

Byung Chan Eu

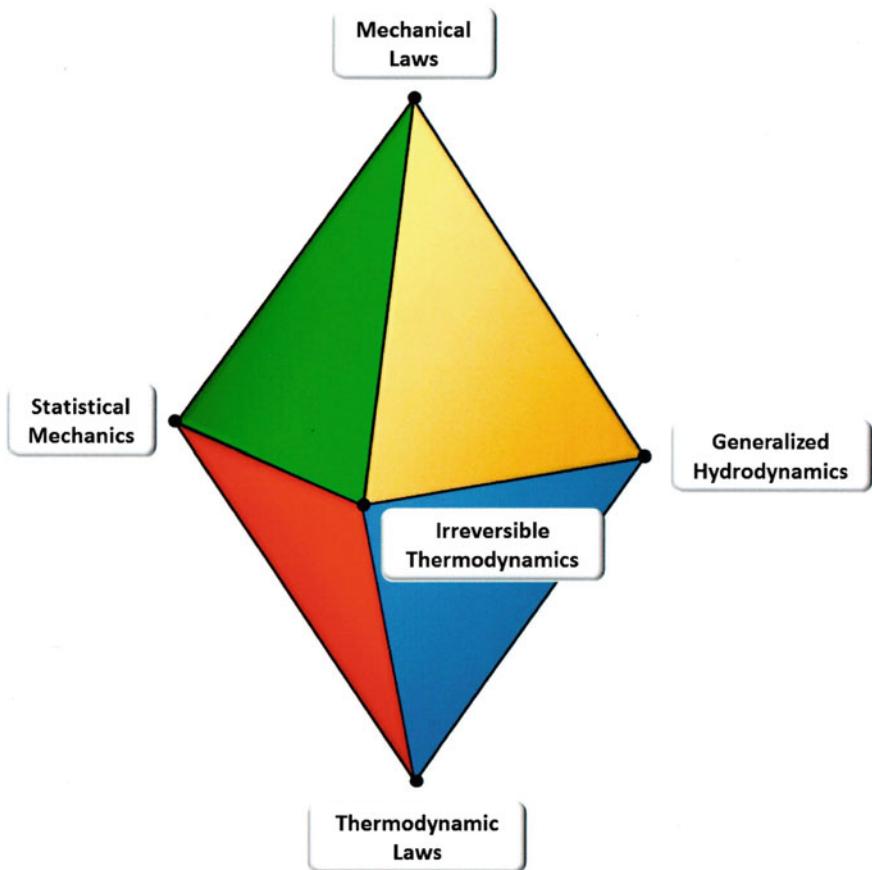
# Kinetic Theory of Nonequilibrium Ensembles, Irreversible Thermodynamics, and Generalized Hydrodynamics

Volume 1. Nonrelativistic Theories



Springer

# Kinetic Theory of Nonequilibrium Ensembles, Irreversible Thermodynamics, and Generalized Hydrodynamics



The tenet under which this work is carried out is figuratively summarized by the hexahedron displayed above: three vertices of subjects in the middle are constrained and in conformation to the two fundamental principles of physics, mechanical laws and laws of thermodynamics, at the two apices at the top and the bottom

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# Kinetic Theory of Nonequilibrium Ensembles, Irreversible Thermodynamics, and Generalized Hydrodynamics

Volume 1. Nonrelativistic Theories



Springer

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# Preface

In this monograph, theories of nonequilibrium statistical mechanics of simple molecules are presented in density ranging from dilute gases to moderately dense gases to liquids. Both single and multiple components are considered for nonrelativistic and relativistic kinetic theories. The nonrelativistic kinetic theories are in classical formalism. In the case of relativistic kinetic theories, classical gases are treated with a relativistic Boltzmann equation, whereas radiation (photons) and matter are treated by means of quantum mechanical kinetic equation—covariant Boltzmann–Nordheim–Uehling–Uhlenbeck kinetic equations for a mixture of photons and material gases. The nonrelativistic theories are presented in Volume 1 and the relativistic theories in Volume 2. The kinetic equations are postulates and hence their predictions are to be verified *a posteriori* against experiments. The laws of thermodynamics serve as the required benchmark for *a posteriori* verification for the present kinetic theories. The postulational kinetic theories presented are formulated for nonequilibrium ensembles of fluids which obey irreversible time-reversal-invariance-breaking kinetic equations modeled after the Boltzmann kinetic equation. Being time-reversal symmetry breaking and hence irreversible, the kinetic equations employed are capable of providing molecular theoretic foundations for irreversible transport processes. The thermodynamic theory of irreversible processes obtained therewith is in full conformation with the laws of thermodynamics as we know of from the phenomenological theories of thermodynamics by S. Carnot, R. Clausius, and W. Thomson (Kelvin) and of J.W. Gibbs. Therefore the consequences of the present kinetic theory for the thermodynamics of irreversible processes and the accompanying hydrodynamics (more precisely, generalized hydrodynamics), may be said to be thermodynamically consistent.

The germ of the present line of work was conceived by the author's realization that the celebrated Boltzmann equation is not derivable, but should be regarded as a postulate for a time-reversal symmetry breaking evolution equation for singlet distribution functions of dilute monatomic gas molecules in the phase space and that it should be also regarded as a phase-space evolution equation of a particular form for an ensemble of uncorrelated molecules. This strand of thought that initially

was put forth in the papers [Ann. Phys. (NY) **118**, 187, 230 (1979); **120**, 423 (1979)] by the present author, however, has taken considerably roundabout ways to come to the present form that the Boltzmann equation should be regarded as a kinetic equation for a simplest possible dynamical ensemble of the many-particle systems consisting of a very dilute monatomic gas. It, in fact, is not derivable from the mechanical laws of motion alone since it requires *extra-mechanical* principles, for example, the probability theory. In this work we, therefore, abandon the pretension that the irreversible kinetic equations are somehow derived from the mechanical principles. This roundabout journey has taken many years, which took a more concrete form with the works underlying the monograph by this author entitled *Kinetic Theory and Irreversible Thermodynamics* published by John Wiley & Sons in 1992 and continued in its sequel, the monograph entitled *Nonequilibrium Statistical Mechanics* (Kluwer 1998) where the idea of the role of ensemble was broached along the line presented in one of my papers [J. Chem. Phys. **107**, 222, (1997)]. In the intervening years there have been made a number of developments and minor corrections in the course of thoughts and applications of the theories developed from the thoughts in the aforementioned monographs. Although there still remains a great deal of further work to be done, it is felt that it is an opportune time to gather materials studied and present a synthesis of them as best as possible in a coherent form. The present monograph is a product of such a sentiment on the part of this author. It is hoped that this work would be useful to readers interested in the subject matter. In the course of this work the author has experienced numerous physical travails, which I could not have overcome without the dedicated cares of numerous physicians and cardiac surgeons at the Royal Victoria Hospital, McGill University, who rescued me from the brink of the abyss of life, and last but not least, of the cares and devoted love of my wife Hui Young. That was about three years ago to this day. Without them this work would not have been possible. I would like to thank them all and, especially, for the encouragement of my wife for this work. I would also like to thank my former students and associates who shared the joys as well as labors with me during the journey along the course of this work. The thoughts of their camaraderie will be cherished. I would also gratefully acknowledge the valuable help from my son David for drawing figures despite his busy schedule.

Montreal, Canada  
March 2016

Byung Chan Eu

# Contents

<b>1</b>	<b>Introduction</b>	<b>1</b>
	References . . . . .	9
 <b>Part I Nonrelativistic Theories</b>		
<b>2</b>	<b>Thermodynamic Theory of Irreversible Processes</b>	<b>13</b>
2.1	The Zeroth Law of Thermodynamics . . . . .	14
2.1.1	The Zeroth Law of Thermodynamics for Temperature . . . . .	14
2.1.2	The Zeroth Law of Thermodynamics Extended . . . . .	17
2.2	The First Law of Thermodynamics . . . . .	18
2.2.1	Internal Energy . . . . .	19
2.2.2	Work . . . . .	20
2.2.3	Local Forms of Evolution Equations . . . . .	24
2.3	The Second Law of Thermodynamics . . . . .	28
2.3.1	Carnot Theorem . . . . .	28
2.3.2	Clausius and Kelvin Principles . . . . .	29
2.3.3	Clausius Inequality . . . . .	31
2.3.4	Clausius Entropy . . . . .	32
2.3.5	Clausius–Duhem Inequality . . . . .	36
2.4	Differential Form for Calortropy . . . . .	40
2.4.1	Local Differential Form for Calortropy . . . . .	41
2.4.2	Calortropy and Thermodynamic Relations . . . . .	47
2.5	Generalized Hydrodynamic Equations . . . . .	48
2.6	Irreversible Thermodynamics of Steady States . . . . .	52
2.7	Inclusion of Chemical Reactions . . . . .	54
2.8	Inclusion of Volume Transport . . . . .	56
2.9	Concluding Remarks . . . . .	57
	References . . . . .	58

<b>3 Boltzmann Kinetic Equation . . . . .</b>	<b>61</b>
3.1 Irreversible Processes in Dilute Monatomic Gases . . . . .	62
3.1.1 Conserved and Nonconserved Macroscopic Variables . . . . .	65
3.1.2 Collision Invariants . . . . .	68
3.1.3 Broken Time Reversal Symmetry and the Boltzmann Kinetic Equation . . . . .	70
3.1.4 The $H$ Theorem and Boltzmann Entropy . . . . .	72
3.2 Equilibrium Distribution Function . . . . .	74
3.2.1 Equilibrium Boltzmann Entropy . . . . .	75
3.2.2 Thermodynamic Correspondence and Equilibrium Gibbs Relation . . . . .	76
3.3 Evolution Equations for Macroscopic Variables . . . . .	78
3.3.1 Boltzmann Entropy Balance Equation . . . . .	79
3.3.2 Conservation Laws of Mass, Momentum, and Energy . . . . .	80
3.3.3 Evolution Equations for Nonconserved Variables . . . . .	83
3.4 Thermodynamics of Irreversible Processes in Dilute Monatomic Gases . . . . .	88
3.4.1 Functional Hypothesis for Distribution Functions . . . . .	89
3.4.2 Calotropy and the Second Law of Thermodynamics . . . . .	90
3.4.3 Thermodynamic Correspondence . . . . .	97
3.5 Statistical Thermodynamics of Irreversible Processes . . . . .	98
3.5.1 Nonequilibrium Intensive Properties . . . . .	100
3.5.2 Nonequilibrium Partition Function . . . . .	104
3.5.3 Calotropy Production in Cumulant Expansion . . . . .	110
3.5.4 Cumulant Expansion for Dissipation Terms . . . . .	113
3.5.5 Collision Bracket Integrals . . . . .	114
3.5.6 Generalized Potentials . . . . .	115
3.5.7 Quasilinear Generalized Hydrodynamics and Transport Processes . . . . .	117
3.5.8 Linear Transport Processes . . . . .	119
3.5.9 A Model for Quasilinear Generalized Hydrodynamic Equations . . . . .	121
3.6 Relative Boltzmann Entropy . . . . .	121
3.6.1 Evolution Equation of Relative Boltzmann Entropy . . . . .	122
3.6.2 Relative Boltzmann Entropy and Fluctuations . . . . .	124
3.6.3 Differential Equations for Fluctuations . . . . .	126
3.6.4 Stochastic Treatment of Fluctuations . . . . .	129
3.7 Concluding Remarks . . . . .	135
References . . . . .	135

<b>4 Equilibrium Ensemble Method . . . . .</b>	137
4.1 Brief Review of Ensemble Methods . . . . .	137
4.2 Ensembles and Fundamental Postulates. . . . .	138
4.2.1 Canonical Ensemble . . . . .	141
4.2.2 Grand Canonical Ensemble . . . . .	148
4.3 Summary of the Gibbs Ensemble Theory . . . . .	154
References . . . . .	154
<b>5 Boltzmann-Like Equation for Moderately Dense Gases . . . . .</b>	157
5.1 Extended Boltzmann Equation . . . . .	158
5.2 Cluster Expansion of the $N$ -Particle Collision Operator. . . . .	173
5.3 Macroscopic Evolution Equations . . . . .	177
5.3.1 Boltzmann Entropy, Calortropy, and Relative Boltzmann Entropy . . . . .	178
5.3.2 Conservation Laws. . . . .	180
5.3.3 Nonconserved Variables and Their Evolution Equations . . . . .	181
5.4 Equilibrium Solution of the Extended Boltzmann Kinetic Equation . . . . .	183
5.5 Thermodynamics of Irreversible Processes and Hydrodynamics . . . . .	184
5.5.1 Nonequilibrium Canonical Distribution Functions. . . . .	185
5.5.2 Calortropy Differential . . . . .	186
5.5.3 Thermodynamic Correspondence . . . . .	188
5.5.4 Nonequilibrium Statistical Thermodynamics of Irreversible Processes . . . . .	189
5.5.5 Generalized Potentials. . . . .	190
5.5.6 Calortropy Production in Cumulant Expansion. . . . .	191
5.5.7 Cumulant Expansion for Dissipation Terms. . . . .	195
5.5.8 Quasilinear Generalized Hydrodynamic Equations . . . . .	196
5.5.9 Collision Bracket Integrals . . . . .	198
5.5.10 Steady Quasilinear and Linear Transport Processes. . . . .	199
5.5.11 A Model for Quasilinear Generalized Hydrodynamic Equations . . . . .	206
5.5.12 Density Expansion of Extended Boltzmann Collision Integral . . . . .	207
5.6 Concluding Remarks . . . . .	211
References . . . . .	212
<b>6 Kinetic Theory of a Simple Dense Fluid . . . . .</b>	213
6.1 Generalized Boltzmann Equation . . . . .	214
6.2 Basic Properties of the Generalized Boltzmann Equation. . . . .	227
6.2.1 Collision Invariants . . . . .	228
6.2.2 The $H$ Theorem and the Stability Condition . . . . .	229
6.2.3 Proof of Conditions (6.C1) and (6.C2) . . . . .	229

6.3	Conservation Laws . . . . .	232
6.3.1	Mass Conservation Law . . . . .	232
6.3.2	Momentum Conservation Law . . . . .	233
6.3.3	Energy Conservation Law . . . . .	236
6.4	Voronoi Volume—a Concept of Molar Volume . . . . .	237
6.5	Evolution Equation of Volume Fluctuations . . . . .	244
6.6	Evolution Equations for Other Nonconserved Variables . . . . .	247
6.6.1	Evolution Equation of Volume Flux . . . . .	249
6.6.2	Shear Stress Evolution Equation . . . . .	250
6.6.3	Evolution Equation for Excess Normal Stress . . . . .	252
6.6.4	Evolution Equation for Heat Flux . . . . .	254
6.7	Thermodynamics of Irreversible Processes . . . . .	258
6.7.1	Boltzmann Entropy . . . . .	258
6.7.2	Calortropy . . . . .	261
6.7.3	Relative Boltzmann Entropy . . . . .	263
6.7.4	Equilibrium Solution of the GBE . . . . .	264
6.7.5	Nonequilibrium Canonical Form for the Distribution Function . . . . .	268
6.7.6	Calortropy and Its Differential Form . . . . .	270
6.7.7	Thermodynamic Correspondence . . . . .	274
6.7.8	Local Form of the Second Law of Thermodynamics . . . . .	275
6.7.9	Nonequilibrium Partition Function . . . . .	278
6.7.10	Nonequilibrium Statistical Thermodynamics . . . . .	279
6.7.11	Determination of Generalized Potentials . . . . .	280
6.7.12	Cumulant Expansion for Dissipation Terms . . . . .	281
6.7.13	Collision Bracket Integrals . . . . .	286
6.7.14	Summary of Generalized Hydrodynamic Equations . . . . .	289
6.8	Linear Constitutive Equations for Nonconserved Moments . . . . .	290
6.8.1	Constitutive Equation for Volume Fluctuation $\Phi^{(0)}$ . . . . .	291
6.8.2	Constitutive Equation for Shear Stress $\Phi^{(1)}$ . . . . .	292
6.8.3	Constitutive Relation for Excess Normal Stress $\Phi^{(2)}$ . . . . .	293
6.8.4	Constitutive Relation for Heat Flux $\Phi^{(3)}$ . . . . .	293
6.8.5	Constitutive Relation for Volume Flux $\Phi^{(4)}$ . . . . .	294
6.8.6	Linear Transport Coefficients . . . . .	294
6.9	Quasilinear Generalized Hydrodynamic Equations . . . . .	297
6.10	Model for Quasilinear Generalized Hydrodynamic Equations . . . . .	297
6.11	Relative Boltzmann Entropy Revisited . . . . .	301
6.11.1	Exponential Form for $\tilde{f}^{(N)}$ . . . . .	301
6.11.2	Relative Boltzmann Entropy Balance Equation . . . . .	303

6.11.3	Stochastic Theory Approach to the Generalized Boltzmann Equation . . . . .	306
6.12	Barycentric Velocity and Its Constitutive Equation . . . . .	308
6.12.1	Cartesian Coordinate Representation . . . . .	308
6.12.2	Transformation to Collective Coordinates . . . . .	313
6.13	Brownian Motion Model . . . . .	315
6.14	Concluding Remarks . . . . .	317
	References . . . . .	318
<b>7</b>	<b>Kinetic Theory of a Dense Simple Fluid Mixture . . . . .</b>	<b>321</b>
7.1	Generalized Boltzmann Equation for a Simple Fluid Mixture . . . . .	322
7.1.1	Nonequilibrium Grand Ensemble . . . . .	322
7.1.2	Generalized Boltzmann Equation for a Mixture . . . . .	324
7.2	Boltzmann Entropy and the $H$ Theorem . . . . .	331
7.2.1	Boltzmann Entropy . . . . .	332
7.2.2	Boltzmann Entropy Balance Equation . . . . .	333
7.2.3	Equilibrium Distribution Function . . . . .	335
7.3	Conserved Variables . . . . .	337
7.4	Nonconserved Variables and Their Evolution Equations . . . . .	341
7.4.1	Generic Form of Evolution Equations . . . . .	342
7.4.2	Physically Most Relevant Nonconserved Moments . . . . .	344
7.5	Set of Macroscopic Moments . . . . .	347
7.5.1	Conserved Moments . . . . .	348
7.5.2	Nonconserved Moments . . . . .	353
7.6	Generalized Hydrodynamic Equations . . . . .	365
7.6.1	Conservation Laws . . . . .	366
7.6.2	Evolution Equations for Nonconserved Variables . . . . .	372
7.7	Thermodynamics of Irreversible Processes in a Mixture . . . . .	386
7.7.1	Nonequilibrium Grand Canonical Ensemble Theory . . . . .	387
7.7.2	Calortropy . . . . .	388
7.7.3	Thermodynamic Correspondence . . . . .	393
7.7.4	Nonequilibrium Statistical Thermodynamics . . . . .	394
7.7.5	Local and Global Representation of Thermodynamic Laws . . . . .	396
7.7.6	Generalized Potentials . . . . .	399
7.7.7	Cumulant Expansion for Calortropy Production and Dissipation Terms . . . . .	401
7.7.8	Collision Bracket Integrals . . . . .	405
7.8	Linear Transport Processes . . . . .	408
7.8.1	Linear Dissipation Terms . . . . .	408
7.8.2	Linear Constitutive Equations . . . . .	409
7.8.3	Linear Transport Coefficients . . . . .	416

7.9	Summary of Generalized Hydrodynamic Equations for a Mixture . . . . .	418
7.9.1	Conservation Laws . . . . .	419
7.9.2	Nonconserved Evolution Equations . . . . .	419
7.10	Quasilinear Generalized Hydrodynamic Equations . . . . .	420
7.11	Relative Boltzmann Entropy . . . . .	423
7.12	Concluding Remarks . . . . .	427
	References . . . . .	428
<b>8</b>	<b>Classical Scattering Theory in Phase Space . . . . .</b>	<b>429</b>
8.1	Preamble to Classical Scattering Theory . . . . .	430
8.2	Eigenvalue Problem for the Classical Liouville Operator . . . . .	431
8.3	Some Mathematical Properties of Eigenfunctions and Eigenvalues . . . . .	437
8.4	Formal Scattering Theory in Phase Space . . . . .	442
8.5	Alternative Form for the Collision Bracket Integral . . . . .	447
8.5.1	Example for Two-Particle Collisions . . . . .	451
8.5.2	Three-Particle Collision . . . . .	452
8.6	Application of the Computational Algorithm . . . . .	453
8.6.1	Linear Transport Coefficients for a Moderately Dense Gas Mixture . . . . .	453
8.6.2	Shear Viscosity . . . . .	456
8.6.3	Bulk Viscosity . . . . .	457
8.6.4	Thermal Conductivity, Thermal Diffusion, and Mass Diffusion . . . . .	458
8.7	Concluding Remarks . . . . .	460
	References . . . . .	461
<b>9</b>	<b>Generalized Hydrodynamics and Transport Processes . . . . .</b>	<b>463</b>
9.1	Generalized Hydrodynamics for Dilute Gases . . . . .	464
9.1.1	Conservation Laws . . . . .	465
9.1.2	Evolution Equations for Nonconserved Variables . . . . .	466
9.1.3	Reduced Generalized Hydrodynamic Equations for Gases . . . . .	472
9.1.4	Quasilinear Transport Phenomena . . . . .	479
9.1.5	Dissipation Function and Thermodynamic Forces . . . . .	482
9.1.6	Nonlinear Transport Coefficients . . . . .	485
9.1.7	Linear Transport Coefficients and Classical Hydrodynamics . . . . .	487
9.1.8	Quasilinear Transport Processes and Hyperbolic-Type Partial Differential Equations . . . . .	488
9.2	Applications of Generalized Hydrodynamic Equations for Gases . . . . .	495
9.2.1	Compressible Poiseuille Gas Flow . . . . .	496
9.2.2	Integration of Conservation Laws . . . . .	498

9.2.3	Reduction of Constitutive Relations to an Independent Set . . . . .	498
9.2.4	Rarefied Gas Flow Past a Circular Cylinder . . . . .	502
9.2.5	The Knudsen Problem . . . . .	504
9.2.6	Light-Induced Gas Flow in Rarefied Gas . . . . .	510
9.3	Generalized Hydrodynamics for Liquids . . . . .	516
9.3.1	Quasilinear Generalized Hydrodynamics and Transport Processes . . . . .	516
9.3.2	Balance Equations for Conserved Variables . . . . .	516
9.3.3	Quasilinear Nonconserved Evolution Equations . . . . .	516
9.3.4	Volume Transport Phenomena . . . . .	519
9.3.5	Shear Viscous Transport . . . . .	520
9.3.6	Heat Conduction, Diffusion, Volume Flux . . . . .	521
9.3.7	Quasilinear and Linear Transport Coefficients . . . . .	524
9.4	Concluding Remarks . . . . .	527
	References . . . . .	528

## Epilogue: Non-Relativistic Theories

### Part II Essays on Equilibrium Theories

<b>10</b>	<b>Molecular Theory of Liquid Mixtures: Equilibrium Properties . . . . .</b>	537
10.1	Kirkwood–Buff Theory of Mixtures . . . . .	538
10.1.1	Chemical Potentials . . . . .	542
10.1.2	Partial Molar Volumes and Isothermal Compressibility . . . . .	543
10.1.3	Equation of State . . . . .	545
10.1.4	Chemical Potentials Revisited . . . . .	545
10.1.5	Osmotic Pressure . . . . .	548
10.2	Ornstein–Zernike Theory of Solutions . . . . .	550
10.3	The KB Theory Recast . . . . .	551
10.3.1	Partial Molar Volumes and Isothermal Compressibility . . . . .	552
10.3.2	Chemical Potentials Recast . . . . .	554
10.3.3	Osmotic Pressure Recast . . . . .	556
10.3.4	Entropy of Mixing . . . . .	558
10.3.5	Enthalpy of Mixtures . . . . .	559
10.4	Monte Carlo Simulation Method for Pair Correlation Functions . . . . .	559
	References . . . . .	560
<b>11</b>	<b>Equilibrium Pair Correlation Functions . . . . .</b>	561
11.1	Integral Equation Method for Pair Correlation Functions . . . . .	561
11.1.1	The Wiener–Hopf Method of Solution for the OZ Equation . . . . .	563

11.1.2	Integral Equation for the Direct Correlation Function . . . . .	566
11.1.3	Integral Equation for the Total Correlation Function . . . . .	568
11.1.4	Thermodynamically Consistent Closure. . . . .	570
11.1.5	Function $\Psi(x)$ . . . . .	572
11.1.6	Equation for Inverse Correlation Length . . . . .	575
11.2	Pair Correlation Function in the Subcritical Regime . . . . .	575
11.3	Concluding Remarks . . . . .	581
	References . . . . .	582
	<b>Appendix A: List of Symbols (Volume 1)</b> . . . . .	585
	<b>Index</b> . . . . .	593

# Chapter 1

## Introduction

Kinetic theory of matter, or more specifically, gases and liquids, has a long history tracing back to the works of Maxwell [1] and Boltzmann [2] in mid 1860s and 1870s. It has evolved since then through the works of Gibbs [3], who established the ensemble theory of statistical mechanics and applied it to equilibrium ensembles, and numerous contributors, most prominently, Enskog [4] and Chapman [5], after him in the twentieth century and in the post-World War II, especially, those led by Bogoliubov [6], Born and Green [7], Kirkwood [8], and Yvon [9] and schools of theoreticians in statistical mechanics following their theoretical developments after 1946. In this work the author hopes to contribute to the ongoing efforts by numerous other research workers on the subject of nonequilibrium statistical mechanics and its relation to the thermodynamics of irreversible processes and hydrodynamics attendant thereto.

In kinetic theory of matter, we hope to describe its macroscopic behavior from the molecular viewpoint in accordance with the particulate concept of matter composed of an astronomical number of particles (electrons, atoms, molecules, etc.). Although the evolution and behaviors of macroscopic material systems are governed not only by the principles of mechanics, classical or quantal, but also by the laws of thermodynamics according to the currently accepted tenets of science, it would not seem unfair to state that the aspects of thermodynamic laws had not been a foremost concern in most of kinetic theory literature. This aspect of kinetic theory has preoccupied the present author's study of kinetic theory beginning from the mid 1970s. This line of study [10] by the author has, unfortunately, evolved over the years unlike the works by some brilliant minds which we see sometimes in science appear to have been achieved in perfection in a single stroke, but it has reached a point where a summing up of the extended study should be made, especially, of the gist of it. That is the aim of this work.

Since the kinetic theory must be developed from the mechanical viewpoint of molecules or particles on the foundation of laws of thermodynamics, so believes this author, the beginning of the discourse on the subject matter in this work is opened

with a phenomenological theory of irreversible processes in matter without restriction to the degree of displacement from equilibrium in Chap. 2. Since the phenomenological theory of such unrestricted irreversible processes is itself not fully verifiable experimentally at present with only some spotty examples of experiment in rarefied gases, carrier mobilities in semiconductors, and some rheological phenomena, we have formulated it axiomatically mainly on the basis of our experience with the thermodynamic theory of linear irreversible processes and a plausible extension of it to nonlinear processes which can be far removed from equilibrium. This axiomatic theory of irreversible processes is formulated in a manner consistent with the principles of thermodynamics and as such it serves as a benchmark to the kinetic theory of irreversible phenomena in matter from the molecular theory point of view in this work. The kinetic theory of irreversible transport processes developed in this work, therefore, is thermodynamically consistent to the extent that the axiomatic theory of phenomenological irreversible processes in macroscopic matter is in conformation to the statistical mechanical representation of laws of thermodynamics.

The phenomenological theory mentioned earlier makes use of Carnot's theorem [11] and the notion of *compensated and uncompensated heats* which Clausius [12] inferred from Carnot's theorem for the second law of thermodynamics and with which he formulated the Clausius inequality for the second law of thermodynamics and the notion of entropy for reversible processes. The Clausius inequality, together with the compensated and uncompensated heats, gives rise to the notion of *calortropy* for nonequilibrium (irreversible) processes in lieu of *entropy*, which was originally defined by Clausius for *reversible processes only*. The internal energy differential and the calortropy differential then can be deduced to give rise to *a pair of vanishing circular integrals in the manifold of thermodynamic variables* that include conserved and nonconserved variables representative of irreversible processes occurring in the system. Since the axiomatically constructed evolution equations for conserved and nonconserved variables are subordinate to the aforementioned pair of exact differential forms as representations of the first and second law of thermodynamics by virtue of the fact that they belong to the thermodynamic manifold described by the differential forms mentioned, the phenomenological theory so constructed is guaranteed to satisfy the thermodynamic laws. In this sense, the macroscopic theory of irreversible processes is consistent with the laws of thermodynamics, and consequently, we have *a continuum theory beacon* to chart the molecular theory of irreversible processes by means of kinetic equations for systems of matter consisting of an enormous number of molecules or particles. Our journey in the rest of this work on kinetic theory of matter is charted by the guiding light of the continuum theory beacon and hence may be said to be thermodynamically consistent since it is in conformation to the laws of thermodynamics.

The first requirement for a molecular theory of irreversible macroscopic processes—namely, kinetic theory—is that the kinetic equation must be irreversible, which means that it must break time reversal invariance, so that it describes irreversible processes. There is available such a kinetic equation in the form of Boltzmann kinetic equation invented by Boltzmann [2] in the case of sufficiently dilute monatomic gases. One of his aims with his celebrated kinetic equation was to show the

uniqueness of the Maxwell velocity distribution function that Maxwell [1] obtained from his kinetic equation less than a decade earlier. With the help of the  $H$  theorem for the kinetic equation he invented, which turned out to precede the Lyapounov stability theorem [13] that appeared much later, he was able to show the uniqueness of Maxwell's equilibrium velocity distribution function. Moreover, the  $H$  theorem enabled him to make connection with Clausius's entropy for reversible (equilibrium) processes [14], which Clausius discovered some 10 years earlier. These well-established features of the Boltzmann kinetic equation suggest that it would be possible to formulate a macroscopic theory of irreversible processes, at least, for dilute gases that would be thermodynamically consistent in the sense mentioned earlier. Therefore, in Chap. 3, we formulate a kinetic theory of irreversible processes in a dilute monatomic gas without restriction as to the degree of removal from equilibrium, which is thermodynamically consistent. We say a macroscopic theory of irreversible processes, regardless of whether it is phenomenological or molecular, is thermodynamically consistent if the theory conforms to the requirement of the laws of thermodynamics, primarily, the first and second law of thermodynamics.

To achieve the stated goal, it was necessary to recognize that the macroscopic variables for the system are, *mathematically*, projections of the distribution functions living in the phase space of molecules comprising the system onto a manifold spanned by macroscopic variables, whose numbers are extremely smaller than the number of particles (molecules) on the order of Avogadro's number comprising the system. Secondly, the nonequilibrium distribution function describing the macroscopic processes in an aforementioned macroscopic manifold of macroscopic variables itself is a “projection” of the phase space distribution function and hence is not exactly the same as the latter. In fact, the former, namely, the projected distribution function, is a *functional of the macroscopic variables spanning the manifold mentioned*—the thermodynamic manifold defined later more precisely—and therefore cannot, in practice, be the exact solution of the kinetic equation. This subtle distinction lies underneath the entire theoretical formulation of kinetic theory of irreversible processes presented throughout this work.

The first step to take in the theoretical formulation of evolution equations for macroscopic variables is in identifying the leading element of the variable set. Since this set is a homologous hierarchy, once the seed element is chosen on the basis of physical phenomena desired to describe, the procedure of collecting the set is fairly easy to find and automatic. Since the phenomena of interest is irreversible flow processes in matter and the fundamental physical laws of nonrelativistic physics demand that the mass must be conserved in a nonrelativistic process, the mass conservation law is sought after from the molecular theory standpoint. Therefore we first look for a statistical mechanical representation of mass of the fluid.

Thus the seed element—henceforth the set will be called moment set—is naturally chosen with the mean mass of particles making up the system. The statistical mechanical mean value—the average—can be readily defined by the local mechanical mass density which is averaged over the phase space weighted by the distribution function obeying the kinetic equation postulated for the system, for example, the Boltzmann kinetic equation in the case of a dilute monatomic gas. Differentiating

with time the statistical mechanical expression for mass, or more precisely, the mass density, the mass balance equation is obtained, which turns out to be the conservation law of mass in the axiomatic phenomenological theory of irreversible phenomena formulated in Chap. 2. This conservation law expression is assured if the mean flux of mass appearing in the divergence term of the equation is identified with the local mean momentum of the flow process in the fluid of interest.

The mean momentum is the moment succeeding the moment of mass—the seed moment of the homologous hierarchy. Thus the second element of the moment set—the hierarchy—is identified and its statistical mechanical formula is definitively defined. Then the evolution equation for the mean momentum density can be derived in exactly the same manner as for the first evolution equation, namely, the mass conservation law, and at the same time the statistical mechanical formula for the moment succeeding the momentum density in the moment set may be defined unambiguously. And it turns out to be the pressure tensor. Repeating this process of deriving all other elements of the moment set and identifying their statistical mechanical formulas, the entire set of evolution equations is derived for macroscopic mean values representing the variables describing flow process of interest.

Sometimes it may be necessary to have additional homologous sets of moments which are distinctive from the homologous moment set led by mass. Then we may repeat the derivation process with an appropriately identified seed moment for each new homologous set and obtain desired evolution equations. In this manner, all the necessary evolution equations can be derived to describe irreversible flow processes in the system of interest and the formal theory of irreversible processes may be completed. However, it must be remembered that the systems of evolution equations are abstract and are not as yet assured of the thermodynamic consistency.

Averaging a mechanical quantity over the phase space with the distribution function  $f$  as a statistical mechanical weight is a projection of  $f$  onto the manifold of mean macroscopic variables, which may be identified with the thermodynamic manifold to be defined later more precisely. The projection is accompanied by a contraction of information.

Since the Boltzmann entropy  $S$  represents the information content for the system from the information theory point of view, a set of quantities represented by the mean values discussed earlier contains far less information than the distribution function  $f$  itself that obeys the kinetic equation exactly and lives in the phase space of the system containing an astronomically large number of molecules or particles. The measure of information contraction of the projected space (or manifold) of macroscopic variables are described by what we call calortropy [15] denoted by  $\Psi$ . This calortropy cannot be equal to the Boltzmann entropy, but can be shown to be subjected to the laws of thermodynamics. As a matter of fact, because its differential can be shown to be exact in the thermodynamic manifold, it may be regarded as a representation of the second law of thermodynamics. In contrast to this, since the Boltzmann entropy  $S$  would not yield an exact differential form in the *thermodynamic manifold*, it is not possible to base the question of thermodynamic consistency on  $S$ . Therefore, with the help of the calortropy it is possible to construct a thermodynamically consistent theory of irreversible processes evolving in the thermodynamic manifold subject to

the control of the calortropy, and consequently we have a thermodynamic theory of irreversible processes fully consistent with the laws of thermodynamics in the case of dilute monatomic gases obeying the Boltzmann kinetic equation. For the present formulation of theory of irreversible thermodynamics the Boltzmann entropy  $S$  plays only an indirect role providing the  $H$  theorem and the notion of calortropy.

The underlying philosophy held for the concepts and procedures taken for formulating kinetic theories of macroscopic irreversible processes in Chap. 3 remains the same for other types of dilute gases, moderately dense gases, and liquids we have studied in this work. In Volume 1, nonrelativistic phenomena are discussed, whereas in Volume 2 relativistic theories are formulated for monatomic gaseous systems and also for a system composed of photons and relativistic gases. The kinetic equation employed in the latter system is quantal, since the Boltzmann–Nordholm–Uehling–Uhlenbeck kinetic equation [15–17], which is a quantal kinetic equation, is made covariant for the kinetic theory of relativistic particles. This treatment therefore would be an example for a macroscopic theory which combines a quantum theory and special relativity theory.

The Boltzmann kinetic equation disguises the fact that the ensemble theory of statistical mechanics of J.W. Gibbs may be said to underlie it, perhaps, in a special form of ensemble of statistically uncorrelated particles. Once we realize this viewpoint in the general context, we may look for kinetic equations for statistically correlated interacting particle systems, which are also irreversible and break time reversal invariance as the Boltzmann equation does. We would like to keep these important features for kinetic equations of interacting particle systems. To implement these two crucially important properties in the kinetic theory we have in mind, in Chap. 4 we first briefly review the gist of equilibrium Gibbs ensemble theory, although we inject some important dynamical elements in the collisional evolution of the ensemble which are absent in the traditional discussion of the equilibrium Gibbs ensemble theory. This would prepare us for the implementation of the notion of ensemble and the heuristic formulations of the ensemble kinetic equations made in the subsequent chapters.

With the aforementioned preparation we devise an ensemble kinetic equation for a moderately dense monatomic gas by recasting the irreversible Boltzmann equation for an ensemble of dilute uncorrelated particles, which may be regarded as a supersystem of one-particle members. Then by replacing the binary collision operator in the aforementioned ensemble kinetic equation with a many-particle collision operator so as to describe interactions of the members of the supersystem representative of the ensemble, we are able to construct an irreversible kinetic equation for a moderately dense gas of statistically uncorrelated particles and discuss irreversible processes therein. This topic is discussed in Chap. 5 in the spirit completely parallel to that taken in Chap. 3 on the Boltzmann kinetic equation. With the so-constructed irreversible kinetic equation and postulated for a moderately dense statistically uncorrelated system, we are not only able to recover the kinetic theory results which one may obtain from the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY hierarchy theory [6–9] in sufficiently low density limit. But we are also able to show the transport coefficients obtained are free from the divergence difficulty arising in connection

with the many-particle collision operator. The generalized hydrodynamic evolution equations are also derived in a manner consistent with the laws of thermodynamics and their mathematical structures are shown to be completely parallel to the theory presented in Chap. 3, thanks to the irreversibility of the kinetic equation constructed for the ensemble.

Adhering to the similar notions and postulates for kinetic equations for appropriate ensembles representative of the systems of molecules used in Chaps. 3 and 5, we are now able to construct and postulate irreversible kinetic equations for ensembles representative of single-component monatomic liquids and liquids mixtures to formulate the thermodynamic theory of irreversible processes, attendant generalized hydrodynamics, and a theory of transport processes in liquids and liquid mixtures. Such theories are presented, respectively, in Chap. 6 for simple single-component liquids and in Chap. 7 for simple liquid mixtures.

In Chaps. 6 and 7, we have generalized the moment set to include the notion of mean volume of influence for interacting molecules—which we simply call the molar volume—and use it as another one of seed moments from which a new moment homologue begins. This “molar volume” enables us to discuss *volume transport phenomena* in fluid mechanics which Brenner [18] put forward in recent years on the phenomenological theory grounds. We have shown that his idea of new volume and associated flux may be formulated on the basis of molecular theory [19, 20] if we make use of the concept of Voronoi volume [21], and that a hydrodynamic theory of volume transport can be more cogently formulated in a logical manner from the molecular theory standpoint. The inclusion of volume transport phenomena represents an extension of the generalized hydrodynamics presented in Chaps. 3 and 5 not only with respect to the formalism itself, but also the scope of conceptual horizon in hydrodynamics. The generalized hydrodynamics presented in Chaps. 6 and 7 therefore may be regarded as a generalization of the generalized hydrodynamic formalism presented in Chaps. 3 and 5. Inclusion of volume transport phenomena in the form presented in these two chapters also extends the thermodynamic manifold and at the same time eliminate, I believe, the uncertain and speculative features of the phenomenological formulation of the idea [18] of Brenner’s “volume”, which appears to be quite elusive to grasp. The generalized hydrodynamics with volume transport phenomena included in this work definitely broadens the horizon and range of traditional hydrodynamics.

The generalized hydrodynamics formulated in this work necessarily accompanies the thermodynamic theory of irreversible processes and nonequilibrium statistical mechanics thereof, which can be carried through in a manner quite parallel to the equilibrium statistical mechanics, thanks to the nonequilibrium canonical or grand canonical distribution function underlying the nonequilibrium ensemble methods. As a matter of fact, the nonequilibrium statistical mechanics formalism accompanying the generalized hydrodynamics facilitates quantification of various intensive parameters appearing in the nonequilibrium canonical or grand canonical distribution functions with the help of the *extended Gibbs relation* for calortropy density—namely, the Pfaffian differential form for calortropy density—and its integrability condition, namely, the nonequilibrium Gibbs–Duhem equation. Thus with

nonequilibrium canonical or grand canonical forms of distribution functions made use of for the calortropy, the extended Gibbs relation, and its integrability condition for the Pfaffian differential form for the calortropy, we are fully equipped with mathematical tools to carry out study of irreversible thermodynamics of transport processes both from the molecular and continuum theory viewpoints supported by the attendant generalized hydrodynamic equations.

The generalized hydrodynamics includes the classical hydrodynamics of Navier, Stokes, Fourier, and Fick as a limiting case as the system tends toward the vicinity of equilibrium, and the accompanying steady-state constitutive equations together with the transport coefficients can be recovered from the generalized hydrodynamic equations. To achieve this goal, it is necessary to investigate the limiting processes required to obtain the limiting forms mentioned. For this purpose, approximate expansion forms—namely, linear approximations—are used for the generalized potentials conjugate to the fluxes, and a cumulant expansion method is used for the dissipation terms in the flux (nonconserved variable) evolution equations. However, some other methods of approximation may be used or explored in the future. As to the linear transport coefficients, in the limit of small fluxes the Chapman–Enskog transport coefficients [5] are recovered from the generalized hydrodynamic equations in the case of dilute monatomic gases, and in the case of liquids molecular-theory expressions for the linear transport coefficients are obtained in terms of collision bracket integrals, which tend to the Chapman–Enskog theory results in the low density limit. They will appear in Chaps. 6 and 7 and also in Chap. 9.

Deviation of distribution functions obeying the kinetic equation from the non-equilibrium canonical or grand canonical distribution function may be regarded as fluctuations. Therefore the difference between the *Boltzmann entropy*  $S$  and the *calortropy*  $\Psi$  may be attributed to fluctuations. Such fluctuations in distribution functions are characterized by the *relative Boltzmann entropy*. Mathematical and quantitative description of such fluctuations would require solution of the kinetic equation in the phase space. Evolution equations of the fluctuations can be generated from the kinetic equations. This part of investigation based on the kinetic equations considered here is rather sketchy primarily owing to the lack of time to study the subject in depth and, more importantly, because formulating the deterministic macroscopic theory from the kinetic theory standpoint is the primary task of the present work. But the relative Boltzmann entropy should be studied in the future for the general interest and completeness of the kinetic theory formulated here. Nevertheless, we would like to point out that with the help of the relative Boltzmann entropy it has been possible to establish a *thermodynamic uncertainty principle* by which various uncertainty inequalities have been established between conjugate variables spanning the thermodynamic manifold and its tangent manifold. Interestingly, they are parallel to the *quantum mechanical uncertainty relations*. This aspect was discussed in some detail, especially, in Chap. 3. It is quite interesting and insightful to see that the thermodynamic uncertainty relations exist in connection with the relative Boltzmann entropy and that they are associated with fluctuations of the Boltzmann entropy from the thermodynamic calortropy. Similar investigations can be made for dense gases, pure liquids, and liquid mixtures discussed in Chaps. 5, 6, and 7 by following the

line of approach taken in Chap. 3. I believe that the surface is hardly scratched on this subject in the kinetic theory of irreversible processes and fluctuations.

The nonequilibrium statistical mechanics and transport coefficients underlying the theories presented in Chaps. 5 through 7 would require practicable knowledge of many-particle collision dynamics of interacting molecules. The collision dynamical information in the present kinetic theory is vested in the collision integrals of the kinetic equations. More specifically, the information on molecular interactions of particles in the system is contained entirely in the form of collision operators in the collision bracket integrals defining transport coefficients. They have to be computed by some means if we wish to make the theory connect with experiments. For this important reason we digress to discuss a classical mechanical technique based on eigenfunctions and eigenvalues for classical Liouville operators and collision operators in Chap. 8. In this chapter is presented a detailed discussion on the eigenvalue problem [22] of classical Liouville operators with an aim to apply it to develop an algorithm to compute numerically—e.g., by using computer simulation techniques—the transport coefficients or collision bracket integrals for liquids and dense gases of interacting molecules. Such an algorithm is presented in Chap. 8 to facilitate computation of linear transport coefficients for liquids and dense gases. Through this study, we find that transport coefficients are expressible in formulas rather reminiscent of the autocorrelation functions in the linear response theory. They appear to be amenable to Monte Carlo simulation methods.

In Chap. 9, the generalized hydrodynamic equations developed in Chaps. 3, 5, 6, and 7 are collected in the case of quasilinear and linear transport processes, and some of their applications are discussed in the case of dilute gas flows far removed from equilibrium—for example, hypersonic flows.

Chapters 2 through 9 constitute Part I for nonequilibrium theories in Volume 1. Any kinetic theory study requires knowledge of methods of equilibrium statistical mechanics. For this reason we have added some results made in our study on them in the past, which we consider should be useful for implementing the kinetic theory results presented in Part I. They are presented in Chaps. 10 and 11 making up Part II of Volume 1 of this work. The materials presented are not at all complete nor are they published as yet, but it is hoped that they may be found useful for some readers.

The relativistic kinetic theories are dealt with in Volume 2 for monatomic relativistic classical gas mixtures and a mixture of photons and material gases. Volume 2, consisting of three chapters, includes a relativistic kinetic theory of monatomic gases (Chap. 1) and a covariant formulation of kinetic theory of photons and material particles (Chap. 2), both of which are treated quantum mechanically, atleast, with respect to the collision integrals. The linear transport coefficients arising from the generalized hydrodynamic theory of photons and gases are calculated explicitly for a radiative system of photons interacting with material particles in the last chapter (Chap. 3) of the volume. The results of this chapter ascertain to some extents the validity of the relativistic kinetic theories presented in the previous two chapters of Volume 2.

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# **Part I**

## **Nonrelativistic Theories**

# Chapter 2

## Thermodynamic Theory of Irreversible Processes

In this work, we are interested in a molecular theory (i.e., statistical mechanics) of time- and space-dependent nonequilibrium (irreversible) processes in matter regarded as composed of many discrete particles. Statistical mechanics is a mathematical model theory of macroscopic observables of gross systems by means of which we hope to theoretically describe the collective state of matter consisting of an astronomical number of discrete constituent particles. By itself, such a mathematical model theory has no physical reality unless it is underpinned by an experimentally founded phenomenological theory of processes fully consistent with the laws of thermodynamics and until verified by experiments to a satisfactory accuracy. In this particular case of theory, it must be done so by an experimentally verifiable or verified phenomenological theory of thermodynamics of irreversible processes.

For the sake of simplicity without losing the essential features of the theory we will begin the discussion with simple fluids. Once this task is accomplished, it then would be comparatively simple to generalize the theory to complex fluids consisting of non-simple molecules. We will assume in this work that the substance does not have an intrinsic angular momentum. We also assume that the system consists of an  $r$ -component non-reactive mixture. Therefore, the case of chemical reactions is excluded at the beginning, but it would be easy to modify the theory at the appropriate places to include the case of chemical reactions. After completing the formulation of the phenomenological theory under the assumptions taken, we will point out where the necessary modifications must be made to include chemical reactions. In this chapter we give a short survey of the essential features of the theory of thermodynamics of irreversible processes, subject to the assumptions mentioned, that we consider necessary in developing a theory of statistical mechanics of irreversible processes in nonequilibrium systems.

In the present work the term thermodynamics used alone without qualifiers will be reserved for equilibrium systems and processes in systems in thermal equilibrium, unless stated otherwise or modified by a suitable qualifier such as an adjective irreversible.

## 2.1 The Zeroth Law of Thermodynamics

### 2.1.1 The Zeroth Law of Thermodynamics for Temperature

If two bodies of different degrees of warmth are put into contact, the bodies eventually reach thermal equilibrium at an equal degree of warmth. This phenomenon is exploited to quantify the measure of hotness or coldness of systems. The zeroth law of thermodynamics [1–3] provides a general procedure of quantifying temperature as a measure of warmth of a system (or body).

*If two systems A and B are, respectively, in thermal equilibrium with system C, then the systems A and B are also in thermal equilibrium.*

This literal statement can be expressed mathematically and more precisely: If there exists thermal equilibrium between A and C, there is a property called temperature  $\theta$  such that if

$$\theta_A = \theta_C \quad (2.1)$$

and similarly for systems B and C

$$\theta_B = \theta_C. \quad (2.2)$$

Then there follows the equality

$$\theta_A = \theta_B. \quad (2.3)$$

In practice, these relations supply a means to devise thermometers and therewith quantify temperature precisely, as described in detail in the literature on measurements of temperature [4]. In our discussion, we will use the absolute temperature scale established in thermometry.

Although the relations (2.1)–(2.3) are mathematically impeccable and are generally used in thermodynamics textbooks [3, 5], they are not too useful from the operational standpoint, especially for irreversible thermodynamics, because there is absent the concept of time duration in which thermal equilibrium is measured between the bodies. A more useful way of saying basically the same thing is to introduce a time interval  $\Delta\tau$  in which the establishment of thermal equilibrium is monitored to a sufficient accuracy. Thus we write instead

$$\frac{\Delta_{ac}\theta}{\Delta\tau} = 0, \quad \frac{\Delta_{bc}\theta}{\Delta\tau} = 0, \quad \frac{\Delta_{ab}\theta}{\Delta\tau} = 0, \quad (2.4)$$

where  $\Delta_{ac}\theta = \theta_a - \theta_c$  and so on. These expressions make it possible to deduce more practical means of measuring temperature and the meanings of temperature for systems where nonequilibrium processes may be in progress. For example, if the

heat transfer per unit time from body  $A$  to body  $C$  is  $Q_{ac}$  and the heat capacity is denoted by  $C_{ac}$  then we may write [6]

$$\frac{\Delta_{ac}\theta}{\Delta\tau} = \frac{\lambda_{ac}}{C_{ac}} Q_{ac}, \quad (2.5)$$

where  $\lambda_{ac}$  is the heat transfer coefficient which is, together with the heat capacity, a characteristic of the materials involved. The  $C_{ac}$  and  $\lambda_{ac}$  are non-vanishing quantities characteristic to the material considered. Therefore, for example, the first condition in (2.4) means that  $Q_{ac} = 0$  at thermal equilibrium of bodies  $A$  and  $C$ .

Determination of the parameter  $\theta$  requires thermal equilibrium between a body  $A$  and another body  $B$  (i.e., thermometer) if it is to be quantified as a well-defined value. However, the term ‘thermal equilibrium’ does not necessarily mean that body  $A$  itself is internally in thermodynamic equilibrium. It may, in fact, be a system where a number of irreversible processes are in progress at a value of temperature  $\theta$ , but the thermal equilibrium is between this body and another that is in contact with the former. The important point is that the value of  $\theta$  remains constant over the time scale  $\Delta\tau$  of measurement. This condition can be readily met if the irreversible processes in bodies  $A$  and  $B$  have reached a steady state at temperature  $\theta$  within  $\Delta\tau$ . An apt example is an animate body (e.g., a human body) where numerous irreversible processes occur, often in conditions far removed from equilibrium, yet the temperature of the body is a well-defined observable and, perhaps more precisely, a local observable, if it meets the condition expressed in (2.4). Another example is a metallic bar subjected to different temperatures at its two ends. It is well known that the temperature has a distribution between the two points. By this we mean that if infinitesimally thin imaginary slices of the metal are taken perpendicular to the direction of heat flow and each slice is put into thermal equilibrium with a thermometer, the recorded temperature values of the slices along the direction of heat flow will be different depending on the position. Even if this distribution changes in time owing to varying boundary conditions (temperatures), the distribution can be quantified as a function of time by a thermometer of an appropriate resolution power, if the relaxation of a transient temperature distribution is achieved within the time scale  $\Delta\tau$  of temperature measurement. The term thermal equilibrium used in stating the zeroth law of thermodynamics therefore must be understood in the sense that equilibrium is between the body and the thermometer over the time span  $\Delta\tau$  irrespective of possible irreversible processes within the bodies involved.

The consideration made here indicates that the zeroth law of thermodynamics is not limited to bodies in equilibrium, but also to bodies where irreversible processes may be in progress as long as the resolution power of the thermometric device permits a meaningful quantification of temperature through the relations in (2.1)–(2.3). This quantification of temperature is often used for a local elementary volume of the body at time  $t$  even if the body is in a nonequilibrium condition in another respect, and temperature becomes a field variable in such a case. If the irreversible

process of interest is such that the conditions in (2.4) are not satisfied within the time interval  $\Delta\tau$  achievable experimentally, then it is no longer possible to describe the process by means of a thermodynamic formalism on that time scale. In other words, thermodynamics has no meaning for such a process on the time scale in question.

There are other field variables to which laws similar to the zeroth law must be applied for their thermodynamic quantification. The collection of such kindred laws for the aforementioned intensive field variables may be simply called the ‘zeroth law of thermodynamics’ in a generalized sense. They will be discussed below. For this purpose, the notions of field variables are properly introduced and defined together with the notion of thermodynamic manifold, which is spanned by macroscopic observables that can be measured in principle in the laboratory on performing experiments on a set of irreversible processes. They include the conserved variables, which obey the conservation laws, and the nonconserved variables, which do not obey conservation laws, but instead are described by the constitutive equations (field equations) characteristic to the material considered.

**Definition 1** Thermodynamic manifold is spanned by the macroscopic variables

$$\mathfrak{P} := (\mathcal{E}, v, \mathfrak{c}_a, \widehat{\Phi}_a^{(s)} : a = 1, 2, \dots, r; s = 1, 2, 3, \dots).$$

The elements of this manifold  $\mathfrak{P}$  are internal energy density  $\mathcal{E}$ , volume  $v$ , concentrations (mass density fraction)  $\mathfrak{c}_a$  for conserved variables and additionally non-conserved variables (fluxes) density  $\widehat{\Phi}_a^{(s)}$ , if the fluid is monatomic. If the fluid has rotational degrees of freedom, the angular momentum and the related should be included. The species subscript  $a$  runs up to  $r$  for an  $r$ -component mixture, and the index for fluxes to  $s$ . The upper bound of index  $s$  can be as large as necessary depending on the fluid and processes of interest.

For a global system the manifold is expressible as

$$\mathfrak{P}_{\text{gl}} := (E, V, M_a, \Gamma_a^{(s)} : 1 \leq a \leq r; s \geq 1).$$

The volume integral of  $\rho \mathfrak{P}$  may be expressible by the integral

$$\mathfrak{P}_{\text{gl}} = \int_V d\mathbf{r} \rho \mathfrak{P}(\mathbf{r}, t). \quad (2.6)$$

The variables spanning manifold  $\mathfrak{P}$  are extensive in the sense that when multiplied by density  $\rho$  (i.e.,  $\rho \times \mathfrak{P}$ ) and integrated over the volume as in (2.6), they are extensive, being proportional to the mass of the system in  $V$ . In the conventional continuum mechanics the element  $v$  of manifold  $\mathfrak{P}$  is generally taken as specific volume<sup>1</sup>—inverse  $\rho$ —of the fluid. The thermodynamic manifold  $\mathfrak{P}$  alone is not

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<sup>1</sup>This viewpoint toward volume (per mole) should be modified because it does not have a molecular representation free from macroscopic variables in its definition. It will be found more appropriate to regard it as a mean volume allowed to molecules in a randomly distributed assembly of particles. Especially, if the fluid is away from equilibrium the latter concept is more appropriate since specific

sufficient to characterize the state of a system (i.e., matter) thermodynamically. A manifold conjugate to  $\mathfrak{P}$  is required for a thermodynamic description of it. It will be called the tangent manifold  $\mathfrak{T}$ , which is defined as follows:

**Definition 2** The manifold  $\mathfrak{T}$  conjugate to  $\mathfrak{P}$  is spanned by observables  $\mathfrak{T} := (T^{-1}, p, \hat{\mu}_a, X_a^{(s)} : a = 1, 2, \dots, r; s = 1, 2, 3, \dots)$ , each element in  $\mathfrak{T}$  being conjugate to the element of  $\mathfrak{P}$  in the same order of sequence of the two sets.

Here  $T := \theta, p, \hat{\mu}_a, X_a^{(s)}$ , as they stand, are merely mathematical symbols for quantities conjugate to the elements of  $\mathfrak{P}$  at the moment, but they will turn out to be, respectively, temperature, pressure, chemical potentials in a generalized sense, and generalized potentials. They are intensive macroscopic variables. The variable  $\theta, p$ , and  $\hat{\mu}_a$  are counterparts of their concepts known in equilibrium phenomena, but the quantity  $X_a^{(s)}$ , which we call the *generalized potential* for species  $a$  of process  $s$  in the nonequilibrium fluid, has no classical equivalent; they are new to the theory developed in this work. As a matter of fact, the operational meaning of parameter  $T$  has been already determined by means of the zeroth law of thermodynamics, but its quantitative determination in practice will be further clarified later. The phenomenological operational procedures for the remaining parameters  $p, \hat{\mu}_a$ , and  $X_a^{(s)}$  can be formalized by applying the idea underlying the zeroth law of thermodynamics for temperature discussed earlier. We thus have extensions of the zeroth law of thermodynamics to parameters spanning the tangent manifold  $\mathfrak{T}$ . Their irreversible thermodynamic meanings will be clarified as the theory of irreversible processes is further developed.

### 2.1.2 The Zeroth Law of Thermodynamics Extended

The parameters  $p, \hat{\mu}_a$ , and  $X_a^{(s)}$  and their temporal behaviors can be quantified through the relations [6] similar to (2.5)

$$\begin{aligned}\frac{\Delta p}{\Delta \tau} &= -\frac{\gamma}{\kappa} \frac{\Delta V}{\Delta \tau}, \\ \frac{\Delta \hat{\mu}_a}{\Delta \tau} &= \frac{\nu_a}{\vartheta_a} \frac{\Delta M_a}{\Delta \tau}, \\ \frac{\Delta X_a^{(s)}}{\Delta \tau} &= \frac{\lambda_{sa}}{\omega_{sa}} \frac{\Delta \Gamma_a^{(s)}}{\Delta \tau},\end{aligned}\tag{2.7}$$

where  $\Delta p = p_1 - p_2$ ,  $\Delta \hat{\mu}_a = \hat{\mu}_{a1} - \hat{\mu}_{a2}$ ,  $\Delta X_a^{(s)} = X_{a1}^{(s)} - X_{a2}^{(s)}$  with the subscripts 1 and 2 denoting the two systems in contact, and  $\kappa, \vartheta_a$ , and  $\omega_{sa}$  are the susceptibilities

(Footnote 1 continued)

volume is not the same as the mean volume per molecule. For the notion of molecular representation of mean volume per molecule, see Ref. [7] and also Ref. [8]. Modification of manifold  $\mathfrak{P}$  will be discussed in a later chapter in which volume transport phenomena are discussed.

of the quantities  $V$ ,  $M_a$ , and  $\Gamma_a^{(s)}$  to the changes  $\Delta p$ ,  $\Delta\hat{\mu}_a$ , and  $\Delta X_a^{(s)}$ , respectively. The time derivatives  $(\Delta V/\Delta\tau)$ ,  $(\Delta M_a/\Delta\tau)$ , and  $(\Delta\Gamma_a^{(s)}/\Delta\tau)$  are functions of the variables in manifolds  $\mathfrak{P}$  and  $\mathfrak{T}$ , which may be empirically determined. The  $\gamma$ ,  $\nu_a$ , and  $\lambda_{sa}$  are the associated transfer coefficients. The differential equations in (2.7) are the zeroth law analogs for pressure, chemical potentials, and generalized potentials. For, as  $(\Delta V/\Delta\tau)$ ,  $(\Delta M_a/\Delta\tau)$ , and  $(\Delta\Gamma_a^{(s)}/\Delta\tau) \rightarrow 0$ , the derivatives on the left vanish:

$$\begin{aligned}\frac{\Delta p}{\Delta\tau} &= 0, \\ \frac{\Delta\hat{\mu}_a}{\Delta\tau} &= 0, \\ \frac{\Delta X_a^{(s)}}{\Delta\tau} &= 0,\end{aligned}\tag{2.8}$$

and the systems in contact reach equilibrium with regards to the variables  $p$ ,  $\hat{\mu}_a$ , and  $X_a^{(s)}$ . They thereby can be quantified experimentally, just as the temperature is measured for the system with a thermometer as the other system, since one of the systems in contact may be the instrument of measurement for the intensive variable. It should be noted, however, that the time scale for  $X_a^{(s)}$  may not be necessarily the same as for those of the conjugate variables to the conserved variables, namely,  $T$ ,  $p$ , and  $\hat{\mu}_a$ . These time scales, however, are not known *a priori* in phenomenological theories, but should be found through experiments, or calculated theoretically if molecular theories are available for them. In any case, (2.5) and (2.7) empirically establish the evolution equations for elements of manifold  $\mathfrak{T}$ . In the subsequent chapters, their evolution equations will be found derived by means of a kinetic theory. They may be also regarded as constitutive equations of the material considered. The natures of these quantities will be clarified as the theory is developed.

To carry out unambiguous discussions of thermodynamic processes it is necessary to establish sign conventions on heat transfer and work performed. We take the following sign conventions:

**Convention on heat transfer:** *Heat transfer is counted negative if heat is given up by the system to the surroundings, and positive if heat is taken up by the system from the surroundings.*

**Convention on work:** *Work is counted as positive if it is done on the system by the surroundings, and negative if it is done on the surroundings by the system.*

## 2.2 The First Law of Thermodynamics

The first law of thermodynamics was a culmination of the understanding of what is meant by heat and its relation to energy. Referring the historical account of the genesis of the idea of equivalence of heat and energy to the literature [3, 9–11], we will simply state it below.

**The First Law of Thermodynamics** may be stated in two equivalent forms:

1. *The energy of an isolated system is constant.*
2. *It is impossible to construct a perpetual machine of the first kind—a machine that, working in a cycle, expends no heat to produce an equivalent work.*

The first statement due to Clausius [12] is a little obtuse, but, more precisely put, it means that the internal energy of an isolated system is conserved over a cycle of processes restoring the system to its original state.

The second equivalent statement, in essence due to Planck [13], can be given a mathematical representation as follows. For this purpose we need the concept of internal energy.

### 2.2.1 Internal Energy

To obtain a mathematical representation of the first law of thermodynamics in the case of an infinitesimal process let us denote the differential heat change by  $dQ$  and the differential work by  $dW$  accompanying the process. The first law of thermodynamics then implies that there exists a quantity called the internal energy  $E$  whose differential  $dE$ , under the sign conventions adopted earlier for heat and work, must be given by the expression

$$dE = dQ + dW, \quad (2.9)$$

whether the process is reversible or irreversible. Thus for a cyclic process<sup>2</sup> the first law of thermodynamics may then be expressible as a vanishing circular integral

$$\oint dE = 0, \quad (2.10)$$

where the cyclic integral is to be performed over the path of a cycle in the space of macroscopic variables characterizing the thermodynamic state of the system—namely, the thermodynamic manifold  $(\mathfrak{P} \cup \mathfrak{T})$ . For by the requirement of the first law the energy of the initial state must be exactly the same as the energy of the final state in the cyclic process. If time is used as a parameter for  $E$ , then the circular integral in (2.10) may be written as an integral over a period  $\tau_c$  of the cyclic motion in the thermodynamic manifold

$$\int_0^{\tau_c} dt \frac{dE}{dt} = 0. \quad (2.11)$$

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<sup>2</sup>A conservation law can be best stated by means of a cyclic process since the state of the system must be exactly restored on completion of the cyclic process and so must be the value of internal energy of the system. Vanishing cyclic integrals consequently play important roles in formulation of thermodynamics of irreversible processes.

It must be reiterated that the first law holds irrespective of whether the process is reversible or irreversible although in equilibrium thermodynamics it is tacitly restricted to a reversible process.

Mathematically, the vanishing circular integral (2.10) means that  $dE$  is an exact differential in the aforementioned thermodynamic manifold  $(\mathfrak{P} \cup \mathfrak{T})$ . Equation (2.10) is also equivalent to the statement that heat is a form of energy, since on substitution of (2.9) into (2.10) we obtain

$$Q = \oint dQ = - \oint dW = -W, \quad (2.12)$$

demonstrating that heat is equal to work (energy) with signs appropriately attached to them. It must be remarked that the mathematical representation (2.10) of the first law is for the global system performing the cycle, namely, the working substance in the whole system which goes through the cyclic process in question. We also note that  $dQ$  and  $dW$  are not by itself an exact differential<sup>3</sup> in the path of the cyclic change unlike  $dE$  is, but the sum of them,  $dE$ , is an exact differential according to the first law of thermodynamics, thus giving rise to (2.10).

## 2.2.2 Work

The meaning of work  $W$  or its differential form  $dW$  will depend on the mechanical task of the cycle (process) in question. It may consist of a number of components, including those attributable to irreversible processes involved. For example, a pressure–volume work may be performed on the system which changes the volume of the system under an external pressure, or work may be done by the system as it transfers a portion of mass to its surroundings under a material potential (chemical potential) between the system and the surroundings. Thus the system generally performs work on its surroundings under the influence of forces that drive changes in the extensive variables of  $\mathfrak{P}_{gl}$  or, more precisely, the densities of extensive variables of  $\mathfrak{P}$ . In all of these kinds of work there are always conjugate pairs of variables associated, one that drives the process of work, namely, the measure of the force, and the other that is the measure of the response by the system to the driving force. For example, in the case of pressure–volume work the pressure is the force and the volume change is the response by the system. In the case of work associated with a transfer of matter, the driving force is the chemical potential and the response is the change in mass. Similarly, in the case of work associated with nonconserved variables, *which is nonclassical*, it is possible to imagine that the system responds by adjusting the value of “flux”  $\Gamma_{ka}$  to the driving force  $X_{ka}$ . The driving forces are all in the set of variables belonging to  $\mathfrak{T}$  introduced earlier, which are conjugate to

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<sup>3</sup>In some textbooks in thermodynamics inexact differentials are denoted with a bar on the differential sign, e.g.,  $\bar{d}Q$  or  $\bar{d}W$ . In this work we do not adopt such a notation.

those in  $\mathfrak{P}$ . If the aforementioned driving forces are in operation, the work done by the system per unit time can be written in the form [6]

$$\frac{dW}{dt} = -p \frac{dV}{dt} + \sum_{a=1}^r \hat{\mu}_a \frac{d_e M_a}{dt} - \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} \frac{d_e \mathfrak{P}_a^{(s)}}{dt} + \frac{d_i W}{dt}. \quad (2.13)$$

The first term on the right represents the pressure–volume work; the second the work of mass transfer; the third the work of ‘transfer’ of  $\mathfrak{P}_a^{(s)}$ , between the system and the surroundings; and the last term the internal work which is not accounted for by the first three kinds of work listed. The sign of the mass transfer suggests that it is a work done on the system by the surroundings. This convention is chosen so that the resulting mathematical formalism agrees with the conventional classical theory in the limit of equilibrium. The time derivative  $d_e/dt$  denotes the transfer (or exchange) rate of the quantity between the system and the surroundings. Since extensive quantities such as  $M_a$  and  $\mathfrak{P}_a^{(s)}$  can also change within the system owing to its inherent internal processes, their total rates of change consist of two components, one arising from the transfer of the quantity mentioned earlier, and the other arising from its internal change [6]:

$$\frac{dA}{dt} = \frac{d_e A}{dt} + \frac{d_i A}{dt} \quad (A = M_a, \mathfrak{P}_a^{(s)}), \quad (2.14)$$

where  $d_i A/dt$  stands for the internal rate of change in  $A$ , which contains basically constitutive information on the substance of interest and  $d_e A/dt$  the rate of transfer of  $A$  between the system and the surroundings. The time derivatives  $d_e A/dt$  and  $d_i A/dt$  will be referred to as the transfer time derivative and the internal time derivative of  $A$ , respectively.

In the conventional theory of macroscopic processes and thermodynamics there is no physical mechanism taken into consideration for an internal volume change and hence the transfer time derivative of volume  $d_e V/dt$  is simply equal to the total time derivative  $dV/dt$  in the case of  $V$ . Therefore there is no need to express the volume derivative as in (2.14) in the conventional theory of thermodynamics and attendant hydrodynamics. This viewpoint would be certainly plausible if we knew nothing of the fluid structure in terms of molecules and the volume inherent to molecules constituting the matter beyond the volume of the hard core of the molecules. If this average inherent volume is called the molar volume of the fluid molecule, then it is reasonable to examine the internal volume change of the fluid. The overall volume derivative of the fluid may be also written as in (2.14). The internal volume then must be regarded as belonging to the submanifold of nonconserved variables of manifold  $\mathfrak{P}$  in the terminology introduced in this work.<sup>4</sup>

<sup>4</sup>This modification of the viewpoint can be implemented if the notion of volume allotted to a molecule is adopted [7] via the Voronoi volume. This notion will be more easily understood if the theory is formulated as a molecular theory as will be done in a later chapter on irreversible processes

Likewise, the heat transfer rate associated with the internal energy conservation law will be denoted by  $dQ_E/dt$  by attaching the subscript  $E$  to  $Q$  because at this point in development, especially if the processes are irreversible, there is no compelling reason that the heat transfer rate in question is necessarily the same as the ‘heat transfer rate’ that will appear in the second law of thermodynamics in the form of compensated heat (see the subsection on the second law of thermodynamics below), which will be denoted by  $dQ/dt$ . Since the two quantities are not necessarily the same, we set [14]

$$\frac{dQ}{dt} = \frac{dQ_E}{dt} + \frac{dQ_n}{dt}. \quad (2.15)$$

The difference  $dQ_n/dt$  must be elucidated by some means, and it will be done when the second law of thermodynamics is discussed. It should be remarked here that this internal transfer rate  $dQ_n/dt$  is essentially in the same level as of other internal changes  $d_i A/dt$  mentioned earlier and, in fact, would be related to them in irreversible thermodynamics.

With the work made more explicit about the nature of its composition as in (2.13) and with the heat transfer rate denoted as indicated, the first law of thermodynamics may be expressed in the form

$$\frac{dE}{dt} = \frac{dQ_E}{dt} - p \frac{dV}{dt} + \sum_{a=1}^r \hat{\mu}_a \frac{d_e M_a}{dt} - \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} \frac{d_e \mathfrak{P}_a^{(s)}}{dt} + \frac{d_i W}{dt}. \quad (2.16)$$

Albeit restricted to within the bounds of the operational meanings of  $p$ ,  $\hat{\mu}_a$ , and  $X_{ka}$ , the form (2.16) will be useful for developing a generalized form of thermodynamics for global processes in a finite bounded system; see Ref. [15]. By using (2.15) the differential form (2.16) for a global irreversible process may be written as

$$\begin{aligned} \frac{dE}{dt} = & \frac{dQ}{dt} - p \frac{dV}{dt} + \sum_{a=1}^r \hat{\mu}_a \frac{d_e M_a}{dt} - \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} \frac{d_e \mathfrak{P}_a^{(s)}}{dt} \\ & + \left( \frac{d_i W}{dt} - \frac{dQ_n}{dt} \right). \end{aligned} \quad (2.17)$$

Before closing this subsection, we would like to examine the notion of ‘work of the task’. A work will be called the ‘work of the task’ if it is the mechanical work specifically designed for a cycle to perform. A particular work of the task is generally accompanied by other kinds of work which are not intended when the cycle of interest is designed for the task of work in question. For example, if a pressure–volume work is the work of the task, it is generally unavoidable to have the working fluid heated

(Footnote 4 continued)

in condensed phase where volume transport is explicitly taken into account. In phenomenological formulation, the notion must be formally accepted, but unfortunately would remain abstract.

by the viscous heating effect accompanying the compression or dilatation of the fluid, although it may be made as small as possible by a careful design of the device performing the cycle. We illustrate this point with the example of pressure–volume work for the work of the task. Over a cycle it is given by

$$W_{\text{task}} = - \oint dV p. \quad (2.18)$$

On substitution of the pressure–volume work term from (2.17) there follows the equation

$$W_{\text{task}} = -Q - W_{\text{ua}}, \quad (2.19)$$

where

$$W_{\text{ua}} = \oint (d_i W - dQ_n) + \sum_{a=1}^r \oint \hat{\mu}_a d_e M_a - \sum_{a=1}^r \sum_{s \geq 1} \oint X_a^{(s)} d_e \mathfrak{P}_a^{(s)} \quad (2.20)$$

and  $Q$  may be expressed as a difference between the input  $Q'_1$  and the output  $Q'_2$  of heat

$$Q = Q'_1 - Q'_2. \quad (2.21)$$

Therefore if it is possible to identify  $Q$  in (2.21) with that in (2.12) we find

$$W = W_{\text{task}} + W_{\text{ua}}. \quad (2.22)$$

This suggests that caution must be exercised when the first law of thermodynamics is used to calculate the work of the task in terms of heat, if there are irreversible processes involved in the course of a cycle. The expression (2.20) for unavailable work clearly indicates that its precise meaning depends on what  $W_{\text{task}}$  is. For example, if  $W_{\text{task}}$  is that of transferring a mass involving the third term on the right hand side of (2.17), then the second integral on the right hand side of (2.20) for  $W_{\text{ua}}$  is replaced by the circular integral

$$- \oint dV p,$$

the pressure–volume work, and hence the meaning of  $W_{\text{ua}}$  is accordingly altered from that of the unavailable work given in (2.20). Therefore, the unavailable work to a given task can become the available work to another task.

In equilibrium thermodynamics the unavailable work does not appear in the formulation of the theory, because *reversible processes considered in equilibrium thermodynamics are precisely the ones that have a vanishing unavailable work*, but when irreversible processes are considered, the notion of unavailable work becomes relevant and worth recognizing its presence to examine its nature.

### 2.2.3 Local Forms of Evolution Equations

The variables spanning manifold  $\mathfrak{P}$  can be endowed their evolution equations and more precise mathematical meanings in this and following subsections. These evolution equations, especially the balance equations for conserved variables, are well established in fluid (or continuum) mechanics, quite apart from the question of irreversible thermodynamics.

#### 2.2.3.1 Local Forms of the Conservation Laws

Many macroscopic processes in nature are described from the local theory viewpoint. Typical examples will be various flow processes in fluid mechanics where local field variables of fluids are assumed to obey partial differential equations—field equations. Since flow phenomena in fluids must obviously be subjected to thermodynamic laws as any macroscopic phenomena should be, it is necessary to cast the internal energy conservation law, namely, the first law of thermodynamics, in local form. In addition to the first law of thermodynamics, the system must obey the mass conservation law and the momentum conservation law as a continuum theory extension of Newton's law of motion. This is easily done by following the method of continuum mechanics [16]. We will simply accept them as phenomenological expressions for the conservation laws and present them as a proposition without going through the details of their derivations.

**Proposition 1** *For non-reacting fluids without a rotational angular momentum the local conservation laws hold for the conserved variables in the following forms: mass:*

$$\rho d_t v = \nabla \cdot \mathbf{u} \quad \text{or} \quad \frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{u}), \quad (2.23)$$

*mass fractions:*

$$\rho d_t c_a = -\nabla \cdot \mathbf{J}_a, \quad (2.24)$$

*momentum:*

$$\rho d_t \mathbf{u} = -\nabla \cdot \mathbf{P} - \rho \hat{\mathbf{F}}, \quad (2.25)$$

*energy:*

$$\rho d_t \mathcal{E} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \hat{\mathbf{F}}_a \cdot \mathbf{J}_a. \quad (2.26)$$

*The symbol  $d_t$  stands for the substantial time derivative*

$$d_t := d/dt = \partial/\partial t + \mathbf{u} \cdot \nabla \quad (2.27)$$

with  $\nabla = \partial/\partial\mathbf{r}$ . In this description, time derivative is calculated in the frame of reference moving with the fluid particle velocity.<sup>5</sup> Henceforth the symbol  $d_t$  is reserved for the substantial time derivative.

In the conservation laws presented,  $v = \rho^{-1}$  is the specific volume of the fluid;  $\rho$  is the (mass) density;  $\mathbf{u}$  is the fluid velocity;  $\mathbf{c}_a$  is the mass fraction

$$\mathbf{c}_a = \rho_a / \rho \quad (2.28)$$

with  $\rho_a$  denoting the (mass) density of species  $a$ ;

$$\mathbf{J}_a = \rho_a (\mathbf{u}_a - \mathbf{u}), \quad (2.29)$$

with  $\mathbf{u}_a$  denoting the velocity of species  $a$ ,  $\mathbf{J}_a$  is the diffusion flux of species  $a$ ;  $\mathbf{Q}$  is the heat flux;  $\widehat{\mathbf{F}}_a$  is the external (body) force per mass density of species  $a$  at position  $\mathbf{r}$ ; and

$$\widehat{\mathbf{F}} = \sum_{a=1}^r \mathbf{c}_a \widehat{\mathbf{F}}_a, \quad (2.30)$$

the total force density. The internal energy density  $\mathcal{E}$  is related to  $E$  by the integral

$$E = \int_V d\mathbf{r} \rho \mathcal{E}(\mathbf{r}, t), \quad (2.31)$$

where the integral is over the volume  $V$  of the fluid. If the assumption of simple fluids—fluids with no internal molecular degrees of freedom such as rotational or vibrational degrees of freedom—is removed, the conserved variables should include the angular momentum and the conservation law, i.e., the angular momentum balance equation.

The pressure tensor  $\mathbf{P}$  can be decomposed into species-component pressure tensors  $\mathbf{P}_a$ :

$$\mathbf{P} = \sum_{a=1}^r \mathbf{P}_a; \quad (2.32)$$

and, similarly, the heat flux  $\mathbf{Q}$  into species-component heat fluxes  $\mathbf{Q}_a$ :

$$\mathbf{Q} = \sum_{a=1}^r \mathbf{Q}_a. \quad (2.33)$$

<sup>5</sup>It should be noted that fluid particle velocity is not the velocity of a molecule comprising the fluid. It is the velocity of the packet of fluid in an elementary volume of fluid at position  $\mathbf{r}$  and time  $t$ . From the molecular theory viewpoint it is the ensemble average of molecular velocities in a sufficiently small volume around the position  $\mathbf{r}$  at time  $t$ . For its molecular theory definition, see Chaps. 3, 5, 6, and 7 of this work.

Equations (2.23)–(2.26) are the local forms for the mass, mass fractions, momentum, and internal energy conservation laws, respectively. These are the field equations for local macroscopic field variables  $v$  or  $\rho$ ,  $c_a$ ,  $\mathbf{u}$ , and  $\mathcal{E}$ . We notice that these field equations contain variables  $\mathbf{J}_a$ ,  $\mathbf{P}$ , and  $\mathbf{Q}$  in addition to the conserved variables, which are so called by the terminology since they obey the conservation laws or balance equations without a dissipation term in them.

### 2.2.3.2 Local Forms for the Evolution Equations of Nonconserved Variables

The additional variables  $\mathbf{J}_a$ ,  $\mathbf{P}$ , and  $\mathbf{Q}$  are examples of nonconserved variables which we have collectively denoted by  $\Phi_a^{(s)}$ ; they span the manifold  $\mathfrak{P}$  defined in the previous subsection. In the theory of linear irreversible processes or in the conventional classical hydrodynamics they are specified by means of constitutive relations characterizing the processes in the substance of interest. The constitutive relations traditionally used in the steady-state linear theory [17, 18] of irreversible processes are not necessarily the most general forms to describe evolutions of the nonconserved variables. There is a considerable body of experimental and kinetic theory evidence that they require suitable generalizations for non-steady and nonlinear regimes. Examples for such necessity can be found in hydrodynamics, rheology [19] and other nonlinear phenomena in semiconductor physics [20], heat transport [21], plasmas [22], etc., covering the entire gamut of macroscopic physics and engineering science. The nonconserved variables  $\Phi_a^{(s)} = \rho \widehat{\Phi}_a^{(s)}$  where  $1 \leq a \leq r$  and  $s \geq 1$ , for which the upper bound of  $s$  is finite in practice, but can be left unspecified at this point in development, are suitably ordered as follows:

$$\begin{aligned}\Phi_a^{(1)} &:= \boldsymbol{\Pi}_a = \frac{1}{2}(\mathbf{P}_a + \mathbf{P}_a^t) - \frac{1}{3}\boldsymbol{\delta}\text{Tr}\mathbf{P}_a, \\ \Phi_a^{(2)} &:= \Delta_a = \frac{1}{3}\text{Tr}\mathbf{P}_a - p_a, \\ \Phi_a^{(3)} &:= \mathbf{Q}'_a = \mathbf{Q}_a - \widehat{h}_a \mathbf{J}_a, \\ \Phi_a^{(4)} &:= \mathbf{J}_a, \\ &\text{etc.}\end{aligned}$$

Here the superscript  $t$  stands for transpose of the tensor; the boldface  $\boldsymbol{\delta}$  denotes the unit second rank tensor;  $p_a$  the *hydrostatic* pressure of species  $a$ ; and  $\widehat{h}_a$  the enthalpy per unit mass of species  $a$ . The set of nonconserved variables can include as many nonconserved variables as necessary for proper description of the system in hand. The variable  $\Phi_a^{(4)}$  is regarded as nonconserved variable since its evolution equation is accompanied by energy dissipation represented by a source term. In some cases, the nonconserved variables may change on different, usually faster time scales and shorter spatial scales than the conserved variables. Since we are looking for a general formalism for macroscopic phenomena in this work, the conserved and nonconserved

variables will be provisionally put on formally equal footing with regard to time and spatial variables. On actual applications of the theory thus formulated, we may take into consideration the relative magnitudes of time and spatial scales of the two classes of field variables and develop approximate theories therewith. This turns out to be usually the case in practice. With this proviso, we now make the following proposition for the evolution equations for nonconserved variables  $\Phi_a^{(s)}$ . Since the nonconserved variables are also field variables, they obey partial differential equations, which take forms of balance equation, but with a source term, which will turn out related to energy dissipation because they are not conserved in time; it is a distinguishing feature from the conserved variables. It will be found convenient to assume a general form for the evolution equation for  $\Phi_a^{(s)} = \rho \widehat{\Phi}_a^{(s)}$  as below:

**Proposition 2** *The nonconserved variables  $\widehat{\Phi}_a^{(s)}$  ( $s \geq 1$ ;  $1 \leq a \leq r$ ) in manifold  $\mathfrak{P}$  obey the evolution equation*

$$\rho d_t \widehat{\Phi}_a^{(s)} = -\nabla \cdot \psi_a^{(s)} + \mathcal{Z}_a^{(s)} + \Lambda_a^{(s)}, \quad (2.34)$$

where  $\psi_a^{(s)}$  is the flux of  $\Phi_a^{(s)}$ ,  $\mathcal{Z}_a^{(s)}$  is called the kinematic term, which contains, at least, a term driving the process  $\Phi_a^{(s)}$  among other terms that nonlinearly depend on nonconserved variables and gradients of the conserved variables, and  $\Lambda_a^{(s)}$  is called the dissipation term which is responsible for energy dissipation arising from the process  $\Phi_a^{(s)}$ . The dissipation term may also be a nonlinear function of variables of the thermodynamic manifold  $\mathfrak{P}$  and its tangent manifold  $\mathfrak{T}$ .

The dissipation terms are generally algebraic functions of conserved and nonconserved variables, satisfying the constraint imposed by the local form of the second law of thermodynamics. They also depend on material parameters such as transport coefficients, density, pressure, etc. Since the kinematic and dissipation terms have different physical origins and characteristics, we have put them as separate terms in the evolution equation (2.34). It is possible to give statistical mechanical definitions for the kinematic and dissipation terms, as will be shown in later chapters on kinetic theory, and calculate them in terms of molecular properties of the fluid. However, their explicit forms in terms of conserved and nonconserved variables are not necessary for the formal theory of irreversible processes we develop axiomatically in this chapter. As will be seen, they will be subject to the constraint of *the second law of thermodynamics*. In this sense, the theory of irreversible processes developed here is fully consistent with the second law of thermodynamics at the formal theory level. Exploiting this thermodynamic consistency and, particularly, making use of the minimum principle provided by the second law of thermodynamics, we may develop a variational method of determining the kinematic and dissipation terms from the standpoint of thermodynamics of irreversible processes.

It should be noted that the linearized versions of the evolution equations for the stress tensor and heat flux were known to Maxwell [23] as transfer equations on which he based his calculation of transport coefficients under the steady-state assumption, and Chapman [24] later used their steady state form in his kinetic theory

of linear transport processes in dilute gases on the basis of the Boltzmann kinetic equation. This aspect will be discussed explicitly in chapters on kinetic theories. It is remarkable to note that the phenomenological theory of irreversible processes can make progress if the laws of thermodynamics are taken advantage of for the kinetic theory of irreversible processes. Here lies the crucial value of the thermodynamic theory of irreversible processes developed axiomatically in this chapter.

## 2.3 The Second Law of Thermodynamics

Unlike the first law of thermodynamics, which does not dictate the direction in which a reversible or irreversible macroscopic process proceeds, the second law of thermodynamics endows spontaneous natural processes with a quality of progressing in a preferred direction in time. This law is a summary of inviolable experimental facts of the unidirectional evolution in which spontaneous macroscopic processes in nature progress. It is presented as an axiom in this work. For a more detailed discussion on it the reader may be referred to *The Second Law of Thermodynamics* edited by Kestin [25] in which history and discussions of the law are given in detail.

### 2.3.1 Carnot Theorem

Historically, the unidirectional temporal evolution of natural phenomena is phrased in a theorem proposed by Carnot [26] as a conclusion of his study of cycles of heat engines. It can be stated as follows<sup>6</sup>:

#### Carnot Theorem

*The efficiency of reversible Carnot cycles is independent of the modes of operation and the materials used and is maximum. It depends only on the temperatures of the heat reservoirs.*

If the efficiency of a reversible cycle is denoted by  $\eta_{\text{rev}}$  and that of an irreversible cycle by  $\eta_{\text{irr}}$ , then regardless of the materials used and the modes of operation

$$\eta_{\text{rev}} \geq \eta_{\text{irr}} \quad \text{and} \quad \eta_{\text{rev}} = \eta'_{\text{rev}}.$$

The  $\eta_{\text{rev}}$  is a function of only the temperatures of the heat reservoirs of the Carnot cycle, and the prime denotes another reversible cycle.

Suppose two cycles (e.g., engines) of the same working material and mode of operation which operate between two heat reservoirs of different temperatures. One cycle is reversible and the other is irreversible. The reversible cycle does work  $W_{\text{rev}}$

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<sup>6</sup>This theorem is proved in Chap. 4, Ref. [3]. See also H. Poincaré, *Thermodynamique* (Georges Carré, Paris, 1892).

whereas the irreversible cycle does work  $W$ , both having received the same amount of heat from the higher temperature heat reservoir. The Carnot theorem then implies that  $W_{\text{rev}} \geq W$ . Therefore, the following can be concluded [3] as a corollary to the Carnot theorem:

*The reversible work is a maximum work, and if a cycle is irreversible, the entirety of the work that can be done by the reversible process is not all available to the irreversible cycle.*

If that amount of unavailable work is denoted by  $W_{\text{ua}}$  as we have earlier, then the reversible work  $W_{\text{rev}}$  may be decomposable into the form

$$W_{\text{rev}} = W + W_{\text{ua}} \quad (2.35)$$

for the pair of irreversible and reversible cycles under consideration. This unavailable work is intrinsic to irreversible cycles in general and was recognized in essence as the *uncompensated heat* (originally called uncompensated transformation value) by Clausius [12].

### 2.3.2 Clausius and Kelvin Principles

The theorem of Carnot led Clausius [27] and Kelvin (Thomson) [28] to formulate the second law of thermodynamics as follows.

#### Clausius Principle

*It is impossible to transfer heat from a colder to a hotter body without converting at the same time a certain amount of work into heat at the end of a cycle of change.*

#### Kelvin Principle

*In a cycle of processes it is impossible to transfer heat from a heat reservoir and convert it all into work without transferring at the same time a certain amount of heat from a hotter to a colder body.*

It can be shown [1] that these two principles are equivalent<sup>7</sup> to each other and also to the Carnot theorem. We note that the second law of thermodynamics is phrased in terms of, and for, cycles only, and for no others. Since even the present form of the second law has not as yet been given a full mathematical expression taking the uncompensated heat into consideration, it must be the goal for theory of irreversible processes before an alternative or amended form of the second law is proposed or formulated, as has been occasionally seen in the literature. Any amended form could

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<sup>7</sup>It must be recognized that the presence and notion of unavailable work in an irreversible cycle is not as apparent in the Clausius and Kelvin principles as in the Carnot theorem, although they are equivalent to the Carnot theorem. In the end, it was the Carnot theorem that Clausius used to formulate the inequality named after him.

be liable to give rise to an unwarranted confusion in the as-yet uncompleted field of thermodynamic theory of irreversible processes.

Either one of the aforementioned literally stated forms of the second law of thermodynamics must be represented in a precise mathematical form, so that it can be used as the starting point of a thermodynamic theory of processes. Such a representation was made feasible by a combination of two important ingredients: One is Kelvin's recognition that the Carnot theorem can be the basis of a universal thermodynamic temperature scale. The other is Clausius's representation of the Carnot theorem for a Carnot cycle in the following manner.

Imagine the aforementioned pair of irreversible and reversible cycles operating between two heat reservoirs of temperatures  $T_1$  and  $T_2$  where  $T_1 > T_2$ . The two cycles take the same amount of heat  $Q_1$  from the higher temperature reservoir and perform work. The irreversible cycle does work  $W$ , discharging heat  $Q_2$  to the lower temperature reservoir, whereas the reversible cycle does a maximum work  $W_{\text{rev}}$ . The efficiency of the reversible cycle is

$$\eta_{\text{rev}} = \frac{W_{\text{rev}}}{Q_1} = 1 - \frac{T_2}{T_1},$$

whereas the efficiency of the irreversible cycle is

$$\eta_{\text{irr}} = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}.$$

By the Carnot theorem

$$1 - \frac{Q_2}{Q_1} \leq 1 - \frac{T_2}{T_1}. \quad (2.36)$$

Clausius [12] rearranges (2.36) to the form

$$-\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \geq 0 \quad (2.37)$$

and argues that this inequality can be cast in an integral form by imagining a series of infinitesimal Carnot cycles (see, for example, Sect. 4.4, Ref. [3].):

$$-\oint \frac{dQ}{T} \geq 0, \quad (2.38)$$

for which the sign convention for heat transfer introduced earlier is used.

An infinitesimal Carnot cycle is the cycle that operates between two heat reservoirs of an infinitesimally small temperature difference. The terminology *infinitesimal* does not mean that the actual physical size of the device performing the cyclic process is infinitesimal; it refers to the temperature difference of the heat reservoirs involved. Note that the temperature  $T$  refers to the heat reservoir at the point in question in the series of infinitesimal cycles making up the entire cycle under consideration. The

$dQ$  is what Clausius called *the compensated heat* which is the heat transfer involved between the system and its surroundings. Clausius also recognized another quantity which is nowadays called *the uncompensated heat* that accompanies a cyclic process when the process is irreversible. This quantity vanishes if the process is reversible. This is an amount of heat that is intrinsic to the system when the system undergoes the irreversible cyclic process in question. It is one of the central quantities that must be elucidated<sup>8</sup> in order to formulate a thermodynamic theory of irreversible processes.

### 2.3.3 Clausius Inequality

Following Clausius, we denote the uncompensated heat by  $N$  and express the Clausius inequality (2.36) as

$$N = - \oint \frac{dQ}{T} \geq 0. \quad (2.39)$$

The uncompensated heat  $N$  is always positive and vanishes only if the process is reversible, and its positivity can be regarded as an expression of the second law of thermodynamics. Clausius [12] suggested to calculate  $N$  by using (2.39) where the circular integral must be computed along an irreversible path, which includes at least one irreversible step. His suggested procedure is mathematically correct since it maintains intact the relation between the compensated and uncompensated heats. However, it ignores his original recognition that the compensated heat  $dQ/T$  and the uncompensated heat  $N$  are two physically distinctive quantities, which cannot tell us about each other.

*Here, we keep Clausius's original understanding of the uncompensated and compensated heats as two independent entities of a natural process and try to elucidate them in terms of the system properties for the irreversible process involved.* As a first step to initiate this endeavor, let us recall that there are two independent physical entities of similar kinds appearing in the guise of work-related quantities in the corollary to the Carnot theorem. According to this corollary, the reversible work is larger by  $W_{ua}$  than the irreversible work  $W$  for the pair of reversible and irreversible cycles in question and, furthermore,  $W_{ua}$  is positive semidefinite, vanishing only if the cycle is reversible. If this unavailable work is taken into account, the Carnot theorem may be written as an equation instead of an inequality as follows:

<sup>8</sup>In this connection, I would like to quote a passage in an article by I. Prigogine in Science **201**, 777 (1978) where he states “150 years after its formulation the second law of thermodynamics still appears to be more a program than a well-defined theory in the usual sense, as nothing precise (except the sign) is said about the  $S$  production”. In view of the fact that entropy was not defined for irreversible processes by Clausius, we interpret that the  $S$  production here is meant for the uncompensated heat despite the notation  $S$  used for entropy in the aforementioned paper. In fact, Prigogine's use of terminology appears to be oblivious to the genesis of the notion of Clausius entropy  $S$ , as is evident from the discussion given below.

$$\frac{T_2}{T_1} = \frac{Q_2}{Q_1} - \frac{W_{\text{ua}}}{Q_1}. \quad (2.40)$$

This means that there exists a positive semidefinite quantity  $N = W_{\text{ua}}/T_2$  such that

$$\frac{Q_2}{T_2} = \frac{Q_1}{T_1} + N. \quad (2.41)$$

This  $N$  vanishes for reversible processes by the Carnot theorem. By using the notion of infinitesimal cycles and the sign convention for heat transfer introduced earlier, we may cast this equation in the form

$$N = - \left( \frac{Q_1}{T_1} - \frac{Q_2}{T_2} \right) = - \sum_i \frac{Q_i}{T_i}, \quad (2.42)$$

which gives rise to (2.39) when passage is made from the sum to the cyclic integral. Clearly, the uncompensated heat  $N$  appears as a quantity related to the work unavailable to the irreversible cycle for the purpose of its task when the work is compared with the work of the reversible cycle. The difference between available work and unavailable work is evidently intrinsic to the system and the irreversible cycle in hand, and the unavailable work should be treated as a separate entity from the compensated heat. It is reasonable to consider  $W_{\text{ua}}$  an energy dissipation to the task of work in question, as we have mentioned in an earlier subsection of this chapter.

### 2.3.4 Clausius Entropy

Since a precise mathematical representation for the uncompensated heat was not known to Clausius except that there should exist such a quantity, he limited the consideration to reversible processes for which  $N = 0$  identically, and developed thereby the theory of equilibrium thermodynamics of reversible processes, namely, thermostatics, with which we are all familiar at present through numerous textbooks on equilibrium thermodynamics. If  $N$  is thus set equal to zero for a reversible cyclic process,<sup>9</sup> then there holds the equality

$$\oint \frac{dQ}{T} = 0, \quad (2.43)$$

which implies that  $dQ/T$  must be an exact differential in  $\mathfrak{P} \cup \mathfrak{T}$  (thermodynamic manifold) for reversible processes and there exists a state function  $S_c$ . Clausius called

<sup>9</sup>Reversible processes are traditionally defined as those of quasistatic processes which are in continuous equilibrium with the surroundings, but it is more mathematically precise to define them as quasistatic processes for which  $N = 0$ . This will be the definition of reversible processes used throughout in this work.

it the entropy [12] of the system and defined by the differential relation

$$dS_e = \left( \frac{dQ}{T} \right)_{\text{rev}}, \quad (2.44)$$

so that

$$\oint dS_e = 0. \quad (2.45)$$

In other words, in mathematical terminology  $dS_e$  is an exact differential in the thermodynamic (variable) space characteristic of the reversible cyclic process. The differential form combined with the differential form (2.9) for the first law of thermodynamics is called the equilibrium Gibbs relation

$$dS_e = T^{-1} (dE - dW). \quad (2.46)$$

It is the fundamental equation of equilibrium thermodynamics. It is important to keep in mind that *the Clausius entropy  $S_e$  is defined for reversible processes only, but not for a nonequilibrium process. Such an entropy will be called the Clausius entropy in this work in order to distinguish it from the Boltzmann entropy defined by the  $H$  theorem in his kinetic theory.*

Before proceeding further to consider irreversible processes in a general context, we briefly mention the gist of the theory of linear irreversible processes as formulated by Onsager [29], Meixner [30], Prigogine [31], and so on. First, by interpreting the differentials of macroscopic observables in (2.46) to mean their substantial time derivatives, the equilibrium Gibbs relation for the Clausius entropy  $S_e$  is cast into a local form which may be written as

$$d_t S_e = T^{-1} (d_t \mathcal{E} - d_t \mathcal{W}), \quad (2.47)$$

where  $S_e$ ,  $\mathcal{E}$ , and  $\mathcal{W}$  are local densities of the Clausius entropy, internal energy, and work, respectively. It is important to recognize that the derivatives in (2.46) are interpreted as substantial time derivatives<sup>10</sup> in the local form (2.47), and it implies that the macroscopic quantities vary in space-time despite the fact that the Gibbs relation is originally obtained for systems in equilibrium, which is a term connoting homogeneity in space and time. The theory of linear irreversible processes [17, 29–31] assumes the validity of the local equilibrium Gibbs formula (2.47) which is combined with the conservation laws presented earlier for the conserved variables appearing in the right-hand side of (2.47). *This assumption is called the local equilibrium hypothesis.* Upon combining this assumption with a set of linear thermodynamic force-flux relations as the constitutive relations for fluxes in the conservation laws—such as stress tensors, heat fluxes, diffusion fluxes—we obtain in essence the thermodynamic theory of linear irreversible processes. The resulting field equations are the

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<sup>10</sup>This interpretation of differentials is usually made in linear theory of irreversible thermodynamics. See [17, 30, 31].

classical hydrodynamic equations, namely, the Navier–Stokes, the Fourier, and the Fick equation in the conventional hydrodynamics [32, 33]. Therefore it may be said that the classical hydrodynamics is within the framework of the thermodynamics of linear irreversible processes.

Since the Clausius entropy can be *defined only for reversible processes* it is not clear under what conditions it is permissible to assume the local equilibrium hypothesis (2.44) when the process in question is not reversible. The thermodynamics of linear irreversible processes at first glance appears to be contradictory to the definition of the Clausius entropy. This question was first raised by Meixner [34] who was also one of the formulators of the theory of linear irreversible processes. His attempt to resolve this vexing question was not successful, however. It is one of the important objectives for the present work to find a solution to the aforementioned question.

Since the early 1960's there have appeared propositions [35–44] in varying forms that extend the thermodynamic space for systems undergoing irreversible processes to include nonconserved variables as a generalization of the local equilibrium hypothesis to nonequilibrium systems. The differential form for the nonequilibrium entropy, *which these theories postulate*, is called the extended Gibbs relation and serves as the starting equation for the subject field of extended irreversible thermodynamics.<sup>11</sup> This postulate for the extended Gibbs relation for irreversible processes, however, has not been shown to be on the support of the foundations of the thermodynamic laws although there have been efforts [35, 37, 40, 41, 43, 44] to provide its kinetic theory basis in terms of the well-known  $H$  theorem of Boltzmann. However, it becomes evident on careful examination of the properties of the Boltzmann entropy that the  $H$  theorem of Boltzmann itself should not simply be taken as an equivalent of the second law of thermodynamics as often and uncritically done in the literatures cited earlier of kinetic theory and irreversible thermodynamics. This statement will be

<sup>11</sup>There are basically two different versions of extended irreversible thermodynamics: one class of versions can be found in Refs. [36, 37, 41, 43, 44] and the other in Refs. [6, 35, 45, 46] and this work. In the former, it is assumed that there exists a nonequilibrium entropy which is a state function in the thermodynamic space and the nonequilibrium entropy is statistically represented by approximations of the Boltzmann entropy or its dense fluid generalization or the information entropy for dynamical systems, without a support of a kinetic equation. In the latter class (i.e., in Refs. [6, 45, 46]), it is shown from the second law of thermodynamics that there exists a quantity called *compensation function* (renamed to calortropy in this and earlier work) and its differential is an exact differential in the thermodynamics space by virtue of the second law. The compensation function, however, is not the same as the Boltzmann entropy appearing in the kinetic theory of dilute gases by Boltzmann. Since thermodynamics of irreversible processes must be securely founded on the thermodynamic laws, it is crucial to show that the basic equations are consistent with the thermodynamic laws and, for example, the extended Gibbs relation is equivalent to the second law of thermodynamics. An assumption for such a basic equation is not acceptable if the resulting theory will have anything to do with the thermodynamic laws in accounting for macroscopic processes in nature. Neither can the thermodynamic laws afford approximate representations. The basic thermodynamic equation in the formulation made in Refs. [6, 46] and in this work is a rigorous consequence of the second law of thermodynamics which mathematically extends equilibrium thermodynamics that is certainly endowed with a physical basis supported by the second law; it is not an assumption as in Refs. [35–44].

supported by the discussion in the subsequent chapters of this work when we discuss the kinetic theory foundations of thermodynamics of irreversible processes.

Besides this point, the extended Gibbs relation for the nonequilibrium entropy raises various subtle questions as to what we really mean by the nonequilibrium entropy; if it really does exist as assumed in the extended irreversible thermodynamics mentioned; whether its differential form is indeed exact in the thermodynamic space taken for description of irreversible processes in hand; what we really mean by the intensive variables appearing in the differential form and their operational thermodynamic significance; and so on. Unless these questions are satisfactorily answered and settled, the theory thus formulated is merely a mathematical formalism that has little to do with thermodynamic laws and the macroscopic reality of the processes under consideration that we hope to describe theoretically. The theory presented below is addressed to help resolve these questions and thereby put the formalism on firmer foundations of the thermodynamic laws. It is also the opinion of the present author that it is not advisable to tamper with the Clausius principle or the Kelvin principle until they are given a complete mathematical representation and such a representation is proven inadequate on application to irreversible processes, as we occasionally see in the literature on thermodynamics.

The Clausius inequality (2.38) is not the most useful mathematical form of representation for the second law of thermodynamics. To proceed further on its mathematical representation, we observe that the uncompensated heat in (2.39) may be written as a circular integral in the thermodynamic manifold over the cycle in hand:

$$N = \oint dN \geq 0, \quad (2.48)$$

where  $dN$ , or more precisely,  $dN/dt$  should be always positive except for reversible processes in which it vanishes. Otherwise, it would be possible to devise<sup>12</sup> a cyclic process in such a way that it vanishes or is negative, violating the second law of thermodynamics.

By combining (2.48) with (2.39), we obtain the equation [45, 47]

$$\oint \left( \frac{dQ}{T} + dN \right) = 0. \quad (2.49)$$

This vanishing circular integral implies that there exists a state function  $\Psi$  in the thermodynamic space such that

$$d\Psi = \frac{dQ}{T} + dN \quad (2.50)$$

<sup>12</sup>A simple, albeit somewhat ideal, example would be a cyclic process consisting of the irreversible segment where  $dN < 0$  and a reversible segment for the remainder of the cycle in which  $dN = 0$ . This cycle, if possible to construct, would violate the second law.

and thus even for a cyclic irreversible process

$$\oint d\Psi = 0. \quad (2.51)$$

The differential form (2.50) and the circular integral (2.51) remain valid regardless of whether the process is reversible or irreversible. Indeed, if the process is reversible, then  $dN = 0$ , or  $dN/dt = 0$ , over the differential segment of the process and we recover the Clausius entropy: namely,

$$d\Psi|_{\text{rev}} = \left. \frac{dQ}{T} \right|_{\text{rev}} = dS_e \quad (2.52)$$

and thus within a constant of integration the reversible calortropy coincides with the Clausius entropy:

$$\Psi_{\text{rev}} = S_e. \quad (2.53)$$

For irreversible processes it is clearly different from the Clausius entropy *which is defined only for reversible processes*. As will be shown in the kinetic theory chapters, it is also different from the Boltzmann entropy or the information entropy [48] for nonequilibrium processes. Since the Boltzmann entropy for a nonequilibrium system is often called the nonequilibrium entropy in the literature, it will be preferable to call  $\Psi$  by another term to remove the possibility of confusion. Henceforth it will be called by a new term [6] *calortropy* which means heat (*calor*) evolution (*tropy*).

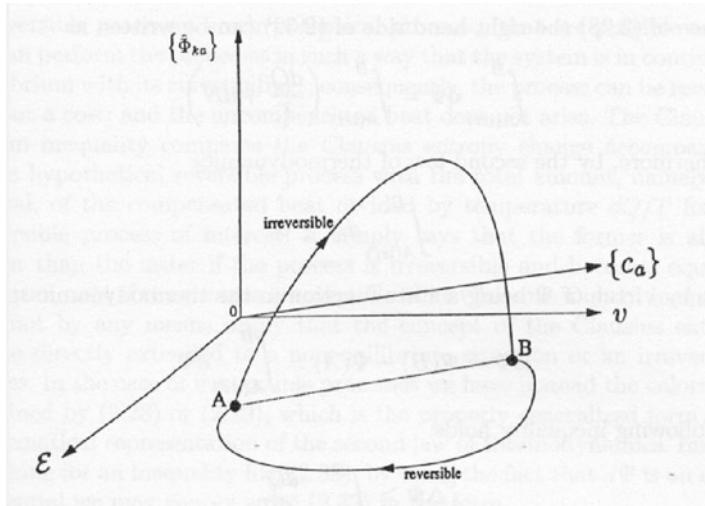
*With (2.10) and (2.51), the first and the second law of thermodynamics are now expressed by a pair of vanishing circular integrals of internal energy and calortropy in the case of a cyclic process.* This pair of vanishing circular integrals, equivalently, the corresponding exact differential forms (2.9) and (2.50), provides us with the starting point of a mathematical theory of thermodynamics of irreversible processes.

### 2.3.5 Clausius–Duhem Inequality

Let us now examine the relation of (2.51) to the Clausius–Duhem inequality . Clausius [12] considered a cyclic process consisting of a segment of irreversible process, which starts from state  $A$  and ends at state  $B$  that are embedded<sup>13</sup> in the equilibrium part of the thermodynamic manifold, and another segment of reversible process which

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<sup>13</sup>In his work, Clausius made no mention of embedding the states  $A$  and  $B$  in the equilibrium part of the thermodynamic manifold. He simply constructed a cycle consisting of an irreversible segment starting from state  $A$  and ending at state  $B$  and a reversible segment starting from state  $B$  and restoring the system to state  $A$ . Since states  $A$  and  $B$  are also part of a reversible process, they must be embedded in the equilibrium part of the thermodynamic manifold. It now may be stated that there was no clear notion of thermodynamic manifold in the Clausius formulation of the second law of thermodynamics.



**Fig. 2.1** A cycle consisting of an irreversible and an reversible segment. This figure is a rendering in the thermodynamic space of the irreversible cycle from which Clausius deduced the Clausius-Duhem inequality. In the formulation of Clausius the concept of thermodynamic manifold is absent. The reversible segment is embedded in the equilibrium part of the thermodynamic manifold. This cycle is a special case, albeit somewhat ideal, because of the presence of a reversible segment. Reproduced from B.C. Eu, Kinetic Theory and Irreversible Thermodynamics copyright © John Wiley & Sons, Inc with permission

reversibly restores the system at state  $B$  to its original thermodynamic state  $A$ ; see Fig. 2.1. In the sense of the conditions imposed on states  $A$  and  $B$ , this cyclic process is rather special since the system must start from an equilibrium state and end at another equilibrium state but through a nonequilibrium path in the thermodynamic state space. For this cyclic process the circular integral (2.51) can be split up into reversible and irreversible segments and written as

$$\int_{A(\text{rev})}^B d\Psi = \int_{A(\text{irr})}^B d\Psi, \quad (2.54)$$

where the subscripts attached to the integrals,  $\text{rev}$  and  $\text{irr}$ , mean that the integration must be performed along the reversible and the irreversible path, respectively. Note that the integration over the reversible path can be reversed by virtue of the process being reversible. Since  $dN = 0$  and hence the calortropy is identified with the Clausius entropy over the reversible segment, we obtain

$$\int_{A(\text{rev})}^B d\Psi = \int_{A(\text{rev})}^B dS_e = S_e(B) - S_e(A) = \Delta S_e. \quad (2.55)$$

By using (2.50), the right-hand side of (2.54) can be written as

$$\int_{A(irr)}^B d\Psi = \int_{A(irr)}^B \left( \frac{dQ}{T} + dN \right). \quad (2.56)$$

Furthermore, by the second law of thermodynamics

$$\int_{A(irr)}^B dN \geq 0. \quad (2.57)$$

Since by virtue of  $\Psi$  being a state function in the thermodynamic space

$$\Delta\Psi = \Psi(B) - \Psi(A) = \int_{A(irr)}^B d\Psi,$$

the following inequality holds

$$\Delta\Psi \geq \int_{A(irr)}^B \frac{dQ}{T}. \quad (2.58)$$

The differential form for this is

$$d\Psi \geq \frac{dQ}{T}, \quad (2.59)$$

which follows from (2.50) since  $dN \geq 0$ . Therefore, it is concluded that  $\Delta\Psi \geq 0$  always for an isolated system. Equations (2.54) and (2.58) with the help of (2.55) give rise to the Clausius–Duhem inequality

$$\Delta S_e \geq \int_{A(irr)}^B \frac{dQ}{T} \quad (2.60)$$

under the sign convention adopted for heat transfer. Thus, the Clausius–Duhem inequality<sup>14</sup> is contained in the present expression for the second law of thermodynamics (2.51).

<sup>14</sup>Inequality (2.60), together with (2.54) and (2.55), means that for an isolated system  $\Delta S_e \geq 0$  as is generally taken in the thermodynamics literature. However, this inequality for an isolated system can be misleading and cause confusion. In applying this inequality, it must be remembered that  $\Delta S_e$  is for the reversible segment complementary to the irreversible step making up the cycle in question and the inequality (2.60) simply means that  $\Delta S_e$  for the reversible segment is always larger than the irreversible compensated heat change. If the system is isolated, the compensated heat  $dQ = 0$  everywhere in the interval of integration and hence  $\Delta S_e = 0$  identically. This conclusion is also consistent with the definition of  $dS_e$  in (2.44). It is clearly convenient to think in terms of  $\Delta\Psi \geq 0$  instead of  $\Delta S_e \geq 0$ .

Reversible processes are hypothetical processes that are possible only if one can perform the processes in such a way that the system is in continuous equilibrium with its surroundings; consequently, the process can be reversed without a cost; and the uncompensated heat does not arise. The Clausius–Duhem inequality compares the Clausius entropy change accompanying such a hypothetical reversible process with the total amount of the compensated heat divided by temperature  $dQ/T$  for the irreversible process of interest. It simply says that the former is always greater than the latter if the process is irreversible and becomes equal to the latter, only if the process is reversible. From the investigation made here we can conclude that the Clausius–Duhem inequality does not by any means imply that the concept of the Clausius entropy can be directly extended to a nonequilibrium situation or an irreversible process. In the case of irreversible processes, we have instead the calortropy  $\Psi$  defined by (2.50) or (2.51), which is a properly generalized form for mathematical representation of the second law of thermodynamics. Instead of looking for an inequality like (2.60), we may simply write, by using the fact that  $d\Psi$  is an exact differential, (2.54) in the form

$$\Delta S_e = \Delta\Psi = \Psi(B) - \Psi(A) \quad (2.61)$$

for the cyclic process considered by Clausius. Therefore, for such a special process starting from an equilibrium state and ending at another equilibrium state the calortropy change for an irreversible process can be simply computed in terms of the Clausius entropy change over a complementary reversible process which with the irreversible segment makes up the cyclic process of Clausius. We emphasize that this equality (2.61) does not mean  $S_e = \Psi$  along the same path, but  $\Delta S_e$  and  $\Delta\Psi$  are computed along two different paths, which are complementary to each other if a cyclic process is possible to construct. This conclusion appears to have considerable significance for understanding and examining from the standpoint of the second law of thermodynamics the thermodynamics of steady irreversible processes and the theory of linear irreversible processes which assumes the local equilibrium hypothesis for Clausius entropy change even if there are irreversible processes present in the system. We will return to this aspect later at a more appropriate stage. Equation (2.61) implies that there are an infinite number of reversible paths that can produce  $\Delta\Psi$  between two states  $A$  and  $B$  in the case of the particular cycle considered. Note, however, that (2.61) is for a global change, but not for a local change.

In the case of a local irreversible process, it is not possible to transcribe (2.61) into the equality

$$d\Psi = dS_e, \quad (2.62)$$

because

$$\int_{A(irr)}^B (d\Psi - dS_e) \neq \int_{A(irr)}^B d\Psi - \int_{A(rev)}^B dS_e = 0.$$

Pursuing this discussion a little further, we remark that in the linear theory of irreversible processes [17, 29–31] the entropy density change  $dS$  in a system is

written as  $dS = dQ/T + dN$  in the present notation. In the light that (2.62) holds for a global process only, this equation for  $dS$  cannot be used for local processes if  $S$  is meant for the Clausius entropy. The discussion presented earlier in connection with calortropy suggests that  $dS$  in the said equation must be interpreted as  $d\Psi$  for it to make sense from the thermodynamic standpoint.

## 2.4 Differential Form for Calortropy

The differential forms for the first and second law of thermodynamics (2.9) and (2.50) can be combined to obtain

$$d\Psi = T^{-1}(dE - dW) + dN. \quad (2.63)$$

If  $dN$  is suitably represented explicitly in terms of global thermodynamic variables, the precise meaning of calortropy  $\Psi$  will be known. Therefore, the subject of irreversible thermodynamics may be said to be centered around the meaning of uncompensated heat. Since such a representation of  $N$  requires the elements of the tangent manifold  $\mathfrak{T}$  conjugate to the manifold  $\mathfrak{P}$ , the zeroth law of thermodynamics and its extension to the variables of  $\mathfrak{T}$  other than temperature  $T$  should be made use of to render them operational. The following proposition is taken for the variables in manifold  $\mathfrak{T}$ :

**Proposition 3** *There exists a set of measurable local intensive variables , namely, temperature  $T$ , pressure  $p$ , chemical potentials  $\widehat{\mu}_a$  ( $1 \leq a \leq r$ ), and generalized potentials  $X_a^{(s)}$ , which are conjugate to the internal energy  $\mathcal{E}$ , specific volume  $v$ , mass fractions  $c_a$  ( $1 \leq a \leq r$ ), and nonconserved variables<sup>15</sup>  $\widehat{\Phi}_a^{(s)}$  ( $s \geq 1$ ,  $1 \leq a \leq r$ ), respectively. These intensive local variables are amenable to measurements, at least in principle, according to the zeroth law of thermodynamics and its extension.*

Thermodynamics of irreversible processes developed below will provide theories of measurements for  $\widehat{\mu}_a$  and  $X_a^{(s)}$  as well as other intensive variables just as equilibrium thermodynamics gives theories of measurements of equilibrium temperature, pressure, and chemical potentials. These intensive variables are basically the constitutive parameters which must be determined as functions of their conjugate variables. Their determinations are therefore a major task of the phenomenological thermodynamics of irreversible processes that emerges in this work. The simplest example for an approximate  $X_a^{(s)}$  that can be used for studies of experimental data is the linear relations between  $X_a^{(s)}$  and  $\widehat{\Phi}_a^{(s)}$ :

$$X_a^{(s)} = -\rho g_a^{(s)} \widehat{\Phi}_a^{(s)}, \quad (2.64)$$

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<sup>15</sup>If the volume transport is included, the range of index  $s$  may be taken  $s \geq 0$ , if we adopt the system of notation used in the kinetic theory chapters in this work. See Chaps. 6 and 7.

in which  $g_{sa}$  is independent of  $\widehat{\Phi}_a^{(s)}$ , but depends on  $\rho$ ,  $T$ , and  $p$ . Rigorously and more generally,  $g_a^{(s)}$  are scalar-valued functions of  $\rho$ ,  $T$ , and  $p$  as well as  $\widehat{\Phi}_a^{(s)}$  ( $r \geq a \geq 1$ ;  $s \geq 1$ ). The functions  $g_a^{(s)}$  may be given in terms of thermodynamic derivatives as will be discussed presently.

### 2.4.1 Local Differential Form for Calortropy

With the preparations made in the previous sections regarding the mathematical representation of the second law of thermodynamics and operational definitions of temperature, pressure, and so on for the intensive variables conjugate to various thermodynamic variables, we are now ready to formulate a thermodynamic theory of irreversible processes in local form. To make the presentation uncluttered with terminologies, we will first define some necessary and recurring quantities.

The calortropy  $\Psi$  for a global system can be given as a volume integral of its density  $\widehat{\Psi}$ :

$$\Psi = \int_V d\mathbf{r} \rho \widehat{\Psi}(\mathbf{r}, t). \quad (2.65)$$

Here the integration is over the volume enclosing the system. Since thermodynamic description of macroscopic processes involves a set of macroscopic variables subject to the laws of thermodynamics, it is clear that  $\widehat{\Psi}(\mathbf{r}, t)$  must be given in terms of variables spanning manifold  $\mathfrak{P} \cup \mathfrak{T}$ . *The union of this set with  $\widehat{\Psi}$  will be called the Gibbs manifold  $\mathfrak{G}$ :*

$$\begin{aligned} \mathfrak{G}: &= \widehat{\Psi} \cup \mathfrak{P} \cup \mathfrak{T} \\ &= (\widehat{\Psi}, \mathcal{E}, v, c_a, \widehat{\Phi}_a^{(s)}, T, p, \widehat{\mu}_a, X_a^{(s)} : 1 \leq a \leq r; s \geq 1). \end{aligned} \quad (2.66)$$

The vanishing circular integral (2.51) may be written in a form similar to (2.11) if the circular path integral is converted into the time integration:

$$\int_0^\tau dt \frac{d\Psi}{dt} = 0, \quad (2.67)$$

where  $\tau$  is the period of the cycle. Noting that the differential form (2.50) can be cast into a derivative form

$$\frac{d\Psi}{dt} = T^{-1} \frac{dQ}{dt} + \frac{dN}{dt} \quad (2.68)$$

and the time derivatives in (2.68) are the global rates of change and by using the well-known procedure in continuum mechanics, it is possible to express the time derivatives as volume integrals of the following forms [6, 14]:

$$\frac{d\Psi}{dt} = \int_V d\mathbf{r} \left[ \frac{\partial}{\partial t} \rho \widehat{\Psi} + \nabla \cdot (\mathbf{u} \rho \widehat{\Psi}) \right], \quad (2.69)$$

$$T^{-1} \frac{dQ}{dt} = - \int_{\mathcal{B}} d\mathbf{B} \cdot \mathbf{Q}^c / T = - \int_V d\mathbf{r} \nabla \cdot [\mathbf{Q}^c / T(\mathbf{r}, t)], \quad (2.70)$$

$$\frac{dN}{dt} = \int_V d\mathbf{r} \rho \widehat{\Xi}_{\text{cal}}(\mathbf{r}, t). \quad (2.71)$$

Here  $\mathbf{u}$  is the fluid velocity. It is assumed for the derivation of (2.69) that the fluid sticks with the boundaries. The subscript  $\mathcal{B}$  to the integral in (2.70) stands for the surface of the enclosing volume whose outward normal direction is counted positive. The vector  $\mathbf{Q}^c$  also is counted positive in the normal direction to the surface. Here, it must be recalled that the differential form (2.68) pertains to one of infinitesimal Carnot cycles which operate between two heat reservoirs of a minute temperature difference and comprise the original Carnot cycle for which (2.39) holds. It is assumed that the temperature is uniform over the surface  $\mathcal{B}$  of the volume of the infinitesimal Carnot cycle which is in contact with the heat reservoir of temperature  $T$ . We remark that except for the terminal infinitesimal Carnot cycles this heat reservoir of temperature  $T$  is not the heat reservoirs of the original finite Carnot cycle, which operates between temperatures  $T_1$  and  $T_2$  and is imagined to consist of infinitesimal Carnot cycles that Clausius used in his derivation of Inequality (2.38).

The first equality in (2.70) can be achieved in this way: Let us observe that since  $T^{-1}dQ$  is the differential form for  $[(Q/T)_i - (Q/T)_{i-1}]$  [see (2.42)],  $T^{-1}dQ/dt$  may be written as the sum over the infinitesimal pistons:

$$T^{-1} \frac{dQ}{dt} = \sum_i \left( T^{-1} \frac{dQ}{dt} \right)_i,$$

which then can be written as

$$\sum_i \left( T^{-1} \frac{dQ}{dt} \right)_i = - \sum_i \int_{\mathcal{B}_i} d\mathbf{B}_i \cdot \frac{\mathbf{Q}^c(\mathcal{B}_i)}{T(\mathcal{B}_i)} = - \int_{\mathcal{B}} d\mathbf{B} \cdot \frac{\mathbf{Q}^c}{T(\mathbf{r}, t)},$$

where  $\mathcal{B} = \cup_i \mathcal{B}_i$ . From this consideration follows the second equality in (2.70). Since the index  $i$  may be regarded as a local position of the global system,  $T$  should be regarded as the local temperature that depends on position  $\mathbf{r}$ . The vector  $\mathbf{Q}^c$  is the net heat flux at the surface; it is the compensated heat flux. The quantity  $\rho \widehat{\Xi}_{\text{cal}}(\mathbf{r}, t)$  is the local rate of uncompensated heat per volume. Use of (2.69)–(2.71) in (2.68) implies, by virtue of continuity, the balance equation for the calortropy density [46, 49]:

$$\rho \frac{d\widehat{\Psi}}{dt} = - \nabla \cdot \left( \frac{\mathbf{Q}^c}{T(\mathbf{r}, t)} \right) + \rho \widehat{\Xi}_{\text{cal}}(\mathbf{r}, t). \quad (2.72)$$

We will call  $\mathbf{J}_c := \mathbf{Q}^c/T$  and  $\rho \widehat{\Xi}_{\text{cal}}$  the calortropy flux and the calortropy production, respectively.

Except that  $\rho\widehat{\Xi}_{\text{cal}}$  must be always positive and vanishes for reversible processes by virtue of Inequality  $dN/dt \geq 0$ , the precise forms for these quantities  $\mathbf{Q}^c$  and  $\widehat{\Xi}_{\text{cal}}$  are not known at this point as to permit deductions on the properties of calortropy. To this end, we reason this way. First of all, since a macroscopic system must evolve in conformation with the conservation laws, the relevant variables to characterize the macroscopic state of the system should include the conserved variables obeying the balance equations in Proposition 1. Since these balance equations require constitutive equations, it is necessary to append the set of the former with the evolution equations for nonconserved variables presented in Proposition 2. Therefore, it is evident that the space of macroscopic variables necessary to describe the calortropy is the manifold  $\mathfrak{P} \cup \mathfrak{T}$ . The desired deductions of the properties of the calortropy will be possible if the calortropy flux and the calortropy production are elucidated in manifold  $\mathfrak{P} \cup \mathfrak{T}$ . We make the following proposition for them.

**Proposition 4** *The calortropy flux  $\mathbf{J}_c := \mathbf{Q}^c/T$  is given by the bilinear form of the intensive variables  $T^{-1}$ ,  $\widehat{\mu}_a T^{-1}$ , and  $X_a^{(s)} T^{-1}$  ( $s \geq 1$ ,  $1 \leq a \leq r$ ) paired, respectively, with  $\mathbf{Q}_a$ ,  $\mathbf{J}_a$ , and  $\psi_a^{(s)}$  (flux of  $\Phi_a^{(s)}$ ) as follows:*

$$\mathbf{J}_c := \sum_{a=1}^r \frac{\mathbf{Q}_a^c}{T} = \sum_{a=1}^r T^{-1} (\mathbf{Q}_a - \widehat{\mu}_a \mathbf{J}_a + \sum_{s \geq 1} X_a^{(s)} \psi_a^{(s)}), \quad (2.73)$$

and the calortropy production  $\Xi_{\text{cal}}$  is given by the bilinear form

$$\begin{aligned} \Xi_{\text{cal}} &:= \rho\widehat{\Xi}_{\text{cal}} \\ &= -T^{-1} \sum_{a=1}^r \left[ (\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q}_a^c \cdot \nabla \ln T + \mathbf{J}_a \cdot (\nabla \widehat{\mu}_a - \widehat{\mathbf{F}}_a) \right. \\ &\quad \left. - \sum_{s \geq 1} \psi_a^{(s)} \cdot \nabla X_a^{(s)} \right] + T^{-1} \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} (\mathcal{Z}_a^{(s)} + \Lambda_a^{(s)}). \end{aligned} \quad (2.74)$$

By the second law of thermodynamics, it must be such that  $\Xi_{\text{cal}} \geq 0$  always, the equality holding for reversible processes only or at equilibrium.

The inequality for the calortropy production imposes the positivity condition that the kinematic and dissipation terms  $\mathcal{Z}_a^{(s)}$  and  $\Lambda_a^{(s)}$  in the evolution equation for  $\widehat{\Phi}_a^{(s)}$  must satisfy, and thus it dictates the acceptable forms for them and hence for the evolution equations for  $\widehat{\Phi}_a^{(s)}$ . Therefore, the evolution equations for nonconserved variables are not free, but must conform to the second law of thermodynamics represented by  $\Xi_{\text{cal}} \geq 0$  in the local theory—namely, the thermodynamic consistency condition. It must be noted that the terms in the square brackets in (2.74) except for the last term involving  $\nabla X_a^{(s)}$  are formally those making up the entropy production in the theory of linear irreversible processes [17, 31]. The last term mentioned is a bilinear product of the gradient of the generalized potential and the flux  $\psi_a^{(s)}$  of nonconserved variable  $\Phi_a^{(s)}$  just as the other terms are bilinear products of the velocity

gradient and the momentum flux (i.e., the stress tensor), of the temperature gradient and the compensated heat flux, and so on. Therefore, it may be said that the gradient  $\nabla X_a^{(s)}$  induces the flux  $\psi_a^{(s)}$  of nonconserved variable  $\Phi_a^{(s)}$  just as  $\nabla \hat{\mu}_a$  induces diffusion flows of species. The occurrence of such a flux gives rise to an uncompensated heat just as do the stress, compensated heat flux, and so on. In addition to the aforementioned contribution from  $\psi_a^{(s)}$ , there are contributions to the uncompensated heat from the kinematic and dissipation terms—the last group of terms in (2.74)—in the evolution equations for the nonconserved variables in the present generalized theory. The calorropy flux proposed is also seen to include the classical terms as well as non-classical terms—the last group of terms in (2.73)—attributable to the nonconserved variables. The calorropy flux and the calorropy production proposed in Proposition 4 are mutually compatible in the sense that they give rise to an integrable differential form for  $d_t \hat{\Psi}$  as will be shown.<sup>16</sup>

Finally, a note on notation: the term  $X_a^{(s)} \hat{\Phi}_a^{(s)}$  or  $X_a^{(s)} \psi_a^{(s)}$  are made up of two tensors appropriately contracted to a scalar in the case of the former and to a vector in the case of the latter. The tensor contraction signs are omitted for brevity of notation.

Use of (2.73) and (2.74) in the calorropy balance equation (2.72) makes it possible to determine  $\hat{\Psi}$  in the Gibbs manifold  $\mathfrak{G}$  if the conservation laws listed in Proposition 1 and the evolution equations in Proposition 2 are used. In particular, if the fluxes  $\mathbf{Q}_a$ ,  $\mathbf{J}_a$ , and  $\psi_a^{(s)}$  are either replaced or rearranged by means of (2.23)–(2.25) and (2.34), then it is possible to put the balance equation for  $\hat{\Psi}$  in a Pfaffian differential form (one-form) in Gibbs manifold  $\mathfrak{G}$ :

$$d_t \hat{\Psi} = T^{-1} \left( d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t \mathfrak{c}_a + \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} d_t \hat{\Phi}_a^{(s)} \right). \quad (2.75)$$

Inasmuch as the calorropy balance equation (2.72) is the local equivalent of the second law of thermodynamics, the Pfaffian differential form<sup>17</sup> (2.75) is an equivalent to the second law in the Gibbs manifold  $\mathfrak{G}$  ( $\mathfrak{G} := \mathfrak{P} \cup \mathfrak{T} \cup \hat{\Psi}$ ) under Proposition 4. This differential form is exact in the Gibbs manifold  $\mathfrak{G}$  by virtue of the vanishing circular integral (2.51). This can be shown as follows. From (2.67) and (2.69) we obtain

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<sup>16</sup>Although (2.73) and (2.74) are sufficient for  $\mathbf{J}_c$  and  $\Xi_c$  to yield a one-form for  $d_t \hat{\Psi}$ , it is not unique. For example, a vector  $\mathbf{A}$  and its divergence  $\nabla \cdot \mathbf{A}$  can be added to  $\mathbf{J}_c$  and  $\Xi_c$ , respectively, with no effect at all on the one-form that can be obtained from the balance equation for the calorropy. In fact, the vector  $\mathbf{A}$  can be taken with  $\sum_{a=1}^r \mathbf{J}_a / m_a$  as can be seen later in Chap. 3. The formulas for  $\mathbf{J}_c$  and  $\Xi_c$  proposed in Proposition 4 therefore are minimal in the sense that they are sufficient to produce a one-form for  $d_t \hat{\Psi}$ .

<sup>17</sup>It must be noted that a Pfaffian differential form is not necessarily an exact differential unless it satisfies a set of integrability conditions [50–53]. In the case of thermodynamics, the second law of thermodynamics preempts the integrability conditions which are partial differential equations not easy to solve in general.

$$\begin{aligned} \int_0^\tau dt \frac{d\Psi}{dt} &= \int_0^\tau dt \int_V d\mathbf{r} \left[ \frac{\partial}{\partial t} \rho \widehat{\Psi} + \nabla \cdot (\mathbf{u} \rho \widehat{\Psi}) \right] \\ &= \int_V d\mathbf{r} \int_0^\tau dt \rho \frac{d\widehat{\Psi}}{dt} = 0 \end{aligned} \quad (2.76)$$

from which, by continuity, follows the vanishing local integral

$$\int_0^\tau dt \rho \frac{d\widehat{\Psi}}{dt} = 0. \quad (2.77)$$

This implies that  $d_t \widehat{\Psi}$  is an exact differential in the Gibbs manifold  $\mathfrak{G}$  since  $\rho(d\widehat{\Psi}/dt)$  may be replaced by  $(d\rho\widehat{\Psi}/dt)$ . It is not simple to prove the exactness of a differential form like (2.75) in  $\mathfrak{G}$  if a purely mathematical approach is taken for the proof, but in the present case, the differential form  $d_t \widehat{\Psi}$  is exact by the demand of the second law of thermodynamics. Thus, when the calortropy flux and the calortropy production are suitably elucidated, the second law assures the integrability of the differential form  $d_t \widehat{\Psi}$  in  $\mathfrak{G}$ , and there exists a hypersurface of  $\widehat{\Psi}$  in manifold  $\mathfrak{G}$ . These results are collected in a theorem.

**Theorem 1** *Under Propositions 1–4 the second law of thermodynamics is expressible, for local irreversible processes in space-time, in the Pfaffian differential form in manifold  $\mathfrak{P} \cup \mathfrak{T}$*

$$d_t \widehat{\Psi} = T^{-1} \left( d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \widehat{\mu}_a d_t \mathfrak{c}_a + \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} d_t \widehat{\Phi}_a^{(s)} \right). \quad (2.78)$$

*This differential form is exact and integrable. Therefore, there exists a state function  $\widehat{\Psi}$  in the Gibbs manifold  $\mathfrak{G}$ . This function may be regarded as a hypersurface in  $\mathfrak{G}$  in conformation to the demand of the second law of thermodynamics.*

The differential form (2.78) is called the extended Gibbs relation for the reason that it reduces to the equilibrium Gibbs relation as  $X_a^{(s)} \rightarrow 0$  at equilibrium. It provides the foundation for a phenomenological theory of thermodynamics of irreversible processes in a fairly general form. We will return to further discussions on the calortropy differential after formulating the kinetic theory version of differential form (2.78). Henceforth the operator  $d_t$  may be written as  $d$  for brevity.

The necessary and sufficient conditions for integrability of the extended Gibbs relation in the Gibbs manifold is the nonequilibrium Gibbs–Duhem equation

$$\mathcal{E} d\left(\frac{1}{T}\right) + v d\left(\frac{p}{T}\right) - \sum_{a=1}^r \mathfrak{c}_a d\left(\frac{\widehat{\mu}_a}{T}\right) + \sum_{a=1}^r \sum_{q \geq 1} \widehat{\Phi}_a^{(q)} d\left(\frac{X_a^{(q)}}{T}\right) = 0. \quad (2.79)$$

If this equation is added to the extended Gibbs relation, then the resulting equation is integrable to the bilinear form for  $\Psi$  in manifold  $\mathfrak{G}$

$$\widehat{\Psi} = T^{-1} \left( \mathcal{E} + pv - \sum_{a=1}^r \widehat{\mu}_a \mathfrak{c}_a + \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} \widehat{\Phi}_a^{(s)} \right) \quad (2.80)$$

apart from a constant, which can be put equal to zero. Thus it is a sufficient condition for (2.78) to be integrable in manifold  $\mathfrak{G}$ . On the other hand, the Gibbs–Duhem equation is evidently the necessary condition for (2.78) to follow from (2.80). Therefore the statement is proved. This integrability condition [54] is a nonequilibrium generalization of the Gibbs–Duhem equation used in equilibrium thermodynamics [1], which is useful for applying the present theory to nonequilibrium phenomena. The nonequilibrium Gibbs–Duhem equation (2.79) may be rearranged to the form

$$d(pv) = \widehat{\Psi} dT + pdv + \sum_{a=1}^r \mathfrak{c}_a d\widehat{\mu}_a - \sum_{q \geq 1} \sum_{a=1}^r \widehat{\Phi}_a^{(q)} dX_a^{(q)}, \quad (2.81)$$

which then may be regarded as the differential form for the thermodynamic potential  $pv$ . The advantage of this differential form lies in the fact that the thermodynamic potential  $pv$  turns out to be given by the local grand canonical partition function appearing in nonequilibrium statistical thermodynamics, which is formulated later based on the Boltzmann kinetic equation and the irreversible kinetic equations for dense fluids treated subsequent to the Boltzmann kinetic equation in this monograph; see Chaps. 5, 6, and 7.

Before proceeding further, we examine how the present theory connects with equilibrium thermodynamics. First of all, we see that as  $X_a^{(s)}$  vanish for all  $s$  and  $a$ , equilibrium thermodynamics is recovered since  $\widehat{\Psi}$  tends to its equilibrium limit  $\widehat{\Psi}_e$  which coincides with the Clausius entropy density  $\mathcal{S}_e$ :

$$\begin{aligned} d_t \widehat{\Psi}_e &= T_e^{-1} \left( d_t \mathcal{E} + p_e d_t v - \sum_{a=1}^r \widehat{\mu}_a^e d_t \mathfrak{c}_a \right) \\ &= d_t \mathcal{S}_e, \end{aligned} \quad (2.82)$$

where

$$T_e = \lim_{X \rightarrow 0} T = \lim_{\Phi \rightarrow 0} T,$$

$$p_e = \lim_{X \rightarrow 0} p = \lim_{\Phi \rightarrow 0} p,$$

$$\widehat{\mu}_a^e = \lim_{X \rightarrow 0} \widehat{\mu}_a = \lim_{\Phi \rightarrow 0} \widehat{\mu}_a.$$

This consideration shows that equilibrium thermodynamics is contained in the formalism based on the concept of calortropy. Since we are not interested in equilibrium thermodynamics here, we will not dwell on this aspect further.

Other thermodynamic functions related to (2.78) and (2.81) can be defined as in equilibrium thermodynamics. For example, we may define generalized work function  $\mathcal{A}$ , generalized Gibbs free energy  $\mathcal{G}$  [6, 46], and generalized enthalpy  $\mathcal{H}$ , which will be found to be another thermodynamic potential:

$$\mathcal{A} = \mathcal{E} - T\widehat{\Psi}, \quad (2.83)$$

$$\mathcal{G} = \mathcal{H} - T\widehat{\Psi}, \quad (2.84)$$

$$\mathcal{H} = \mathcal{E} + pv, \quad (2.85)$$

We remark that  $\mathcal{H}$  is basically a mechanical quantity because  $\mathcal{E}$  and  $p$  are mechanically calculable from their molecular expressions. In this sense,  $\mathcal{H}$  is different from  $\mathcal{A}$  and  $\mathcal{G}$ , which is defined with  $\widehat{\Psi}$  instead of  $\mathcal{S}_e$  used in equilibrium thermodynamics. Since the properties of the functions  $\mathcal{A}$  and  $\mathcal{G}$  can be discussed in complete parallel to the equilibrium thermodynamics by using the fundamental equation (2.75) we will discuss about them only briefly in this section.

### 2.4.2 Calortropy and Thermodynamic Relations

Differential forms equivalent to (2.78) and (2.81) can be easily obtained for  $\mathcal{H}$ ,  $\mathcal{A}$ , and  $\mathcal{G}$ , respectively:

$$d_t \mathcal{H} = T d_t \widehat{\Psi} + v d_t p + \sum_{a=1}^r \widehat{\mu}_a d_t \mathfrak{c}_a - \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} d_t \widehat{\Phi}_a^{(s)}, \quad (2.86)$$

$$d_t \mathcal{A} = -\widehat{\Psi} d_t T - p d_t v + \sum_{a=1}^r \widehat{\mu}_a d_t \mathfrak{c}_a - \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} d_t \widehat{\Phi}_a^{(s)}, \quad (2.87)$$

$$d_t \mathcal{G} = -\widehat{\Psi} d_t T + p d_t v + \sum_{a=1}^r \widehat{\mu}_a d_t \mathfrak{c}_a - \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} d_t \widehat{\Phi}_a^{(s)}. \quad (2.88)$$

These extended Gibbs relations yield Maxwell relations between thermodynamic derivatives which are generalized to take nonequilibrium states into account. For example, there holds the relations between generalized potential derivatives

$$\left( \frac{\partial X_a^{(s)}}{\partial \widehat{\Phi}_b^{(q)}} \right)_{v, \mathfrak{c}, \widehat{\Phi}'} = \left( \frac{\partial X_b^{(q)}}{\partial \widehat{\Phi}_a^{(s)}} \right)_{v, \mathfrak{c}, \widehat{\Phi}'}, \quad etc., \quad (2.89)$$

which relate a generalized potential  $X_a^{(s)}$  to other generalized potentials as well as other variables—these are examples for generalized Maxwell relations. These derivative relations also serve as symmetry relations between generalized potentials relating one irreversible process to another. Furthermore, there follow from (2.78) the relations between  $\widehat{\Psi}$  and intensive variables  $T^{-1}$ ,  $pT^{-1}$ , etc.

$$\begin{aligned} T^{-1} &= \left( \frac{\partial \widehat{\Psi}}{\partial \mathcal{E}} \right)_{v, c, \hat{\Phi}}, \quad p T^{-1} = \left( \frac{\partial \widehat{\Psi}}{\partial v} \right)_{\mathcal{E}, c, \hat{\Phi}}, \\ \widehat{\mu}_a T^{-1} &= \left( \frac{\partial \widehat{\Psi}}{\partial c_a} \right)_{\mathcal{E}, c', \hat{\Phi}}, \quad X_a^{(s)} T^{-1} = \left( \frac{\partial \widehat{\Psi}}{\partial \Phi_a^{(s)}} \right)_{\mathcal{E}, c, \hat{\Phi}'}. \end{aligned} \quad (2.90)$$

These derivatives or their analogues can be used to calculate the nonequilibrium contributions to intensive variables from the variables of the tangential manifold  $\mathfrak{T}$ , given the information on  $\widehat{\Psi}$ . We will return to this question in the kinetic theory chapters later. Other forms of generalized Maxwell relations can be obtained from the differential forms presented here in a parallel manner to equilibrium thermodynamics. Furthermore, a theory of thermodynamics of irreversible processes can be formulated on the basis of the differential forms for  $\widehat{\Psi}$ ,  $\mathcal{A}$ ,  $\mathcal{G}$ , or  $\mathcal{H}$ . Since the main objective of this section is not in developing this particular subject, but also for lack of space, we will not pursue it further; see Ref. [6] for more details of the subject. Instead, we would like to discuss the role of hydrodynamics of flow phenomena within the present framework of the thermodynamic theory of irreversible processes acquired.

## 2.5 Generalized Hydrodynamic Equations

The extended Gibbs relations suggest they can be integrated in manifold  $\mathfrak{G}$  and, for example, the calortropy may be expressed in terms of a bilinear form of the variables spanning the thermodynamic manifold  $\mathfrak{P}$  and the tangential manifold  $\mathfrak{T}$ , but such a form tells us little about the materials undergoing irreversible transport processes. To answer these questions it is necessary to examine the generalized hydrodynamic equations, especially, elucidate the kinematic terms  $Z_a^{(s)}$  and the dissipation terms  $\Lambda_a^{(s)}$  therein more explicitly in terms of material functions as well as the variables of  $\mathfrak{P} \cup \mathfrak{T}$ , and then solve the evolution equations to test against measurements made in experiments on transport processes. The evolution equations (i.e., generalized hydrodynamic equations) so obtained constitute a generalized theory of hydrodynamics. To find them a little more explicitly we may first consider near-equilibrium flow phenomena, for which  $\widehat{\Psi}$  may be quadratic with respect to  $\Phi_a^{(\alpha)}$ . In such cases, the generalized potentials  $X_a^{(s)}$  now are simply proportional to  $\Phi_a^{(s)}$  as suggested by the last relation in (2.90). Phenomenologically, we may write

$$X_a^{(s)} = -g_a^{(s)} \Phi_a^{(s)}, \quad (2.91)$$

where the proportionality coefficients  $g_a^{(s)}$  are scalar functions of  $T, p, c_a$ , but may be independent of  $\Phi_a^{(s)}$  in the leading-order approximation model. However, a phenomenological theory is incapable of predicting explicit forms for  $g_a^{(s)}$ . They may be obtained more explicitly if a molecular theory model is used. For the leading members they are given by

$$g_a^{(1)} = \frac{1}{2p_a}; \quad g_a^{(2)} = \frac{3}{2p_a}; \quad g_a^{(3)} = \frac{1}{Tp_a \widehat{C}_{pa}}; \quad g_a^{(4)} = \frac{1}{\rho_a}, \quad (2.92)$$

where  $\widehat{C}_{pa}$  is the specific heat per unit mass of  $a$  at constant pressure. We will return to (2.91) in later chapters dealing with molecular theories of irreversible processes.

The kinematic term  $\mathcal{Z}_a^{(s)}$  in the generalized hydrodynamic equations should contain, at least, the thermodynamic driving force of the process, and it can be deduced that they should be of the following forms in the near-equilibrium regime of transport processes:

$$\begin{aligned} \mathcal{Z}_a^{(1)} &= -2p_a [\nabla \mathbf{u}]^{(2)}, \quad \mathcal{Z}_a^{(2)} = -p_a d_t \ln(p_a v^{5/3}/c_a), \\ \mathcal{Z}_a^{(3)} &= -Tp_a \widehat{C}_{pa} \nabla \ln T, \quad \mathcal{Z}_a^{(4)} = -p \mathbf{d}_a, \end{aligned} \quad (2.93)$$

where  $\mathbf{d}_a$  is the thermodynamic force for mass diffusion

$$\mathbf{d}_a = \nabla \left( \frac{n_a}{n} \right) + \left( \frac{n_a}{n} - \frac{\rho_a}{\rho} \right) \nabla \ln p + \frac{\rho_a}{p} (\widehat{\mathbf{F}} - \widehat{\mathbf{F}}_a). \quad (2.94)$$

This form implies that mass diffusion can be driven by gradients of concentration and pressure and by the (external) body force. We remark that  $\mathbf{d}_a$  in (2.94) can be recast into the form

$$\mathbf{d}_a = \nabla c_a + \left( \frac{n_a}{n} - \frac{\rho_a}{\rho} \right) \nabla \ln \left[ \left( \frac{n_a}{n} - \frac{\rho_a}{\rho} \right) p \right] + \frac{\rho_a}{p} (\widehat{\mathbf{F}} - \widehat{\mathbf{F}}_a), \quad (2.95)$$

if the mass fraction  $c_a$  is desired for concentrations instead of the mole fraction  $n_a/n$ . The gradients listed in (2.93) are thermodynamic driving forces of the processes in question. Here we remark that the kinematic terms in (2.93) are empirical and gleaned from experimental studies on linear transport processes in fluids [17, 18].

The dissipation terms may be deduced to be proportional to  $\Phi_a^{(s)}$ —for example, on the basis of Rayleigh dissipation principle [55]—in the case of near-equilibrium transport phenomena: for a scalar process

$$\Lambda_a^{(s)} = - \sum_{b=1}^r L_{ab}^{(s)} \Phi_a^{(s)}, \quad (2.96)$$

or for a vector process

$$\Lambda_a^{(s)} = - \sum_{\gamma=3}^4 \sum_{b=1}^r L_{ab}^{(s\gamma)} \Phi_a^{(\gamma)} \quad (s = 3, 4), \quad (2.97)$$

where  $L_{ab}^{(s)}$  are phenomenological coefficients. A scalar process can be coupled to other scalar processes, whereas a vector can be coupled to other vector processes

(e.g., heat and mass diffusions), in a manner consistent with the Curie principle [17]. The phenomenological coefficients are symmetric on account of the generalized Maxwell relations and thus in accord with the Onsager reciprocal relations [29]. Their molecular theory formulas are found in the kinetic theory chapters in this work. Putting the aforementioned forms for  $\mathcal{Z}_a^{(s)}$  and  $\Lambda_a^{(s)}$  into the evolution equations for  $\Phi_a^{(s)}$ , we obtain the hydrodynamic equations for near equilibrium phenomena as given below:

$$\rho d_t v = \nabla \cdot \mathbf{u} \text{ or } \frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{u}), \quad (2.98)$$

$$\rho d_t c_a = -\nabla \cdot \mathbf{J}_a, \quad (2.99)$$

$$\rho d_t \mathbf{u} = -\nabla \cdot \mathbf{P} - \rho \widehat{\mathbf{F}}, \quad (2.100)$$

$$\rho d_t \mathcal{E} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \widehat{\mathbf{F}}_a, \quad (2.101)$$

for the conservation laws and

$$\rho d_t \widehat{\Phi}_a^{(1)} = -2p_a [\nabla \mathbf{u}]^{(2)} - \rho \sum_{b=1}^r L_{ab}^{(1)} \widehat{\Phi}_a^{(1)}, \quad (2.102)$$

$$\rho d_t \widehat{\Phi}_a^{(2)} = -p_a d_t \ln(p_a v^{5/3} / c_a) - \rho \sum_{b=1}^r L_{ab}^{(2)} \widehat{\Phi}_a^{(2)}, \quad (2.103)$$

$$\rho d_t \widehat{\Phi}_a^{(3)} = -p_a \widehat{C}_{pa} \nabla \ln T - \rho \sum_{\gamma=3}^4 \sum_{b=1}^r L_{ab}^{(3\gamma)} \widehat{\Phi}_a^{(\gamma)}, \quad (2.104)$$

$$\rho d_t \widehat{\Phi}_a^{(4)} = -p \mathbf{d}_a - \rho \sum_{\gamma=3}^4 \sum_{b=1}^r L_{ab}^{(4\gamma)} \widehat{\Phi}_a^{(\gamma)}. \quad (2.105)$$

Equations (2.98)–(2.105) are the generalized hydrodynamic equations for linear transport processes. If  $d_t \widehat{\Phi}_a^{(s)} = 0$  for all  $s$  and  $a$ , then (2.98)–(2.105) become the Navier–Stokes, Fourier, and Fick’s equations—i.e., the classical hydrodynamic equations [32, 33]—holding near-equilibrium phenomena when viewed from the thermodynamic standpoint. In other words, the conventional hydrodynamics is within the framework of thermodynamics of linear irreversible processes holding near-equilibrium flow phenomena. The evolution equations (2.98)–(2.105) should be subjected to the demand of the laws of thermodynamics according to the formalism described earlier, and we find the second law of thermodynamics require the phenomenological coefficients<sup>18</sup>  $L_{ab}^{(s)}$  or  $L_{ab}^{(s\gamma)}$  must satisfy the inequalities demanded by the second law of thermodynamics—namely, positivity conditions. In this manner,

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<sup>18</sup>These phenomenological transport coefficients may be identified with their molecular theory (i.e., kinetic theory) formulas in the forms of collision bracket integrals, which appear in the kinetic theory chapters.

the classical hydrodynamic equations are made consistent with the laws of thermodynamics. Therefore they may be regarded as macroscopic evolution equations within the framework of the laws of thermodynamics.

For a class of nonlinear phenomena—e.g., rheological phenomena or nonlinear flow phenomena subjected to high spatial gradients which are observed, for example, in rarefied gas dynamics or rheology—the dissipation terms  $\Lambda_a^{(s)}$  are no longer linear, but highly nonlinear with respect to  $\Phi_a^{(s)}$  or the thermodynamic gradients—i.e., spatial gradients of variables belonging to manifold  $\mathfrak{T}$ . For example, they may be put into the form

$$\Lambda_a^{(s)} = \sum_{\gamma \geq 1} \sum_{b=1}^r L_{ab}^{(s,\gamma)} \Phi_b^{(\gamma)} \frac{\sinh \kappa}{\kappa}, \quad (2.106)$$

where  $\kappa$  is the square root of a quadratic form in  $\Phi_b^{(\gamma)}$ . This function  $\kappa$  is rather reminiscent of the Rayleigh dissipation function,<sup>19</sup> since it is quadratic with respect to  $\Phi_a^{(\alpha)}$ , which may be regarded as a generalized velocity:

$$\kappa = \sqrt{\sum_{\alpha, \gamma \geq 1} \sum_{a,b=1}^r \Phi_a^{(\alpha)} L_{ab}^{(\alpha, \gamma)} \Phi_b^{(\gamma)}}. \quad (2.107)$$

It should be noted that this form of the dissipation functions can be deduced if the calorentropy production  $\sigma_{\text{ent}}$  is approximated by the formula

$$\sigma_{\text{c}} = k_B g^{-1} \kappa \sinh \kappa, \quad (2.108)$$

where

$$g = \frac{1}{n^2 d^2} \sqrt{\frac{m}{2k_B T}} \quad (2.109)$$

with  $m$  denoting the mean reduced mass and  $d$  the mean diameter of molecules. The dimension of factor  $g$  is inverse time or the mean intermolecular force range. With the nonlinear dissipation functions given in (2.106) in the hydrodynamic equations (2.98)–(2.105) numerous nonlinear flow phenomena [19–22] observed in the laboratory have been successfully accounted for in the fields of rheology, semiconductor carrier mobility, rarefied gas flows, and heat conduction in plasmas. Therefore, such generalized hydrodynamic equations are rather practical forms for numerous hydrodynamic phenomena observed in the laboratory conditions. In Chap. 9, we will return to some of examples of applications of the generalized hydrodynamic equations, linear and quasilinear, presented in this section.

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<sup>19</sup> Originally, the Rayleigh dissipation function was quadratic with respect to velocities. Here we are generalizing not only the original definition for fluxes (velocities) to  $\Phi_a^{(s)}$ , but also the flux dependence of the dissipation function to a highly nonlinear form from a quadratic function of velocities.

## 2.6 Irreversible Thermodynamics of Steady States

Experiments are often performed in steady-state conditions where fluxes remain stationary in time. Such examples [56, 57] can be seen in many transport processes in fluids and solids, and rheological experiments [19], transport phenomena in semiconductors [20], rarefied gas dynamics [21], etc. In fact, linear irreversible thermodynamics discussed in the previous section can deal with such situations in more simpler and definitive fashions. Therefore, it is useful to consider them and relate the present general theory to such special cases. Here we will examine cases in which the nonconserved variables do not change in time in the frame of reference moving with the fluid velocity. That is, we consider the cases of

$$d_t \widehat{\Phi}_a^{(s)} = 0.$$

However, the kinematic and dissipation terms in the evolution equation for  $\widehat{\Phi}_a^{(s)}$  can be linear or nonlinear. We will separately consider the case of linear evolution equations for  $\Phi_a^{(s)}$  in the next section.

If  $d_t \widehat{\Phi}_a^{(s)} = 0$  for all  $s$  and  $a$ , then the extended Gibbs relation for calortropy becomes

$$d_t \widehat{\Psi}_{ss} = T^{-1} \left( d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \widehat{\mu}_a d_t c_a \right), \quad (2.110)$$

where the subscript ss denotes the steady state of the nonconserved variables. Henceforth in this section we use the term steady state to mean the steady state of nonconserved variables. Since the differential form on the right-hand side of (2.110) is simply the same as the local equilibrium entropy change, the calortropy at the steady state coincides with the local equilibrium entropy  $S_e$  given by the same differential form as in (2.82) except for the meanings of the coefficients  $T$ ,  $p$ , and  $\widehat{\mu}_a$  to the differentials since they may depend on  $\widehat{\Phi}_a^{(s)}$ :

$$d_t \widehat{\Psi}_{ss} = d_t S_e = T^{-1} \left( d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \widehat{\mu}_a d_t c_a \right). \quad (2.111)$$

In this case, the local equilibrium hypothesis, which is usually made in the linear theory of irreversible thermodynamics [17, 18, 30, 31] is a perfectly acceptable differential form for a thermodynamic description of the process in hand, provided that the steady-state evolution equations for  $\widehat{\Phi}_a^{(s)}$  are given by<sup>20</sup>

<sup>20</sup>In actual applications of the present theory, the nonconserved variables require closure relations. For example, in the case of single-component fluids it will be found useful to take the first thirteen moments (i.e., density, pressure, three velocity components, three components of heat flux, two normal stresses, three components of shear stress) for macroscopic variables and then assume the closure relations  $\psi_a^{(1)} = \psi_a^{(3)} = 0$ . Applications discussed in a later chapter take this kind of closure relations.

$$-\nabla \cdot \psi_a^{(s)} + \mathcal{Z}_a^{(s)} + \Lambda_a^{(s)} = 0 \quad (2.112)$$

for all  $s$  and  $a$ . See the examples for the kinematic and dissipation terms which have been already given in the previous section. In fact, the steady-state evolution equations (2.112) may give rise to nonlinear thermodynamic force–flux relations, namely, the constitutive equations for fluxes whose solutions yield nonlinear transport coefficients, if the dissipation terms are nonlinear with respect to  $\Phi_a^{(s)}$ . At this juncture of discussion, we would like to remark that the nature of (2.111) can be put in a better light if (2.111) is compared with (2.61) which was seen to hold for a cyclic process where the initial and final states  $A$  and  $B$  are embedded in the equilibrium part of the thermodynamic space. The embedded equilibrium states may be interpreted to be steady states which are characterized by (2.111) and (2.112).

The solutions of (2.112) give  $\Phi_a^{(s)}$ , for example, the stress tensor, heat flux, and diffusion fluxes, etc. as nonlinear functions of thermodynamic forces, temperature, density, etc.:

$$\mathbf{P} = \sum_{a=1}^r \mathbf{P}_a = F_p(T, \rho | \nabla \mathbf{u}, \nabla \ln T, \dots), \quad (2.113)$$

$$\mathbf{Q} = \sum_{a=1}^r \mathbf{Q}_a = F_q(T, \rho | \nabla \mathbf{u}, \nabla \ln T, \dots), \quad (2.114)$$

$$\mathbf{J}_a = F_a(T, \rho | \nabla \mathbf{u}, \nabla \ln T, \dots) \quad (1 \leq a \leq r), \quad (2.115)$$

and in general

$$\Phi_a^{(s)} = F_{sa}(T, \rho | \nabla \mathbf{u}, \nabla \ln T, \dots). \quad (2.116)$$

The functions  $F_p$ ,  $F_q$ , and  $F_a$  are generally nonlinear tensor or vector functions of thermodynamic forces,  $\nabla \mathbf{u}$ ,  $\nabla \ln T$ , and  $(\nabla \hat{\mu}_a - \hat{\mathbf{F}}_a)$ , owing to the fact that the constitutive equations (2.112) are generally nonlinear with respect to the nonconserved variables or the thermodynamic forces. On substitution of, for example, (2.113)–(2.115) into the conservation laws (2.24)–(2.26), we obtain hydrodynamic equations which generalize the classical hydrodynamic equations such as the Navier–Stokes, Fourier, and Fick equations [32, 33]. It must be noted that in the present theory the nonlinear steady-state constitutive equations (2.112) still conform to the second law of thermodynamics since they satisfy the inequality  $\Xi_{\text{cal}} \geq 0$  demanded by the second law of thermodynamics.

The deduction made here from the general theory, therefore, shows that the theory of nonlinear steady-state irreversible phenomena can be put within the framework of the present extended theory of irreversible thermodynamics in a form fully consistent with the second law of thermodynamics. If the theory for steady-state irreversible phenomena for nonlinear processes were formulated on the basis of the local equilibrium hypothesis as usually is the case in the literature on linear irreversible thermodynamics [17, 18, 56], then the form for the entropy production would not be obvious and the second law of thermodynamics would not play a role in determining

the forms for the constitutive equations for fluxes in contrast to the present theory. Some examples for application of steady-state irreversible phenomena are discussed in Refs. [6, 45, 46].

Finally, we point out that the steady-state description will be appropriate for non-conserved variables if they change on faster time scales than the conserved variables so that on the time scale of interest for the conserved variables the nonconserved variables have already relaxed to their steady-state values. There are many such situations realizable in laboratory experiments, and for such situations the steady-state theory with nonlinear constitutive equations can be sufficient. As a matter of fact, such steady-state constitutive equations coincide with those in the adiabatic approximation as will be seen later in this work, for example, Chap. 3.

The case of steady linear irreversible processes has been already discussed in the previous section, and they give rise to the traditional Navier–Stokes–Fourier hydrodynamics. Therefore there is little to add here about its relation to the linear irreversible thermodynamics.

## 2.7 Inclusion of Chemical Reactions

We now would like to take chemical reactions into consideration. Let us denote by  $R_l$  the rate of reaction  $l$ , and by  $\nu_{al}$  the associated stoichiometric coefficient times the mass of species  $a$ . This stoichiometric coefficient is counted positive for the products and negative for the reactants. In this convention the chemical reactions may be written in the form

$$\sum_{a=1}^r \nu_{al} B_a = 0, \quad (2.117)$$

where  $B_a$  denotes chemical species  $a$ . There are  $m$  chemical reactions:  $m \geq l \geq 1$ , and  $r$  chemical species are involved in the reactions. The presence of chemical reactions requires a modification of the mass fraction balance equations, whereas other macroscopic evolution equations retain the same form as (2.34) although the dissipation terms may contain reactive contributions, but they do not have to be written out explicitly for our purpose here. The mass fraction balance equation now reads

$$\rho d_t c_a = -\nabla \cdot \mathbf{J}_a + \sum_{l=1}^m \nu_{al} R_l. \quad (2.118)$$

The calortropy balance equation remains invariant to chemical reactions. Let us define the affinity  $A_l$  by the expression

$$A_l = \sum_{a=1}^r \nu_{al} \hat{\mu}_a. \quad (2.119)$$

The presence of chemical reactions then requires the following modification of Proposition 4c:

**Proposition 4c** *For the system where there are  $m$  chemical reactions  $\sum_a^r \nu_{al} B_a = 0$  ( $m \geq l \geq 1$ ) the calortropy flux  $\mathbf{J}_c := \mathbf{Q}^c/T$  is given by the bilinear form of the intensive variables  $T^{-1}$ ,  $\widehat{\mu}_a T^{-1}$ , and  $X_a^{(s)} T^{-1}$  ( $s \geq 1$ ,  $1 \leq a \leq r$ ) paired, respectively, with  $\mathbf{Q}_a$ ,  $\mathbf{J}_a$ , and  $\psi_a^{(s)}$  (flux of  $\Phi_a^{(s)}$ ) as follows:*

$$\mathbf{J}_c := \sum_{a=1}^r \frac{\mathbf{Q}_a^c}{T} = \sum_{a=1}^r T^{-1} (\mathbf{Q}_a - \widehat{\mu}_a \mathbf{J}_a + \sum_{s \geq 1} X_a^{(s)} \psi_a^{(s)}), \quad (2.120)$$

and the calortropy production  $\Xi_{cal}$  is given by the bilinear form

$$\begin{aligned} \Xi_{cal} &:= \rho \widehat{\Xi}_{cal} \\ &= -T^{-1} \sum_{a=1}^r [(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q}_a^c \cdot \nabla \ln T \\ &\quad + \mathbf{J}_a \cdot (\nabla \widehat{\mu}_a - \mathbf{F}_a) + \sum_{l=1}^m \nu_{al} \widehat{\mu}_a R_l - \sum_{s \geq 1} \psi_a^{(s)} \cdot \nabla X_a^{(s)}] \\ &\quad + T^{-1} \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} (\mathcal{Z}_a^{(s)} + \Lambda_a^{(s)}). \end{aligned} \quad (2.121)$$

Here contributions to  $\Lambda_a^{(s)}$  by the chemical reactions are implicit. By the second law of thermodynamics,  $\Xi_{cal} \geq 0$  always, the equality holding for reversible processes only.

Therefore, the calortropy flux formally remains the same as for nonreactive systems, but the calortropy production is modified by the presence of a term given below, since there is an energy dissipation term which arises from chemical reactions present:

$$\Xi_{cal}^{\text{chem}} := -T^{-1} \sum_{a=1}^r \sum_{l=1}^m \nu_{al} \widehat{\mu}_a R_l = -T^{-1} \sum_{l=1}^m A_l R_l. \quad (2.122)$$

It is a familiar looking form for the entropy production in the linear theory [17] of irreversible processes. We emphasize that this additional term is not arbitrary, but a consequence of the modification of the mass fraction balance equations which is necessitated by the chemical reactions. When used in the calortropy balance equation, Proposition 4c gives rise to the same differential form for  $d_t \widehat{\Psi}$  as (2.78) in Theorem 1. Therefore, the differential form for  $d_t \widehat{\Psi}$  remains invariant in its formal structure, but the meaning of the chemical potentials changes since they now get contributions from the chemical reactions and the mass fractions become nonconserved variables joining the ranks of  $\Phi_a^{(s)}$  ( $s \geq 1$ ) whose evolution equations are also modified in

the dissipation terms. Thus hydrodynamic equations are modified, but the basic thermodynamic structure of the theory remains formally the same whether the fluid is reactive or not. If other irreversible processes, such as shearing, heat flow, and so on, are absent and chemical reactions are the only irreversible process in the system, then  $d_t \widehat{\Psi}$  becomes the local equilibrium formula for  $d_t \mathcal{S}_e$ . The local equilibrium formula also arises if the nonconserved variables are at the steady state in the moving frame of reference.

## 2.8 Inclusion of Volume Transport

In the traditional approach to continuum mechanics [16] the volume variable is described by the specific volume of the fluid, which is given by the inverse of density (or mass density in the present phenomenological theory). Recently, it has been pointed out that such a description would not yield a sufficiently general description of fluid behavior [58]. In the recent kinetic theory investigation in Ref. [8] it is shown that the specific volume is not the most appropriate quantity to describe the molar volume of a fluid, but in its place the notion of Voronoi volume [59] may be used, which may be regarded a free volume available to particles at a given state of the fluid or more generally matter. The mean Voronoi volume is a nonconserved variable, and obeys a constitutive equation with a dissipative term like other nonconserved variables we have taken into consideration in this chapter. Thus recognizing the mean Voronoi volume as a nonconserved variable on the same footing as heat flux, stress tensor, diffusion flux, etc. we extend the manifold of nonconserved variables  $\widehat{\Phi}_a^{(s)}$  to include the mean Voronoi volume, which we denote by  $\widehat{\Phi}_a^{(0)}$ , so that the set of nonconserved variables now reads  $\widehat{\Phi}_a^{(s)} (s \geq 0; 1 \leq a \leq r)$ . This requires a slight modification of Proposition 2 to the following:

**Proposition 2v** *The nonconserved variables  $\widehat{\Phi}_a^{(s)} (s \geq 0; 1 \leq a \leq r)$  including the mean Voronoi volume obey the evolution equation*

$$\rho d_t \widehat{\Phi}_a^{(s)} = -\nabla \cdot \psi_a^{(s)} + \mathcal{Z}_a^{(s)} + \Lambda_a^{(s)}, \quad (2.123)$$

where  $\psi_a^{(s)}$  is the flux of  $\Phi_a^{(s)}$ ,  $\mathcal{Z}_a^{(s)}$  is called the kinematic term, which contains, at least, a term driving the process  $\Phi_a^{(s)}$  among other terms that nonlinearly depend on nonconserved variables and gradients of the conserved variables, and  $\Lambda_a^{(s)}$  is called the dissipation term which is responsible for energy dissipation arising from the process  $\Phi_a^{(s)}$ . The dissipation term may also be a nonlinear function of variables of manifold  $\mathfrak{P}$  as well as its tangent manifold.

Except for the fact that the set includes  $\widehat{\Phi}_a^{(0)}$  in addition to  $\widehat{\Phi}_a^{(s)} (s \geq 1; 1 \leq a \leq r)$ , that is, the range of  $\widehat{\Phi}_a^{(s)}$  should be  $s \geq 0$  and  $1 \leq a \leq r$ , Proposition 2v remains the same as Proposition 2. Of course, the evolution equation for  $\widehat{\Phi}_a^{(0)}$  and its higher-order homologues must be added to the evolution equation set for the nonconserved variables.

The form for the evolution equation for  $\widehat{\Phi}_a^{(0)}$  is not sufficiently known phenomenologically, and it is one of the aims of this work to establish it with the help of a statistical mechanical theory as will be shown in later chapters. In any case, with so modified Proposition 2 a phenomenological theory of irreversible processes in the presence of volume transport phenomena is now appropriately formulated such that it is thermodynamically consistent. The inclusion of volume transport phenomena in hydrodynamic description of flows significantly generalizes the classical hydrodynamic theory and widens our perspective toward the subject.

## 2.9 Concluding Remarks

Theory of thermodynamics is based on empirical observations of natural phenomena in macroscopic material systems in nature and laboratory. Such observations and experiences, stretching over millennia and ever made more quantitative with the progress of time, have crystallized to a set of laws axiomatic in their nature, which constitutes the laws of thermodynamic science and which all branches of macroscopic physics in matter believed to conform to and obey. Here in this chapter we have presented a summary of the subject matter in a form to cover as widely as possible according to the author's point of view on linear and nonlinear irreversible phenomena and their study in the past. In this work, the representations of the first and second laws of thermodynamics are presented as a pair of exact differentials in the Gibbs manifold  $\mathfrak{G} = \mathfrak{P} \cup \mathfrak{T} \cup \Psi$ , which includes nonequilibrium fluxes among the variables spanning the manifold of variables. Therefore the dimension of  $\mathfrak{G}$  is as large as necessary for properly describing the irreversible processes in question. The aforementioned exact differential pairs can, therefore, be expressed in a pair of circular integrals in  $\mathfrak{G}$ , if the irreversible processes are made cyclic. Moreover, the exact differential forms are on the support of generalized hydrodynamic equations attendant on the irreversible transport processes undergoing in the macroscopic material system in hand. The generalized hydrodynamic equations are in conformation with the laws of thermodynamics. Therefore they are said to be thermodynamically consistent.

The generalized hydrodynamic equations attending the differential forms mentioned tend to the classical hydrodynamic equations of Navier, Stokes, Fourier, and Fick, as the system approaches the vicinity of thermodynamic equilibrium and, therefore, the transport processes becomes linear with respect to applied thermodynamic spatial gradients or forces. In this limit the theory of irreversible thermodynamics presented tends to the thermodynamics of linear irreversible processes. Therefore the generalized hydrodynamics extends the classical hydrodynamics to nonlinear transport processes.

The present theory of irreversible processes and the generalized hydrodynamic equations are also extended to include volume transport phenomena, which the conventional hydrodynamic theory and the previous version of generalized hydrodynamic equations and theory of irreversible thermodynamics by the present author

did not take into account. In this sense, the present version is a revision of the previous theory of irreversible thermodynamics by the present author, which is intended to cover a wider range of irreversible processes.

The theory of irreversible thermodynamics presented in this chapter serves a guiding light for formulating kinetic theories of irreversible nonlinear macroscopic processes in gases and liquids in later chapters in conformation to the laws of thermodynamics. This assures us to formulate theories of transport processes, linear or nonlinear, and nonequilibrium statistical thermodynamics in gases and liquids in complete consistency with the laws of thermodynamics.

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# Chapter 3

## Boltzmann Kinetic Equation

Once we accept the particulate concept of matter it is inevitable to try to understand thermodynamics and thermodynamic processes in continuum systems in terms of atoms and molecules constituting matter, and formulate molecular theories of macroscopic processes and thermodynamics. To this aim, statistical mechanics or, rather, kinetic theory of matter may be formulated and applied. At least, in the case of sufficiently dilute monatomic gases, the phenomenological theory presented in Chap. 2 can be given undisputable statistical mechanical foundations if the Boltzmann kinetic equation [1, 2] is made use of in a manner completely consistent with the laws of thermodynamics.

In this chapter we would like to show that the Boltzmann equation can enable us to adequately achieve the desired aim and thus point the direction in which to explore formulation of kinetic theory of irreversible processes in condensed phase of matter in forms comparable to the phenomenological theories presented in Chap. 2. Furthermore, since the Boltzmann equation provides us with an opportunity of examining the concept of ensemble in the context of the Gibbs ensemble theory [3–5] we would like to begin with the application of the Boltzmann equation to achieve the main objective of the present work, namely, formulation of a theory of irreversible macroscopic processes in condensed phase of matter in a way consistent with the laws of thermodynamics. In order to help us comprehend the Boltzmann kinetic theory from the viewpoint of the Gibbs ensemble theory by connecting them in the conceptual plane, in the next chapter we will briefly review the gist of the Gibbs equilibrium ensemble theory which we know provides statistical mechanical foundations [3, 5] to equilibrium thermodynamics. We reiterate that the molecular theories of macroscopic irreversible thermodynamic processes are the main objects of attention in this work, and as such the theory should be formulated in accordance with the laws of thermodynamics.

We have learned from the previous investigations [6, 7] that the aforementioned objective can be achieved with the Boltzmann kinetic equation, thanks to its char-

acteristic properties for a kinetic equation. The principal reason that the Boltzmann kinetic equation is useful for such a formulation is that it is *an irreversible kinetic equation* that breaks the time reversal invariance unlike the mechanical equations of motion such as Newton's equations of motion or the Liouville equation, owing to the presence of the time-reversal-symmetry breaking collision term in it. In this connection, it should be remarked that it is not possible to formulate a theory of irreversible processes on the basis of time-reversal symmetry invariant equations of motion or an equation, such as the reversible Liouville equation for probability distribution functions, because one cannot hope to obtain irreversible macroscopic dynamic evolution equations from reversible equations of motion. Clearly, something more than the reversible equations of motion is required. The Boltzmann kinetic equation is a typical example of irreversible kinetic equation, which is valid, at least, for dilute gases, that provides the essential feature for description of irreversibility.

Thus the example of formulating an irreversible theory of macroscopic transport processes with the Boltzmann kinetic equation would clearly expose the essential qualities that are required for a kinetic equation to possess if a thermodynamically consistent theory of irreversible processes is desired in the dense fluid regime in which particles are correlated statistically at arbitrary strength. For this reason it would be very useful to illustrate the basic ideas with the example of the Boltzmann kinetic equation for dilute monatomic gases to illustrate the required qualities that the kinetic equation should have if the theory is to have a chance to fulfill the desired thermodynamic consistency. The theory so formulated then can be tested against experiment and observations in the light of the thermodynamic laws. For the aforementioned reason we start our discourse with the Boltzmann kinetic equation and uncover the gist of what it implies for the goal we set out for this work, namely, a molecular theory of irreversible processes in condensed phase and, in particular, in liquids in conformation to the law of thermodynamics.

### 3.1 Irreversible Processes in Dilute Monatomic Gases

We shall assume that the fluid consists of a monatomic gaseous mixture contained in volume  $V$  and the mixture is sufficiently dilute, so that the statistical correlations between molecules are negligible to a good approximation. The Boltzmann kinetic equation provides an adequate mathematical model for the kinetic equation for such a system. We will briefly discuss how a thermodynamic theory of irreversible processes is formulated on the basis of the Boltzmann equation, listing the essential features and steps in this chapter.

Let us imagine the phase space of  $N_1, N_2, \dots, N_r$  molecules of species  $1, 2, \dots, r$  with position coordinates and momenta of particles, respectively, denoted  $\mathbf{r}_{ia}$  and  $\mathbf{p}_{ia}$  in the Euclidean phase space where  $i$  and  $a$  refer to the  $i$ th particle of species  $a$  of mass  $m_a; i \in a$ . The global scale number density of species  $a$  therefore is  $n_a = N_a/V$  and the mixture is of  $r$  components. The phase space volume element of particles numbering

$$N = N_1 + N_2 + \cdots + N_r$$

will be abbreviated for brevity of notation by

$$d\mathbf{x}^{(N)} = \prod_{a=1}^r d\mathbf{r}_{1a} \cdots d\mathbf{r}_{N_1 a} d\mathbf{p}_{1a} \cdots d\mathbf{p}_{N_1 a} = \prod_{a=1}^r d\mathbf{x}_a^{(N_a)}, \quad (3.1)$$

where the range of position coordinates is limited by  $V$ , whereas the range of momenta is from  $-\infty$  to  $+\infty$ . The probability—namely, the distribution function—of finding particles in phase volume element  $d\mathbf{x}^{(N)}$  around the phase point (or just phase for simplicity)  $\mathbf{x}_{ia} = (\mathbf{r}_{ia}, \mathbf{p}_{ia})$  for all  $i \in a$  and at time  $t$  is denoted by  $F^{(N)}(\mathbf{x}^{(N)}, t)$ . By the assumption that particles are not statistically correlated and thus statistically independent of each other, the distribution function  $F^{(N)}(\mathbf{x}^{(N)}, t)$  of  $N$  particles, consequently, is a product of singlet distribution functions  $f_a(\mathbf{x}_{ia}, t)$ :

$$F^{(N)}(\mathbf{x}^{(N)}, t) = \prod_{a=1}^r \prod_{i=1}^{N_a} f_a(\mathbf{x}_{ia}, t). \quad (3.2)$$

In the Boltzmann kinetic theory it is assumed that the singlet distribution functions obey the Boltzmann kinetic equation. Since the particles of the same species are indistinguishable it is sufficient to consider  $f_a(\mathbf{r}, \mathbf{v}_a, t) := f_a(\mathbf{x}_{ia}, t)$  for species  $a$ , which is assumed to obey the kinetic equation

$$\left( \frac{\partial}{\partial t} + \mathbf{v}_a \cdot \frac{\partial}{\partial \mathbf{r}} + \mathbf{F}_a \cdot \frac{\partial}{\partial \mathbf{p}_a} \right) f_a(\mathbf{r}, \mathbf{p}_a, t) = \mathbf{R}[f_a], \quad (3.3)$$

where  $\mathbf{v}_a = \mathbf{p}_a/m_a$  and  $\mathbf{R}[f_a]$  is the Boltzmann collision integral defined by [1, 2]

$$\mathbf{R}[f_a] = \sum_{b=1}^r C(f_a, f_b), \quad (3.4)$$

$$C(f_a, f_b) = \int d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} \mathbf{b} \mathbf{g}_{ab} [f_a^*(\mathbf{r}, \mathbf{v}_a^*, t) f_b^*(\mathbf{r}, \mathbf{v}_b^*, t) - f_a(\mathbf{r}, \mathbf{v}_a, t) f_b(\mathbf{r}, \mathbf{v}_b, t)] \quad (3.5)$$

with  $\varphi$  denoting the deflection angle of scattering,  $\mathbf{b}$  the impact parameter,  $\mathbf{g}_{ab} = |\mathbf{v}_a - \mathbf{v}_b|$ , and the asterisk the post-collision value.  $\mathbf{F}_a$  is the external force on mass  $m_a$  of species  $a$ . It is assumed to vary slowly in space and remain constant over the intermolecular interaction range, so that molecular collisions are not affected by it. Here indices  $a$  and  $b$  play a dual role of simultaneously standing for particle and its species. This notational device is for brevity of equations. The singlet distribution functions are assumed spatially coarse-grained over the intermolecular force range, so that they remain unchanged over the course of collision. This, often overlooked but important, point should be kept in mind in applying the Boltzmann kinetic equation. Here we have presented the Boltzmann kinetic equation in the conventional form in

deference to the tradition, but we will slightly alter it to a more general form that will help later to design a kinetic equation for correlated systems.

Despite assertions made in the literature [8] that the Boltzmann kinetic equation can be derived from the basic mechanical equations, it is important to recognize that it, in essence, is *a postulate for dynamic evolution of singlet distribution functions*  $f_a(\mathbf{r}, \mathbf{v}_a, t)$  in the phase space, which is based on the assumptions made to “arrive at it” from the reversible equations of motion: *the molecular chaos assumption, the absence of statistical correlations of particles, and spatial and time coarse-grainings over the range of intermolecular forces*. We will find that these assumptions enter in one form or another in devising a suitable kinetic equation for the distribution function for a liquid, but they are not attributes of the mechanical laws of motion in true sense of words.

The distribution function  $f_a(\mathbf{r}, \mathbf{v}_a, t)$  is normalized to number density  $n_a(\mathbf{r}, t)$  as follows:

$$n_a(\mathbf{r}, t) = \int d\mathbf{v}_a f_a(\mathbf{r}, \mathbf{v}_a, t). \quad (3.6)$$

Here the integration over the velocity ranges from  $-\infty$  to  $+\infty$ . With  $f_a(\mathbf{r}_a, \mathbf{v}_a, t)$  obeying (3.3), the mean value (statistical average)  $\langle A(\mathbf{v}_a) f_a \rangle$  of mechanical quantity  $A(\mathbf{v}_a)$  can be computed by the formula

$$\langle Af_a \rangle = \int d\mathbf{v}_a A(\mathbf{v}_a) f_a(\mathbf{r}, \mathbf{v}_a, t). \quad (3.7)$$

Henceforth angular brackets  $\langle Af_a \rangle$  denotes the mean value of dynamical quantity  $A$  calculated with the distribution function  $f_a$ . It is also useful to note the following properties associated with the Boltzmann collision integrals, such as

$$\mathbf{g}_{ab} = \mathbf{g}_{ab}^* \quad (3.8)$$

and, if  $d\Omega$  is denoted by

$$d\Omega = \sin \theta d\theta d\varphi, \quad (3.9)$$

the relation between the phase space volumes before and after collision

$$d\mathbf{v}_a d\mathbf{v}_b d\Omega = d\mathbf{v}_a^* d\mathbf{v}_b^* d\Omega. \quad (3.10)$$

If the scattering cross section  $\sigma(\mathbf{g}_{ab}|\mathbf{g}_{ab}^*)$  is defined as is done in mechanics [9, 10] by the relation

$$\mathbf{b} d\mathbf{b} d\varphi = \sigma(\mathbf{g}_{ab}|\mathbf{g}_{ab}^*) d\Omega, \quad (3.11)$$

owing to (3.8) the microscopic reversibility implies

$$\sigma(\mathbf{g}_{ab}|\mathbf{g}_{ab}^*) = \sigma(\mathbf{g}_{ab}^*|\mathbf{g}_{ab}). \quad (3.12)$$

The relations (3.8), (3.10), and (3.12) owe their validity to the reversibility of the collision dynamics on the microscopic scale. It is also important to observe that the distribution functions  $f_a(\mathbf{r}, \mathbf{v}_a, t)$ , etc. in  $C(f_a, f_b)$  remain unchanged over the collision volume. In this sense, the Boltzmann equation describes the evolution of spatially coarse-grained distribution functions. These features show that the mechanical laws of particles and their interactions are Newtonian at the classical particle dynamical level, but the statistical evolution equation for the distribution function or probability distribution function obeying the Boltzmann equation is not exactly of Newtonian (classical) mechanics, although it is built on the Newtonian mechanics at the microscopic dynamical level as far as the collision process involved is concerned. Thus it is appropriate to regard the Boltzmann kinetic equation as *a fundamental postulate* for a dynamic, statistical description of evolution of probability distribution functions for macroscopic systems (in this case, fluids) in the phase space. Its validity is then justified *a posteriori* in comparison with observations and experiment on the system modeled by the kinetic equation—the approach therefore is deductive under a set of postulates, as statistical mechanics is in general.

### 3.1.1 *Conserved and Nonconserved Macroscopic Variables*

As we have found it convenient to distinguish conserved and nonconserved variables in developing the phenomenological theory of irreversible processes described in Chap. 2, we will adopt the same scheme of variable classification in the kinetic theory approach so that we hope to provide a molecular theory foundation of the phenomenological theory. The former set of variables obeys conservation laws, examples being the mass, momentum, and energy balance equation, and the latter are variables for which their evolution equations have a source term responsible for energy dissipation which arises from the fact that their microscopic dynamic observables are not conserved over the molecular collision processes attendant on their collisional evolution. This distinction between the conserved and nonconserved variables is the essential and manifest advantage of the Boltzmann kinetic theory over a Liouville equation that does not have an irreversible collision term and thus has no mechanism for energy dissipation built into it. We will find that the Boltzmann collision integral-weighted averages of nonconserved variables are intimately associated with energy dissipation arising in the irreversible processes involving nonconserved variables.

#### 3.1.1.1 **Conserved Variables**

In the case of dilute monatomic gases describable by the Boltzmann kinetic equation the conserved variables, mass density, momentum density, and energy density or internal energy density, are defined as follows:

### Mass Density

The local mass density of species  $a$  is given evidently by the statistical mechanical formula

$$\rho_a(\mathbf{r}, t) = \langle m_a f_a \rangle, \quad (3.13)$$

where the angular brackets stand for averaging over velocity space as defined by (3.7). Henceforth in this chapter the arguments in the distribution function  $f_a(\mathbf{r}, \mathbf{v}_a, t)$  will be suppressed for the sake of notational brevity, wherever there is no danger of confusion arising thereby. The total local density  $\rho(\mathbf{r}, t)$  is then given by the expression

$$\rho(\mathbf{r}, t) = \sum_{a=1}^r \rho_a(\mathbf{r}, t) = \sum_{a=1}^r \langle m_a f_a \rangle. \quad (3.14)$$

### Momentum Density

The mean velocity  $\mathbf{u}_a(\mathbf{r}, t)$  consistent with (3.14) is then defined by the average of molecular momentum

$$\rho_a(\mathbf{r}, t) \mathbf{u}_a(\mathbf{r}, t) = \langle m_a \mathbf{v}_a f_a \rangle, \quad (3.15)$$

whose sum over species gives the total momentum density

$$\rho(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t) = \sum_{a=1}^r \rho_a(\mathbf{r}, t) \mathbf{u}_a(\mathbf{r}, t) = \sum_{a=1}^r \langle m_a \mathbf{v}_a f_a \rangle. \quad (3.16)$$

Note that the left hand side of (3.16) is evidently the momentum of the fluid mixture. The mean velocity  $\mathbf{u}(\mathbf{r}, t)$  defined by (3.16) is simply called the fluid velocity or fluid-particle velocity. Thus from the molecular theory viewpoint the fluid velocity is seen as the mean velocity of a packet of molecules in the elementary volume of fluid located around position  $\mathbf{r}$  in the coordinate system at time  $t$ . It is then convenient to define the peculiar velocity  $\mathbf{C}_a$  of particle  $a$  by the formula

$$\mathbf{C}_a = \mathbf{v}_a - \mathbf{u}(\mathbf{r}, t). \quad (3.17)$$

We note that peculiar velocity had been originally an astronomical term which was adopted in kinetic theory; it is a velocity relative to  $\mathbf{u}(\mathbf{r}, t)$ , more precisely, the center of mass velocity of a packet of fluid at  $\mathbf{r}$ . In kinetic theory it is found convenient to define mean values of velocity-related quantities in terms of peculiar velocities. Clearly, the peculiar velocity has the property

$$\sum_{a=1}^r \langle m_a \mathbf{C}_a f_a \rangle = 0. \quad (3.18)$$

### Energy Density

The total kinetic energy density of the fluid is evidently defined by the mean kinetic energy formula

$$E_k(\mathbf{r}, t) = \sum_{a=1}^r \left\langle \frac{1}{2} m_a (\mathbf{v}_a \cdot \mathbf{v}_a) f_a \right\rangle, \quad (3.19)$$

which motivates us to define the internal energy density by the formula

$$\rho(\mathbf{r}, t) \mathcal{E}(\mathbf{r}, t) = \sum_{a=1}^r \left\langle \frac{1}{2} m_a (\mathbf{C}_a \cdot \mathbf{C}_a) f_a \right\rangle. \quad (3.20)$$

This may be interpreted as the mean kinetic energy of a packet of fluid particles moving relative to the mean velocity  $\mathbf{u}(\mathbf{r}, t)$ . If the peculiar velocity is used in the kinetic energy expression (3.19),  $E_k$  is expressed by the formula

$$E_k(\mathbf{r}, t) = E_{\text{kin}} + \rho(\mathbf{r}, t) \mathcal{E}(\mathbf{r}, t), \quad (3.21)$$

where  $E_{\text{kin}}$  is the convective kinetic energy of the fluid

$$E_{\text{kin}} = \frac{1}{2} \rho \mathbf{u} \cdot \mathbf{u}. \quad (3.22)$$

In the case of a dilute monatomic gas mixture, there are no other conserved variables than those listed above.

#### 3.1.1.2 Nonconserved Macroscopic Variables

In continuum mechanical description of macroscopic processes in gas and fluid in general there can occur a number of macroscopic observables other than the conserved variables as we have observed in Chap. 2, and the number of such variables may vary depending on the processes under consideration. In kinetic theory the set of such nonconserved variables is generally kept open. For dilute monatomic gases such a set may be generated from the mean value of the quantity obtained upon operating on it the one-particle Liouville operator, namely, the streaming terms of the Boltzmann equation, defined by

$$\mathbf{L}^{(1)} = \mathbf{v}_a \cdot \nabla + \widehat{\mathbf{F}}_a \cdot \nabla_{\mathbf{v}_a} = \mathbf{C}_a \cdot \nabla + \mathbf{u} \cdot \nabla + \widehat{\mathbf{F}}_a \cdot \nabla_{\mathbf{v}_a}, \quad (3.23)$$

where  $\nabla = \partial/\partial \mathbf{r}$ ,  $\nabla_{\mathbf{v}_a} = \partial/\partial \mathbf{v}_a$ , and  $\widehat{\mathbf{F}}_a = \mathbf{F}_a/m_a$ .

If  $\mathbf{C}_a$  is a  $d$ -dimensional vector, let its unit vector directions indexed  $1, 2, \dots, d$ . Let  $A_a^{(s)}$  denote a product (moment) of components of  $\mathbf{C}_a$

$$h_a^{(s)} = m_a C_a^{s_1} C_a^{s_2} \cdots C_a^{s_m}, \quad (3.24)$$

where superscripts  $s_1, s_2, \dots, s_m$  stand for integers. For example, if  $h_a^{(ii)} = m_a C_a^i C_a^i$  with the repeated superscript  $i$  meaning the sum over  $i$  (Einstein convention), which therefore implies the scalar product of vector  $\mathbf{C}_a$ . However, if  $h_a^{(ij)} = m_a C_a^i C_a^j$  with  $i \neq j$ , then it is a direct ordered product of two vector components.

Let us operate the linear operator  $\mathbf{L}^{(1)}$  on  $h_a^{(s)} f_a$ :

$$\mathbf{L}^{(1)}(h_a^{(s)} f_a) = (\mathbf{C}_a \cdot \nabla + \mathbf{u} \cdot \nabla + \widehat{\mathbf{F}}_a \cdot \nabla_{\mathbf{v}_a})(h_a^{(s)} f_a), \quad (3.25)$$

where  $f_a$  is standing for the distribution function. Operating the Liouville operator in turn on the quantities on its right we obtain

$$\begin{aligned} \mathbf{L}^{(1)}(h_a^{(s)} f_a) &= (\mathbf{C}_a \cdot \nabla h_a^{(s)} + \mathbf{u} \cdot \nabla h_a^{(s)} + \widehat{\mathbf{F}}_a \cdot \nabla_{\mathbf{v}_a} h_a^{(s)}) f_a \\ &\quad + h_a^{(s)} (\mathbf{C}_a \cdot \nabla f_a + \mathbf{u} \cdot \nabla f_a + \widehat{\mathbf{F}}_a \cdot \nabla_{\mathbf{v}_a} f_a). \end{aligned} \quad (3.26)$$

This shows that operation of  $\mathbf{L}^{(1)}$  on  $h_a^{(s)} f_a$  generates a combination of moments of  $\mathbf{C}_a$  including a moment one-order higher than the original moment  $h_a^{(s)}$ , namely,

$$h_a^{(s+1)} = h_a^{(s)} \mathbf{C}_a \quad (3.27)$$

appearing in the term  $h_a^{(s)} \mathbf{C}_a \cdot \nabla f_a$ —the first term in the second line of (3.26). Thus repeated operations of  $\mathbf{L}^{(1)}$  on a product of  $\mathbf{C}_a$  give rise to an open hierarchical set of moments with the order of moment increasing by one every time  $\mathbf{L}^{(1)}$  is operated on  $h_a^{(s)}$ . This feature is ever present in kinetic theory—molecular theory—approach to macroscopic processes regardless of whether the approach taken is for equilibrium or nonequilibrium processes. One must therefore be prepared to contend with this problem of an open hierarchical set appearing in molecular theory approach.

### 3.1.2 Collision Invariants

We have mentioned that the evolution equations for the conserved variables do not have a source term associated with energy dissipation by the process. Within the framework of the Boltzmann kinetic equation this distinguishing characteristic is intimately associated with the collision invariance property of the equation. This feature of the Boltzmann equation is important for the macroscopic theory formulated. It is what sets apart the Boltzmann equation from the reversible Liouville equation, which lacks irreversibility essential for irreversible kinetic equations.

Let us denote by  $\psi_a$  a function of  $\mathbf{v}_a$  and  $\mathbf{r}$  and consider the integral

$$I[\psi] = \sum_{a=1}^r \sum_{b=1}^r \int d\mathbf{v}_a \psi_a(\mathbf{v}_a, \mathbf{r}) C(f_a f_b). \quad (3.28)$$

Upon substitution of the explicit expression for  $C (f_a f_b)$  in (3.5), adding the result to (3.28), and dividing the result by 2, we obtain

$$I [\psi] = \frac{1}{2} \sum_{a=1}^r \sum_{b=1}^r \int \int d\mathbf{v}_a d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} \mathbf{b} \mathbf{g}_{ab} (\psi_a + \psi_b) \times \\ [f_a^* (\mathbf{r}, \mathbf{v}_a^*, t) f_b^* (\mathbf{r}, \mathbf{v}_b^*, t) - f_a (\mathbf{r}, \mathbf{v}_a, t) f_b (\mathbf{r}, \mathbf{v}_b, t)]. \quad (3.29)$$

The collision process involved for this expression is accompanied by the transformation of velocity pair from the initial to the final state:  $(\mathbf{v}_a, \mathbf{v}_b) \rightarrow (\mathbf{v}_a^*, \mathbf{v}_b^*)$ . On reversal of this collision process the integral  $I [\psi]$  takes the form

$$I [\psi] = \frac{1}{2} \sum_{a=1}^r \sum_{b=1}^r \int \int d\mathbf{v}_a^* d\mathbf{v}_b^* \int_0^{2\pi} d\varphi^* \int_0^\infty d\mathbf{b}^* \mathbf{b}^* \mathbf{g}_{ab}^* (\psi_a^* + \psi_b^*) \times \\ [f_a (\mathbf{r}, \mathbf{v}_a, t) f_b (\mathbf{r}, \mathbf{v}_b, t) - f_a^* (\mathbf{r}, \mathbf{v}_a^*, t) f_b^* (\mathbf{r}, \mathbf{v}_b^*, t)]. \quad (3.30)$$

We remark that since the distribution functions are coarse-grained over the collision volume of an order of the intermolecular force range, the position coordinate  $\mathbf{r}$  in the distribution functions is not affected by the collision. Add this equation to (3.29) to obtain

$$I [\psi] = -\frac{1}{4} \sum_{a=1}^r \sum_{b=1}^r \int \int d\mathbf{v}_a d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} \mathbf{b} \mathbf{g}_{ab} (\psi_a^* + \psi_b^* - \psi_a - \psi_b) \times \\ [f_a^* (\mathbf{r}, \mathbf{v}_a^*, t) f_b^* (\mathbf{r}, \mathbf{v}_b^*, t) - f_a (\mathbf{r}, \mathbf{v}_a, t) f_b (\mathbf{r}, \mathbf{v}_b, t)]. \quad (3.31)$$

If  $\psi_a$  is a conserved quantity in the collision process, then there holds the relation

$$\psi_a^* + \psi_b^* = \psi_a + \psi_b. \quad (3.32)$$

The conserved quantities listed earlier satisfy this relation as can be easily verified by means of the mechanical equations of motion. Therefore for conserved quantities

$$I [\psi] = 0 \quad (3.33)$$

identically. Such a quantity is called a collision invariant. As will be seen later, this is responsible for the absence of the energy dissipating source term in the evolution equations of conserved variables—conservation laws. This property is a prerequisite among other necessary properties for a kinetic equation, if the theory is to obey the conservation laws as it should.

In addition to this property of collision invariants, there are other noticeable properties of the collision integral  $C (f_a f_b)$ . We list them below:

- $C(f_a f_b)$  is evidently symmetric with respect to interchange of indices  $a$  and  $b$ :

$$C(f_a f_b) = C(f_b f_a). \quad (3.34)$$

- If we express  $C(f_a f_b)$  in a way to distinguish pre- and post-collision distribution function as in  $C(f_a f_b) := C(f_a f_b | f_a^* f_b^*)$ , then the reversal of collision process results in the change in sign of  $C(f_a f_b | f_a^* f_b^*)$ . Thus under the reversal of collision process  $(\mathbf{v}_a^*, \mathbf{v}_b^*) \rightarrow (\mathbf{v}_a, \mathbf{v}_b)$

$$C(f_a f_b | f_a^* f_b^*) \rightarrow C(f_a^* f_b^* | f_a f_b) = -C(f_a f_b | f_a^* f_b^*). \quad (3.35)$$

- If  $f_a^{\text{eq}}$  and  $f_b^{\text{eq}}$  are equilibrium solutions of the Boltzmann equation then

$$C(f_a^{\text{eq}} f_b^{\text{eq}} | f_a^{\text{eq}} f_b^{\text{eq}}) = 0 \quad (3.36)$$

identically. This property is easy to see since at equilibrium the distribution functions remain constant in time and space,  $f_a^{\text{eq}}$  is such that

$$\left( \frac{\partial}{\partial t} + \mathbf{L}^{(1)} \right) f_a^{\text{eq}} = 0. \quad (3.37)$$

Hence (3.36) holds. Because of properties (3.34) and (3.35) the following inequality holds:

$$I_H = \sum_{a=1}^r \sum_{b=1}^r \langle -\ln f_a C(f_a f_b) \rangle \geq 0. \quad (3.38)$$

By virtue of properties (3.34) and (3.35)  $I_H$  can be put in the form

$$I_H = \frac{1}{4} \sum_{a=1}^r \sum_{b=1}^r \left\langle \ln \left( \frac{f_a^* f_b^*}{f_a f_b} \right) \left[ f_a^* f_b^* - \frac{f_a^* f_b^*}{f_a f_b} \right] \right\rangle \geq 0, \quad (3.39)$$

where the angular brackets  $\langle \dots \rangle$  stands for integration over  $\mathbf{v}_a$  and  $\mathbf{v}_b$  of the Boltzmann collision integral, and the inequality holds because  $\ln(y/x)(y-x) \geq 0$ . The existence of this distinguishing property of the Boltzmann equation, namely, the positivity of  $I_H$ , is what makes it essential for understanding the molecular theory of irreversible processes in the fluid under consideration.

### 3.1.3 Broken Time Reversal Symmetry and the Boltzmann Kinetic Equation

We have mentioned earlier the necessity of the kinetic equation being of broken time reversal symmetry if it is going to properly describe irreversible phenomena in macroscopic systems, at least, with respect to time reversal symmetry breaking.

Unlike the Newtonian equations of motion or Schrödinger equation the Boltzmann kinetic equation breaks time reversal symmetry. If an equation breaks time reversal symmetry, it does not remain invariant to the reversal of the direction of time and velocity. In the case of evolution equations for irreversible phenomena, since the evolution of the processes is unidirectional the evolution equations must not remain invariant to the transformation reversing the direction of time and velocities. We show it is indeed the case for the Boltzmann kinetic equation.

Let us reverse the direction of flow of time,  $t \rightarrow -t$  in the equation while the velocity is also simultaneously reversed:  $\mathbf{v}_a \rightarrow -\mathbf{v}_a$ ; in other words, operate the time reversal operator  $\vartheta$  on the Boltzmann kinetic equation

$$\vartheta \left[ \frac{\partial}{\partial t} + \mathbf{L}_1(\mathbf{v}_a) \right] f_a(\mathbf{r}, \mathbf{v}_a, t) = \sum_{b=1}^r \vartheta C(f_a f_b). \quad (3.40)$$

The left-hand side of this equation is then given by

$$\begin{aligned} \vartheta \left[ \frac{\partial}{\partial t} + \mathbf{L}_1(\mathbf{v}_a) \right] f_a(\mathbf{r}, \mathbf{v}_a, t) &= \left[ \frac{\partial}{\partial(-t)} + \mathbf{L}_1(-\mathbf{v}_a) \right] f_a(\mathbf{r}, -\mathbf{v}_a, -t) \\ &= - \left[ \frac{\partial}{\partial t} + \mathbf{L}_1(\mathbf{v}_a) \right] f_a(\mathbf{r}, -\mathbf{v}_a, -t), \end{aligned}$$

whereas the right-hand side is given by

$$\begin{aligned} \sum_{b=1}^r \vartheta C(f_a f_b) &= \sum_{b=1}^r \int d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} \mathbf{b} \mathbf{g}_{ab} \times \\ &\quad [f_a^*(\mathbf{r}, -\mathbf{v}_a^*, -t) f_b^*(\mathbf{r}, -\mathbf{v}_b^*, -t) \\ &\quad - f_a(\mathbf{r}, -\mathbf{v}_a, -t) f_b(\mathbf{r}, -\mathbf{v}_b, -t)], \end{aligned} \quad (3.41)$$

where the collision volume—the phase volume—remains unchanged under the operation of  $\vartheta$ . The final form of the equation takes the form

$$\left[ \frac{\partial}{\partial t} + \mathbf{L}_1(\mathbf{v}_a) \right] f_a(\mathbf{r}, -\mathbf{v}_a, -t) = - \sum_{b=1}^r C[f_a(\mathbf{r}, -\mathbf{v}_a, -t) f_b(\mathbf{r}, -\mathbf{v}_b, -t)]. \quad (3.42)$$

Thus we see that the Boltzmann kinetic equation does not remain invariant under time reversal and neither does the time reversed distribution function  $f_a(\mathbf{r}, -\mathbf{v}_a, -t)$  obey the same kinetic equation as the original kinetic equation for  $f_a(\mathbf{r}, \mathbf{v}_a, t)$ . That is, the Boltzmann kinetic equation is of broken time reversal symmetry. This would not be the case if a kinetic equation is without a collision integral, for example, collisionless Boltzmann equation for which  $\mathbf{R}[f_a] = 0$  identically. This equation with  $\mathbf{R}[f_a] = 0$ , as a matter of fact, is the one-particle Liouville equation and, as is well known, the Liouville equation of an arbitrary number of particles is time

reversal invariant regardless of the number of particles involved. For this reason the Liouville equation cannot produce a dissipation term in the macroscopic evolution equations derived from it.

The distinguishing characteristic of broken time reversal symmetry in the Boltzmann equation is the very property that makes it useful for formulating a molecular theory of thermodynamics of irreversible processes. A kinetic equation of such a property is not a derivative of Newtonian mechanics proper, such as Newtonian equations of motion, free from *extra-mechanical* assumptions, and hence must be taken as a postulate for molecular description of evolution for macroscopic processes in large systems of interacting molecules in the strict mechanical standpoint of view. For this reason the macroscopic theory formulated with a time-reversal symmetry breaking kinetic equation is a postulate and deductive as noted earlier and must be justified *a posteriori* of its validity with the help of experiment or in conformation to the laws of thermodynamics.<sup>1</sup>

### 3.1.4 The *H* Theorem and Boltzmann Entropy

The Boltzmann kinetic equation is a nonlinear partial differential equation for distribution functions for sufficiently dilute gas. Boltzmann's motivation to study his kinetic equation was, most importantly, to show the uniqueness and stability of the Maxwell velocity distribution, which J. C. Maxwell obtained about seven years earlier in his kinetic theory. To achieve the aim Boltzmann specifically invented the *H* function, and in doing it he, in fact, preceded Lyapounov [11] who proposed to employ what is now called the Lyapounov function in stability theory [12, 13] of solutions of differential equations. The *H* function for the Boltzmann equation is defined by

$$S(t) = -k_B \sum_{a=1}^r \int_V d\mathbf{r} \langle f_a(\mathbf{r}, \mathbf{v}_a, t) \ln f_a(\mathbf{r}, \mathbf{v}_a, t) \rangle. \quad (3.43)$$

Traditionally, in the literature [2, 6, 7, 14], on the Boltzmann kinetic theory  $[\ln f_a(\mathbf{r}, \mathbf{v}_a, t) - 1]$  is used in place of  $\ln f_a(\mathbf{r}, \mathbf{v}_a, t)$  in (3.43). We, however, find the factor  $(-1)$  is not necessary and troublesome in developing the nonequilibrium theory of transport processes discussed in this work. As a matter of fact, in the original definition by Boltzmann [1] the  $(-1)$  factor is absent, but later authors inserted it because it was found that it does not change the conclusion or utility of the *H* function, yet we find it inconvenient to have for discussing the thermodynamics of irreversible phenomena in a general context. Therefore we will adhere to Boltzmann's original definition of *S*.

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<sup>1</sup>In this viewpoint it is reasonable to regard the Boltzmann equation as a fundamental postulate for a molecular theory of dilute uncorrelated monatomic gases. And this is our position taken for all the kinetic equations for correlated fluids considered in this work.

Later in his theory, when the equilibrium solution for the Boltzmann equation, namely, the Maxwell distribution function [2], is used for  $S$ , Boltzmann discovered that the  $H$  function gave rise to the equilibrium entropy that Clausius [15] discovered some seven years earlier in his study of thermodynamics. In this regard, it should be emphasized that in thermodynamics Clausius's entropy is definable only for reversible (equilibrium) processes as discussed in Chap. 2. It is not immediately answerable at this point to what extent  $S(t)$  is related to the Clausius entropy for reversible processes, but it is clear that  $S(t)$  is certainly beyond the realm of Clausius's entropy defined for reversible processes, because the system described by the Boltzmann equation can be far removed from equilibrium and, in fact, the Boltzmann equation describes nonequilibrium phenomena in the phase space but not only in the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T}$  introduced in Chap. 2. In fact, in the terminology of information theory developed by Shannon [16]  $S(t)$  is the negative of average information. Since the distribution functions describe probabilities of microscopic states in the phase space of particles in the systems of particles on the order of  $10^{23}$  in number, the information content of  $S(t)$  in a nonequilibrium state is certainly larger than those of the macroscopic thermodynamic system (matter) at equilibrium, and it would be reasonable to expect that the manifold of the states characteristic of such a nonequilibrium system would be larger than that of the equilibrium system. With this note of the subtlety of entropy with regard to the Clausius entropy of reversible processes and the nature of  $S(t)$ , we will henceforth refer to  $S(t)$  as *the Boltzmann entropy* in contrast to *the Clausius entropy*, which is reserved for reversible processes or systems in equilibrium only, as we have done in Chap. 2.

On differentiation of  $S(t)$  and use of the Boltzmann equation and applying the boundary conditions on the distribution functions upon integrating the resulting expression, there follows from (3.43) the derivative of  $S$  in the form

$$\frac{dS}{dt} = -k_B \sum_{a=1}^r \int_V d\mathbf{r} \langle \ln f_a(\mathbf{r}, \mathbf{v}_a, t) \mathbf{R}[f_a] \rangle. \quad (3.44)$$

By property (3.38) of the Boltzmann equation, especially, with regard to the collision integral  $\mathbf{R}[f_a]$ , it follows

$$\frac{dS}{dt} \geq 0, \quad (3.45)$$

where the equality holds at equilibrium established in the long time limit. This is the content of Boltzmann's  $H$  theorem. It thus implies that the equilibrium solution of the Boltzmann equation is stable in accordance with the Lyapounov criteria of stability [12, 13]. It, however, is not the same as the second law of thermodynamics which is about an inequality holding for macroscopically measurable variables near the equilibrium state of a macroscopic thermodynamic system described in the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T}$ ; see the discussions given in Chap. 2.

## 3.2 Equilibrium Distribution Function

The  $H$  theorem makes it possible to prove that the equilibrium solution of the Boltzmann kinetic equation is not only unique, but also a Maxwell distribution function. For at equilibrium it follows from (3.44) that

$$\ln f_a^{*eq} + \ln f_b^{*eq} - \ln f_a^{eq} - \ln f_b^{eq} = 0, \quad (3.46)$$

which implies that  $\ln f_a^{eq}$  and  $\ln f_b^{eq}$  are made up of collision invariants. Since the Hamiltonian (energy), momentum, and density (or mass density) are only invariants of a collision process,  $\ln f_a^{eq}$  must be given as a linear combination of five collision invariants, namely, mass  $m_a$ , three momenta  $m_a v_{ax}, m_a v_{ay}, m_a v_{az}$ , and energy. Determining the five expansion coefficients of the linear combination by using the mean values of the five collision invariants and comparing them with their thermodynamic correspondents; namely,  $n_a^0$  for the equilibrium bulk density,  $\mathbf{u}$  for the fluid velocity, and the kinetic energy density of the fluid

$$\rho^0 \mathcal{E} := \frac{3}{2} n_a^0 k_B T_e = \sum_{a=1}^r \left\langle \frac{1}{2} m_a C_a^2 f_a^{eq} \right\rangle, \quad (3.47)$$

it is possible to find a unique distribution function, which has the form

$$f_a^{eq} = n_a^e \exp \left( \frac{m_a \hat{\mu}_a^e}{k_B T_e} - \frac{m_a C_a^2}{2k_B T_e} - \ln \Gamma_a^e \right), \quad (3.48)$$

$$\Gamma_a^e = \left\langle \exp \left( \frac{m_a \hat{\mu}_a^e}{k_B T_e} \right) \exp \left( -\frac{m_a C_a^2}{2k_B T_e} \right) \right\rangle^{-1}, \quad (3.49)$$

$$m_a \hat{\mu}_a^e = k_B T_e \ln \left[ n_a^e \left( \frac{m_a}{2\pi k_B T} \right)^{3/2} \right], \quad (3.50)$$

$$n_a^e = n_a^0 \exp \left[ -\frac{U_a(\mathbf{r})}{k_B T_e} \right], \quad (3.51)$$

where  $U_a(\mathbf{r})$  denotes the external potential energy on species  $a$ ,  $T_e$  is a parameter with a dimension of temperature,  $n_a^0$  is the density at  $U_a = 0$ , and  $\hat{\mu}_a^e$  is the chemical potential per unit mass of species  $a$ . We emphasize that the precise meaning of  $T_e$  is not clarified as yet except that it is a symbolical representation of the internal energy at this point.<sup>2</sup> The details of the derivation of the expression  $f_a^{eq}$  given here is available in the literature; see, for example, Ref. [7]. This form of the equilibrium distribution function is unique, because there are no other forms for expansion in the collision invariants possible and hence for  $f_a^{eq}$ . This uniqueness proof for  $f_a^{eq}$  is possible, thanks to the  $H$  theorem.

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<sup>2</sup>The operational meaning of  $T_e$  is clarified through thermodynamics when  $S_e$  is corresponded to the Clausius entropy of a reversible process, as will be shown later.

### 3.2.1 Equilibrium Boltzmann Entropy

The equilibrium distribution function (3.48) makes it possible to explicitly calculate the equilibrium Boltzmann entropy  $S_e$

$$S_e = -k_B \sum_{a=1}^r \int_V d\mathbf{r} \langle f_a^{\text{eq}}(\mathbf{r}, \mathbf{v}_a) \ln f_a^{\text{eq}}(\mathbf{r}, \mathbf{v}_a) \rangle, \quad (3.52)$$

which, on substitution of (3.48), yields the formula

$$\begin{aligned} S_e = & -k_B \sum_{a=1}^r \int_V d\mathbf{r} \left\langle \left\{ \ln \left[ n_a^e \left( \frac{m_a}{2\pi k_B T_e} \right)^{3/2} \right] - \frac{m_a C_a^2}{2k_B T_e} \right\} f_a^{\text{eq}} \right\rangle \\ & + \frac{1}{T_e} \int_V d\mathbf{r} (k_B T_e \ln \Gamma^e), \end{aligned} \quad (3.53)$$

where

$$\Gamma^e = \prod_{a=1}^r (\Gamma_a^e)^{N_a}, \quad (3.54)$$

with  $N_a$  denoting the total number of species  $a$  in  $V$ . The total number of molecules in  $V$  is then given by

$$N = \sum_{a=1}^r N_a = \sum_{a=1}^r \int_V d\mathbf{r} \rho_a^0. \quad (3.55)$$

If the integrability or the Gibbs–Duhem equation is made use of, the differential form of  $S_e$  is easily integrated to yield

$$\int_V d\mathbf{r} (k_B T_e \ln \Gamma^e) = p_e V, \quad (3.56)$$

where  $p_e$  denotes the equilibrium pressure. Thus we finally obtain the equilibrium Boltzmann entropy in the form

$$S_e = \frac{5}{2} k_B N - k_B \sum_{a=1}^r N_a \ln \left[ \frac{N_a}{V} \left( \frac{m_a}{2\pi k_B T_e} \right)^{3/2} \right]. \quad (3.57)$$

It is the well-known Sackur-Tetrode formula [3] for the Clausius entropy. Boltzmann obtained it from his  $H$  function evaluated with the equilibrium (i.e., Maxwell) distribution function. This shows that as equilibrium is approached, the Boltzmann entropy coincides with the Clausius entropy in thermodynamics, which Clausius introduced for *reversible processes only*, as shown in Chap. 2. Note that this identification is possible when the conserved variables calculated by statistical mechanics

are corresponded to or identified with the thermodynamic counterparts of density and internal energy. This way, the mathematical model, statistical mechanics, is endowed the physical significance and reality through thermodynamics.

### 3.2.2 Thermodynamic Correspondence and Equilibrium Gibbs Relation

The thermodynamic correspondence alluded to earlier can be formalized for the purposes of more general situations that we are going to deal with later, for example, irreversible processes. Since it would not make a difference even if  $U_a$  is absent we will set  $U_a = 0$  to make the discussion simpler. Since

$$N = \sum_{a=1}^r N_a = \sum_{a=1}^r \int_V d\mathbf{r} \langle f_a^{\text{eq}}(\mathbf{r}, \mathbf{v}_a) \rangle, \quad (3.58)$$

$$E_e = \sum_{a=1}^r \int_V d\mathbf{r} \left\langle \frac{1}{2} m_a C_a^2 f_a^{\text{eq}}(\mathbf{r}, \mathbf{v}_a) \right\rangle, \quad (3.59)$$

the formula (3.57) for  $S_e$  can be recast in the form

$$S_e = T_e^{-1} \left( E_e + N k_B T_e - \sum_{a=1}^r m_a \hat{\mu}_a^e N_a \right), \quad (3.60)$$

where  $\hat{\mu}_a^e$  is defined by (3.50). To make progress further from here let us observe that pressure of a gas is the mean momentum transfer per unit area per unit time, which is generally identified with the trace of momentum tensor divided by 3, namely,

$$\begin{aligned} p_e &= \frac{1}{3V} \sum_{a=1}^r \langle \text{Tr}(m_a \mathbf{C}_a \mathbf{C}_a) f_a^{\text{eq}}(\mathbf{r}, \mathbf{v}_a) \rangle \\ &= \frac{1}{3V} \sum_{a=1}^r \langle m_a \mathbf{C}_a \cdot \mathbf{C}_a f_a^{\text{eq}}(\mathbf{r}, \mathbf{v}_a) \rangle \\ &= \frac{N k_B T_e}{V}. \end{aligned} \quad (3.61)$$

Thus (3.60) is now given by the formula

$$S_e = T_e^{-1} \left( E_e + p_e V - \sum_{a=1}^r \mu_a^e N_a \right). \quad (3.62)$$

Taking differential of this equation and also owing to (3.50) for  $\hat{\mu}_a^e$ , we find the differential form

$$T_e dS_e = dE_e + p_e dV - \sum_{a=1}^r \mu_a^e dN_a \quad (\mu_a^e = m_a \hat{\mu}_a^e) \quad (3.63)$$

together with the differential

$$\sum_{a=1}^r N_a d\mu_a^e = V dp_e - S_e dT_e, \quad (3.64)$$

which follows from (3.50). It is called the Gibbs–Duhem equation [17, 18]. It is simply the integrability condition [19] in the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T}$  (See Chap. 2 for the definitions of these symbols.) for the differential (3.63), which in thermodynamics is called the equilibrium Gibbs relation—a fundamental equation of equilibrium thermodynamics [17, 18]. At this point these differential forms are simply statistical mechanical in their origin, no more than mathematical relations, and  $T_e$ ,  $p_e$ , and  $\mu_a^e$  are merely mathematical symbols defined by (3.47), (3.50), and (3.61). These statistical and mathematical objects are endowed a thermodynamic reality by means of thermodynamic correspondence. It is useful to note the rearranged form of (3.64):

$$d(p_e V) = S_e dT_e + p_e dV + \sum_{a=1}^r N_a d\mu_a^e, \quad (3.65)$$

which suggests  $p_e V$  is a thermodynamic potential like the Gibbs free energy or Helmholtz free energy.

In thermodynamics [17, 18], the Clausius entropy  $S$  obeys the differential form

$$TdS = dE + pdV - \sum_{a=1}^r \mu_a dN_a, \quad (3.66)$$

where  $E$ ,  $p$ , and  $\mu_a$  are the internal energy, pressure, and chemical potential of species  $a$ , respectively; see Chap. 2. It should be noted that the temperature  $T$  is endowed with its thermodynamic and operational meaning by means of the second law and the zeroth law of thermodynamics. In comparing the differential forms (3.63) and (3.66) we now make the following correspondences between the statistical mechanical and thermodynamic quantities:

$$\begin{aligned} S_e|_{st} &\Leftrightarrow S|_{th}; & E_e|_{st} &\Leftrightarrow E|_{th}; \\ V|_{st} &\Leftrightarrow V|_{th}; & N_a|_{st} &\Leftrightarrow N_a|_{th} \end{aligned} \quad (3.67)$$

for the extensive variables, and

$$T_e|_{st} \Leftrightarrow T|_{th}; \quad p_e|_{st} \Leftrightarrow p|_{th}; \quad \mu_a^e|_{st} \Leftrightarrow \mu_a|_{th} \quad (3.68)$$

for the conjugate intensive variables. By this correspondence the parameter  $T_e$  is now identified with the thermodynamic temperature, which in thermodynamics is given in the absolute temperature scale. With this identification other quantities given in terms of  $T_e$  [e.g.,  $p_e$  in (3.61) and  $\mu_a^e$  in (3.50)] are now endowed with thermodynamic and operational meanings and can be compared with experimental data for them. In this manner, statistical mechanics, which is a mathematical model for the system of interest, is made a physical theory of the macroscopic many-particle system under consideration. From the results obtained so far, we also conclude

$$T_e^{-1} = \left( \frac{\partial S_e}{\partial E_e} \right)_{V,N} = \left( \frac{\partial S}{\partial E} \right)_{V,N} = T^{-1}. \quad (3.69)$$

The important point we have learned from the discussion in the present subsection is that the uniqueness of the equilibrium solution for the Boltzmann equation is assured by the  $H$  theorem. It is also the  $H$  theorem that provides the equilibrium Boltzmann entropy with the differential forms, the equilibrium Gibbs relation and the Gibbs–Duhem equation, which facilitate the thermodynamic correspondences of statistical mechanical and thermodynamic observables and, as a consequence, endow the physical reality on the mathematical model that is statistical mechanics or, more specifically, the Boltzmann kinetic theory of dilute monatomic gases. This is a most important lesson we have learned from the example provided by the Boltzmann kinetic equation, which will be useful for us to develop a kinetic theory of many-correlated-particle systems in condensed phase, for example, liquids studied in later chapters of this work: *that the mathematical model, kinetic theory of fluids, is made a physical theory of processes, reversible or irreversible, in molecular systems, thanks to the principles of thermodynamics*, which in the present work appears in the form of the phenomenological thermodynamic theory of macroscopic (irreversible or reversible) processes in Chap. 2. For this the  $H$  theorem has played the crucial role in the case of equilibrium (reversible) processes providing a statistical mechanical representation of the Clausius entropy for reversible processes.

### 3.3 Evolution Equations for Macroscopic Variables

We have seen in Sect. 3.1 of this chapter that description of irreversible processes would generally require a set of macroscopic observables consisting of conserved and nonconserved variables that span the thermodynamic manifold. The Boltzmann kinetic equation (BKE) provides their evolution equations in space and time, when the observables are appropriately defined as averages of their molecular formulas over the phase space; see (3.7). Here we derive them in general forms in the case of dilute monatomic gases modeled with the BKE. To describe the evolution in space-time it is necessary to consider the density of an extensive macroscopic observable  $\mathcal{A}(t)$  defined by

$$\mathcal{A}(t) = \int_V d\mathbf{r} \rho(\mathbf{r}, t) \mathcal{A}(\mathbf{r}, t), \quad (3.70)$$

where  $\rho(\mathbf{r}, t)$  is the mass density of the fluid and  $\mathcal{A}(\mathbf{r}, t)$  is the density per unit mass of  $\mathfrak{A}(t)$  of the fluid in volume element at  $\mathbf{r}$  and time  $t$ . In fact, we may simply use  $\mathfrak{A}(t)$  per unit volume instead of  $\mathcal{A}(\mathbf{r}, t)$ , but we find it more convenient to use  $\mathcal{A}(\mathbf{r}, t)$  for formulation of the theory.

### 3.3.1 Boltzmann Entropy Balance Equation

Differentiating (3.43) with time and making use of the BKE, we obtain the differential equation for  $\rho\mathcal{S}$

$$\frac{\partial}{\partial t} [\rho(\mathbf{r}, t) \mathcal{S}(\mathbf{r}, t)] = -\nabla \cdot [\mathbf{J}_s + \mathbf{u}\rho\mathcal{S}(\mathbf{r}, t)] + \sigma_{\text{ent}}(\mathbf{r}, t), \quad (3.71)$$

where  $\mathbf{J}_s$  and  $\sigma_{\text{ent}}$  are defined by the statistical mechanical formulas

$$\mathbf{J}_s(\mathbf{r}, t) = -k_B \sum_{a=1}^r \langle \mathbf{C}_a \ln f_a(\mathbf{r}, \mathbf{v}_a, t) f_a \rangle, \quad (3.72)$$

$$\sigma_{\text{ent}}(\mathbf{r}, t) = -k_B \sum_{a=1}^r \langle \ln f_a(\mathbf{r}, \mathbf{v}_a, t) \mathbf{R}[f_a] \rangle. \quad (3.73)$$

Using the substantial time derivative

$$d_t := \frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla, \quad (3.74)$$

the Boltzmann entropy balance equation or the evolution equation (3.71) for  $\mathcal{S}(\mathbf{r}, t)$  is written in the form

$$\rho \frac{d}{dt} \mathcal{S}(\mathbf{r}, t) = -\nabla \cdot \mathbf{J}_s + \sigma_{\text{ent}}(\mathbf{r}, t), \quad (3.75)$$

where  $\mathbf{J}_s$  is the Boltzmann entropy flux defined by statistical mechanical formula (3.72) and  $\sigma_{\text{ent}}$  is the Boltzmann entropy production. Its statistical formula is given by (3.73) for gases obeying the BKE. It is noted that  $\sigma_{\text{ent}}$  is directly related to the collision integral of the BKE describing the collisional evolution of the gas in the collision volume enclosing position  $\mathbf{r}$  at time  $t$ . It is easy to show by using the properties of the BKE that  $\sigma_{\text{ent}}$  is always positive, but vanishes at equilibrium only:

$$\sigma_{\text{ent}}(\mathbf{r}, t) = k_B \sum_{a=1}^r \left\langle \ln \left( \frac{f_a^* f_b^*}{f_a f_b} \right) (f_a^* f_b^* - f_a f_b) \right\rangle_{\text{col}} \geq 0 \quad (3.76)$$

where  $\langle \cdots \rangle_{\text{col}}$  is the abbreviation for the integrals

$$\langle \cdots \rangle_{\text{col}} = \int \int d\mathbf{v}_a d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} \mathbf{b} \mathbf{g}_{ab} \cdots . \quad (3.77)$$

The inequality is a local form of the  $H$  theorem shown in (3.45). Later, we will investigate (3.75) in more detail in connection with the thermodynamic theory of irreversible processes in dilute monatomic gases.

### 3.3.2 Conservation Laws of Mass, Momentum, and Energy

#### 3.3.2.1 Mass Conservation Law

Differentiating (3.14) for mass density  $\rho$  with time and making use of the BKE—basically the same procedure as for the Boltzmann entropy balance Eq. (3.75)—we obtain the mass density balance equation, namely, the conservation law of mass:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot [\rho \mathbf{u}(\mathbf{r}, t)], \quad (3.78)$$

for which we have made use of the fact that the molecular mass is a collision invariant of the collision integral of the BKE, so that

$$\sum_{a=1}^r \langle m_a \mathbf{R}[f_a] \rangle = 0. \quad (3.79)$$

Note that the source term is absent in (3.78) and the mean velocity  $\mathbf{u}$  is defined by (3.16). The specific volume is defined in fluid mechanics or continuum mechanics by

$$v = \rho^{-1}. \quad (3.80)$$

Then the equation of continuity—mass balance equation—may be written as

$$\rho \frac{dv}{dt} = \nabla \cdot \mathbf{u}, \quad (3.81)$$

which shows that if the velocity is sourceless, that is,  $\nabla \cdot \mathbf{u} = 0$ , then the fluid is incompressible. Eqs. (3.78) and (3.81) represent the kinetic theory derivation of their phenomenological counterparts presented in Chap. 2, as would other evolution equations derived below.

Here we note an important point of the procedure of deriving the evolution equations for macroscopic variables: that is, for example, the momentum  $\rho \mathbf{u}$ , which appears in the divergence term of (3.78) as a moment one-order higher than the

density  $\rho$ , is necessarily and sufficiently defined by the statistical mechanical formula (3.15) so that (3.78) becomes the mass conservation law. There is no alternative form for the statistical formula for the mean momentum other than (3.15). This appearance of a moment one-order higher than the moment for which the time derivative is calculated is a general pattern for the divergence term in the derivation of macroscopic evolution equations from the kinetic equation and for emergence of an open hierarchy of macroscopic evolution equations. The basic mathematical reason for such an appearance of the moment one-order higher in the divergence term has been already illustrated by the discussion leading to (3.27): such a moment is generated by the Liouville operator whenever it operates on a function depending on velocity and position coordinates.

### 3.3.2.2 Mass Fraction (Concentration) Balance Equation

If (3.15) is differentiated with  $t$  and the same procedure is followed as for (3.78), in the case of chemically inactive fluids we obtain the balance equation of mass fraction  $c_a = \rho_a / \rho$ —concentration of species  $a$ :

$$\rho \frac{dc_a}{dt} = -\nabla \cdot \mathbf{J}_a, \quad (3.82)$$

where  $\mathbf{J}_a$  is the diffusion flux defined by the formula

$$\mathbf{J}_a = \langle m_a \mathbf{C}_a f_a \rangle = \rho_a (\mathbf{u}_a - \mathbf{u}). \quad (3.83)$$

The source term is absent in Eq. (3.82) because  $m_a \mathbf{C}_a$  is a collision invariant of the collision integral of the BKE, but if the fluid were chemically reactive, there would have been a collisional dissipation term present owing to the chemical reactions. The second equality in (3.83) follows from the definition of  $\mathbf{u}_a$  and  $\rho_a$ . This formula for  $\mathbf{J}_a$  in (3.83) implies that the diffusion flux is the mean relative momentum of molecule  $a$  with respect to the mean fluid velocity.

### 3.3.2.3 Momentum Conservation Law

If (3.16) is differentiated with  $t$  and the same procedure is employed as for  $S$  and  $\rho$  using the BKE, the momentum balance equation—momentum conservation law—is obtained:

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla \cdot \mathbf{P} + \rho \widehat{\mathbf{F}}, \quad (3.84)$$

where  $\mathbf{P}$  is the pressure (stress) tensor defined by

$$\mathbf{P} = \sum_{a=1}^r \langle m_a \mathbf{C}_a \mathbf{C}_a f_a \rangle \quad (3.85)$$

and  $\widehat{\mathbf{F}}$  is the body force per unit mass defined by

$$\rho \widehat{\mathbf{F}} = \sum_{a=1}^r \rho_a \widehat{\mathbf{F}}_a = \sum_{a=1}^r \langle m_a \widehat{\mathbf{F}}_a f_a \rangle. \quad (3.86)$$

For (3.84) the collision invariance of molecular momentum  $m_a \mathbf{v}_a$  is made use of. Therefore there is absent the source term associated with collisional energy dissipation in (3.84). We remark that in the language of moment method  $\mathbf{P}$  appearing in the divergence term in (3.84) is a moment one-order higher than momentum  $\rho \mathbf{u}$ .

### 3.3.2.4 Internal Energy Balance Equation

The kinetic energy of a molecule is also a collision invariant, and the internal energy balance equation can be obtained by following the procedure used for the balance equations presented earlier. We thus obtain internal energy balance equation—energy conservation law—from (3.20):

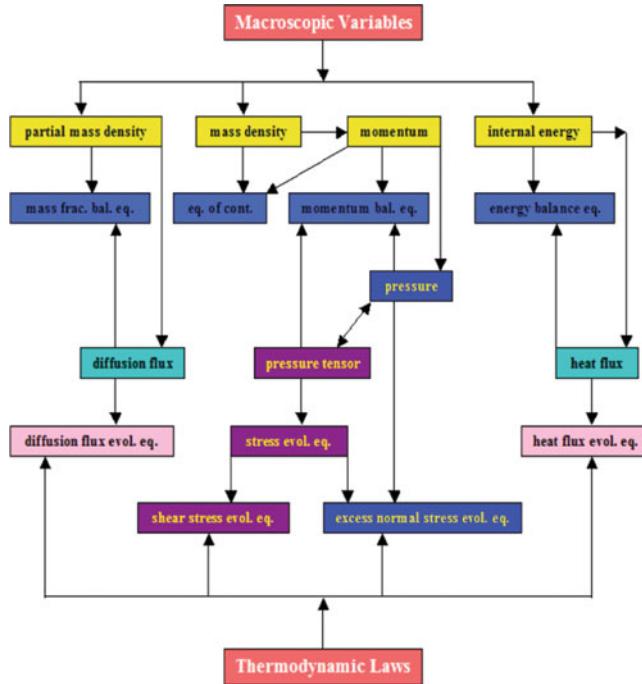
$$\rho \frac{d\mathcal{E}}{dt} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \widehat{\mathbf{F}}_a, \quad (3.87)$$

where the vector  $\mathbf{Q}$  is the heat flux defined by

$$\mathbf{Q} = \sum_{a=1}^r \left\langle \frac{1}{2} m_a C_a^2 \mathbf{C}_a f_a \right\rangle. \quad (3.88)$$

Because of the collisional invariance of the kinetic energy of the molecules, also absent in the energy balance equation is the source term arising from the collision integral of the BKE that is the seat of energy dissipation originating from molecular collisions in the case of nonconserved variables.

Before proceeding further it is useful to observe that the balance equations presented in the following are dilute monatomic gas examples for evolution equations derived from the Boltzmann kinetic equation for moments  $h_a^{(s)}$  defined in (3.24). Notice that we have begun with moment  $m_a$  that yields the equation of continuity, which involves a moment one-order higher than  $m_a \mathbf{v}_a = m_a \mathbf{C}_a + m_a \mathbf{u}$ , and so on. The higher order moment is generated as a result of operating  $\mathbf{L}^{(1)}$  on the moment of interest. Thus, as noted earlier, we see that the moment evolution equations can be progressively and hierarchically generated with the help of the kinetic equation and



**Fig. 3.1** Flow chart for moment evolution equations. The seed moments are, density, mass fraction, momentum, and internal energy indicated on the *top* of the flow chart. From the seed moments follow higher-order moments sequentially upon making use of the kinetic equation (BKE). The Liouville operator of the BKE generates them

the BKE in the particular case of dilute monatomic gases under consideration. Once we choose the leading moment, the succeeding moments are uniquely determined from the kinetic equation, but unfortunately, the set generated is open. Therefore the open set must be suitably closed. The procedure of obtaining the entire hierarchy of evolution equations is summarized in Fig. 3.1. The question of closure for the moment set will be discussed later when some examples of evolution equations closely relevant to the formulation of a theory of irreversible processes are obtained explicitly.

### 3.3.3 Evolution Equations for Nonconserved Variables

The evolution equations for nonconserved variables can be derived by taking time derivatives of their statistical mechanical definitions and making use of the BKE; in this connection it is useful to recall the property of  $\mathbf{L}^{(1)}$  discussed in Sect. 3.1.2;

**Table 3.1** Examples of moments for dilute monatomic gases

Name	Conventional symbols	Molecular definition $h_a^{(s)}$
Shear stress $\Phi_a^{(1)}$	$\Pi_a = [\mathbf{P}_a]^{(2)}$	$m_a [\mathbf{C}_a \mathbf{C}_a]^{(2)}$
Bulk stress $\Phi_a^{(2)}$	$\Delta_a = \frac{1}{3} \text{Tr} \mathbf{P}_a - p_a$	$\frac{1}{3} m_a \text{Tr}(\mathbf{C}_a \mathbf{C}_a) - m_a p_a / \rho_a$
Heat flux $\Phi_a^{(3)}$	$\mathbf{Q}'_a = \mathbf{Q}_a - \hat{h}_a \mathbf{J}_a$	$(\frac{1}{2} m_a C_a^2 - \hat{h}_a m_a) \mathbf{C}_a$
Diffusion flux $\Phi_a^{(4)}$	$\mathbf{J}_a$	$m_a \mathbf{C}_a$

see (3.23)–(3.27). Since the process is straightforward, we simply present only the results with some comments.

### 3.3.3.1 Generic Evolution Equation for Moments

Let  $h_a^{(s)}$  denote the  $s$ th element of moments representative of the molecular expressions of nonconserved variables. On taking average of this moment we obtain non-conserved variable  $\Phi_a^{(s)}$ :

$$\Phi_a^{(s)} = \rho \widehat{\Phi}_a^{(s)} = \langle h_a^{(s)} f_a \rangle. \quad (3.89)$$

The moment  $h_a^{(s)}$  generally is a vector or tensor corresponding to the diffusion flux, heat flux, stress tensor of species  $a$ , etc. as shown in Table 3.1 where the notation  $[\mathbf{A}]^{(2)}$  stands for the traceless symmetric part of second rank tensor  $\mathbf{A}$ , for example,

$$[\mathbf{C}_a \mathbf{C}_a]^{(2)} = \frac{1}{2} [\mathbf{C}_a \mathbf{C}_a + (\mathbf{C}_a \mathbf{C}_a)^t] - \frac{1}{3} \delta \text{Tr}(\mathbf{C}_a \mathbf{C}_a), \quad (3.90)$$

$\delta$  is the unit second rank tensor, and the superscript  $t$  stands for transpose. Therefore  $\Phi_a^{(1)}$  represents the shear stress,  $\Phi_a^{(2)}$  the excess normal stress in excess of hydrostatic pressure  $p_a$  ( $p_a := p_a^e$ ), simply, the bulk stress;  $\hat{h}_a$  the enthalpy per unit mass of species  $a$ . Therefore,  $\Phi_a^{(3)}$  is the heat flux in excess of energy carried by convective mass flux  $m_a \mathbf{u}$ .

The evolution equation for  $\Phi_a^{(s)}$  is derived from the BKE upon using its molecular definition (3.89) by following the same procedure as used for the conservation laws already presented. It is useful to write it in a generic form which indicates three different categories of term, each of which may be worked out in more detail:

$$\rho \frac{d \widehat{\Phi}_a^{(s)}}{dt} = -\nabla \cdot \boldsymbol{\psi}_a^{(s)} + \mathcal{Z}_a^{(s)} + \Lambda_a^{(s)} \quad (s \geq 1, a = 1, \dots, r), \quad (3.91)$$

where

$$\Lambda_a^{(s)} = \langle h_a^{(s)} \mathbf{R} [f_a] \rangle, \quad (3.92)$$

$$\boldsymbol{\psi}_a^{(s)} = \langle \mathbf{C}_a h_a^{(s)} f_a \rangle, \quad (3.93)$$

$$\mathcal{Z}_a^{(s)} = \langle f_a \mathcal{D}_t h_a^{(s)} \rangle \quad (3.94)$$

with  $\mathcal{D}_t$  denoting a differential operator defined by

$$\mathcal{D}_t h_a^{(s)} = \left( \frac{d}{dt} + \mathbf{C}_a \cdot \nabla + \widehat{\mathbf{F}}_a \cdot \nabla_{\mathbf{v}_a} \right) h_a^{(s)}. \quad (3.95)$$

Here  $d/dt$  is the substantial time derivative. Therefore, operator  $\mathcal{D}_t$  is a moving frame version of the streaming operator of the BKE equation, namely, the left hand side of the BKE on account of the operator  $\mathbf{L}^{(1)}$ . The nonvanishing source term  $\Lambda_a^{(s)}$  in (3.91) is called the dissipation term, which is closely associated with the energy dissipation owing to  $h_a^{(s)}$  in the collision integral of the BKE, and  $\mathcal{Z}_a^{(s)}$  is called the kinematic term arising from space-time evolution of  $h_a^{(s)}$  independent of molecular collisions. It contains the thermodynamic driving force term for the process as well as other nonlinear causes for the process. When  $h_a^{(s)}$  is specialized to the conserved moments  $m_a$ ,  $m_a \mathbf{v}_a$ , and  $\frac{1}{2} m_a C_a^2$  the conservation laws are obtained from the generic form of evolution equation (3.91). The leading examples for the kinematic terms for nonconserved variables presented in Table 3.1 will be given below. The generic form of evolution equations represents an open set of partial differential equations for macroscopic variables owing to the divergence term, which always consists of a moment one-order higher than  $h_a^{(s)}$ . When they are suitably closed and made to conform to the laws of thermodynamics, the set of evolution equations constitute generalized hydrodynamic equations of the fluid under consideration, which we apply to study fluid flows—namely, hydrodynamics of the fluid. A quasilinear model for generalized hydrodynamic equations will be discussed in Chap. 9 of this work. When the generalized hydrodynamic equations are solved subjected to appropriate initial and boundary conditions, a hydrodynamic description of the flow process of interest can be made to compare it with experimental observation in a generalized manner than by the classical hydrodynamics. The flow processes, for example, may be far removed from equilibrium.

### 3.3.3.2 Shear Stress

It is convenient to discuss the stress evolution of  $\mathbf{P}_a$  before describing the evolution of shear stress  $\boldsymbol{\Pi}_a := \Phi_a^{(1)}$  because both the shear stress and the excess trace part  $\Delta_a := \Phi_a^{(2)}$  of  $\mathbf{P}_a$  can be trivially generated from the evolution equation of  $\mathbf{P}_a$ . Let the kinematic term for  $\mathbf{P}_a$  be denoted by  $\mathcal{Z}_a^{(P)}$ , which is given by

$$\mathcal{Z}_a^{(P)} = \langle f_a \mathcal{D}_t (m_a \mathbf{C}_a \mathbf{C}_a) \rangle. \quad (3.96)$$

This formula is worked out as follows. Since  $\mathcal{Z}_a^{(P)}$  is a tensor of rank 2 its  $ij$  (Cartesian) component is found given by the formula

$$\begin{aligned} \mathcal{Z}_a^{(P)ij} &= - (d_t \mathbf{u}^i) \mathbf{J}_a^j - \mathbf{J}_a^i (d_t \mathbf{u}^j) - (\nabla^k \mathbf{u}^i) \mathbf{P}_a^{kj} - \mathbf{P}_a^{ik} (\nabla^k \mathbf{u}^j) \\ &\quad + \widehat{\mathbf{F}}_a^j \mathbf{J}_a^i + \widehat{\mathbf{F}}_a^i \mathbf{J}_a^j. \end{aligned} \quad (3.97)$$

The repeated superscripts mean the sum over the index. Therefore taking the traceless symmetric part of  $\mathcal{Z}_a^{(P)}$ , we obtain

$$\mathcal{Z}_a^{(1)} = -2 \left[ (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) \cdot \mathbf{J}_a \right]^{(2)} - 2 [\mathbf{P}_a \cdot \nabla \mathbf{u}]^{(2)}. \quad (3.98)$$

The excess trace part is then given by

$$\begin{aligned} \mathcal{Z}_a^{(2)} &= -\frac{2}{3} (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) \cdot \mathbf{J}_a - \frac{2}{3} \mathbf{P}_a \cdot \nabla \mathbf{u} - p_a \left\langle f_a m_a \mathcal{D}_t \left( \frac{1}{\rho_a} \right) \right\rangle \\ &= p_a d_t \ln \rho_a - \frac{2}{3} \mathbf{P}_a \cdot \nabla \mathbf{u} + \frac{p_a}{\rho_a} \mathbf{J}_a \cdot \nabla \ln \rho_a - \frac{2}{3} (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) \cdot \mathbf{J}_a, \end{aligned} \quad (3.99)$$

since

$$\left\langle f_a m_a \mathcal{D}_t \left( \frac{1}{\rho_a} \right) \right\rangle = -d_t \ln \rho_a - \frac{1}{\rho_a} \mathbf{J}_a \cdot \nabla \ln \rho_a. \quad (3.100)$$

It should be noted that the tensor  $\psi_a^{(P)}$  is a third-rank tensor which is symmetric with respect to the last two indices in the same manner as the stress tensor is. Therefore

$$\psi_a^{(1)} = \langle m_a \mathbf{C}_a [\mathbf{C}_a \mathbf{C}_a]^{(2)} f_a \rangle, \quad (3.101)$$

$$\psi_a^{(2)} = \left\langle \mathbf{C}_a \left[ \frac{1}{3} m_a (\mathbf{C}_a \cdot \mathbf{C}_a) - \frac{p_a}{\rho_a} m_a \right] f_a \right\rangle = \frac{2}{3} \mathbf{Q}_a - p_a v_a \mathbf{J}_a, \quad (3.102)$$

where

$$v_a = \rho_a^{-1}, \quad (3.103)$$

the partial specific volume of species  $a$ . Therefore  $\psi_a^{(2)}$  represents the mean relative kinetic energy flux in excess of the mean thermal energy carried by mass in motion. In a manner similar to this interpretation,  $\psi_a^{(1)}$  may be regarded as a flux of mean momentum transfer per unit area. The calculations presented here show that the evolution equations for the traceless symmetric part, excess trace part, and trace of tensor  $\mathbf{P}_a$  can be easily obtained from the evolution equation for  $\mathbf{P}_a$  itself.

### 3.3.3.3 Heat Flux

In the case of the heat flux, we find

$$\begin{aligned} \mathcal{Z}_a^{(3)} &= - (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) \cdot (\mathbf{P}_a - p_a \boldsymbol{\delta}) - \boldsymbol{\varphi}_a : \nabla \mathbf{u} \\ &\quad - \mathbf{Q}'_a \cdot \nabla \mathbf{u} - \mathbf{J}_a d_t \widehat{h}_a - \mathbf{P}_a \cdot \nabla \widehat{h}_a, \end{aligned} \quad (3.104)$$

where  $\boldsymbol{\varphi}_a$  is a third-rank tensor defined by

$$\boldsymbol{\varphi}_a^{ijk} = \langle f_a m_a \mathbf{C}_a^i \mathbf{C}_a^k \mathbf{C}_a^j \rangle \quad (3.105)$$

and  $\mathbf{Q}'_a$  is defined by

$$\mathbf{Q}'_a = \mathbf{Q}_a - \hat{h}_a \mathbf{J}_a. \quad (3.106)$$

The tensor  $\varphi_a$  is an example for a contracted third-rank tensor—e.g., heat flux—becoming a full third-rank tensor on operation of operator  $\mathcal{D}_t$  just like the operator  $\mathbf{L}^{(1)}$ .

### 3.3.3.4 Diffusion Flux

The kinematic term for the diffusion flux is given by

$$\begin{aligned} \mathcal{Z}_a^{(4)} &= \langle f_a \mathcal{D}_t (m_a \mathbf{C}_a) \rangle \\ &= -\rho_a (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) - \mathbf{J}_a \cdot \nabla \mathbf{u}. \end{aligned} \quad (3.107)$$

Note that in the case of diffusion fluxes

$$\psi_a^{(4)} = \mathbf{P}_a, \quad (3.108)$$

which may be regarded as a moment one-order higher<sup>3</sup> than  $\mathbf{J}_a$ . The examples of the evolution equations considered here are those appearing within the so-called thirteen moment approximation theory [20] for transport processes. We remark that the evolution equation for  $\Phi_a^{(4)}$ , as a matter of fact, may be regarded as the equation of motion for the mean species velocity  $\mathbf{u}_a$  since

$$\widehat{\Phi}_a^{(4)} = \mathbf{J}_a / \rho = c_a (\mathbf{u}_a - \mathbf{u}) \quad (3.109)$$

and hence it is possible to write the evolution equation for  $\widehat{\Phi}_a^{(4)}$  in the form

$$\rho_a \frac{d\mathbf{u}_a}{dt} = \rho_a \widehat{\mathbf{F}}_a - \nabla p_a - \mathbf{J}_a \frac{d}{dt} \ln c_a + c_a \Lambda_a^{(4)}. \quad (3.110)$$

This equation of motion for  $\mathbf{u}_a$  may be applied to a molecular theory investigation of the mobility [21] of charged particles subjected to Brownian motions if the external force is an external electric field.

We collect the evolution equations for the leading nonconserved moments presented here as a summary:

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<sup>3</sup>In the terminology of tensor analysis  $\mathbf{P}_a$ , a second rank tensor, is one rank higher than diffusion flux  $\mathbf{J}_a$ , which is a vector.

$$\begin{aligned}\rho d_t \widehat{\boldsymbol{\Pi}}_a = & -\nabla \cdot \boldsymbol{\psi}_a^{(1)} - 2[(d_t \mathbf{u} - \widehat{\mathbf{F}}_a) \mathbf{J}_a]^{(2)} - 2[\boldsymbol{\Pi}_a \cdot \nabla \mathbf{u}]^{(2)} \\ & - 2\Delta_a [\nabla \mathbf{u}]^{(2)} - \frac{2}{3} \boldsymbol{\Pi}_a \nabla \cdot \mathbf{u} - 2p_a [\nabla \mathbf{u}]^{(2)} + \Lambda_a^{(1)},\end{aligned}\quad (3.111)$$

$$\begin{aligned}\rho d_t \widehat{\Delta}_a = & -\nabla \cdot \boldsymbol{\psi}_a^{(2)} - \frac{2}{3} (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) \cdot \mathbf{J}_a - \frac{2}{3} \boldsymbol{\Pi}_a : \nabla \mathbf{u} \\ & - \frac{2}{3} \boldsymbol{\Delta}_a \nabla \cdot \mathbf{u} - p_a d_t \ln(p_a \rho_a^{5/3}) + \nabla \cdot \left( \frac{p_a}{\rho_a} \mathbf{J}_a \right) + \Lambda_a^{(2)},\end{aligned}\quad (3.112)$$

$$\begin{aligned}\rho d_t \widehat{\mathbf{Q}}'_a = & -\nabla \cdot \boldsymbol{\psi}_a^{(3)} - (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) \cdot (\mathbf{P}_a - p_a \boldsymbol{\delta}) - \boldsymbol{\varphi}_a : \nabla \mathbf{u} \\ & - \mathbf{Q}'_a \cdot \nabla \mathbf{u} - \mathbf{J}_a d_t \widehat{h}_a - (\boldsymbol{\Pi}_a + \Delta_a \boldsymbol{\delta}) \cdot \nabla \widehat{h}_a \\ & - p_a \nabla \widehat{h}_a + \Lambda_a^{(3)},\end{aligned}\quad (3.113)$$

$$\rho d_t \widehat{\mathbf{J}}_a = -\nabla \cdot \mathbf{P}_a - \rho_a (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) - \mathbf{J}_a \cdot \nabla \mathbf{u} + \Lambda_a^{(4)}. \quad (3.114)$$

The dissipation terms in these equations will be worked out in more detail at a more appropriate stage in the theory; they may be expressed as algebraic functions of  $\boldsymbol{\Pi}_a$ , etc. and conserved variables.

### 3.4 Thermodynamics of Irreversible Processes in Dilute Monatomic Gases

In the continuum theory treatment of macroscopic processes in space and time, we investigate a finite number of macroscopic observables and their evolution in space-time subject to initial and boundary conditions compatible with experiments performed to measure them. Thus the fluid mechanics was invented as mathematical models for flow problems in continuous material systems. It is clear that such flow processes must be subjected to the laws of thermodynamics. It is well known and established that the near-equilibrium phenomena in fluid mechanics are consistent with the laws of thermodynamics according to the thermodynamics of linear irreversible processes [21] and in such processes linear constitutive relations, such as Newton's law of viscosity, Fourier's law of heat conduction, and Fick's law of diffusion, are assumed to hold. In the case of near equilibrium phenomena the manifold of macroscopic observables, namely, the manifold  $\mathfrak{P}$ , is finite, its dimension numbering only ten and some.

In this work, we are aiming to go beyond the linear regime of constitutive relations, so that the fluid system can be removed from equilibrium to an arbitrary degree. Nevertheless, it is reasonable to imagine the dimension of the manifold of macroscopic observables must be the same as those of near-equilibrium phenomena. The dimension of such manifold may be denumerably infinite, yet we are able to practically retain the same dimension as for the linear theory, provided that the time and space scales of observables beyond the linear theory are quite shorter than those of the former, so that chances of observing higher-order moments are quite small

by the present experimental means. Under this proviso we could liberate ourselves from the dimensional restriction and work with infinite dimension of the manifold of macroscopic observables.

### 3.4.1 Functional Hypothesis for Distribution Functions

Since macroscopic irreversible processes must be subjected to the laws of thermodynamics and, for this to be facilitated, since it is necessary to have the distribution functions of the BKE evolve in the same manner as for the macroscopic observables constrained by the laws of thermodynamics, it is inevitable to assume that the distribution functions are functionals of the macroscopic observables. This is what is commonly called the functional hypothesis. Such a functional hypothesis lies in the foundation of the Chapman–Enskog solution method [2] for the BKE. But the precise manner of employing the hypothesis in this work differs from that in the Chapman–Enskog method of solution for the BKE. Obviously, the distribution function so obtained under the functional hypothesis and denoted by  $f_a^c$  will differ from the solution of the BKE in the phase space obtained without the hypothesis. It must be approximate because it will turn out to be a projection of the distribution function  $f_a(\mathbf{r}, \mathbf{v}_a, t)$  onto the thermodynamic manifold and, as such, it differs from  $f_a$  by the complement of the projection, which may be regarded as a deviation from the exact and true phase space solution of the BKE. This deviation will be called the fluctuation  $\delta f_a$  and defined by

$$\delta f_a = f_a - f_a^c. \quad (3.115)$$

This fluctuation unfortunately cannot be treated in the same manner as for  $f_a^c$  and hence will require a separate treatment; see Sect. 3.6 and thereafter for treatments of  $\delta f_a$ . Such a distribution function  $f_a^c$  obtained under the functional hypothesis will be sometimes referred to as the thermodynamic branch of the solution of the BKE. The functional hypothesis is formalized by the following proposition:

**Proposition 5** *Functional Hypothesis*

*The nonequilibrium canonical form  $f_a^c$  (thermodynamic branch) for the distribution functions of the Boltzmann kinetic equation evolve as a functional of macroscopic observables consistent with the constraints of the laws of thermodynamics. The space-time evolution of the macroscopic observables consistent with the aforementioned laws are field-equations in space and time which are ultimately determined by approximate solutions of the Boltzmann kinetic equation in the sense that  $\delta f_a$  is neglected, especially, in the calculation of dissipation terms and variables spanning the tangent manifold.*

Therefore according to this hypothesis there are fluctuations of distribution functions from the thermodynamic branch  $f_a^c$  which will be the object of a fluctuation theory discussed later. The fluctuations will not be our immediate concern in the

thermodynamics of irreversible processes here. We remark that the last part of the hypothesis makes it possible to keep the evolution equations for macroscopic observables derived earlier from the BKE unchanged except when the dissipation terms and the divergence terms are either explicitly calculated in terms of macroscopic observables or examined for the purpose of closure for the open hierarchy of macroscopic evolution equations.

### 3.4.2 Calortropy and the Second Law of Thermodynamics

In the previous chapter, we have shown that Clausius inequality (2.39), when approached alternatively from Clausius's treatment, gives rise to a new notion of calortropy as an extension of the Clausius entropy to nonequilibrium processes, and the equilibrium thermodynamics of Clausius and Gibbs can be extended therewith to nonequilibrium processes in a rational manner. The BKE approach will now be shown to provide a way to represent the calortropy and the related by means of statistical mechanics.

#### 3.4.2.1 Statistical Mechanical Treatment of Calortropy

The distribution function  $f_a(\mathbf{r}, \mathbf{v}_a, t)$  obeying the BKE contains information on molecular states of an enormous number of molecules comprising the system. However, all the initial and boundary conditions are not available for all degrees of freedom if the BKE is attempted for solution as a partial differential equation in the phase space, since in phenomenological thermodynamic treatment of macroscopic processes we are accessible to only a finite (in fact, a small) number of macroscopic observables at our disposal to determine the flow processes, which are not enough to determine distribution functions in the phase space. Thus we are in practice compelled to have an information shedding by means of a projection onto the manifold  $\mathfrak{P}$  introduced in Chap. 2. The precise manner of information shedding is facilitated by the functional hypothesis and the nonequilibrium canonical form  $f_a^c$ . This implies that since the Boltzmann entropy is in fact the information content of the system in the phase space of dimension  $6N$ , a thermodynamic treatment of irreversible macroscopic processes by means of the functional hypothesis is not able to achieve their molecular description fully in the phase space, only their projections onto manifold  $\mathfrak{P}$  being provided by them. We instead acquire an irreversible continuum thermodynamic description of flow processes.

In statistical mechanics of transport processes we define the calortropy as that part of the Boltzmann entropy that corresponds to the thermodynamic branch  $f_a^c(\mathbf{r}, \mathbf{v}_a, t)$  of  $f_a(\mathbf{r}, \mathbf{v}_a, t)$ . The definition of calortropy is formalized as a proposition:

**Proposition 6** *The calortropy for a dilute monatomic gas is defined by the statistical mechanical formula*

$$\Psi(t) = -k_B \int_V d\mathbf{r} \sum_{a=1}^r \langle f_a \ln f_a^c \rangle. \quad (3.116)$$

Its local density  $\widehat{\Psi}$  is then given by

$$\rho \widehat{\Psi}(\mathbf{r}, t) = -k_B \sum_{a=1}^r \langle f_a \ln f_a^c \rangle \quad (3.117)$$

and the attendant flux of calortropy  $\mathbf{J}_c$  and the calortropy production  $\sigma_c$  are, respectively, defined by

$$\mathbf{J}_c = -k_B \sum_{a=1}^r \langle f_a \mathbf{C}_a \ln f_a^c \rangle, \quad (3.118)$$

$$\sigma_c = -k_B \sum_{a=1}^r \langle \ln f_a^c \mathbf{R}[f_a] \rangle. \quad (3.119)$$

These definitions are consistent with the functional hypothesis. From the definition of the calortropy density  $\widehat{\Psi}$  and given the definitions of  $\mathbf{J}_c$  and  $\sigma_c$  there easily follows its evolution equation for  $\widehat{\Psi}$ :

$$\rho \frac{d\widehat{\Psi}}{dt} = -\nabla \cdot \mathbf{J}_c + \Xi_{cal}, \quad (3.120)$$

where the source term  $\Xi_{cal}$  is defined by

$$\Xi_{cal} = \sigma_c - k_B \sum_{a=1}^r \langle f_a \mathcal{D}_t \ln f_a^c \rangle. \quad (3.121)$$

The balance Eq. (3.120) for  $\widehat{\Psi}$  is then seen formally in the same form as the phenomenological counterpart (2.72) in Chap. 2, and the source term  $\Xi_{cal}$  is now given a statistical mechanical representation. This evolution equation should be compared with the Boltzmann entropy balance Eq. (3.75) to appreciate their difference. As a matter of fact, the second term on the right of (3.121) will be found to play a crucial role in making the calortropy a keystone of the mathematical edifice of irreversible thermodynamics, since its presence makes it possible to integrate (3.120) in the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T}$  unlike the Boltzmann entropy balance equation, which is not integrable in manifold  $\mathfrak{P} \cup \mathfrak{T}$ .

As a preparation for proceeding further, we define the thermodynamic manifold, a concept introduced in Chap. 2, by the statistical averages of molecular observables that can be measured in principle in the laboratory on performing experiments on a

set of irreversible processes according to the theory developed in what follows. The thermodynamic manifold would certainly include the conserved variables as well as nonconserved variables.

**Definition 3** Manifold  $\mathfrak{P} := (\mathcal{E}, v, \mathfrak{c}_a, \widehat{\Phi}_a^{(q)} : a = 1, \dots, r; q \geq 1)$  defined previously in the phenomenological theory is represented by the molecular expressions of the set<sup>4</sup>  $\mathfrak{M} := \left(\frac{1}{2}m_a C_a^2, m_a/\rho, m_a, h_a^{(q)} : 1 \leq a \leq r; q \geq 1\right)$ , which on taking statistical mechanical average yields  $\mathfrak{P} = \rho^{-1} \langle \mathfrak{M} f_a \rangle$ .

Note that averaging  $\mathfrak{M}$  over distribution function  $f_a$  is mathematically equivalent to a projection onto  $\mathfrak{P}$ .

In addition to the manifold  $\mathfrak{P}$  of macroscopic variables we define a manifold  $\mathfrak{T}$  which is tangent to the manifold of  $\mathfrak{P}$ .

**Definition 4** Manifold  $\mathfrak{T} := (T^{-1}, p, \widehat{\mu}_a, X_a^{(q)} : 1 \leq a \leq r; q \geq 1)$  is spanned by elements tangent to the elements of manifold  $\mathfrak{P}$ . The elements of  $\mathfrak{T}$  will turn out to be inverse temperature  $T^{-1}$ , pressure  $p$ , chemical potential  $\widehat{\mu}_a$ , and generalized potential  $X_a^{(q)}$  of the nonequilibrium fluid.

Unlike the variables of manifold  $\mathfrak{P}$  the elements of the tangent manifold  $\mathfrak{T}$  do not have simple molecular representations. As will be seen, their statistical mechanical formulas can be derived from nonequilibrium partition function through thermodynamic relations—derivatives of nonequilibrium partition function.

We now determine the calortropy density as a linear functional of variables spanning the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T}$ . The equilibrium distribution function determined from the equilibrium condition of the  $H$  theorem in Sect. 3.2 we may make the functional hypothesis for  $f_a^c$  more concrete mathematically and take it in the form

<sup>4</sup>Here to maintain a continuity of the present theory with the tradition of kinetic theory so far, for example, the Chapman–Enskog theory of the Boltzmann equation, in which the mean volume is represented by the specific volume, we are taking the molecular representation of the volume occupied a molecule with  $m_a/\rho$  which gives the element of manifold  $\Omega$  corresponding to volume,  $v$ , because

$$\Omega = \rho^{-1} \langle \mathfrak{M} f_a \rangle,$$

namely,

$$v = \rho^{-1} \sum_{a=1}^r \left\langle \frac{m_a}{\rho} f_a \right\rangle = \rho^{-1} \sum_{a=1}^r \mathfrak{c}_a = \rho^{-1}.$$

It must be pointed out that the molecular representation taken here is merely the molecular theory interpretation of the viewpoint taken in the traditional approach in continuum theory of fluids and fluid mechanics. This viewpoint can be appropriately corrected to represent the volume occupied by a molecule from a molecular picture. This will be discussed in detail when we discuss volume transport phenomena later in this work; Chaps. 6 and 7.

$$f_a^c(\mathbf{r}, \mathbf{v}_a, t) = \frac{n_a}{\Gamma_a} \exp \left[ -\beta \left( \frac{1}{2} m_a C_a^2 + \sum_{q \geq 1} \sum_{a=1}^r X_a^{(q)} h_a^{(q)} - m_a \hat{\mu}_a \right) \right], \quad (3.122)$$

where

$$\beta = \frac{1}{k_B T} \quad (3.123)$$

and the normalization factor  $f_a^0$  is given by<sup>5</sup>

$$f_a^0 = n_a / \Gamma_a. \quad (3.124)$$

with  $\Gamma_a$  is defined by the integral

$$\Gamma_a = \left\langle \exp \left[ -\beta \left( \frac{1}{2} m_a C_a^2 + \sum_{q \geq 1} \sum_{a=1}^r X_a^{(q)} h_a^{(q)} - m_a \hat{\mu}_a \right) \right] \right\rangle. \quad (3.125)$$

It will be found that  $\Gamma_a$  is the local form of nonequilibrium grand canonical partition function of species  $a$ .

Substitution of  $f_a^c$  in (3.122) yields the expression for the local calortropy density in the form

$$\widehat{\Psi} = T^{-1} \left( \mathcal{E} - \sum_{a=1}^r \hat{\mu}_a \mathfrak{c}_a + \sum_{a=1}^r \sum_{q \geq 1} X_a^{(q)} \widehat{\Phi}_a^{(q)} + v (k_B T \ln \Gamma) \right), \quad (3.126)$$

where

$$\Gamma = \prod_{a=1}^r \Gamma_a^{n_a} \quad (3.127)$$

and  $v = \rho^{-1}$  is the specific volume of the fluid. At this point it is not known in what manner  $\ln \Gamma$  belongs to the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T}$ .

To help us decide on the question, take differential of  $\widehat{\Psi}$ . Then we find

$$d_t \widehat{\Psi} = d_t \left( \mathcal{E} \bar{I} + \sum_{a=1}^r \sum_{q \geq 1} \bar{X}_a^{(q)} \widehat{\Phi}_a^{(q)} - \sum_{a=1}^r \bar{\mu}_a \mathfrak{c}_a \right) + d_t \left[ \frac{1}{T} v (k_B T \ln \Gamma) \right], \quad (3.128)$$

---

<sup>5</sup>Here the potential of the external body force  $\mathbf{F}_a = m_a \widehat{\mathbf{F}}_a$ , which is assumed to be uniform over the intermolecular force range, is absorbed into  $n_a$ , which may be written as  $n_a = n_a^0 e^{-\beta U_a}$ , where  $U_a$  is the potential of the external body force. Thus  $n_a^0$  is the density for the case of  $U_a = 0$ . This is easy to see if the kinetic energy in manifold  $\mathfrak{M}$  is replaced with  $\frac{1}{2} m_a C_a^2 + U_a$ . The range of index  $q$  should be also such that the normalization factor exists. This may be achieved by making an appropriate closure.

where

$$\bar{I} = T^{-1}, \quad \bar{\mu}_a = \frac{\hat{\mu}_a}{T}, \quad \bar{X}_a^{(q)} = \frac{X_a^{(q)}}{T}. \quad (3.129)$$

Comparing—namely, making thermodynamic correspondence—between the phenomenological and the statistical mechanical calortropy differentials for  $d\hat{\Psi}$  in (2.78) and (3.128) term by term, we conclude that

$$k_B T \ln \Gamma = p(\mathbf{r}, t) v. \quad (3.130)$$

Translated into global representation this equation may be written as

$$k_B T \ln \mathbb{Z} = \int_V d\mathbf{r} \rho (k_B T \ln \Gamma) = \int_V d\mathbf{r} \rho (pv)(\mathbf{r}, t) := pV. \quad (3.131)$$

where  $p$  is defined by the volume average of  $p(\mathbf{r}, t)$ :

$$\langle p \rangle_{vol} = \frac{1}{V} \int_V d\mathbf{r} p(\mathbf{r}, t). \quad (3.132)$$

We then finally obtain  $d_t \hat{\Psi}$  in the form

$$d_t \hat{\Psi} = d_t \left( \mathcal{E} \bar{I} + \sum_{a=1}^r \sum_{q \geq 1} \bar{X}_a^{(q)} \hat{\Phi}_a^{(q)} - \sum_{a=1}^r \bar{\mu}_a \mathfrak{c}_a + \bar{p}v \right), \quad (3.133)$$

where

$$\bar{p} = \frac{p}{T}. \quad (3.134)$$

Therefore, apart from a constant which may be taken equal to zero, integration of  $d\hat{\Psi}$  in manifold  $\mathfrak{P} \cup \mathfrak{T}$  yields a bilinear form for the calortropy density

$$\hat{\Psi} = \frac{1}{T} \left( \mathcal{E} - \sum_{a=1}^r \hat{\mu}_a \mathfrak{c}_a + pv + \sum_{a=1}^r \sum_{q \geq 1} X_a^{(q)} \hat{\Phi}_a^{(q)} \right). \quad (3.135)$$

Furthermore, from (3.133) we obtain

$$\begin{aligned} d_t \hat{\Psi} &= T^{-1} \left[ d_t \mathcal{E} + pd_t v - \sum_{a=1}^r \hat{\mu}_a d_t \mathfrak{c}_a + \sum_{q \geq 1} \sum_{a=1}^r X_a^{(q)} d_t \hat{\Phi}_a^{(q)} \right] \\ &\quad + \mathcal{E} d_t \left( \frac{1}{T} \right) + vd_t \left( \frac{p}{T} \right) - \sum_{a=1}^r \mathfrak{c}_a d_t \left( \frac{\hat{\mu}_a}{T} \right) + \sum_{q \geq 1} \sum_{a=1}^r \hat{\Phi}_a^{(q)} d_t \left( \frac{X_a^{(q)}}{T} \right). \end{aligned} \quad (3.136)$$

Provided that<sup>6</sup>

$$\mathcal{E}d_t\left(\frac{1}{T}\right) + vd_t\left(\frac{p}{T}\right) - \sum_{a=1}^r \mathfrak{c}_a d_t\left(\frac{\hat{\mu}_a}{T}\right) + \sum_{q \geq 1} \sum_{a=1}^r \hat{\Phi}_a^{(q)} d_t\left(\frac{X_a^{(q)}}{T}\right) = 0, \quad (3.137)$$

there follows the extended the Gibbs relation for  $d_t\hat{\Psi}$

$$d_t\hat{\Psi} = T^{-1} \left[ d_t\mathcal{E} + pd_tv - \sum_{a=1}^r \hat{\mu}_a d_t\mathfrak{c}_a + \sum_{q \geq 1} \sum_{a=1}^r X_a^{(q)} d_t\hat{\Phi}_a^{(q)} \right]. \quad (3.138)$$

Equation (3.137) is called the nonequilibrium Gibbs-Duhem (NGD) equation. It is the necessary and sufficient condition [19] for integrability of the differential form—the extended Gibbs relation (3.138)—in the manifold  $\mathfrak{P} \cup \mathfrak{T}$ . In other words, the calortropy differential (3.138) is found to be an exact differential in the thermodynamic manifold. Therefore, when thermodynamic correspondence with the phenomenological ones in Chap. 2 is made use of, the statistical mechanical parameters  $T^{-1}$ ,  $pT^{-1}$ ,  $\hat{\mu}_a T^{-1}$ , and  $X_a^{(q)} T^{-1} \in \mathfrak{T}$ , which are conjugate to the variables in manifold  $\mathfrak{P}$ , acquire physical meanings grounded on experiments performed on nonequilibrium fluids. This way, the statistical mechanics formalism, which is launched as a mathematical model, finally acquires the status of a physical theory and provides us with a thermodynamic theory of irreversible processes in the fluid under consideration. We note that the NGD Eq. (3.137) can be recast into an alternative form, which may be regarded as the differential form for thermodynamic potential  $pv$ :

$$d(pv) = \hat{\Psi}dT + \sum_{a=1}^r \mathfrak{c}_a d\hat{\mu}_a + pdv - \sum_{a=1}^r \sum_{q \geq 1} \hat{\Phi}_a^{(q)} dX_a^{(q)}. \quad (3.139)$$

This form is more useful for the purpose of formulating nonequilibrium statistical mechanics, since Eq. (3.130) then suggests (3.139) may be regarded as for the differential form for the nonequilibrium partition function:

$$d(k_B T \ln \Gamma) = \hat{\Psi}dT + \sum_{a=1}^r \mathfrak{c}_a d\hat{\mu}_a + pdv - \sum_{a=1}^r \sum_{q \geq 1} \hat{\Phi}_a^{(q)} dX_a^{(q)}. \quad (3.140)$$

---

<sup>6</sup>This equation, in fact, follows from the normalization

$$\langle f_a^c(x_a, t) \rangle = \text{constant}.$$

If this condition is varied by varying the variables in manifold  $\mathfrak{T}$  holding the molecular variables giving rise to the manifold  $\mathfrak{P}$  (namely, the energy, mass, moments, etc.) held fixed, then there follows the Gibbs-Duhem equation (3.137). Therefore, (3.137) is not an arbitrary assumption or assertion.

This differential form bridges the statistical mechanics to the phenomenological irreversible thermodynamics as will be shown later.

We now change the tag and look for the differential form (3.138) for  $\widehat{\Psi}$  from another angle by starting from the formal evolution equation (3.120) we have obtained. Specifically, we examine if (3.120) is integrable in the manifold  $\mathfrak{P} \cup \mathfrak{T}$ . For this purpose we calculate  $\mathbf{J}_c$  and  $\Xi_{\text{cal}}$  given in (3.118) and (3.121), respectively, by using the functional hypothesis form for  $f_a^c$  in (3.122). Upon using  $f_a^c$  in (3.118) and (3.121), respectively, for  $\mathbf{J}_c$  and  $\Xi_{\text{cal}}$  we obtain

$$\mathbf{J}_c = \sum_{a=1}^r T^{-1} \mathbf{Q}_a^c, \quad (3.141)$$

$$\Xi_{\text{cal}} = \Xi_l^X + \sum_{a=1}^r \sum_{q \geq 1} T^{-1} X_a^{(q)} \Lambda_a^{(q)}, \quad (3.142)$$

where  $\mathbf{Q}_a^c$  and  $\Xi_l^X$  are defined by the expressions

$$\mathbf{Q}_a^c = \mathbf{Q}_a - \widehat{\mu}_a \mathbf{J}_a + \sum_{q \geq 1} \boldsymbol{\psi}_a^{(q)} X_a^{(q)}, \quad (3.143)$$

$$\begin{aligned} \Xi_l^X &= -T^{-1} \sum_{a=1}^r [(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla u + Q_a^c \cdot \nabla \ln T + \mathbf{J}_a \cdot (\nabla \widehat{\mu}_a - \mathbf{F}_a)] \\ &\quad + T^{-1} \sum_{a=1}^r \sum_{q \geq 1} \boldsymbol{\psi}_a^{(q)} \cdot \nabla X_a^{(q)} + T^{-1} \sum_{a=1}^r \sum_{q \geq 1} X_a^{(q)} \mathcal{Z}_a^{(q)}. \end{aligned} \quad (3.144)$$

On substituting (3.141) and (3.142) and in turn (3.143) and (3.144) into (3.120), there follows the differential form (3.136). And, with the nonequilibrium Gibbs–Duhem equation (3.137) imposed, the extended Gibbs relation for  $d_t \widehat{\Psi}$  given in (3.138) is obtained. As a matter of fact, since (3.136) is integrable in the manifold  $\mathfrak{P} \cup \mathfrak{T}$ , we have shown that the calortropy density balance equation is integrable in the manifold  $\mathfrak{P} \cup \mathfrak{T}$ . Therefore, with the integrability condition (3.137)—i.e., the nonequilibrium Gibbs–Duhem equation—the extended Gibbs relation (3.138) is integrable in  $\mathfrak{P} \cup \mathfrak{T}$ . This conclusion is agreement with Theorem 1 in Chap. 2, leading us to state that the calortropy density (or global calortropy  $\Psi$ ) is a surface in the Gibbs manifold  $\mathfrak{G} := \mathfrak{P} \cup \mathfrak{T} \cup \widehat{\Psi}$ . In any case, we have shown that the extended Gibbs relation is obtained from both the statistical mechanical formula for  $\widehat{\Psi}$  and the balance equation for  $\widehat{\Psi}$ .

Finally, we should emphasize that the integrability of the calortropy balance Eq. (3.120) in  $\mathfrak{P} \cup \mathfrak{T}$  is what makes it sharply distinguishable from the Boltzmann entropy balance equation, which is defined in terms of distribution function  $f_a(x, t)$  evolving in the phase space but not in the manifold  $\mathfrak{G}$ . This crucial difference ultimately lies in the term  $-k_B \sum_{a=1}^r \langle f_a \mathcal{D}_t \ln f_a^c \rangle$  in (3.121) of the source term of the

calortropy balance equation, its absence rendering the Boltzmann entropy balance equation nonintegrable in  $\mathfrak{P} \cup \mathfrak{T}$ .

Before proceeding further, we remark that the source term  $\Xi_{\text{cal}}$  of the calortropy balance Eq. (3.142) consists of two distinctive components; one consisting of gradients of intensive variables and the other consisting of the dissipation terms in the evolution equations of nonconserved variables. The terms involving the gradients are rather reminiscent of the entropy production terms in linear irreversible thermodynamics [21], which make up the Rayleigh dissipation function [22] in the linear theory of irreversible processes. Thus we see that  $\Xi_{\text{cal}}$  is intimately related to the generalized Rayleigh dissipation function appearing in the present theory.

### 3.4.3 Thermodynamic Correspondence

The mathematical formalism developed by means of statistical mechanics is made a physical theory if the differential form (3.138) for  $\widehat{\Psi}$  is corresponded to the phenomenological calortropy differential [23] deduced from the second law of thermodynamics through the Clausius inequality. This correspondence is formalized in the form of proposition:

**Proposition 7** *The statistically defined macroscopic extensive variables (labeled by subscript st) are corresponded to their phenomenological counterpart (labeled by th) in manifold  $\mathfrak{G} = (\widehat{\Psi}, \mathcal{E}, v, \mathfrak{c}_a, \widehat{\Phi}_a^{(q)} : a = 1, \dots, r; q \geq 1)$ :*

$$\begin{aligned}\widehat{\Psi}|_{st} &\Leftrightarrow \widehat{\Psi}|_{th}, & \mathcal{E}|_{st} &\Leftrightarrow \mathcal{E}|_{th}, & v|_{st} &\Leftrightarrow v|_{th}, \\ \mathfrak{c}_a|_{st} &\Leftrightarrow \mathfrak{c}_a|_{th}, & \widehat{\Phi}_a^{(q)}|_{st} &\Leftrightarrow \widehat{\Phi}_a^{(q)}|_{th}.\end{aligned}\quad (3.145)$$

*This correspondence fixes the physical meanings of the intensive variables spanning the tangent manifold  $\mathfrak{T}$  in the differential form (3.138) and provides them with thermodynamic (i.e., experimental) means to determine them operationally:*

$$T|_{st} \Leftrightarrow T|_{th}, \quad p|_{st} \Leftrightarrow p|_{th}, \quad \widehat{\mu}_a|_{st} \Leftrightarrow \widehat{\mu}_a|_{th}, \quad X_a^{(q)}|_{st} \Leftrightarrow X_a^{(q)}|_{th}. \quad (3.146)$$

The results obtained up to this point for dilute monatomic gases described by the BKE can be summarized as a theorem:

**Theorem 2** *The statistical mechanical calortropy differential (3.138) is a molecular representation of the phenomenological calortropy differential (2.75) deduced from the second law of thermodynamics, and the source term  $\Xi_{\text{cal}}$  in the calortropy balance Eq. (3.120) is a local expression for the second law of thermodynamics. It is positive semidefinite for all irreversible processes everywhere in space and time and vanishes at equilibrium.*

On the strength of this theorem the thermodynamic theory of irreversible processes on the basis of the extended Gibbs relation (3.138) is thermodynamically consistent,

that is, in conformation to the laws of thermodynamics. Consequently, the generalized hydrodynamic equations subordinated to the extended Gibbs relation are also found to be thermodynamically consistent. And we now have a statistical thermodynamics foundation of nonequilibrium macroscopic processes in dilute monatomic gases.

### 3.5 Statistical Thermodynamics of Irreversible Processes

Since the thermodynamic branch  $f_a^c$  of the nonequilibrium distribution function  $f_a$  is now elucidated to yield the calortropy and other related quantities thanks to the functional hypothesis, it is possible to carry on formulating statistical thermodynamics of nonequilibrium processes with the help of the extended Gibbs relation. As a matter of fact,  $f_a^c$  in (3.122) is a nonequilibrium grand canonical distribution function for a monatomic dilute gas in which various irreversible processes represented by the variables in manifold  $\mathfrak{P}$  are in progress. In the following discussion in this section we would like to sketch briefly the essential feature of the procedure. The thermodynamic theory of irreversible processes can certainly be developed to the full, but the present discussion will be sufficient for conveying the essential idea. One can devote another monograph to this subject alone.

For the purpose in mind, we return to the Gibbs–Duhem equation (3.140) and recall that the nonequilibrium thermodynamic potential  $pv$  is given by the local form of the grand canonical partition function  $\mathbb{Z}$

$$k_B T \ln \mathbb{Z} = \int_V d\mathbf{r} \rho k_B T \ln \Gamma = \int_V d\mathbf{r} \rho (pv) \quad (3.147)$$

and

$$pv = k_B T \ln \Gamma = k_B T \ln \prod_{a=1}^r \Gamma_a^{n_a}. \quad (3.148)$$

See (3.125) for  $\Gamma_a$ . Therefore, it is possible to calculate all the variables spanning the Gibbs manifold  $\mathfrak{G}$ , which can be expressed in the following forms:

$$\widehat{\Psi} = k_B \ln \Gamma + k_B T \left( \frac{\partial \ln \Gamma}{\partial T} \right)_{v, \widehat{\mu}, X}, \quad (3.149)$$

$$p = k_B T \left( \frac{\partial \ln \Gamma}{\partial v} \right)_{T, \widehat{\mu}, X}, \quad (3.150)$$

$$\epsilon_a = k_B T \left( \frac{\partial \ln \Gamma}{\partial \widehat{\mu}_a} \right)_{T, v, \widehat{\mu}', X} \quad (1 \leq a \leq r), \quad (3.151)$$

$$\widehat{\Phi}_{av}^{(q)} = -k_B T \left( \frac{\partial}{\partial X_a^{(q)}} \ln \Gamma \right)_{T, v, \widehat{\mu}, X'} \quad (1 \leq a \leq r; q \geq 1), \quad (3.152)$$

where the prime on the subscript  $\hat{\mu}'$  in (3.151) or  $X'$  in (3.152) means excluding the differentiating variable from the subscripts. These statistical mechanical formulas are nonequilibrium generalizations of the equilibrium ensemble theory except for the last formula which does not appear in equilibrium theory [3].

In addition to the thermodynamic potential  $p v$  presented in (3.148) and (3.139), other thermodynamic functions such as nonequilibrium Gibbs free energy, nonequilibrium work function, and nonequilibrium enthalpy can be defined by means of Legendre transformations. Thus we define nonequilibrium Gibbs free energy  $\mathcal{G}$ , non-equilibrium work function (Helmholtz free energy)  $\mathcal{A}$ , and nonequilibrium enthalpy  $\mathcal{H}$ , respectively, by the Legendre transformations

$$\mathcal{G} = \mathcal{E} + p v - T \hat{\Psi}, \quad (3.153)$$

$$\mathcal{A} = \mathcal{E} - T \hat{\Psi}, \quad (3.154)$$

$$\mathcal{H} = \mathcal{E} + p v, \quad (3.155)$$

whose differential forms are then given by [23]

$$d_t \mathcal{G} = -\hat{\Psi} d_t T + v d_t p + \sum_{a=1}^r \hat{\mu}_a d_t \mathfrak{c}_a - \sum_{a=1}^r \sum_{q \geq 1} X_a^{(q)} d_t \hat{\Phi}_a^{(q)}, \quad (3.156)$$

$$d_t \mathcal{A} = -\hat{\Psi} d_t T - p d_t v + \sum_{a=1}^r \hat{\mu}_a d_t \mathfrak{c}_a - \sum_{a=1}^r \sum_{q \geq 1} X_a^{(q)} d_t \hat{\Phi}_a^{(q)}, \quad (3.157)$$

$$d_t \mathcal{H} = T d_t \hat{\Psi} + v d_t p + \sum_{a=1}^r \hat{\mu}_a d_t \mathfrak{c}_a - \sum_{a=1}^r \sum_{q \geq 1} X_a^{(q)} d_t \hat{\Phi}_a^{(q)}. \quad (3.158)$$

We may also rearrange the extended Gibbs relation to obtain a differential form for  $\mathcal{E}$ :

$$d_t \mathcal{E} = T d_t \hat{\Psi} - p d_t v + \sum_{a=1}^r \hat{\mu}_a d_t \mathfrak{c}_a - \sum_{a=1}^r \sum_{q \geq 1} X_a^{(q)} d_t \hat{\Phi}_a^{(q)}. \quad (3.159)$$

The relations (3.156)–(3.159) are nonequilibrium extensions of the thermodynamic fundamental equations well known in equilibrium thermodynamics [17, 18]. From these fundamental equations—namely, exact differential forms—follow the extended Maxwell relations which can be made use of to derive numerous practical relations between thermodynamic quantities and use them to measure and correlate macroscopic thermodynamic observables. We will examine some examples below, where examples for extended Maxwell relations are also made use of; see, for example, (3.160) below.

### 3.5.1 Nonequilibrium Intensive Properties

The intensive variables such as  $T$ ,  $p$ ,  $\hat{\mu}_a$ , or  $X_a^{(s)}$  can be in principle obtained by making use of nonequilibrium statistical mechanical expressions (3.149)–(3.152) and the partition function  $\Gamma_a$  expressed in terms of variables spanning the manifold  $\mathfrak{P} \cup \mathfrak{T}$ . Recall that in the phenomenological theory the thermodynamic operational meanings of variables in  $\mathfrak{T}$  are fixed by the zeroth law of thermodynamics and its extension. It would be now interesting to discuss what would be required to quantify them without making use of the knowledge of the nonequilibrium partition function, solely in terms of observables measurable in the laboratory. This will make us better appreciate the utility of the present theory of thermodynamics of irreversible processes developed here, albeit for dilute monatomic gases.

#### 3.5.1.1 Generalized Potentials

We begin the intended discussion on intensive variables with the generalized potentials  $X_a^{(s)}$  because the methods of determining other intensive variables must make use of the formula for  $X_a^{(s)}$ . From the extended Gibbs relation for  $\widehat{\Psi}$  follows the generalized Maxwell relations

$$\left( \frac{\partial X_a^{(s)}}{\partial \widehat{\Phi}_b^{(q)}} \right)_{v, c, \widehat{\Phi}''} = \left( \frac{\partial X_b^{(q)}}{\partial \widehat{\Phi}_a^{(s)}} \right)_{v, c, \widehat{\Phi}'}, \quad (3.160)$$

for all values of indices  $a, b, s, q$ . Since

$$X_a^{(s)} = \left( \frac{\partial \widehat{\Psi}}{\partial \widehat{\Phi}_a^{(s)}} \right)_{v, c, \widehat{\Phi}'}, \quad (3.161)$$

the Maxwell relation is nothing but the symmetry of the order of differentiation of  $\widehat{\Psi}$  with respect to  $\widehat{\Phi}_a^{(s)}$  and  $\widehat{\Phi}_b^{(q)}$ . Let the derivatives be denoted by

$$\begin{aligned} g_{ab}^{(sq)} &:= \left( \frac{\partial X_a^{(s)}}{\partial \widehat{\Phi}_b^{(q)}} \right)_{v, c, \widehat{\Phi}''} \\ &= \left( \frac{\partial^2 \widehat{\Psi}}{\partial \widehat{\Phi}_b^{(q)} \partial \widehat{\Phi}_a^{(s)}} \right)_{v, c, \widehat{\Phi}''} = \left( \frac{\partial^2 \widehat{\Psi}}{\partial \widehat{\Phi}_a^{(s)} \partial \widehat{\Phi}_b^{(q)}} \right)_{v, c, \widehat{\Phi}''} \\ &= \left( \frac{\partial X_b^{(q)}}{\partial \widehat{\Phi}_a^{(s)}} \right)_{v, c, \widehat{\Phi}'} := g_{ba}^{(qs)}. \end{aligned} \quad (3.162)$$

Evidently,  $g_{ab}^{(sq)}$  is a function of variables of manifolds  $\mathfrak{T}$  and  $\mathfrak{P}$  and generally a tensor of rank  $(s+q)$ , as  $\widehat{\Psi}$  is of manifold  $\mathfrak{G}$ . That is, the tensor  $g_{ab}^{(sq)}$  is symmetric in the sense:

$$g_{ab}^{(sq)} = g_{ba}^{(qs)}. \quad (3.163)$$

The generalized Maxwell relation (3.162) implies that the calortropy  $\widehat{\Psi}$  is of the form

$$\widehat{\Psi} = \widehat{\Psi}_0 + \sum_{a,b=1}^r \sum_{s,q \geq 1} \widehat{\Phi}_a^{(s)} g_{ab}^{(sq)} \widehat{\Phi}_b^{(q)}, \quad (3.164)$$

which suggests

$$X_a^{(s)} = \sum_{b=1}^r \sum_{q \geq 1} g_{ab}^{(sq)} \widehat{\Phi}_b^{(q)}. \quad (3.165)$$

This form is possible since different irreversible processes  $\widehat{\Phi}_a^{(s)}$  and  $\widehat{\Phi}_b^{(q)}$  of different tensorial ranks, for example, stress and heat flux, couple in the nonlinear regime. Such a coupling means, for example, thermo-viscous coupling, which arises beyond the regime of linear processes that exclude such couplings on account of the Curie principle.<sup>7</sup> When such couplings occur, the constitutive relations, for which (3.165) is an example, may arise. If we again take a thermo-viscous coupling as an example, and if  $\widehat{\Phi}_a^{(s)}$  is rank 2 and  $\widehat{\Phi}_b^{(q)}$  is rank 1, then

$$X_a^{(2)} = \sum_{b=1}^r \widehat{g}_{ab}^{(2)} \widehat{\Phi}_b^{(2)} + \sum_{b=1}^r \widehat{g}_{ab}^{(21)} \widehat{\Phi}_b^{(1)} \widehat{\Phi}_b^{(1)} + \dots, \quad (3.166)$$

where  $\widehat{g}_{ab}^{(2)}$  and  $\widehat{g}_{ab}^{(21)}$  are scalars independent of  $\widehat{\Phi}_a^{(s)}$ ,  $\widehat{\Phi}_b^{(q)}$ , ..., and hence  $\widehat{\Phi}_a^{(2)} \widehat{\Phi}_b^{(1)} \widehat{\Phi}_b^{(1)} = \widehat{\Phi}_a^{(2)} : \widehat{\Phi}_b^{(1)} \widehat{\Phi}_b^{(1)}$  is a scalar. Thus in Eq. (3.165), if we assume that

$$g_{ab}^{(sq)} = -g_a^{(s)} \delta_{ab} \delta_{sq}, \quad (3.167)$$

where  $g_a^{(s)}$  is a scalar function of variables of  $\mathfrak{T}$  and  $\mathfrak{P}$  to be determined phenomenologically or from the nonequilibrium partition function, we obtain

$$X_a^{(s)} = -g_a^{(s)} \widehat{\Phi}_a^{(s)}, \quad (3.168)$$

a form we have found as an approximation in the previous studies of thermodynamics of irreversible processes. This relation will be used as an approximation of the more general form in (3.165) in the following discussion of  $T$ ,  $p$ , and  $\widehat{\mu}_a$ .

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<sup>7</sup>This is a mathematical statement that different irreversible processes of different tensorial ranks cannot linearly couple because of the symmetry reason.

### 3.5.1.2 Nonequilibrium Temperature

A method of determining nonequilibrium temperature in terms of variables of  $\mathfrak{T}$  and  $\mathfrak{P}$  can be devised if the thermodynamics of irreversible processes presented up to this point is used, and in particular, the extended Gibbs relation and the generalized Maxwell relations. We obtain the desired Maxwell relation from the extended Gibbs relation

$$\left( \frac{\partial T}{\partial \widehat{\Phi}_a^{(s)}} \right)_{v,c,\widehat{\Psi},\widehat{\Phi}'} = \left( \frac{\partial X_a^{(s)}}{\partial \widehat{\Psi}} \right)_{v,c,\widehat{\Phi}'}, \quad (3.169)$$

which is rearranged to the form

$$\left( \frac{\partial \ln T}{\partial \widehat{\Phi}_a^{(s)}} \right)_{v,c,\widehat{\Psi},\widehat{\Phi}'} = \frac{1}{T} \left( \frac{\partial X_a^{(s)}}{\partial \widehat{\Psi}} \right)_{v,c,\widehat{\Phi}'}. \quad (3.170)$$

Integrating this equation we obtain

$$\ln (T/T_0) = \int_0^{\widehat{\Phi}_a^{(s)}} d\widehat{\Phi}^{(s)} \frac{1}{T} \left( \frac{\partial X_a^{(s)}}{\partial \widehat{\Psi}} \right)_{v,c,\widehat{\Phi}'} \quad (3.171)$$

with  $T_0$  denoting the temperature at  $\widehat{\Phi}^{(s)} = 0$

$$T_0 = T \left( \widehat{\Phi}^{(s)} \right)_{\widehat{\Phi}^{(s)}=0}, \quad (3.172)$$

that is, the equilibrium temperature. Since by using (3.168) we may write the derivative on the right of (3.171) as

$$\begin{aligned} \left( \frac{\partial X_a^{(s)}}{\partial \widehat{\Psi}} \right)_{v,c,\widehat{\Phi}'} &= \left( \frac{\partial X_a^{(s)}}{\partial T} \right)_{v,c,\widehat{\Phi}'} / \left( \frac{\partial \widehat{\Psi}}{\partial T} \right)_{v,c,\widehat{\Phi}} \\ &= -\frac{T}{\widehat{C}_{v,\widehat{\Phi}}} \left( \frac{\partial g_a^{(s)}}{\partial T} \right)_{v,c,\widehat{\Phi}'} \widehat{\Phi}_a^{(s)}, \end{aligned} \quad (3.173)$$

where  $\widehat{C}_{v,\widehat{\Phi}}$  is a nonequilibrium specific heat per mass defined by

$$\widehat{C}_{v,\widehat{\Phi}} = T \left( \frac{\partial \widehat{\Psi}}{\partial T} \right)_{v,c,\widehat{\Phi}}, \quad (3.174)$$

we finally obtain

$$T = T_0 \exp \left[ - \int_0^{\widehat{\Phi}_a^{(s)}} d\widehat{\Phi}_a^{(s)} \widehat{C}_{v,\widehat{\Phi}}^{-1} \left( \frac{\partial g_a^{(s)}}{\partial T} \right)_{v,c,\widehat{\Phi}'} \widehat{\Phi}_a^{(s)} \right]. \quad (3.175)$$

in the case that all processes  $\{\widehat{\Phi}_b^{(s)}\}$  except for  $\widehat{\Phi}_a^{(s)}$  are kept frozen. Near equilibrium

$$T \simeq T_0 - T_0 \int_0^{\widehat{\Phi}_a^{(s)}} d\widehat{\Phi}_a^{(s)} \widehat{C}_{v,\widehat{\Phi}}^{-1} \left( \frac{\partial g_a^{(s)}}{\partial T} \right)_{v,c,\widehat{\Phi}'} \widehat{\Phi}_a^{(s)}. \quad (3.176)$$

Here the factor  $\widehat{C}_{v,\widehat{\Phi}}^{-1} (\partial g_a^{(s)} / \partial T)_{v,c,\widehat{\Phi}'}$  may be taken at equilibrium to an approximation. Otherwise, (3.176) should be regarded as an integral equation for  $T$ . In the approximation indicated, the nonequilibrium temperature is a quadratic function of  $\widehat{\Phi}_a^{(s)}$  near equilibrium. Depending on the sign of the derivative  $(\partial g_a^{(s)} / \partial T)_{v,c,\widehat{\Phi}'}$ , the temperature  $T$  either increases or decreases as the nonequilibrium process  $\widehat{\Phi}_a^{(s)}$  progresses. It is possible to formulate a similar effect by using the fundamental equation for enthalpy  $\widehat{H}$  given earlier, but in this case  $\widehat{C}_{v,\widehat{\Phi}}$  will be replaced by  $\widehat{C}_{p,\widehat{\Phi}}$ .

### 3.5.1.3 Nonequilibrium Pressure

The effect on pressure by a nonequilibrium process can be investigated similarly to the effect on temperature. For the purpose we first calculate the generalized Maxwell relation

$$-\left( \frac{\partial p}{\partial \widehat{\Phi}_a^{(s)}} \right)_{v,c,\widehat{\Psi},\widehat{\Phi}} = \left( \frac{\partial X_a^{(s)}}{\partial v} \right)_{\widehat{\Psi},c,\widehat{\Phi}}. \quad (3.177)$$

Integrating this with respect to  $\widehat{\Phi}_a^{(s)}$  we obtain

$$\begin{aligned} p - p_0 &= - \int_0^{\widehat{\Phi}_a^{(s)}} d\widehat{\Phi}_a^{(s)} \left( \frac{\partial X_a^{(s)}}{\partial v} \right)_{\widehat{\Psi},c,\widehat{\Phi}} \\ &= - \int_0^{\widehat{\Phi}_a^{(s)}} d\widehat{\Phi}_a^{(s)} \frac{\widehat{\Phi}_a^{(s)}}{\kappa_{\widehat{\Psi}}} \left( \frac{\partial g_a^{(s)}}{\partial p} \right)_{\widehat{\Psi},c,\widehat{\Phi}}, \end{aligned} \quad (3.178)$$

where  $\kappa_{\widehat{\Psi}}$  is the adiabatic compressibility defined by

$$\kappa_{\widehat{\Psi}} = -\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_{\widehat{\Psi},c,\widehat{\Phi}}. \quad (3.179)$$

This is the nonequilibrium extension of the equilibrium adiabatic compressibility of the fluid in the presence of irreversible processes  $\{\widehat{\Phi}_a^{(s)}\}$ . Strictly speaking, (3.178) is an integral equation for  $p$ , but if the factor  $\frac{1}{\kappa_{\widehat{\Psi}}} (\partial g_a^{(s)} / \partial p)_{\widehat{\Psi},c,\widehat{\Phi}}$  is approximated by a form near  $p = p_0$  it becomes approximate as is (3.176) for  $T$ .

### 3.5.1.4 Nonequilibrium Chemical Potentials

We employ the same procedure as for temperature and pressure to devise a procedure to determine the nonequilibrium chemical potentials. Integrating the generalized Maxwell relation

$$\left( \frac{\partial \widehat{\mu}_a}{\partial \widehat{\Phi}_a^{(s)}} \right)_{\widehat{\Psi}, v, \mathfrak{c}', \widehat{\Phi}} = - \left( \frac{\partial X_a^{(s)}}{\partial \mathfrak{c}_a} \right)_{\widehat{\Psi}, v, \mathfrak{c}', \widehat{\Phi}} \quad (3.180)$$

with respect to  $\widehat{\Phi}_a^{(s)}$  from equilibrium state  $\widehat{\Phi}_a^{(s)} = 0$  to arbitrary nonequilibrium state along a fixed  $(\widehat{\Psi}, v, \mathfrak{c}', \widehat{\Phi}')$  path, we obtain

$$\widehat{\mu}_a - \widehat{\mu}_a^0 = - \int_0^{\widehat{\Phi}_a^{(s)}} d\widehat{\Phi}_a^{(s)} \left( \frac{\partial X_a^{(s)}}{\partial \mathfrak{c}_a} \right)_{\widehat{\Psi}, v, \mathfrak{c}', \widehat{\Phi}}, \quad (3.181)$$

which may be recast into the form

$$\widehat{\mu}_a - \widehat{\mu}_a^0 = \int_0^{\widehat{\Phi}_a^{(s)}} d\widehat{\Phi}_a^{(s)} \left( \frac{\partial g_a^{(s)}}{\partial \mathfrak{c}_a} \right)_{\widehat{\Psi}, v, \mathfrak{c}', \widehat{\Phi}} \widehat{\Phi}_a^{(s)}. \quad (3.182)$$

If the derivative  $(\partial g_a^{(s)} / \partial \mathfrak{c}_a)_{\widehat{\Psi}, v, \mathfrak{c}', \widehat{\Phi}}$  is independent of  $\widehat{\Phi}$  as usually is near equilibrium and is also independent of  $\widehat{\mu}_a$ , we obtain

$$\widehat{\mu}_a = \widehat{\mu}_a^0 + \frac{1}{2} \left( \frac{\partial g_a^{(s)}}{\partial \mathfrak{c}_a} \right)_{\widehat{\Psi}_0, v, \mathfrak{c}'} \widehat{\Phi}_a^{(s)} \odot^s \widehat{\Phi}_a^{(s)}, \quad (3.183)$$

where  $\odot^s$  is the symbol for contraction of tensor  $\widehat{\Phi}_a^{(s)}$ . The nonequilibrium chemical potential  $\widehat{\mu}_a$  therefore is quadratic with respect to  $\widehat{\Phi}_a^{(s)}$  at the order of approximations made.

Nonequilibrium (irreversible) processes can be further pursued on the basis of the formalism developed here, but since a full exposition of irreversible thermodynamics is not the aim of this monograph we conclude the discussions of the nonequilibrium statistical thermodynamics based on the calortropy of dilute monatomic gases. Before closing this section we consider an approximate method of calculating the constitutive equations for the generalized potentials by using the ensemble method developed here.

### 3.5.2 Nonequilibrium Partition Function

We have seen that the nonequilibrium partition function  $\Gamma$  provides the thermodynamic potential  $pv$  whose derivatives with respect to the generalized potentials give the fluxes  $\widehat{\Phi}_a^{(q)}$ . It can be shown by using the derivative

$$\widehat{\Phi}_a^{(q)} = -k_B T \left( \frac{\partial}{\partial X_a^{(q)}} \ln \Gamma \right)_{T,v,\mu,X'}, \quad (3.184)$$

since the nonequilibrium partition function  $\Gamma$  is expressible in the form

$$\begin{aligned} \ln \Gamma = & \sum_{a=1}^r n_a \ln \left[ n_a^{-1} \left( \frac{2\pi}{m\beta} \right)^{3/2} \right] \\ & + \sum_{a=1}^r n_a \ln \left\langle \exp \left[ - \sum_{q \geq 1} \sum_{a=1}^r \beta X_a^{(q)} h_a^{(q)} \right] \right\rangle_0 \end{aligned} \quad (3.185)$$

with the angular brackets  $\langle \dots \rangle_0$  denoting the integral over the reduced (dimensionless) velocities—an equilibrium average:

$$\langle A \rangle_0 = (2\pi)^{-3/2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\mathbf{w}_a e^{-\frac{1}{2} w_a^2} A(\mathbf{w}_a). \quad (3.186)$$

Here  $\mathbf{w}$  is dimensionless velocity vector reduced as in

$$\mathbf{w}_a = \sqrt{m_a \beta} \mathbf{C}_a. \quad (3.187)$$

Therefore, we find

$$\Phi_a^{(q)} = -k_B T \sum_{a=1}^r n_a \left( \frac{\partial \ln \mathfrak{Z}_a}{\partial X_a^{(q)}} \right)_{T,p,N,X'}, \quad (3.188)$$

where  $\mathfrak{Z}_a$  stands for the mean value of the nonequilibrium part of the partition function  $\Gamma$

$$\mathfrak{Z}_a = \left\langle \exp \left[ - \sum_{q \geq 1} \sum_{a=1}^r \beta X_a^{(q)} h_a^{(q)} \right] \right\rangle_0. \quad (3.189)$$

This mean value can be calculated by a number of methods. We find the cumulant method applicable if nonlinear relations are desired.

### 3.5.2.1 Cumulant Method for the Nonequilibrium Partition Function

We calculate the mean value  $\mathfrak{Z}_a$  by means of cumulants [6, 24, 25]. To achieve this objective it is convenient to express the moments  $h_a^{(s)}$  in orthogonal Hermite tensors as used in Ref. [7]. For the leading order of moments we have chosen in this chapter, we find

$$\begin{aligned}
\text{shear stress: } h_a^{(1)} &= \beta^{-1} \left[ \mathcal{H}_a^{(2)} - \frac{1}{3} \delta \text{Tr} \mathcal{H}_a^{(2)} \right], \\
\text{normal stress difference: } h_a^{(2)} &= \beta^{-1} \left[ \frac{1}{3} \text{Tr} \mathcal{H}_a^{(2)} + \left( 1 - \frac{p\beta}{n_a} \right) \mathcal{H}_a^{(0)} \right], \\
\text{heat flux: } h_{ai}^{(3)} &= \frac{1}{2\sqrt{m_a}\beta^{3/2}} \mathcal{H}_{aijj}^{(3)}, \\
\text{diffusion flux: } h_a^{(4)} &= \sqrt{\frac{m_a}{\beta}} \mathcal{H}_a^{(1)}, \tag{3.190}
\end{aligned}$$

where  $\mathcal{H}_a^{(m)}$  is tensor Hermite polynomial of rank  $m$ : for example,  $\mathcal{H}_{aijk}^{(3)} = (\mathbf{w}_a \mathbf{w}_a \mathbf{w}_a - \mathbf{w}_a \boldsymbol{\delta})_{ijk}$ . Here  $\boldsymbol{\delta}_{jk}$  denotes the Kronecker delta. Thus, in the case of  $\mathcal{H}_{aijj}^{(3)}$ , trace is taken over the last two indices, and the result is a vector. Then the expansion in moments (3.189) can be rearranged into an expansion in tensor Hermite polynomials; e.g.,

$$\sum_{s \geq 1} \beta X_a^{(s)} h_a^{(s)} = \sum_{m \geq 1} \bar{X}_a^{(m)} \mathcal{H}_a^{(m)}, \tag{3.191}$$

where

$$\begin{aligned}
\bar{X}_a^{(0)} &= (1 - p\beta/n_a) X_a^{(2)}; \text{ normal stress difference,} \\
\bar{X}_a^{(1)} &= \sqrt{m_a \beta} X_a^{(4)}; \quad \text{diffusion flux,} \\
\bar{X}_a^{(2)} &= X_a^{(1)}; \quad \text{shear stress,} \\
\bar{X}_a^{(3)} &= \frac{1}{2\sqrt{m_a \beta}} X_a^{(3)} \quad \text{heat flux,} \\
&\text{etc.} \tag{3.192}
\end{aligned}$$

We have excluded the term involving  $\text{Tr} \mathcal{H}_a^{(2)}$  because its average is identically equal to zero. With this preparation the cumulant expansion for  $\mathfrak{Z}_a$  making up the nonequilibrium partition function  $\Gamma$  may be written as

$$\mathfrak{Z}_a = \exp \left[ \exp \left( \sum_{l=2}^{\infty} \frac{(-1)^l}{l!} \kappa_l^a \right) - 1 \right] \tag{3.193}$$

where cumulants are:

$$\kappa_2^a = \sum_{k \geq 0} \sum_{m \geq 0} \bar{X}_a^{(k)} \bar{X}_a^{(m)} [\langle \mathcal{H}_a^{(m)} \mathcal{H}_a^{(k)} \rangle_0 - \langle \mathcal{H}_a^{(m)} \rangle \langle \mathcal{H}_a^{(k)} \rangle_0], \tag{3.194}$$

$$\begin{aligned}\kappa_3^a &= \sum_{k \geq 0} \sum_{m \geq 0} \sum_{p \geq 0} \bar{X}_a^{(k)} \bar{X}_a^{(m)} \bar{X}_a^{(p)} [\langle \mathcal{H}_a^{(m)} \mathcal{H}_a^{(k)} \mathcal{H}_a^{(p)} \rangle_0 \\ &\quad - \langle \mathcal{H}_a^{(m)} \rangle_0 \langle \mathcal{H}_a^{(k)} \mathcal{H}_a^{(p)} \rangle_0 - \langle \mathcal{H}_a^{(k)} \rangle_0 \langle \mathcal{H}_a^{(m)} \mathcal{H}_a^{(p)} \rangle_0 \\ &\quad - \langle \mathcal{H}_a^{(p)} \rangle_0 \langle \mathcal{H}_a^{(m)} \mathcal{H}_a^{(k)} \rangle_0 + 2 \langle \mathcal{H}_a^{(k)} \rangle_0 \langle \mathcal{H}_a^{(m)} \rangle_0 \langle \mathcal{H}_a^{(p)} \rangle_0], \text{ etc.}\end{aligned}\quad (3.195)$$

Since  $\langle \mathcal{H}_a^{(k)} \rangle_0 = 0$  for all  $k$  owing to the orthogonality of tensor polynomials of different orders, the first cumulant vanishes identically:

$$\kappa_1^a = \sum_{k \geq 0} \langle \bar{X}_a^{(k)} \mathcal{H}_a^{(k)} \rangle_0 = \sum_{k \geq 0} \bar{X}_a^{(k)} \langle \mathcal{H}_a^{(k)} \rangle_0 = 0,$$

and for this reason we obtain

$$\kappa_2^a = \sum_{k \geq 0} \sum_{m \geq 0} \bar{X}_a^{(k)} \bar{X}_a^{(m)} \langle \mathcal{H}_a^{(m)} \mathcal{H}_a^{(k)} \rangle_0, \quad (3.196)$$

$$\kappa_3^a = \sum_{k \geq 0} \sum_{m \geq 0} \sum_{p \geq 0} \bar{X}_a^{(k)} \bar{X}_a^{(m)} \bar{X}_a^{(p)} \langle \mathcal{H}_a^{(m)} \mathcal{H}_a^{(k)} \mathcal{H}_a^{(p)} \rangle_0, \quad (3.197)$$

etc.

It is easy to calculate various mean values  $\langle \mathcal{H}_a^{(m)} \mathcal{H}_a^{(k)} \rangle_0$ ,  $\langle \mathcal{H}_a^{(m)} \mathcal{H}_a^{(k)} \mathcal{H}_a^{(p)} \rangle_0$ , etc. by using the orthogonality of tensor Hermite polynomials and their recurrence relations. They can be calculated in generality for a mixture, but for the sake of simplicity we will limit the discussion here to the case of an approximation retaining the second cumulant in the case of a single-component gas. In such an approximation the mean value  $\mathfrak{Z}$  is given by

$$\mathfrak{Z} = \exp \left( e^{\frac{1}{2} \kappa_2} - 1 \right), \quad (3.198)$$

where the species index  $a$  is now omitted. Thus the nonequilibrium flux  $\Phi^{(s)}$  ( $s = 1, 2, 3, 4$ ) is now given by

$$\Phi^{(s)} = -n k_B T \left( \frac{\partial e^{\frac{1}{2} \kappa_2}}{\partial X_a^{(s)}} \right)_{T, p, N, X'} = -\frac{1}{2} n k_B T \left( \frac{\partial \kappa_2}{\partial X_a^{(s)}} \right)_{T, p, N, X'} e^{\frac{1}{2} \kappa_2}, \quad (3.199)$$

where

$$\frac{1}{2} \kappa_2 = X^{(p)} : X^{(p)} + \frac{5 k_B T}{4m} X^{(h)} X^{(h)} := K, \quad (3.200)$$

if we limit the number of moments to shear stress and heat flux. Note that there is no contribution from the diffusion fluxes because they vanish in the case of a single component fluid. Finally, we obtain the expressions

$$\frac{1}{2nk_B T} \Phi^{(1)} = -X^{(p)} \exp \left( X^{(p)} : X^{(p)} + \frac{5k_B T}{4m} X^{(h)} \cdot X^{(h)} \right), \quad (3.201)$$

$$\begin{aligned} \frac{1}{nk_B T} \sqrt{\frac{m}{5k_B T}} \Phi^{(3)} &= -\frac{1}{2} \sqrt{\frac{5k_B T}{m}} X^{(h)} \times \\ &\exp \left( X^{(p)} : X^{(p)} + \frac{5k_B T}{4m} X^{(h)} \cdot X^{(h)} \right). \end{aligned} \quad (3.202)$$

These two coupled algebraic equations must be solved for the constitutive relations for  $X^{(p)}$  and  $X^{(h)}$ . To the aim we contract the tensor with itself and similarly for the vector and then add them up to obtain the expression

$$\Re(\Phi) = K(X) e^{2K(X)}, \quad (3.203)$$

where

$$\Re(\Phi) = \left( \frac{1}{2nk_B T} \right)^2 \Phi^{(1)} : \Phi^{(1)} + \frac{m}{5n^2 (k_B T)^3} \Phi^{(3)} : \Phi^{(3)}. \quad (3.204)$$

This relation can be solved by a LambertW function [26]:

$$X^{(1)} : X^{(1)} + \frac{5k_B T}{4m} X^{(3)} \cdot X^{(3)} = \Re(e^{-\text{LambertW}(l, 2\Re)}) \quad (l \geq 0) \quad (3.205)$$

A particular solution of this quadratic form is given by

$$X^{(1)} = -\frac{1}{2nk_B T} \Phi^{(1)} e^{-\frac{1}{2} \text{LambertW}(l, 2\Re)} \quad (l \geq 0), \quad (3.206)$$

$$X^{(3)} = -\frac{2m}{5n (k_B T)^2} \Phi^{(3)} e^{-\frac{1}{2} \text{LambertW}(l, 2\Re)} \quad (l \geq 0). \quad (3.207)$$

This is a set of desired nonlinear constitutive relations for the generalized potentials  $X^{(p)}$  and  $X^{(h)}$ . We recover the previously employed approximate forms for them in the linear regime. It is useful to note that the Taylor series for the LambertW function is given by

$$\text{LambertW}(0, 2\Re) = 2\Re - 4\Re^2 + 12\Re^3 - \frac{128}{3}\Re^4 + \frac{500}{3}\Re^5 - \dots, \quad (3.208)$$

whereas its asymptotic expansion is

$$\begin{aligned} \text{LambertW}(0, 2\Re) &= \ln(2\Re) - \ln \ln(2\Re) \\ &+ \sum_{l \geq 0} \sum_{m \geq 1} \frac{(-1)^l}{m!} \begin{bmatrix} l+m \\ l+1 \end{bmatrix} \frac{(\ln \ln(2\Re))^m}{(\ln(2\Re))^{l+m}}, \end{aligned} \quad (3.209)$$

where

$$\begin{bmatrix} l+m \\ l+1 \end{bmatrix} = \text{Stirling cycle number}, \quad (3.210)$$

which is the number generated by the formula

$$x(x+1)(x+2)\cdots(x+n-1) = \sum_{k=0}^n \begin{bmatrix} n \\ k \end{bmatrix} x^k. \quad (3.211)$$

Having obtained the constitutive relations for generalized potentials, we are now in a position to compute the calortropy with respect to fluxes. According to the extended Gibbs relation (3.138) for  $d\hat{\Psi}$  the calortropy density change arising from the change in shear stress and heat flux at fixed energy and volume is given by

$$d\hat{\Psi} = T^{-1} (X^{(1)} d\hat{\Phi}^{(1)} + X^{(3)} d\hat{\Phi}^{(3)}). \quad (3.212)$$

Integrating this differential form with the constitutive relation inserted, we find the calortropy given in terms of line integrals along the path  $0 \rightarrow \hat{\Phi}^{(p)}$  or  $0 \rightarrow \hat{\Phi}^{(h)}$ :

$$\begin{aligned} \hat{\Psi} = \hat{\Psi}_0 - \frac{1}{2nk_B T^2} & \int_0^{\hat{\Phi}^{(1)}} d\hat{\Phi}^{(1)} \hat{\Phi}^{(1)} \times \\ & \exp \left[ -\frac{1}{2} \text{LambertW} \left( 0, \frac{\hat{\Phi}^{(1)2}}{2(nk_B T)^2} + \frac{2m\hat{\Phi}^{(3)2}}{5(nk_B T)^2} \right) \right] \\ & - \frac{2m}{5nT(k_B T)^2} \int_0^{\hat{\Phi}^{(3)}} d\hat{\Phi}^{(3)} \hat{\Phi}^{(3)} \times \\ & \exp \left[ -\frac{1}{2} \text{LambertW} \left( 0, \frac{\hat{\Phi}^{(1)2}}{2(nk_B T)^2} + \frac{2m\hat{\Phi}^{(3)2}}{5(nk_B T)^2} \right) \right], \end{aligned} \quad (3.213)$$

where  $\hat{\Psi}_0$  is an integration constant which may be identified with the equilibrium entropy, and we have taken the principal branch  $l = 0$ . These integrals can be numerically computed rather simply. This shows that the calortropy is maximum at equilibrium with the value identical with the Clausius entropy and decreases as the fluxes increases, that is, the fluid is removed from equilibrium. This result thus agrees with what we understand of the calortropy from the phenomenological consideration.

If the cumulant approximation is extended to include the fourth order cumulant, then in the case of a single-component gas and one-dimensional transport processes, after a rather lengthy calculation we obtain the equations

$$\begin{aligned} \frac{1}{2nk_B T} \Phi^{(1)} = - & \left( X^{(2)} - X^{(2)2} - \frac{3k_B T}{8m} X^{(h)2} \right. \\ & \left. + 2X^{(2)3} + \frac{5k_B T}{8m} X^{(2)} X^{(h)2} \right) e^{K_4}, \end{aligned} \quad (3.214)$$

$$\frac{1}{nk_B T} \sqrt{\frac{m}{5k_B T}} \Phi^{(3)} = - \left( 2X^{(h)} - \frac{6}{5} X^{(h)} X^{(2)} + X^{(2)2} + \frac{103}{2} \left( \frac{k_B T}{m} \right)^2 X^{(h)3} \right) e^{K_4}, \quad (3.215)$$

where

$$K_4 = X^{(2)2} + \frac{5k_B T}{4m} X^{(h)2} - \frac{2}{3} X^{(2)3} - \frac{3k_B T}{4m} X^{(h)2} + X^{(2)4} + \frac{5k_B T}{8m} X^{(2)2} X^{(h)2} + \frac{203 (k_B T)^2}{16m^2} X^{(h)4}. \quad (3.216)$$

The solutions  $X^{(2)}$  and  $X^{(h)}$  of these equations numerically behave similarly to Expressions (3.206) and (3.207). The second cumulant approximation, therefore, seems to be a reasonable approximation if we are concerned with the qualitative aspects of the constitutive relations between the generalized potentials and the fluxes.

### 3.5.3 Calortropy Production in Cumulant Expansion

Instead of calculating the nonequilibrium partition function by means of the Lambert W function, which is in essence equivalent to a cumulant expansion method, we may calculate the calortropy production by a cumulant expansion method. The advantage of this method is in ensuring the inevitable approximation for the calortropy production and consequently the dissipation terms to confirm to the requirement of the second law of thermodynamics. The desired cumulant expansion method is facilitated by first calculating the calortropy production with the nonequilibrium canonical form  $f_a^c(x_a, t)$  introduced earlier. This approximation is tantamount to discarding the fluctuations  $\Delta f_a = f_a(\mathbf{r}, \mathbf{v}_a, t) - f_a^c(\mathbf{r}, \mathbf{v}_a, t)$  of the distribution function from  $f_a^c(x_a, t)$ . That is, the distribution function is approximated by the formula

$$f_a(\mathbf{r}, \mathbf{v}_a, t) = f_a^c(\mathbf{r}, \mathbf{v}_a, t) + O(\Delta f_a), \quad (3.217)$$

where the nonequilibrium canonical form may be written in terms of dimensionless reduced variables as

$$f_a^c(\mathbf{r}, \mathbf{v}_a, t) = f_a^0 \exp(-x_a), \quad (3.218)$$

where

$$x_a = \beta (H_a^{(1)} - \mu_a + \mu_a^0), \quad (3.219)$$

$$f_a^0 = n_a \left( \frac{m_a}{2\pi k_B T} \right)^{3/2} \exp\left(-\frac{1}{2} w_a^2\right), \quad (3.220)$$

$$\mathbf{w}_a = \sqrt{\frac{m_a}{k_B T}} \mathbf{C}_a. \quad (3.221)$$

In this approximation the calortropy production is then given by the expression

$$\sigma_c = \frac{1}{4} k_B \sum_{a,b=1}^r \int d\Theta_{ab} f_a^0 f_b^0 (x_{ab} - y_{ab}) [\exp(-y_{ab}) - \exp(-x_{ab})], \quad (3.222)$$

where

$$x_{ab} = x_a + x_b, \quad y_{ab} = y_a + y_b := x_{ab}^*, \quad (3.223)$$

and  $d\Theta_{ab}$  is abbreviation for the integral

$$\int d\Theta_{ab} \cdots = \int d\mathbf{v}_a \int d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} \mathbf{b} \mathbf{g}_{ab} \cdots \quad (3.224)$$

$\mathbf{g}_{ab}$  being the relative speed of colliding particles  $a$  and  $b$ . The symbols  $y_a$  and  $y_b$  are the post-collision values of  $x_a$  and  $x_b$ , respectively. The relative speed is made dimensionless by scaling it as follows:

$$\bar{\mathbf{g}}_{ab} = \mathbf{g}_{ab} \sqrt{\frac{m_r}{2k_B T}}. \quad (3.225)$$

With the parameter  $\mathbf{g}$  defined by

$$\mathbf{g} := \frac{1}{(nd)^2} \sqrt{\frac{m_r}{2k_B T}}, \quad (3.226)$$

where  $m_r$  is the mean mass of molecules,  $d$  is a length (e.g., interaction range) characteristic of molecules, and  $n$  is the density, the calortropy production  $\sigma_c$  in (3.222) is rendered dimensionless as follows:

$$\begin{aligned} \bar{\sigma}_c &= \sigma_c \mathbf{g} / k_B \\ &= \frac{1}{4} \sum_{a,b=1}^r \langle (x_{ab} - y_{ab}) [\exp(-y_{ab}) - \exp(-x_{ab})] \rangle_c, \end{aligned} \quad (3.227)$$

where

$$\langle A \rangle_c = \int d\bar{\Theta}_{ab} \omega_{ab} A \quad (3.228)$$

with  $\omega_{ab}$  denoting the reduced distribution function

$$\omega_{ab} = (2\pi)^{-3} \exp\left(-\frac{1}{2} w_a^2 - \frac{1}{2} w_b^2\right) \quad (3.229)$$

and  $d\bar{\Theta}_{ab}$  stands for the reduced form of  $d\Theta_{ab}$  defined in (3.224). It is now convenient to write  $\bar{\sigma}_c$  in terms of two components

$$\mathcal{R}^{(+)}(\lambda) = \sum_{a,b=1}^r \langle (x_{ab} - y_{ab}) [\exp(-\lambda y_{ab}) - 1] \rangle_c, \quad (3.230)$$

$$\mathcal{R}^{(-)}(\lambda) = \sum_{a,b=1}^r \langle (x_{ab} - y_{ab}) [\exp(-\lambda x_{ab}) - 1] \rangle_c, \quad (3.231)$$

where  $\lambda$  is a constant parameter introduced for the bookkeeping purpose when the calortropy production is expanded in series of cumulants. When the expansion procedure is completed, it will be set equal to unity. With  $\mathcal{R}^{(\pm)}(\lambda)$  the calortropy production is now given by

$$\bar{\sigma}_c = \frac{1}{4} [\mathcal{R}^{(+)}(\lambda) - \mathcal{R}^{(-)}(\lambda)]_{\lambda=1}. \quad (3.232)$$

With the preparation presented above,  $\mathcal{R}^{(\pm)}(\lambda)$  are expanded in cumulants [24, 25] as follows:

$$\mathcal{R}^{(\pm)}(\lambda) = \kappa \left\{ \exp \left[ \sum_{l=1}^{\infty} \frac{(-\lambda)^l}{l!} \kappa_l^{(\pm)} \right] - 1 \right\}, \quad (3.233)$$

where  $\kappa$  is defined by a collision-weighted average of a quadratic form of  $x_{ab}$  and  $y_{ab}$ :

$$\kappa := \frac{1}{2} \sqrt{\sum_{a,b=1}^r \langle (x_{ab} - y_{ab})^2 \rangle_c}, \quad (3.234)$$

and the leading order cumulants  $\kappa_l^{(\pm)}$  are easily found:

$$\kappa_1^{(\pm)} = \mp \kappa, \quad (3.235)$$

$$\kappa_2^{(\pm)} = \mp \frac{\kappa_2}{\kappa} - \kappa^2, \quad (3.236)$$

$$\kappa_3^{(\pm)} = \mp \frac{\kappa_3}{\kappa} - 3\kappa_2 \mp 2\kappa^3, \text{ etc.} \quad (3.237)$$

Here  $\kappa_2$  and  $\kappa_3$  are defined by the integrals

$$\kappa_2 = \frac{1}{4} \sum_{a,b=1}^r \langle (x_{ab} - y_{ab}) (x_{ab}^2 - y_{ab}^2) \rangle_c, \quad (3.238)$$

$$\kappa_3 = \frac{1}{4} \sum_{a,b=1}^r \langle (x_{ab} - y_{ab}) (x_{ab}^3 - y_{ab}^3) \rangle_c. \quad (3.239)$$

These expressions for the cumulants are found by expanding (3.227) and (3.232) in power series of  $\lambda$  and comparing the terms of the like power of  $\lambda$ . A more general method well known in the cumulant expansion method [24, 25] can be made use of to obtain the general formula for cumulants, but we would find the leading order

formulas given in (3.235)–(3.237) sufficient for practical purposes. In fact, we find the first order cumulant approximation sufficient for many nonlinear problems. The first-order cumulant approximation is given by

$$\bar{\sigma}_c = \kappa \sinh \kappa. \quad (3.240)$$

Since  $\kappa \geq 0$ , the first-order calortropy production is found to be positive semi-definite:  $\bar{\sigma}_c \geq 0$  satisfying the second law of thermodynamics for all irreversible processes. The equality holds if the nonequilibrium variables (fluxes) of manifold  $\mathfrak{P}$  vanish; in other words, at equilibrium.

### 3.5.4 Cumulant Expansion for Dissipation Terms

On substitution of (3.219) for  $x_a$  and  $y_a$  it can be shown that  $\kappa^2$  is a quadratic form in generalized potentials  $X_a^{(q)}$  as in

$$\kappa^2 = \sum_{a,b=1}^r \sum_{q,s \geq 1} X_a^{(q)} \mathbf{R}_{ab}^{(qs)} X_b^{(s)}, \quad (3.241)$$

where the coefficients  $\mathbf{R}_{ab}^{(qs)}$ , which are made up of collision bracket integrals of moments  $h_a^{(q)}$  and  $h_b^{(s)}$  introduced earlier, will be explicitly given later. Comparing the first-order cumulant approximation for  $\bar{\sigma}_c$  with the calortropy production given in terms of dissipation function [see (3.92)]

$$\sigma_c = T^{-1} \sum_{a=1}^r \sum_{q \geq 1} X_a^{(q)} \Lambda_a^{(q)}, \quad (3.242)$$

we obtain the first-order cumulant approximation for the dissipation term

$$\Lambda_a^{(q)} = (\beta g)^{-1} \sum_{b=1}^r \sum_{s \geq 1} \mathbf{R}_{ab}^{(qs)} X_b^{(s)} q_n(\kappa), \quad (3.243)$$

where

$$q_n(\kappa) = \frac{\sinh \kappa}{\kappa}, \quad (3.244)$$

which is a nonlinear function of the generalized potentials. If higher order cumulant approximations are taken that make use of  $\kappa_2^{(\pm)}$ ,  $\kappa_3^{(\pm)}$ , etc., the calortropy production will have the corresponding approximation and the dissipation functions  $\Lambda_a^{(q)}$  will accordingly change their forms. The dissipation functions given in (3.244) appear in the quasilinear model for transport processes presented in Sect. 3.5.7 and discussed

in Chap. 9. They give rise to nonlinear transport coefficients, such as non-Newtonian viscosity [27], non-Fourier thermal conductivity, etc., which interestingly describe nonlinear transport processes in terms of linear transport coefficients and thermodynamic gradients only, even if the transport processes occur far removed from equilibrium. In this regard the quasilinear generalized hydrodynamic equations are of considerable practical utility as will be seen in Chap. 9.

### 3.5.5 Collision Bracket Integrals

We now show the expansion coefficients  $\mathbf{R}_{ab}^{(qs)}$ , which are tensors, are given by the collision bracket integrals directly related to the collision integral  $\mathbf{R}[f_a]$  of the Boltzmann kinetic equation and hence to collision dynamics of the molecules in the gas. Therefore the present theory is connected to molecular aspects and, in particular, interactions of particles in the fluid. Since  $x_a$  [see (3.219) and (3.223)] appearing in  $\kappa$  is given in terms of moments  $h_i^{(q)}$ , with the definitions

$$\Delta h_a^{(q)} = h_a^{(q)} - h_a^{(q)*}, \quad (3.245)$$

$$\Delta A_a = A_a - A_a^*, \text{ etc.} \quad (3.246)$$

and collision bracket integrals

$$[A_a B_a]_{ab} := \frac{n_a n_b}{4n^2} \int d\bar{\Theta}_{ab} \omega_{ab} (\mathbf{w}_a, \mathbf{w}_b) (\Delta A_a + \Delta A_b) (\Delta B_a + \Delta B_b), \quad (3.247)$$

$$[A_a B_a]_{ab}' := \frac{n_a n_b}{2n^2} \int d\bar{\Theta}_{ab} \omega_{ab} (\mathbf{w}_a, \mathbf{w}_b) \Delta A_a \Delta B_a, \quad (3.248)$$

$$[A_a B_a]_{ab}'' := \frac{n_a n_b}{2n^2} \int d\bar{\Theta}_{ab} \omega_{ab} (\mathbf{w}_a, \mathbf{w}_b) \Delta A_a \Delta B_b, \quad (3.249)$$

the tensor coefficient  $\mathbf{R}_{ab}^{(qs)}$  reduces to a scalar coefficients  $R_{ab}^{(qs)}$ :

$$\mathbf{R}_{ab}^{(qs)} X_b^{(s)} = R_{ab}^{(qs)} X_b^{(s)}. \quad (3.250)$$

The scalar coefficients  $R_{ab}^{(qs)}$  on the right of (3.250) are given by the collision bracket integrals

$$R_{aa}^{(11)} = \frac{1}{5} \beta^2 [h_a^{(1)} : h_a^{(1)}]_{aa'} + \sum_{a \neq b}^r [h_a^{(1)} : h_a^{(1)}]_{ab}', \quad (3.251)$$

$$R_{aa}^{(11)} = \frac{1}{5} \beta^2 [h_a^{(1)} : h_b^{(1)}]_{ab}'' \quad (a \neq b), \quad (3.252)$$

$$R_{aa}^{(22)} = \beta^2 [h_a^{(2)} h_a^{(2)}]_{aa'} + \sum_{a \neq b}^r [h_a^{(2)} h_a^{(2)}]_{ab}', \quad (3.253)$$

$$R_{aa}^{(22)} = \beta^2 [h_a^{(2)} h_b^{(2)}]_{ab}'' \quad (a \neq b), \quad (3.254)$$

$$R_{aa}^{(qs)} = \frac{1}{3} \beta^2 [h_a^{(q)} \cdot h_a^{(s)}]_{aa'} + \sum_{a \neq b}^r [h_a^{(q)} \cdot h_a^{(s)}]_{ab}', \quad (3.255)$$

$$R_{ab}^{(qs)} = \frac{1}{3} \beta^2 [h_a^{(q)} \cdot h_b^{(s)}]_{ab}'' \quad (a \neq b; q, s = 3, 4). \quad (3.256)$$

In these expressions for the collision bracket integrals the prime on the subscript to  $[\dots]_{aa'}$  means another particle of species  $a$ . Therefore the collision involved is between two particles of the same species  $a$ . The fractional coefficients such as  $\frac{1}{5}$  or  $\frac{1}{3}$  arises because the integral involving the tensor product  $h_a^{(1)} h_a^{(1)}$  contracts to a scalar  $h_a^{(1)} : h_a^{(1)}$  or the vector product  $h_a^{(q)} h_a^{(s)}$  contracts to a scalar product  $h_a^{(q)} \cdot h_a^{(s)}$  of vectors. The collision bracket integrals in (3.251)–(3.256) are the entire set of collision bracket integrals necessary to compute the coefficients  $\mathbf{R}_{ab}^{(qs)}$  for the quadratic form for  $\kappa^2$  in the present theory. Thus within the “13 moment” approximation for the moment set considered in this work the dissipation terms in the first-order cumulant approximation is given by

$$\Lambda_a^{(q)} = (\beta g)^{-1} \sum_{b=1}^r \sum_{s \geq 1} R_{ab}^{(qs)} X_b^{(s)} q_n(\kappa). \quad (3.257)$$

We conclude the discussion on collision bracket integrals in this subsection by noting that (3.251)–(3.256) are identical with the collision bracket integrals in the first-order Chapman–Enskog theory [2] of the Boltzmann equation. This indicates that the present generalized hydrodynamic equations approach to the transport processes contains the Chapman–Enskog theory in the limit of  $\kappa \rightarrow 0$  in linear approximations for  $X_a^{(q)}$  as in (3.304).

### 3.5.6 Generalized Potentials

The generalized potentials can be calculated by using the statistical mechanical expression

$$\widehat{\Phi}_{av}^{(q)} = -k_B T \left( \frac{\partial \ln \Gamma}{\partial X_a^{(q)}} \right)_{T, v, \widehat{\mu}, X'} \quad (1 \leq a \leq r; q \geq 1) \quad (3.258)$$

relating a flux to generalized potentials, if the (local) nonequilibrium partition function  $\Gamma$  is computed as a function of  $X_a^{(q)}$  by some means. Earlier we have taken the Lambert W function approach to the aim. As a matter of fact, the Lambert W function method is similar to the cumulant expansion method. However, we may use the simple-minded method of perturbation theory to obtain the lowest order relation of fluxes to generalized potentials. Thus we will calculate the partial derivative in (3.258) by a perturbation theory method by expanding  $\Gamma$  in series of generalized potentials.

Since  $\Gamma$  is given by

$$\Gamma = \prod_{a=1}^r \Gamma_a^{n_a}, \quad (3.259)$$

where

$$\Gamma_a = n_a^{-1} \left\langle \exp \left[ -\beta \left( \frac{1}{2} m_a C_a^2 + \sum_{q \geq 1} \sum_{a=1}^r X_a^{(q)} h_a^{(q)} \right) \right] \right\rangle, \quad (3.260)$$

the partial derivative in (3.258) is given, to first order in  $X_a^{(q)}$ , by the series as follows:

$$\left( \frac{\partial \ln \Gamma}{\partial X_a^{(q)}} \right)_{T, v, \hat{\mu}, X'} = n_a \left\langle h_a^{(q)} h_a^{(q)} \right\rangle_{\text{eq}} X_a^{(q)} + O(X^2).$$

Therefore we find

$$\Phi_a^{(q)} = -n_a \left\langle h_a^{(q)} h_a^{(q)} \right\rangle_{\text{eq}} X_a^{(q)}$$

or

$$X_a^{(q)} = -\frac{1}{n_a \left\langle h_a^{(q)} h_a^{(q)} \right\rangle_{\text{eq}}} \Phi_a^{(q)} + O(\Phi^2), \quad (3.261)$$

where  $\left\langle h_a^{(q)} h_a^{(q)} \right\rangle_{\text{eq}}$  is the equilibrium average of the (contracted) moments:

$$\left\langle h_a^{(q)} h_a^{(q)} \right\rangle_{\text{eq}} = \left\langle f_a^{\text{eq}} h_a^{(q)} h_a^{(q)} \right\rangle. \quad (3.262)$$

Thus we obtain the approximate expression for  $\mathbf{g}_a^{(q)}$  in (3.304):

$$\mathbf{g}_a^{(q)} = \frac{1}{n_a \left\langle f_a^{\text{eq}} h_a^{(q)} \odot h_a^{(q)} \right\rangle}. \quad (3.263)$$

This can be calculated case by case for all  $q$ . We find

$$\mathbf{g}_a^{(1)} = \frac{1}{2p_a}; \quad \mathbf{g}_a^{(2)} = \frac{3}{2p_a}; \quad \mathbf{g}_a^{(3)} = \frac{1}{p_a \widehat{C}_{pa} T}; \quad \mathbf{g}_a^{(4)} = \frac{1}{\rho_a}. \quad (3.264)$$

Here  $\hat{C}_{pa}$  is the specific heat per mass of  $a$  at constant pressure.

Now, all the parameters in the generalized hydrodynamic equations are explicitly determined in complete consistency with the laws of thermodynamics, and we have shown that the irreversible thermodynamics can be formulated for dilute gases on the basis of the Boltzmann kinetic equation, attended by thermodynamically consistent generalized hydrodynamic equations. The generalized hydrodynamics formulated therefore can be applied to flow problems and transport processes also in complete consistency with the laws of thermodynamics. In the next subsection, we collect quasilinear generalized hydrodynamic equations obtained in various approximations described earlier. These generalized hydrodynamic equations enable us to discuss steady-state quasilinear and linear transport processes, which either extend, or are completely equivalent to, the first-order Chapman–Enskog theory results [2] of linear transport processes in dilute monatomic gases.

### 3.5.7 Quasilinear Generalized Hydrodynamics and Transport Processes

The generalized hydrodynamic equations consist of two subsets, one consisting of balance equations for the conserved variables  $\mathbf{u}$ ,  $c_a$  or  $n_a$ ,  $v$ , and  $\mathcal{E}$ :

$$\begin{aligned} \rho \frac{dv}{dt} &= \nabla \cdot \mathbf{u}, \\ \rho \frac{dc_a}{dt} &= -\nabla \cdot \mathbf{J}_a, \\ \rho \frac{d\mathbf{u}}{dt} &= -\nabla \cdot \mathbf{P} + \rho \widehat{\mathbf{F}}, \\ \rho \frac{d\mathcal{E}}{dt} &= -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \widehat{\mathbf{F}}_a, \end{aligned} \quad (3.265)$$

and the other, made up of the evolution equations for the nonconserved variables (3.111)–(3.114), is generically expressed by (3.91). If the closure relations are introduced, if the kinematic terms are linearized with respect to the thermodynamic forces—spatial gradients of variables of  $\mathbf{u}$ ,  $c_a$  or  $n_a$ ,  $v$ , and  $T$  spanning the manifold  $\mathfrak{T}$ —and, moreover, if dissipation terms are approximated by the first-order cumulant, we then obtain what we call quasilinear generalized hydrodynamic equations. The quasilinear evolution equations for nonconserved variables thus obtained are:

$$\rho d_t \widehat{\mathbf{\Pi}}_a = -2p_a [\nabla \mathbf{u}]^{(2)} - (\beta g g_a^{(1)})^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(11)} \Phi_b^{(1)} q_n(\kappa), \quad (3.266)$$

$$\rho d_t \widehat{\Delta}_a = -\frac{5}{3} p_a \nabla \cdot \mathbf{u} - (\beta g g_a^{(2)})^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(22)} \Phi_b^{(2)} q_n(\kappa), \quad (3.267)$$

$$\rho d_t \widehat{\mathbf{Q}}'_a = -p_a \widehat{C}_{pa} \nabla \ln T - (\beta g g_a^{(3)})^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(33)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(34)} \Phi_b^{(4)} \right) q_n(\kappa), \quad (3.268)$$

$$\rho d_t \widehat{\mathbf{J}}_a = -p \mathbf{d}_a - (\beta g g_a^{(4)})^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(43)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(44)} \Phi_b^{(4)} \right) q_n(\kappa). \quad (3.269)$$

In these equations  $\mathbf{d}_a$  is the driving force of mass diffusion defined by

$$\mathbf{d}_a = \nabla \left( \frac{n_a}{n} \right) + \left( \frac{n_a}{n} - \frac{\rho_a}{\rho} \right) \nabla \ln p + \frac{\rho_a}{p} (\widehat{\mathbf{F}} - \widehat{\mathbf{F}}_a). \quad (3.270)$$

With the generalized potentials  $X_a^{(q)}$  approximated linearly with respect to  $\Phi_a^{(q)}$ , the first cumulant  $\kappa$  in (3.241) is now seen to be in essence a generalized form of the Rayleigh dissipation function [22]

$$\kappa = \sqrt{\sum_{a,b=1}^r \sum_{q,s \geq 1} \mathfrak{R}_{ab}^{(qs)} \Phi_a^{(q)} \odot \Phi_b^{(s)}}, \quad (3.271)$$

where

$$\mathfrak{R}_{ab}^{(qs)} = g_a^{(q)} \mathbf{R}_{ab}^{(qs)} g_b^{(s)}, \quad (3.272)$$

and  $g$  is a parameter defined by (3.226). The symbol  $\odot$  stands for contraction of tensors to a scalar. Rayleigh [22] originally introduced the eponymous dissipation function in connection with the energy dissipation in sound wave propagation. In the present theory  $\kappa$  is intimately associated with calortropy production which is a measure of energy dissipation in the course of irreversible processes in the fluid—a measure that may be said to be the true physical meaning of  $\kappa$ . It should be recalled that the irreversible processes are described by the nonconserved variables:  $\Phi_a^{(1)} = \Pi_a$ ;  $\Phi_a^{(2)} = \Delta_a$ ;  $\Phi_a^{(3)} = \mathbf{Q}'_a$ ;  $\Phi_a^{(4)} = \mathbf{J}_a$ .

If the time scales of evolutions are examined for the two subsets—i.e., the conservation laws and the evolution equations for the nonconserved variables—of quasilinear generalized hydrodynamic equations, they are found widely separated. This can be seen if we consider, for example, the ratio of the rate of stress change to the rate of velocity change, which is proportional to the ratio of hydrodynamic relaxation time  $\tau_h$  to stress relaxation time  $\tau_s$ , namely, the inverse of Deborah number  $N_{De}$

$$\frac{(d\widehat{\Pi}/dt)L}{(d\mathbf{u}/dt)\eta_r} \sim \frac{\left(\frac{\Pi_r}{\eta_r}\right)}{\left(\frac{U_r}{L}\right)} \sim \frac{\tau_h}{\tau_s} = N_{De}^{-1}. \quad (3.273)$$

We note that  $N_{\text{De}}^{-1} \ll 1$  in the normal state of fluids. This implies that the stress tensor relaxes to a steady state value well before the velocity evolves to a steady state. Similar arguments hold for other nonconserved variables. Therefore in the hydrodynamic time scale of  $O(\tau_h)$  evolution equations (3.266)–(3.269) become quasilinear steady-state constitutive equations

$$-2p_a [\nabla \mathbf{u}]^{(2)} - (\beta g g_a^{(1)})^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(11)} \Phi_b^{(1)} q_n(\kappa) = 0, \quad (3.274)$$

$$-\frac{5}{3} p_a \nabla \cdot \mathbf{u} - (\beta g g_a^{(2)})^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(22)} \Phi_b^{(2)} q_n(\kappa) = 0, \quad (3.275)$$

$$-p_a \hat{C}_{pa} \nabla \ln T - (\beta g g_a^{(3)})^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(33)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(34)} \Phi_b^{(4)} \right) q_n(\kappa) = 0, \quad (3.276)$$

$$-p \mathbf{d}_a - (\beta g g_a^{(4)})^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(43)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(44)} \Phi_b^{(4)} \right) q_n(\kappa) = 0. \quad (3.277)$$

These nonlinear constitutive equations describe *non-Newtonian flows* of shear and bulk (compression/dilatation) processes, *non-Fourier heat conduction*, and *non-Fickian diffusion*, respectively. Upon solving these steady-state equations for  $\Phi_b^{(q)}$  ( $q = 1, \dots, 4$ ), it is possible to derive quasilinear transport coefficients depending nonlinearly on the thermodynamic gradients, as will be shown later in Chap. 9. For example, they provide a non-Newtonian shear viscosity, non-Fourier thermal conductivity, non-Fickian diffusion coefficients, etc. The steady-state quasilinear constitutive equations (3.274)–(3.277) together with the conservation laws (3.265) represent an extension of the classical hydrodynamic equations [28, 29] of Navier, Stokes, Fourier, and Fick. This extension of the classical hydrodynamic equations still remains consistent with the laws of thermodynamics unlike, for example, the Burnett order solutions [2] of the Chapman–Enskog theory of the Boltzmann equation, which become inconsistent with the second law of thermodynamics.

### 3.5.8 Linear Transport Processes

Since  $\kappa \rightarrow 0$  as the system approaches equilibrium the nonlinear factor  $q_n(\kappa)$  tends to unity:

$$\lim_{\kappa \rightarrow 0} q_n(\kappa) = \lim_{\kappa \rightarrow 0} \frac{\sinh \kappa}{\kappa} = 1. \quad (3.278)$$

Therefore, if the nonlinear factor  $q_n(\kappa)$  is set equal to 1, linear transport processes are described by the linearized evolution equations

$$\rho d_t \widehat{\boldsymbol{\Pi}}_a = -2p_a [\nabla \mathbf{u}]^{(2)} - (\beta g \mathbf{g}_a^{(1)})^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(11)} \Phi_b^{(1)}, \quad (3.279)$$

$$\rho d_t \widehat{\Delta}_a = -\frac{5}{3} p_a \nabla \cdot \mathbf{u} - (\beta g \mathbf{g}_a^{(2)})^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(22)} \Phi_b^{(2)}, \quad (3.280)$$

$$\rho d_t \widehat{\mathbf{Q}}'_a = -p_a \widehat{C}_{pa} \nabla \ln T - (\beta g \mathbf{g}_a^{(3)})^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(33)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(34)} \Phi_b^{(4)} \right), \quad (3.281)$$

$$\rho d_t \widehat{\mathbf{J}}_a = -p \mathbf{d}_a - (\beta g \mathbf{g}_a^{(4)})^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(43)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(44)} \Phi_b^{(4)} \right). \quad (3.282)$$

In Chap. 9, we will resume discussions on applications of generalized hydrodynamics attending irreversible thermodynamics just outlined above. The topics discussed will include linear transport processes and acquisition of the associated transport coefficients, and thereafter formal theories dealing with nonlinear transport processes, such as non-Newtonian flows seen in rheological studies of flow on the basis of quasilinear generalized hydrodynamic equations, in addition to some examples of studies in hydrodynamic flow problems with the generalized hydrodynamic equation formulated here.

By reasoning in the same manner as for the quasilinear generalized hydrodynamic equations presented above, it is possible to deduce the constitutive equations for linear transport processes. We thus obtain the linear constitutive equations for nonconserved variables ( $\boldsymbol{\Pi}_a$ ,  $\Delta_a$ ,  $\mathbf{Q}'_a$ ,  $\mathbf{J}_a$ ):

$$-2p_a [\nabla \mathbf{u}]^{(2)} - (\beta g \mathbf{g}_a^{(1)})^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(11)} \Phi_b^{(1)} = 0, \quad (3.283)$$

$$-\frac{5}{3} p_a \nabla \cdot \mathbf{u} - (\beta g \mathbf{g}_a^{(2)})^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(22)} \Phi_b^{(2)} = 0, \quad (3.284)$$

$$-p_a \widehat{C}_{pa} \nabla \ln T - (\beta g \mathbf{g}_a^{(3)})^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(33)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(34)} \Phi_b^{(4)} \right) = 0, \quad (3.285)$$

$$-p \mathbf{d}_a - (\beta g \mathbf{g}_a^{(4)})^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(43)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(44)} \Phi_b^{(4)} \right) = 0. \quad (3.286)$$

The linear transport coefficients, such as the shear viscosity, bulk viscosity, heat conductivity, and diffusion coefficients, can be extracted from these linear constitutive equations in terms of the collision bracket integrals  $\mathfrak{R}_{ab}^{(qs)}$ . These linear constitutive equations together with the conservation laws (3.265) give rise to the classical hydrodynamic equations [28, 29]. These aspects will be further discussed in Chap. 9.

### 3.5.9 A Model for Quasilinear Generalized Hydrodynamic Equations

If the fluxes  $\Phi_b^{(q)}$  ( $q = 1, \dots, 4$ ) in the quadratic form in  $q_n(\kappa)$ —namely, the Rayleigh dissipation function—are replaced with the solutions  $\Phi_b^{(q)}$  obtained from (3.274)–(3.277) and if the resulting nonlinear factor  $q_L$ , which is obtained from  $q_n$  (see Chap. 9, Sect. for details), replaces  $q_n(\kappa)$  in (3.266)–(3.269), then we obtain a model for quasilinear generalized hydrodynamic equations:

$$\rho d_t \widehat{\Pi}_a = -2p_a [\nabla \mathbf{u}]^{(2)} - (\beta g g_a^{(1)})^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(11)} \Phi_b^{(1)} q_L(\kappa), \quad (3.287)$$

$$\rho d_t \widehat{\Delta}_a = -\frac{5}{3} p_a \nabla \cdot \mathbf{u} - (\beta g g_a^{(2)})^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(22)} \Phi_b^{(2)} q_L(\kappa), \quad (3.288)$$

$$\rho d_t \widehat{\mathbf{Q}}_a = -p_a \widehat{C}_{pa} \nabla \ln T - (\beta g g_a^{(3)})^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(33)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(34)} \Phi_b^{(4)} \right) q_L(\kappa), \quad (3.289)$$

$$\rho d_t \widehat{\mathbf{J}}_a = -p \mathbf{d}_a - (\beta g g_a^{(4)})^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(43)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(44)} \Phi_b^{(4)} \right) q_L(\kappa). \quad (3.290)$$

These equations are coupled to the conservation laws (3.265). We reiterate that  $\kappa$  in  $q_L(\kappa)$  now is a quadratic form of thermodynamic gradients. Further discussions and applications of the model quasilinear generalized hydrodynamic equations will be given in Chap. 9.

## 3.6 Relative Boltzmann Entropy

Since the calortropy is a measure of information shedding—a projection of phase space information onto the thermodynamic manifold—from the full Boltzmann entropy, there is a complement to the projection. It is called the relative Boltzmann entropy (RBE)  $\rho \mathcal{S}_r[f|f^c]$ , which is the difference between  $\mathcal{S}$  and  $\Psi$  defined by

$$\rho \widehat{\mathcal{S}} = \rho \widehat{\Psi} - \rho \mathcal{S}_r[f|f^c]. \quad (3.291)$$

If knowledge of the Boltzmann entropy is desired fully, it is necessary to learn about the RBE. Its statistical mechanical expression is readily found in the form

$$\rho \mathcal{S}_r[f|f^c] = k_B \sum_{a=1}^r \langle f_a \ln (f_a/f_a^c) \rangle, \quad (3.292)$$

which follows from the definition of  $\widehat{\mathcal{S}}$  and  $\widehat{\Psi}$ . Since by Klein's inequality

$$x \ln x - x + 1 \geq 0,$$

the RBE is positive semidefinite:

$$\mathcal{S}_r[f|f^c] \geq 0, \quad (3.293)$$

the equality holding if  $f_a = f_a^c$ . This means that

$$\widehat{\mathcal{S}} \leq \widehat{\Psi}. \quad (3.294)$$

This inequality implies that the information content of the Boltzmann entropy is always larger than that of the calortropy, since the latter is a projection onto the thermodynamic manifold of the former whose dimension is smaller than that of the phase space of the system.

### 3.6.1 Evolution Equation of Relative Boltzmann Entropy

The evolution equation of the relative Boltzmann entropy is also naturally obtained from the Boltzmann entropy balance equation and the calortropy balance equation

$$\rho \frac{d}{dt} \mathcal{S}_r[f|f^c] = -\nabla \cdot \mathbf{J}_r[f|f^c] + \sigma_r[f|f^c], \quad (3.295)$$

where  $\mathbf{J}_r[f|f^c]$  is the relative Boltzmann entropy flux and  $\sigma_r[f|f^c]$  is the relative Boltzmann entropy production respectively defined by the statistical mechanical formulas

$$\mathbf{J}_r[f|f^c] = k_B \sum_{a=1}^r \langle f_a \mathbf{C}_a \ln (f_a/f_a^c) \rangle, \quad (3.296)$$

$$\sigma_r[f|f^c] = k_B \sum_{a=1}^r \langle \ln (f_a/f_a^c) \mathbf{R}[f_a] \rangle - k_B \sum_{a=1}^r \langle f_a \mathcal{D}_t \ln f_a^c \rangle. \quad (3.297)$$

To calculate more explicitly these quantities in the statistical mechanical approach, we may reason that the distribution function  $f_a$  should be dependent on the variables of manifold  $\mathfrak{M}$  representative of manifold  $\mathfrak{P}$ . Then, since it would be natural to imagine that the mathematical structure of  $f_a$  in manifold  $\mathfrak{M}$  is isomorphic to that of  $f_a^c$ , it is logical to think that the fluctuations of  $f_a$  should be vested in the variables of tangent manifold  $\mathfrak{T}$ . That is, the variables of  $\mathfrak{T}$  in  $f_a$  are fluctuating variables. Under this reasoning we look for  $f_a$  in the form

$$f_a = \exp \left\{ -k_B^{-1} \left[ \frac{1}{2} m_a C_a^2 I + \sum_{q \geq 1} \bar{X}_a^{(q)} h_a^{(q)} - m_a \bar{\mu}_a \right] \right\}, \quad (3.298)$$

where

$$I = \frac{1}{T}, \quad \bar{\mu}_a = \frac{\hat{\mu}_a}{T}, \quad \bar{X}_a^{(q)} = \frac{X_a^{(q)}}{T}. \quad (3.299)$$

On the other hand, the thermodynamic branch  $f_a^c$  is written by the expression

$$f_a^c = \exp \left\{ -k_B^{-1} \left[ \frac{1}{2} m_a C_a^2 I^t + \sum_{s \geq 1} \bar{X}_a^{(s)t} h_a^{(s)} - m_a \bar{\mu}_a^t \right] \right\}, \quad (3.300)$$

where  $I^t$ ,  $\bar{\mu}_a^t$ , and  $\bar{X}_a^{(s)t}$  are the intensive variables of the thermodynamic branch of  $\mathfrak{T}$  which are determined either by phenomenological thermodynamic methods or as described earlier by means of the statistical mechanical method based on  $f_a^c$ :

$$I^t = \frac{1}{T^t}, \quad \bar{\mu}_a^t = \frac{\hat{\mu}_a^t}{T^t}, \quad \bar{X}_a^{(q)t} = \frac{X_a^{(q)t}}{T^t}, \quad (3.301)$$

where  $T^t$ ,  $\hat{\mu}_a^t$ , and  $X_a^{(s)t}$  are thermodynamically determined intensive variables, which are fully deterministic. Here we emphasize that the nonequilibrium canonical form  $f_a^c$  is fully on the support of the generalized hydrodynamic equations consistent with the laws of thermodynamics. We also stress that in the present approach all the phase space information provided by the solution  $f_a$  of the Boltzmann kinetic equation subjected to the initial and boundary conditions is vested in the intensive variables  $I$ ,  $\bar{\mu}_a$ ,  $\bar{X}_a^{(q)}$ .

Thus we see that in this line of approach the distribution function  $f_a$  may be sought as a solution of the BKE in the phase space in the form

$$f_a/f_a^c = \exp \left\{ -k_B^{-1} \left[ \frac{1}{2} m_a C_a^2 \delta I + \sum_{s \geq 1} h_a^{(s)} \delta \bar{X}_a^{(s)} - m_a \delta \bar{\mu}_a \right] \right\}, \quad (3.302)$$

where  $\delta I$ ,  $\delta \bar{\mu}_a$ , and  $\delta \bar{X}_a^{(s)}$  are fluctuations defined by

$$\delta \bar{I} = I - I^t, \quad \delta \bar{\mu}_a = \bar{\mu}_a - \bar{\mu}_a^t, \quad \delta \bar{X}_a^{(q)} = \bar{X}_a^{(q)} - \bar{X}_a^{(q)t}, \quad (3.303)$$

which are measures of fluctuations of  $f_a$  from the thermodynamic branch. Since the distribution function is normalized to number density

$$n_a = \langle f_a \rangle,$$

we obtain

$$n_a = \left\langle \exp \left\{ -k_B^{-1} \left[ \frac{1}{2} m_a C_a^2 I + \sum_{q \geq 1} \bar{X}_a^{(q)} h_a^{(q)} - m_a \bar{\mu}_a \right] \right\} \right\rangle. \quad (3.304)$$

Varying Eq. (3.304) with  $\frac{1}{2} m_a C_a^2$  and  $h_a^{(s)}$  held fixed, we obtain

$$\sum_{a=1}^r \delta n_a = -k_B^{-1} \left( \rho \mathcal{E} \delta I + \sum_{a=1}^r \sum_{q \geq 1} \rho \hat{\Phi}_a^{(q)} \delta \bar{X}_a^{(q)} - \rho \sum_{a=1}^r \mathfrak{c}_a \delta \bar{\mu}_a \right), \quad (3.305)$$

which may be rearranged to the form

$$\mathcal{E} \delta \bar{I} - v \delta \bar{p} + \sum_{a=1}^r \sum_{q \geq 1} \hat{\Phi}_a^{(q)} \delta \bar{X}_a^{(q)} - \sum_{a=1}^r \mathfrak{c}_a \delta \bar{\mu}_a = 0, \quad (3.306)$$

where

$$\delta \bar{p} = \frac{p}{T} - \frac{p^t}{T^t}. \quad (3.307)$$

To obtain (3.306) we have made use of the fact that for a mole of dilute gases the equation of state is given by

$$pv = k_B T. \quad (3.308)$$

Equation (3.306), as a matter of fact, is the Gibbs–Duhem equation in the presence of fluctuations in the intensive variables. It should be noted that the variables in (3.308) are not of thermodynamic equilibrium nor are the variables  $\delta \bar{I}$ ,  $\delta \bar{X}_a^{(q)}$ ,  $\delta \bar{\mu}_a$ —i.e., fluctuations—in contrast to  $I^t$ ,  $\bar{\mu}_a^t$ ,  $p^t$ ,  $\bar{X}_a^{(q)t}$ , which are determined deterministically in the thermodynamics theory of irreversible processes presented earlier.

### 3.6.2 Relative Boltzmann Entropy and Fluctuations

On use of  $f_a/f_a^c$  given in Eq. (3.302) the RBE flux and production are easily found:

$$\mathbf{J}_r [f|f^c] = -\mathbf{Q} \delta I - \sum_{a=1}^r \sum_{q \geq 1} \boldsymbol{\psi}_a^{(q)} \delta \bar{X}_a^{(q)} + \sum_{a=1}^r \mathbf{J}_a \delta \bar{\mu}_a, \quad (3.309)$$

$$\sigma_r [f|f^c] = - \sum_{a=1}^r \sum_{q \geq 1} \Lambda_a^{(q)} \delta \bar{X}_a^{(q)} - k_B \sum_{a=1}^r \langle f_a \mathcal{D}_t \ln f_a^c \rangle, \quad (3.310)$$

where

$$\begin{aligned}
& -k_B \sum_{a=1}^r \langle f_a \mathcal{D}_t \ln f_a^c \rangle \\
& = \rho \mathcal{E} d_t I^t - \rho \sum_{a=1}^r \mathfrak{c}_a d_t \bar{\mu}_a^t + \rho \sum_{a=1}^r \sum_{q \geq 1} \widehat{\Phi}_a^{(q)} d_t \bar{X}_a^{(q)t} \\
& - I^t \left[ \mathbf{P} : \nabla \mathbf{u} + \mathbf{Q}^{\text{ch}} \cdot \nabla \ln T^t + \sum_{a=1}^r \mathbf{J}_a \cdot (\nabla \widehat{\mu}_a^t - \widehat{\mathbf{F}}_a) \right. \\
& \quad \left. - \sum_{a=1}^r \sum_{q \geq 1} \boldsymbol{\psi}_a^{(q)} \cdot \nabla X_a^{(q)t} \right] \\
& - \sum_{a=1}^r \sum_{q \geq 1} \left[ \bar{X}_a^{(q)t} \left\langle f_a \frac{\partial h_a^{(q)}}{\partial \mathbf{C}_a} \right\rangle \cdot (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) \right. \\
& \quad \left. - \sum_{a=1}^r \sum_{s \geq 1} \bar{X}_a^{(q)t} \left\langle f_a \mathbf{C}_a \frac{\partial h_a^{(q)}}{\partial \mathbf{C}_a} \right\rangle : \nabla u \right]
\end{aligned} \tag{3.311}$$

with the definition of  $\mathbf{Q}^{\text{ch}}$  by the expression

$$\mathbf{Q}^{\text{ch}} = \mathbf{Q} - \sum_{a=1}^r \widehat{\mu}_a^t \mathbf{J}_a + \sum_{a=1}^r \sum_{s \geq 1} \boldsymbol{\psi}_a^{(s)} \bar{X}_a^{(s)t}. \tag{3.312}$$

Therefore, since there holds the relation

$$vd_t \bar{p}^t + Ipd_t v = vd_t \bar{p}^t + \bar{p} d_t v = vd_t \bar{p}^t - vd_t \bar{p} = vd_t \delta \bar{p}, \tag{3.313}$$

the RBE balance equation can be given by the expression

$$\begin{aligned}
\rho d_t S_r [f | f^c] & = -\rho \delta Id_t \mathcal{E} - \rho vd_t \delta \bar{p} + \rho \sum_{a=1}^r \delta \bar{\mu}_a d_t \mathfrak{c}_a \\
& - \rho \sum_{a=1}^r \sum_{s \geq 1} \delta \bar{X}_a^{(s)} d_t \widehat{\Phi}_a^{(s)} - I \Xi_l \\
& + \sum_{a=1}^r \sum_{s \geq 1} \bar{X}_a^{(s)t} K_a^{(s)},
\end{aligned} \tag{3.314}$$

where

$$K_a^{(q)} = \langle f_a \mathcal{D}_t h_a^{(q)} \rangle = - \left\langle f_a \frac{\partial h_a^{(q)}}{\partial \mathbf{C}_a} \cdot \mathcal{D}_t \mathbf{u} \right\rangle, \quad (3.315)$$

$$\begin{aligned} \Xi_l &= (\mathbf{P} - p\delta) : \nabla u + \mathbf{Q}^{\text{ch}} \cdot \nabla \ln T + \sum_{a=1}^r \mathbf{J}_a \cdot (\nabla \mu_a - \widehat{\mathbf{F}}_a) \\ &\quad - \sum_{a=1}^r \sum_{q \geq 1} \psi_a^{(q)} \cdot \nabla X_a^{(q)}. \end{aligned} \quad (3.316)$$

Here  $K_a^{(q)}$  is an abbreviation for the last line on the right of (3.311). Recall that

$$\mathcal{D}_t h_a^{(q)} = \left( \frac{d}{dt} + \mathbf{C}_a \cdot \nabla + \widehat{\mathbf{F}}_a \cdot \nabla_{\mathbf{v}_a} \right) h_a^{(q)}.$$

The presence of the last two terms, in particular, on the right hand side of (3.314) implies that  $d_t S_r[f|f_c]$  is not an exact differential in the manifold  $\mathfrak{G}$  unlike the calortropy differential. Owing to this important distinction  $d_t S_r[f|f_c]$  is a non-exact differential in manifold  $\mathfrak{G}$ , and consequently neither is the Boltzmann entropy differential integrable in the Gibbs manifold  $\mathfrak{G}$ , whereas the calortropy differential is, as shown earlier. This was the principal reason that the Boltzmann entropy was not used to formulate a thermodynamic theory of irreversible processes and the notion of calortropy was put forward. The RBE is possible to integrate as *a path-dependent line integral* in manifold  $\mathfrak{G}$  and contains all the phase space information left out when the distribution function is projected onto the manifold  $\mathfrak{P} \cup \mathfrak{T}$  in order to construct the calortropy. But its description is no longer in the realm of irreversible thermodynamics as is for the calortropy. The complete solution of the BKE would require the relative Boltzmann entropy and solutions of the accompanying fluctuation evolution equations derived from the Boltzmann kinetic equation.

### 3.6.3 Differential Equations for Fluctuations

Having shown the intimate connection between fluctuations and the relative Boltzmann entropy in the forms of derivatives in (3.314), it is now necessary to devise a procedure to determine fluctuations from the relative Boltzmann entropy or the Boltzmann equation itself. To achieve this aim, we may take either statistical mechanics using the distribution functions or a stochastic method approach.

Here we will begin with the former method to prepare for future study. We would like to describe how to obtain differential equations for fluctuations  $\delta \bar{I}$ ,  $\delta \bar{\mu}_a$ ,  $\delta \bar{X}_a^{(q)}$ , etc. from the Boltzmann kinetic equation, which can be written in the form

$$\begin{aligned} d_t \left[ f_a \ln \left( \frac{f_a}{f_a^c} \right) \right] &= f_a d_t \ln \left( \frac{f_a}{f_a^c} \right) - \ln \left( \frac{f_a}{f_a^c} \right) [(\mathbf{C}_a \cdot \nabla + \widehat{\mathbf{F}}_a \cdot \nabla_{\mathbf{v}_a}) f_a] \\ &\quad + \ln \left( \frac{f_a}{f_a^c} \right) \mathbf{R}[f_a]. \end{aligned} \quad (3.317)$$

The left hand side of this equation, upon integration over the momentum space, is expressible as the derivative of  $\mathcal{S}_r[f|f_c]$  whereas the right hand side may be calculated by using the distribution functions given in (3.298) and (3.300). Such calculation would be very much facilitated if we make use of orthogonal tensor Hermite polynomials  $\mathcal{H}^{(q)}(\mathbf{C}_a)$  for the distribution functions involved and its conjugate variable  $Y_a^{(q)}$ . The distribution functions  $f_a$  and  $f_a^c$  in (3.298) and (3.300) may then be expressed as follows:

$$f_a = \exp \left\{ -\beta \left[ \frac{1}{2} m_a C_a^2 + \sum_{q \geq 1} Y_a^{(q)} \mathcal{H}^{(q)}(\mathbf{C}_a) - m_a \widehat{\mu}_a \right] - \Upsilon_a \right\}, \quad (3.318)$$

$$f_a^c = \exp \left\{ -\beta^t \left[ \frac{1}{2} m_a C_a^2 + \sum_{q \geq 1} Y_a^{(q)t} \mathcal{H}^{(q)}(\mathbf{C}_a) - m_a \widehat{\mu}_a^t \right] - \Upsilon_a^c \right\} \quad (3.319)$$

where the normalization factors  $\exp \Upsilon_a$  and  $\exp \Upsilon_a^c$  are defined by

$$\Upsilon_a = -\ln \left\{ n_a^{-1} \left\langle \exp \left[ -\beta \left( \frac{1}{2} m_a C_a^2 + \sum_{q \geq 1} Y_a^{(q)} \mathcal{H}^{(q)}(\mathbf{C}_a) \right) \right] \right\rangle \right\}, \quad (3.320)$$

$$\Upsilon_a^c = -\ln \left\{ n_a^{-1} \left\langle \exp \left[ -\beta^t \left( \frac{1}{2} m_a C_a^2 + \sum_{q \geq 1} Y_a^{(q)t} \mathcal{H}^{(q)}(\mathbf{C}_a) \right) \right] \right\rangle \right\} \quad (3.321)$$

with  $\beta = 1/k_B T$  and  $\beta^t = 1/k_B T^t$ . Here, as before, the superscript  $t$  denotes the quantity determined according to the irreversible thermodynamics based on the calortropy and generalized hydrodynamics already described. The symbol  $Y_a^{(q)}$  denotes the generalized potential in the orthogonal Hermite polynomial basis set. The angular brackets denote integration over the momentum space. Therefore writing the distribution functions as in (3.318) and (3.319) we claim that the difference between  $f_a$  and  $f_a^c$  is vested in the fluctuations of  $(\beta, Y_a^{(q)})$  from  $(\beta^t, Y_a^{(q)t})$ .

Since with the nonequilibrium canonical forms, it is possible to express  $\ln(f_a/f_a^c)$  as

$$\ln(f_a/f_a^c) = -k_B^{-1} \left[ \delta \bar{I} \mathcal{H}_a + \sum_{k \geq 1} \delta \bar{Y}_{ka} \mathcal{H}^{(k)}(\mathbf{w}_a) - m_a \delta \bar{\mu}_a \right], \quad (3.322)$$

where

$$\delta\bar{I} = T^{-1} - T^{t-1}, \quad \delta\bar{Y}_{ka} = Y_a^{(k)}/T - Y_a^{(k)t}/T^t, \quad \delta\bar{\mu}_a = \mu_a/T - \mu_a^t/T^t.$$

The Boltzmann equation therefore can be recast into the form

$$d_t \ln \left( \frac{f_a}{f_a^c} \right) = (\mathbf{C}_a \cdot \nabla + \widehat{\mathbf{F}}_a \cdot \nabla_{\mathbf{v}a}) \ln \left( f_a/f_a^c \right) + (1/f_a) \mathbf{R}[f_a] - D_t \ln f_a^c. \quad (3.323)$$

Since the left-hand side of this equation may be written as

$$d_t \ln \left( \frac{f_a}{f_a^c} \right) = -k_B^{-1} \left( \mathcal{H}_a d_t \delta\bar{I} + \sum_{k \geq 1} \mathcal{H}^{(k)}(\omega_a) d_t \delta\bar{Y}_{ka} - m_a d_t \delta\bar{\mu}_a \right), \quad (3.324)$$

on combining the two equations given above we obtain

$$\begin{aligned} f_a^c \mathcal{H}_a d_t \delta\bar{I} + f_a^c \sum_{k \geq 1} \mathcal{H}^{(k)}(\omega_a) d_t \delta\bar{Y}_{ka} - f_a^c m_a d_t \delta\bar{\mu}_a \\ = k_B f_a^c (\mathbf{C}_a \cdot \nabla + \widehat{\mathbf{F}}_a \cdot \nabla_{\mathbf{v}a}) \ln \left( f_a/f_a^c \right) - k_B (f_a^c/f_a) \mathbf{R}[f_a] \\ + k_B D_t f_a^c. \end{aligned} \quad (3.325)$$

On integrating over momentum after multiplication of 1,  $\mathcal{H}_a$ , or  $\mathcal{H}^{(q)}(\omega_a)$  ( $q \geq 1$ ) in turn and taking advantage of the orthogonality of tensor Hermite polynomials, we obtain from (3.325) a coupled set of equations for  $d_t \delta\bar{I}$ ,  $d_t \delta\bar{\mu}_a$ , and  $d_t \delta\bar{Y}_{ka}$  in terms of  $\delta\bar{I}$ ,  $\delta\bar{\mu}_a$ , and  $\delta\bar{Y}_{ka}$  as well as variables in manifold  $\mathfrak{P}$ . The set is in the form:

$$\begin{aligned} \langle f_a^c \mathcal{H}_a \rangle d_t \delta\bar{I} - m_a n_a d_t \delta\bar{\mu}_a \\ = \langle k_B f_a^c (\mathbf{C}_a \cdot \nabla + \widehat{\mathbf{F}}_a \cdot \nabla_{\mathbf{v}a}) \ln \left( f_a/f_a^c \right) \rangle \\ - \langle k_B (f_a^c/f_a) \mathbf{R}[f_a] \rangle + k_B \langle D_t f_a^c \rangle, \end{aligned} \quad (3.326)$$

$$\begin{aligned} \langle f_a^c \mathcal{H}_a^2 \rangle d_t \delta\bar{I} - m_a \langle f_a^c \mathcal{H}_a \rangle d_t \delta\bar{\mu}_a \\ = \langle k_B \mathcal{H}_a f_a^c (\mathbf{C}_a \cdot \nabla + \widehat{\mathbf{F}}_a \cdot \nabla_{\mathbf{v}a}) \ln \left( f_a/f_a^c \right) \rangle \\ - \langle k_B \mathcal{H}_a (f_a^c/f_a) \mathbf{R}[f_a] \rangle + k_B \langle \mathcal{H}_a D_t f_a^c \rangle, \end{aligned} \quad (3.327)$$

$$\begin{aligned} \langle f_a^c \mathcal{H}_a^{(q)} \mathcal{H}_a^{(q)}(\omega_a) \rangle d_t \delta\bar{Y}_{qa} = \langle k_B \mathcal{H}_a^{(q)} f_a^c (\mathbf{C}_a \cdot \nabla + \widehat{\mathbf{F}}_a \cdot \nabla_{\mathbf{v}a}) \ln \left( f_a/f_a^c \right) \rangle \\ - \langle k_B \mathcal{H}_a^{(q)} (f_a^c/f_a) \mathbf{R}[f_a] \rangle + k_B \langle \mathcal{H}_a^{(q)} D_t f_a^c \rangle. \end{aligned} \quad (3.328)$$

The right-hand side of these equations can be explicitly calculated in terms of variables in manifold  $\mathfrak{P} \cup \mathfrak{T}$  if the mathematical machinery developed so far in this chapter is made use of, although they are unfortunately rather complicated. This coupled set for  $d_t \delta\bar{I}$ ,  $d_t \delta\bar{\mu}_a$ , and  $d_t \delta\bar{Y}_{ka}$  may be expressed formally as the differential equations as follows:

$$d_t \delta \bar{I} = F_I(\delta \bar{I}, \delta \bar{\mu}_a, \dots, \delta \bar{Y}_{qa} \dots | \mathfrak{P}, \mathfrak{T}), \quad (3.329)$$

$$d_t \delta \bar{\mu}_a = F_{\mu a}(\delta \bar{I}, \delta \bar{\mu}_a, \dots, \delta \bar{Y}_{qa} \dots | \mathfrak{P}, \mathfrak{T}), \quad (3.330)$$

$$d_t \delta \bar{Y}_{qa} = F_{Y_q a}(\delta \bar{I}, \delta \bar{\mu}_a, \dots, \delta \bar{Y}_{qa} \dots | \mathfrak{P}, \mathfrak{T}) \quad (q \geq 1), \quad (3.331)$$

where  $F_I, F_\mu, F_{Y_q a}$  are functionals of variables in manifold  $\mathfrak{P} \cup \mathfrak{T}$

$$\begin{aligned} F_I &= \frac{\partial}{\partial \mathcal{E}} F(\delta \bar{I}, \delta \bar{\mu}_a, \dots, \delta \bar{Y}_{qa} \dots | \mathfrak{P}, \mathfrak{T}), \\ F_{\mu a} &= \frac{\partial}{\partial c_a} F(\delta \bar{I}, \delta \bar{\mu}_a, \dots, \delta \bar{Y}_{qa} \dots | \mathfrak{P}, \mathfrak{T}), \\ F_{Y_q a} &= \frac{\partial}{\partial Y_{qa}} F(\delta \bar{I}, \delta \bar{\mu}_a, \dots, \delta \bar{Y}_{qa} \dots | \mathfrak{P}, \mathfrak{T}) \end{aligned} \quad (3.332)$$

depending on the fluctuations. This coupled set of differential equations for fluctuations  $\delta \bar{I}$ ,  $\delta \bar{\mu}_a$ , and  $\delta \bar{Y}_{qa}$  provides the evolution equations of fluctuations. When the function  $F(\delta \bar{I}, \delta \bar{y}_{aq}, \delta \bar{\mu}_a, \nabla \delta \bar{I}, \nabla \delta \bar{y}_{aq}, \nabla \delta \bar{\mu}_a | \mathfrak{P}, \mathfrak{T})$  is explicitly calculated,<sup>8</sup> this formal procedure would be completed to obtain the fluctuation evolution equations. Integrating this set of equations over the reduced velocity space and observing that the moments are orthogonal, we obtain fluctuations  $\delta \bar{I}$ ,  $\delta \bar{Y}_{qa}$ , and  $\delta \bar{\mu}_a$ . To do so would be comparable to solving the Boltzmann equation in the phase space, subject to the initial and boundary conditions on the distribution functions or the fluctuations. However, such an endeavor would take us from the question of the theory of thermodynamics of irreversible processes and hydrodynamics as the main objective of this work. Therefore we leave it to one of the future tasks to be taken up on the subject matter.

### 3.6.4 Stochastic Treatment of Fluctuations

Fluctuations in distribution functions obeying the Boltzmann kinetic equation have been vested in the intensive variables conjugate to the molecular representations of variables spanning the manifold  $\mathfrak{P}$ , and they can be deterministically found if their evolution equations are solved subject to the initial and boundary conditions. This approach, however, is as difficult as solving the kinetic equation directly in the phase space.

We could depart from this approach and take an alternative but purely stochastic theory approach without relying on the deterministic kinetic equation. There is a considerably wide scope of topics to explore in this approach, but here we will confine the discussion to a limited topic in which the probability of fluctuations of  $f_a$  from the thermodynamic branch  $f_a^c$  is examined. First of all, we will limit the discussion

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<sup>8</sup>For explicit forms for  $F(\delta \bar{I}, \delta \bar{y}_{aq}, \delta \bar{\mu}_a, \nabla \delta \bar{I}, \nabla \delta \bar{y}_{aq}, \nabla \delta \bar{\mu}_a | \mathfrak{P}, \mathfrak{T})$  see Ref. [7], Sect. 7.4.2, pp. 154–159, where the fluctuation evolution equations are derived from the Boltzmann kinetic equation.

to a dilute monatomic single-component gas that can be described by the Boltzmann kinetic equation and to an introductory discussion of stochastic differential equations based on the relative Boltzmann entropy. For the sake of simplicity we limit the discussion to a single component. Therefore the species subscript will be omitted for the distribution functions and related variables.

To construct a suitable probability distribution function in the stochastic theory of fluctuations, we will assume that the non-fluctuating part of the distribution function is described by the thermodynamic branch in the case of a single-component monatomic dilute gas, which is described by formula (3.298). The thermodynamic branch of the distribution function of these particles in (3.298) is recast in terms of the tensor Hermite polynomials as follows:

$$f^c = \exp \left\{ - \left[ \frac{1}{2} w^2 + \beta^t \sum_{q \geq 1} Y^{(q)t} \mathcal{H}^{(q)}(\mathbf{w}) - \beta^t m \hat{\mu}^t \right] \right\}, \quad (3.333)$$

$$m \hat{\mu}^t = -k_B T^t \ln \left\{ n^{-1} \left\langle \exp \left[ - \left( \frac{1}{2} w^2 + \beta^t \sum_{q \geq 1} Y^{(q)t} \mathcal{H}^{(q)} \right) \right] \right\rangle \right\}. \quad (3.334)$$

Here the angular brackets denote integration over the reduced momentum; and  $\omega(\mathbf{w}) = (2\pi)^{-3} \exp(-\frac{1}{2}w^2)$  could serve as the weight function for the orthonormal tensor Hermite polynomials. (See, for example, Ref. [7] for tensor Hermite polynomials.)

Now let us divide the momentum space into small cells of an equal magnitude. The total number of cells can be made sufficiently large and cells will be indexed by  $i$  according to the momentum values in the momentum space at a fixed value of position coordinate. Suppose there are  $N_i$  particles assigned to cell  $i$ .

If measurements are performed of the distribution of particles in an arbitrary nonequilibrium condition of the system, the number of states of randomly distributed  $N_i$  particles in cell  $i$  is proportional to the ways to distribute the particles randomly without restriction

$$W = N! \prod_i \frac{1}{N_i!}. \quad (3.335)$$

However, since these events are assumed to occur around  $f^c$ , the occurrence in each cell should be weighted by  $(V f^c)^{N_i}$ . Here volume  $V$  is multiplied because of the way normalization is made for  $f^c$ . Thus the probability  $\mathcal{P}$  of distribution  $W$  to occur is modified to the form

$$\mathcal{P} = N! \prod_i \frac{(V f_i^c)^{N_i}}{N_i!}. \quad (3.336)$$

Since the probability of finding  $N_i$  particles in cell  $i$  randomly without restriction is given by the ratio  $N_i/N$  the distribution function  $f_i$  is proportional to this ratio:

$$f_i \propto \frac{N_i}{NV}. \quad (3.337)$$

If the Stirling approximation<sup>9</sup> for the factorials in (3.336) is used in the limit of large  $N_i$ , we find  $\mathcal{P}$  is proportional to the form

$$\mathcal{P} = C \exp \left\langle - \sum_i f_i \ln \left( f_i / f_i^c \right) \right\rangle, \quad (3.338)$$

where  $C$  is the normalization factor and the exponent is simply the discrete space version of the relative Boltzmann entropy. It should be noted that the sum over index  $i$  should be regarded as integration over the momentum space. Therefore the exponent in (3.338) is identified with the relative Boltzmann entropy. Thus we may write it in the form

$$\mathcal{P} = C \exp \left( -k_B^{-1} \mathcal{S}_r [f | f^c] \right) = C \exp \left[ k_B^{-1} (\widehat{\Psi} - \mathcal{S}) \right], \quad (3.339)$$

where

$$\mathcal{S}_r [f | f^c] = k_B \sum_i f_i \ln \left( f_i / f_i^c \right) = k_B \langle f \ln (f/f^c) \rangle. \quad (3.340)$$

It is remarkable that the probability  $\mathcal{P}$  of the distribution  $f$  fluctuating from the thermodynamic branch  $f^c$  is given by an exponential of the relative Boltzmann entropy  $\mathcal{S}_r [f | f^c]$  and, furthermore, that a probability distribution function, which is rather akin and related to the Einstein formula for the distribution function in his fluctuation theory, comes about from the reasoning given above. It is quite natural that it is given in terms of the relative Boltzmann entropy that describes fluctuations of macroscopic states of the system from those described by the calortropy corresponding to the thermodynamic branch of the distribution function obeying the Boltzmann equation. The reasoning leading to  $\mathcal{P}$  given above can be generalized to a gas mixture, and we easily arrive at the formula for  $\mathcal{P}$  for the mixture.

Thus, if we look for  $f_a$  in a form isomorphic to  $f_a^c$  as has been done in previous sections, then it follows that

$$\mathcal{S}_r [f | f^c] = -\mathcal{E} \delta I - v \delta \bar{p} + \sum_{a=1}^r c_a \delta \bar{\mu}_a - \sum_{a=1}^r \sum_{q \geq 1} \widehat{\Theta}_a^{(q)} \delta \bar{Y}_a^{(q)}. \quad (3.341)$$

This is seen to be identical with the RBE and can be obtained with expressions (3.298) and (3.300) for  $f_a^c$  and  $f_a$  if the extensive variables are replaced with their

<sup>9</sup>The Stirling approximation for Gamma function  $\Gamma(x)$  is as follows:

$$\Gamma(x) = e^{-x} x^{x-\frac{1}{2}} \sqrt{2\pi} \left[ 1 + \frac{1}{12x} + O(x^{-2}) \right].$$

densities. From this formula it follows the relations

$$\begin{aligned}\frac{\partial \mathcal{S}_r[f|f^c]}{\partial \mathcal{E}} &= -\delta I, \\ \frac{\partial \mathcal{S}_r[f|f^c]}{\partial v} &= -\delta \bar{p}, \\ \frac{\partial \mathcal{S}_r[f|f^c]}{\partial c_a} &= \delta \bar{\mu}_a, \\ \frac{\partial \mathcal{S}_r[f|f^c]}{\partial \widehat{\Theta}_a^{(q)}} &= -\delta \bar{Y}_a^{(q)} \quad (q \geq 1; a = 1, 2, \dots, r).\end{aligned}\quad (3.342)$$

Applied to the expression for  $\mathcal{P}$ , these derivatives mean that

$$\begin{aligned}k_B \frac{\partial \mathcal{P}}{\partial E} &= \delta I \mathcal{P}, \\ k_B \frac{\partial \mathcal{P}}{\partial V} &= \delta \bar{p} \mathcal{P}, \\ k_B \frac{\partial \mathcal{P}}{\partial c_a} &= -\delta \bar{\mu}_a \mathcal{P}, \\ k_B \frac{\partial \mathcal{P}}{\partial \widehat{\Theta}_a^{(q)}} &= \delta \bar{Y}_a^{(q)} \mathcal{P} \quad (q \geq 1; a = 1, 2, \dots, r).\end{aligned}\quad (3.343)$$

As in mechanics, classical or quantum, observables in thermodynamics and irreversible thermodynamics occur in conjugate pairs. Notice, for examples, momenta and position variables in mechanics, and energy and inverse temperature in thermodynamics, are conjugate pairs. When classical mechanics makes transition to probabilistic description in quantum mechanics, the conjugate pairs of variables follow certain quantization rules. Likewise, when thermodynamic fluctuations make transition to stochastic (probabilistic) description under suitable stochastic assumptions, there appear mathematical relations akin to the mechanical quantization rules in quantum mechanics. Thus for example, the calortropy is a bilinear function of variables of the thermodynamic manifold and the tangent manifold, and if the relative Boltzmann entropy is looked for in a bilinear form similar to the calortropy, but with respect to fluctuations, we arrive at relations for fluctuations as described above. The equations in (3.343) are the mathematical relations for the case in point. We may regard them as thermodynamic quantization rules. Thus when stochastic (probabilistic) theories are made use of on the basis of the probability formula (3.339) given in terms of the relative Boltzmann entropy, the following “*thermodynamic quantization rules*” may be assumed in analogy to quantum mechanics:

$$\begin{aligned}\delta I &= k_B \frac{\partial}{\partial \mathcal{E}}, & \delta \bar{p} &= k_B \frac{\partial}{\partial v}, \\ \delta \bar{\mu}_a &= -k_B \frac{\partial}{\partial c_a}, & \delta \bar{Y}_a^{(q)} &= k_B \frac{\partial}{\partial \widehat{\Theta}_a^{(q)}}.\end{aligned}\quad (3.344)$$

The thermodynamic quantization rules suggest that the thermodynamic commutators of conjugate variables have the values between conjugate variables:

$$[\delta I, \mathcal{E}] = \delta I \mathcal{E} - \mathcal{E} \delta I = k_B, \text{ etc.} \quad (3.345)$$

Relations in (3.343) can be made use of to evaluate the mean values involving fluctuations by using  $\mathcal{P}$  considered given in manifold  $\mathfrak{P}$ . Let us denote the volume element in manifold  $\mathfrak{P}$ :

$$d\omega = d\mathcal{E} dv \prod_{a=1}^r d\mathfrak{c}_a \prod_{q \geq 1} d\widehat{\Theta}_a^{(q)}. \quad (3.346)$$

Thus we define mean values, for example,

$$\langle \delta I \mathcal{E} \rangle = \int d\omega \delta I \mathcal{E} \mathcal{P}(\omega) \quad (3.347)$$

and then make use of (3.343). It yields

$$\begin{aligned} \langle \delta I \mathcal{E} \rangle &= -k_B, & \langle v \delta \bar{p} \rangle &= -k_B, \\ \langle \mathfrak{c}_a \delta \bar{\mu}_a \rangle &= -k_B, & \left\langle \widehat{\Theta}_a^{(q)} \delta \bar{Y}_a^{(q)} \right\rangle &= -k_B. \end{aligned} \quad (3.348)$$

Applying these results to the mean value of  $S_r$

$$\langle S_r[f|f_c] \rangle \geq 0 \quad (3.349)$$

which is consistent with the Klein inequality applied to the statistical mechanical formula for the relative Boltzmann entropy (3.293). If the mean values of fluctuations are calculated, it follows

$$\langle \delta I \rangle = \langle \delta \bar{p} \rangle = \langle \delta \bar{\mu}_a \rangle = \left\langle \delta \bar{Y}_a^{(q)} \right\rangle = 0 \quad (3.350)$$

as they should, and if we define

$$\begin{aligned} \delta \mathcal{E} &= \mathcal{E} - \langle \mathcal{E} \rangle, & \delta v &= v - \langle v \rangle, \\ \delta \mathfrak{c}_a &= \mathfrak{c}_a - \langle \mathfrak{c}_a \rangle, & \delta \widehat{\Theta}_a^{(q)} &= \widehat{\Theta}_a^{(q)} - \langle \widehat{\Theta}_a^{(q)} \rangle \end{aligned} \quad (3.351)$$

it is possible to write

$$\langle \delta I \delta \mathcal{E} \rangle + \langle \delta \bar{p} \delta v \rangle - \sum_{a=1}^r \langle \delta \mathfrak{c}_a \delta \bar{\mu}_a \rangle + \sum_{a=1}^r \sum_{q \geq 1} \left\langle \delta \widehat{\Theta}_a^{(q)} \delta \bar{Y}_a^{(q)} \right\rangle \geq 0 \quad (3.352)$$

as a direct consequence of the fact that  $\langle S_r[f|f^c] \rangle \geq 0$ . Furthermore, by Schwartz inequality

$$\langle \delta I \delta \mathcal{E} \rangle^2 \leq \langle (\delta I)^2 \rangle \langle (\delta \mathcal{E})^2 \rangle, \quad \text{etc.} \quad (3.353)$$

we find

$$\sqrt{\langle (\delta I)^2 \rangle \langle (\delta \mathcal{E})^2 \rangle} \geq -\langle \delta I \mathcal{E} \rangle = k_B, \quad \text{etc.} \quad (3.354)$$

Therefore if we define

$$\Delta \bar{I} = \sqrt{\langle (\delta I)^2 \rangle}, \quad \Delta \mathcal{E} = \sqrt{\langle (\delta \mathcal{E})^2 \rangle}, \quad \text{etc.} \quad (3.355)$$

we obtain the thermodynamic uncertainty relations for the nonequilibrium system

$$\Delta \bar{I} \Delta \mathcal{E} \geq k_B, \quad \Delta \bar{p} \Delta v, \quad \Delta \bar{\mu}_a \Delta c_a \geq k_B, \quad \Delta \bar{Y}_a^{(q)} \Delta \widehat{\Theta}_a^{(q)} \geq k_B \quad (3.356)$$

in a manner analogous to Heisenberg uncertainty relations in quantum mechanics [30].

The possibility of such relations in thermodynamics were considered by Bohr [31], Heisenberg [32], and others [33]. Later, Lindhard [34] made an attempt at their derivation, but did not quite get them. Schlogl [35] eventually got them for the case of equilibrium. Here, we have derived for nonequilibrium [7, 36] by using the Boltzmann equation for dilute gases. It is interesting to see that the relative Boltzmann entropy plays an essential role in the statistical treatment of fluctuations in intensive variables when the system is in nonequilibrium. The probability distribution function  $\mathcal{P}$  is expected to be in the basis of a thermodynamic fluctuation theory for nonequilibrium systems, and the relative Boltzmann entropy plays the central role in it. We finally note that within the framework of the fluctuation theory described above, the substantial time derivatives of fluctuations such as  $d_t \delta \bar{I}$ , etc. can be easily obtained from the relations

$$\begin{aligned} d_t \delta I &= -\frac{\partial}{\partial \mathcal{E}} d_t S_r[f|f^c], \\ d_t \delta \bar{p} &= -\frac{\partial}{\partial v} d_t S_r[f|f^c], \\ d_t \delta \bar{\mu}_a &= \frac{\partial}{\partial c_a} d_t S_r[f|f^c], \\ d_t \delta \bar{Y}_a^{(q)} &= -\frac{\partial}{\partial \widehat{\Theta}_a^{(q)}} d_t S_r[f|f^c] \quad (q \geq 1; a = 1, 2, \dots, r). \end{aligned} \quad (3.357)$$

The right-hand side of these equations can be calculated more explicitly in terms of fluctuations as well as variables in manifold  $\mathfrak{P} \cup \mathfrak{T}$  in forms similar to  $F_I$ , etc. (3.332).

### 3.7 Concluding Remarks

In this chapter, it is shown that the Boltzmann kinetic equation can be made use of in order to construct the nonequilibrium canonical distribution function and therewith formulate a thermodynamic theory of irreversible transport processes in a monatomic gaseous fluid and the accompanying hydrodynamics in a manner consistent with the phenomenological laws of thermodynamics. The resulting irreversible thermodynamics and the attendant hydrodynamics (i.e., generalized hydrodynamics) are thus endowed with molecular theories and the nonequilibrium statistical mechanics equipped with the nonequilibrium canonical form that provides molecular theory tools to calculate various macroscopic quantities involved in the theory of irreversible thermodynamics and generalized hydrodynamics, at least, for statistically uncorrelated monatomic dilute gases. Thus the Boltzmann kinetic equation serves as the prototype and a model for irreversible kinetic equations to use in order to formulate a thermodynamic theory of irreversible transport processes and hydrodynamics for correlated molecular fluids at any density and state. It should be borne in mind that the nonequilibrium canonical distribution function used is not an exact solution of the Boltzmann kinetic equation in the phase space of the particles, because it is merely a projection onto the thermodynamic manifold of the exact distribution function obeying the kinetic equation, which lives in the phase space of molecules. The key quantity making the theory of irreversible thermodynamics and the accompanying nonequilibrium statistical thermodynamics possible to be formulated is the calentropy. The aforementioned nonequilibrium canonical distribution function used for formulating the irreversible thermodynamics and hydrodynamics neglects the fluctuations and hence represents only the deterministic part of the solution for the Boltzmann equation. The fluctuation parts of the distribution function should be obtained by solving the kinetic equation, but it does not represent the deterministic theory in the sense that irreversible processes and hydrodynamics are determined in the Gibbs manifold  $\mathcal{G} = \mathfrak{P} \cup \mathfrak{T} \cup \widehat{\Psi}$  evolving in space and time. For this reason, the subject has not been studied in depth in this work except for some interesting aspects of it, such as thermodynamic uncertainty relations and the relative Boltzmann entropy because the principal objective of this work is the molecular theory foundations of deterministic irreversible thermodynamics and hydrodynamics. The stochastic part of study on the subject involving fluctuations is left virtually untouched. It should constitute a potentially fruitful starting point of study on stochastic theory of fluctuating hydrodynamics based on the foundations of an irreversible kinetic equation and irreversible thermodynamics.

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# Chapter 4

## Equilibrium Ensemble Method

### 4.1 Brief Review of Ensemble Methods

Although controversial initially because of its irreversibility that contradicts the time reversal invariance of mechanical equations from which it was perceived to have descended, Boltzmann's kinetic equation [1] has drawn enduring attractions from kinetic theorists owing to its alluring features for studying nonequilibrium phenomena in gases and has been made use of by numerous authors in the kinetic theory in the literature [2–5].

By using a modified moment method [6, 7], which is a generalized version of the conventional moment method of Grad [8], we have shown in Chap. 3 that it is possible to develop a theory of irreversible thermodynamic processes in macroscopic systems of gaseous matter in a manner consistent with the laws of thermodynamics. Thus we have been able to show a way to comprehend irreversible thermodynamic processes in gases with the ideas of Maxwell and Boltzmann if the Boltzmann equation is made use of in the way described in Chap. 3; see also Refs. [7, 9].

Although the kinetic equations of Maxwell [10] and Boltzmann [1] are capable of describing nonequilibrium processes in dilute gas systems, they are not applicable to condensed matter in which particles (or molecules) are interacting with each other and statistically correlated owing to their interparticle interaction forces. To overcome these limitations in the case of condensed matter, by synthesizing the Maxwell and Boltzmann's original idea of probability distribution functions in the momentum space Gibbs [11] had made, in his path-breaking monograph published in 1902, a conceptual leap to formulate the ensemble theory of statistical mechanics, both terms of which he coined for the first time in science. However, although his ensemble theory of statistical mechanics is applicable to all systems regardless of the states of aggregation of matter, it was formulated only for systems in equilibrium. Linear response theories [12–14] and the BBGKY hierarchy theories [15–18] are some prominent examples of theories developed to describe nonequilibrium phenomena. For the same reason numerous later research workers [7, 19, 20] in the

field of statistical mechanics have pursued studies to this day in attempt to formulate theories along different lines of approach to statistical mechanics of nonequilibrium phenomena.

In this chapter the Gibbs ensemble theory [21–23] will be discussed, but, only for the gist of it, to convey the basic ideas which will be useful for formulating macroscopic thermodynamic theories of nonequilibrium processes in condensed phases of matter in this work.

## 4.2 Ensembles and Fundamental Postulates

In molecular theoretic studies of the macroscopic behavior of matter we need to treat a system on the basis of mechanics, classical or quantum, but we only have some knowledge of the system, such as the initial and boundary conditions, but not enough of them to completely predict its macroscopic states and behavior mechanically from the molecular point of view. Moreover, even if we have a complete set of information, such as initial and boundary conditions, necessary for dynamic description of the system with the mechanical equations of motion, there are simply too numerous particles for us to describe the evolution of the system by a purely mechanical approach alone. In any case, we can only hope to describe the average behavior of a collection of systems made up of an astronomically large number of constituent particles (atoms or molecules or other kinds of particles) that have the same structure as the system of interest and are distributed over a range of different possible microscopic states. For this purpose of treating macroscopic properties of matter Gibbs [11] put forward the notion of ensemble. The terminology was coined by Gibbs for the first time. An ensemble is said to consist of systems representative of the actual matter of interest. A gross system made up of an astronomical number of particles indeed can have an equally astronomical number of representative systems because they are capable of having particles of different states and different configurations that are accessible and admissible, if they all satisfy the same given gross conditions (e.g., the fixed number of particles, volume, or total energy, etc.) on the system we observe macroscopically.

In the discussion in this chapter we shall use the language and concepts of classical mechanics. However, quantum description (namely, discrete energy level) can be used with a suitable modification of terminology employed, and the reasoning presented below is equally well applicable to quantum systems.

Assume that a system consists of  $N$  monatomic molecules whose positions in the phase space are collectively denoted by phase  $x^{(N)} = (\mathbf{r}_1, \mathbf{p}_1, \dots, \mathbf{r}_N, \mathbf{p}_N)$  as we have introduced in Chap. 3. This phase space is then partitioned into cells of magnitude  $\delta\mathbf{p}\delta\mathbf{x} \sim O(h^3)$  ( $h$  = Planck constant) into which particles may be assigned. Since the energy (Hamiltonian)  $E$  depends on  $x^{(N)}$ , it may be seen as discretized. This discretized energy may be expressed  $E_{\mathbf{k}} = E_{\mathbf{k}}(x^{(N)}, N, V) := H(x^{(N)}, N, V)$  for the system of  $N$  particles contained in volume  $V$ .

To guide us in constructing an ensemble of representative systems we make a fundamental postulate of statistical mechanics that:

subject to the constraints imposed, all accessible mechanical states of the system are equally probable.

This postulate is called *equal a priori probability hypothesis* for construction of an ensemble. Together with the *ergodic hypothesis* stated later, it is one of two fundamental postulates in the Gibbs ensemble theory of statistical mechanics. This postulate may be illustrated as follows: Take, for example, a system consisting of  $N$  monatomic molecules. The state of the system continuously follows the trajectory in the phase space spanned by  $x^{(N)}$ . Nevertheless, since the representative points of the system are randomly distributed over the accessible space, it is reasonable to think of the frequency of finding the representative systems of the ensemble in an elementary volume in the phase space in terms of the density  $\rho = \rho(x^{(N)}, t)$  of points (states) in the phase space. The number of systems  $d\mathcal{N}$ , which would be found at time to have the phase points lying in the interval<sup>1</sup>  $dx^{(N)} := d\mathbf{r}_1 d\mathbf{p}_1 \cdots d\mathbf{r}_N d\mathbf{p}_N$  around point  $x^{(N)}$ , is then given by

$$d\mathcal{N} = \rho(x^{(N)}, t) dx^{(N)}. \quad (4.1)$$

Integrating it over the entire phase space, we find the total number  $\mathcal{N}$  of the systems in the ensemble or the phase points in the phase space representative of the system:

$$\mathcal{N} = \int dx^{(N)} \rho(x^{(N)}, t). \quad (4.2)$$

We may then define the probability of observing the system—namely, states—at time  $t$  in the interval  $dx^{(N)} := d\mathbf{x}_1 \cdots d\mathbf{x}_N$  ( $dx_i = d\mathbf{r}_i d\mathbf{p}_i$ ) around the phase point  $x^{(N)}$  by the formula

$$f^{(N)}(x^{(N)}, t) := \frac{\rho(x^{(N)}, t)}{\mathcal{N}} = \frac{\rho(x^{(N)}, t)}{\int dx^{(N)} \rho(x^{(N)}, t)}. \quad (4.3)$$

This probability is evidently normalized:

$$\int dx^{(N)} f^{(N)}(x^{(N)}, t) = 1. \quad (4.4)$$

This distribution function  $f^{(N)}(x^{(N)}, t)$  enables us to calculate the average of mechanical quantity  $M(x^{(N)})$  from the knowledge of solutions of the equations of motion for the system:

$$\langle M \rangle = \int dx^{(N)} M(x^{(N)}) f^{(N)}(x^{(N)}, t). \quad (4.5)$$

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<sup>1</sup>The phase volume of this interval is  $O(h^{3N})$  if the cell volumes are  $O(h^3)$  according to the method discretizing the phase space mentioned earlier.

Thus to have a complete knowledge of  $\langle M \rangle$  mechanically, it is first necessary to find solutions of mechanical equations of motion—Hamilton's equations of motion—and therewith the distribution function  $f^{(N)}(x^{(N)}, t)$  in the phase space, which will make it possible to compute the integral in (4.5). This represents the method of ensemble average of mechanical quantity  $M(x^{(N)})$ . Therefore calculation of  $\langle M \rangle$  would first of all require the evolution equation for  $f^{(N)}(x^{(N)}, t)$  and its solution. Such evolution equation must be found and appropriately solved.

In principle, it is also conceivable to obtain macroscopic observables by taking the time average of  $M(x^{(N)})$  over the course of a sufficiently long trajectory in the phase space of the system, which may be computed by solving the mechanical equations of motion subject to appropriate initial and boundary conditions of particles. This approach indeed can be put into practice, albeit for a limited number of particles, if an electronic computation method is employed to integrate the mechanical equations of motion at a considerable cost of labor and resources. It would provide the time average of  $M(x^{(N)})$ :

$$\overline{M}^{\text{time}} = \frac{1}{\tau} \int_0^\tau dt M(x^{(N)}), \quad (4.6)$$

where  $\tau$  is the duration of time sufficiently long for the system to evolve from the initial to final time to make the time average meaningful. In contrast to  $\langle M \rangle$ , calculation of the time average  $\overline{M}^{\text{time}}$  would require simply the knowledge of the trajectory followed in the phase space from the initial to the final state by the system. The two averages  $\langle M \rangle$  and  $\overline{M}^{\text{time}}$  are not necessarily the same, however, and the range of their identicalness must be studied.

In the ensemble theory of statistical mechanics it is postulated that:

*the time average  $\overline{M}^{\text{time}}$  may be replaced by the ensemble average  $\langle M \rangle$ :*

$$\overline{M}^{\text{time}} = \langle M \rangle. \quad (4.7)$$

This is *the second fundamental postulate* of the Gibbs ensemble theory, and it is called *the ergodic hypothesis*. The subject studying this question is called the ergodic theory. The reader interested in this subject is referred to the relevant literature [24].

The Gibbs ensemble theory of statistical mechanics is based on the aforementioned two postulates. In this chapter we shall discuss the gist of the conventionally available version of it followed when the system of interest is in equilibrium, in order to give the reader the basic idea underlying the nonequilibrium statistical mechanics developed later in this work—namely, the method of nonequilibrium ensembles and the accompanying kinetic equations.

To implement the ensemble theory for a system in thermodynamic equilibrium it is necessary to determine the equilibrium distribution function representative of the system with respect to the thermodynamic behavior. We shall first consider the case of a canonical ensemble of systems with a fixed number  $N$  of particles at a fixed volume  $V$  but with variable energies, which are immersed in a sufficiently large thermal reservoir of temperature  $T$ . Therefore the constraints imposed on the

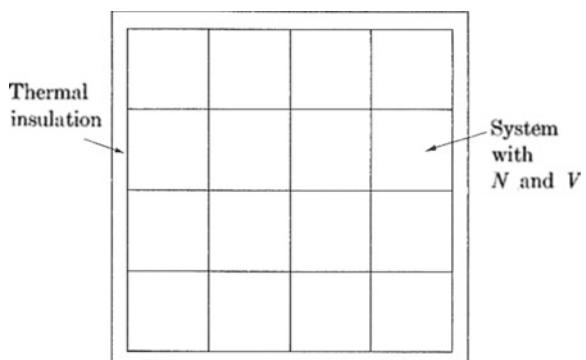
ensemble are the fixed  $N$ ,  $V$ , and  $T$  for canonical ensembles. The next case to consider would be the grand canonical ensemble in which the constraint on the number of particles is relaxed and made arbitrary, but members of the ensemble are allowed to reach an equilibrium with respect to matter by exchanging particles between them, attaining fixed chemical potentials  $\mu_a$  with respect to species  $a$ . Therefore the external constraints imposed on the grand canonical ensemble are  $V$ ,  $T$ , and  $\mu_1, \mu_2, \dots, \mu_r$ , in which the subscript  $r$  denotes the number of species. There can be other kinds of external constraints possible, but only the aforementioned two ensembles will be considered in this work, because they would be sufficient for our purpose in this work and for most cases in practice.

### 4.2.1 Canonical Ensemble

Assume the experimental system is maintained at temperature  $T$  and at a fixed number of particles in volume  $V$ . This condition can be achieved if the system is immersed in a heat reservoir of temperature  $T$ . Such systems are assembled to form an assembly in accordance with the *equal a priori hypothesis* (postulate 1) and are allowed to reach thermal equilibrium with each other and the heat reservoir enclosing the assembly (i.e., the canonical ensemble). Recall that the number  $\mathcal{N}$  of systems in the ensemble can be practically infinite owing to the enormous number of particles in each system, which are distributed over an enormous number of accessible states. Except for the exchange of thermal energy and their reaching thereby thermal equilibrium the members of the ensemble are statistically independent (Fig. 4.1).

It is important to realize that the system we are dealing with is extremely degenerate with regard to energy because in a large system, such as we are contemplating on here, there can be possible a large number of different state configurations with a same numerical value of energy or Hamiltonian. For example, the energies of two different members with different sets of phases, say, cells of  $O(h^{3N})$  around phase points  $x^{(N)}$  and  $x^{(N)'}$ , may be equal in value:

**Fig. 4.1** Canonical ensemble. Systems of  $N$  particles contained in volume  $V$  are enclosed as a whole and put in a thermal reservoir of temperature  $T$ . And the systems are thus allowed to equilibrate with each other and with the heat reservoir, and then the whole assembly is isolated



$$E_k(x^{(N)}|N, V) = E_k(x^{(N)\prime}|N, V)$$

because different distributions of phases  $x^{(N)} = (x_1, x_2, \dots, x_N)$  in the phase space can result in an identical value of the Hamiltonian (energy). Let us then assume the frequencies of members of the ensemble with energies (Hamiltonians)  $E_1, E_2, \dots, E_k, \dots$  are  $n_1, n_2, \dots, n_k, \dots$ , respectively. It should be noted that there can be many different distributions, that is, the set  $\mathbf{n} := (n_1, n_2, \dots, n_k, \dots)$  runs over a gamut of all possible values given the constraints on the system. It then follows that for a given frequency distribution there holds the relation

$$\mathcal{N} = \sum_k n_k \quad (4.8)$$

and the total energy of the ensemble is given by

$$\mathfrak{E}_t = \sum_k n_k E_k, \quad (4.9)$$

which are both at a fixed value of  $\mathcal{N}$  and  $\mathfrak{E}_t$ . Equation (4.9) follows from the fact that the members of the ensemble, which may be regarded as a supersystem, are independent except that they are in thermal equilibrium with each other and with the heat reservoir. The number of states (configurations in phase space) consistent with the distribution  $\mathbf{n} := (n_1, n_2, \dots, n_k, \dots)$  is given by

$$\Omega_t(\mathbf{n}) = \frac{\mathcal{N}!}{\prod_k n_k!}, \quad (4.10)$$

which is the number of ways arranging  $\mathcal{N}$  distinguishable objects into groups of  $n_1, n_2, \dots, n_k, \dots$ . The total number of states or phase volume of the ensemble is given by

$$\Omega = \sum_{\mathbf{n}} \Omega_t(\mathbf{n}), \quad (4.11)$$

and the probability of observing the arrangement as for  $\Omega_t(\mathbf{n})$  is proportional to  $\Omega_t$ . In (4.11) the sum is over all possible distributions. The probability of observing the system in the narrow strip of energy  $\mathfrak{E}_t$  is then given by

$$W_{\mathbf{n}} = \frac{\Omega_t(\mathbf{n})}{\Omega} \quad (4.12)$$

for the isolated ensemble. Therefore, the probability of realizing state  $k$  is given by

$$P_k = \frac{\bar{n}_k}{\mathcal{N}} = \sum_{\mathbf{n}} \frac{n_k}{\mathcal{N}} W_{\mathbf{n}} = \frac{\sum_{\mathbf{n}} n_k \Omega_t(\mathbf{n})}{\mathcal{N} \Omega}. \quad (4.13)$$

This probability  $P_k$  provides the desired function  $f(x^{(N)})$  in (4.5) for the distribution function with which to calculate averages in the case of a system in equilibrium. It, however, is desirable to obtain an explicit expression for  $\bar{n}_k$  to put the theory into practice. This aim can be achieved if  $\Omega_t(\mathbf{n})$  is expressed in a more practical and explicit form. For this purpose one can use either the method of steepest descent of Darwin and Fowler [25] or the variational method of undetermined multipliers [26], which provides us with the maximum term in the distribution of  $\Omega_t(\mathbf{n})$  with respect to  $\mathbf{n}$  subject to the conditions (4.8) and (4.9).

If  $\Omega_t(\mathbf{n})$  is examined with respect to its dependence of  $\mathbf{n}$ , it has a narrow distribution sharply peaked at a value of  $\mathbf{n}^* := \{n_k^*\}$ . The maximum term calculated thereby will replace the sum in (4.13) and practical computation of averages will be facilitated therewith. The aforementioned variational method will be made use of to calculate the maximum term in the following.

In the method of undetermined multipliers we consider

$$\ln \Omega_t(\mathbf{n}) = \ln \mathcal{N}! - \sum_k \ln n_k!. \quad (4.14)$$

Variation of this expression is subject to the constraints of (4.8) and (4.9). Since  $\mathcal{N}$  and  $n_k$  are extremely large, their factorials can be written in the asymptotic form by applying the Stirling approximation [27] for the gamma function  $\Gamma(x+1) = x!$

$$\ln x! = e^{-(x+1)}(x+1)^{x+\frac{1}{2}}\sqrt{2\pi} \left[ 1 + \frac{1}{12(x+1)} + O\left(\frac{1}{(x+1)^2}\right) \right] \quad (4.15)$$

$$\simeq x \ln x - x \quad (4.16)$$

if  $x$  is sufficiently large. In the present case, it is sufficient to use the second line (4.16) without incurring a noticeable error for the mean values calculated therewith on account of the fact that  $n_k$  is  $O(10^{20})$ . Henceforth the second line of approximation will be used for the Stirling approximation. Upon use of the Stirling approximation (4.16) we may write (4.14) in the form

$$\ln \Omega_t(\mathbf{n}) = \mathcal{N} \ln \mathcal{N} - \sum_k n_k \ln n_k. \quad (4.17)$$

Varying this equation we obtain

$$\delta \ln \Omega_t(\mathbf{n}) = - \sum_k \delta n_k \ln n_k. \quad (4.18)$$

Subtracting from (4.18) the variations of the conditions (4.8) and (4.9), each multiplied by undetermined multipliers  $\alpha$  and  $\beta$ , respectively,

$$0 = \alpha \sum_j \delta n_k, \quad (4.19)$$

$$0 = \beta \sum_k E_k \delta n_k, \quad (4.20)$$

we obtain

$$\delta \ln \Omega_t(\mathbf{n}) = - \sum_k (\ln n_k + \alpha + \beta E_k) \delta n_k. \quad (4.21)$$

Therefore for the left hand side to be a maximum there should exist  $n_k^*$  such that

$$\ln n_k^* + \alpha + \beta E_k = 0, \quad (4.22)$$

because  $\delta n_k$  are arbitrary for all  $k$ ; that is,  $n_k^*$  must be of the form

$$n_k^*(N, V) = e^{-\alpha} e^{-\beta E_k(N, V)}. \quad (4.23)$$

Here it is emphasized that in the classical description

$$E_k(N, V) = H(x^{(N)}; N, V) \quad (4.24)$$

an energy of the system in state  $k$  or configuration  $k$  in the phase space of the system of dimension  $6N$  in the case of a monatomic molecular system. Therefore we obtain

$$P_k^* = \frac{n_k^*(N, V)}{\mathcal{N}} := f_{\text{eq}}^{(N)}(x^{(N)}) \quad (4.25)$$

for the equilibrium distribution function of the canonical ensemble of a monatomic system of matter, which takes the form

$$f_{\text{eq}}^{(N)}(x^{(N)}) = \frac{1}{Q(N, V, \beta)} e^{-\beta H(x^{(N)}, N, V)}, \quad (4.26)$$

$$Q(N, V, \beta) := e^\alpha = \int dx^{(N)} e^{-\beta H(x^{(N)}, N, V)}, \quad (4.27)$$

where we have reverted back to the continuous Hamiltonian notation and written the equilibrium distribution function in the form given for  $f_{\text{eq}}^{(N)}(x^{(N)})$  in (4.26) when the system is in equilibrium. The normalization factor  $Q(N, V, \beta)$  is called the (canonical) partition function, by which the meaning of undetermined multiplier  $\alpha$  is fixed. The determination of the remaining multiplier  $\beta$  is made in the following. This multiplier is determined with the help of the phenomenological theory of thermodynamics [28–30], whose validity is experimentally established on the phenomenological grounds; see Chap. 2 on the phenomenological theory of thermodynamics.

Before proceeding further in the Gibbs ensemble theory, it would be useful to digress a little and compare the manners in which the Gibbs ensemble theory gives rise to  $f_{\text{eq}}^{(N)}(x^{(N)})$  for equilibrium distribution function for an interacting particle system, and the Boltzmann kinetic theory to the equilibrium distribution function  $f_a^{\text{eq}}$  (see

Sect. 3.2.) for a dilute noninteracting molecular gas. For it might provide valuable insights possibly for a kinetic theory of ensembles. First of all, whereas the Boltzmann kinetic theory is dynamic albeit for a noninteracting gas, the Gibbs ensemble theory is for both interacting and noninteracting systems regardless of their states of aggregation, but only at equilibrium. Despite a seemingly wide gulf between the two theories it is possible to discern some faintly disguised connections between the two theories. In the Boltzmann kinetic equation the two distribution functions for two independent particles of the system are dynamically connected through a binary collision in the collision integral of the kinetic equation which has collision invariants—energy, momentum, and number—remaining unchanged over the course of collision, whereas in the Gibbs ensemble theory the members of the ensemble somehow reach equilibrium thermally (in the case of a canonical ensemble) under the constraints of a fixed energy, number of particles, and volume of the system. Therefore nothing is said about how the members of the ensemble interact at the molecular level to attain the equilibrium in the Gibbs ensemble theory, but such information is not necessary since the members have already reached equilibrium and the state of the ensemble is static. Despite the differences there are faint but noticeable connections between them, and in later chapters in this work we would like to bridge the gulf between them by strengthening the faint connection we discern between them.

We now would like to return to the main discussion of the equilibrium ensemble theory. According to (4.5), the equilibrium average of mechanical observable  $M(x^{(N)})$  is calculated by using  $f_{\text{eq}}^{(N)}(x^{(N)})$ :

$$\overline{M} := \langle M \rangle_{\text{eq}} = \int dx^{(N)} M(x^{(N)}) f_{\text{eq}}^{(N)}(x^{(N)}). \quad (4.28)$$

Therefore, the average energy  $\overline{E}$  is given by

$$\overline{E}(N, V) = \int dx^{(N)} H(x^{(N)}, N, V) f_{\text{eq}}^{(N)}(x^{(N)}). \quad (4.29)$$

To make use of thermodynamics [28, 29], let us examine the differential of average energy  $\overline{E}$ . Taking differential of (4.29) for  $\overline{E}$  we obtain

$$\begin{aligned} d\overline{E}(N, V) &= \int dx^{(N)} H(x^{(N)}, N, V) df_{\text{eq}}^{(N)} \\ &\quad + dV \int dx^{(N)} \frac{\partial H(x^{(N)}, N, V)}{\partial V} f_{\text{eq}}^{(N)}. \end{aligned} \quad (4.30)$$

Eliminating  $H(x^{(N)}, N, V)$  from (4.30) by using (4.26) yields the equation

$$d\bar{E} = -\beta^{-1} d \left[ \int dx^{(N)} f_{\text{eq}}^{(N)} \ln f_{\text{eq}}^{(N)} \right] + dV \int dx^{(N)} \frac{\partial H(x^{(N)}, N, V)}{\partial V} f_{\text{eq}}^{(N)}. \quad (4.31)$$

Here we now define

$$\bar{p} = - \int dx^{(N)} \frac{\partial H(x^{(N)}, N, V)}{\partial V} f_{\text{eq}}^{(N)}. \quad (4.32)$$

Mathematically, this is a mean quantity of  $-(\partial H / \partial V)_N$ , a mean work per unit volume arising from volume change of the system. It may be interpreted as the statistical mechanical expression for pressure. With this interpretation, we finally obtain the differential

$$d\bar{E} = -\beta^{-1} d \left[ \int dx^{(N)} f_{\text{eq}}^{(N)} \ln f_{\text{eq}}^{(N)} \right] + \bar{p} dV. \quad (4.33)$$

This is as far as the present mathematical theory based on the distribution function can proceed. To endow the physical meanings on the differential form (4.33) and find the meaning of the multiplier  $\beta$  it is necessary to invoke thermodynamic correspondence between the differential for (4.33) and the phenomenological Gibbs relation for equilibrium thermodynamic process

$$dE = TdS + pdV, \quad (4.34)$$

which is a mathematical representation of the second law of thermodynamics *for reversible processes* [31, 32] in the system at equilibrium. Thus we make thermodynamic correspondences

$$d\bar{E} \Leftrightarrow dE; \quad (4.35)$$

$$-(T\beta)^{-1} d \left[ \int dx^{(N)} f_{\text{eq}}^{(N)} \ln f_{\text{eq}}^{(N)} \right] \Leftrightarrow dS; \quad (4.36)$$

$$\bar{p} \Leftrightarrow p. \quad (4.37)$$

The left hand side of correspondence (4.36) becomes an exact differential if  $(T\beta)^{-1}$  is a constant. Therefore setting

$$\beta = \frac{1}{k_B T}, \quad (4.38)$$

where  $k_B$  is the Boltzmann constant we not only find the undetermined multiplier  $\beta$  but also a statistical mechanical expression for the *entropy* of Clausius [31] for a

*reversible process* in the system at equilibrium. It is, apart from a constant, given by the statistical mechanical formula

$$S = -k_B \int dx^{(N)} f_{\text{eq}}^{(N)} \ln f_{\text{eq}}^{(N)}. \quad (4.39)$$

In this manner, the mathematical (statistical mechanical) theory of thermodynamic processes in the system at equilibrium is made a physical theory based on the molecular picture, and thermodynamic quantities can be calculated from the knowledge of the distribution function  $f_{\text{eq}}^{(N)}(x^{(N)}, N, V)$  for reversible processes in the system at equilibrium. Here we would like to emphasize that the correspondence (4.36) and the identification  $dS$  with *an exact differential*<sup>2</sup> of the Clausius entropy is only for *reversible processes*. On this point, recall the conclusion we have reached in the analysis of Chap. 3 on the basis of the Boltzmann kinetic equation.

Since the Helmholtz free energy (work function)  $A$  is given by [28, 29]

$$A = E - TS, \quad (4.40)$$

substitution of (4.26)  $\ln f_{\text{eq}}^{(N)}$  in (4.39) yields the statistical mechanical expression for  $A$ :

$$A = -k_B T \ln Q(N, V, T). \quad (4.41)$$

Recalling the exact differential form for the work function  $A$

$$dA = -SdT - pdV, \quad (4.42)$$

from which we find

$$S = - \left( \frac{\partial A}{\partial T} \right)_{V,N}, \quad (4.43)$$

$$p = - \left( \frac{\partial A}{\partial V} \right)_{T,N}, \quad (4.44)$$

it is now possible to deduce the statistical mechanical expressions for various thermodynamic quantities in terms of the canonical partition function  $Q$ :

$$S = k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N} + k_B \ln Q, \quad (4.45)$$

$$E = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N}, \quad (4.46)$$

---

<sup>2</sup>For in the case of nonequilibrium processes the statistical mechanical entropy formula cannot be shown to give rise to an exact differential and to be identical with Clausius's entropy for reversible processes as we have shown in Chap. 3.

$$p = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{T,N}, \quad (4.47)$$

etc. from which all other thermodynamic relations can be derived in terms of the canonical partition function  $Q(N, V, T)$ .

This formalism can be generalized to a closed composite system consisting of different species in which case the number  $N$  of particles should be generalized to  $(N_1, N_2, \dots, N_r)$  where the subscript  $r$  denotes the species, and the distribution function, in the case of an  $r$ -component non-interacting mixture, should be also generalized to

$$f_{\text{eq}}(x^{(N)}) = \frac{1}{Q} \exp \left[ \alpha - \beta \sum_{\alpha=1}^r H_{\alpha}(x^{(N_{\alpha})}, N_{\alpha}, V) \right] \quad (4.48)$$

$$Q = \prod_{\alpha=1}^r Q_{\alpha}(N_{\alpha}, V) = \prod_{\alpha=1}^r \int dx_{\alpha}^{(N_{\alpha})} e^{-\beta H_{\alpha}(x^{(N_{\alpha})}, N_{\alpha}, V)}. \quad (4.49)$$

The characteristic function (Helmholtz free energy) has the differential form [28, 29]

$$dA = -TdS - pdV + \sum_{\alpha=1}^r \mu_{\alpha} dN_{\alpha}, \quad (4.50)$$

where  $\mu_{\alpha}$  is the chemical potential of species  $\alpha$ . Following the procedure for the single-component system presented earlier in this section, statistical mechanical expressions for various thermodynamic functions can be obtained in terms of the partition function in forms similar to (4.45)–(4.47). In particular, the chemical potential  $\mu_{\alpha}$  is obtained in terms of partition function  $Q(N_1, N_2, \dots, V, T)$  from the statistical mechanical formula

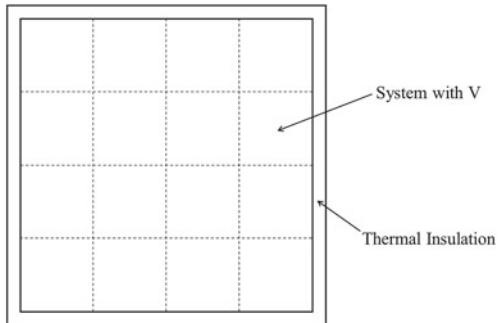
$$\mu_{\alpha} = -k_B T \left( \frac{\partial \ln Q}{\partial N_{\alpha}} \right)_{T,V,N'}. \quad (4.51)$$

Here the subscript  $N'$  denotes the set  $(N_1, N_2, \dots, N_r)$  excluding  $N_{\alpha}$ . The theory for the case of mixtures will be discussed in more detail and more appropriately when the grand canonical ensemble is discussed in the next section (Fig. 4.2).

### 4.2.2 Grand Canonical Ensemble

There are experimental systems that consist of certain regions of space into and out of which particles of different species freely pass through. For example, a liquid solution of many components may exist contiguously in space to its vapor phase, and compositions of the phases may change as the conditions of the phases change as the molecules are exchanged between them. The canonical ensemble method is

**Fig. 4.2** Grand canonical ensemble. The whole system is allowed to equilibrate with respect to heat and matter and then isolated. Systems contained in volume  $V$  are allowed to come to equilibrium with each other with respect to heat and matter



not well suited for developing a statistical mechanical theory for thermodynamic observables in that case, since the particle numbers and hence the dimensions of phase spaces change in the course of a process. It must be suitably generalized, and the grand canonical ensemble discussed achieves the aim.

Let us introduce the notion of petit ensembles, each of which consists of a fixed number of particles at constant volume  $V$ , but may be composed of a mixture of an  $r$  components of  $N_1, N_2, \dots, N_r$  particles (molecules). This set of particle numbers will be denoted by  $\mathbf{N} = (N_1, N_2, \dots, N_r)$  for a petit ensemble. Therefore petit ensembles are like canonical ensembles of a fixed  $\mathbf{N}$ . Similarly to the notations used in the previous section on the canonical ensemble, the phases of particles will be abbreviated by  $\mathbf{x}^{(\mathbf{N})} = (x^{(N_1)}, x^{(N_2)}, \dots, x^{(N_r)}) := (\mathbf{x}^{(\mathbf{N})})$ , each component  $x^{(N_a)}$  of the set representing collectively the phase of  $N_a$  particles of species  $a$  of the petit ensemble:  $x^{(N_a)} := (\mathbf{r}_{1a}, \mathbf{p}_{1a}, \dots, \mathbf{r}_{Na}, \mathbf{p}_{Na})$ , where the subscript  $1a$  denoting particle 1 of species  $a$ , etc. Equations (4.1)–(4.6) are then accordingly generalized.

First we assemble *petit ensembles* [11] of fixed number  $\mathbf{N}$  and volume  $V$  and then the grand ensemble is assembled with all the possible petit ensembles of varying  $\mathbf{N}$  at fixed  $V$ . Therefore the grand ensemble may be regarded as a supersystem of made up of petit ensembles<sup>3</sup> of a fixed composition  $\mathbf{N}$  and volume  $V$ . The supersystem is then made equilibrate thermally and materially with a heat reservoir and a material reservoir, which is then isolated. Thus, the subsystems of the isolated supersystem have equilibrated with respect to heat and matter (see Fig. 4.2).

If we denote the density of observing  $\mathbf{N} := \sum_{\alpha=1}^r \mathbf{N}_\alpha$  particles by  $\rho(\mathbf{x}^{(\mathbf{N})})$  the number of particles in the interval  $d\mathbf{x}^{(\mathbf{N})} := \prod_{\alpha=1}^r d\mathbf{x}^{(N_\alpha)}$  is given by

$$d\mathcal{N} = \rho(\mathbf{x}^{(\mathbf{N})}) d\mathbf{x}^{(\mathbf{N})}. \quad (4.52)$$

<sup>3</sup>In the ensemble theory the dimension of phase space should remain invariant over time. But in the case of open systems and mixtures the numbers of particles of different species are not constant. To overcome this difficulty in the case of open systems and mixtures Gibbs invented petit ensembles which make it possible to avoid the difficulty.

The total number of particles in the grand ensemble is obtained if (4.52) is integrated over  $\mathbf{x}^{(N)}$  and summed over all possible values of set  $\mathbf{N}$ . We thus find

$$\mathcal{N} = \sum_{\mathbf{N} \geq \mathbf{0}} \int d\mathbf{x}^{(N)} \rho(\mathbf{x}^{(N)}) \quad (4.53)$$

for the total number of particles in the grand ensemble (supersystem). We may now define the probability of observing the system at phase point  $\mathbf{x}^{(N)}$ —namely, states—at time  $t$  in the interval  $d\mathbf{x}^{(N)}$  by the formula

$$f^{(N)}(\mathbf{x}^{(N)}) := \frac{\rho(\mathbf{x}^{(N)})}{\mathcal{N}} = \frac{\rho(\mathbf{x}^{(N)})}{\sum_{\mathbf{N} \geq \mathbf{0}} \int d\mathbf{x}^{(N)} \rho(\mathbf{x}^{(N)})}, \quad (4.54)$$

which is normalized to unity:

$$\sum_{\mathbf{N} \geq \mathbf{0}} \int d\mathbf{x}^{(N)} f^{(N)}(\mathbf{x}^{(N)}) = 1. \quad (4.55)$$

This distribution function  $f^{(N)}(\mathbf{x}^{(N)})$  enables us to calculate the average of mechanical quantity  $M(\mathbf{x}^{(N)})$  from the knowledge of solutions of the equations of motion for the system:

$$\langle M \rangle_G = \sum_{\mathbf{N} \geq \mathbf{0}} \int d\mathbf{x}^{(N)} M(\mathbf{x}^{(N)}) f^{(N)}(\mathbf{x}^{(N)}). \quad (4.56)$$

In order to obtain explicitly the probability of finding the system at equilibrium in the interval  $d\mathbf{x}^{(N)}$  around  $\mathbf{x}^{(N)}$  it is convenient to discretize the energy spectrum of petit ensembles as has been done for canonical ensembles, since then it is simpler to enumerate distributions of particles in the states. Afterward, we may take the limit to continuous spectrum appropriate to the classical description we are carrying out here. If we wish to avoid this devise we may simply adopt a quantum mechanical formulation and then take the classical limits of the results obtained.

The Hamiltonian (energy) of the ensemble of  $N$  particles in volume  $V$  is denoted  $H(\mathbf{x}^{(N)}, \mathbf{N}, V)$ . Its numerical value of a particular distribution of particles, which is consistent with the constraints on the isolated grand ensemble that is made equilibrate with the heat reservoir, is denoted  $E_{\mathbf{k}}(\mathbf{N}, V)$ . The subscript  $\mathbf{k}$  here is the collective set of index specifying the energy states corresponding to the distribution of phases  $\mathbf{x}^{(N)}$  consistent with the constraints. The supersystem as well as the subsystems (petit ensembles) are degenerate since there can be  $n_{\mathbf{k}}(\mathbf{N}, V)$  occurrence for  $E_{\mathbf{k}}(\mathbf{N}, V)$ . The constraints of the so-assembled isolated supersystem is then

$$\mathcal{N} = \sum_{\mathbf{k}, \mathbf{N}} n_{\mathbf{k}}(\mathbf{N}, V), \quad (4.57)$$

$$\mathbf{N}_t = \sum_{\mathbf{k}, \mathbf{N}} n_{\mathbf{k}}(\mathbf{N}, V) \mathbf{N}, \quad (4.58)$$

$$E_t = \sum_{\mathbf{k}, \mathbf{N}} n_{\mathbf{k}}(\mathbf{N}, V) E_{\mathbf{k}}(\mathbf{N}, V). \quad (4.59)$$

It should be noted that  $\mathbf{N}_t$  here is a vector of dimension  $r$  as is  $\mathbf{N}$ . For the so-assembled isolated supersystem the number of states is enumerated to be

$$\Omega_t = \sum_{\{\mathbf{N}\} \geq 0} \Omega(\mathbf{N}) = \sum_{\{\mathbf{N}\} \geq 0} \frac{\mathcal{N}!}{\prod_{\mathbf{k}, \mathbf{N}} n_{\mathbf{k}}(\mathbf{N}, V)!}, \quad (4.60)$$

where  $\{\mathbf{N}\}$  denotes all the possible distributions of set  $\mathbf{N}$ . Varying  $\Omega(\mathbf{N})$  subject to the constraints (4.57)–(4.60) by using the method of undetermined multipliers as for the canonical ensemble, we obtain

$$f_{\text{eq}}^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, \beta, \boldsymbol{\mu}) = \frac{n_{\mathbf{k}}^*(\mathbf{N}, V)}{\mathcal{N}} = \frac{1}{\Xi_{\text{eq}}} \exp [\beta \boldsymbol{\mu} \cdot \mathbf{N} - \beta H(\mathbf{x}^{(\mathbf{N})}, \mathbf{N}, V)], \quad (4.61)$$

$$\Xi_{\text{eq}}(\beta, \boldsymbol{\mu}, V) = \sum_{\mathbf{N} \geq 0} \int d\mathbf{x}^{(\mathbf{N})} \exp \{ \beta [\boldsymbol{\mu} \cdot \mathbf{N} - H(\mathbf{x}^{(\mathbf{N})}, \mathbf{N}, V)] \}. \quad (4.62)$$

With this grand canonical distribution function  $f_{\text{eq}}^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})})$  the ensemble average of mechanical observable  $M(\mathbf{x}^{(\mathbf{N})})$  is calculated:

$$\overline{M} := \langle M \rangle_G = \sum_{\mathbf{N} \geq 0} \int d\mathbf{x}^{(\mathbf{N})} M(\mathbf{x}^{(\mathbf{N})}) f_{\text{eq}}^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}), \quad (4.63)$$

where the sum is over all possible distribution of  $\mathbf{N} = (\mathbf{N}_1, \mathbf{N}_2, \dots, \mathbf{N}_r)$ . The undetermined multiplier  $\beta$  and  $r$  undetermined multipliers  $\boldsymbol{\mu} := \mu_1, \dots, \mu_r$  must be determined through thermodynamic correspondence with the phenomenological thermodynamic differential form for the energy as was the case for canonical ensemble. Since the average energy of the system is given by

$$\overline{E}(\mathbf{N}, V) = \sum_{\mathbf{N} \geq 0} \int d\mathbf{x}^{(\mathbf{N})} f_{\text{eq}}^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, \beta, \boldsymbol{\mu}) H(\mathbf{x}^{(\mathbf{N})}, \mathbf{N}, V), \quad (4.64)$$

its differential is found in the form

$$\begin{aligned} d\overline{E}(\mathbf{N}, V) &= \sum_{\mathbf{N} \geq 0} \int d\mathbf{x}^{(\mathbf{N})} \left[ H(\mathbf{x}^{(\mathbf{N})}, \mathbf{N}, V) df_{\text{eq}}^{(\mathbf{N})} \right. \\ &\quad \left. + f_{\text{eq}}^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, \beta, \boldsymbol{\mu}) \frac{\partial H}{\partial V} dV \right]. \end{aligned} \quad (4.65)$$

By using (4.61), this equation may be rearranged to the expression

$$\begin{aligned} d\bar{E} &= -\beta^{-1} \sum_{N \geq 0} \int d\mathbf{x}^{(N)} df_{eq}^{(N)} \left[ \ln f_{eq}^{(N)} + \beta \boldsymbol{\mu} \cdot \mathbf{N} - \ln \Xi_{eq} \right] \\ &\quad - \sum_{N \geq 0} \int d\mathbf{x}^{(N)} f_{eq}^{(N)}(\mathbf{x}^{(N)}, \beta \boldsymbol{\mu}) p(\mathbf{N}, V) dV \\ &= -\beta^{-1} \sum_{N \geq 0} d \left[ \int d\mathbf{x}^{(N)} f_{eq}^{(N)} \ln f_{eq}^{(N)} \right] - \beta^{-1} \boldsymbol{\mu} \cdot d\bar{\mathbf{N}} - \bar{p} dV, \end{aligned} \quad (4.66)$$

where

$$\bar{p} = - \int d\mathbf{x}^{(N)} f_{eq}^{(N)}(\mathbf{x}^{(N)}, \beta, \boldsymbol{\mu}) \left( \frac{\partial H}{\partial V} \right)_N \quad (4.67)$$

and

$$\bar{\mathbf{N}} = \sum_{N \geq 0} \int d\mathbf{x}^{(N)} f_{eq}^{(N)}(\mathbf{x}^{(N)}, \beta, \boldsymbol{\mu}) \mathbf{N}. \quad (4.68)$$

Since the thermodynamic differential form for  $E$  is given by [28, 29]

$$dE = TdS - pdV + \sum_{\alpha=1}^r \mu_\alpha dn_\alpha, \quad (4.69)$$

where  $n_\alpha$  denotes the number density of species  $\alpha$ , making correspondence of the statistical mechanical expression (4.66) with the thermodynamic differential form (4.69)

$$E \Leftrightarrow \bar{E}; \quad n_\alpha \Leftrightarrow \bar{N}_\alpha, \quad (4.70)$$

we conclude that the statistical expression for the Clausius entropy for reversible processes is, within a constant, given by the statistical mechanical formula

$$S \Leftrightarrow -k_B \sum_{N \geq 0} \int d\mathbf{x}^{(N)} f_{eq}^{(N)}(\mathbf{x}^{(N)}, \mathbf{N}, V) \ln f_{eq}^{(N)}. \quad (4.71)$$

The undetermined multipliers are also identifiable as follows:

$$\beta = \frac{1}{k_B T}, \quad (4.72)$$

$$\boldsymbol{\mu} = (\mu_1, \dots, \mu_r). \quad (4.73)$$

Thus, in summary, the equilibrium grand canonical distribution function is found in the form

$$f_{\text{eq}}^{(\mathbf{N})} (\mathbf{x}^{(\mathbf{N})}, \beta, \boldsymbol{\mu}) = \frac{1}{\Xi_{\text{eq}}} \exp \left\{ (k_B T)^{-1} [\boldsymbol{\mu} \cdot \mathbf{N} - H(\mathbf{x}^{(\mathbf{N})}, \mathbf{N}, V)] \right\}, \quad (4.74)$$

$$\Xi_{\text{eq}}(T, \boldsymbol{\mu}, V) = \sum_{\mathbf{N} \geq 0} \int d\mathbf{x}^{(\mathbf{N})} \exp \left[ (k_B T)^{-1} \boldsymbol{\mu} \cdot \mathbf{N} \right] \times \\ \exp \left[ - (k_B T)^{-1} H(\mathbf{x}^{(\mathbf{N})}, \mathbf{N}, V) \right], \quad (4.75)$$

where  $\Xi_{\text{eq}}(T, \boldsymbol{\mu}, V)$  is the equilibrium grand canonical partition function, and the (Clausius) entropy is finally found given by the formula

$$S = -k_B \sum_{\mathbf{N} \geq 0} \int d\mathbf{x}^{(\mathbf{N})} f_{\text{eq}}^{(\mathbf{N})} (\mathbf{x}^{(\mathbf{N})}, \mathbf{N}, V) \ln f_{\text{eq}}^{(\mathbf{N})}. \quad (4.76)$$

If (4.61) is substituted into (4.76) and the resulting expression is rearranged, it is found

$$k_B T \ln \Xi_{\text{eq}} = TS + \sum_{\alpha=1}^r \mu_\alpha N_\alpha - E = pV. \quad (4.77)$$

This implies that the exact differential form for the thermodynamic potential is given in terms of the grand canonical partition function:

$$d(pV) = SdT + \sum_{\alpha=1}^r N_\alpha d\mu_\alpha + pdV \quad (4.78)$$

$$= d(k_B T \ln \Xi_{\text{eq}}). \quad (4.79)$$

Thus  $pV$  is found to be the thermodynamic potential for the equilibrium grand canonical ensemble. From this differential form are obtained the following thermodynamic quantities related to the equilibrium grand canonical partition function  $\Xi_{\text{eq}}$ :

$$p = k_B T \left( \frac{\partial \ln \Xi_{\text{eq}}}{\partial V} \right)_{T, \mu}, \quad (4.80)$$

$$N_\alpha = k_B T \left( \frac{\partial \ln \Xi_{\text{eq}}}{\partial \mu_\alpha} \right)_{T, V, \mu'}, \quad (4.81)$$

$$S = \left( \frac{\partial k_B T \ln \Xi_{\text{eq}}}{\partial T} \right)_{V, \mu}. \quad (4.82)$$

All the thermodynamic relations and results can be calculated if the formalism presented for the equilibrium grand canonical ensemble is applied.

### 4.3 Summary of the Gibbs Ensemble Theory

The Gibbs ensemble method is a deductive theory based on two fundamental hypotheses, *equal a priori probability assumption* and *ergodic hypothesis*, which makes it possible to calculate equilibrium thermodynamic functions of matter in an arbitrary number of phases. *The former hypothesis is for assembling ensembles representative of experimental macroscopic systems*, which enables us to deduce the most probable equilibrium distribution functions, *and the latter replaces the time average of a thermodynamic observable with its ensemble average calculated with the equilibrium distribution function used as a weight function*. The distribution function obtained contains undetermined multipliers, which can be determined upon making the statistical mechanically calculated energy—more precisely—the energy differential correspond to the thermodynamic energy differential deducible from the first and second laws of thermodynamics in the case of reversible processes (or a system in equilibrium). Thus the complete determination of equilibrium distribution functions in the Gibbs ensemble method is facilitated with the help of the laws of thermodynamics, if processes are reversible. Once the equilibrium distribution function is completely determined, all thermodynamic functions and relations are deducible by mean of statistical mechanics in terms of partition functions, and the task of equilibrium molecular theory of matter is reduced to calculation of appropriate partition functions.

Later in this work, it will be found fruitful to implement the *equal a priori hypothesis* in a slightly different form than the conventional approach [22] discussed here if we apply the hypothesis to the distribution functions for the members of an ensemble instead of the number of states or phase volume of the ensemble assembled and replace the variation method of undetermined multipliers with a dynamic collision operator method as alluded to earlier. This aspect will be discussed in the subsequent chapters.

In this work, the ideas underlying the Gibbs equilibrium ensemble theory will be applied to formulate, with the help of appropriately constructed irreversible kinetic equations for the ensemble distribution functions, nonequilibrium ensemble theories for nonequilibrium processes progressing in matter at any density.

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# Chapter 5

## Boltzmann-Like Equation for Moderately Dense Gases

We have shown in Chap. 3 that, if the concept of calortropy is made use of in place of the Boltzmann entropy, the Boltzmann equation [1] is capable of providing a satisfactory formalism for a theory of irreversible processes in dilute monatomic fluids and the attendant generalized hydrodynamics in a manner consistent with the laws of thermodynamics. It also provides a molecular theory framework for fluctuations of irreversible processes through the concept of relative Boltzmann entropy, which describes fluctuations of macroscopic variables from the deterministic macroscopic variables that span the thermodynamic manifold and obey the generalized hydrodynamic equations.

The Boltzmann equation is capable of producing the thermodynamic theory of irreversible processes mainly owing to the irreversibility built into it. The most prominent drawback of the Boltzmann kinetic theory, however, is that it is a theory of gases so dilute that the effects of collisions of more than two particles can be ignored and spatial correlations of particles are insignificant. These assumptions are not true at an elevated density.

The aforementioned drawback has historically motivated numerous investigations that have attempted to extend the density range of the Boltzmann kinetic theory beyond the sufficiently dilute gas regime. Such investigations began with the attempt of Enskog [2], who was able to include a three-particle collision term in the collision integral in an *ad hoc* manner, and by later researchers led by Bogoliubov [3], Born and Green [4], Kirkwood [5], and Yvon [6] (BBGKY) and their followers [7–10], who investigated theories to generalize the Boltzmann kinetic equation by partially integrating the Liouville equation for an isolated system consisting of many particles. The linear response theory of Green [11], Kubo [12], and Mori [13] is another line of theory distinctively different from those of the BBGKY hierarchy theory.

The BBGKY hierarchy theory in effect tries to improve the Enskog theory, which accounts for the effects of three-particle collisions and correlations in a hard sphere fluid in a nonsystematic but intuitive fashion. The BBGKY theory is, in fact, an

attempt to integrate the Liouville equation of an isolated fluid consisting of correlated particles in a density series for the singlet distribution function. The basic deficiency of the BBGKY theory is that it tries to draw out an irreversible kinetic equation from a reversible equation invariant to time reversal. For this reason it is incapable of describing irreversible phenomena that break time reversal invariance inherent to irreversible processes observed in nature or laboratory. Therefore, somewhere in the process of “derivation” of such an irreversible equation a time reversal symmetry breaking step must be entered by a device of either an assumption or approximation that basically breaks time reversal invariance. It is not the aim of this work to identify and discuss such a step here.

As shown in Chap. 3, the Boltzmann kinetic equation [1] manifestly breaks the time reversal invariance, contrary to the mechanical (Newtonian or quantum) equations of motion or the Liouville equation. It should be emphasized that this is the most important feature of the Boltzmann equation that enables us to formulate a thermodynamic theory of irreversible processes, as is presented in Chap. 3. However, as is well known historically [14], this irreversible feature of the equation unfortunately got the author of the equation (Ludwig Boltzmann) in a considerable difficulty with his peers. As alluded to it earlier, *the present author would like to take the Boltzmann equation as a fundamental postulate for singlet distribution functions for dilute monatomic gases that is built on the foundations of classical mechanics and probability theory*. We then would like to explore in this chapter a way to keep this important feature of the Boltzmann equation, that is, the irreversibility, and simultaneously extend the density range of validity by including many-particle collisions, so that the density range is extended beyond that of the Boltzmann equation, at least, to a moderate density regime. This attempt is, in a way, in the same spirit as Enskog’s, but there are important differences in the viewpoint and also in the absence of correlations as well as in the approach taken in the present investigation. The differences will become evident as we proceed. The principal motivation for the present discussion lies in the fact that the method we employ here, in fact, provides important clues and stepping stones for the later development of the ensemble theory presented for dense fluids of statistically correlated particles in the subsequent two chapters of this work.

## 5.1 Extended Boltzmann Equation

In this chapter, in order to make the discussion as simple as possible we shall limit it to a single-component monatomic gas of moderate density. The theory formulated can then be easily generalized to mixtures. In the notation of Chap. 3, the Boltzmann kinetic equation can be written as

$$\left( \frac{\partial}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} + \mathbf{F} \cdot \frac{\partial}{\partial \mathbf{p}} \right) f(\mathbf{r}, \mathbf{p}, t) = \mathbf{R}[f], \quad (5.1)$$

where  $\mathbf{v} = \mathbf{p}/m$  and the Boltzmann collision integral  $\mathbf{R}[f]$  is defined by

$$\mathbf{R}[f] = \sum_{b=1}^r C(f, f_b), \quad (5.2)$$

$$C(f, f_b) = \int d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} g_{1b} [f^*(\mathbf{r}, \mathbf{v}^*, t) f_b^*(\mathbf{r}, \mathbf{v}_b^*, t) - f(\mathbf{r}, \mathbf{v}, t) f_b(\mathbf{r}, \mathbf{v}, t)]. \quad (5.3)$$

Here the subscript  $b$  refers to the second particle of species  $b$  colliding with the first (unsubscripted) particle.

It is necessary for our purpose to recast the Boltzmann collision integral into a more general form by using the classical collision operator, because the complexity of dynamics in a fluid lies in the collision integral of a kinetic equation. The idea underlying the Gibbs equilibrium ensemble theory motivates us to recast the collision term of the kinetic equation (5.1) into a form suitable for the ensemble theory we finally obtain.

In the classical theory of scattering [15], the collision of a pair of particles interacting in the field of a finite-ranged potential  $U_{12}$  is described by the classical collision operator  $\mathcal{T}_{12}$  obeying the classical Lippmann–Schwinger equation [15, 16]

$$\mathcal{T}_{12}(z) = \mathcal{L}_{12} - \mathcal{L}_{12}\mathcal{R}_0(z)\mathcal{T}_{12}(z), \quad (5.4)$$

where  $\mathcal{L}_{12}$  is the interaction Liouville operator defined by

$$\mathcal{L}_{12} = -i\mathbf{F}_{12} \cdot \left( \frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2} \right) \quad \left( \mathbf{F}_{12} = -\frac{\partial U_{12}}{\partial \mathbf{r}_{12}} \right) \quad (5.5)$$

with  $i = \sqrt{-1}$ , and  $\mathcal{R}_0(z)$  is the resolvent operator defined by

$$\mathcal{R}_0(z) = (\mathcal{L}_0 - z)^{-1} \quad (z = i\varepsilon; \quad \varepsilon > +0). \quad (5.6)$$

Here  $\mathcal{L}_0$  denotes the Liouville operator of non-interacting particles:

$$\mathcal{L}_0 = -i \sum_{k \neq 1}^2 \mathbf{v}_k \cdot \frac{\partial}{\partial \mathbf{r}_k}. \quad (5.7)$$

The operator equation (5.4) can be rearranged to equivalent forms

$$\mathcal{R}(z)\mathcal{L}_{12} = \mathcal{R}_0(z)\mathcal{L}_{12}(z), \quad (5.8)$$

$$\mathcal{L}_{12}\mathcal{R}(z) = \mathcal{L}_{12}(z)\mathcal{R}_0(z), \quad (5.9)$$

where  $\mathcal{R}(z)$  is the resolvent operator for the full Liouville operator

$$\mathcal{R}(z) = (\mathcal{L} - z)^{-1} = (\mathcal{L}_0 + \mathcal{L}_{12} - z)^{-1}. \quad (5.10)$$

It can be written in a form of integral equation equivalent to (5.4)

$$\mathcal{R}(z) = \mathcal{R}_0(z) - \mathcal{R}_0(z)\mathcal{T}_{12}(z)\mathcal{R}_0(z). \quad (5.11)$$

Here the integral equation for the collision operator  $\mathcal{T}_{12}(z)$  may be also written as

$$\mathcal{T}_{12}(z) = \mathcal{L}_{12} - \mathcal{L}_{12}\mathcal{R}(z)\mathcal{L}_{12}, \quad (5.12)$$

which may be cast into an integral equation for  $\mathcal{T}_{12}(z)$  if (5.8) is made use of:

$$\mathcal{T}_{12}(z) = \mathcal{L}_{12} - \mathcal{L}_{12}\mathcal{R}_0(z)\mathcal{T}_{12}(z). \quad (5.13)$$

If we recall that the Boltzmann collision integral implicitly assumes a spatial coarse-graining over the collision volume on the same order of magnitude as the cube of intermolecular force range, the distribution functions  $f(\mathbf{r}, \mathbf{v}, t)$  and  $f_2(\mathbf{r}, \mathbf{v}_2, t)$  must be regarded as spatially uniform within the so-defined collision volume. Under this condition it is possible to show [15, 17] that the collision integral  $C(f, f_2)$  can be written in terms of the collision operator  $\mathcal{T}_{12}$ :

$$C[f(x_1, t), f_2(x_2, t)] = \int dx_2 (-i) \mathcal{T}_{12}(z) f(\mathbf{r}_1, \mathbf{p}_1, t) f(\mathbf{r}_1, \mathbf{p}_2, t), \quad (5.14)$$

where  $x_1$  denotes the phase  $(\mathbf{r}, \mathbf{p}_1)$  of particle 1,  $x_2$  the phase  $(\mathbf{r}, \mathbf{p}_2)$  of particle 2,  $dx_2 = d\mathbf{r}_2 d\mathbf{p}_2$ , and  $\mathbf{r}_1 = \mathbf{r}$ . Note that when the right hand side of (5.14) is fully calculated over the time scale of two-particle collision and the collision process is over, then the limit  $z \rightarrow +0$  can be finally taken in the expression in (5.14). The aforementioned limit is implicit in (5.14). *The distribution functions  $f(\mathbf{r}, \mathbf{p}_1, t)$  and  $f(\mathbf{r}, \mathbf{p}_2, t)$  are spatially uniform within the collision volume owing to the spatial coarse graining implicit.*

Upon use of transformation of the Boltzmann collision operator as in (5.14) the Boltzmann equation can be written as

$$\left( \frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}} + m \widehat{\mathbf{F}}_1 \cdot \frac{\partial}{\partial \mathbf{p}_1} \right) f(\mathbf{r}, \mathbf{p}_1, t) = \int dx_2 (-i) \mathcal{T}_{12}(z) \times f(\mathbf{r}, \mathbf{p}_1, t) f(\mathbf{r}, \mathbf{p}_2, t). \quad (5.15)$$

Here  $\widehat{\mathbf{F}}_1$  is the external force per unit mass on particle 1:  $\widehat{\mathbf{F}}_1 = \mathbf{F}_1/m$ .

Comparing (5.3) and (5.14), we see that the collision operator  $\mathcal{T}_{12}$ , upon operating on the product of distribution functions  $f(\mathbf{r}, \mathbf{p}_1, t) f(\mathbf{r}, \mathbf{p}_2, t)$ , which are spatially coarse-grained in the collision volume, transforms the product  $f(\mathbf{r}, \mathbf{p}_1, t) f(\mathbf{r}, \mathbf{p}_2, t)$

into their difference between post- and pre-collision values; namely, the right hand side of (5.15) is transformed into the Boltzmann collision integral in (5.3). *The collision operator  $T_{12}$  retains the entire set of properties of the original  $C(f_1, f_2)$ : that is, the mass, momentum, and energy of the particle pair are its collision invariants, and also the  $H$  theorem of the Boltzmann equation.* Therefore the form of the Boltzmann equation given in (5.15) preserves the original properties of (5.3): most importantly, the irreversibility,  $H$ -theorem, and collision invariance. We will attempt to preserve this important feature for a moderately dense gas in which statistical correlations can be neglected. It is a model kinetic equation that resembles the Boltzmann kinetic equation and helps us grasp the essential idea of preserving irreversibility in the kinetic equation of a fluid which is not so dilute as to be described by the Boltzmann equation; yet it is an irreversible kinetic equation distinctive from the Liouville equation or the Boltzmann kinetic equation. For the present particular model the fluid is, nevertheless, sufficiently dilute so that spatial correlations are negligible between particles.

Let there be  $N$  particles contained in volume  $V$ , whose total distribution function in the phase space is denoted by  $F^{(N)}(x^{(N)}, t)$  where  $x^{(N)}$  denotes the total phase  $x^{(N)} := (x_1, x_2, \dots, x_N) = (\mathbf{r}_1, \mathbf{p}_1; \mathbf{r}_2, \mathbf{p}_2; \dots; \mathbf{r}_N, \mathbf{p}_N)$ . Now let  $F_s(x^{(s)}, t)$  be the distribution function of an  $s$ -particle subset of  $N$  particles. It is defined by

$$F_s(x^{(s)}, t) = V^s \int dx_{s+1} \cdots dx_N F^{(N)}(x^{(N)}, t). \quad (5.16)$$

This is according to the conventional definition [3] of reduced distribution functions. Since  $F^{(N)}(x^{(N)}, t)$  is assumed to be normalized to unity, for example, the singlet reduced distribution function  $F_1(x_1, t)$  is normalized to unity such that

$$V^{-1} \int dx_i F_1(x_i, t) = 1. \quad (5.17)$$

Let us simplify the notation: define

$$f^{(1)}(x_i, t) = V^{-1} F_1(x_i, t). \quad (5.18)$$

Consider a macroscopic system consisting of  $N$  monatomic particles contained in volume  $V$ . Assume that it is so dilute that statistical correlations of particles are negligible—incidentally, it is one of the conditions assumed in the derivation [18] of the Boltzmann equation in the studies of the kinetic theory of dilute monatomic fluids. Then the total distribution function  $F^{(N)}(x^{(N)}, t)$  is given by the product of singlet distribution functions

$$F^{(N)}(x^{(N)}, t) = \prod_{i=1}^N f^{(1)}(x_i, t) \quad (5.19)$$

owing to the fact that particles are statistically uncorrelated. The total distribution function  $F^{(N)}(x^{(N)}, t)$  written as a product in (5.19) normalizes to unity in view of (5.17). It represents the probability of observing  $N$  statistically independent uncorrelated particles at  $x^{(N)}$  in volume  $V$  at time  $t$ . Furthermore,  $f^{(1)}(x_i, t)$  may be regarded as a reduced distribution function of finding particle  $i$  at  $x_i$ , given  $(N - 1)$  particles at  $x_1, \dots, x_{i-1}, x_{i+1}, \dots, x_N$  in  $V$ :

$$f^{(1)}(x_i, t) = \int dx_i^{(N-1)} F^{(N)}(x^{(N)}, t), \quad (5.20)$$

where

$$dx_i^{(N-1)} = \prod_{i \neq k=1}^N dx_k. \quad (5.21)$$

The distribution function  $F^{(N)}(x^{(N)}, t)$  is governed by the Liouville equation

$$\left( \frac{\partial}{\partial t} + \mathbf{L}^{(N)} \right) F^{(N)}(x^{(N)}, t) = 0, \quad (5.22)$$

if the subsystems of one particle are allowed to interact with each other, but *the whole system of  $N$  particles is isolated*. Then the Liouville operator  $\mathbf{L}^{(N)}$  is given by

$$\mathbf{L}^{(N)} = \mathbf{L}_0^{(N)} + \mathbf{L}_1^{(N)} \quad (5.23)$$

where the free Liouville operator  $\mathbf{L}_0^{(N)}$  is given by

$$\mathbf{L}_0^{(N)} = \sum_{i=1}^N \mathbf{L}_{0i} := \sum_{i=1}^N \mathbf{v}_i \cdot \nabla_i, \quad (5.24)$$

and the interaction Liouville operator  $\mathbf{L}_1^{(N)}$  by

$$\mathbf{L}_1^{(N)} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1(j \neq i)}^N \mathbf{L}_{ij} + \mathbf{L}_{ex}^{(N)} \quad (5.25)$$

with the intermolecular and the external interaction terms given by

$$\mathbf{L}_{ij} := \mathbf{F}_{ij} \cdot (\nabla_{pi} - \nabla_{pj}) \quad (5.26)$$

$$\mathbf{L}_{ex}^{(N)} := \sum_{i=1}^N m_i \hat{\mathbf{F}}_i \cdot \nabla_{pi}. \quad (5.27)$$

Here  $\mathbf{F}_{ij}$  and  $\widehat{\mathbf{F}}_i$  denote intermolecular and external interaction (body) forces. If we regard the aforementioned  $N$  particle system as an assembly of single particle systems distributed in their  $\mu$ -phases the whole assembly of subsystems interacts through  $\mathbf{L}_1^{(N)}$  and evolves.

Therefore, we may picture the assembly of  $N$  subsystems, which are initially well separated from each other, approach each other toward mutual interaction zone and exchange energies, and then separate from each other, having reached equilibrium mechanically and thermally. The entire process may be regarded as a collision process of  $N$  particles. We are especially interested in the evolution of singlet distribution functions. It is described by an equation obtained by integrating (5.22) over  $(N - 1)$  phases— $(N - 1)$   $\mu$ -phases, in fact—and the resulting evolution equation is given by

$$\left( \frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \nabla_1 + m_1 \widehat{\mathbf{F}}_1 \cdot \nabla_{p1} \right) f^{(1)}(x_1, t) = \int dx_1^{(N-1)} \sum_{j>1}^N \mathbf{L}_{1j} \prod_{j=1}^N f^{(1)}(x_j, t), \quad (5.28)$$

where  $dx_1^{(N-1)} = dx_2 \cdots dx_N$ . This evolution equation is then time-coarse-grained by taking time average over a time span longer than the order of collision time. In terms of spatial distance it would be longer than the order of the interaction force range. We define the time-coarse-grained distribution function by

$$\bar{f}^{(1)}(x_1, t) = \frac{1}{\tau_c} \int_{-\tau_c}^0 ds f^{(1)}(x_1, t + s) := \epsilon \int_{-\infty}^0 ds f^{(1)}(x_1, t + s) \quad (5.29)$$

where we regard the collision time  $\tau_c = 1/\epsilon$  of  $O(10^{-9}$  sec) as sufficiently long compared to the scale of time of molecular movement, which is on the order of  $10^{-12}$  s. The initial time is set at remote past when the particles (subsystems) are well separated from each other beyond the interaction range, and the time span is from  $s = -\tau_c$  taken  $\tau_c = -\infty$  to the present time  $s = 0$  in the relative scale mentioned. Thus  $\epsilon$  may be taken to the limit of 0. This time-coarse graining is according to the idea of Kirkwood [5], who introduced the notion of irreversibility through time-coarse graining in his work on kinetic equation. When thus time-coarse-grained, the mean evolution equation is obtained from (5.28) in the form

$$\begin{aligned} & \left( \frac{\partial}{\partial t} + \mathbf{v}_1 \cdot \nabla_1 + m_1 \widehat{\mathbf{F}}_1 \cdot \nabla_{p1} \right) \bar{f}^{(1)}(x_1, t) \\ &= \epsilon \int_{-\infty}^0 ds \int dx_1^{(N-1)} \sum_{j>1}^N \mathbf{L}_{1j} F^{(N)}(x^{(N)}, t + s), \end{aligned} \quad (5.30)$$

where  $x_1 = (\mathbf{r}_1, \mathbf{p}_1)$ .

It is convenient to introduce a Hermitean Liouville operators  $\mathcal{L}^{(N)}$ , etc. defined by

$$\mathcal{L}^{(N)} = -i\mathbf{L}^{(N)}; \quad \mathcal{L}_{jk}^{(N)} = -i\mathbf{L}_{jk}^{(N)}. \quad (5.31)$$

Being Hermitean, the eigenvalues of  $\mathcal{L}^{(N)}$  are real. Then it is possible to express

$$F^{(N)}(x^{(N)}, t + s) = e^{-is\mathcal{L}^{(N)}} F^{(N)}(x^{(N)}, t). \quad (5.32)$$

Inserting a convergence factor  $\exp(\epsilon s)$  in the right hand side of (5.30) in accordance with the Abel-Tauber theorem [19, 20], we obtain

$$\begin{aligned} \left( \frac{\partial}{\partial t} + \mathbf{L}_{01} \right) \bar{f}^{(1)}(x_1, t) &= \int dx_1^{(N-1)} \sum_{j>1}^N \mathbf{L}_{1j} \times \\ &\quad \epsilon \int_{-\infty}^0 ds e^{\epsilon s} e^{is\mathcal{L}^{(N)}} F^{(N)}(x^{(N)}, t), \end{aligned} \quad (5.33)$$

where  $\lim \epsilon \rightarrow +0$  is understood and  $\mathbf{L}_{01}$  is defined by the abbreviation

$$\mathbf{L}_{01} = \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} + m\widehat{\mathbf{F}}_1 \cdot \frac{\partial}{\partial \mathbf{p}_1}. \quad (5.34)$$

Henceforth the limit  $\epsilon \rightarrow +0$  is implicitly understood with  $\epsilon$ , even if the limit sign is not present. Performing the integration over  $s$  and defining the resolvent operator  $\mathcal{R}^{(N)}(\epsilon)$ :

$$\mathcal{R}^{(N)}(\epsilon) = (\mathcal{L}^{(N)} - i\epsilon)^{-1}, \quad (5.35)$$

we cast (5.33) in the form

$$\left( \frac{\partial}{\partial t} + \mathbf{L}_{01} \right) \bar{f}^{(1)}(x_1, t) = -i\epsilon \int dx_1^{(N-1)} \sum_{j>1}^N \mathcal{L}_{1j} \mathcal{R}(\epsilon) F^{(N)}(x^{(N)}, t). \quad (5.36)$$

In general, the resolvent operator  $\mathcal{R}(z)$  is defined by

$$\mathcal{R}^{(N)}(z) = (\mathcal{L}^{(N)} - z)^{-1} \quad (5.37)$$

with  $z$  defined by a complex number  $z$  given in terms of the eigenvalue  $\lambda$  of the Liouville operator  $\mathcal{L}^{(N)}$ :

$$z = \lambda + i\epsilon. \quad (5.38)$$

Therefore the resolvent operator  $\mathcal{R}(\epsilon)$  may be said to be in the null class of eigenvalues because  $\lambda = 0$ . Since the product distribution function  $F^{(N)}(x^{(N)}, t)$  on

the right hand side of (5.36) is still fine-grained in time, we can time-coarse-grain (5.36) once again to obtain the fully coarse-grained equation

$$\left( \frac{\partial}{\partial t} + \mathbf{L}_{01} \right) \overline{f}^{(1)}(x_1, t) = \epsilon \int dx_1^{(N-1)} \sum_{j>1}^N \mathcal{L}_{1j} \mathcal{R}^{(N)}(\epsilon) \overline{F}^{(N)}(x^{(N)}, t), \quad (5.39)$$

where

$$\begin{aligned} \overline{F}^{(N)}(x^{(N)}, t) &= \epsilon \int_{-\infty}^0 ds F^{(N)}(x^{(N)}, t+s) \\ &= \epsilon \int_{-\infty}^0 ds \prod_{j=1}^N f^{(1)}(x_j, t+s). \end{aligned} \quad (5.40)$$

We now assume that  $\overline{F}^{(N)}(x^{(N)}, t)$  is given by the product of

$$\overline{F}^{(N)}(x^{(N)}, t) \simeq \prod_{j=1}^N \overline{f}^{(1)}(x_j, t) \quad (5.41)$$

under the assumption that the phases of  $f^{(1)}(x_j, t+s)$  of different subsystems on average cancel out and vanish to an approximation. With this approximation and recalling the classical time-dependent scattering formalism [16, 21], we may define the classical collision operator<sup>1</sup>  $\mathcal{T}^{(N)}$  in terms of the Møller operator by the formula

$$\mathcal{T}^{(N)} \mathcal{R}_0^{(N)}(\epsilon) = \sum_{i=1}^N \mathcal{T}_{ij}^{(N)} \Omega^{(N)}(0, -\infty) = \sum_{i=1}^N \sum_{j>1}^N \mathcal{L}_{1j} \Omega^{(N)}(0, -\infty), \quad (5.42)$$

where the Møller operator  $\Omega^{(N)}(0, -\infty)$  is defined by

$$\Omega^{(N)}(0, -\infty) = \lim_{\epsilon \rightarrow +0} \epsilon \int_{-\infty}^0 dt e^{\epsilon t} e^{it\mathcal{L}^{(N)}}. \quad (5.43)$$

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<sup>1</sup>The classical collision operator  $\mathcal{T}^{(N)}$  appearing in the kinetic theory formulated here is basically a differential operator operating on a distribution function and producing the difference in the distribution function before and after collisions of particles in the assembly represented by the distribution function. In this sense the classical collision operator is different from the transition or collision operator appearing in the scattering theory of particles in, for example, the Lippmann-Schwinger theory of particle in quantum mechanics. This difference should be kept in mind when applying the scattering theory formulated below and made use of in this work. Nevertheless, one can show their relations.

We then obtain (5.39) in terms of the collision operator

$$\bar{f}^{(1)}(x_1, t) = \epsilon \int dx_1^{(N-1)} \sum_{j>1}^N \mathcal{T}_{1j}^{(N)}(\epsilon) \mathcal{R}_0^{(N)}(\epsilon) \prod_{j=1}^N \bar{f}^{(1)}(x_j, t), \quad (5.44)$$

where  $\mathcal{R}_0^{(N)}(\epsilon)$  denotes the free resolvent operator defined by

$$\mathcal{R}_0^{(N)}(\epsilon) = (\mathcal{L}_0^{(N)} - i\epsilon)^{-1}. \quad (5.45)$$

In the time-independent collision theory language, the collision operator  $\mathcal{T}_{1j}^{(N)}(\epsilon)$  is also defined by the relation

$$\mathcal{T}_{1j}^{(N)}(\epsilon) \mathcal{R}_0^{(N)}(\epsilon) = \mathcal{L}_{1j} \mathcal{R}^{(N)}(\epsilon). \quad (5.46)$$

Let us now observe that the collision process of  $N$  particles constituting the assembly of  $N$  particles preserves the total energy and momentum as well as the number of particles. In other words, the aforementioned quantities (i.e., total energy and momentum) are collision invariants of the assembly and the eigenvalues of the Liouville operators  $\mathcal{L}_0^{(N)}$  and  $\mathcal{L}^{(N)}$  are not only equal, but also identically equal to zero, because of their invariance property. This means that if we denote the eigenvalue of the Liouville operator (5.46) by  $\lambda$ , the collision process considered evolves in the phase space of  $\lambda = 0$ . It will be said that such a motion is in the phase plane of the  $\lambda = 0$  class. This implies that

$$\mathcal{R}_0^{(N)}(\epsilon) \prod_{j=1}^N \bar{f}^{(1)}(x_j, t) = -i/\epsilon. \quad (5.47)$$

Therefore the kinetic equation for  $\bar{f}^{(1)}(x_1, t)$  is finally given by

$$\left( \frac{\partial}{\partial t} + \mathbf{L}_{01} \right) \bar{f}^{(1)}(x_1, t) = \int dx_1^{(N-1)} \sum_{j>1}^N (-i) \mathcal{T}_{1j}^{(N)}(\epsilon) \prod_{j=1}^N \bar{f}^{(1)}(x_j, t). \quad (5.48)$$

Since the integrals involving  $\mathcal{T}_{kj}^{(N)}(\epsilon)$  for  $k > 1$  in (5.48) identically vanish, the sum of collision operators  $\sum_{j>1}^N \mathcal{T}_{1j}^{(N)}(\epsilon)$  may be replaced with the total collision operator  $\mathcal{T}^{(N)}$  defined by

$$\mathcal{T}^{(N)} = \sum_{k=1}^N \sum_{j>1}^N \mathcal{T}_{kj}^{(N)}(\epsilon). \quad (5.49)$$

It should be noted that  $\mathcal{T}_{kj}^{(N)}$  is not a binary collision operator of an isolated particle pair  $(k, j)$ , but a collision operator of particle  $k$  and particle  $j$  embedded

in the group of  $(N - 1)$  particles; see a cluster expansion discussed in Ref. [15], Chap. 9, Ref. [21], and the discussion presented in Sect. 5.2 of this chapter. We then have the kinetic equation in the form

$$\begin{aligned} \left( \frac{\partial}{\partial t} + \mathbf{L}_{01} \right) \bar{f}^{(1)}(x_1, t) &= \int dx_1^{(N-1)} (-i) \mathcal{T}^{(N)}(z) \prod_{j=1}^N \bar{f}^{(1)}(x_j, t) \\ &:= \Re \left[ \bar{F}^{(N)}(x^{(N)}, t) \right]. \end{aligned} \quad (5.50)$$

This is the kinetic equation for  $\bar{f}^{(1)}(x_1, t)$ , which describes the evolution of singlet distribution function  $\bar{f}^{(1)}(x_1, t)$ , that we use to study moderate dense gases in this chapter. As will be shown, *it is not only irreversible, but also has the required properties for formulation of irreversible thermodynamics in the gases consisting of statistically uncorrelated particles*. It should be noted at this point that the left-hand side of (5.50) is not exactly identical with that of Boltzmann equation in (5.15) because  $\bar{f}^{(1)}(x_1, t)$  is not quite the same as  $f(\mathbf{r}, \mathbf{p}_1, t)$ , even though they are related to each other in the following sense:

$$\begin{aligned} f(\mathbf{r}, \mathbf{p}_1, t) &= \frac{1}{V} \sum_{i=1}^N \int d\mathbf{r}_i f^{(1)}(x_i, t) \delta(\mathbf{r}_i - \mathbf{r}) \\ &= \frac{1}{V} \sum_{i=1}^N f^{(1)}(\mathbf{r}, \mathbf{p}_i, t) := n f^{(1)}(\mathbf{r}, \mathbf{p}_i, t). \end{aligned} \quad (5.51)$$

In this sense (5.15) can be shown related to (5.50) as will become evident, when we demonstrate the Boltzmann collision integral  $\mathbf{R}[f]$  emerges as the lowest order term in the density expansion of collision integral  $\Re \left[ \bar{F}^{(N)}(x^{(N)}, t) \right]$  of the kinetic equation (5.50).

In the case of gas mixtures the extended Boltzmann equation (5.50) can be trivially generalized by changing the particle subscript  $i$  to a compound subscript  $ia$ , meaning particle  $i$  of species  $a$  and adding another product sign over species ranging from 1 to  $r$  if the mixture consists of  $r$  components. Thus the extended Boltzmann kinetic equation would read

$$\left( \frac{\partial}{\partial t} + \mathbf{L}_{01a} \right) \bar{f}_a^{(1)}(x_{1a}, t) = \int dx_{1a}^{(N-1)} (-i) \mathcal{T}^{(N)}(z) \prod_{b=a}^r \prod_{jb=1}^{N_b} \bar{f}_b^{(1)}(x_{jb}, t) \quad (5.52)$$

with  $N = N_1 + \dots + N_r$  for the  $r$ -component gas mixture. This kinetic equation will be used to derive evolution equations for macroscopic variables of the mixture, such as balance equations of conserved variables, stress tensor evolution equations, etc.

Comparing the Boltzmann equation written in the form of (5.15) with the model kinetic equation (5.50) for a moderately dense but statistically uncorrelated fluid, we may gain useful insights and ways to generalize the Boltzmann kinetic equation in a number of directions. Equation (5.50) certainly extends the range of the Boltzmann equation with respect to the density in the case of  $N$  statistically uncorrelated particles interacting via finite-ranged interaction potentials. For in this case we may regard the binary collision operator  $T_{12}(z)$  as a leading order collision operator for binary clusters in the connected cluster expansion<sup>2</sup> [15] of  $N$ -particle collision operator  $\mathcal{T}^{(N)}(z)$ , as will be shown in a later section. Thus it would be possible to say that as the density reduces to a sufficiently low value, so that the collision operator  $\mathcal{T}^{(N)}(z)$  may be approximated by binary collision operator  $T_{12}(z)$ , the Boltzmann equation is recovered from the kinetic equation (5.50). *The most salient point of (5.50) is that the collision integral  $\Re[\bar{F}^{(N)}(x^{(N)}, t)]$  describes the collisional evolution of an assembly of  $N$  uncorrelated particles which are distributed in their own  $\mu$  space, time-coarse grained over a span of collision time scale.* This idea of ensemble and its evolution holds a key to devise kinetic equations<sup>3</sup> for interacting and correlated fluids, which are irreversible and capable of producing a theory of irreversible thermodynamics. It is therefore reasonable to call the kinetic equation (5.50) *the extended Boltzmann equation for a moderately dense gas* because the density does not have to be sufficiently low as is for the case of the Boltzmann kinetic equation.

It should be emphasized that the kinetic equation (5.50) is irreversible on account of the irreversibility of the collision integral involving operator  $\mathcal{T}^{(N)}(z)$ . Moreover, this equation satisfies the  $H$  theorem and has the total energy, momentum, and particle number as collision invariants as the Boltzmann kinetic equation does. Furthermore, since its right-hand side—i.e.,  $\Re[\bar{F}^{(N)}(x^{(N)}, t)]$ —yields a density series of higher order than that of the Boltzmann kinetic equation on account of the fact that the connected cluster expansion [15] of  $\mathcal{T}^{(N)}$  yields a density series involving triple, quadruple, ··· collision events, the linear transport coefficients predicted by (5.50) are expected to be similarly density-dependent. From the standpoint of transport coefficients it extends the latter in the sense that the linear transport coefficients obtained from the collision integral  $\Re[\bar{F}^{(N)}(x^{(N)}, t)]$  are density-dependent unlike the case for the Boltzmann kinetic equation which yields first-order Chapman–Enskog transport coefficients independent of density [22]. This feature will be discussed in a later section.

<sup>2</sup>Especially, Sects. 9.4 and 9.5 of Ref. [15] for the cluster expansion of classical many-particle collision operators.

<sup>3</sup>The collision integral (5.52) incorporates for dilute gases the approximations of two distinctive ideas for evolution of the assembly (ensemble) of  $N$  particles: (1) statistical correlations of distribution functions of subsystems of the ensemble and (2) dynamical correlations of the  $N$  particles. The former is probabilistic correlations, whereas the latter is dynamical correlations confined in the intermolecular force range. We are assuming the two factors of correlations are separable in the collision integral.

Lastly, we show that the collision integral  $\Re[\bar{F}^{(N)}(x^{(N)}, t)]$  of the extended Boltzmann equation satisfies the following conditions:

**Condition 1:** If the mass, momentum, and energy density are denoted by

$$I_j = \left( m_j, m_j \mathbf{v}_j, \frac{1}{2} m_j v_j^2 : 1 \leq j \leq N \right)$$

then they give rise to summation invariants of  $\Re[\bar{F}^{(N)}]$ :

$$\int_V d\mathbf{r} \int dx^{(N)} \sum_{j=1}^N I_j \delta(\mathbf{r}_j - \mathbf{r}) \Re[\bar{F}^{(N)}(x^{(N)}, t)] = 0. \quad (5.C1)$$

**Condition 2:** There holds the positive semidefinite integral

$$-\sum_{i=1}^N \int dx_i \ln \bar{f}^{(1)}(x_i, t) \Re[\bar{F}^{(N)}(x^{(N)}, t)] \geq 0 \quad (5.C2)$$

with the equality holding at equilibrium. From this inequality follows the  $H$  theorem for the Boltzmann entropy.

**Condition 3:** The collision operator  $\Re[\bar{F}^{(N)}(x^{(N)}, t)]$  is invariant under canonical transformation. At equilibrium  $\bar{F}^{(N)} = \bar{F}_{\text{eq}}^{(N)}$  and

$$\Re[\bar{F}_{\text{eq}}^{(N)}(x^{(N)})] = 0. \quad (5.C2\text{eq})$$

We prove the aforementioned conditions are indeed true. For the purpose we first note that the collision operator  $\mathcal{T}^{(N)}$  for an  $N$ -particle system obeys the classical Lippmann–Schwinger equation [15, 16, 23]

$$\mathcal{T}^{(N)}(z) = \mathcal{L}_1^{(N)} - \mathcal{L}_1^{(N)} \mathcal{R}_0^{(N)}(z) \mathcal{T}^{(N)}(z). \quad (5.53)$$

This is the  $N$ -particle version of (5.13). The equivalent integral equation for the resolvent operator  $\mathcal{R}^{(N)}(z)$  is

$$\mathcal{R}^{(N)}(z) = \mathcal{R}_0^{(N)}(z) - \mathcal{R}_0^{(N)}(z) \mathcal{L}_1^{(N)} \mathcal{R}^{(N)}(z). \quad (5.54)$$

By using (5.46) holding between the resolvent and the collision operator the integral equation (5.54) can be written as

$$\mathcal{R}^{(N)}(z) = \mathcal{R}_0^{(N)}(z) - \mathcal{R}_0^{(N)}(z) \mathcal{T}^{(N)} \mathcal{R}_0^{(N)}(z). \quad (5.55)$$

Using this equation, the collision integral  $\Re[\bar{F}^{(N)}(x^{(N)}, t)]$  can be formally recast into the form

$$\Re[\bar{F}^{(N)}(x^{(N)}, t)] = \int dx_1^{(N-1)} (-i) \mathcal{R}_0^{(N)-1}(z) [\mathcal{R}_0^{(N)}(z) - \mathcal{R}^{(N)}(z)] \times \mathcal{R}_0^{(N)-1}(z) \bar{F}^{(N)}(x^{(N)}, t). \quad (5.56)$$

Recalling that the eigenvalue of the Liouville operators for  $\bar{F}^{(N)}(x^{(N)}, t)$  is zero because the function is in the null class, we obtain

$$\Re[\bar{F}^{(N)}] = \int dx_1^{(N-1)} \epsilon^2 \int_0^\infty dt [e^{-(\epsilon+i\mathcal{L}^{(N)})t} - e^{-(\epsilon+i\mathcal{L}_0^{(N)})t}] \bar{F}^{(N)}(x^{(N)}, t) \quad (5.57)$$

for which we have made use of the integral representations for the resolvent operators

$$\mathcal{R}^{(N)}(z) = i \int_0^\infty dt e^{-(\epsilon+i\mathcal{L}^{(N)})t}, \quad (5.58)$$

$$\mathcal{R}_0^{(N)}(z) = i \int_0^\infty dt e^{-(\epsilon+i\mathcal{L}_0^{(N)})t}. \quad (5.59)$$

If we let the asterisk on the phases stand for the post-collision value, then the post-collision value of distribution function  $\bar{F}^{(N)}(x^{(N)}, t)$  may be written as

$$\bar{F}^{(N)*}(x^{(N)*}, t) = \prod_{j=1}^N \bar{f}^{(1)*}(x_j^*, t) = \epsilon \int_0^\infty dt e^{-(\epsilon+i\mathcal{L}^{(N)})t} \prod_{j=1}^N \bar{f}^{(1)}(x_j, t). \quad (5.60)$$

Here the phases  $x_j$  are turned into the post collision value  $x_j^*$  by the propagator  $e^{-(\epsilon+i\mathcal{L}^{(N)})t}$ . On the other hand, in the case of the free propagator  $e^{-(\epsilon+i\mathcal{L}_0^{(N)})t}$  it leaves the phases of the operand essentially unchanged, so that the distribution function remains unchanged from the pre-collision value:

$$\bar{F}^{(N)}(x^{(N)}, t) = \epsilon \int_0^\infty dt e^{-(\epsilon+i\mathcal{L}_0^{(N)})t} \prod_{j=1}^N \bar{f}^{(1)}(x_j, t). \quad (5.61)$$

If this notation is adopted and made use of, the collision integral  $\Re[\bar{F}^{(N)}]$  finally can be written in the form

$$\Re[\bar{F}^{(N)}(x^{(N)}, t)] = \epsilon \int dx_1^{(N-1)} [\bar{F}^{(N)*}(x^{(N)*}, t) - \bar{F}^{(N)}(x^{(N)}, t)]. \quad (5.62)$$

Now let the density of kinetic energy be denoted by

$$E = \sum_{j=1}^N \frac{1}{2} m_j v_j^2 \delta(\mathbf{r}_j - \mathbf{r}). \quad (5.63)$$

Then

$$\begin{aligned}
I_E &:= \int_V d\mathbf{r} \int dx_1 \sum_{j=1}^N \frac{1}{2} m_j v_j^2 \delta(\mathbf{r}_j - \mathbf{r}) \Re \left[ \bar{F}^{(N)}(x^{(N)}, t) \right] \\
&= \epsilon \int_V d\mathbf{r} \int dx_1 \int dx_1^{(N-1)} \sum_{k=1}^N \frac{1}{2} m_k v_k^2 \delta(\mathbf{r}_k - \mathbf{r}) \times \\
&\quad \left[ \bar{F}^{(N)*}(x^{(N)*}, t) - \bar{F}^{(N)}(x^{(N)}, t) \right] \\
&= \epsilon \int dx^{(N)} \sum_{k=1}^N \frac{1}{2} m_k v_k^2 \left[ \bar{F}^{(N)*}(x^{(N)*}, t) - \bar{F}^{(N)}(x^{(N)}, t) \right].
\end{aligned}$$

On reversing the collision process this integral can be written as

$$I_E = \epsilon \int dx^{*(N)} \sum_{k=1}^N \frac{1}{2} m_k v_k^{*2} \left[ \bar{F}^{(N)}(x^{(N)}, t) - \bar{F}^{(N)*}(x^{(N)*}, t) \right] \quad (5.64)$$

but since the phase volume remains invariant over the collision there holds

$$dx^{*(N)} = dx^{(N)} \quad (5.65)$$

and we obtain

$$I_E = -\epsilon \int dx^{(N)} \sum_{k=1}^N \frac{1}{2} m_k v_k^{*2} \left[ \bar{F}^{(N)*}(x^{(N)*}, t) - \bar{F}^{(N)}(x^{(N)}, t) \right]. \quad (5.66)$$

Adding (5.65) and (5.66), we finally obtain

$$\begin{aligned}
I_E &= \frac{1}{2} \epsilon \int dx^{(N)} \sum_{k=1}^N \left( \frac{1}{2} m_k v_k^2 - \frac{1}{2} m_k v_k^{*2} \right) \times \\
&\quad \left[ \bar{F}^{(N)*}(x^{(N)*}, t) - \bar{F}^{(N)}(x^{(N)}, t) \right].
\end{aligned} \quad (5.67)$$

Since the energy of the  $N$ -particle assembly also remains constant before and at the end of the collision process, we have

$$\sum_{k=1}^N \frac{1}{2} m_k v_k^2 = \sum_{k=1}^N \frac{1}{2} m_k v_k^{*2}$$

and hence

$$I_E = 0. \quad (5.68)$$

This proves Condition (5.C1) for energy. For other conserved quantities the condition can be proved similarly.

As for Condition (5.C2), if a similar procedure leading to (5.68) is applied to the integral

$$I_L := - \sum_{i=1}^N \int dx_i \ln \bar{f}^{(1)}(x_i, t) \Re \left[ \bar{F}^{(N)}(x^{(N)}, t) \right],$$

then  $I_L$  can be put in the form

$$\begin{aligned} I_L &= - \int dx^{(N)} \ln \left[ \frac{\bar{F}^{(N)}(x^{(N)}, t)}{\bar{F}^{(N)*}(x^{(N)*}, t)} \right] \left[ \bar{F}^{(N)*}(x^{(N)*}, t) - \bar{F}^{(N)}(x^{(N)}, t) \right] \\ &\geq 0 \end{aligned} \quad (5.69)$$

which is always positive.

Therefore Condition (5.C2) is proved. Condition (5.C2eq) follows from this, since at equilibrium

$$\bar{F}_{\text{eq}}^{(N)*}(x^{(N)*}) = \bar{F}_{\text{eq}}^{(N)}(x^{(N)}). \quad (5.70)$$

On the basis of the discussion presented above, the extended Boltzmann kinetic equation (5.50) allows the following interpretation: *an isolated group of uncorrelated (statistically independent) monatomic particles of N, which can be arbitrarily large as possible, forms an ensemble of completely uncorrelated particles that evolves from the initial to the final state according to the dictate of the collision operator  $\mathcal{T}^{(N)}(z)$  operating on  $\bar{F}^{(N)}$ , and such a collisional evolution is a source of irreversible evolution of a singlet distribution function  $\bar{f}(\mathbf{x}_i, t)$  on the left of the kinetic equation (5.50).* In particular, the collision term of (5.50) mimics an evolving ensemble of subsystems described by as-yet-undetermined singlet distribution functions, which will reach an equilibrium among the subsystems at the completion of their collision processes dictated by operator  $\mathcal{T}^{(N)}(z)$ . Thus, if the ensemble is immersed in a heat bath of temperature  $T$ , we have in our hand a situation mimicking Gibbs ensemble theory situation except that a dynamical collision operator  $\mathcal{T}^{(N)}(z)$  replaces the step in the Gibbs equilibrium ensemble theory by which the isolated supersystem is allowed to reach equilibrium with the heat reservoir and, at the same time, the subsystems in the ensemble reach equilibrium between themselves by some unspecified means of interaction [24–26].

It should be noted that the original formulation of the Gibbs equilibrium ensemble theory such a collision operator is absent, but the supersystem (i.e. the assembly) reaches equilibrium somehow by letting the subsystems exchange heat (energy) by unspecified means, except that the subsystems are constrained to a fixed total energy, volume, and number of particles. By introducing the  $N$ -particle collision operator into the collision integral, we are explicitly specifying the energy exchange mechanism according to the collision dynamics—an aspect left unspecified in the equilibrium Gibbs ensemble theory.

We will show later that since the collision operator  $\mathcal{T}^{(N)}(z)$  admits collision invariants it is possible to ascertain that the equilibrium solution  $\bar{f}_{\text{eq}}(x)$  of (5.50) is Maxwellian in the case of the subsystems of the ensemble, each of which is made up of a single particle. The existence of such equilibrium solution owes to Condition (5.C2), namely, the  $H$  theorem, and (5.50) consequently is irreversible.

By the example demonstrated here, we have shown the Boltzmann equation can serve as a rather suggestive prototype of irreversible kinetic equations for subsystem distribution functions of an ensemble of representative systems. The irreversible kinetic equation (5.50) is, however, not an equation that can be derived from the laws of mechanics alone—e.g., Newtonian laws of mechanics or quantum equations of motion—the Schrödinger equations. It requires something extra-mechanical as is the case for the Boltzmann equation. The discussion presented here clearly points the direction in which the development of kinetic theory of irreversible processes should be taken for dense gases and liquids.

## 5.2 Cluster Expansion of the $N$ -Particle Collision Operator

For  $N$ -particle the collision operator  $\mathcal{T}^{(N)}$  obeys the classical Lippmann–Schwinger integral equation [15] for  $N$  particles, similar to (5.4)

$$\mathcal{T}^{(N)}(z) = \mathcal{L}_1^{(N)} - \mathcal{L}_1^{(N)} \mathcal{R}_0^{(N)}(z) \mathcal{T}^{(N)}(z). \quad (5.71)$$

Here  $\mathcal{L}_1^{(N)}$  is the interaction Liouville operator

$$\begin{aligned} \mathcal{L}_1^{(N)} &= \sum_{j < k}^N \mathcal{L}_{jk} \\ &= -i \sum_{j < k}^N \mathbf{F}_{jk} \cdot \left( \frac{\partial}{\partial \mathbf{p}_j} - \frac{\partial}{\partial \mathbf{p}_k} \right) \quad \left( \mathbf{F}_{jk} = -\frac{\partial U_{jk}}{\partial \mathbf{r}_{jk}} \right) \end{aligned} \quad (5.72)$$

and  $\mathcal{R}_0^{(N)}(z)$  is the free resolvent operator

$$\mathcal{R}_0^{(N)}(z) = \left( \mathcal{L}_0^{(N)} - z \right)^{-1} \quad (5.73)$$

with  $\mathcal{L}_0^{(N)}$  denoting the  $N$ -particle free Liouville operator

$$\mathcal{L}_0^{(N)} = -i \sum_{j=1}^N \mathbf{v}_j \cdot \frac{\partial}{\partial \mathbf{r}_j}. \quad (5.74)$$

Let us define binary collision operator  $\mathcal{T}_{jk}$  for two interacting particles  $j$  and  $k$  imbedded in  $N - 2$  noninteracting spectator particles. This operator obeys the integral equation

$$\mathcal{T}_{jk}(z) = \mathcal{L}_{jk} - \mathcal{L}_{jk}\mathcal{R}_0^{(N)}(z) \quad \mathcal{T}_{jk}(z) = \mathcal{L}_{jk} - \mathcal{T}_{jk}(z)\mathcal{R}_0^{(N)}(z)\mathcal{L}_{jk}. \quad (5.75)$$

Then it is formally solved by

$$\mathcal{T}_{jk}(z) = (1 + \mathcal{L}_{jk}\mathcal{R}_0)^{-1}\mathcal{L}_{jk}. \quad (5.76)$$

Now define subcollision operator  $\mathcal{T}_N^{(\alpha)}$  for particle pair  $\alpha$  by the equation

$$\mathcal{T}_N^{(\alpha)} = \mathcal{L}_\alpha - \mathcal{L}_\alpha\mathcal{R}_0^{(N)}(z)\mathcal{T}^{(N)}(z), \quad (5.77)$$

where  $\alpha$  denotes a pair of particles, e.g.,  $(j, k)$ . It should be noted that pairs  $\alpha$  are not isolated. There are  $\frac{1}{2}N(N - 1)$  independent pairs for  $N$  particles. This means that  $\mathcal{T}^{(N)}$  is decomposable into  $\frac{1}{2}N(N - 1)$  groups of  $\mathcal{T}_N^{(\alpha)}$ :

$$\mathcal{T}^{(N)} = \sum_{j < k N}^N \mathcal{T}_N^{(jk)} := \sum_\alpha \mathcal{T}_N^{(\alpha)}. \quad (5.78)$$

On substituting (5.78) into the right hand side of (5.77) and making use of (5.76), the interaction Liouville operator  $\mathcal{L}_{jk}$  can be removed from (5.77), and we finally obtain coupled integral equations

$$\mathcal{T}_N^{(\alpha)} = \mathcal{T}_\alpha - \sum_{\alpha \neq \beta} \mathcal{T}_\alpha \mathcal{R}_0^{(N)} \mathcal{T}_N^{(\beta)}. \quad (5.79)$$

When solved iteratively, this set of equations produces a binary collision expansion for  $\mathcal{T}^{(N)}$ . The so-generated binary collision expansion, however, contains disconnected clusters, which give rise to divergences.<sup>4</sup> This means that the binary collision expansion for  $N > 3$  is not appropriate to use many-particle systems if  $N > 3$ . This difficulty is remedied by expanding  $\mathcal{T}^{(N)}$  in terms of collision operators of connected

<sup>4</sup>This point was discovered by L.D. Faddeev, who proposed the well-known quantum theory of three-body scattering [27]. He found that after three iterations of Eq. (5.79) the disconnected diagrams disappear and the integral kernel becomes completely continuous and that the iterative solution of the three-body collision operator becomes free from divergence-causing terms. Later, Yakubovskii [28] generalized the Faddeev theory to many-particle collisions. The present classical theory is an adaptation of the quantum theory to the classical formalism using the Liouville equation of  $N$  particles [15]. This adaptation is legitimate because the Faddeev theory can be formulated with the Liouville-von Neumann equation—the quantum version of the classical Liouville equation and then the classical limit of the results of the theory may be taken to obtain the classical theory of collisions.

clusters. Such an expansion is assured if the equation for  $\mathcal{T}_N^{(\alpha)}$  is recast into the form of integral equations [15]

$$\begin{aligned} \mathcal{T}_N^{(jk)} &= \sum_{s=1}^{N-1} \frac{1}{s} \sum_{\{C_s\}}^{(N)} \delta(jk; C_1, C_2, \dots, C_s) \mathcal{T}_{C_1, C_2, \dots, C_s}^{(jk)} \\ &\quad - \frac{1}{2} \sum_{\{C_{s'}, C_{s''}\}} \delta(jk; s', s'') \mathcal{T}_{C_1, C_2}^{(jk)} \mathcal{R}_0^{(N)} \sum_{(s's'') \neq (jk)} \mathcal{T}_N^{(s's'')}, \end{aligned} \quad (5.80)$$

which makes up the full  $\mathcal{T}^{(N)}$  operator for  $N$  particles:

$$\mathcal{T}^{(N)} = \sum_{i < j}^N \mathcal{T}_N^{(jk)}. \quad (5.81)$$

Here  $\{C_s\}$  stands for all the possible partitions of  $N$  particles into clusters  $(C_1)(C_2) \cdots (C_s)$  such that particles  $j$  and  $k$  appear in the same cluster  $C_i$ ,  $1 \leq j \leq s$ . Symbol  $\{C_{s'}, C_{s''}\}$  means all possible two-cluster sets formed by partition of the  $N$  particle system such that the particles  $j$  and  $k$  are contained in the same cluster either  $C_{s'}$  or  $C_{s''}$ . The sum over  $(s's'')$  runs over all pairs of particles, one belonging to  $C_{s'}$  and the other to  $C_{s''}$ . The Kronecker delta denotes

$$\delta(jk; C_1, C_2, \dots, C_s) = \begin{cases} 1 & \text{if } jk \in C_1 \text{ or } C_2, \dots, \text{ or } C_s \\ 0 & \text{otherwise} \end{cases}. \quad (5.82)$$

Expansion (5.80) is proved inductively in Chap. 9 of Ref. [15]. It gives rise to a divergence-free expansion of  $\mathcal{T}_N^{(jk)}$  in binary collision operators  $\mathcal{T}_{kl}$  ( $1 \leq k \neq l \leq N$ ).

The collision operator appearing in the collision term of the kinetic equation (5.50) should be understood and calculated according to the expansion (5.80). To show this point, it is useful to illustrate the cluster expansion for a single-component fluid. In that case, the cluster expansion of the collision term of the kinetic equation (5.50) is given by

$$\begin{aligned} \mathcal{T}^{(N)} &= \sum_{i=1}^N \sum_{j>i}^N \mathcal{T}_{ij} + \sum_{1=i < j < k}^N \mathcal{T}_{ijk} + \sum_{1=i < j < k < l}^N \mathcal{T}_{ijkl} \cdots + \mathcal{T}_{12\dots N} \\ &\quad + \sum_{1=i < j < k < l} \mathcal{T}_{ij;kl} + \cdots, \end{aligned} \quad (5.83)$$

where  $\mathcal{T}_{ij}$ ,  $\mathcal{T}_{ijk}$ , etc. are two-particle, three-particle connected cluster operators, etc. whereas  $\mathcal{T}_{ij;kl}, \dots$ , are the disconnected cluster collision operator of disconnected particle pair  $(ij; kl)$ , etc. Substitution of expansion (5.83) into the collision integral  $\Re [\bar{F}^{(N)}]$  in (5.50) yields the expansion consisting of connected clusters only:

$$\begin{aligned} \Re \left[ \bar{F}^{(N)} \right] = & \int dx_1^{(N-1)} (-i) \sum_{i=1}^N \sum_{j>i}^N T_{ij} \bar{F}^{(N)}(x^{(N)}, t) \\ & + \int dx_1^{(N-1)} (-i) \sum_{i=1}^N \sum_{1=i < j < k}^N T_{ijk} \bar{F}^{(N)}(x^{(N)}, t) + \dots \end{aligned} \quad (5.84)$$

In fact, when we implement the theory in the study of transport processes we would be working with integrals of the form

$$I_h = \int dx_1^{(N)} h(x_1^{(N)}) \Re \left[ \bar{F}^{(N)} \right], \quad (5.85)$$

where  $h(x_1^{(N)})$  is a function of  $x_1^{(N)}$ . On substitution of the expansion of  $\Re \left[ \bar{F}^{(N)} \right]$  in (5.84) into (5.85) the integral  $I_h$  is expressible in its cluster expansion as below:

$$\begin{aligned} I_h = & \int dx^{(N)} h(x_1^{(N)}) (-i) \sum_{j=1}^N \sum_{k>j}^N T_{jk} \bar{F}^{(N)}(x^{(N)}, t) \\ & + \int dx^{(N)} h(x_1^{(N)}) (-i) \sum_{1=j < k < l}^N T_{jkl} \bar{F}^{(N)}(x^{(N)}, t) + \dots \end{aligned} \quad (5.86)$$

Note that  $dx^{(N)} = dx_1^{(N)} dx_1^{(N-1)}$ .

Because the particles are identical, the binary collision term, namely, the first term on the right of (5.86) contributes  $\frac{1}{2}N(N-1) \approx \frac{1}{2}N^2$  equivalent terms, whereas the three-body collision term, namely, the second term on the right, contributes  $\frac{1}{3!}N(N-1)(N-2) \approx \frac{1}{6}N^3$ , etc. It should be emphasized here that the expansion (5.86) contains only connected clusters which are free from divergence-causing terms. Symbolically, the density series of  $T_N$  may be expressed as follows:

$$T^{(N)} = \frac{1}{2}N^2 T_{12} + \frac{1}{6}N^3 T_{123} + \dots \quad (5.87)$$

where  $T_{12}$  is the binary collision operator of particle pair (12) and  $T_{123}$  the three connected particle cluster (123), etc. Therefore the integral  $I_h$  is also similarly expressible. Expansion (5.87) will be referred to as a lower order example of the cluster expansion of  $T^{(N)}$ . Hence in the lowest order in density the collision operator  $T^{(N)}$  may be approximated by

$$T^{(N)} \approx \frac{1}{2}N^2 T_{12} \quad (5.88)$$

and the binary collision contribution to  $I_h$  becomes

$$I_h = \frac{1}{2} N^2 \int dx^{(N)} h\left(x_1^{(N)}\right) (-i) T_{12} \bar{F}^{(N)}(x^{(N)}, t). \quad (5.89)$$

This is the lowest order approximation for  $I_h$  in the limit of low density. In this approximation the collision integral of (5.50) evidently reduces to the collision integral of the Boltzmann equation. This result supports what we have earlier said about the relation of the collision integral  $\mathfrak{R}[\bar{F}]$  to the Boltzmann collision integral  $\mathbf{R}[f]$ .

From the illustration made above, it should be also evident that the dissipation terms in the generalized hydrodynamic equations derived from (5.50) or (5.52) would be different in their density dependence from the dissipation terms obtained from the Boltzmann equation. And this difference would result in the differences in the transport coefficients predicted by the aforementioned dissipation terms. As will be shown later, the present extended Boltzmann kinetic equation predicts a density dependence of the linear transport coefficients which arises from the density dependence of the collision operator when it is expanded into clusters of connected collision operators, whereas the linear transport coefficients predicted by the Boltzmann equation are simply density-independent in the first-order Chapman–Enskog solution.

### 5.3 Macroscopic Evolution Equations

The kinetic equation (5.50) gives rise to the same mathematical structures of thermodynamics of irreversible processes and generalized hydrodynamic equations as the Boltzmann equation, except for the parts associated with the collision integral in (5.50). The same comment applies to (5.52) for the mixture. Since we would prefer to formulate the theory of macroscopic processes for a gas mixture, the extended kinetic equation for a mixture (5.52) will be used in the following discussion on irreversible thermodynamics and attendant generalized hydrodynamics of a gas mixture. The procedure to obtain macroscopic evolution equations from (5.52) is the same as for the original Boltzmann equation, provided that statistical mechanical definitions of macroscopic variables are appropriately adjusted to the mixture. Therefore, we simply present definitions of macroscopic variables including the Boltzmann entropy, density, momentum, internal energy, and nonconserved variables compatible with the kinetic equation and their evolution equations of a mixture. On comparing the theoretical structures of the evolution equations obtained by both kinetic equations, we will be able to ascertain what we have claimed earlier regarding the identical formal theoretical structures of the irreversible thermodynamics and generalized hydrodynamics obtained by both Boltzmann and extended Boltzmann kinetic equations.

### 5.3.1 Boltzmann Entropy, Calortropy, and Relative Boltzmann Entropy

The Boltzmann entropy is given by the formula

$$S(t) = \int_V d\mathbf{r} \rho \mathcal{S}(\mathbf{r}, t) \quad (5.90)$$

with the local Boltzmann entropy density  $\mathcal{S}(\mathbf{r}, t)$  defined by

$$\rho \mathcal{S}(\mathbf{r}, t) = -k_B \sum_{a=1}^r \sum_{i=1}^{N_a} \langle [\ln \bar{f}_a(x_{ia}, t) - 1] \delta(\mathbf{r}_{ia} - \mathbf{r}) \bar{f}_a(x_{ia}, t) \rangle. \quad (5.91)$$

Here the angular brackets stand for the integral

$$\langle A \rangle = \int dx_{ia} A(x_{ia}) \quad (dx_{ia} = d\mathbf{r}_{ia} d\mathbf{p}_{ia}). \quad (5.92)$$

On differentiating (5.91) and using the extended Boltzmann equation (5.50), the balance equation for Boltzmann entropy density is obtained:

$$\frac{\partial}{\partial t} \rho \mathcal{S}(\mathbf{r}, t) = -\nabla \cdot [\mathbf{J}_s(\mathbf{r}, t) + \mathbf{u} \rho \mathcal{S}(\mathbf{r}, t)] + \sigma_{\text{ent}}(\mathbf{r}, t), \quad (5.93)$$

where the Boltzmann entropy flux  $\mathbf{J}_s(\mathbf{r}, t)$  and the Boltzmann entropy production  $\sigma_{\text{ent}}(\mathbf{r}, t)$  are respectively defined by the formulas

$$\mathbf{J}_s(\mathbf{r}, t) = -k_B \sum_{a=1}^r \sum_{i=1}^{N_a} \langle \mathbf{C}_{ia} [\ln \bar{f}_{ia}(x_{ia}, t) - 1] \delta(\mathbf{r}_{ia} - \mathbf{r}) \bar{f}_a(x_{ia}, t) \rangle, \quad (5.94)$$

$$\sigma_{\text{ent}}(\mathbf{r}, t) = -k_B \sum_{a=1}^r \sum_{i=1}^{N_a} \left\langle \ln \bar{f}_a(x_{ia}, t) \delta(\mathbf{r}_{ia} - \mathbf{r}) \Re \left[ \bar{F}^{(N)}(x^{(N)}, t) \right] \right\rangle. \quad (5.95)$$

The formal structure of the balance equation (5.93) evidently remains the same as the Boltzmann entropy balance equation derived from the Boltzmann kinetic equation, but the Boltzmann entropy production (5.95) differs from (3.73) for the Boltzmann equation in that the collision integral  $\mathbf{R}[f_a]$  is replaced by the extended Boltzmann collision integral  $\Re[\bar{F}^{(N)}]$ . Nevertheless, owing to the property (5.C2), the  $H$  theorem holds, and we find the positive semidefinite inequality for  $\sigma_{\text{ent}}(\mathbf{r}, t)$ :

$$\sigma_{\text{ent}}(\mathbf{r}, t) = -k_B \sum_{a=1}^r \sum_{i=1}^{N_a} \left\langle \ln \bar{f}_a(x_{ia}, t) \delta(\mathbf{r}_{ia} - \mathbf{r}) \Re \left[ \bar{F}^{(N)} \right] \right\rangle \geq 0. \quad (5.96)$$

The calortropy [21, 29]  $\Psi(t)$  is given by its local density  $\widehat{\Psi}(\mathbf{r}, t)$

$$\Psi(t) = \int_V d\mathbf{r} \rho \widehat{\Psi}(\mathbf{r}, t), \quad (5.97)$$

where the local calortropy density  $\widehat{\Psi}(\mathbf{r}, t)$  is defined similarly to Chap. 3:

$$\rho \widehat{\Psi}(\mathbf{r}, t) = -k_B \sum_{a=1}^r \sum_{i=1}^{N_a} \left\langle \ln \overline{f}_a^c(x_{ia}, t) \delta(\mathbf{r}_{ia} - \mathbf{r}) \overline{f}_a(x_{ia}, t) \right\rangle, \quad (5.98)$$

where  $\overline{f}_a^c(x_{ia}, t)$  is the thermodynamic branch of the distribution function  $\overline{f}_a(x_{ia}, t)$ , which may be taken in the same form as for Chap. 3 under the functional hypothesis. Since  $\overline{f}_a^c(x_{ia}, t)$  is not the same as  $\overline{f}_a(x_{ia}, t)$ , the relative Boltzmann entropy  $S_r[\overline{f}|\overline{f}^c]$  is defined by [29]

$$S = \widehat{\Psi} - S_r[\overline{f}|\overline{f}^c], \quad (5.99)$$

where  $S_r[\overline{f}|\overline{f}^c]$  is defined by the statistical mechanical formula

$$S_r[\overline{f}|\overline{f}^c] = k_B \sum_{a=1}^r \sum_{i=1}^{N_a} \left\langle \left[ \ln \overline{f}_a(x_a, t) - \ln \overline{f}_a^c(x_a, t) \right] \delta(\mathbf{r}_a - \mathbf{r}) \overline{f}_a(x_a, t) \right\rangle. \quad (5.100)$$

It can be easily shown that by the Klein inequality

$$S_r[\overline{f}|\overline{f}^c] \geq 0 \quad (5.101)$$

the equality holding only if  $\overline{f}_a = \overline{f}_a^c$ , that is, if  $\overline{f}_a^c$  is an exact solution of the kinetic equation (5.50). The relative Boltzmann entropy describes the evolution of fluctuations of  $\overline{f}_a(x_a, t)$  from the nonequilibrium canonical form  $\overline{f}_a^c(x_{ia}, t)$ . Inequality (5.101) implies that

$$S \leq \widehat{\Psi}. \quad (5.102)$$

The balance equations for  $\widehat{\Psi}$  and  $S_r[\overline{f}|\overline{f}^c]$  have the same formal structures as the corresponding balance equations by the Boltzmann kinetic equation in Chap. 3:

$$\rho \frac{d\widehat{\Psi}}{dt} = -\nabla \cdot \mathbf{J}_c + \sigma_c - k_B \sum_{a=1}^r \sum_{i=1}^{N_a} \left\langle \overline{f}_a \delta(\mathbf{r}_{ia} - \mathbf{r}) \mathcal{D}_t \ln \overline{f}_a^c \right\rangle, \quad (5.103)$$

$$\begin{aligned} \rho \frac{d}{dt} \mathcal{S}_r \left[ \overline{f} | \overline{f}^c \right] &= -\nabla \cdot \mathbf{J}_r \left[ \overline{f} | \overline{f}^c \right] + \sigma_r \left[ \overline{f} | \overline{f}^c \right] \\ &\quad - k_B \sum_{a=1}^r \sum_{i=1}^{N_a} \left\langle \overline{f}_a \delta(\mathbf{r}_{ia} - \mathbf{r}) \mathcal{D}_t \ln \overline{f}_a^c \right\rangle, \end{aligned} \quad (5.104)$$

where calortropy flux  $\mathbf{J}_c$ , calortropy production  $\sigma_c$ , relative Boltzmann entropy flux  $\mathbf{J}_r \left[ \overline{f} | \overline{f}^c \right]$ , and relative Boltzmann entropy production  $\sigma_r \left[ \overline{f} | \overline{f}^c \right]$  for moderately dense gas are defined by the statistical mechanical formulas

$$\mathbf{J}_c = -k_B \sum_{a=1}^r \sum_{i=1}^{N_a} \left\langle \mathbf{C}_{ia} \ln \overline{f}_a^c(x_{ia}, t) \delta(\mathbf{r}_{ia} - \mathbf{r}) \overline{f}_a(x_{ia}, t) \right\rangle, \quad (5.105)$$

$$\sigma_c = -k_B \sum_{a=1}^r \sum_{i=1}^{N_a} \left\langle \ln \overline{f}_a^c(x_{ia}, t) \delta(\mathbf{r}_{ia} - \mathbf{r}) \Re \left[ \overline{F}^{(N)} \right] \right\rangle, \quad (5.106)$$

$$\mathbf{J}_r \left[ \overline{f} | \overline{f}^c \right] = k_B \sum_{a=1}^r \sum_{i=1}^{N_a} \left\langle \mathbf{C}_a \ln \left( \overline{f}_a / \overline{f}_a^c \right) \delta(\mathbf{r}_{ia} - \mathbf{r}) \overline{f}_a(x_a, t) \right\rangle, \quad (5.107)$$

$$\sigma_r \left[ \overline{f} | \overline{f}^c \right] = k_B \sum_{a=1}^r \sum_{i=1}^{N_a} \left\langle \ln \left( \overline{f}_a / \overline{f}_a^c \right) \delta(\mathbf{r}_{ia} - \mathbf{r}) \Re \left[ \overline{F}^{(N)} \right] \right\rangle. \quad (5.108)$$

Although (5.103) and (5.104) as well as  $\mathbf{J}_c$  and  $\mathbf{J}_r \left[ \overline{f} | \overline{f}^c \right]$  have the same formal structure as their Boltzmann equation counterparts (3.120) and (3.295) in Chap. 3, the details of  $\sigma_c$  and  $\sigma_r \left[ \overline{f} | \overline{f}^c \right]$  are different from their Boltzmann equation counterparts because of the difference in the collision integrals; see (3.119) and (3.297).

### 5.3.2 Conservation Laws

The conserved variables, namely, density  $\rho$ , momentum  $\rho\mathbf{u}$ , and internal energy  $\rho\mathcal{E}$ , are defined by the statistical mechanical formulas

$$\rho(\mathbf{r}, t) = \sum_{a=1}^r \sum_{i=1}^{N_a} \left\langle m_a \delta(\mathbf{r}_{ia} - \mathbf{r}) \overline{f}_a(x_{ia}, t) \right\rangle, \quad (5.109)$$

$$\rho\mathbf{u}(\mathbf{r}, t) = \sum_{a=1}^r \sum_{i=1}^{N_a} \left\langle m_a \mathbf{v}_{ia} \delta(\mathbf{r}_{ia} - \mathbf{r}) \overline{f}_a(x_{ia}, t) \right\rangle, \quad (5.110)$$

$$\rho \mathcal{E}(\mathbf{r}, t) = \sum_{a=1}^r \sum_{i=1}^{N_a} \left\langle \frac{1}{2} m_a C_{ia}^2 \delta(\mathbf{r}_{ia} - \mathbf{r}) \bar{f}_a(x_{ia}, t) \right\rangle. \quad (5.111)$$

The conserved variables obey the balance equations—the conservation laws

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla \cdot \mathbf{u}, \quad (5.112)$$

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla \cdot \mathbf{P} + \rho \hat{\mathbf{F}}, \quad (5.113)$$

$$\rho \frac{d\mathcal{E}}{dt} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \hat{\mathbf{F}}_a, \quad (5.114)$$

$$\rho \frac{d\mathbf{c}_a}{dt} = -\nabla \cdot \mathbf{J}_a \quad (5.115)$$

with  $\mathbf{P}$ ,  $\mathbf{Q}$ , and  $\mathbf{J}_a$  defined by the statistical mechanical formulas

$$\mathbf{P}(\mathbf{r}, t) = \sum_{a=1}^r \sum_{i=1}^{N_a} \left\langle m_a \mathbf{C}_{ia} \mathbf{C}_{ia} \delta(\mathbf{r}_{ia} - \mathbf{r}) \bar{f}_a(x_{ia}, t) \right\rangle, \quad (5.116)$$

$$\mathbf{Q}(\mathbf{r}, t) = \sum_{a=1}^r \sum_{i=1}^{N_a} \left\langle \frac{1}{2} m_a C_{ia}^2 \mathbf{C}_{ia} \delta(\mathbf{r}_{ia} - \mathbf{r}) \bar{f}_a(x_{ia}, t) \right\rangle, \quad (5.117)$$

$$\mathbf{J}_a(\mathbf{r}, t) = \sum_{i=1}^{N_a} \left\langle m_a \mathbf{C}_{ia} \delta(\mathbf{r}_{ia} - \mathbf{r}) \bar{f}_a(x_{ia}, t) \right\rangle. \quad (5.118)$$

The balance equations (5.112)–(5.115) and definitions (5.116)–(5.118) are formally identical with their Boltzmann equation counterparts in their mathematical structure, but it should be noted that their density dependence would be different from those by the Boltzmann equation owing to the different density dependence of the distribution functions involved.

### 5.3.3 Nonconserved Variables and Their Evolution Equations

We define the generic form of the nonconserved moments  $h_{ia}^{(q)}$  in the same form as for the case of the Boltzmann equation

$$h_{ia}^{(q)} = m_a \mathbf{C}_{ia}^{(1)} \mathbf{C}_{ia}^{(2)} \cdots \mathbf{C}_{ia}^{(q)} \quad (q \geq 1). \quad (5.119)$$

Its mean value is given by the formula

$$\Phi_a^{(q)}(\mathbf{r}, t) = \rho \widehat{\Phi}_a^{(q)} = \sum_{i=1}^{N_a} \left\langle h_{ia}^{(q)} \delta(\mathbf{r}_{ia} - \mathbf{r}) \overline{f}_a(x_{ia}, t) \right\rangle. \quad (5.120)$$

The evolution equation for  $\widehat{\Phi}_a^{(q)}$  is then given by

$$\rho \frac{d \widehat{\Phi}_a^{(q)}}{dt} = -\nabla \cdot \psi_a^{(q)} + \mathcal{Z}_a^{(q)} + \Lambda_a^{(q)}, \quad (5.121)$$

where the dissipation term  $\Lambda_a^{(q)}$ , the flux of the nonconserved variable  $\psi_a^{(q)}$ , and the kinematic term  $\mathcal{Z}_a^{(q)}$  are defined by the formulas

$$\Lambda_a^{(q)}(\mathbf{r}, t) = \sum_{i=1}^{N_a} \left\langle h_{ia}^{(q)} \delta(\mathbf{r}_{ia} - \mathbf{r}) \Re \left[ \overline{F}^{(N)} \right] \right\rangle, \quad (5.122)$$

$$\psi_a^{(q)}(\mathbf{r}, t) = \sum_{i=1}^{N_a} \left\langle \mathbf{C}_{ia} h_{ia}^{(q)} \delta(\mathbf{r}_{ia} - \mathbf{r}) \overline{f}_a(x_{ia}, t) \right\rangle, \quad (5.123)$$

$$\mathcal{Z}_a^{(q)}(\mathbf{r}, t) = \sum_{i=1}^{N_a} \left\langle \overline{f}_a(x_{ia}, t) \delta(\mathbf{r}_{ia} - \mathbf{r}) \mathcal{D}_t h_{ia}^{(q)} \right\rangle, \quad (5.124)$$

with  $\mathcal{D}_t$  denoting an operator defined by

$$\mathcal{D}_t h_{ia}^{(q)} = \left( \frac{d}{dt} + \mathbf{C}_{ia} \cdot \nabla + \widehat{\mathbf{F}}_{ia} \cdot \nabla_{\mathbf{v}_{ia}} \right) h_{ia}^{(q)}. \quad (5.125)$$

Equation (5.121), despite the same formal structure as for the Boltzmann equation counterpart (3.91) of Chap. 3, is different from the latter because of the difference in the collision integral  $\Re \left[ \overline{F}^{(N)} \right]$  and the Boltzmann collision integral  $\mathbf{R} [f_a]$ , although  $\psi_a^{(q)}$  and  $\mathcal{Z}_a^{(q)}$  have formally the same structures for both cases. In Table 5.1 are listed the first four kinematic terms  $\mathcal{Z}_a^{(q)}$  representing the kinematic terms in the evolution equation for the shear stress ( $q = 1$ ), the excess normal stress ( $q = 2$ ), the heat flux ( $q = 3$ ), and the mass diffusion flux ( $q = 4$ ). Together with the conservation laws of mass, momentum, and internal energy these four evolution equations constitute the generalized hydrodynamic equations generalizing the conventional Navier–Stokes–Fourier hydrodynamic equations—the classical hydrodynamics. In Table 5.1 the meanings of the symbols used are the same as defined in Chap. 3. In particular,  $\Phi_a^{(1)} = \mathbf{P}_a - \frac{1}{3} \delta \text{Tr} \mathbf{P}_a := [\mathbf{P}_a]^{(2)}$ ;  $\Phi_a^{(2)} = \frac{1}{3} \text{Tr} \mathbf{P}_a - p_a$ ;  $\Phi_a^{(3)} = \mathbf{Q}'_a = \mathbf{Q}_a - \widehat{h}_a \mathbf{J}_a$ ; the excess heat flux over and above the heat carried by mass diffusion,  $\widehat{h}_a$  the enthalpy per unit mass of species  $a$ ;  $\Phi_a^{(4)} = \mathbf{J}_a$ . Table (5.1) shows that the kinematic terms are the same as those calculated with the Boltzmann equation. The higher-order flux  $\psi_a^{(q)}$

**Table 5.1** Four leading kinematic terms in the generalized hydrodynamic equations

Flux	$\mathcal{Z}_a^{(q)}$
$\Phi_a^{(1)}$ shear stress	$-2[\mathbf{J}_a(d_t \mathbf{u} - \widehat{\mathbf{F}}_a)]^{(2)} - 2[\Pi_a \cdot [\nabla \mathbf{u}]^{(2)}]^{(2)}$ $-2\Delta_a [\nabla \mathbf{u}]^{(2)} - \frac{2}{3}\Pi_a (\nabla \cdot \mathbf{u}) - 2\rho_a [\nabla \mathbf{u}]^{(2)}$
$\Phi_a^{(2)}$ excess normal stress	$-\frac{2}{3}\mathbf{J}_a \cdot (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) - \frac{2}{3}\Pi_a : \nabla \mathbf{u} - \frac{2}{3}\Delta_a \nabla \cdot \mathbf{u}$ $-\rho_a d_t \ln(p_a v^{5/3}) - \nabla \cdot (\mathbf{J}_a p_a / \rho_a)$
$\Phi_a^{(3)}$ heat flux	$-(d_t \mathbf{u} - \widehat{\mathbf{F}}_a) \cdot (\mathbf{P}_a - p_a \boldsymbol{\delta}) - \mathbf{Q}'_a \cdot \nabla \mathbf{u}$ $-\varphi^{(3)} : \nabla \mathbf{u} - \mathbf{J}_a d_t \widehat{h}_a - \mathbf{P}_a \cdot \nabla \widehat{h}_a$
$\Phi_a^{(4)}$ diffusion flux	$-\rho_a (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) - \mathbf{J}_a \cdot \nabla \mathbf{u}$

in the divergence term  $\nabla \cdot \psi_a^{(q)}$  is also the same as in the Boltzmann kinetic theory, and  $\varphi_a^{(3)}$  is defined by the mean value of a rank 3 tensor

$$\varphi_a^{(3)} = \sum_{i=1}^{N_a} \langle m_a \mathbf{C}_{ia} \mathbf{C}_{ia} \mathbf{C}_{ia} \delta(\mathbf{r}_{ia} - \mathbf{r}) \bar{f}_a(x_{ia}, t) \rangle. \quad (5.126)$$

It is a tensor of rank 3.

Since the linear transport coefficients are determined by the linearized dissipation term  $\Lambda_a^{(q)}$ , it is expected that the linear transport coefficients for the Boltzmann equation and the extended Boltzmann equation will be different because the density dependence of  $\Re[\bar{F}^{(N)}]$  is different from that of the Boltzmann collision integral  $\mathbf{R}[f_a]$ . Therefore the generalized hydrodynamic equations obtained from the Boltzmann and extended Boltzmann equations will be different with regard to the linear transport coefficients predicted by them. We will discuss this difference in a later section.

## 5.4 Equilibrium Solution of the Extended Boltzmann Kinetic Equation

Since Condition (5.C2) on  $\Re[\bar{F}^{(N)}]$  also holds at equilibrium, it follows that, if the equilibrium solution of the extended Boltzmann kinetic equation is denoted by  $\bar{F}_{\text{eq}}^{(N)}(x^{(N)})$ , then upon use of integration by parts we obtain the equation

$$T^{(N)} \ln \bar{F}_{\text{eq}}(x^{(N)}) = 0. \quad (5.127)$$

For this we may recall that the operator  $\mathcal{T}^{(N)}$  also obeys an integral equation in the form of (5.71) in the time-independent scattering theory formalism [15, 16] and in particular (5.43).

Equation (5.127) means that  $\ln \overline{F}_{\text{eq}}(x^{(N)})$  must be a linear combination of collision invariants of the collision operator  $\mathcal{T}^{(N)}$  for the ensemble: the total energy, momentum, and number of particles in volume  $V$ , namely, the constraints on the ensemble in the Gibbs ensemble theory; see Chap. 4. Therefore  $\overline{F}_{\text{eq}}(x^{(N)})$  may be written as

$$\overline{F}_{\text{eq}}(x^{(N)}) = \exp \left[ \alpha - \beta_e \sum_{a=1}^r \sum_{j=1}^{N_a} \frac{1}{2} m C_{ja}^2 \right]. \quad (5.128)$$

The constant factor  $\alpha$  is found upon normalizing  $\overline{F}_{\text{eq}}(x^{(N)})$  to unity:

$$e^{-\alpha} = \prod_{a=1}^r \prod_{j=1}^{N_a} \langle e^{-\frac{1}{2} \beta_e m C_{ja}^2} \rangle. \quad (5.129)$$

Therefore we see that  $\overline{F}_{\text{eq}}(x^{(N)})$  is simply a product of Maxwell velocity distribution functions.<sup>5</sup> It should be noted that this result is unique since there is no other equilibrium solution. This uniqueness of equilibrium solution is due to the  $H$  theorem. The meaning of the remaining parameter  $\beta_e$  can be obtained by appealing to the thermodynamic correspondence of equilibrium statistical mechanical quantities to the thermodynamic quantities. Since this part is completely the same as for the discussion given in Chap. 3, we will dispense with it.

## 5.5 Thermodynamics of Irreversible Processes and Hydrodynamics

Since the equilibrium solution of the extended Boltzmann equation is simply a product of Maxwell velocity distribution functions, namely, the product of the equilibrium solutions of the Boltzmann kinetic equations of different subsystems, the nonequilibrium canonical form for the extended Boltzmann equation may be preferably

<sup>5</sup>The Maxwell distribution function  $f_a(\mathbf{r}, \mathbf{p}, t)$  should be understood by its relation to time-coarse grained distribution function  $\overline{f}_a(x_{ia}, t)$  as follows:

$$\begin{aligned} f_a(\mathbf{r}, \mathbf{p}, t) &= \sum_{i=1}^{N_a} V^{-1} \int dx_{ia} \overline{f}_a(x_{ia}, t) \delta(\mathbf{r}_{ia} - \mathbf{r}) \delta(p_{ia} - \mathbf{p}) \\ &= V^{-1} \sum_{i=1}^{N_a} \overline{f}_a(\mathbf{r}, \mathbf{p}_i, t), \end{aligned}$$

where  $n_a = N_a/V$ .

assumed in a form isomorphic to that for the Boltzmann equation. Furthermore, since it has been already shown that the extended Boltzmann equation yields macroscopic variables obeying formally the same forms of evolution equations as those by the Boltzmann equation except for the dissipation terms, it is expected to produce and, it indeed does, also the same structure for the thermodynamics of irreversible processes and generalized hydrodynamic equations as by the Boltzmann kinetic equation, of course, except for the differences in the transport coefficients and their density dependences. This difference inevitably arises because the collision integrals of the Boltzmann and extended Boltzmann equations are different, one being made up of a binary collision operator  $T_{12}$  only, whereas the other is given by a many-particle collision operator  $T^{(N)}$ . This in turn implies that the dissipation terms in the evolution equations are different in their density dependence and, consequently, the energy dissipation mechanisms are evidently different as the fluid density varies for the two kinetic equations mentioned. Despite this subtle difference in the density dependence of energy dissipation, we can show that the calortropy differential have the same mathematical structure for both kinetic equations since they give rise to the same formal mathematical structures of the kinematic terms in their attendant generalized hydrodynamic equations. Therefore discussing the theory of thermodynamics of irreversible processes with the extended Boltzmann equation would be a repetition of the theory formulated for the Boltzmann equation in Chap. 3. Nevertheless, for the sake of completeness of the discourse we summarize the results for the extended Boltzmann equation trivially generalized to a gas mixture of  $r$  components.

### 5.5.1 Nonequilibrium Canonical Distribution Functions

The nonequilibrium canonical form for distribution function under the functional hypothesis is taken as

$$\bar{F}_a^{(1)c}(x_{ia}, t) = f_a^0 \exp \left[ -\beta \left( \frac{1}{2} m_a C_{ia}^2 + \sum_{q \geq 1} X_a^{(q)} h_{ia}^{(q)} - m_a \hat{\mu}_a \right) \right], \quad (5.130)$$

where  $f_a^0$  is the normalization factor

$$f_a^0 = \left\langle \exp \left[ -\beta \left( \frac{1}{2} m_a C_{ia}^2 + \sum_{q \geq 1} X_a^{(q)} h_{ia}^{(q)} - m_a \hat{\mu}_a \right) \right] \right\rangle^{-1}. \quad (5.131)$$

The exponential factor is exactly in the same form as for the Boltzmann equation. The normalization factor may be cast in the form

$$f_a^0 = 1 / \Gamma_a, \quad (5.132)$$

with  $\Gamma_a$  denoting the nonequilibrium partition function

$$\Gamma_a = \left\langle \exp \left[ -\beta \sum_{i=1}^{N_a} \left( \frac{1}{2} m_a C_{ia}^2 + \sum_{q \geq 1} X_a^{(q)} h_{ia}^{(q)} - m_a \hat{\mu}_a \right) \right] \right\rangle. \quad (5.133)$$

The nonequilibrium partition function for the  $N$ -particle system is therefore given by

$$\Gamma = \prod_{a=1}^r \Gamma_a^{N_a}. \quad (5.134)$$

The particular form taken for  $\bar{F}_a^{(1)c}(\mathbf{r}_a, \mathbf{v}_a, t)$  is partly motivated by the equilibrium distribution function (5.128). Therefore the nonequilibrium canonical form  $\bar{f}_a^{(1)c}(x_{ia}, t)$  is taken with the form

$$\bar{f}_a^{(1)c}(x_{ia}, t) = (\Gamma_a v)^{-1} \exp \left[ -\beta \left( \frac{1}{2} m_a C_{ia}^2 + \sum_{q \geq 1} X_a^{(q)} h_{ia}^{(q)} - m_a \hat{\mu}_a \right) \right]. \quad (5.135)$$

Another reason to choose (5.130) lies in the fact that the form gives rise to a formalism for irreversible thermodynamics consistent with the laws of thermodynamics. The second term in the exponent in (5.130) is the nonequilibrium contribution, which, apart from the intensive variables such as  $\beta$  and  $\hat{\mu}_a$ , carries all the information on nonequilibrium evolution of the fluid. It should be recalled that this form of nonequilibrium canonical form is identical with that for the Boltzmann equation in Chap. 3 and taken in the same spirit as for the Boltzmann equation.

### 5.5.2 Calortropy Differential

Upon inserting  $\bar{f}_a^{(1)c}(x_{ia}, t)$  into (5.103), (5.105), and (5.106) and making use of the conservation laws, the calortropy differential form—extended Gibbs relation for  $\widehat{\Psi}$ —can be shown given by

$$\begin{aligned} d_t \widehat{\Psi} &= T^{-1} d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \widehat{\mu}_a d_t \mathfrak{c}_a + \sum_{a=1}^r \sum_{q \geq 1} X_a^{(q)} d_t \widehat{\Phi}_a^{(q)} \\ &+ \mathcal{E} d_t T^{-1} + v d_t \left( \frac{p}{T} \right) - \sum_{a=1}^r \mathfrak{c}_a d_t \left( \frac{\widehat{\mu}_a}{T} \right) + \sum_{a=1}^r \sum_{q \geq 1} \widehat{\Phi}_a^{(q)} d_t \left( \frac{X_a^{(q)}}{T} \right), \end{aligned} \quad (5.136)$$

provided we set

$$k_B T \ln \Gamma = p v, \quad (5.137)$$

where  $p$  is a macroscopic observable, which will turn out to be the nonequilibrium pressure when the resulting calortropy differential is corresponded to its thermodynamic equivalent, namely, the thermodynamic calortropy differential as shown below. Now, if (5.137) is substituted into (5.133) and the resulting expression is varied with respect to the intensive variables, we obtain the equation

$$\mathcal{E} d_t T^{-1} + v d_t \left( \frac{p}{T} \right) - \sum_{a=1}^r \mathfrak{c}_a d_t \left( \frac{\hat{\mu}_a}{T} \right) + \sum_{a=1}^r \sum_{q \geq 1} \hat{\Phi}_a^{(q)} d_t \left( \frac{X_a^{(q)}}{T} \right) = 0, \quad (5.138)$$

which is the nonequilibrium Gibbs–Duhem (NGD) equation. We note that the NGD equation (5.138) can be cast into the form

$$\hat{\Psi} d_t T + \sum_{a=1}^r \mathfrak{c}_a d_t \hat{\mu}_a - v d_t p - \sum_{a=1}^r \sum_{q \geq 1} \hat{\Phi}_a^{(q)} d_t X_a^{(q)} = 0. \quad (5.139)$$

Equation (5.136) then gives rise to the extended Gibbs relation for  $\hat{\Psi}$ :

$$d_t \hat{\Psi} = T^{-1} d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t \mathfrak{c}_a + \sum_{a=1}^r \sum_{q \geq 1} X_a^{(q)} d_t \hat{\Phi}_a^{(q)}. \quad (5.140)$$

In other words, the nonequilibrium Gibbs–Duhem equation (5.138) is the integrability condition [30] for the extended Gibbs relation (5.140)—namely, a Pfaffian differential form. Indeed, if the nonequilibrium canonical form  $\overline{f}_a^c(\mathbf{r}, \mathbf{v}_a, t)$  is inserted into (5.98), we obtain, apart from a constant which may be set equal to zero, the calortropy density

$$\hat{\Psi} = T^{-1} \mathcal{E} + p v - \sum_{a=1}^r \hat{\mu}_a \mathfrak{c}_a + \sum_{a=1}^r \sum_{q \geq 1} X_a^{(q)} \hat{\Phi}_a^{(q)}, \quad (5.141)$$

provided (5.137) holds. On the other hand, in the phenomenological theory approach, if (5.140) and (5.138) are added side by side, the integral (5.141) of the Pfaffian differential form (5.140) arises in a bilinear form in manifold  $\mathfrak{P} \cup \mathfrak{T}$ .

By this, it is therefore fully demonstrated that the calortropy balance equation is integrable to an integral in manifold  $\mathfrak{P} \cup \mathfrak{T} \cup \Psi$ , and the nonequilibrium Gibbs–Duhem equation is the integrability condition for (5.140). On the other hand, the Boltzmann entropy balance equation cannot give rise to an exact differential form in manifold  $\mathfrak{P} \cup \mathfrak{T}$  that can be integrated to an integral in bilinear form in  $\mathfrak{P} \cup \mathfrak{T} \cup \mathcal{S}$ . For this reason there is no underlying mathematical structure of thermodynamics of

irreversible processes possible to obtain for the Boltzmann entropy in contrast to the calortropy. This is the reason we have introduced the concept of calortropy.

The differential forms (5.140) and (5.138) are supported by the attendant generalized hydrodynamic equations summarized below:

$$\begin{aligned}\rho \frac{dv}{dt} &= \nabla \cdot \mathbf{u}, \\ \rho \frac{dc_a}{dt} &= -\nabla \cdot \mathbf{J}_a, \\ \rho \frac{d\mathbf{u}}{dt} &= -\nabla \cdot \mathbf{P} + \rho \hat{\mathbf{F}}, \\ \rho \frac{d\mathcal{E}}{dt} &= -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \hat{\mathbf{F}}_a,\end{aligned}\quad (5.142)$$

for the conservation laws, and for nonconserved variables by the evolution equations

$$\rho \frac{d\hat{\Phi}_a^{(q)}}{dt} = -\nabla \cdot \psi_a^{(q)} + \mathcal{Z}_a^{(q)} + \Lambda_a^{(q)} \quad (s \geq 1, a = 1, \dots, r), \quad (5.143)$$

for which  $\psi_a^{(q)}$ ,  $\mathcal{Z}_a^{(q)}$ , and  $\Lambda_a^{(q)}$  are already given; see Table 5.1. The collision bracket integrals in the linear transport coefficients, which are obtained by linearizing the dissipation terms  $\Lambda_a^{(q)}$ , have different density dependences than those by the Boltzmann kinetic equation as mentioned earlier in connection with the density dependence of dissipation terms. However, the difference in density dependence of the dissipation terms or the linear transport coefficients, interestingly, would not affect the structure of the thermodynamic theory of irreversible processes, as is evident from the derivation of the extended Gibbs relation for the calortropy density. Therefore the thermodynamics of irreversible processes remains the same as for both the Boltzmann and extended Boltzmann kinetic equations.

### 5.5.3 Thermodynamic Correspondence

At this point in the development of the theory the parameters such as  $\beta$  (or  $1/k_B T$ ),  $\hat{\mu}_a$ ,  $p$ ,  $X_a^{(q)} \in \mathfrak{T}$  in the postulated nonequilibrium canonical form are merely mathematical symbols, which appear as conjugate variables to the observables  $\mathcal{E}$ ,  $v$ ,  $c_a$ ,  $\Phi_a^{(q)} \in \mathfrak{P}$  in the extended Gibbs relation. They have as yet no physical (or thermodynamic) meanings as they stand in the differential forms (5.136) and (5.138). They would be endowed thermodynamic meanings by making the statistical mechanical calortropy correspond to the thermodynamic calortropy deduced from the laws of thermodynamics. The thermodynamic calortropy has been deduced from the laws of thermodynamics in Chap. 2, which has been shown to obey an exact differential

form in manifold  $\mathfrak{P} \cup \mathfrak{T}$ . By making thermodynamic correspondence between statistical mechanical (st) and thermodynamic (th) observables of differential forms of calortropy

$$\begin{aligned}\widehat{\Psi}|_{\text{st}} &\Leftrightarrow \widehat{\Psi}|_{\text{th}}, & \mathcal{E}|_{\text{st}} &\Leftrightarrow \mathcal{E}|_{\text{th}}, & v|_{\text{st}} &\Leftrightarrow v|_{\text{th}}, \\ \mathfrak{c}_a|_{\text{st}} &\Leftrightarrow \mathfrak{c}_a|_{\text{th}}, & \Phi_a^{(q)}|_{\text{st}} &\Leftrightarrow \Phi_a^{(q)}|_{\text{th}},\end{aligned}\quad (5.144)$$

we necessarily arrive at the correspondences between the intensive variables (parameters) in manifold  $\mathfrak{T}$ :

$$T|_{\text{st}} \Leftrightarrow T|_{\text{th}}, \quad p|_{\text{st}} \Leftrightarrow p|_{\text{th}}, \quad \mu_a|_{\text{st}} \Leftrightarrow \mu_a|_{\text{th}}, \quad X_a^{(q)}|_{\text{st}} \Leftrightarrow X_a^{(q)}|_{\text{th}}. \quad (5.145)$$

By these correspondences the differential forms (5.136) and (5.138) are endowed the thermodynamic meanings and status, and therewith we are now able to formulate a theory of irreversible transport processes. In other words, as the Boltzmann kinetic equation does for dilute gases, the extended Boltzmann equation for moderately dense gases provides statistical mechanical foundations for a theory of irreversible transport processes for moderately dense gases and the generalized hydrodynamic equations thereof, thanks to the extended Gibbs relation permitting the thermodynamic correspondences.

#### 5.5.4 Nonequilibrium Statistical Thermodynamics of Irreversible Processes

Since we are now equipped with the nonequilibrium partition function and the extended Gibbs relation it is now possible to formulate nonequilibrium statistical thermodynamics as we have done in Chap. 3. To this aim it is convenient to recast the NGD equation (5.139) into the differential form

$$d_t(pv) = \widehat{\Psi} d_t T + \sum_{a=1}^r \mathfrak{c}_a d_t \widehat{\mu}_a + pd_t v - \sum_{a=1}^r \sum_{q \geq 1} \widehat{\Phi}_a^{(q)} d_t X_a^{(q)} \quad (5.146)$$

and then observe it is a differential form for the thermodynamic potential  $p v$ . But it is also given by the nonequilibrium partition function  $k_B T \ln \Gamma$ ; see (5.137). Therefore there holds the differential form

$$d_t(k_B T \ln \Gamma) = \widehat{\Psi} d_t T + \sum_{a=1}^r \mathfrak{c}_a d_t \widehat{\mu}_a + pd_t v - \sum_{a=1}^r \sum_{q \geq 1} \widehat{\Phi}_a^{(q)} d_t X_a^{(q)}. \quad (5.147)$$

This differential form gives the thermodynamic quantities  $(\widehat{\Psi}, p, c_a, \widehat{\Phi}_a^{(q)})$  as derivatives of the nonequilibrium partition function  $\Gamma$ . We list the following basic thermodynamic derivatives of the nonequilibrium partition function:

$$\widehat{\Psi} = k_B \ln \Gamma + k_B T \left( \frac{\partial \ln \Gamma}{\partial T} \right)_{T,\mu,X}, \quad (5.148)$$

$$p = k_B T \left( \frac{\partial \ln \Gamma}{\partial v} \right)_{T,\widehat{\mu},X}, \quad (5.149)$$

$$c_a = k_B T \left( \frac{\partial \ln \Gamma}{\partial \widehat{\mu}_a} \right)_{T,v,\widehat{\mu}',X} \quad (1 \leq a \leq r), \quad (5.150)$$

$$\widehat{\Phi}_a^{(q)} = -k_B T \left( \frac{\partial \ln \Gamma}{\partial X_a^{(q)}} \right)_{T,p,\widehat{\mu},X'} \quad (1 \leq a \leq r; q \geq 1). \quad (5.151)$$

With these derivatives various nonequilibrium thermodynamic variables can be calculated from the knowledge of nonequilibrium partition function  $\Gamma$  and the foundation of formal nonequilibrium statistical thermodynamics is now in place. We have shown in Chap. 3 that  $\Gamma$  can be computed by means of a cumulant expansion method or its variation in the form of Lambert W function. Since this part of discussion would be a repetition of discussions given in Chap. 3 owing to the nonequilibrium partition function (5.133) that is exactly in the same form as for that in Chap. 3, the reader is referred to the sections in the aforementioned chapter.

### 5.5.5 Generalized Potentials

Having derived the statistical thermodynamic relations of thermodynamic observables to the nonequilibrium partition function, it is possible to calculate the thermodynamic observables in terms of molecular parameters and the variables in the thermodynamic manifold explicitly. In particular, the relation of the generalized potential  $X_a^{(q)}$  to  $\Phi_a^{(q)}$  can be calculated by using (5.151). Since the generalized hydrodynamics formalism has remained formal because of the absence of an explicit relation of  $X_a^{(q)}$  to  $\Phi_a^{(q)}$ , their explicit relation will put the formalism closer to completion. A linear approximation for their relation turns out to be sufficient for most of practical applications so far. We find their relation remains the same as for that in Chap. 3. Therefore the leading order results will be presented for the generalized potentials without going through their derivation. The relations are:

$$\Phi_a^{(q)} = -g_a^{(q)} X_a^{(q)} + O(X^2), \quad (5.152)$$

where

$$g_a^{(1)} = \frac{1}{2p_a}; \quad g_a^{(2)} = \frac{3}{2p_a}; \quad g_a^{(3)} = \frac{1}{p_a \widehat{C}_{pa} T}; \quad g_a^{(4)} = \frac{1}{\rho_a}. \quad (5.153)$$

We find the relations given in (5.152) appear to be sufficient for many cases of transport processes within the framework of generalized hydrodynamics formulated.

### 5.5.6 Calortropy Production in Cumulant Expansion

The calortropy production is first approximated by replacing  $\bar{f}_b(x_{jb}, t)$  with the nonequilibrium canonical forms  $\bar{f}_b^c(x_{jb}, t)$  given in (5.135) in the expression for  $\sigma_c$ . This approximation should be regarded as being tantamount to neglecting fluctuations of the distribution function  $\bar{f}_b(x_{jb}, t)$  from the nonequilibrium canonical form  $\bar{f}_b^c(x_{jb}, t)$ :

$$\Delta \bar{f}_b = \bar{f}_b(x_{jb}, t) - \bar{f}_b^c(x_{jb}, t). \quad (5.154)$$

In this approximation the calortropy production is given by the expression

$$\begin{aligned} \bar{\sigma}_c = - \sum_{a=1}^r \sum_{i=1}^{N_a} \int dx^{(N)} \ln \bar{f}_a^c(x_{1a}, t) \delta(\mathbf{r}_{1a} - \mathbf{r}) \times \\ \left[ \bar{f}_1^{c*}(x_{11}, t) \bar{f}_1^{c*}(x_{21}, t) \cdots \bar{f}_r^{c*}(x_{rN_r}, t) \right. \\ \left. - \bar{f}_1^c(x_{11}, t) \bar{f}_1^c(x_{21}, t) \cdots \bar{f}_r^c(x_{rN_r}, t) \right], \end{aligned} \quad (5.155)$$

where we have reduced the calortropy production as follows:

$$\bar{\sigma}_c = \sigma_c g / k_B \quad (5.156)$$

with  $g$  denoting the same scaling parameter as defined by (3.226) in Chap. 3, namely,

$$g = \frac{1}{n^2 d^2} \sqrt{\frac{m_r}{2k_B T}}. \quad (5.157)$$

If  $\epsilon$  is chosen such that

$$\sqrt{\frac{m_r}{2k_B T}} \epsilon = 1 \quad (5.158)$$

then  $g\epsilon$  becomes simply

$$g\epsilon = \frac{1}{n^2 d^2}. \quad (5.159)$$

The reduced calortropy production  $\bar{\sigma}_c$  is now dimensionless.

Now we take the exponential form for the nonequilibrium canonical distribution function

$$\bar{f}_a^c(x_{ia}, t) = \frac{1}{V\Gamma_a} \exp \left[ -\beta \left( \frac{1}{2} m_a C_{ia}^2 + \sum_{q \geq 1} X_a^{(q)} h_{ia}^{(q)} - m_a \hat{\mu}_a \right) \right], \quad (5.160)$$

$$\Gamma_a = \left\langle \exp \left[ -\beta \left( \frac{1}{2} m_a C_{ia}^2 + \sum_{q \geq 1} X_a^{(q)} h_{ia}^{(q)} - m_a \hat{\mu}_a \right) \right] \right\rangle, \quad (5.161)$$

and factorize the distribution function  $\bar{F}^{(N)}(x^{(N)}, t)$  for the system into the equilibrium distribution function  $\bar{F}_0^{(N)}$  and the nonequilibrium part. Then  $\bar{F}^{(N)}$  can be written as

$$\bar{F}^{(N)}(x^{(N)}, t) = \bar{F}_0^{(N)}(x^{(N)}) \exp \left( -\beta \sum_{a=1}^r \sum_{i=1}^{N_a} \sum_{q \geq 1} X_a^{(q)} h_{ia}^{(q)} \right), \quad (5.162)$$

where  $\bar{F}_0^{(N)}(x^{(N)})$  is defined by

$$\bar{F}_0^{(N)}(x^{(N)}) = V^{-N} \exp \left[ -\beta \sum_{a=1}^r \sum_{i=1}^{N_a} \left( \frac{1}{2} m_a C_{ia}^2 - m_a \hat{\mu}_a \right) - \ln \Gamma \right]. \quad (5.163)$$

This distribution function  $\bar{F}_0^{(N)}(x^{(N)})$  not only resembles the equilibrium distribution function  $\bar{F}_{eq}^{(N)}(x^{(N)})$  except for  $\hat{\mu}_a$  and  $\Gamma$ , but also assures convergence of the collision integral involved. The reduced calortropy production is then given by the formula

$$\bar{\sigma}_c = \frac{1}{2} \langle (\bar{X} - \bar{Y}) (e^{-\lambda Y} - e^{-\lambda X}) \rangle_{col} |_{\lambda=1}, \quad (5.164)$$

where  $\langle A \rangle_{col}$  is the abbreviation for the collision integral

$$\langle A \rangle_{col} = g\epsilon V^{-N} \int dx^{(N)} \bar{F}_0^{(N)} A \quad (5.165)$$

and  $X$ ,  $Y$ ,  $\bar{X}$ , and  $\bar{Y}$  are defined by

$$X = \sum_{a=1}^r \sum_{i=1}^{N_a} \xi_{ia} = \beta \sum_{a=1}^r \sum_{i=1}^{N_a} \sum_{q \geq 1} X_a^{(q)} h_{ia}^{(q)}, \quad (5.166)$$

$$Y = \sum_{a=1}^r \sum_{i=1}^{N_a} \xi_{ia}^* = \beta \sum_{a=1}^r \sum_{i=1}^{N_a} \sum_{q \geq 1} X_a^{(q)} h_{ia}^{(q)*}, \quad (5.167)$$

$$\bar{X} = \sum_{a=1}^r \sum_{i=1}^{N_a} \xi_{ia} \delta(\mathbf{r}_{ia} - \mathbf{r}) = \beta \sum_{a=1}^r \sum_{i=1}^{N_a} \sum_{q \geq 1} X_a^{(q)} h_{ia}^{(q)} \delta(\mathbf{r}_{ia} - \mathbf{r}), \quad (5.168)$$

$$\bar{Y} = \sum_{a=1}^r \sum_{i=1}^{N_a} \xi_{ia}^* \delta(\mathbf{r}_{ia} - \mathbf{r}) = \beta \sum_{a=1}^r \sum_{i=1}^{N_a} \sum_{q \geq 1} X_a^{(q)} h_{ia}^{(q)*} \delta(\mathbf{r}_{ia} - \mathbf{r}). \quad (5.169)$$

The reduced calortropy production  $\bar{\sigma}_c$  in (5.164) is in a form suitable for cumulant expansion. We have inserted a parameter  $\lambda$  for the purpose of bookkeeping. It will be set equal to unity upon completing the cumulant expansion process presented.

To implement the cumulant expansion we introduce

$$\mathcal{R}^{(+)}(\lambda) = \langle (\bar{X} - \bar{Y}) [\exp(-\lambda Y) - 1] \rangle_{\text{col}}, \quad (5.170)$$

$$\mathcal{R}^{(-)}(\lambda) = \langle (\bar{X} - \bar{Y}) [\exp(-\lambda X) - 1] \rangle_{\text{col}}, \quad (5.171)$$

so that  $\bar{\sigma}_c$  is expressed in the form

$$\bar{\sigma}_c = \lim_{\lambda \rightarrow 1} 2^{-1} [\mathcal{R}^{(+)}(\lambda) - \mathcal{R}^{(-)}(\lambda)]. \quad (5.172)$$

Now expanding  $\mathcal{R}^{(\pm)}(\lambda)$  in cumulants  $\kappa_l^{(\pm)}$  as follows

$$\mathcal{R}^{(\pm)}(\lambda) = \kappa \left[ \exp \left( \sum_{l=1}^{\infty} \frac{(-\lambda)^l}{l!} \kappa_l^{(\pm)} \right) - 1 \right], \quad (5.173)$$

we obtain  $\bar{\sigma}_c$  in terms of cumulants  $\kappa_l^{(\pm)}$ :

$$\bar{\sigma}_c(\lambda) = \frac{1}{2} \kappa \left\{ \exp \left[ \sum_{l=1}^{\infty} \frac{(-\lambda)^l}{l!} \kappa_l^{(+)} \right] - \exp \left[ \sum_{l=1}^{\infty} \frac{(-\lambda)^l}{l!} \kappa_l^{(-)} \right] \right\}. \quad (5.174)$$

Here  $\kappa$ ,  $\kappa_l^{(+)}$ , and  $\kappa_l^{(-)}$  are to be determined in terms of their molecular expressions.

The leading order cumulants are easily determined by expanding (5.164), (5.170), and (5.171) in power series of  $\lambda$ , and comparing the terms of like-powers of  $\lambda$  we

obtain a set of relations between cumulants and collision integrals of products of  $(\bar{X} - \bar{Y})$  and  $(X - Y)$ :

$$\kappa_1^{(+)} - \kappa_1^{(-)} = -\frac{\langle (\bar{X} - \bar{Y})(X - Y) \rangle_{\text{col}}}{\kappa}, \quad (5.175)$$

$$\kappa_1^{(+2)} - \kappa_1^{(-2)} + \kappa_2^{(+)} - \kappa_2^{(-)} = -\frac{\langle (\bar{X} - \bar{Y})(X^2 - Y^2) \rangle_{\text{col}}}{\kappa}, \quad (5.176)$$

$$\begin{aligned} \kappa_1^{(+3)} - \kappa_1^{(-3)} + 3 \left( \kappa_2^{(+)} \kappa_1^{(+)} - \kappa_2^{(-)} \kappa_1^{(-)} \right) + \kappa_3^{(+)} - \kappa_3^{(-)} \\ = -\frac{\langle (\bar{X} - \bar{Y})(X^3 - Y^3) \rangle_{\text{col}}}{\kappa}, \quad \text{etc.} \end{aligned} \quad (5.177)$$

With the definitions of basic cumulants  $\kappa, \kappa_2, \kappa_3$  by the formulas

$$\kappa = \frac{1}{\sqrt{2}} \sqrt{\langle (\bar{X} - \bar{Y})(X - Y) \rangle_{\text{col}}} \quad (5.178)$$

$$\kappa_2 = \frac{1}{2} \langle (\bar{X} - \bar{Y})(X^2 - Y^2) \rangle_{\text{col}}, \quad (5.179)$$

$$\kappa_3 = \frac{1}{2} \langle (\bar{X} - \bar{Y})(X^3 - Y^3) \rangle_{\text{col}}, \quad (5.180)$$

etc.,

it is possible to solve the set (5.175)–(5.177) systematically. We obtain the cumulants  $\kappa_l^{(\pm)}$  in terms of  $\kappa, \kappa_2, \kappa_3, \dots$ :

$$\kappa_1^{(\pm)} = \mp \kappa, \quad (5.181)$$

$$\kappa_2^{(\pm)} = \mp \frac{\kappa_2}{\kappa}, \quad (5.182)$$

$$\kappa_3^{(\pm)} = \mp \left( \frac{\kappa_3}{\kappa} + \kappa^3 \right), \quad \text{etc.} \quad (5.183)$$

With these results the leading-order cumulant expansion for  $\bar{\sigma}_c(\lambda)$  is determined in terms collision integrals of various orders.

If the cumulant expansion is limited to the first-order cumulants  $\kappa_1^{(\pm)}$  as an approximation, then the reduced calortropy production to the first-order cumulants is obtained:

$$\bar{\sigma}_c = \frac{1}{2} \kappa [e^{\lambda \kappa} - e^{-\lambda \kappa}]_{\lambda=1} = \kappa \sinh \kappa. \quad (5.184)$$

If the hyperbolic sine function is approximated to the lowest order then we obtain the lowest order approximation for  $\bar{\sigma}_c$

$$\bar{\sigma}_c = \kappa^2. \quad (5.185)$$

This will be found in the same order as for the calortropy production in the Chapman–Enskog theory [22] of the kinetic equation of interest. Therefore (5.184) still is rather highly nonlinear with respect to  $\kappa$ . Nevertheless, it would require only the information on the same transport coefficients as for the first-order Chapman–Enskog transport process—a linear-order—theory to describe highly nonlinear transport processes. This intriguing aspect will be further discussed later.

### 5.5.7 Cumulant Expansion for Dissipation Terms

Since the calortropy production is intimately related to the dissipation terms in the generalized hydrodynamic equations, it is possible to deduce the dissipation terms in the cumulant approximation used for  $\bar{\sigma}_c$ . The first-order cumulant approximant for the dissipation functions therefore can be obtained from  $\bar{\sigma}_c$ . Since  $\bar{\sigma}_c$  may be written in the form

$$\bar{\sigma}_c = \kappa^2 q_n, \quad (5.186)$$

where the nonlinear factor  $q_n$  is defined by formula given in terms of cumulants defined earlier

$$q_n = \frac{\sinh(\kappa + \kappa_2/\kappa + \kappa^3 + \dots)}{\kappa}, \quad (5.187)$$

it is straightforward to deduce the cumulant approximation for the dissipation term  $\Lambda_a^{(q)}$ : With the definition of collision bracket integrals

$$\mathbb{R}_{ab}^{(qs)} = \frac{1}{2} \beta^2 \left\langle \left( \bar{h}_{ia}^{(q)} - \bar{h}_{ia}^{(q)*} \right) \left( h_{jb}^{(s)} - h_{jb}^{(s)*} \right) \right\rangle, \quad (5.188)$$

we obtain for the dissipation term

$$\Lambda_a^{(q)} = \beta^{-1} \sum_{b=1}^r \sum_{s \geq 1} \mathbb{R}_{ab}^{(qs)} X_b^{(s)} q_n(\kappa). \quad (5.189)$$

The first-order cumulant approximation for  $\Lambda_a^{(q)}$  then follows if only the first-order cumulant  $\kappa$  is retained:

$$\Lambda_a^{(q)} = \beta^{-1} \sum_{s \geq 1} \mathbb{R}_{ab}^{(qs)} X_b^{(s)} q_n(\kappa), \quad (5.190)$$

where

$$q_n(\kappa) = \frac{\sinh \kappa}{\kappa}. \quad (5.191)$$

We will use this first-order cumulant approximant for  $\Lambda_a^{(q)}$  when nonlinear transport processes are discussed later. If the generalized potentials  $X_b^{(s)}$  are expressed by the approximation linearized with respect to  $\Phi_b^{(s)}$  as in (5.152), then the dissipation term  $\Lambda_a^{(q)}$  in (5.190) reads

$$\Lambda_a^{(q)} = -\left(\beta g_a^{(q)}\right)^{-1} \sum_{b=1}^r \sum_{s \geq 1} \mathfrak{R}_{ab}^{(qs)} \Phi_b^{(s)} q_n(\kappa), \quad (5.192)$$

where the collision bracket integral  $\mathbb{R}_{ab}^{(qs)}$  is transformed to  $\mathfrak{R}_{ab}^{(qs)}$  defined by

$$\mathfrak{R}_{ab}^{(qs)} = g_a^{(q)} \mathbb{R}_{ab}^{(qs)} g_b^{(q)}. \quad (5.193)$$

Equation (5.192) is the quasilinear form for the dissipation term appearing in the quasilinear generalized hydrodynamic equations in the following.

### 5.5.8 Quasilinear Generalized Hydrodynamic Equations

Past experience in generalized hydrodynamics finds it sufficient for many practical applications to use the results for the relation (5.152) of  $\Phi_a^{(q)}$  to  $X_a^{(q)}$  presented earlier and also the first-order cumulant approximation (5.190) for the dissipation terms  $\Lambda_a^{(q)}$ . Linearizing the kinematic terms  $\mathcal{Z}_a^{(q)}$  in the evolution equations (5.121) for  $\Phi_a^{(q)}$  with respect to the thermodynamic driving forces, we obtain quasilinear generalized hydrodynamic equations, presented below. According to the previous applications of the quasilinear generalized hydrodynamic equations derived from the Boltzmann kinetic equation in Chap. 3, they should be equally well applicable to moderately dense gases. They are summarized below. The conservation laws are:

$$\begin{aligned} \rho \frac{dv}{dt} &= \nabla \cdot \mathbf{u}, \\ \rho \frac{dc_a}{dt} &= -\nabla \cdot \mathbf{J}_a, \\ \rho \frac{d\mathbf{u}}{dt} &= -\nabla \cdot \mathbf{P} + \rho \hat{\mathbf{F}}, \\ \rho \frac{d\mathcal{E}}{dt} &= -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \hat{\mathbf{F}}_a. \end{aligned} \quad (5.194)$$

The quasilinear evolution equations for nonconserved variables are obtained by linearizing the kinematic terms in (5.143) with respect to the thermodynamic forces—namely, gradients of  $\mathbf{u}$ ,  $c_a$  or  $n_a$ ,  $v$ , and  $T$ :

$$\rho d_t \widehat{\Pi}_a = -2p_a [\nabla \mathbf{u}]^{(2)} - (g_a^{(1)} \beta)^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(11)} \Phi_b^{(1)} q_n(\kappa), \quad (5.195)$$

$$\rho d_t \widehat{\Delta}_a = -\frac{5}{3} p_a \nabla \cdot \mathbf{u} - (g_a^{(2)} \beta)^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(22)} \Phi_b^{(2)} q_n(\kappa), \quad (5.196)$$

$$\rho d_t \widehat{\mathbf{Q}}'_a = -p_a \widehat{C}_{pa} \nabla \ln T - (g_a^{(3)} \beta)^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(33)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(34)} \Phi_b^{(4)} \right) q_n(\kappa), \quad (5.197)$$

$$\rho d_t \widehat{\mathbf{J}}_a = -p \mathbf{d}_a - (g_a^{(4)} \beta)^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(43)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(44)} \Phi_b^{(4)} \right) q_n(\kappa), \quad (5.198)$$

where  $\widehat{C}_{pa}$  is the specific heat at constant pressure per unit mass of species  $a$  and  $\mathbf{d}_a$  is the driving force of mass flow. It is defined by

$$\mathbf{d}_a = \nabla \left( \frac{n_a}{n} \right) + \left( \frac{n_a}{n} - \frac{\rho_a}{\rho} \right) \nabla \ln p + \frac{\rho_a}{p} (\widehat{\mathbf{F}} - \widehat{\mathbf{F}}_a). \quad (5.199)$$

The first cumulant  $\kappa$  with the approximation for the generalized potentials given in (5.152) is now seen to be in essence a generalized form of the Rayleigh dissipation function [32]

$$\kappa = \sqrt{\sum_{a,b=1}^r \sum_{q,s \geq 1} \mathfrak{R}_{ab}^{(qs)} \Phi_a^{(q)} \odot \Phi_b^{(s)}}. \quad (5.200)$$

The symbol  $\odot$  stands for contraction of tensors to a scalar. Rayleigh originally introduced the eponymous dissipation function in connection with the energy dissipation in sound wave propagation. In the present theory  $\kappa$  is intimately associated with calortropy production which is a measure of energy dissipation in the course of irreversible processes in the fluid.

A comment is in order with regard to the quasilinear generalized hydrodynamic equations presented above. First of all, in the quasilinear approximation the divergence terms  $\nabla \cdot \psi_a^{(q)}$  in (5.143) are neglected because  $\psi_a^{(q)}$  are generally of a higher order in thermodynamic forces. Thereby, the open set of nonconserved variable evolution equations is naturally and automatically closed. Furthermore, the kinematic terms  $\mathcal{Z}_a^{(q)}$  simply consist of the thermodynamic driving force for  $\Phi_a^{(q)}$ . With so approximated  $\mathcal{Z}_a^{(q)}$  and the approximations made for the quasilinear dissipation terms as in (5.195)–(5.198), the generalized hydrodynamic equations given above indeed generalize the classical hydrodynamic equations of Navier, Stokes, Fourier, and Fick, which are recovered if the processes are steady in the moving coordinate system, namely, if  $\rho d_t \widehat{\Phi}_a^{(q)} = 0$  and  $q_n(\kappa) = 1$ . Note that

$$q_n(\kappa) = \frac{\sinh \kappa}{\kappa} \rightarrow 1, \quad (5.201)$$

as  $\kappa \rightarrow 0$ , as the system tends to equilibrium in which limit  $\Phi_a^{(q)} \rightarrow 0$ . Therefore the classical Navier–Stokes, Fourier, and Fick’s equation are recovered from the quasi-linear generalized hydrodynamic equation (5.194)–(5.198) in the neighborhood of equilibrium. Consequently, the quasilinear generalized hydrodynamic equations presented above generalize the classical hydrodynamic equations in the aforementioned sense. Further aspects of the quasilinear generalized hydrodynamic equations will be discussed in more details in Chap. 9 of this work.

### 5.5.9 Collision Bracket Integrals

The collision bracket integral (5.193) needs further consideration before it is compared with the Boltzmann equation counterpart. More explicitly written, it is given by the formula

$$\mathfrak{R}_{ab}^{(qs)} = \frac{1}{2} g_a^{(q)} g_b^{(s)} \beta^2 \left\langle \left( \bar{h}_{ia}^{(q)} - \bar{h}_{ia}^{(q)*} \right) \left( h_{jb}^{(s)} - h_{jb}^{(s)*} \right) \right\rangle_{\text{col}}. \quad (5.202)$$

Here it should be noted that the integrand in (5.202) is a tensor product since  $\bar{h}_{ia}^{(q)}$  and  $h_{jb}^{(s)}$  are tensors of rank corresponding to the moments. In the context of the approximation employed with regards to the moment set taken here they are either second rank or vector (rank 1 tensor) or scalar (rank 0). Since they are integrated (i.e., averaged) over an isotropic space owing to the fact that the distribution function  $\bar{F}_0^{(N)}$  is essentially of equilibrium, the integral in (5.202) gives rise to a completely isotropic irreducible tensor of rank 4 if  $q, s = 1$  (shear stress  $\Pi_a$ ); of rank 2 if  $q, s = 3$  or 4 (heat flux  $\mathbf{Q}'_a$  or diffusion flux  $\mathbf{J}_a$ ); of rank 0 if  $q, s = 2$  (excess normal stress) in the present order of definitions for the moments employed. Translated into the conventional terminology, the meanings of the ordering of moments are indicated in the parentheses after  $q$  or  $s$ . The collision bracket integrals for various cases are as given below:

1. shear stress  $\Pi_a, q = s = 1$ :

$$\begin{aligned} \left( \mathfrak{R}_{ab}^{(11)} \right)_{\mu\nu\eta\omega} &= \frac{1}{5} \cdot \frac{1}{2} g_a^{(1)} g_b^{(1)} \beta^2 \left\langle \left( \bar{h}_{ia}^{(1)} - \bar{h}_{ia}^{(1)*} \right) : \left( h_{jb}^{(1)} - h_{jb}^{(1)*} \right) \right\rangle_{\text{col}} \\ &\times \left[ \frac{1}{2} (\delta_{\mu\eta}\delta_{\nu\omega} + \delta_{\mu\omega}\delta_{\nu\eta}) - \frac{1}{3} \delta_{\mu\nu}\delta_{\eta\omega} \right]. \end{aligned} \quad (5.203)$$

2. excess normal stress  $\Delta_a, q = s = 2$ :

$$\mathfrak{R}_{ab}^{(22)} = \frac{1}{2} g_a^{(2)} g_b^{(2)} \beta^2 \left\langle \left( \bar{h}_{ia}^{(2)} - \bar{h}_{ia}^{(2)*} \right) \left( h_{jb}^{(2)} - h_{jb}^{(2)*} \right) \right\rangle_{\text{col}}. \quad (5.204)$$

3. heat flux  $\mathbf{Q}'_a$ ,  $q = 3$ ,  $s = 3$  or 4:

$$\begin{aligned} \left(\mathfrak{R}_{ab}^{(33)}\right)_{\mu\nu} &= \frac{1}{3} \cdot \frac{1}{2} g_a^{(3)} g_b^{(3)} \beta^2 \left\langle \left(\bar{h}_{ia}^{(3)} - \bar{h}_{ia}^{(3)*}\right) \cdot \left(h_{jb}^{(3)} - h_{jb}^{(3)*}\right) \right\rangle_{\text{col}} \delta_{\mu\nu}, \\ \left(\mathfrak{R}_{ab}^{(34)}\right)_{\mu\nu} &= \frac{1}{3} \cdot \frac{1}{2} g_a^{(3)} g_b^{(4)} \beta^2 \left\langle \left(\bar{h}_{ia}^{(3)} - \bar{h}_{ia}^{(3)*}\right) \cdot \left(h_{jb}^{(4)} - h_{jb}^{(4)*}\right) \right\rangle_{\text{col}} \delta_{\mu\nu}, \\ \left(\mathfrak{R}_{ab}^{(43)}\right)_{\mu\nu} &= \left(\mathfrak{R}_{ab}^{(34)}\right)_{\mu\nu}. \end{aligned} \quad (5.205)$$

4. diffusion flux  $\mathbf{J}_a$ ,  $q = 4$ ,  $s = 3$  or 4:

$$\begin{aligned} \left(\mathfrak{R}_{ab}^{(44)}\right)_{\mu\nu} &= \frac{1}{3} \cdot \frac{1}{2} g_a^{(4)} g_b^{(4)} \beta^2 \left\langle \left(\bar{h}_{ia}^{(4)} - \bar{h}_{ia}^{(4)*}\right) \cdot \left(h_{jb}^{(4)} - h_{jb}^{(4)*}\right) \right\rangle_{\text{col}} \delta_{\mu\nu}, \\ \left(\mathfrak{R}_{ab}^{(43)}\right)_{\mu\nu} &= \frac{1}{2} g_a^{(4)} g_b^{(3)} \beta^2 \left\langle \left(\bar{h}_{ia}^{(4)} - \bar{h}_{ia}^{(4)*}\right) \cdot \left(h_{jb}^{(3)} - h_{jb}^{(3)*}\right) \right\rangle_{\text{col}} \delta_{\mu\nu}. \end{aligned} \quad (5.206)$$

For the details of the mathematical backgrounds for these kinds of integrals involving isotropic Cartesian tensors see pp. 97–107, Chap. 5, Ref. [15] or Ref. [22].

The collision bracket integrals presented in (5.202) are integrals in the  $N$ -particle phase space, which do not manifestly display the  $N$ -particle dynamical aspect. As a matter of fact, the many-particle dynamical aspects only begin to manifest themselves when the tensor products—more precisely, contracted tensors making up the collision bracket integrals—are computed in terms of tensors of 2 particles, 3 particles … contracted over the particle field. Then we begin to see the collision bracket integral expanded in density in terms of the collision dynamics of two particles, three particles, …, etc. This aspect can become explicit and clear when the collision bracket integral is put into a equivalent form by means of the  $N$ -particle collision operator  $\mathcal{T}^{(N)}(z)$  from which (5.202) descends. The density expansion of  $\mathcal{T}^{(N)}(z)$  will be discussed in Sect. 5.6 of this chapter.

### 5.5.10 Steady Quasilinear and Linear Transport Processes

#### 5.5.10.1 Linear Transport Processes

The quasilinear generalized hydrodynamic equations (5.194)–(5.198) consist of two subsets (5.194) and (5.195)–(5.198), which evolve on two distinctive time scales, because the conserved variables  $(v, \mathbf{c}_a, \mathbf{u}, \mathcal{E})$  evolve on a much longer time scale than the nonconserved variables  $(\Pi_a, \Delta_a, \mathbf{Q}'_a, \mathbf{J}_a)$ . In other words, the latter variables relax much faster than the hydrodynamic time scale for the former. Therefore the evolution equations for the latter variables reach a steady state well before the conserved variables reach steady states. Here we would like to examine the aforementioned two subsets on hydrodynamic time scales. In such a time scale the evolution equations (5.195)–(5.198) become steady-state equations:

$$-2p_a [\nabla \mathbf{u}]^{(2)} - (g_a^{(1)} \beta)^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(11)} \Phi_b^{(1)} q_n(\kappa) = 0, \quad (5.207)$$

$$-\frac{5}{3} p_a \nabla \cdot \mathbf{u} - (g_a^{(2)} \beta)^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(22)} \Phi_b^{(2)} q_n(\kappa) = 0, \quad (5.208)$$

$$-p_a \widehat{C}_{pa} \nabla \ln T - (g_a^{(3)} \beta)^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(33)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(34)} \Phi_b^{(4)} \right) q_n(\kappa) = 0, \quad (5.209)$$

$$-p \mathbf{d}_a - (g_a^{(4)} \beta)^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(43)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(44)} \Phi_b^{(4)} \right) q_n(\kappa) = 0, \quad (5.210)$$

where we now understand collision bracket integrals  $\mathfrak{R}_{ab}^{(qs)}$  as

$$\mathfrak{R}_{ab}^{(11)} = \frac{1}{10} g_a^{(1)} g_b^{(1)} \beta^2 \left\langle \left( \bar{h}_{ia}^{(1)} - \bar{h}_{ia}^{(1)*} \right) : \left( h_{jb}^{(1)} - h_{jb}^{(1)*} \right) \right\rangle_{\text{col}}, \quad (5.211)$$

$$\mathfrak{R}_{ab}^{(22)} = \frac{1}{2} g_a^{(2)} g_b^{(2)} \beta^2 \left\langle \left( \bar{h}_{ia}^{(2)} - \bar{h}_{ia}^{(2)*} \right) \left( h_{jb}^{(2)} - h_{jb}^{(2)*} \right) \right\rangle_{\text{col}}, \quad (5.212)$$

$$\mathfrak{R}_{ab}^{(33)} = \frac{1}{6} g_a^{(3)} g_b^{(3)} \beta^2 \left\langle \left( \bar{h}_{ia}^{(3)} - \bar{h}_{ia}^{(3)*} \right) \cdot \left( h_{jb}^{(3)} - h_{jb}^{(3)*} \right) \right\rangle_{\text{col}}, \quad (5.213)$$

$$\mathfrak{R}_{ab}^{(44)} = \frac{1}{6} g_a^{(4)} g_b^{(4)} \beta^2 \left\langle \left( \bar{h}_{ia}^{(4)} - \bar{h}_{ia}^{(4)*} \right) \cdot \left( h_{jb}^{(4)} - h_{jb}^{(4)*} \right) \right\rangle_{\text{col}}, \quad (5.214)$$

$$\mathfrak{R}_{ab}^{(34)} = \mathfrak{R}_{ab}^{(43)}. \quad (5.215)$$

Equations (5.207)–(5.210) are the steady-state quasilinear constitutive equations for nonconserved variables  $(\Pi_a, \Delta_a, \mathbf{Q}'_a, \mathbf{J}_a)$ , which would become the Newton's law of viscosity, the bulk viscosity equation, the Fourier law of heat conduction, and Fick's law of diffusion in the limit in which  $\kappa$  is small, namely, in the neighborhood of equilibrium:

$$-2p_a [\nabla \mathbf{u}]^{(2)} - (g_a^{(1)} \beta)^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(11)} \Phi_b^{(1)} = 0, \quad (5.216)$$

$$-\frac{5}{3} p_a \nabla \cdot \mathbf{u} - (g_a^{(2)} \beta)^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(22)} \Phi_b^{(2)} = 0, \quad (5.217)$$

$$-p_a \widehat{C}_{pa} \nabla \ln T - (g_a^{(3)} \beta)^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(33)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(34)} \Phi_b^{(4)} \right) = 0, \quad (5.218)$$

$$-p \mathbf{d}_a - (g_a^{(4)} \beta)^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(43)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(44)} \Phi_b^{(4)} \right) = 0. \quad (5.219)$$

When the solutions for these linear equations for  $(\Phi_b^{(1)}, \Phi_b^{(2)}, \Phi_b^{(3)}, \Phi_b^{(4)}) = (\Pi_a, \Delta_a, \mathbf{Q}'_a, \mathbf{J}_a)$  are substituted into the conservation laws in (5.194) the classical hydrodynamic equations are obtained as for the case of the Boltzmann kinetic equation discussed in Chap. 3. From the aforementioned solutions of the linear constitutive equations we are able to obtain the statistical mechanical expressions for linear transport coefficients, such as shear viscosity, bulk viscosity, diffusion coefficients, etc. in completely isomorphic forms to those given in Chap. 3 except that the density dependence of the transport coefficients obtained thereby would be different from those of the first-order Chapman–Enskog results [22] for the linear transport coefficients.

The solutions of the linear constitutive equations (5.216)–(5.219) are simply the well-known laws of linear transport processes: For example, Newtonian law of viscosity

$$\Pi_a = -2\eta_a^0 [\nabla \mathbf{u}]^{(2)}; \quad (5.220)$$

the bulk viscosity law

$$\Delta_a = -\eta_{Ba}^0 \nabla \cdot \mathbf{u}, \quad (5.221)$$

where the Newtonian shear viscosity  $\eta_a^0$  and bulk viscosity  $\eta_{Ba}^0$  are given by the statistical mechanical formulas

$$\eta_a^0 = \sum_{b=1}^r 2p_b g_b^{(1)} \beta (\mathfrak{R}^{(11)})_{ab}^{-1}, \quad (5.222)$$

$$\eta_{Ba}^0 = \sum_{b=1}^r \frac{5p_b g_b^{(2)} \beta}{3} (\mathfrak{R}^{(22)})_{ab}^{-1}. \quad (5.223)$$

The Fourier law of heat conduction and Fick's law of diffusion take a little more complicated forms because the two processes are coupled with each other. Their constitutive relations (5.218) and (5.219) may be written in matrix form

$$\begin{pmatrix} \mathfrak{R}^{(33)} & \dots & \mathfrak{R}^{(34)} & \dots \\ \vdots & \ddots & \vdots & \ddots \\ \mathfrak{R}^{(43)} & \dots & \mathfrak{R}^{(44)} & \dots \\ \vdots & \ddots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \mathbf{Q}'_a \\ \vdots \\ \mathbf{J}_a \\ \vdots \end{pmatrix} = - \begin{pmatrix} p_a \widehat{C}_{pa} g_a^{(3)} \beta \nabla \ln T \\ \vdots \\ p g_a^{(4)} \beta \mathbf{d}_a \mathbf{J}_a \\ \vdots \end{pmatrix}.$$

Solving this matrix equation we obtain

$$\begin{pmatrix} \mathbf{Q}'_a \\ \vdots \\ \mathbf{J}_a \\ \vdots \end{pmatrix} = - \begin{pmatrix} \mathfrak{R}^{(33)} & \dots & \mathfrak{R}^{(34)} & \dots \\ \vdots & \ddots & \vdots & \ddots \\ \mathfrak{R}^{(43)} & \dots & \mathfrak{R}^{(44)} & \dots \\ \vdots & \ddots & \vdots & \ddots \end{pmatrix}^{-1} \begin{pmatrix} p_a \widehat{C}_{pa} g_a^{(3)} \beta \nabla \ln T \\ \vdots \\ p g_a^{(4)} \beta \mathbf{d}_a \\ \vdots \end{pmatrix}.$$

Denoting the supermatrix by

$$\mathfrak{S} := \begin{pmatrix} \mathfrak{R}^{(33)} & \dots & \mathfrak{R}^{(34)} & \dots \\ \vdots & \ddots & \vdots & \ddots \\ \mathfrak{R}^{(43)} & \dots & \mathfrak{R}^{(44)} & \dots \\ \vdots & \ddots & \vdots & \ddots \end{pmatrix}^{-1} := \begin{pmatrix} \mathfrak{S}^{(hh)} & \mathfrak{S}^{(hd)} \\ \mathfrak{S}^{(dh)} & \mathfrak{S}^{(dd)} \end{pmatrix} \quad (5.224)$$

and the corresponding column vector by

$$\begin{pmatrix} \mathfrak{h} \nabla \ln T \\ \mathfrak{d}\mathbf{d}_a \end{pmatrix} := \begin{pmatrix} \frac{p_a \hat{C}_{pa} g_a^{(3)} \beta}{\epsilon} \nabla \ln T \\ \vdots \\ \frac{p g_a^{(4)} \beta}{\epsilon} \mathbf{d}_a \\ \vdots \end{pmatrix}, \quad (5.225)$$

we obtain  $\mathbf{Q}'_a$  and  $\mathbf{J}_a$  expressed in linear combinations of column vector components of  $\mathfrak{h} \nabla \ln T$  and  $\mathfrak{d}\mathbf{d}_a$ :

$$\mathbf{Q}'_a = - \sum_b \mathfrak{S}_{ab}^{(hh)} \mathfrak{h}_b \nabla \ln T - \sum_b \mathfrak{S}_{ab}^{(hd)} \mathfrak{d}_b \mathbf{d}_b, \quad (5.226)$$

$$\mathbf{J}_a = - \sum_b \mathfrak{S}_{ab}^{(dh)} \mathfrak{h}_b \nabla \ln T - \sum_b \mathfrak{S}_{ab}^{(dd)} \mathfrak{d}_b \mathbf{d}_b. \quad (5.227)$$

These linear relations are the Fourier's law and the Fick's law. From these coupled constitutive relations, we can identify the thermal conductivity  $\lambda_{ab}^0$ , diffusive thermal conductivity  $\zeta_{ab}^0$ , thermo-diffusion coefficient  $\xi_{ab}^0$ , and diffusion coefficients  $\mathcal{D}_{ab}^0$  of the mixture:

$$\lambda_{ab}^0 = \mathfrak{S}_{ab}^{(hh)} \mathfrak{h}_b, \quad (5.228)$$

$$\zeta_{ab}^0 = \mathfrak{S}_{ab}^{(hd)} \mathfrak{d}_b, \quad (5.229)$$

$$\xi_{ab}^0 = \mathfrak{S}_{ab}^{(dh)} \mathfrak{h}_b, \quad (5.230)$$

$$\mathcal{D}_{ab}^0 = \mathfrak{S}_{ab}^{(dd)} \mathfrak{d}_b, \quad (5.231)$$

all of which are given in terms of collision bracket integrals presented earlier. Thus we have now obtained the molecular theory representations of linear transport coefficients. They coincide exactly with the first-order Chapman–Enskog theory results for transport coefficients [22].

### 5.5.10.2 Quasilinear Transport Processes

The constitutive relations for steady quasilinear transport processes described by the set (5.207)–(5.210) can be obtained by if the aforementioned set is formally solved by treating the nonlinear factor  $q_n(\kappa)$  as if it is a constant. This step simply would yield the constitutive relations

$$\Pi_a = -2\eta_a^0 q_n^{-1} [\nabla \mathbf{u}]^{(2)}, \quad (5.232)$$

$$\Delta_a = -\eta_{Ba}^0 q_n^{-1} \nabla \cdot \mathbf{u}, \quad (5.233)$$

$$\mathbf{Q}'_a = -q_n^{-1} \sum_b \lambda_{ab}^0 \nabla \ln T - q_n^{-1} \sum_b \zeta_{ab}^0 \mathbf{d}_b, \quad (5.234)$$

$$\mathbf{J}_a = -q_n^{-1} \sum_b \xi_{ab}^0 \nabla \ln T - q_n^{-1} \sum_b \mathcal{D}_{ab}^0 \mathbf{d}_b, \quad (5.235)$$

where  $\lambda_{ab}^0$ ,  $\zeta_{ab}^0$ ,  $\xi_{ab}^0$ , and  $\mathcal{D}_{ab}^0$  are given by their statistical mechanical formulas (5.228)–(5.231). Now observing that the Rayleigh dissipation function  $\kappa^2$  is a quadratic form of  $(\Pi_a, \Delta_a, \mathbf{Q}'_a, \mathbf{J}_a)$ ,

$$\begin{aligned} \kappa^2 &= \sum_{a,b} \left( \mathfrak{R}_{ab}^{(11)} \Pi_a : \Pi_b + \mathfrak{R}_{ab}^{(22)} \Delta_a \Delta_b \right) \\ &\quad + \sum_{a,b} \left( \mathfrak{R}_{ab}^{(33)} \mathbf{Q}'_a \cdot \mathbf{Q}'_b + \mathfrak{R}_{ab}^{(34)} \mathbf{Q}'_a \cdot \mathbf{J}_b \right) \\ &\quad + \sum_{a,b} \left( \mathfrak{R}_{ab}^{(43)} \mathbf{J}_a \cdot \mathbf{Q}'_b + \mathfrak{R}_{ab}^{(44)} \mathbf{J}_a \cdot \mathbf{J}_b \right), \end{aligned} \quad (5.236)$$

substitution of (5.232)–(5.235) into (5.236) yields

$$\begin{aligned} (q_n \kappa)^2 &= \sum_{a,b} \left[ 4\eta_a^{02} \mathfrak{R}_{ab}^{(11)} [\nabla \mathbf{u}]^{(2)} : [\nabla \mathbf{u}]^{(2)} + \eta_B^{02} \mathfrak{R}_{ab}^{(22)} (\nabla \cdot \mathbf{u})^2 \right] \\ &\quad + \sum_{a,b,c} \mathfrak{R}_{ab}^{(33)} \left( \mathfrak{S}_{ab}^{(hh)} \mathfrak{h}_b \nabla \ln T + \mathfrak{S}_{ab}^{(dd)} \mathfrak{d}_b \mathbf{d}_b \right) \cdot \\ &\quad \quad \left( \mathfrak{S}_{bc}^{(hh)} \mathfrak{h}_c \nabla \ln T + \mathfrak{S}_{bc}^{(hd)} \mathfrak{d}_c \mathbf{d}_c \right) \\ &\quad + \sum_{a,b,c} \mathfrak{R}_{ab}^{(34)} \left( \mathfrak{S}_{ab}^{(hh)} \mathfrak{h}_b \nabla \ln T + \mathfrak{S}_{ab}^{(hd)} \mathfrak{d}_b \mathbf{d}_b \right) \cdot \\ &\quad \quad \left( \mathfrak{S}_{bc}^{(dh)} \mathfrak{h}_c \nabla \ln T + \mathfrak{S}_{bc}^{(dd)} \mathfrak{d}_c \mathbf{d}_c \right) \\ &\quad + \sum_{a,b,c} \mathfrak{R}_{ab}^{(43)} \left( \mathfrak{S}_{ab}^{(dh)} \mathfrak{h}_b \nabla \ln T + \mathfrak{S}_{ab}^{(dd)} \mathfrak{d}_b \mathbf{d}_b \right) \cdot \\ &\quad \quad \left( \mathfrak{S}_{bc}^{(hh)} \mathfrak{h}_c \nabla \ln T + \mathfrak{S}_{bc}^{(hd)} \mathfrak{d}_c \mathbf{d}_c \right) \end{aligned}$$

$$+ \sum_{a,b,c} \mathfrak{R}_{ab}^{(44)} \left( (\mathfrak{S}_{ab}^{(dh)} \mathfrak{h}_b \nabla \ln T + \mathfrak{S}_{ab}^{(dd)} \mathfrak{d}_b \mathbf{d}_b) \cdot \right. \\ \left. (\mathfrak{S}_{bc}^{(dd)} \mathfrak{h}_b \nabla \ln T + \mathfrak{S}_{bc}^{(dd)} \mathfrak{d}_c \mathbf{d}_c) \right).$$

The right-hand side of this expression is rearranged to a quadratic form of thermodynamic gradients

$$\kappa_L^2 := \sum_{a,b} 4\eta_a^{02} \mathfrak{R}_{ab}^{(11)} [\nabla \mathbf{u}]^{(2)} : [\nabla \mathbf{u}]^{(2)} + \sum_{a,b} \eta_{Bb}^{02} \mathfrak{R}_{ab}^{(22)} (\nabla \cdot \mathbf{u})^2 \\ + \sum_{a,b,c} \mathfrak{C}_{abc}^{(TT)} \nabla \ln T \cdot \nabla \ln T + \sum_{a,b,c} \mathfrak{C}_{abc}^{(TD)} \mathbf{d}_c \cdot \nabla \ln T \\ \sum_{a,b,c} \mathfrak{C}_{abc}^{(DT)} \mathbf{d}_b \cdot \nabla \ln T + \sum_{a,b,c} \mathfrak{C}_{abc}^{(DD)} \mathbf{d}_b \cdot \mathbf{d}_c, \quad (5.237)$$

so that (5.236) can be written

$$(q_n \kappa)^2 = \kappa_L^2. \quad (5.238)$$

In (5.237) for  $\kappa_L$  the coefficients  $\mathfrak{C}_{abc}^{(TT)}$ , etc. are defined in terms of collision bracket integrals as follows:

$$\mathfrak{C}_{abc}^{(TT)} = \left[ \mathfrak{R}_{ab}^{(33)} \mathfrak{S}_{ab}^{(hh)} \mathfrak{S}_{bc}^{(hh)} + \mathfrak{R}_{ab}^{(34)} \left( \mathfrak{S}_{ab}^{(hh)} \mathfrak{S}_{bc}^{(dh)} + \mathfrak{S}_{ab}^{(dh)} \mathfrak{S}_{bc}^{(hh)} \right) \right. \\ \left. + \mathfrak{R}_{ab}^{(44)} \mathfrak{S}_{ab}^{(dh)} \mathfrak{S}_{bc}^{(dd)} \right] \mathfrak{h}_b \mathfrak{h}_b, \quad (5.239)$$

$$\mathfrak{C}_{abc}^{(TD)} = \left[ \mathfrak{R}_{ab}^{(33)} \mathfrak{S}_{ab}^{(hh)} \mathfrak{S}_{bc}^{(hd)} + \mathfrak{R}_{ab}^{(34)} \left( \mathfrak{S}_{ab}^{(hh)} \mathfrak{S}_{bc}^{(dd)} + \mathfrak{S}_{ab}^{(dh)} \mathfrak{S}_{bc}^{(hd)} \right) \right. \\ \left. + \mathfrak{R}_{ab}^{(44)} \mathfrak{S}_{ab}^{(dh)} \mathfrak{S}_{bc}^{(dd)} \right] \mathfrak{h}_b \mathfrak{d}_c, \quad (5.240)$$

$$\mathfrak{C}_{abc}^{(DT)} = \left[ \mathfrak{R}_{ab}^{(33)} \mathfrak{S}_{ab}^{(dd)} \mathfrak{S}_{bc}^{(dh)} + \mathfrak{R}_{ab}^{(34)} \left( \mathfrak{S}_{ab}^{(hd)} \mathfrak{S}_{bc}^{(dh)} + \mathfrak{S}_{ab}^{(dd)} \mathfrak{S}_{bc}^{(hh)} \right) \right. \\ \left. + \mathfrak{R}_{ab}^{(44)} \mathfrak{S}_{ab}^{(dd)} \mathfrak{S}_{bc}^{(dd)} \right] \mathfrak{d}_b \mathfrak{h}_c, \quad (5.241)$$

$$\mathfrak{C}_{abc}^{(DD)} = \left[ \mathfrak{R}_{ab}^{(33)} \mathfrak{S}_{ab}^{(dd)} \mathfrak{S}_{bc}^{(hd)} + \mathfrak{R}_{ab}^{(34)} \left( \mathfrak{S}_{ab}^{(hd)} \mathfrak{S}_{bc}^{(dd)} + \mathfrak{S}_{ab}^{(dd)} \mathfrak{S}_{bc}^{(hd)} \right) \right. \\ \left. + \mathfrak{R}_{ab}^{(44)} \mathfrak{S}_{ab}^{(dd)} \mathfrak{S}_{bc}^{(dd)} \right] \mathfrak{d}_b \mathfrak{d}_c. \quad (5.242)$$

Here we emphasize that  $\kappa_L^2$  in (5.237) is a quadratic form of thermodynamic gradients. But since

$$q_n(\kappa) \kappa = \sinh \kappa,$$

by virtue of (5.237) we obtain

$$\sinh \kappa = \kappa_L.$$

Inverting the hyperbolic sine function, we find the Rayleigh dissipation function  $\kappa$  is expressible in terms of  $\kappa_L$  given by a quadratic form of thermodynamic gradients:

$$\kappa = \sinh^{-1} \kappa_L.$$

Therefore, the inverse of  $q_n(\kappa)$  is simply identified with the formula

$$q_n^{-1}(\kappa) = \frac{\kappa}{\sinh \kappa} = \frac{\sinh^{-1} \kappa_L}{\kappa_L}. \quad (5.243)$$

It is useful to define the nonlinear factor on the right of (5.243) by  $q_L$ :

$$q_L(\kappa_L) := \frac{\sinh^{-1} \kappa_L}{\kappa_L}. \quad (5.244)$$

This relation essentially solves the quasilinear constitutive equations (5.232)–(5.235) in terms of thermodynamic gradients, since the solutions of the quasilinear constitutive equations are now expressible in terms of the thermodynamic gradients only ( $[\nabla \mathbf{u}]^{(2)}, \nabla \cdot \mathbf{u}, \nabla \ln T, \mathbf{d}_a$ ) as follows:

$$\Pi_a = -2\eta_a [\nabla \mathbf{u}]^{(2)}, \quad (5.245)$$

$$\Delta_a = -\eta_{Ba} \nabla \cdot \mathbf{u}, \quad (5.246)$$

$$\mathbf{Q}'_a = -\sum_b \lambda_{ab} \nabla \ln T - \sum_b \zeta_{ab} \mathbf{d}_b, \quad (5.247)$$

$$\mathbf{J}_a = -\sum_b \xi_{ab} \nabla \ln T - \sum_b \mathcal{D}_{ab} \mathbf{d}_b, \quad (5.248)$$

where

$$\begin{aligned} \eta_a &= \eta_a^0 q_L, \\ \eta_{Ba} &= \eta_{Ba}^0 q_L, \\ \lambda_{ab} &= \lambda_{ab}^0 q_L, \\ \mathcal{D}_{ab} &= \mathcal{D}_{ab}^0 q_L, \\ \zeta_{ab} &= \zeta_{ab}^0 q_L, \\ \xi_{ab} &= \xi_{ab}^0 q_L. \end{aligned} \quad (5.249)$$

The quasilinear transport coefficients in (5.249) define the non-Newtonian viscosity  $\eta_a$ , non-Newtonian bulk viscosity  $\eta_{Ba}$ , non-Fourier heat conductivity  $\lambda_{ab}$ , non-Fickian diffusion coefficients  $\mathcal{D}_{ab}$ , etc. They depend nonlinearly on thermodynamic gradients because of the nonlinear factor  $q_L$ , but tend to the linear transport coefficients as the thermodynamic forces diminish as the system tends to equilibrium. It should be noted that the quasilinear transport processes described by the

constitutive parameters of (5.249) breaks Curie's principle because of the nonlinear factor  $q_L$  on all the thermodynamic gradients, tensorial, vectorial and scalar, present in the fluid, although the constitutive relations described by the set (5.245)–(5.248) superficially appears to obey the Curie principle.

### 5.5.11 A Model for Quasilinear Generalized Hydrodynamic Equations

If we restore the substantial time derivative terms in the steady state constitutive equations (5.207)–(5.210) and, at the same time, replace  $q_n(\kappa)$  with  $q_L$  defined in (5.243), then we obtain a set of model quasilinear generalized hydrodynamic equations given below:

$$\rho \frac{d\widehat{\Phi}_a^{(1)}}{dt} = -2p_a [\nabla \mathbf{u}]^{(2)} - (g_a^{(1)}\beta)^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(11)} \Phi_b^{(1)} q_L, \quad (5.250)$$

$$\rho \frac{d\widehat{\Phi}_a^{(2)}}{dt} = -\frac{5}{3} p_a \nabla \cdot \mathbf{u} - (g_a^{(2)}\beta)^{-1} \sum_{b=1}^r \mathfrak{R}_{ab}^{(22)} \Phi_b^{(2)} q_L, \quad (5.251)$$

$$\rho \frac{d\widehat{\Phi}_a^{(3)}}{dt} = -p_a \widehat{C}_{pa} \nabla \ln T - (g_a^{(3)}\beta)^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(33)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(34)} \Phi_b^{(4)} \right) q_L, \quad (5.252)$$

$$\rho \frac{d\widehat{\Phi}_a^{(4)}}{dt} = -p \mathbf{d}_a - (g_a^{(4)}\beta)^{-1} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(43)} \Phi_b^{(3)} + \mathfrak{R}_{ab}^{(44)} \Phi_b^{(4)} \right) q_L. \quad (5.253)$$

In these equations the collision bracket integrals  $\mathfrak{R}_{ab}^{(qs)}$  may be eliminated in favor of the linear transport coefficients. Recall that  $\Phi_a^{(1)} = \Pi_a$ ,  $\Phi_a^{(2)} = \Delta_a$ ,  $\Phi_a^{(3)} = \mathbf{Q}_a$ ,  $\Phi_a^{(4)} = \mathbf{J}_a$ . The model presented in (5.250)–(5.253) differs from the model for (3.287)–(3.290) of Chap. 3 with regard to the density dependence of the collision bracket integrals, because the collision bracket integrals in (5.250)–(5.253) involve a many-particle collision operator whereas the Boltzmann collision integral is for binary collisions only. Therefore the present model is applicable to moderately dense gases.

Together with the conservation laws (5.194) the evolution equations (5.250)–(5.253) serve as practically useful models for generalized hydrodynamic equations, which are thermodynamically consistent. Applications of these equations will be discussed in Chap. 9 of this work.

Finally, we make a comment on the mathematical basis of the model for the quasilinear generalized hydrodynamic equations (5.250)–(5.253) presented above. Mathematically, the model is obtained by following the well-known procedure to analyze the stability of the steady-state of a nonlinear dynamical system, because the differential equations (5.250)–(5.253) are simply the evolution equations for

the perturbed state around the steady state of the generic evolution equations (5.195)–(5.198). Equations (5.250)–(5.253) therefore determine the stability of the steady state defined by (5.207)–(5.210) and the behavior of the perturbed state in space-time. The steady state will turn out to be stable in the present nonlinear model of  $q_n(\kappa)$ .

### 5.5.12 Density Expansion of Extended Boltzmann Collision Integral

The generalized hydrodynamic equations in the Boltzmann kinetic theory, when the dissipation terms are linearized with respect to the thermodynamic driving forces (or fluxes) as described in Chap. 3, give rise to density-independent linear transport coefficients in the first-order Chapman–Enskog theory [22] of the Boltzmann equation. However, the extended Boltzmann equation (5.50) would give rise to density-dependent collision terms even at the linear level of approximation for the Chapman–Enskog-type solution, because if either the collision bracket integrals (5.188) or the collision operator  $\mathcal{T}^{(N)}$  is expanded in clusters, there arises a density series for the transport coefficients. Thus in the case of the extended Boltzmann equation the first-order Chapman–Enskog transport coefficients are corrected with respect to the density dependence. This aspect can be shown equivalently by either using the collision bracket integral (5.188) or collision operator  $\mathcal{T}^{(N)}$ . Since the collision bracket integrals (5.188) descend from the collision integral  $\Re \left[ \overline{F}^{(N)} \right]$  expressed with the collision operator  $\mathcal{T}^{(N)}$ , we may safely investigate the density dependence of collision operator  $\mathcal{T}^{(N)}$  itself instead of (5.188). This approach is, especially, preferable since it enables us to recover a theoretical result akin to the Enskog theory that includes three-body collision terms as the leading order correction to the first-order Chapman–Enskog transport coefficients, although the correlation effect will be absent in the present theory primarily owing to the absence of correlation in the distribution functions in the case of the extended Boltzmann equation. When we investigate the density dependence of dense fluid transport coefficients in Chap. 6, the correlation effect will emerge naturally and the Enskog theory result will be recovered as a special case for hard spheres of the theory under investigation in the limit of the statistical correlations vanishing between molecules.

By taking the mathematical steps in operator algebra leading to (5.61) from (5.53), we have shown the collision integral  $\Re \left[ \overline{F}^{(N)}(x^N, t) \right]$  can be cast into an equivalent form of (5.61). Therefore it is sufficient to examine the density dependence of the collision operator  $\mathcal{T}^{(N)}$  itself. As briefly discussed in Sect. 5.2 of this chapter, the  $N$ -particle collision operator  $\mathcal{T}^{(N)}$  obeying the classical Lippmann–Schwinger equation (5.71), upon applying the dynamic cluster expansion discussed earlier, can be written in the following expanded form

$$\begin{aligned} \mathcal{T}^{(N)} = & \sum_{j < k}^N \mathcal{T}_{jk} + \sum_{j < k < l}^N \mathcal{T}_{jkl} + \sum_{j < k < l < m}^N \mathcal{T}_{jklm} + \cdots + \mathcal{T}_{12\cdots N} \\ & + \sum_{j < k < l < m}^N \mathcal{T}_{jk;lm} + \cdots , \end{aligned} \quad (5.254)$$

where  $\mathcal{T}_{jkl}$ , etc. in the first line of (5.254) denote connected clusters of three particles ( $jkl$ ) imbedded in ( $N - 3$ ) non-interacting spectator particles, etc., whereas  $\mathcal{T}_{jk;lm}$ , etc. in the second line denote a disconnected cluster of four particle ( $jk; lm$ ) imbedded in ( $N - 4$ ) non-interacting spectator, etc. Therefore,  $\mathcal{T}_{jk}$  represents the binary cluster ( $jk$ ) in ( $N - 2$ ) non-interacting spectator particles. In the case of the uncorrelated fluids described by the present extended Boltzmann equation the disconnected cluster collision operators, such as ( $jk; lm$ ), do not contribute to the collision bracket integrals of the transport coefficients. As a matter of fact, the  $\mathcal{T}_{jk}$  terms in the first line of (5.254) contribute  $\frac{1}{2}N(N - 1)$  equivalent two-particle collision bracket integrals, the  $\mathcal{T}_{jkl}$  terms  $\frac{1}{6}N(N - 1)(N - 2)$  equivalent three-particle collision bracket integrals, and so on. Thus it is possible to see that when expanded in clusters as in (5.254) the collision operator,  $\mathcal{T}^{(N)}$  gives rise to a density dependence of the collision bracket integrals for the transport coefficients.

To show this feature in the context of transport coefficients it is sufficient to consider as an example the collision bracket integral  $\mathfrak{R}_{ab}^{(qp)}$  for a mixture of gases, which may be defined by the formula [15, 32]

$$\mathfrak{R}_{ab}^{(qp)} = g\mathcal{C}_q g_a^{(q)} g_b^{(s)} \beta^2 \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \int dx^{(N)} F_{\text{eq}}^{(N)} h_{ja}^{(q)} \odot i\mathcal{T}^{(N)} h_{kb}^{(p)}, \quad (5.255)$$

where  $\odot$  stands for contraction of tensors or vectors  $h_{ja}^{(q)}$  and  $h_{kb}^{(p)}$  and  $\mathcal{C}_q = 1/5$  for  $q = 1$ ; 1 for  $q = 2$ ;  $1/3$  for  $q = 3, 4$ , which is the numerical factor associated with contraction of the tensor to irreducible isotropic tensors. The collision bracket integral  $\mathfrak{R}_{ab}^{(qp)}$  has non-vanishing cross terms, because of symmetries of the integrand involved, only for  $q, p = 3$  or  $4$  in which case moments  $h_{ja}^{(q)}$  and  $h_{kb}^{(p)}$  are vectors. This mathematical fact is explained by means of the Curie principle in the theory of linear irreversible processes.

In the case of single-component fluids the collision bracket integral becomes

$$\mathfrak{R}^{(qq)} = \mathcal{C}_q g g^{(q)2} \beta^2 \sum_{j=1}^N \sum_{k=1}^N \int dx^{(N)} F_{\text{eq}}^{(N)} h_j^{(q)} \odot i\mathcal{T}^{(N)} h_k^{(q)} \quad (5.256)$$

with  $q = 1, 2, 3$  since there is no mass diffusion flux possible. Now there do not appear species indices in the expression. For simplicity of illustration we will consider  $\mathfrak{R}^{(qq)}$  only.

It is convenient to simplify the notation for the purpose of calculating the collision bracket integral. We define the abbreviation

$$\mathbb{T}^{(q)} := \langle A | i\mathcal{T}^{(N)} | B \rangle = \int dx^{(N)} F_{\text{eq}}^{(N)} A \odot i\mathcal{T}^{(N)} B. \quad (5.257)$$

Inserting the cluster expansion for  $\mathcal{T}^{(N)}$  in (5.254) we obtain the expansion

$$\begin{aligned} \mathbb{T}^{(q)} = \sum_{j=1}^N \sum_{k=1}^N & \left[ \sum_{k < l}^N \left\langle h_j^{(q)} | i\mathcal{T}_{kl} | h_l^{(q)} \right\rangle + \sum_{k < l < m}^N \left\langle h_j^{(q)} | i\mathcal{T}_{klm} | h_l^{(q)} \right\rangle + \dots \right. \\ & \left. + \sum_{k < l < m}^N \left\langle h_j^{(q)} | i\mathcal{T}_{kl;mp} | h_l^{(q)} \right\rangle + \dots \right]. \end{aligned} \quad (5.258)$$

Here for simplicity we abbreviate the terms as follows:

$$\mathbb{T}_2^{(q)} = \sum_{j=1}^N \sum_{k=1}^N \sum_{k < l}^N \left\langle h_j^{(q)} | i\mathcal{T}_{kl} | h_l^{(q)} \right\rangle, \quad (5.259)$$

$$\mathbb{T}_3^{(q)} = \sum_{j=1}^N \sum_{k=1}^N \sum_{k < l < m}^N \left\langle h_j^{(q)} | i\mathcal{T}_{klm} | h_l^{(q)} \right\rangle, \quad (5.260)$$

⋮

Since the moments  $h_j^{(q)}$  are functions of peculiar velocities only in the present case of dilute gases, we find that for  $l, m \neq j, k$

$$\left\langle h_j^{(q)} | \mathcal{T}_{lm} | h_k^{(q)} \right\rangle = 0, \quad (5.261)$$

and also the disconnected diagrams representing  $\left\langle h_j^{(q)} | \mathcal{T}_{kl;mp} | h_l^{(q)} \right\rangle$ , etc. vanish identically:

$$\left\langle h_j^{(q)} | \mathcal{T}_{kl;mp} | h_l^{(q)} \right\rangle = 0. \quad (5.262)$$

For these results, recall that collision operators are basically operators involving momentum derivative operators; Sect. 5.2 of this chapter. We therefore find

$$\mathbb{T}_2^{(q)} = \sum_{j < k}^N \left\langle h_j^{(q)} | i\mathcal{T}_{jk} | h_k^{(q)} \right\rangle. \quad (5.263)$$

Since there are  $\frac{1}{2}N(N - 1)$  two-particle contributions the right-hand side of (5.263) can be written

$$\mathbb{T}_2^{(q)} = n^2 \epsilon^{-1} \left\langle h_1^{(q)} | i \mathcal{T}_{12} | h_1^{(q)} + h_2^{(q)} \right\rangle_2, \quad (5.264)$$

where  $\langle A \rangle_2$  now stands for an integral in two-particle phase space

$$\langle A \rangle_2 = \int dx_1 \int dx_2 \frac{e^{-\frac{1}{2}\beta m C_1^2}}{\left\langle e^{-\frac{1}{2}\beta m C_1^2} \right\rangle_{eq}} \frac{e^{-\frac{1}{2}\beta m C_2^2}}{\left\langle e^{-\frac{1}{2}\beta m C_2^2} \right\rangle_{eq}} A \quad (5.265)$$

and

$$n = \lim_{N, V \rightarrow \infty} \frac{N}{V}. \quad (5.266)$$

Let us define

$$K_l^{(q)} = \sum_{j=1}^l h_j^{(q)}. \quad (5.267)$$

Then

$$\mathbb{T}_2^{(q)} = \frac{1}{2} n^2 \epsilon^{-1} \left\langle K_2^{(q)} | i \mathcal{T}_{12} | K_2^{(q)} \right\rangle. \quad (5.268)$$

The right hand side of (5.268) therefore is seen reminiscent of the two-particle collision bracket integrals in the Chapman–Enskog theory of solution for the Boltzmann equation [22]. Similarly to (5.268),  $\mathbb{T}_3^{(q)}$  can be written in the form

$$\mathbb{T}_3^{(q)} = \frac{1}{6} n^3 \epsilon^{-1} \left\langle K_3^{(q)} | i \mathcal{T}_{123} | K_3^{(q)} \right\rangle_3 \quad (5.269)$$

with  $\langle A \rangle_3$  defined similarly to (5.265) in the three-particle phase space. This process can be continued for all the connected cluster terms in the cluster expansion (5.258). In this manner, the collision bracket integrals in (5.256) can be expanded in the dynamic connected cluster expansion [15]

$$\mathfrak{R}^{(qq)} = \frac{1}{2} \epsilon^{-1} \mathcal{C}_q g^{(q)2} \beta^2 \left[ \left\langle K_2^{(q)} | i \mathcal{T}_{12} | K_2^{(q)} \right\rangle + \frac{1}{3} n \left\langle K_3^{(q)} | i \mathcal{T}_{123} | K_3^{(q)} \right\rangle + \dots \right]. \quad (5.270)$$

For more detailed accounts on this aspect see Sect. 13.5 of Ref. [15]. The first term on the right corresponds to the first-order Chapman–Enskog collision bracket integral and the second to the Enskog theory result for the three-particle collision term except for the absence of the correlation effect factor. Such correlations effects are not present in the present theory by the very nature of the extended Boltzmann equation, which does not take particle correlations into account—a defect which can be remedied in later chapters on dense fluids and liquids.

To calculate explicitly the connected cluster collision operators two-particle, three-particle collision problems should be solved. However, for arbitrary continuous potentials they are not possible to solve in closed analytic forms. Therefore, it is necessary to resort to numerical solution methods one way or another. In fact, they can be converted into collision bracket integrals that are similar in form to two-particle, three-particle collision bracket integrals in Chapman–Enskog theory [22] or Enskog theory [2, 22], if we apply the method developed for classical collision operators in a recent paper [16]. They can then be computed by a Monte Carlo simulation method [33]. In this connection Chap. 8 of this volume. We leave further computational development for the collision bracket integrals  $\mathfrak{R}_{ab}^{(qp)}$  to future studies.

## 5.6 Concluding Remarks

The salient point of this chapter is the following: The Boltzmann kinetic equation may be looked upon as a special case of the kinetic equation used in the present chapter, namely, the extended Boltzmann equation, because to obtain the Boltzmann kinetic equation from the extended Boltzmann equation it is only necessary to take a sufficiently low density limit of the expansion in (5.254) or arbitrarily mutilate the cluster expansion at the two-particle collision level throwing away the three-particle or higher-order collision terms. Then the collision integral  $\mathfrak{R} \left[ \overline{F}^{(N)} \right]$  simply collapses to the Boltzmann collision integral  $\mathbf{R}[f]$  and we recover the Boltzmann kinetic equation. This implies that the Boltzmann kinetic equation is a special case [34] (i.e., low density limit) of the ensemble kinetic equation for an ensemble of completely uncorrelated fluid particle systems. This feature is not obvious at a quick glance of the Boltzmann equation, but it is not difficult to see it once we learn about and manipulate the underlying collision operators sufficiently well as discussed in Ref. [34] and Ref. [21] and in this chapter. Thus we now see that the Boltzmann kinetic theory is a special dynamic theory form of ensemble theory that J.W. Gibbs formulated for equilibrium thermodynamic phenomena, and that there is an underlying theoretical structure of dynamic ensemble theory in Gibbs's equilibrium ensemble theory as we have shown in this chapter. Even if for nothing else, there lies the worth of the present chapter on the extended Boltzmann equation as a model for an insight into a kinetic theory of dense systems. As does the Boltzmann equation, it also allows formulation of a thermodynamic theory of irreversible phenomena consistent with the laws of thermodynamics for moderately dense uncorrelated fluids as does the Boltzmann equation. The generalized hydrodynamic equations derived from the aforementioned kinetic equation are thermodynamically consistent, but also provide a theoretical framework for a theory of linear and nonlinear transport processes in moderately dense gases. Therefore the generalized hydrodynamic theory enables us to carry out thermodynamically consistent macroscopic and deterministic studies of flow in moderately dense monatomic fluids.

In this chapter, we, however, have not discussed about the relative Boltzmann entropy beyond what has been formally presented, since the topics about it can be treated similarly to the treatments given in Chap. 3 in a completely parallel fashion. Therefore, here we forego the discussion on them to avoid a repetition.

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# Chapter 6

## Kinetic Theory of a Simple Dense Fluid

In Chap. 5, we have glimpsed into the possibility that the Boltzmann equation may be an archetype, but only in a special form, of irreversible kinetic equation for fluids, after which the kinetic equation for dense fluids of correlated particles may be fashioned and therewith the Gibbs ensemble theory can be formulated for time-dependent irreversible processes in dense fluids. As a first step to realize this goal, we would like to make an attempt to extend the Boltzmann-like kinetic equation for moderately dense gases, which we have formulated in Chap. 5, to dense correlated gases and liquids. We will thereby acquire a class of irreversible kinetic equations in the form of generalized Boltzmann equation (BGE), which will enable us to derive various evolution equations for macroscopic variables in the thermodynamic manifold necessary to describe macroscopic evolution of a fluid. Then, on the basis of them, we hope to comprehend the phenomenological thermodynamic theory of irreversible (transport) processes discussed in Chap. 2 from the molecular theory standpoint. The kinetic theory foundations of irreversible thermodynamics and generalized hydrodynamics will be hopefully laid thereby.

We will begin with the system consisting of a single-component simple fluid. The set of macroscopic evolution equations for variables spanning the thermodynamic manifold will turn out to be the dense fluid versions of generalized hydrodynamic equations of gases, which consist of the balance equations for conserved variables—the conservation laws—and the evolution equations of nonconserved variables. Unlike the dilute uncorrelated gases discussed in Chap. 3 the distribution functions, however, are no longer made up of singlet distribution functions only, but fully involve effects of spatial correlations which would be indispensable in describing the fluid behaviors in the dense fluid regime. Therefore the macroscopic variables for the fluid must be computed with spatial correlations explicitly taken to account.

Nevertheless, their evolution equations still consist of the equation of continuity or the mass balance equation, momentum balance equation, and internal energy balance equation for the conserved variables, and various constitutive equations for the

shear stress, excess normal stress, heat flux, etc., plus the volume transport equation in the case when volume transport phenomena are non-negligible in the dense fluid regime. By including a variable characterizing the representative volume of the fluid—the Voronoi volume, more specifically—among the nonconserved variables in the thermodynamic manifold, we are able to explicitly extend the thermodynamic manifold. The structure of generalized hydrodynamic equations obtained thereby broadens the scope of hydrodynamic description beyond the traditional range of macroscopic variables. In that sense, the present form of generalized hydrodynamics is more general than the previous version we have discussed in Refs. [1, 2], since it would be endowed a capability of discussing volume transport phenomena hitherto neglected in the study of flow phenomena—namely, fluid dynamics. It is believed that volume transport phenomena [3–6] have some subtle effects that have not been suspected to exist in the fluid phenomena.

## 6.1 Generalized Boltzmann Equation

To deduce the kinetic equation for a dense correlated fluid of monatomic molecules we adopt the basic idea of the equilibrium Gibbs ensemble theory of statistical mechanics and modify it suitably for a nonequilibrium version of the theory in the spirit of the kinetic theory of moderately dense gases discussed in Chap. 5.

In the Gibbs equilibrium ensemble theory, a canonical ensemble, for example, is assembled with independent subsystems of a fixed number  $N$  of particles in constant volume  $V$  which are distributed in the phase space of dimension  $6N$  in accordance with the *equal a priori probability hypothesis*: *This hypothesis states that all physically accessible states subject to the constraints imposed are equally probable, and hence systems of such states should be admitted as a member of the assembly*. The number of admissible systems can be very large owing to  $N$  being astronomically large. In any case, the ensemble as a whole may be regarded as a supersystem consisting of a large—practically, infinitely large—number of subsystems. In the Gibbs ensemble theory, the members (subsystems) of the ensemble, however, do not interact with each other except that they exchange heat<sup>1</sup> and thereby reach thermal equilibrium. In the case of a nonequilibrium ensemble described below, it is necessary to be explicit about interactions between the subsystems of a fixed  $N$  and  $V$  if we wish to describe their dynamical evolution through a kinetic equation, preferably irreversible, and thereby to replace the vague notion of heat exchange between the subsystems employed in the equilibrium ensemble theory. We will also have to be more explicit how such subsystems come to equilibrium eventually.

Let the number of subsystems in the ensemble be  $v$ . This number is very large since the value of  $N$  itself is very large being of the order of Avogadro's number.

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<sup>1</sup>In the equilibrium Gibbs ensemble theory it is not stated how heat is exchanged between the subsystems nor is there mention of the molecular origin and nature of heat.

The total number of particles in the ensemble (supersystem) then is  $\mathcal{N} = \nu N$  and the volume of the supersystem<sup>2</sup> (ensemble) is  $\mathbb{V} = \nu V$ .

Let us denote the coordinate and momentum of particle  $i$  in a suitably fixed coordinate system by  $\mathbf{r}_i$  and  $\mathbf{p}_i$ , respectively, and the phase of particle  $i$  by  $x_i = (\mathbf{r}_i, \mathbf{p}_i)$ , which is a 6-dimensional vector in the phase space. The phase of  $N$  molecules therefore is a  $6N$ -dimensional vector in the phase space spanned by  $\mathbf{r}_i$  and  $\mathbf{p}_i$  ( $i = 1, \dots, N$ ). We will abbreviate the phase of  $N$  monatomic particles by  $\mathbf{x}^{(N)} := (x_1, x_2, \dots, x_N)$  for brevity. To count the number of possible states in the ensemble let us divide the  $6N$ -dimensional phase space of  $N$  particles into cells of  $O(h^3)$  ( $h$  = Planck constant) enclosing phase points  $x_i$  ( $i = 1, \dots, N$ ) at their centers. We then enumerate the number of ways to randomly distribute  $\mathcal{N}$  particles in the cells in  $6N$ -dimensional phase space of  $N$  particles embedded in the  $6\mathcal{N}$ -dimensional phase space of the whole ensemble. If the frequency of cell  $k$  being occupied by particles is  $n_k(N, V)$ , then the number of ways of randomly distributing (identical but distinguishable classical) particles into such cells is given by

$$\Omega_n = \prod_k \frac{\mathcal{N}!}{n_k(N, V)!}.$$

In the equilibrium Gibbs ensemble theory this number gives the probability of finding the system at a mechanical state in equilibrium, which is usually derived by using the method of Lagrange method [7] of undetermined multipliers associated with the conditions [8] on the isolated ensemble

$$\mathcal{N} = \sum_k n_k(N, V), \quad (6.1)$$

$$E_t = \sum_k H(N, V) n_k(N, V). \quad (6.2)$$

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<sup>2</sup>The volume of the supersystem  $\mathbb{V} = \nu V$  is a sum of  $V$ . It may be written as

$$\mathbb{V} = \sum_{\alpha=1}^{\nu} V(\alpha)$$

where  $V(\alpha)$  is the volume of the  $\alpha$ th subsystem. Since all the subsystems have the same volume  $V$ , naturally  $\mathbb{V} = \nu V$ . In integral form under the assumption that the volumes are contiguously arranged, we write

$$\mathbb{V} = \int_{\mathbb{V}} d\mathbf{r} = \sum_{\alpha=1}^{\nu} \int_{V(\alpha)} d\mathbf{r} = \sum_{\alpha=1}^{\nu} V(\alpha).$$

In (6.2)  $H(N, V)$  is the Hamiltonian (energy) of the  $N$ -particle subsystem free from the body force. The ensemble being isolated,  $\mathcal{N}$  and  $E_t$  are fixed and confined in the total volume<sup>3</sup>  $\mathbb{V} = vV$ .

In the case of nonequilibrium such a counting of the number of states does not suffice for our purpose, since the configuration of the whole system changes with time because the subsystems interact with each other. To describe the evolution of the ensemble and the subsystems therein we need to have an evolution equation for probability distribution functions, which describes the evolution of the ensemble from the time it is assembled and let interact with each other to the time when it reaches equilibrium. The evolution equation then would provide the attendant macroscopic evolution of the system over the course of time and space. Such an evolution equation of the ensemble is especially desired if the aim is to understand the behavior of the fluid from the molecular theory viewpoint by employing the method of statistical mechanics.

The evolution equation and the ensemble distribution function are such that (6.1) and (6.2) are satisfied over the course of collisions between the subsystems making up the ensemble. Since the system (i.e., the ensemble) lives in the phase space, the conditions (6.1) and (6.2) imply that it is evolving in the plane characterized by constant  $\mathcal{N}$  and  $E_t$  in the phase space of the ensemble. These conditions in turn mean the eigenvalue of the Liouville operator is of a value satisfying the aforementioned conditions, namely, *null since they should remain constant in time*. Further comments will be made on this point later in this chapter. Also see the analysis on this point made in Chap. 8, where the eigenvalue problem [9] of the Liouville operator is discussed in more detail.

The probability of finding the system in the  $6\mathcal{N}$ -dimensional phase volume  $dx^{(\mathcal{N})} := dx_1 dx_2 \dots dx_{\mathcal{N}}$  enclosing point  $x^{(\mathcal{N})}$  at time  $t$  will be denoted by the distribution function  $\mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t)$ . In the equilibrium ensemble theory [8, 10], the supersystem—the entire assembly (ensemble) of the subsystems—is isolated and let attain thermal equilibrium with the heat reservoir of temperature  $T$  and between the subsystems by some means unspecified. However, in the nonequilibrium Gibbs ensemble theory formulated here, the initially well-separated noninteracting subsystems are allowed to interact (or collide) with each other, exchanging energy, and their evolution is followed over the course of their collision process until they equilibrate with respect to energy and separate from each other, having attained their final state still satisfying conditions (6.1) and (6.2). Therefore equilibrium is achieved by molecular interactions between the subsystems in the course of their collisions. Since the ensemble of representative systems (subsystems) is isolated as a whole, the evolution of the distribution function  $\mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t)$  for entire ensemble (supersystem) obeys the Liouville equation for an isolated system

<sup>3</sup>The condition  $\mathbb{V} = vV$  may be added to the set of condition (6.1) and (6.2), but in the nonequilibrium ensemble theory being formulated here the constant  $\mathbb{V}$  condition is not necessary because the subsystems of the ensemble must be separated from each other before and after their collisions.

$$\left( \frac{\partial}{\partial t} + \mathbf{L}^{(\mathcal{N})} \right) \mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t) = 0, \quad (6.3)$$

where the Liouville operator is given by

$$\mathbf{L}^{(\mathcal{N})} = \mathbf{L}_0^{(\mathcal{N})} + \mathbf{L}_1^{(\mathcal{N})}, \quad (6.4)$$

$$\mathbf{L}_0^{(\mathcal{N})} = \sum_{\alpha=1}^v \mathbf{L}_{\alpha}^{(N)}, \quad (6.5)$$

$$\mathbf{L}_1^{(\mathcal{N})} = \sum_{\beta < \alpha}^v \mathbf{L}_{\alpha\beta}^{(N,N')}. \quad (6.6)$$

Here the Liouville operator  $\mathbf{L}_{\alpha}^{(N)}$  of the  $\alpha$ th “free” (separated) subsystem of  $N$  particles<sup>4</sup> is defined by

$$\mathbf{L}_{\alpha}^{(N)} = \sum_{j\alpha=1}^N \left[ \mathbf{v}_{j\alpha} \cdot \nabla_{j\alpha} + \frac{1}{2} \sum_{j\alpha \neq k\beta=1}^v \mathbf{F}_{j\alpha k\beta}(\mathbf{r}_{j\alpha k\beta}) \cdot (\nabla_{\mathbf{p}_{j\alpha}} - \nabla_{\mathbf{p}_{k\beta}}) + m_{j\alpha} \widehat{\mathbf{F}}(\mathbf{r}_{j\alpha}) \cdot \nabla_{\mathbf{p}_{j\alpha}} \right] \quad (6.7)$$

with  $\mathbf{v}_{j\alpha} = \mathbf{p}_{j\alpha}/m_{j\alpha}$  denoting the velocity of particle  $j\alpha$  of mass  $m_{j\alpha}$ , and operator  $\mathbf{L}_{\alpha\beta}^{(N,N')}$  is the intersubsystem interaction Liouville operator of subsystems  $\alpha$  and  $\beta$ . It is defined by

$$\mathbf{L}_{\alpha\beta}^{(N,N')} = \frac{1}{2} \sum_{j\alpha=1}^N \sum_{\substack{k\beta=1 \\ (\alpha \neq \beta)}}^N \mathbf{F}_{j\alpha k\beta}(\mathbf{r}_{j\alpha k\beta}) \cdot (\nabla_{\mathbf{p}_{j\alpha}} - \nabla_{\mathbf{p}_{k\beta}}). \quad (6.8)$$

In (6.8) the subscript pair  $j\alpha$  denotes particle  $j \in \alpha$ , and other symbols are defined by

$$\begin{aligned} \mathbf{r}_{j\alpha k\beta} &= \mathbf{r}_{j\alpha} - \mathbf{r}_{j\beta}, & \nabla_{j\alpha} &= \frac{\partial}{\partial \mathbf{r}_{j\alpha}}, & \nabla_{\mathbf{p}_{j\alpha}} &= \frac{\partial}{\partial \mathbf{p}_{j\alpha}}, \\ \mathbf{F}_{j\alpha k\alpha}(\mathbf{r}_{j\alpha k\alpha}) &= -\frac{\partial U_{j\alpha k\alpha}(\mathbf{r}_{j\alpha k\alpha})}{\partial \mathbf{r}_{j\alpha k\alpha}}, & \mathbf{F}(\mathbf{r}_{j\alpha}) &= -\frac{\partial U_{j\alpha}(\mathbf{r}_{j\alpha})}{\partial \mathbf{r}_{j\alpha}}. \end{aligned} \quad (6.9)$$

In (6.9)  $U_{j\alpha k\beta}(\mathbf{r}_{j\alpha k\beta})$  denotes the intermolecular pair potential of particle pair  $(j\alpha, k\beta)$ , and  $U_{j\alpha}(\mathbf{r}_{j\alpha})$  the external potential on particle  $j \in \alpha$  located at

<sup>4</sup>We might imagine the subsystems are aggregates of  $N$  particles each or  $N$  loosely bound polyatomic molecules, the subsystems being well separated spatially from each other at the beginning of their collision process.

position  $\mathbf{r}_{j\alpha}$ . The pairwise additive potential assumption implicit in the definition of Liouville operators can be removed without causing a problem at the formal theory level. This pairwise additivity assumption would not impair the formulation of the theory we have in mind in this work. It can be easily removed but with a slight complication of the some of resulting formulas.  $\mathbf{F}(\mathbf{r}_{j\alpha})$  is the external body-force on molecule  $j \in \alpha$  at  $\mathbf{r}_{j\alpha}$ . This body-force is assumed to vary slowly over the range of intermolecular forces. Thus the intermolecular collision processes of particle pairs remain unaffected by the presence of the external body-force. It will be convenient to abbreviate by  $H'_{j\alpha}$  the associated Hamiltonian of molecule  $j$  in the frame of reference moving at the mean velocity  $\mathbf{u}$  of the fluid:

$$H'_{j\alpha} = H_{j\alpha} + U_{j\alpha}(\mathbf{r}_{j\alpha}), \quad (6.10)$$

$$H_{j\alpha} = \frac{1}{2}m_{j\alpha}C_{j\alpha}^2 + \frac{1}{2}\sum_{j\alpha \neq k\beta=1}^N U_{j\alpha k\beta}(\mathbf{r}_{j\alpha k\beta}). \quad (6.11)$$

In (6.11) the symbol  $\mathbf{C}_{j\alpha}$  denotes the peculiar velocity of particle  $j \in \alpha$  defined by

$$\mathbf{C}_{j\alpha} = \mathbf{v}_{j\alpha} - \mathbf{u}. \quad (6.12)$$

The statistical mechanical meaning of  $\mathbf{u}$  will be given later, but for the moment it may be considered a phenomenological fluid velocity.<sup>5</sup> Therefore  $H'_{j\alpha}$  is the energy of particle  $j \in \alpha$  relative to the fluid particle moving at velocity  $\mathbf{u}$  in the field of a sufficiently slowly varying body force. The density of the fluid is given by

$$n = \lim_{\mathcal{N}, \mathbb{V} \rightarrow \infty} \frac{\mathcal{N}}{\mathbb{V}} = \lim_{N, V \rightarrow \infty} \frac{N}{V}. \quad (6.13)$$

The distribution function  $\mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t)$  is normalized to unity:

$$\int dx^{(\mathcal{N})} \mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t) = 1, \quad (6.14)$$

where the integral over  $x^{(\mathcal{N})}$  is an abbreviation of the  $6\mathcal{N}$ -dimensional integrals:

$$\int dx^{(\mathcal{N})} \dots = \int_V d\mathbf{r}_1 \dots \int_V d\mathbf{r}_v \int_{-\infty}^{\infty} d\mathbf{p}_1 \dots \int_{-\infty}^{\infty} d\mathbf{p}_v \dots, \quad (6.15)$$

each integral on the right being three-dimensional integrals in either coordinate or momentum space. Each coordinate space integration is limited to within the volume  $\mathbb{V}$  for the center of mass position of the subsystem and to  $V$  for the  $3(N-1)$  degree

<sup>5</sup>By fluid velocity we mean the mean velocity of a packet of fluid containing a sufficiently large number of molecules (or particles) in an elementary volume around point  $\mathbf{r}$ .

of freedom of  $N$  particles in the subsystem; more explicitly written out

$$\int_V d\mathbf{r}_1 = \int_V d\mathbf{R}_1 \int d\xi_1^{(N-1)}, \quad (6.16)$$

where  $\mathbf{R}_1$  is the center of mass position vector for subsystem 1 in  $V$  and  $\xi_1^{(N-1)} := (\xi_1, \xi_2, \dots, \xi_{N-1})$  is the position vectors of particles in subsystem 1 relative to  $\mathbf{R}_1$  and limited to  $V$ . The other coordinate integrals in (6.15) can be similarly expressed.

The solution of the Liouville equation, as a first-order partial differential equation, can be in principle obtained by integrating the characteristic equations subject to the initial and boundary conditions [11], but, as is well known in statistical mechanics, this approach is not taken because of its impracticality owing to the too-many particles involved and too much information required to obtain the solutions of characteristic differential equations—we do not have all the initial and boundary conditions of entire particles of the system. The present work is concerned with an alternative way to treat the problem for dense correlated fluids at arbitrary density, and the main aim is to comprehend the thermodynamics of irreversible transport processes and the attendant fluid dynamics from the molecular theory viewpoint. The method of classical scattering theory in phase space will be employed to guide us to the aim.

The collision process in question is initiated at the initial time  $t = t_i$  and finished at the final time  $t = t_f$ . Since at  $t = t_i$  the ensemble is assembled with independent subsystems subject to conditions (6.1) and (6.2), the distribution function of the ensemble (supersystem) may be written as a product of probabilities  $f^{(N)}(\mathbf{x}_\alpha^{(N)}, t_i)$  of subsystems assembled in the ensemble under the *equal a priori probability hypothesis*:

$$\mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t_i) = \prod_{\alpha=1}^v f^{(N)}(\mathbf{x}_\alpha^{(N)}, t_i). \quad (6.17)$$

Here we assume  $f^{(N)}(\mathbf{x}_\alpha^{(N)}, t)$  is normalized to unity

$$\int d\mathbf{x}_\alpha^{(N)} f^{(N)}(\mathbf{x}_\alpha^{(N)}, t) = 1 \quad (\alpha = 1, \dots, v). \quad (6.18)$$

Consequently

$$\int dx^{(\mathcal{N})} \mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t) = 1. \quad (6.19)$$

Since the classical scattering theory [1], the results of which we are going to make use of here, is most conveniently formulated with self-adjoint Liouville operators, it is necessary to use alternative notation for the self-adjoint (i.e., Hermitian) Liouville operators:

$$\mathcal{L}^{(\mathcal{N})} = -i\mathbf{L}^{(\mathcal{N})}; \quad \mathcal{L}^{(N)} = -i\mathbf{L}^{(N)}; \quad \mathcal{L}_{\alpha\beta}^{(N,N')} = -i\mathbf{L}_{\alpha\beta}^{(N,N')}, \quad etc., \quad (6.20)$$

where  $i = \sqrt{-1}$ . In this notation the Liouville equation (6.3) reads

$$\left( i \frac{\partial}{\partial t} - \mathcal{L}^{(\mathcal{N})} \right) \mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t) = 0, \quad (6.21)$$

where

$$\mathcal{L}^{(\mathcal{N})} = \mathcal{L}_0^{(\mathcal{N})} + \mathcal{L}_1^{(\mathcal{N})} \quad (6.22)$$

with the “free” and “interaction” Liouville operators  $\mathcal{L}_0^{(\mathcal{N})}$  and  $\mathcal{L}_1^{(\mathcal{N})}$  of the supersystem defined by

$$\mathcal{L}_0^{(\mathcal{N})} = -i\mathbf{L}_0^{(\mathcal{N})}, \quad \mathcal{L}_1^{(\mathcal{N})} = -i\mathbf{L}_1^{(\mathcal{N})}. \quad (6.23)$$

As  $t \rightarrow t_i$ ,  $\mathcal{L}_1^{(\mathcal{N})}$  tends to vanish because the interactions<sup>6</sup> between the subsystems vanish as they separate beyond the intersubsystem molecular force range. Consequently,  $\mathcal{L}^{(\mathcal{N})} \rightarrow \mathcal{L}_0^{(\mathcal{N})}$  in the limit. The same limit also holds as the subsystems separate well from each other on completion of the collision process as  $t \rightarrow t_f$ .

As  $t \rightarrow t_i$ , the Liouville equation (6.21) tends to the form

$$\left( i \frac{\partial}{\partial t} - \mathcal{L}_0^{(\mathcal{N})} \right) \mathbb{F}_{\text{in}}^{(\mathcal{N})}(x^{(\mathcal{N})}, t) = 0, \quad (6.24)$$

where

$$\mathbb{F}_{\text{in}}^{(\mathcal{N})}(x^{(\mathcal{N})}, t) = \prod_{\alpha=1}^v f_{\text{in } \alpha}^{(N)}(\mathbf{x}_{\alpha}^{(N)}, t) \quad (6.25)$$

with  $f_{\text{in } \alpha}^{(N)}(\mathbf{x}_{\alpha}^{(N)}, t)$  denoting the solutions of the equations

$$\left( i \frac{\partial}{\partial t} - \mathcal{L}_{0\alpha}^{(N)} \right) f_{\text{in } \alpha}^{(N)}(\mathbf{x}_{\alpha}^{(N)}, t) = 0, \quad (6.26)$$

because (6.24) is separable in the long time limit; (6.26) is in fact the Liouville equation for the independent subsystem  $\alpha$ . If we set

$$f_{\text{in } \alpha}^{(N)}(\mathbf{x}_{\alpha}^{(N)}, t) = e^{-i\lambda_{\alpha} t} \rho_{\alpha}(\mathbf{x}_{\alpha}^{(N)}; \lambda_{\alpha}), \quad (6.27)$$

where  $\rho_{\alpha}(\mathbf{x}_{\alpha}^{(N)}; \lambda_{\alpha})$  denotes the time-independent part of the solution, (6.26) may be turned into an eigenvalue problem [9] of Liouville operator  $\mathcal{L}_{0\alpha}^{(N)}$ :

$$\mathcal{L}_{0\alpha}^{(N)} \rho_{\alpha} = \lambda_{\alpha} \rho_{\alpha}. \quad (6.28)$$

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<sup>6</sup>The intersubsystem forces may be regarded as consisting mainly of intermolecular forces between molecules in the peripheries of different subsystems, since the interactions with molecules well inside the subsystems are screened off by the peripheral molecules. Because the number of peripheral molecules should be relatively small compared to the numbers of molecules in the subsystems, the subsystem interaction Liouville operators are relatively weak (i.e., small in magnitude) compared to the interaction Liouville operators of the subsystems.

Since  $\rho_\alpha(\mathbf{x}_\alpha^{(N)}; \lambda_\alpha)$  is a function of  $N$  and energy satisfying conditions (6.1) and (6.2), it follows that

$$\lambda = \sum_{\alpha=1}^v \lambda_\alpha = 0, \quad (6.29)$$

because the energy and  $N$  are constant (i.e., constants of motion) over the course of collision. Therefore, the distribution function  $\mathbb{F}_{in}^{(N)}(x^{(N)}, t_i)$  belongs to the (extremely degenerate) null eigenvalue class. As shown by the analysis [9] discussed in Chap. 8, *the distribution function  $\mathbb{F}^{(N)}(x^{(N)}, t)$  of the ensemble would remain in the same eigenvalue class (i.e., the null eigenvalue class) over the entire course of the collision process of the subsystems owing to the conditions (6.1) and (6.2), even if the interactions of subsystems in the course of evolution might give rise to the component distribution functions quite different from those of  $\mathbb{F}_{in\alpha}^{(N)}(x_\alpha^{(N)}, t)$  initially.*

In summary, in the present theory we let the  $v$  independent subsystems of the ensemble begin to collide at  $t = t_i$  (i.e., remote past), exchange energy as they come within their interaction range, and finally separate from each other, having reached equilibrium with respect to energy in the course of time (e.g., in the distant future). The initial state of the supersystem is described by the aforementioned product of distribution functions because the ensemble consists of  $v$  independent subsystems by construction of the ensemble in compliance with *the equal a priori probability hypothesis*. This collision process of  $v$  independent subsystems is described by the Liouville equation (6.21).

To implement the nonequilibrium ensemble theory we define reduced distribution function  $f^{(N)}(\mathbf{x}^{(N)}, t)$  ( $1 \leq N < v$ ) of finding a subsystem of  $N$  particles in the interval  $\mathbf{x}^{(N)} + d\mathbf{x}^{(N)} \sim \mathbf{x}^{(N)}$  around phase point  $\mathbf{x}^{(N)} = (x_1, \dots, x_N)$  regardless of the distribution of the rest of particles in the supersystem by the integral

$$f^{(N)}(\mathbf{x}^{(N)}, t) = \int dx^{(N-N)} \mathbb{F}^{(N)}(x^{(N)}, t), \quad (6.30)$$

where  $dx^{(N-N)}$  abbreviates the partial phase volume

$$dx^{(N-N)} = dx_{N+1} dx_{N+2} \cdots dx_N.$$

Henceforth, for brevity of notation, wherever confusion would not arise, the subsystem index  $\alpha$  is omitted in the reduced distribution function  $f^{(N)}(\mathbf{x}_\alpha^{(N)}, t)$ . In this notational convention,  $f^{(N)}(\mathbf{x}^{(N)}, t)$ , for example, in (6.30) may be regarded as the distribution function for subsystem 1.

The evolution equation for  $f^{(N)}(\mathbf{x}^{(N)}, t)$  is then easily obtained from the Liouville equation (6.21) for  $\mathbb{F}^{(N)}(x^{(N)}, t)$  if (6.21) is integrated over  $x^{(N-N)} := (x_{N+1}, x_{N+2}, \dots, x_N)$ . Regrouping  $(x_{N+1}, x_{N+2}, \dots, x_N)$  from the particle sequence to the subsystem sequence and writing  $x^{(N-N)}$  in the form  $x^{(N-N)} := (\mathbf{x}_2^{(N)}, \mathbf{x}_3^{(N)}, \dots, \mathbf{x}_v^{(N)})$ , we may write the evolution equation for  $f^{(N)}(\mathbf{x}^{(N)}, t)$  in the form

$$\begin{aligned} & \left( i \frac{\partial}{\partial t} - \mathcal{L}^{(N)} \right) f^{(N)}(\mathbf{x}^{(N)}, t) \\ &= \int d\mathbf{x}^{(N-N)} \sum_{\alpha=1}^v \sum_{\beta>1(\alpha\neq\beta)}^v \mathcal{L}_{\alpha\beta}^{(N,N')} \mathbb{F}^{(N)}(\mathbf{x}^{(N')}, t), \end{aligned} \quad (6.31)$$

where  $\mathcal{L}^{(N)}$  is the Liouville operator for subsystem 1 defined by (6.7). The index for subsystem 1 is omitted from  $\mathcal{L}^{(N)}$  and  $f^{(N)}(\mathbf{x}^{(N)}, t)$  for brevity in the left hand side of the equation. This is the fine-grained kinetic equation for  $f^{(N)}(\mathbf{x}^{(N)}, t)$  before time-coarse-graining is applied.

The distribution functions in this equation are now coarse-grained with respect to time by taking time average over a time scale much longer than the subsystem collision time ( $\tau_c$ ), which is taken longer than molecular collision time ( $\tau_m$ ), but shorter than the hydrodynamic scale  $\tau_h$  ( $\tau_c \ll \tau \ll \tau_h$ ):

$$\bar{f}^{(N)}(\mathbf{x}^{(N)}, t) = \tau^{-1} \int_0^\tau ds f^{(N)}(\mathbf{x}^{(N)}, t + s). \quad (6.32)$$

The time-coarse graining by time averaging taken in the spirit of Kirkwood [12] is aimed at removing rapid fluctuations of distribution functions that arise from rapid molecular motions owing to the molecular interactions on a short time scale of  $O(\tau_m)$ . It should be noted that this averaging is a key step in formulating an irreversible kinetic equation for the time-coarse grained distribution function. The subsystem collision time scale  $\tau_c$  should be taken to be longer than molecular interaction time. Therefore the time-coarse grained distribution function  $\bar{f}^{(N)}(\mathbf{x}^{(N)}, t)$  would remain unchanged over the molecular collision time because it is a quantity averaged over a time span  $\tau$  much longer than  $\tau_c$  but less than  $\tau_h$  (hydrodynamic time scale). Performing such a time-coarse-graining of (6.31) we obtain

$$\begin{aligned} & \left( i \frac{\partial}{\partial t} - \mathcal{L}^{(N)} \right) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) = \sum_{\alpha=1}^v \sum_{\beta>1(\alpha\neq\beta)}^v \int d\mathbf{x}^{(N-N)} \mathcal{L}_{\alpha\beta}^{(N,N')} \times \\ & \lim_{\epsilon \rightarrow +0} \epsilon \int_0^\infty ds e^{-\epsilon s} e^{-is\mathcal{L}^{(N)}} \mathbb{F}^{(N)}(\mathbf{x}^{(N')}, t) \end{aligned} \quad (6.33)$$

with  $\epsilon$  defined by

$$\epsilon = \frac{1}{\tau}. \quad (6.34)$$

In the right-hand side of (6.33) we have inserted the exponential factor  $e^{-\epsilon s}$  to ensure the convergence of the integral in accordance with the Abel–Tauber theorem [13, 14]. Henceforth the limit sign will be omitted from (6.33) but understood to apply when calculation is completed for the right hand side of the equation. Upon performing integration over  $s$  we obtain (6.33) in the form

$$\begin{aligned} & \left( \frac{\partial}{\partial t} + \mathbf{L}^{(N)} \right) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \\ &= \int d\mathbf{x}^{(N-N)}(-\epsilon) \sum_{\alpha=1}^v \sum_{\beta>1(\alpha \neq \beta)}^v \mathcal{L}_{\alpha\beta}^{(N,N')} \mathcal{R}^{(N)}(\epsilon) \mathbb{F}^{(N)}(\mathbf{x}^{(N')}, t), \end{aligned} \quad (6.35)$$

where  $\mathcal{R}(\epsilon)$  is the resolvent operator<sup>7</sup> defined by

$$\mathcal{R}^{(N)}(\epsilon) = \frac{1}{\mathcal{L}^{(N)} - i\epsilon}. \quad (6.36)$$

The resolvent operator, more generally, is given by

$$\mathcal{R}^{(N)}(z) = \frac{1}{\mathcal{L}^{(N)} - z} \quad (6.37)$$

with  $z$  defined by a complex number in terms of the eigenvalue  $\lambda$  of the Liouville operator  $\mathcal{L}^{(N)}$ :

$$z = \lambda + i\epsilon. \quad (6.38)$$

Therefore the resolvent operator  $\mathcal{R}(\epsilon)$  in (6.35) is in the null class mentioned earlier because  $\lambda = 0$ , which in turn implies that the distribution function  $\mathbb{F}^{(N)}(\mathbf{x}^{(N)}, t)$  of the ensemble still evolves [9] in the constant total energy–total number plane of the  $6N$ -dimensional phase space of the supersystem because of the conditions (6.C1) and (6.C1) listed below in Sects. 6.2.1 and 6.2.2.

Since according to the classical scattering theory [1] the classical collision operator  $\mathcal{T}^{(N)}(z)$  is related to the resolvent operator by the equation

$$\mathcal{T}_{1\beta}^{(N)}(z) \mathcal{R}_0^{(N)}(z) = \mathcal{L}_{1\beta}^{(N,N')} \mathcal{R}^{(N)}(z), \quad (6.39)$$

where  $\mathcal{R}_0^{(N)}(z)$  is the free resolvent operator defined by

$$\mathcal{R}_0^{(N)}(z) = \frac{1}{\mathcal{L}_0^{(N)} - z}, \quad (6.40)$$

the integral on the right of (6.35) may be written in terms of collision operator  $\mathcal{T}_{1\beta}^{(N)}(z)$  describing collisions of the subsystems in the ensemble (i.e., supersystem).

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<sup>7</sup>See Chap. 9 of Ref. [1] for detailed discussions on classical and quantum scattering theories of particles which we make use of in the following.

Before proceeding further, we digress a little to mention the following general relations regarding the collision operator  $T_{1\beta}^{(\mathcal{N})}(z)$ . Equation (6.39) may be more generally written for the full interaction Liouville operator instead of  $\mathcal{L}_{1\beta}^{(N,N')}$ :

$$T^{(\mathcal{N})}(z) \mathcal{R}_0^{(\mathcal{N})}(z) = \mathcal{L}_1^{(\mathcal{N})} \mathcal{R}^{(\mathcal{N})}(z). \quad (6.41)$$

The corresponding integral equation for  $T^{(\mathcal{N})}(z)$  is the full classical Lippmann–Schwinger equation [15]

$$\begin{aligned} T^{(\mathcal{N})}(z) &= \mathcal{L}_1^{(\mathcal{N})} - \mathcal{L}_1^{(\mathcal{N})} \mathcal{R}_0^{(\mathcal{N})}(z) T^{(\mathcal{N})}(z) \\ &= \mathcal{L}_1^{(\mathcal{N})} - T^{(\mathcal{N})}(z) \mathcal{R}_0^{(\mathcal{N})}(z) \mathcal{L}_1^{(\mathcal{N})}. \end{aligned} \quad (6.42)$$

Therefore the full collision operator  $T^{(\mathcal{N})}(z)$  is given by

$$\begin{aligned} T^{(\mathcal{N})}(z) &= \sum_{\alpha < \beta}^v T_{\alpha\beta}^{(\mathcal{N})} \\ &= \sum_{\alpha < \beta}^v \left[ \mathcal{L}_{\alpha\beta}^{(N,N')} - \mathcal{L}_{\alpha\beta}^{(N,N')} \mathcal{R}_0^{(\mathcal{N})}(z) T^{(\mathcal{N})}(z) \right]. \end{aligned} \quad (6.43)$$

Before implementing the replacement mentioned in connection with (6.39), it is also useful to note that the free resolvent operator operating on the null class distribution function  $\mathbb{F}^{(\mathcal{N})}(\mathbf{x}^{(\mathcal{N})}, t)$  gives rise<sup>8</sup> to a term of  $O(1/i\epsilon)$ . Combining this and (6.39) together in (6.35) and time-coarse graining the resulting equation once again, we finally obtain the evolution equation for the time-coarse grained distribution function  $\bar{f}^{(N)}(\mathbf{x}^{(N)}, t)$ :

$$\begin{aligned} \left( \frac{\partial}{\partial t} + \mathbf{L}^{(N)} \right) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \\ = \frac{1}{v} \sum_{\beta > \alpha=1}^v \int d\mathbf{x}^{(\mathcal{N}-N)} (-i) T_{\alpha\beta}^{(\mathcal{N})}(z) \bar{\mathbb{F}}^{(\mathcal{N})}(\mathbf{x}^{(\mathcal{N})}, t), \end{aligned} \quad (6.44)$$

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<sup>8</sup>If this step is not taken at this stage, Eq. (6.44) below would read

$$\left( \frac{\partial}{\partial t} + \mathbf{L}^{(N)} \right) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) = - \sum_{\beta > 1}^v \epsilon \int d\mathbf{x}^{(\mathcal{N}-N)} T_{1\beta}^{(\mathcal{N})}(z) \mathcal{R}_0^{(N)}(z) \bar{f}^{(\mathcal{N})}(\mathbf{x}^{(\mathcal{N})}, t).$$

However, when the right hand side of this equation is explicitly calculated with the null class functions for the distribution functions

$$\epsilon \mathcal{R}_0^{(N)}(i\epsilon) = -i$$

would results.

where  $z = i\epsilon$  and

$$\begin{aligned}\bar{\mathbb{F}}^{(\mathcal{N})}(x^{(\mathcal{N})}, t) &= \tau^{-1} \int_0^\tau ds \mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t+s) \\ &= \tau^{-1} \int_0^\tau ds \prod_{\alpha=1}^v f^{(N)}(\mathbf{x}_\alpha^{(N)}, t+s).\end{aligned}\quad (6.45)$$

For (6.44) we have made use of the identity

$$\int d\mathbf{x}_2^{(N)} \cdots \int d\mathbf{x}_v^{(N)} \sum_{\alpha=2}^v \sum_{\beta>\alpha}^v \mathcal{L}_{\alpha\beta}^{(N,N')} \prod_{\beta=1}^v \bar{f}^{(N)}(\mathbf{x}_\beta^{(N)}, t) = 0 \quad (6.46)$$

owing to the property of the interaction Liouville operators; recall that  $\mathcal{L}_{\alpha\beta}^{(N,N')}$  is a differential operator.

We may further approximate  $\bar{\mathbb{F}}^{(\mathcal{N})}(x^{(\mathcal{N})}, t)$  as a product of time-coarse grained distribution functions of the subsystems under the assumption that the phases of the cross products of subsystem distribution functions are random and thus vanishes or negligible upon time coarse graining:

$$\begin{aligned}\bar{\mathbb{F}}^{(\mathcal{N})}(x^{(\mathcal{N})}, t) &= \overline{\prod_{\alpha=1}^v f^{(N)}(\mathbf{x}_\alpha^{(N)}, t)} \\ &\simeq \prod_{\alpha=1}^v \bar{f}^{(N)}(\mathbf{x}_\alpha^{(N)}, t).\end{aligned}\quad (6.47)$$

A remark is in order for this product form for the distribution function  $\bar{\mathbb{F}}^{(\mathcal{N})}(\mathbf{x}^{(\mathcal{N})}, t)$ . The subsystems representative of the macroscopic system under consideration here consist of a large number of molecules and are initially independent of each other. Moreover, their interactions are mainly contributed by the molecules of peripheral regions of the subsystems since the molecular interaction range is shorter than the subsystem size and the effects of the molecules well inside a subsystem would be screened off to be significant on other subsystems. Since the number of surface molecules is of a small fraction of the bulk molecules, the intersubsystem interactions are, therefore, expected to be relatively weak compared to the energy of the subsystems. Consequently, it is reasonable to think that the states of the subsystems would not be altered significantly by the collision process of the subsystems under consideration. For this reason it would be reasonable to assume the initial product form would remain virtually the same for  $\bar{\mathbb{F}}^{(\mathcal{N})}(\mathbf{x}^{(\mathcal{N})}, t)$  in the entire course of their collision except that the arguments of the subsystem distribution functions are disturbed and altered by the collisions of subsystems. Since the phases of  $f^{(N)}(\mathbf{x}_\alpha^{(N)}, t)$  are random and their time average should, therefore, be vanishingly small, the distribution func-

tion  $\bar{F}^{(N)}(x^{(N)}, t)$  of the ensemble<sup>9</sup> should be expected of the product form as in (6.47), if the random fluctuating terms are neglected.

With the approximation (6.47) the evolution equation for  $\bar{f}^{(N)}(\mathbf{x}^{(N)}, t)$  is then given by the kinetic equation

$$\left( \frac{\partial}{\partial t} + \mathbf{L}^{(N)} \right) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) = \Re[\bar{F}^{(N)}(x^{(N)}, t)], \quad (6.48)$$

$$\Re[\bar{F}^{(N)}] = \frac{1}{v} \int dx^{(N-N)} (-i) \mathcal{T}^{(N)}(z) \bar{F}^{(N)}(x^{(N)}, t), \quad (6.49)$$

where (6.47) is used for  $\bar{F}^{(N)}(x^{(N)}, t)$  in the collision integral. We reiterate that  $\bar{f}_\alpha^{(N)}(\mathbf{x}_\alpha^{(N)}, t)$  is the coarse-grained distribution function for the  $\alpha$ th subsystem, and equations similar to (6.48) hold for all  $\alpha$ . Equation (6.48) is the kinetic equation<sup>10</sup> we have strived to deduce in the approach taken for nonequilibrium ensemble theory in this chapter. We should note the deduction presented here is not exactly derivation from the Liouville equation equivalently representing the Newtonian equations of motion owing to the approximations and notions of probability theory—a non-mechanical mathematical theory. This point will be further elaborated on shortly.

If the subsystems consist of a single particle, namely,  $N = 1$ , randomly distributed in the phase space and hence if the ensemble is an assembly of single-particle subsystems, (6.48) reduces to the extended Boltzmann equation (5.50) for a moderately dense gas that we have obtained in Chap. 5 for the one-particle distribution function of each member of the ensemble. Recall that we have deduced it from the Boltzmann equation in an approach different from the approach taken in this chapter—in fact, opposite to the present approach. The extended Boltzmann equation (5.50) tends to the Boltzmann equation as the density diminishes to a sufficiently dilute gas value. Thus the name extended Boltzmann equation. For this reason (6.48) will be called the generalized Boltzmann equation (GBE) for the coarse-grained distribution functions of a dense correlated particle system—e.g., a monatomic liquid; the three kinetic equations mentioned are in the class of kindred kinetic equations, covering the density range from sufficiently dilute to moderate to dense or liquid regime. The Boltzmann kinetic equation is therefore the limiting density form that can be obtained from the generalized Boltzmann equation. Recall that we have built the extended Boltzmann equation for moderately dense gases from the Boltzmann equation for sufficiently dilute gases.

<sup>9</sup>We may imagine this situation as follows: Internal correlations of molecules in subsystems may be assumed to be stronger than the interactions between the peripheral molecules of different subsystems, so that intersubsystem interactions do not change the integrity of the subsystems when the latter collide, as if the subsystems are polymers of  $N$ -mers, which collide with each other, exchanging energy, but still remain  $N$ -mers.

<sup>10</sup>The germ of the idea for this kinetic theory was sown in the 1979 papers by the author; see Eu [63]. It is the outgrowth and evolution of the idea over the years.

The collision term of the GBE evidently describes the collisional evolution of an isolated assembly (supersystem) of subsystems, each made up of  $N$  particles, and the collisional evolution of the supersystem determines the evolution of the distribution function  $\bar{f}^{(N)}(\mathbf{x}_\alpha^{(N)}, t)$  for a subsystem of the supersystem which consists of an arbitrarily large number  $v$  of subsystems made up of  $N$  particles. Therefore it may be said to be an implementation of the basic idea underlying the Gibbs equilibrium ensemble theory when time-dependent macroscopic dynamical processes are present in dense fluids. This kinetic equation will enable us to study fluid dynamics underlying the thermodynamics of irreversible transport processes at arbitrary degree of removal from equilibrium in fluids of arbitrary density later in this chapter.

Before proceeding to discuss hydrodynamics and irreversible thermodynamics of transport processes on the basis of (6.48), we remark that *the GBE is found time-reversal symmetry breaking because of collision operator  $T^{(N)}(z)$  and hence irreversible and that the equation is not derived from the mechanical equations of motion in the strict sense of word “derivation”* because of the extramechanical steps such as time-coarse graining and random phase approximation inherent to (6.47). For, strictly speaking, the time-reversal symmetry broken equation is not derived from the mechanical equations of motion that strictly preserves time reversal symmetry owing to the presence of a step or steps<sup>11</sup> that break the time reversal symmetry introduced in the course of “derivation”. Rather, it is more appropriate to say that the GBE is formulated on the foundations of mechanical laws of motion and the probability theory in such a way that a theory of irreversible transport processes may be constructed on the basis of it in a thermodynamically consistent manner just as the Boltzmann equation was formulated by blending the ideas of probability theory and laws of mechanics. And we have made use of the combination of deterministic and stochastic theories to formulate a kinetic theory of irreversible thermodynamics and hydrodynamics in a thermodynamically consistent manner as in Chap. 3. For this reason it is more appropriate to take the kinetic equation (6.48) as *a postulate* for the evolution equation describing the distribution function  $\bar{f}^{(N)}(\mathbf{x}_\alpha^{(N)}, t)$  and therewith irreversible processes in a dense fluid. As such, the deductions made from the GBE must be confirmed *a posteriori* in correspondence to the results with phenomenological observations, particularly, in confirmation to the laws of thermodynamics.

## 6.2 Basic Properties of the Generalized Boltzmann Equation

The generalized Boltzmann equation owes its time reversal symmetry breaking property to the collision operator  $T^{(N)}(z)$  appearing in the collision integral  $\mathfrak{R}[\mathbb{F}^-(x^{(N)}, t)]$ . Besides this crucially important property, the collision integral has two basic properties related to  $T^{(N)}(z)$ : (1) It has collision invariants  $\mathcal{N}$  for the

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<sup>11</sup>The time coarse graining is one of such steps.

total number of members (subsystems) of the ensemble—alternatively, the mass—and  $E_t$  the total energy of the ensemble, both listed in (6.1) and (6.2); (2) The  $H$  theorem is satisfied by the collision integral. These properties are delineated below and shown valid in the third subsection of the present section.

### 6.2.1 Collision Invariants

The collision operator  $\mathcal{T}^{(\mathcal{N})}(z)$  has collision invariants  $\mathcal{N}$  and  $E_t$  both of which remain unchanged before and after collisions of  $v$  subsystems (i.e., members of the ensemble), because the ensemble is constructed such that they are at a fixed value and remain fixed for all time after its construction. Therefore their values are the same as their initial values even after the subsystems of the ensemble have reached mutual equilibrium internally at the end of their collision process described by the many-particle collision operator  $\mathcal{T}^{(\mathcal{N})}(z)$ .

We may make use of the mass instead of the number of particles. Although the total momenta of subsystems are not used to construct the ensemble, we may include it in the set of invariants, because the total mass of the ensemble is evidently a constant of motion over the collision process. Thus collision invariants may be taken as the mass, momentum, and energy of the ensemble. We denote the collision invariants by the symbol  $I_\gamma$  with subscript  $\gamma$  standing for the mass, momentum, and energy

$$I_\gamma = \sum_{\alpha=1}^v I_\gamma^{(\alpha)} \delta(\mathbf{r}_i - \mathbf{r}), \quad (6.50)$$

where

$$I_\gamma^{(\alpha)} = \sum_{j \in \alpha}^N m_j, \quad \sum_{j \in \alpha}^N m_j \mathbf{v}_j, \quad \text{or} \quad \sum_{j \in \alpha}^N H_j$$

with  $H_j$  denoting the Hamiltonian of molecule  $j$ . See (6.11) for  $H_j$ . The collision invariance of  $I_\gamma$  with respect to the collision operator  $\mathcal{T}^{(\mathcal{N})}(z)$  may be mathematically expressed by the formula

$$\int_V d\mathbf{r} \int dx^{(\mathcal{N})} I_\gamma(-i) \mathcal{T}^{(\mathcal{N})}(z) \prod_{\alpha=1}^v \bar{f}^{(N)}(\mathbf{x}_\alpha^{(N)}, t) = 0 \quad (6.C1)$$

in the space of distribution functions  $\mathbb{F}^{-(\mathcal{N})}(x^{(\mathcal{N})}, t)$ . As will be presently shown, this property assures the existence of conservation laws of the invariant quantity  $I_\gamma$  and also a unique equilibrium solution for the kinetic equation, the GBE. This property may be expressed as a vanishing commutator of  $\mathcal{T}^{(\mathcal{N})}$  and  $I_\gamma$ :

$$[T^{(\mathcal{N})}, I_\gamma] = 0 \quad (6.51)$$

in the space of  $\mathbb{F}^{-(\mathcal{N})}(x^{(\mathcal{N})}, t)$ . Condition (6.C1) will be used to construct the equilibrium solution of the GBE in a later section.

### 6.2.2 The $H$ Theorem and the Stability Condition

In addition to Condition (6.C1), there also holds the inequality

$$-\int_V d\mathbf{r} \int dx^{(\mathcal{N})} \ln \left( \prod_{\alpha=1}^{\mathcal{N}} \bar{f}^{(\mathcal{N})}(\mathbf{x}_\alpha^{(\mathcal{N})}, t) \right) \left[ (-i) T^{(\mathcal{N})}(z) \prod_{\alpha=1}^{\mathcal{N}} \bar{f}^{(\mathcal{N})}(\mathbf{x}_\alpha^{(\mathcal{N})}, t) \right] \geq 0. \quad (6.C2)$$

This condition will be seen as the  $H$  theorem. As a matter of fact, it is a form of Lyapounov stability condition [16, 17] of the equilibrium solution, since the GBE is a quasi-linear first-order partial differential equations from the mathematical point of view.

Conditions (6.C1) and (6.C2) are the dense fluid equivalents of Conditions (3.33) and (3.38) in Chap. 3 and Conditions (C1) and (C2) in Chap. 5, which assure the GBE the existence of conservation laws and the  $H$  theorem. The equality holds when the system reaches equilibrium. Recall similar conditions hold for the Boltzmann kinetic equation. For Conditions (6.C1) and (6.C2) to be fulfilled, the coarse-grained distribution functions  $\bar{f}^{(\mathcal{N})}(\mathbf{x}_\alpha^{(\mathcal{N})}, t)$  are required. We now show these conditions are indeed true.

### 6.2.3 Proof of Conditions (6.C1) and (6.C2)

For this line of discussion, let us first simplify the notation for the collision operator and omit the superscript  $\mathcal{N}$  from  $T^{(\mathcal{N})}(z)$  for brevity of notation. The classical collision operator  $T(z)$  obeys the classical Lippmann–Schwinger equation [1] (6.42), which is rewritten as

$$T(z) = \mathcal{L}_1 - \mathcal{L}_1 \mathcal{R}_0(z) T(z) = \mathcal{L}_1 - T(z) \mathcal{R}_0(z) \mathcal{L}_1. \quad (6.52)$$

The free resolvent operator  $\mathcal{R}_0(z)$  describes free propagation of phases of  $v$  groups (subsystems) of  $\mathcal{N}$  particles when it operates on a function of phase  $x^{(\mathcal{N})}$  whereas the resolvent operator (i.e., propagator)  $\mathcal{R}(z)$  takes into account the propagation of states under the effects of interactions between the  $v$  groups. The resolvent operator  $\mathcal{R}(z)$  formally can be written in an integral equation—a classical Lippmann–Schwinger equation [1] equivalent to (6.52)

$$\mathcal{R}(z) = \mathcal{R}_0(z) - \mathcal{R}_0(z) \mathcal{L}_1 \mathcal{R}(z) = \mathcal{R}_0(z) - \mathcal{R}(z) \mathcal{L}_1 \mathcal{R}_0(z), \quad (6.53)$$

which upon use of (6.52) can be also written as

$$\mathcal{R}(z) = \mathcal{R}_0(z) - \mathcal{R}_0(z) \mathcal{T}(z) \mathcal{R}_0(z). \quad (6.54)$$

Therefore it is possible to write it in the form

$$\mathcal{T}(z) = -\mathcal{R}_0^{-1}(z) [\mathcal{R}(z) - \mathcal{R}_0(z)] \mathcal{R}_0^{-1}(z). \quad (6.55)$$

This form is used in the collision integral, which can be written as

$$\Re[\bar{\mathbb{F}}^{(\mathcal{N})}(x^{(\mathcal{N})}, t)] = \frac{1}{v} \epsilon^2 \int dx^{(\mathcal{N}-N)} i [\mathcal{R} - \mathcal{R}_0] \bar{\mathbb{F}}^{(\mathcal{N})}(x^{(\mathcal{N})}, t). \quad (6.56)$$

Here it should be noted that  $\bar{\mathbb{F}}^{(\mathcal{N})}(x^{(\mathcal{N})}, t)$  is a function in the null eigenvalue class. Since the resolvent operators in this expression can be replaced by the integrals of time-displacement operators

$$\mathcal{R}(i\epsilon) = i \int_0^\infty ds e^{-s(\epsilon + i\mathcal{L}^{(\mathcal{N})})}, \quad (6.57)$$

$$\mathcal{R}_0(i\epsilon) = i \int_0^\infty ds e^{-s(\epsilon + i\mathcal{L}_0^{(\mathcal{N})})}, \quad (6.58)$$

the collision integral (6.56) may be written as

$$\Re[\bar{\mathbb{F}}^{(\mathcal{N})}(x^{(\mathcal{N})}, t)] = \frac{1}{v} \epsilon \int dx^{(\mathcal{N}-N)} \left[ \bar{\mathbb{F}}^{(\mathcal{N})}(x^{(\mathcal{N})}, t) - \bar{\mathbb{F}}^{(\mathcal{N})*}(x^{(\mathcal{N})*}, t) \right], \quad (6.59)$$

where

$$\bar{\mathbb{F}}^{(\mathcal{N})*}(x^{(\mathcal{N})*}, t) = \epsilon \int_0^\infty ds e^{-s(\epsilon + i\mathcal{L}^{(\mathcal{N})})} \bar{\mathbb{F}}^{(\mathcal{N})}(x^{(\mathcal{N})}, t), \quad (6.60)$$

$$\bar{\mathbb{F}}^{(\mathcal{N})}(x^{(\mathcal{N})}, t) = \epsilon \int_0^\infty ds e^{-s(\epsilon + i\mathcal{L}_0^{(\mathcal{N})})} \bar{\mathbb{F}}^{(\mathcal{N})}(x^{(\mathcal{N})}, t). \quad (6.61)$$

In (6.60), the asterisk on  $\bar{\mathbb{F}}^{(\mathcal{N})*}(x^{(\mathcal{N})*}, t)$  stands for the post-collision value. Since  $\mathcal{L}_0^{(\mathcal{N})}$  is a free Liouville operator the phase  $x^{(\mathcal{N})}$  does not change. It is not difficult to see, because the resolvent operator  $\mathcal{R}(z)$  propagates the phase  $x^{(\mathcal{N})}$  from the initial to the final state through interactions between the  $v$  subsystems, whereas the free resolvent operator  $\mathcal{R}_0(z)$  does not cause such a propagation. Therefore the net effect of the collision operator on  $\bar{\mathbb{F}}^{(\mathcal{N})}(x^{(\mathcal{N})}, t)$  may be written as a difference in

$\bar{\mathbb{F}}^{(\mathcal{N})}(x^{(\mathcal{N})}, t)$ , with regard to the phase before and after collisions. This basic property of the collision operator  $\mathcal{T}(z)$  can be exploited to show the conditions (6.C1) and (6.C2) are true. For: (1) before and after the collision process of the subsystems of the ensemble (supersystem) the masses, momentum, and energy remain unchanged. Therefore it follows that

$$\int dx^{(\mathcal{N})} \sum_{\alpha=1}^v \sum_{j=1}^N \left( I_{\gamma j}^{(\alpha)*} - I_{\gamma j}^{(\alpha)} \right) = 0, \quad (6.62)$$

which means (6.C1) is true owing to the continuity of the integrand; (2) because of the form of (6.59) and the symmetry of the phase integrals for different index  $\alpha$ , i.e., equivalence of subsystems and the invariance of the phase volume under canonical transformation from the pre- and post-collision phase, the phase volume remains the same, so that

$$dx^{(\mathcal{N})*} = dx^{(\mathcal{N})}, \quad (6.63)$$

after symmetrization of the logarithmic factor  $v$  times (6.C2) can be written in the form

$$\begin{aligned} & \frac{1}{2v^2} \int dx^{(\mathcal{N})} \ln \left[ \prod_{\alpha=1}^v \bar{f}^{(N)*}(\mathbf{x}_\alpha^{(N)}) / \prod_{\alpha=1}^v \bar{f}^{(N)}(\mathbf{x}_\alpha^{(N)}) \right] \times \\ & \left[ \prod_{\alpha=1}^v \bar{f}^{(N)*}(\mathbf{x}_\alpha^{(N)}) - \prod_{\alpha=1}^v \bar{f}^{(N)}(\mathbf{x}_\alpha^{(N)}) \right] \geq 0. \end{aligned} \quad (6.64)$$

This integral is definitely positive semidefinite because of the inequality

$$\ln(x/y)(x-y) \geq 0.$$

The equality holds only if

$$\prod_{\alpha=1}^N \bar{f}_{\text{eq}}^{(N)*}(\mathbf{x}_\alpha^{(N)}) = \prod_{\alpha=1}^N \bar{f}_{\text{eq}}^{(N)}(\mathbf{x}_\alpha^{(N)}), \quad (6.65)$$

the equality being achieved at equilibrium attained in long time. This proves the  $H$  theorem. Thus Conditions (6.C1) and (6.C2) are shown to be true.

The consequences of these conditions (6.C1) and (6.C2) will be further elaborated later when we discuss the equilibrium solution in detail and show that the GBE gives rise to a kinetic theory of thermodynamics of irreversible processes consistent with the laws of thermodynamics.

### 6.3 Conservation Laws

The GBE, (6.48), gives rise to conservation laws and the accompanying evolution equations for macroscopic variables. We derive them in the following. Let  $M(x^{(N)})$  be a mechanical quantity depending on the phase  $x^{(N)}$  in the phase space of  $N$  particles. Upon averaging  $M(x^{(N)})$  with the distribution function  $\bar{f}^{(N)}(\mathbf{x}^{(N)}, t)$  of  $N$  particles in the phase space we obtain the local mean macroscopic observable  $\langle M \rangle(\mathbf{r}, t)$  corresponding to mechanical quantity  $M_i(x^{(N)})$  of particle  $i$ :

$$\langle M \rangle(\mathbf{r}, t) = \left\langle \sum_{i=1}^N M_i(x^{(N)}) \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (6.66)$$

where the angular brackets  $\langle \dots \rangle$  stand for integrals over the phase  $\mathbf{x}^{(N)}$  in the phase space of  $N$  particles.

#### 6.3.1 Mass Conservation Law

The statistical mechanical definition of mean mass density is now given by the formula

$$\rho(\mathbf{r}, t) = \left\langle \sum_{i=1}^N m_i \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \quad (6.67)$$

The physical meaning of this expression is self-evident.

Taking time derivative we obtain

$$\frac{\partial}{\partial t} \rho(\mathbf{r}, t) = \left\langle \sum_{i=1}^N m_i \delta(\mathbf{r}_i - \mathbf{r}) \frac{\partial}{\partial t} \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle.$$

By making use of the GBE (6.48) and the condition that  $\bar{f}^{(N)}(\mathbf{x}^{(N)}, t)$  vanishes at the boundaries of the system contained in volume  $V$  as well as Condition (6.C1) owing to the fact that the mass is a collision invariant of  $\mathcal{T}^{(N)}$ , we obtain the macroscopic evolution equation for the mass density

$$\frac{\partial}{\partial t} \rho(\mathbf{r}, t) = -\nabla \cdot [\rho \mathbf{u}(\mathbf{r}, t)], \quad (6.68)$$

where  $\nabla = \partial/\partial \mathbf{r}$ , provided that mean velocity  $\mathbf{u}(\mathbf{r}, t)$  is defined by the statistical mechanical formula

$$\rho \mathbf{u}(\mathbf{r}, t) = \left\langle \sum_{i=1}^N m_i \mathbf{v}_i \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \quad (6.69)$$

This is evidently seen as the mean local momentum. Its statistical mechanical definition is naturally suggested in the course of derivation of the evolution equation for mass density  $\rho$ , which is the mass conservation law. Therefore the existence of mass conservation law naturally requires the statistical definition of momentum density  $\rho\mathbf{u}(\mathbf{r}, t)$  as given by (6.69), if the equation of continuity is to be obtained. As a matter of fact, apart from the collision invariance of mass, (6.69) is a necessary and sufficient condition for the mass conservation law to hold. It is useful to observe that if we set  $v_{sp} = 1/\rho$  (specific volume) there follows from (6.68) that

$$\rho \frac{dv_{sp}}{dt} = \nabla \cdot \mathbf{u}(\mathbf{r}, t), \quad (6.70)$$

and the evolution equation for  $v_{sp}$  does not have a source term. Equation (6.70) therefore shows that  $v_{sp}$  is also a conserved variable as is  $\rho$ , because there is no dissipation term in it.

### 6.3.2 Momentum Conservation Law

Upon using the statistical mechanical formula for the mean momentum (6.69) and applying a procedure similar to the one employed for the mass conservation law it is possible to derive the momentum balance equation

$$\frac{\partial}{\partial t} \rho \mathbf{u}(\mathbf{r}, t) = -\nabla \cdot (\mathbf{P} + \rho \mathbf{u} \mathbf{u}) + \rho \widehat{\mathbf{F}}(\mathbf{r}), \quad (6.71)$$

provided that the second-rank tensor  $\mathbf{P}(\mathbf{r}, t)$  in the divergence term is defined by the statistical mechanical formula

$$\mathbf{P}(\mathbf{r}, t) = \mathbf{P}_k(\mathbf{r}, t) + \mathbf{P}_v(\mathbf{r}, t), \quad (6.72)$$

$$\mathbf{P}_k(\mathbf{r}, t) = \left\langle \sum_i^N m_i \mathbf{C}_i \mathbf{C}_i \delta(\mathbf{r}_i - \mathbf{r}) \overline{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (6.73)$$

$$\mathbf{P}_v(\mathbf{r}, t) = \frac{1}{2} \left\langle \sum_{i \neq j}^N \overline{f}^{(N)}(\mathbf{x}^{(N)}, t) \mathbf{W}_{ij} \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle, \quad (6.74)$$

where  $\widehat{\mathbf{F}}$  is the external body force per mass density and  $\mathbf{F}_{ij}$  denotes the intermolecular force between particles  $i$  and  $j$

$$\mathbf{F}_{ij} = -\frac{\partial U_{ij}(\mathbf{r}_i - \mathbf{r}_j)}{\partial \mathbf{r}_{ij}}, \quad (6.75)$$

and  $\mathbf{W}_{ij}$  is a tensor operator defined by

$$\mathbf{W}_{ij} = \int_0^1 d\lambda \mathbf{r}_{ij} \mathbf{F}_{ij} \exp(-\lambda \mathbf{r}_{ij} \cdot \nabla). \quad (6.76)$$

The collision invariance of momentum is made use of for (6.71). The second rank tensor  $\mathbf{W}_{ij}$  is called the virial tensor operator, which operates on the delta function to its right. It is basically a displacement operator. Tensor  $\mathbf{P}(\mathbf{r}, t)$  is identified with the pressure tensor (or stress tensor). Although the details of deriving (6.71) is available in, for example, Ref. [2], we illustrate in the following how it is obtained as a typical example for deriving the evolution equations for dense fluids we are presenting in this work. This would be an illustration of the comment in the previous subsection.

Differentiating (6.69) with  $t$ , making use of the GBE (6.48), and the fact that  $m_i \mathbf{v}_i$  are one of the collision invariants, we obtain

$$\frac{\partial}{\partial t} \rho \mathbf{u} = \left\langle \sum_i^N \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \mathbf{L}^{(N)} m_i \mathbf{v}_i \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle. \quad (6.77)$$

Upon insertion of the expression for  $\mathbf{L}^{(N)}$  the right hand side of this equation can be recast into the form

$$\begin{aligned} RHS = & \left\langle \sum_i^N \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \sum_{i=1}^N m_i \mathbf{v}_i \mathbf{v}_i \cdot \nabla_{\mathbf{r}_i} \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle \\ & + \left\langle \frac{1}{2} \sum_{i \neq j}^N \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \mathbf{F}_{ij} [\delta(\mathbf{r}_i - \mathbf{r}) - \delta(\mathbf{r}_j - \mathbf{r})] \right\rangle \\ & + \left\langle \sum_{i=1}^N \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) m_i \hat{\mathbf{F}} \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle. \end{aligned} \quad (6.78)$$

Since the Dirac delta function has the property

$$\nabla_{\mathbf{r}_i} \delta(\mathbf{r}_i - \mathbf{r}) = -\nabla \delta(\mathbf{r}_i - \mathbf{r}), \quad (6.79)$$

the first line of (6.78) can be easily recast into the form

$$(RHS)_1 = -\nabla \cdot (\mathbf{P}_k + \rho \mathbf{u} \mathbf{u}),$$

if the definition of the peculiar velocity is made use of. As for the second line in (6.78), using the identity of a difference of Dirac delta functions

$$\begin{aligned}
\delta(\mathbf{r}_i - \mathbf{r}) - \delta(\mathbf{r}_j - \mathbf{r}) &= [\exp(-\mathbf{r}_{ij} \cdot \nabla) - 1] \delta(\mathbf{r}_j - \mathbf{r}) \\
&= \int_0^1 d\lambda \frac{d}{d\lambda} \exp(-\lambda \mathbf{r}_{ij} \cdot \nabla) \delta(\mathbf{r}_j - \mathbf{r}) \\
&= -\nabla \cdot \int_0^1 d\lambda \mathbf{r}_{ij} \exp(-\lambda \mathbf{r}_{ij} \cdot \nabla) \delta(\mathbf{r}_j - \mathbf{r}),
\end{aligned} \tag{6.80}$$

where  $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ , it can be cast into the form

$$\begin{aligned}
(RHS)_2 &= -\nabla \cdot \left\langle \int_0^1 d\lambda \frac{1}{2} \sum_{i \neq j}^N \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \mathbf{r}_{ij} \mathbf{F}_{ij} e^{-\lambda \mathbf{r}_{ij} \cdot \nabla} \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle \\
&= -\nabla \cdot \left\langle \frac{1}{2} \sum_{i \neq j}^N \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \mathbf{W}_{ij} \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle \\
&= -\nabla \cdot \mathbf{P}_v
\end{aligned}$$

by making use of the definition of the virial tensor operator given in (6.76). The third term of  $RHS$  can be trivially written as

$$(RHS)_3 = \left\langle \sum_{i=1}^N \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) m_i \widehat{\mathbf{F}} \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle = \rho \widehat{\mathbf{F}},$$

since  $\widehat{\mathbf{F}}$  is independent of  $\mathbf{x}^{(N)}$ . On combining  $(RHS)_1$ ,  $(RHS)_2$ , and  $(RHS)_3$ , the momentum balance equation (6.71) is easily obtained in the form presented in (6.71).

The statistical mechanical definition of  $\mathbf{P}(\mathbf{r}, t)$  and its components, (6.72)–(6.74), are therefore the necessary and sufficient conditions for the momentum balance equation (i.e., momentum conservation law) to exist and match the phenomenological form. Moreover, their definitions are unique. In the conventional kinetic theory [18] the virial tensor  $\mathbf{W}_{ij}$  is usually taken with the virial

$$\mathbf{W}_{ij} = \mathbf{r}_{ij} \mathbf{F}_{ij}, \tag{6.81}$$

which arises if one neglects the contributions from the effects of the neighboring particles surrounding the particle pair  $(ij)$ ; in other words, if the exponential factor in (6.76) is set equal to unity. However, the contribution of the exponential factor to the virial tensor is not negligible, but plays an important role in heat transport and other related transport processes as can be shown later.

Some authors in the literature debate on the question of how the pressure tensor should be defined in statistical mechanics, but in the viewpoint of the present approach there cannot be room for a question with regard to the definition of stress tensor (i.e., pressure tensor), because the momentum balance equation unambiguously dictates how and in what form it should be defined in terms of molecular variables and quantities in statistical mechanics.

### 6.3.3 Energy Conservation Law

By now it is clear how the internal energy conservation law should be derived with the help of a kinetic equation, for example, the GBE. The only difference from the previous two conservation laws is that the procedure gets progressively complicated and lengthy as the moment gets more complicated mathematically. The guide employed for the purpose is the phenomenological form of the internal energy conservation law we obtained in Chap. 2 in conformation to the laws of thermodynamics.

First, we define the internal energy in statistical mechanics as the mean mechanical energy (Hamiltonian) relative to the convective kinetic energy of flow of the fluid:

$$\rho\mathcal{E}(\mathbf{r}, t) = \left\langle \sum_{i=1}^N \left( \frac{1}{2}m_i \mathbf{C}_i^2 + \frac{1}{2} \sum_{i \neq j=1}^N U_{ij} \right) \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (6.82)$$

where many-particle contributions to the potential energy is neglected for simplicity, but their inclusion would not cause a drastic alteration of the formalism presented below.

By following the same procedure as for the derivation of the momentum balance equation, we obtain the energy conservation law, or the balance equation for internal energy, by differentiating (6.82) with  $t$  and using the GBE (6.48). The internal energy balance equation is thereby obtained in the form

$$\frac{\partial}{\partial t} \rho\mathcal{E}(\mathbf{r}, t) = -\nabla \cdot [\mathbf{Q}(\mathbf{r}, t) + \rho\mathcal{E}\mathbf{u}(\mathbf{r}, t)] - \mathbf{P} : \nabla \mathbf{u}, \quad (6.83)$$

provided that the heat flux  $\mathbf{Q}(\mathbf{r}, t)$  is identified with the statistical mechanical formula

$$\mathbf{Q}(\mathbf{r}, t) = \mathbf{Q}^{(h)}(\mathbf{r}, t) + \mathbf{Q}^{(v)}(\mathbf{r}, t), \quad (6.84)$$

$$\mathbf{Q}^{(h)} = \left\langle \sum_i^N H'_i \mathbf{C}_i \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (6.85)$$

$$\mathbf{Q}^{(v)} = \left\langle \frac{1}{2} \sum_{i \neq j}^N \mathbf{W}_{ij} \mathbf{C}_j \delta(\mathbf{r}_j - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (6.86)$$

$$H'_i = \frac{1}{2}m_i C_i^2 + \sum_{j>i}^N U_{ij}(\mathbf{r}_i - \mathbf{r}_j). \quad (6.87)$$

Here again, there is no ambiguity with regard to the statistical mechanical definitions of heat fluxes to obtain (6.83) from the definition of internal energy in (6.82) with the help of the GBE, so that the form for the phenomenological internal energy balance equation is obtained. Here we note that (6.83) can be put into an exact differential for internal energy as an expression for the first law of thermodynamics.

This point will be elaborated later at a more appropriate point, when we discuss irreversible thermodynamics.

It is useful to observe that the component  $\mathbf{Q}^{(v)}$  appears associated with the virial tensor in the statistical mechanical formula for heat flux, but it is not easily expected from the phenomenological theory. However, the kinetic theory consideration indicates that there is an energy flux associated with the virial of Clausius or its extension in the case of a dense fluid or a fluid in condensed phase—namely, the virial tensor  $\mathbf{W}_{ij}$ . The appearance of  $\mathbf{Q}^{(v)}$  given in terms of  $\mathbf{W}_{ij}$  indicates that the heat flux, therefore, is a more complex form of energy flow than a flow of Hamiltonian form of energy one might conceive to be of heat flux as an energy flow on the phenomenological theory grounds.

We now would like to make an important comment on the characteristic feature recurrent in derivation of evolution equations in kinetic theory: In the language of moment methods in kinetic theory, the conserved variables used up to this point in the derivations of three balance equations presented are moments, the leading moment being the mass density, which is the germinal element of the homologous set. Each succeeding moment evolution equation contains a moment one-order higher than the previous moment evolution equation, which usually appears in the divergence term. For example, the momentum balance equation contains a moment one-order higher than the mass density in the divergence term in the form of the stress tensor which is of rank 2 whereas the momentum density is of rank 1, namely, a vector. The Liouville operator  $\mathbf{L}^{(N)}$  is the generator of such higher order moments. The higher order moment invariably appears in the divergence term of the evolution equation. This observation holds true for the entire moment set generated from each germinal element, for example, the mass density. But other distinctive germinal moments may be required, and we will see an example for them presently, when we discuss volume transport phenomena. Unfortunately, the evolution equations so generated form an open homologous hierarchy. We will have to deal with the problem of closing the open hierarchy.

## 6.4 Voronoi Volume—a Concept of Molar Volume

The mean volume allotted to a molecule in a fluid is a physical concept that appears intuitively simple, but its molecular theory definition is not as simple. In equilibrium thermodynamics, the molar volume may be defined by using mean density; in fact, it is defined by the so-called specific volume, which is defined by the inverse density or the inverse mass density. This definition, however, does not faithfully reflect the fluid structure and its relation to the volume allotted to each particle. From the molecular theory standpoint the definition of specific volume does not appear to be a suitable candidate for the molar volume, although in equilibrium the specific volume clearly coincides with the molar volume as one can show it to be true by means of the mathematical machinery of equilibrium thermodynamics [19]. Therefore, there remains the fundamental question of what is the molecular theory definition of molar

volume—the mean volume that can be assigned to each molecule as its proper realm (or domain) in condensed phase—if a fluid (gas or liquid) is displaced from the state of equilibrium.

In fluids or macroscopic matter in general, particles (molecules) are surrounded by other continuously moving particles whether the matter is in equilibrium or not. According to Voronoi [20], if constituent particles are each positioned at the center of a Voronoi polyhedron formed by the nearest neighbors to the particle in a given configuration of the particles contained in the volume, such Voronoi polyhedra are contiguous throughout the space and thus the whole volume  $V$  is completely packed without a gap by the Voronoi volumes representative of the given configuration—this covering is called the Voronoi tessellation. Therefore, if we regard the molar volume as a representative of the mean allotted space to each particle in a fluid, the concept of Voronoi volume is eminently suitable for a molecular theoretic representation of molar volume. In the present work, we would like to take the Voronoi volume as a molecular theory representation of molar volume and hence the space (volume)<sup>12</sup> allotted to each particle in the fluid in any state of condensation. And with this concept and its molecular representation we study its macroscopic and fluid dynamic consequences. Inclusion of such a quantity (mean volume per molecule) in the macroscopic variable set extends the traditional range of fluid dynamics and irreversible thermodynamics into the new unfamiliar realm of description of transport processes in fluids.

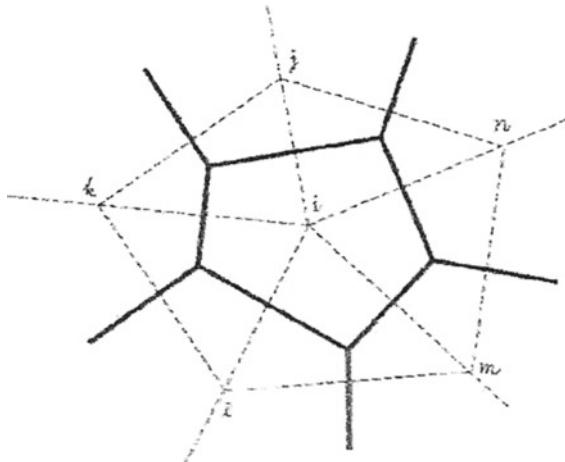
The Voronoi polyhedron of a particle is constructed in an assembly of particles as follows: Bisect the distances of a particle from the nearest-neighbor particle positions with perpendicular planes. The intersections of such planes form a polyhedron at the center of which is located the particle of attention. This polyhedron whose faces are made up of polygons is the *Voronoi polyhedron* of the particle at the center. Figure 6.1 is a two-dimensional rendering of the Voronoi polyhedron—namely, a Voronoi polygon, which graphically illustrates how polygons and polyhedra may be constructed. Since the center particles can be chosen with the next neighboring particles for the contiguous polyhedra, obviously such polyhedra<sup>13</sup> completely cover the entire volume of the fluid contained in volume  $V$ . This covering is the Voronoi tessellation mentioned earlier.

Since particles are randomly distributed in space in the case of fluids, such polyhedra and their volumes vary and must be averaged over the distribution of particles to obtain the mean value. In the case of a homogeneous equilibrium fluid, since the fluid is uniform and translationally symmetric in space the mean Voronoi volume

<sup>12</sup>van der Waals coined the term free volume in a fluid, which he used in formulating his famous equation of state and searched for its true molecular representation, but unsuccessfully. In the present author's opinion the mean Voronoi volume comes close to the notion of free volume of van der Waals.

<sup>13</sup>The concept of Voronoi polyhedra for fluids is a fluid version of the concept of Wigner–Seitz cell [21] in solid-state physics. It, however, precedes the latter concept in time.

**Fig. 6.1** Two-dimensional rendering of Voronoi volume. The polygon in solid line is the Voronoi region of particle  $i$  whose nearest neighbors at time  $t$  are particle  $j$  through  $n$ . Such polygons form faces of Voronoi polyhedron in a three-dimensional rendering of Voronoi volume at the center of which particle  $i$  is positioned. Such Voronoi polyhedra cover the entire fluid volume contained in volume  $V$



must have a uniform value over the space. If its mean value is denoted by  $\bar{v}_{\text{vo}}$  for a mole of particles then the total volume  $V$  must be evidently given by

$$V = n\bar{v}_{\text{vo}}, \quad (6.88)$$

where  $n$  is the mole number of the fluid. *This means that volume  $V$  of the fluid is a first-degree homogeneous function of  $n$*  with respect to the mean Voronoi volume  $\bar{v}_{\text{vo}}$ . This also means the Voronoi volume is a function of  $n$ ,  $T$ , and  $p$  in the case of pure fluids, where  $T$  and  $p$  are temperature and pressure, respectively. Even if the fluid is displaced from equilibrium and thus in a nonequilibrium state Relation (6.88) still holds valid, if the mean value is calculated with a suitable nonequilibrium distribution function for the fluid. In this latter case, the precise meanings of density, temperature, and pressure will accordingly be altered from those of equilibrium.

Let the Voronoi polyhedron of particle  $i$  in a fluid has  $\mathfrak{V}$  vertices which make  $p_1, p_2, \dots, p_\omega$  polygons. That is, there are  $\omega$  faces of polygons of a varying number of vertices, which form the polyhedron. The algorithms to find Voronoi polyhedra are known in the literature [22, 23]. Assume polygon  $j$  constructed therewith has  $\eta_j$  vertices. Take a vertex  $\alpha = 1$  of this polygon and join it to the non-adjacent vertices in turn to partition the polygon into triangles. Let the coordinates of the vertices with respect to the center  $O$  of the polyhedron be  $\mathbf{r}_\alpha^{(j)} = (x_\alpha^{(j)}, y_\alpha^{(j)}, z_\alpha^{(j)})$ . Then the volume of a tetrahedron is

$$\Omega_{\alpha\beta}^{(j)} = \frac{1}{6} \begin{vmatrix} x_\alpha^{(j)} & y_\alpha^{(j)} & z_\alpha^{(j)} \\ x_{\alpha+\beta}^{(j)} & y_{\alpha+\beta}^{(j)} & z_{\alpha+\beta}^{(j)} \\ x_{\alpha+\beta+1}^{(j)} & y_{\alpha+\beta+1}^{(j)} & z_{\alpha+\beta+1}^{(j)} \end{vmatrix}, \quad (6.89)$$

where  $\alpha < \beta \in \eta_j$ . The volume of the pyramid whose base is the polygon  $p_j$  and with the apex at the center  $O$  of the polyhedron is

$$\Omega_{\text{vo}}^{(j)} = \sum_{\alpha < \beta \in \eta_j} \Omega_{\alpha\beta}^{(j)}, \quad (6.90)$$

and hence the volume of the polyhedron is given by the sum of the tetrahedral volumes

$$\begin{aligned} \Omega_{\text{vo}} &= \sum_j \Omega_{\text{vo}}^{(j)} = \sum_j \sum_{\alpha < \beta \in \eta_j} \Omega_{\alpha\beta}^{(j)} \\ &= \frac{1}{6} \sum_j \sum_{\alpha < \beta \in \eta_j} \begin{vmatrix} x_\alpha^{(j)} & y_\alpha^{(j)} & z_\alpha^{(j)} \\ x_{\alpha+\beta}^{(j)} & y_{\alpha+\beta}^{(j)} & z_{\alpha+\beta}^{(j)} \\ x_{\alpha+\beta+1}^{(j)} & y_{\alpha+\beta+1}^{(j)} & z_{\alpha+\beta+1}^{(j)} \end{vmatrix}. \end{aligned} \quad (6.91)$$

In (6.91)  $x_\alpha^{(j)}$  stands for the distance between the vertices, namely,  $i$  and  $j$  particles constituting the polygon surrounding molecule  $\alpha$

$$\begin{aligned} x_\alpha^{(j)} &:= (\mathbf{r}_\alpha^j - \mathbf{r}_\alpha^i)_x \text{ component,} \\ \mathbf{r}_\alpha^i &= \text{coordinate vector of the center molecule.} \end{aligned}$$

The vector  $\mathbf{r}_\alpha^i$  varies from point to point and also with time and nonuniformity in space if the fluid is in nonequilibrium. We remark that (6.91) requires the implicit assumption that the polyhedron is convex. Regardless of whether the fluid is in equilibrium or nonequilibrium,  $\Omega_{\text{vo}}$  is a function of relative distance vector  $\mathbf{r}_{ij}^\alpha = \mathbf{r}_\alpha^j - \mathbf{r}_\alpha^i$ . If the fluid is in equilibrium, we obtain  $\bar{v}_{\text{vo}}^{(\text{eq})}$  by taking average with the equilibrium configuration distribution function  $g_{\text{eq}}^{(N)}(\mathbf{r}^{(N)})$  of the fluid:

$$n\bar{v}_{\text{vo}}^{(\text{eq})} = \langle \Omega_{\text{vo}} g_{\text{eq}}^{(N)}(\mathbf{r}^{(N)}) \rangle, \quad (6.92)$$

where  $\mathbf{r}^{(N)}$  stands for the totality of position coordinates of  $N$  particles in  $V$ . Computation of this average is not simple, however. We may employ an alternative [23], but simpler route to calculate  $\bar{v}_{\text{vo}}$  in practice without directly using a distribution function. However, the present distribution function method suffices for our purpose of developing macroscopic evolution equations related to the Voronoi volume.

If the fluid is in nonequilibrium, the nonequilibrium distribution function must be taken to perform the averaging. The nonequilibrium version of Eq. (6.92) may be written as

$$n\bar{v}_{\text{vo}} = \langle \Omega_{\text{vo}} g_{\text{eq}}^{(N)}(\mathbf{r}^{(N)}) \rangle + \langle \Omega_{\text{vo}} \Delta g^{(N)}(\mathbf{r}^{(N)}, t) \rangle, \quad (6.93)$$

where  $\Delta g^{(N)}(\mathbf{r}^{(N)}, t)$  is the nonequilibrium correction to  $g_{\text{eq}}^{(N)}(\mathbf{r}^{(N)})$ , which depends on nonconserved flow variables for the assembly of particles; for example, stress tensors, heat fluxes, etc., which vary with time and position. The nonequilibrium

correction  $\Delta g^{(N)}(\mathbf{r}^{(N)}, t)$  is provided by a suitable kinetic equation for the system. The point we would like to emphasize here is that the molecular expression  $\Omega_{vo}$  for the Voronoi volume is not a collision invariant, because its value is not conserved over a collision process of a pair of particles. Therefore in the terminology we are using in connection with the set of moments,  $\Omega_{vo}$  is a nonconserved moment unlike the mass density, momentum, or internal energy. Consequently, the set led by Voronoi volume  $\Omega_{vo}$  consists of nonconserved variables only—one may call it the Voronoi volume homolog of moments.

Before passing on to the discussion of volume transport incorporating the mean Voronoi volume, it would be useful to discuss its relation to molar volume, so that we have a thermodynamic grounding of the concept of Voronoi volume and its relation to the molar volume and specific volume, and perhaps to free volume.

To the aim we have in mind, we first examine the specific and molar volumes of the fluid by means of statistical mechanics. If density is denoted by  $\rho$  (in the units of moles per unit volume), specific volume is defined by

$$v_{sp} = 1/\rho. \quad (6.94)$$

If the equation of state is given,  $v_{sp}$  is computable from it as a function of temperature and pressure. If a mole of fluid molecules is contained in the volume it is clearly the molar volume of the fluid, denoted by  $\bar{v}$ . Thermodynamically and phenomenologically, it is expressible in the form [24]

$$\bar{v} = \frac{1}{p} [RT + B(T)p + C(T)p^2 + D(T)p^3 + \dots], \quad (6.95)$$

where  $R$  is the gas constant and  $B, C$ , etc. are the second, third, . . . , virial coefficients, which are experimentally available or may be calculated with the statistical mechanical formulas of the virial coefficients. For equilibrium fluids, the molar volume  $\bar{v}$  is derivable from the equation of state since clearly

$$\bar{v} = v_{sp}. \quad (6.96)$$

It is assumed that the expansion in (6.95) converges uniformly and sufficiently fast for this approach to be practical.

On the other hand, in thermodynamics the molar volume  $\bar{v}$  of a pure fluid may be defined by the partial derivative

$$\bar{v} = \left( \frac{\partial V}{\partial n} \right)_{T,p} \quad (6.97)$$

as a special case of the partial molar (molal) volumes [24, 25] defined in thermodynamics of mixtures by the formula

$$\bar{v}_a = \left( \frac{\partial V}{\partial n_i} \right)_{T,p,n'}, \quad (6.98)$$

where  $a$  stands for species component and  $n'$  means excluding  $n_a$ , the number density of component  $a$ . Equation (6.98) means that  $V$  is a first-degree homogeneous function of density with respect to the molar volume  $\bar{v}$  and hence

$$V = n\bar{v} \quad (6.99)$$

for a pure fluid. For a mixture

$$V = \sum_a n_a \bar{v}_a. \quad (6.100)$$

In the case of pure fluids, there is no need for (6.100) because (6.99) obviously holds. From the thermodynamic definition (6.97) it, however, is not obvious that  $\bar{v} = v_{sp}$ . It is proved below that it is indeed so.

For this purpose we write the equation of state in the form

$$pV = Nk_B T + NZ(\rho, T), \quad (6.101)$$

where  $N$  is the number of particles and  $k_B$  is the Boltzmann constant and  $Z$  is the compressibility factor. It can be expressed either phenomenologically or, if statistical mechanics is used, by the formula in terms of the pair correlation function  $g(r)$  and intermolecular potential  $u(r)$

$$Z(\rho, T) = -\frac{\rho}{6} \int_V d\mathbf{r} \mathbf{r} \cdot \frac{\partial u(r)}{\partial \mathbf{r}} g(r). \quad (6.102)$$

Either way, we obtain

$$\bar{v} = \left( \frac{\partial V}{\partial N} \right)_{T,p} = \frac{k_B T (1 + Z)}{p} + \frac{N}{p} \left( \frac{\partial \rho}{\partial N} \right)_{T,p} \left( \frac{\partial Z}{\partial \rho} \right)_{T,p}. \quad (6.103)$$

Since  $\rho = N/V$ , it follows

$$\left( \frac{\partial \rho}{\partial N} \right)_{T,p} = \frac{1}{V} (1 - \rho \bar{v}) \quad (6.104)$$

and on substituting it into Eq. (6.103) and rearranging the result, we find [19]

$$\bar{v} = \frac{k_B T + Z + \rho \left( \frac{\partial Z}{\partial \rho} \right)_{T,p}}{p \left[ 1 + \rho^2 \left( \frac{\partial Z}{\partial \rho} \right)_{T,p} \right]} = \frac{1}{\rho} = v_{sp}. \quad (6.105)$$

This proves that indeed  $\bar{v} = v_{\text{sp}}$  for equilibrium fluids. The same conclusion can be drawn for mixtures. For nonequilibrium fluids, since the equation of state is generally not known to be in the form of Eq. (6.101), the conclusion drawn above for equilibrium fluids cannot be simply extended to nonequilibrium fluids. In any case, this demonstrates the equivalence of molar volume and mean Voronoi volume if the fluid is in equilibrium, but, if the fluid is removed from equilibrium, from the standpoint of kinetic theory the Voronoi volume is not equivalent to the equilibrium specific volume that is a collision invariant. This is the reason that the theory of volume transport may be based on the concept of mean Voronoi volume.

For real fluids the equation of state can be sufficiently accurately computed by numerical methods, including computer simulation methods [26, 27]. With the so-obtained equation of state,  $v(T, p)$  can be tabulated and compared with experimental data. Nevertheless, even for equilibrium fluids the simple-looking quantities like the molar volume or specific volume are not so simple to obtain directly as an explicit function of temperature and pressure in a closed form by means of a molecular (statistical mechanical) theory, as investigation into the literature would indicate, perhaps except for hard sphere fluids. In the latter case, the Carnahan–Starling equation of state [28] may be used to a good approximation. In any case, their molecular theory definitions have not been explicitly given as other thermodynamic quantities are in the literature, but we see that the Voronoi volume now fills this lacuna.

The local mean value of the Voronoi volume of particle  $i$  surrounded by  $z_i$  nearest neighbors  $j \in z_i$  is denoted by

$$\rho(\mathbf{r}, t) v(\mathbf{r}, t) = \left\langle \sum_{i=1}^N m \Omega(\{\mathbf{r}_i - \mathbf{r}_j\}; j \in z_i) \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(x^{(N)}, t) \right\rangle. \quad (6.106)$$

Its local equilibrium value  $\rho v_0(\mathbf{r})$  is then evidently given by its local equilibrium average

$$\rho v_0(\mathbf{r}) = \left\langle \sum_{i=1}^N m \Omega(\{\mathbf{r}_i - \mathbf{r}_j\}; j \in z_i) \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}_{\text{eq}}^{(N)}(x^{(N)}) \right\rangle, \quad (6.107)$$

where  $\bar{f}_{\text{eq}}^{(N)}(x^{(N)})$  is the local equilibrium distribution function. We then find it convenient to work with the moment defined by

$$h_i^{(0)} = m_i \Omega(\{\mathbf{r}_i - \mathbf{r}_j\}; j \in z_i) - m_i v_0(\mathbf{r}). \quad (6.108)$$

Therefore the local mean value of moment  $h_i^{(0)}$  is evidently a fluctuation of the Voronoi volume from the equilibrium Voronoi volume:

$$\Phi^{(0)} = \rho \hat{\Phi}^{(0)} = \left\langle \sum_i h_i^{(0)} \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(x^{(N)}, t) \right\rangle, \quad (6.109)$$

which is evidently given by

$$\Phi^{(0)} = \rho \widehat{\Phi}^{(0)} = \rho (v - v_0). \quad (6.110)$$

Henceforth, this moment  $h_i^{(0)}$  is the leading element of the volume homolog of moments. It is notationally convenient to define

$$\bar{h}_i^{(0)} = h_i^{(0)} \delta(\mathbf{r}_i - \mathbf{r}) \quad (6.111)$$

with  $h_i^{(0)}$  defined by (6.108). Therefore

$$\Phi_{\text{eq}}^{(0)} = \sum_{i=1}^N \left\langle \bar{h}_i^{(0)} \bar{f}_{\text{eq}}^{(N)}(x^{(N)}) \right\rangle = 0. \quad (6.112)$$

We emphasize that, precisely speaking,  $v(\mathbf{r}, t) \neq v_{\text{sp}}$ , but would tend to  $v_{\text{sp}}$  as shown in a numerical study<sup>14</sup> of Hunjan and Eu [19]. Moment  $\Phi^{(0)}$  is a functional of  $\boldsymbol{\varsigma} := (\rho, \mathbf{u}, T)$  through which the distribution functions  $\bar{f}^{(N)}(x^{(N)}, t)$  evolve to  $\bar{f}_{\text{eq}}^{(N)}(x^{(N)})$  on account of the fact that their space-time evolution is locally determined by the hydrodynamic modes, if the system is in a nonequilibrium condition away from equilibrium.

## 6.5 Evolution Equation of Volume Fluctuations

The evolution equation of volume fluctuation  $\Phi^{(0)}$  also can be obtained by making use of the GBE in a manner similar to the equation of continuity, etc.

Differentiating (6.109) with respect to time and making use of the GBE (6.48), we obtain the evolution equation for  $\widehat{\Phi}^{(0)}$ :

$$\rho \frac{d\widehat{\Phi}^{(0)}}{dt} = -\nabla \cdot \Phi^{(4)} + d_t \boldsymbol{\varsigma} \cdot \mathbf{v}_{\boldsymbol{\varsigma}} + f_v + \Lambda^{(0)}, \quad (6.113)$$

where the dissipation term  $\Lambda^{(0)}$  is defined by

$$\Lambda^{(0)} = \left\langle \sum_{i=1}^N h_i^{(0)} \delta(\mathbf{r}_i - \mathbf{r}) \mathfrak{R}[\bar{\mathbb{F}}^{(N)}(x^{(N)}, t)] \right\rangle, \quad (6.114)$$

---

<sup>14</sup>This implies that  $v_{\text{sp}}$  should not be regarded as the molar volume in the liquid density regime.

and  $f_v$  by the statistical mechanical formula

$$f_v = \left\langle \sum_{i=1}^N \sum_{i \neq j \in \varepsilon_i} \mathbf{C}_i \cdot \frac{\partial h_i^{(0)}}{\partial \mathbf{r}_{ij}} \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \quad (6.115)$$

The rest of the symbols in (6.113) are as follows:

$$\mathbf{v}_\zeta = \left\langle \sum_{i=1}^N \frac{\delta \bar{h}_i^{(0)}}{\delta \zeta} \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle \quad (6.116)$$

with the abbreviation

$$\frac{\delta \bar{h}_i^{(0)}}{\delta \zeta} = d_t \mathbf{u} \cdot \frac{\delta \bar{h}_i^{(0)}}{\delta \mathbf{u}} + d_t \rho \frac{\delta \bar{h}_i^{(0)}}{\delta \rho} + d_t T \frac{\delta \bar{h}_i^{(0)}}{\delta T}, \quad (6.117)$$

and  $\Phi^{(4)}$  denotes the moment one-order higher than  $\Phi^{(0)}$ , that is, a volume flux, akin to the mass flux in the equation of continuity. It is defined by

$$\Phi^{(4)} = \rho \hat{\Phi}^{(4)} := \mathbf{J}_v = \left\langle \sum_{i=1}^N h_i^{(4)} \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle \quad (6.118)$$

with the definition of  $h_i^{(4)}$  as the expression of the flux of  $h_i^{(4)}$  in the coordinate frame moving at the flow velocity  $\mathbf{u}$

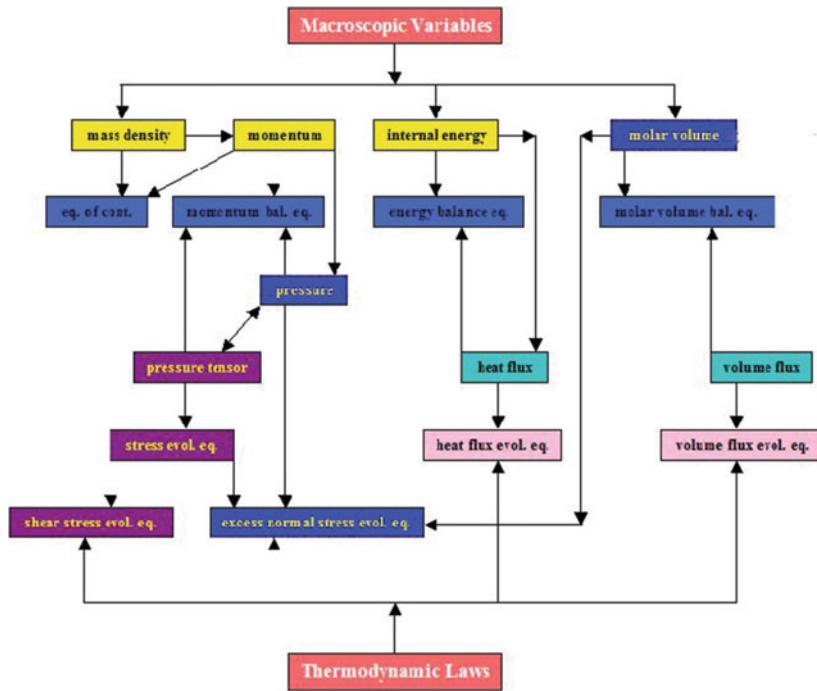
$$h_i^{(4)} = \mathbf{C}_i h_i^{(0)}, \quad (6.119)$$

$$\bar{h}_i^{(4)} = \mathbf{C}_i h_i^{(0)} \delta(\mathbf{r}_i - \mathbf{r}) = \mathbf{C}_i \bar{h}_i^{(0)}. \quad (6.120)$$

It is important to note that the dissipation term  $\Lambda^{(0)}$  is generally not equal to zero, and hence it makes  $\Phi^{(0)}$  a nonconserved moment. Therefore it thus may be correct to say that the evolution of Voronoi volume in a nonequilibrium fluid, in general, dissipates energy unlike the specific volume  $v_{sp} = 1/\rho$ , whose evolution equation has no dissipation term, as easily deduced from the equation of continuity; see (6.70).

The appearance of this Voronoi volume evolution equation is the new aspect that distinguishes the present theory of macroscopic evolution from the conventional ones, and we now have a version of generalized hydrodynamics extended from the old version [1, 2, 29, 30]. Consequently, the manifold of macroscopic variables for nonequilibrium fluids is accordingly enlarged to include the mean Voronoi volume and its flux as legitimate macroscopic variables necessary for proper description of fluid behaviors in nonequilibrium conditions. Besides, the concept of volume is endowed a desired molecular theory representation in the form of Voronoi volume just like other macroscopic observables in statistical mechanics.

Just like the leading moments listed earlier giving rise to their evolution equations with the help of the GRE, their evolution equations naturally and logically determine their fluxes. Thus the fluxes of the leading moments sequentially give rise to their evolution equation with the help of the GRE. This way an entire hierarchy of moment evolution equations can be logically derived by using the GBE—an irreversible kinetic equation. This process of generating the hierarchy of evolution equations in the present kinetic theory is schematically illustrated in Fig. 6.2. So generated hierarchies of evolution equations are open sets. The sets are eventually closed by closures and also made to confirm the laws of thermodynamics.



**Fig. 6.2** Flow chart for moments is displayed in the case of a pure simple fluid. Beginning from the conserved moments and Voronoi volume on the top of the flow chart, when operated on by the Liouville operator they give rise to various macroscopic evolution equations displayed at different levels of tensorial order denoted in different shades of color. In the present theory, the evolution equations at the level of shear stress, excess normal stress, heat flux, and volume flux evolution equations are subjected to the laws of thermodynamics, so that they are made thermodynamically consistent

## 6.6 Evolution Equations for Other Nonconserved Variables

To implement the general process of deriving evolution equations for non-conserved variables, it is useful to construct a set of nonconserved moments including the moments for volume fluctuation and volume flux. We explicitly define the leading elements of nonconserved moment set<sup>15</sup> arranged in a suitable sequence as follows:

$$\mathfrak{H} = \left( \bar{h}_i^{(0)}, \bar{h}_i^{(1)}, \bar{h}_i^{(2)}, \bar{h}_i^{(3)}, \bar{h}_i^{(4)}, \dots \right), \quad (6.121)$$

where  $\bar{h}_i^{(0)}$  and  $\bar{h}_i^{(4)}$  are already defined by (6.111) and (6.120) and the remaining moments are defined as follows:

$$\begin{aligned} \bar{h}_i^{(1)} &:= m_i [\mathbf{C}_i \mathbf{C}_i]^{(2)} \delta(\mathbf{r}_i - \mathbf{r}) + \frac{1}{2} \sum_{j \neq i} [\mathbf{W}_{ij}]^{(2)} \delta(\mathbf{r}_j - \mathbf{r}) \\ &:= h_i^{(1)} \delta(\mathbf{r}_i - \mathbf{r}), \end{aligned} \quad (6.122)$$

$$\begin{aligned} \bar{h}_i^{(2)} &= \left[ \frac{1}{3} \text{Tr}(m_i \mathbf{C}_i \mathbf{C}_i) - m_i p / \rho \right] \delta(\mathbf{r}_i - \mathbf{r}) \\ &\quad + \frac{1}{6} \sum_{j \neq i}^N \text{Tr} \mathbf{W}_{ij} \delta(\mathbf{r}_j - \mathbf{r}) - \alpha_2 h_i^{(0)} \delta(\mathbf{r}_i - \mathbf{r}) \\ &:= h_i^{(2)} \delta(\mathbf{r}_i - \mathbf{r}) - \alpha_2 h_i^{(0)} \delta(\mathbf{r}_i - \mathbf{r}), \end{aligned} \quad (6.123)$$

$$\begin{aligned} \bar{h}_i^{(3)} &= \mathbf{C}_i H'_i \delta(\mathbf{r}_i - \mathbf{r}) \\ &\quad + \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ (i \neq j)}}^N \mathbf{W}_{ij} \cdot \mathbf{C}_j \delta(\mathbf{r}_j - \mathbf{r}) - \alpha_3 h_i^{(4)} \delta(\mathbf{r}_i - \mathbf{r}) \\ &:= h_i^{(3)} \delta(\mathbf{r}_i - \mathbf{r}) - \alpha_3 h_i^{(4)} \delta(\mathbf{r}_i - \mathbf{r}). \end{aligned} \quad (6.124)$$

In (6.122)–(6.124) the coefficients  $\alpha_2$  and  $\alpha_3$  are determined, by applying the Schmidt orthogonalization method, such that

$$\left\langle \bar{h}_i^{(2)} \cdot h_i^{(0)} \right\rangle_0 = 0, \quad \left\langle \bar{h}_i^{(3)} \cdot h_i^{(4)} \right\rangle_0 = 0, \quad etc., \quad (6.125)$$

with  $\langle \dots \rangle_0$  denoting an equilibrium average as in (6.112). As a consequence, the moments are orthogonal to each other and irreducible. These conditions yield the constants  $\alpha_2$  and  $\alpha_3$  in the forms

<sup>15</sup>The moment set constructed in this work is a dense fluid extension of the Grad moment set [31] which is used in the moment method for the Boltzmann kinetic equation for dilute monatomic gases. As the density is diluted sufficiently low to the level of dilute gas density, the present moment set reduces to the Grad moment set.

$$\alpha_2 = \frac{\langle \bar{h}_i^{(2)} \cdot h_i^{(0)} \rangle_0}{\langle \bar{h}_i^{(0)} \cdot h_i^{(0)} \rangle_0}, \quad (6.126)$$

$$\alpha_3 = \frac{\langle \bar{h}_i^{(4)} \cdot \bar{h}_i^{(3)} \rangle_0}{\langle \bar{h}_i^{(4)} \cdot h_i^{(4)} \rangle_0}, \dots \quad (6.127)$$

The rest of the set  $\mathfrak{H}$  then can be systematically defined, step by step, when the evolution equations are derived from the kinetic equation and the moments are orthogonalized and made irreducible by employing the Schmidt method. Since we will confine our discussion to the elements shown above (i.e., the leading moments), the remainder of the set is not explicitly listed here for brevity of presentation. These moments can be systematically and unambiguously identified in the course of generating moment series and their evolution equations. The moment one order higher than  $h_i^{(q)}$  is identified with  $\psi_i^{(q)}$  in the divergence term of the evolution equation generated; see (6.129) below. The moments  $h_i^{(1)}, h_i^{(2)}, h_i^{(3)}$  are the molecular expression for the shear stress tensor, excess normal stress, heat flux of the fluid, which have appeared in the divergence terms in the conservation laws. As can be seen evidently, these moment evolution equations not only are coupled with each other, but also include contributions from the Voronoi volume and the moments generated from them in the course of derivations of their evolution equations; see, for example,  $\alpha_2$  and  $\alpha_3$ , both of which involve either  $h_i^{(0)}$  or  $h_i^{(4)}$  that are associated with the volume fluctuation and the volume flux. This pattern of sequence persists for higher order moments. It is useful to note that the Liouville operator in the streaming term in the GBE is the generator of the moment set. Thus by examining the macroscopic variable manifold together with their evolution equations it would be possible to investigate the effects of volume transport processes on the moments in the course of transport processes in the fluid of interest and, consequently, on the structure of hydrodynamics by the presence of volume transport and the modifications of the traditional hydrodynamics thereby.<sup>16</sup>

Given the set  $\mathfrak{H}$ , the evolution equations for macroscopic observables (moments)  $\Phi^{(q)}$  defined by

$$\Phi^{(q)} = \rho \widehat{\Phi}^{(q)} = \left\langle \sum_{i=1}^N h_i^{(q)} \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle \quad (6.128)$$

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<sup>16</sup>The notion of volume transport in a quite different and roundabout form was proposed by Brenner [3, 4] in a series of papers. We find a precise molecular concept of volume (e.g., Voronoi volume) allotted to a molecule in a fluid is missing in his phenomenological formulation. As a consequence, the phenomenological equations employed are difficult to comprehend from the phenomenological and kinetic theory standpoints, if not misleading.

can be derived from the kinetic equation in the generic form

$$\rho \frac{d}{dt} \widehat{\Phi}^{(q)} = -\nabla \cdot \psi^{(q)} + \mathcal{Z}^{(q)} + \Lambda^{(q)} (q \geq 0). \quad (6.129)$$

Here the symbols are defined by the statistical mechanics formulas

$$\psi^{(q)} = \left\langle \sum_{i=1}^N \mathbf{C}_i h_i^{(q)} \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (6.130)$$

$$\mathcal{Z}^{(q)} = \left\langle \sum_{i=1}^N \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \mathcal{D}_t h_i^{(q)} \right\rangle, \quad (6.131)$$

$$\Lambda^{(q)} = \left\langle \sum_{i=1}^N h_i^{(q)} \delta(\mathbf{r}_i - \mathbf{r}) \mathfrak{R}[\bar{\mathbb{F}}^{(N)}(x^{(N)}, t)] \right\rangle, \quad (6.132)$$

with the definition of substantial time derivative in the phase space of  $N$  particles  $\mathcal{D}_t$  defined by

$$\mathcal{D}_t = \frac{d}{dt} + \mathbf{L}^{(N)} + \mathbf{C}_i \cdot \nabla. \quad (6.133)$$

The  $\mathcal{Z}^{(q)}$  is called the kinematic term and  $\Lambda^{(q)}$  the dissipation term, which is responsible for energy dissipation by the process  $\Phi^{(q)} = \rho \widehat{\Phi}^{(q)}$ . Equations (6.113) and (6.134) below as well as other evolution equations, or their suitable rearrangements, presented below for nonconserved variables (moments), are examples of the generic form, (6.129), for the evolution equation of a nonconserved moment. The evolution equations for the shear stress, excess normal stress, and heat flux are presented in the following.

### 6.6.1 Evolution Equation of Volume Flux

Equation (6.113) contains a new macroscopic variable  $\Phi^{(4)}$  that is one order higher than  $\Phi^{(0)}$  as a macroscopic moment. It is a vector as opposed to a scalar  $\Phi^{(0)}$ . Using a procedure similar for the previously presented evolution equations, we are able to obtain the evolution equation for the volume flux  $\Phi^{(4)}$  with the help of the kinetic equation (GBE) as presented below:

$$\rho \frac{d \widehat{\Phi}^{(4)}}{dt} = -\nabla \cdot \psi^{(4)} + \widehat{\Phi}^{(0)} \nabla \cdot (\mathbf{P} - \rho \widehat{\mathbf{F}}) - \rho \widehat{\Phi}^{(4)} \cdot \nabla \mathbf{u} + \mathbf{T}_F + \Lambda^{(4)}, \quad (6.134)$$

where  $\widehat{\Phi}_0$  is a scalar and

$$\Lambda^{(4)} = \left\langle \sum_{i=1}^N h_i^{(4)} \delta(\mathbf{r}_i - \mathbf{r}) \mathfrak{R}[\mathbb{F}^{-(N)}(x^{(N)}, t)] \right\rangle, \quad (6.135)$$

$$\psi^{(4)} = \left\langle \sum_{i=1}^N \mathbf{C}_i h_i^{(4)} \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (6.136)$$

$$\mathbf{T}_F = \left\langle \sum_{i=1}^N \sum_{k \neq i}^N \frac{1}{m_i} \mathbf{F}_{ik} h_i^{(0)} \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \quad (6.137)$$

Since  $h_i^{(4)}$  is clearly a nonconserved variable, the dissipation function  $\Lambda^{(4)}$  does not vanish. As for other macroscopic evolution equations, (6.134) may, in fact, be regarded as the constitutive equation for the volume flux. It may not be ignored if volume transport is significant. As we will see presently, this evolution equation is a member of an open hierarchy of evolution equations that are directly associated with volume transport phenomena in macroscopic irreversible processes.

### 6.6.2 Shear Stress Evolution Equation

It is possible to show the evolution equation for the traceless symmetric part of the stress tensor  $\widehat{\Phi}^{(1)} := [\mathbf{P}]^{(2)} / \rho = \boldsymbol{\Pi} / \rho$  is given by

$$\frac{d\widehat{\Phi}^{(1)}}{dt} = -\nabla \cdot [\bar{\psi}^{(1)}]^{(2)} - 2[\mathbf{P} \cdot \nabla \mathbf{u}]^{(2)} + 2[\mathbf{V}_1]^{(2)} + \Lambda^{(1)}, \quad (6.138)$$

where the symbol  $[\mathbf{A}]^{(2)}$  denotes the traceless symmetric part of second rank tensor  $\mathbf{A}$  and  $\bar{\psi}^{(1)}$  is defined by a renormalized third rank tensor

$$\bar{\psi}^{(1)} = \psi^{(1)} + \psi^{(1W)} \quad (6.139)$$

with  $\psi^{(1)}$  and  $\psi^{(1W)}$ , respectively, defined by

$$\psi^{(1)} = \sum_{i=1}^N \left\langle \bar{f}^{(N)} m_i \mathbf{C}_i \mathbf{C}_i \mathbf{C}_i \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle, \quad (6.140)$$

$$\psi_{\gamma\alpha\beta}^{(1W)} = \frac{1}{2} \sum_{j=1}^N \sum_{k=1}^N \left( \bar{f}^{(N)} \left( \mathbf{C}_{jk}^\gamma \mathbf{W}_{jk}^{\alpha\beta} + \mathbf{C}_{jk}^\alpha \mathbf{W}_{jk}^{\gamma\beta} + \mathbf{C}_{jk}^\beta \mathbf{W}_{jk}^{\gamma\alpha} \right) \delta(\mathbf{r}_k - \mathbf{r}) \right). \quad (6.141)$$

Therefore  $\bar{\psi}^{(1)}$  is a renormalized third-rank tensor making up the divergence term in the stress tensor evolution equation. The symbol  $[\psi^{(1)}]^{(2)}$  in (6.138) denotes the traceless symmetric part of the last two Greek indices on vectors or tensors:

$$[\psi^{(1)}]_{\alpha\beta\gamma}^{(2)} = \frac{1}{2} \left( \psi_{\gamma\alpha\beta}^{(1)} + \psi_{\gamma\beta\alpha}^{(1)} \right) - \frac{1}{3} \delta_{\alpha\beta} \psi_{\gamma\delta\delta}^{(1)}, \quad (6.142)$$

which thus makes up a third rank tensor that is traceless symmetric with respect to the last two Cartesian indices. The trace taken over the last two indices is denoted by

$$\text{Tr}' \psi^{(1)} := \psi_{\gamma\delta\delta}^{(1)}, \quad (6.143)$$

where the prime on  $\text{Tr}'$  means taking trace of the last two indices of the third rank tensor. Therefore  $\psi^{(1)}$  may be decomposed into the two parts as in the expression

$$\psi^{(1)} = [\psi^{(1)}]^{(2)} + \frac{1}{3} \delta \text{Tr}' \psi^{(1)}. \quad (6.144)$$

Evolution equation (6.138) is structurally in the same form as the evolution equation for the traceless symmetric part of the stress tensor for a mixture in Refs. [1, 2], which were derived without the volume transport taken into consideration. The diffusion flux dependent terms are absent here because the diffusion fluxes are equal to zero if the fluid is pure. The tensor  $\mathbf{V}_1$  is closely related to the tensor whose vector component is the torque of the relative motion of particle pairs  $(i,j)$  as will be shown presently

$$\begin{aligned} \mathbf{V}_1 = & \frac{1}{2} \sum_{i=1}^N \sum_{k \neq i}^N \left\langle \bar{f}^{(N)} \left( \mathbf{F}_{ik}^\alpha \mathbf{C}_{ik}^\beta + \mathbf{C}_{ik}^\alpha \mathbf{F}_{ik}^\beta \right) \delta(\mathbf{r}_k - \mathbf{r}) \right\rangle \\ & + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \left\langle \bar{f}^{(N)} \mathbf{C}_{ij} \cdot \nabla_{ij} \mathbf{W}_{ij} \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle \\ & + \sum_{i=1}^N \left\langle \bar{f}^{(N)} \left( \widehat{\mathbf{F}}_i m_i \mathbf{C}_i + m_i \mathbf{C}_i \widehat{\mathbf{F}}_i \right) \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle. \end{aligned} \quad (6.145)$$

Similarly to (6.144), the second rank tensor  $\mathbf{V}_1$  can be decomposed into two parts

$$\mathbf{V}_1 = [\mathbf{V}_1]^{(2)} + \frac{1}{3} \delta \text{Tr} \mathbf{V}_1. \quad (6.146)$$

To comprehend the significance of tensors  $\mathbf{V}_1$ , let us digress and assume<sup>17</sup> Hooke's law for the intermolecular forces  $\mathbf{F}_{jk}$ :

$$\mathbf{F}_{ik}(\mathbf{r}_{ik}) \simeq -k_{ik}\mathbf{r}_{ik}, \quad (6.147)$$

where  $k_{ik}$  is the force constant. Then, for example, there follows the approximation

$$\mathbf{F}_{jk}\mathbf{C}_{jk} \simeq -k_{jk}\mathbf{r}_{jk}\mathbf{C}_{jk}[1 + O(\mathbf{r}_{jk} \cdot \nabla)] \quad (6.148)$$

and  $\mathbf{r}_{jk}m_{ij}\mathbf{C}_{jk}[m_{jk} = m_jm_k/(m_k + m_k)]$  is an angular momentum tensor of the relative motion of particle pair  $(jk)$ . Therefore the tensor  $\mathbf{V}_1$  will have an intimate relation to local rotations of binary pairs in the fluid. A similar related interpretation may be given to  $\psi^{(1W)}$ , since we find it is a mean value of the flux of such a tensor associated with the torque of rotational motion in liquids. The volume flux may be also attributed to such a local rotation arising in the fluid flow in liquid states.

We also notice that the stress evolution equation presented does not explicitly involve the moment  $\Phi^{(0)}$  for volume fluctuations, although the effects of volume fluctuations appear implicitly through the moments  $h_i^{(1)}$ , especially, in the dissipation term. The basic reason for this lies in the Curie principle which does not allow direct couplings between macroscopic moments of different tensorial ranks, or alternatively put, of different symmetries. We will see such couplings will occur in the case of, for example, the excess normal stress presented below.

### 6.6.3 Evolution Equation for Excess Normal Stress

In the absence of volume transport it is natural to choose for excess normal stress the moment

$$h_j^{(2)}\delta(\mathbf{r}_j - \mathbf{r}) = m_j \left( \frac{1}{3}C_j^2 - p/\rho \right) \delta(\mathbf{r}_j - \mathbf{r}) + \frac{1}{6} \sum_{\substack{k=1 \\ (j \neq k)}}^N \text{Tr} \mathbf{W}_{jk} \delta(\mathbf{r}_k - \mathbf{r}) \quad (6.149)$$

to be consistent with the moment chosen for the traceless symmetric part of the stress tensor in the same situation. The average of this molecular moment gives the excess normal stress

$$\bar{\Delta} = \left\langle \sum_{j=1}^N h_j^{(2)}\delta(\mathbf{r}_j - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (6.150)$$

which is related to compression/dilatation and thus the bulk viscosity of the fluid.

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<sup>17</sup>In this model the potential energies of interaction is those of harmonic oscillators.

If the volume transport is taken into consideration, the molecular moment for molar volume fluctuation  $h_i^{(0)}$ , which is scalar, is coupled to the excess normal stress for symmetry reason. Thus we define the molecular moment in the form

$$\bar{h}_j^{(2)} := h_j^{(2)} \delta(\mathbf{r}_j - \mathbf{r}) - \alpha_2 h_j^{(0)} \delta(\mathbf{r}_j - \mathbf{r}). \quad (6.151)$$

Recall  $h_j^{(0)}$  is the molecular expression for molar domain given in terms of the Voronoi volume  $\bar{h}_i^{(0)}/m_i := \Omega_i (|\mathbf{r}_i - \mathbf{r}_j|, j \in z_i | \boldsymbol{\varsigma})$  introduced earlier. The mean value of the moment  $h_j^{(2)}$  defines the modified excess normal stress

$$\Phi^{(2)} := \Delta = \left\langle \sum_{j=1}^N \bar{h}_j^{(2)} \bar{f}^{(N)}(x^{(N)}, t) \right\rangle = \bar{\Delta} - \alpha_2 \Phi^{(0)}, \quad (6.152)$$

where  $\bar{\Delta}$  is defined by (6.150).

By proceeding in a similar manner to the derivation of the evolution equation (6.138), we obtain the evolution equation for  $\Delta := \Phi^{(2)} = \rho \hat{\Phi}^{(2)}$  in the form

$$\begin{aligned} \rho \frac{d\hat{\Phi}^{(2)}}{dt} &= -\nabla \cdot \bar{\psi}^{(2)} - \rho \frac{d}{dt} (p/\rho) \\ &\quad - \frac{2}{3} (\mathbf{P} : \nabla \mathbf{u}) + \frac{2}{3} \text{Tr} \mathbf{V}_1 - \alpha^{(2)} \rho \frac{dv}{dt} + \Lambda^{(2)}. \end{aligned} \quad (6.153)$$

Here the vector in the divergence term  $\bar{\psi}^{(2)}$  is renormalized as follows:

$$\bar{\psi}^{(2)} = (\psi^{(2)} + \psi^{(2W)}), \quad (6.154)$$

where  $\psi^{(2)}$  and  $\psi^{(2W)}$  are defined by

$$\psi^{(2)} = \frac{1}{3} \sum_{i=1}^N \left\langle m_i \mathbf{C}_i C_i^2 \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)} \right\rangle - \alpha_2 \sum_{i=1}^N \left\langle \mathbf{C}_i h_i^{(0)} \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)} \right\rangle, \quad (6.155)$$

$$\psi_\gamma^{(2W)} = \frac{1}{6} \left\langle \sum_{j,k=1(j \neq k)}^N \bar{f}^{(N)} \left( \mathbf{C}_j^\gamma \mathbf{W}_{jk}^{\alpha\alpha} + \mathbf{C}_j^\alpha \mathbf{W}_{jk}^{\gamma\alpha} + \mathbf{C}_j^\alpha \mathbf{W}_{jk}^{\alpha\gamma} \right) \delta(\mathbf{r}_k - \mathbf{r}) \right\rangle \quad (6.156)$$

with the repeated indices denoting trace (i.e., summation over the index). Lastly,  $\Lambda^{(2)}$  is the dissipation term

$$\Lambda^{(2)} = \left\langle \sum_{i=1}^N \bar{h}_i^{(2)} \mathfrak{R}[\bar{F}^{(N)}] \right\rangle. \quad (6.157)$$

The tensor  $\mathbf{V}_1$  was defined previously in connection with the derivation of the evolution equation for  $\boldsymbol{\Pi}$ . It should be noted that  $\psi^{(2)}$  and  $\psi^{(2W)}$  are vectors, whose mathematical structures are reminiscent of that of the heat flux. Indeed, it can be shown that they are related to each other. The evolution equation for the excess normal stress in the absence of volume transport is thus modified by the appearance of the term  $-\alpha_2 \Phi^{(0)}$  in  $\psi^{(2)}$  and the appearance of the term  $-\alpha_2 \rho (dv/dt)$  in the kinematic term. Note also that  $\bar{h}_i^{(2)}$  in  $\Lambda^{(2)}$  is modified by the presence of  $-\alpha_2 h_j^{(0)}$ . We reiterate the difference between the specific volume  $\hat{v} = 1/\rho$  and the molar domain or volume  $v$  in the present theory and that  $\alpha_2$  is associated with molar domain fluctuations; see (6.108) and (6.109).

### 6.6.4 Evolution Equation for Heat Flux

The evolution equation for heat flux  $\mathbf{Q}$  requires much more involved calculations than those related to the stress tensor because of the complexity of the moment for heat flux. If volume transport is taken into account, the moment for the heat flux must be orthogonalized with respect to the vectorial moment generated from the moment for the volume flux, because they couple with each other for symmetry reason. Therefore, if we denote the molecular moment for the heat flux in the absence of volume transport by  $h_j^{(3)}$

$$h_j^{(3)} = H'_j \mathbf{C}_j + \frac{1}{2} \sum_{\substack{j=1 \\ (j \neq k)}}^N \sum_{k=1}^N \mathbf{W}_{jk} \cdot \mathbf{C}_k, \quad (6.158)$$

the moment for the heat flux  $h_j^{(3)}$  in the presence of volume flux must be defined such that it is orthogonal to the moment for the volume flux  $h_i^{(4)}$ , which is a vector and hence must be coupled to  $h_j^{(3)}$ . We therefore define

$$\bar{h}_j^{(3)} := h_j^{(3)} \delta(\mathbf{r}_j - \mathbf{r}) - \alpha_3 h_j^{(4)} \delta(\mathbf{r}_j - \mathbf{r}), \quad (6.159)$$

and the coefficient  $\alpha_3$  is chosen such that  $h_j^{(3)}$  is orthogonal to  $h_i^{(4)}$  as we have noted earlier; see (6.124) and (6.125). The heat flux  $\mathbf{Q}'$  in the presence of volume transport is then defined by the statistical mechanical average of  $h_j^{(3)}$

$$\begin{aligned} \Phi^{(3)} &= \left\langle \sum_{j=1}^N \left( h_j^{(3)} - \alpha_3 h_j^{(4)} \right) \delta(\mathbf{r}_j - \mathbf{r}) \bar{f}^{(N)}(x^{(N)}, t) \right\rangle \\ &:= \mathbf{Q}' = \mathbf{Q} - \alpha_3 \Phi^{(4)}. \end{aligned} \quad (6.160)$$

Here  $\Phi^{(4)}$  is the volume flux defined by (6.118) and obeys (6.134).

Differentiating (6.160) with  $t$  and making use of the kinetic equation and following the procedure similar to the evolution equations for the nonconserved variables already presented, we obtain the evolution equation for  $\widehat{\Phi}^{(3)} = \mathbf{Q}'/\rho$ :

$$\begin{aligned}\rho \frac{d\widehat{\Phi}^{(3)}}{dt} &= -\nabla \cdot (\psi^{(3)} + \psi^{(3W)}) - \varphi^{(3)} : \nabla \mathbf{u} + \mathbf{V}_3 \\ &\quad - \mathbf{P} \cdot \nabla \widehat{h} - \Phi^{(3)} \cdot \nabla \mathbf{u} - [d_t \mathbf{u} - \widehat{\mathbf{F}}(\mathbf{r})] \cdot (\mathbf{P} - p\delta) \\ &\quad - \alpha_3 [(v - v_0) \nabla \cdot (\mathbf{P} + \rho \widehat{\mathbf{F}}) - \Phi^{(4)} \cdot \nabla \mathbf{u} + \mathbf{T}_F] + \Lambda^{(3)}. \end{aligned} \quad (6.161)$$

See (6.137) for  $\mathbf{T}_F$ , which is coupled to volume fluctuation. This heat flux evolution equation formally looks similar to its dilute gas or moderately dense gas counterpart presented in Chaps. 3 and 5. However, the similarity in appearance is deceptive, because it is rather complicated owing to the intermolecular interaction contributions as can be seen below. The various symbols in (6.161) are defined as follows:  $\widehat{h}$  is the enthalpy per mass and

$$\overline{\psi}^{(3)} = \psi^{(3)} + \psi^{(3W)}, \quad (6.162)$$

$$\psi^{(3)} = \sum_{j=1}^N \left\langle \overline{f}^{(N)} \mathbf{C}_j \left( h_j^{(3)} - \alpha_3 \psi_4 \right) \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle, \quad (6.163)$$

$$\psi^{(3W)} = \psi^{(3,W1)} + \psi^{(3,W2)}, \quad (6.164)$$

with  $\psi^{(3,W1)}$  and  $\psi^{(3,W2)}$  standing for the statistical mechanics formulas

$$\begin{aligned}\psi^{(3,W1)} &= \frac{1}{2} \left\langle \sum_{j=1}^N \sum_{k=1}^N \overline{f}^{(N)} \mathbf{W}_{jk} \cdot \mathbf{C}_j \mathbf{C}_j \delta(\mathbf{r}_k - \mathbf{r}) \right\rangle \\ &\quad + \frac{1}{2} \left\langle \sum_{j=1}^N \sum_{k=1}^N \overline{f}^{(N)} \mathbf{W}_{jk} \cdot \left( H'_j/m_j - \widehat{h} \right) \delta \delta(\mathbf{r}_k - \mathbf{r}) \right\rangle, \end{aligned} \quad (6.165)$$

$$\psi^{(3,W2)} = \frac{1}{4} \left\langle \sum_{j=1}^N \sum_{k=1}^N \sum_{l=1}^N \overline{f}^{(N)} \frac{1}{m_j} \mathbf{W}_{jk} \cdot \mathbf{W}_{jkl} \delta(\mathbf{r}_l - \mathbf{r}) \right\rangle. \quad (6.166)$$

In addition to these,  $\varphi^{(3)}$  is given by the sum of terms

$$\varphi^{(3)} = \varphi_{kin}^{(3)} + \varphi_1^{(W)} + \varphi_2^{(W)} + \varphi_3^{(W)}, \quad (6.167)$$

where the components on the right are defined by the statistical mechanics formulas

$$\varphi_{kin}^{(3)} = \left\langle \sum_{j=1}^N \bar{f}^{(N)} \delta(\mathbf{r}_j - \mathbf{r}) m_j \mathbf{C}_j \mathbf{C}_j \mathbf{C}_j \right\rangle, \quad (6.168)$$

$$\varphi_{1\alpha\beta\gamma}^{(W)} = \frac{1}{2} \left\langle \sum_{j=1}^N \sum_{k=1}^N \sum_{\substack{j \neq k}} \bar{f}^{(N)} \mathbf{W}_{jk}^{\alpha\beta} \mathbf{C}_j^\gamma \delta(\mathbf{r}_k - \mathbf{r}) \right\rangle, \quad (6.169)$$

$$\varphi_{2\alpha\beta\gamma}^{(W)} = \frac{1}{2} \left\langle \sum_{j=1}^N \sum_{k=1}^N \sum_{\substack{j \neq k}} \bar{f}^{(N)} \mathbf{C}_j^\alpha \mathbf{W}_{jk}^{\beta\gamma} \delta(\mathbf{r}_k - \mathbf{r}) \right\rangle, \quad (6.170)$$

$$\varphi_{3\alpha\beta\gamma}^{(W)} = \frac{1}{2} \left\langle \sum_{j=1}^N \bar{f}^{(N)} \mathbf{W}_{jk}^{\alpha\gamma} \mathbf{C}_j^\beta \delta(\mathbf{r}_k - \mathbf{r}) \right\rangle, \quad (6.171)$$

with the superscripts  $\alpha$ ,  $\beta$ , and  $\gamma$  standing for Cartesian components of the tensor.

The vector  $\mathbf{V}_3$  consists of 5 component vectors

$$\mathbf{V}_3 = \mathbf{V}_1^{(3)} + \mathbf{V}_2^{(3)} + \mathbf{V}_3^{(3)} + \mathbf{V}_4^{(3)} + \mathbf{V}_5^{(3)} \quad (6.172)$$

with the components on the right defined by the formulas

$$\mathbf{V}_1^{(3)} = \frac{1}{2} \left\langle \sum_{j=1}^N \sum_k \sum_{\substack{j \neq k}} \bar{f}^{(N)} \mathbf{F}_{jk} \cdot (\mathbf{C}_j \mathbf{C}_j - \mathbf{C}_k \mathbf{C}_k) \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle, \quad (6.173)$$

$$\mathbf{V}_2^{(3)} = \frac{1}{2} \left\langle \sum_{j=1}^{N_a} \sum_k \sum_{\substack{j \neq k}} \bar{f}^{(N)} (H'_j/m_j - H'_k/m_k) \mathbf{F}_{jk} \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle, \quad (6.174)$$

$$\mathbf{V}_3^{(3)} = \frac{1}{2} \left\langle \sum_{j=1}^N \sum_{k=1}^N \sum_{\substack{j \neq k}} \bar{f}^{(N)} \delta(\mathbf{r}_j - \mathbf{r}) \mathbf{C}_{jk} \cdot (\nabla_{\mathbf{r}_{jk}} \mathbf{W}_{jk}) \cdot \mathbf{C}_j \right\rangle, \quad (6.175)$$

$$\mathbf{V}_4^{(3)} = \frac{1}{2} \left\langle \sum_{j=1}^N \sum_{k=1}^N \sum_{\substack{j \neq k}} \bar{f}^{(N)} \frac{1}{m_j} \mathbf{W}_{jk} \cdot \mathbf{F}_{jk} \delta(\mathbf{r}_k - \mathbf{r}) \right\rangle, \quad (6.176)$$

$$\mathbf{V}_5^{(3)} = \frac{1}{4} \left\langle \sum_{j=1}^N \sum_{k=1}^N \sum_{l=1}^N \sum_{\substack{j \neq k \neq l}} \bar{f}^{(N)} \frac{1}{m_j} (\mathbf{W}_{jk} \cdot \mathbf{F}_{jl} + \mathbf{W}_{jl} \cdot \mathbf{F}_{kj}) \delta(\mathbf{r}_k - \mathbf{r}) \right\rangle. \quad (6.177)$$

The intermolecular force-dependent terms in (6.161) originate from the intermolecular interactions and their coupling with flow, which are not present in the evolution equation for the heat flux if the fluid is dilute; they are absent in, for example, the evolution equation derived from the Boltzmann equation for dilute monatomic gases. But they are expected to contribute to the intermolecular force effects on flow phenomena in the dynamic evolution of liquids in flow. These effects have not as yet been studied in liquid flow phenomena.

The effects of volume transport manifestly appear as the terms in the square brackets in the last line of (6.161) with  $\alpha_3$  as the coefficient, although its effects are also implicit in the definitions of  $\widehat{\Phi}^{(3)}$ ,  $\overline{\psi}^{(3)}$ , and  $\Lambda^{(3)}$ . We will see that the aforementioned square-bracketed terms are a hallmark of the volume transport in the case of heat flux.

The molecular nature of vector  $\mathbf{V}_3$  can be better seen if the intermolecular forces are approximated as in (6.147), which shows couplings of vectors  $\mathbf{C}_{ij} = \mathbf{C}_i - \mathbf{C}_j$  and  $\mathbf{r}_{ij}$  and related quantities; for example, the torque tensor of rotational motion of pairs or its contraction. Although these couplings do not manifest themselves in the linear regime of transport processes, they are expected to yield subtle nonlinear effects, especially, in liquids and if the thermodynamic gradients are large in magnitude, for example, as in the rarefied gas regime. It is useful to remark that  $\psi^{(3)}$  and  $\psi^{(3W)}$  are second-rank tensors, which may be related to the stress tensors.

The conservation laws (the equation of continuity, momentum balance equation, energy balance equation, and angular momentum conservation appearing in the case of diatomic fluids, for example) and the evolution equations for the shear stress, excess normal stress, and heat flux supplemented by the evolution equations for molar volume and volume flux, which we have presented up to this point, constitute *the generalized hydrodynamic equations*. We may employ them to study flow phenomena when volume transport processes are explicitly taken into account.

The equations are still open since there appear in them additional higher-order moments that generally must be included in a complete theory of nonequilibrium phenomena. These higher-order moments rarely appear in most of flow problems in practice, but, if necessary, their evolution equations can be derived from the kinetic equation by using their statistical mechanics expressions. From this vantage point our first task would be to explore the range of the applicability of the evolution equations presented and then decide whether it is warranted to include extra moments outside the first thirteen moments plus the moments corresponding to diffusion and volume transport presented. Therefore we will not pursue their evolution equations further in this work until generalized hydrodynamic equations presented are tested against experiments and found deficient in some aspects.

The macroscopic evolution equation presented in Sects. 6.3–6.5 constitute the generalized hydrodynamic equations attendant on the theory of thermodynamics of irreversible processes discussed in the following sections. They will be made thermodynamically consistent by making them to confirm to the laws of thermodynamics.

## 6.7 Thermodynamics of Irreversible Processes

In this section, we explicitly demonstrate that the generalized hydrodynamic equations presented are not only consistent with the laws of thermodynamics, but also the hydrodynamic theory of irreversible processes based on the former is within the framework of the thermodynamic theory of transport processes in liquids. To facilitate this aim we show the kinetic equation gives rise to the theoretical structure comparable to the phenomenological thermodynamic theory of transport processes we have presented in Chap. 2.

### 6.7.1 Boltzmann Entropy

As is for moderately dense fluids, the (global) Boltzmann entropy of the fluid considered is defined by the statistical mechanical formula<sup>18</sup>

$$S = -k_B \left\langle \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \ln \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (6.178)$$

in which the subsystem subscript  $\alpha$  is omitted from  $\bar{f}^{(N)}$ . This is the Boltzmann  $H$  function. It is a global formula defined for the whole volume  $V$ . The local density  $\hat{\mathcal{S}}(\mathbf{r}, t)$  of  $S$  is related to it by the relation

$$S = \int_V d\mathbf{r} \rho \mathcal{S}(\mathbf{r}, t). \quad (6.179)$$

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<sup>18</sup>The Boltzmann entropy for the ensemble should be defined by

$$\begin{aligned} \mathbb{S} &= -k_B \sum_{\alpha=1}^v \left\langle \bar{f}^{(N)}(\mathbf{x}_\alpha^{(N)}, t) \ln \bar{f}^{(N)}(\mathbf{x}_\alpha^{(N)}, t) \right\rangle \\ &= \sum_{\alpha=1}^v S_\alpha \end{aligned}$$

since the supersystem consists of  $v$  subsystems. Since  $v$  subsystems are statistically uncorrelated by construction of the ensemble, the mean values for  $v$  subsystems are numerically identical. Therefore we may write  $\mathbb{S} = vS$  with  $S$  defined by (6.178). Henceforth we refer  $S$  to the Boltzmann entropy of the system represented by the ensemble. And similarly to the calorentropy, relative Boltzmann entropy, etc. it should be kept in mind that the ensemble kinetic theory we are discussing here for a system of  $N$  interacting particles resembles the ideal gas kinetic theory of Boltzmann in the sense that the ensemble distribution function is a product of distribution functions of members of the ensemble representative of the system under consideration.

Differentiating (6.178) and using the GBE (6.48), we obtain

$$\frac{dS}{dt} = -k_B \left\langle \ln \bar{f}^{(N)}(x^{(N)}, t) \Re[\bar{\mathbb{F}}^{(\mathcal{N})}(x^{(\mathcal{N})}, t)] \right\rangle. \quad (6.180)$$

It is possible to show the right hand side of this equation satisfies Condition (6.C2) and hence the time derivative of  $S$  is positive semidefinite

$$\frac{dS}{dt} \geq 0, \quad (6.181)$$

the equality holding in the limit of long time at which the system reaches the equilibrium. This is the  $H$  theorem for the GBE (6.48) in the phase space. This is, in fact, a global stability theorem satisfied by the solution of the coarse-grained kinetic equation, because the  $H$  function (6.178) may be regarded as a Lyapounov function [16, 17] for the set of differential equations that happens to be the generalized Boltzmann equation (6.48). It must be kept in mind that the Boltzmann entropy  $S$  is a quantity that lives in the phase space of the entire system of  $O(10^{23})$  particles in number for which the dynamical equations of motion govern the evolution of the system (ensemble).

The statistical mechanical formula (6.178) suggests it would be useful to represent the distribution functions in an exponential form

$$k_B \ln \bar{f}^{(N)}(\mathbf{x}_\alpha^{(N)}, t) = - \int_V d\mathbf{r} \sum_{i=1(i \in \alpha)}^N G_i^{(N)}(\mathbf{x}_\alpha^{(N)}, t) \delta(\mathbf{r}_i - \mathbf{r}), \quad (6.182)$$

where  $G_i^{(N)}(\mathbf{x}_\alpha^{(N)}, t)$  is a local density depending on phases  $\mathbf{x}_\alpha^{(N)}$  of particles in the subsystem  $\alpha$ . Note that each subsystem consists of  $N$  particles and index  $\alpha$  enumerates the subsystems comprising the ensemble. The precise meaning of  $G_i^{(k)}(\mathbf{x}_\alpha^{(N)}, t)$  is yet to be determined from the solution of the GBE (6.48), subject to the initial and boundary conditions on the system. Upon combining (6.178) and (6.182) the statistical mechanical expression for the local Boltzmann entropy density  $\mathcal{S}(\mathbf{r}, t)$  is obtained:

$$\rho \mathcal{S}(\mathbf{r}, t) = \left\langle \sum_{i=1(i \in \alpha)}^N G_i^{(N)}(\mathbf{x}^{(N)}, t) \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \quad (6.183)$$

Recall that  $\mathcal{N} = vN$ . As it stands, this formal expression does not tell us much about the Boltzmann entropy density. To make progress on the question we first derive the Boltzmann entropy balance equation. As was for the other evolution equations for macroscopic variables presented earlier, differentiating (6.183) and making use of

the GBE (6.48) we obtain the evolution equation—i.e., balance equation—for the Boltzmann entropy density  $\mathcal{S}$ :

$$\rho \frac{d\mathcal{S}(\mathbf{r}, t)}{dt} = -\nabla \cdot \mathbf{J}_s + \sigma_{\text{ent}}(\mathbf{r}, t). \quad (6.184)$$

Here  $\mathbf{J}_s$  and  $\sigma_{\text{ent}}(\mathbf{r}, t)$  are the Boltzmann entropy flux and the Boltzmann entropy production, respectively, defined by the statistical mechanical formulas

$$\mathbf{J}_s(\mathbf{r}, t) = \left\langle \sum_{i=1}^N \mathbf{C}_i G_i^{(N)}(\mathbf{x}^{(N)}, t) \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (6.185)$$

$$\sigma_{\text{ent}}(\mathbf{r}, t) = \left\langle \sum_{i=1}^N G_i^{(N)}(\mathbf{x}^{(N)}, t) \delta(\mathbf{r}_i - \mathbf{r}) \Re[\bar{\mathbb{F}}^{-(N)}(x^{(N)}, t)] \right\rangle. \quad (6.186)$$

For the derivation of (6.184) we have made use of the identity

$$\begin{aligned} \sum_{i=1}^N & \left\langle \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \delta(\mathbf{r}_i - \mathbf{r}) \mathcal{D}_t G_i^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle \\ &= k_B \left\langle \Re[\bar{\mathbb{F}}^{-(N)}(x^{(N)}, t)] \right\rangle \\ &= 0. \end{aligned} \quad (6.187)$$

See (6.133) for the definition of operator  $\mathcal{D}_t$ . Note that the Liouville operator  $\mathbf{L}^{(N)}$  here pertains to a subsystem  $\alpha$  of the ensemble. Henceforth, we omit the subscript  $\alpha$  for subsystem  $\alpha$  of the ensemble for notational brevity. It can be shown that by Condition (6.C2)

$$\sigma_{\text{ent}}(\mathbf{r}, t) \geq 0, \quad (6.188)$$

the equality holding at equilibrium reached in long time. This is the local form of the  $H$  theorem.

As is for the Boltzmann equation in Chap. 3 and the extended Boltzmann equation in Chap. 5, the  $H$  theorem is not to be identified with the second law of thermodynamics, as is popularly thought to be, because, if the system is away from equilibrium (or the macroscopic processes are irreversible), the Boltzmann entropy  $S$  is not the same as the Clausius entropy defined only for reversible processes in the thermodynamic manifold. This point will be clarified as we develop the theory of irreversible thermodynamics in the light of (6.48) and (6.184).

Before closing this subsection we note that the inequality (6.181) may be decomposed into two parts representing the change due to the exchange of  $S$  between the system and its surroundings and the production of  $S$  arising from the energy dissipation caused by various transport processes occurring within the system:

$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt}, \quad (6.189)$$

where

$$\frac{d_e S}{dt} = - \int_V d\mathbf{r} \nabla \cdot (\mathbf{J}_s + \mathbf{u}\rho\mathcal{S}), \quad (6.190)$$

$$\frac{d_i S}{dt} = \int_V d\mathbf{r} \sigma_{\text{ent}}(\mathbf{r}, t) \geq 0. \quad (6.191)$$

This inequality may be regarded as the global form of the  $H$  theorem.  $d_e S/dt$  is the exchange part and  $d_i S/dt$  the inherent dissipation part.

### 6.7.2 Calortropy

Thermodynamics is phenomenologically described by the variables spanning the thermodynamic manifold, which is a union of manifold  $\mathfrak{P}$  and its tangent manifold  $\mathfrak{T}$ : namely,  $\mathfrak{P} \cup \mathfrak{T}$ . The thermodynamic manifold is spanned by a finite number of macroscopic observables, although its dimension could be quite large, but finite in number much smaller than the dimension  $6\mathcal{N}$  of the phase space of an ensemble consisting of  $\mathcal{N}$  particles [ $\mathcal{N} = O(10^{23})$  in number].

Since macroscopic observables are averages of mechanical quantities depending on phases  $\mathbf{x}^{(N)}$ , from the statistical mechanical and mathematical points of view the thermodynamic manifold may be regarded as a finite dimensional projection of the information of the system in the phase space of an ensemble of an astronomically large dimension onto a much dimensionally contracted manifold  $\mathfrak{P} \cup \mathfrak{T}$ . Inasmuch as the thermodynamic manifold is a projection of such a phase space it is mathematically legitimate to look for a class of distribution functions that evolve as functionals of variables spanning the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T}$ . We will denote such distribution functions by  $\bar{f}_c^{(N)}(x_\alpha^{(N)}, t)$  ( $\alpha = 1, \dots, v$ ), which will be called the *nonequilibrium canonical form* of distribution function—more generally, the thermodynamic branch of the phase space distribution function  $\bar{f}^{(N)}(x_\alpha^{(N)}, t)$ . Similarly to the case of dilute gases obeying the Boltzmann kinetic equation, associated with this functional form is a quantity  $\Psi$  which we call calortropy. It is defined in terms of the nonequilibrium canonical form  $\bar{f}_c^{(N)}(\mathbf{x}_\alpha^{(N)}, t)$  by the statistical mechanical formula

$$\Psi = -k_B \int_V d\mathbf{r} \left\langle \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \ln \bar{f}_c^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \quad (6.192)$$

Therefore  $\Psi$  is a mean value of  $-k_B \ln \bar{f}_c^{(N)}$ . It is the Boltzmann entropy-like, but is not the same as the Boltzmann entropy inasmuch as  $\bar{f}_c^{(N)} \neq \bar{f}^{(N)}$ . The calortropy

evolves in manifold  $\mathfrak{P} \cup \mathfrak{T}$  through the variables, which obey the generalized hydrodynamic equations, whereas the Boltzmann entropy lives, and obeys the GBE, in the phase space of the system. The difference between  $S$  and  $\Psi$  then is called the relative Boltzmann entropy. It is defined by the statistical mechanical formula

$$S_r[\bar{f}|\bar{f}^c] = k_B \int_V d\mathbf{r} \langle \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \ln [\bar{f}^{(N)}(\mathbf{x}^{(N)}, t)/\bar{f}_c^{(N)}(\mathbf{x}^{(N)}, t)] \rangle, \quad (6.193)$$

which is always positive by the Klein inequality  $\ln x \geq 1 - x$ :

$$S_r[\bar{f}|\bar{f}^c] \geq 0. \quad (6.194)$$

This inequality means that

$$S \leq \Psi. \quad (6.195)$$

Evidently, the Boltzmann entropy, calortropy, and relative Boltzmann entropy given by (6.178), (6.192), and (6.193) are dense fluid generalizations of their dilute gas equivalents defined in Chaps. 3 and 5.

Since from the viewpoint of information theory [32, 33] the Boltzmann entropy may be regarded as an information content of the system, the calortropy  $\Psi$  arising from a projection of  $\bar{f}^{(N)}(\mathbf{x}^{(N)}, t)$  onto the thermodynamic manifold describes an information content reduced compared to that of  $S$ . As we have seen in Chaps. 3 and 5, a thermodynamic theory of irreversible transport processes in the system of dense fluids or liquids may be formulated on the basis of the calortropy. A thermodynamic theory based on the calortropy necessarily contains an information content much reduced compared to that of the Boltzmann entropy that may be obtained by solving the GBE fully in the phase space of the system under the initial and boundary conditions on the system of an astronomically large number of particles contained therein. For the manifolds  $\mathfrak{P}$  and  $\mathfrak{T}$  pertain to macroscopic variables and, as such, their information contents are much contracted than that of the full phase space of the ensemble.

The calortropy balance equation can be derived from the GBE (6.48) by using a procedure similar for the Boltzmann entropy balance Eq. (6.184). To achieve this aim we first write  $k_B \ln \bar{f}_c^{(N)}(\mathbf{x}^{(N)}, t)$  as the volume integral of a local function  $\mathfrak{S}_i^{(N)}(\mathbf{x}^{(N)}, t)$ :

$$k_B \ln \bar{f}_c^{(N)}(\mathbf{x}^{(N)}, t) = - \int_V d\mathbf{r} \sum_{i=1}^N \mathfrak{S}_i^{(N)}(\mathbf{x}^{(N)}, t) \delta(\mathbf{r}_i - \mathbf{r}). \quad (6.196)$$

Since the global calortropy is expressible in terms of calortropy density  $\widehat{\Psi}$  by the formula

$$\Psi(t) = \int_V d\mathbf{r} \rho \widehat{\Psi}(\mathbf{r}, t), \quad (6.197)$$

we find the statistical mechanical formula for  $\widehat{\Psi}(\mathbf{r}, t)$ :

$$\rho \widehat{\Psi}(\mathbf{r}, t) = \left\langle \sum_{i=1}^N \mathfrak{S}_i^{(N)}(\mathbf{x}^{(N)}, t) \delta(\mathbf{r}_i - \mathbf{r}) \overline{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \quad (6.198)$$

Therefore,  $\widehat{\Psi}$  may be interpreted as a measure of information loss owing to the description of the system made in the thermodynamic manifold instead of the phase space.

Differentiating (6.198) with  $t$  and using the GBE, (6.48), we obtain the local balance equation for  $\widehat{\Psi}(\mathbf{r}, t)$ :

$$\rho \frac{d\widehat{\Psi}}{dt} = -\nabla \cdot \mathbf{J}_c + \sigma_c + \mathbb{D}, \quad (6.199)$$

where calortropy flux  $\mathbf{J}_c$ , calortropy production  $\sigma_c$ , and  $\mathbb{D}$  are, respectively, defined by the statistical mechanical formulas

$$\mathbf{J}_c(\mathbf{r}, t) = \left\langle \sum_{i=1}^N \mathbf{C}_i \mathfrak{S}_i^{(N)}(\mathbf{x}^{(N)}, t) \delta(\mathbf{r}_i - \mathbf{r}) \overline{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (6.200)$$

$$\sigma_c(\mathbf{r}, t) = \sum_{i=1}^N \mathfrak{S}_i^{(N)}(\mathbf{x}^{(N)}, t) \delta(\mathbf{r}_i - \mathbf{r}) \Re[\mathbb{F}^{-(\mathcal{N})}(x^{(\mathcal{N})}, t)], \quad (6.201)$$

$$\mathbb{D}(\mathbf{r}, t) = k_B \left\langle \sum_{i=1}^N \overline{f}^{(N)}(\mathbf{x}^{(N)}, t) \delta(\mathbf{r}_i - \mathbf{r}) \mathcal{D}_t \mathfrak{S}_i^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \quad (6.202)$$

Here, it is understood  $i \in \alpha \in \nu$ .

The calortropy density evolution equation therefore remains formally isomorphic to the Boltzmann entropy balance Eq. (6.184) in that it contains a divergence term and source terms. The meaning and the mathematical structure of  $\mathfrak{S}_i^{(N)}$  however, will be seen quite different from those of  $G_i^{(N)}(\mathbf{x}^{(N)}, t)$  for  $\mathcal{S}$  because  $\mathfrak{S}_i^{(N)}(\mathbf{x}^{(N)}, t)$ , given in terms of macroscopic observables in manifold  $\mathfrak{P} \cup \mathfrak{T}$  has to be such that the calortropy density is thermodynamically consistent. To this end, the term  $\mathbb{D}$  plays a crucial and indispensable role. This aspect will be further elucidated later when we discuss the thermodynamics of irreversible processes in the system.

### 6.7.3 Relative Boltzmann Entropy

Since the relative Boltzmann entropy(RBE)<sup>19</sup> can be also expressed in terms of its density by the relation

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<sup>19</sup>A similar notion appears in the work of Lindbald [34] on irreversibility and also in semigroup theories [35] in a different context.

$$S_r[\bar{f}|\bar{f}^c] = \int_V d\mathbf{r} \rho S_r[\bar{f}|\bar{f}^c](\mathbf{r}, t), \quad (6.203)$$

the representation of  $\bar{f}_c^{(N)}(\mathbf{x}_k^{(N)}, t)$  by the exponential form—nonequilibrium canonical form—in (6.196) gives rise to its statistical mechanical expression

$$\begin{aligned} \rho S_r[\bar{f}|\bar{f}^c] = - & \left\langle \sum_{i=1}^N \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \delta(\mathbf{r}_i - \mathbf{r}) \times \right. \\ & \left. \left[ G_i^{(N)}(\mathbf{x}^{(N)}, t) - \mathfrak{G}_i^{(N)}(\mathbf{x}^{(N)}, t) \right] \right\rangle, \end{aligned} \quad (6.204)$$

and the evolution equation for the relative Boltzmann entropy density can be found in the same manner as for the evolution equation for the calortropy density (6.199):

$$\rho \frac{dS_r[\bar{f}|\bar{f}^c]}{dt} = -\nabla \cdot \mathbf{J}_{rB} + \sigma_{rB} + \mathbb{D}_{rB}, \quad (6.205)$$

where the relative Boltzmann entropy flux  $\mathbf{J}_{rB}$ , the relative Boltzmann entropy production  $\sigma_{rB}$ , and  $\mathbb{D}_{rB}$  are defined by statistical mechanical formulas

$$\mathbf{J}_{rB} = \left\langle \sum_{i=1}^N \mathbf{C}_i \left( G_i^{(N)} - \mathfrak{G}_i^{(N)} \right) (\mathbf{x}^{(N)}, t) \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (6.206)$$

$$\sigma_{rB} = \left\langle \sum_{i=1}^N \left( G_i^{(N)} - \mathfrak{G}_i^{(N)} \right) (\mathbf{x}^{(N)}, t) \delta(\mathbf{r}_i - \mathbf{r}) \mathfrak{R}[\bar{\mathbb{F}}^{(N)}(x^{(N)}, t)] \right\rangle, \quad (6.207)$$

$$\mathbb{D}_{rB} = k_B \left\langle \sum_{i=1}^N \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \delta(\mathbf{r}_i - \mathbf{r}) \mathcal{D}_t \left( G_i^{(N)} - \mathfrak{G}_i^{(N)} \right) (\mathbf{x}^{(N)}, t) \right\rangle. \quad (6.208)$$

Cast in the forms presented for  $S$ ,  $\widehat{\Psi}$ , and  $S_r[\bar{f}|\bar{f}^c]$  their formal evolution equations (6.184), (6.199), and (6.205) suggest merely their potential significance and possibilities for formulating the solutions of the kinetic equation underlying them and a thermodynamic theory of irreversible processes. To develop the thermodynamic theory of irreversible processes it will be necessary to study the meanings and mathematical structures of  $G_i^{(N)}$  and  $\mathfrak{G}_i^{(N)}$  in more detail.

### 6.7.4 Equilibrium Solution of the GBE

#### 6.7.4.1 Equilibrium Distribution Function

To learn about  $G_i^{(N)}$  and  $\mathfrak{G}_i^{(N)}$  we first look for the equilibrium solution of the GBE. It will guide us to find a suitable nonequilibrium canonical form. Since the equilib-

rium distribution function  $\bar{f}_{\text{eq}}^{(N)}$  does not change in time and space for a system at equilibrium, which means  $\mathbf{L}^{(N)} \bar{f}_{\text{eq}}^{(N)} = 0$ , there follows the equation

$$\Re[\prod_{\alpha=1}^v \bar{f}_{\text{eq}}^{(N)}(\mathbf{x}_{\alpha}^{(N)})] = 0. \quad (6.209)$$

Therefore, according to the properties of the collision operator  $\mathcal{T}^{(N)}(z)$  established in connection with Conditions (6.C1) and (6.C2), the product of distribution functions for the ensemble must be a function of collision invariants. If we distinguish the values of the operand of the collision integral  $\Re[\prod_{\alpha=1}^v \bar{f}_{\text{eq}}^{(N)}]$  before and after collision process by affixing an asterisk on the post-collision values, we may write (6.209) as

$$\prod_{\alpha=1}^v \bar{f}_{\text{eq}}^{(N)*}(\mathbf{x}_{\alpha}^{(N)*}) = \prod_{\alpha=1}^v \bar{f}_{\text{eq}}^{(N)}(\mathbf{x}_{\alpha}^{(N)}), \quad (6.210)$$

where the quantity with the asterisk means the post-collision value of the quantity asterisked. Take logarithm of this expression to obtain

$$\sum_{\alpha=1}^v \ln \bar{f}_{\text{eq}}^{(N)*}(\mathbf{x}_{\alpha}^{(N)*}) = \sum_{\alpha=1}^v \ln \bar{f}_{\text{eq}}^{(N)}(\mathbf{x}_{\alpha}^{(N)}). \quad (6.211)$$

We then find the logarithmic functions  $\ln \bar{f}_{\text{eq}}^{(N)*}(\mathbf{x}_{\alpha}^{(N)*})$  and  $\ln \bar{f}_{\text{eq}}^{(N)}(\mathbf{x}_{\alpha}^{(N)})$  must be a linear combination of collision invariants  $I_{\gamma}$ , namely, energy (Hamiltonian), momentum, and mass if the system consists of monatomic molecules, and there are no other invariants. It is therefore sufficient for our purpose here to take for  $G_{i\text{eq}}^{(N)}$  the form

$$\begin{aligned} \sum_{i=1}^N G_{i\text{eq}}^{(N)} \delta(\mathbf{r}_i - \mathbf{r}) &= k_B \int_V d\mathbf{r} \beta_{\text{eq}} \sum_{i=1}^N \left( H_i^{(N)} - m_i \hat{\mu}_{\text{e}} \right) \delta(\mathbf{r}_i - \mathbf{r}) \\ &\quad + k_B \ln \mathbb{Z}_{\text{eq}}^{(N)}, \end{aligned} \quad (6.212)$$

where  $H_i$  is the Hamiltonian of particle  $i$ ,  $\beta_{\text{eq}}$  and  $\hat{\mu}_{\text{e}}$  are constant parameters<sup>20</sup> that will have to be determined, upon making thermodynamic correspondence, and  $\ln \mathbb{Z}_{\text{eq}}^{(N)}$  assures  $\bar{f}_{\text{eq}}^{(N)}$  to be normalized to unity. The index  $\alpha$  is omitted because the same form should hold for every subsystem of the ensemble at equilibrium. Therefore the equilibrium distribution functions of subsystems are found to have the form

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<sup>20</sup>For an equilibrium system that is spatially uniform the parameter  $\hat{\mu}_{\text{e}}$  is not necessary. Here we have inserted it anticipating the case of local equilibrium when the system is not spatially uniform. In this case,  $\hat{\mu}_{\text{e}}$  can be dependent on space as the parameter  $\beta_{\text{eq}}$  is.

$$\bar{f}_{\text{eq}}^{(N)}(\mathbf{x}^{(N)}) = \frac{1}{Z_{\text{eq}}^{(N)}} \exp \left[ - \int_V d\mathbf{r} \beta_{\text{eq}} \sum_{i=1}^N (H_i^{(N)} - m_i \hat{\mu}_e) \delta(\mathbf{r}_i - \mathbf{r}) \right], \quad (6.213)$$

Since the distribution function  $\bar{f}_{\text{eq}}^{(N)}$  should be normalized to unity we find the normalization factor

$$\begin{aligned} Z_{\text{eq}}^{(N)} &= \int d\mathbf{x}^{(N)} \exp \left[ - \int_V d\mathbf{r} \beta_{\text{eq}} \sum_{i=1}^N (H_i^{(N)} - m_i \hat{\mu}_e) \delta(\mathbf{r}_i - \mathbf{r}) \right] \\ &:= \left\langle \exp \left[ - \int_V d\mathbf{r} \beta_{\text{eq}} \sum_{i=1}^N (H_i^{(N)} - m_i \hat{\mu}_e) \delta(\mathbf{r}_i - \mathbf{r}) \right] \right\rangle. \end{aligned} \quad (6.214)$$

At equilibrium the distribution function is uniform in space. Therefore we find the local equilibrium partition function  $\Gamma_{\text{eq}}^{(N)}$  is simply given by

$$\begin{aligned} \Gamma_{\text{eq}}^{(N)} &= \left\langle \exp \left[ - \beta_{\text{eq}} \sum_{i=1}^N (H_i^{(N)} - m_i \hat{\mu}_e) \right] \right\rangle \\ &= e^{\beta_{\text{eq}} N m \hat{\mu}_e} \left\langle \exp \left[ - \beta_{\text{eq}} \sum_{i=1}^N H_i^{(N)} \right] \right\rangle \\ &:= e^{\beta_{\text{eq}} N m \hat{\mu}_e} Q_{\text{eq}}. \end{aligned} \quad (6.215)$$

With the definition of symbol  $A_{\text{eq}}^{(N)}$

$$A_{\text{eq}}^{(N)} = -\beta_{\text{eq}}^{-1} \ln Q_{\text{eq}}, \quad (6.216)$$

we obtain

$$\ln \Gamma_{\text{eq}}^{(N)} = \beta_{\text{eq}} \left( N m \hat{\mu}_e - A_{\text{eq}}^{(N)} \right). \quad (6.217)$$

The integral  $Q_{\text{eq}}$  over the phase space will turn out to be the equilibrium canonical partition function. Upon use of  $\bar{f}_{\text{eq}}^{(N)}$  in (6.213) the formula in (6.183) becomes the equilibrium Boltzmann entropy density

$$\rho S_{\text{eq}} = \left\langle \sum_{i=1}^N G_{ie}^{(N)}(\mathbf{x}^{(N)}) \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}_{\text{eq}}^{(N)}(\mathbf{x}^{(N)}) \right\rangle,$$

from which we find

$$S_{\text{eq}} = k_B \beta_{\text{eq}} (\mathcal{E} - \hat{\mu}_e) - k_B \ln \Gamma_{\text{eq}}^{(N)}. \quad (6.218)$$

It should be noted that  $\rho = Nm/V$ . The parameters  $\beta_{\text{eq}}$  and  $\hat{\mu}_e$  can be determined on correspondence with the equilibrium thermodynamic relations as shown below.

Anticipating the later result obtained upon using the thermodynamic correspondence we set

$$p_{\text{eq}}v = \beta_{\text{eq}}^{-1} \ln \Gamma_{\text{eq}}^{(N)} \quad (6.219)$$

with  $v = 1/\rho$ . For with this identification the differential of  $\mathcal{S}_{\text{eq}}$  yields a differential form for  $\mathcal{S}_{\text{eq}}$  identical with the equilibrium Gibbs relation [25, 36, 37], so that the parameter  $\beta_{\text{eq}}$  may be identified with the inverse absolute (thermodynamic) temperature  $T_e$

$$\beta_{\text{eq}} = \frac{1}{k_B T_e} \quad (6.220)$$

and the parameter  $\widehat{\mu}_e$  with the equilibrium chemical potential per mass. Consequently, there holds the differential form for the thermodynamic potential  $p_{\text{eq}}v$  [25, 36, 37]

$$d(p_{\text{eq}}v) = \mathcal{S}_{\text{eq}}dT_e + p_{\text{eq}}dv + d\widehat{\mu}_e. \quad (6.221)$$

By making correspondence of this differential form with the phenomenological differential form

$$\mathcal{S}_{\text{eq}}|_{\text{st}} \Leftrightarrow \mathcal{S}_{\text{eq}}|_{\text{th}}, T_e|_{\text{st}} \Leftrightarrow T_e|_{\text{th}}, p_{\text{eq}}|_{\text{st}} \Leftrightarrow p_{\text{eq}}|_{\text{th}}, \widehat{\mu}_e|_{\text{st}} \Leftrightarrow \widehat{\mu}_e|_{\text{th}}, \quad (6.222)$$

it is possible to ascertain  $T_e$  is indeed the thermodynamic temperature and  $\widehat{\mu}_e$  the chemical potential per mass at equilibrium. Therefore  $p_{\text{eq}}v$  given by the statistical mechanical formula (6.219) is the statistical mechanics formula for the thermodynamic potential  $p_{\text{eq}}v$ .

#### 6.7.4.2 Equilibrium Boltzmann Entropy and Calortropy

Since the distribution function should be replaced by  $\overline{f}_{\text{eq}}^{(N)}(\mathbf{x}^{(N)})$  at equilibrium, and  $\overline{f}_c^{(N)}(\mathbf{x}^{(N)})$  in the expression for the calortropy should be replaced also with  $\overline{f}_{\text{eq}}^{(N)}(\mathbf{x}^{(N)})$ , the relative Boltzmann entropy is found equal to zero at equilibrium. That is, the equilibrium Boltzmann entropy and calortropy or their densities are found identical if the system is at equilibrium:

$$\mathcal{S}_{\text{eq}} = \widehat{\Psi}_{\text{eq}}, \quad (6.223)$$

and the statistical mechanical calortropy at equilibrium, or the Boltzmann entropy, is therefore given by the bilinear formula

$$\widehat{\Psi}_{\text{eq}} = T_e^{-1} (\mathcal{E} - \widehat{\mu}_e + p_e v). \quad (6.224)$$

Hence the symbol  $A_{\text{eq}} := \rho \widehat{A}_{\text{eq}}$ , given by the statistical mechanical formula

$$A_{\text{eq}} = -k_B T_e \ln Q_{\text{eq}}, \quad (6.225)$$

turns out to be the Helmholtz work function [25, 36, 37]. It should be remembered that this is closely associated with the normalization factor for  $\bar{f}_{\text{eq}}^{(N)}$  of a subsystem of the assembly and that the parameters  $\beta_{\text{eq}}$  and  $\hat{\mu}_{\text{e}}$  in the equilibrium distribution function  $\bar{f}_{\text{eq}}^{(N)}(\mathbf{x}^{(N)})$  are determined through the thermodynamic correspondence between the phenomenological thermodynamic quantities and the statistical mechanical counterparts. This way, a mathematical model theory, namely, statistical mechanics, or kinetic theory, employed here, is given the connection to the physical theory, namely, thermodynamics, at least, in the case of a system at equilibrium.

### 6.7.5 Nonequilibrium Canonical Form for the Distribution Function

The nonequilibrium canonical form can be employed to calculate the calentropy and associated quantities in a manner quite parallel to those for a dilute monatomic gas obeying the Boltzmann equation in Chap. 3 and for a moderately dense gas described by the kinetic equation described in Chap. 5.

Therefore, without further ado about what motivates the particular form chosen for it under the functional hypothesis, we choose  $\mathfrak{S}_i^{(N)}$  in (6.196) for the nonequilibrium canonical form  $\bar{f}_{\text{c}}^{(N)}(\mathbf{x}^{(N)}, t)$  in the form

$$\sum_{i=1}^N \mathfrak{S}_i^{(N)}(\mathbf{x}^{(N)}, t) \delta(\mathbf{r}_i - \mathbf{r}) = k_B \beta \sum_{i=1}^N \mathcal{H}_i^{(N)} \delta(\mathbf{r}_i - \mathbf{r}) + k_B \ln \Gamma^{(N)}. \quad (6.226)$$

In this expression  $\mathcal{H}_i^{(N)}$  consists of the Hamiltonian of the fluid relative to the convective kinetic energy of flow and a linear combination of moments  $h_i^{(q)}$ , which when averaged give rise to the macroscopic variables in the manifold  $\mathfrak{P}$ :

$$\mathcal{H}_i^{(N)} = H_i^{(N)} + \sum_{q \geq 0} X^{(q)} h_i^{(q)} - m_i \hat{\mu}. \quad (6.227)$$

Therefore  $\bar{f}_{\text{c}}^{(N)}(\mathbf{x}^{(N)}, t)$  can be written in the form

$$\bar{f}_{\text{c}}^{(N)}(\mathbf{x}^{(N)}, t) = \frac{1}{\mathbb{Z}^{(N)}} \exp \left[ - \int_V d\mathbf{r} \beta \sum_{i=1}^N \mathcal{H}_i^{(N)} \delta(\mathbf{r}_i - \mathbf{r}) \right]. \quad (6.228)$$

Keep it in mind that  $\bar{f}_{\text{c}}^{(N)}(\mathbf{x}^{(N)}, t)$  pertains to generic subsystem  $\alpha$  of the ensemble. The expansion coefficients  $X^{(q)}$  in (6.227) depend on variables in the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T}$  through which space-time dependence of the nonequilibrium

canonical form<sup>21</sup>  $\bar{f}_c^{(N)}$  enters the theory. Since the variables in  $\mathfrak{P}$  obeys the evolution equations—field equations—namely, the generalized hydrodynamic equations presented earlier,  $\bar{f}_c^{(N)}$  evolves in space-time as a functional of variables (e.g.,  $\Phi^{(q)}$  and their conjugate variables) in the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T}$ .

Since  $\bar{f}_c^{(N)}(\mathbf{x}^{(N)}, t)$  is normalized to unity, we find

$$\mathbb{Z}^{(N)} = \left\langle \exp \left[ - \int_V d\mathbf{r} \beta \sum_{i=1}^N \left( H_i^{(N)} + \sum_{q \geq 0} X^{(q)} h_i^{(q)} - m_i \hat{\mu} \right) \delta(\mathbf{r}_i - \mathbf{r}) \right] \right\rangle \quad (6.229)$$

Here  $\mathbb{Z}^{(N)}$  may be regarded as the nonequilibrium partition function for a whole subsystem, say,  $\alpha$ , of the ensemble and the volume  $V$  is the same for all subsystems of the ensemble. We remark here that the nonequilibrium term on the right of (6.227) must be such that the integral in (6.229) should be normalizable. This means the choice of the moment set  $\{h_i^{(q)} : q \geq 0\}$  and, particularly, the number of moments, should be appropriate to meet the normalizability<sup>22</sup> of  $\bar{f}_c^{(N)}(\mathbf{x}^{(N)}, t)$ . Assuming that this condition is met, we will later examine the consequence of the functional hypothesis with regard to the calortropy and irreversible thermodynamics of transport processes. At this point, in anticipation of the thermodynamic correspondence and in the light of  $\beta_{\text{eq}}$  in (6.220) we look for the parameter  $\beta$  in the form

$$\beta = \frac{1}{k_B T}. \quad (6.230)$$

The meaning of parameter  $T$  will be clarified presently.

The expansion coefficients  $X^{(q)}$  in (6.227) as well as  $\beta$  and  $\mathbb{Z}^{(N)}$  depend on variables in the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T}$  through which space-time dependence of the nonequilibrium canonical form  $\bar{f}_c^{(N)}$  enters. Since the variables in  $\mathfrak{P}$  obeys the evolution equations, namely, the generalized hydrodynamic equations presented earlier,  $\bar{f}_c^{(N)}$  evolves in space-time as a functional of the variables (e.g.,  $\Phi^{(q)}$  and their conjugate variables) spanning the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T}$ .

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<sup>21</sup>As noted in the footnote on  $\hat{\mu}_{\text{eq}}$  in Sect. 6.7.4, the term  $m_i \hat{\mu}$  is inserted for the event the system is spatially nonuniform as generally is if the system is in a nonequilibrium state. Thus the ensemble may be imagined to consist of petit ensembles of spatially varying parameters  $\hat{\mu}(\mathbf{r})$ .

<sup>22</sup>This normalizability condition is accompanied by the closure relation. It necessarily demands an approximation to the dimension of the manifold  $\mathfrak{P}$ . This approximation is reflected on the meaning of calortropy and its representation in the thermodynamic manifold, which therefore permits us to comprehend the thermodynamic and molecular theory meanings of calortropy within the bounds of validity of the approximation and the phenomenological thermodynamic theory to which the calortropy and its attributes are corresponded in the present scheme of theory.

### 6.7.6 Calortropy and Its Differential Form

#### 6.7.6.1 Calortropy

With  $\mathfrak{S}_i^{(N)}$  in (6.226) and  $\mathcal{H}_i^{(N)}$  given by (6.227), the local calortropy density  $\widehat{\Psi}$  in (6.198) is easily calculated from (6.198) in the form

$$\rho\widehat{\Psi} = \frac{\rho}{T} \left( \mathcal{E} + \sum_{q \geq 0} X^{(q)} \widehat{\Phi}^{(q)} - \widehat{\mu} \right) + \rho k_B \ln \Gamma(\mathbf{r}, t), \quad (6.231)$$

where  $\ln \Gamma(\mathbf{r}, t)$  is the local density of the global normalization factor  $\ln \mathbb{Z}^{(N)}$  defined as follows:

$$\begin{aligned} \ln \mathbb{Z}^{(N)} &= \int_V d\mathbf{r} \sum_{i=1}^N \left\langle \overline{f}^{(N)} m_i \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle \ln \Gamma(\mathbf{r}, t) \\ &= \int_V d\mathbf{r} \rho \ln \Gamma(\mathbf{r}, t) \end{aligned} \quad (6.232)$$

with the definition of  $\delta$

$$\sum_{i=1}^N \left\langle \overline{f}^{(N)} m_i \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle = \int d\mathbf{x}^{(N)} \overline{f}^{(N)} m_i \delta(\mathbf{r}_i - \mathbf{r}) = \rho.$$

Comparing (6.232) with the definition of  $\mathbb{Z}$  (6.229), we find

$$\exp \left[ \int_V d\mathbf{r} \rho k_B \ln \Gamma(\mathbf{r}, t) \right] = \left\langle \exp \left[ - \int_V d\mathbf{r} \beta \sum_{i=1}^N \mathcal{H}_i^{(N)} \delta(\mathbf{r}_i - \mathbf{r}) \right] \right\rangle, \quad (6.233)$$

which provides a way to relate  $\ln \Gamma(\mathbf{r}, t)$  to its molecular theory expression given in terms of  $\mathcal{H}_i^{(N)}$ .

To elucidate the meaning of  $\ln \Gamma(\mathbf{r}, t)$  from the phenomenological viewpoint, we first calculate the calortropy balance Eq. (6.199) by making use of the nonequilibrium canonical form (6.228) and the statistical mechanical formulas (6.200)–(6.202) for the calortropy flux and calortropy production, and  $\mathbb{D}$ . The calortropy flux  $\mathbf{J}_c$  is given by the formula

$$\begin{aligned} \mathbf{J}_c &= \frac{1}{T} \sum_{i=1}^N \left\langle \mathbf{C}_i \left( H_i^{(N)} + \sum_{q \geq 0} X^{(q)} h_i^{(q)} - m_i \widehat{\mu} \right) \times \right. \\ &\quad \left. \delta(\mathbf{r}_i - \mathbf{r}) \overline{f}^{(N)}(x^{(N)}, t) \right\rangle \\ &= \frac{1}{T} \left( \mathbf{Q} + \sum_{q \geq 0} X^{(q)} \boldsymbol{\psi}^{(q)} \right), \end{aligned} \quad (6.234)$$

where we have made use of the fact that

$$\sum_{i=1}^N \left\langle m_i \mathbf{C}_i \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)} \right\rangle = 0. \quad (6.235)$$

On the other hand, the calortropy production  $\sigma_c$  is given by the formula

$$\sigma_c = k_B \beta \sum_{i=1}^N \sum_{q \geq 0} \left\langle X^{(q)} h_i^{(q)} \delta(\mathbf{r}_i - \mathbf{r}) \mathfrak{R}[\bar{\mathbb{F}}^{(N)}(\mathbf{x}^{(N)}, t)] \right\rangle \quad (6.236)$$

owing to the fact that  $H_i^{(N)}$  and  $m_i$  are collision invariants of the collision integral  $\mathfrak{R}[\bar{\mathbb{F}}^{(N)}(\mathbf{x}^{(N)}, t)]$ . If the expression (6.132) for dissipation term  $\Lambda^{(q)}$  is made use of,  $\sigma_c$  can be written in a compact form in terms of dissipation terms:

$$\sigma_c = T^{-1} \sum_{q \geq 0} X^{(q)} \Lambda^{(q)}. \quad (6.237)$$

This expression not only elucidates a close connection of the dissipation terms to the calortropy production, but also endows on the calortropy production  $\sigma_c$ , which has so far remained an abstract quantity, a more definitive physical significance as the seat of energy dissipation accompanying transport processes described by the generalized hydrodynamic equations. In addition, we now see that the dissipation terms  $\Lambda^{(q)}$  unambiguously provide the energy dissipation mechanisms arising from the transport processes in terms of molecular interactions and collisions: they are the seat of energy dissipation in the course of transport processes. Furthermore, they can be shown to be in conformation to the laws of thermodynamics as any natural processes should be. The desired thermodynamic consistency will be assured if  $\sigma_c$  is calculated to remain always positive semidefinite irrespective of approximations made to the distribution functions. We will show this aim is possible to achieve explicitly, if  $\sigma_c$  is calculated in a cumulant expansion.

As to  $\mathbb{D}$ , it takes little more elaborate calculations. If we set

$$\ln \mathbb{Z}^{(N)} = \int_V d\mathbf{r} \rho \ln \Gamma(\mathbf{r}, t), \quad (6.238)$$

it can be shown to take the form

$$\begin{aligned} \mathbb{D} = & \rho \left( \mathcal{E} d_t T^{-1} + \sum_{q \geq 0} \widehat{\Phi}^{(q)} d_t \bar{X}^{(q)} + d_t (k_B \ln \Gamma) \right) \\ & - T^{-1} [\mathbf{Q} \cdot \nabla \ln T + \mathbf{P} : \nabla \mathbf{u}] - \nabla \cdot (T^{-1} \mathbf{Q}_v) + \sum_{q \geq 0} \bar{X}^{(q)} d_t \widehat{\Phi}^{(q)} \\ & + \sum_{q \geq 0} \nabla \cdot (\boldsymbol{\psi}^{(q)} \bar{X}^{(q)}) - \sum_{q \geq 0} \bar{X}^{(q)} \Lambda^{(q)}, \end{aligned} \quad (6.239)$$

where

$$\bar{X}^{(q)} = T^{-1} X^{(q)}. \quad (6.240)$$

It is also convenient to define for brevity of notation the symbols

$$\bar{\mu} = T^{-1} \hat{\mu}; \quad \bar{p} = T^{-1} p. \quad (6.241)$$

We will also find it useful, for the sake of maintaining the balance of two parts of the differential form presented below, to define the mass density fraction  $\mathfrak{c}$  by

$$\mathfrak{c} = mn/\rho, \quad (6.242)$$

which in fact turns out to be equal to unity in the case of a single-component fluid and hence unity. In the case of a mixture it will turn out to be a way to express concentrations of species in the mixture.

### 6.7.6.2 Calortropy Differential Form

Inserting  $\mathbf{J}_c$ ,  $\sigma_c$ , and  $\mathbb{D}$  calculated above into (6.199) and making use of the internal energy balance equation we obtain the calortropy balance equation in the differential form

$$\begin{aligned} \frac{d\hat{\Psi}}{dt} &= \frac{1}{T} \left[ \frac{d\mathcal{E}}{dt} + \sum_{q \geq 0} X^{(q)} \frac{d\hat{\Phi}^{(q)}}{dt} - \hat{\mu} \frac{d\mathfrak{c}}{dt} \right] \\ &+ \left[ \mathcal{E} \frac{d}{dt} \frac{1}{T} + \sum_{q \geq 0} \hat{\Phi}^{(q)} \frac{d}{dt} \frac{X^{(q)}}{T} - \mathfrak{c} \frac{d}{dt} \frac{\hat{\mu}}{T} \right] + \frac{d}{dt} (k_B \ln \Gamma). \end{aligned} \quad (6.243)$$

Here for the present case of a pure fluid

$$\mathfrak{c} = 1$$

and hence

$$\frac{d\mathfrak{c}}{dt} = 0$$

and the last term in the first line of (6.243) is therefore vanishes, but we have kept it to maintain the formal balance between the first two terms on the right hand side of (6.243). Note that in the case of a mixture  $d\mathfrak{c}/dt \neq 0$ . Furthermore, if we set

$$k_B T \ln \Gamma = pv, \quad (6.244)$$

where  $p$  is a parameter whose meaning is yet to be elucidated, we obtain the differential form (6.243) in a more insightful form

$$\begin{aligned} \frac{d\widehat{\Psi}}{dt} = & \frac{1}{T} \left[ \frac{d\mathcal{E}}{dt} + p \frac{dv}{dt} + \sum_{q \geq 0} X^{(q)} \frac{d\widehat{\Phi}^{(q)}}{dt} - \widehat{\mu} \frac{dc}{dt} \right] \\ & + \left[ \mathcal{E} \frac{d}{dt} \left( \frac{1}{T} \right) + v \frac{d}{dt} \left( \frac{p}{T} \right) + \sum_{q \geq 0} \widehat{\Phi}^{(q)} \frac{d}{dt} \left( \frac{X^{(q)}}{T} \right) - c \frac{d}{dt} \left( \frac{\widehat{\mu}}{T} \right) \right]. \end{aligned} \quad (6.245)$$

This differential form implies that it can be integrated in the manifold  $\mathfrak{P} \cup \mathfrak{T}$  to the bilinear form

$$\widehat{\Psi} = \frac{1}{T} \left( \mathcal{E} + pv + \sum_{q \geq 0} X^{(q)} \widehat{\Phi}^{(q)} - \widehat{\mu}c \right) \quad (6.246)$$

within a constant. As a matter of fact, this is identical with (6.231) since (6.244) holds. Moreover, if (6.246) is varied with respect to the variables in manifold  $\mathfrak{T}$ —namely, intensive variables—then we find the equation

$$\mathcal{E} d_t \left( \frac{1}{T} \right) + vd_t \left( \frac{p}{T} \right) + \sum_{q \geq 0} \widehat{\Phi}^{(q)} d_t \left( \frac{X^{(q)}}{T} \right) - cd_t \left( \frac{\widehat{\mu}}{T} \right) = 0, \quad (6.247)$$

where  $d_t = d/dt$ . This equation will be found to be the nonequilibrium Gibbs–Duhem equation, which is the necessary and sufficient condition for the integrability [39] in manifold  $\mathfrak{P} \cup \mathfrak{T}$  of the Pfaffian differential form [38, 40, 41]

$$d_t \widehat{\Psi} = T^{-1} \left( d_t \mathcal{E} + pd_t v - \widehat{\mu} d_t c + \sum_{q \geq 0} X^{(q)} d_t \widehat{\Phi}^{(q)} \right). \quad (6.248)$$

This is the extended Gibbs relation for the calortropy density, which is equivalent to the calortropy balance equation. Keep it in mind that  $d_t c = 0$  in (6.248) for a pure fluid. Therefore it may be safely said that, subject to the nonequilibrium Gibbs–Duhem equation, the calortropy balance equation is integrable to a surface in manifold  $\mathfrak{P} \cup \mathfrak{T} \cup \widehat{\Psi}$ . This feature is in sharp contrast to the Boltzmann entropy and its balance equation, because the Boltzmann entropy balance equation cannot be put into an exact differential form in manifold  $\mathfrak{P} \cup \mathfrak{T}$ . Therefore it is possible to state that the Boltzmann entropy balance equation cannot be integrated in the manifold  $\mathfrak{P} \cup \mathfrak{T}$ . This is, as a matter of fact, the very reason that we have introduced the notion of calortropy in place of the Boltzmann entropy when the system is removed from equilibrium and that a theory of thermodynamics of irreversible processes cannot be formulated with the Boltzmann entropy  $S$  in the manifold  $\mathfrak{P} \cup \mathfrak{T}$ . As will be seen in a later section on the relative Boltzmann entropy, neither is the Boltzmann entropy

balance equation integrable in the manifold  $\mathfrak{P} \cup \mathfrak{T}$ . It is therefore possible to state that the Boltzmann entropy and the relative Boltzmann entropy are quantities living in a wider space than  $\mathfrak{P} \cup \mathfrak{T}$ —namely, the phase space of dimension  $6\mathcal{N}$ .

### 6.7.7 Thermodynamic Correspondence

As it stands, the calortropy and its differential are mathematical objects derived from the GBE. To endow physical and operational meanings on them, the calortropy differential form (6.248) is corresponded to the phenomenological (thermodynamic) calortropy differential form in Chap. 2:

$$\begin{aligned}\widehat{\Psi}|_{\text{st}} &\Leftrightarrow \widehat{\Psi}|_{\text{th}}; \quad \mathcal{E}|_{\text{st}} \Leftrightarrow \mathcal{E}|_{\text{th}}; \quad v|_{\text{st}} \Leftrightarrow v|_{\text{th}}; \\ \mathfrak{c}|_{\text{st}} &\Leftrightarrow \mathfrak{c}|_{\text{th}}; \quad \widehat{\Phi}^{(q)}|_{\text{st}} \Leftrightarrow \widehat{\Phi}^{(q)}|_{\text{th}}.\end{aligned}\quad (6.249)$$

These thermodynamic correspondences identify not only the statistical mechanical quantities  $\widehat{\Psi}$ ,  $\mathcal{E}$ , etc. belonging to manifold  $\mathfrak{P}$  (i.e., extensive quantities). But they also provide identifications of the conjugate variables of the variables in manifold  $\mathfrak{P}$ —namely, the parameters  $T$  and  $p$ ,  $\mu$ ,  $X^{(q)}$  belonging to manifold  $\mathfrak{T}$  (i.e., intensive variables) with the respective thermodynamic quantities:

$$T|_{\text{st}} \Leftrightarrow T|_{\text{th}}; \quad p|_{\text{st}} \Leftrightarrow p|_{\text{th}}; \quad \mu|_{\text{st}} \Leftrightarrow \mu|_{\text{th}}; \quad X^{(q)}|_{\text{st}} \Leftrightarrow X^{(q)}|_{\text{th}}. \quad (6.250)$$

They thereby endow the thermodynamic meanings on them:  $T$  as thermodynamic (absolute) temperature;  $p$  as pressure;  $\mu$  as chemical potential;  $X^{(q)}$  as the generalized potentials and similarly for the extensive quantities. Evidently,  $T$  may be characterized by the derivative

$$T^{-1} = \left( \frac{\partial \widehat{\Psi}}{\partial \mathcal{E}} \right)_{v, \mathfrak{c}, \widehat{\Phi}} \quad (6.251)$$

and similarly for other conjugate parameters  $p$ ,  $\widehat{\mu}$ , and  $X^{(q)}$ . In particular,

$$X^{(q)} = T \left( \frac{\partial \widehat{\Psi}}{\partial \widehat{\Phi}^{(q)}} \right)_{v, \mathfrak{c}, \widehat{\Phi}'}. \quad (6.252)$$

Furthermore, with the help of (6.247) we are able to ascertain the normalization factor  $\mathbb{Z}$  is related to local pressure

$$k_B \ln \mathbb{Z}^{(N)} = \int_V d\mathbf{r} \frac{p}{T}, \quad (6.253)$$

which confirms (6.244). If  $p/T$  is uniform in space, (6.253) may be written as

$$k_B T \ln \mathbb{Z}^{(N)} = pV, \quad (6.254)$$

a well recognizable equilibrium statistical mechanics expression relating the partition function  $\mathbb{Z}^{(N)}$  to the pressure. We will return to the relation (6.253) presently to determine its local nonequilibrium partition function  $\Gamma(\mathbf{r}, t)$  more explicitly.

### 6.7.8 Local Form of the Second Law of Thermodynamics

Let us return to the calortropy balance equation, from which the differential form (6.248) has descended

$$\begin{aligned} \rho d_t \widehat{\Psi} &= -\nabla \cdot \left( T^{-1} \mathbf{Q} - \sum_{q \geq 0} \overline{X}^{(q)} \widehat{\Phi}^{(q)} \right) \\ &\quad + \rho \widehat{\Sigma}_{\text{loc}} + \sum_{q \geq 0} \overline{X}^{(q)} (\mathcal{Z}^{(q)} + \Lambda^{(q)}), \end{aligned} \quad (6.255)$$

where

$$\rho \widehat{\Sigma}_{\text{loc}} = -T^{-1} [(\mathbf{P} - p\boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q}^{\text{ch}} \cdot \nabla \ln T] + T^{-1} \sum_{q \geq 0} \boldsymbol{\psi}^{(q)} \cdot \nabla X^{(q)}, \quad (6.256)$$

$$\mathbf{Q}^{\text{ch}} = \mathbf{Q} + \sum_{q \geq 0} X^{(q)} \boldsymbol{\psi}^{(q)}. \quad (6.257)$$

If this balance equation is integrated over the volume of the system then the left-hand side of the balance equation may be expressed as

$$\frac{d\Psi}{dt} = \int_V d\mathbf{r} \rho \left( \frac{\partial \widehat{\Psi}}{\partial t} + \mathbf{u} \cdot \frac{\partial \widehat{\Psi}}{\partial \mathbf{r}} \right).$$

which represents the total change in  $\Psi$  within the volume of the system; on the other hand, the right-hand side of the balance equation consists of two components, one arising from the exchange of calortropy represented by  $\mathbf{J}_c$ , the flux of calortropy, and the other the source term represented by  $\Xi_{\text{cal}}$

$$\Xi_{\text{cal}} := \rho \widehat{\Sigma}_{\text{loc}} + \sum_{q \geq 0} X^{(q)} (\mathcal{Z}^{(q)} + \Lambda^{(q)}) \geq 0. \quad (6.258)$$

The integral of the divergence term may be written as

$$\frac{d_e \Psi}{dt} = - \int_{\mathbf{B}} d\mathbf{B} \cdot \mathbf{J}_c, \quad (6.259)$$

which represents the exchange of calortropy between the system and its surroundings, whereas the integral of  $\Xi_{\text{cal}}$  may be written as

$$\frac{d_i \Psi}{dt} = \int_V d\mathbf{r} \Xi_{\text{cal}}(\mathbf{r}, t), \quad (6.260)$$

which represents a creation of calortropy within the system owing to the irreversible transport processes therein. Thus we obtain in place of the calortropy balance equation the time derivative relation for the global calortropy

$$\frac{d\Psi}{dt} = \frac{d_e \Psi}{dt} + \frac{d_i \Psi}{dt}. \quad (6.261)$$

The first term on the right ( $d_e \Psi/dt$ ) representing the change arising from exchange of calortropy with the surroundings can be positive or negative depending on the direction of exchange in  $\Psi$  with the surroundings, but owing to the inequality (6.258) the second term ( $d_i \Psi/dt$ ) representing the intrinsic change within the system is always positive:

$$\frac{d_i \Psi}{dt} \geq 0, \quad (6.262)$$

the equality holding only at equilibrium at which  $\Xi_{\text{cal}}$  vanishes.

Clausius [42] put forward the notions of *compensated* and *uncompensated heats* in the course of his work on thermodynamics [43]. The first term ( $d_e \Psi/dt$ ) may be interpreted as the compensated heat because it represents a heat exchanged between the system and its surroundings, whereas the second term ( $d_i \Psi/dt$ ), may be regarded as the uncompensated heat, which is a heat unavoidably created within the system owing to the irreversible transport processes. The uncompensated heat is always positive in the sign convention we have adopted in this work. The reasoning leading to (6.261) and (6.262) provides a cogent basis to assert that the notions of calortropy, calortropy flux, and calortropy production can represent a nonequilibrium and molecular (kinetic) theory representation of Clausius's notions of compensated and uncompensated heats. Therefore it may be said that calortropy is a nonequilibrium generalization of the equilibrium entropy (or, simply, entropy) he invented for *reversible processes* in thermodynamics. On the grounds of the reasoning and discussion presented up to this point the local form of the second law of thermodynamics can now be said given by the inequality of  $\Xi_{\text{cal}}$  represented by (6.258).

We have shown that the Pfaffian differential form  $d_t \widehat{\Psi}$  for the calortropy accompanying irreversible processes is exact in the thermodynamic manifold. Therefore, if an irreversible process is performed from state  $A$  to state  $B$  such that the inequality (6.262) is satisfied, then the difference in the calortropy values at state  $B$  and state  $A$  would be

$$\Delta \widehat{\Psi} = \widehat{\Psi}(B) - \widehat{\Psi}(A).$$

Therefore, if a cyclic process is performed such that the inequality (6.262) is met everywhere on the path of the cyclic process in the manifold  $\mathfrak{P} \cup \mathfrak{T} \cup \widehat{\Psi}$  then

$$\int_0^{\tau_p} dt \frac{d\widehat{\Psi}}{dt} = \oint d\widehat{\Psi} = 0, \quad (6.263)$$

because  $d_t \widehat{\Psi}$  is exact in  $\mathfrak{P} \cup \mathfrak{T}$ . Here the integral is over the cyclic process of period  $\tau_p$ . This vanishing circular integral of  $\widehat{\Psi}$  agrees with the phenomenological expression for the second law deduced from the Clausius inequality inferred from the Carnot theorem, namely, the second law of thermodynamics. Therefore this vanishing cyclic integral of  $\widehat{\Psi}$  with the inequality (6.262) satisfied everywhere on the cyclic path may be said to be also a local representation of the second law of thermodynamics, and in the present work we have obtained their statistical mechanical representations for dense fluids or liquids. It should be noted that the evolution of  $\widehat{\Psi}$  is on the support of generalized hydrodynamic equations accompanying the irreversible processes and the generalized hydrodynamics are in conformation to the second law of thermodynamics.

In connection with this vanishing cyclic integral representation of the second law of thermodynamics, it should be also noted that the energy conservation law, that is, the first law of thermodynamics, may also be expressed as a vanishing circular integral of the internal energy along the cyclic path (or process)

$$\oint d\mathcal{E} = 0, \quad (6.264)$$

because the energy balance Eq.(6.83) can be put in an exact differential form in  $\mathfrak{P} \cup \mathfrak{T}$  and its cyclic integral over the process vanishes identically. Therefore the local forms of the first and second law of thermodynamics may be expressed in a pair of vanishing circular integrals (6.264) and (6.263) in  $\mathfrak{P} \cup \mathfrak{T} \cup \widehat{\Psi}$ , which are the kinetic theory counterparts of similar circular integrals appearing in the phenomenological theory in Chap. 2. For this reason the underlying generalized hydrodynamic equations derived from the GBE may be said to be consistent with the laws of thermodynamics.

### 6.7.9 Nonequilibrium Partition Function

To develop formal relations for calentropy density  $\widehat{\Psi}$  we have made use of local nonequilibrium partition function  $\Gamma$  through relations (6.231), (6.233), and (6.238) relating the global nonequilibrium partition function  $\mathbb{Z}^{(N)}$  to  $\Gamma$ . The integral relation (6.238), however, remains rather formal. It is necessary to obtain an explicit local representation for  $\Gamma$ , if we wish to carry through the desired formulation of nonequilibrium statistical thermodynamics we have set out to establish in a practicable form. We first attend to this essential step.

To achieve the aim we return to (6.233), which may be written in terms of  $\mathbb{Z}^{(N)}$ :

$$\mathbb{Z}^{(N)} = \left\langle \exp \left[ - \int_V d\mathbf{r} \sum_{i=1}^N \beta \mathcal{H}_i^{(N)} \delta(\mathbf{r}_i - \mathbf{r}_l) \right] \right\rangle. \quad (6.265)$$

The integral over the whole volume of the assembly may be written as a sum over elementary volume elements  $\Delta V(\mathbf{r}_l)$  into which volume  $V$  is partitioned around points  $\mathbf{r}_l$  in  $V$ . Thus the global  $\mathbb{Z}^{(N)}$  may be written as

$$\mathbb{Z}^{(N)} = \left\langle \exp \left[ - \sum_{i=1}^N \beta \mathcal{H}_i^{(N)} \delta(\mathbf{r}_i - \mathbf{r}_l) \right] \right\rangle^{\sum_l \Delta V(\mathbf{r}_l)}. \quad (6.266)$$

Let us multiply a constant parameter  $\lambda$  to  $\Delta V(\mathbf{r}_l)$  which will be taken equal to unity at the end when the analysis is finished. The global partition function  $\mathbb{Z}^{(N)}$  may then be written as

$$\mathbb{Z}^{(N)}(\lambda) = \left\langle \exp \left[ - \sum_{i=1}^N \beta \mathcal{H}_i^{(N)}(\mathbf{r}_{ia}) \delta(\mathbf{r}_i - \mathbf{r}_l) \right] \right\rangle^{\sum_l \lambda \Delta V(\mathbf{r}_l)} \quad (6.267)$$

Differentiating  $\mathbb{Z}^{(N)}(\lambda)$  with parameter  $\lambda$  it is possible to show that  $\ln \mathbb{Z}^{(N)}(\lambda)$  is a first-degree homogeneous function of  $\Delta V(\mathbf{r}_l)$ , so that we obtain

$$\begin{aligned} \ln \mathbb{Z}^{(N)}(\lambda) |_{\lambda=1} &= \sum_{l \geq 0} \Delta V_l \ln \left\langle \exp \left[ - \sum_{i=1}^N \beta \mathcal{H}_i^{(N)}(\mathbf{r}_i) \delta(\mathbf{r}_i - \mathbf{r}_l) \right] \right\rangle \\ &= \int_V d\mathbf{r} \ln \left\langle \exp \left[ - \sum_{i=1}^N \beta \mathcal{H}_i^{(N)}(\mathbf{r}_i) \delta(\mathbf{r}_i - \mathbf{r}) \right] \right\rangle, \end{aligned} \quad (6.268)$$

which means

$$\Gamma(\mathbf{r}, t) = \left\langle \exp \left[ - \sum_{i=1}^N \beta(\mathbf{r}) \mathcal{H}_i^{(N)} \delta(\mathbf{r}_i - \mathbf{r}) \right] \right\rangle^{1/\rho}. \quad (6.269)$$

This is the desired local form of nonequilibrium partition function we set out to obtain. This nonequilibrium partition function provides molecular theory representations for all nonequilibrium thermodynamic functions appearing in the thermodynamic theory of irreversible transport processes and generalized hydrodynamics formulated in this chapter.

### 6.7.10 Nonequilibrium Statistical Thermodynamics

The most convenient differential form for developing nonequilibrium statistical thermodynamics is obtained if (6.231) is rearranged to the form

$$k_B \ln \Gamma(\mathbf{r}, t) = \widehat{\Psi} - \frac{1}{T} \left( \mathcal{E} + \sum_{q \geq 0} X^{(q)} \Phi^{(q)} - c\widehat{\mu} \right),$$

which with relation (6.244) may be written as

$$pv = T\widehat{\Psi} - \mathcal{E} - \sum_{q \geq 0} X^{(q)} \Phi^{(q)} + c\widehat{\mu}. \quad (6.270)$$

By operating  $d_t$  and making use of the differential for  $\widehat{\Psi}$  in (6.248) there follows the differential form for  $(pv)$  which now may be regarded as a thermodynamic potential whose differential form is given by the exact differential

$$d_t(pv) = \widehat{\Psi} d_t T + pd_t v + cd_t \widehat{\mu} - \sum_{q \geq 0} \widehat{\Phi}^{(q)} d_t X^{(q)} = d_t(k_B T \ln \Gamma). \quad (6.271)$$

Recall (6.244) that  $pv = k_B T \ln \Gamma$  is the local form of the logarithm of nonequilibrium partition function  $\mathbb{Z}$ . With this differential form we are now able to express its coefficients as derivatives of the thermodynamic potential  $pv$  or nonequilibrium partition function as follows:

$$\widehat{\Psi} = k_B \ln \Gamma + k_B T \left( \frac{\partial \ln \Gamma}{\partial T} \right)_{v, \widehat{\mu}, X}, \quad (6.272)$$

$$p = k_B T \left( \frac{\partial \ln \Gamma}{\partial v} \right)_{T, \widehat{\mu}, X}, \quad (6.273)$$

$$c = k_B T \left( \frac{\partial \ln \Gamma}{\partial \widehat{\mu}} \right)_{T, v, X}, \quad (6.274)$$

$$\widehat{\Phi}^{(q)} = -k_B T \left( \frac{\partial \ln \Gamma}{\partial X^{(q)}} \right)_{T, v, X'}, \quad (6.275)$$

where the prime on the subscript  $X$  in the derivative denotes excluding the variable  $X^{(q)}$  from the set of  $X^{(q)}$  ( $q \geq 0$ ). Therefore knowledge of the local nonequilibrium partition function  $\Gamma$  would make it possible to compute the macroscopic variables on the right in (6.272)–(6.275). These derivatives together with the differential forms for the calortropy and the related are the principal formal results of nonequilibrium statistical mechanics based on the nonequilibrium canonical form  $\bar{f}_c^{(N)}$  for the GBE. Numerous other irreversible thermodynamic relations may be obtained from (6.272)–(6.275). Consequently, computation of local nonequilibrium partition function would be one of the principal concerns of the theory of nonequilibrium statistical thermodynamics. A note of caution: Eq. (6.274) must be disregarded in the case of a pure fluid, since then  $c = 1$ , as noted earlier, and consequently  $dc/dt = 0$ .

We have seen an example of how we might compute  $\Gamma$  or  $Z^{(N)}$  in Chap. 3 and therewith the generalized potentials  $X^{(q)}$ . A similar method may be applied to the case of dense fluids, albeit the task will be much more complicated to accomplish owing to the presence of molecular interactions. With these formal results the thermodynamic theory of irreversible processes is fully established, at least formally, by means of the kinetic equation for the ensemble.

Equations (6.248) and (6.271) and the associated thermodynamic results verify that the assertion made in connection with (6.247) must be true in the light of self-consistency in the formalism obtained for the thermodynamic theory of irreversible processes. In fact, (6.247) is the necessary and sufficient conditions for the calortropy balance equation is integrable in the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T} \cup \widehat{\Psi}$ , and we are thereby assured of the existence of a theoretical structure of thermodynamics of irreversible processes satisfying the laws of thermodynamics [25, 36, 37].

In any case, with the extended Gibbs relations obtained above, it is possible to develop a complete molecular theory of thermodynamics of irreversible processes in dense fluids. It may be said that the present work lays the kinetic theory foundation of nonequilibrium thermodynamics. Some applications of the theory to flow problems is referred to the monograph on generalized thermodynamics [30] by the present author and Chap. 9 of this work.

### 6.7.11 Determination of Generalized Potentials

The dissipation terms  $\Lambda^{(q)}$  in the generalized hydrodynamic equations must be given in terms of, primarily, the variables spanning the manifold  $\mathfrak{P}$ . To achieve this aim it is first necessary to replace  $f^{(N)}$  with  $f_c^{(N)}$  in the statistical mechanics expression for  $\Lambda^{(q)}$ . However, this step of replacing  $f^{(N)}$  with  $f_c^{(N)}$  itself is an approximation neglecting the fluctuation of  $f^{(N)}$  from  $f_c^{(N)}$ . Then the generalized potentials  $X^{(q)} \in \mathfrak{T}$  appearing in the nonequilibrium canonical form  $f_c^{(N)}$  should be expressed in terms of variables in manifold  $\mathfrak{P}$  first of all.

For this aim we may follow the idea developed in Chap. 3 by using the Lambert W function approach [44] for this purpose. Alternatively, by using the derivative (6.275) we may calculate the relation between  $X^{(q)}$  and  $\widehat{\Phi}^{(q)}$ .

$$\widehat{\Phi}^{(q)} = -k_B T \left( \frac{\partial \ln \Gamma}{\partial X^{(q)}} \right)_{T, p, X'} . \quad (6.276)$$

This derivative is not only a function of generalized potentials  $X^{(q)}$ , but also must be of the same tensorial rank as  $\widehat{\Phi}^{(q)}$ . Therefore, if the derivative is expanded in series of  $X^{(q)}$ , the leading term must be proportional to  $X^{(q)}$  itself. Hence we may write (6.276) in the form

$$X^{(q)} = -g^{(q)} \widehat{\Phi}^{(q)}, \quad (6.277)$$

where  $g^{(q)}$  is generally given by the inverse logarithmic derivative

$$g^{(q)} = \frac{1}{k_B T} \left( \frac{\partial \ln \Gamma}{\partial \ln X^{(q)}} \right)_{T, p, X'}^{-1} \quad (q \geq 0). \quad (6.278)$$

The coefficient  $g^{(q)}$  is a scalar function of variables of manifold  $\mathfrak{P}$  and their thermodynamic tangents such as  $T$ ,  $p$ , etc., which may be generally given in terms of statistical mechanical averages of moments  $h_i^{(q)}$ . To compute explicitly the detailed mathematical structure of  $g^{(q)}$  would take the same amount of effort as for the non-equilibrium partition function itself. Nevertheless, as the system tends to near equilibrium in the low density regime,  $g^{(q)}$  would tend to the dilute gas forms as shown in Chap. 3. Therefore we may express  $g^{(q)}$  in the form

$$g^{(q)} = g_0^{(q)} + g_1^{(q)} \widehat{\Phi}^{(q)} \odot \widehat{\Phi}^{(q)} + \dots , \quad (6.279)$$

where  $g_0^{(q)}$  is a limit of  $g^{(q)}$  independent of  $\widehat{\Phi}^{(q)}$

$$g_0^{(q)} = \lim_{\Phi \rightarrow 0} g^{(q)}(n, T, p, \dots) \quad (6.280)$$

and  $g_1^{(q)}$  depends on  $n$ ,  $T$ ,  $p$ . The examples for  $g_0^{(q)}$  excluding those associated with the volume transport phenomena can be seen in Chap. 3, where the Boltzmann (dilute monatomic gas) kinetic theory is discussed.

### 6.7.12 Cumulant Expansion for Dissipation Terms

The formal expression for the dissipation term  $\Lambda^{(q)}$  must be also properly computed as a function of variables in manifold  $\mathfrak{P}$  before we attempt to apply the generalized hydrodynamic equations to study transport processes and related hydrodynamic flow

problems. Fortunately, this goal can be simultaneously achieved if the calortropy production  $\sigma_c$  is calculated by using  $\bar{f}_c^{(N)}$  in (6.196) and (6.228) since then the two quantities are seen closely related to each other:

$$\sigma_c = \frac{1}{T} \sum_{q \geq 0} X^{(q)} \Lambda^{(q)}. \quad (6.281)$$

Since  $\sigma_c$  is partly given in terms of the full distribution function  $\bar{f}_c^{(N)}$  as is evident from its definition (6.201),  $\bar{f}^{(N)}$  appearing in the collision term  $\mathfrak{R}[\mathbb{F}]$  must be approximated with the nonequilibrium canonical form  $\bar{f}_c^{(N)}$  if we wish to make further progress. This approximation is tantamount to neglecting fluctuations of  $\bar{f}$  from  $\bar{f}_c^{(N)}$ . As a matter of fact, the aforementioned approximation assures the positivity of  $\sigma_c$  because then Condition (6.C2) is satisfied. However, it will be found that further approximations are necessary to put  $\sigma_c$  in a more practical form. They must be made such that the positivity of  $\sigma_c$  remains inviolate so as to make the result of approximations thermodynamically consistent. We find that such a controlled approximation of  $\sigma_c$  is possible to achieve if a cumulant expansion method [45, 46] is applied.

The nonequilibrium canonical form  $\bar{f}_c^{(N)}$  is given by

$$\bar{f}_c^{(N)}(\mathbf{x}_\alpha^{(N)}, t) = \exp \left[ - \int_V d\mathbf{r} \beta \sum_{i\alpha=1}^N \mathcal{H}_{i\alpha}^{(N)} \delta(\mathbf{r}_{i\alpha} - \mathbf{r}) - \ln \mathbb{Z}_\alpha^{(N)} \right], \quad (6.282)$$

where

$$\mathcal{H}_{i\alpha}^{(N)} = H_{i\alpha}^{(N)} + \sum_{q \geq 0} X_\alpha^{(q)} h_{i\alpha}^{(q)} - m_{i\alpha} \hat{\mu}_\alpha \quad (6.283)$$

and

$$\mathbb{Z}_\alpha^{(N)} = \left\langle \exp \left[ - \int_V d\mathbf{r} \beta \sum_{i\alpha=1}^N \left( H_{i\alpha}^{(N)} + \sum_{q \geq 0} X_\alpha^{(q)} h_{i\alpha}^{(q)} - m_{i\alpha} \hat{\mu}_\alpha \right) \delta(\mathbf{r}_{i\alpha} - \mathbf{r}) \right] \right\rangle \quad (6.284)$$

with the definition of the brackets  $\langle A \rangle$  by

$$\langle A \rangle = \int d\mathbf{x}^{(N)} A. \quad (6.285)$$

The subsystems (i.e., ensemble members) are distinguished by the subscript  $\alpha$ , and to remind us that the chemical potentials may be a local function of position in the case of nonequilibrium the subscript  $\alpha$  is affixed on  $\mu$ . It, however, has nothing to do with species. The functional hypothesis form for the ensemble distribution function

$$\underline{\mathbb{F}}_c^{(\mathcal{N})} = \prod_{\alpha=1}^v \overline{f}_c^{(N)}(\mathbf{x}_{\alpha}^{(N)}, t) \quad (6.286)$$

may then be written as

$$\underline{\mathbb{F}}_c^{(\mathcal{N})} = \underline{\mathbb{F}}_0^{(\mathcal{N})} e^{-\underline{\mathbb{H}}^{(1)}}. \quad (6.287)$$

In (6.287)  $\underline{\mathbb{F}}_0^{(\mathcal{N})}$  is the “equilibrium part” defined by

$$\underline{\mathbb{F}}_0^{(\mathcal{N})} = \frac{1}{Z^{(\mathcal{N})}} \exp \left[ - \sum_{\alpha=1}^v \int_{V_{\alpha}} d\mathbf{r} \sum_{i=1(i \in \alpha)}^N \beta_{\alpha} (H_{i\alpha} - m_{i\alpha} \hat{\mu}_{\alpha}) \delta(\mathbf{r}_{i\alpha} - \mathbf{r}) \right], \quad (6.288)$$

$$Z^{(\mathcal{N})} = \prod_{\alpha=1}^v Z_{\alpha}^{(N)} \quad (\mathcal{N} = vN), \quad (6.289)$$

and  $\underline{\mathbb{H}}^{(1)}$  is defined by the nonequilibrium part

$$\underline{\mathbb{H}}^{(1)} = \sum_{\alpha=1}^v k_B^{-1} \int_{V_{\alpha}} d\mathbf{r} \sum_{i=1(i \in \alpha)}^N \overline{H}_{i\alpha}^{(1)} \delta(\mathbf{r}_{i\alpha} - \mathbf{r}). \quad (6.290)$$

The form (6.287) for  $\underline{\mathbb{F}}_c^{(\mathcal{N})}$  replaces the full distribution function in the formula for the calortropy production

$$\sigma_c = k_B \sum_{q \geq 0} \beta X^{(q)} \left\langle \overline{\mathbb{H}}_{\bullet}^{(1)} \Re[\underline{\mathbb{F}}_0^{(\mathcal{N})} e^{-\underline{\mathbb{H}}^{(1)}}] \right\rangle, \quad (6.291)$$

where we have used the abbreviation for the nonequilibrium part  $\overline{\mathbb{H}}_{\bullet}^{(1)}$  for brevity:

$$\overline{\mathbb{H}}_{\bullet}^{(1)} = \sum_{q \geq 0} \beta X^{(q)} \sum_{i=1}^N h_i^{(q)} \delta(\mathbf{r}_i - \mathbf{r}) \quad (6.292)$$

with the subscript  $\bullet$  standing<sup>23</sup> for a subsystem over which the term will be summed when  $\sigma_c$  is to be symmetrized presently. If we follow the procedure used for the proof of Condition (6.C2) in Sect. 6.2.3, the collision integral in (6.291) can be written in the form

$$\Re[\underline{\mathbb{F}}^{(\mathcal{N})}(x^{(\mathcal{N})}, t)] = \frac{\epsilon}{v} \int dx^{(\mathcal{N}-N)} \underline{\mathbb{F}}_0^{(\mathcal{N})} \left[ e^{-\underline{\mathbb{H}}^{(1)*}} - e^{-\underline{\mathbb{H}}^{(1)}} \right], \quad (6.293)$$

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<sup>23</sup>The dot  $\bullet$  is a subscript place holder.

where  $\bar{H}^{(1)*}$  is the post-collision value of  $H^{(1)}$

$$e^{-\bar{H}^{(1)*}} = \epsilon \int_0^\infty ds e^{-(\epsilon + i\mathcal{L}^{(\mathcal{N})})s} e^{-\bar{H}^{(1)}(x^{(\mathcal{N})})} \quad (6.294)$$

$$e^{-\bar{H}^{(1)}} = \epsilon \int_0^\infty ds e^{-(\epsilon + i\mathcal{L}_0^{(\mathcal{N})})s} e^{-\bar{H}^{(1)}(x^{(\mathcal{N})})}. \quad (6.295)$$

Finally, the calortropy production in (6.291) can be written a fully symmetrized form as follows:

$$\begin{aligned} \hat{\sigma}_c &= \frac{1}{2v^2} \int dx^{(\mathcal{N})} \left( \bar{H}^{(1)} - \bar{H}^{(1)*} \right) \left[ e^{-\bar{H}^{(1)*}} - e^{-\bar{H}^{(1)}} \right] \bar{\mathbb{F}}_0^{(\mathcal{N})} \\ &:= \frac{1}{2} \left\langle \left( \bar{H}^{(1)} - \bar{H}^{(1)*} \right) \left[ e^{-\bar{H}^{(1)*}} - e^{-\bar{H}^{(1)}} \right] \right\rangle_c, \end{aligned} \quad (6.296)$$

where  $\bar{H}^{(1)}$  is now given by

$$\bar{H}^{(1)} = \sum_{\alpha=1}^v \left( \bar{H}_{\bullet}^{(1)} \right)_{\bullet=\alpha} = \sum_{\alpha=1}^v \bar{H}_{\alpha}^{(1)} \quad (6.297)$$

and  $\hat{\sigma}_c$  is the reduced calortropy production defined by

$$\hat{\sigma}_c = \sigma_c / k_B \epsilon. \quad (6.298)$$

Here we now may take  $\epsilon$ , which is the time for subsystems to collide, in the form

$$\epsilon = l \sqrt{\frac{2k_B T}{m}}, \quad (6.299)$$

where  $m$  is the reduced mass and  $l$  is the mean free path.

The right hand side of (6.296) is now ready for a cumulant expansion. We apply the cumulant expansion method of Meeron [45] and Kubo [46]. For the aim in mind it is convenient to split  $\hat{\sigma}_c$  into two parts as in

$$\hat{\sigma}_c = \frac{1}{2} \left[ \mathcal{R}^{(+)}(\lambda) - \mathcal{R}^{(-)}(\lambda) \right]_{\lambda=1}, \quad (6.300)$$

where

$$\mathcal{R}^{(+)}(\lambda) = \left\langle \left( \bar{H}^{(1)} - \bar{H}^{(1)*} \right) \left( e^{-\lambda \bar{H}^{(1)*}} - 1 \right) \right\rangle_c, \quad (6.301)$$

$$\mathcal{R}^{(-)}(\lambda) = \left\langle \left( \bar{H}^{(1)} - \bar{H}^{(1)*} \right) \left( e^{-\lambda \bar{H}^{(1)}} - 1 \right) \right\rangle_c. \quad (6.302)$$

Then  $\mathcal{R}^{(\pm)}(\lambda)$  are expanded in cumulant series as follows:

$$\mathcal{R}^{(\pm)}(\lambda) = \kappa \left\{ \exp \left[ \sum_{l=1}^{\infty} \frac{(-\lambda)^l}{l!} \kappa_l^{(\pm)} \right] - 1 \right\}, \quad (6.303)$$

where

$$\kappa = \frac{1}{2} \left\langle \left( \bar{\mathbb{H}}^{(1)} - \bar{\mathbb{H}}^{(1)*} \right) \left( \mathbb{H}^{(1)} - \mathbb{H}^{(1)*} \right) \right\rangle_c^{1/2}. \quad (6.304)$$

To find the cumulants  $\kappa_l^{(\pm)}$ , (6.303), (6.301), and (6.302) are expanded in power series in  $\lambda$  and the terms of like powers of  $\lambda$  are compared. With the definition of symbols for basic cumulants

$$\begin{aligned} \kappa_2 &= \frac{1}{4} \left\langle \left( \bar{\mathbb{H}}^{(1)} - \bar{\mathbb{H}}^{(1)*} \right) \left( \mathbb{H}^{(1)2} - \mathbb{H}^{(1)*2} \right) \right\rangle_c, \\ \kappa_3 &= \frac{1}{4} \left\langle \left( \bar{\mathbb{H}}^{(1)} - \bar{\mathbb{H}}^{(1)*} \right) \left( \mathbb{H}^{(1)3} - \mathbb{H}^{(1)*3} \right) \right\rangle_c, \\ &\text{etc.} \end{aligned} \quad (6.305)$$

the leading order cumulants are then found given by the formulas

$$\begin{aligned} \kappa_1^{(\pm)} &= \mp \kappa, \\ \kappa_2^{(\pm)} &= \mp \frac{\kappa_2}{\kappa} - \kappa^2, \\ \kappa_3^{(\pm)} &= \mp \frac{\kappa_3}{\kappa} - 3\kappa_2 \mp 2\kappa^3, \\ &\text{etc.} \end{aligned} \quad (6.306)$$

When  $\lambda$  is set equal to 1, the reduced calortropy production is obtained in terms of cumulants. And the first-order cumulant approximation is identified by the simple formula given in terms of first-order cumulant  $\kappa$ :

$$\hat{\sigma}_c = \kappa \sinh \kappa. \quad (6.307)$$

This formula is always positive. Therefore it is a simplest, yet nonlinear, thermodynamically consistent approximation for the calortropy production, which we will use later in this work. The second-order cumulant approximation does not yield a positive  $\hat{\sigma}_c$  everywhere, making it an unsuitable approximation, whereas the third-order cumulant approximation is positive everywhere. However, it is rather unwieldy because it produces collision bracket integrals very complicated and unwieldy to compute in practice. However, it contains quite a physically interesting feature because there is a distinctive possibility of a nonzero second minimum emerging [47] beyond equilibrium. *Such a second minimum is rather intriguing, because the system may self-organize beyond equilibrium in a minimum calortropy production state.*

To deduce the dissipation terms in the first-order cumulant approximation we first calculate  $\kappa^2$  explicitly. We find that  $\kappa^2$  is a quadratic form in the generalized potentials  $X^{(q)}$ :

$$\kappa^2 = \sum_{q,s \geq 0} X^{(q)} \mathbb{R}^{(qs)} X^{(s)}, \quad (6.308)$$

where the coefficients  $\mathbb{R}^{(qs)}$  are the collision bracket integrals discussed in the next subsection. Since we may write the first-order cumulant approximation for  $\sigma_c$  as

$$\sigma_c = k_B \epsilon \kappa^2 \frac{\sinh \kappa}{\kappa} = k_B T \epsilon \sum_{q,s \geq 0} \frac{X^{(q)}}{T} \mathbb{R}^{(qs)} X^{(s)} \left( \frac{\sinh \kappa}{\kappa} \right),$$

on comparing it with (6.281) we obtain the first order cumulant approximation for  $\Lambda^{(q)}$ :

$$\Lambda^{(q)} = \sum_{s \geq 0} k_B T \epsilon \mathbb{R}^{(qs)} X^{(s)} \left( \frac{\sinh \kappa}{\kappa} \right). \quad (6.309)$$

With these dissipation terms in terms of collision bracket integrals and the generalized potentials given in terms of variables in manifold  $\mathfrak{P}$  in the previous subsection, the generalized hydrodynamic equations are now free from undetermined parameters initially present in  $\bar{\mathcal{F}}_c^{(N)}$  given in (6.282). The set is now closed with respect to variables in manifold  $\mathfrak{P} \cup \mathfrak{T}$  and ready for solution. We note that the collision dynamical information of the generalized hydrodynamic equations are wholly contained in the collision bracket integrals  $\mathbb{R}^{(qs)}$  as will be seen later when we explicitly list them. Being derived from the thermodynamically consistent  $\sigma_c$  given in (6.307), the generalized hydrodynamic equations with  $\Lambda^{(q)}$  given by (6.309) are also thermodynamically consistent.

### 6.7.13 Collision Bracket Integrals

In kinetic theory of macroscopic transport processes all the molecular dynamical information on the substance of interest is contained in the collision integral of the kinetic equation and, particularly, in the collision bracket integrals  $\mathbb{R}^{(qs)}$ , if the first-order cumulant approximation is taken for the dissipation terms. It is, therefore, sufficient to pay attention to  $\kappa^2$  in (6.43), which on substitution of  $\bar{\mathbb{H}}^{(1)}$  and  $\mathbb{H}^{(1)}$  yields the formula

$$\kappa^2 = \frac{1}{4\nu^2} \int d\mathbf{x}^{(\mathcal{N})} \bar{\mathbb{F}}_0^{(\mathcal{N})} \sum_{\alpha=1}^v \sum_{i\alpha=1}^{N_\alpha} \sum_{q \geq 0} \left[ \beta X^{(q)} \left( h_i^{(q)} - h_i^{(q)*} \right) \delta(\mathbf{r}_i - \mathbf{r}) \right]_\alpha \times \\ \sum_{\gamma=1}^v \sum_{j\gamma=1}^{N_\gamma} \sum_{s \geq 0} \left[ \int_V d\mathbf{r}' \beta X^{(s)} \left( h_j^{(s)} - h_j^{(s)*} \right) \delta(\mathbf{r}_{j\gamma} - \mathbf{r}') \right]_\gamma. \quad (6.310)$$

Because the terms of different  $\alpha$  and  $\gamma$  contribute  $v$  identical values of the integrals, (6.310) is reduced to the form

$$\kappa^2 = \frac{1}{4} \int_V d\mathbf{r}' \int d\mathbf{x}^{(\mathcal{N})} \bar{\mathbb{F}}_0^{(\mathcal{N})} \sum_{i=1}^N \sum_{q \geq 0} \beta X^{(q)} \left( h_i^{(q)} - h_i^{(q)*} \right) \delta(\mathbf{r}_i - \mathbf{r}) \times \\ \sum_{j=1}^N \sum_{s \geq 0} \beta X^{(s)} \left( h_j^{(s)} - h_j^{(s)*} \right) \delta(\mathbf{r}_j - \mathbf{r}'). \quad (6.311)$$

Now, if the integration over  $\mathbf{r}'$  is performed, we find  $\kappa^2$  can be put into an integral over a single set of phase  $x^{(\mathcal{N})}$ :

$$\kappa^2 = \frac{1}{4} \beta^2 \sum_{q \geq 0} \sum_{s \geq 0} \sum_{i=1}^N \sum_{j=1}^N X^{(q)} X^{(s)} \left\langle \left( h_i^{(q)} - h_i^{(q)*} \right) \left( h_j^{(s)} - h_j^{(s)*} \right) \right\rangle_0. \quad (6.312)$$

For this we have defined the abbreviation  $\langle \dots \rangle_0$  for the integral which we have used to construct the set of moments:

$$\left\langle \left( h_i^{(q)} - h_i^{(q)*} \right) \left( h_j^{(s)} - h_j^{(s)*} \right) \right\rangle_0 \\ = \int d\mathbf{x}^{(\mathcal{N})} \bar{\mathbb{F}}_0^{(\mathcal{N})} \left( h_i^{(q)} - h_i^{(q)*} \right) \left( h_j^{(s)} - h_j^{(s)*} \right) \delta(\mathbf{r}_i - \mathbf{r}). \quad (6.313)$$

If  $h_i^{(q)}$  and  $h_i^{(s)}$  are of different tensorial ranks, the integral vanishes by symmetry. We therefore obtain

$$\kappa^2 = X^{(1)} \mathbb{R}^{(11)} X^{(1)} \\ + X^{(0)} \mathbb{R}^{(00)} X^{(0)} + 2X^{(0)} \mathbb{R}^{(02)} X^{(2)} + X^{(2)} \mathbb{R}^{(22)} X^{(2)} \\ + X^{(3)} \mathbb{R}^{(33)} X^{(3)} + 2X^{(3)} \mathbb{R}^{(34)} X^{(4)} + X^{(4)} \mathbb{R}^{(44)} X^{(4)}, \quad (6.314)$$

where

$$\mathbb{R}^{(qs)} = \mathbb{R}^{(sq)} \\ = \frac{1}{4} \beta^2 \sum_{i=1}^N \sum_{j=1}^N \left\langle \left( h_i^{(q)} - h_i^{(q)*} \right) \left( h_j^{(s)} - h_j^{(s)*} \right) \right\rangle_0. \quad (6.315)$$

The coefficients  $\mathbb{R}^{(qs)}$  can be decomposed into components in the case  $h_i^{(q)}$  and  $h_i^{(s)}$  are either vectors or scalar, because they are coupled with other vectorial moments or scalar moments, respectively, in the Schmidt orthogonalization method used for the moment set. That is, we have

$$h_i^{(2)} = \bar{h}_i^{(2)} - \alpha_2 h_i^{(0)}, \quad h_i^{(3)} = \bar{h}_i^{(3)} - \alpha_3 h_i^{(4)}. \quad (6.316)$$

For the expressions of  $\bar{h}_i^{(2)}$  and  $\bar{h}_i^{(3)}$  and  $\alpha_2$  and  $\alpha_3$ , see Sect. 6.5, where the moment set is constructed by the Schmidt orthogonalization method. The coefficients  $\mathbb{R}^{(22)}$  and  $\mathbb{R}^{(02)}$  of the quadratic form for  $\kappa^2$  are then further decomposed into components as follows:

$$\kappa^2 = \sum_{q,s \geq 1} X^{(q)} \mathbb{R}^{(qs)} X^{(s)}, \quad (6.317)$$

where the coefficients  $\mathbb{R}^{(qs)}$  consist of the following combination of collision bracket integrals  $\mathbb{M}^{(qs)}$ :

$$\begin{aligned} \mathbb{R}^{(qq)} &= \mathbb{M}^{(qq)} \quad (q = 0, 1, 4), \\ \mathbb{R}^{(02)} &= \mathbb{M}^{(02)} - \alpha_2 \mathbb{M}^{(00)}, \\ \mathbb{R}^{(22)} &= \mathbb{M}^{(22)} - \alpha_2 (\mathbb{M}^{(02)} + \mathbb{M}^{(20)}) + \alpha_2^2 \mathbb{M}^{(00)}, \\ \mathbb{R}^{(33)} &= \mathbb{M}^{(33)} - \alpha_3 (\mathbb{M}^{(34)} + \mathbb{M}^{(43)}) + \alpha_3^2 \mathbb{M}^{(44)}, \\ \mathbb{R}^{(34)} &= \mathbb{M}^{(34)} - \alpha_3 \mathbb{M}^{(44)}. \end{aligned} \quad (6.318)$$

The explicit forms for  $\mathbb{M}^{(qs)}$  are given by the collision bracket integrals of moments:

$$\begin{aligned} \mathbb{M}^{(qq)} &= \frac{\beta^2}{4} \sum_{i=1}^N \sum_{j=1}^N \left\langle \left( h_i^{(q)} - h_i^{(q)*} \right) \left( h_j^{(q)} - h_j^{(q)*} \right) \right\rangle_0 \quad (q = 0, 1, 4), \\ \mathbb{M}^{(02)} &= \frac{\beta^2}{4} \sum_{i=1}^N \sum_{j=1}^N \left\langle \left( h_i^{(0)} - h_i^{(0)*} \right) \left( \bar{h}_j^{(2)} - \bar{h}_j^{(2)*} \right) \right\rangle_0, \\ \mathbb{M}^{(20)} &= \frac{\beta^2}{4} \sum_{i=1}^N \sum_{j=1}^N \left\langle \left( \bar{h}_i^{(2)} - \bar{h}_i^{(2)*} \right) \left( h_j^{(0)} - h_j^{(0)*} \right) \right\rangle_0, \\ \mathbb{M}^{(34)} &= \frac{\beta^2}{4} \sum_{i=1}^N \sum_{j=1}^N \left\langle \left( \bar{h}_i^{(3)} - \bar{h}_i^{(3)*} \right) \left( h_j^{(4)} - h_j^{(4)*} \right) \right\rangle_0, \\ \mathbb{M}^{(43)} &= \frac{\beta^2}{4} \sum_{i=1}^N \sum_{j=1}^N \left\langle \left( h_i^{(4)} - h_i^{(4)*} \right) \left( \bar{h}_j^{(3)} - \bar{h}_j^{(3)*} \right) \right\rangle_0. \end{aligned} \quad (6.319)$$

Finally, upon inserting into (6.317) the generalized potentials  $X^{(q)}$  given in terms of  $\Phi^{(q)}$  (6.277), we finally obtain  $\kappa^2$  in terms of coefficients  $\mathfrak{R}^{(qs)}$  that define linear transport coefficients:

$$\kappa^2 = \sum_{q,s \geq 1} \Phi^{(q)} \mathfrak{R}^{(qs)} \Phi^{(s)}, \quad (6.320)$$

$$\mathfrak{R}^{(qs)} = g^{(q)} \mathbb{R}^{(qs)} g^{(s)}. \quad (6.321)$$

This is the form for  $\kappa^2$  that we will make use of in the cumulant expansion formula for  $\sigma_c$  and for the dissipation terms  $\Lambda^{(q)}$  in the generalized hydrodynamic equations, which are now explicitly given in terms of collision bracket integrals. We remark that  $\kappa^2$  is a generalization of the Rayleigh dissipation function [48].

### 6.7.14 Summary of Generalized Hydrodynamic Equations

We present a summary of generalized hydrodynamic equations derived from the GBE for simple dense fluids. We thus would like to conclude the deterministic part of the present kinetic theory, which supports the theory of irreversible thermodynamics of matter removed from equilibrium at arbitrary degree yet in conformation to the laws of thermodynamics.

#### 6.7.14.1 Conservation Laws

$$\frac{\partial}{\partial t} \rho(\mathbf{r}, t) = -\nabla \cdot [\rho \mathbf{u}(\mathbf{r}, t)] \quad \text{or} \quad \rho \frac{dv}{dt} = \nabla \cdot \mathbf{u} \quad (6.322)$$

$$\rho \frac{d}{dt} \mathbf{u}(\mathbf{r}, t) = -\nabla \cdot \mathbf{P} + \rho \widehat{\mathbf{F}}(\mathbf{r}), \quad (6.323)$$

$$\rho \frac{d}{dt} \mathcal{E}(\mathbf{r}, t) = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} \quad (6.324)$$

#### 6.7.14.2 Evolution Equations for Nonconserved Variables

$$\rho \frac{d\widehat{\Phi}^{(0)}}{dt} = -\nabla \cdot \Phi^{(4)} + d_t \boldsymbol{\varsigma} \cdot \mathbf{v}_\varsigma + f_v + \Lambda^{(0)}, \quad (6.325)$$

$$\rho \frac{d\widehat{\Phi}^{(1)}}{dt} = -\nabla \cdot \overline{\boldsymbol{\psi}}^{(1)} - 2[\mathbf{P} \cdot \nabla \mathbf{u}]^{(2)} + 2[\mathbf{V}_1]^{(2)} + \Lambda^{(1)}, \quad (6.326)$$

$$\rho \frac{d\widehat{\Phi}^{(2)}}{dt} = -\nabla \cdot \overline{\boldsymbol{\psi}}^{(2)} - \rho \frac{d}{dt} (p/\rho) - \alpha^{(2)} \rho \frac{dv}{dt}$$

$$-\frac{2}{3}\text{Tr}(\mathbf{P} \cdot \nabla \mathbf{u}) + \frac{2}{3}\text{Tr}\mathbf{V}_1 + \Lambda^{(2)}, \quad (6.327)$$

$$\begin{aligned} \rho \frac{d\widehat{\Phi}^{(3)}}{dt} = & -\nabla \cdot (\boldsymbol{\psi}^{(3)} + \boldsymbol{\psi}^{(3B)}) - \boldsymbol{\varphi}^{(3)} : \nabla \mathbf{u} + \mathbf{V}_3 \\ & - \mathbf{P} \cdot \nabla \widehat{h} - \boldsymbol{\Phi}^{(3)} \cdot \nabla \mathbf{u} - [d_t \mathbf{u} - \widehat{\mathbf{F}}(\mathbf{r})] \cdot (\mathbf{P} - p\delta) \\ & - \alpha_3 [(v - v_0) \nabla \cdot (\mathbf{P} + \rho \widehat{\mathbf{F}}) - \boldsymbol{\Phi}^{(4)} \cdot \nabla \mathbf{u} + \mathbf{T}_F] + \Lambda^{(3)}, \end{aligned} \quad (6.328)$$

$$\rho \frac{d\widehat{\Phi}^{(4)}}{dt} = -\nabla \cdot \boldsymbol{\psi}^{(4)} + \widehat{\Phi}^{(0)} \nabla \cdot (\mathbf{P} - \rho \widehat{\mathbf{F}}) - \rho \widehat{\boldsymbol{\Phi}}^{(4)} \cdot \nabla \mathbf{u} + \mathbf{T}_F + \Lambda^{(4)}, \quad (6.329)$$

where  $\Phi^{(0)} = \rho(v - v_0)$  is the volume fluctuation;  $\boldsymbol{\Phi}^{(1)} = \boldsymbol{\Pi}$ , the shear stress;  $\Phi^{(2)} = \overline{\Delta} - \alpha_2 \Phi^{(0)}$ , the excess normal stress in excess of volume fluctuation; and  $\boldsymbol{\Phi}^{(3)} = \mathbf{Q} - \alpha_3 \boldsymbol{\Phi}^{(4)}$ , heat flux in excess of volume flux. The dissipation terms  $\Lambda^{(q)}$  in the aforementioned nonconserved evolution equations are the first-order cumulant approximation formulas given in (6.309). With the collision bracket integrals described in the previous subsubsection  $\Lambda^{(q)}$  takes the form

$$\Lambda^{(q)} = -(\epsilon/\beta g^{(q)}) \sum_{s \geq 0} \mathfrak{R}^{(qs)} \Phi^{(s)} q_n(\kappa), \quad (6.330)$$

and the nonlinear factor  $q_n(\kappa)$  the form

$$q_n(\kappa) = \frac{\sinh \kappa}{\kappa}. \quad (6.331)$$

Here we may finally take  $\epsilon$  as the estimate of the inverse collision time:

$$\epsilon = \frac{1}{l} \sqrt{\frac{2k_B T}{m_r}}, \quad (6.332)$$

where  $l$  may be taken with the mean free path and  $m_r$  is for the reduced mass. With this form for  $\Lambda^{(q)}$  the generalized hydrodynamic equations are examined for linear transport processes occurring near equilibrium in the next section.

## 6.8 Linear Constitutive Equations for Nonconserved Moments

If irreversible processes occur in the neighborhood of equilibrium the linear constitutive relations for nonconserved variables  $\boldsymbol{\Pi}$ ,  $\Delta$ ,  $\mathbf{Q}'$ , etc. can be extracted in linear forms if the steady-state evolution equations are linearized with respect to the thermodynamic gradients. The objective of this section is to derive constitutive relations that will account for linear transport processes in a dense fluid, taking into account

the volume transport phenomena, which the present author believes that H. Brenner appeared to try to include in his bivelocity theory [3, 4] of fluid dynamics.

Since Brenner in his proposal is believed to take volume transport processes into consideration and thereby modify, in essence, the conventional phenomenological linear constitutive relations [18, 49] for transport processes, it is particularly important to examine how linear constitutive relations are modified when volume transport processes are taken into account in the present kinetic theory. It should be recalled that in the present kinetic theory, we have, in addition to the usual specific volume used in the conventional fluid dynamics and also Brenner's theory, a new concept of molar volume in the form of Voronoi volume as a volume inherent to molecules in the fluid, it is useful and also important to compare the linearized steady-state approximations for the present kinetic theory-based evolution equations with Brenner's phenomenological theory counterparts. In any case, we hope the present discussion on linear constitutive equations for the nonconserved variables will help us understand the kinetic theory foundations and significance of volume transport phenomena and related constitutive relations and at the same time assess them from the molecular theory viewpoint and relate them to experimental verification, if that is possible.

For linearized constitutive relations it is found sufficient to linearize the dissipation terms  $\Lambda^{(q)}$  in the generalized hydrodynamic equations. Therefore we consider  $\Lambda^{(q)}$  in the form

$$\Lambda^{(q)} = -(\epsilon/\beta g^{(q)}) \sum_{s \geq 0} \mathfrak{R}^{(qs)} \Phi^{(s)}, \quad (6.333)$$

for which we have set

$$q_n(\kappa) = \frac{\sinh \kappa}{\kappa} = 1,$$

namely, in the limit of  $\kappa = 0$ . In the generalized potentials

$$X^{(q)} = -g^{(q)} \Phi^{(q)} = -g_0^{(q)} \Phi^{(q)} + O(\Phi^2) \quad (6.334)$$

the coefficient  $g_0^{(q)}$  is assumed to be independent of all  $\Phi^{(q)}$ . This is true in the linear regime near equilibrium. With the dissipation terms given by (6.333) the linear transport coefficients will be found in terms of, principally, the collision bracket integrals  $\mathfrak{R}^{(qs)}$ .

### 6.8.1 Constitutive Equation for Volume Fluctuation $\Phi^{(0)}$

The linear constitutive equation for  $\Phi^{(0)}$  follows if the steady state form of evolution equation (6.325) is linearized with respect to the thermodynamic forces and variables of manifold  $\mathfrak{P}$ . The term  $f_v$  in (6.325) can be linearized with respect to fluxes to the form

$$f_v = \beta g_0^{(4)} \lambda_{04} \cdot \Phi^{(4)}, \quad (6.335)$$

but  $\lambda_{04}$  in this expression is a mean value of a gradient of volume

$$\lambda_{04} = \left\langle \sum_{i=1}^N \sum_{j \neq i \in z_i}^N \mathbf{C}_i \cdot \frac{\partial h_i^{(0)}}{\partial \mathbf{r}_{ij}} h_j^{(4)} \bar{f}_{\text{eq}}^{(N)} \right\rangle. \quad (6.336)$$

Therefore  $f_v$  is of second order and hence must not be included in the linear constitutive equation. Consequently, the linearized steady-state form of (6.325) is given by the equation

$$g_0^{(0)} \mathfrak{R}^{(00)} \Phi^{(0)} + g_0^{(2)} \mathfrak{R}^{(02)} \Phi^{(2)} = 0. \quad (6.337)$$

This constitutive equation indicates that volume fluctuation  $\Phi^{(0)}$  is coupled to the excess normal stress  $\Phi^{(2)}$ , which is associated with compression or decompression of the fluid. Their relation (6.337) seems to be physically reasonable. Its solution will be examined presently when we obtain the constitutive equation for  $\Phi^{(2)}$ .

### 6.8.2 Constitutive Equation for Shear Stress $\Phi^{(1)}$

The tensor  $\mathbf{V}_1$  in the evolution equation (6.326) for  $\Phi^{(1)}$  can be shown directly related to the torque of the rotational motion of particle pairs, but it is a higher-order effect. This higher-order effect is ignored in the linear regime. The other higher-order moments and nonlinear effects are neglected for the linear constitutive equation for  $\Phi^{(1)}$ . We then obtain the constitutive equation for the shear stress tensor  $\Phi^{(1)}$  in the form

$$\beta g_0^{(1)} \mathfrak{R}^{(11)} \Phi^{(1)} = -2p [\nabla \mathbf{u}]^{(2)}, \quad (6.338)$$

Here  $\mathfrak{R}^{(qs)}$  is a collision bracket integral of the contraction of traceless symmetric tensor moments  $h_i^{(1)}$ —therefore, a scalar. In the linear regime for the shear stress, since there is no flux associated with volume transport, this is consistent with Curie's principle [50]. Moreover, we find that nowhere in (6.338) does the volume velocity  $\mathbf{v}_v$  appear unlike in Brenner's phenomenological theory [4].

Nevertheless, we note that  $\nabla \mathbf{u}$  consists of two components, one arising from the spatial variation of the barycentric velocity  $\mathbf{u}_c$  that may be used to define the shear rate observed in the laboratory and the other arising from the diffusive motion of internal collective modes that originates from mass density variation in space, that is,

$$[\nabla \mathbf{u}]^{(2)} = [\nabla \mathbf{u}_c]^{(2)} - [\nabla (\mathbf{D} \cdot \nabla \ln \rho)]^{(2)}. \quad (6.339)$$

Here  $\mathbf{D}$  is the diffusion tensor of the fluid; see Ref. [51] for the constitutive relation for  $\mathbf{u}$  underlying (6.339). Therefore if  $[\nabla \mathbf{u}_c]^{(2)}$  is designated as the shear rate experimentally observed in the laboratory, then the diffusive contribution—the second term on the right—appears to affect the viscous phenomena, but it is a second

order effect, which should be negligible if the density of the fluid is uniform in the spatial scale of diffusion.

### 6.8.3 Constitutive Relation for Excess Normal Stress $\Phi^{(2)}$

In contrast to the shear stress, the situation regarding  $\Phi^{(2)}$ , namely, the excess normal stress phenomena related to the bulk viscosity accompanying compression or dilatation of the fluid, will be altered if the volume transport is taken into consideration. In the same order of approximation neglecting the effects of the torque tensor  $\mathbf{V}_1$ , the constitutive relation for the excess normal stress  $\Phi^{(2)}$  in the linear regime is then given by

$$g_0^{(2)} \mathfrak{R}^{(20)} \Phi^{(0)} + g_0^{(2)} \mathfrak{R}^{(22)} \Phi^{(2)} = -\frac{\beta}{\epsilon} \left( \frac{5}{3} p + \alpha^{(2)} \right) \nabla \cdot \mathbf{u}. \quad (6.340)$$

To obtain this, we have used the closure relation

$$\psi^{(2)} + \psi^{(2B)} = 0$$

and, in addition, the fact that the term

$$d_t \boldsymbol{\varsigma} \cdot \mathbf{v}_{\boldsymbol{\varsigma}} + f_v,$$

being of second order in gradients, should be also neglected. The resulting equation (6.340) is found coupled to (6.337), and it is simple to see that volume fluctuations contribute to the excess normal stress and thus affect, for example, compression or dilatation of the fluid. It also should be noted that H. Brenner proposed to modify [3] hydrodynamics. In his proposal, only “the volume velocity” appears in the constitutive equation for the stress tensor, whereas the kinetic theoretic constitutive equation for  $\Delta$  obtained here in the present generalized hydrodynamic theory is given in terms of  $\nabla \cdot \mathbf{u}$  only. This is a logical consequence of the fact that  $\mathbf{u}$  is the mean fluid velocity appearing in the equation of continuity and other evolution equations of macroscopic variables that we have shown to be equivalent to the mass velocity  $\mathbf{v}_m$  in Brenner’s theory. We believe the inclusion of volume transport makes his proposal unnecessary and hydrodynamics resulting thereby becomes simpler and straightforward.

### 6.8.4 Constitutive Relation for Heat Flux $\Phi^{(3)}$

On linearization of the evolution equation for  $\Phi^{(3)}$  we obtain a linear constitutive equation for the heat flux  $\Phi^{(3)}$

$$g_0^{(3)} \mathfrak{R}^{(33)} \Phi^{(3)} + g_0^{(3)} \mathfrak{R}^{(34)} \Phi^{(4)} = -\frac{\beta}{\epsilon} \left[ p \widehat{C}_p \nabla T + \alpha_3 (v - v_0) \nabla p \right]. \quad (6.341)$$

Since this equation is coupled to the constitutive equation for volume flux  $\Phi_4$  given below, the heat flux  $\Phi^{(3)}$  is modified by the presence of volume transport. A quick glance at this constitutive equation suggests that the Fourier law of heat conduction is significantly modified because a heat flux can be modified by the presence of volume transport phenomena.

### 6.8.5 Constitutive Relation for Volume Flux $\Phi^{(4)}$

Linearizing the steady state volume flux evolution equation with respect to thermodynamic gradients, we obtain the steady-state constitutive equation for  $\Phi^{(4)}$ :

$$-\left(\epsilon/\beta g_0^{(4)}\right) \mathfrak{R}^{(43)} \Phi^{(3)} - \left(\epsilon/\beta g_0^{(4)}\right) \mathfrak{R}^{(44)} \Phi^{(4)} = 0. \quad (6.342)$$

This equation must be solved together with (6.341).

### 6.8.6 Linear Transport Coefficients

Having obtained the steady-state linear constitutive equations we can derive linear transport coefficients by solving them. Since the constitutive equations are algebraic and linear, it is straightforward to find the transport coefficients.

#### 6.8.6.1 Shear Viscosity

Equation (6.338) can be put in the form of Newton's law of viscosity. It is then straightforward to deduce the shear viscosity of the fluid from it:

$$\Phi^{(1)} = -\frac{2p}{\beta g_0^{(1)} \mathfrak{R}^{(11)}} [\nabla \mathbf{u}]^{(2)} = -2\eta_0 [\nabla \mathbf{u}]^{(2)}, \quad (6.343)$$

where the Newtonian shear viscosity  $\eta_0$  is given in terms of collision bracket integral  $\mathfrak{R}^{(11)}$  by the formula

$$\eta_0 = \frac{p}{\beta g_0^{(1)} \mathfrak{R}^{(11)}} \quad (6.344)$$

with  $g_0^{(1)}$  given by

$$g_0^{(1)} = \frac{1}{2p}. \quad (6.345)$$

### 6.8.6.2 Bulk Viscosity and Volume Transport Coefficient

The transport coefficients associated with  $\Phi^{(0)}$  and  $\Phi^{(2)}$  can be deduced from the solutions for their constitutive equations (6.337) and (6.340). Their solutions are:

$$\Phi^{(0)} = \zeta_v \nabla \cdot \mathbf{u}, \quad (6.346)$$

$$\Phi^{(2)} = -\eta_B \nabla \cdot \mathbf{u}, \quad (6.347)$$

where the volume transport coefficient  $\zeta_v$  is given by the statistical mechanical formula

$$\zeta_v = \frac{\beta \mathfrak{R}^{(02)} \left(\frac{5}{3} p + \alpha^{(2)}\right)}{\epsilon g_0^{(2)} (\mathfrak{R}^{(00)} \mathfrak{R}^{(22)} - \mathfrak{R}^{(02)} \mathfrak{R}^{(20)})} \quad (6.348)$$

and the bulk viscosity  $\eta_b$  by the formula

$$\eta_B = \frac{\beta \mathfrak{R}^{(00)} \left(\frac{5}{3} p + \alpha^{(2)}\right)}{\epsilon g_0^{(2)} (\mathfrak{R}^{(00)} \mathfrak{R}^{(22)} - \mathfrak{R}^{(02)} \mathfrak{R}^{(20)})}. \quad (6.349)$$

Equation (6.346) can be written out in terms of volume

$$\rho v = \rho v_0 + \zeta_v \nabla \cdot \mathbf{u}, \quad (6.350)$$

which suggests that volume fluctuation arises because of the compressibility of the fluid and the measure of such fluctuation is provided by the volume transport coefficient  $\zeta_v$ . This is *a new transport coefficient* not seen in the conventional theory in which the Voronoi volume or, more generically, molar volume domain of a molecule is not taken into consideration. Because of the volume fluctuations taken into consideration in the present theory, compression or dilatation of the fluid is affected and, as a consequence, the bulk viscosity is accordingly modified from its kinetic theory expression for the case of volume transport absent. Therefore, we may look for the evidence of volume transport phenomena in the behavior of bulk viscosity.

### 6.8.6.3 Heat Flow and Volume Transpiration

We have seen that the linear constitutive equations for heat flux and volume flux are coupled. Therefore to extract transport coefficients from them, the coupled constitutive equations must be solved together. We thus obtain the Fourier law of heat conduction in the presence of volume transport and the linear force–flux equation for volume flux by solving (6.341) and (6.342):

$$\Phi^{(3)} = -\lambda_0 \nabla T - \lambda_{Tp} \nabla p, \quad (6.351)$$

$$\Phi^{(4)} = \zeta_{vT} \nabla T + \zeta_{vp} \nabla p, \quad (6.352)$$

where  $\lambda_0$  is the thermal conductivity in the presence of volume transport and  $\lambda_{\text{Tp}}$ ,  $\zeta_{\text{vT}}$ ,  $\zeta_{\text{vp}}$  are transport coefficients defined by the molecular theory formulas

$$\lambda_0 = \frac{\beta g_0^{(4)} \mathfrak{R}^{(44)} p \widehat{C}_p}{\epsilon \left( g_0^{(3)} \mathfrak{R}^{(33)} g_0^{(4)} \mathfrak{R}^{(44)} - g_0^{(3)} \mathfrak{R}^{(34)} g_0^{(4)} \mathfrak{R}^{(43)} \right)}, \quad (6.353)$$

$$\lambda_{\text{Tp}} = \frac{\beta \alpha_3 g_0^{(4)} \mathfrak{R}^{(44)} (v - v_0)}{\epsilon \left( g_0^{(3)} \mathfrak{R}^{(33)} g_0^{(4)} \mathfrak{R}^{(44)} - g_0^{(3)} \mathfrak{R}^{(34)} g_0^{(4)} \mathfrak{R}^{(43)} \right)}, \quad (6.354)$$

$$\zeta_{\text{vT}} = \frac{\beta g_0^{(4)} \mathfrak{R}^{(43)} p \widehat{C}_p}{\epsilon \left( g_0^{(3)} \mathfrak{R}^{(33)} g_0^{(4)} \mathfrak{R}^{(44)} - g_0^{(3)} \mathfrak{R}^{(34)} g_0^{(4)} \mathfrak{R}^{(43)} \right)}, \quad (6.355)$$

$$\zeta_{\text{vp}} = \frac{\beta \alpha_3 g_0^{(4)} \mathfrak{R}^{(43)} (v - v_0)}{\epsilon \left( g_0^{(3)} \mathfrak{R}^{(33)} g_0^{(4)} \mathfrak{R}^{(44)} - g_0^{(3)} \mathfrak{R}^{(34)} g_0^{(4)} \mathfrak{R}^{(43)} \right)}. \quad (6.356)$$

The transport coefficients  $\lambda_{\text{Tp}}$ ,  $\zeta_{\text{vT}}$ , and  $\zeta_{\text{vp}}$  are new to the kinetic theory because they are associated with the volume transport phenomena taken into consideration in the present work. In any case, the transport coefficients presented in this section are affected implicitly or explicitly by the volume transport phenomena. Since  $\nabla p$  may be expressed in terms of isothermal compressibility coefficient

$$\kappa_T = -\rho \left( \frac{\partial v_{\text{sp}}}{\partial p} \right)_T \quad (v_{\text{sp}} = 1/\rho), \quad (6.357)$$

we may express (6.351) and (6.352) in alternative forms

$$\Phi^{(3)} = -\lambda_0 \nabla T + \frac{\lambda_{\text{Tp}}}{\kappa_T} \nabla \ln \rho, \quad (6.358)$$

$$\Phi^{(4)} = \zeta_{\text{vT}} \nabla T - \frac{\zeta_{\text{vp}}}{\kappa_T} \nabla \ln \rho \quad (6.359)$$

to show that an effect of volume transport manifests itself in transport of heat and volume flux, which we may regard as a volume transpiration phenomenon. Equation (6.359) clearly indicates that the volume flux vanishes if the density and temperature are uniform in the fluid; in other words, the volume flux—volume transpiration—is driven by volume and temperature gradient present in the fluid. This means that volume transport phenomena should be taken into account if the fluid is spatially nonuniform with respect to density and temperature.

## 6.9 Quasilinear Generalized Hydrodynamic Equations

Having derived the linear transport coefficients as presented in the previous section, as we have done in the previous chapters for dilute gases and moderately dense gases, we are now ready to examine approximations of the evolution equations (6.325)–(6.329) for the nonconserved variables  $\Phi^{(q)}$  ( $q = 0, 1, \dots, 4$ ). Together with the conservation laws (6.322)–(6.324) they constitute the generalized hydrodynamic equations for dense fluids.

By linearizing the kinematic terms and divergence terms in the evolution equations for  $\Phi^{(q)}$  and also using the first-order cumulant approximation for the dissipation terms  $\Lambda^{(q)}$ , we obtain quasilinear generalized hydrodynamic equations, whose evolution equations for  $\Phi^{(q)}$  have now the forms given below:

$$\rho \frac{d\widehat{\Phi}^{(0)}}{dt} = -g_0^{(0)} \mathfrak{R}^{(00)} \Phi^{(0)} q_n(\kappa) - g_0^{(2)} \mathfrak{R}^{(02)} \Phi^{(2)} q_n(\kappa), \quad (6.360)$$

$$\rho \frac{d\widehat{\Phi}^{(1)}}{dt} = -2p [\nabla \mathbf{u}]^{(2)} - \beta g_0^{(1)} \mathfrak{R}^{(11)} \Phi^{(1)} q_n(\kappa), \quad (6.361)$$

$$\begin{aligned} \rho \frac{d\widehat{\Phi}^{(2)}}{dt} = & -\frac{\beta}{\epsilon} \left( \frac{5}{3} p + \alpha^{(2)} \right) \nabla \cdot \mathbf{u} - g_0^{(2)} \mathfrak{R}^{(20)} \Phi^{(0)} q_n(\kappa) \\ & - g_0^{(2)} \mathfrak{R}^{(22)} \Phi^{(2)} q_n(\kappa), \end{aligned} \quad (6.362)$$

$$\begin{aligned} \rho \frac{d\widehat{\Phi}^{(3)}}{dt} = & -\frac{\beta}{\epsilon} [p \widehat{C}_p \nabla T + \alpha_3 (v - v_0) \nabla p] - g_0^{(3)} \mathfrak{R}^{(33)} \Phi^{(3)} q_n(\kappa) \\ & - g_0^{(3)} \mathfrak{R}^{(34)} \Phi^{(4)} q_n(\kappa), \end{aligned} \quad (6.363)$$

$$\rho \frac{d\widehat{\Phi}^{(4)}}{dt} = -\left(\epsilon/\beta g_0^{(4)}\right) \mathfrak{R}^{(43)} \Phi^{(3)} q_n(\kappa) - \left(\epsilon/\beta g_0^{(4)}\right) \mathfrak{R}^{(44)} \Phi^{(4)} q_n(\kappa). \quad (6.364)$$

These evolution equations are coupled to conservation laws (6.322)–(6.324) to form quasilinear generalized hydrodynamic equations. In Chap. 9, we will discuss further on the quasilinear generalized hydrodynamic equations to derive nonlinear transport coefficients such as non-Newtonian viscosity, non-Fourier thermal conductivity, etc. and their applications. They will be found to extend the linear transport coefficients obtained in the previous section into the nonlinear regime of transport processes.

## 6.10 Model for Quasilinear Generalized Hydrodynamic Equations

As was done in Chaps. 3 and 5, if the Rayleigh dissipation function  $\kappa$  in the nonlinear factor  $q_n(\kappa)$  is replaced with the solutions of the linear constitutive equations for  $\Phi^{(q)}$  ( $q = 0, 1, \dots, 4$ ) and the resulting  $q_n(\kappa)$  is inverted, then the net effect of the

procedure is tantamount to replacing the nonlinear factor  $q_n(\kappa)$  with  $q_L(\kappa) = q_n^{-1}(\kappa)$  in the constitutive equations for  $\Phi^{(q)}$ , where the Rayleigh dissipation function  $\kappa$  is now given in terms of a quadratic form of thermodynamic gradients; see Sect. 9.3.6, Chap. 9 for details and also Sect. 5.5.10, Chap. 5 for the case of a moderately dense gas. With such a nonlinear factor  $q_L(\kappa)$  replacing  $q_n(\kappa)$ , we then obtain a new set of evolution equations for  $\Phi^{(q)} (q = 0, 1, \dots, 4)$ , in which the nonlinear factor in the dissipation terms has the form  $q_L(\kappa) = \sinh^{-1} \kappa_T / \kappa_T$  with  $\kappa_T$  denoting a quadratic form of thermodynamic gradients and thus no longer depending on  $\Phi^{(q)} (q = 0, 1, \dots, 4)$ . We may call the so-obtained set a model for the quasilinear generalized hydrodynamic equations. The evolution equations so obtained are presented below:

$$\rho \frac{d\widehat{\Phi}^{(0)}}{dt} = -g_0^{(0)} \mathfrak{R}^{(00)} \Phi^{(0)} q_L(\kappa) - g_0^{(2)} \mathfrak{R}^{(02)} \Phi^{(2)} q_L(\kappa), \quad (6.365)$$

$$\rho \frac{d\widehat{\Phi}^{(1)}}{dt} = -2p [\nabla \mathbf{u}]^{(2)} - \beta g_0^{(1)} \mathfrak{R}^{(11)} \Phi^{(1)} q_L(\kappa), \quad (6.366)$$

$$\begin{aligned} \rho \frac{d\widehat{\Phi}^{(2)}}{dt} = & -\frac{\beta}{\epsilon} \left( \frac{5}{3} p + \alpha^{(2)} \right) \nabla \cdot \mathbf{u} - g_0^{(2)} \mathfrak{R}^{(20)} \Phi^{(0)} q_L(\kappa) \\ & - g_0^{(2)} \mathfrak{R}^{(22)} \Phi^{(2)} q_L(\kappa), \end{aligned} \quad (6.367)$$

$$\begin{aligned} \rho \frac{d\widehat{\Phi}^{(3)}}{dt} = & -\frac{\beta}{\epsilon} [p \widehat{C}_p \nabla T + \alpha_3 (v - v_0) \nabla p] - g_0^{(3)} \mathfrak{R}^{(33)} \Phi^{(3)} q_L(\kappa) \\ & - g_0^{(3)} \mathfrak{R}^{(34)} \Phi^{(4)} q_L(\kappa), \end{aligned} \quad (6.368)$$

$$\rho \frac{d\widehat{\Phi}^{(4)}}{dt} = -\left(\epsilon/\beta g_0^{(4)}\right) \mathfrak{R}^{(43)} \Phi^{(3)} q_L(\kappa) - \left(\epsilon/\beta g_0^{(4)}\right) \mathfrak{R}^{(44)} \Phi^{(4)} q_L(\kappa). \quad (6.369)$$

The evolution equations are now linear with respect to  $\Phi^{(q)} (q = 0, 1, \dots, 4)$ , which may be correctly regarded as fluctuations from the steady-state fluxes. These evolution equations are, of course, coupled to the conservation laws. Together, they form a model for generalized hydrodynamic equations which we find a considerable range of applications for flow problems in fluids. See Chap. 9.

We conclude this part of irreversible thermodynamics and generalized hydrodynamics with the following remarks:

The novel feature that distinguishes the present generalized hydrodynamics from the previous version of generalized hydrodynamics [1, 2, 30] and the conventional hydrodynamics [52, 53] is the inclusion of molar volume in the form of Voronoi volume and its flux, namely, the volume flux—volume transpiration—in the set of hydrodynamic macroscopic variables. Especially, the concept of molar volume in terms of the Voronoi volume of the fluid is novel. It, in fact, makes it possible to calculate the constitutive relation for the molar volume, which is distinctive from the thermodynamic formula usually based on the equation of state. The Voronoi volume is the most natural and rigorous choice for the molecular representation of molar volume. The inclusion of the Voronoi volume as the molar volume in the formulation

not only endows the theory of irreversible processes in fluids with more flexibility than otherwise, but also gives rise to new effects on the excess normal stress (or the bulk viscosity) and the heat flux even at the level of linear approximation that have not been seen in the conventional theories in which the molar volume is excluded from the nonconserved variable set. *This latter feature is absent in pure fluids in the linear regime in the traditional theory in which volume transport is absent.* (See p. 122, Ref. [49].) Therefore it might be a readily observable phenomenon to ascertain the concept of volume transport, since it is probably much easier to detect than the effect on the excess normal stress phenomena, which usually give rise to rather small bulk viscosities compared to the shear viscosity. In this connection, it should be noted that heat fluxes are proportional to the density gradients of species for a mixture even if volume transport phenomena are absent, because in that case the heat fluxes are coupled to diffusion fluxes—it is known as thermal diffusion (Soret) effect [50]. In such an event, the effect of volume transport can be masked by diffusion fluxes and, probably, indistinguishable from the normal diffusion effect of a mixture.

The concept of Voronoi volume was used before in the context of fluid dynamics, although in a considerably different form. In a line of theories called discrete dissipative particle dynamics (DPD) [54–56], which was developed in connection with computer simulations of complex fluids, the Voronoi volume, or a semblance of it, has been used, but only to discretize the microscopic (mechanical) forms of conservation laws—the mass, momentum, and internal energy balance equations before averaging over an assembly of particles. Since the usage of Voronoi volume in the DPD approach and the present theory is different, it is useful to point out where the differences lie between the two approaches to avoid a possible confusion with regard to their distinction, before we discuss what we have found about the statistical mechanical implications of the present theory to Brenner's phenomenological theory [3, 4] of volume transport.

In the DPD, the dynamic evolution of the observables defined in the cells on the Voronoi lattice is examined only for the conserved variables, i.e., mass, momentum, and internal energy, but not for the non-conserved variables such as the Voronoi volume, volume flux, stress tensor, heat flux, etc. The evolution equations for the latter, which are essentially dissipative variables that break the time reversal invariance symmetry of irreversible processes, are in fact not microscopically derivable from the mechanical equations of motion (e.g., Newtonian equations of motion) in a form manifesting dissipation unless an irreversible equation is made use of. Hence they cannot be included as correct basic evolution equations of macroscopic variables in the DPD approach. Therefore, for example, for the stress tensor and heat flux their mean values are necessarily assumed to obey the Newtonian law of viscosity and Fourier's law of heat conduction, but they are not determined in a self-consistent manner within the framework of a theory incorporating the concept of volume transport. In addition to this, the fluctuating parts of the evolution equations for the mass, momentum, and internal energy are assumed describable by a theory of stochastic processes obeying the fluctuation-dissipation theorem, which in essence serves as the seat of irreversibility.

In contrast to the aforestated procedure of the DPD approach, in the present theory for the generalized hydrodynamics an irreversible kinetic equation, for example, the generalized Boltzmann equation, is assumed and the evolution equations for the conserved and nonconserved macroscopic variables are derived from the irreversible kinetic equation in a thermodynamically consistent manner. The Voronoi volume and the associated volume flux are explicitly included without difficulty in the set of nonconserved variables for the generalized hydrodynamics. This is in distinctive contrast to the DPD approach in which the Voronoi volume is not included among the macroscopic variables considered, but it is simply used to define the conserved variables for “the Voronoi cells on a Voronoi lattice”. (Even if included, its dissipation is not correctly expressible owing to the absence of an appropriate irreversible kinetic equation.) Therefore, the fundamental difference in the two approaches may be said to lie in the irreversible kinetic equation—e.g., the generalized Boltzmann equation—used in the present theory from the outset. This most outstanding difference between the two approaches also brings about secondary differences, although some of the latter may disappear when linear approximations are made to the generalized hydrodynamic equations. It should be noted that in the generalized hydrodynamics the linear constitutive relations for the stress tensor and heat flux are simply the linear approximations of the evolution equations for the nonconserved variables, but not relations extrinsic to the generalized hydrodynamics equations. In any case, the generalized hydrodynamics includes the classical Navier–Stokes–Fourier hydrodynamics as a special case holding near equilibrium. This aspect of generalized hydrodynamics will be further studied in a separate chapter later in this work.

Since the volume flux is also proportional to  $\nabla \ln \rho$  and may also be given in terms [5, 6] of  $\mathbf{v}_v - \mathbf{v}_m = \mathbf{v}_v - \mathbf{u}$  as shown previously [5, 6], one may relate the aforementioned diffusive term in (6.339) to the volume velocity if one specifically strives to do so, but such an argument may be regarded as contrived and does not appear compelling, especially, because  $\mathbf{u}$  and  $\nabla \mathbf{u}$  appear naturally in the statistical mechanics expressions for macroscopic variables and their evolution equations derived by the present approach to statistical mechanics. As a matter of fact, this diffusive contribution might be said to be of the same order as the Burnett-order terms [49] in the constitutive equation for the shear stress tensor, which is of higher order than the first-order Chapman–Enskog approximation giving rise to the linear constitutive relations such as Newton’s law of viscosity and Fourier’s law of heat conduction. Therefore if we insist that Relation (6.339) be used in the constitutive equation for  $\Phi^{(1)}$  the effects of volume transport might be said contained in the Burnett or higher order solutions in the Chapman–Enskog approach to gas dynamics. Hence, at the linear order for the Newtonian law of viscosity the volume transport is found to play no role when looked at from the kinetic theory standpoint. From the consideration made earlier we find Brenner’s constitutive relation—given in terms of the volume velocity—for the traceless symmetric part of the stress tensor does not have a kinetic theory foundation.

## 6.11 Relative Boltzmann Entropy Revisited

The calorropy and related topics discussed earlier provide only a partial information on the Boltzmann entropy because the nonequilibrium canonical form  $\bar{f}_c^{(N)}$  only approximately represents the solution of the kinetic equation in the sense that the former is a projection of the latter, even if  $\bar{f}^{(N)}$  does not deviate from  $\bar{f}_c^{(N)}$  to a significant degree. Alternatively stated,  $\bar{f}_c^{(N)}$  may be said to be a projection onto the thermodynamic manifold of the full distribution function  $\bar{f}^{(N)}$  obeying the kinetic equation (6.48) in the phase space. Therefore it is important to learn about the complement of the projection, which is closely related to the relative Boltzmann entropy. This point was true for the case of Boltzmann equation and remains true also for the generalized Boltzmann equation. Until the complement of the projection is appropriately obtained from the generalized Boltzmann equation, it is not possible to state the generalized Boltzmann equation is solved, although we may claim we have acquired a formal theory of thermodynamics of irreversible processes consistent with the laws of thermodynamic laws. Solution of the generalized Boltzmann equation and formulation of the theory of irreversible thermodynamics accompanying the kinetic equation are two separate levels of question.

The complement to the projection itself, however, is as difficult to solve for as solving the kinetic equation of a dense fluid in the full phase space of the system. Nevertheless, we notice that the complement of the projection represents some sort of fluctuations from the states described by the thermodynamic states characterized by the nonequilibrium canonical form  $\bar{f}_c^{(N)}$ . There is a large body of knowledge to treat fluctuations of macroscopic thermodynamic systems in the literature. We may avail ourselves to it. However, since our aim in this work is in acquiring a kinetic theory foundation for thermodynamics of irreversible processes we shall not have a sufficient space allotted to discuss the subject matter. For this reason we will close this section by laying only a foundation for the discussion on a fluctuation theory dealing with the relative Boltzmann entropy for a dense fluid in the future.

### 6.11.1 Exponential Form for $\bar{f}^{(N)}$

If we regard the full distribution function  $\bar{f}^{(N)}$  obeying the GBE (6.48) as consisting of fluctuations from the nonequilibrium canonical form  $\bar{f}_c^{(N)}$  it is reasonable and expedient to seek  $\bar{f}^{(N)}$  in an exponential form similar to that of  $\bar{f}_c^{(N)}$ . Therefore, we express them both in exponential form with similar mathematical structures as below:

$$k_B \ln \bar{f}^{(N)} = - \int_V d\mathbf{r} \sum_{i=1}^N \frac{1}{T} \mathcal{H}_i^{(N)} \delta(\mathbf{r}_i - \mathbf{r}) - k_B \ln \mathbb{Z}^{(N)}, \quad (6.370)$$

$$k_B \ln \bar{f}_c^{(N)} = - \int_V d\mathbf{r} \sum_{q=1}^N \frac{1}{T^t} \mathcal{H}_i^{(N)} \delta(\mathbf{r}_i - \mathbf{r}) - k_B \ln \mathbb{Z}^{(N)t}, \quad (6.371)$$

where we have defined the symbols

$$\frac{1}{T} \mathcal{H}_i^{(N)} = H_i^{(N)} I + \sum_{q \geq 0} \bar{X}^{(q)} h_i^{(q)} - m_i \bar{\mu}, \quad (6.372)$$

$$\frac{1}{T^t} \mathcal{H}_i^{(N)} = H_i^{(N)} I^t + \sum_{q \geq 0} \bar{X}^{(q)t} h_i^{(q)} - m_i \bar{\mu}^t, \quad (6.373)$$

with definitions

$$I = \frac{1}{T}, \quad \bar{X}^{(q)} = \frac{X^{(q)}}{T}, \quad \bar{\mu} = \frac{\hat{\mu}}{T}. \quad (6.374)$$

Affixing a superscript  $t$  on the temperature  $T$ , generalized potentials  $X^{(q)}$ , and  $\hat{\mu}$ , the following symbols are used in the exponential form for the nonequilibrium canonical form  $\bar{f}_c^{(N)}$ :

$$I^t = \frac{1}{T^t}, \quad \bar{X}^{(q)t} = \frac{X^{(q)t}}{T^t}, \quad \bar{\mu}^t = \frac{\hat{\mu}^t}{T^t}. \quad (6.375)$$

In addition to these symbols, it is convenient to cast the normalization factors  $\langle k_B \bar{f}^{(N)} \ln \mathbb{Z}^{(N)} \rangle$  and  $\langle k_B \bar{f}_c^{(N)} \ln \mathbb{Z}^{(N)t} \rangle$  in the forms

$$\langle k_B \bar{f}^{(N)} \ln \mathbb{Z}^{(N)} \rangle = \int_V d\mathbf{r} \bar{p}(\mathbf{r}, t) = \int_V d\mathbf{r} \rho(\bar{p}v), \quad (6.376)$$

$$\langle k_B \bar{f}_c^{(N)} \ln \mathbb{Z}^{(N)t} \rangle = \int_V d\mathbf{r} \bar{p}^t(\mathbf{r}, t) = \int_V d\mathbf{r} \rho(\bar{p}^tv) \quad (6.377)$$

where  $\bar{p}$  and  $\bar{p}^t$  are local parameters depending on  $\mathbf{r}$ , and  $t$  defined by

$$\bar{p} = \frac{p}{T}, \quad \bar{p}^t = \frac{p^t}{T^t}. \quad (6.378)$$

The meanings of  $p^t$  has been already clarified in connection with the calortropy and its calortropy differential. A similar meaning will be assigned to  $p$ , but it will involve fluctuations from  $p^t$ . We will find it convenient to define fluctuations in variables of  $\bar{I}$ ,  $\bar{p}$ ,  $\bar{\mu}$ , and  $\bar{X}^{(q)}$  from the corresponding variables of the thermodynamic theory of irreversible transport processes described by the calortropy and its differential:

$$\begin{aligned} \delta \bar{I} &= T^{-1} - T^{t-1}, & \delta \bar{p} &= \bar{p} - \bar{p}^t, \\ \delta \bar{\mu} &= \bar{\mu} - \bar{\mu}^t, & \delta \bar{X}^{(q)} &= \bar{X}^{(q)} - \bar{X}^{(q)t}. \end{aligned} \quad (6.379)$$

It should be noted that the fluctuations  $\delta\bar{I}$ , etc. are non-deterministic in contrast to the variables  $T^t$ ,  $\bar{p}^t$ ,  $\bar{\mu}^t$ , and  $\bar{X}^{(q)t}$ , which are deterministically solved for by the generalized hydrodynamic equations within the framework of the irreversible thermodynamic theory described earlier. Observing that

$$\rho = \sum_{i=1}^N \left\langle m_i \delta(\mathbf{r}_i - \mathbf{r}) \bar{f}^{(N)} \right\rangle, \quad (6.380)$$

in the system of notation adopted, (6.370) and (6.371) can be combined to the expression as follows:

$$\left\langle k_B \bar{f}^{(N)} \ln \left( \frac{\bar{f}^{(N)}}{\bar{f}_c^{(N)}} \right) \right\rangle = - \int_V d\mathbf{r} \rho \left( \mathcal{E} \delta\bar{I} + v \delta\bar{p} - \delta\bar{\mu} + \sum_{q \geq 0} \hat{\Phi}^{(q)} \delta\bar{X}^{(q)} \right). \quad (6.381)$$

Therefore, with the exponential forms for the distribution functions the relative Boltzmann entropy is then given by by fluctuations as well:

$$\mathcal{S}_r \left[ \bar{f}^{(N)} | \bar{f}_c^{(N)} \right] = \mathcal{E} \delta\bar{I} + v \delta\bar{p} + \sum_{q \geq 0} \hat{\Phi}^{(q)} \delta\bar{X}^{(q)} - \delta\bar{\mu}. \quad (6.382)$$

This implies that the relative Boltzmann entropy is determined by the fluctuations on the one hand and the variables of manifold  $\mathfrak{T}$  on the other hand. By the Klein's inequality it evidently is positive semidefinite:

$$\mathcal{E} \delta\bar{I} + v \delta\bar{p} - \delta\bar{\mu} + \sum_{q \geq 0} \hat{\Phi}^{(q)} \delta\bar{X}^{(q)} \geq 0. \quad (6.383)$$

Therefore only in the limit of all fluctuations vanishing does the relative Boltzmann entropy vanish and the calortropy becomes identical with the Boltzmann entropy in the limit.

### 6.11.2 Relative Boltzmann Entropy Balance Equation

The relative entropy balance equation can then be shown given by the form

$$\begin{aligned} \frac{d}{dt} \mathcal{S}_r \left[ \bar{f}^{(N)} | \bar{f}_c^{(N)} \right] &= - (\delta\bar{I}) d_t \mathcal{E} - (\delta\bar{p}) d_t v - \sum_{q \geq 0} (\delta\bar{X}^{(q)}) d_t \hat{\Phi}^{(q)} \\ &\quad + \hat{\Sigma}_{\text{loc}} + \rho^{-1} \sum_{q \geq 0} \bar{X}^{(q)} \mathcal{Z}^{(q)}. \end{aligned} \quad (6.384)$$

Even if all fluctuations vanish, the rate of relative Boltzmann entropy does not vanish because it contains nonvanishing source terms:

$$\frac{d}{dt} \mathcal{S}_r \left[ \bar{f}^{(N)} | \bar{f}_c^{(N)} \right] = \widehat{\Sigma}_{\text{loc}} + \rho^{-1} \sum_{q \geq 0} \bar{X}^{(q)} \mathcal{Z}^{(q)}, \quad (6.385)$$

where  $\widehat{\Sigma}_{\text{loc}}$  is defined by (6.256). The right hand side of this equation does not vanish as long as there is an irreversible process that is driven by nonvanishing spatial gradients  $\nabla \mathbf{u}$ ,  $\nabla \ln T$ , or  $\nabla X^{(q)}$  present in the system; it should be remarked that  $X^{(q)}$  are generally proportional to  $\{\Phi^{(q)}; q \geq 0\}$ . The rate of change in the relative Boltzmann entropy therefore depends on the path of evolution in irreversible processes in the thermodynamics manifold.

The conclusion in turn implies that the Boltzmann entropy balance equation would not give rise to an exact differential in the thermodynamic manifold unlike the calortropy balance equation. This conclusion points to the basic physical significance of the relative Boltzmann entropy, which is further amplified by the fluctuations of the intensive variables  $\delta \bar{I}$ ,  $\delta \bar{p}$ ,  $\delta \bar{\mu}$ ,  $\delta \bar{X}^{(q)}$  whose evolution equations can be derived from the GBE (6.48) in a manner parallel to the derivations from the Boltzmann equation; see Sect. 3.6.3 of Chap. 3.

To derive the evolution equations for fluctuations  $\delta \bar{I}$ ,  $\delta \bar{p}$ ,  $\delta \bar{\mu}$ ,  $\delta \bar{X}^{(q)}$  from the generalized Boltzmann equation we follow the same procedure as used for the case of the Boltzmann equation for a dilute gas. For simplicity of notation we first limit the discussion to a single-component system and then the results obtained will be generalized to the case of a liquid mixture. We thus consider the following:

$$\begin{aligned} & \langle \mathfrak{M}_k \left( \frac{\partial}{\partial t} + \mathbf{L}^{(N)} \right) k_B \bar{f}^{(N)} \ln \left( \bar{f}^{(N)} / \bar{f}_c^{(N)} \right) \rangle \\ &= - \int_V d\mathbf{r} \sum_{i=1}^N \mathfrak{M}_k \bar{f}^{(N)} \left( \frac{\partial}{\partial t} + \mathbf{L}^{(N)} \right) \times \\ & \quad \left\langle \left( H_i^{(N)} \delta \bar{I} + \sum_{q \geq 0} h_i^{(q)} \delta \bar{X}_q - m_i \delta \bar{\mu} + m_i v \delta \bar{p} \right) \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle, \end{aligned} \quad (6.386)$$

where  $\mathfrak{M}_k$  is a phase function representing moments such as  $H_i$ ,  $h_i^{(k)}$ ,  $m_i$ , or 1. Rearranging this equation, we obtain a coupled set of differential equations for  $d_t \delta \bar{I}$ ,  $d_t \delta \bar{X}_q$ ,  $d_t \delta \bar{\mu}$ ,  $d_t \delta \bar{p}$ :

$$\begin{aligned}
& \mathfrak{M}_k^{(I)} d_t \delta \bar{I} + \sum_{q \geq 0} \mathfrak{M}_k^{(q)} d_t \delta \bar{X}^{(q)} - \mathfrak{M}_k^{(m)} d_t \delta \bar{\mu} + v \mathfrak{M}_k^{(m)} d_t \delta \bar{p} \\
&= -k_B \left\langle \mathfrak{M}_k \Re[\bar{\mathbb{F}}^{(\mathcal{N})}] \right\rangle - \sum_{i=1}^N \left\langle \bar{f}^{(N)} \mathfrak{M}_k \left( \frac{\partial}{\partial t} + \mathbf{L}^{(N)} \right) \frac{\mathcal{H}_i^{(N)}}{T^t} \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle \\
&\quad - \sum_{i=1}^N \left\langle \bar{f}^{(N)} \mathfrak{M}_k \mathbf{L}^{(N)} H_i^{(N)} \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle \delta \bar{I} \\
&\quad - \sum_{i=1}^N \sum_{q \geq 0} \left\langle \bar{f}^{(N)} \mathfrak{M}_k \mathbf{L}^{(N)} h_i^{(q)} \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle \delta \bar{X}^{(q)} \\
&\quad + \sum_{i=1}^N \left\langle \bar{f}^{(N)} \mathfrak{M}_k \mathbf{L}^{(N)} m_i \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle (\delta \bar{\mu} - v \delta \bar{p}) \\
&\quad + \sum_{i=1}^N \left\langle \bar{f}^{(N)} \mathfrak{M}_k H_i^{(N)} \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle \mathbf{u} \cdot \nabla \delta \bar{I} \\
&\quad + \sum_{i=1}^N \left\langle \bar{f}^{(N)} \mathfrak{M}_k \sum_{q \geq 0} h_i^{(q)} \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle \mathbf{u} \cdot \nabla \delta \bar{X}^{(q)} \\
&\quad + \sum_{i=1}^N \left\langle \bar{f}^{(N)} \mathfrak{M}_k m_i \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle \mathbf{u} \cdot \nabla (\delta \bar{\mu} - v \delta \bar{p}),
\end{aligned} \tag{6.387}$$

where

$$\begin{aligned}
\mathfrak{M}_k^{(I)} &= \sum_{i=1}^N \left\langle \bar{f}^{(N)} \mathfrak{M}_k H_i^{(N)} \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle, \\
\mathfrak{M}_k^{(q)} &= \sum_{i=1}^N \left\langle \bar{f}^{(N)} \mathfrak{M}_k h_i^{(q)} \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle, \\
\mathfrak{M}_k^{(m)} &= \sum_{i=1}^N \left\langle \bar{f}^{(N)} \mathfrak{M}_k m_i \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle.
\end{aligned} \tag{6.388}$$

When solved for  $d_t \delta \bar{I}$ ,  $d_t \delta \bar{X}_q$ ,  $d_t \delta \bar{\mu}$ ,  $d_t \delta \bar{p}$ —i.e., when the left-hand side of (6.387) is diagonalized—this set can be written as a set of coupled differential equations

$$\begin{aligned}
d_t \delta \bar{I} &= -F_I (\delta \bar{I}, \delta \bar{X}_q, \delta \bar{\mu}, \delta \bar{p} | \mathfrak{P}, \mathfrak{T}), \\
d_t \delta \bar{X}^{(k)} &= -F_{Xk} (\delta \bar{I}, \delta \bar{X}_q, \delta \bar{\mu}, \delta \bar{p} | \mathfrak{P}, \mathfrak{T}), \\
d_t \delta \bar{\mu} &= F_\mu (\delta \bar{I}, \delta \bar{X}_q, \delta \bar{\mu}, \delta \bar{p} | \mathfrak{P}, \mathfrak{T}), \\
d_t \delta \bar{p} &= -F_p (\delta \bar{I}, \delta \bar{X}_q, \delta \bar{\mu}, \delta \bar{p} | \mathfrak{P}, \mathfrak{T}),
\end{aligned} \tag{6.389}$$

where  $F_I(\delta\bar{I}, \delta\bar{X}_q, \delta\bar{\mu}, \delta\bar{p}|\mathfrak{P}, \mathfrak{T})$ , etc. are functions depending on fluctuations  $\delta\bar{I}, \delta\bar{X}_q, \delta\bar{\mu}, \delta\bar{p}$  and their spatial derivatives; in fact, the right-hand side is functionals of variables in manifold  $\mathfrak{P} \cup \mathfrak{T}$ . Their details can be worked out explicitly if the right-hand side of (6.387) is explicitly calculated with the generalized Boltzmann equation; see Sect. 3.6.3 of Chap. 3 where the Boltzmann equation was used for kinetic equation. Since our aim in this work is not in fluctuations beyond this point we would not dwell on the details of (6.389). This set of equations can be easily generalized to the case of a liquid mixture. They may be written in the forms

$$\begin{aligned} d_t \delta\bar{I} &= -F_I \left( \delta\bar{I}, \delta\bar{X}_b^{(q)}, \delta\bar{\mu}_b, \delta\bar{p} | \mathfrak{P}, \mathfrak{T} \right), \\ d_t \delta\bar{X}_a^{(k)} &= -F_{Xka} \left( \delta\bar{I}, \delta\bar{X}_b^{(q)}, \delta\bar{\mu}_b, \delta\bar{p} | \mathfrak{P}, \mathfrak{T} \right), \\ d_t \delta\bar{\mu}_a &= F_{\mu a} \left( \delta\bar{I}, \delta\bar{X}_b^{(q)}, \delta\bar{\mu}_b, \delta\bar{p} | \mathfrak{P}, \mathfrak{T} \right), \\ d_t \delta\bar{p} &= -F_p \left( \delta\bar{I}, \delta\bar{X}_b^{(q)}, \delta\bar{\mu}_b, \delta\bar{p} | \mathfrak{P}, \mathfrak{T} \right), \end{aligned} \quad (6.390)$$

where the subscripts  $a$  and  $b$  stand for species in the mixture. There are a number of avenues open for obtaining approximate solutions, including the Chapman–Enskog line of approach.

### 6.11.3 Stochastic Theory Approach to the Generalized Boltzmann Equation

We have shown in the case of gases obeying the Boltzmann kinetic equation that, if the fluctuations are treated as stochastic variables, the probability  $\mathcal{P}$  observing fluctuations follows an exponential form given in terms of relative Boltzmann entropy

$$\mathcal{P} = \exp \left( -k_B^{-1} S_r \left[ \bar{f}^{(N)} | \bar{f}_c^{(N)} \right] \right), \quad (6.391)$$

which is as a matter of fact the Einstein probability in his fluctuation theory:

$$\mathcal{P} = \exp \left[ -k_B^{-1} (\mathcal{S} - \hat{\Psi}) \right] \quad (6.392)$$

That is, fluctuations from the thermodynamic states described by the calortropy are probabilistically described by (6.391). In the case of liquids, making the same line of argument as for (6.391) we find the same probability formula holds.

Since the relative Boltzmann entropy is given for an  $r$ -component mixture by

$$S_r \left[ \bar{f}^{(N)} | \bar{f}_c^{(N)} \right] = - \left( \mathcal{E} \delta\bar{I} + v \delta\bar{p} + \sum_{a=1}^r \sum_{q \geq 1} \hat{\Phi}_a^{(q)} \delta\bar{X}_a^{(q)} - \sum_{a=1}^r c_a \delta\bar{\mu}_a \right), \quad (6.393)$$

it is possible to first formulate the thermodynamic quantization rules as we have done for the case of the Boltzmann kinetic theory for dilute monatomic gases, and then use the results to show the thermodynamic uncertainty relations as well as the stochastic evolution equations for fluctuations  $\delta\bar{I}$ ,  $\delta\bar{p}$ ,  $\delta\bar{X}_a^{(q)}$ , and  $\delta\bar{\mu}_a$  as follows:

$$\begin{aligned} d_t \delta\bar{I} &= -\frac{\partial}{\partial \mathcal{E}} d_t \mathcal{S}_r \left[ \bar{f}^{(N)} | \bar{f}_c^{(N)} \right], \\ d_t \delta\bar{p} &= -\frac{\partial}{\partial v} d_t \mathcal{S}_r \left[ \bar{f}^{(N)} | \bar{f}_c^{(N)} \right], \\ d_t \delta\bar{X}_a^{(q)} &= -\frac{\partial}{\partial \hat{\Phi}_a^{(q)}} d_t \mathcal{S}_r \left[ \bar{f}^{(N)} | \bar{f}_c^{(N)} \right], \\ d_t \delta\bar{\mu}_a &= \frac{\partial}{\partial \mathfrak{c}_a} d_t \mathcal{S}_r \left[ \bar{f}^{(N)} | \bar{f}_c^{(N)} \right]. \end{aligned} \quad (6.394)$$

Expressing the relative Boltzmann entropy balance equation in the form

$$d_t \mathcal{S}_r \left[ \bar{f}^{(N)} | \bar{f}_c^{(N)} \right] = F \left( \delta\bar{I}, \delta\bar{p}, \delta\bar{X}_a^{(q)}, \delta\bar{\mu}_a | \mathfrak{P} \cup \mathfrak{T} \right), \quad (6.395)$$

we obtain the set of coupled differential equations

$$\begin{aligned} d_t \delta\bar{I} &= -\frac{\partial}{\partial \mathcal{E}} F \left( \delta\bar{I}, \delta\bar{p}, \delta\bar{X}_a^{(q)}, \delta\bar{\mu}_a | \mathfrak{P} \cup \mathfrak{T} \right), \\ d_t \delta\bar{p} &= -\frac{\partial}{\partial v} F \left( \delta\bar{I}, \delta\bar{p}, \delta\bar{X}_a^{(q)}, \delta\bar{\mu}_a | \mathfrak{P} \cup \mathfrak{T} \right), \\ d_t \delta\bar{X}_a^{(q)} &= -\frac{\partial}{\partial \hat{\Phi}_a^{(q)}} F \left( \delta\bar{I}, \delta\bar{p}, \delta\bar{X}_a^{(q)}, \delta\bar{\mu}_a | \mathfrak{P} \cup \mathfrak{T} \right), \\ d_t \delta\bar{\mu}_a &= \frac{\partial}{\partial \mathfrak{c}_a} F \left( \delta\bar{I}, \delta\bar{p}, \delta\bar{X}_a^{(q)}, \delta\bar{\mu}_a | \mathfrak{P} \cup \mathfrak{T} \right). \end{aligned} \quad (6.396)$$

For a single-component liquid the last equation is absent, and we have the equations

$$\begin{aligned} d_t \delta\bar{I} &= -\frac{\partial}{\partial \mathcal{E}} F \left( \delta\bar{I}, \delta\bar{p}, \delta\bar{X}^{(q)} | \mathfrak{P} \cup \mathfrak{T} \right), \\ d_t \delta\bar{p} &= -\frac{\partial}{\partial v} F \left( \delta\bar{I}, \delta\bar{p}, \delta\bar{X}^{(q)} | \mathfrak{P} \cup \mathfrak{T} \right), \\ d_t \delta\bar{X}^{(q)} &= -\frac{\partial}{\partial \hat{\Phi}^{(q)}} F \left( \delta\bar{I}, \delta\bar{p}, \delta\bar{X}^{(q)} | \mathfrak{P} \cup \mathfrak{T} \right). \end{aligned} \quad (6.397)$$

It should be recalled that the thermodynamic uncertainty relations are contained in this stochastic theory formalism. They are not discussed here to avoid repetition; see Chap. 3.

## 6.12 Barycentric Velocity and Its Constitutive Equation

In the continuum theory of irreversible processes, the term barycentric velocity is commonly used for the fluid velocity. This describes motion of a packet of fluid in motion and defines the kinetic energy density of the convective motion of the fluid. In statistical mechanics the internal energy as well as all other macroscopic variables of the fluid is then defined relative to the barycentric velocity in the coordinate system moving with the barycentric velocity. In fluid dynamics the barycentric velocity, denoted by  $\mathbf{u}$ , obeys the momentum balance equation, which is coupled to the equation describing the pressure tensor, which in turn is described by its constitutive equation. However, in nonrelativistic theory, unlike other fluid dynamic variables the barycentric velocity do not appear by itself except in the form of time derivative or spatial derivatives. For this reason we are not compelled to think about it and its characteristics in the course of formulating theories of macroscopic variables. As a consequence, a molecular theory of  $\mathbf{u}$  has been neglected until recently [57]. It is found that its constitutive relation has some interesting features which would help elucidate fluid behaviors from the molecular theory standpoint. We would like to review the results of our investigation [57], which give a fresh insight into the nature of the barycentric velocity. It is believed they might be useful for investigating some questions on nano scale flows and velocity boundary conditions in fluid mechanics.

### 6.12.1 Cartesian Coordinate Representation

We consider a single-component simple fluid. Its mean density and the barycentric velocity are given by

$$\rho(\mathbf{r}, t) = \left\langle \sum_{i=1}^N m_i \delta(\mathbf{r}_i - \mathbf{r}) f^{(N)}(x^{(N)}, t) \right\rangle, \quad (6.398)$$

$$\mathbf{u}(\mathbf{r}, t) = \frac{1}{\rho(\mathbf{r}, t)} \left\langle \sum_{i=1}^N m_i \mathbf{v}_i \delta(\mathbf{r}_i - \mathbf{r}) f^{(N)}(x^{(N)}, t) \right\rangle. \quad (6.399)$$

We would like to calculate (6.399) by using molecular theory methods.

To deal with a many-particle system collectively and its motion, the following change of variables is made:

$$\mathbf{R} = \frac{1}{M_N} \sum_{i=1}^N m_i \mathbf{r}_i \quad \left( M_N = \sum_{i=1}^N m_i \right), \quad (6.400)$$

$$\xi_i = \mathbf{R} - \mathbf{r}_i \quad (i = 1, 2, \dots, N), \quad (6.401)$$

where  $\xi_i$  is the displacement of particle  $i$  from the center of mass  $\mathbf{R}$  of the system. The Jacobian of transformation

$$(\dot{\mathbf{r}}_i \quad i = 1, 2, \dots, N) \rightarrow (\mathbf{R}, \xi_1, \dots, \xi_N)$$

is unity. The center-of-mass and relative velocities are respectively given by

$$\dot{\mathbf{V}} = \dot{\mathbf{R}} = \frac{1}{M_N} \sum_{i=1}^N m_i \dot{\mathbf{r}}_i, \quad (6.402)$$

$$\dot{\xi}_i = \dot{\mathbf{R}} - \dot{\mathbf{r}}_i = \dot{\mathbf{V}} - \dot{\mathbf{v}}_i. \quad (6.403)$$

Here the overdot denotes time derivative: for example,  $\dot{\mathbf{R}} = \frac{d}{dt} \mathbf{R}$ . The relative distances and velocities satisfy the conditions

$$\sum_{i=1}^N m_i \dot{\xi}_i = 0, \quad (6.404)$$

$$\sum_{i=1}^N m_i \ddot{\xi}_i = 0. \quad (6.405)$$

With the transformations the barycentric velocity in (6.399) may be written in two components as

$$\mathbf{u}(\mathbf{r}, t) = \mathbf{u}_c + \mathbf{u}_d, \quad (6.406)$$

where

$$\mathbf{u}_c = \frac{1}{\rho} \left\langle \sum_{i=1}^N m_i \mathbf{V} \delta(\mathbf{r}_i - \mathbf{r}) f^{(N)}(x^{(N)}, t) \right\rangle, \quad (6.407)$$

$$\mathbf{u}_d = \frac{1}{\rho} \left\langle \sum_{i=1}^N m_i \dot{\xi}_i \delta(\mathbf{r}_i - \mathbf{r}) f^{(N)}(x^{(N)}, t) \right\rangle. \quad (6.408)$$

In (6.407)  $\mathbf{u}_c$  is evidently the center-of-mass velocity of the fluid packet, which we may identify with the barycentric velocity in the fluctuation-free generalized hydrodynamic equations. Therefore  $\mathbf{u}_c$  may be thought of the solution for fluid velocity of fluctuationless completely deterministic hydrodynamic equations. For a moving fluid  $\mathbf{u}_c$  is not equal to zero. Neither is  $\mathbf{u}_d$  equal to zero despite (6.406), because of the delta function present in (6.408). Therefore the barycentric velocity  $\mathbf{u}$  consists of the mean center-of-mass velocity of the fluid packet and mean velocities of modes relative to the moving center of mass. It is now necessary to elucidate  $\mathbf{u}_d$  further on the basis of a physically more accessible concept.

To achieve this aim we make use of the following identity regarding the Dirac delta function:

$$\delta(\mathbf{r}_i - \mathbf{r}) = \delta(\mathbf{R} - \boldsymbol{\xi}_i - \mathbf{r}) = \exp(\boldsymbol{\xi}_i \cdot \nabla) \delta(\mathbf{R} - \mathbf{r}), \quad (6.409)$$

where  $\nabla = \partial/\partial\mathbf{r}$ . The exponential factor on the right is a displacement operator. This displacement operator can be recast into a more useful form for our purpose by using the identity

$$\exp(\boldsymbol{\xi}_i \cdot \nabla) = 1 + \int_0^1 d\lambda \boldsymbol{\xi}_i \cdot \nabla \exp(\lambda \boldsymbol{\xi}_i \cdot \nabla), \quad (6.410)$$

where  $\lambda$  is a parameter ranging from 0 to 1. On inserting this identity into (6.408), we obtain

$$\rho \mathbf{u}_d = - \int_0^1 d\lambda \left\langle \sum_{i=1}^N m_i \dot{\boldsymbol{\xi}}_i \boldsymbol{\xi}_i \exp(\lambda \boldsymbol{\xi}_i \cdot \nabla) \cdot \nabla \delta(\mathbf{R} - \mathbf{r}) f^{(N)}(x^{(N)}, t) \right\rangle, \quad (6.411)$$

for which we have used Condition (6.405). To make further progress, the distribution function  $f^{(N)}(x^{(N)}, t)$  can be factorized into a product of the center-of-mass distribution function and the distribution function for the “internal” (relative) modes of the moving packet of particles,

$$f^{(N)}(x^{(N)}, t) = f(\mathbf{R}, \mathbf{V}, t) f_I^{(N)}\left(\left\{\dot{\boldsymbol{\xi}}_i\right\}, \{\boldsymbol{\xi}_i\}, t\right), \quad (6.412)$$

where  $f(\mathbf{R}, \mathbf{V}, t)$  is the center-of-mass distribution function, which is normalized to  $N$ ,

$$N = \int d\mathbf{R} \int d\mathbf{V} f(\mathbf{R}, \mathbf{V}, t) \quad (6.413)$$

and  $f_I^{(N)}\left(\left\{\dot{\boldsymbol{\xi}}_i\right\}, \{\boldsymbol{\xi}_i\}, t\right)$  is the internal distribution function for motions of  $\boldsymbol{\xi}_i$  modes with respect to the center of the packet. It is normalized to unity:

$$\int d\left\{\dot{\boldsymbol{\xi}}_i\right\} \int d\{\boldsymbol{\xi}_i\} f_I^{(N)}\left(\left\{\dot{\boldsymbol{\xi}}_i\right\}, \{\boldsymbol{\xi}_i\}, t\right) = 1. \quad (6.414)$$

If we imagine the packet to be a giant molecule, then  $\{\boldsymbol{\xi}_i\}$  may be regarded as internal coordinates relative to the center of mass of the giant “polyatomic” molecule. Since the distribution function  $f^{(N)}(x^{(N)}, t)$  factorizes into the center-of-mass and internal relative motion parts we find

$$n(\mathbf{r}, t) = \int d\mathbf{R} \int d\mathbf{V} \delta(\mathbf{R} - \mathbf{r}) f(\mathbf{R}, \mathbf{V}, t), \quad (6.415)$$

which is the density of packets—fluid particles, and the mass density  $\rho(\mathbf{r}, t)$  is given by

$$\rho(\mathbf{r}, t) = mn(\mathbf{r}, t). \quad (6.416)$$

The diffusive part  $\mathbf{u}_d$  of the barycentric velocity then can be written in the form

$$\mathbf{u}_d = -\rho^{-1} \mathbb{D}_{gen} \cdot \nabla \rho(\mathbf{r}, t) \quad (6.417)$$

with the definition

$$\mathbb{D}_{gen} = \int_0^1 d\lambda \left\langle \sum_{i=1}^N \dot{\xi}_i \xi_i \exp(\lambda \dot{\xi}_i \cdot \nabla) f_I^{(N)} \left( \left\{ \dot{\xi}_i \right\}, \left\{ \xi_i \right\}, t \right) \right\rangle. \quad (6.418)$$

The averaging in this expression is performed in the space of  $\left( \left\{ \dot{\xi}_i \right\}, \left\{ \xi_i \right\} \right)$ . The coefficient tensor  $\mathbb{D}_{gen}$  has the dimension of [length<sup>2</sup>/time], which is the same dimension of diffusion coefficient. Therefore it may be thought of as a generalized diffusion tensor. Equation (6.417) is an exact, but formal, constitutive relation for  $\mathbf{u}_d$ . It clearly shows that  $\mathbf{u}_d$  is proportional to the density gradient with a generalized diffusion tensor as a material parameter. Finally, the constitutive relation for the barycentric velocity  $\mathbf{u}$  is given by the expression

$$\mathbf{u} = \mathbf{u}_c - \rho^{-1} \mathbb{D}_{gen} \cdot \nabla \rho(\mathbf{r}, t). \quad (6.419)$$

It is possible to see that the generalized diffusion tensor reduces to the Einstein diffusion coefficient [58] in the lowest order approximation. Noting that the exponential operator in (6.418) must be understood in terms of its Taylor expansion we find

$$\mathbb{D}_{gen} = \sum_{l=0}^{\infty} \frac{1}{(l+1)!} \left\langle \sum_{i=1}^N \dot{\xi}_i \xi_i^{l+1} \exp(\lambda \dot{\xi}_i \cdot \nabla) f_I^{(N)} \left( \left\{ \dot{\xi}_i \right\}, \left\{ \xi_i \right\}, t \right) \right\rangle \odot^l \nabla^l, \quad (6.420)$$

where  $\odot^l$  stands for contraction of tensor  $\xi_i^{l+1}$  of rank  $l+1$  with tensor  $\nabla^l$  of rank  $l$ . Thus we may write (6.419) in the form

$$\mathbf{u} = \mathbf{u}_c - \sum_{l=0}^{\infty} \frac{1}{(l+1)!\rho} \mathfrak{D}_{l+2} \odot^{l+1} \nabla^{l+1} \rho(\mathbf{r}, t), \quad (6.421)$$

where

$$\mathfrak{D}_{l+2} = \left\langle \sum_{i=1}^N \dot{\xi}_i \xi_i^{l+1} f_I^{(N)} \left( \left\{ \dot{\xi}_i \right\}, \left\{ \xi_i \right\}, t \right) \right\rangle. \quad (6.422)$$

Therefore in the small density gradient regime

$$\mathbf{u} = \mathbf{u}_c - \mathbf{D} \cdot \nabla \ln \rho + O(\nabla^2 \rho), \quad (6.423)$$

where

$$\mathbf{D} = \mathfrak{D}_2 = \left\langle \sum_{i=1}^N \dot{\xi}_i \xi_i f_I^{(N)} \left( \left[ \dot{\xi}_i \right], \{ \xi_i \}, t \right) \right\rangle. \quad (6.424)$$

If the approximation for  $\dot{\xi}_i$  is permitted such that

$$\dot{\xi}_i = \tau^{-1} \xi_i, \quad (6.425)$$

where  $\tau$  is the relaxation time for internal mode  $\xi_i$ , then  $\mathbf{D}$  in (6.424) can be approximated as the Einstein diffusion tensor

$$\mathbf{D} = \frac{1}{\tau} \left\langle \sum_{i=1}^N \xi_i \dot{\xi}_i f_I^{(N)} \left( \left[ \dot{\xi}_i \right], \{ \xi_i \}, t \right) \right\rangle. \quad (6.426)$$

For an isotropic fluid this may be further simplified as

$$\mathbf{D} = D \delta \quad (6.427)$$

with  $D$  given by the scalar quantity

$$D = \frac{1}{3\tau} \left\langle \sum_{i=1}^N \xi_i \dot{\xi}_i f_I^{(N)} \left( \left[ \dot{\xi}_i \right], \{ \xi_i \}, t \right) \right\rangle, \quad (6.428)$$

which is the well-known Einstein formula for the diffusion coefficient in the theory of Brownian motion [58]. Therefore in this approximation the constitutive relation for  $\mathbf{u}$  becomes

$$\mathbf{u} = \mathbf{u}_c - D \nabla \ln \rho(\mathbf{r}, t). \quad (6.429)$$

We remark that the expansion parameter for (6.419) is not  $\xi_i$ , but  $\lambda \nabla \rho$ . Therefore, if the density gradient is small in magnitude, the expansion is sufficiently fast convergent. In any case, away from a possible singularity in  $\rho$  the Taylor expansion is uniformly convergent.

Having carried out the analysis of the barycentric velocity this far, we can easily conclude that the mean velocity of a packet of fluid particles in statistical mechanics consists of the center-of-mass velocity and a diffusive contribution of internal collective modes relative to the center-of-gravity motion. We may depict the motion of a fluid particle as if it is the motion of a jellyfish whose main body moves forward

with velocity  $\mathbf{u}_c$  with the rest of the body entrained diffusively at  $\mathbf{u}_d$  relative to its center of gravity. It appears to be an apt cartoon for the mathematical result for the fluid motion in a liquid.

### 6.12.2 Transformation to Collective Coordinates

The coordinate transformation  $\{\mathbf{r}_i\} \rightarrow \{\mathbf{R}, \xi_i\}$  is essential for obtaining the constitutive relation (6.429) for  $\mathbf{u}$ , but the new variables  $\{\xi_i\}$  are not the most suitable for studying dynamics of diffusive motions. We would like to explore another set of collective coordinates. We find the collective coordinates proposed by Hirschfelder and his collaborators [59, 60] many years ago in connection with quantum chemistry. We have used them to study three-particle collisions associated with three-body transport cross sections [1].

The Dahler-Hirschfelder (DH) collective coordinates are constructed as follows: with the definitions

$$\mathbf{r}_{21} = \mathbf{r}_2 - \mathbf{r}_1, \quad (6.430)$$

$$\mathbf{r}_{3,21} = \mathbf{r}_3 - \frac{1}{M_2} \sum_{i=1}^2 m_i \mathbf{r}_i := \mathbf{r}_3 - \mathbf{R}_{12}, \quad (6.431)$$

...

$$\mathbf{r}_{N,N-1\dots 321} = \mathbf{r}_N - \frac{1}{M_{N-1}} \sum_{i=1}^{N-1} m_i \mathbf{r}_i := \mathbf{r}_N - \mathbf{R}_{12\dots N-1}, \quad (6.432)$$

$$M_l = \sum_{i=1}^l m_i, \quad (6.433)$$

a set of mass-normalized collective coordinates is then defined by transformations

$$\begin{aligned} \mathbf{Q}_1 &= \sqrt{\frac{m_1 m_2}{M_2}} \mathbf{r}_{21}, \\ \mathbf{Q}_k &= \sqrt{\frac{m_{k+1}}{M_k M_{k+1}}} \sum_{j=1}^k m_j \mathbf{r}_{k+1,j} \\ &:= \sqrt{\frac{m_{k+1} M_k}{M_{k+1}}} \sum_{j=1}^k m_j \mathbf{r}_{k+1,k\dots 21} \quad (k = 3, \dots, N-1), \\ \mathbf{Q}_N &= \frac{1}{\sqrt{M_N}} \sum_{j=1}^N m_j \mathbf{r}_j \\ &:= \sqrt{M_N} \mathbf{R}. \end{aligned} \quad (6.434)$$

Since  $\mathbf{Q}_k$  are linear combinations of particle position coordinates, they are collective coordinates. These transformations leave the kinetic energy of the system invariant in form, namely,

$$K_E = \sum_{j=1}^N m_j \dot{\mathbf{r}}_j^2 = \sum_{j=1}^N \frac{1}{2} \dot{\mathbf{Q}}_j^2 \quad (6.435)$$

where the overdot means time derivative and  $\dot{\mathbf{r}}_j^2 = \dot{\mathbf{r}}_j \cdot \dot{\mathbf{r}}_j$  and similarly for  $\dot{\mathbf{Q}}_j^2$ . Therefore  $\mathbf{Q}_k$  are collective coordinates akin to the normal modes, but unlike the normal modes they do not diagonalize the potential energy. Since

$$\mathbf{r}_i = \sum_{i=1}^N S_{ik} \mathbf{Q}_k = \mathbf{R} + \sum_{k=1}^{N-1} S_{ik} \mathbf{Q}_k, \quad (6.436)$$

where  $\mathbf{S}$  is the orthogonal matrix defining the transformation  $\{\mathbf{Q}_k\} \rightarrow \{\mathbf{r}_k\}$  and  $S_{iN} = 1/\sqrt{M_N}$  for all  $i$ . The associated elementary volume is found given by

$$\begin{aligned} \prod_{k=1}^N d\mathbf{r}_k &= |\det \mathbf{S}| \prod_{k=1}^N d\mathbf{Q}_k \\ &= \left( \prod_{k=1}^N m_k \right)^{3/2} M_N^{3/2} d\mathbf{R} \prod_{k=1}^{N-1} d\mathbf{Q}_k \end{aligned} \quad (6.437)$$

and the phase integral for statistical mechanical average can be accordingly transformed to the  $(\mathbf{Q}_k, \mathbf{P}_k : k = 1, 2, \dots, N)$  space—the phase space of collective modes. Here momentum  $\mathbf{P}_k$  conjugate to  $\mathbf{Q}_k$  is given by

$$\mathbf{P}_i = \sum_{k=1}^N m_i S_{ik} \dot{\mathbf{Q}}_k, \quad (6.438)$$

$$\mathbf{P} = \sum_{i=1}^N \mathbf{P}_i = \sum_{i=1}^N \mu_i \dot{\mathbf{Q}}_i, \quad (6.439)$$

where

$$\mu_k = \sum_{i=1}^N m_i S_{ik}. \quad (6.440)$$

On comparing (6.436) with (6.401) we find the transformation between  $\xi_i$  and  $\mathbf{Q}_k$ :

$$\xi_i = - \sum_{k=1}^{N-1} S_{ik} \mathbf{Q}_k, \quad (6.441)$$

$$\dot{\xi}_i = - \sum_{k=1}^{N-1} S_{ik} \dot{\mathbf{Q}}_k. \quad (6.442)$$

The normal-coordinate-like collective coordinates  $\{\mathbf{Q}_k\}$  are rather suggestive of some physically motivated models for description of liquids. The transformations (6.441) and (6.442) may be used in the diffusion tensor  $\mathbb{D}_{gen}$  and its approximations in Sect. 6.10.1.

In summary, in the analysis presented, the elementary packet of a fluid flows with  $\mathbf{u}_c$  entraining the constituent parts (particles) in a diffusive motion toward the center of gravity of the fluid packet. Therefore, fluid motion consists of two velocities: one, that of the center of mass and the other diffusive, that has to do with a volume gradient. In the sense that there are two distinctive velocities it reminds us of the bivelocity concept of Brenner [3, 4], who has attempted to formulate fluid dynamics on the basis of a two-velocity concept, but without a guidance of a molecular theory. The present analysis seems to elucidate what one might mean by two velocities from the molecular theory point of view, if one insists that there are two velocities involved in fluid dynamic description of flow. In any case, in our approach described in the main body of this chapter, the inclusion of volume transport obviates the bivelocity concept.

## 6.13 Brownian Motion Model

The Brownian motion model considered below does not fall in the category of kinetic equations we envisage in this work, but we would like to briefly discuss it for its interesting aspects of its kinetic theory origin the way Kirkwood [12] approached it, and for its potential for applications to irreversible phenomena in general. Despite its interesting features and potentials for irreversible phenomena and transport processes in liquids little has been studied of them in the literature except for his work with his collaborators [61].

Liquids can be also treated by means of Brownian motion model by following Kirkwood [12] who obtained a Fokker-Planck equation for the singlet distribution function  $f^{(1)}(x_1, t)$  for a monatomic molecule (designated molecule 1) assumed to undergo Brownian motion constantly bombarded by surrounding particles of medium. For this purpose the singlet reduced distribution function  $\bar{f}^{(1)}(x_1, t)$  is coarse-grained over a molecular interaction time on the order of molecular collision time  $\tau$  much less than hydrodynamic time:

$$\bar{f}^{(1)}(x_1, t) = \frac{1}{\tau} \int_0^\tau ds f^{(1)}(x_1, t + s). \quad (6.443)$$

The leading member of the BBGKY hierarchy for  $f^{(1)}(x_1, t)$  is similarly time-coarse-grained.

Then assuming the  $(N - 1)$  particles act as a constant temperature reservoir (medium) that perturbs the Brownian particle of attention, he obtained a Fokker–Planck equation for the coarse-grained singlet distribution function  $\bar{f}^{(1)}(x_1, t)$ . We may adopt this idea to study the Brownian motion model for the subsystem distribution function  $f^{(N)}(\mathbf{x}^{(N)}, t)$  for members of the ensemble representative of the fluid of interest. The distribution function  $\bar{f}^{(N)}(\mathbf{x}^{(N)}, t)$ , which is coarse-grained in the same manner as in (6.32), can be found [1] to obey a Fokker–Planck equation of Kirkwood

$$\left( \frac{\partial}{\partial t} + \mathbf{L}^{(N)} \right) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) = \mathfrak{R}_{\text{FP}} \left[ \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right], \quad (6.444)$$

where collision operator  $\mathfrak{R}_{\text{FP}} \left[ \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right]$  is found to be the Fokker–Planck operator<sup>24</sup>

$$\mathfrak{R}_{\text{FP}} \left[ \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \right] = \sum_{i=1}^N \sum_{j=1}^N \frac{\partial}{\partial \mathbf{p}_i} \cdot \boldsymbol{\zeta}_{ij} \cdot \left( \frac{\mathbf{p}_j}{m} + k_B T \frac{\partial}{\partial \mathbf{p}_j} \right) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t). \quad (6.445)$$

Here  $\boldsymbol{\zeta}_{ij}$  is the friction tensor defined by

$$\boldsymbol{\zeta}_{ij} = \frac{1}{k_B T \tau} \int_0^\tau ds \int_0^{s'} ds' \left\langle \mathbf{f}_i e^{-(s-s')\mathbf{L}^{(n-N)}} \mathbf{f}_j \right\rangle_{(\mathfrak{N}-N)} \quad (6.446)$$

with  $\mathbf{f}_i$  denoting the force on particle  $i$  in the Brownian particle consisting of  $N$  particles

$$\mathbf{f}_i = - \sum_{j \notin (N)}^{\mathfrak{N}} \frac{\partial U_{ij}}{\partial \mathbf{r}_i} \quad (U_{ij} = \text{intermolecular potential of particles } i \text{ and } j), \quad (6.447)$$

$$\mathbf{f}_j = - \sum_{i=1}^N \frac{\partial U_{ij}}{\partial \mathbf{r}_j} \text{ for } j \in \mathfrak{N} - N. \quad (6.448)$$

The symbol  $\langle \dots \rangle_{(\mathfrak{N}-N)}$  in (6.446) stands for the equilibrium average

$$\langle X \rangle_{(\mathfrak{N}-N)} = \mathfrak{V}^N \int_{\mathfrak{V}} d\mathbf{x}^{(\mathfrak{N}-N)} X \bar{f}_{\text{eq}} \quad (6.449)$$

with  $\bar{f}_{\text{eq}}$  denoting the equilibrium distribution function defined by

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<sup>24</sup>This kind of Fokker–Planck equation for the coarse-grained distribution function was derived in pp. 486–493, Ref. [1], to which the reader is referred for more details.

$$\mathbf{L}^{(N)} \bar{f}_{\text{eq}} = 0. \quad (6.450)$$

The  $T$  is the temperature of the rest of the system ( $\mathfrak{N} - N$ ) treated as the medium and heat bath. The kinetic equation (6.444) is irreversible and may be used to derive the evolution equations of macroscopic variables—e.g., hydrodynamic equations by the Brownian motion model. In this connection, we remark that the possibility of formulating a theory of irreversible thermodynamics and accompanying generalized hydrodynamics was discussed in Ref. [62] in the case in which the potential condition is satisfied.

## 6.14 Concluding Remarks

It seems appropriate to have a retrospect of what we have acquired in this chapter of a considerable length. The present chapter represents a synthesis of what the present author has pursued in subjects of kinetic theory, scattering theory of particles, and irreversible thermodynamics in the last few decades since the publication of the 1979 papers [63]. We have shown in the present chapter that the equilibrium Gibbs ensemble theory can be generalized to nonequilibrium fluids in which irreversible transport processes are present. By utilizing the classical scattering theory formalism we have been able to deduce a coarse-grained kinetic equation which is irreversible and reduces to the Boltzmann kinetic equation as the density diminishes to a dilute gas value. The coarse-grained kinetic equation obtained is called the generalized Boltzmann equation (GBE) for the canonical ensemble considered. The deduction of the GBE is a result of realization that the Boltzmann kinetic equation may be regarded as a kinetic equation within the framework of nonequilibrium Gibbs ensemble theory of statistical mechanics. Based on this realization, the equilibrium Gibbs ensemble theory underlying the equilibrium statistical mechanics is generalized to nonequilibrium phenomena. It is then shown that the irreversible GBE is capable of producing a theory of thermodynamics of irreversible processes in fluids of arbitrary density, condensed phases of matter included, with attendant hydrodynamic equations that manifestly generalize the classical hydrodynamics of Navier–Stokes and Fourier, if the concept of calortropy is made use of in place of the Boltzmann entropy.

*The important characteristic of the calortropy is that its balance equation (i.e., evolution equation) is integrable in the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T}$  thanks to the fact that its (Pfaffian) differential form is an exact differential in manifold  $\mathfrak{P} \cup \mathfrak{T} \cup \widehat{\Psi}$ , whereas the Boltzmann entropy balance equation is not.* Mathematically, the calortropy is a projection onto manifold  $\mathfrak{P} \cup \mathfrak{T}$  of the phase space information of the molecular system contained in the Boltzmann entropy, while the complement of the projection is carried by the relative Boltzmann entropy. For the relative Boltzmann entropy the GBE must be solved in the full phase space of the system under the initial and boundary conditions on the full distribution function obeying the kinetic equation. In this line of approach, the GBE therefore requires two levels of description; one at the level of the calortropy and the related in manifold  $\mathfrak{P} \cup \mathfrak{T} \cup \widehat{\Psi}$

and the other at the level of the relative Boltzmann entropy characterizing fluctuations from the deterministic descriptions provided by the calortropy and associated hydrodynamic equations. The hydrodynamic field evolution equations derived from the generalized Boltzmann equation are called the generalized hydrodynamic equations, because they reduce to the classical hydrodynamic equations as the irreversible processes tend to those occurring near equilibrium. The generalized hydrodynamic equations, as a matter of fact, are field equations for the nonequilibrium canonical distribution function. Since the deterministic thermodynamic theory of irreversible transport processes and generalized hydrodynamics is the principal objective in this work, we have not much devoted our effort to the investigation of the relative Boltzmann entropy and fluctuations of macroscopic variables underlying it.

They have been successfully applied to some typical nonlinear hydrodynamic flow problems in literatures cited. Some examples for applications will be briefly discussed in Chap. 9. The present version of generalized hydrodynamic evolution equations explicitly includes evolution equations for volume transport phenomena and thereby broaden the scope of hydrodynamics. The study of relative Boltzmann entropy and its evolution equation is left for future work.

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# Chapter 7

## Kinetic Theory of a Dense Simple Fluid Mixture

In Chap. 6 we have confined the formulation of the kinetic theory to a pure dense fluid for simplicity of formulation. To develop a theory of irreversible thermodynamics in a general form covering liquid mixtures it is now necessary to generalize the theories formulated in the previous chapters. It is possible to achieve this goal if we first formulate a kinetic theory of a mixture of dense simple fluids by using a grand canonical ensemble method and then develop therewith a thermodynamic theory of irreversible transport processes and attendant generalized hydrodynamics of a fluid mixture. The grand canonical ensemble kinetic theory is parallel in structure to the GBE theory of a pure simple fluid—described in Chap. 6. For this reason the general methodology and various concepts remain unaltered from those employed in Chap. 6. Therefore we will not go into details of derivation of the coarse-grained kinetic equation for dense fluid mixtures, but briefly mention the important steps with appropriate definitions of notation used for the fluid mixture necessary to follow the discussion. However, since hydrodynamics of a mixture often involves generalized forms of equations sometimes considerably different from those for a pure fluid we will find it necessary to derive them again. Nevertheless, the generic structures of generalized hydrodynamic equations and irreversible thermodynamics formalism for a mixture will be found to remain basically unchanged, but they reduce to their counterparts for a pure simple fluid discussed in Chap. 6 as the fluid becomes pure, and to the dilute simple gas counterparts as the density diminishes to a dilute gas value.

## 7.1 Generalized Boltzmann Equation for a Simple Fluid Mixture

### 7.1.1 Nonequilibrium Grand Ensemble

We consider a fluid of a nonreactive mixture of  $r$  species of  $N_1, N_2, \dots$ , and  $N_r$  monatomic molecules contained in a fixed volume  $V$ . The density and composition of the fluid mixture are arbitrary. This volume of the fluid exchanges matter as well as energy with its surroundings. Therefore the numbers of different species particles of the system are not fixed and the dimension of the phase space accordingly varies for the system over time in the course of exchange processes. For this reason the canonical ensemble method [1] discussed in Chap. 6 cannot be applied in a straightforward manner, if a statistical mechanical theory is sought. It is necessary to resort to the grand canonical ensemble method devised by Gibbs [2] to overcome the difficulty of the varying phase space dimension as the particle exchange process progresses with time. To discuss this method we would like to define the notation to be employed.

The different species will be distinguished by subscript  $a, b, c$ , etc. and particles by subscripts,  $i, j, k$ , etc. Accordingly, for example, the composite subscript  $ja$  denotes particle  $j$  belonging to species  $a$ ; i.e.,  $j \in a$ . The position vectors of particles will be accordingly denoted by  $\mathbf{r}_{ja}$  for particle  $ja$  in a suitably fixed coordinate system, and its conjugate momentum vector by  $\mathbf{p}_{ja}$ . It will be convenient to denote the phase of particle  $j$  of species  $a$  by  $x_{ja} = (\mathbf{p}_{ja}, \mathbf{r}_{ja})$ , which is a vector of dimension 6 in the phase space (i.e.,  $\mu$  space). If the fluid consists of an  $r$  component mixture of  $N_1$  particles for species 1,  $N_2$  particles for species 2,  $\dots$ ,  $N_r$  particles for species  $r$ , so that there are  $N$  particles in total

$$N = \sum_{a=1}^r N_a, \quad (7.1)$$

the total phase vector of  $N$  particles in the system will be denoted by  $\mathbf{x}^{(N)} = (\mathbf{x}^{(N_1)}, \mathbf{x}^{(N_2)}, \dots, \mathbf{x}^{(N_r)})$  in which the component phase vectors  $\mathbf{x}^{(N_b)}$  of the set are denoted by

$$\mathbf{x}^{(N_b)} = (x_{1b}, x_{2b}, \dots, x_{Nb}) \quad (1 \leq b \leq r). \quad (7.2)$$

This number  $N$  of particles is variable because  $N_b$  ( $b = 1, \dots, r$ ) changes as the system exchanges particles with the surroundings.<sup>1</sup> As a consequence, the indeterminate dimension of the phase space would give rise to a difficulty if the canonical ensemble method [3] of Chap. 6 were applied to formulate statistical mechanics of an open system because the dimension of the phase space would change over the course of particle exchange between the system and its surroundings, but a fixed dimension

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<sup>1</sup>If chemical reactions are allowed,  $N_a$  will change also owing to the chemical reactions occurring within the system. However, this case is excluded in the present consideration for simplicity of discussion. This restriction, however, is easy to remove.

of phase space is necessary to define distribution functions and formulate a statistical mechanics theory of macroscopic processes in the system. This difficulty is overcome in Gibbs's grand ensemble method as elaborated below. Gibbs constructs a grand ensemble made up of *petit ensembles* of all possible values of particle number  $N$ . But although the value of  $N$  and the distribution of  $N_a$  over species  $\{a\}$  change from petit ensemble to petit ensemble, the value of  $N$  is fixed for each petit ensemble representative of the system.

The grand ensemble is assembled with all possible petit ensembles constructed under the *equal a priori probability hypothesis that all physically accessible states of the system are equally probable and thus admissible as a member of the ensemble*. The grand ensemble therefore may be imagined consisting of subsystems of fixed numbers of particles contained each in volume  $V$  and hence as a *supersystem*<sup>2</sup> consisting of  $\nu$  subsystems of variable particle number  $N$ . The value of  $\nu$  can be as large as the equal a priori probability hypothesis permits in assembling the ensemble. The volume of the supersystem is  $\mathbb{V} = \nu V$ . The phase vector of the grand ensemble (supersystem) has  $6\nu$  components in a  $6\nu$ -dimensional phase space. It will be abbreviated by

$$\mathbf{x}^{(\nu)} = (\mathbf{x}_1^{(N)}, \mathbf{x}_2^{(N)}, \dots, \mathbf{x}_{\nu}^{(N)}).$$

Since the system may be composed of a different composition of petit ensembles consisting of different but fixed numbers of particles for each representative of the varying composition of the system, the indeterminacy of phase space dimension arising from particle exchange is thus neatly overcome, and we can implement the ensemble method free from the difficulty of varying phase space dimensions.

As we have done in the previous chapter, the following consideration is rather helpful for illustrating the general scheme of formulation. The phase space of each petit ensemble is divided into cell of  $O(h^3)$  ( $h$  = Planck constant) centered at  $x_{ia}$  ( $1 \leq i \leq N_a$ ;  $1 \leq a \leq r$ ). As particles are assigned into the cells, the state of the petit ensemble is specified by the distribution of particles in the cells. Thus the frequency of distribution of  $x_{ia}$  among the petit ensembles determines the state of the grand ensemble. If the frequency of particles distributed into such cells in the grand ensemble is denoted by  $n(\mathbf{N}, k)$  subsystems (petit ensembles), where

$$\mathbf{N} := (N_1, N_2, \dots, N_r)$$

and  $k$  is the index for location of cell  $k$  in the phase space of all petit ensembles, then summing  $n_k(\mathbf{N}, V)$  over all  $k$  and species distribution  $\mathbf{N}$  gives the number of petit ensembles

$$\nu = \sum_{\{\mathbf{N}\} \geq 0} \sum_k n_k(\mathbf{N}, V) \quad (7.3)$$

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<sup>2</sup>For a schematic illustration of the equilibrium grand ensemble, see Fig. 4.2 in Chap. 4. A similar schematic representation may be used for a nonequilibrium grand ensemble.

in the grand ensemble. The total number of particles in the grand ensemble is then given by the sum

$$\mathcal{N} = \sum_{\{\mathbf{N}\} \geq 0} \sum_k N n_k(\mathbf{N}, V) \quad (7.4)$$

and the total energy by the sum of energies

$$E_t = \sum_{\{\mathbf{N}\} \geq 0} \sum_k H(\mathbf{N}, V; k) n_k(\mathbf{N}, V), \quad (7.5)$$

where  $H(\mathbf{N}, V; k)$  is the energy of the subsystem in state  $k$ . The total number of particles  $\mathcal{N}$  is fixed for the grand ensemble although individual values of  $\mathbf{N}$  may be varied from petit ensemble to petit ensemble.<sup>3</sup> Thus even if the dimensions of the phase spaces for petit ensembles vary as the number of particles in a system varies or the dimensions of component phases vary as particles are exchanged between component phases, each subsystem has a fixed phase space dimension and hence the phase space dimension of the grand ensemble is fixed. This theoretical device of Gibbs enables us to neatly overcome the difficulty of getting the fixed dimension of the phase space that would arise if the canonical ensemble method were used in the case of open systems. Having devised the system of notation as described above, conditions (7.4) and (7.5) resemble the conditions (6.1) and (6.2) in Chap. 6 except for the additional summation over the distribution over  $\mathbf{N}$ , and the formulation of the grand ensemble kinetic equation can proceed parallel to the canonical ensemble theory in Chap. 6.

### 7.1.2 Generalized Boltzmann Equation for a Mixture

The Liouville operator for the subsystem (petit ensemble)  $\alpha$  consisting of  $\mathbf{N}$  particles is given for the system of interest by the expressions

$$\mathcal{L}_\alpha^{(\mathbf{N})} = -i \mathbf{L}_\alpha^{(\mathbf{N})}, \quad (7.6)$$

$$\begin{aligned} \mathbf{L}_\alpha^{(\mathbf{N})} = & \sum_{a=1}^r \sum_{ja=1}^{N_a} \left[ \mathbf{v}_{ja} \cdot \nabla_{ja} + \frac{1}{2} \sum_{b=1}^r \sum_{ja \neq kb=1}^{N_b} \mathbf{F}_{jakb}(\mathbf{r}_{jakb}) \cdot (\nabla_{\mathbf{p}_{ja}} - \nabla_{\mathbf{p}_{kb}}) \right. \\ & \left. + m_a \widehat{\mathbf{F}}_a(\mathbf{r}_{ja}) \cdot \nabla_{\mathbf{p}_{ja}} \right]_\alpha, \end{aligned} \quad (7.7)$$

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<sup>3</sup>The total number of states of the grand ensemble for a particular distribution  $n$  consistent with (7.3) and (7.4) therefore is given by

$$\Omega_n = \frac{\mathcal{N}!}{\prod_{\{\mathbf{N}\} \geq 0, k} n_k(\mathbf{N}, V)!}.$$

where  $\mathbf{v}_{ja} = \mathbf{p}_{ja}/m_a$  is the velocity of particle  $j \in a$ ,  $m_a$  being the mass of species  $a$ , and other symbols are defined by

$$\begin{aligned}\mathbf{r}_{jakb} &= \mathbf{r}_{ja} - \mathbf{r}_{jb}; \quad \nabla_{ja} = \frac{\partial}{\partial \mathbf{r}_{ja}}; \quad \nabla_{\mathbf{p}_{ja}} = \frac{\partial}{\partial \mathbf{p}_{ja}}; \\ \mathbf{F}_{jakb}(\mathbf{r}_{jakb}) &= -\frac{\partial U_{jakb}(\mathbf{r}_{jakb})}{\partial \mathbf{r}_{jakb}}; \quad \mathbf{F}_a(\mathbf{r}_{ja}) = -\frac{\partial U_{ja}(\mathbf{r}_{ja})}{\partial \mathbf{r}_{ja}}\end{aligned}\quad (7.8)$$

with  $U_{jakb}(\mathbf{r}_{jakb})$  denoting the intermolecular pair potential of particle pair  $(ja, kb)$ , and  $U_{ja}(\mathbf{r}_{ja})$  the external potential on particle  $ja$ . The pairwise additive potential assumption implicit in the definition of Liouville operator can be removed without causing a problem at the formal level. This pairwise additivity assumption would not impair the formulation of the theory we have in mind in this work. It can be easily removed but with a slight complication of the some of resulting formulas.  $\hat{\mathbf{F}}_a(\mathbf{r}_{ja}) := \mathbf{F}_a/m_a$  is the external body-force per unit mass of species  $a$  at  $\mathbf{r}_{ja}$ . This body-force is assumed to vary slowly over the range of intermolecular forces. Thus the intermolecular collision processes of particle pairs remain unaffected by the presence of the external body-force. It will be convenient to abbreviate by  $H'_{ja}$  the Hamiltonian of molecule  $ja$  in the frame of reference moving at the mean velocity  $\mathbf{u}$  of the fluid:

$$H'_{ja} = H_{ja} + U_{ja}(\mathbf{r}_{ja}), \quad (7.9)$$

$$H_{ja} = \frac{1}{2}m_a C_{ja}^2 + \frac{1}{2} \sum_{b=1}^r \sum_{ja \neq kb=1}^{N_b} U_{jakb}(\mathbf{r}_{jakb}), \quad (7.10)$$

where  $\mathbf{C}_{ja}$  denotes the peculiar velocity of particle  $ja$  defined by

$$\mathbf{C}_{ja} = \mathbf{v}_{ja} - \mathbf{u}. \quad (7.11)$$

The statistical mechanical meaning of  $\mathbf{u}$  will be given later, but for the moment it may be considered a phenomenological fluid velocity. Therefore  $H'_{ja}$  is the Hamiltonian (energy) of particle  $ja$  relative to the fluid particle moving at velocity  $\mathbf{u}$ .

The intersubsystem interaction Liouville operator between subsystems  $\alpha$  and  $\beta$  is denoted by

$$\mathcal{L}_{\alpha\beta}^{(\mathbf{N}, \mathbf{N}')} = -i \mathbf{L}_{\alpha\beta}^{(\mathbf{N}, \mathbf{N}')}, \quad (\alpha \neq \beta), \quad (7.12)$$

where

$$\mathbf{L}_{\alpha\beta}^{(\mathbf{N}, \mathbf{N}')} = \frac{1}{2} \sum_{a,b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} [\mathbf{F}_{jakb}(\mathbf{r}_{jakb}) \cdot (\nabla_{\mathbf{p}_{ja}} - \nabla_{\mathbf{p}_{kb}})]_{(a, ja) \in \alpha, (b, kb) \in \beta}. \quad (7.13)$$

In this expression the subscript pair  $ja$  belongs to subsystem  $\alpha$  whereas the subscript pair  $kb$  belongs to subsystem  $\beta \neq \alpha$ . Therefore intermolecular force  $\mathbf{F}_{jakb}$  ( $\mathbf{r}_{jakb}$ ) represents the force between the particles belonging to two different subsystems (petit ensembles)  $\alpha$  and  $\beta$ . The Liouville operator for the grand ensemble (supersystem) may then be written as

$$\begin{aligned}\mathcal{L}^{(\mathcal{N})} &= -i\mathbf{L}^{(\mathcal{N})} \\ &= \mathcal{L}_0^{(\mathcal{N})} + \mathcal{L}_1^{(\mathcal{N})},\end{aligned}\quad (7.14)$$

$$\mathcal{L}_0^{(\mathcal{N})} = -i \sum_{\alpha=1}^{\nu} \mathbf{L}_{\alpha}^{(\mathbb{N})}, \quad (7.15)$$

$$\mathcal{L}_1^{(\mathcal{N})} = -i \frac{1}{2} \sum_{\alpha \neq \beta} \mathbf{L}_{\alpha\beta}^{(\mathbb{N}, \mathbb{N}')}. \quad (7.16)$$

The intersubsystem interactions are mainly provided by molecules on the peripheries of the subsystems because the interactions with inside particles are screened off, especially, owing to the relatively short range (on the order of a few hundred nanometers ( $10^{-9}$  m)) of intermolecular interaction forces. Since the number of molecules in the periphery of a subsystem is relatively small compared with the size of the subsystems if the subsystems are macroscopic in size, the intersubsystem interactions are relatively weak compared to the energies of the subsystems themselves.

In the ensemble kinetic theory the distribution function is sought for the system mechanically described in its phase space. Therefore, if the probability of finding the supersystem at state  $x^{(\mathcal{N})}$  and time  $t$  is denoted by  $\mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t)$ , since the grand ensemble, namely, the supersystem, is isolated, its distribution (more precisely, distribution function) obeys the Liouville equation for an isolated system

$$\left( i \frac{\partial}{\partial t} - \mathcal{L}^{(\mathcal{N})} \right) \mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t) = 0. \quad (7.17)$$

Since the grand ensemble (supersystem) consists of weakly interacting subsystems in comparison to individual interparticle interactions according to the qualitative reasoning made earlier, the Liouville equation (7.17) describes evolution of weakly interacting subsystems. We should emphasize that except for the meaning of the superscript  $\mathcal{N}$  regarding the number and meaning of particles in the ensemble, which is now a supersystem, the Liouville equation is identical in form to the Liouville equation for the canonical ensemble theory. In the present case, the distribution function  $\mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t)$  is normalized to unity for all time:

$$\int dx^{(\mathcal{N})} \mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t) = 1. \quad (7.18)$$

Now imagine an isolated grand ensemble (supersystem) assembled with well-separated petit ensembles (subsystems) at time  $t_i$ . The subsystems being well sep-

arated and therefore independent of each other, the probability  $\mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t_i)$  of finding the grand ensemble assembled at  $t = t_i$  in state  $x^{(\mathcal{N})}$  is given by the product of subsystem distribution functions  $f^{(N)}(\mathbf{x}_k^{(N)}, t_i)$ , where  $k$  is the index for the subsystems in the phase space of the grand ensemble:

$$\mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t_i) = \prod_{\{\mathbf{N}\} \geq 0, k} f^{(N)}(\mathbf{x}_k^{(N)}, t_i). \quad (7.19)$$

This distribution function describes the initial state of the grand ensemble embarking on collisions of its constituent subsystems. Compare this product for  $\mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t_i)$  with a similar product (6.17) for the canonical ensemble theory of Chap. 6. As time progresses, its evolution for the distribution function is described by the Liouville equation (7.17), and the form for  $\mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t)$  would not remain in a product form as in (7.19), although, the intersubsystem interaction being sufficiently weak, it is expected to be approximately in a product form of some sort, which reflects the integrity<sup>4</sup> of subsystems. In any case, the entire supersystem evolves toward the equilibrium in time through interactions (i.e., collisions) between the subsystems and between particles in each subsystem.

The most important objective here is the evolution of the probability of a subsystem (a petit ensemble) of  $N$  particles to acquire phase  $\mathbf{x}^{(N)}$  at time  $t$ , given the supersystem at the initial state  $x^{(\mathcal{N})}$  at  $t = t_i$ . It will be denoted by  $f^{(N)}(\mathbf{x}_k^{(N)}, t)$  for subsystem  $k$ . From the viewpoint of  $\mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t)$  the distribution function  $f^{(N)}(\mathbf{x}_k^{(N)}, t)$  is, in fact, a reduced distribution function of observing subsystem  $k$  of an  $N$  particle petit ensemble, say, petit ensemble (subsystem) 1, regardless of states assumed by all other  $(\mathcal{N} - N)$  particles—i.e., the rest of petit ensembles—in the subspace of  $x^{(\mathcal{N}-N)}$  at  $t$ :

$$f^{(N)}(\mathbf{x}_1^{(N)}, t) = \int d\mathbf{x}^{(\mathcal{N}-N)} \mathbb{F}^{(\mathcal{N})}(x^{(\mathcal{N})}, t), \quad (7.20)$$

where

$$d\mathbf{x}^{(\mathcal{N}-N)} = d\mathbf{x}_2^{(N)} d\mathbf{x}_3^{(N)} \dots d\mathbf{x}_{\nu}^{(N)}. \quad (7.21)$$

In the system of notation for  $N$  used here the symbol  $N$  itself distinguishes the subsystem composition owing to the fact that subsystems have a different distribution of  $N$  and the value of  $\mathbf{x}_k^{(N)}$  stands for the state because the distribution of phase points  $\mathbf{x}_k^{(N)}$  in phase space characterizes the state of petit ensemble  $k$ . For this reason we may omit the subscript from  $\mathbf{x}_k^{(N)}$  for notational brevity, if there is no danger arising from the omission of the subscript. Therefore it follows

$$\int d\mathbf{x}^{(N)} f^{(N)}(\mathbf{x}^{(N)}, t) = 1. \quad (7.22)$$

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<sup>4</sup>In this respect, the subsystems may be regarded as if they are giant polyatomic molecules that preserve their chemical compositions but can change their states, as they interact with each other in the course collisions.

The evolution equation for  $f^{(N)}(\mathbf{x}^{(N)}, t)$  is easily obtained from the Liouville equation (7.17) upon integrating it over phase  $x^{(\mathcal{N}-N)} := x^{(\nu-1)}$ :

$$\left( i \frac{\partial}{\partial t} - \mathcal{L}^{(N)} \right) f^{(N)}(\mathbf{x}^{(N)}, t) = - \int dx^{(\mathcal{N}-N)} \sum_{\beta>1}^{\nu} \mathcal{L}_{1\beta}^{(N,N)} \bar{\mathbb{F}}^{(N)}(\mathbf{x}^{(N)}, t). \quad (7.23)$$

Here index 1 referring to subsystem 1 is omitted from the Liouville operator and the reduced distribution function on the left hand side of the equation. Equation (7.23) is the evolution equation for the reduced distribution function  $f^{(N)}(\mathbf{x}^{(N)}, t) := f^{(N)}(\mathbf{x}_1^{(N)}, t)$  of subsystem 1. It is the grand canonical ensemble equivalent of (6.31), which, if the meanings of  $N$  and  $\mathbf{N}$  are appropriately interpreted, is in fact isomorphic to (7.23) except for the product sign over  $\{N\}$  in (7.19) for  $\bar{\mathbb{F}}^{(N)}(x^{(N)}, t_i)$ . Note that  $\mathbf{N}$  is a variable distributed over all possible values owing to varying compositions in the case of a grand ensemble.

The evolution equation (7.23) for  $f^{(N)}(\mathbf{x}^{(N)}, t)$  is a generic kinetic equation for subsystems. It is also a member of a hierarchy of kinetic equations, which includes the kinetic equations for subsystem pairs, subsystem triplets, etc. We can also obtain a set of coarse-grained evolution equations for distribution function  $f^{(N)}(\mathbf{x}_k^{(N)}, t)$  as shown in the following.

Since the deduction of closed evolution equations from Eq.(7.23) for a time-coarse-grained distribution function

$$\bar{f}^{(N)}(\mathbf{x}_k^{(N)}, t) = \tau^{-1} \int_0^\tau ds f^{(N)}(\mathbf{x}_k^{(N)}, t+s) \quad (7.24)$$

is completely parallel to the procedure for the generalized Boltzmann equation, (6.48) and (6.49), in Chap. 6, we simply list the kinetic equation for  $\bar{f}^{(N)}(\mathbf{x}^{(N)}, t)$  obtained after twice performing time-coarse graining:

$$\left( \frac{\partial}{\partial t} + \mathbf{L}^{(N)} \right) \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) = \Re[\bar{\mathbb{F}}^{(N)}(x^{(N)}, t)], \quad (7.25)$$

where the collision integral is given by

$$\Re[\bar{\mathbb{F}}^{(N)}(x^{(N)}, t)] = \int dx^{(N-N)} \sum_{\alpha<\beta}^{\nu} (-i) T_{\alpha\beta}^{(N)}(z) \bar{\mathbb{F}}^{(N)}(x^{(N)}, t) \quad (7.26)$$

with  $z = i\epsilon$  and the overbar over the distribution function  $\bar{\mathbb{F}}^{(N)}$  denotes the time averaging in the same sense as (7.24)

$$\bar{\mathbb{F}}^{(N)}(x^{(N)}, t) = \prod_{\{N\} \geq 0, k} \bar{f}^{(N)}(\mathbf{x}_k^{(N)}, t). \quad (7.27)$$

Note that the subsystem index is omitted in the Liouville operator and the reduced distribution function on the left hand side of the kinetic equation. In (7.26)  $\mathcal{T}_{\alpha\beta}^{(N)}(\epsilon)$  stands for the classical transition operator describing many-subsystem (petit ensemble) collisions. It obeys the classical Lippmann–Schwinger equation [4] for scattering operators.<sup>5</sup> See also (6.42) and the related discussion in Chap. 3. It should be noted that, as for pure fluids in Chap. 6, (7.27) requires the assumption that the phases of the product of  $\bar{f}^{(N)}(\mathbf{x}_k^{(N)}, t)$  vanish when time coarse grained, so that (7.27) holds for  $\bar{\mathbb{F}}^{(N)}(x^{(N)}, t)$ .

Equation (7.25) is the generalized Boltzmann equation (GBE) for a mixture of fluids (gases or liquids). It is a closed equation deduced from the Liouville equation for the grand ensemble distribution function. Completely isomorphic to the GBE (6.48) for the canonical ensemble version for a single-component fluid, it is irreversible, breaking the time reversal invariance symmetry characteristic of the Liouville equation. This irreversibility element was introduced in the course of time averaging and emergence of transition operators defined in the complex eigenvalue plane<sup>6</sup> that ends up breaking the time reversal symmetry inherent to the Liouville equation. This is the desired feature of the kinetic equation that allows the formulation of a theory of irreversible thermodynamics and hydrodynamics consistent with the laws of thermodynamics for which the arrow of time is unidirectional. Here we again emphasize that the kinetic equation (7.25) is not derived from the Liouville equation (7.17) by means of mechanics alone. But it rather may be said that it is deduced from the Liouville equation in a manner consistent with the principles of classical mechanics and theory of probability. It should be taken as *a postulate* for the kinetic equation of the time-coarse-grained distribution function  $\bar{f}^{(N)}(\mathbf{x}_k^{(N)}, t)$  whose predictions for macroscopic properties must be verified *a posteriori* against experiments. It represents a closed set of evolution equations for  $\bar{f}^{(N)}$  and produces a thermodynamics theory of irreversible processes and a theory of generalized hydrodynamics attendant on the former, both of which are consistent with the laws of thermodynamics as will be shown.

The collision integral (7.26), as is for the collision integral of the extended Boltzmann kinetic equation (5.52), incorporates two separable ideas for evolution of the assembly of  $N$  particles: (1) weak probabilistic correlations of distribution functions of petit ensembles, which are negligible and (2) dynamical correlations arising from collisions of particles, which are described the collision operator  $\mathcal{T}^{(N)}$  that operates on  $\bar{\mathbb{F}}^{(N)}$  dynamically modifying its phases. We are assuming that the aforementioned

<sup>5</sup> Since the interactions between subsystems (petit ensembles) are through the particles in the peripheries of the subsystems and hence are relatively smaller compared to the total interaction energies, a perturbation treatment of the Lippmann–Schwinger equation for  $\mathcal{T}_{ss'}^{(N)}(\epsilon)$  is quite justifiable and permissible. Nevertheless, we will pursue the present formulation, deferring such an approximation to the last stage where the transport coefficients are calculated.

<sup>6</sup> In this connection, it should be recognized the transition operators are defined in the complex eigenvalue plane, and in fact in the upper positive plane  $\lambda + i\epsilon$ , whereas the Liouville operator  $\mathcal{L}^{(N)}$  has real eigenvalues.

two factors are separable in the collision integral. The first part of the assumption serves as a closure of the set of distribution functions  $\bar{f}^{(N)}$ .

### 7.1.2.1 Basic Properties of the GBE for Mixtures

As is the case for the GBE in the canonical ensemble theory, the time-coarse grained collision integral of (7.25) has the following properties with respect to the collision invariants  $I(\mathbf{r})$  expressed in the form

$$I^{(N)}(\mathbf{r}) = \sum_{a=1}^r \sum_{ja=1}^{N_a} I_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}), \quad (7.28)$$

where  $I_{ja}$  stands for mass, momentum, and energy.

### 7.1.2.2 Condition 1

The  $I^{(N)}(\mathbf{r})$  is a collision invariant of the collision integral (7.26) for which its collision-integral-weighted integral vanishes:

$$\sum_{\{N\} \geq 0} \int d\mathbf{x}^{(N)} \sum_{a=1}^r \sum_{ja=1}^{N_a} I_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \Re[\bar{\mathbb{F}}^{(N)}(x^{(N)}, t)] = 0. \quad (7.C1)$$

### 7.1.2.3 Condition 2

The  $H$ -theorem and the stability condition of equilibrium hold for it:

$$-\sum_{\{N\} \geq 0} \int d\mathbf{x}^{(N)} \ln \bar{f}^{(N)}(\mathbf{x}^{(N)}, t) \Re[\bar{\mathbb{F}}^{(N)}(x^{(N)}, t)] \geq 0 \quad (7.C2)$$

with the equality holding for equilibrium only. At equilibrium reached in long time there holds the equality for the equilibrium condition

$$\Re[\bar{\mathbb{F}}_{\text{eq}}^{(N)}(x^{(N)})] = 0, \quad (7.C2\text{eq})$$

where  $\bar{\mathbb{F}}_{\text{eq}}^{(N)}(x^{(N)})$  is the equilibrium distribution function obeying the GBE.

### 7.1.2.4 Condition 3

The collision integral  $\Re[\bar{\mathbb{F}}^{(N)}(x^{(N)}, t)]$  is evidently invariant under canonical transformations, since the dynamics of molecules is described by Newtonian equations of motion. It is useful to note that the phase volume

$$dx^{(N)} = dp^{(N)} dr^{(N)}$$

is invariant under canonical transformation. Later when collision bracket integrals and transport coefficients are discussed, more details will be given of (7.26). Proof of conditions (7.C1) and (7.C2) is omitted, because it can be shown to proceed in exactly the same way as for conditions (6.C1) and (6.C2).

The first condition guarantees the conservation laws of mass, momentum, and energy. The second condition assures the existence of the Boltzmann entropy satisfying the  $H$  theorem [5] and thereby assuring the stability of the equilibrium solution at equilibrium defined by (7.C2eq). All these conditions enable us to formulate a thermodynamically consistent macroscopic theory of material processes, at least, at the formal theory level. In the subsequent sections we apply the generalized Boltzmann equation for a mixture of monatomic molecules to study various irreversible processes. Throughout this work the phase space average of mechanical quantity  $M(\mathbf{x}^{(N)}, t)$  will be abbreviated with angular brackets as in the formula

$$\langle M(\mathbf{x}^{(N)}, t) f^{(N)} \rangle = \sum_{\{N\} \geq 0} \int d\mathbf{x}^{(N)} M(\mathbf{x}^{(N)}, t) f^{(N)}(\mathbf{x}^{(N)}, t), \quad (7.29)$$

where we have omitted the overbar for the sake of notational brevity

$$f^{(N)}(\mathbf{x}^{(N)}, t) := \bar{f}^{(N)}(\mathbf{x}^{(N)}, t). \quad (7.30)$$

Henceforth,  $f^{(N)}(\mathbf{x}^{(N)}, t)$  stands for the time-coarse-grained distribution function.

## 7.2 Boltzmann Entropy and the $H$ Theorem

For achieving the objective outlined earlier the concept of the Boltzmann entropy and the  $H$  theorem thereof play a crucial role in laying the foundation for the concepts descending from it on which the thermodynamic theory of irreversible thermodynamics for transport processes and hydrodynamics described by the generalized Boltzmann equation, albeit its role is indirect in that the concept of calortropy is introduced in reference to it. Its role is clarified presently.

### 7.2.1 Boltzmann Entropy

The generalized Boltzmann equation (7.25) admits the Boltzmann entropy which satisfies the  $H$  theorem. This theorem makes it possible to show the stability of the equilibrium solution  $f_{\text{eq}}^{(\mathbf{N})} = \bar{f}_{\text{eq}}^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})})$  defined by Condition (7.C2eq), to the details of which we will return later. Following Boltzmann, we define the Boltzmann entropy  $S(t)$  by the statistical mechanical formula

$$S(t) = -k_B \langle f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t) \ln f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t) \rangle, \quad (7.31)$$

where the angular brackets have the same meaning as in (7.29). This global formula suggests the local Boltzmann entropy density  $\mathcal{S}(\mathbf{r}, t)$  in local volume at point  $\mathbf{r}$  may be defined by the integral relation

$$S(t) = \int_V d\mathbf{r} \rho \mathcal{S}(\mathbf{r}, t). \quad (7.32)$$

By using this relation between the global  $S(t)$  and its local density  $\mathcal{S}(\mathbf{r}, t)$  and the exponential representation for  $f^{(\mathbf{N})}$  suggested by the statistical formula (7.31) for  $S(t)$  we find the statistical mechanical expression for the Boltzmann entropy density. To achieve this aim we first observe that it is appropriate to represent  $f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t)$  in an exponential form

$$k_B \ln f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t) = - \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} G_{ja}(\mathbf{x}^{(\mathbf{N})}, t) \delta(\mathbf{r}_{ja} - \mathbf{r}), \quad (7.33)$$

where  $G_{ja}(\mathbf{x}^{(\mathbf{N})}, t)$  is an as-yet-undetermined function of phase  $\mathbf{x}^{(\mathbf{N})}$ , which in principle must be determined as a solution of the kinetic equation GBE, such that  $f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t)$  is normalized in phase space  $\mathbf{x}^{(\mathbf{N})}$ . It should, of course, must satisfy the boundary and initial conditions demanded of the distribution function  $f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t)$ . Inserting (7.33) into (7.31) we obtain

$$S(t) = \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} \langle G_{ja}(\mathbf{x}^{(\mathbf{N})}, t) \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t) \rangle \quad (7.34)$$

suggesting that  $S(t)$  may be expressed as local mean density of  $G_{ja}(\mathbf{x}^{(\mathbf{N})}, t)$ :

$$\rho \mathfrak{G} = \sum_{a=1}^r \sum_{ja=1}^{N_a} \langle G_{ja}(\mathbf{x}^{(\mathbf{N})}, t) \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t) \rangle. \quad (7.35)$$

It should be recalled that written more explicitly

$$\rho\mathfrak{G} = \sum_{\{\mathbf{N}\} \geq 0} \sum_{a=1}^r \sum_{ja=1}^{N_a} \int d\mathbf{x}^{(\mathbf{N})} G_{ja}(\mathbf{x}^{(\mathbf{N})}, t) \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t). \quad (7.36)$$

We remark that  $\rho\mathfrak{G}$  in its present form does not tell us much about the nature of  $S(t)$ . To this end, we look for the evolution equation for the local entropy density.

### 7.2.2 Boltzmann Entropy Balance Equation

Differentiation of Formula (7.34) with time and use of the kinetic equation yields the equation

$$\begin{aligned} \frac{dS(t)}{dt} &= \int_V d\mathbf{r} \frac{\partial}{\partial t} \rho\mathcal{S}(\mathbf{r}, t) \\ &= \int_V d\mathbf{r} [-\nabla \cdot (\mathbf{J}_s + \mathbf{u}\rho\mathcal{S}) + \sigma_{\text{ent}}(\mathbf{r}, t)] \\ &\quad + \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t) \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathcal{D}_t^{(\mathbf{N})} G_{ja}(\mathbf{x}^{(\mathbf{N})}, t) \right\rangle. \end{aligned} \quad (7.37)$$

Here the operator  $\mathcal{D}_t^{(N)}$  is defined by the differential operator

$$\mathcal{D}_t^{(\mathbf{N})} = \frac{d}{dt} + \mathbf{L}^{(\mathbf{N})} + \mathbf{C}_{ja} \cdot \nabla \quad (7.38)$$

with  $d/dt$  denoting the substantial time derivative:

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla, \quad (7.39)$$

and

$$\mathbf{J}_s(\mathbf{r}, t) = \sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle f^{(\mathbf{N})} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathbf{C}_{ja} G_{ja}(\mathbf{x}^{(\mathbf{N})}, t) \right\rangle, \quad (7.40)$$

$$\sigma_{\text{ent}}(\mathbf{r}, t) = \sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle f^{(\mathbf{N})} \delta(\mathbf{r}_{ja} - \mathbf{r}) G_{ja}(\mathbf{x}^{(\mathbf{N})}, t) \Re[\bar{\mathbb{F}}^{(\mathcal{N})}] \right\rangle. \quad (7.41)$$

That is,  $\mathbf{J}_s(\mathbf{r}, t)$  is the Boltzmann entropy flux and  $\sigma_{\text{ent}}(\mathbf{r}, t)$  the Boltzmann entropy production, which is positive semi-definite owing to Condition (7.C2). The last term in (7.37) vanishes by virtue of Condition (7.C2), or rather its special case, since it is possible to show

$$\int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle f^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) D_t^{(N)} G_{ja}(\mathbf{x}^{(N)}, t) \right\rangle = k_B \left\langle \Re[\bar{\mathbb{F}}_{\text{eq}}^{(N)}] \right\rangle = 0. \quad (7.42)$$

Therefore the local balance equation for the Boltzmann entropy density is given by

$$\rho \frac{dS(\mathbf{r}, t)}{dt} = -\nabla \cdot \mathbf{J}_s(\mathbf{r}, t) + \sigma_{\text{ent}}(\mathbf{r}, t), \quad (7.43)$$

where by Condition (7.C2) or the local form of the  $H$  theorem

$$\sigma_{\text{ent}}(\mathbf{r}, t) \geq 0. \quad (7.44)$$

We remark that the  $H$  theorem should be distinguished from the second law of thermodynamics as it was shown to be distinguishable in the case of the Boltzmann equation. For the thermodynamic laws govern the evolution of deterministic macroscopic variables spanning manifolds of a finite number of macroscopic variables, such as fluid velocity, energy (more precisely, internal energy), heat flux, mass diffusion flux, stress tensor, etc., namely, manifold  $\mathfrak{P}$  and their conjugate variables in manifold  $\mathfrak{T}$ , whereas the Boltzmann entropy density  $S(\mathbf{r}, t)$  is a statistical quantity defined and living in the phase space of particles of Avogadro's number in the system. *Therefore, except at equilibrium the Boltzmann entropy  $S(\mathbf{r}, t)$  is not the same as the Clausius entropy, which, by definition, holds only for thermodynamic reversible processes and is subject to the thermodynamic laws and in particular the second law of thermodynamics.* In fact, the second law of thermodynamics is concerned about the thermodynamic stability of a thermodynamic system described by deterministic macroscopic variables in a manifold (space) much contracted in dimension than the phase space in which the distribution functions and the Boltzmann entropy  $S(\mathbf{r}, t)$  reside. It will be found that the Boltzmann entropy does not yield an exact differential form in the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T}$  in which thermodynamic states of a nonequilibrium system evolve.<sup>7</sup> Therefore, the  $H$  theorem is broader than the second law of thermodynamics as a stability theorem for equilibrium. This point will be become evident as we proceed in formulating the theory.

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<sup>7</sup>It should be recalled that the manifold  $\mathfrak{P} \cup \mathfrak{T}$  is of nonequilibrium and a projection of the  $6N$ -dimensional phase space of particles.

The global Boltzmann entropy balance equation corresponding to (7.37) may be split into the exchange and internal part, each representing respectively the exchange of  $S$  between the system and its surroundings and the internal production of  $S$ , which is a manifestation of the energy dissipation as a consequence of interactions between constituent particles:

$$\begin{aligned}\frac{dS}{dt} &= \frac{d_e S}{dt} + \frac{d_i S}{dt} \\ &\geq \frac{d_e S}{dt},\end{aligned}\quad (7.45)$$

where

$$\frac{d_e S}{dt} = - \int_V d\mathbf{r} \nabla \cdot (\mathbf{J}_s + \mathbf{u} \rho \mathcal{S}), \quad (7.46)$$

$$\frac{d_i S}{dt} = \int_V d\mathbf{r} \sigma_{\text{ent}}(\mathbf{r}, t) \geq 0. \quad (7.47)$$

In (7.46) and (7.47) the derivatives  $d_e S/dt$  and  $d_i S/dt$  respectively represent the exchange and dissipative contributions to the total entropy derivative  $dS/dt$ . Therefore, (7.47) may deceptively look like a statistical mechanical representation of the second law of thermodynamics. It will be evident that what we have found out about the nature of the second law of thermodynamics in the case of the Boltzmann equation still holds true for the generalized Boltzmann equation for liquids.

### 7.2.3 Equilibrium Distribution Function

Since at equilibrium

$$\Re[\bar{\mathbb{F}}_{\text{eq}}^{(N)}] = 0 \quad (7.48)$$

and, furthermore, by Condition (7.C2), there holds the equation

$$\int_V d\mathbf{r} \sum_{\{N\} \geq 0} \int d\mathbf{x}^{(N)} \sum_{a=1}^r \sum_{ja=1}^{N_a} I_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \Re[\bar{\mathbb{F}}_{\text{eq}}^{(N)}] = 0, \quad (7.49)$$

where

$$I_{ja} = m_a, \mathbf{p}_{ja}, \text{ or } H_{ja}^{(N)}, \quad (7.50)$$

which are collision invariants, the Boltzmann entropy production vanishes at equilibrium, that is,  $\sigma_{\text{ent}}(\mathbf{r}, t)|_{\text{eq}} = 0$ , and this means that  $f_{\text{eq}}^{(N)}$  must be a linear combination of the collision invariants. Moreover, the listed linear combination of collision

invariants<sup>8</sup> in (7.50) is unique since there are no other linearly independent linear combinations for the monatomic fluid mixture.

It is useful to note that the discussion leading to the uniqueness of  $f_{\text{eq}}^{(\mathbf{N})}$  presented here is one of the important motivations for developing the kinetic theory with the help of the GBE, and it is a feature absent in Gibbs's equilibrium ensemble theory [2]. An additional feature absent in the kinetic theory making use of the Liouville equation is that it does not provide the dissipation terms in the evolution equations for nonconserved variables, whereas the kinetic equation GBE employed here provides molecular theory expressions for the dissipation terms in the evolution equations and concrete dynamical energy dissipation mechanisms, as will be seen later.

The equilibrium distribution  $f_{\text{eq}}^{(\mathbf{N})}$  now can be written in the form

$$f_{\text{eq}}^{(\mathbf{N})} = \exp \left\{ - \int_V d\mathbf{r} \beta_{\text{eq}} [H^{(\mathbf{N})}(\mathbf{r}) - \rho g_e] - \ln \mathbb{Z}_{\text{eq}}^{(\mathbf{N})} \right\}, \quad (7.51)$$

where with  $\mathbf{N} = \sum_{a=1}^r N_a$  and

$$H^{(\mathbf{N})} = \sum_{a=1}^r \sum_{ja=1}^{N_a} H_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}), \quad (7.52)$$

$$g_e = \sum_{a=1}^r c_a \hat{\mu}_a^e, \quad (7.53)$$

and  $\mathbb{Z}_{\text{eq}}^{(\mathbf{N})}$  is the normalization factor defined by

$$\mathbb{Z}_{\text{eq}}^{(\mathbf{N})} = \sum_{\{\mathbf{N}\} \geq 0} c^{-1} \int d\mathbf{x}^{(\mathbf{N})} \exp \left\{ - \int_V d\mathbf{r} \beta_{\text{eq}} [H^{(\mathbf{N})}(\mathbf{r}) - \rho g_e] \right\} \quad (7.54)$$

with<sup>9</sup>  $c = h^{3\mathbf{N}} \mathbf{N}!$ . For notational brevity, the phase integral in (7.54) for  $\mathbb{Z}_{\text{eq}}^{(\mathbf{N})}$  will be abbreviated by the symbol:

$$\mathbb{Z}_{\text{eq}}^{(\mathbf{N})} = \left\langle \exp \left\{ - \int_V d\mathbf{r} \beta_{\text{eq}} [H^{(\mathbf{N})}(\mathbf{r}) - \rho g_e] \right\} \right\rangle. \quad (7.55)$$

<sup>8</sup>If there are angular momenta for the particles, then they must be included to the list shown. Since the external force is assumed to remain unchanged over the elementary volume around the position  $\mathbf{r}$ , the external potential energy  $U_a^{(ex)}$  per molecule may be added to the particle Hamiltonian  $H_{ja}''$ .

<sup>9</sup>It should be noted that this factor  $c$  can be disposed of with no effect on the theory formulated in the present formulation.

Since the variables such as  $\beta_{\text{eq}} = 1/k_B T_{\text{e}}$  and equilibrium chemical potentials  $\hat{\mu}_a^{\text{e}}$  are uniform in space if the system is in equilibrium the volume integral in (7.54) may be simply replaced with  $V\beta_{\text{eq}}(H^{(\text{N})} - \rho g_{\text{e}})$ .

The equilibrium state described by  $f_{\text{eq}}^{(\text{N})}$  in the phase space is stable and the variation of the Boltzmann entropy is a Lyapounov function [6, 7] in the following sense. First, define

$$\delta S = S(t) - S_{\text{e}}, \quad (7.56)$$

where  $S_{\text{e}}$  is defined by

$$S_{\text{e}} = -k_B \left\langle f^{(\text{N})} \ln f_{\text{eq}}^{(\text{N})} \right\rangle. \quad (7.57)$$

Then, by Klein's inequality

$$\delta S \leq 0 \quad (7.58)$$

whereas by virtue of the  $H$  theorem and under the assumption that there is no contribution from the boundary term

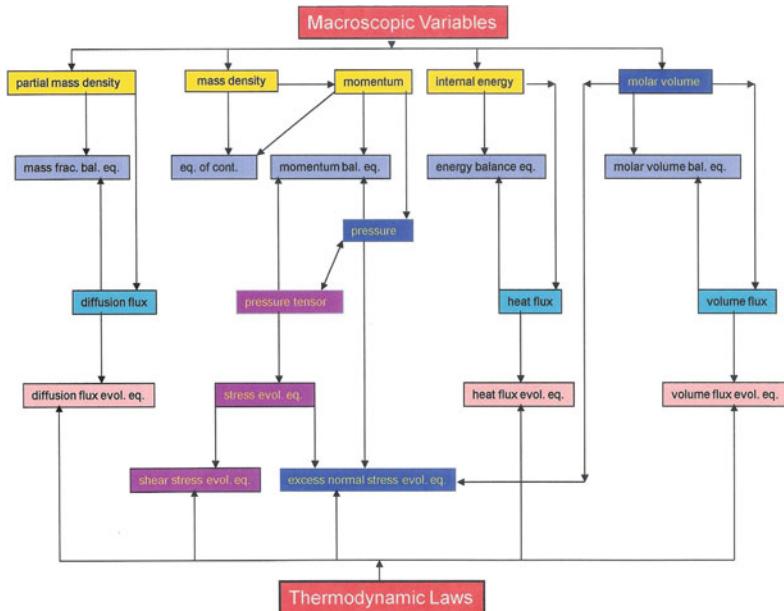
$$\frac{d\delta S}{dt} \geq 0. \quad (7.59)$$

This means that  $\delta S$  may be regarded as a Lyapounov function and the state characterized by  $f_{\text{eq}}^{(\text{N})}$  is a stable stationary state asymptotically approached in time from a nonequilibrium state in the phase space. This shows that the  $H$  theorem is a stability theorem of the equilibrium solution of the kinetic equation in the sense of Lyapounov, but not a statistical mechanical representation of the second law of thermodynamics. Inequality (7.59) just happens to coincide with the second law of thermodynamics in the case of the system at equilibrium.

The kinetic equation postulated implies macroscopic evolution equations including balance equations for conserved variables—conservation laws—and macroscopic observables, which may be formally calculated therewith. They are calculated in the following sections.

### 7.3 Conserved Variables

In mechanics, there are three basic (primitive) building blocks of physical concepts of mass, momentum, and energy. In macroscopic physics involving a large number of particles, in addition to the aforementioned three basic physical quantities, we find it necessary to pay close attention to the concept of molecular domains in the scale smaller than the global spatial scale in which the globally averaged mean density is characterized. We would find such a volume representable by the *Voronoi* volume



**Fig. 7.1** Flow chart for moments giving rise to various macroscopic evolution equations displayed at different levels of tensorial order in different shades of color. The evolution equations at the level of diffusion flux, shear stress, excess normal stress, heat flux, and volume flux evolution equations are subjected to the laws of thermodynamics, so that they are made thermodynamically consistent

characteristic of the molecular volume<sup>10</sup> in condensed phase. It therefore is necessary to add the mean Voronoi volume (molar volume) to the aforementioned basic set. The subsequent members of the set is then possible to generate unambiguously and systematically starting from the basic four members of the set, if the kinetic equation, more specifically, the Liouville operator comprising the kinetic equation, is made use of to derive the evolution equations for the mean macroscopic variables appearing therein. This way, a hierarchy of evolution equations is obtained in the form of Eq. (7.80) given below. The hierarchy is depicted figuratively in Fig. 7.1.

Owing to Condition (7.C1), the GBE implies the conservation laws of mass, momentum, and energy. The balance (evolution) equations can be derived for them by differentiating their appropriate statistical mechanical average and then making use of the generalized Boltzmann equation (GBE), (7.25), for the mixture of interest. The conserved variables, namely, mass density, mass fractions, momentum, and internal energy, are defined by the statistical mechanical averages of the molecular

<sup>10</sup>In the traditional description of hydrodynamic processes the concept of molar volume or, simply, volume assignable to each particle appears in the form of specific volume  $v_{sp} = 1/\rho$ , where  $\rho$  is mass density. However, this specific volume is not equal to the molar volume per particle at all densities of the fluid [11]. It becomes the molar volume at the limit of low density. Therefore it is reasonable to count the molar volume among the macroscopic variables at the same level as density, momentum, energy, etc. used for hydrodynamic description of flow processes.

expressions of the aforementioned quantities. The macroscopic variables in this class are density-homologues that begins with the mass density:

**Mass Density of Species  $a$**  The species mass density is defined by

$$\rho_a(\mathbf{r}, t) = \sum_{ja=1}^{N_a} \langle m_a \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \rangle. \quad (7.60)$$

**Mass Density** The total mass density is defined by

$$\begin{aligned} \rho(\mathbf{r}, t) &= \sum_{a=1}^r \rho_a(\mathbf{r}, t) \\ &= \sum_{a=1}^r \sum_{ja=1}^{N_a} \langle m_a \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \rangle. \end{aligned} \quad (7.61)$$

**Momentum Density** The momentum density is defined by

$$\begin{aligned} \rho\mathbf{u}(\mathbf{r}, t) &= \sum_{a=1}^r \rho_a \mathbf{u}_a(\mathbf{r}, t) \\ &= \sum_{a=1}^r \sum_{ja=1}^{N_a} \langle m_a \mathbf{v}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \rangle, \end{aligned} \quad (7.62)$$

In (7.62)  $\mathbf{u}_a(\mathbf{r}, t)$  is the mean velocity of species  $a$ . From this mode of definition the mean fluid velocity  $\mathbf{u}$  may be interpreted as an average of mean species velocities:

$$\mathbf{u}(\mathbf{r}, t) = \sum_{a=1}^r c_a \mathbf{u}_a(\mathbf{r}, t), \quad (7.63)$$

where  $c_a = \rho_a / \rho$  is the mass fraction of species  $a$ .

**Internal Energy Density** The internal energy density is defined by

$$\begin{aligned} \rho\mathcal{E}(\mathbf{r}, t) &= \sum_{a=1}^r \rho_a \mathcal{E}_a(\mathbf{r}, t) \\ &= \sum_{a=1}^r \sum_{ja=1}^{N_a} \langle H'_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \rangle. \end{aligned} \quad (7.64)$$

By differentiating the conserved variables with time and making use of the GBE the following equations for the conserved variables are obtained:

$$\partial_t \rho = -\nabla \cdot (\rho \mathbf{u}) \text{ or } \rho d_t v = \nabla \cdot \mathbf{u} \quad (v = 1/\rho), \quad (7.65)$$

$$\rho d_t \mathbf{c}_a = -\nabla \cdot \mathbf{J}_a, \quad (7.66)$$

$$\rho d_t \mathbf{u} = -\nabla \cdot \mathbf{P} + \rho \widehat{\mathbf{F}}, \quad (7.67)$$

$$\rho d_t \mathcal{E} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a, \quad (7.68)$$

where various symbols are defined as follows:  $\mathbf{J}_a$  is the diffusion flux of species  $a$ ;  $\mathbf{P}$  is the pressure (stress) tensor, which may be regarded as the momentum flux;  $\mathbf{Q}$  is the heat flux, which is the flux of internal energy;  $\widehat{\mathbf{F}}$  is the external force per unit mass of the mixture; and  $\widehat{\mathbf{F}}_a$  is the external force on species  $a$  per unit mass

$$\rho \widehat{\mathbf{F}} = \sum_{a=1}^r \rho_a \widehat{\mathbf{F}}_a. \quad (7.69)$$

The nonconserved variables, such as  $\mathbf{J}_a$ ,  $\mathbf{P}$ ,  $\mathbf{Q}$ , etc., are defined by the statistical mechanical averages given below:

$$\mathbf{J}_a = \sum_{ja=1}^{N_a} \langle m_a \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \rangle, \quad (7.70)$$

$$\mathbf{P} = \sum_{a=1}^r \mathbf{P}_a = \mathbf{P}^{(k)} + \mathbf{P}^{(v)} = \sum_{a=1}^r (\mathbf{P}_a^{(k)} + \mathbf{P}_a^{(v)}), \quad (7.71)$$

$$\mathbf{P}_a^{(k)} = \sum_{ja=1}^{N_a} \langle m_a \mathbf{C}_{ja} \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \rangle, \quad (7.72)$$

$$\mathbf{P}_a^{(v)} = \frac{1}{2} \sum_{b=1}^r \sum_{ja \neq kb=1}^{N_a, N_b} \langle \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \rangle, \quad (7.73)$$

$$\mathbf{W}_{jakb} = \int_0^1 d\lambda \mathbf{r}_{jakb} \mathbf{F}_{jakb} \exp(-\lambda \mathbf{r}_{jakb} \cdot \nabla), \quad (7.74)$$

and

$$\mathbf{Q} = \sum_{a=1}^r \mathbf{Q}_a = \mathbf{Q}^{(k)} + \mathbf{Q}^{(v)} = \sum_{a=1}^r (\mathbf{Q}_a^{(k)} + \mathbf{Q}_a^{(v)}) \quad (7.75)$$

$$\mathbf{Q}_a^{(k)} = \sum_{ja=1}^{N_a} \langle H'_{ja} \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \rangle, \quad (7.76)$$

$$\mathbf{Q}_a^{(v)} = \frac{1}{2} \sum_{b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \langle \mathbf{W}_{jakb} \cdot \mathbf{C}_{ja} \delta(\mathbf{r}_{kb} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \rangle. \quad (7.77)$$

It is helpful to make some remarks on the definitions of the various macroscopic variables given above. First of all, these statistical mechanical definitions are not arbitrary and at our disposal, but are naturally led to the forms given above when the derivations of mass, momentum, internal energy, etc. are made in manner consistent with the phenomenological conservation laws. Their derivations begin with the most obvious definition of mass density and the internal energy in the light of Newtonian mechanics. Then the derivations of the rest of evolution equations logically follow from the particulate theory viewpoint of matter together with the statistical mechanical mean velocity formula, which are listed in (7.65)–(7.77). Given the kinetic equation GBE, these statistical mechanical definitions are not only unique, but also independent of the collision term present in the kinetic equation.

It would be also helpful to note in connection with the definition of the virial tensor operator  $\mathbf{W}_{jakk}$  the following identity [3, 8] regarding the Dirac delta functions:

$$\delta(\mathbf{r}_{ja} - \mathbf{r}) - \delta(\mathbf{r}_{kb} - \mathbf{r}) = -\nabla \cdot \int_0^1 d\lambda \mathbf{r}_{jakk} \exp(-\lambda \mathbf{r}_{jakk} \cdot \nabla) \delta(\mathbf{r}_{kb} - \mathbf{r}), \quad (7.78)$$

where  $\mathbf{r}_{jakk} = \mathbf{r}_{ja} - \mathbf{r}_{kb}$ . Note that the exponential operator in (7.78) is a displacement operator acting on the operand on its right. The identity (7.78) is the mixture version of Identity (6.80) and will be frequently made use of in the derivations of evolution equations in this chapter. We note that the mixture version of the virial tensor operator  $\mathbf{W}_{jakk}$  is completely parallel to its pure fluid version in Sect. 6.3.2 of Chap. 6.

## 7.4 Nonconserved Variables and Their Evolution Equations

The balance equations for the conserved variables derived earlier contain the nonconserved variables such as  $\mathbf{J}_a$ ,  $\mathbf{P}$ , and  $\mathbf{Q}$ , although they do not have dissipation terms owing to the fact that the conserved variables do not dissipate energy in the course of their evolution. The nonconserved variables obey their own evolution equations, and these evolution equations can be derived from the kinetic equation GBE in the same manner as for the balance equations for the conserved variables except that the balance equations contain a source term responsible for energy dissipation in the course of evolution of the nonconserved variables. As is for pure liquids, this feature is a major difference between the evolution equations of conserved and nonconserved variables and the reason for the terminology nonconserved variables used in this work. Their derivations are more involved than for the conserved variables. Nevertheless, the derivations are mathematically straightforward. Compare the evolution equations with their pure fluid counterparts in Chap. 6.

**Table 7.1** Terminology for symbols  $\Phi_a^{(q)}$ 

Terminology	Symbol	Hydrodynamic symbol
Volume fluctuation	$\Phi_a^{(0)}$	$v - v_0$
Mass flux	$\Phi_a^{(1)}$	$\mathbf{J}_a$
Volume flux	$\Phi_a^{(2)}$	$\mathcal{F}_{\Omega a}$
Heat flux	$\Phi_a^{(3)}$	$\mathbf{Q}'_a = \mathbf{Q}_a - \hat{h}_a \mathbf{J}_a$
Shear stress	$\Phi_a^{(4)}$	$\boldsymbol{\Pi}_a$
Excess normal stress	$\Phi_a^{(5)}$	$\Delta_a = \text{Tr} \mathbf{P}_a - p/\rho_a$

### 7.4.1 Generic Form of Evolution Equations

We define the generic form of the nonconserved variables by the formula

$$\Phi_a^{(q)} = \rho \widehat{\Phi}_a^{(q)} := \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (7.79)$$

where  $h_{ja}^{(q)}$  is the molecular expression of the nonconserved moment; the examples for them can be found in the definitions of the pressure tensor, heat flux, and diffusion flux presented earlier. See Table 7.1 for the names of  $\Phi_a^{(q)}$ . The evolution equation for the density  $\widehat{\Phi}_a^{(q)}$  of nonconserved variable  $\Phi_a^{(q)}$  is formally expressible in the generic form

$$\rho d_t \widehat{\Phi}_a^{(q)} = -\nabla \cdot \psi_a^{(q)} + \mathcal{Z}_a^{(q)} + \Lambda_a^{(q)}, \quad (7.80)$$

where  $\psi_a^{(q)}$  may be regarded as the flux of  $h_{ja}^{(q)}$ ;  $\mathcal{Z}_a^{(q)}$  is called the kinematic term; and  $\Lambda_a^{(q)}$  is the dissipation term which is the seat of energy dissipation arising during the evolution process of  $\widehat{\Phi}_a^{(q)}$ . Such variables will be more specifically discussed in the subsequent sections where the generalized hydrodynamic equations underlying irreversible processes in the fluid are derived; see Sects. 7.5 and 7.6 below. The dissipation term  $\Lambda_a^{(q)}$  arises because  $h_{ja}^{(q)}$  are not collision invariants of the collision term  $\mathfrak{R}[\overline{\mathbb{F}}^{(N)}]$  of the GBE. As will be seen, the presence of the collision term in the kinetic equation is crucial to account for dissipative processes in nonequilibrium fluids and the consistency of the generalized hydrodynamic theory with the thermodynamic laws. It is important to recognize that such a dissipation term would not arise if the Liouville equation for an isolated system were used to derive the evolution equation à la Irving–Kirkwood method [9]. The present approach to the macroscopic theory of irreversible processes gives rise to an open hierarchy of evolution equations as in most of molecular theories, and for this reason the hierarchy must be closed on the basis of suitable mathematical approximations or physical assumptions. Consequently, the resulting theory and its limit of validity must be tested against experiment. This requirement, however, would be necessary for any mathematical (statistical

mechanical) theory of macroscopic processes in nature, which is based on molecular theory models in the form of kinetic equation.

The nonconserved variable defined by the statistical mechanical formula (7.79) and obeying (7.80) has the statistical mechanical formulas for the flux, kinematic term, and dissipation term as follows:

$$\psi_a^{(q)} = \sum_{ja=1}^{N_a} \left\langle \mathbf{C}_{ja} h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t) \right\rangle, \quad (7.81)$$

$$\mathcal{Z}_a^{(q)} = \sum_{ja=1}^{N_a} \left\langle f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t) \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathcal{D}_t^{(\mathbf{N})} h_{ja}^{(q)} \right\rangle, \quad (7.82)$$

$$\Lambda_a^{(q)} = \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \Re[\bar{\mathbb{F}}^{(\mathcal{N})}] \right\rangle. \quad (7.83)$$

In (7.82) differential operator  $\mathcal{D}_t^{(\mathbf{N})}$  is the mixture version of  $\mathcal{D}_t$  in (6.133):

$$\mathcal{D}_t^{(\mathbf{N})} = d_t + \mathbf{L}^{(\mathbf{N})} + \mathbf{C}_{ja} \cdot \nabla. \quad (7.84)$$

The virial tensor operator  $\mathbf{W}_{jakk}$  in the potential part of the pressure tensor  $\mathbf{P}^{(v)}$  and also in the non-classical part  $\mathbf{Q}^{(v)}$  of heat flux  $\mathbf{Q}$  is a tensor operator associated with the intermolecular interactions; see (6.76) in Chap. 6. For inhomogeneous fluids the tensor operator  $\mathbf{W}_{jakk}$  will play important roles in transport processes, contributing non-classical contributions not seen in the conventional theory of linear transport processes as we have seen in Chap. 6.

The conservation law of orbital angular momentum can be deduced by using the momentum balance equation. In fact, the orbital angular momentum is conserved if the pressure tensor is symmetric [8]. Indeed, for simple fluids the pressure tensor defined by (7.71)–(7.73) is symmetric owing to the spherical symmetry of intermolecular forces. Thus the orbital angular momentum conservation is simply stated by the equation

$$\mathbf{P} = \mathbf{P}^t, \quad (7.85)$$

where  $t$  denotes the transpose of the tensor. The set of evolution equations—the conservation laws and the generic nonconserved variable evolution equation (7.80)—is called generalized hydrodynamic equations, because they generalize the classical Navier–Stokes hydrodynamic equations [10] to nonlinear regime as will be discussed later.

### 7.4.2 Physically Most Relevant Nonconserved Moments

In the previous subsection we have shown a homologous series of conserved and nonconserved moments systematically descend from the seed element. In the case of the homologous series presented in the previous section, the mass density itself is a conserved moment. It has given rise to an open set of moments including nonconserved moments. This scheme, however, gives rise to an incomplete set of macroscopic moments to describe irreversible behavior of the matter of interest because it fails to include the moments homologous to the volume per molecule among the macroscopic observables necessary to properly describe the fluid behavior in general. In the traditional approach to irreversible behavior of matter the volume homologues of variables were not taken into consideration, but their absence leaves out an important and interesting aspect of fluid behavior in its description.

To remedy this unfortunate oversight we introduce *the concept of volume per molecule of each species and its molecular representation* as we have in Chap. 6. In this connection, we note that the conventionally used notion for molar volume, namely, the specific volume defined by the inverse density of the fluid, does not sufficiently well represent molar volume, because it does not have its own molecular representation like other macroscopic variables, such as momentum density, internal energy density, stress tensor, etc., all of which have their own unique molecular representations with which their statistical mechanical (i.e., molecular theoretical) mean values can be calculated. We recall that in the case of pure simple fluids we were able to introduce the Voronoi volume [11] per molecule to define the molar volume per molecule in the fluid in a nonequilibrium condition in general, and it had its homologues of macroscopic variables as shown in Chap. 6. Here we argue that the same method can be applied to the case of a fluid mixture. For the purpose we consider the Voronoi volume per molecule for a fluid mixture.

#### 7.4.2.1 Voronoi Volume in a Simple Fluid Mixture

The result established in Chap. 6 can be simply taken over if the index for molecule  $j$  is replaced by the index  $ja$  for molecule  $j$  belonging to species  $a$  according to the system of notations adopted in this chapter for a mixture and the sum over  $j$  is replaced by sums over species  $a$  as well, and similarly for other particle indices. The vertices of the Voronoi polyhedron will now be characterized by different particles belonging to different species. Regardless of whether the fluid is pure or a mixture, there will be nearest neighbors distributed around the center molecule of a species, although the probabilities of finding particular species among them would depend on characteristic dynamics of different molecular species subjected to different interaction laws. These particular distributions of particles in the neighboring sets will be determined by the kinetic equation for the distribution functions. The vertices  $\alpha$  thus depend on position vectors of different species. Nevertheless, given a particular distribution of nearest neighbors with regard to their positions and species the Voronoi volume for molecule

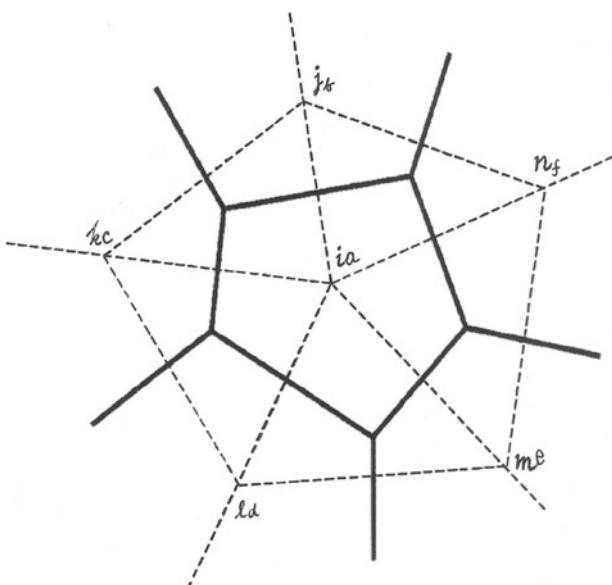
$ja$  would be formally the same as the one given in (6.89) of Chap.6. Thus we obtain the molecular representation of Voronoi volume per molecule. A Voronoi volume can be regarded as the sum of constituent tetrahedra whose bases are triangles consisting of the polygons of the Voronoi polyhedra. The volumes of tetrahedra  $\Omega_{\alpha\beta}^{(j)}$  are given with the formula

$$\Omega_{\alpha\beta}^{(j_a)} = \frac{1}{6} \begin{vmatrix} x_{\alpha}^{(j_a)} & y_{\alpha}^{(j_a)} & z_{\alpha}^{(j_a)} \\ x_{\alpha+\beta}^{(j_a)} & y_{\alpha+\beta}^{(j_a)} & z_{\alpha+\beta}^{(j_a)} \\ x_{\alpha+\beta+1}^{(j_a)} & y_{\alpha+\beta+1}^{(j_a)} & z_{\alpha+\beta+1}^{(j_a)} \end{vmatrix}, \quad (7.86)$$

where indices  $\alpha < \beta \in \eta_{j_a}$  label the vertex positions of polyhedron  $\Omega^{(j_a)}$  of molecule  $ja$ , which depend on positions and species of molecules at the vertices. Given a distribution of particles and their species the molecular position and species dependence can be precisely determined. Here, in the case of two dimensions (see Fig. 7.2 for a two-dimensional rendering of  $\Omega^{(j_a)}$ ),  $x_{\alpha}^{(j_a)}$  stands for the distance between the vertices, namely,  $ib$  ( $i \in b$  at vertex  $\alpha$ ) and  $ja$  particle constituting the polygon surrounding molecule  $j \in a$

$$x_{\alpha}^{(j_a)} := (\mathbf{r}_{\alpha}^{ja} - \mathbf{r}_{\alpha}^{ia})_x \text{ component,}$$

$\mathbf{r}_{\alpha}^{ia}$  = coordinate vector of the center molecule.



**Fig. 7.2** Two-dimensional rendering of Voronoi volume for a mixture. At vertices particles of different species are located in this figure

The vector  $\mathbf{r}_\alpha^{ia}$  varies from point to point and also with time and nonuniformity in space if the fluid is in nonequilibrium. The volume of the pyramid (tetrahedron) whose base is the polygon (triangle)  $p_{ja}$  with the apex at the center  $O$  of the Voronoi polyhedron is then given by

$$\Omega_{ja} = \sum_{\alpha < \beta \in \eta_{ja}} \Omega_{\alpha\beta}^{(ja)} \quad (7.87)$$

and hence the volume of the polyhedron by the sum of the tetrahedral volumes

$$\Omega = \sum_{a=1}^r \sum_{ja=1}^{N_a} \Omega_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) = \sum_{a=1}^r \sum_{ja=1}^{N_a} \sum_{\alpha < \beta \in \eta_{ja}} \Omega_{\alpha\beta}^{(ja)} \delta(\mathbf{r}_{ja} - \mathbf{r}). \quad (7.88)$$

We remark that (7.88) requires the implicit assumption that the polyhedron is convex. Regardless of whether the fluid is in equilibrium or nonequilibrium,  $\Omega$  is a function of the relative distance vector  $\mathbf{r}_{ibja}^\alpha = \mathbf{r}_\alpha^{ja} - \mathbf{r}_\alpha^{ib}$ . If the fluid is in equilibrium, we obtain the equilibrium Voronoi volume  $\bar{v}_{vo}^{(eq)}$  by taking average of  $\Omega$  with the equilibrium configuration distribution function  $g_{eq}^{(N)}(\mathbf{x}^{(N)})$  of the fluid:

$$n\bar{v}_{vo}^{(eq)} = \sum_{a=1}^r \sum_{ja=1}^{N_a} \langle \Omega_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) g_{eq}^{(N)}(\mathbf{r}^{(N)}) \rangle, \quad (7.89)$$

where  $\mathbf{r}^{(N)}$  stands for the totality of position coordinates of  $N$  particles in  $V$ . Since computation of this average is not simple, we may employ an alternative, but simpler route available in the literature<sup>11</sup> to calculate  $\bar{v}_{vo}$  in practice without directly using a distribution function. However, the present distribution function method suffices for our purpose of developing macroscopic evolution equations related to the Voronoi volume.

If the fluid is in nonequilibrium, the nonequilibrium distribution function must be taken to perform the averaging. The nonequilibrium version of (7.89) may be written as

$$\begin{aligned} \rho\hat{v}(\mathbf{r}, t) &:= n\bar{v}_{vo}(\mathbf{r}, t) \\ &= \sum_{a=1}^r \sum_{ja=1}^{N_a} \langle \Omega_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{r}^{(N)}, t) \rangle \\ &= \sum_{a=1}^r \rho_a \hat{v}_a(\mathbf{r}, t), \end{aligned} \quad (7.90)$$

where  $\hat{v}(\mathbf{r}, t)$  is defined as the molar volume density; in other words, molar volume per unit mass density. This may be regarded as the ratio of the mean Voronoi volume to the specific volume. These two quantities are identical in the equilibrium state of the

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<sup>11</sup>See, for example, Refs. [21] and [23] quoted in Chap. 6.

fluid, but not equal to each other if the system is in a nonequilibrium state [11]. Molar volume  $\rho\hat{v}(\mathbf{r}, t)$  may be further decomposed into partial molar volumes  $\hat{v}_a(\mathbf{r}, t)$  of the fluid in nonequilibrium. In any case, the nonequilibrium molar volume  $\rho\hat{v}(\mathbf{r}, t)$  is not a conserved quantity, because  $\Omega_{ja}$  is not a collision invariant with respect to

the collision integral  $\mathfrak{R}[\mathcal{F}^-(x^{(N)}, t)]$  of the GBE, because evidently  $\Omega_{ja}$  does not remain invariant on completion of the collision process of the constituent members of the ensemble. We will see this aspect better when we examine the evolution equations of the volume-homologues of macroscopic variables.

## 7.5 Set of Macroscopic Moments

Nonequilibrium states of a fluid are described by the spatial and temporal evolutions of the macroscopic observables representative of the processes of interest. Generally, such macroscopic observables consist of conserved variables such as the density, volume, velocity or momentum, and internal energy in the case of monatomic fluids and, if the fluid consists of molecular species other than monatomic molecules, other conserved variables such as the angular momentum may be included among the conserved variable set. This set of variables is supplemented with the addition of nonconserved variables such as pressure tensor, heat flux, diffusion fluxes of species, in the traditional 13-moment formulation [3, 8, 12], but in the present work we will also add additional nonconserved variables such as the Voronoi (molar) volume and the related flux of volume and possibly the related to the set of nonconserved observables. Therefore the entire set of observables is enlarged by macroscopic variables related to the (molar) volume and the related variables beyond the traditional notion of the macroscopic variable set in the continuum theory of matter. The molecular expressions of this macroscopic observable set will be called simply the moments. Thus the  $q$ th member appearing in the set, called the  $q$ th moment, will be denoted

$$\bar{h}_{ja}^{(q)} = m_a h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}). \quad (7.91)$$

Here  $h_{ja}^{(q)}$  is then the  $q$ th moment per unit mass of species  $a$ . Thus, taking average with the distribution function  $f^{(N)}(\mathbf{x}^{(N)}, t)$  obeying a kinetic equation, e.g., the GBE, we obtain the corresponding macroscopic observable denoted by  $\Phi^{(q)}$  as the  $q$ th element of the set of macroscopic observables:

$$\Phi_a^{(q)} = \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (7.92)$$

$$\begin{aligned} \Phi^{(q)} &= \rho \widehat{\Phi}^{(q)} = \sum_{a=1}^r \rho_a \widehat{\Phi}_a^{(q)} \\ &= \sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \end{aligned} \quad (7.93)$$

In (7.93)  $\widehat{\Phi}^{(q)}$  is the density of  $\Phi^{(q)}$  defined by the relation

$$\widehat{\Phi}^{(q)} := \frac{1}{\rho} \Phi^{(q)} = \frac{1}{\rho} \sum_{a=1}^r \rho_a \widehat{\Phi}_a^{(q)} = \sum_{a=1}^r c_a \widehat{\Phi}_a^{(q)}, \quad (7.94)$$

where  $c_a = \rho_a / \rho$  is the mass density fraction of  $a$ , an expression for concentration. With this preparation various moments and corresponding observables are defined in the following.

### 7.5.1 Conserved Moments

#### 7.5.1.1 Mass Density

The molecular moment for the mass density at position  $\mathbf{r}$  is given by

$$m_a \delta(\mathbf{r}_{ja} - \mathbf{r}). \quad (7.95)$$

On taking statistical average, it gives rise to the partial mass density  $\rho_a$  of species  $a$ :

$$\rho_a = \sum_{ja=1}^{N_a} \left\langle m_a \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \quad (7.96)$$

If the partial mass density  $\rho_a$  is summed over all species, we obtain the total mass density of the mixture:

$$\rho = \sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle m_a \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \quad (7.97)$$

Division of the partial mass density  $\rho_a$  by fluid mass density  $\rho$  yields mass density fraction  $c_a$  mentioned earlier:

$$c_a = \frac{\rho_a}{\rho}. \quad (7.98)$$

The mass density fraction serves as the concentration variable of species  $a$  of the mixture.

As will be seen, these scalar conserved moments  $c_a$  and  $\rho$ , with the help of the GBE, give rise, respectively, to the mass fraction balance equation and the equation of continuity, provided that the statistical formulas for their fluxes in the moving coordinate system are identified with either the fluid velocity, namely, the mean velocity of the fluid in the case of the equation of continuity, or the mass diffusion flux relative to the fluid velocity in the mass density fraction balance equation. We remark, on a point of observation, that in the present scheme of theory, once the conserved moment for mass is given as a molecular definition on the basis of physical grounds the entire hierarchy of observables beginning with the seed moment, for example, such as mass density of species  $a$ , is systematically and uniquely deducible together with their evolution equations within the framework of the kinetic equation postulated in this work. And similarly for the volume fluctuation as a seed moment. In this connection, it should be also remarked that the Liouville operator, as the generator of the homologous moment sets, determines the molecular details of the evolution equations more than anything else.

### 7.5.1.2 Momentum Density (Velocity)

The vectorial elements appearing as the next members of the evolution equations in the homologue of moments beginning with the mass moment acting as the seed moment are: the velocities, partial and total, and the diffusion flux of the species and thereafter the heat flux, if no other higher-order vectorial moments are taken into consideration. The first two are defined by the statistical mechanical averages by the formulas

$$\rho\mathbf{u} = \sum_{a=1}^r \rho_a \mathbf{u}_a = \sum_{a=1}^r \sum_{ja=1}^{N_a} \langle m_a \mathbf{v}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \rangle \quad (7.99)$$

and

$$\mathbf{J}_a = \sum_{ja=1}^{N_a} \langle m_a \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \rangle, \quad (7.100)$$

where  $\mathbf{C}_{ja}$  is the peculiar velocity of particle  $j \in a$  defined relative to the mean velocity  $\mathbf{u}$  of the fluid by formula

$$\mathbf{C}_{ja} = \mathbf{v}_{ja} - \mathbf{u}. \quad (7.101)$$

The symbol  $\mathbf{u}_a$  in (7.99) is the mean velocity of species  $a$  in the mixture. As can be recognized later when the evolution equations are derived using the kinetic equations (e.g., GBE), the vectorial moments just introduced, momentum density  $\rho\mathbf{u}$  and diffusion flux  $\mathbf{J}_a$ , are defined naturally in the course of deriving the evolution equations

of mass density and mass fraction density by demanding that the kinetic equation produce, respectively, the equation of continuity and the mass fraction balance equation in the light of phenomenological theory of mechanics of continua [13]. In this sense, there is no room for arbitrariness in the definitions of macroscopic variables from the standpoint of the theory of irreversible processes once the seed moment is given on the obvious physical grounds. They are unique within the framework of the kinetic theory employed.

### 7.5.1.3 Internal Energy

The next member of the hierarchy in the mass homologue of molecular moments is a scalar that consists of a contracted second rank dyadic, which we call the internal energy density  $\mathcal{E}$ . It is defined by the statistical mechanical average of the Hamiltonian of a kinetic energy relative to the mean velocity of the moving fluid:

$$\rho\mathcal{E} = \sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle \left( \frac{1}{2} m_a C_{ja}^2 + U_{ja} \right) \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (7.102)$$

where  $U_{ja}$  is the potential energy of particle  $ja$ . The internal energy is not as primitive as the density or mass density, since it is defined as the energy of the system in a moving coordinate system relative to the fluid velocity  $\mathbf{u}$ . In this sense, its definition is anthropomorphic<sup>12</sup> to the extent it is intimately related to the fundamental concept of heat whose precise statistical mechanical meaning changes, depending on what is precisely meant by the internal energy from the mechanical viewpoint. The potential energy  $U_{ja}$  may be often expressed by an approximate representation consisting of the pairwise additive potentials in which case we have

$$U_{ja} = \frac{1}{2} \sum_{ja \neq kb=1}^{N_b} U_{jakb} (\mathbf{r}_{ja} - \mathbf{r}_{kb}). \quad (7.103)$$

We will abbreviate the internal energy Hamiltonian of particle  $ja$  by the symbol  $H'_{ja}$

$$H'_{ja} = \frac{1}{2} m_a C_{ja}^2 + \frac{1}{2} \sum_{ja \neq kb=1}^{N_b} U_{jakb} (\mathbf{r}_{ja} - \mathbf{r}_{kb}). \quad (7.104)$$

It should be noted that it is not necessary to assume the pairwise additive potential model for the interaction potential energy. Even if many-body potentials are included,

<sup>12</sup>The histocial evolution of the concept of energy and heat has taken a considerably winding path, which is intimately tied with the development of thermodynamics. For histocial account of the concept of energy and heat, see S.G. Brush, *The Kind of Motion We Call Heat* (North-Holland, Amsterdam, 1976), vols. 1 and 2.

the formalism developed in this work would not fundamentally altered. In this work, for the simplicity's sake we will take pairwise additive potentials only.

Using the expression for the internal energy density in (7.102) and the GBE for kinetic equation we are led, uniquely, to the expression for the heat flux upon comparison of the statistical mechanical energy balance equation with the phenomenological and continuum mechanical version [13] of the internal energy balance equation. It has the statistical mechanical form

$$\begin{aligned} \mathbf{Q} = & \sum_{a=1}^r \sum_{ja=1}^{N_a} \langle \mathbf{C}_{ja} H'_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \rangle \\ & + \frac{1}{2} \sum_{a,b=1}^r \sum_{ja \neq ka=1}^{N_a, N_b} \langle f^{(N)}(\mathbf{x}^{(N)}, t) \mathbf{C}_{ja} \cdot \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) \rangle, \end{aligned} \quad (7.105)$$

which clearly can be interpreted as the flux consisting of internal energy and virial—a mechanical work. This latter part of  $\mathbf{Q}$ , namely, the flux of virial, is not obvious in the phenomenological theory in which one might simply think that heat flow is a flow of mechanical energy in the form of Hamiltonian as the mechanical theory of heat suggests. However, it is not as simple as that in the molecular theory. Therefore, the present form of heat flux given in (7.105) must be regarded as an important dividend from the molecular theory, namely, the kinetic theory of matter we are formulating here. It is convenient to define the abbreviating symbol

$$\mathcal{H}_{ja}^{(h)} := H'_{ja} + \frac{1}{2} \sum_{b=1}^r \sum_{ja \neq ka=1}^{N_b} \mathbf{C}_{kb} \cdot \mathbf{W}_{kbja}, \quad (7.106)$$

which will appear in connection with the heat flux and the related moments later on. It is useful to symmetrize the virial tensor

$$\mathbf{W}_{jakb} = 2 \int_0^1 d\lambda \{ \mathbf{r}_{jakb} \mathbf{F}_{jakb}(\mathbf{r}_{jakb}) \} \exp(-\lambda \mathbf{r}_{jakb} \cdot \nabla), \quad (7.107)$$

where

$$\{ \mathbf{r}_{jakb} \mathbf{F}_{jakb}(\mathbf{r}_{jakb}) \} = \frac{1}{2} [\mathbf{r}_{jakb} \mathbf{F}_{jakb}(\mathbf{r}_{jakb}) + \mathbf{F}_{jakb}(\mathbf{r}_{jakb}) \mathbf{r}_{jakb}], \quad (7.108)$$

which can be seen indeed symmetric, if  $\mathbf{F}_{jakb}(\mathbf{r}_{jakb})$  is written as

$$\mathbf{F}_{jakb}(\mathbf{r}_{jakb}) = - \frac{\mathbf{r}_{jakb}}{|\mathbf{r}_{jakb}|} \frac{\partial U_{jakb}}{\partial |\mathbf{r}_{jakb}|} = \mathbf{r}_{jakb} \frac{F_{jakb}}{|\mathbf{r}_{jakb}|} \quad (7.109)$$

with  $F_{jakb} = (\partial U_{jakb} / \partial |\mathbf{r}_{jakb}|)$  being the scalar force.

With the momentum density defined in a fixed coordinate frame its evolution equation, namely, the momentum balance equation, or the momentum conservation law, can be derived with the help of the GBE. By putting the momentum balance equation in the form isomorphic to the phenomenological momentum conservation law it is possible to unambiguously identify the pressure tensor (stress tensor) in molecular theory (i.e., statistical mechanics) form. The pressure tensor is given by the statistical mechanical expression

$$\mathbf{P} = \mathbf{P}^{(k)} + \mathbf{P}^{(v)}, \quad (7.110)$$

$$\mathbf{P}^{(k)} = \sum_{a=1}^r \sum_{ja=1}^{N_a} \langle m_a \mathbf{C}_{ja} \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(\mathbb{N})}(\mathbf{x}^{(\mathbb{N})}, t) \rangle, \quad (7.111)$$

$$\mathbf{P}^{(v)} = \frac{1}{2} \sum_{a=1}^r \sum_{ja=1}^{N_a} \sum_{b=1}^r \sum_{ja \neq ka=1}^{N_b} \langle f^{(\mathbb{N})}(\mathbf{x}^{(\mathbb{N})}, t) \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) \rangle \quad (7.112)$$

with the virial tensor  $\mathbf{W}_{jakb}$  defined by (7.107). It would be convenient to abbreviate the (local) tensor molecular moment for the pressure tensor by the symbol  $\mathbf{T}_{ja}$

$$\mathbf{T}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) = m_a \mathbf{C}_{ja} \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) + \frac{1}{2} \sum_{b=1}^r \sum_{ja \neq ka=1}^{N_b} \mathbf{W}_{kbja} \delta(\mathbf{r}_{kb} - \mathbf{r}). \quad (7.113)$$

Thus the pressure tensor  $\mathbf{P}$  is an average of  $\mathbf{T}_{ja}$ :

$$\mathbf{P} = \sum_{a=1}^r \sum_{ja=1}^{N_a} \langle \mathbf{T}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(\mathbb{N})}(\mathbf{x}^{(\mathbb{N})}, t) \rangle. \quad (7.114)$$

We note that, as a matter of fact,  $U_{jakb}(\mathbf{r}_{jakb})$  does not have to be a pair potential in the aforementioned expressions as noted earlier. We emphasize that these definitions given above are uniquely made once the momentum density definition is accepted together with the kinetic equation.

The equilibrium hydrostatic pressure is easily deduced by using the equilibrium solution of the kinetic equation and the statistical formula for the pressure tensor. The so-defined equilibrium pressure is used in the definition of excess normal stress defined later as a normal stress in excess of equilibrium pressure. In the conventional theory, the virial tensor  $\mathbf{W}_{jakb}$  is replaced by Clausius's virial  $\mathbf{r}_{jakb} \mathbf{F}_{jakb}$  as an approximation, but the remainder of  $\mathbf{W}_{jakb}$  makes a significant contribution that should not be ignored from the quantitative and qualitative standpoints of macroscopic theory of matter as will be seen later.

The macroscopic observables, mass density  $\rho$ , momentum density  $\rho\mathbf{u}$ , and internal energy density  $\rho\mathcal{E}$ , are conserved variables, each of which obeys, respectively, the mass conservation law (equation of continuity), the momentum conservation law (momentum balance equation), and the energy conservation law (internal energy

balance equation) as will be shown later when the evolution equations are specifically discussed. For the fluid under consideration there are no other conserved variables for the density homologue of moments.

### 7.5.2 Nonconserved Moments

Macroscopic variables necessary for description of a fluid form a hierarchy in the theory of macroscopic processes. The conserved variables are followed by nonconserved variables in the hierarchy. This hierarchical ordering may be viewed figuratively as shown in Fig. 7.1. The hierarchy of macroscopic observables, through their evolution equations, are eventually subjected to the constraints of the laws of thermodynamics and thereby the theory of macroscopic processes is made thermodynamically consistent, as will be discussed.

#### 7.5.2.1 Mean Voronoi Volume—Molar Volume

In addition to the mass and internal energy densities, there is another scalar observable. That observable is the Voronoi (molar) volume, which has been defined earlier in the case of a simple fluid mixture as for a pure fluid. Unlike the aforementioned two scalar observables it is nonconserved. As shown previously, this observable is different from the specific volume defined as the inverse density or mass density, which obeys the equation of continuity or its equivalent. We have shown that in the case of a pure simple fluid the molecular representation of this particular volume is given by the Voronoi volume. Let us denote by  $\Omega_{ja}$  the volume of Voronoi polyhedron for molecule  $ja$  at position  $\mathbf{r}_{ja}$  in a suitable coordinate system; see Fig. 7.2 for a schematic two-dimensional example of a Voronoi polygon. This volume may be taken for a molecular representation  $m_a V_{ja}$  of the molar volume (area in two-dimension) of the fluid:

$$m_a V_{ja} := \Omega_{ja}.$$

It is the volume enclosing the molecule  $ja$  at  $\mathbf{r}_{ja}$  in the mixture at time  $t$ . It must be a function of all the coordinates of nearest neighbor molecules that determine the vertices surrounding the center molecule  $ja$  of the polyhedron. As such, it is also a functional of the fluid state characterized by  $\rho, \mathbf{u}, T$ , where  $T$  is the temperature of the fluid, because the Voronoi volume is bound to change accordingly as  $\rho, \mathbf{u}, T$  vary. Thus we write the Voronoi volume as a functional of the variables  $\varsigma := (\rho, \mathbf{u}, T)$ :

$$m_a V_{ja} = \Omega_{ja} (\{\mathbf{r}_{ja} - \mathbf{r}_{ib}\}; ib \in z_{ja} | \varsigma), \quad (7.115)$$

where  $z_{ja}$  is the number of nearest neighbors of  $ja$ —the coordination number. This molecular representation is for the molar volume of the fluid of interest or matter in

general, and it is evidently different from the inverse mass density, that is, the specific volume

$$v_{\text{sp}} = \rho^{-1}. \quad (7.116)$$

As shown elsewhere [11] and in Chap. 6, the mean value of  $m_a V_{ja}$  tends to  $v_{\text{sp}}$  as the fluid approaches the state of thermodynamic equilibrium.

On taking statistical average, we find the molar volume or the volume density at a nonequilibrium state:

$$\begin{aligned} \rho \hat{v}(\mathbf{r}, t) &= \sum_{a=1}^r \rho_a \hat{v}_a(\mathbf{r}, t) \\ &= \sum_{a=1}^r \sum_{ja=1}^{N_a} \langle m_a V_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \rangle, \end{aligned} \quad (7.117)$$

$\hat{v}_a(\mathbf{r}, t)$  being the partial molar volume, which is given by the statistical mechanical average

$$\rho_a \hat{v}_a(\mathbf{r}, t) = \sum_{ja=1}^{N_a} \langle m_a V_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \rangle. \quad (7.118)$$

With this preparatory remark on molar volume, we proceed to construct a set of moments employed in the present theory. The general idea made use of in its construction makes use of the Schmidt orthogonalization method, so that the set  $\{h_{ja}^{(q)} : q \geq 0\}$  of nonconserved moments is mutually orthogonal, and the theory would be rendered simpler thereby. We begin with the moment corresponding to the molar volume.

### 7.5.2.2 Molecular Moment for Volume

Using  $m_a V_{ja}$  defined in Eq.(7.115) we take the molecular expression for moment  $h_{ja}^{(0)}$

$$h_{ja}^{(0)} := m_a \hat{h}_{ja}^{(0)} = m_a (V_{ja} + A_a^{(0)}), \quad (7.119)$$

$$\bar{h}_{ja}^{(0)} = h_{ja}^{(0)} \delta(\mathbf{r}_{ja} - \mathbf{r}), \quad (7.120)$$

where  $A_a^{(0)}$  is a constant. We require the equilibrium average of  $\bar{h}_{ja}^{(0)}$  vanish. Thus setting

$$\left\langle \mathbf{1} \cdot \bar{h}_{ja}^{(0)} \right\rangle_0 = 0,$$

where the subscript 0 to the angular brackets in  $\left\langle \mathbf{1} \cdot \bar{h}_{ja}^{(0)} \right\rangle_0$  stands for the equilibrium average

$$\left\langle \mathbf{1} \cdot \bar{h}_{ja}^{(0)} \right\rangle_0 = \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(0)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f_{\text{eq}}^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}) \right\rangle \quad (7.121)$$

with  $f_{\text{eq}}^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})})$  denoting the equilibrium distribution function; see (7.51) for  $f_{\text{eq}}^{(\mathbf{N})}$ . With the definition of the equilibrium partial molar volume of species  $a$  by the statistical mechanical expression

$$v_a^{(0)} = \rho_a \hat{v}_a^{(0)} = \sum_{ja=1}^{N_a} \left\langle m_a V_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f_{\text{eq}}^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}) \right\rangle, \quad (7.122)$$

we find the constant:

$$A_a^{(0)} = -\hat{v}_a^{(0)}. \quad (7.123)$$

Hence the leading moment of the set is given by

$$h_{ja}^{(0)} = m_a (V_{ja} - \hat{v}_a^{(0)}). \quad (7.124)$$

If the partial molar volume of the nonequilibrium fluid is denoted by

$$\rho_a \hat{v}_a = \sum_{ja=1}^{N_a} \left\langle m_a V_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t) \right\rangle, \quad (7.125)$$

then the macroscopic moment  $\Phi_a^{(0)}$  corresponding to  $h_{ja}^{(0)}$  is given by

$$\begin{aligned} \Phi_a^{(0)} &= \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(0)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t) \right\rangle \\ &= \rho_a (\hat{v}_a - \hat{v}_a^{(0)}). \end{aligned} \quad (7.126)$$

It is seen to be a fluctuation of partial molar volume of special  $a$  from the equilibrium partial molar volume. Summing it over all species we obtain the macroscopic moment for the volume fluctuation in the mixture

$$\begin{aligned} \Phi^{(0)} &= \rho \hat{\Phi}^{(0)} = \sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(0)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t) \right\rangle \\ &= \sum_{a=1}^r \rho_a (\hat{v}_a - \hat{v}_a^{(0)}) = \rho (\hat{v} - \hat{v}^{(0)}). \end{aligned} \quad (7.127)$$

It is a molar volume fluctuation from the equilibrium molar volume; see Table 7.1. Therefore  $\widehat{\Phi}^{(0)}$  can be written as

$$\widehat{\Phi}^{(0)} = \widehat{v} - \widehat{v}^{(0)} = \sum_{a=1}^r c_a (\widehat{v}_a - \widehat{v}_a^{(0)}). \quad (7.128)$$

We now choose the volume flux for the next molecular moment of the set  $\left\{ h_{ja}^{(q)} : q \geq 0 \right\}$  such that it is orthogonal to  $h_{ja}^{(0)}$ , and similarly for the subsequent elements, which are sequentially orthogonalized according to the Schmidt orthogonalization method. The details of this process is given below for the leading members of the set.

### 7.5.2.3 Molecular Moment for Mass Flux

The ordering of the moment set is arbitrary to some extent. We choose the molecular moment for mass flux for the next member of the set. Since its principal part is dictated by the momentum balance equation for the species of interest, say, species  $a$ , it is taken in the form

$$h_{ja}^{(1)} = m_a \mathbf{C}_{ja} + A_1^{(a)} h_{ja}^{(0)}, \quad (7.129)$$

$$\bar{h}_{ja}^{(1)} = h_{ja}^{(1)} \delta(\mathbf{r}_{ja} - \mathbf{r}), \quad (7.130)$$

where the constant  $A_1^{(a)}$  is determined such that  $h_{ja}^{(1)}$  is orthogonal to the previous moments in the set in the sense of Schmidt's orthogonalization method. Therefore  $h_{ja}^{(1)}$  is chosen such that

$$\left\langle h_a^{(0)} \odot \bar{h}_a^{(1)} \right\rangle_0 := \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(0)} \bar{h}_{ja}^{(1)} f_{eq}^{(N)} \right\rangle = 0, \quad (7.131)$$

and upon substituting (7.129) we find

$$A_1^{(a)} = - \frac{\left\langle \bar{h}_{ja}^{(0)} \odot m_a \mathbf{C}_{ja} \right\rangle_0}{\left\langle \bar{h}_{ja}^{(0)} \odot h_{ja}^{(0)} \right\rangle_0} = 0,$$

because  $\left\langle h_{ja}^{(0)} \odot m_a \mathbf{C}_{ja} \right\rangle_0 = 0$  identically on account of symmetry of the integrand in the momentum space. The symbol  $\odot$  stands for taking the scalar product or contraction of tensors in this work. Therefore we find

$$h_{ja}^{(1)} = m_a \mathbf{C}_{ja} \quad (7.132)$$

and its nonequilibrium average is the mass diffusion flux itself:

$$\Phi_a^{(1)} := \mathbf{J}_a = \sum_{ja=1}^{N_a} \langle m_a \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)} \rangle, \quad (7.133)$$

which has already appeared in connection with the mass fraction  $c_a$ .

#### 7.5.2.4 Molecular Moment for Volume Flux

For the next moment, we take with the molecular moment for volume flux. It is orthogonalized to the two preceding moments of the set, that is,  $h_{ja}^{(0)}$  and  $h_{ja}^{(1)}$ . In essence, we construct it in the form of a flux of  $h_{ja}^{(0)}$

$$h_{ja}^{(2)} = \mathbf{C}_{ja} h_{ja}^{(0)} + A_{20}^{(a)} h_{ja}^{(0)} + A_{21}^{(a)} h_{ja}^{(1)}, \quad (7.134)$$

$$\bar{h}_{ja}^{(2)} = h_{ja}^{(2)} \delta(\mathbf{r}_{ja} - \mathbf{r}), \quad (7.135)$$

where the coefficients  $A_{20}^{(a)}$  and  $A_{21}^{(a)}$  are determined such that  $\bar{h}_{ja}^{(2)}$  is orthogonal to  $h_{ja}^{(0)}$  and  $h_{ja}^{(1)}$  in the mean at equilibrium. On taking average this yields the macroscopic observable  $\Phi_a^{(2)}$ :

$$\Phi_a^{(2)} = \sum_{ja=1}^{N_a} \left\langle \bar{h}_{ja}^{(2)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \quad (7.136)$$

On inserting (7.134) into (7.136) and applying the Schmidt orthogonalization method the following orthogonality conditions are obtained:

$$\begin{aligned} 0 &= \left\langle \bar{h}_a^{(0)} \odot \mathbf{C}_a h_a^{(0)} \right\rangle_0 + A_{20}^{(a)} \left\langle \bar{h}_a^{(0)} \odot h_a^{(0)} \right\rangle_0 + A_{21}^{(a)} \left\langle \bar{h}_a^{(0)} \odot h_a^{(1)} \right\rangle_0, \\ 0 &= \left\langle \bar{h}_a^{(1)} \odot \mathbf{C}_a h_a^{(0)} \right\rangle_0 + A_{20}^{(a)} \left\langle \bar{h}_a^{(1)} \odot h_a^{(0)} \right\rangle_0 + A_{21}^{(a)} \left\langle \bar{h}_a^{(1)} \odot h_a^{(1)} \right\rangle_0, \end{aligned}$$

which yield the solutions for the coefficients

$$A_{20}^{(a)} = -\frac{\left\langle \bar{h}_a^{(0)} \odot \mathbf{C}_a h_a^{(0)} \right\rangle_0}{\left\langle h_a^{(0)} \odot h_a^{(0)} \right\rangle_0} = 0, \quad (7.137)$$

$$A_{21}^{(a)} = -\frac{\left\langle \bar{h}_a^{(1)} \odot \mathbf{C}_a h_a^{(0)} \right\rangle_0}{\left\langle \bar{h}_a^{(1)} \odot h_a^{(1)} \right\rangle_0} = -\frac{\left\langle \bar{h}_a^{(1)'} \odot \mathbf{C}_a h_a^{(0)} \right\rangle_0}{\sqrt{\left\langle \bar{h}_a^{(1)} \odot h_a^{(1)} \right\rangle_0}} := -\alpha_a^{(2)}. \quad (7.138)$$

Here we have defined  $\bar{h}_a^{(1)'} \text{ as below:}$

$$\bar{h}_a^{(1)'} = \frac{\bar{h}_a^{(1)}}{\sqrt{\langle \bar{h}_a^{(1)} \odot h_a^{(1)} \rangle_0}}. \quad (7.139)$$

Finally, the moment  $h_{ja}^{(2)}$  is given by the expression

$$\begin{aligned} h_{ja}^{(2)} &:= \mathbf{C}_{ja} h_{ja}^{(0)} - \alpha_a^{(2)} h_{ja}^{(1)} \\ &= m_a \left( \mathbf{C}_{ja} \hat{h}_{ja}^{(0)} - \alpha_a^{(2)} \hat{h}_{ja}^{(1)} \right) = m_a \mathbf{C}_{ja} \left( \hat{h}_{ja}^{(0)} - \alpha_a^{(2)} \right). \end{aligned} \quad (7.140)$$

and its average  $\Phi_a^{(2)}$  gives rise to the volume flux  $\mathcal{F}_{\Omega a}$

$$\begin{aligned} \Phi_a^{(2)} &:= \mathcal{F}_{\Omega a} \\ &= \sum_{ja=1}^{N_a} \left\langle \mathbf{C}_{ja} h_{ja}^{(0)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle - \alpha_a^{(2)} \rho_a \widehat{\Phi}_a^{(1)}. \end{aligned} \quad (7.141)$$

The total volume flux is given by

$$\begin{aligned} \Phi^{(2)} &:= \mathcal{F}_{\Omega} = \sum_{a=1}^r \Phi_a^{(2)} \\ &= \sum_{a=1}^r \left[ \sum_{ja=1}^{N_a} \left\langle \mathbf{C}_{ja} h_{ja}^{(0)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle - \alpha_a^{(2)} \rho_a \widehat{\Phi}_a^{(1)} \right]. \end{aligned} \quad (7.142)$$

Formula (7.142) is, from the physical standpoints, seen as a volume flux relative to the mass diffusion flux. It indicates that the volume flux would be coupled to the mass diffusion flux present in the mixture. Note that all terms on the right are vectorial quantities and therefore of same (rotational) symmetry—that is, they transform like a vector. It is interesting that the presence of volume flux implies an accompanying mass diffusion flux, and vice versa in the present scheme of theory. This presages the coupling between the mass flux and the volume flux in consistency with the Curie principle that states the macroscopic fluxes of the same spatial symmetry can be coupled to each other. The presence of volume fluctuation and accompanying volume flux is a new feature in generalized hydrodynamics, which is absent in the classical theory of hydrodynamics.

### 7.5.2.5 Heat Flux

We find it convenient to choose for the next member of the moment set the internal energy flux (i.e., heat flux) whose molecular expression can be deduced from the internal energy balance equation to have the molecular expression

$$\begin{aligned} \mathbf{C}_{ja}\mathcal{H}_{ja}^{(h)} &= \left( \frac{1}{2}m_a C_{ja}^2 + U_{ja} \right) \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \\ &\quad + \frac{1}{2} \sum_{b=1}^r \sum_{ja \neq kb=1}^{N_a} \mathbf{C}_{ja} \cdot \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}), \end{aligned} \quad (7.143)$$

where  $\mathbf{W}_{jakb}$  is the virial tensor operator already defined. This moment is then orthogonalized to the previous moments of the set. If the moment in question is denoted  $h_{ja}^{(3)}$ , it then may be written as a linear combination of  $\mathbf{C}_{ja}\mathcal{H}_{ja}^{(h)}$  and the previous moments of the set

$$h_{ja}^{(3)} := \mathbf{C}_{ja}\mathcal{H}_{ja}^{(h)} + A_{30}^{(a)} h_{ja}^{(0)} + A_{31}^{(a)} h_{ja}^{(1)} + A_{32}^{(a)} h_{ja}^{(2)}, \quad (7.144)$$

$$\bar{h}_{ja}^{(3)} = h_{ja}^{(3)} \delta(\mathbf{r}_{ja} - \mathbf{r}). \quad (7.145)$$

The coefficients  $A_{30}^{(a)}$ ,  $A_{31}^{(a)}$ , and  $A_{32}^{(a)}$  are then determined by the orthogonality conditions:

$$\begin{aligned} 0 &= \left\langle \bar{h}_a^{(0)} \odot \mathbf{C}_a \mathcal{H}_a^{(h)} \right\rangle_0 + A_{30}^{(a)} \left\langle \bar{h}_a^{(0)} \odot h_a^{(0)} \right\rangle_0 + A_{31}^{(a)} \left\langle \bar{h}_a^{(0)} \odot h_a^{(1)} \right\rangle_0 \\ &\quad + A_{32}^{(a)} \left\langle \bar{h}_a^{(0)} \odot h_a^{(2)} \right\rangle_0, \\ 0 &= \left\langle \bar{h}_a^{(1)} \odot \mathbf{C}_a \mathcal{H}_a^{(h)} \right\rangle_0 + A_{30}^{(a)} \left\langle \bar{h}_a^{(1)} \odot h_a^{(0)} \right\rangle_0 + A_{31}^{(a)} \left\langle \bar{h}_a^{(1)} \odot h_a^{(1)} \right\rangle_0 \\ &\quad + A_{32}^{(a)} \left\langle \bar{h}_a^{(1)} \odot h_a^{(2)} \right\rangle_0, \\ 0 &= \left\langle \bar{h}_a^{(2)} \odot \mathbf{C}_a \mathcal{H}_a^{(h)} \right\rangle_0 + A_{30}^{(a)} \left\langle \bar{h}_a^{(2)} \odot h_a^{(0)} \right\rangle_0 + A_{31}^{(a)} \left\langle \bar{h}_a^{(2)} \odot h_a^{(1)} \right\rangle_0 \\ &\quad + A_{32}^{(a)} \left\langle \bar{h}_a^{(2)} \odot h_a^{(2)} \right\rangle_0. \end{aligned}$$

Owing to the orthogonality of moments in the sense of Schmidt's method

$$\left\langle \bar{h}_a^{(0)} \odot h_a^{(1)} \right\rangle_0 = 0, \quad \left\langle \bar{h}_a^{(0)} \odot h_a^{(2)} \right\rangle_0 = 0, \quad \text{etc.},$$

the three orthogonality conditions yield the coefficient as follows:

$$A_{30}^{(a)} = -\frac{\langle \bar{h}_a^{(0)} \odot \mathbf{C}_a \mathcal{H}_a^{(h)} \rangle_0}{\langle \bar{h}_a^{(0)} \odot h_a^{(0)} \rangle_0} = -\frac{\langle \bar{h}_a^{(0)'} \odot \mathbf{C}_a \mathcal{H}_a^{(h)} \rangle_0}{\sqrt{\langle \bar{h}_a^{(0)} \odot h_a^{(0)} \rangle_0}} = 0, \quad (7.146)$$

$$A_{31}^{(a)} = -\frac{\langle \bar{h}_a^{(1)} \odot \mathbf{C}_a \mathcal{H}_a^{(h)} \rangle_0}{\langle \bar{h}_a^{(1)} \odot h_a^{(1)} \rangle_0} = -\frac{\langle \bar{h}_a^{(1)'} \odot \mathbf{C}_a \mathcal{H}_a^{(h)} \rangle_0}{\sqrt{\langle \bar{h}_a^{(1)} \odot h_a^{(1)} \rangle_0}} := -\alpha_a^{(31)}, \quad (7.147)$$

$$A_{32}^{(a)} = -\frac{\langle \bar{h}_a^{(2)} \odot \mathbf{C}_a \mathcal{H}_a^{(h)} \rangle_0}{\langle \bar{h}_a^{(2)} \odot h_a^{(2)} \rangle_0} = -\frac{\langle \bar{h}_a^{(2)'} \odot \mathbf{C}_a \mathcal{H}_a^{(h)} \rangle_0}{\sqrt{\langle \bar{h}_a^{(2)} \odot h_a^{(2)} \rangle_0}} := -\alpha_a^{(32)}. \quad (7.148)$$

In these expressions

$$\bar{h}_a^{(l)'} = \frac{\bar{h}_a^{(l)}}{\sqrt{\langle \bar{h}_a^{(l)} \odot h_a^{(l)} \rangle_0}}, \quad (l = 1, 2). \quad (7.149)$$

Finally, we obtain the moment  $h_{ja}^{(3)}$  in the form

$$\begin{aligned} h_{ja}^{(3)} &= m_a \hat{h}_{ja}^{(3)} \\ &= \mathbf{C}_{ja} \mathcal{H}_{ja}^{(h)} - \alpha_a^{(31)} h_{ja}^{(1)} - \alpha_a^{(32)} h_{ja}^{(2)} \\ &= \mathbf{C}_{ja} \left( \mathcal{H}_{ja}^{(h)} - m_a \hat{h}_a \right) - \alpha_a^{(32)} h_{ja}^{(2)}. \end{aligned} \quad (7.150)$$

It is remarkable that, when explicitly evaluated,  $\alpha_a^{(31)}$  gives rise to the equilibrium enthalpy density. The moment  $h_{ja}^{(3)}$  is the molecular expression for heat flux in the presence of the volume flux in a liquid mixture. It implies that the heat flux is influenced by the presence of the mass diffusion flux and the volume flux. Note that  $h_{ja}^{(1)}$  and  $h_{ja}^{(2)}$  on the right of (7.149) are vectors.

On taking statistical average of  $h_{ja}^{(3)}$  the partial heat flux of species  $a$  is obtained:

$$\begin{aligned} \Phi_a^{(3)} &= \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(3)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(\mathbf{N})} (\mathbf{x}^{(\mathbf{N})}, t) \right\rangle \\ &= \sum_{ja=1}^{N_a} \left\langle \mathbf{C}_{ja} \left( \mathcal{H}_{ja}^{(h)} - m_a \hat{h}_a \right) \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(\mathbf{N})} (\mathbf{x}^{(\mathbf{N})}, t) \right\rangle \end{aligned}$$

$$-\alpha_a^{(32)} \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(2)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \quad (7.151)$$

The flux  $\Phi_a^{(3)}$  may be alternatively expressed as a linear combination of other fluxes:

$$\begin{aligned} \Phi_a^{(3)} &= \mathbf{Q}'_a - \alpha_a^{(32)} \Phi_a^{(2)} \\ &= \mathbf{Q}_a - \widehat{h}_a \Phi_a^{(1)} - \alpha_a^{(32)} \Phi_a^{(2)} \\ &= \mathbf{Q}_a - \widehat{h}_a \mathbf{J}_a - \alpha_a^{(32)} \Phi_a^{(2)}. \end{aligned} \quad (7.152)$$

The total heat flux is then given by the sum of  $\Phi_a^{(3)}$  over species:

$$\Phi^{(3)} = \sum_{a=1}^r \Phi_a^{(3)} = \sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(3)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \quad (7.153)$$

### 7.5.2.6 Shear Stress

The next elements of the moment set are the molecular expressions for the shear stress and the excess normal stress. The pressure (stress) tensor appears in the momentum balance equation, as shown earlier. Since the pressure tensor is a second-rank tensor, there is no possibility of their coupling between the shear stress and either scalar or vectors moments, at least, in the linear regime. Nevertheless, formally, we may tentatively define the molecular moment corresponding to  $h_{ja}^{(4)}$  as a linear combination of the moments preceding  $h_{ja}^{(4)}$  in the set constructed so far and then determine the coefficients by applying the Schmidt orthogonalization method:

$$h_{ja}^{(4)} := [\mathbf{T}_{ja}]^{(2)} + A_{40}^{(a)} h_{ja}^{(0)} + A_{41}^{(a)} h_{ja}^{(1)} + A_{42}^{(a)} h_{ja}^{(2)} + A_{43}^{(a)} h_{ja}^{(3)}, \quad (7.154)$$

$$\bar{h}_{ja}^{(4)} = h_{ja}^{(4)} \delta(\mathbf{r}_{ja} - \mathbf{r}), \quad (7.155)$$

where

$$[\mathbf{T}_{ja}]^{(2)} = m_a [\mathbf{C}_{ja} \mathbf{C}_{ja}]^{(2)} + \frac{1}{2} \sum_{b=1}^r \sum_{ja \neq kb}^{N_a, N_b} [\mathbf{W}_{jakb}]^{(2)}. \quad (7.156)$$

The symbol  $[\mathbf{B}]^{(2)}$  denotes the traceless symmetric part of the second rank tensor  $\mathbf{B}$ . The expansion coefficients  $A_{40}^{(a)}$ ,  $A_{41}^{(a)}$ ,  $A_{42}^{(a)}$ , and  $A_{43}^{(a)}$  are determined by the orthogonality conditions in the same manner as for the preceding moments discussed earlier. Since we find

$$\left\langle \bar{h}_{ja}^{(l)} \odot [\mathbf{T}_{ja}]^{(2)} \right\rangle_0 = 0 \quad l = 0, 1, 2, 3,$$

because  $h_{ja}^{(l)}$  are scalar or vectors whereas  $[\mathbf{T}_{ja}]^{(2)}$  is a traceless symmetric second-rank tensor, which is of different spatial symmetry from the former. Therefore, according to the orthogonality conditions on the moments  $h_{ja}^{(0)}, h_{ja}^{(1)}, h_{ja}^{(2)}, h_{ja}^{(3)}$  already orthogonalized, we find

$$A_{4l}^{(a)} = 0 \quad \text{for } l = 0, 1, 2, 3.$$

Consequently, we finally conclude that  $h_{ja}^{(4)}$  is simply given by

$$h_{ja}^{(4)} := m_a \hat{h}_{ja}^{(4)} = m_a [\mathbf{C}_{ja} \mathbf{C}_{ja}]^{(2)} + \frac{1}{2} \sum_{b=1}^r \sum_{ja \neq kb}^{N_a, N_b} [\mathbf{W}_{jakb}]^{(2)}. \quad (7.157)$$

Upon taking average, we obtain the traceless symmetric part of the pressure (stress) tensor—namely, the shear stress

$$\Phi^{(4)} = \rho \hat{\Phi}^{(4)} = \sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(4)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t) \right\rangle. \quad (7.158)$$

Of course, the partial stress tensor  $\Phi_a^{(4)}$  is defined by the formula

$$\Phi_a^{(4)} = \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(4)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t) \right\rangle. \quad (7.159)$$

We emphasize that  $[\mathbf{T}_{ja}]^{(2)}$  is not coupled with either scalar moments or vector moments, and it is in accordance with the Curie principle.

### 7.5.2.7 Excess Normal Stress

The trace part of the pressure tensor gives rise to another nonconserved moment, which is a scalar moment. Being a scalar, it is expected to be coupled also with the preceding scalar moments such as the mass  $m_a$  of species  $a$  and  $h_{ja}^{(0)}$ . Thus we take the molecular moment for the excess normal stress (for bulk viscosity phenomena) of dense gases and liquids in the form

$$\begin{aligned} h_{ja}^{(5)} &:= \frac{1}{3} \text{Tr} \mathbf{T}_{ja} - m_a p / \rho + A_5^{(a)} h_{ja}^{(0)} \\ &= \left[ \frac{1}{3} m_a C_{ja}^2 + \frac{1}{6} \sum_{ja \neq kb=1}^{N_b} \text{Tr} \mathbf{W}_{jakb} - m_a p / \rho \right] + A_5^{(a)} h_{ja}^{(0)}, \end{aligned} \quad (7.160)$$

$$\bar{h}_{ja}^{(5)} = h_{ja}^{(5)} \delta(\mathbf{r}_{ja} - \mathbf{r}). \quad (7.161)$$

It should be recalled that the excess normal stress is associated with compression or decompression of the fluid under the total equilibrium (hydrostatic local equilibrium) pressure  $p$  defined by the formula

$$\begin{aligned} p &= \sum_{a=1}^r \mathfrak{c}_a p_a \\ &= \sum_{a=1}^r \mathfrak{c}_a \sum_{ja=1}^{N_a} \left\langle \frac{1}{3} \text{Tr} \mathbf{T}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f_{\text{eq}}^{(N)} \right\rangle \\ &= \sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle \left[ \frac{1}{3} m_a C_{ja}^2 + \frac{1}{6} \sum_{b=1}^r \sum_{ja \neq kb=1}^{N_b} \text{Tr} \mathbf{W}_{jakb} \right] \delta(\mathbf{r}_{ja} - \mathbf{r}) f_{\text{eq}}^{(N)} \right\rangle. \quad (7.162) \end{aligned}$$

Note that

$$\frac{1}{\rho} \left\langle m_a \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle = \rho_a / \rho = \mathfrak{c}_a. \quad (7.163)$$

We perform the Schmidt orthogonalization for  $h_{ja}^{(5)}$ , making it orthogonal to the previous moments, especially, the scalar moments in this case. Other non-scalar moments are orthogonal to it for symmetry reason. For this reason we do not consider them in implementing this particular procedure. We find

$$\left\langle \bar{h}_{ja}^{(0)} \odot h_{ja}^{(5)} \right\rangle_0 = \left\langle h_{ja}^{(0)} \frac{1}{3} \text{Tr} \mathbf{T}_a \right\rangle_0 + A_5^{(a)} \left\langle h_{ja}^{(0)} h_{ja}^{(0)} \right\rangle_0 = 0,$$

which yields

$$A_5^{(a)} = - \frac{\left\langle \bar{h}_{ja}^{(0)} \odot \frac{1}{3} \text{Tr} \mathbf{T}_a \right\rangle_0}{\left\langle \bar{h}_{ja}^{(0)} \odot h_{ja}^{(0)} \right\rangle_0} := -\alpha_a^{(5)}. \quad (7.164)$$

Finally, with  $A_5^{(a)}$  so identified we obtain the moment  $h_{ja}^{(5)}$  in the form

$$h_{ja}^{(5)} = \frac{1}{3} \text{Tr} \mathbf{T}_{ja} - m_a p / \rho - \alpha_a^{(5)} h_{ja}^{(0)}, \quad (7.165)$$

$$\bar{h}_{ja}^{(5)} = h_{ja}^{(5)} \delta(\mathbf{r}_{ja} - \mathbf{r}). \quad (7.166)$$

Taking average of (7.165) we obtain the partial excess normal stress in the presence of volume transport:

$$\Phi_a^{(5)} = \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(5)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle$$

$$= \frac{1}{3} \text{Tr} \mathbf{P}_a - c_a p - \alpha_a^{(5)} \Phi_a^{(0)}. \quad (7.167)$$

The total excess normal stress is given by

$$\begin{aligned} \Phi^{(5)} = \rho \widehat{\Phi}^{(5)} &= \sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(5)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle \\ &= \frac{1}{3} \text{Tr} \mathbf{P} - p - \sum_{a=1}^r \alpha_a^{(5)} \Phi_a^{(0)}. \end{aligned} \quad (7.168)$$

We notice that the excess normal stress difference (i.e., a pressure fluctuation from equilibrium pressure) in the presence of volume transport is now modified by the volume fluctuation  $\Phi^{(0)}$ . Since the excess normal stress difference is associated with bulk viscous phenomena, which have to do with compression or decompression, the presence of volume fluctuations in the macroscopic variable  $\Phi^{(5)}$  appears physically quite sensible, when bulk viscous phenomena are considered.

By this we have completed the construction of a molecular moment set corresponding to the so-called “thirteen moment theory” of hydrodynamic processes in the presence of volume transport phenomena. For the reason that the volume transport is included in the set the traditional thirteen moment set is extended, and we expect to have an extended theory of generalized hydrodynamics. It is, of course, possible to continue the present method of constructing the moment set, but in practice it is not necessary to do so because the set of moments constructed so far is expected to be sufficient for many experimental situations we encounter in the laboratory and nature. In the present work, we will confine our discussion on generalized hydrodynamics and accompanying irreversible thermodynamics to those moments listed earlier.

Having constructed the molecular moments, it is possible to calculate the macroscopic nonconserved observables, which we collect in a generic form

$$\Phi^{(q)} = \rho \widehat{\Phi}^{(q)} = \sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \quad (7.169)$$

Here molecular moments  $h_{ja}^{(q)}$  are given already for the leading elements in the set.

The following point should be remembered: In the derivation of evolution equations given below,  $\widehat{\Phi}_a^{(q)}$  is defined by

$$\Phi_a^{(q)} = \rho \widehat{\Phi}_a^{(q)} \quad (7.170)$$

and, according to the statistical mechanical definition of  $\Phi_a^{(q)}$  given in (7.169), it follows that

$$\Phi^{(q)} = \sum_{a=1}^r \Phi_a^{(q)}. \quad (7.171)$$

Hence we obtain

$$\widehat{\Phi}^{(q)} = \sum_{a=1}^r \widehat{\Phi}_a^{(q)}. \quad (7.172)$$

The five seed moments—four scalar and one vector molecular moments—as indicated in the flow chart in Fig. 7.1 give rise to their evolution equations appearing in the second level of moments in the flow chart, and in the third level they are followed by either vectorial fluxes (i.e., diffusion flux, heat flux, and volume flux) shaded in light blue or the tensorial flux in purple. These five seed (leading) moments have series of homologous moments increasing in tensorial order, which are generated on operation of a generator—namely, the Liouville operator  $\mathbf{L}^{(N)}$ . It serves as the generator on account of the kinetic equation used to derive the evolution equations for macroscopic variables as will be shown below.

## 7.6 Generalized Hydrodynamic Equations

The evolution equations, which turn out to be generalized hydrodynamic equations, can be derived from the kinetic equation postulated—for example, the GBE—for the set of molecular moments representing macroscopic observables constructed in the previous section. The GBE, in fact, appears to be the most suitable irreversible kinetic equation requiring a least number of postulates, but any other empirically postulated irreversible kinetic equations may be employed as long as their predicted macroscopic behaviors are found *a posteriori* thermodynamically consistent.

The evolution equations derived from such a kinetic equation would consist of the balance equations for conserved variables and the irreversible evolution equations for nonconserved variables presented earlier, all of which have irreversible dissipation terms responsible for energy dissipation arising from irreversible processes. The appearance of such dissipation terms is a characteristic feature of irreversible evolution equations (i.e., kinetic equations), which is absent in the evolution equations for nonconserved variables derived from the reversible Liouville equation taken as the kinetic equation, for example, as in the Irving-Kirkwood method [9] or in the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy theory [14]. The totality of the conserved and irreversible nonconserved variable evolution equations generated from the GBE constitutes the generalized hydrodynamic equations for the fluid under consideration in the present kinetic theory.

The generalized hydrodynamic equations in the presence of volume transport phenomena extend the classical hydrodynamics of Navier, Stokes, and Fourier as well

as the previous version of the generalized hydrodynamic equations [3, 8] formulated in the absence of volume transport. The basis for this claim is that, as will be shown later, the generalized hydrodynamic equations extend the linear force-flux relations for the constitutive equations, such as Newtonian law of viscosity, Fourier's law of heat conduction, and Fick's law of diffusion, that underlie the thermodynamics of linear irreversible processes [15, 16].

### 7.6.1 Conservation Laws

The balance equations of mass, momentum, and internal energy are three conservation laws if the fluid is monatomic. They are also called the equation of continuity and the momentum and internal energy conservation laws. Such balance equations of conserved variables are possible to derive because mass, momentum, and internal energy are collision invariants of the collision term of the GBE from which we derive them in the following.

#### 7.6.1.1 Equation of Continuity

The equation of continuity representing the mass conservation law follows on differentiation of the statistical mechanical expression for mass density  $\rho(\mathbf{r}, t)$ , (7.97), and use of the GBE. We illustrate the derivation. Differentiating it with time  $t$  and making use of the GBE gives rise to the expression

$$\begin{aligned} \frac{\partial \rho(\mathbf{r}, t)}{\partial t} = & - \sum_{a=1}^r \sum_{ja=1}^{N_a} \langle m_a \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathbf{L}^{(N)} f^{(N)}(\mathbf{x}^{(N)}, t) \rangle \\ & + \sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle m_a \delta(\mathbf{r}_{ja} - \mathbf{r}) \Re[\bar{\mathbb{F}}^{(N)}] \right\rangle. \end{aligned} \quad (7.173)$$

Because mass  $m_a$  is a collision invariant of the collision integral of the GBE, the second term on the right of (7.173) vanishes:

$$\sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle m_a \delta(\mathbf{r}_{ja} - \mathbf{r}) \Re[\bar{\mathbb{F}}^{(N)}] \right\rangle = 0. \quad (7.174)$$

On substitution of the expression for the Liouville operator, (7.7), and performing integration by parts subject to the boundary conditions on the distribution functions that  $f^{(N)}$  vanishes at the boundaries of the phase space, (7.173) can be written as

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = -\nabla \cdot [\rho \mathbf{u}(\mathbf{r}, t)], \quad (7.175)$$

where  $\mathbf{u}(\mathbf{r}, t)$  is identified with the statistical mechanical expression for mean velocity, (7.97), at position  $\mathbf{r}$  and time  $t$  of the fluid in motion

$$\rho \mathbf{u} = \sum_{a=1}^r \sum_{ja=1}^{N_a} \langle m_a \mathbf{v}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \rangle.$$

The property of the Dirac delta function

$$\nabla_{\mathbf{r}_{ja}} \delta(\mathbf{r}_{ja} - \mathbf{r}) = -\nabla \delta(\mathbf{r}_{ja} - \mathbf{r}) \quad (7.176)$$

is used to obtain (7.175). This property will be used throughout the derivation of evolution equations from the GBE in this work. Equation (7.175) is the equation of continuity, locally expressing the mass conservation law in continuum mechanics [13]. Therefore we see that the statistical mechanical expression for the momentum density, (7.97), is a necessary condition for the equation of continuity to hold in the present kinetic theory. This statistical formula is unique in the fixed coordinate frame of reference employed here. Similar methods of derivation may be used for other conserved variables, although their derivations get progressively lengthy, but they are mathematically straightforward. Therefore we will simply present only the results, especially, in the light of the derivations discussed of their pure fluid counterparts in Chap. 6.

The equation of continuity may be given an alternative form if the specific volume defined by

$$v := v_{sp} = \frac{1}{\rho} \quad (7.177)$$

is made use of. With this transformation the equation of continuity can be written as

$$\rho \frac{dv}{dt} = \nabla \cdot \mathbf{u}, \quad (7.178)$$

where symbol  $d/dt$  stands for the substantial time derivative defined by

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla. \quad (7.179)$$

It is the time derivative in the coordinate system moving at velocity  $\mathbf{u}$ . Thus the incompressibility of the fluid is expressible with  $\nabla \cdot \mathbf{u} = \mathbf{0}$  in the steady state  $\frac{dv}{dt} = 0$  in the frame of reference of the vanishing substantial time derivative of  $v_{sp}$ ; see (7.177).

### 7.6.1.2 Mass Fraction Balance Equations

Differentiating the formula for  $\rho_a$  in (7.96) and making use of the equation of continuity, (7.175), just derived yields the mass fraction balance equation for species  $a$ . Thereby we necessarily arrive at the statistical mechanical expression for the mass diffusion flux formula given in (7.100) in the divergence term in the evolution equation:

$$\rho \frac{d\epsilon_a(\mathbf{r}, t)}{dt} = -\nabla \cdot \mathbf{J}_a(\mathbf{r}, t) \quad (1 \leq a \leq r, \quad r = \text{number of species}) \quad (7.180)$$

in the case of a non-reacting fluid. For a reacting fluid this equation is modified by the appearance of a source term on the right that accounts for the change in concentration arising from the chemical reactions progressing within the fluid; see p. 148, Ref. [17].

### 7.6.1.3 Momentum Balance Equation

To derive the momentum balance equation we apply to the statistical mechanical expression for  $\rho\mathbf{u}$  the same procedure as used for the preceding balance equations. The momentum balance equation is thereby obtained for the fluid

$$\rho \frac{d\mathbf{u}(\mathbf{r}, t)}{dt} = -\nabla \cdot \mathbf{P}(\mathbf{r}, t) + \rho \hat{\mathbf{F}}, \quad (7.181)$$

where  $\hat{\mathbf{F}}$  is the external force (body force) density per unit mass on the fluid particle at position  $\mathbf{r}$  and  $\mathbf{P}(\mathbf{r}, t)$  is the pressure (stress) tensor on the fluid, defined earlier by (7.110)–(7.112). The external force density is expressible as

$$\rho \hat{\mathbf{F}} = \sum_{a=1}^r \rho_a \hat{\mathbf{F}}_a, \quad (7.182)$$

where  $\hat{\mathbf{F}}_a$  is the external force density per mass of  $a$ . It should be noted that, in general, these forces are mean local external forces (i.e., body-forces). It is assumed that the external forces vary slowly in space, remaining constant over the intermolecular force ranges so that intermolecular collisions are not affected by the presence of external forces.

The statistical mechanical formula for the pressure tensor is not quite straightforward as for other quantities such as the velocity and diffusion flux. For this reason and also for the reason that it was not discussed in Chap. 6, we discuss it in a more general context. We begin with the statistical mechanical definition of momentum density, (7.97).

Taking time derivative of (7.97) and making use of the GBE we obtain

$$\frac{\partial \rho \mathbf{u}}{\partial t} = - \sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle m_a \mathbf{v}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathbf{L}^{(N)} f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (7.183)$$

where the dissipation term related to the collision term in the GBE does not appear owing to the fact that the momentum is a collision invariant as is mass  $m_a$ ; see (7.174). Upon substitution of the Liouville operator the right hand side of (7.183) is split into the kinetic and potential energy contributions,

$$\text{RHS} = \mathbf{T}_K + \mathbf{T}_P + \mathbf{T}_{Ex},$$

where

$$\begin{aligned} \mathbf{T}_K &= - \sum_{a=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left\langle m_a \mathbf{v}_{ja} \mathbf{v}_{kb} \delta(\mathbf{r}_{ja} - \mathbf{r}) \cdot \frac{\partial f^{(N)}}{\partial \mathbf{r}_{kb}} \right\rangle, \\ \mathbf{T}_{Ex} &= - \sum_{a=1}^r \sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle m_a \mathbf{v}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathbf{F}_a(\mathbf{r}_{ja}) \cdot \frac{\partial f^{(N)}}{\partial \mathbf{p}_{ja}} \right\rangle, \\ \mathbf{T}_P &= - \sum_{a=1}^r \sum_{ja \neq kb=1}^{N_a, N_b} \left\langle \frac{1}{2} m_a \mathbf{v}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathbf{F}_{jakb} \cdot \left( \frac{\partial}{\partial \mathbf{p}_{ja}} - \frac{\partial}{\partial \mathbf{p}_{kb}} \right) f^{(N)} \right\rangle. \end{aligned}$$

Performing integration by parts and making use of the property of Dirac delta function in (7.176), the term  $\mathbf{T}_K$  can be put into a divergence form

$$\mathbf{T}_K = -\nabla \cdot (\mathbf{P}^{(k)} + \rho \mathbf{u} \mathbf{u}),$$

where  $\mathbf{P}^{(k)}$  is the statistical mechanical formula for the kinetic part of the pressure (stress) tensor

$$\mathbf{P}^{(k)} = \sum_{a=1}^r \mathbf{P}_a^{(k)} = \sum_{ja=1}^{N_a} \left\langle m_a \mathbf{C}_{ja} \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N_a)}(\mathbf{x}^{(N_a)}, t) \right\rangle. \quad (7.184)$$

As for  $\mathbf{T}_{Ex}$ , carrying out integration by parts once over the momentum, we obtain  $\mathbf{T}_{Ex}$  in the form

$$\mathbf{T}_{Ex} = \sum_{a=1}^r \rho_a \widehat{\mathbf{F}}_a(\mathbf{r}),$$

where  $\widehat{\mathbf{F}}_a$  is the external force density per mass of species  $a$  at position  $\mathbf{r}$ .

As for the term  $\mathbf{T}_P$ , performing integration by parts over the momenta involved, we obtain

$$\mathbf{T}_P = - \sum_{a,b=1}^r \sum_{ja \neq kb=1}^{N_a, N_b} \left\langle \frac{1}{2} [\delta(\mathbf{r}_{ja} - \mathbf{r}) \mathbf{F}_{jakb} - \delta(\mathbf{r}_{kb} - \mathbf{r}) \mathbf{F}_{kbja}] f^{(N)} \right\rangle,$$

but since

$$\mathbf{F}_{jakb} = \mathbf{F}_{kbja},$$

it follows

$$\mathbf{T}_P = \sum_{a,b=1}^r \sum_{ja \neq kb=1}^{N_a, N_b} \left\langle \frac{1}{2} \mathbf{F}_{jakb} [\delta(\mathbf{r}_{ja} - \mathbf{r}) - \delta(\mathbf{r}_{kb} - \mathbf{r})] f^{(N)} \right\rangle.$$

Upon use of the identity (7.78), the term  $\mathbf{T}_P$  can be written in terms of the virial tensor  $\mathbf{W}_{jakb}$ :

$$\begin{aligned} \mathbf{T}_P &= -\nabla \cdot \sum_{a,b=1}^r \sum_{ja \neq kb=1}^{N_a, N_b} \left\langle f^{(N_a)} (\mathbf{x}^{(N)}, t) \frac{1}{2} \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle \\ &= -\nabla \cdot \mathbf{P}^{(v)}. \end{aligned}$$

Combining the results obtained above, the momentum balance equation is derived together with the statistical mechanical expression for the pressure tensor defined in (7.110)–(7.112):

$$\rho \frac{d\mathbf{u}(\mathbf{r}, t)}{dt} = -\nabla \cdot \mathbf{P} + \rho \hat{\mathbf{F}}. \quad (7.185)$$

We reiterate that the statistical mechanical formula for the pressure tensor  $\mathbf{P}$  obtained is not arbitrary, but uniquely determined, given the kinetic equation and the molecular moments preceding it in the hierarchy of moments for the fluid, because the statistical mechanical formula for  $\mathbf{P}$  we have arrived at is, as a matter of fact, a necessary condition for the momentum balance equation to hold in the present kinetic theory.

Perhaps, a remark on this derivation is in order at this juncture. Equation (7.185) as well as the two preceding conservation equations may be obtained with the Liouville equation as is done in the Irving-Kirkwood method [9], simply because the Liouville equation has no collision term, which automatically guarantees a vanishing dissipation term. However, the absence of a collision term in the Liouville equation makes a fundamental difference in the evolution equations for nonconserved variables in the generalized hydrodynamics theory obtained, especially, because the appearance of dissipation terms in the generalized hydrodynamic equations makes it feasible to study the thermodynamics of irreversible transport processes. This is an important reason why the Liouville equation cannot be used as a kinetic equation.

### 7.6.1.4 Internal Energy Balance Equation

Following the procedure used for the conserved variables discussed earlier, it is possible to derive the internal energy balance equation from the kinetic equation and the statistical mechanical definition of internal energy. The complexity of derivation involved for the internal energy balance equation is roughly similar to that of the momentum balance equation. Therefore, to avoid the repetition we will simply present the result of derivation, leaving the derivation as an exercise to the reader.

The internal energy balance equation can be shown to have the form

$$\rho \frac{d\mathcal{E}(\mathbf{r}, t)}{dt} = -\nabla \cdot \mathbf{Q}(\mathbf{r}, t) - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \widehat{\mathbf{F}}_a, \quad (7.186)$$

where the heat flux  $\mathbf{Q}$  is given by the statistical mechanical formula

$$\begin{aligned} \mathbf{Q} = & \sum_{a=1}^r \sum_{ja=1}^r \langle \mathbf{C}_{ja} H'_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \rangle \\ & + \frac{1}{2} \sum_{a,b=1}^r \sum_{ja \neq kb=1}^{N_a, N_b} \langle f^{(N)}(\mathbf{x}^{(N)}, t) \mathbf{W}_{jakb} \cdot \mathbf{C}_{ja} \delta(\mathbf{r}_{kb} - \mathbf{r}) \rangle. \end{aligned} \quad (7.187)$$

We stress that this statistical mechanical formula for  $\mathbf{Q}$  is uniquely obtained once the molecular moment for the mechanical energy, namely, the Hamiltonian given in (7.104), is taken on the physical grounds and if we ensure that the internal energy balance equation is isomorphic to its continuum mechanics counterpart. In (7.186) the dissipation term is absent because the Hamiltonian  $H'_{ja}$  is invariant in the molecular collision processes. Physically, according to the statistical mechanical expression the heat flux is made up of the flux of dynamical energy and mechanical work represented by the virial tensor arising from particles interacting through intermolecular forces of the particles in the fluid. But from the continuum theory standpoint the form of the virial tensor contribution is not as obvious as is in the statistical mechanical consideration. As a matter of fact, the energy flux arising from the flux of the virial tensor generally makes up a sizable portion of the heat flux if the fluid is in condensed phase. Therefore, in practice it would be necessary to make a careful estimate the virial flux contribution. At this juncture, it is useful to remark the following important features of the momentum and energy fluxes in: tensor  $\mathbf{P}$  and vector  $\mathbf{Q}$  in the divergence terms of (7.185) and (7.186) are not simply the momentum flux and the flux of Hamiltonian  $H'_{ja}$ , but, in addition to them, the contributions from the fluxes of work (a form of energy) to bring particles from infinity to the point of interest  $\mathbf{r}$  against the forces on them by all other particles in the system. This type of contributions occurs in other evolution equations appearing in the present dense fluid kinetic theory.

### 7.6.2 Evolution Equations for Nonconserved Variables

In the course of deriving the evolution equations for conserved variables shown in the previous subsection, we have noticed that once the physically most logically obvious definition of mean mass density is given, the subsequent molecular moment of the homologous set is generated by the Liouville operator and naturally suggested by the statistical mechanical expression of the “flux” in the divergence term of the evolution equation for the mean mass density as a necessary condition for the evolution equation of mean density—in this case, the equation of continuity—to exist. The term in question is the divergence of mean momentum of the fluid describing mass flow in and out of a local volume. An analogous situation arises for the evolution equation for the mean momentum; namely, the momentum balance equation, and from the divergence term we may uniquely deduce the statistical mechanical definition of the stress (pressure) tensor; recall the remark made at the end of Sect. 7.3. And similarly, the statistical mechanical expression for the heat flux in the internal energy balance equation may be deduced such that the energy balance equation is isomorphic to its continuum mechanics counterpart. In this manner, evolution equations for the hierarchy of molecular moments can be systematically and uniquely made use of to construct a unique hierarchy of moments and the corresponding evolution equations. This strategy is obviously suggested on inspection of the procedure taken in Chap. 6 and also described in this chapter.

There are two physically distinctive seed moments if volume transport phenomena are taken into consideration; one starting from the mass density and the other with the volume per molecule, which depends on position coordinates of the particles involved. They produce two distinctive, but eventually coupled sets of molecular moments as the process of derivation is continued as suggested by the flow chart in Fig. 7.1.

Before presenting the evolution equation for each nonconserved variable it is convenient to present the generic form of the evolution equations for them to indicate the generic difference between the conserved and nonconserved variables in the mathematical structures of the evolution equations. As alluded to earlier, the fundamental difference between the evolution equations of conserved and nonconserved variables lies in the appearance of dissipation terms in the evolution equations for the latter owing to the fact that the nonconserved moments are not collision invariants of the kinetic equation, for example, GBE. They are the seats of energy dissipation as we have seen in the phenomenological formulation of irreversible processes and in Chap. 6. They are intimately associated with the second law of thermodynamics as shown previously [3, 8].

If we denote the nonconserved variable  $\Phi_a^{(q)}$  by the statistical mechanical formula

$$\Phi_a^{(q)} := \rho \widehat{\Phi}_a^{(q)} = \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t) \right\rangle, \quad (7.188)$$

its evolution equation can be derived from the kinetic equation in a generic form

$$\rho \frac{d\widehat{\Phi}_a^{(q)}}{dt} = -\nabla \cdot \psi_a^{(q)} + \mathcal{Z}_a^{(q)} + \Lambda_a^{(q)}, \quad (7.189)$$

where  $\psi_a^{(q)}$  is the mean flux of  $h_{ja}^{(q)}$ ,  $\mathcal{Z}_a^{(q)}$  is called the kinematic term which contains mechanical and kinematic information on the process including macroscopic driving force of  $\Phi_a^{(q)}$ , and  $\Lambda_a^{(q)}$  the dissipation term. Their statistical mechanical formulas are given by the following expressions:

$$\psi_a^{(q)} = \sum_{ja=1}^{N_a} \left\langle \mathbf{C}_{ja} h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t) \right\rangle, \quad (7.190)$$

$$\mathcal{Z}_a^{(q)} = \sum_{ja=1}^{N_a} \left\langle \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(\mathbf{N})}(\mathbf{x}^{(\mathbf{N})}, t) \mathcal{D}_t^{(\mathbf{N})} h_{ja}^{(q)} \right\rangle, \quad (7.191)$$

$$\Lambda_a^{(q)} = \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \Re[\mathbb{F}^{-(\mathcal{N})}] \right\rangle \quad (7.192)$$

with  $\mathcal{D}_t^{(\mathbf{N})}$  denoting an operator consisting of the substantial time derivative operator  $d_t$ ,  $\mathbf{L}^{(\mathbf{N})}$ , and  $\nabla$ :

$$\begin{aligned} \mathcal{D}_t^{(\mathbf{N})} &= d_t + \mathbf{L}^{(\mathbf{N})} + \mathbf{C}_{ja} \cdot \nabla, \\ d_t &= \partial_t + \mathbf{u} \cdot \nabla. \end{aligned} \quad (7.193)$$

The kinematic term  $\mathcal{Z}_a^{(q)}$ , together with dissipation term  $\Lambda_a^{(q)}$ , contains the molecular dynamical and physical characteristics of process  $\widehat{\Phi}_a^{(q)}$  in the fluid that also include macroscopic (i.e., irreversible thermodynamic) driving forces and transport coefficients of the process of interest. These driving forces are called thermodynamic forces in irreversible thermodynamics [15, 16] for which the present theory provides the statistical mechanical foundation.

On summing (7.189) over species index  $a$ , we find the quantities for the whole fluid

$$\Phi^{(q)} = \sum_{a=1}^r \Phi_a^{(q)}, \quad \psi^{(q)} = \sum_{a=1}^r \psi_a^{(q)}, \quad \mathcal{Z}^{(q)} = \sum_{a=1}^r \mathcal{Z}_a^{(q)} \quad (7.194)$$

and the evolution equation for component  $\Phi^{(q)}$  can be obtained in the form

$$\rho \frac{d\widehat{\Phi}^{(q)}}{dt} = -\nabla \cdot \psi^{(q)} + \mathcal{Z}^{(q)} + \Lambda^{(q)}, \quad (7.195)$$

where

$$\rho \hat{\Phi}^{(q)} = \Phi^{(q)}. \quad (7.196)$$

The flux  $\psi_a^{(q)}$  of  $\Phi_a^{(q)}$  and the kinematic term  $\mathcal{Z}_a^{(q)}$  in the evolution equation for  $\hat{\Phi}_a^{(q)}$  can be explicitly calculated and their statistical mechanical formulas explicitly obtained in terms of macroscopic observables if the procedures used for the conserved variables shown earlier are followed.

It should be noted here that the final forms for the kinematic term  $\mathcal{Z}^{(q)}$  and the flux of  $\hat{\Phi}_a^{(q)}$ , namely,  $\psi^{(q)}$  will often appear redefined because the kinematic term  $\mathcal{Z}_a^{(q)}$  derived from its statistical mechanical formula can be rearranged upon subtracting from it the divergence terms involving the virial tensors which are then absorbed into the divergence term  $\nabla \cdot \psi_a^{(q)}$ ; in other words, the evolution equation for  $\hat{\Phi}_a^{(q)}$  can be renormalized<sup>13</sup> so that the resulting evolution equation appears as irreducible mathematically as possible, still retaining the generic form consisting of a divergence term, kinematic terms, and a dissipation term as in (7.195).

### 7.6.2.1 Evolution Equation for Voronoi (Molar) Volume

One of the two homologous sets of moments is led by the molecular expression for the molar volume represented by the Voronoi volume introduced in (7.115) and (7.117). This representation of molar volume by the Voronoi volume is not unique, but seems eminently reasonable. This question, however, is besides the point, because the point we would like make here is that the concept of molar volume is accepted into the rank of macroscopic hydrodynamic variables. In this sense, the viewpoint of hydrodynamics is broadened also in the case of a mixture.

Using the kinetic equation and the statistical mechanical expression for molar volume the evolution equation for partial molar volume  $\hat{\Phi}_a^{(0)}$  of species  $a$  can be shown given by

$$\rho \frac{d}{dt} \hat{\Phi}_a^{(0)} = -\nabla \cdot \psi_a^{(0)} + \mathcal{Z}_a^{(0)} + \Lambda_a^{(0)}, \quad (7.197)$$

where

$$\psi_a^{(0)} := \varphi_a^{(1)} = \left\langle \sum_{ja=1}^{N_a} \mathbf{C}_{ja} h_{ja}^{(0)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (7.198)$$

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<sup>13</sup>A remark on terminology *renormalization*: In the mathematical procedure of recasting some of terms in  $\mathcal{Z}_a^{(1)}$ , the divergence of vectors or tensors  $\nabla \cdot \phi$  arising from intermolecular forces, is combined with the divergence term in the evolution equation  $\nabla \cdot \psi^{(q)}$  to a form similar to the original form. This procedure will be henceforth called renormalization for a want of a better terminology. This procedure produces a physically better balanced system of evolution equations, especially, when they are approximated in the linear regime of thermodynamic driving forces of the processes, and for the purpose of formulating the theory of irreversible thermodynamics presented later.

$$\mathcal{Z}_a^{(0)} = \frac{\delta \psi_a^{(0)}}{\delta \varsigma} \cdot \nabla \varsigma + \frac{\delta \Phi_a^{(0)}}{\delta \varsigma} \cdot \frac{d\varsigma}{dt} + f_{va}^{(0)}, \quad (7.199)$$

$$f_{va}^{(0)} = \sum_{b=1}^r \sum_{ja=1}^{N_a} \sum_{\substack{kb \in z_{ja} \\ (ja \neq kb)}} \left\langle \delta(\mathbf{r}_{ja} - \mathbf{r}) \left( \mathbf{v}_{kb} \cdot \frac{\partial h_{ja}^{(0)}}{\partial \mathbf{r}_{kb}} \right) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \quad (7.200)$$

In (7.199)  $\varsigma$  stands for the set of three conserved variables  $\rho, \mathbf{u}, T$ :  $\varsigma = (\rho, \mathbf{u}, T)$  and, owing to the fact that  $\psi_a^{(0)}$  and  $\Phi_a^{(0)}$  are generally functionals of  $\varsigma$ , the functional derivatives  $\psi_a^{(0)}$  and  $\Phi_a^{(0)}$  must be expressed as

$$\frac{\delta \psi_a^{(0)}}{\delta \varsigma} \cdot \nabla \varsigma = \frac{\delta \psi_a^{(0)}}{\delta \rho} \cdot \nabla \rho + \frac{\delta \psi_a^{(0)}}{\delta \mathbf{u}} \cdot \nabla \mathbf{u} + \frac{\delta \psi_a^{(0)}}{\delta T} \cdot \nabla T, \quad (7.201)$$

$$\frac{\delta \Phi_a^{(0)}}{\delta \varsigma} \cdot \frac{d\varsigma}{dt} = \frac{\delta \Phi_a^{(0)}}{\delta \rho} \frac{d\rho}{dt} + \frac{\delta \Phi_a^{(0)}}{\delta \mathbf{u}} \cdot \frac{d\mathbf{u}}{dt} + \frac{\delta \Phi_a^{(0)}}{\delta T} \frac{dT}{dt}. \quad (7.202)$$

This set of equations implies that the volume fluctuations are determined by density, velocity, and temperature variations over space and time in the fluid, in addition to the inherent energy dissipation arising from the variation in the Voronoi volume in the course of molecular collisions. Therefore, if there are density, or temperature, or flow velocity gradients present in the fluid, volume fluctuations are expected to occur in mean molar volume and the associated transport coefficients to appear in the evolution equation. These new effects have been overlooked in the classical formulation of Navier–Stokes–Fourier hydrodynamics [10], and in the case of a mixture the effects are amplified by the coupling of volume fluctuations to mass diffusion and heat flow as will be seen shortly. However, at this point in development of the theory we do not have a precise idea of their magnitude of their coupling. The theory we formulate will provide ways to estimate theoretically or measure it experimentally.

The evolution equation for the total molar volume  $\Phi^{(0)}$  is obtained if (7.197) is summed over all species:

$$\begin{aligned} \rho \frac{d}{dt} \widehat{\Phi}^{(0)} &= -\nabla \cdot \psi^{(0)} + \frac{\delta \Phi^{(0)}}{\delta \varsigma} \cdot \frac{d\varsigma}{dt} \\ &\quad + \frac{\delta \varphi^{(1)}}{\delta \varsigma} \cdot \nabla \varsigma + f_v^{(0)} + \Lambda^{(0)}, \end{aligned} \quad (7.203)$$

where

$$\psi^{(0)} := \varphi^{(1)} = \sum_{a=1}^r \psi_a^{(0)}, \quad (7.204)$$

$$\mathcal{Z}^{(0)} = \sum_{a=1}^r \mathcal{Z}_a^{(0)}, \quad (7.205)$$

$$f_v^{(0)} = \sum_{a=1}^r f_{va}^{(0)}. \quad (7.206)$$

### 7.6.2.2 Evolution Equation for Diffusion Flux

The evolution equation for mass diffusion flux  $\Phi_a^{(1)}$  is obtained if the general procedure for (7.189) is followed with its statistical mechanical formula  $\Phi_a^{(1)}$  defined in (7.133). Its renormalized form is given by

$$\rho \frac{d\widehat{\Phi}_a^{(1)}}{dt} = -\nabla \cdot \overline{\psi}_a^{(1)} + \underline{\mathcal{Z}}_a^{(1)} + \Lambda_a^{(1)}, \quad (7.207)$$

where  $\nabla \cdot \overline{\psi}_a^{(1)}$  is obtained on combining the flux of mass flux with the divergence of virial tensor arising from the force term in the kinematic term, that is,  $\overline{\psi}_a^{(1)}$  is the renormalized flux of mass flux, which we find is related to the stress tensor of species  $a$ :

$$\overline{\psi}_a^{(1)} = \mathbf{P}_a - \mathfrak{c}_a \mathbf{P}. \quad (7.208)$$

The renormalized kinematic term  $\underline{\mathcal{Z}}_a^{(1)}$  is then given by

$$\begin{aligned} \underline{\mathcal{Z}}_a^{(1)} &= -p \mathbf{d}_a - \mathbf{J}_a \cdot \nabla \mathbf{u} + \mathbf{V}_a^{(1)} + \mathfrak{c}_a \nabla \cdot (\mathbf{P} - p \boldsymbol{\delta}) \\ &\quad - \nabla \cdot (\mathbf{P}_a - p_a \boldsymbol{\delta}). \end{aligned} \quad (7.209)$$

On the other hand, the pre-renormalized kinematic term  $\mathcal{Z}_a^{(1)}$  may be written as

$$\begin{aligned} \mathcal{Z}_a^{(1)} &= -p \mathbf{d}_a - \mathbf{J}_a \cdot \nabla \mathbf{u} + \mathbf{V}_a^{(1)} + \mathfrak{c}_a \nabla \cdot (\mathbf{P} - p \boldsymbol{\delta}) \\ &\quad - \nabla \cdot (\mathbf{P}_a^{(v)} - p_a \boldsymbol{\delta}), \end{aligned} \quad (7.210)$$

in which  $\mathbf{V}_a^{(1)}$  is the mean intermolecular force defined by

$$\mathbf{V}_a^{(1)} = \sum_{ja=1}^{N_a} \sum_{b=1}^r \sum_{kb>ja}^{N_b} \left\langle f^{(N)}(\mathbf{x}^{(N)}, t) \frac{1}{2} \mathbf{F}_{jakb} [\delta(\mathbf{r}_{ja} - \mathbf{r}) + \delta(\mathbf{r}_{kb} - \mathbf{r})] \right\rangle \quad (7.211)$$

and  $p_a$  is the partial pressure of species  $a$ . Note that in the last term on the right-hand side of (7.210)  $\mathbf{P}_a^{(v)}$  is replaced by  $\mathbf{P}_a$ , the full stress tensor, in (7.209). In both (7.209) and (7.210),  $\mathbf{d}_a$  is the thermodynamic force for diffusion defined by

$$\mathbf{d}_a = \nabla x_a + (x_a - \mathfrak{c}_a) \nabla \ln p + \frac{\rho_a}{p} (\widehat{\mathbf{F}} - \widehat{\mathbf{F}}_a) \quad (x_a = \frac{n_a}{n}). \quad (7.212)$$

It may sometimes be convenient to express  $\mathbf{d}_a$  in terms of  $\nabla \mathfrak{c}_a$  instead of  $\nabla x_a$  as follows:

$$\mathbf{d}_a = \nabla \mathfrak{c}_a + \frac{\rho}{p} \mathfrak{c}_a (\widehat{\mathbf{F}} - \widehat{\mathbf{F}}_a) + (x_a - \mathfrak{c}_a) \nabla \ln [(x_a - \mathfrak{c}_a) p]. \quad (7.213)$$

In the derivation of the kinematic term in (7.209),  $\mathbf{V}_a^{(1)}$  originally appears in the statistical mechanical form

$$\mathbf{V}_a^{(1)} = \sum_{ja=1}^{N_a} \sum_{b=1}^r \sum_{kb>ja}^{N_b} \left\langle f^{(N)}(\mathbf{x}^{(N)}, t) \mathbf{F}_{jakb} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle. \quad (7.214)$$

The right-hand side of this statistical mechanical formula can be written in a sum of two terms, one symmetric and the other antisymmetric with respect to interchange of  $ja$  and  $kb$  particle coordinates. The antisymmetric part of  $\mathbf{V}_a^{(1)}$  gives rise to a quantity involving the virial tensor  $\mathbf{W}_{jakb}$ , which is combined with the kinetic part of the pressure tensor  $\mathbf{P}^{(k)}$  appearing in the kinematic term to produce the full pressure tensor  $\mathbf{P}$ , leaving behind the symmetric part given in (7.211), where  $\mathbf{F}_{jakb} = m_a \widehat{\mathbf{F}}_{jakb}$  is the mean intermolecular force on species  $a$  at position  $\mathbf{r}$ , and  $\mathbf{F}_a$  is the external force per mass of species  $a$ :

$$\mathbf{F}_a = \rho_a \widehat{\mathbf{F}}_a = \frac{1}{2} \sum_{b=1}^r \sum_{ja=1}^{N_a} \sum_{ja<kb}^{N_b} \left\langle m_{ja} \widehat{\mathbf{F}}_a \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \quad (7.215)$$

The dissipation term  $\Lambda_a^{(1)}$  is, of course, given by the statistical mechanical formula

$$\Lambda_a^{(1)} = \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(1)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \Re[\mathbb{F}^{(N)}] \right\rangle. \quad (7.216)$$

Note that  $\Lambda_a^{(1)}$  does not vanish because  $h_{ja}^{(1)}$ , unless summed over species  $a$ , is not a collision invariant. This equation is superficially in the same form as the dissipation term for mass diffusion flux in the absence of volume transport phenomena, but it is coupled to the volume flux evolution equation through the dissipation term, which also depends on the volume flux in accordance with the symmetry constraints, namely, the Curie principle [15, 16].

### 7.6.2.3 Evolution Equation for Volume Flux

Since its molecular expression of volume flux  $\Phi^{(2)}$  is given by

$$h_{ja}^{(2)} = \mathbf{C}_{ja} h_{ja}^{(0)} - \alpha_a^{(2)} h_{ja}^{(1)} = m_a \mathbf{C}_{ja} \left( \widehat{h}_{ja}^{(0)} - \alpha_a^{(2)} \right), \quad (7.217)$$

differentiating its statistical mechanical average

$$\Phi^{(2)} = \sum_{a=1}^r \Phi_a^{(2)} = \sum_{a=1}^r \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(2)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (7.218)$$

we obtain its renormalized evolution equation in the form

$$\rho \frac{d\widehat{\Phi}_a^{(2)}}{dt} = -\nabla \cdot \overline{\psi}_a^{(2)} + \underline{\mathcal{Z}}_a^{(2)} + \Lambda_a^{(2)} \quad (7.219)$$

with  $\overline{\psi}_a^{(2)}$  defined by the formula

$$\overline{\psi}_a^{(2)} = \psi_a^{(2)} + \psi_a^{(2W)}; \quad (7.220)$$

the renormalized kinematic term by

$$\begin{aligned} \underline{\mathcal{Z}}_a^{(2)} &= -\rho (\widehat{\Phi}_a^{(0)} - \epsilon_a \alpha_a^{(2)}) \left( \frac{d\mathbf{u}}{dt} - \widehat{\mathbf{F}}_a \right) - \Phi_a^{(2)} \cdot \nabla \mathbf{u} - \mathbf{P}_a \cdot \nabla \alpha_a^{(2)} \\ &+ \mathbf{V}_a^{(2)} + \mathbf{f}_{va}^{(2)} + \frac{\partial \Phi_a^{(2)}}{\partial \varsigma} \odot \frac{d\varsigma}{dt} + \frac{\partial \varphi_a^{(2W)}}{\partial \varsigma} \odot \nabla \varsigma; \end{aligned} \quad (7.221)$$

and the dissipation term by the statistical mechanical formula

$$\Lambda_a^{(2)} = \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(2)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \Re[\underline{\mathbb{F}}^{(N)}(x^{(N)}, t)] \right\rangle. \quad (7.222)$$

The as-yet undefined symbols in (7.220) and (7.221) are defined as follows:

$$\psi_a^{(2W)} = \frac{1}{2} \sum_{b=1}^r \sum_{ja \neq kb=1}^{N_a, N_b} \left\langle f^{(N)} \left( \widehat{h}_{ja}^{(0)} - \alpha_a^{(2)} \right) \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle, \quad (7.223)$$

$$\psi_a^{(2)} = \sum_{ja=1}^{N_a} \left\langle f^{(N)} m_a \mathbf{C}_{ja} \mathbf{C}_{ja} (\widehat{h}_{ja}^{(0)} - \alpha_a^{(2)}) \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle, \quad (7.224)$$

and

$$\mathbf{f}_{va}^{(2)} = \sum_{b=1}^r \sum_{ja \neq kb \in z_{ja}}^{N_a, N_b} \left\langle f^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) m_a \mathbf{C}_{ja} \mathbf{C}_{kbja} \cdot \nabla_{\mathbf{r}_{kbja}} \widehat{h}_{ja}^{(0)}(\mathbf{r}_{jakb}) \right\rangle,$$

$$\mathbf{V}_a^{(2)} = \frac{1}{2} \sum_{b=1}^r \sum_{kb \neq ja=1}^{N_a, N_b} \left\langle f^{(N)} m_a \left( \widehat{h}_{ja}^{(0)} - \alpha_a^{(2)} \right) \right\rangle$$

$$\widehat{\mathbf{F}}_{jakb} [\delta(\mathbf{r}_{ja} - \mathbf{r}) + \delta(\mathbf{r}_{kb} - \mathbf{r})], \quad (7.225)$$

$$\varphi_a^{(2W)} = \psi^{(0K)} + \psi^{(0W)}$$

with  $\psi^{(0K)}$  and  $\psi^{(0W)}$  defined by

$$\psi_a^{(0K)} = \sum_{ja=1}^{N_a} \left\langle f^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathbf{C}_{ja} \mathbf{C}_{ja} m_a \widehat{h}_{ja}^{(0)} \right\rangle, \quad (7.226)$$

$$\psi_a^{(0W)} = \frac{1}{2} \sum_{b=1}^r \sum_{ja \neq kb=1}^{N_a, N_b} \left\langle f^{(N)} \widehat{h}_{ja}^{(0)} \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle. \quad (7.227)$$

In the expression for  $\mathbf{f}_{va}^{(2)}$  the sum over indices  $c$  and  $k$  must be restricted to particles making up the Voronoi volume around particle  $ja$ , and  $z_{ja}$  denotes the coordination number around particle  $j \in a$ .

Summing over species we obtain the evolution equation for the total volume flux:

$$\rho \frac{d\widehat{\Phi}^{(2)}}{dt} = -\nabla \cdot \overline{\psi}^{(2)} + \overline{\mathcal{Z}}^{(2)} + \Lambda^{(2)}, \quad (7.228)$$

where  $\widehat{\Phi}^{(2)}$ ,  $\overline{\psi}^{(2)}$ ,  $\overline{\mathcal{Z}}^{(2)}$ , and  $\Lambda^{(2)}$  are sums of their species components  $\widehat{\Phi}_a^{(2)}$ , etc.

This evolution equation would be of particular interest in the study of volume transport phenomena. This is a new addition to the generalized hydrodynamic equations in the presence of volume transport phenomena in the case of a liquid mixture.

#### 7.6.2.4 Evolution Equation of Heat Flux

The evolution equation for heat flux  $\Phi^{(3)}$  can be derived similarly for the evolution equations for  $\Phi^{(2)}$ ,  $\Phi^{(1)}$ , and  $\Phi^{(0)}$  presented. We find the renormalized evolution equation for heat flux in the form

$$\rho \frac{d\widehat{\Phi}_a^{(3)}}{dt} = -\nabla \cdot \overline{\psi}_a^{(3)} + \overline{\mathcal{Z}}_a^{(3)} + \Lambda_a^{(3)}, \quad (7.229)$$

where the dissipation term  $\Lambda_a^{(3)}$  is given by

$$\Lambda_a^{(3)} = \sum_{ja=1}^{N_a} \left\langle h_a^{(3)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \Re[\overline{\mathbb{F}}^{(N)}(x^{(N)}, t)] \right\rangle; \quad (7.230)$$

the renormalized flux  $\bar{\psi}_a^{(3)}$  of  $\Phi_a^{(3)}$  is defined by the statistical expressions

$$\bar{\psi}_a^{(3)} = \sum_{ja=1}^{N_a} \left\langle f^{(N)} \mathbf{C}_{ja} \left( \mathcal{H}_{ja}^{(h)} - m_a \hat{h}_a \right) \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle + \psi_a^{(3W)}, \quad (7.231)$$

$$\begin{aligned} \psi_a^{(3W)} &= \frac{1}{2} \sum_{b=1}^r \sum_{ja \neq kb=1}^{N_a, N_b} \left\langle f^{(N)} \mathbf{C}_{ja} \mathbf{C}_{ja} \cdot \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle \\ &\quad + \frac{1}{2} \sum_{b=1}^r \sum_{ja \neq kb=1}^{N_a, N_b} \left\langle f^{(N)} \mathbf{C}_{ja} \left( \mathcal{H}_{ja}^{(h)} - m_a \hat{h}_a \right) \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle \\ &\quad + \frac{1}{4} \sum_{b,c=1}^r \sum_{ja \neq kb \neq lc=1}^{N_a, N_b, N_c} \left\langle f^{(N)} \frac{1}{m_a} \mathbf{W}_{jakb} \cdot \mathbf{W}_{jalc} \delta(\mathbf{r}_{lc} - \mathbf{r}) \right\rangle; \end{aligned} \quad (7.232)$$

and the renormalized kinematic term  $\bar{\mathcal{Z}}_a^{(3)}$  by

$$\begin{aligned} \bar{\mathcal{Z}}_a^{(3)} &= - \left[ \rho_a (\mathcal{E}_a - \hat{h}_a) d_t \mathbf{u} + d_t \mathbf{u} \cdot \mathbf{P}_a - \mathbf{J}_a \cdot d_t \hat{h}_a \right] \\ &\quad - \mathbf{Q}'_a \cdot \nabla \mathbf{u} + \mathbf{P}_a \cdot \nabla \hat{h}_a - \varphi_a^{(3W)} \odot \nabla \mathbf{u} + \mathbf{V}_a^{(3)} \\ &\quad - \alpha_a^{(32)} \left[ \alpha_a^{(2)} \rho_a (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) - \Phi_a^{(0)} (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) \right. \\ &\quad \quad \left. + \mathbf{V}_a^{(2)} + \mathbf{f}_{va}^{(2)} + d_t \boldsymbol{\varsigma} \cdot \frac{\delta \psi_a^{(0)}}{\delta \boldsymbol{\varsigma}} + \frac{\delta \varphi_a^{(2W)}}{\delta \boldsymbol{\varsigma}} : \nabla \boldsymbol{\varsigma} \right. \\ &\quad \quad \left. - \Phi_a^{(1)} d_t \alpha_a^{(2)} - \mathbf{P}_a \cdot \nabla \alpha_a^{(2)} - (\psi_a^{(0)} - \Phi_a^{(1)} \alpha_a^{(2)}) \cdot \nabla \mathbf{u} \right] \\ &\quad - \Phi_a^{(2)} d_t \alpha_a^{(32)} - \sum_{a=1}^r \psi_a^{(2W)} \nabla \alpha_a^{(32)} \end{aligned} \quad (7.233)$$

with various symbols defined by

$$\begin{aligned} \sum_{a=1}^r \mathbf{V}_a^{(3)} &= - \frac{1}{2} \sum_{a,b=1}^r \sum_{ja \neq kb=1}^{N_a, N_b} \left\langle f^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) m_a \mathbf{C}_{ja} \mathbf{C}_{jakb} \cdot \widehat{\mathbf{F}}_{jakb} \right\rangle \\ &\quad - \frac{1}{2} \sum_{a,b=1}^r \sum_{ja \neq kb=1}^{N_a, N_b} \left\langle f^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathbf{C}_{kb} \mathbf{C}_{jakb} : \nabla_{\mathbf{r}_{kbja}} \mathbf{W}_{kbja} \right\rangle \\ &\quad + \frac{1}{2} \sum_{a,b=1}^r \sum_{ja \neq kb=1}^{N_a, N_b} \left\langle f^{(N)} [\delta(\mathbf{r}_{ja} - \mathbf{r}) + \delta(\mathbf{r}_{kb} - \mathbf{r})] \times \right. \\ &\quad \quad \left. \widehat{\mathbf{F}}_{jakb} \cdot [(H_{ja} - m_a \hat{h}_a) \delta + \mathbf{T}_{jakb}] \right\rangle, \end{aligned} \quad (7.234)$$

$$\varphi_a^{(3W)} = \varphi_a^{(3)} + \frac{1}{2} \sum_{b=1}^r \sum_{ja \neq kb=1}^{N_a, N_b} \langle f^{(N)} \mathbf{C}_{ja} \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) \rangle, \quad (7.235)$$

$$\begin{aligned} \psi^{(2W)} &= \sum_{a=1}^r \psi_a^{(2W)} \\ &= \frac{1}{2} \sum_{a,b=1}^r \sum_{ja \neq kb=1}^{N_a, N_b} \left\langle f^{(N)} \left( \hat{h}_{ja}^{(0)} - \alpha_a^{(2)} \right) \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle. \end{aligned} \quad (7.236)$$

Finally, on summing (7.229) over all species, we obtain the evolution equation for the total heat flux  $\Phi^{(3)}$ :

$$\rho \frac{d\widehat{\Phi}^{(3)}}{dt} = -\nabla \cdot \overline{\psi}^{(3)} + \underline{\mathcal{Z}}^{(3)} + \Lambda^{(3)}, \quad (7.237)$$

where

$$\begin{aligned} \Phi^{(3)} &= \sum_{a=1}^r \Phi_a^{(3)}; & \underline{\mathcal{Z}}^{(3)} &= \sum_{a=1}^r \underline{\mathcal{Z}}_a^{(3)}; \\ \Lambda^{(3)} &= \sum_{a=1}^r \Lambda_a^{(3)}; & \overline{\psi}^{(3)} &= \sum_{a=1}^r \overline{\psi}_a^{(3)}. \end{aligned} \quad (7.238)$$

The heat flux evolution equation is most complicated to derive among the leading moment evolution equations discussed in this work, but mathematically straightforward to derive.

We will present a physically more transparent, but approximate form for the evolution equation when we discuss transport coefficients in the presence of volume transport phenomena in a later section. Even at the formal theory level, we see that heat flux evolution is coupled to the volume flux evolution equation and, more generally, volume transport phenomena. Therefore it is expected that the heat conductivity would exhibit its dependence on a volume transport effect as will be shown more explicitly in a later section.

### 7.6.2.5 Evolution Equation for Shear Stress

Unlike the preceding nonconserved macroscopic scalars and vectors in the moment set, the shear stress  $\Phi_a^{(4)}$  is not directly coupled to either of them. In any case, the evolution equation for  $\Phi_a^{(4)}$  is relatively simpler to derive than, for example, the heat flux evolution equation. Following the same procedure as used for the previous evolution equations, we obtain the shear flux evolution equation in the form

$$\rho \frac{d\widehat{\Phi}_a^{(4)}}{dt} = -\nabla \cdot \overline{\psi}_a^{(4)} + \overline{\mathcal{Z}}_a^{(4)} + \Lambda_a^{(4)}, \quad (7.239)$$

where the dissipation term is given by

$$\Lambda_a^{(4)} = \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(4)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \Re[\bar{\mathbb{F}}^{(N)}(x^{(N)}, t)] \right\rangle. \quad (7.240)$$

The renormalized flux  $\overline{\psi}_a^{(4)}$  of  $\Phi_a^{(4)}$  is given by

$$\overline{\psi}_a^{(4)} = \psi_a^{(4K)} + \psi_a^{(4W)}, \quad (7.241)$$

where  $\psi_a^{(4)}$  and  $\psi_a^{(4W)}$  are, respectively, defined by the statistical mechanical formulas

$$\psi_a^{(4K)} = \sum_{ja=1}^{N_a} \left\langle f^{(N)}(\mathbf{x}^{(N)}, t) \mathbf{C}_{ja} [m_a \mathbf{C}_{ja} \mathbf{C}_{ja}]^{(2)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle, \quad (7.242)$$

$$\psi_a^{(4W)} = \frac{1}{2} \sum_{b=1}^r \sum_{kb \neq ja=1}^{N_a, N_b} \left\langle f^{(N)}(\mathbf{x}^{(N)}, t) \left\{ \mathbf{C}_{ja} [\mathbf{W}_{jakb}]^{(2)} \right\} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle. \quad (7.243)$$

In (7.243) the curly brackets denote symmetrization of the third-rank tensor  $\mathbf{C}_{ja} [\mathbf{W}_{jakb}]^{(2)}$ :

$$\begin{aligned} \left\{ \mathbf{C}_{ja} [\mathbf{W}_{jakb}]^{(2)} \right\}^{\gamma\alpha\beta} &= \mathbf{C}_{ja}^\gamma [\mathbf{W}_{jakb}]^{(2)\alpha\beta} + \mathbf{C}_{ja}^\alpha [\mathbf{W}_{jakb}]^{(2)\gamma\beta} \\ &\quad + \mathbf{C}_{ja}^\beta [\mathbf{W}_{jakb}]^{(2)\alpha\gamma}. \end{aligned} \quad (7.244)$$

The renormalized kinematic term  $\overline{\mathcal{Z}}_a^{(4)}$  is given by

$$\overline{\mathcal{Z}}_a^{(4)} = -2 [\mathbf{P}_a \cdot \nabla \mathbf{u}]^{(2)} - 2 \left[ \mathbf{J}_a \frac{d\mathbf{u}}{dt} \right]^{(2)} + 2 [\widehat{\mathbf{F}}_a \mathbf{J}_a]^{(2)} + \mathbf{V}_a^{(4)} \quad (7.245)$$

with traceless symmetric tensor  $\mathbf{V}_a^{(4)}$  given by the expression

$$\begin{aligned} \mathbf{V}_a^{(4)} &= \sum_{b=1}^r \sum_{ia=1}^{N_a} \sum_{kb \neq ia}^{N_b} \left\langle \overline{f}^{(N)} [\mathbf{F}_{iakb} \mathbf{C}_{iakb}]^{(2)} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle \\ &\quad + \frac{1}{2} \sum_{ia=1}^{N_a} \sum_{jb \neq ia}^{N_b} \left\langle \overline{f}^{(N)} \mathbf{C}_{iajb} \cdot \nabla_{iajb} [\mathbf{W}_{iajb}]^{(2)} \delta(\mathbf{r}_{jb} - \mathbf{r}) \right\rangle. \end{aligned} \quad (7.246)$$

In this expression  $\mathbf{C}_{iakb}$  is defined by

$$\begin{aligned}\mathbf{C}_{jakk} &= \mathbf{C}_{ja} - \mathbf{C}_{kb}, \\ m_{ab} &= \frac{m_a m_b}{m_a + m_b} \text{ (reduced mass).}\end{aligned}\quad (7.247)$$

Upon summing (7.239) over species we obtain the total shear stress evolution equation:

$$\rho \frac{d\widehat{\Phi}^{(4)}}{dt} = -\nabla \cdot \overline{\psi}^{(4)} + \overline{\mathcal{Z}}^{(4)} + \Lambda^{(4)}, \quad (7.248)$$

where

$$\overline{\psi}^{(4)} = \sum_{a=1}^r \overline{\psi}_a^{(4)}, \quad \overline{\mathcal{Z}}^{(4)} = \sum_{a=1}^r \overline{\mathcal{Z}}_a^{(4)}, \quad \Lambda^{(4)} = \sum_{a=1}^r \Lambda_a^{(4)} \quad (7.249)$$

Experimentally, since we are not usually interested in evolution of component stress tensors, the evolution equation for total stress tensor will be sufficient for studying shear flow phenomena. The evolution equation (7.239) is not coupled to evolution equations for scalars and vectors particularly in the linear regime of thermodynamic driving forces in accordance with the Curie principle, as will be seen later.

### 7.6.2.6 Evolution Equation for Excess Normal Stress

In the absence of volume transport it is natural to choose for the excess normal stress the molecular moment

$$\begin{aligned}h_{ja}^{(5)} \delta(\mathbf{r}_{ja} - \mathbf{r}) &= \left( \frac{1}{3} m_a C_{ja}^2 - m_a p / \rho \right) \delta(\mathbf{r}_{ja} - \mathbf{r}) \\ &+ \frac{1}{6} \sum_{b=1}^r \sum_{ja \neq kb=1}^{N_b} \text{Tr} \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r})\end{aligned}\quad (7.250)$$

to be consistent with the moment chosen for the traceless symmetric part of the stress tensor in the same experimental conditions. Physically, the average of this molecular moment represents the excess normal stress over and above the equilibrium pressure  $p$ . The average of  $h_{ja}^{(5)}$  gives the excess normal stress

$$\overline{\Delta} = \sum_{a=1}^r \overline{\Delta}_a = \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} h_{ja}^{(5)} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle, \quad (7.251)$$

which is related to compression/decompression of the fluid and thus its bulk viscosity in the absence of volume transport phenomena.

If the volume transport is taken into account, the molecular moment for molar volume  $h_{ja}^{(0)}$ , which is scalar, is coupled to the excess normal stress for symmetry reason. It turns out  $h_{ja}^{(0)}$  is the only scalar in the set of moments introduced so far. Thus we define the molecular moment for the excess normal stress in the form

$$\bar{h}_{ja}^{(5)} = \left( h_{ja}^{(5)} - \alpha_a^{(5)} h_{ja}^{(0)} \right) \delta(\mathbf{r}_{ja} - \mathbf{r}). \quad (7.252)$$

Recall  $h_{ja}^{(0)}$  is the molecular expression for molar domain given in terms of the Voronoi volume  $m_a V_{ja}(|\mathbf{r}_{ja} - \mathbf{r}|, j \in z_{ja}|\varsigma|)$  of particle  $ja$  introduced earlier. The mean value of moment  $\bar{h}_{ja}^{(5)}$  defines the modified excess normal stress

$$\begin{aligned} \Phi_a^{(5)} &:= \Delta_a \\ &= \left\langle \sum_{ja=1}^{N_a} \left( h_{ja}^{(5)} - \alpha_a^{(5)} h_{ja}^{(0)} \right) \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle \\ &= \overline{\Delta}_a - \alpha_a^{(5)} \Phi_a^{(0)} \end{aligned} \quad (7.253)$$

and we obtain the evolution equation for  $\Phi_a^{(5)} = \rho \widehat{\Phi}_a^{(5)}$  in the renormalized form

$$\rho \frac{d\widehat{\Phi}_a^{(5)}}{dt} = -\nabla \cdot \overline{\psi}_a^{(5)} + \overline{\mathcal{Z}}_a^{(5)} + \Lambda_a^{(5)}. \quad (7.254)$$

Here the dissipation term  $\Lambda_a^{(5)}$  and  $\overline{\psi}_a^{(5)}$  are, respectively, defined by the statistical mechanical formulas

$$\Lambda_a^{(5)} = \left\langle \sum_{ja=1}^{N_a} h_{ja}^{(5)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \Re[\overline{\mathbb{F}}^{(N)}(\mathbf{x}^{(N)}, t)] \right\rangle; \quad (7.255)$$

$$\begin{aligned} \overline{\psi}_a^{(5)} &= \sum_{b=1}^r \sum_{ia=1}^{N_a} \frac{1}{3} \left\langle \overline{f}^{(N)} m_{ia} \mathbf{C}_{ia} \mathbf{C}_{ia} \cdot \mathbf{C}_{ia} \delta(\mathbf{r}_{ia} - \mathbf{r}) \right\rangle \\ &\quad + \frac{1}{6} \sum_{ia=1}^{N_a} \sum_{jb \neq ia}^{N_b} \left\langle f^{(N)} \{ \mathbf{C}_{ia} \mathbf{W}_{iab} \} \delta(\mathbf{r}_{jb} - \mathbf{r}) \right\rangle - \alpha_a^{(5)} \varphi_a^{(1)} - \alpha_a^{(5)} \Phi_a^{(2)}, \end{aligned} \quad (7.256)$$

and the renormalized kinematic term  $\overline{\mathcal{Z}}_a^{(5)}$  by

$$\begin{aligned} \overline{\mathcal{Z}}_a^{(5)} &= -\rho \frac{d}{dt} (\mathfrak{c}_a p v) - \frac{2}{3} \mathbf{P}_a : \nabla \mathbf{u} - \frac{2}{3} \mathbf{J}_a \cdot \frac{d\mathbf{u}}{dt} + \frac{2}{3} \widehat{\mathbf{F}}_a \cdot \mathbf{J}_a - \rho \frac{d\alpha_a^{(5)}}{dt} \widehat{\Phi}_a^{(0)} \\ &\quad - \rho \widehat{\Phi}^{(2)} \cdot \nabla \alpha^{(5)} - \alpha_a^{(5)} (d_t \mathfrak{c}_a \cdot \mathbf{v}_s + f_{va}) + V_a^{(5)}. \end{aligned} \quad (7.257)$$

Here  $V_a^{(5)}$  consists of intermolecular interaction potential contributions:

$$\begin{aligned} V_a^{(5)} = & \frac{1}{3} \sum_{b=1}^r \sum_{ja \neq kb=1}^{N_a, N_b} \langle f^{(N)} \widehat{\mathbf{F}}_{jakb} \cdot \mathbf{C}_{jakb} \delta(\mathbf{r}_{ja} - \mathbf{r}) \rangle \\ & + \frac{1}{6} \sum_{b=1}^r \sum_{ja \neq kb=1}^{N_a, N_b} \langle f^{(N)} \mathbf{C}_{jakb} \cdot (\nabla_{\mathbf{r}_{jakb}} \text{Tr} \mathbf{W}_{jakb}) \delta(\mathbf{r}_{kb} - \mathbf{r}) \rangle. \end{aligned} \quad (7.258)$$

On summing (7.254) over species we obtain the evolution equation for the total excess normal stress density  $\widehat{\Phi}^{(5)}$  in the presence of volume transport phenomena:

$$\rho \frac{d\widehat{\Phi}^{(5)}}{dt} = -\nabla \cdot \overline{\psi}^{(5)} + \overline{\mathcal{Z}}^{(5)} + \Lambda^{(5)}. \quad (7.259)$$

The evolution equation for the excess normal stress in the absence of volume transport would be obtained if  $\alpha_a^{(5)}$  and  $\Phi_a^{(0)}$  were set equal to zero in (7.254). In connection with the volume transport phenomena, we reiterate the difference between the specific volume  $\widehat{v} = 1/\rho$  and the molar domain or volume  $v$  in the present theory and that  $\alpha_a^{(5)}$  is associated with molar domain fluctuations. The volume fluctuations of this kind have an effect on bulk viscosity. Therefore the volume transport should manifest itself in bulk viscous phenomena and thus would leave its signature experimentally on the bulk viscosity coefficient. It will also have effects on the heat conductivity and mass diffusion. We will see this feature more explicitly when we discuss linear transport processes in later sections.

By this, we have completed, within the framework of moment method, the derivations of evolution equations for the generalized hydrodynamics in the presence of volume transport phenomena in a simple fluid mixture. *The 10 evolution equations presented above constitute the generalized hydrodynamic equations for mixtures in the presence of volume transport phenomena that we will use within the framework of 16 moments in all.* Because the volume transport processes are included in them, the generalized hydrodynamic equations are extended beyond those of the conventional “13 moments” considered by Grad [12] in the cases of dilute gases obeying the Boltzmann equation and single-component liquids obeying the generalized Boltzmann equation discussed in the previous chapters. The dissipation terms will be given in more explicit forms, when the underlying theory of irreversible processes is formulated and the generalized hydrodynamics is thereby made thermodynamically consistent by subjecting the evolution equations to the thermodynamic laws in the subsequent sections.

## 7.7 Thermodynamics of Irreversible Processes in a Mixture

The evolution equations presented for macroscopic variables in the previous sections do not directly represent the solutions of the kinetic equation. Not only are they merely projections of the kinetic equation onto the manifold of macroscopic variables, but also incomplete, because the dissipation terms are not as yet calculated more explicitly in forms useful for practical study of fluid phenomena, in particular, the transport properties. The calculation of dissipation terms, unlike the kinematic terms, would demand a little more explicit description of many-particle dynamics and some appropriate systematic description of the solution for the kinetic equation. This important task cannot be achieved in a single step, but must be broken up into smaller sequential steps. It will be useful to briefly consider what is done in the case of the Boltzmann equation for dilute monatomic gases, the extended Boltzmann equation, and the GBE for a simple dense fluid in Chaps. 4, 5, and 6, respectively.

The kinetic equation should in principle give rise to a distribution function such that it faithfully contains and reflects the molecular dynamical information of the systems, so that we are able to comprehend the molecular cause for the observed phenomena of the fluid system in hand. Since the kinetic equation is a set of first-order nonlinear partial differential equations in the phase space, one might be tempted to solve it as such, provided that initial and boundary conditions are supplied. However, it is not a productive approach to try as we would a partial differential equation in other context because of the many-body dynamics of astronomically large number of particles (molecules) involved and insufficient knowledge on initial and boundary conditions necessary for solving the kinetic equation as partial differential equations. Neither is the many-particle collision problem itself possible to solve in simple tractable forms. In such circumstances we look for more practicable methodologies to extract molecular information from the molecular theoretic viewpoint.

We have learned in the case of dilute gas kinetic theory how we might approach the subject. Here we will follow the same trail of thoughts with the postulated kinetic equation—the GBE—for the dense gases and liquids. Other alternative forms may be equally well used for the kinetic equation, if they are capable of yielding a thermodynamic theory of irreversible phenomena in a way consistent with the laws of thermodynamics.

Historically, in the Chapman–Enskog theory [18] of solution for the Boltzmann kinetic equation a functional hypothesis is taken for the distribution functions obeying the kinetic equation in which the distribution functions are regarded as functionals of conserved variables ( $\rho, \mathbf{u}, \mathcal{E}$ ) (or  $T$  in place of  $\mathcal{E}$ ) and their time and spatial derivatives. In the Chapman–Enskog expansion method of solution, the Boltzmann equation is turned into hydrodynamic equations given in terms of the functional derivatives. These equivalent hydrodynamic equations, finite in number, are then solved subject to initial and boundary conditions on hydrodynamic variables of the conserved variables. Therefore, the kinetic equation (Boltzmann equation) is not directly solved as partial differential equations as the usual mathematical method would suggest. Nevertheless, the Boltzmann equation is deemed solved thereby and

the macroscopic and hydrodynamic properties of the dilute gases described by the Boltzmann equation are understood from the molecular theory viewpoint through hydrodynamic field variables. This is one approach to the “solution” of the Boltzmann equation in kinetic theory.

On the other hand, in Grad’s method [12] (or moment method) of “solution” for the Boltzmann equation the Chapman–Enskog functional hypothesis is broadened by extending the thermodynamic manifold spanned by  $(\rho, \mathbf{u}, \mathcal{E})$  such that it includes fluxes such as mass fluxes, heat fluxes, pressure tensors, etc. We will call these fluxes, collectively, moments in this work. Therefore, in Grad’s moment method the Boltzmann equation describing the distribution functions for particles in the phase space of Avogadro’s number of particles are projected onto a finite number of macroscopic evolution equations for moments (macroscopic variables), which may then be solved suitably subjected to their initial and boundary conditions. Thus, “solution” of the Boltzmann equation is replaced by solutions of the macroscopic evolution equations—partial differential equations—for the variables spanning the thermodynamic manifold. This method is evidently distinctive from the Chapman–Enskog method, although their connection may be established in some sense.

The terminology we use for solution must be understood in the sense of the Chapman–Enskog method or Grad’s moment method as described earlier. In the present work, the moment method approach is taken with the GBE as the kinetic equation for dense gases and liquids. In the previous sections we have derived the kinematic terms in the evolution equations mentioned. Now, we are going to lay the methodological foundation for calculating the dissipation terms in the evolution equations and their thermodynamic consistency, which have been deferred to the end, because a theory of irreversible thermodynamics must be formulated before demonstrating that the generalized hydrodynamic equations presented are consistent with the laws of thermodynamics. We attend to this subject in the following.

### 7.7.1 Nonequilibrium Grand Canonical Ensemble Theory

#### 7.7.1.1 Functional Hypothesis

We assume the following hypothesis [3, 8] for the distribution functions:

*The distribution functions  $f^{(N)}(\mathbf{x}^{(N)}, t)$  are functionals of macroscopic observables spanning the thermodynamic manifold, which is a union of manifold  $\mathfrak{P} := (\rho, v_a, \mathbf{u}, \mathcal{E}, \Phi_a^{(q)} : 1 \leq a \leq r; q \geq 0)$  and their conjugate tangent manifold  $\mathfrak{T} := (T, p, \mu_a, X_a^{(q)} : 1 \leq a \leq r; q \geq 0)$ . The variables spanning the thermodynamic manifold  $(\mathfrak{P} \cup \mathfrak{T})$  obey their evolution equations derived from the kinetic equation and presented earlier.*

Therefore the distribution functions evolve according to the time and spatial scales determined by the variables spanning the thermodynamic manifold, constrained by thermodynamic laws, as will be shown presently. Since the elements of the thermo-

dynamic manifold are subjected to the constraints imposed by the thermodynamic laws, the evolutions of the variables spanning the thermodynamic manifold can be made consistent with the thermodynamic laws, and we have a thermodynamically consistent theory of macroscopic irreversible processes in the present theory.

### 7.7.1.2 Nonequilibrium Grand Canonical Form

Under the functional hypothesis the (nonequilibrium) grand canonical form  $f_c^{(N)}$  will be taken to be a functional of variables spanning the thermodynamic manifold in the form

$$\bar{f}_c^{(N)}(\mathbf{x}^{(N)}, t) = \exp \left[ - \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ia=1}^{N_a} \beta \mathcal{H}_{ia}^{(N)} \delta(\mathbf{r}_{ia} - \mathbf{r}) - \ln \mathbb{Z}^{(N)} \right], \quad (7.260)$$

where  $\mathbb{Z}^{(N)}$  is the normalization factor

$$\mathbb{Z}^{(N)} = \left\langle \exp \left[ - \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ia=1}^{N_a} \beta \mathcal{H}_{ia}^{(N)} \delta(\mathbf{r}_{ia} - \mathbf{r}) \right] \right\rangle. \quad (7.261)$$

Here recall that angular brackets  $\langle A \rangle$  stands for the integral

$$\langle A \rangle = \sum_{\{N\} \geq 0} \int d\mathbf{x}^{(N)} A \quad (7.262)$$

and it should be kept in mind that the volume  $V$  is the same for all subsystems of the ensemble. The parameter  $\beta = 1/k_B T(\mathbf{r}, t)$  is proportional to the local inverse temperature  $T(\mathbf{r}, t)$ , which remains an as-yet undetermined parameter. A more explicit form for  $\mathcal{H}_{ia}^{(N)}$  will be stated in the next subsection where the notion of calortropy is introduced.

### 7.7.2 Calortropy

The exponential form for  $f_c^{(N)}$  for the nonequilibrium grand canonical form is suggested by the  $H$  function (i.e., Boltzmann entropy) and, more specifically, by its projection of  $H$  function onto the thermodynamic manifold. The aforementioned projection of  $S$  is called the calortropy  $\Psi$ . We have earlier seen that the  $H$  theorem is a stability theorem of the equilibrium solution of the kinetic equation and the associated  $H$  function is a Lyapounov function [6, 7] characterizing the stability of equilibrium solution in the phase space. In other words, the Boltzmann's entropy characterizes the stability of the equilibrium solution in the phase space.

Consequently, the  $H$  theorem of Boltzmann on entropy is wider and larger than the second law of thermodynamics in the sense that it is a stability theorem for the solution of the kinetic equation in the phase space, but not in the thermodynamic manifold that is a projection of the phase space onto a space of much smaller than the former. In contrast to the Boltzmann entropy  $S$ , the calortropy  $\Psi$  is thermodynamic in its basic nature and a function depending on the variables spanning the thermodynamic manifold, and it characterizes the thermodynamic equilibrium of the system in the thermodynamic manifold as the system tends to equilibrium. It is, therefore, related to the Boltzmann entropy  $S$ , but *not equal to the Boltzmann entropy itself* except at equilibrium. It is defined by the statistical mechanical formula

$$\Psi = -k_B \langle f^{(N)} \ln f_c^{(N)} \rangle, \quad (7.263)$$

which may be interpreted as a projection of the Boltzmann entropy onto the thermodynamic manifold in the sense that  $f_c^{(N)}$  is a projection of  $f^{(N)}$  onto the thermodynamic manifold. Since this calortropy  $\Psi$  must be a linear combination of the variables spanning the thermodynamic manifold, we have found it natural to take an exponential form for  $f_c^{(N)}$  as in (7.260) to meet the phenomenological theory requirement for  $\Psi$ . To formulate the thermodynamics [17] of irreversible processes,  $\mathcal{H}_{ja}^{(N)}$  in  $\bar{f}_c^{(N)}(\mathbf{x}^{(N)}, t)$  is represented more explicitly by taking as follows<sup>14</sup>:

$$\mathcal{H}_{ja}^{(N)} = H'_{ja}^{(N)} + \sum_{q \geq 0} X_a^{(q)} h_{ja}^{(q)} - m_{ja} \hat{\mu}_a. \quad (7.264)$$

Here  $H'_{ja}^{(N)}$  denotes the Hamiltonian of particle  $j \in a$ , and  $T, \hat{\mu}_a$ , and  $X_a^{(q)}$  macroscopic parameters<sup>15</sup> as yet undetermined. The latter will turn out to be the thermodynamic temperature, the nonequilibrium chemical potential per unit mass of species  $a$ , and the generalized potentials, all of which generally depend on the variables of the thermodynamic manifold when the theory of irreversible thermodynamics is fully in place in a way consistent with the laws of thermodynamics. They are going to be determined self-consistently within the framework of the theory of irreversible processes formulated. The moments  $h_{ja}^{(q)}$  have been already defined and their meanings discussed.

<sup>14</sup>In the following expression for  $\mathcal{H}_{ja}^{(N)}$  the nonequilibrium terms do not involve more than one species. This is a special model for the nonequilibrium contribution to which we will confine the theory. It may be generalized with a more complicated structure of the theory resulting thereby. Such a complication is not warranted at this point in development.

<sup>15</sup>At this point in development of theory it would be more appropriate to regard  $T, \hat{\mu}_a$ , and  $X_a^{(q)}$ , respectively, as parameters conjugate to energy, mass, and moments characterizing nonequilibrium, but we are using the term temperature, *nonequilibrium chemical potential*, and *generalized potentials* in anticipation of their identification as such through thermodynamic correspondences made between the statistical mechanical and phenomenological quantities.

Since the global calortropy  $\Psi$  may be expressed in terms of calortropy density  $\widehat{\Psi}(\mathbf{r}, t)$  by the formula

$$\Psi = \int_V d\mathbf{r} \rho \widehat{\Psi}(\mathbf{r}, t), \quad (7.265)$$

the calortropy density can be deduced, with the help of the functional hypothesis (7.260), from the formula

$$\rho \widehat{\Psi}(\mathbf{r}, t) = \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} f^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \left( T^{-1} \mathcal{H}_{ja}^{(N)} \right) + k_B \ln \mathbb{Z}^{(N)} \right\rangle. \quad (7.266)$$

Now, if the local density of  $\ln \mathbb{Z}^{(N)}$  is looked for in the form

$$\ln \mathbb{Z}^{(N)} = \int_V d\mathbf{r} \rho \ln \Gamma, \quad (7.267)$$

where  $\ln \Gamma$  is the local density of  $\ln \mathbb{Z}^{(N)}$ , then since the right hand side of (7.267) can be written in the form

$$\int_V d\mathbf{r} \rho \ln \Gamma = \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} f^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) m_{ja} \right\rangle \ln \Gamma,$$

substitution of  $\mathcal{H}_{ja}^{(N)}$  given in (7.264) yields the calortropy density in the bilinear form

$$\widehat{\Psi} = \frac{1}{T} \left( \mathcal{E} + \sum_{a=1}^r \sum_{q \geq 0} X_a^{(q)} \widehat{\Phi}_a^{(q)} - \sum_{a=1}^r \widehat{\mu}_a \mathfrak{c}_a + k_B T \ln \Gamma \right). \quad (7.268)$$

We will return to the relation of  $\mathbb{Z}^{(N)}$  to  $\Gamma$  in (7.267). The relation will enable us to obtain statistical mechanical expression for  $\Gamma$ .

Differentiating (7.263) with time, using  $\overline{f}_c^{(N)}$  in (7.260) and the GBE, yields the calortropy density balance equation

$$\rho \frac{d\widehat{\Psi}}{dt} = -\nabla \cdot \mathbf{J}_c + \sigma_c + \mathbb{D}, \quad (7.269)$$

for which we define, respectively, the calortropy flux  $\mathbf{J}_c$ , the calortropy production  $\sigma_c$ , and  $\mathbb{D}$ , the kinematic contribution to the calortropy, by the statistical mechanical formulas

$$\mathbf{J}_c = \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} f^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathcal{H}_{ja}^{(N)} \mathbf{C}_{ja} \right\rangle, \quad (7.270)$$

$$\sigma_c = \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} f^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathcal{H}_{ja}^{(N)} \mathfrak{R}[\mathbb{F}^{(N)}] \right\rangle, \quad (7.271)$$

$$\mathbb{D} = k_B \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} f^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathcal{D}_t \left( T^{-1} \mathcal{H}_{ja}^{(N)} + m_{ja} \ln \Gamma \right) \right\rangle. \quad (7.272)$$

To make further progress from here we investigate the integrability of the calortropy balance equation in the thermodynamic manifold. For the purpose we show how a Pfaffian differential form may be obtained from the calortropy density balance equation (7.269).

### 7.7.2.1 Pfaffian Form for Calortropy Density

With the form (7.264) for  $\mathcal{H}^{(N)}$  the calortropy flux and production can be easily calculated from their statistical mechanical expressions (7.270) and (7.271), respectively. They are given by the formulas:

$$\mathbf{J}_c = T^{-1} \mathbf{Q}^{(h)} + \sum_{a=1}^r \sum_{q \geq 0} T^{-1} X_a^{(q)} \psi_a^{(q)} - \sum_{a=1}^r T^{-1} \hat{\mu}_a \mathbf{J}_a, \quad (7.273)$$

$$\sigma_c = \sum_{a=1}^r \sum_{q \geq 0} T^{-1} X_a^{(q)} \Lambda_a^{(q)}, \quad (7.274)$$

where  $\mathbf{Q}^{(h)}$  is a heat flux defined by the formula

$$\mathbf{Q}^{(h)} = \sum_{a=1}^r \mathbf{Q}_a^{(h)} = \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} H'_{ja} \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) f^{(N)}(\mathbf{x}^{(N)}, t) \right\rangle. \quad (7.275)$$

The part of the source term  $\mathbb{D}$  in (7.269) can be calculated by making use of the methods employed for derivations of evolution equations for nonconserved variables. We obtain the formula for  $\mathbb{D}$ :

$$\begin{aligned} \mathbb{D} = & \rho \left[ \mathcal{E} d_t T^{-1} - \sum_{a=1}^r \mathfrak{c}_a d_t \bar{\mu}_a + \sum_{a=1}^r \sum_{q \geq 0} \widehat{\Phi}_a^{(q)} d_t \bar{X}_a^{(q)} + d_t (k_B \ln \Gamma) \right] \\ & - T^{-1} \left[ \mathbf{Q} \cdot \nabla \ln T + \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot (T \nabla \hat{\mu}_a - \widehat{\mathbf{F}}_a) \right] \\ & - \nabla \cdot \left( \frac{\mathbf{Q}_v}{T} \right) + \sum_{a=1}^r \sum_{q \geq 0} \bar{X}_a^{(q)} d_t \widehat{\Phi}_a^{(q)} + \sum_{a=1}^r \sum_{q \geq 0} \nabla \cdot (\psi_a^{(q)} \bar{X}_a^{(q)}) \end{aligned}$$

$$- \sum_{a=1}^r \sum_{q \geq 0} \bar{X}_a^{(q)} \Lambda_a^{(q)}, \quad (7.276)$$

where

$$\bar{p} = \frac{p}{T}, \quad \bar{\mu}_a = \frac{\hat{\mu}_a}{T}, \quad \bar{X}_a^{(q)} = \frac{X_a^{(q)}}{T} \quad (7.277)$$

and  $d_t$  stands for the substantial time derivative.

Substitution of (7.273)–(7.276) yields the calortropy density balance equation in the differential form

$$\begin{aligned} d_t \hat{\Psi} &= T^{-1} \left[ d_t \mathcal{E} - \sum_{a=1}^r \hat{\mu}_a d_t \mathfrak{c}_a + \sum_{a=1}^r \sum_{q \geq 0} X_a^{(q)} d_t \hat{\Phi}_a^{(q)} \right] \\ &+ \left[ \mathcal{E} d_t T^{-1} - \sum_{a=1}^r \mathfrak{c}_a d_t \hat{\mu}_a + \sum_{a=1}^r \sum_{q \geq 0} \hat{\Phi}_a^{(q)} d_t \bar{X}_a^{(q)} \right] + d_t (k_B \ln \Gamma). \end{aligned} \quad (7.278)$$

The calortropy balance equation in (7.278) now is easily integrated to the form in (7.268) within a constant.

Now, (7.278) becomes a surface in manifold  $\mathfrak{P} \cup \mathfrak{T}$ , if parameters  $T$ ,  $\hat{\mu}_a$ , and  $X_a^{(q)}$  are regarded as elements of manifold  $\mathfrak{T}$  and, furthermore, if  $k_B T \ln \Gamma$  is given by the product of element  $p \in \mathfrak{T}$  and  $v \in \mathfrak{P}$  as below:

$$pv = k_B T \ln \Gamma. \quad (7.279)$$

Then (7.278) can be put into the differential form in manifold  $\mathfrak{P} \cup \mathfrak{T}$ :

$$\begin{aligned} d_t \hat{\Psi} &= T^{-1} \left[ d_t \mathcal{E} + pd_t v - \sum_{a=1}^r \hat{\mu}_a d_t \mathfrak{c}_a + \sum_{a=1}^r \sum_{q \geq 0} X_a^{(q)} d_t \hat{\Phi}_a^{(q)} \right] \\ &+ \left[ \mathcal{E} d_t T^{-1} + vd_t \bar{p} - \sum_{a=1}^r \mathfrak{c}_a d_t \bar{\mu}_a + \sum_{a=1}^r \sum_{q \geq 0} \hat{\Phi}_a^{(q)} d_t \bar{X}_a^{(q)} \right]. \end{aligned} \quad (7.280)$$

On integration, this differential form yields its integral in a bilinear form in the thermodynamic manifold within a constant:

$$\hat{\Psi} = T^{-1} \mathcal{E} + \bar{p}v - \sum_{a=1}^r \bar{\mu}_a \mathfrak{c}_a + \sum_{a=1}^r \sum_{q \geq 0} \bar{X}_a^{(q)} \hat{\Phi}_a^{(q)}. \quad (7.281)$$

Therefore the identification of  $k_B T \ln \Gamma$  with  $pv$  as in (7.279) can be seen as a necessary and sufficient condition for the integrability of the calortropy balance equation in the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T}$ . As a matter of fact, the differential form

$$\mathcal{E} d_t T^{-1} + v d_t \bar{p} - \sum_{a=1}^r c_a d_t \bar{\mu}_a + \sum_{a=1}^r \sum_{q \geq 0} \widehat{\Phi}_a^{(q)} d_t \bar{X}_a^{(q)} = 0 \quad (7.282)$$

is the *nonequilibrium Gibbs-Duhem (NGD) equation*, which is the necessary and sufficient condition for the integrability in manifold  $\mathfrak{P} \cup \mathfrak{T}$  of the Pfaffian differential form for  $\widehat{\Psi}$

$$d_t \widehat{\Psi} = T^{-1} \left[ d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \widehat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{q \geq 0} X_a^{(q)} d_t \widehat{\Phi}_a^{(q)} \right]. \quad (7.283)$$

This differential form is called the *extended Gibbs (EG) relation*—a fundamental equation of the present theory of thermodynamics of irreversible processes. It forms a cornerstone for the thermodynamic theory of irreversible processes. It is an exact differential in manifold  $\mathfrak{P} \cup \mathfrak{T}$  and yields numerous derivative relations between macroscopic variables in  $\mathfrak{P} \cup \mathfrak{T}$ . Using (7.283) and (7.282) we will be able to calculate in principle all local nonequilibrium macroscopic quantities of the fluid of interest in the theory of nonequilibrium statistical thermodynamics of a fluid mixture on the basis of the formulas developed in the present theory, if the nonequilibrium grand partition function is explicitly calculated.

The differential forms (7.283) and (7.282) are isomorphic to the differential forms for calortropy in the axiomatic phenomenological theory of irreversible processes in Chap. 2 and in Ref. [17]. Taking advantage of this isomorphism we are now able to endow the as-yet undetermined parameters  $T, p, \widehat{\mu}_a$ , and  $X_a^{(q)}$  with their phenomenological theoretic meanings and thereby make the present theory connect with the physical reality.

### 7.7.3 Thermodynamic Correspondence

The EG equation (7.283) supplies relations between the variables spanning the tangential manifold  $(T, p, \widehat{\mu}_a, X_a^{(q)} : a \geq 1, q \geq 0)$  and their conjugate manifold  $(\mathcal{E}, v, c_a, \widehat{\Phi}_a^{(q)} : a \geq 1, q \geq 0)$ . As a matter of fact, the former can be determined in terms of the latter, which obey their evolution equations already derived. Nevertheless, the variables of the tangential manifold can be endowed with thermodynamic meanings in the light of the phenomenological theory of irreversible processes.

This aim is achieved on making thermodynamic correspondence between the extensive variables of the thermodynamic manifold calculated by statistical mechanics and their phenomenological thermodynamic counterparts as below:

$$\mathcal{E}|_{\text{st}} \Leftrightarrow \mathcal{E}|_{\text{th}}, \quad v|_{\text{st}} \Leftrightarrow v|_{\text{th}}, \quad c_a|_{\text{st}} \Leftrightarrow c_a|_{\text{th}}, \quad \widehat{\Phi}_a^{(q)}|_{\text{st}} \Leftrightarrow \widehat{\Phi}_a^{(q)}|_{\text{th}}. \quad (7.284)$$

These correspondences then enable us to identify their conjugate variables with their phenomenological counterparts:

$$T|_{\text{st}} \Leftrightarrow T|_{\text{th}}, \quad p|_{\text{st}} \Leftrightarrow p|_{\text{th}}, \quad \hat{\mu}_a|_{\text{st}} \Leftrightarrow \hat{\mu}_a|_{\text{th}}, \quad X_a^{(q)}|_{\text{st}} \Leftrightarrow X_a^{(q)}|_{\text{th}}. \quad (7.285)$$

The subscripts st and th in the preceding expressions stand for statistical mechanical and phenomenological thermodynamic, respectively. This set of correspondences will be referred to as *thermodynamic correspondences*, which enable us to identify the statistical mechanical parameters ( $T, p, \hat{\mu}_a, X_a^{(q)}$ ) with the corresponding phenomenological thermodynamic intensive variables of manifold  $\mathcal{T}$ . With the identifications of the parameters the statistical mechanical formulas developed below provide molecular theoretic expressions—i.e., statistical mechanical formulas—for all quantities relevant to irreversible macroscopic processes. Thus the mathematical model for fluids is now fully endowed with meanings of experimental and physical reality and becomes a physical theory.

### 7.7.4 Nonequilibrium Statistical Thermodynamics

#### 7.7.4.1 Local Nonequilibrium Partition Function

Having acquired a thermodynamically consistent theory of irreversible processes, we would like to provide it with a nonequilibrium statistical mechanics machinery, so that molecular theory calculations can be performed. This aim is achieved with a nonequilibrium partition function, which can be made use of to compute various macroscopic observables described by the theory of irreversible processes. However, as it stands, Relation (7.267) is formal and, at a glance of it, the relation would not easily reveal how the local function  $\Gamma(\mathbf{r}, t)$  might be calculated, given the statistical mechanical formula for  $\mathbb{Z}^{(N)}$ . However, it is crucial to have a precise statistical mechanical formula for  $\Gamma(\mathbf{r}, t)$  for a statistical thermodynamic theory underlying the theory of irreversible thermodynamics. In the following we prove the relation (7.267) indeed yields an expression for  $\Gamma(\mathbf{r}, t)$  in a local form.

We observe that the integration over volume in the exponential factor of  $\mathbb{Z}^{(N)}$  may be written as a sum over elementary volume elements  $\Delta V(\mathbf{r}_l)$  into which volume  $V$  is partitioned around points  $\mathbf{r}_l$ :

$$\begin{aligned} \mathbb{Z}^{(N)} &= \left\langle \exp \left[ - \sum_l \Delta V(\mathbf{r}_l) \sum_{a=1}^r \sum_{ia=1}^{N_a} \beta \mathcal{H}_{ia}^{(N)} \delta(\mathbf{r}_{ia} - \mathbf{r}_l) \right] \right\rangle \\ &= \left\langle \exp \left[ - \sum_{a=1}^r \sum_{ia=1}^{N_a} \beta \mathcal{H}_{ia}^{(N)} \delta(\mathbf{r}_{ia} - \mathbf{r}_l) \right] \right\rangle^{\sum_l \Delta V(\mathbf{r}_l)}. \end{aligned} \quad (7.286)$$

Let us multiply a constant parameter  $\lambda$  to  $\Delta V(\mathbf{r}_l)$  which will be taken equal to unity at the end when the analysis is finished. The global partition function  $\mathbb{Z}^{(N)}$  may then be written as

$$\mathbb{Z}^{(N)}(\lambda) = \left\langle \exp \left[ - \sum_{a=1}^r \sum_{ia=1}^{N_a} \beta \mathcal{H}_{ia}^{(N)}(\mathbf{r}_{ia}) \delta(\mathbf{r}_{ia} - \mathbf{r}_l) \right] \right\rangle^{\sum_l \lambda \Delta V(\mathbf{r}_l)}, \quad (7.287)$$

Differentiating  $\mathbb{Z}^{(N)}(\lambda)$  with parameter  $\lambda$  it is possible to show that  $\ln \mathbb{Z}^{(N)}(\lambda)$  is a first-degree homogeneous function of  $\Delta V(\mathbf{r}_l)$ , so that we obtain

$$\begin{aligned} \ln \mathbb{Z}^{(N)}(\lambda) |_{\lambda=1} &= \sum_{l \geq 0} \Delta V_l \ln \left\langle \exp \left[ - \sum_{a=1}^r \sum_{ia=1}^{N_a} \beta \mathcal{H}_{ia}^{(N)}(\mathbf{r}_{ia}) \delta(\mathbf{r}_{ia} - \mathbf{r}_l) \right] \right\rangle \\ &= \int_V d\mathbf{r} \rho \ln \left\langle \exp \left[ - \sum_{a=1}^r \sum_{ia=1}^{N_a} \beta \mathcal{H}_{ia}^{(N)}(\mathbf{r}_{ia}) \delta(\mathbf{r}_{ia} - \mathbf{r}) \right] \right\rangle^{1/\rho}, \end{aligned} \quad (7.288)$$

which means

$$\Gamma(\mathbf{r}, t) = \left\langle \exp \left[ - \sum_{a=1}^r \sum_{ia=1}^{N_a} \beta(\mathbf{r}) \mathcal{H}_{ia}^{(N)} \delta(\mathbf{r}_{ia} - \mathbf{r}) \right] \right\rangle^{1/\rho}. \quad (7.289)$$

Equation (7.267) is now proved and at the same time we have acquired the molecular (i.e., statistical mechanical) expression for the local function  $\Gamma(\mathbf{r}, t)$  for the nonequilibrium partition function that can be easily amenable to more detailed and explicit analysis. For example, it can be calculated as a function of nonequilibrium parameters such as  $\Phi_a^{(q)}$  if a cumulant expansion method or a method of Lambert W functions described earlier is applied.

#### 7.7.4.2 Nonequilibrium Statistical Thermodynamics

Although it is possible to formulate nonequilibrium statistical thermodynamics on the basis of the extended Gibbs relation (7.283), it is necessary to include the non-equilibrium partition function  $\Gamma$  given by (7.289) in the differential form. Therefore we rearrange (7.282) to the differential form

$$\begin{aligned} d_t(pv) &= \widehat{\Psi} d_t T + p d_t v + \sum_{a=1}^r \mathfrak{c}_a d_t \widehat{\mu}_a - \sum_{a=1}^r \sum_{q \geq 0} \widehat{\Phi}_a^{(q)} d_t X_a^{(q)} \\ &= d(k_B T \ln \Gamma) \end{aligned} \quad (7.290)$$

as we did in Chap. 6. This is the nonequilibrium EG relation for the thermodynamic potential  $p\mathbf{v}$  of a fluid mixture.

Equipped with the differential form (7.290) we are now able to relate the phenomenological thermodynamic variables to the nonequilibrium (grand canonical) partition function, which is evidently a local function. We obtain from (7.290) the following derivatives of  $\ln \Gamma(\mathbf{r}, t)$ :

$$\widehat{\Psi} = k_B \left[ \frac{\partial}{\partial T} T \ln \Gamma(\mathbf{r}, t) \right]_{v, \widehat{\mu}, X}, \quad (7.291)$$

$$p = k_B T \left( \frac{\partial \ln \Gamma(\mathbf{r}, t)}{\partial v} \right)_{T, \widehat{\mu}, X}, \quad (7.292)$$

$$\mathfrak{c}_a = k_B T \left( \frac{\partial \ln \Gamma(\mathbf{r}, t)}{\partial \widehat{\mu}_a} \right)_{T, v, \widehat{\mu}', X}, \quad (7.293)$$

$$\widehat{\Phi}_a^{(q)} = -k_B T \left( \frac{\partial \ln \Gamma(\mathbf{r}, t)}{\partial X_a^{(q)}} \right)_{T, v, \widehat{\mu}, X'}, \quad (7.294)$$

$$(1 \leq a \leq r; q \geq 0).$$

The prime on the subscript of the derivatives means excluding  $\widehat{\mu}_a$  or  $X_a^{(q)}$  from the set. It should be recalled that the nonconserved variables include the molar volume and volume flux of various species of the mixture.

The differential forms (7.282), (7.283), and (7.290) together with (7.291)–(7.294) and (7.289) form the basis of nonequilibrium statistical thermodynamics of processes including volume transport in a manner parallel to the equilibrium statistical thermodynamics [19]. We would like to supplement the following for completeness of the statistical mechanical description of calortropy density.

### 7.7.5 Local and Global Representation of Thermodynamic Laws

On substitution of (7.273), (7.274), and (7.276) and using the integrability condition (7.282) the calortropy density balance equation (7.269) can be written as

$$\begin{aligned} \rho \frac{d\widehat{\Psi}}{dt} &= -\nabla \cdot \left( T^{-1} \mathbf{Q}^{(h)} - \sum_{a=1}^r \bar{\mu}_a \mathbf{J}_a - \sum_{a=1}^r \sum_{q \geq 0} \bar{X}_a^{(q)} \widehat{\Phi}_a^{(q)} \right) \\ &\quad + \rho \widehat{\Sigma}_{\text{loc}} + \sum_{a=1}^r \sum_{q \geq 0} X_a^{(q)} (\mathcal{Z}_a^{(q)} + \Lambda_a^{(q)}), \end{aligned} \quad (7.295)$$

where  $\rho\widehat{\Sigma}_{\text{loc}}$  is defined by the expression

$$\begin{aligned}\rho\widehat{\Sigma}_{\text{loc}} &= -T^{-1} \sum_{a=1}^r [(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q}_a^{\text{ch}} \cdot \nabla \ln T + \mathbf{J}_a \cdot (\nabla \widehat{\mu}_a - \widehat{\mathbf{F}}_a)] \\ &\quad + T^{-1} \sum_{a=1}^r \sum_{q \geq 0} \psi_a^{(q)} \cdot \nabla X_a^{(q)}\end{aligned}\quad (7.296)$$

with  $\mathbf{Q}_a^{\text{ch}}$  denoting an effective heat flux

$$\mathbf{Q}_a^{\text{ch}} = \mathbf{Q}_a^{(h)} - \widehat{\mu}_a \mathbf{J}_a + \sum_{q \geq 0} X_a^{(q)} \psi_a^{(q)}. \quad (7.297)$$

The local form of the second law of thermodynamics is then given as the inequality

$$\Xi_{\text{cal}} := \rho\widehat{\Sigma}_{\text{loc}} + \sum_{a=1}^r \sum_{q \geq 0} X_a^{(q)} (\mathcal{Z}_a^{(q)} + \Lambda_a^{(q)}) \geq 0. \quad (7.298)$$

For the derivation of (7.295) the following expressions obtained from the statistical mechanical formula for  $\mathbb{D}$  are made use of:

$$\mathbb{D} = \mathbb{D}_1 + \mathbb{D}_2 + \mathbb{D}_3, \quad (7.299)$$

where each component on the right is given below:

$$\begin{aligned}\mathbb{D}_1 &= \rho \left[ \mathcal{E} d_t T^{-1} - \sum_{a=1}^r \mathfrak{c}_a d_t \overline{\mu}_a + \sum_{a=1}^r \sum_{q \geq 0} \widehat{\Phi}_a^{(q)} d_t \overline{X}_a^{(q)} + d_t (\overline{\rho} v) \right] \\ &\quad + \sum_{a=1}^r \sum_{q \geq 0} \overline{X}_a^{(q)} \left\langle f^{(\mathbb{N})} \sum_{ja=1}^{N_a} \delta(\mathbf{r}_{ja} - \mathbf{r}) d_t h_{ja}^{(q)} \right\rangle,\end{aligned}\quad (7.300)$$

$$\begin{aligned}\mathbb{D}_2 &= -\nabla \cdot \left( \frac{\mathbf{Q}^{(v)}}{T} \right) - T^{-1} \sum_{a=1}^r (\mathbf{Q}_a^{(v)} \cdot \nabla \ln T + \mathbf{P}_a^{(v)} : \nabla \mathbf{u} - \mathbf{J}_a \cdot \widehat{\mathbf{F}}_a) \\ &\quad + \sum_{a=1}^r \sum_{q \geq 0} \overline{X}_a^{(q)} \left\langle f^{(\mathbb{N})} \sum_{ja=1}^{N_a} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathbf{L}^{(N)} h_{ja}^{(q)} \right\rangle,\end{aligned}\quad (7.301)$$

$$\begin{aligned} \mathbb{D}_3 = & -T^{-1} \sum_{a=1}^r (\mathbf{Q}_a^{(h)} \cdot \nabla \ln T + \mathbf{P}_a^{(k)} : \nabla \mathbf{u}) \\ & - \sum_{a=1}^r \mathbf{J}_a \cdot \nabla \bar{\mu}_a + \sum_{a=1}^r \sum_{q \geq 0} \psi_a^{(q)} \nabla \bar{X}_a^{(q)} \\ & + \sum_{a=1}^r \sum_{q \geq 0} \bar{X}_a^{(q)} \left\langle f^{(\mathrm{N})} \sum_{ja=1}^{N_a} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathbf{C}_{ja} \cdot \nabla h_{ja}^{(q)} \right\rangle. \end{aligned} \quad (7.302)$$

Recall that in (7.301)

$$\mathbf{Q}^{(v)} = \sum_{a=1}^r \mathbf{Q}_a^{(v)}, \quad (7.303)$$

where  $\mathbf{Q}_a^{(v)}$  is the virial tensor contribution to the heat flux; see (7.77) for the statistical mechanical formula for  $\mathbf{Q}_a^{(v)}$ .

Expressed in global forms, the local calortropy balance equation (7.295) together with the inequality (7.298) is given in the form

$$\frac{d\Psi}{dt} = \frac{d_e\Psi}{dt} + \frac{d_i\Psi}{dt}, \quad (7.304)$$

where  $(d_e\Psi/dt)$  is the rate of change arising from exchange of  $\Psi$  between the system and its surroundings

$$\frac{d_e\Psi}{dt} = - \int d\mathbf{r} \nabla \cdot \mathbf{J}_c(\mathbf{r}, t), \quad (7.305)$$

and  $(d_i\Psi/dt)$  represents the rate of creation of  $\Psi$  owing to the irreversible processes within the system

$$\frac{d_i\Psi}{dt} = \int d\mathbf{r} \Xi_{\text{cal}}(\mathbf{r}, t) = \int d\mathbf{r} \rho \widehat{\Xi}_{\text{cal}}(\mathbf{r}, t) \geq 0, \quad (7.306)$$

which is always positive semidefinite. Equation (7.304) together with Inequality (7.306) represents the second law of thermodynamics as stated by Clausius [20] for systems undergoing irreversible processes. The  $(d_e\Psi/dt)$  represents the *compensated heat* of Clausius and  $(d_i\Psi/dt)$  the *uncompensated heat*. The global representations by (7.304)–(7.306) can be equivalently expressed, in local representations, by a vanishing circular integral in the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T}$

$$\oint d\widehat{\Psi} = 0 \quad (7.307)$$

subject to the condition that the uncompensated heat  $\Xi_{\text{cal}}$  remains positive everywhere along the cyclic path of irreversible processes.

In addition to this vanishing integral of  $\widehat{\Psi}$ , there also holds the vanishing cyclic integral of internal energy in the manifold  $\mathfrak{P} \cup \mathfrak{T}$

$$\oint d\mathcal{E} = 0, \quad (7.308)$$

representing the exact differential form for  $d_t \mathcal{E}$ . Thus the first and second law of thermodynamics can be mathematically expressed by the pair of vanishing cyclic integrals (7.307) and (7.308)—or exact differentials—subject to the local condition  $\Xi_{\text{cal}}(\mathbf{r}, t) \geq 0$  in the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T}$ .

In contrast to these properties of  $\widehat{\Psi}$  yielding an exact differential form and a vanishing circular integral in manifold  $\mathfrak{P} \cup \mathfrak{T}$ , the Boltzmann entropy equation cannot be put into an equivalent exact differential form for  $d_t S$  in the thermodynamic manifold ( $\mathfrak{P} \cup \mathfrak{T}$ ) and consequently cannot give rise to a vanishing cyclic integral representing the second law of thermodynamics in the thermodynamic manifold—in other words, the Boltzmann entropy balance equation is not integrable to a bilinear function in manifold  $\mathfrak{P} \cup \mathfrak{T}$ , if there exist a nonequilibrium irreversible process in the system. This, as a matter of fact, was the very reason why the concept of calortropy was conceived and invented in place of the Boltzmann entropy.

### 7.7.6 Generalized Potentials

Since in the linear theory of irreversible thermodynamics [15, 16] the generalized potentials do not appear and hence are not as familiar to us as chemical potentials or pressure, phenomenological theories of irreversible processes cannot be of help when we try to develop constitutive equations for generalized potentials. Therefore it must be necessarily resorted to the method of statistical mechanics applied beyond the realm of linear irreversible thermodynamics. By using the statistical expression<sup>16</sup> for  $\Gamma(\mathbf{r}, t)$  given in (7.289) the nonconserved variables  $\widehat{\Phi}_a^{(q)}$  can be calculated in terms of  $X_a^{(q)}$  from (7.294). Inverting this relation we then obtain the constitutive relations for  $X_a^{(q)}$ , (7.311) below. This inversion procedure was already illustrated in Chap. 3 by using Lambert's W function [21] in the case of dilute single component fluids. The same procedure is applicable to liquid mixtures, albeit more complicated. Near equilibrium where the exponential form can be expanded to linear order in  $X_a^{(q)}$ , it is easy to calculate  $\Gamma(\mathbf{r}, t)$  from which we obtain the relation between  $X_a^{(q)}$  and  $\widehat{\Phi}_a^{(q)}$ :

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<sup>16</sup>It should be kept in mind that by using the nonequilibrium statistical thermodynamics formalism developed earlier, the nonequilibrium distribution function  $f^{(N)}$  is necessarily replaced by  $f_c^{(N)}$ . Therefore, fluctuations inherent to  $f^{(N)}$  are neglected. This means the generalized potentials are without fluctuations.

$$\begin{aligned}\rho\widehat{\Phi}_a^{(q)} &= \sum_{\{\mathbf{N}\} \geq 0} \Gamma^{-1} \int d\mathbf{x}^{(\mathbf{N})} \exp \left( -\beta \sum_{a=1}^r \sum_{ja=1}^{N_a} \mathcal{H}_{ja}^{(N_a)} \right) h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \\ &= \sum_{\{\mathbf{N}\} \geq 0} \Gamma^{-1} \int d\mathbf{x}^{(\mathbf{N})} h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) e^{-\beta\mathcal{H}_0^{(\mathbf{N})}} e^{-\beta\Delta\mathcal{H}^{(\mathbf{N})}}.\end{aligned}\quad (7.309)$$

The right-hand side of the second line may be expanded in cumulants of the nonequilibrium contributions  $\beta\Delta\mathcal{H}^{(\mathbf{N})}$  and, more precisely, of generalized potentials  $\{X_a^{(q)}\}$ .

The so-obtained cumulant expansion in  $\{X_a^{(q)}\}$  may be inverted to obtain the generalized potentials  $X_a^{(q)}$  in terms of  $\rho\widehat{\Phi}_a^{(q)}$ . Here we will look for a linear relation between them for simplicity. It would be the lowest-order approximation for their relation.

Expanding the exponential factor  $e^{-\beta\Delta\mathcal{H}^{(\mathbf{N})}}$  in the second line of (7.309) to linear order in  $\Delta\mathcal{H}^{(\mathbf{N})}$  we obtain

$$\rho\widehat{\Phi}_a^{(q)} = -\beta \sum_{\{\mathbf{N}\} \geq 0} \int d\mathbf{x}^{(\mathbf{N})} e^{-\beta\mathcal{H}_0^{(\mathbf{N})}} \sum_{b=1}^r \sum_{p \geq 0} X_b^{(p)} \odot \sum_{kb=1}^{N_b} h_{kb}^{(p)} h_{ja}^{(q)} + O(X^2). \quad (7.310)$$

Therefore, to first order in  $X$  there follows the expression

$$X_a^{(q)} = -g_a^{(q)} \widehat{\Phi}_a^{(q)} + O(\widehat{\Phi}^2), \quad (7.311)$$

where

$$g_a^{(q)} = \frac{1}{\beta \langle h_{kb}^{(p)} h_{ja}^{(q)} \rangle_0} \quad (7.312)$$

with  $\langle h_{ja}^{(q)} h_{ja}^{(q)} \rangle_0$  defined by the equilibrium grand canonical ensemble average of  $h_{ja}^{(q)} h_{ja}^{(q)}$ :

$$\langle h_{ja}^{(q)} h_{ja}^{(q)} \rangle_0 = \sum_{\{\mathbf{N}\} \geq 0} \Gamma_0^{-1} \int d\mathbf{x}^{(\mathbf{N})} e^{-\beta\mathcal{H}_0^{(\mathbf{N})}} h_{ja}^{(q)} h_{ja}^{(q)}, \quad (7.313)$$

where

$$\Gamma_0^{-1} = \langle e^{-\beta\mathcal{H}_0^{(\mathbf{N})}} \rangle. \quad (7.314)$$

Here it should be noted that by virtue of Schmidt's orthogonalization used for constructing  $h_{ja}^{(q)}$  we have used the orthogonality of moments

$$\langle h_{kb}^{(p)} h_{ja}^{(q)} \rangle_0 = \delta_{ab} \delta_{pq} \delta_{jk} \langle h_{ja}^{(q)} h_{ja}^{(q)} \rangle_0. \quad (7.315)$$

The result presented shows that  $X_a^{(q)}$  is proportional to  $\widehat{\Phi}_a^{(q)}$  to first order in the generalized potentials. The linear relation between  $\widehat{\Phi}_a^{(q)}$  and  $X_a^{(q)}$  will be used in the first-order theory discussed later in this work. Such a linear relation is often found sufficient in practice.

### 7.7.7 Cumulant Expansion for Calortropy Production and Dissipation Terms

Since the statistical mechanical expression for the calortropy production in a mixture is formally identical with that of a pure fluid except for the sum over species and the difference in the numbers of moments, the expressions obtained in the case of a pure fluid discussed in Chap. 6 can be directly transcribed into the formulas for a mixture, and the same is true for the dissipation terms appearing in the generalized hydrodynamic equations. Therefore we will not repeat the derivations by the cumulant expansion method for the calortropy production and the dissipation terms associated with the calortropy production for a mixture, but simply present the final results for

them. If the nonequilibrium grand canonical form for  $\bar{f}_c^{(N)}(\mathbf{x}^{(N)}, t)$  is used,  $\bar{\mathbb{F}}_c^{(N)}$  can be written in the form

$$\bar{\mathbb{F}}_c^{(N)} = \bar{\mathbb{F}}_0^{(N)} e^{-\bar{\mathbb{H}}^{(1)}}. \quad (7.316)$$

Here  $\bar{\mathbb{F}}_0^{(N)}$  is the “equilibrium part” defined by

$$\bar{\mathbb{F}}_0^{(N)} = \frac{1}{Z^{(N)}} \exp \left[ - \sum_{\gamma=1}^{\nu} \sum_{\{\mathbf{N}_{\gamma}\} \geq 0} \int_{V_{\gamma}} d\mathbf{r} \sum_{ia=1}^{N_a} \beta \left( H_{ia}^{(N_{\gamma})} - m_{ia} \widehat{\mu}_{\alpha} \right) \delta(\mathbf{r}_{ia} - \mathbf{r}) \right], \quad (7.317)$$

$$Z^{(N)} := \prod_{\gamma=1}^{\nu} Z_{\gamma}^{(N)}, \quad (7.318)$$

where the subscript  $\gamma$  stands for subsystems and  $\bar{\mathbb{H}}^{(1)}$  is defined by the nonequilibrium part

$$\bar{\mathbb{H}}^{(1)} = \sum_{\gamma=1}^{\nu} \sum_{\{\mathbf{N}_{\gamma}\} \geq 0} k_B^{-1} \int_{V_{\gamma}} d\mathbf{r} \sum_{ia=1}^{N_{\gamma}} \bar{H}_{ia}^{(1,\gamma)} \delta(\mathbf{r}_{ia} - \mathbf{r}). \quad (7.319)$$

Since the subsystems contribute identical values when averaged over the entire phase space of the ensemble the index  $\gamma$  is just used for the bookkeeping purpose,

and it can be removed at the end of calculations. The form (7.316) for  $\bar{\mathbb{F}}_c^{(N)}$  replaces the full distribution function in the formula for the calortropy production

$$\sigma_c = k_B \sum_{q \geq 0} \beta X^{(q)} \left\langle \overline{\mathbb{H}}_{\bullet}^{(1)} \Re[\mathbb{F}_0^{-(\mathcal{N})} e^{-\overline{\mathbb{H}}^{(1)}}] \right\rangle, \quad (7.320)$$

where we have used the abbreviation for the nonequilibrium part  $\overline{\mathbb{H}}_{\bullet}^{(1)}$  for brevity:

$$\overline{\mathbb{H}}_{\bullet}^{(1)} = \sum_{q \geq 0} \sum_{i=1}^N \beta X^{(q)} h_i^{(q)} \delta(\mathbf{r}_i - \mathbf{r}) \quad (7.321)$$

with the subscript  $\bullet$  standing for subsystems over which the term will be summed when  $\sigma_c$  is to be symmetrized presently.

If we follow the procedure used for the proof of Condition (6.C2) in Sect. 6.2.3, the collision integral in (7.320) can be written in the form

$$\Re[\mathbb{F}^{-(\mathcal{N})}(x^{(\mathcal{N})}, t)] = \frac{\epsilon}{\nu} \int dx^{(\mathcal{N}-N)} \mathbb{F}_0^{-(\mathcal{N})} \left[ e^{-\overline{\mathbb{H}}^{(1)*}} - e^{-\overline{\mathbb{H}}^{(1)}} \right], \quad (7.322)$$

where  $\overline{\mathbb{H}}^{(1)*}$  is the post-collision value of  $\overline{\mathbb{H}}^{(1)}$

$$e^{-\overline{\mathbb{H}}^{(1)*}} = \epsilon \int_0^\infty ds e^{-(\epsilon + i \mathcal{L}^{(\mathcal{N})})s} e^{-\overline{\mathbb{H}}^{(1)}(x^{(\mathcal{N})})}, \quad (7.323)$$

$$e^{-\overline{\mathbb{H}}^{(1)}} = \epsilon \int_0^\infty ds e^{-(\epsilon + i \mathcal{L}_0^{(\mathcal{N})})s} e^{-\overline{\mathbb{H}}^{(1)}(x^{(\mathcal{N})})}. \quad (7.324)$$

Finally, upon substituting (7.322) the calortropy production in (7.320) can be written in a fully symmetrized form as follows:

$$\begin{aligned} \widehat{\sigma}_c &= \frac{1}{2\nu^2} \int dx^{(\mathcal{N})} \left( \overline{\mathbb{H}}^{(1)} - \overline{\mathbb{H}}^{(1)*} \right) \left[ e^{-\overline{\mathbb{H}}^{(1)*}} - e^{-\overline{\mathbb{H}}^{(1)}} \right] \mathbb{F}_0^{-(\mathcal{N})} \\ &:= \frac{1}{2} \left\langle \left( \overline{\mathbb{H}}^{(1)} - \overline{\mathbb{H}}^{(1)*} \right) \left[ e^{-\overline{\mathbb{H}}^{(1)*}} - e^{-\overline{\mathbb{H}}^{(1)}} \right] \right\rangle_c, \end{aligned} \quad (7.325)$$

where  $\overline{\mathbb{H}}^{(1)}$  is now given by

$$\begin{aligned} \overline{\mathbb{H}}^{(1)} &= \sum_{\alpha=1}^{\nu} \left( \overline{\mathbb{H}}_{\bullet}^{(1)} \right)_{\bullet=\gamma} = \sum_{\gamma=1}^{\nu} \overline{\mathbb{H}}_{\gamma}^{(1)} \\ &= \sum_{\gamma=1}^{\nu} k_B^{-1} \int_V d\mathbf{r} \sum_{ia=1}^{N_\gamma} \overline{H}_{ia}^{(1,\gamma)} \delta(\mathbf{r}_{ia} - \mathbf{r}) \end{aligned} \quad (7.326)$$

and  $\hat{\sigma}_c$  is the reduced calortropy production defined by

$$\hat{\sigma}_c = \sigma_c / k_B \epsilon. \quad (7.327)$$

Expanding the right hand side of (7.327) in cumulants [22, 23], we obtain a cumulant expansion in the same form as in Chap. 6. Casting  $\hat{\sigma}_c$  in the form

$$\hat{\sigma}_c = \frac{1}{2} [\mathcal{R}^{(+)}(\lambda) - \mathcal{R}^{(-)}(\lambda)]_{\lambda=1}, \quad (7.328)$$

where

$$\mathcal{R}^{(+)}(\lambda) = \left\langle \left( \bar{\mathbb{H}}^{(1)} - \bar{\mathbb{H}}^{(1)*} \right) \left( e^{-\lambda \bar{\mathbb{H}}^{(1)*}} - 1 \right) \right\rangle_c, \quad (7.329)$$

$$\mathcal{R}^{(-)}(\lambda) = \left\langle \left( \bar{\mathbb{H}}^{(1)} - \bar{\mathbb{H}}^{(1)*} \right) \left( e^{-\lambda \bar{\mathbb{H}}^{(1)}} - 1 \right) \right\rangle_c \quad (7.330)$$

and expanding  $\mathcal{R}^{(\pm)}(\lambda)$  in a cumulant series as in

$$\mathcal{R}^{(\pm)}(\lambda) = \kappa \left\{ \exp \left[ \sum_{l=1}^{\infty} \frac{(-\lambda)^l}{l!} \kappa_l^{(\pm)} \right] - 1 \right\}, \quad (7.331)$$

where

$$\kappa = \frac{1}{2} \left\langle \left( \bar{\mathbb{H}}^{(1)} - \bar{\mathbb{H}}^{(1)*} \right) (\mathbb{H}^{(1)} - \mathbb{H}^{(1)*}) \right\rangle_c^{1/2} \quad (7.332)$$

and  $\lambda$  is a bookkeeping parameter to keep track of the order of expansion, we find the leading order cumulants  $\kappa_l^{(\pm)}$

$$\begin{aligned} \kappa_1^{(\pm)} &= \mp \kappa, \\ \kappa_2^{(\pm)} &= \mp \frac{\kappa_2}{\kappa} - \kappa^2, \\ \kappa_3^{(\pm)} &= \mp \frac{\kappa_3}{\kappa} - 3\kappa_2 \mp 2\kappa^3, \\ &\text{etc.} \end{aligned} \quad (7.333)$$

Setting  $\lambda = 1$ , we find the reduced calortropy production in the first-order cumulant approximation

$$\hat{\sigma}_c = \kappa \sinh \kappa. \quad (7.334)$$

This formula is always positive. Therefore it is a simplest, yet highly nonlinear, thermodynamically consistent approximation for the calortropy production, as it was in the case of a pure fluid. This would be found sufficient for many purposes in

studies of nonlinear transport processes. Therefore we will not pursue higher-order cumulant approximations<sup>17</sup> in the present work.

To deduce the dissipation terms in the first-order cumulant approximation we first calculate  $\kappa^2$  more explicitly. We find that  $\kappa^2$  is a quadratic form in the generalized potentials  $X_a^{(q)}$ :

$$\kappa^2 = \sum_{a,b=1}^r \sum_{q,s \geq 0} X_a^{(q)} \mathbb{R}_{ab}^{(qs)} X_b^{(s)}, \quad (7.335)$$

where the coefficients  $\mathbb{R}_{ab}^{(qs)}$  are the collision bracket integrals for a coupled transport processes  $q$  and  $s$ , involving species  $a$  and  $b$ . They will be calculated in terms of collision bracket integrals in the next subsection. Since we may express more explicitly the first-order cumulant approximation for  $\sigma_c$  in terms of collision bracket integrals

$$\sigma_c = k_B \epsilon \kappa^2 \frac{\sinh \kappa}{\kappa} = k_B T \epsilon \sum_{a,b=1}^r \sum_{q,s \geq 0} \frac{X_a^{(q)}}{T} \mathbb{R}_{ab}^{(qs)} X_b^{(s)} \left( \frac{\sinh \kappa}{\kappa} \right),$$

on comparing it with (7.274) we obtain the first-order cumulant approximation for the dissipation term  $\Lambda_a^{(q)}$ :

$$\Lambda_a^{(q)} = \sum_{b=1}^r \sum_{s \geq 0} k_B T \epsilon \mathbb{R}_{ab}^{(qs)} X_b^{(s)} \left( \frac{\sinh \kappa}{\kappa} \right). \quad (7.336)$$

Substitution of the approximate generalized potentials given in (7.311) renders the dissipation terms more explicit:

$$\Lambda_a^{(q)} = - \sum_{b=1}^r \sum_{s \geq 0} k_B T \epsilon \mathbb{R}_{ab}^{(qs)} g_b^{(s)} \Phi_b^{(s)} \left( \frac{\sinh \kappa}{\kappa} \right). \quad (7.337)$$

Here as we have done in Chap. 6, we now may take  $\epsilon$ , for time for subsystems to collide, in the form

$$\epsilon = l \sqrt{\frac{2k_B T}{m}},$$

where  $m$  is the reduced mass and  $l$  is the mean free path; Ref. [18]. This interpretation of  $\epsilon$  will be understood in the following.

<sup>17</sup>The second-order cumulant approximation is not suitable owing to the possibility it produces a negative calorropy production in some region of thermodynamic manifold, but the third-order cumulant approximation is always positive. It, in fact, offers an intriguing possibility of producing a second minimum in  $\sigma_c$  away from equilibrium, so that the system self-organizes around the state of the second minimum removed away from equilibrium. For a study of the third-order cumulant approximation in the case of a dilute gas transport phenomena, see B.C. Eu, J. Chem. Phys. **75**, 4031 (1981).

With this first-order cumulant approximation (7.337) for the dissipation terms substituted for  $\Lambda_a^{(q)}$ , the generalized hydrodynamic equations presented in the previous subsections—i.e., (7.195)—become free from undetermined parameters and closed with respect to variables in the manifold  $\mathfrak{P} \cup \mathfrak{T}$ . With suitable initial and boundary conditions supplied for the flow problem of interest, they are ready for solution of generalized hydrodynamic equations and thereby studying flow processes in liquid mixtures. Moreover, transport processes associated therewith can be related to the collision dynamical information on the fluid which is contained in the collision integral of the GBE. Being derived from the thermodynamically consistent calortropy production  $\sigma_c$  given in (7.334), the generalized hydrodynamic equations with  $\Lambda^{(q)}$  given by (7.336), or (7.337), are also thermodynamically consistent. For example, the hydrodynamic flow profiles derived therefrom are, therefore, expected to conform to the laws of thermodynamics.

### 7.7.8 Collision Bracket Integrals

In kinetic theory of macroscopic transport processes all the molecular dynamical information on the substance of interest is contained in the collision integral of the kinetic equation and, particularly, in the collision bracket integrals  $\mathbb{R}_{ab}^{(qs)}$ , if the first-order cumulant approximation is taken for the dissipation terms. It is, therefore, sufficient to pay attention to the first-order cumulant in (7.332), which on substitution of  $\mathbb{H}^{(1)}$  and  $\overline{\mathbb{H}}^{(1)}$  in (7.319) and (7.321) yields the dissipation function in the form

$$\begin{aligned} \kappa^2 = & \frac{1}{4\nu^2} \int dx^{(\mathcal{N})} \overline{\mathbb{F}_0}^{(\mathcal{N})} \sum_{\alpha=1}^{\nu} \sum_{q \geq 0} \sum_{\{\mathbf{N}_\alpha\} \geq 0} \sum_{a=1}^r \sum_{i\alpha=1}^{N_\alpha} \left[ \beta X^{(q)} \Delta h_{ia}^{(q)} \delta(\mathbf{r}_{ia} - \mathbf{r}) \right]_\alpha \\ & \times \int_V d\mathbf{r}' \sum_{\gamma=1}^{\nu} \sum_{s \geq 0} \sum_{\{\mathbf{N}_\gamma\} \geq 0} \sum_{b=1}^r \sum_{j\gamma=1}^{N_\gamma} \left[ \beta X^{(s)} \Delta h_{jb}^{(s)} \delta(\mathbf{r}_{jb} - \mathbf{r}') \right]_\gamma, \end{aligned} \quad (7.338)$$

where

$$\Delta h_{ia}^{(q)} = h_{ia}^{(q)} - h_{ia}^{(q)*}, \quad \Delta h_{jb}^{(s)} = h_{jb}^{(s)} - h_{jb}^{(s)*}. \quad (7.339)$$

Because the terms of different  $\alpha$  and  $\gamma$  contribute  $\nu$  identical values of the integrals, (7.338) is reduced to the form

$$\begin{aligned} \kappa^2 = & \frac{1}{4} \int dx^{(\mathcal{N})} \overline{\mathbb{F}_0}^{(\mathcal{N})} \sum_{\{\mathbf{N}_\alpha\} \geq 0} \sum_{a=1}^r \sum_{ia=1}^{N_a} \sum_{q \geq 0} \beta X_a^{(q)} \Delta h_{ia}^{(q)} \delta(\mathbf{r}_{ia} - \mathbf{r}) \\ & \times \sum_{\{\mathbf{N}_\gamma\} \geq 0} \sum_{b=1}^r \sum_{jb=1}^{N_b} \sum_{s \geq 0} \int_V d\mathbf{r}' \beta X_b^{(s)} \Delta h_{jb}^{(s)} \delta(\mathbf{r}_{jb} - \mathbf{r}'), \end{aligned} \quad (7.340)$$

where subsystem indices  $\alpha$  and  $\gamma$  are now omitted and the interparticle collisions are those of a single subsystem. Now, perform the integration over  $\mathbf{r}'$  to get rid of the second delta function. Let us define the abbreviation of the phase integral with the symbol

$$\langle A_{ia} B_{jb} \rangle_m := \sum_{\{\mathbf{N}\} \geq 0} \sum_{\{\mathbf{N}\} \geq 0} \int d\mathbf{x}^{(\mathcal{N})} \bar{\mathbb{F}}_0^{(\mathcal{N})} A_{ia} B_{jb}, \quad (7.341)$$

where  $A_{ia}$  and  $B_{jb}$  are defined by formulas

$$\begin{aligned} A_{ia} &= \beta X_a^{(q)} \Delta h_{ia}^{(q)} \delta(\mathbf{r}_{ia} - \mathbf{r}), \\ B_{jb} &= \beta X_b^{(s)} \Delta h_{jb}^{(s)}. \end{aligned}$$

We then find  $\kappa^2$  in the quadratic form of  $X^{(q)}$ :

$$\kappa^2 = \sum_{a=1}^r \sum_{a=1}^r \sum_{q \geq 0} \sum_{s \geq 0} X_a^{(q)} X_b^{(s)} \mathbb{R}_{ab}^{(qs)}, \quad (7.342)$$

where the coefficients  $\mathbb{R}_{ab}^{(qs)}$  are defined by the collision bracket integral

$$\mathbb{R}_{ab}^{(qs)} = \frac{\beta^2}{4} \sum_{i\alpha=1}^{N_\alpha} \sum_{jb=1}^{N_b} \left\langle \Delta h_{ia}^{(q)} \Delta h_{jb}^{(s)} \right\rangle_m. \quad (7.343)$$

The collision bracket integrals  $\mathbb{R}_{ab}^{(qs)}$  are symmetric with respect to both subscript pairs or superscript pairs. Therefore the coefficients  $\mathbb{R}_{ab}^{(qs)}$  in (7.342) have the following symmetry with respect to interchange of indices:

$$\mathbb{R}_{ab}^{(qs)} = \mathbb{R}_{ba}^{(sq)}. \quad (7.344)$$

Moreover, they vanish if  $h_i^{(q)}$  and  $h_i^{(s)}$  are of different tensorial ranks for symmetry reason.

Since some moments are coupled with each other according to the Schmidt orthogonalization method employed to construct the moment set, the coefficients  $\mathbb{R}^{(qs)}$  can be decomposed into components. Since the maximum rank of tensor is 2 in the moment set taken in this work, if  $h_i^{(q)}$  and  $h_i^{(s)}$  are either vectors or scalar, then they are coupled with other. Consequently, we have the following linear combinations

$$\begin{aligned} h_{ia}^{(2)} &= \bar{h}_{ia}^{(2)} - \alpha_a^{(2)} h_{ia}^{(1)}, \\ h_{ia}^{(3)} &= \bar{h}_{ia}^{(3)} - \alpha_a^{(3)} \bar{h}_{ia}^{(2)} + \alpha_a^{(2)} \alpha_a^{(3)} h_{ia}^{(1)}, \\ h_{ia}^{(5)} &= \bar{h}_{ia}^{(5)} - \alpha_a^{(5)} h_{ia}^{(0)}, \end{aligned} \quad (7.345)$$

as shown in the previous sections. Hence the coefficients  $\mathbb{R}_{ab}^{(qs)}$  can be expressed in linear combinations of basic collision bracket integrals  $\mathbb{M}_{ab}^{(qs)}$  as follows:

$$\begin{aligned}
 \mathbb{R}_{ab}^{(00)} &= \mathbb{M}_{ab}^{(00)}, \\
 \mathbb{R}_{ab}^{(11)} &= \mathbb{M}_{ab}^{(11)}, \\
 \mathbb{R}_{ab}^{(12)} &= \mathbb{M}_{ab}^{(12)} - \alpha_b^{(2)} \mathbb{M}_{ab}^{(11)}, \\
 \mathbb{R}_{ab}^{(23)} &= \mathbb{M}_{ab}^{(23)} - \alpha_a^{(2)} \mathbb{M}_{ab}^{(13)} - \alpha_b^{(3)} \mathbb{M}_{ab}^{(22)} + \alpha_a^{(2)} \alpha_b^{(3)} \mathbb{M}_{ab}^{(12)} \\
 &\quad + \alpha_b^{(2)} \alpha_b^{(3)} \mathbb{M}_{ab}^{(21)} - \alpha_a^{(2)} \alpha_b^{(2)} \alpha_b^{(3)} \mathbb{M}_{ab}^{(11)}, \\
 \mathbb{R}_{ab}^{(50)} &= \mathbb{M}_{ab}^{(50)} - \alpha_a^{(5)} \mathbb{M}_{ab}^{(00)}, \\
 \mathbb{R}_{ab}^{(22)} &= \mathbb{M}_{ab}^{(22)} - \alpha_a^{(2)} \left( \mathbb{M}_{ab}^{(21)} + \mathbb{M}_{ab}^{(12)} \right) + \alpha_a^{(2)} \alpha_b^{(2)} \mathbb{M}_{ab}^{(11)} \\
 \mathbb{R}_{ab}^{(33)} &= \mathbb{M}_{ab}^{(33)} + \alpha_a^{(3)} \alpha_b^{(3)} \mathbb{M}_{ab}^{(22)} + \alpha_a^{(2)} \alpha_a^{(3)} \alpha_b^{(2)} \alpha_b^{(3)} \mathbb{M}_{ab}^{(11)} \\
 &\quad - \alpha_a^{(3)} \mathbb{M}_{ab}^{(23)} - \alpha_b^{(3)} \mathbb{M}_{ab}^{(32)} + \alpha_a^{(2)} \alpha_a^{(3)} \mathbb{M}_{ab}^{(31)} + \alpha_b^{(2)} \alpha_b^{(3)} \mathbb{M}_{ab}^{(13)} \\
 &\quad - \alpha_a^{(3)} \alpha_b^{(2)} \alpha_b^{(3)} \mathbb{M}_{ab}^{(21)} - \alpha_b^{(3)} \alpha_a^{(2)} \alpha_a^{(3)} \mathbb{M}_{ab}^{(12)}, \\
 \mathbb{R}_{ab}^{(44)} &= \mathbb{M}_{ab}^{(44)}, \\
 \mathbb{R}_{ab}^{(55)} &= \mathbb{M}_{ab}^{(55)} - \alpha_b^{(5)} \mathbb{M}_{ab}^{(50)} - \alpha_a^{(5)} \mathbb{M}_{ab}^{(05)} + \alpha_a^{(5)} \alpha_b^{(5)} \mathbb{M}_{ab}^{(00)}. 
 \end{aligned} \tag{7.346}$$

Here the basic collision bracket integrals  $\mathbb{M}_{ab}^{(qs)}$  are defined by

$$\begin{aligned}
 \mathbb{M}_{ab}^{(ss)} &= \frac{\beta^2}{4} \sum_{i\alpha=1}^{N_\alpha} \sum_{jb=1}^{N_b} \left\langle \Delta h_{ia}^{(s)} \Delta h_{jb}^{(s)} \right\rangle_m \quad (s = 0, 1, 4), \\
 \mathbb{M}_{ab}^{(qq)} &= \frac{\beta^2}{4} \sum_{i\alpha=1}^{N_\alpha} \sum_{jb=1}^{N_b} \left\langle \Delta h_{ia}^{(q)} \Delta h_{jb}^{(q)} \right\rangle_m \quad (q = 2, 3, 5), 
 \end{aligned} \tag{7.347}$$

$$\mathbb{M}_{ab}^{(qs)} = \frac{\beta^2}{4} \sum_{i\alpha=1}^{N_\alpha} \sum_{jb=1}^{N_b} \left\langle \Delta h_{ia}^{(q)} \Delta h_{jb}^{(s)} \right\rangle_m \tag{7.348}$$

$$(q \neq s; q = 1, 2, 5; s = 0, 1, 2, 3).$$

Upon inserting the generalized potentials  $X_a^{(q)}$  given in terms of  $\Phi^{(q)}$  (7.311) into (7.342), we finally obtain the dissipation function  $\kappa^2$  in terms of the final forms of collision bracket integrals  $\mathfrak{R}^{(qs)}$ . This will be used to define linear transport coefficients:

$$\kappa^2 = \sum_{q,s \geq 1} \Phi^{(q)} \mathfrak{R}^{(qs)} \Phi^{(s)}, \tag{7.349}$$

$$\mathfrak{R}^{(qs)} = g^{(q)} \mathbb{R}^{(qs)} g^{(s)}. \tag{7.350}$$

The form for  $\kappa^2$  in (7.349) will be used in the cumulant expansion formula for the calortropy production  $\sigma_c$  and for the dissipation terms  $\Lambda^{(q)}$  in (7.337) for generalized hydrodynamic equations. We remark that  $\kappa^2$  is a generalization of the Rayleigh dissipation function [24] for a liquid mixture.

## 7.8 Linear Transport Processes

### 7.8.1 Linear Dissipation Terms

A great deal of attention has been paid so far to the kinematic terms of evolution equations, because they indicate how macroscopic evolutions of processes are driven by external conditions as well as mutual couplings of observables, and the role of intermolecular forces to produce the couplings. The major role of kinematic terms lies in providing thermodynamic driving forces in the forms of spatial gradients of conserved variables. We have seen an example for this feature in the case of diffusion flux evolution equation.

On the other hand, although the dissipation terms  $\Lambda_a^{(q)}$  have been relegated to an inconspicuous role in the derivations of evolution equations up to this point, they contain the most important molecular dynamic information on the mechanical origin of the irreversible processes from the molecular theory standpoint. Since the molecular collision dynamical information is contained in the transport coefficients provided by the dissipation terms, we gain our ultimate molecular theory understanding of transport processes, hydrodynamics, and irreversible thermodynamics, through them. However, the dissipation terms also pose the most computationally difficult and technically demanding part of the kinetic theory of fluids from the molecular theory standpoint because of the many-body collision problems involved. Our strategy in this work is to defer the computational task to the question of transport coefficients in which all the molecular theory information is vested. Then the computation of transport coefficients will be performed by suitable methods, either by approximate analytical methods or numerical methods—e.g., molecular dynamical methods [25] or Monte Carlo methods [26] on an electronic computer.

If irreversible processes occur near equilibrium, the nonlinear dissipation terms, for example, given in (7.336) can be linearized with respect to fluxes. We thus obtain

$$\Lambda_a^{(q)} = -\frac{\epsilon}{\beta g_a^{(q)}} \sum_{b=1}^r \sum_{s \geq 0} \mathfrak{R}_{ab}^{(qs)} \Phi_b^{(s)}, \quad (7.351)$$

where  $\mathfrak{R}_{ab}^{(qs)}$  are given by the collision bracket integral in (7.350):

$$\mathfrak{R}_{ab}^{(qs)} = g_a^{(q)} \mathbb{R}_{ab}^{(qs)} g_b^{(s)}. \quad (7.352)$$

It should be remarked that in this linear approximation the quadratic form for the dissipation function is still positive:

$$\sum_{a=1}^r \sum_{b=1}^r \sum_{q \geq 0} \sum_{s \geq 0} \Phi_a^{(q)} \mathfrak{R}_{ab}^{(qs)} \Phi_b^{(s)} \geq 0 \quad (7.353)$$

As will be shown presently, the linear dissipation terms give rise to linear constitutive equations if the kinematic terms in the generalized hydrodynamic equations are linearized with respect to the thermodynamic forces—namely, gradients of density, concentrations, molar volume, fluid velocity, and temperature—in order to be consistent with the linear approximations made for the dissipation terms.

## 7.8.2 *Linear Constitutive Equations*

### 7.8.2.1 Volume Transport Equation

Traditionally, the molar (or partial molar) volume gradient does not occur among the thermodynamic gradients, but in the present theory the volume fluctuations could be also driven by a volume gradient which appears as a mean value of spatial gradients of the Voronoi volume of molecules. The presence of this aspect represents a significant departure from the conventional mode of thought in fluid mechanics. Such effects are contained in the kinematic term.

To ascertain whether or not they are in the linear order, the kinematic term in the volume evolution equation

$$\mathcal{Z}_a^{(0)} = \frac{\delta \psi_a^{(0)}}{\delta \zeta} \cdot \nabla \zeta + \frac{\delta \Phi_a^{(0)}}{\delta \zeta} \cdot \frac{d\zeta}{dt} + f_{va}^{(0)}$$

is now examined closely. Since the first two terms on the right of  $\mathcal{Z}_a^{(0)}$  are evidently seen to be, at least, of second order in gradients  $\nabla \zeta$  or derivatives of nonequilibrium variables, we may neglect it in the linear-order approximation holding near equilibrium. As to the remaining term  $f_{va}^{(0)}$ , upon expanding  $f_c^{(N)}$  to first order in generalized potentials  $X_a^{(1)}$

$$f_c^{(N)} = f_{eq}^{(N)} \left[ 1 - \sum_{q \geq 0} \sum_{a=1}^r \sum_{ja=1}^{N_a} \beta X_a^{(q)} h_{ja}^{(q)} + O(X^2) \right], \quad (7.354)$$

which has given rise to the linear relation between  $\Phi_a^{(q)}$  and  $X_a^{(q)}$  in (7.311), to linear order in  $\Phi_a^{(q)}$  there follows the approximation:

$$f_{va}^{(0)} = \beta \sum_{b=1}^r \left( \boldsymbol{\lambda}_{ab}^{(01)} \cdot \Phi_b^{(1)} + \boldsymbol{\lambda}_{ab}^{(02)} \cdot \Phi_b^{(2)} \right) + O(X^2). \quad (7.355)$$

In (7.355)  $\boldsymbol{\lambda}_{ab}^{(0k)}$  ( $k = 1, 2$ ) are defined by the averages listed below:

$$\boldsymbol{\lambda}_{ab}^{(01)} = \sum_{ja=1}^{N_a} \sum_{\substack{kb \in z_{ja} \\ (ja \neq kb)}}^{N_b} g_b^{(1)} \left\langle f_0^{(\mathbb{N})} \delta(\mathbf{r}_{ja} - \mathbf{r}) \left( \mathbf{C}_{kb} \cdot \frac{\partial h_{ja}^{(0)}}{\partial \mathbf{r}_{kb}} \right) h_{kb}^{(1)} \right\rangle_e, \quad (7.356)$$

$$\boldsymbol{\lambda}_{ab}^{(02)} = \sum_{ja=1}^{N_a} \sum_{\substack{kb \in z_{ja} \\ (ja \neq kb)}}^{N_b} g_b^{(2)} \left\langle f_0^{(\mathbb{N})} \delta(\mathbf{r}_{ja} - \mathbf{r}) \left( \mathbf{C}_{kb} \cdot \frac{\partial h_{ja}^{(0)}}{\partial \mathbf{r}_{kb}} \right) h_{kb}^{(2)} \right\rangle_e. \quad (7.357)$$

It should be remembered that the averages presented in (7.356) and (7.357) are not collisional averages as is the case for the collision bracket integrals, but local equilibrium averages involving particles  $kb$  at the vertex of Voronoi polyhedron of particle  $ja$ . Consequently,  $\left( \mathbf{C}_{kb} \cdot \frac{\partial h_{ja}^{(0)}}{\partial \mathbf{r}_{kb}} \right)$  represents a mean spatial gradient of the flux of Voronoi volume at position  $\mathbf{r}$  weighted by mass velocity  $h_{kb}^{(1)}$  or volume velocity  $h_{kb}^{(2)}$ . Therefore, despite being linear with respect to  $\Phi_b^{(1)}$  and  $\Phi_b^{(2)}$ , which are vectors, we are inclined to conclude that the first two terms in (7.355) should be regarded as also of second order in spatial gradients. Moreover, the first two terms in (7.355) break the Curie principle in the constitutive equation for the volume fluctuation  $\Phi_a^{(0)}$ . Based on this observation we conclude that

$$\mathcal{Z}_a^{(0)} = O(X^2) \quad (7.358)$$

and hence it should be neglected in the first order approximation.

Combining the linear dissipation and kinematic terms, the linear constitutive equations are obtained for volume transport to first order in generalized potentials in the form

$$\frac{\epsilon}{\beta g_a^{(0)}} \sum_{b=1}^r \mathfrak{R}_{ab}^{(00)} \Phi_b^{(0)} + \frac{\epsilon}{\beta g_a^{(0)}} \sum_{b=1}^r \mathfrak{R}_{ab}^{(05)} \Phi_b^{(5)} = 0. \quad (7.359)$$

As will be seen later, this set of equations is coupled with the constitutive equations for excess normal stresses. When these coupled equations are solved, there naturally will appear the transport coefficients to account for volume transport processes of the mixture. It means the volume transport phenomena will affect the bulk viscosity of the mixture, and vice versa.

### 7.8.2.2 Mass Diffusion Equations

The kinematic term for mass diffusion flux is given, to linear order in gradients, by the thermodynamic force  $\mathbf{d}_a$  only:

$$\underline{\mathcal{Z}}_a^{(1)} = -p\mathbf{d}_a + \text{nonlinear terms.} \quad (7.360)$$

The dissipation term  $\Lambda_a^{(1)}$  for diffusion flux consists of a linear combination of diffusion fluxes, heat fluxes, and volume fluxes to first order in generalized potentials for all the species of the mixture. Thus we find

$$\Lambda_a^{(1)} = -\frac{\epsilon}{\beta g_a^{(1)}} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(11)} \Phi_b^{(1)} + \mathfrak{R}_{ab}^{(12)} \Phi_b^{(2)} + \mathfrak{R}_{ab}^{(13)} \Phi_b^{(3)} \right) + O(X^2), \quad (7.361)$$

where the coefficients  $\mathfrak{R}_{ab}^{(1s)}$  are collision bracket integrals :

$$\mathfrak{R}_{ab}^{(1s)} = \frac{\beta^2}{4} \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left\langle \Delta h_{ja}^{(1)} \odot \Delta h_{kb}^{(s)} \right\rangle_m \quad (s = 1, 2, 3), \quad (7.362)$$

See (7.339) and (7.341) for the definition of the symbols in (7.362). Therefore, the constitutive equations for mass diffusion fluxes are given by linear constitutive equations

$$\mathbf{d}_a - \frac{\epsilon}{\beta g_a^{(1)}} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(11)} \Phi_b^{(1)} + \mathfrak{R}_{ab}^{(12)} \Phi_b^{(2)} + \mathfrak{R}_{ab}^{(13)} \Phi_b^{(3)} \right) = 0 \quad (7.363)$$

$$(1 \leq a \leq r).$$

These are coupled to the linear constitutive equation for volume fluctuation (7.359).

### 7.8.2.3 Volume Flux Equations

The renormalized kinematic term  $\underline{\mathcal{Z}}_a^{(2)}$  for the volume flux can be linearized with respect to thermodynamic forces. We thus obtain it in the form

$$\underline{\mathcal{Z}}_a^{(2)} = -\mathfrak{c}_a \alpha_a^{(2)} \nabla p - p_a \nabla \alpha_a^{(2)} - \alpha_a^{(2)} \rho_a \widehat{\mathbf{F}}_a + O(X^2). \quad (7.364)$$

Since  $\alpha_a^{(2)}$  is a function of  $T$  and  $v$  or  $p$  we may write  $\nabla \alpha_a^{(2)}$  in terms of derivatives of  $T$  and  $p$ :

$$\nabla \alpha_a^{(2)} = \frac{\partial \alpha_a^{(2)}}{\partial T} \nabla T + \frac{\partial \alpha_a^{(2)}}{\partial p} \nabla p. \quad (7.365)$$

The dissipation term is given by a linear combination of vectorial fluxes:

$$\Lambda_a^{(2)} = -\frac{\epsilon}{\beta g_a^{(2)}} \sum_{b=1}^r \sum_{s=1}^3 \mathfrak{R}_{ab}^{(2s)} \Phi_b^{(s)} + O(X^2), \quad (7.366)$$

where the collision bracket integrals are given by the formula

$$\mathfrak{R}_{ab}^{(2s)} = \frac{\beta^2}{4} \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left\langle \Delta h_{ja}^{(2)} \odot \Delta h_{kb}^{(s)} \right\rangle_m. \quad (7.367)$$

Combining (7.364) and (7.366), the linear constitutive equations for volume fluxes are obtained:

$$\frac{\epsilon}{\beta g_a^{(2)}} \sum_{b=1}^r \sum_{s=1}^3 \mathfrak{R}_{ab}^{(2s)} \Phi_b^{(s)} = -\alpha_a^{(2)} \left( A_{Ta}^{(2)} \nabla T + A_{pa}^{(2)} \nabla p + \rho_a \widehat{\mathbf{F}}_a \right), \quad (7.368)$$

where the coefficients  $A_{Ta}^{(2)}$  and  $A_{pa}^{(2)}$  are defined below:

$$A_{Ta}^{(2)} = p_a \frac{\partial \ln \alpha_a^{(2)}}{\partial T}, \quad (7.369)$$

$$A_{pa}^{(2)} = \mathfrak{c}_a + p_a \frac{\partial \ln \alpha_a^{(2)}}{\partial p}. \quad (7.370)$$

The linear constitutive equation (7.368) are also coupled to constitutive equations (7.359) and (7.363).

#### 7.8.2.4 Heat Flux

The kinematic term for the heat flux is similarly linearized to obtain

$$\begin{aligned} \underline{\mathcal{Z}}_a^{(3)} &= -p_a \widehat{C}_p \nabla T - \alpha_a^{(32)} \alpha_a^{(2)} \mathbf{d}_a + \alpha_a^{(32)} p_a \nabla \alpha_a^{(2)} \\ &\quad + \text{nonlinear terms.} \end{aligned} \quad (7.371)$$

This linear approximation for  $\underline{\mathcal{Z}}_a^{(3)}$  is written in a linear combination of spatial gradients  $\nabla T$ ,  $\nabla p$ , and  $\mathbf{d}_a$ :

$$\underline{\mathcal{Z}}_a^{(3)} = -C_{Ta}^{(3)}\nabla T + C_{pa}^{(3)}\nabla p - C_{da}^{(3)}\mathbf{d}_a, \quad (7.372)$$

where

$$\begin{aligned} C_{Ta}^{(3)} &= p_a \left( \widehat{C}_p + \alpha_a^{(32)} \alpha_a^{(2)} \frac{\partial \ln \alpha_a^{(2)}}{\partial T} \right), \\ C_{pa}^{(3)} &= p_a \alpha_a^{(32)} \alpha_a^{(2)} \frac{\partial \ln \alpha_a^{(2)}}{\partial p}, \\ C_{da}^{(3)} &= \alpha_a^{(32)} \alpha_a^{(2)}. \end{aligned} \quad (7.373)$$

The dissipation term is also linearized with respect to  $\Phi_b^{(1)}$ ,  $\Phi_b^{(2)}$ , and  $\Phi_b^{(3)}$ :

$$\Lambda_a^{(3)} = -\frac{\epsilon}{\beta g_a^{(3)}} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(31)} \Phi_b^{(1)} + \mathfrak{R}_{ab}^{(32)} \Phi_b^{(2)} + \mathfrak{R}_{ab}^{(33)} \Phi_b^{(3)} \right) + O(X^2). \quad (7.374)$$

Here the collision bracket integrals are given by

$$\mathfrak{R}_{ab}^{(3s)} = \frac{\beta^2}{4} \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left\langle \Delta h_{ja}^{(3)} \odot \Delta h_{kb}^{(s)} \right\rangle_m \quad (s = 1, 2, 3). \quad (7.375)$$

Upon combining (7.371) and (7.374), we obtain the linear constitutive equations for heat fluxes

$$\begin{aligned} \frac{\epsilon}{\beta g_a^{(3)}} \sum_{b=1}^r \left( \mathfrak{R}_{ab} \Phi_b^{(1)} + \mathfrak{R}_{ab}^{(32)} \Phi_b^{(2)} + \mathfrak{R}_{ab}^{(33)} \Phi_b^{(3)} \right) \\ = -C_{Ta}^{(3)}\nabla T + C_{pa}^{(3)}\nabla p - C_{da}^{(3)}\mathbf{d}_a. \end{aligned} \quad (7.376)$$

Thus we see that three constitutive equations for vector processes (7.363), (7.368), and (7.376) are coupled.

### 7.8.2.5 Shear Stress

The linearized kinematic term for shear stress is given by

$$\underline{\mathcal{Z}}_a^{(4)} = -2p_a [\nabla \mathbf{u}]^{(2)} \quad (7.377)$$

and the dissipation term is linearized with respect to the shear stress by

$$\Lambda_a^{(4)} = - \sum_{b=1}^r \mathfrak{R}_{ab}^{(44)} \Phi_b^{(4)}. \quad (7.378)$$

There are no coupling terms with other fluxes than shear stresses. Thus there are no cross terms with other processes in the collision bracket integrals

$$\mathfrak{R}_{ab}^{(44)} = \frac{\beta^2}{4} \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left\langle \Delta h_{ja}^{(4)} \odot \Delta h_{kb}^{(4)} \right\rangle_m. \quad (7.379)$$

The linear constitutive equations therefore are:

$$\frac{\epsilon}{\beta g_a^{(4)}} \sum_{b=1}^r \mathfrak{R}_{ab}^{(44)} \Phi_b^{(4)} = -2p_a [\nabla \mathbf{u}]^{(2)} \quad (r \geq a \geq 1). \quad (7.380)$$

So, the shear stresses of these linear constitutive equations are not coupled to other scalar or vectorial fluxes but to shear stresses of other species in the linear regime even in the presence of volume transport.

### 7.8.2.6 Excess Normal Stress

The kinematic term is linearized to the form

$$\bar{\mathcal{Z}}_a^{(5)} = -\rho \frac{d}{dt} (p/\rho) - \alpha_a^{(5)} \rho \frac{dv}{dt} - \frac{2}{3} p \nabla \cdot \mathbf{u} + O(X^2). \quad (7.381)$$

This is rearranged to another form by using the relation

$$\rho \frac{d}{dt} (pv) = \left( p - \frac{1}{\kappa_{\hat{\Psi}}} \right) \nabla \cdot \mathbf{u}, \quad (7.382)$$

where

$$\kappa_{\hat{\Psi}} = -\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_{\hat{\Psi}}, \quad (7.383)$$

which is the constant calortropy compressibility. Therefore the kinematic term can be written for the linear excess normal stress as

$$\bar{\mathcal{Z}}_a^{(5)} = - \left( \frac{5}{3} p_a + \alpha_a^{(5)} - \frac{1}{\kappa_{\hat{\Psi}a}} \right) \nabla \cdot \mathbf{u}. \quad (7.384)$$

The corresponding dissipation term is linearized to the form

$$\Lambda_a^{(5)} = -\frac{\epsilon}{\beta g_a^{(5)}} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(50)} \Phi_b^{(0)} + \mathfrak{R}_{ab}^{(55)} \Phi_b^{(5)} \right) + O(X^2), \quad (7.385)$$

where the coefficients are collision bracket integrals

$$\mathfrak{R}_{ab}^{(5s)} = \frac{\beta^2}{4} \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left\langle \Delta h_{ja}^{(5)} \odot \Delta h_{kb}^{(s)} \right\rangle_m \quad (s = 0, 5) \quad (7.386)$$

The linear constitutive equations for excess normal stresses therefore are given by the equation

$$\frac{\epsilon}{\beta g_a^{(5)}} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(50)} \Phi_b^{(0)} + \mathfrak{R}_{ab}^{(55)} \Phi_b^{(5)} \right) = - \left( \frac{5}{3} p_a + \alpha_a^{(5)} - \frac{1}{\kappa \hat{\Psi}_a} \right) \nabla \cdot \mathbf{u}. \quad (7.387)$$

Notice that volume fluctuations  $\Phi_b^{(0)}$  appear explicitly in this linear constitutive equation indicating that volume fluctuations and the excess normal stress are coupled. It is, therefore, expected that the bulk viscosity would be influenced by volume fluctuations present in the fluid in nonequilibrium, and vice versa. It may be possible to look for the evidence of volume fluctuation effect in, for example, ultrasonic experiments [27].

### 7.8.2.7 Summary of Linear Constitutive Equations

The linear constitutive equations are collected below as a summary of the results of this section:

$$\frac{\epsilon}{\beta g_a^{(0)}} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(00)} \Phi_b^{(0)} + \mathfrak{R}_{ab}^{(05)} \Phi_b^{(5)} \right) = 0, \quad (7.388)$$

$$\frac{\epsilon}{\beta g_a^{(5)}} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(50)} \Phi_b^{(0)} + \mathfrak{R}_{ab}^{(55)} \Phi_b^{(5)} \right) = - \left( \frac{5}{3} p_a + \alpha_a^{(5)} - \frac{1}{\kappa \hat{\Psi}_a} \right) \nabla \cdot \mathbf{u}, \quad (7.389)$$

$$\sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(11)} \Phi_b^{(1)} + \mathfrak{R}_{ab}^{(12)} \Phi_b^{(2)} + \mathfrak{R}_{ab}^{(13)} \Phi_b^{(3)} \right) = \frac{\beta g_a^{(1)}}{\epsilon} \mathbf{d}_a, \quad (7.390)$$

$$\sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(21)} \Phi_b^{(1)} + \mathfrak{R}_{ab}^{(22)} \Phi_b^{(2)} + \mathfrak{R}_{ab}^{(23)} \Phi_b^{(3)} \right) = -c_a \alpha_a^{(2)} \frac{\beta g_a^{(2)}}{\epsilon} \left( A_{Ta}^{(2)} \nabla T + A_{pa}^{(2)} \nabla p + \rho_a \hat{\mathbf{F}}_a \right), \quad (7.391)$$

$$\sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(31)} \Phi_b^{(1)} + \mathfrak{R}_{ab}^{(32)} \Phi_b^{(2)} + \mathfrak{R}_{ab}^{(33)} \Phi_b^{(3)} \right) = -p_a \hat{C}_p \frac{\beta g_a^{(3)}}{\epsilon} \nabla T - c_a^{(32)} \alpha_a^{(2)} \mathbf{d}_a, \quad (7.392)$$

$$\sum_{b=1}^r \mathfrak{R}_{ab}^{(44)} \Phi_b^{(4)} = -2 p_a \frac{\beta g_a^{(4)}}{\epsilon} [\nabla \mathbf{u}]^{(2)}. \quad (7.393)$$

It is noteworthy that the linear constitutive equations consist of three subsets, namely, (7.388) and (7.389), (7.390)–(7.392), and (7.393). Equation (7.393) is not coupled to either scalar or vector equations. The three subsets will be separately solved to determine the linear transport coefficients.

### 7.8.3 Linear Transport Coefficients

If the linear constitutive equations are solved for various fluxes  $\Phi_a^{(q)}$  in terms of thermodynamic forces, the linear transport coefficients can be obtained in terms of collision bracket integrals. We thus obtain shear viscosity, bulk viscosity, thermal conductivity, diffusion coefficients and related transport coefficients such as thermodiffusion, etc. in terms of collision bracket integrals. In addition to these usually known linear transport coefficients, we obtain new transport coefficients associated with volume transport coefficients. It is preferable to summarize them into three subsets—a subset consisting of a single constitutive equation for shear stress; another consisting of volume fluctuations coupled with excess normal stresses and driven by diffusion and volume flux; the third subset consisting of vectorial fluxes driven by spatial gradients of temperature, pressure or volume, and concentrations. Since the subsets consist of linear algebraic equations they are easily solved in terms of the driving forces and yield  $\Phi_b^{(q)}$  ( $q = 0, 1, \dots, 5$ ) for all species components, from which linear transport coefficients can be extracted. Thus we derive:

#### 7.8.3.1 Law of Viscosity

From (7.393) the Newtonian law of viscosity is obtained and the shear viscosity is identified:

$$\begin{aligned} \Phi_a^{(4)} &= -2 \sum_{b=1}^r (\mathfrak{R}^{(44)})_{ab}^{-1} \frac{p_a \beta g_a^{(4)}}{\epsilon} [\nabla \mathbf{u}]^{(2)} \\ &= -2 \eta_a^{(0)} [\nabla \mathbf{u}]^{(2)} \end{aligned} \quad (7.394)$$

where  $(\mathfrak{R}^{(44)})^{-1}$  stands for the inverse square matrix consisting of  $\mathfrak{R}_{ab}^{(44)}$  and the partial linear shear viscosity  $\eta_a^{(0)}$  is identified by the formula

$$\eta_a^{(0)} = \sum_{b=1}^r \frac{p_b \beta g_b^{(4)}}{\epsilon} (\mathfrak{R}^{(44)})_{ab}^{-1}. \quad (7.395)$$

Since the shear viscosity is usually measured for the mixture, but not for the components this formula should be summed over all species contributions to obtain the viscosity of the mixture:

$$\eta_0 = \sum_{a=1}^r \eta_a^{(0)}. \quad (7.396)$$

In this sense, the kinetic theory of mixtures has advantages over experiment on a mixture, unless experiment is such that it distinguishes species contributions.

### 7.8.3.2 Diffusion, Heat Flow, and Volume Flux

The vectorial processes associated with mass diffusion, heat flow, and volume flow are determined from the subset of coupled equations (7.390)–(7.392). Solving the coupled linear equations, we obtain the diffusion fluxes  $\Phi_a^{(1)}$ , volume fluxes  $\Phi_a^{(2)}$ , and heat fluxes  $\Phi_a^{(3)}$  for all species in terms of their driving forces,  $\mathbf{d}_a$ ,  $\nabla T$ ,  $\nabla p$ , or  $\nabla v$ , and the external forces  $\widehat{\mathbf{F}}_a$ . The three fluxes are expressible as linear combinations of the aforementioned driving forces with the coefficients given in terms of corresponding elements of an inverse matrix consisting of  $\mathfrak{R}_{ab}^{(qs)}$  ( $q, s = 1, 2, 3$ ) and the coefficients of the inhomogeneous terms in (7.390)–(7.392), namely, the driving forces mentioned. They are expressible as

$$\Phi_a^{(q)} = - \sum_{b=1}^r \left( D_{ab}^{(q1)} \mathbf{d}_b + \lambda_{ab}^{(q1)} \nabla T + \lambda_{ab}^{(q2)} \nabla v + \zeta_{ab}^{(q2)} \widehat{\mathbf{F}}_b \right) \quad (q = 1, 2, 3), \quad (7.397)$$

where  $D_{ab}^{(q1)}$  are diffusion related coefficients (e.g., thermal diffusion, etc.),  $\lambda_{ab}^{(q1)}$  thermal conduction-related transport coefficients, and  $\lambda_{ab}^{(q2)}$  the transport coefficients related to volume transport, and, finally,  $\zeta_{ab}^{(q2)}$  the transport coefficients associated with the external body-forces. The coefficients  $\lambda_{ab}^{(q2)}$  are new; they arise from volume transport phenomena, which have been conventionally overlooked. The transport coefficients can be expressed in terms of a matrix consisting of collision bracket integrals  $\mathfrak{R}_{ab}^{(qs)}$ , but this topic is deferred to Chap. 9. We do not take up the topic here since they are bulky and distracting. Another reason for not showing at this point is that it is necessary to eliminate dependent diffusion fluxes before explicitly identifying the diffusion-related transport coefficients by using the condition

$$\sum_{a=1}^r \Phi_a^{(1)} = 0. \quad (7.398)$$

For the aforementioned question, see Chap. 9 where linear hydrodynamic theories satisfying the condition (7.398) are constructed, discussed, and applied.

### 7.8.3.3 Excess Normal Stress and Volume Fluctuations

The subset of coupled (7.388) and (7.389) indicates that  $\Phi_a^{(0)}$  and  $\Phi_a^{(5)}$  are driven by  $\nabla \cdot \mathbf{u}$ . Thus by solving the coupled set we obtain the transport coefficients for bulk viscous phenomena associated with compression/dilatation of the fluid that result in the bulk viscosity, but also transport coefficients associated with volume fluctuations, which are intimately associated with  $\nabla \cdot \mathbf{u}$ . The latter is new to the conventional theory of transport processes which usually ignores volume transport phenomena, as we have mentioned earlier. The constitutive relations thus obtained have the form

$$\Phi_a^{(q)} = - \sum_{b=1}^r \lambda_{ab}^{(q5)} \nabla \cdot \mathbf{u} \quad (q = 0, 5), \quad (7.399)$$

where the transport coefficients  $\lambda_{ab}^{(q5)}$  can be easily identified from the solutions of (7.388) and (7.389). The volume fluctuations have therefore the same kinematic origin as the excess normal stress in the linear approximation.

Thus we have seen that transport phenomena associated with the vectorial processes are affected by volume transport processes through the volume fluxes. The effects thereof may be small, but still amenable to careful measurements and alters the conventional understanding of fluid flow phenomena through bulk viscous phenomena as well as mass diffusion and heat flow phenomena. The linear transport coefficients may be computed by means of computer simulation methods. One may use the method discussed in Refs. [28] and [29], where the possibility of applying a Monte Carlo type simulation logarithm is discussed for transport coefficients for liquids.

## 7.9 Summary of Generalized Hydrodynamic Equations for a Mixture

It is now appropriate to summarize the thermodynamically consistent generalized hydrodynamic equations, which we have derived from the ensemble kinetic equation, i.e., the GBE, and may apply to study fluid flow phenomena in a mixture. These generalized hydrodynamic equations are in the first-order cumulant approximation

for the dissipation terms. Also the generalized potentials  $X_a^{(q)}$  are linearized with respect to  $\Phi_a^{(q)}$ .

The kinematic terms and the divergence terms also can be linearized to first order with respect to the thermodynamic driving forces as described in the previous section where the linearized constitutive equations are discussed. As a matter of fact, most of nonlinear flow analysis can be made even if linear approximations are made for the kinematic terms including the divergence terms, provided that the first-order cumulant approximation is retained for the dissipation terms as presented earlier. In the following the generalized hydrodynamic equations in the first-order cumulant approximation for the dissipation terms are summarized.

### 7.9.1 Conservation Laws

$$\partial_t \rho = -\nabla \cdot (\rho \mathbf{u}), \quad (7.400)$$

$$\rho d_t \mathbf{c}_a = -\nabla \cdot \mathbf{J}_a, \quad (7.401)$$

$$\rho d_t \mathbf{u} = -\nabla \cdot \mathbf{P} + \rho \widehat{\mathbf{F}}, \quad (7.402)$$

$$\rho d_t \mathcal{E} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a. \quad (7.403)$$

### 7.9.2 Nonconserved Evolution Equations

$$\begin{aligned} \rho \frac{d}{dt} \widehat{\Phi}_a^{(0)} &= -\nabla \cdot \psi_a^{(0)} + \frac{\delta \psi_a^{(0)}}{\delta \boldsymbol{\varsigma}} \cdot \nabla \boldsymbol{\varsigma} + \frac{\delta \Phi_a^{(0)}}{\delta \boldsymbol{\varsigma}} \cdot \frac{d \boldsymbol{\varsigma}}{dt} \\ &+ f_{va}^{(0)} - \frac{\epsilon}{\beta g_a^{(0)}} \sum_{b=1}^r \sum_{s=1,2,3} \mathfrak{R}_{ab}^{(0s)} \Phi_b^{(s)} q_n(\kappa), \end{aligned} \quad (7.404)$$

$$\begin{aligned} \rho \frac{d \widehat{\Phi}_a^{(1)}}{dt} &= -\nabla \cdot \bar{\psi}_a^{(1)} - p \mathbf{d}_a - \mathbf{J}_a \cdot \nabla \mathbf{u} + \mathbf{V}_a^{(1)} + \mathbf{c}_a \nabla \cdot (\mathbf{P} - p \boldsymbol{\delta}) \\ &- \nabla \cdot (\mathbf{P}_a - p_a \boldsymbol{\delta}) - \frac{\epsilon}{\beta g_a^{(1)}} \sum_{b=1}^r \sum_{s=1,2,3} \mathfrak{R}_{ab}^{(1s)} \Phi_b^{(s)} q_n(\kappa), \end{aligned} \quad (7.405)$$

$$\begin{aligned} \rho \frac{d \widehat{\Phi}_a^{(2)}}{dt} &= -\nabla \bar{\psi}_a^{(2)} - \rho (\widehat{\Phi}_a^{(0)} - \mathbf{c}_a \alpha_a^{(2)}) \left( \frac{d \mathbf{u}}{dt} - \widehat{\mathbf{F}}_a \right) - \Phi_a^{(2)} \cdot \nabla \mathbf{u} \\ &- \mathbf{P}_a \cdot \nabla \alpha_a^{(2)} + \mathbf{V}_a^{(2)} + \mathbf{f}_{va}^{(2)} + \frac{\partial \Phi_a^{(2)}}{\partial \boldsymbol{\varsigma}} \odot \frac{d \boldsymbol{\varsigma}}{dt} + \frac{\partial \varphi_a^{(2W)}}{\partial \boldsymbol{\varsigma}} \odot \nabla \boldsymbol{\varsigma} \\ &- \frac{\epsilon}{\beta g_a^{(2)}} \sum_{b=1}^r \sum_{s=1,2,3} \mathfrak{R}_{ab}^{(2s)} \Phi_b^{(s)} q_n(\kappa), \end{aligned} \quad (7.406)$$

$$\begin{aligned}
\rho \frac{d\widehat{\Phi}_a^{(3)}}{dt} = & -\nabla \cdot \overline{\psi}_a^{(3)} - [\rho_a (\mathcal{E}_a - \widehat{h}_a) d_t \mathbf{u} + d_t \mathbf{u} \cdot \mathbf{P}_a - \mathbf{J}_a \cdot d_t \widehat{h}_a] \\
& - \mathbf{Q}'_a \cdot \nabla \mathbf{u} + \mathbf{P}_a \cdot \nabla \widehat{h}_a - \varphi_a^{(3W)} \odot \nabla \mathbf{u} + \mathbf{V}_a^{(3)} \\
& - \alpha_a^{(32)} [(\alpha_a^{(2)} \rho_a - \Phi_a^{(0)}) (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) + \mathbf{V}_a^{(2)} + \mathbf{f}_{va}^{(2)} \\
& + d_t \varsigma \cdot \frac{\delta \psi_a^{(0)}}{\delta \varsigma} + \frac{\delta \varphi_a^{(2W)}}{\delta \varsigma} \odot \nabla \varsigma - \Phi_a^{(1)} d_t \alpha_a^{(2)} \\
& - \mathbf{P}_a \cdot \nabla \alpha_a^{(2)} - (\psi_a^{(0)} - \Phi_a^{(1)} \alpha_a^{(2)}) \cdot \nabla \mathbf{u}] - \Phi_a^{(2)} d_t \alpha_a^{(32)} \\
& - \sum_{a=1}^r \psi_a^{(2W)} \nabla \alpha - \frac{\epsilon}{\beta g_a^{(3)}} \sum_{b=1}^r \sum_{s=1,2,3} \mathfrak{R}_{ab}^{(3s)} \Phi_b^{(s)} q_n(\kappa), \quad (7.407)
\end{aligned}$$

$$\begin{aligned}
\rho \frac{d\widehat{\Phi}_a^{(4)}}{dt} = & -\nabla \cdot \overline{\psi}_a^{(4)} - 2 [\mathbf{P}_a \cdot \nabla \mathbf{u}]^{(2)} - 2 \left[ \mathbf{J}_a \frac{d\mathbf{u}}{dt} \right]^{(2)} + 2 [\widehat{\mathbf{F}}_a \mathbf{J}_a]^{(2)} \\
& + 2 \mathbf{V}_a^{(4)} + [\mathfrak{P}_a]^{(2)} - \frac{\epsilon}{\beta g_a^{(4)}} \sum_{b=1}^r \mathfrak{R}_{ab}^{(44)} \Phi_b^{(4)} q_n(\kappa), \quad (7.408)
\end{aligned}$$

$$\begin{aligned}
\rho \frac{d\widehat{\Phi}_a^{(5)}}{dt} = & -\nabla \cdot \overline{\psi}_a^{(5)} - \rho \frac{d}{dt} (p/\rho) - \frac{2}{3} \text{Tr} (\mathbf{P}_a \cdot \nabla \mathbf{u}) + V_a^{(5)} - \rho \alpha_a^{(5)} \frac{d\widehat{\Phi}_a^{(0)}}{dt} \\
& - \rho \frac{d\alpha_a^{(5)}}{dt} \widehat{\Phi}_a^{(0)} - \frac{\epsilon}{\beta g_a^{(5)}} \sum_{b=1}^r \sum_{s=0,5} \mathfrak{R}_{ab}^{(5s)} \Phi_b^{(s)} q_n(\kappa). \quad (7.409)
\end{aligned}$$

In (7.404)–(7.409) the nonlinear factor  $q_n$  is defined by

$$q_n(\kappa) = \frac{\sinh \kappa}{\kappa} \quad (7.410)$$

with  $\kappa$  denoting the dissipation function. Because of this nonlinear factor the generalized hydrodynamic equations are highly nonlinear with respect to  $\Phi_b^{(s)}$ . Entire molecular theoretic information including interactions is contained in the linear transport coefficients.

## 7.10 Quasilinear Generalized Hydrodynamic Equations

If the kinematic terms and the divergence terms in the evolution equations (7.404)–(7.409) can be linearized with respect to  $\Phi_b^{(s)}$  ( $s = 0, 1, \dots, 5$ ) and the thermodynamic forces as we have described in Sect. 7.8.2, we obtain quasilinear evolution equations for nonconserved variables (i.e., macroscopic moments):

$$\rho \frac{d}{dt} \widehat{\Phi}_a^{(0)} = - \frac{\epsilon}{\beta g_a^{(0)}} \sum_{b=1}^r \sum_{s=0,5} \mathfrak{R}_{ab}^{(0s)} \Phi_b^{(s)} q_n(\kappa), \quad (7.411)$$

$$\rho \frac{d\widehat{\Phi}_a^{(1)}}{dt} = -p \mathbf{d}_a - \frac{\epsilon}{\beta g_a^{(1)}} \sum_{b=1}^r \sum_{s=1,2,3} \mathfrak{R}_{ab}^{(1s)} \Phi_b^{(s)} q_n(\kappa), \quad (7.412)$$

$$\begin{aligned} \rho \frac{d\widehat{\Phi}_a^{(2)}}{dt} &= -\alpha_a^{(2)} \left( A_{Ta}^{(2)} \nabla T + A_{pa}^{(2)} \nabla p + \rho_a \widehat{\mathbf{F}}_a \right) \\ &\quad - \frac{\epsilon}{\beta g_a^{(2)}} \sum_{b=1}^r \sum_{s=1,2,3} \mathfrak{R}_{ab}^{(2s)} \Phi_b^{(s)} q_n(\kappa), \end{aligned} \quad (7.413)$$

$$\begin{aligned} \rho \frac{d\widehat{\Phi}_a^{(3)}}{dt} &= -p_a \widehat{C}_p \frac{\beta g_a^{(3)}}{\epsilon} \nabla T - \alpha_a^{(32)} \alpha_a^{(2)} \mathbf{d}_a \\ &\quad - \frac{\epsilon}{\beta g_a^{(3)}} \sum_{b=1}^r \sum_{s=1,2,3} \mathfrak{R}_{ab}^{(3s)} \Phi_b^{(s)} q_n(\kappa), \end{aligned} \quad (7.414)$$

$$\rho \frac{d\widehat{\Phi}_a^{(4)}}{dt} = -2p_a [\nabla \mathbf{u}]^{(2)} - \frac{\epsilon}{\beta g_a^{(4)}} \sum_{b=1}^r \mathfrak{R}_{ab}^{(44)} \Phi_b^{(4)} q_n(\kappa), \quad (7.415)$$

$$\rho \frac{d\widehat{\Phi}_a^{(5)}}{dt} = - \left( \frac{5}{3} p_a + \alpha_a^{(5)} - \frac{1}{\kappa_{\Psi a}} \right) \nabla \cdot \mathbf{u} - \frac{\epsilon}{\beta g_a^{(5)}} \sum_{b=1}^r \sum_{s=0,5} \mathfrak{R}_{ab}^{(5s)} \Phi_b^{(s)} q_n(\kappa). \quad (7.416)$$

On combining these evolution equations for  $\Phi_a^{(s)}$  (7.411)–(7.416) with the conservation laws (7.400)–(7.403), quasilinear generalized hydrodynamic equations are obtained for a liquid mixture. Recall that  $\Phi_a^{(0)}$  is the volume fluctuation;  $\Phi_a^{(1)}$  the mass diffusion flux;  $\Phi_a^{(2)}$  the volume flux;  $\Phi_a^{(3)}$  the heat flux;  $\Phi_a^{(4)}$  the shear stress tensor; and  $\Phi_a^{(5)}$  the excess normal stress of species  $a$ .

Before making an attempt to solve nonlinear differential equations such as the quasilinear hydrodynamic equations presented, it is useful to pay attention to steady states and the stability of the solutions at the steady states. We have noticed there is a spectrum of relaxation times of states at steady states. In particular, conserved variables relax generally at much slower rates than the nonconserved variables obeying evolution equations (7.411)–(7.416). Thus studying the steady states of the latter equations we are naturally led to a theory of nonlinear transport processes. On further linearization of the steady state equations, we have, as a matter of fact, obtained the linear constitutive equations discussed in Sect. 7.8.2. The intermediate step of this particular procedure, namely, the steady-state equations of (7.411)–(7.416), are of considerable interest by themselves since they provide a set of model quasilinear generalized hydrodynamic equations. Here we give an outline of how they are obtained. The details of the model is deferred to Chap. 9 where nonlinear transport processes are discussed in more detail together with their applications.

Based on the concept of relaxation time separation between conserved and nonconserved variables, we examine the steady state of the nonconserved variable evolution equations (7.411)–(7.416) obtained by setting their left-hand side equal to zero:

$$0 = -\frac{\epsilon}{\beta g_a^{(0)}} \sum_{b=1}^r \sum_{s=0,5} \mathfrak{R}_{ab}^{(0s)} \Phi_b^{(s)} q_n(\kappa), \quad (7.417)$$

$$0 = -p \mathbf{d}_a - \frac{\epsilon}{\beta g_a^{(1)}} \sum_{b=1}^r \sum_{s=1,2,3} \mathfrak{R}_{ab}^{(1s)} \Phi_b^{(s)} q_n(\kappa), \quad (7.418)$$

$$0 = -\alpha_a^{(2)} \left( A_{Ta}^{(2)} \nabla T + A_{pa}^{(2)} \nabla p + \rho_a \widehat{\mathbf{F}}_a \right) - \frac{\epsilon}{\beta g_a^{(2)}} \sum_{b=1}^r \sum_{s=1,2,3} \mathfrak{R}_{ab}^{(2s)} \Phi_b^{(s)} q_n(\kappa), \quad (7.419)$$

$$0 = -p_a \widehat{C}_p \frac{\beta g_a^{(3)}}{\epsilon} \nabla T - \alpha_a^{(32)} \alpha_a^{(2)} \mathbf{d}_a - \frac{\epsilon}{\beta g_a^{(3)}} \sum_{b=1}^r \sum_{s=1,2,3} \mathfrak{R}_{ab}^{(3s)} \Phi_b^{(s)} q_n(\kappa), \quad (7.420)$$

$$0 = -2p_a [\nabla \mathbf{u}]^{(2)} - \frac{\epsilon}{\beta g_a^{(4)}} \sum_{b=1}^r \mathfrak{R}_{ab}^{(44)} \Phi_b^{(4)} q_n(\kappa), \quad (7.421)$$

$$0 = - \left( \frac{5}{3} p_a + \alpha_a^{(5)} - \frac{1}{\kappa_{\widehat{\Psi}a}} \right) \nabla \cdot \mathbf{u} - \frac{\epsilon}{\beta g_a^{(5)}} \sum_{b=1}^r \sum_{s=0,5} \mathfrak{R}_{ab}^{(5s)} \Phi_b^{(s)} q_n(\kappa). \quad (7.422)$$

These steady-state equations are nonlinear on account of the nonlinear factor  $q_n(\kappa)$ . Nevertheless, they are solvable algebraic equations for nonconserved variables  $\Phi_b^{(s)}$  ( $s = 0, 1, \dots, 5$ ) and give rise to nonlinear (e.g., non-Newtonian, non-Fourier, and non-Fickian) transport coefficients and steady-state nonlinear constitutive equations as will be described in Chap. 9. If so-obtained steady state solutions are used to calculate the Rayleigh dissipation function in the nonlinear factor  $q_n(\kappa)$ , the nonlinear factor  $q_n(\kappa)$  can be replaced by  $q_L(\kappa_L)$  defined by the formula

$$q_L(\kappa_L) = \frac{\sinh^{-1} \kappa_L}{\kappa_L}, \quad (7.423)$$

where the Rayleigh dissipation function  $\kappa_L$  is now a quadratic form of thermodynamic gradients [see Sect. 9.1.5 of Chap. 9 for the formula for  $\kappa$  and the derivation of  $q_L(\kappa)$ . Also see Sect. 5.5.10 of Chap. 5.]. It should be noted that the procedure of replacing  $q_n(\kappa)$  with  $q_L(\kappa_L)$  is exact and not arbitrary. Therefore evolution equations for the deviation of  $\Phi_b^{(s)}$  ( $s = 0, 1, \dots, 5$ ) from the steady-state are described by the same equations as (7.411)–(7.416) except that the nonlinear factor  $q_n(\kappa)$  is replaced by  $q_L(\kappa_L)$  in which the Rayleigh dissipation function is now given by a quadratic form of thermodynamic gradients. This is the reason that the quasilinear evolution equations are attractive. When combined with the conservation equations, a model is obtained for quasilinear generalized hydrodynamic equations. The solutions of the model quasilinear generalized hydrodynamic equations are stable by virtue of the second law of thermodynamics and the Lyapounov stability theorem. Therefore, they are of considerable practical interest to studies of fluid flows in systems removed far from equilibrium.

## 7.11 Relative Boltzmann Entropy

The calortropy discussed earlier provides the information on the thermodynamic branch of solution of the kinetic equation, but only a partial information on the distribution function because the nonequilibrium grand canonical form  $f_c^{(N)}$  is merely a projection onto the thermodynamic manifold of the full distribution function  $f^{(N)}$  obeying the kinetic equation. Therefore it is important to learn about the complement of the projection. However, the complement is as difficult to compute explicitly as solving the kinetic equation itself in the full phase space of the system. Nevertheless, we notice that the complement of the projection represents some sort of fluctuations from the states represented by the thermodynamic states characterized by the non-equilibrium grand canonical form  $f_c^{(N)}$ . Since there is a large body of knowledge in the literature to treat fluctuations of macroscopic thermodynamic systems, we may avail ourselves to it to develop a theory about the complement mentioned. Since the principal objective of the present work lies in the thermodynamic theory of irreversible processes, it is not a place to develop a full theory for the aforementioned in the limited space for this work. Nevertheless, we have devoted some space on the topic in Chap. 6 for a pure liquid. Since a version of the theory for a liquid mixture would be easy to acquire, we would not repeat the formulation in order to save the space. For these reasons we will close this section by only laying a foundation for the discussion on a fluctuation theory dealing with the relative Boltzmann entropy for liquid mixtures in a future work.

The relative Boltzmann entropy relative to the calortropy defined earlier is given by the formula

$$S_r[f^{(N)}|f_c^{(N)}](t) = k_B \left\langle f^{(N)}(\mathbf{x}^{(N)}, t) \ln \left( \frac{f^{(N)}}{f_c^{(N)}} \right) \right\rangle. \quad (7.424)$$

The relative Boltzmann entropy density  $\mathcal{S}_r$  then may be defined by the integral relation

$$S_r[f^{(N)}|f_c^{(N)}](t) = \int_V d\mathbf{r} \rho \mathcal{S}_r[f^{(N)}|f_c^{(N)}](\mathbf{x}^{(N)}, t), \quad (7.425)$$

which, in light of the exponential representation (7.35) of  $f^{(N)}$ , suggests the relative Boltzmann entropy density in the form

$$\begin{aligned} \rho \mathcal{S}_r[f^{(N)}|f_c^{(N)}] = & - \left\langle \sum_{a=1}^r \sum_{j=1}^{N_a} f^{(N)} \left( G_{ja}^{(N)} - \mathcal{H}_{ja}^{(N)} + m_a \gamma \right) \right. \\ & \times \left. \delta(\mathbf{r}_{ja} - \mathbf{r}) \ln \left( \frac{f^{(N)}}{f_c^{(N)}} \right) \right\rangle. \end{aligned} \quad (7.426)$$

Use of this statistical formula and the kinetic equation yields the local balance equation for the relative Boltzmann entropy density

$$\begin{aligned} \rho \frac{d}{dt} \mathcal{S}_r[f^{(N)}|f_c^{(N)}] &= -\nabla \cdot \mathbf{J}_r[f^{(N)}|f_c^{(N)}] + \sigma_r[f^{(N)}|f_c^{(N)}] \\ &\quad + \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} f^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathcal{D}_t^{(N)} (\mathcal{H}_{ja}^{(N)} - m_a \Upsilon) \right\rangle, \end{aligned} \quad (7.427)$$

where the relative Boltzmann entropy flux  $\mathbf{J}_r[f^{(N)}|f_c^{(N)}]$  and the relative Boltzmann entropy production  $\sigma_r[f^{(N)}|f_c^{(N)}]$  are, respectively, defined by the statistical formula

$$\mathbf{J}_r[f^{(N)}|f_c^{(N)}] = - \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} f^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) (G_{ja}^{(N)} - \mathcal{H}_{ja}^{(N)}) \mathbf{C}_{ja} \right\rangle, \quad (7.428)$$

$$\sigma_r[f^{(N)}|f_c^{(N)}] = - \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} \delta(\mathbf{r}_{ja} - \mathbf{r}) (G_{ja}^{(N)} - \mathcal{H}_{ja}^{(N)}) \Re \left[ \bar{\mathbb{F}}^{(N)} \right] \right\rangle. \quad (7.429)$$

To evaluate the right hand side of (7.427) we write  $G_{ja}^{(N)}$  and  $\mathcal{H}_{ja}^{(N)}$  in the forms

$$G_{ja}^{(N)} = T^{-1} H'_{ja} + \sum_{q \geq 0} \bar{X}_a^{(q)} h_{ja}^{(q)} - m_a \bar{\mu}_a + m_a \bar{p} v, \quad (7.430)$$

$$\mathcal{H}_{ja}^{(N)} = T^{t-1} H''_{ja} + \sum_{q \geq 0} \bar{X}_a^{(q)t} h_{ja}^{(q)} - m_a \bar{\mu}_a^t, \quad (7.431)$$

$$\Upsilon = -\bar{p}^t v \quad (7.432)$$

with the superscript  $t$  on  $T$ ,  $\mu_a$ , and  $p$  denoting the intensive variables as determined by nonequilibrium thermodynamics described in the previous section by using the calortropy, namely,

$$\bar{X}_a^{(q)t} = T^{t-1} X_a^{(q)}, \quad \bar{\mu}_a^t = T^{t-1} \hat{\mu}_a, \quad \bar{p}^t = T^{t-1} p. \quad (7.433)$$

As a matter of fact, (7.427)–(7.430) are obtained if the distribution functions are written in exponential forms

$$\begin{aligned} k_B \ln f^{(N)} &= - \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} \left( T^{-1} H'_{ja} + \sum_{q \geq 0} \bar{X}_a^{(q)} h_{ja}^{(q)} \right) \delta(\mathbf{r}_{ja} - \mathbf{r}) \\ &\quad + \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} m_a (\bar{\mu}_a - \bar{p} v) \delta(\mathbf{r}_{ja} - \mathbf{r}), \end{aligned} \quad (7.434)$$

$$\begin{aligned} k_B \ln f_c^{(N)} = & - \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} \left( T^{t-1} H'_{ja} + \sum_{q \geq 0} \bar{X}_a^{(q)t} h_{ja}^{(q)} \right) \delta(\mathbf{r}_{ja} - \mathbf{r}) \\ & + \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} m_a (\bar{\mu}_a^t - \bar{p}^t v) \delta(\mathbf{r}_{ja} - \mathbf{r}). \end{aligned} \quad (7.435)$$

It should be remembered that although  $f^{(N)}$  is written in a form isomorphic to  $f_c^{(N)}$ , the former is a function defined in the full phase space of the system and, as such, should be determined from the solution of the kinetic equation, fully subject to its initial and boundary conditions on  $f^{(N)}$  in the phase space. This implies that  $T$ ,  $\bar{X}_a^{(q)}$ ,  $\bar{\mu}_a$ ,  $\bar{p}$  are not determined as for their thermodynamic counterparts  $T^t$ ,  $\bar{X}_a^{(q)t}$ ,  $\bar{\mu}_a^t$ ,  $\bar{p}^t$  which may be determined by the thermodynamic theory of irreversible processes described in the previous subsections, but as full phase space functions. In other words, the former set represents parameters that must be determined from the solution of the kinetic equation,  $G_{ja}^{(N)}$  in the phase space. The purpose of this particular subsection is then to lay a foundation for a stochastic theory alternative to a theory of partial differential equations represented by the kinetic equation in the phase space.

For the aforementioned purpose we define fluctuations in the parameters  $T$ ,  $\bar{X}_a^{(q)}$ ,  $\bar{\mu}_a$ ,  $\bar{p}$  from the thermodynamically determined parameters  $T^t$ ,  $\bar{X}_a^{(q)t}$ ,  $\bar{\mu}_a^t$ ,  $\bar{p}^t$ :

$$\begin{aligned} \delta \bar{I} &= T^{-1} - T^{t-1}, \quad \delta \bar{X}_a^{(q)} = \bar{X}_a^{(q)} - \bar{X}_a^{(q)t}, \\ \delta \bar{\mu}_a &= \bar{\mu}_a - \bar{\mu}_a^t, \quad \delta \bar{p} = \bar{p} - \bar{p}^t. \end{aligned} \quad (7.436)$$

By using the formulas for  $G_{ja}^{(N)}$  and  $\mathcal{H}_{ja}^{(N)}$  given in (7.430) and (7.431), we find the relative Boltzmann entropy density in the bilinear form

$$\mathcal{S}_r[f^{(N)}|f_c^{(N)}] = \mathcal{E} \delta \bar{I} + v \delta \bar{p} - \sum_{a=1}^r \mathfrak{c}_a \delta \bar{\mu}_a + \sum_{a=1}^r \sum_{q \geq 0} \hat{\Phi}_a^{(q)} \delta \bar{X}_a^{(q)}. \quad (7.437)$$

We observe that this is in a form similar to the integral of the calortropy density in thermodynamic manifold obtained on integration of the extended Gibbs relation with the help of the nonequilibrium Gibbs–Duhem equation.

Upon applying the Klein inequality  $\ln x \geq 1 - x^{-1}$  to (7.426) for the statistical mechanical formula for  $\mathcal{S}_r[f^{(N)}|f_c^{(N)}]$ , there follows the inequality

$$\mathcal{S}_r[f^{(N)}|f_c^{(N)}] \geq 0 \quad (7.438)$$

with the equality holding only if  $f^{(N)} = f_c^{(N)}$ , which holds if all the fluctuations vanish for  $\bar{I}$ ,  $\bar{\mu}_a$ ,  $\bar{p}$ , and  $\bar{X}_a^{(q)}$ . Since

$$\mathcal{S} = \hat{\Psi} - \mathcal{S}_r[f^{(N)}|f_c^{(N)}], \quad (7.439)$$

the inequality (7.438) means that

$$\mathcal{S} \leq \widehat{\Psi}, \quad (7.440)$$

which from the standpoint of information theory [30–32] implies a loss of information content when the nonequilibrium grand canonical form  $f_c^{(N)}$  is constructed by projecting  $f^{(N)}$  onto the thermodynamic manifold of a smaller dimension than the full phase space of the system. This lost information content is contained in the relative Boltzmann entropy density, which is expressible in terms of fluctuations introduced earlier.

We also see that the fluctuations are such that

$$\mathcal{E}\delta\bar{I} + v\delta\bar{p} - \sum_{a=1}^r \mathfrak{c}_a \delta\bar{\mu}_a + \sum_{a=1}^r \sum_{q \geq 0} \widehat{\Phi}_a^{(q)} \delta\bar{X}_a^{(q)} \geq 0. \quad (7.441)$$

By applying the same method as for the calortropy density balance equation in the previous subsection, we can express the relative Boltzmann entropy balance equation in the form

$$\begin{aligned} \frac{d}{dt} \mathcal{S}_r[f^{(N)}|f_c^{(N)}] = & -(\delta\bar{I}) d_t \mathcal{E} - (\delta\bar{p}) d_t v + \sum_{a=1}^r (\delta\bar{\mu}_a) d_t \mathfrak{c}_a \\ & - \sum_{a=1}^r \sum_{q \geq 0} \left( \delta\bar{X}_a^{(q)} \right) d_t \widehat{\Phi}_a^{(q)} + \widehat{\Sigma}_l + \rho^{-1} \sum_{a=1}^r \sum_{q \geq 0} \bar{X}_a^{(q)} \mathcal{Z}_a^{(q)}. \end{aligned} \quad (7.442)$$

In the limit of all the fluctuations vanishing we find the rate of change in  $\mathcal{S}_r[f^{(N)}|f_c^{(N)}]$

$$\frac{d}{dt} \mathcal{S}_r[f^{(N)}|f_c^{(N)}] = \widehat{\Sigma}_l + \rho^{-1} \sum_{a=1}^r \sum_{q \geq 0} \bar{X}_a^{(q)} \mathcal{Z}_a^{(q)}, \quad (7.443)$$

the right hand side of which does not generally vanish if the system is away from equilibrium. Therefore we may conclude that, if the solution of evolution equation (7.442) is sought in the manifold  $\mathfrak{P} \cup \mathfrak{T}$  as the solution of the calortropy balance equation has been, the relative Boltzmann entropy  $\mathcal{S}_r[f^{(N)}|f_c^{(N)}]$  would not give rise to an exact differential in  $\mathfrak{P} \cup \mathfrak{T}$  in contrast for the calortropy differential, which is an exact differential in manifold  $\mathfrak{P} \cup \mathfrak{T}$ . Moreover, its value would depend on the path taken by the process in the thermodynamic manifold. The manner in which  $\mathcal{S}_r[f^{(N)}|f_c^{(N)}]$  vanishes in the vicinity of vanishing limit of fluctuations can be investigated by integrating (7.443) over time along a path described by the thermodynamic theory of irreversible processes (namely, by calortropy) in  $\mathfrak{P} \cup \mathfrak{T}$ .

The formal theory presented in this section can be made use of if a set of differential equations for fluctuations are sought for irreversible processes. Such evolution equations would be the mixture versions of the fluctuation evolution equations pre-

sented for a pure liquid in Chap. 6. Therewith a full description of evolution of fluctuations may be achieved for liquids via the relative Boltzmann entropy and the fluctuation theory. It is also possible to develop a stochastic theory of the relative Boltzmann entropy for a liquid mixture in a manner similar to the theory described in Chap. 6. In this line of approach, the thermodynamic uncertainty relations would also hold for liquid mixtures. All of such tasks may be achieved if the discussions made on the subject in Chap. 6 are followed for the mixtures, but they are beyond the objectives of the present work on the theory of irreversible thermodynamics and hydrodynamics from the molecular theory viewpoint. Consequently, their studies are left for future work.

## 7.12 Concluding Remarks

In this chapter a molecular theory of monatomic liquids is presented in a general form for a liquid mixture. It can be made theories for nonequilibrium statistical thermodynamics, irreversible thermodynamics of transport processes, and hydrodynamics of a fluid either for gas or a liquid when an appropriate density limit is taken with respect to the density, or for a pure fluid when specialized to a single component. In this sense, it summarizes and serves as a summary of the theories developed in the preceding chapters which we believe have been tested for various gas dynamic problems and carrier transport problems in the past, albeit limited in number, and also have thus served the role of the stepping stones for a general theory for a liquid mixture presented in this chapter. Having reached the goal and looking back, the roles of the stepping stones seem limited, but it must be kept in mind that we are not usually capable of taking a large jump in a single stride when exploring a new territory. In this connection, we should note that the irreversible thermodynamics of transport processes and hydrodynamics in liquids and liquid mixtures remain theoretically at least explored terrain, presenting numerous challenges in the molecular theoretic approach to fluids in condensed phase—perhaps, rheology may be an exception. In the case of rheology of simple fluids of gases and liquids the generalized hydrodynamic equations, especially, the quasilinear approximation model has produced correct theoretical results comparable to experimental data. Therefore, there is a reason to expect similarly successful theoretical results for other aspects of flows of dense fluids by means of generalized hydrodynamic equations presented. The thermodynamic theory of irreversible processes in fluids far removed from equilibrium is, we believe, ready for further development and various applications. It would be interesting to see the theory tested against experimental observations.

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# Chapter 8

## Classical Scattering Theory in Phase Space

The statistical mechanical theories of transport processes and attendant irreversible thermodynamics presented in the previous chapters are formal and their computational implementation to make them compared with experiments would require knowledge of dynamics of many particles in the phase space. In fact, formulating the statistical mechanical theories of hydrodynamic processes, although essential from the molecular theory standpoint, is merely putting the foundations for the edifice of molecular theories of macroscopic processes in matter, leaving the question of solving many-body dynamic problems involved in the macroscopic processes and actual computational methodologies to the investigations in the next stage. In particular, computation of transport coefficients would require such knowledge and mathematical techniques.

However, we are not in a barren terrain with regard to molecular treatments of transport processes from the theoretical and methodological standpoints because there have been much progress made through numerous studies on them in the past in equilibrium and nonequilibrium statistical mechanics. They are too numerous to quote them all here except for some typical examples. Nevertheless, it would be helpful to add some useful thoughts toward general methods of treating many-particle dynamics in the phase space which would help to computationally implement the formal theories developed in this work, so that they can be applied to experimental systems studied in the laboratory and to make us comprehend them sufficiently well from the molecular theory viewpoint. From this vantage point we would like to discuss some thoughts on treating dynamics of many-particle systems in the phase space, which is described by the Liouville operator. The potentially useful theoretical results would be the formulas for collision bracket integrals for dense fluids which we believe are alternatives to the linear response theory formulas for the transport coefficients, since they appear to be well suited for computer simulation methods. From the standpoint of the kinetic theory of liquids described in the previous chapters in this work they furnish a much desired computational tool that enables us to utilize well-known computational algorithms in the modern simulation methods [1, 2]. The Monte Carlo simulation methods appear particularly suited for them.

## 8.1 Preamble to Classical Scattering Theory

As shown in the previous chapters, classical collision operators [3–5] appear in the statistical formulas of transport coefficients in kinetic theory of matter and pose an important problem to resolve in the final stage of implementing the kinetic theory to make it connect with experiments. Although practical methods of their calculation is essential to making kinetic theory a useful molecular theory of matter, they have not been given much attention in contrast to their quantum mechanical collision operators in scattering theory of particles in the literature [6–9]. In this chapter, we would like to take up the subject for study and make an attempt to mitigate the situation. Classical collision operators are generally defined in formal analogy [10, 11] to quantum mechanical collision operators, but their definitions have been made without much attention paid to the space of functions in which the operators live.

Clearly, study of classical collision operators would require a space of eigenfunctions for the underlying Liouville operator in the phase space. Here we first consider the classical eigenvalue problems for Liouville operators, especially when the spectrum is continuous, and then apply the eigenfunctions to recast many-particle collision bracket integrals appearing in transport coefficients for dense fluids, which in their exact forms are given in terms of classical collision operators.

Some 30 years ago, the present author made a study of eigenvalue problems for Liouville operators in Ref. [12], but the problem posed then was regarded as the classical limit of the molecular scattering theory formulated in quantum mechanics, and for this reason it was not further pursued because the latter approach was more desirable. However, now that the kinetic theory of dense fluids has been formulated as presented in the previous chapters, it is necessary to study the classical collision operators in the forms they appear in the context of kinetic theory of matter. In the present chapter, we revisit the problem to improve upon the method of calculating eigenfunctions before applying the notion of eigenfunctions to examine and develop algorithms to numerically calculate the collision bracket integrals appearing in the classical kinetic theory of transport processes. We first will examine the eigenfunctions in classical scattering theory of particles in phase space and then make use of the acquired results to cast the classical collision operators in the collision bracket integrals into forms more suitable for numerical computation, especially, by computer simulation methods [1, 2]. Since the many-body problems involved in such integrals do not allow simple analytic forms for the collision cross sections or transition probabilities for physically realistic dynamical events and pose a barrier to overcome to put the kinetic theory into practice, it is imperative to devise alternative forms of the transport coefficients suitable for efficient numerical computation. Therefore, this line of study is quite relevant to implementing kinetic theory of matter to apply the theory of transport properties of dense fluids to experimental systems. It is precisely the reason for discussing the subject matter at this particular juncture of this work on kinetic theory and macroscopic physics of matter. As a matter of fact, we have deferred to this chapter discussions on computational aspects of transport coefficients presented in the previous chapters.

Classical collision operators [3–5] defined in the phase space and appearing in the statistical mechanical formulas of transport coefficients in kinetic theory of matter are classical mechanical analogs of quantum mechanical collision operators defined in terms of Liouville-von Neumann operators [13] and, as a matter of fact, the classical limits of the latter. Despite their importance to make kinetic theory validated in comparison with experiment, they have not been given much attention as their quantum mechanical scattering theory analogs have been in the literature [6–9], especially, in connection with quantum mechanics of few-body systems. Computation of classical collision operators and related formulas appearing in kinetic theory of dense fluids still poses a theoretical challenge in nonequilibrium statistical mechanics. In this chapter, we would like to take up the subject for study and make an attempt to mitigate the situation.

Classical collision operators are generally defined in formal analogy [10, 11] to quantum mechanical collision operators, but their definitions and applications have been made without much attention paid to the space of functions in which the operators live. Clearly, study of classical collision operators would require a space of eigenfunctions for the underlying Liouville operator in the phase space. Here we first consider the classical eigenvalue problems for Liouville operators, especially when the spectrum is continuous. We then apply the eigenfunctions to recast many-particle collision bracket integrals which are given in terms of classical collision operators in kinetic theory of dense fluids. In a recent paper [14], we have revisited the eigenvalue problem of the Liouville operator and improved upon the method of calculating eigenfunctions before applying the notion and existence of eigenfunctions to examine a way to calculate the collision bracket integrals in the context of kinetic theory of transport processes, particularly, in liquids. We reproduce the principal results of the paper here and refine the results therein wherever possible.

## 8.2 Eigenvalue Problem for the Classical Liouville Operator

In classical kinetic theory of matter, as we have seen, the formalism is usually formulated in terms of the Liouville operator and, in the kinetic equation, classical collision operators associated with the Liouville operators appear in close analogy to quantum scattering theory. Formal theory [6–9] of quantum scattering has been studied in depth from the mathematical standpoint and the mathematical properties [8, 9], such as the Hilbert space for the operators, of quantum scattering operators are well understood at present. On the other hand, it cannot be said the same of the classical scattering theory based on classical Liouville operators, and even the mathematical nature of the function space for the classical Liouville operator is not well clarified at present, almost all of mathematical operations involving the classical Liouville operators being performed by simple analogy to the quantum counterparts; see, for example, Refs. [4–7, 10, 11]. In this section we will consider an aspect of

the problem, limiting the study to construction of eigenfunctions. This aim may be achieved by means of the Hamilton–Jacobi characteristic function [15].

The eigenfunctions are  $L^2$  functions normalized to unity and have a closure in the phase space. If the Hamilton–Jacobi equation is separable, then the eigenfunctions can be given in terms of well-defined quadratures. Otherwise, a numerical solution method is the only way left to treat the problem adequately. Nevertheless, the eigenfunctions can be used to formulate formal classical scattering theory in analogy to quantum scattering theory, and the theory thus formulated can provide a mathematically sensible computational algorithm for the classical collision problems associated with transport coefficients of gases and liquids. An interesting outcome of the efforts in this line is, as will be shown below, the acquisition of collision bracket integrals for various transport coefficients of liquids in forms readily computable by means of computer simulation methods. In fact, they appear to be computable as readily as the linear response theory formulas in the Green–Kubo theory without requiring to solve the classical Lippmann–Schwinger equations [11] for the classical collision operators. A simple Monte–Carlo simulation method [2] would appear to be necessary to compute them.

To make the posed eigenvalue problem definite and sufficiently simple, we first consider a two-particle problem in the center-of-mass coordinate system. The same idea as used for the two-particle problem presented here can be applied and extended to many-particle situations without difficulty, at least, formally.

The particles interact by the potential energy  $V(\mathbf{r})$  where  $\mathbf{r}$  is the relative coordinate vector between the two particles. The Hamiltonian will be denoted by  $H(\mathbf{p}, \mathbf{r})$ :

$$H(\mathbf{p}, \mathbf{r}) = \frac{p^2}{2m} + V(\mathbf{r}). \quad (8.1)$$

The Liouville operator is then defined by the Poisson bracket times  $-i$  where  $i = \sqrt{-1}$ :

$$\mathcal{L} = -i[H, \cdot]_{\mathbf{p}\mathbf{r}} = -i \sum_k \left( \frac{\partial H}{\partial p_k} \frac{\partial}{\partial r_k} - \frac{\partial H}{\partial r_k} \frac{\partial}{\partial p_k} \right). \quad (8.2)$$

The subscript  $k$  denotes Cartesian components of vectors  $\mathbf{p}$  and  $\mathbf{r}$ . With this definition of Liouville operator the Liouville equation can be written as

$$i \frac{\partial f}{\partial t} = \mathcal{L}f(x, t), \quad (8.3)$$

where  $x$  denotes the phase  $x = (\mathbf{p}, \mathbf{r})$  and  $f$  is the probability distribution function.

Since it is possible to expand  $f$  into Fourier components as in the integral

$$f(x, t) = \int_{-\infty}^{\infty} d\lambda \exp(-i\lambda t) \psi_{\lambda}(x), \quad (8.4)$$

we arrive at an eigenvalue problem [3] of  $\mathcal{L}$ :

$$\mathcal{L}(x) \psi_\lambda(x) = \lambda \psi_\lambda(x), \quad (8.5)$$

where  $\lambda$  is an eigenvalue and  $\psi_\lambda$  the eigenfunction belonging to  $\lambda$ . This eigenvalue problem is intimately related to the Hamilton–Jacobi theory in classical mechanics [15] as will be shown below.

Since the Liouville operator is invariant to canonical transformation  $(\mathbf{p}, \mathbf{r}) \rightarrow (\mathbf{P}, \mathbf{Q})$ , where  $\mathbf{P}$  and  $\mathbf{Q}$  are the new canonical momentum and coordinate preserving the forms of Hamilton's canonical equations of motion, in the new canonical variables the eigenvalue problem takes the form

$$\mathcal{L}(X) \psi_\lambda(X) = \lambda \psi_\lambda(X), \quad (8.6)$$

where  $X = (\mathbf{P}, \mathbf{Q})$  and

$$\mathcal{L}(X) = -i[H, ]_{\mathbf{PQ}} = -i \sum_k \left( \frac{\partial H}{\partial P_k} \frac{\partial}{\partial Q_k} - \frac{\partial H}{\partial Q_k} \frac{\partial}{\partial P_k} \right). \quad (8.7)$$

Here  $H$  is the new Hamiltonian  $H = H(\mathbf{P}, \mathbf{Q})$ . If the new Hamiltonian is independent of  $\mathbf{Q}$ , then we have

$$\mathcal{L}(X) = -i[H, ]_{\mathbf{PQ}} = -i \sum_k \frac{\partial H}{\partial P_k} \frac{\partial}{\partial Q_k}. \quad (8.8)$$

We will return to examine this form for  $\mathcal{L}$  later.

We now consider (8.5). The Liouville operator  $\mathcal{L}$  is Hermitian in the space of square-integrable functions  $\psi_\lambda$  which are generally complex. If  $\psi_\lambda(x)$  is sought in the form

$$\psi_\lambda(x) = A(x) \exp[i\Gamma(x)], \quad (8.9)$$

then the eigenvalue problem can be cast in a pair of equations

$$[H, \Gamma]_{\mathbf{pr}} = \lambda, \quad (8.10)$$

$$[H, A]_{\mathbf{pr}} = 0. \quad (8.11)$$

Equation (8.11) indicates that the amplitude  $A(x)$  is a function of canonical invariants. Therefore  $A(x)$  is a function of basic invariants of  $H$ ; for example, a function of the Hamiltonian alone.

Let us assume<sup>1</sup>  $S(\mathbf{P}, \mathbf{r}, t)$  to be the generating function [15] of canonical transformation such that

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<sup>1</sup>In this chapter,  $S(\mathbf{P}, \mathbf{r}, t)$  does not stand for the Boltzmann entropy appearing frequently in the previous chapters.

$$p_k = \frac{\partial S}{\partial r_k}, \quad Q_k = \frac{\partial S}{\partial P_k}. \quad (8.12)$$

The generating function  $S$  obeys the Hamilton–Jacobi equation

$$\frac{\partial S}{\partial t} + H\left(\frac{\partial S}{\partial \mathbf{r}}, \mathbf{r}\right) = 0. \quad (8.13)$$

Under this canonical transformation the amplitude function is given by

$$A(x) = \delta\left(\mathbf{p} - \frac{\partial S}{\partial \mathbf{r}}\right) \frac{\partial(p_1, \dots, p_f)}{\partial(\alpha_1, \dots, \alpha_f)}, \quad (8.14)$$

where  $\alpha_1, \dots, \alpha_f$  are the values of  $P_1, \dots, P_f$ , respectively, with subscript  $f$  denoting the degrees of freedom and  $\partial(p_1, \dots, p_f) / \partial(\alpha_1, \dots, \alpha_f)$  is the Jacobian of transformation. It can be shown that  $A(x)$  in (8.14) satisfies (8.11).

To find the phase function  $\Gamma$ , we observe that (8.10), on canonical transformation, can be written as

$$[H, \Gamma]_{\mathbf{PQ}} = \lambda. \quad (8.15)$$

Explicitly written out, it has the form

$$\lambda = \sum_k \frac{\partial H}{\partial P_k} \frac{\partial \Gamma}{\partial Q_k}. \quad (8.16)$$

In this equation we may put

$$\omega_k = \frac{\partial H}{\partial P_k}, \quad (8.17)$$

but  $\omega_k$  is independent of  $\mathbf{Q}$  since  $H = H(\mathbf{P})$  is independent of  $\mathbf{Q}$ . Notice that  $\omega_k$  is a frequency. Therefore, (8.16) is readily solved, and we find

$$\Gamma = \sum_k \frac{\lambda_k}{\omega_k} Q_k + \Gamma_0, \quad (8.18)$$

where  $\Gamma_0$  is a constant, and constants  $\lambda_k$  are such that

$$\lambda = \sum_k \lambda_k. \quad (8.19)$$

The constants  $\lambda_k$  will be determined on imposing suitable boundary conditions on the eigenfunctions  $\psi_\lambda$ . It should be noted that  $Q_k$  is a function of  $\mathbf{r}$  and since  $Q_k = Q_k(\mathbf{r}, \cdot)$ .

In summary of the results up to this point, we have found the eigenfunctions in the form

$$\begin{aligned}\psi_{\lambda}(\mathbf{p}, \mathbf{r}) &= A_0 \delta\left(\boldsymbol{\alpha} - \frac{\partial S}{\partial \mathbf{r}}\right) \exp\left(i \sum_k \frac{\lambda_k}{\omega_k} \frac{\partial S}{\partial \alpha_k}\right) \\ &= A_0 \delta(\boldsymbol{\alpha} - \mathbf{p}) \exp\left(i \sum_k \frac{\lambda_k}{\omega_k} Q_k\right),\end{aligned}\quad (8.20)$$

where  $A_0$  is the normalization factor, and  $p_k$  and  $Q_k$  are made use of in place of the derivatives of the generating function  $S$  in the second equality of (8.20). Since the generating function  $S$  can be written in terms of the characteristic function  $W$  as

$$S = W - Et,\quad (8.21)$$

where  $E$  is a constant (energy), the eigenfunction can be written as

$$\psi_{\lambda}(\mathbf{p}, \mathbf{r}) = A_0 \delta(\boldsymbol{\alpha} - \mathbf{p}) \exp\left(i \sum_k \frac{\lambda_k}{\omega_k} \frac{\partial W}{\partial \alpha_k}\right).\quad (8.22)$$

This result shows that the eigenfunction will be explicitly found if the Hamilton–Jacobi equation is solved, given the initial conditions for  $(\mathbf{p}, \mathbf{r})$ . It would be more appropriate to write

$$\psi_{\lambda}(\mathbf{p}, \mathbf{r}) = \psi(\mathbf{p}, \mathbf{r}; \boldsymbol{\alpha}, \boldsymbol{\lambda})$$

to indicate that there are two sets  $(\boldsymbol{\alpha}, \boldsymbol{\lambda})$  of eigenvalues involved. This set of eigenfunctions can be easily shown orthogonal and normalizable.

To prove it we use the identity that under the canonical transformation and subject to the condition  $\delta(\boldsymbol{\alpha} - \mathbf{p})$  the Jacobian of transformation is unity:

$$\frac{\partial(Q_1, \dots, Q_f)}{\partial(r_1, \dots, r_f)} = \frac{\partial(p_1, \dots, p_f)}{\partial(\alpha_1, \dots, \alpha_f)} = 1.\quad (8.23)$$

Here  $f$  denotes the degrees of freedom.

Before closing this line of discussion it would be useful to note that the eigenfunctions obtained can be cast in a form of a classical action integral. This action integral is convenient to use for numerical computation.

Recalling that the generating function  $S$  can be expressed in an action integral

$$S(t) = - \int_{t_0}^t ds \mathcal{L}_g(\mathbf{p}, \mathbf{r}, s),\quad (8.24)$$

where  $\mathcal{L}_g(\mathbf{p}, \mathbf{r}, s)$  is the Lagrangian, the eigenfunction  $\psi(\mathbf{p}, \mathbf{r}; \boldsymbol{\alpha}, \boldsymbol{\lambda})$  may be written as

$$\psi(\mathbf{p}, \mathbf{r}; \boldsymbol{\alpha}, \boldsymbol{\lambda}) = \frac{A_0}{(2\pi)^{3f}} \exp \left[ -i \sum_{j=1}^f \frac{\lambda_j}{\omega_j} \frac{\partial}{\partial \alpha_j} \int_{t_0}^t ds \mathcal{L}_g(\mathbf{p}, \mathbf{r}, s) \right] \times \int_{-\infty}^{\infty} d\xi \exp \left[ i\xi \cdot \left( \boldsymbol{\alpha} - \frac{\partial}{\partial \mathbf{r}} \int_{t_0}^t ds \mathcal{L}_g(\mathbf{p}, \mathbf{r}, s) \right) \right]. \quad (8.25)$$

This form reminds us of the Feynman path integral [16] in quantum mechanics in that it is given in terms of action integrals along the classical trajectory. We remark that the action integral may be written in the form of a phase integral

$$\int_{t_0}^t ds \mathcal{L}_g(\mathbf{p}, \mathbf{r}, s) = \sum_{j=1}^f \int_{r_{j0}}^{r_j} dr_j p_j - E(t - t_0). \quad (8.26)$$

The action integral form (8.25) for the eigenfunction is rather suggestive in that *the eigenfunction can be numerically computed by performing molecular dynamic simulations for classical trajectories from the initial to the final state.* It thus provides a practicable numerical algorithm for eigenfunctions which usually cannot be calculated in closed form except for dynamically trivial or simple cases.

We now consider a special case of a periodic motion in phase space. A periodic box normalization may be imposed on the eigenfunctions. This implies eigenfunctions are periodic. Imposing periodic boundary conditions on the eigenfunctions

$$\psi_\lambda(\mathbf{r} + \mathbf{L}) = \psi_\lambda(\mathbf{r}), \quad (8.27)$$

where  $L$  is the edge length of a cubic box, we find

$$\frac{\lambda_k}{\omega_k} \frac{\partial}{\partial \alpha_k} [W(\mathbf{r} + \mathbf{L}) - W(\mathbf{r})] = 2\pi l_k. \quad (8.28)$$

Here  $l_k$  is an integer. Since this condition should hold even at infinite separation of the colliding particles where

$$\frac{\partial W}{\partial r_k} = \sqrt{2mE} = \omega_k, \quad (8.29)$$

we find

$$\lambda_k = \frac{2\pi m l_k}{L} := mn_k \quad (8.30)$$

with  $n_k$  denoting the wave number

$$n_k = \frac{2\pi l_k}{L} \quad (l_k = \pm 1, \pm 2, \dots). \quad (8.31)$$

Since the characteristic function  $W$  is a constant energy surface in the phase space and the trajectories are perpendicular to the family of surfaces, the eigenfunctions represent waves propagating in the phase space with the phase

$$\Gamma = \sum_k \frac{\lambda_k}{\omega_k} \frac{\partial W}{\partial \alpha_k} = \sum_k \frac{m n_k}{\omega_k} \frac{\partial W}{\partial \alpha_k}. \quad (8.32)$$

Equations (8.20) and (8.30) represent the formal solution of the eigenvalue problem in terms of the Hamilton–Jacobi characteristic function  $W$ . This method of constructing the eigenfunctions is different from, and simpler and more direct than, that used in a previous work [12].

For noninteracting particles we easily obtain

$$\psi_\lambda(\mathbf{p}, \mathbf{r}) = A_0 \delta(\mathbf{p} - \boldsymbol{\alpha}) \exp\left(i \sum_k n_k r_k\right) \quad (8.33)$$

in agreement with the known result in the literature [3]. Its Fourier components are given by

$$\psi(\mathbf{p}, \mathbf{r}; \boldsymbol{\lambda}, \boldsymbol{\xi}) = \frac{A_0}{(2\pi)^3} \exp[i(\mathbf{n} \cdot \mathbf{r} + \mathbf{p} \cdot \boldsymbol{\xi} - \boldsymbol{\alpha} \cdot \boldsymbol{\xi})], \quad (8.34)$$

where

$$\mathbf{n} \cdot \mathbf{r} = \sum_k n_k r_k, \quad \boldsymbol{\alpha} \cdot \boldsymbol{\xi} = \sum_k \xi_k \alpha_k, \quad \boldsymbol{\xi} \cdot \mathbf{p} = \sum_k \xi_k p_k. \quad (8.35)$$

It is an interesting exercise to construct the eigenfunctions for separable bound-state problems in the case of two interacting particles. Such examples are given for a few cases in Ref. [12]. Such eigenfunctions can be used for calculations in molecular dynamic problems related to bound states in a classical approximation.

### 8.3 Some Mathematical Properties of Eigenfunctions and Eigenvalues

Having introduced the eigenfunctions and eigenvalues of the Liouville operator  $\mathcal{L}$ , it will be useful and also necessary for developing physical theory with it, and for comprehending the mathematical basis for steps involved, to discuss some of their important mathematical properties. We list them in the following.

**Property 1** *The Liouville operator is Hermitian.*

Consider the integral

$$l_{\lambda\lambda'} = \int dx \psi_{\lambda'}^* \mathcal{L} \psi_\lambda,$$

where the asterisk denotes complex conjugation. Then

$$\begin{aligned}
 l_{\lambda\lambda'}^* &= \int dx (\psi_{\lambda'}^* \mathcal{L} \psi_\lambda)^* \\
 &= \int dx \psi_{\lambda'} i [H, \psi_\lambda^*]_{pq} \\
 &= \int dx \psi_\lambda^* (-i) [H, \psi_{\lambda'}]_{pq} \\
 &= \int dx \psi_\lambda^* \mathcal{L} \psi_{\lambda'} \\
 &= l_{\lambda'\lambda}.
 \end{aligned}$$

Therefore  $\mathcal{L}$  is Hermitian and hence  $\mathcal{L}$  is self-adjoint:

$$\mathcal{L}^\dagger = \mathcal{L}. \quad (8.36)$$

**Property 2** *Since  $\mathcal{L}$  is Hermitian, its eigenvalues are real.*

Let

$$\mathcal{L} \psi_\lambda = \lambda \psi_\lambda.$$

Then take its complex conjugate

$$\mathcal{L}^* \psi_\lambda^* = \lambda^* \psi_\lambda^*.$$

Hence it follows that

$$\begin{aligned}
 \int dx (\psi_\lambda^* \mathcal{L} \psi_\lambda - \psi_\lambda^* \mathcal{L} \psi_\lambda^*) &= (\lambda - \lambda^*) \int dx \psi_\lambda^* \psi_\lambda \\
 &= \lambda - \lambda^*.
 \end{aligned}$$

But by virtue of hermiticity

$$\int dx (\psi_\lambda^* \mathcal{L} \psi_\lambda - \psi_\lambda^* \mathcal{L} \psi_\lambda^*) = 0.$$

Therefore

$$\lambda = \lambda^*, \quad (8.37)$$

which implies  $\lambda$  is real.

**Property 3** *The eigenfunctions belonging to different eigenvalues are orthogonal.*

Proof for this follows from Property 2.

**Property 4** Any function in the phase space can be expanded into the eigenfunctions of  $\mathcal{L}$ :

$$f(\mathbf{p}, \mathbf{q}) = \sum_k a_k \psi_k(\mathbf{p}, \mathbf{q}),$$

where

$$a_k = \int d\Gamma f(\mathbf{p}, \mathbf{q}) \psi_k^*(\mathbf{p}, \mathbf{q}).$$

This property follows from the fact that  $L$  is a linear operator. In the case of time-dependent functions

$$f(\mathbf{p}, \mathbf{q}, t) = \sum_k a_k(t) \psi_k(\mathbf{p}, \mathbf{q}). \quad (8.38)$$

Inserting it into the Liouville equation yields

$$\begin{aligned} i \frac{\partial f}{\partial t} &= \sum_k a_k(t) \mathcal{L} \psi_k(\mathbf{p}, \mathbf{q}) \\ &= \sum_k a_k(t) \lambda_k \psi_k(\mathbf{p}, \mathbf{q}) \\ &= i \sum_k \frac{da_k}{dt} \psi_k(\mathbf{p}, \mathbf{q}), \end{aligned}$$

which gives rise to the ordinary differential equation for the expansion coefficients

$$i \frac{da_k}{dt} = \lambda_k a_k(t). \quad (8.39)$$

Integrating this equation we obtain

$$a_k(t) = c_k \exp(-i\lambda_k t).$$

Finally,

$$\rho(\mathbf{p}, \mathbf{q}, t) = \sum_k c_k e^{-i\lambda_k t} \psi_k(\mathbf{p}, \mathbf{q}). \quad (8.40)$$

Of course, the eigenvalues and eigenfunctions appearing here are not known explicitly in terms of the system properties. Nevertheless, it is possible to deduce some general properties of the expansion, eigenvalues, and eigenfunctions, and they may help assess the utility of eigenvalues and eigenfunctions we will obtain later.

**Property 5** Since the distribution function is normalized

$$\int dx f(\mathbf{p}, \mathbf{q}, t) = 1, \quad (8.41)$$

it follows

$$\sum_k c_k e^{-i\lambda_k t} \int dx \psi_k(\mathbf{p}, \mathbf{q}) = 1.$$

Since

$$\int dx \mathcal{L} \psi_k(\mathbf{p}, \mathbf{q}) = \lambda_k \int dx \psi_k(\mathbf{p}, \mathbf{q}),$$

but

$$\begin{aligned} \int dx \mathcal{L} \psi_k(\mathbf{p}, \mathbf{q}) &= -i \sum_j \int dx \left( \frac{\partial H}{\partial p_j} \frac{\partial \psi_k}{\partial q_j} - \frac{\partial H}{\partial q_j} \frac{\partial \psi_k}{\partial p_j} \right) \\ &= i \sum_j \int dx \left( \frac{\partial H}{\partial q_j \partial p_j} - \frac{\partial H}{\partial p_j \partial q_j} \right) \psi_k \\ &\quad - i \sum_j \int dx \left( \frac{\partial H}{\partial p_j} \psi_k|_{q_j=\text{boundary}} - \frac{\partial H}{\partial q_j} \psi_k|_{p_j=\text{boundary}} \right) \\ &= 0, \end{aligned}$$

if

$$\frac{\partial H}{\partial p_j} \psi_k|_{q_j=\text{boundary}} = \frac{\partial H}{\partial q_j} \psi_k|_{p_j=\text{boundary}} = 0,$$

it follows

$$\lambda_k \int dx \psi_k(\mathbf{p}, \mathbf{q}) = 0. \quad (8.42)$$

This means

$$\int dx \psi_k(\mathbf{p}, \mathbf{q}) = 0 \quad (8.43)$$

if  $\lambda_k \neq 0$ . However,  $\lambda_k \neq 0$  for  $k = 0$ . Therefore the integral of eigenfunctions for  $k \neq 0$  vanish. It thus follows

$$c_0 \int dx \psi_0(\mathbf{p}, \mathbf{q}) = 1.$$

That is,

$$c_0 = 1 / \int dx \psi_0(\mathbf{p}, \mathbf{q}) \quad (8.44)$$

and the normalization of  $f(\mathbf{p}, \mathbf{q}, t)$  is fulfilled.

In this manner, the distribution function in the phase space is expandable in the eigenfunctions, and its expansion is reconciled with the notion of eigenfunctions being  $\mathcal{L}^2$  functions in the Hilbert space.

**Property 6** *It is well known that the Liouville operator is invariant to time reversal operator times complex conjugation operator. That is, if we denote by  $\theta$  the time reversal operator then*

$$\theta \mathcal{L} = -\mathcal{L}.$$

*Therefore if we denote the compound operator of time reversal and complex conjugation by  $\vartheta$*

$$\vartheta := \theta (*) = (*) \theta$$

*then*

$$\vartheta \mathcal{L} = \mathcal{L}.$$

*Consequently the time reversed distribution function  $f(-\mathbf{p}, \mathbf{q}, -t)$  obeys the same Liouville equation as  $f(\mathbf{p}, \mathbf{q}, t)$ .*

We note that this is in the root cause of the difficulty in kinetic theory of matter when we try to develop it by means of the Liouville equation, which is time reversal invariant.<sup>2</sup>

In connection with the compound operator  $\vartheta$ , we note the following: Since

$$\mathcal{L}^* = -\mathcal{L}$$

and the eigenvalues are real, we have

$$\mathcal{L}^* \psi_{\lambda_k}^* = \lambda_k \psi_{\lambda_k}^* \quad (8.45)$$

and hence

$$\mathcal{L} \psi_{\lambda_k}^* = -\lambda_k \psi_{\lambda_k}^*.$$

This means that  $\psi_{\lambda_k}^*$  is the eigenfunction belonging to  $-\lambda_k$ . Furthermore, since

$$\theta^2 = 1,$$

it also follows

$$\theta \mathcal{L}^* = -\theta \mathcal{L} = \vartheta \mathcal{L} = \mathcal{L}.$$

Now operating  $\theta$  on Eq. (8.45) we obtain

$$\theta \mathcal{L}^* \psi_{\lambda_k}^* = \lambda_k \theta \psi_{\lambda_k}^*$$

<sup>2</sup>On the other hand, for example, the Boltzmann kinetic equation breaks the time reversal invariance characteristic of the Liouville equation, because the latter has no time reversal invariance breaking collision term. It should be noted that the generalized Boltzmann equation (GBE)—shown in Chaps. 6 and 7—has that property essential for irreversible kinetic equation even though it is for a dense gases and liquids. On this important aspect of the GBE, see also B.C. Eu, J. Chem. Phys. **107**, 222 (1997).

but

$$\theta \mathcal{L}^* \psi_{\lambda_k}^* = \mathcal{L} \theta \psi_{\lambda_k}^*$$

and hence

$$\mathcal{L} \theta \psi_{\lambda_k}^* = \lambda_k \theta \psi_{\lambda_k}^*,$$

which implies that

$$\begin{aligned}\theta \psi_{\lambda_k}^* &= \text{an eigenfunction of } \mathcal{L} \text{ belonging to } \lambda_k \\ &= \psi_{\lambda_k}.\end{aligned}$$

That is,

$$\psi_{\lambda_k}^* = \theta \psi_{\lambda_k}. \quad (8.46)$$

This auxiliary property is important for proving the orthogonality of eigenfunctions.

**Property 7** *The eigenfunctions  $\psi_\lambda$  are generally complex and hence they can be written in terms of amplitude and phase:*

$$\psi_\lambda(\mathbf{p}, \mathbf{q}) = A_\lambda(\mathbf{p}, \mathbf{q}) \exp[i\Gamma_\lambda(\mathbf{p}, \mathbf{q})], \quad (8.47)$$

where

$$\mathcal{L} A_\lambda(\mathbf{p}, \mathbf{q}) = 0, \quad (8.48)$$

$$\mathcal{L} \Gamma_\lambda(\mathbf{p}, \mathbf{q}) = -i\lambda. \quad (8.49)$$

This easily follows from the eigenvalue problem of  $\mathcal{L}$  on substituting (8.47). Equation (8.48) implies  $A_\lambda(\mathbf{p}, \mathbf{q})$  is made up of invariants of motion and  $\Gamma_\lambda(\mathbf{p}, \mathbf{q})$  is the phase of a wave in the  $\Gamma$  space that corresponds to the eigenvalue  $\lambda$ . The eigenvalue problem of  $\mathcal{L}$  is now reduced to finding the amplitude and the phase of waves.

On the basis of the mathematical properties enumerated above, we are fairly on safe mathematical grounds to develop a formal theory of classical scattering in phase space in close analogy to quantum scattering theory [5–7, 17].

## 8.4 Formal Scattering Theory in Phase Space

To express collision bracket integrals involving classical collision operators in an equivalent but computationally more practical form and also to make this work self-contained with respect to the subject matter, we briefly review classical scattering theory.

Formal classical theory of scattering [3, 5, 10, 11] can be formulated in phase space. It has considerable advantages in nonequilibrium statistical mechanics and, especially, in kinetic theory, as has been frequently demonstrated in kinetic theory investigations in which classical collision operators are used in analogy [18] to quantum scattering theory [6, 7]. In fact, the mathematical basis of such collision operators have not been studied beyond the formal symbolic level. Since they are, nevertheless, often used in such investigations, it is all the more important to try to comprehend their mathematical basis, so that one can perform calculations systematically, for example, in connection with collision integrals appearing in the theory of transport processes. For this reason we have reviewed the mathematical aspects of the space of phase space eigenfunctions in the previous section. Our aim here, however, is not in developing classical scattering theory in depth, but rather in exposing the essential features that may be relevant to their mathematical treatments and approximations for them which one might use in future computations of transport properties. For this purpose the eigenfunctions presented in the previous section provide valuable insights and a conceptual framework for computation.

Consider a scattering situation where particles (in fact, collimated beams of particles) at infinite separation converge toward each other, interact, and then separate to infinite relative distance from each other. In classical mechanics, there is no concept of waves for particle motion. However, when the collision problem is formulated in the phase space, there appears a notion of waves as we have seen in the previous section where the eigenfunctions are calculated for continuous spectra of the Liouville operator. The Liouville equation (8.3) governs this scattering process of waves in phase space. We describe the basic aspects of the theory here.

The collision process of particles is governed by the Liouville equation (8.3). Since at remote past and distant future where colliding particles do not interact with each other, the probability distribution function  $f$  obeys the free particle Liouville equation

$$i \frac{\partial f}{\partial t} = \mathcal{L}_0 f, \quad (8.50)$$

where  $\mathcal{L}_0$  is the free Liouville operator defined by

$$\mathcal{L}_0 = -i \sum_k \frac{p_k}{m} \frac{\partial}{\partial r_k}. \quad (8.51)$$

If the system is prepared at an eigenstate  $\lambda$  at remote past and thus we set

$$f(x, t) = \exp(-i\lambda t) \Phi_\lambda(x), \quad (8.52)$$

the corresponding eigenvalue problem is

$$\mathcal{L}_0 \Phi_\lambda(x) = \lambda \Phi_\lambda(x). \quad (8.53)$$

This eigenfunction is of the form as in (8.33). To describe scattering, it is useful to introduce the interaction representation. To this aim, we define a transformation of  $f$

$$\tilde{f}(t) = \exp(i\mathcal{L}_0 t)f(t). \quad (8.54)$$

This puts the Liouville equation (8.3) in the form

$$i\frac{\partial \tilde{f}}{\partial t} = \tilde{\mathcal{L}}_1(t)\tilde{f}(t), \quad (8.55)$$

where

$$\tilde{\mathcal{L}}_1(t) = \exp(i\mathcal{L}_0 t)\mathcal{L}_1 \exp(-i\mathcal{L}_0 t), \quad (8.56)$$

with  $\mathcal{L}_1$  denoting the interaction Liouville operator

$$\mathcal{L}_1 = i \sum_k \frac{\partial H}{\partial r_k} \frac{\partial}{\partial p_k}. \quad (8.57)$$

The formal solution for (8.55) can be written in the form

$$\tilde{f}(t) = \exp(i\mathcal{L}_0 t) \exp[-i\mathcal{L}(t - t_0)] \exp(-i\mathcal{L}_0 t)\tilde{f}(t_0). \quad (8.58)$$

As  $t_0 \rightarrow -\infty$  at which point in time the interaction<sup>3</sup> between the particles vanishes, there holds the limit  $\mathcal{L} \rightarrow \mathcal{L}_0$  and therefore

$$\tilde{f}(t) \rightarrow \exp(i\mathcal{L}_0 t) \exp(-i\mathcal{L}_0 t)\Phi_\lambda = \Phi_\lambda, \quad (8.59)$$

and similarly as  $t \rightarrow \infty$ . Consequently, in the limit of  $t_0 \rightarrow -\infty$  the distribution function is given by

$$\begin{aligned} f(t) &= \lim_{t_0 \rightarrow -\infty} \exp[-i\mathcal{L}(t - t_0)] \exp(-i\mathcal{L}_0 t_0)\tilde{f}(t_0) \\ &= \lim_{t_0 \rightarrow -\infty} \exp[-i\mathcal{L}(t - t_0)] \exp(-i\mathcal{L}_0 t_0)\Phi_\lambda. \end{aligned} \quad (8.60)$$

This is a strong limit which may be written in an equivalent form by using the Abel–Tauber theorem [19, 20]:

$$\begin{aligned} f(t) &= \lim_{\epsilon \rightarrow 0^+} \epsilon \int_{-\infty}^0 ds e^{\epsilon s} \exp[-i\mathcal{L}(t - s)] \exp(-i\mathcal{L}_0 s)\Phi_\lambda \\ &= \exp(-i\mathcal{L}t) \lim_{\epsilon \rightarrow 0^+} \epsilon \int_{-\infty}^0 ds e^{\epsilon s} \exp(i\mathcal{L}s) \exp(-i\lambda s)\Phi_\lambda. \end{aligned} \quad (8.61)$$

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<sup>3</sup>Here the assumption is implicit that the interaction force is of finite range, so that it vanishes sufficiently fast and would not persist indefinitely.

Physically, this form implies a time average<sup>4</sup> of a wave train released from remote past until  $t = 0$ . We define a time-independent function  $\psi_\lambda^{(+)}$  by the formula

$$\psi_\lambda^{(+)} = \lim_{\epsilon \rightarrow +0} \epsilon \int_{-\infty}^0 ds e^{\epsilon s} \exp(i\mathcal{L}s) \exp(-i\lambda s) \Phi_\lambda \quad (8.62)$$

to formulate a time-independent scattering theory, since it contains all the necessary dynamical information on the scattering system. The mathematical nature of the scattered function  $\psi_\lambda^{(+)}$  can be better understood by recasting (8.62) on performing integration: With the definition of a complex number

$$z = \lambda + i\epsilon,$$

we find

$$\psi_\lambda^{(+)} = -i\epsilon (\mathcal{L} - z)^{-1} \Phi_\lambda, \quad (8.63)$$

where the limit sign  $\epsilon \rightarrow +0$  is omitted for notational brevity. The limit must be taken when the calculation of the right-hand side is completed. This limit will be understood henceforth. Multiplying  $(\mathcal{L} - z)$  to (8.62) from left and taking the limit  $\epsilon \rightarrow +0$ , we obtain

$$\mathcal{L}\psi_\lambda^{(+)} = \lambda\psi_\lambda^{(+)}. \quad (8.64)$$

This equation suggests that  $\psi_\lambda^{(+)}$  is an eigenfunction of  $\mathcal{L}$  belonging to the same eigenvalue  $\lambda$  as for  $\mathcal{L}_0$ . If it is recalled that the free state of the scattering system prepared in the remote past also has the eigenvalue  $\lambda$  with eigenfunction  $\Phi_\lambda$ , we see that the full scattering eigenfunction  $\psi_\lambda^{(+)}$  and the free eigenfunction  $\Phi_\lambda$  belong to the same eigenvalue spectrum, that is, *the scattering process occurs on the shell of a given eigenvalue  $\lambda$  of the Liouville operators and the total eigenvalue of the system does not change even if there is scattering of particles by each other*. This is an important point worth keeping in mind when we apply the classical scattering theory formalism to prove a number of formal relations (e.g., the  $H$  theorem) in kinetic theory and also to calculate collision bracket integrals given in terms of classical collision operators.

The classical resolvent operator in (8.63) can be recast into another alternative form—an operator integral equation

<sup>4</sup>By employing the idea of time coarse graining of Kirkwood [17], a similar time averaging has been used to derive the collision term in the generalized Boltzmann equation in Chaps. 6 and 7 in a different viewpoint that does not invoke the Abel-Tauber theorem. However, it should be noted that even if the collision terms in the kinetic equation could have been treated by the same method as used here to obtain (8.61) from the Liouville equation, the resulting kinetic equation would need time-coarse graining in order to make it a kinetic equation for time-coarse-grained distribution function.

$$\begin{aligned}
\mathcal{R}(z) &= (\mathcal{L} - z)^{-1} \\
&= \mathcal{R}_0(z) - \mathcal{R}_0(z) \mathcal{L}_1 \mathcal{R}(z) \\
&= \mathcal{R}_0(z) - \mathcal{R}(z) \mathcal{L}_1 \mathcal{R}_0(z),
\end{aligned} \tag{8.65}$$

where the free resolvent operator  $\mathcal{R}_0(z)$  is defined by

$$\mathcal{R}_0(z) = (\mathcal{L}_0 - z)^{-1}. \tag{8.66}$$

Equation (8.63), upon use of (8.65), can be written in a more formally familiar form

$$\psi_\lambda^{(+)} = \Phi_\lambda - \mathcal{R}_0(z) \mathcal{L}_1 \psi_\lambda^{(+)}, \tag{8.67}$$

which may be thought of the classical analog of the Lippmann–Schwinger equation in quantum scattering theory [6, 7, 21]. We will call it the classical Lippmann–Schwinger equation for the scattered eigenfunction  $\psi_\lambda^{(+)}$ . It is an integral equation for  $\psi_\lambda^{(+)}$  in phase space in contrast to the quantum mechanical counterpart that lives in either coordinate or momentum space. By defining the classical collision operator  $\mathcal{T}(z)$

$$\mathcal{T}(z) = \mathcal{L}_1 - \mathcal{L}_1 \mathcal{R}_0(z) \mathcal{T}(z), \tag{8.68}$$

we may put the classical Lippmann–Schwinger equation in an alternative form

$$\psi_\lambda^{(+)} = \Phi_\lambda - \mathcal{R}_0(z) \mathcal{T}(z) \Phi_\lambda. \tag{8.69}$$

The operator relations (8.65) and (8.68) can be rearranged to obtain the relations

$$\mathcal{R}(z) \mathcal{L}_1 = \mathcal{R}_0(z) \mathcal{T}(z), \tag{8.70}$$

$$\mathcal{L}_1 \mathcal{R}(z) = \mathcal{T}(z) \mathcal{R}_0(z), \tag{8.71}$$

$$\mathcal{R}(z) = \mathcal{R}_0(z) - \mathcal{R}_0(z) \mathcal{T}(z) \mathcal{R}_0(z), \tag{8.72}$$

$$\mathcal{T}(z) = \mathcal{L}_1 - \mathcal{L}_1 \mathcal{R}(z) \mathcal{L}_1. \tag{8.73}$$

These relations will be found useful in various calculations involving collision operators since the classical collision operators appear in the theory of transport processes.

The formal classical scattering theory presented here for the case of two-body collision can be generalized [18] to the case of many-particle collision. The equations presented remain structurally the same as for the case of many-particle collision. Therefore, we will simply consider the equations presented applicable to a many-particle situation.

However, there are some precautions that must be taken when many-particle collision and resolvent operators are calculated in terms of operators involving smaller numbers of particles, for example, two-particle, three-particle operators, and so on in the lower order collision operators, because then such a procedure may give rise to a divergent expansion. Since many-particle operators cannot be computed in closed form in practice unless they are decomposed into such lower-order

operators involving smaller numbers of interacting particles, the precautions mentioned become important when kinetic theory results are computed for experimental comparison. To avoid divergences of expansion for many-body collision operators it is necessary to use *an expansion in connected cluster collision operators*. Detailed discussions on these points are given in Chap. 9 of Ref. [5] to which the reader is referred.

## 8.5 Alternative Form for the Collision Bracket Integral

As we have seen in the previous chapters on kinetic theory, the kinetic equation is either based on the Liouville equation<sup>5</sup> or postulated on the basis of the viewpoint that the kinetic equation is a fundamental (irreversible) equation<sup>6</sup> for mesoscopic description of a many-particle system, built a priori on (reversible) classical or quantum mechanics just like mechanical equations of motion. The difference between the two approaches is not merely philosophical: Although either way, we are treating macroscopic systems from the molecular viewpoint by using Newtonian equations of motion or Schrödinger equations to describe molecular interactions, the kinetic equation of the second approach (e.g., the Boltzmann equation) is time-reversal symmetry breaking whereas the kinetic equation of the first approach (i.e., the Liouville equation) is time-reversal invariant. The time reversal symmetry is broken by the irreversible kinetic equation (e.g., Boltzmann equation) in the second approach because of the time-reversal symmetry breaking collision term in which energy dissipation accompanying irreversible processes is vested.

The collision term is given in terms of the collision cross section or collision operator (alternatively, transition operator) which is relatively simple to calculate in the case of two-particle elastic scattering, but becomes hard to calculate as the complexity of the system increases with the increasing number of particles involved. All material functions such as transport coefficients are given as collision-weighted averages of dynamical quantities, and the theoretical formulas for material functions by any kinetic theory cannot transcend the formalistic level to make connection with experimental data unless a practicable method of computing collision-weighted averages is developed. By method, we do not mean some sort of analytical theoretic method, but an algorithm by which the aforementioned averages can be efficiently calculated on an electronic computer.

Therefore, the aim here is to transform the formal expressions for material functions, such as transport coefficients, obtained in irreversible kinetic theory to forms

<sup>5</sup>This line of approach is typically represented by the BBGKY hierarchy theory [17, 22–24], for which a number of review articles by Cohen [25] are available. In this approach, the distribution function obeying the Liouville equation is hierarchically expanded in a density series and the leading order equations are determined, obtaining the Boltzmann equation for the lowest order member of hierarchy.

<sup>6</sup>To this class of approach belongs the kinetic theory formulated in the present work as well as relaxation time models for kinetic equations for dense fluids in the literature.

readily computable electronically by using computer simulation methods or numerical computational methods. It is the main objective in this section to provide a necessary algorithm for them.

To achieve the stated aim, it is sufficient to consider the following collision bracket integral appearing in the dense fluid kinetic theory formulated in the previous chapters and elsewhere in Refs. [5, 26]:

$$I_c = i \langle h(x) \mathcal{T}(z) h(x) f_{\text{eq}}(x) \rangle := i \mathcal{J}_c \quad (8.74)$$

where  $h(x)$  is a function of phase  $x = (\mathbf{p}^{(N)}, \mathbf{r}^{(N)})$  for an  $N$  particle system,  $f_{\text{eq}}(x)$  is the equilibrium distribution function,  $\mathcal{T}(z)$  is the  $N$ -particle collision operator obeying the  $N$ -particle version of the classical Lippmann-Schwinger equation (8.68), and  $i = \sqrt{-1}$ . The angular brackets stand for integration over the phase space. The limit  $\epsilon \rightarrow 0^+$  must be taken on completion of calculation for the average in (8.74).

Since it is not clear how the classical collision operator  $\mathcal{T}(z)$  may be numerically calculated on a computer unless the integral equation for  $\mathcal{T}(z)$  is solved in the phase space of eigenfunctions, we aim to cast the phase space average in (8.74) in an alternative, more readily computable form.

It is convenient to use bra and ket vector notation, so that we can write

$$\mathcal{J}_c := \langle g | \mathcal{T}(z) | g \rangle, \quad (8.75)$$

where the bra vector is defined by

$$|g\rangle = \left| h(x) f_{\text{eq}}^{1/2} \right\rangle, \quad (8.76)$$

and the ket vector as the hermitean adjoint of the bra vector in an analogous manner to quantum mechanics. Note that since  $\mathcal{T}(z)f_{\text{eq}} = 0$  owing to the fact that  $f_{\text{eq}}$  is a function of collision invariants and, in particular, of the Hamiltonian and hence  $\mathcal{L}(z)f_{\text{eq}} = 0$ , it is clear that

$$\mathcal{T}(z) h(x) f_{\text{eq}} = f_{\text{eq}} \mathcal{T}(z) h(x). \quad (8.77)$$

Let  $\Phi_\lambda$  denote the complete set of eigenfunctions for  $\mathcal{L}_0$ —the free Liouville operator for the  $N$  particles. The complete set has the closure

$$\sum_{\lambda} |\Phi_{\lambda}(x)\rangle \langle \Phi_{\lambda}(x)| = \mathbf{1}. \quad (8.78)$$

The collision integral  $\mathcal{J}_c$  then can be written as

$$\mathcal{J}_c = \sum_{\lambda} \sum_{\lambda'} \langle g | \Phi_{\lambda}(x) \rangle \langle \Phi_{\lambda}(x) | \mathcal{T}(z) | \Phi_{\lambda'}(x) \rangle \langle \Phi_{\lambda'}(x) | g \rangle. \quad (8.79)$$

On rearranging (8.72) into the following form

$$\mathcal{T}(z) = \mathcal{R}_0^{-1}(z)[\mathcal{R}_0(z) - \mathcal{R}(z)]\mathcal{R}_0^{-1}(z), \quad (8.80)$$

which implies that the result of  $\mathcal{T}(z)$  operating on its operand  $F(x)$  is the difference between the post- and pre-collision values of  $F(x)$ , and upon using this result in (8.79), the collision integral can be written as

$$\begin{aligned} \mathcal{J}_c = & \sum_{\lambda, \lambda'} (\lambda - z)^* (\lambda' - z) \langle g | \Phi_\lambda(x) \rangle \langle \Phi_\lambda(x) | \mathcal{R}(z) | \Phi_{\lambda'}(x) \rangle \langle \Phi_{\lambda'}(x) | g \rangle \\ & - \sum_{\lambda, \lambda'} (\lambda' - z) \langle g | \Phi_\lambda(x) \rangle \langle \Phi_\lambda(x) | \Phi_{\lambda'}(x) \rangle \langle \Phi_{\lambda'}(x) | g \rangle. \end{aligned} \quad (8.81)$$

Since the eigenfunctions are orthogonal, the collision integral is further simplified to the form

$$\begin{aligned} \mathcal{J}_c = & \sum_{\lambda} \sum_{\lambda'} (\lambda - z)^* (\lambda' - z) \langle g | \Phi_\lambda(x) \rangle \langle \Phi_\lambda(x) | \mathcal{R}(z) | \Phi_{\lambda'}(x) \rangle \langle \Phi_{\lambda'}(x) | g \rangle \\ & - \sum_{\lambda} (\lambda - z) \langle g | \Phi_\lambda(x) \rangle \langle \Phi_\lambda(x) | g \rangle. \end{aligned} \quad (8.82)$$

According to the scattering theory consideration made in the previous section, the collision occurs on the shell of a given  $\lambda$ . This means that there will be a negligible contribution from the off-shell  $\lambda$ . Furthermore, the collisions relevant to the collision bracket integrals in the present kinetic theory occur in the  $\lambda = 0$  shell. Therefore it follows that

$$(\lambda - z)^* (\lambda' - z) = -(i\epsilon)^2 = \epsilon^2.$$

In this regard, it should be recognized that the equilibrium distribution is also on the shell of  $\lambda = 0$  and that the eigenfunctions of  $\lambda \neq 0$  represent the wave propagation transversal to the surface of the  $\lambda = 0$  shell in the phase space. The collision bracket integrals under consideration is, therefore, on the  $\lambda = 0$  shell; for this point recall the basic constraints of the ensemble kinetic theory in Chaps. 6 and 7. Therefore, neglecting the off-shell contribution, we obtain

$$\begin{aligned} \mathcal{J}_c = & \epsilon^2 \sum_{\lambda} \sum_{\lambda'} \langle g | \Phi_\lambda(x) \rangle \langle \Phi_\lambda(x) | \mathcal{R}(z) | \Phi_{\lambda'}(x) \rangle \langle \Phi_{\lambda'}(x) | g \rangle \\ & - i\epsilon \sum_{\lambda} \langle g | \Phi_\lambda(x) \rangle \langle \Phi_\lambda(x) | g \rangle \\ = & \epsilon^2 \langle g | \mathcal{R}(z) | g \rangle - i\epsilon \langle g | g \rangle. \end{aligned} \quad (8.83)$$

The resolvent operator in this expression can be written in the form of integral. We consequently find

$$\mathcal{J}_c = i\epsilon \int_0^\infty dt e^{-\epsilon t} \langle e^{i\mathcal{L}t} g | g \rangle - i\epsilon \langle g | g \rangle. \quad (8.84)$$

Therefore, the collision integral  $I_c$  in (8.74) may be written as

$$I_c = \epsilon \left[ \langle g | g \rangle - \epsilon \int_0^\infty dt e^{-\epsilon t} \langle e^{i\mathcal{L}t} g | g \rangle \right]. \quad (8.85)$$

Since  $g(t) = e^{i\mathcal{L}t} g = f_{\text{eq}}^{1/2} e^{i\mathcal{L}t} h$ , we finally obtain

$$\begin{aligned} I_c &= \epsilon \left[ \langle g | g \rangle - \epsilon \int_0^\infty dt e^{-\epsilon t} \langle g(t) | g \rangle \right] \\ &= -\epsilon^2 \int_0^\infty dt e^{-\epsilon t} \langle [g(t) - g] | g \rangle. \end{aligned} \quad (8.86)$$

This form and, particularly, the second term on the right in the first line, is rather reminiscent of the time autocorrelation functions appearing in the linear response theory [27, 28]. Here  $\epsilon$  may be taken with the inverse of a sufficiently large value of time,  $\tau_c$ , so that

$$I_c = -\tau_c^{-2} \int_0^\infty dt e^{-t/\tau_c} \langle [g(t) - g] | g \rangle. \quad (8.87)$$

This is an alternative form for the collision bracket integral in (8.74). It is given in terms of a time correlation function of  $g(t)$  which is certainly more readily amenable to molecular dynamic simulation methods than the one involving the classical  $N$ -particle collision operator  $\mathcal{T}(z)$ . For  $\tau_c$  we may take the time to traverse the intermolecular force range, for example, or a distance of that order of magnitude or the mean free time.

If  $\Delta g(t) = g(t) - g$  may be approximated by  $\Delta g(\tau_c)$ —that is, if there is a plateau value for  $\Delta g(t)$ —the integral may be approximated by

$$I_c = -\frac{1}{\tau_c} \langle \Delta g(\tau_c) | g \rangle, \quad (8.88)$$

By reversing the collision process in the phase space and using the time reversal invariance of the phase volume, it is possible to put this integral in a symmetric form

$$I_c = \frac{1}{2\tau_c} \langle \Delta g(\tau_c) | \Delta g(\tau_c) \rangle, \quad (8.89)$$

which is reminiscent of the collision bracket integrals in the Chapman-Enskog theory [29] of dilute gases. It should be noted that the angular brackets denote averaging over the equilibrium ensemble. Eq. (8.89) is an alternative, and practically important,

form for the collision bracket integral [26] we have set out to show in this chapter. All the collision bracket integrals appearing in the present line of kinetic theory based on the GBE, and hence all transport coefficients [26] associated with the generalized hydrodynamic equations, can be expressed in terms of the general formula (8.89). This formula is amenable to classical trajectory calculations or molecular dynamic simulations [2].

### 8.5.1 Example for Two-Particle Collisions

Formula (8.89) indeed can be shown to be the Chapman-Enskog collision bracket integral for  $\Delta g(\tau_c)$  if we consider the case of  $I_c$  for two particles, since in the dilute gas kinetic theory the collision bracket integrals involve two-particle collisions. For this purpose, let us write  $I_c$  explicitly for two particles:

$$I_c = \frac{1}{2\tau_c} \int dx^{(2)} \Delta g(\tau_c) \Delta g(\tau_c) f_{\text{eq}}^{(2)}(x^{(2)}) . \quad (8.90)$$

If  $\Delta g(\tau_c)$  is assumed to depend only on the momenta and if  $f_{\text{eq}}^{(2)}(x^{(2)}) = f_{\text{eq}}(\mathbf{p}_1)f_{\text{eq}}(\mathbf{p}_2)$  as is the case of the Chapman-Enskog collision bracket integrals for dilute monatomic gases, it then is possible to show [4, 5, 29] that

$$\int dx^{(2)} \dots = \tau_c V \int d\mathbf{v}_1 \int d\mathbf{v}_2 \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} \mathbf{b} g_{12} \dots \quad (8.91)$$

in the standard notation. Here  $V$  is the volume of the container,  $\mathbf{b}$  is the impact parameter,  $\varphi$  is the azimuthal scattering angle,  $g_{12}$  is the relative speed, and  $f_{\text{eq}}(\mathbf{p}_i)$  is a singlet equilibrium momentum distribution function—the Maxwell distribution function. By using this result, we finally get

$$I_c^{(2)} = \frac{1}{2} V \int d\mathbf{v}_1 \int d\mathbf{v}_2 \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} \mathbf{b} g_{12} \Delta g(\tau_c) \Delta g(\tau_c) f_{\text{eq}}(\mathbf{p}_1) f_{\text{eq}}(\mathbf{p}_2), \quad (8.92)$$

which, apart from the constant factor omitted in the definition of  $I_c$ , is clearly the Chapman-Enskog collision bracket integral [29, 30] for  $\Delta g(\tau_c) = g(\tau_c) - g$  where  $g(\tau_c)$  is the post-collision value of  $g$  if  $\tau_c$  is taken for the collision time for the particles. For example,  $g(\tau_c) = m(\mathbf{v} - \mathbf{u})(\mathbf{v} - \mathbf{u})$ , where  $\mathbf{v}$  is the particle velocity and  $\mathbf{u}$  is the fluid velocity, which would be the case for the stress phenomena. This shows that Formula (8.89) tends to the collision bracket integral in the Chapman-Enskog theory results for transport coefficients, and hence it generalizes dilute gas Boltzmann kinetic theory results to dense gases or liquids, if  $f_{\text{eq}}^{(2)}(x^{(2)})$  is for correlated particle pairs so that

$$f_{\text{eq}}^{(2)}(x^{(2)}) = f_{\text{eq}}(\mathbf{p}_1)f_{\text{eq}}(\mathbf{p}_2)g_{\text{eq}}(\mathbf{r}_1, \mathbf{r}_2), \quad (8.93)$$

where  $g_{\text{eq}}(\mathbf{r}_1, \mathbf{r}_2)$  is the equilibrium pair correlation function.

### 8.5.2 Three-Particle Collision

In the case of  $I_c$  involving three particles, we employ mass-normalized coordinates [5, 31, 32], which are then subsequently expressed in hyperspherical coordinates [33]. In the aforementioned mass-normalized hyperspherical coordinates the three-particle phase integral can be written as

$$\int dx^{(3)} \dots = \tau_c V \int d\mathbf{P}_c \int d\boldsymbol{\pi}_1 \int d\boldsymbol{\pi}_2 \int d\Omega_4 \int_0^\infty d\mathfrak{b} \mathfrak{b}^4 (P/\mu) \dots, \quad (8.94)$$

where  $\mathbf{P}_c$  is the center of mass momentum,  $\boldsymbol{\pi}_1$  and  $\boldsymbol{\pi}_2$  are two components of mass-normalized relative momenta of the three particles,  $P = |\boldsymbol{\pi}_1 + \boldsymbol{\pi}_2|$ ,  $\mu^2 = m_1 m_2 m_3 / (m_1 + m_2 + m_3) = m^2/3$ ,

$$d\Omega_4 = \sin^3 \theta_4 \sin^2 \theta_3 \sin \theta_2 d\theta_1 d\theta_2 d\theta_3 d\theta_4 \quad (8.95)$$

with  $\theta_2$ ,  $\theta_3$ ,  $\theta_4$  denoting the hyperpolar angles ( $0 \leq \theta_i \leq \pi : i = 2, 3, 4$ ),  $\theta_1$  is the hyperazimuthal angle ( $0 \leq \theta_1 \leq 2\pi$ ), and  $\mathfrak{b}$  is the generalized impact parameter for three-body collision. For details of the coordinate transformation and the collision dynamics leading to (8.94) and (8.95), see Sect. 13.6 of Ref. [5]. By using this result, the three-particle collision bracket integral can be written as

$$I_c^{(3)} = \frac{1}{2} V \int d\mathbf{P}_c \int d\boldsymbol{\pi}_1 \int d\boldsymbol{\pi}_2 \int d\Omega_4 \int_0^\infty d\mathfrak{b} \mathfrak{b}^4 (P/\mu) \Delta g(\tau_c) \Delta g(\tau_c) \times \\ f_{\text{eq}}(\boldsymbol{\pi}_1) f_{\text{eq}}(\boldsymbol{\pi}_2) f_{\text{eq}}(\mathbf{P}_c), \quad (8.96)$$

in the case where  $\Delta g(\tau_c)$  depends on the momenta of three particles only and

$$f_{\text{eq}}^{(3)} = f_{\text{eq}}(\boldsymbol{\pi}_1) f_{\text{eq}}(\boldsymbol{\pi}_2) f_{\text{eq}}(\mathbf{P}_c).$$

It must be noted that parameter  $\tau_c$  is canceled out in  $I_c^{(3)}$  if  $\tau_c$  is taken as the collision time of the three particles.

Here we remark that  $I_c$  in Eq. (8.90) may be expanded into a cluster expansion [5] where  $I_c^{(2)}$  and  $I_c^{(3)}$  appear as the leading order contributions in a density series. Since such an expansion is not the aim of this work, we will not discuss it in this chapter, but this example suggests that formula (8.89) may be expanded in clusters, which results in a density series whose expansion coefficients consisting of collision

bracket integrals may be computed by means of simulation methods—either an MD simulation method or an MC simulation method—on the basis of the algorithm presented above.

## 8.6 Application of the Computational Algorithm

In this section we resume the discussion on computational algorithms of transport coefficients for moderately dense gases in Chap. 5 and also in Chaps. 6 and 7. If the density is not sufficiently low, the method holding for dilute gases could not be used to obtain satisfactory results for them. We should use some sort of numerical computational method, but the collision bracket integrals are not easily amenable to a numerical simulation method.

Since we now are equipped with alternative forms for them that appear to be amenable to a numerical method on a computer, we would like to devote this section to the question to show a typical example for transport coefficients and collision bracket integrals appearing in the kinetic theory based on the GBE. Specifically, we will consider the case of pure fluids to make the discussion as simple as possible. We will also exclude volume transport phenomena, whose effects should be small in the density regime considered. Including volume transport processes would not alter the basic procedure of calculating the transport coefficients discussed below.

### 8.6.1 Linear Transport Coefficients for a Moderately Dense Gas Mixture

In the linear regime near equilibrium, the linear transport processes in a gas mixture are described by the linear constitutive relations<sup>7</sup>

$$\mathcal{Z}_a^{(q)} - (\beta g g_a^{(q)})^{-1} \sum_{b=1}^r \sum_{s \geq 1} \mathfrak{R}_{ab}^{(qp)} \Phi_b^{(s)} = 0 \quad (q \geq 1; r \geq a \geq 1), \quad (8.97)$$

where coefficients  $\mathfrak{R}_{ab}^{(qp)}$  are given by collision bracket integrals whose precise expressions are defined in Chap. 5; see (5.255). The symbols  $g$  and  $g_a^{(q)}$  are, respectively, defined by

$$g = \frac{1}{n^2 d^2} \sqrt{\frac{m}{2k_B T}} \quad (8.98)$$

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<sup>7</sup>In the case of  $\mathfrak{R}_{ab}^{(as)}$  for dense fluids and liquids discussed in Chaps. 6 and 7  $g^{-1}$  in (8.97) must be replaced by  $\epsilon = 1/\tau_c$ .

and

$$g_a^{(1)} = \frac{1}{2p_a}, \quad g_a^{(2)} = \frac{3}{2p_a}, \quad g_a^{(3)} = \frac{1}{\tilde{C}_{pa} T p_a}, \quad g_a^{(4)} = \frac{1}{\rho_a} \quad (8.99)$$

in the linear regime with  $d$  denoting a quantity of order of a typical collision cross section and  $m$  the reduced mass. The collision bracket integrals  $\mathfrak{R}_{ab}^{(qs)}$  appear as coefficients in the linear relations. They are summarized in Table 8.1, where the angular brackets  $\langle \cdots \rangle_c$  denote the collision integral and  $h_{kb}^{(q)}$  are moments defined in Chap. 5. For the reader's convenience they are summarized in the following. In the linear approximations for the kinematic terms  $\mathcal{Z}_a^{(q)}$  are as below:

$$\begin{aligned} \mathcal{Z}_a^{(1)} &= -2p_a [\nabla \mathbf{u}]^{(2)}, \quad \mathcal{Z}_a^{(2)} = -\frac{2}{3}p_a \nabla \cdot \mathbf{u}, \\ \mathcal{Z}_a^{(3)} &= -\tilde{C}_{pa} p_a T \nabla \ln T, \quad \mathcal{Z}_a^{(4)} = -p \mathbf{d}_a + \rho_a \hat{\mathbf{F}}_a, \\ \mathbf{d}_a &= \nabla \left( \frac{n_a}{n} \right) + \left( \frac{n_a}{n} - \frac{\rho_a}{\rho} \right) \nabla \ln p + \frac{\rho_a}{p} (\hat{\mathbf{F}} - \hat{\mathbf{F}}_a). \end{aligned} \quad (8.100)$$

If volume transport processes are taken into account, the driving forces in the kinematic terms would involve the thermodynamic forces (gradients) driving volume transport.

In Table 8.1,

$$\bar{h}_{ja}^{(q)} = \delta(\mathbf{r}_{ja} - \mathbf{r}) h_{ja}^{(q)} \quad (q \geq 1)$$

and the collision bracket integrals  $\mathfrak{R}_{ab}^{(pq)}$  are given in terms of the collision operator  $\mathbf{T}(z)$  in the expressions for the linear transport coefficients of simple dense fluid mixtures in the ensemble kinetic theory:

$$\mathfrak{R}_{ab}^{(pq)} = \int dx^{(N)} f_{\text{eq}}^{(N)}(x^{(N)}) \sum_{ja, ka=1}^N \delta(\mathbf{r}_{ja} - \mathbf{r}) h_{ja}^{(p)} \odot i \mathbf{T}^{(N)}(z) h_{kb}^{(q)}. \quad (8.101)$$

**Table 8.1** Collision bracket integrals for linear constitutive equations

Type	CBI	Kinetic theory formula
Shear viscosity	$\mathfrak{R}_{ab}^{(11)}$	$\frac{1}{5} \beta^2 \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \langle -\bar{h}_{ja}^{(1)} : h_{kb}^{(1)} \rangle_c$
Bulk viscosity	$\mathfrak{R}_{ab}^{(22)}$	$\beta^2 \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \langle -\bar{h}_{ja}^{(2)} h_{kb}^{(2)} \rangle_c$
Heat conductivity	$\mathfrak{R}_{ab}^{(33)}$	$\frac{1}{3} \beta^2 \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \langle -\bar{h}_{ja}^{(3)} \cdot h_{kb}^{(3)} \rangle_c$
Thermal diffusion	$\mathfrak{R}_{ab}^{(34)}$	$\frac{1}{3} \beta^2 \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \langle -\bar{h}_{ja}^{(3)} \cdot h_{kb}^{(4)} \rangle_c$
Thermal diffusion	$\mathfrak{R}_{ab}^{(43)}$	$\frac{1}{3} \beta^2 \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \langle -\bar{h}_{ja}^{(4)} \cdot h_{kb}^{(3)} \rangle_c$
Mass diffusion	$\mathfrak{R}_{ab}^{(44)}$	$\frac{1}{3} \beta^2 \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \langle -\bar{h}_{ja}^{(4)} \cdot h_{kb}^{(4)} \rangle_c$

In (8.101)  $h_{ja}^{(p)}$  and  $h_{kb}^{(q)}$  are the molecular moments for particle  $ja$  or  $kb$  for processes  $p$  and  $q$  ( $p, q \geq 0$ ), respectively, and their molecular expressions are given in Chap. 5. According to the results given in the previous section of this chapter the collision bracket integrals  $\mathfrak{R}_{ab}^{(pq)}$  are expressible<sup>8</sup> in a form of time correlation function

$$\mathfrak{R}_{ab}^{(pq)} = -\frac{1}{\tau_c} \sum_{ja,ka=1}^N \left\langle \Delta g_{ja}^{(p)}(\tau_c) | g_{kb}^{(q)} \right\rangle_c, \quad (8.102)$$

where

$$g_{ja}^{(p)} = h_{ja}^{(p)}(x) f_{eq}^{1/2}, \quad (8.103)$$

if the procedure is followed as made use of subsequent to (8.75) leading to (8.89).

In the following we explicitly show various linear transport coefficients expressed in terms of  $\mathfrak{R}_{ab}^{(pq)}$ . In the absence of volume transport phenomena the moments  $h_{ja}^{(q)}$  are defined in the same order as in Chap. 5 of this monograph. The leading nonconservative moments are summarized below:

### 1. Shear viscosity

$$h_{ja}^{(1)} \delta(\mathbf{r}_{ja} - \mathbf{r}) = m_a [\mathbf{C}_{ja} \mathbf{C}_{ja}]^{(2)} \delta(\mathbf{r}_{ja} - \mathbf{r}). \quad (8.104)$$

### 2. Bulk viscosity

$$h_{ja}^{(2)} \delta(\mathbf{r}_{ja} - \mathbf{r}) = \frac{1}{3} m_a \text{Tr} \mathbf{C}_{ja} \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}). \quad (8.105)$$

### 3. Heat flux

$$h_{ja}^{(3)} \delta(\mathbf{r}_{ja} - \mathbf{r}) = \frac{1}{2} m_a C_{ja}^2 \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}). \quad (8.106)$$

### 4. Diffusion flux (mass flux)

$$h_{ja}^{(4)} \delta(\mathbf{r}_{ja} - \mathbf{r}) = m_a \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}). \quad (8.107)$$

Here  $\mathbf{C}_{ja}$  is the peculiar velocity  $\mathbf{C}_{ja} = \mathbf{v}_{ja} - \mathbf{u}$ . It should be recalled that in Chap. 5 the streaming term in the kinetic equation is that of noninteracting molecules. Therefore it is a rather special model taken to illustrate the idea of ensemble theory on the basis of the Boltzmann kinetic theory. The moments listed above can be easily extended to the case of dense interacting fluids as discussed in Chaps. 6 and 7.

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<sup>8</sup>In this form of collision bracket integrals it is understood that the coordinates of  $\mathbf{r}_{ja}$  are transformed relative to the center of gravity  $\mathbf{R}$  of the  $N$  particles and then the integration over  $\mathbf{R}$  is performed to get rid of the Diract delta function. This procedure puts the integrand in terms of the relative distance  $\xi_{ja} = \mathbf{r}_{ja} - \mathbf{R}$ .

We now discuss the general procedure of extracting the transport coefficients in terms of the collision bracket integrals from the coupled linear constitutive equations (8.97). The coupled linear constitutive equations are solved for  $\Phi_b^{(s)}$ . On comparison of the solution for  $\Phi_b^{(s)}$  with the phenomenological constitutive relations we are able to identify the molecular representations for the linear transport coefficients. In implementing this solution procedure we make use of the Curie principle [34], according to which we find only the linear relations of fluxes  $\Phi_b^{(s)}$  of same tensorial rank are coupled with each other. Thus the linear equations of different tensorial ranks can be separated out. This means that shear tensor equations can be separated out from the vectorial flux equations and the scalar flux equations such as for the normal stress differences, which do not get coupled with either of shear tensor and vectorial equations. Since we have already discussed this aspect in previous chapters, the reader should recall the general idea.

### 8.6.2 Shear Viscosity

In the case of shear stresses, (8.97) becomes

$$\sum_{b=1}^r \mathfrak{R}_{ab}^{(11)} \Phi_b^{(1)} = -2\beta g g_a^{(1)} p_a [\nabla \mathbf{u}]^{(2)}, \quad (8.108)$$

which is readily solved. The solution may be put in a form comparable with the phenomenological theory formula

$$\Phi_a^{(1)} = -2\eta_a^0 [\nabla \mathbf{u}]^{(2)}, \quad (8.109)$$

where the phenomenological shear viscosity  $\eta_a^0$  is now identified with the statistical mechanical formula

$$\eta_a^0 = \beta g \sum_{b=1}^r (\mathfrak{R}^{(11)})_{ab}^{-1} g_b^{(1)} p_b. \quad (8.110)$$

This may be regarded as the partial shear viscosity of species  $a$  in the mixture. The symbol  $(\mathfrak{R}^{(11)})$  stands for the  $(r \times r)$  square matrix consisting of collision bracket integrals  $\mathfrak{R}_{ab}^{(11)}$ .

In the conventional experiment based on a fluid dynamic method, shear viscosities of species components in a mixture are usually not measured separately. The principal reason for this is that it is difficult to measure them independently. Therefore, to obtain a theoretical shear viscosity of a mixture in a molecular theory approach we must first calculate the constitutive equations for the shear stress tensors for each species and then sum them over species contributions to obtain the total shear stress tensor before deducing the shear viscosity of the mixture. The shear viscosity for the solution may be calculated from the sum of partial viscosities [26]:

$$\eta_0 = \sum_{a=1}^r \eta_a^0 = \beta g \sum_{a,b=1}^r (\mathfrak{R}^{(11)})_{ab}^{-1} g_b^{(1)} p_b. \quad (8.111)$$

According to the analysis made in Sect. 5 of this chapter, the collision bracket integral  $\mathfrak{R}^{(11)}$  on the right can be expressed in the alternative form

$$\mathfrak{R}^{(11)} = \tau_c^{-1} \int_0^\infty ds \langle \Delta h(s\tau_c) | \Delta h(s\tau_c) \rangle_c, \quad (8.112)$$

$$\Delta h(s\tau_c) = \sum_j \left[ h_j^{(1)}(s\tau_c) - h_j^{(1)}(0) \right]^{(2)}. \quad (8.113)$$

where  $[A]^{(2)}$  denotes the traceless symmetric part of rank 2 tensor  $\left[ h_j^{(1)}(s\tau_c) - h_j^{(1)}(0) \right]$  with  $h_j^{(1)}$  presented in (8.104); see the previous section. Separating the center of mass part of  $d\mathbf{x}^{(N)}$  so that  $d\mathbf{x}^{(N)} = d\mathbf{r}d\mathbf{P}d\mathbf{x}^{(N/c)}$  where  $\mathbf{x}^{(N)}$  is the phase vector of  $N$  particles and  $\mathbf{x}^{(N/c)}$  the phase vector relative to the center of mass phase vector  $(\mathbf{r}, \mathbf{P})$ , the integrand  $\langle \Delta h(s\tau_c) | \Delta h(s\tau_c) \rangle_c$  in (8.112) can be cast into the form

$$\langle \Delta h(s\tau_c) | \Delta h(s\tau_c) \rangle_c = \int d\mathbf{P} \int d\mathbf{x}^{(N/c)} f_{\text{eq}}^{(N/c)}(\mathbf{x}^{(N/c)}) \Delta h(s\tau_c) : \Delta h(s\tau_c), \quad (8.114)$$

where  $f_{\text{eq}}^{(N/c)}$  is the equilibrium distribution function excluding the center of mass motion part of the  $N$  particles. This is in a form similar to the Chapman–Enskog collision bracket integral of dilute gases. Thus the viscosity of the dense fluid is inversely proportional to the collision bracket integral in a form analogous to the transport coefficients of dilute gases in the Boltzmann kinetic theory, but not exactly the same as the Chapman–Enskog form.

### 8.6.3 Bulk Viscosity

The statistical mechanical formula for bulk viscosity  $\eta_B^0$  can be obtained if the phenomenological constitutive equation

$$\Delta = -\eta_B^0 \nabla \cdot \mathbf{u}, \quad (8.115)$$

is compared with the kinetic theory formula. Since (8.115) may be decomposed into components

$$\Delta_a = \Phi_a^{(2)} = -\eta_B^0 \nabla \cdot \mathbf{u}, \quad (8.116)$$

on comparing it with the solution of coupled constitutive relations (8.97) for the case of  $q = 2$  we find the bulk viscosity in terms of collision bracket integrals:

$$\eta_{Ba}^0 = 2\beta g \sum_{b=1}^r (\mathfrak{R}^{(22)-1})_{ab} g_b^{(2)} p_b \quad (8.117)$$

and hence the bulk viscosity formula for the mixture

$$\eta_B^0 = \sum_{a=1}^r \eta_{Ba}^0 = 2\beta g \sum_{a,b=1}^r (\mathfrak{R}^{(22)-1})_{ab} g_b^{(2)} p_b. \quad (8.118)$$

The collision bracket integrals in (8.117) are expressible in the form given in (8.102) for which we have

$$g_{ja}^{(2)} = h_{ja}^{(2)}(x) f_{\text{eq}}^{1/2} \quad (8.119)$$

or more precisely

$$\mathfrak{R}^{(22)} = \tau_c^{-1} \int_0^\infty ds \langle \Delta h(s\tau_c) | \Delta h(s\tau_c) \rangle_c \quad (8.120)$$

with  $\Delta h(s\tau_c)$  given by.

$$\Delta h(s\tau_c) = \sum_j \left[ h_j^{(2)}(s\tau_c) - h_j^{(2)}(0) \right]. \quad (8.121)$$

This collision bracket integral can be further analyzed in a manner similar for (8.114). The analysis is left to the reader as an exercise.

### 8.6.4 Thermal Conductivity, Thermal Diffusion, and Mass Diffusion

Heat fluxes are coupled to mass diffusion fluxes simultaneously occurring in the mixture either directly caused by a driving force applied to the system or induced indirectly. In such a case, the kinematic terms generally are composed of temperature or concentration or density gradients as given in (8.100), and the dissipation terms also are given in linear combinations of heat and mass fluxes. This situation therefore requires solving coupled constitutive equations<sup>9</sup>

<sup>9</sup>In the case of mixtures, diffusion fluxes are not all independent, since the condition

$$\sum_{a=1}^r \Phi_a^{(4)} = \sum_{a=1}^r \mathbf{J}_a = 0$$

must hold for diffusion fluxes. Therefore one diffusion flux, say,  $\mathbf{J}_r$ , is dependent on  $(r-1)$  diffusion fluxes. If the dependent diffusion flux is eliminated from the constitutive equations, the

$$\mathcal{Z}_a^{(3)} - (\beta g g_a^{(3)})^{-1} \sum_{b=1} \sum_{s=3,4} \mathfrak{R}_{ab}^{(3s)} \Phi_b^{(s)} = 0, \quad (8.122)$$

$$\mathcal{Z}_a^{(4)} - (\beta g g_a^{(4)})^{-1} \sum_{b=1} \sum_{s=3,4} \mathfrak{R}_{ab}^{(4s)} \Phi_b^{(s)} = 0, \quad (8.123)$$

where both  $\mathcal{Z}_a^{(3)}$  and  $\mathcal{Z}_a^{(4)}$  are given in (8.100). Let us construct the supermatrix  $\mathbb{R}$  made up of  $\mathfrak{R}_{ab}^{(3s)}$  and  $\mathfrak{R}_{ab}^{(4s)}$  as well as their coupling matrices  $\mathfrak{R}_{ab}^{(34)}$  and  $\mathfrak{R}_{ab}^{(43)}$ :

$$\mathbb{R} = \begin{pmatrix} \mathfrak{R}^{(33)} & \mathfrak{R}^{(34)} \\ \mathfrak{R}^{(43)} & \mathfrak{R}^{(44)} \end{pmatrix} \quad (8.124)$$

and supercolumn vector

$$\Phi = \begin{pmatrix} \Phi^{(3)} \\ \Phi^{(4)} \end{pmatrix}, \quad (8.125)$$

where  $\Phi^{(3)} := (\Phi_a^{(3)}, \dots, \Phi_r^{(3)})$  and  $\Phi^{(4)} := (\Phi_a^{(4)}, \dots, \Phi_r^{(4)})$ , column vectors spanned by species components. Then the solutions to the coupled set (8.122) and (8.123) may be written in the forms

$$\Phi_a^{(3)} = \beta g g_a^{(3)} \sum_{b=1}^r (\mathbb{R}^{-1})_{ab}^{(33)} \mathcal{Z}_b^{(3)} + \beta g g_a^{(3)} \sum_{b=1}^{r-1} (\mathbb{R}^{-1})_{ab}^{(34)} \mathcal{Z}_b^{(4)}, \quad (8.126)$$

$$\Phi_a^{(4)} = \beta g g_a^{(4)} \sum_{b=1}^{r-1} (\mathbb{R}^{-1})_{ab}^{(43)} \mathcal{Z}_b^{(3)} + \beta g g_a^{(4)} \sum_{b=1}^{r-1} (\mathbb{R}^{-1})_{ab}^{(44)} \mathcal{Z}_b^{(4)}, \quad (8.127)$$

where, for example,  $(\mathbb{R}^{-1})_{ab}^{(33)}$  stands for the  $(a, b)$  element in the  $(3, 3)$  block of the inverse  $\mathbb{R}^{-1}$ . If the heat flux is measured for the entire mixture, but not each component, the thermal conductivity of the mixture is obtained upon summing (8.126)

$$\mathbf{Q} = \sum_{a=1}^r \Phi_a^{(3)} = -\lambda^0 \nabla \ln T - \beta g \sum_{a=1}^r \sum_{b=1}^r g_a^{(3)} (\mathbb{R}^{-1})_{ab}^{(34)} (p \mathbf{d}_b - \rho_b \widehat{\mathbf{F}}_b), \quad (8.128)$$

where the thermal conductivity  $\lambda^0$  is identified with the statistical mechanical formula

$$\lambda^0 = \beta T g \sum_{a,b=1}^r g_a^{(3)} (\mathbb{R}^{-1})_{ab}^{(33)} \widehat{C}_{pb} p_b. \quad (8.129)$$

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(Footnote 9 continued)

collision bracket integrals  $\mathfrak{R}_{ab}^{(34)}$ ,  $\mathfrak{R}_{ab}^{(43)}$  and  $\mathfrak{R}_{ab}^{(44)}$  are modified. For modifications, see Chap. 9. Here we are assuming that the collision bracket integrals have been appropriately modified.

The thermodiffusion coefficients  $L_{ab}$  may be defined in the form

$$L_{ab}^{(34)} = \beta g g_a^{(3)} (\mathbb{R}^{-1})_{ab}^{(34)} \quad (8.130)$$

by the second group of the terms on the right of (8.129). Similarly, the mass diffusion coefficients  $D_{ab}$  can be identified with the coefficient of the thermodynamic force  $p\mathbf{d}_b - \rho_b \hat{\mathbf{F}}_b$

$$D_{ab} = \beta g g_a^{(4)} (\mathbb{R}^{-1})_{ab}^{(44)}. \quad (8.131)$$

It can be shown that the reciprocal relations are satisfied by the collision bracket integrals in the form

$$g_a^{(3)} (\mathbb{R}^{-1})_{ab}^{(34)} = g_a^{(4)} (\mathbb{R}^{-1})_{ab}^{(43)}. \quad (8.132)$$

The collision bracket integrals in the expressions above are given by the time-correlation-like forms in (8.102) and (8.103) with upper index for  $h_j^{(p)}(s\tau_c)$  chosen appropriately. They are again time correlation-like integrals similar to (8.112) and (8.120), which can be cast to forms reminiscent of the first-order Chapman–Enskog theory formulas for collision bracket integrals similar to (8.114). We refrain from writing them out to avoid the appearance of repetition and leave them to the reader for exercise.

The two-particle example can be shown to give rise to the traditional Chapman–Enskog theory result for dilute monatomic gases. We have also presented a three-particle collision bracket integral in the case of dilute gases where there is no statistical correlation. The alternative forms of the collision bracket integral present a possibility of developing a new way (i.e., computer simulation methods) of computing many-particle collision bracket integrals on a computer.

With the investigation presented above, we now have acquired a set of formulas with which to compute numerically the transport coefficients appearing in the kinetic theory; their expressions are formally comparable to those of the linear response theory, but their numerical simulation methods also might be similarly implemented as for the time autocorrelation functions. In fact, they should be amenable to Monte Carlo simulation method [2]. This would be in contrast to the time autocorrelation functions of the linear response theory which require a molecular dynamic simulation method.

## 8.7 Concluding Remarks

In this Chapter, we have revisited the eigenvalue problem of the Liouville operator in the context of kinetic theory. We have shown a general and, perhaps, simpler way of obtaining the eigenfunctions of the Liouville operator than the previously reported method [12]. The eigenfunctions obtained enable us to consider formal classical scattering theory of particles in a mathematically precise manner. An important point

realized in this investigation is that the classical scattering involves waves propagating perpendicularly to the characteristic function  $W$  with phases given by (8.32) and occurs on the shell of a fixed eigenvalue which is shared by both the incident and scattered waves in the phase space. By using this latter notion in the calculation of the collision bracket integrals appearing in kinetic theory of dense gases and liquids it is possible to recast the collision bracket integrals in terms of time correlation functions reminiscent of time correlation functions in the linear response theory, but distinctively different from those in the latter theory. The two-particle example is shown to give rise to the traditional Chapman-Enskog theory result for dilute monatomic gases. We have also presented a three-particle collision bracket integral in the case of dilute gases where there is no statistical correlation present. The recast forms for the collision bracket integral appear to be more suitable for numerical computation on a computer than the forms given in terms of the classical collision operator, which is otherwise difficult to compute numerically. The alternative forms of the collision bracket integral seems to offer a new avenue of approach to compute many-particle collision bracket integrals on a computer and quantitatively study transport processes and attendant hydrodynamic processes in dense fluids or liquids with no further approximations on the dynamics of many particles.

The fact that the eigenfunctions can be expressed in action integrals of the Lagrangian of the system presents an intriguing possibility for computationally tackling dynamical problems of classical many-particle systems in a manner parallel to the Feynman path integral theory for quantum systems. Since the classical dynamic collision operator formalism, especially, for nonequilibrium processes in condensed phases appears to be quite difficult to implement computationally, the action integral formalism based on the eigenfunctions of Liouville operators seems to offer a way to resolve the difficulty inherent to the classical theory of many-particle systems. Here we unfortunately have to pass on the tantalizing possibility merely having had a glimpse of it, but hoping it would be taken up by another researcher in the future.

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# Chapter 9

## Generalized Hydrodynamics and Transport Processes

The generalized hydrodynamic equations derived from various kinetic equations for nonequilibrium ensembles in the previous chapters are capable of describing transport processes and hydrodynamic phenomena in fluids. They can describe transport processes occurring in states far removed from equilibrium under fairly steep flow gradients and high external force fields. Applications of the generalized hydrodynamic theory have been made in the literature to study rarefied gas dynamic flows [1], shock waves [2], rheological flows [3] in high shear fields, and charge carrier mobility and conductance [4] under steep electric field gradients. Since such applications have been discussed in the previous monographs [5, 6] and reviewed in the literature by the present author [7, 8], we do not wish to repeat them here. But there are some recent works by other authors on applications of generalized hydrodynamics. We would like to discuss them in this chapter. In any case, it will be of interest to the reader to show the conditions and the limits under which the generalized hydrodynamic equations reduce to the conventional Navier–Stokes–Fourier hydrodynamics [9, 10] as a benchmark and guide to apply the present formalism of generalized hydrodynamics to flow problems for which the classical theory becomes theoretically ineffective. For this purpose in mind the generalized hydrodynamic equations are collected for mixtures when generalized potentials  $X_a^{(q)}$  are approximated by forms proportional to fluxes (nonconserved variables)  $\Phi_a^{(q)}$  ( $1 \leq a \leq r$ ;  $q \geq 0$ ) and the first-order cumulant approximation is used for the dissipation terms  $\Lambda_a^{(q)}$ . We find that this combination of approximations well describes diverse nonlinear flow problems, which the classical Navier–Stokes–Fourier hydrodynamic theory is incapable of describing accurately. One may take the generalized hydrodynamic equations in the aforementioned approximations as a model for treating flows removed far from equilibrium. For flow problems they fail to describe accurately one may then, at least, have the direction in which to look for improvement by taking higher order approximations for the generalized potentials and dissipation terms beyond the level of approximations mentioned.

Since hydrodynamic flows can be generally characterized by various fluid dynamic numbers such as Reynolds, Mach, Knudsen numbers, etc., it will be useful to cast the generalized hydrodynamic equations in reduced variables appropriately defined. For this reason we will first recast the generalized hydrodynamic equations used in this chapter into dimensionless reduced forms by scaling them with appropriately chosen reference variables. Such reduced forms of equations would also naturally indicate in which limit of the fluid dynamic numbers the generalized hydrodynamic equations approach the classical hydrodynamic equations of Navier, Stokes, and Fourier. In contrast to the classical hydrodynamic equations being parabolic, the generalized hydrodynamic equations will be generally found to be hyperbolic. In any case, the dimensionless reduced equations will help to devise suitable approximations for the generalized hydrodynamic equations.

## 9.1 Generalized Hydrodynamics for Dilute Gases

The generalized hydrodynamic equations are simpler for dilute gases than for liquids, for which they contain various extra terms arising from molecular interactions in liquids. Therefore we will first discuss them for gases and then for liquids in which case the volume transport phenomena will be also included. The volume transport phenomena become necessary to include in hydrodynamic equations as the specific volume gets increasingly different from the molar volume or the volume of the domain characteristic to a molecule in condensed phase, as the density of the fluid becomes denser. In such a range of density, we find the molar volume may be most appropriately represented by the Voronoi volume.

As we have seen in Chaps. 6 and 7, inclusion of volume transport phenomena in the hydrodynamic description of flow not only increases the complexity of the formalism, but also raises the question of the limit of validity of the conventional hydrodynamic description without volume transport phenomena taken into account. For this reason it would be appropriate to compare the two hydrodynamic equations. It thus would be worthwhile to expend a little more space in this monograph to have them as a separate section in this chapter.

We have formulated the generalized hydrodynamic equations in Chaps. 3 and 4 for dilute gases and in Chap. 5 for moderately dense gases, which we find formally identical except for the details of their dissipation terms. The difference in collision dynamics results in different dissipation terms in the two cases of dilute gases and moderately dense gases, since the kinetic theory of moderately dense gases requires multiple collisions between the molecules in the gas. This difference in turn results in the linear transport coefficients, which are density-independent in the case of a dilute gas, but density-dependent if the gas becomes moderately dense. Therefore for gases it would be sufficient to carry on discussion with the generalized hydrodynamic equations derived for the former, because for the case of moderately dense gases the theory can be made applicable by simply replacing the linear transport coefficients with appropriate density-dependent ones. For liquids discussed in Chaps. 6 and 7,

since the generalized hydrodynamic equations contain a new feature not seen in the macroscopic theory of gases—namely, volume transport phenomena—a separate section will be devoted for a summary and discussion.

With the generalized potentials  $X_a^{(q)}$  approximated to linear order in fluxes  $\Phi_a^{(q)}$  and the dissipation terms  $\Lambda_a^{(q)}$  calculated in the first-order cumulant approximation, the generalized hydrodynamic equations are collected in the following sections.

### 9.1.1 Conservation Laws

Mass, momentum, and energy conservation laws are described by the following balance equations:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot [\rho \mathbf{u}(\mathbf{r}, t)] \quad \text{or} \quad \rho \frac{dv}{dt} = \nabla \cdot \mathbf{u}(\mathbf{r}, t), \quad (9.1)$$

$$\rho \frac{dc_a}{dt} = -\nabla \cdot \mathbf{J}_a(\mathbf{r}, t) \quad (c_a = \rho_a / \rho), \quad (9.2)$$

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla \cdot \mathbf{P}(\mathbf{r}, t) + \rho \widehat{\mathbf{F}}, \quad (9.3)$$

$$\rho \frac{d\mathcal{E}}{dt} = -\nabla \cdot \mathbf{Q}(\mathbf{r}, t) - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \widehat{\mathbf{F}}_a. \quad (9.4)$$

The variables  $\rho$ ,  $c_a$ ,  $\mathbf{u}$ , and  $\mathcal{E}$  are examples of conserved variables obeying conservation laws. They are conserved over the course of molecular collision processes. The first equation of the set is the mass balance equation—equation of continuity—or its alternative version in terms of specific volume  $v = 1/\rho$ ; the second is the mass fraction balance equation; the third is the momentum balance equation—momentum conservation law; and the fourth is the internal energy balance equation—simply, the energy balance equation, respectively. It should be noted that in the case of non-reacting fluids the dissipation term is absent in the mass fraction balance equation.<sup>1</sup> Notice also that these balance equations for conserved variables cannot describe the flow problems by themselves because they contain diffusion flux  $\mathbf{J}_a$ , pressure tensor  $\mathbf{P}$ , and heat flux  $\mathbf{Q}$ , whose evolution equations, or constitutive relations, must be supplied. The aforementioned observables  $\mathbf{J}_a$ ,  $\mathbf{P}$ , and  $\mathbf{Q}$  are examples of nonconserved variables. They are called so because unlike the conserved variables their evolutions do not conserve them over the course of molecular collisions progressing in the system, but they evolve at the expense of energy. Consequently, energy is dissipated through the dissipation terms in the evolution equations in the course of their evolution.

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<sup>1</sup>If the fluid is chemically reactive, there appears a dissipation term representing reaction rates in (9.2). See Chap. 2 for the phenomenological treatment of chemical reacting fluids.

### 9.1.2 Evolution Equations for Nonconserved Variables

There could be a denumerably infinite number of nonconserved variables. The nonconserved variables are observables that should be amenable to macroscopic measurement together with the conserved variables in the laboratory. Since experiment can be performed on finite number of observables only, a relatively small number of nonconserved variables are experimentally accessible and available for observations in practice. In this sense, hydrodynamic description of transport processes in the system of matter is anthropomorphic and in essence approximate. The selected nonconserved variables for dilute gases of  $r$  components in the absence of volume transport will be denoted by  $\Phi_a^{(q)}$  ( $1 \leq a \leq r; q \geq 1$ ) and ordered in the following sequence:

$$\begin{aligned}\Phi_a^{(1)} &:= \mathbf{\Pi}_a = [\mathbf{P}_a]^{(2)}; & \Phi_a^{(2)} &:= \Delta_a = \frac{1}{3} \text{Tr} \mathbf{P}_a - p_a; \\ \Phi_a^{(3)} &:= \mathbf{Q}'_a = \mathbf{Q}_a - \widehat{h}_a \mathbf{J}_a; & \Phi_a^{(4)} &:= \mathbf{J}_a; \quad \text{etc.,}\end{aligned}\quad (9.5)$$

where  $p_a$  denotes the hydrostatic pressure;  $\widehat{h}_a$  is the enthalpy density per unit mass of species  $a$ ; and the symbol  $[\mathbf{P}_a]^{(2)}$  stands for the traceless symmetric part; and  $\Delta_a$  for excess trace part of the pressure tensor  $\mathbf{P}_a$ . The generic form of evolution equation may be written as

$$\rho \frac{d\widehat{\Phi}_a^{(q)}}{dt} = -\nabla \cdot \psi_a^{(q)} + \mathcal{Z}_a^{(q)} + \Lambda_a^{(q)}, \quad (9.6)$$

where  $\widehat{\Phi}_a^{(q)} = \Phi_a^{(q)}/\rho$  is the density of  $\Phi_a^{(q)}$ , and  $\psi_a^{(q)}$  is, generally, given by a tensor one-order higher than the rank of tensor  $\Phi_a^{(q)}$ . For a dilute monatomic gas  $\psi_a^{(q)}$  ( $q = 1, \dots, 4$ ) are defined by the statistical mechanical formulas

$$\psi_a^{(1)} = \langle m_a \mathbf{C}_a [\mathbf{C}_a \mathbf{C}_a]^{(2)} f_a \rangle, \quad (9.7)$$

$$\psi_a^{(2)} = \frac{2}{3} \mathbf{Q}_a - p_a v_a \mathbf{J}_a, \quad (9.8)$$

$$\psi_a^{(3)} = \left\langle \frac{1}{2} m_a C_a^2 \mathbf{C}_a \mathbf{C}_a f_a \right\rangle - \widehat{h}_a \mathbf{P}_a, \quad (9.9)$$

$$\psi_a^{(4)} = \mathbf{P}_a. \quad (9.10)$$

The dissipation terms  $\Lambda_a^{(q)}$  are in general given by the formula

$$\Lambda^{(q)} = \left\langle \sum_{i=1}^N h_i^{(q)} \delta(\mathbf{r}_i - \mathbf{r}) \mathfrak{R}[\mathbb{F}^{-(\mathcal{N})}(x^{(\mathcal{N})}, t)] \right\rangle \quad (9.11)$$

in terms of the collision integral  $\mathfrak{R}[\mathbb{F}^{-(\mathcal{N})}]$ . In the case of dilute gases considered here  $\mathfrak{R}[\mathbb{F}^{-(\mathcal{N})}]$  should be replaced with either the Boltzmann collision integral (Chap. 3)

or its extended version for moderately dense gases (Chap. 5). With the linear approximation for the generalized potentials  $X_a^{(q)}$

$$X_a^{(s)} = -g_a^{(s)} \Phi_a^{(s)}, \quad (9.12)$$

where  $g_a^{(s)}$  is a scalar function of conserved variables defined in previous chapters, the dissipation term  $\Lambda_a^{(q)}$  in the first-order cumulant approximation is given by the formula

$$\Lambda_a^{(q)} = -(\beta g g_a^{(q)})^{-1} \sum_{b=1}^r \sum_{s \geq 1} \mathfrak{R}_{ab}^{(qs)} \Phi_a^{(s)} (\sinh \kappa / \kappa). \quad (9.13)$$

In this expression the dissipation function  $\kappa$  is given by statistical mechanical formula

$$\kappa = \sqrt{\sum_{a,b=1}^r \sum_{q,s \geq 1} \mathfrak{R}_{ab}^{(qs)} \Phi_a^{(q)} \odot \Phi_b^{(s)}}. \quad (9.14)$$

The symbol  $\odot$  stands for contraction of tensors or vectors to a scalar. The quadratic form of  $\Phi_a^{(q)}$  in (9.14) is, in essence, a generalization of the Rayleigh dissipation function [11] and the coefficients  $\mathfrak{R}_{ab}^{(qs)}$  for both gases and liquids are defined by

$$\mathfrak{R}_{ab}^{(qs)} = g_a^{(q)} \mathbb{R}_{ab}^{(qs)} g_b^{(q)}. \quad (9.15)$$

Here  $\mathbb{R}_{ab}^{(qs)}$  are the collision bracket integrals given in terms of the Boltzmann collision integral or its moderately dense gas version given in terms of the extended Boltz-

$-\langle \mathcal{N} \rangle$ mann collision integral or  $\mathfrak{R}[\mathbb{F}]$  for the extended Boltzmann collision integral for gases; see Chaps. 3 and 5. For liquids the collision integral stands for the generalized Boltzmann integrals; see Chaps. 6 and 7 for their details. It should be recalled that the Rayleigh dissipation function is related to the Boltzmann or extended Boltzmann or generalized Boltzmann collision integral in the kinetic theory. In the phenomenological theory of irreversible processes [12] and hydrodynamics [9, 10]  $\mathfrak{R}_{ab}^{(qs)}$  may be taken as phenomenological coefficients. The coefficients  $\mathfrak{R}_{ab}^{(qs)}$  are tensors, vectors, or scalars and obey the Onsager reciprocal relations [12, 13]. Thus  $\mathfrak{R}_{ab}^{(qs)} = \mathfrak{R}_{ba}^{(sq)}$  or  $\mathfrak{R}_{ab}^{(qs)} = \mathfrak{R}_{ba}^{(qs)}$  for tensors or vectors or scalars belonging to the same rank. Since the collision bracket integrals will be seen related to linear transport coefficients, they may be replaced by the latter as will be shown later.

The kinematic terms  $\mathcal{Z}_a^{(q)}$  for the leading nonconserved variables for gases listed in (9.5) are given by

$$\begin{aligned} \mathcal{Z}_a^{(1)} &= -2 [(d_t \mathbf{u}) \mathbf{J}_a]^{(2)} - [\widehat{\mathbf{F}}_a \mathbf{J}_a]^{(2)} - 2 [\mathbf{P}_a \cdot \nabla \mathbf{u}]^{(2)}, \\ \mathcal{Z}_a^{(2)} &= p_a d_t \ln \rho_a + \frac{p_a}{\rho_a} \mathbf{J}_a \cdot \nabla \ln \rho_a - \frac{2}{3} (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) \cdot \mathbf{J}_a \end{aligned} \quad (9.16)$$

$$-\frac{2}{3}\mathbf{P}_a \cdot \nabla \mathbf{u}, \quad (9.17)$$

$$\begin{aligned} \mathcal{Z}_a^{(3)} = & - (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) \cdot (\mathbf{P}_a - p_a \boldsymbol{\delta}) - \boldsymbol{\varphi}_a : \nabla \mathbf{u} \\ & - \mathbf{Q}'_a \cdot \nabla \mathbf{u} - \mathbf{J}_a d_t \widehat{h}_a - \mathbf{P}_a \cdot \nabla \widehat{h}_a, \end{aligned} \quad (9.18)$$

$$\mathcal{Z}_a^{(4)} = -\rho_a d_t \mathbf{u} + \rho_a \widehat{\mathbf{F}}_a - \mathbf{J}_a \cdot \nabla \mathbf{u}. \quad (9.19)$$

The pressure tensor  $\mathbf{P}_a$  may be split into traceless symmetric part  $\mathbf{\Pi}_a$ , trace part  $p\boldsymbol{\delta}$ , and asymmetric vorticity part  $\boldsymbol{\omega}$ . But in the present discussion we will assume the vorticity tensor  $\boldsymbol{\omega}$  is absent for the reason that most of flow phenomena we consider are generally satisfied by the assumption because the stress tensor is symmetric in the case of dilute monatomic gases, and dropping it makes the equations simpler. It is, however, simple to restore it, if necessary, at a minor expense of complication. In some applications of the theory shown later, the vorticity tensor is indeed taken into account. The symbol  $\boldsymbol{\varphi}_a^{ijk}$  stands for a tensor of rank 3 defined by the formula

$$\boldsymbol{\varphi}_a = \langle m_a \mathbf{C}_a \mathbf{C}_a \mathbf{C}_a f_a \rangle. \quad (9.20)$$

This quantity may be regarded as a mean flux of stress tensor, more precisely, its kinetic part and similarly for tensor  $\psi_a^{(1)}$ .

If the evolution equations for variables in the manifold  $\mathfrak{P}$  of nonconserved macroscopic variables are limited to the set  $(\mathbf{\Pi}_a, \Delta_a, \mathbf{Q}'_a, \mathbf{J}_a; a = 1, \dots, r)$  by taking the so-called “first 13 moments<sup>2</sup>”, then the evolution equations contain higher-order moments such as  $\psi_a^{(1)}$  and  $\psi_a^{(3)}$ , which are outside the aforementioned chosen set. They must be either set equal to zero or suitably expressed in terms of the chosen set  $(\mathbf{\Pi}_a, \Delta_a, \mathbf{Q}'_a, \mathbf{J}_a)$ . This procedure of truncating the moment set is called the closure.

There is no unique way of implementing the closure. It is usually guided by physical or other (e.g., mathematical) consideration. For example,  $\psi_a^{(1)}$  and  $\psi_a^{(3)}$  may be expandable in a finite number of moments  $\{\Phi_a^{(q)}; q \geq 1\}$ . Furthermore, if the nonequilibrium canonical form  $f_a^c$  approximates the distribution function  $f_a$  and if the expansions for  $\psi_a^{(1)}$  and  $\psi_a^{(3)}$  are included in the exponent of the nonequilibrium canonical form  $f_a^c$ , the expansions in question should render the nonequilibrium canonical form for  $f_a^c$  normalizable.

With this proviso we expand  $\psi_a^{(1)}$  and  $\psi_a^{(3)}$  as follows:

$$\psi_a^{(1)} = \phi_a^{(13)} \Phi_a^{(3)} + \phi_a^{(14)} \Phi_a^{(4)} + \text{higher order in } \Phi_a^{(q)}, \quad (9.21)$$

$$\psi_a^{(3)} = \phi_a^{(31)} \Phi_a^{(1)} + \phi_a^{(32)} \Phi_a^{(2)} \boldsymbol{\delta} - \widehat{h}_a \mathbf{P}_a + \text{higher order in } \Phi_a^{(q)}, \quad (9.22)$$

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<sup>2</sup>It, in fact, should be 13 plus  $3(r-1)$  moments if the independent diffusion fluxes are included. We use this pure fluid terminology for want of a more appropriate terminology, even if the system is a mixture and diffusions are present.

where  $\phi_a^{(13)}$ ,  $\phi_a^{(14)}$ ,  $\phi_a^{(31)}$  and  $\phi_a^{(32)}$  are coefficients depending on  $T$ ,  $c_a$ , and  $\rho$  (or  $p$  through the equation of state) only, which can be obtained explicitly with the local equilibrium distribution function  $f_a^c$ . They are given by the formulas:

$$\begin{aligned}\phi_a^{(13)} &= \frac{9(k_B T)^2}{5} \mathbf{T}^{(4,1)}, & \phi_a^{(14)} &= \frac{2k_B T}{m_a} \mathbf{T}^{(4,1)}, \\ \phi_a^{(31)} &= \frac{7k_B T}{2m_a} \mathbf{T}^{(4,1)}, & \phi_a^{(32)} &= \frac{5k_B T}{m_a} \boldsymbol{\delta},\end{aligned}\quad (9.23)$$

where  $\boldsymbol{\delta}$  is the unit second-rank tensor

$$\boldsymbol{\delta} = (\delta_{ij})$$

and  $\mathbf{T}^{(4,1)}$  is traceless symmetric isotropic fourth-rank tensor [5]

$$\mathbf{T}_{ijkl}^{(4,1)} = \frac{1}{2} (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) - \frac{1}{3} \delta_{ij}\delta_{kl}, \quad (9.24)$$

$\delta_{ij}$  being Kronecker's delta. The higher order moment on the right of (9.21) should then be a tensor of rank 4, whereas the higher order moment on the right of (9.22) should be a tensor of rank 5, owing to the symmetry requirement.

Now approximating  $f_a$  with the nonequilibrium canonical form  $f_a^c$  under the functional hypothesis

$$f_a \approx f_a^c,$$

where the exponent of  $f_a^c$  in its exponential form contains the higher order terms in (9.21) and (9.22). The so-expressed  $f_a^c$  should be normalizable. To meet this essential requirement and at the same time determine the higher order moments in (9.21) and (9.22), we would find sufficient to assume in the evolution equations the closure relations

$$\psi_a^{(1)} = \psi_a^{(3)} = 0. \quad (9.25)$$

These closure relations not only determine the higher order moments in expansions (9.21) and (9.22), but also close the open set of evolution equations for  $\Phi_a^{(q)}$  ( $q = 1, 2, 3, 4$ ). At the same time they also render the nonequilibrium canonical form  $f_a^c$  normalizable [14]. This procedure of closing the open set of evolution equations has been successfully employed for studies of hypersonic shock wave structures [15–17]. We may employ variations of this line of approach to the closure problem for the set of evolution equations for  $\Phi_a^{(q)}$  and particularly for approximating the kinematic terms  $Z_a^{(q)}$  and the divergence terms therein. The kinematic terms for the case of liquids are examined in linearized forms in Sect. 9.3.

The procedure of closure described not only closes the open set of evolution equations, but also ensures the normalizability of the nonequilibrium canonical form taken. In the following we summarize the set of evolution equations for gases in (9.6) so closed as described:

$$\begin{aligned} \rho \frac{d\widehat{\Pi}_a}{dt} = & - \left[ \nabla \left( \frac{9k_B T}{5} \mathbf{Q}'_a \right) \right]^{(2)} - \left[ \nabla \left( \frac{2k_B T}{m_a} \mathbf{J}_a \right) \right]^{(2)} \\ & - 2 [(d_t \mathbf{u}) \mathbf{J}_a]^{(2)} - [\widehat{\mathbf{F}}_a \mathbf{J}_a]^{(2)} - 2 [\mathbf{P}_a \cdot \nabla \mathbf{u}]^{(2)} \\ & - \frac{1}{\beta g g_1^{(1)}} \sum_{b=1}^r \mathfrak{R}_{ab}^{(11)} \Pi_b q_n(\kappa), \end{aligned} \quad (9.26)$$

$$\begin{aligned} \rho \frac{d\widehat{\Delta}_a}{dt} = & - \nabla \cdot \left( \frac{2}{3} \mathbf{Q}_a - p_a v_a \mathbf{J}_a \right) + p_a d_t \ln \rho_a + \frac{p_a}{\rho_a} \mathbf{J}_a \cdot \nabla \ln \rho_a \\ & - \frac{2}{3} (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) \cdot \mathbf{J}_a - \frac{2}{3} \mathbf{P}_a \cdot \nabla \mathbf{u} \\ & - \frac{1}{\beta g g_2^{(2)}} \sum_{b=1}^r \mathfrak{R}_{ab}^{(22)} \Delta_b q_n(\kappa), \end{aligned} \quad (9.27)$$

$$\begin{aligned} \rho \frac{d\widehat{\mathbf{Q}}'_a}{dt} = & - \nabla \cdot \left[ \frac{k_B T}{m_a} \left( \frac{7}{2} \boldsymbol{\Pi}_a : \mathbf{T}^{(4,1)} - \frac{5}{2} \mathbf{P}_{aij} \right) \right] - \nabla \left[ \frac{5(k_B T)}{m_a} \Delta_a \right] \\ & - (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) \cdot (\mathbf{P}_a - p_a \boldsymbol{\delta}) - \mathbf{J}_a d_t \widehat{h}_a - \mathbf{P}_a \cdot \nabla \widehat{h}_a \\ & - \left( \frac{4}{5} \mathbf{Q}'_a + \frac{2k_B T}{m_a} \mathbf{J}_a \right) \cdot \mathbf{T}^{(4,1)} : \nabla \mathbf{u} - \mathbf{Q}'_a \cdot \nabla \mathbf{u} \\ & - \frac{1}{\beta g g_a^{(3)}} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(33)} \mathbf{Q}'_b + \mathfrak{R}_{ab}^{(34)} \mathbf{J}_b \right) q_n(\kappa), \end{aligned} \quad (9.28)$$

$$\begin{aligned} \rho \frac{d\widehat{\mathbf{J}}_a}{dt} = & - \nabla \cdot \mathbf{P}_a - \rho_a d_t \mathbf{u} + \rho_a \widehat{\mathbf{F}}_a - \mathbf{J}_a \cdot \nabla \mathbf{u} \\ & - \frac{1}{\beta g g_a^{(4)}} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(43)} \mathbf{Q}'_b + \mathfrak{R}_{ab}^{(44)} \mathbf{J}_b \right) q_n(\kappa), \end{aligned} \quad (9.29)$$

where  $q_n(\kappa)$  is the nonlinear factor defined by

$$q_n(\kappa) = \frac{\sinh \kappa}{\kappa}. \quad (9.30)$$

Since the diffusion fluxes are not all independent because

$$\sum_{a=1}^r \mathbf{J}_a = 0, \quad (9.31)$$

it is necessary to remove a dependent diffusion flux. We will choose  $\mathbf{J}_r$  as the dependent diffusion flux given by

$$\mathbf{J}_r = - \sum_{a=1}^{r-1} \mathbf{J}_a. \quad (9.32)$$

Replacing  $\mathbf{J}_r$  in (9.28) and (9.29) with (9.32), the evolution equations for  $\mathbf{Q}'_a$  and  $\mathbf{J}_a$  are recast in terms of independent diffusion fluxes only. With the collision bracket integrals appropriately redefined, the evolution equations for nonconserved variables are as follows:

$$\begin{aligned} \rho \frac{d\widehat{\Pi}_a}{dt} = & -\nabla \cdot \psi_a^{(1)} - 2[(d_t \mathbf{u}) \mathbf{J}_a]^{(2)} - [\widehat{\mathbf{F}}_a \mathbf{J}_a]^{(2)} \\ & - 2[\mathbf{P}_a \cdot \nabla \mathbf{u}]^{(2)} - 2p_a \sum_{b=1}^r \mathfrak{B}_{ab} \Pi_b q_n(\kappa), \end{aligned} \quad (9.33)$$

$$\begin{aligned} \rho \frac{d\widehat{\Delta}_a}{dt} = & -\nabla \cdot \left( \frac{2}{3} \mathbf{Q}_a - p_a v_a \mathbf{J}_a \right) + p_a d_t \ln \rho_a + \frac{p_a}{\rho_a} \mathbf{J}_a \cdot \nabla \ln \rho_a \\ & - \frac{2}{3} (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) \cdot \mathbf{J}_a - \frac{2}{3} \mathbf{P}_a \cdot \nabla \mathbf{u} \\ & - \frac{2p_a}{3} \sum_{b=1}^r \mathfrak{V}_{ab} \Delta_b q_n(\kappa), \end{aligned} \quad (9.34)$$

$$\begin{aligned} \rho \frac{d\widehat{\mathbf{Q}}'_a}{dt} = & -\nabla \cdot \psi_a^{(3)} - (d_t \mathbf{u} - \widehat{\mathbf{F}}_a) \cdot (\mathbf{P}_a - p_a \boldsymbol{\delta}) \\ & - \varphi_a \odot \nabla \mathbf{u} - \mathbf{Q}'_a \cdot \nabla \mathbf{u} - \mathbf{J}_a d_t \widehat{h}_a - \mathbf{P}_a \cdot \nabla \widehat{h}_a \\ & - \widehat{C}_{pa} p_a T \left( \sum_{b=1}^r \mathfrak{T}_{ab} \mathbf{Q}'_b + \sum_{b=1}^{r-1} \mathfrak{H}_{ab} \mathbf{J}_b \right) q_n(\kappa), \end{aligned} \quad (9.35)$$

$$\begin{aligned} \rho \frac{d\widehat{\mathbf{J}}_a}{dt} = & -\nabla \cdot [(\Pi_a + \Delta_a) - \mathfrak{c}_a (\boldsymbol{\Pi} + \boldsymbol{\Delta} \boldsymbol{\delta})] \\ & - (\boldsymbol{\Pi} + \boldsymbol{\Delta} \boldsymbol{\delta}) \cdot \nabla \mathfrak{c}_a - \mathbf{J}_a \cdot \nabla \mathbf{u} \\ & - p \mathbf{d}_a - \rho_a \left( \sum_{b=1}^r \mathfrak{K}_{ab} \mathbf{Q}'_b + \sum_{b=1}^{r-1} \mathfrak{D}_{ab} \mathbf{J}_b \right) q_n(\kappa), \end{aligned} \quad (9.36)$$

where the new coefficients are defined by the expressions

$$\begin{aligned} \mathfrak{B}_{ab} &= \frac{\mathfrak{R}_{ab}^{(11)}}{\beta g}, & \mathfrak{V}_{ab} &= \frac{\mathfrak{R}_{ab}^{(22)}}{\beta g}, & \mathfrak{T}_{ab} &= \frac{\mathfrak{R}_{ab}^{(33)}}{\beta g}, \\ \mathfrak{H}_{ab} &= \frac{\mathfrak{R}_{ab}^{(34)} - \mathfrak{R}_{ar}^{(34)}}{\beta g}, & \mathfrak{K}_{ab} &= \frac{\mathfrak{R}_{ab}^{(43)} - \mathfrak{R}_{rb}^{(43)}}{\beta g}, \\ \mathfrak{D}_{ab} &= \frac{\mathfrak{R}_{ab}^{(44)} + \mathfrak{R}_{rr}^{(44)} - \mathfrak{R}_{ar}^{(44)} - \mathfrak{R}_{rb}^{(44)}}{\beta g}; \end{aligned} \quad (9.37)$$

and  $\mathbf{d}_a$  are the thermodynamic force for diffusion —concentration gradient—defined by

$$\mathbf{d}_a = \nabla c_a + \frac{\rho}{p} c_a (\widehat{\mathbf{F}} - \widehat{\mathbf{F}}_a) + (x_a - c_a) \nabla \ln [(x_a - c_a) p] \quad (9.38)$$

with  $x_a = n_a/n$  the mole fraction of species  $a$ . We remark that the thermodynamic force  $\mathbf{d}_a$  in (9.38) is an alternative form for  $\mathbf{d}_a$  defined in (3.270), (5.199), (7.212), respectively, of Chaps. 3, 5, and 7.

$$\mathbf{d}_a = \nabla x_a + \frac{\rho_a}{p} (\widehat{\mathbf{F}} - \widehat{\mathbf{F}}_a) + (x_a - c_a) \nabla \ln p.$$

Expressing  $\mathbf{d}_a$  in terms of mass fraction  $c_a$  instead of mole fraction  $x_a$  is closer to the conventional practice using a concentration unit other than mole fraction. The evolution equations (9.33)–(9.36) together with the conservations laws (9.1)–(9.4) constitute a nonlinear model of generalized hydrodynamics for transport processes in monatomic molecular gas mixtures. It should be noted here that we have kept the terms  $\nabla \cdot \psi_a^{(1)}$  and  $\nabla \cdot \psi_a^{(3)}$  in (9.33) and (9.35) since one may elect to take another manner of implementing closure than discussed earlier. They should be absent if the closure discussed earlier were taken.

With simply setting  $\psi_a^{(1)} = \psi_a^{(3)} = 0$  for closure in (9.33) and (9.35) and linearization with respect to fluxes  $\Phi_a^{(q)}$ , not only can the linear transport processes be studied with (9.33)–(9.36), but also the classical hydrodynamic equations of Navier, Stokes, and Fourier can be recovered from them. It thus shows that the set indeed generalizes the classical hydrodynamics to nonlinear regimes of thermodynamic gradients.

If the evolution equations were made dimensionless by suitably scaling various variables with appropriately chosen reference variables, various approximation methods would present themselves naturally. On scaling the equations in this manner, various well-known dimensionless fluid dynamic numbers appear in the equations, and upon taking suitable limits of the fluid dynamic numbers the evolution equations can be approximated such that, for example, the linear constitutive relations naturally emerge and the classical Navier–Stokes–Fourier–Fick hydrodynamic equations—or simply put, the classical hydrodynamic equations—are recovered from the generalized hydrodynamic equations presented. This would in fact indicate in what manner the present generalized hydrodynamics generalize the classical hydrodynamics, assuring us the appropriateness of the terminology generalized hydrodynamics used this work.

### 9.1.3 Reduced Generalized Hydrodynamic Equations for Gases

For practical applications it is generally convenient to have the equations in non-dimensional forms by scaling variables involved with appropriate reference variables.

**Table 9.1** List of reduced variables and parameters

$\xi = \mathbf{r}L^{-1}$	$\zeta = t\tau_r^{-1}$	$\mathbf{u}^* = \mathbf{u}U_r^{-1}$
$T^* = TT_r^{-1}$	$\rho^* = \rho\rho_r^{-1}$	$\mathcal{E}^* = \mathcal{E}\mathcal{E}_r^{-1}$
$p^* = pp_r^{-1}$	$\eta^* = \eta\eta_r^{-1}$	$\lambda^* = \lambda\lambda_r^{-1}$
$D^* = DD_r^{-1}$	$[\nabla\mathbf{u}]^{(2)*} = [\nabla\mathbf{u}]^{(2)}LU_r^{-1}$	$\omega^* = \omega LU_r^{-1}$
$\Pi_a^* = \Pi_a L(\eta_r U_r)^{-1}$	$\Delta_a^* = \Delta_a L(\eta_{Br} U_r)^{-1}$	$\mathbf{Q}_a^* = \mathbf{Q}_a L(\lambda_r \Delta_r T)^{-1}$
$\mathbf{J}_a^* = \mathbf{J}_a \frac{L}{\mathfrak{D}_r \Delta_r c_r}$	$\mathbf{d}^* = \mathbf{d} \frac{L}{\Delta c_r}$	$\mathfrak{D}_r = D_r \rho_r$

The precise choice of reference variables depends on the flow problem in hand, but the following reduction scheme appears to be generic.

By reduced generalized hydrodynamic equations it is meant the entire set of generalized hydrodynamic equations rendered dimensionless. Such a set will be found useful not only for studying numerical computation methods for practical problems in hydrodynamics, but also for investigating the existing theories of transport processes in the conventional kinetic theories [18, 19] and classical hydrodynamics [9, 10]. We will also find the existing theories are, in fact, possible to recover systematically, if the generalized hydrodynamic equations are taken to an appropriate limit of parameters one way or another. In Table 9.1 dimensionless scaled variables appearing in the theory are summarized. Such scalings naturally give rise to dimensionless reduced variables and a slew of fluid dynamic numbers which will be given in the course of discussion.

### 9.1.3.1 Dimensionless Variables

We will denote the typical geometric length by  $L$  and the reference (e.g., hydrodynamic) time by  $\tau_r$ . Variables subscripted by  $r$  mean the reference variables:

They are denoted by  $U_r$  for hydrodynamic velocity;  $\rho_r$  for density;  $\mathcal{E}_r$  for internal energy;  $p_r$  for pressure;  $\eta_r$  for shear viscosity;  $\lambda_r$  for thermal conductivity;  $D_r$  for diffusion coefficient;  $T_r = \frac{1}{2}(T_1 + T_2)$  for the mean value of temperatures at two typical points in space;  $\Delta_r T = T_2 - T_1$  for the temperature difference between two typical points in space, and  $\Delta c_a = c_{a2} - c_{a1}$  for the typical density fraction difference between two points, and  $\omega = \frac{1}{2}[\nabla\mathbf{u} - (\nabla\mathbf{u})']$ , the rotation tensor or vorticity tensor. Thus the reduced gradient operator will be denoted by  $\nabla^* = \partial/\partial\xi$ .

The diffusion coefficient is defined in the literature [18, 19] on the basis of velocity  $\mathbf{V}_a = \mathbf{u}_a - \mathbf{u}$ , not with  $\mathbf{J}_a = \rho_a \mathbf{V}_a$ , and the thermal conductivity is defined in reference to  $\nabla T$ , not to  $\nabla \ln T$  as in this work. That is,  $\mathbf{Q}_a \sim \lambda_a \nabla \ln T$  and  $\mathbf{J}_a \sim -D_a \rho_a \mathbf{d}_a$  where  $D_a$  is such that  $\mathbf{V}_a = \mathbf{u}_a - \mathbf{u} = -D_a \mathbf{d}_a$ . These points will be elaborated at more appropriate points later, but should be kept in mind to avoid confusion.

With the reference variables used here we can define various dimensionless fluid dynamic numbers appearing in the dimensionless generalized hydrodynamic equations. They are as follows [20]:

$$\begin{aligned}
\text{Mach number: } & N_M = U_r / \sqrt{\gamma_0 \mathcal{R} T_r}, \\
\text{Reynolds number: } & N_{Re} = \rho_r U_r L / \eta_r, \\
\text{Eckert number: } & N_E = U_r^2 / \tilde{C}_{pr} \Delta T_r, \\
\text{Prandtl number: } & N_{Pr} = \tilde{C}_{pr} \eta_r / \lambda_r \\
\text{Knudsen number: } & N_{Kn} = l / L, \\
\text{Schmidt number: } & N_S = \eta_r / \mathfrak{D}_r := \eta_r / D_r \rho_r \\
\text{Critical number: } & N_\delta = \eta_r U_r / p_r L,
\end{aligned}$$

where  $l$  is the mean free path and  $\mathcal{R}$  is the gas constant per mass, and  $\gamma_0$  is the polytropic ratio (ratio of specific heats), i.e.,  $\gamma_0 = \tilde{C}_p / \tilde{C}_v$ .

It should be noted that the Prandtl number is defined without the  $T_r$  factor because  $\lambda_r$  is defined on the basis of  $\nabla T$ , not with regard to  $\nabla \ln T$ . The definition of Prandtl number made here is in contrast to its definition made in Refs. [5, 6]. The critical number  $N_\delta$ , which is a measure of nonlinearity range of flow phenomena, determines the degree of nonlinearity of flow phenomena and in which part of the range the generalized hydrodynamic equations go over to the classical hydrodynamics. This is the reason why it is called the critical number.

Some of these fluid dynamic numbers are not independent of each other, since they are related to others. For example, there holds the relation

$$N_{Re} = \sqrt{\frac{\pi \gamma_0}{2}} \frac{N_M}{N_{Kn}}. \quad (9.39)$$

We find it useful to elaborate on the composite nature of the critical number  $N_\delta$ , since it can be expressed in alternative manners in terms of other fluid dynamic numbers: for example,

$$N_\delta = \gamma_0 N_M^2 N_{Re}^{-1} = \sqrt{\frac{2\pi}{\gamma_0}} N_M N_{Kn}. \quad (9.40)$$

If the stress is examined from the viewpoint of its relaxation time, the critical number  $N_\delta$  may be put in terms of stress relaxation time  $\tau_s$  relative to the hydrodynamic relaxation time to  $\tau_r := \tau_h$ .

Since we may put

$$\frac{\eta_r}{p_r \tau_s} = \frac{\Pi_r}{p_r},$$

the critical number is seen to be of the same order of magnitude as the Weissenberg number  $N_{We}$  appearing in rheology [3]

$$N_\delta = \frac{\eta_r U_r}{p_r L} = \frac{\tau_s}{\tau_h} \sim N_{We},$$

where  $\tau_s$  is the relaxation time for stress which then makes the ratio  $\tau_s / \tau_h$  proportional to  $N_{We}$ .

It should be recalled that the Mach number is traditionally defined by the ratio of  $U_r$  to the sound wave speed  $c_s$

$$N_M = \frac{U_r}{c_s}. \quad (9.41)$$

Since the speed of sound  $c_s$  is given in thermodynamic terms by the formula

$$c_s = \sqrt{\left(\frac{\partial p}{\partial \rho}\right)_S},$$

where  $S$  denotes the equilibrium entropy (i.e., Clausius entropy), and, furthermore, since there holds the thermodynamic relation

$$\left(\frac{\partial p}{\partial \rho}\right)_S = \frac{C_p}{C_v} \left(\frac{\partial p}{\partial \rho}\right)_T = \gamma_0 \left(\frac{\partial p}{\partial \rho}\right)_T,$$

we find the Mach number may be defined by the formula

$$N_M = \frac{U_r}{\sqrt{\gamma_0 \left(\frac{\partial p}{\partial \rho}\right)_T}} = \frac{U_r}{\sqrt{\gamma_0 k_B T_r / m}} = \frac{U_r}{\sqrt{\gamma_0 \mathcal{R} T_r}}.$$

This is the formula for  $N_M$  in the list of fluid dynamic numbers assembled earlier.

There are other dimensionless fluid dynamic numbers characterizing flow problems associated with nonlinear hydrodynamic processes that can be described by the generalized hydrodynamic equations presented. For example, the Deborah number associated with shear flow is defined by the ratio of the characteristic time  $\tau_s$  of stress relaxation to the characteristic time  $\tau_h$  of flow:

$$\begin{aligned} N_{De} &= \frac{\tau_s}{\tau_h} \\ &= \frac{(\eta_r / \Pi_r)}{(L/U_r)} = \frac{(\eta_r U_r / L)}{\Pi_r}, \end{aligned}$$

which gives a measure of deviation of flow from that of Newtonian flow. Another number often used in rheology is the aforementioned Weissenberg number defined as the product of characteristic time for stress and shear rate:

$$N_{We} = \tau_s \frac{U_r}{L}.$$

In fact, this number was introduced to characterize the ratio of the first normal stress difference to the shear stress, indicating the relative importance of the first normal stress difference and shear stress. However, this number may be regarded as a dimensionless shear rate. As shown earlier, since it, in fact, may be written as

$$N_{\text{We}} = \frac{\tau_s}{\tau_h},$$

it may be thought that  $N_{\text{De}}$  and  $N_{\text{We}}$  are related to each other. As mentioned earlier, the Weissenberg number also may be regarded as related to the critical number  $N_\delta$ , which is not necessarily limited to rheological phenomena. It is also useful to define a characteristic number associated with heat flow by taking the ratio of the characteristic time  $\tau_q$  of heat flow to the characteristic time  $\tau_h$  of hydrodynamic flow:

$$N_Q = \frac{\tau_q}{\tau_h} = \frac{(h_r U_r / L^3)}{Q_r},$$

where  $h_r$  is the reference enthalpy. This number is interpretable as the ratio of ballistic heat flow ( $h_r U_r / L^3$ ) to diffusive heat flow.

The dimensionless fluid dynamic numbers presented will be found useful making systematic approximations to the generalized hydrodynamic equations in diverse applications of them to study flow phenomena, as shown in the examples shown in later sections.

### 9.1.3.2 Dimensionless Generalized Hydrodynamic Equations

With the system of reduced variables introduced, the generalized hydrodynamic equations—in the first-order cumulant approximation to the dissipation term, or the calortropy, and the linear approximations to the generalized potentials  $X_a^{(q)}$ , (9.12)—are made dimensionless as follows:

$$\rho^* \frac{dv^*}{d\zeta} = \nabla^* \cdot \mathbf{u}^*, \quad (9.42)$$

$$\frac{N_{\text{Re}} N_S}{\Delta \mathfrak{c}_r} \rho^* \frac{d\mathfrak{c}_a^*}{d\zeta} = -\nabla^* \cdot \mathbf{J}_a^*, \quad (9.43)$$

$$\gamma_0 N_M^2 \rho^* \frac{d\mathbf{u}^*}{d\zeta} = -(\nabla^* p^* - \rho^* \widehat{\mathbf{F}}) - N_\delta (\nabla^* \cdot \boldsymbol{\Pi}^* + \nabla^* \Delta^*), \quad (9.44)$$

$$\begin{aligned} \gamma_0 N_M^2 \rho^* \frac{d\mathcal{E}}{dt} = & - \left( p^* \nabla^* \cdot \mathbf{u}^* - \sum_{a=1}^r \widehat{\mathbf{J}}_a \cdot \mathbf{F}_a \right) - \frac{N_\delta}{N_{\text{Pr}} N_E} \nabla^* \cdot \mathbf{Q}^* \\ & - N_\delta (\boldsymbol{\Pi}^* : \nabla^* \mathbf{u}^* + \Delta^* \nabla^* \cdot \mathbf{u}^*), \end{aligned} \quad (9.45)$$

$$\begin{aligned} N_\delta \rho^* \frac{d\widehat{\mathbf{\Pi}}_a^*}{d\zeta} = & -2p_a^* [\nabla^* \mathbf{u}^*]^{(2)} - 2p_a^* \sum_{b=1}^r \mathfrak{B}_{ab}^* \boldsymbol{\Pi}_b^* q_n(\kappa) \\ & - N_\delta \nabla^* \cdot \psi_a^{(1)*} - 2 \frac{N_\delta \Delta \mathfrak{c}_r}{N_S} \left[ \frac{d\mathbf{u}^*}{d\zeta} \mathbf{J}_a^* \right]^{(2)} \\ & - 2N_\delta \left[ [\boldsymbol{\Pi}_a^* \cdot \nabla^* \mathbf{u}^*]^{(2)} + \Delta_a^* [\nabla^* \mathbf{u}^*]^{(2)} \right] \\ & + \frac{N_\delta \Delta \mathfrak{c}_r}{N_S} [\widehat{\mathbf{F}}_a^* \mathbf{J}_a^*]^{(2)}, \end{aligned} \quad (9.46)$$

$$\begin{aligned}
N_\delta \rho \frac{d\widehat{\Delta}_a^*}{d\zeta} = & -\frac{5}{3} p_a^* \nabla^* \cdot \mathbf{u}^* - \frac{2}{3} p_a^* \sum_{b=1}^r \mathfrak{V}_{ab}^* \Delta_b^* q_n(\kappa) \\
& - \frac{2N_\delta}{3N_{\text{Pr}}N_{\text{E}}} \nabla^* \mathbf{Q}_a^* - \frac{2}{3} N_\delta [(\boldsymbol{\Pi}_a^* + \Delta_a^* \boldsymbol{\delta}) : \nabla^* \mathbf{u}^*] \\
& + \frac{\Delta \mathfrak{c}_r}{N_{\text{Re}}N_{\text{S}}} \left[ \frac{2}{3} \nabla^* \cdot (p_a^* v_a^* \mathbf{J}_a^*) - p_a^* v_a^* \mathbf{J}_a^* \cdot \nabla^* \ln v_a^* \right] \\
& - \frac{2N_\delta \Delta \mathfrak{c}_r}{3N_{\text{S}}} d_\zeta \mathbf{u}^* \cdot \mathbf{J}_a^* + \frac{N_\delta \Delta \mathfrak{c}_r}{N_{\text{S}}} \widehat{\mathbf{F}}_a^* \cdot \mathbf{J}_a^*, \tag{9.47}
\end{aligned}$$

$$\begin{aligned}
\frac{N_\delta}{N_{\text{Pr}}} \rho^* \frac{d\widehat{\mathbf{Q}}_a'^*}{d\zeta} = & -\widehat{C}_{pa}^* P_a^* \nabla^* T^* - \widehat{C}_{pa}^* P_a^* T^* \sum_{b=1}^r \mathfrak{T}_{ab}^* \mathbf{Q}_b'^* q_n(\kappa) \\
& - \epsilon_{QJ} \widehat{C}_{pa}^* P_a^* T^* \sum_{b=1}^{r-1} \mathfrak{H}_{ab}^* \mathbf{J}_b^* q_n(\kappa) - \frac{N_\delta}{N_{\text{Pr}}} \mathbf{Q}_a'^* \cdot \nabla^* \mathbf{u}^* \\
& - N_\delta \widehat{C}_{pa}^* (\boldsymbol{\Pi}_a^* + \Delta_a^* \boldsymbol{\delta}) \cdot \nabla^* T^* - \frac{N_\delta}{N_{\text{S}}} \Delta \mathfrak{c}_r \mathbf{J}_a^* d_\zeta \widehat{h}_a^* \\
& - N_{\text{Re}} N_{\text{E}} [\boldsymbol{\Pi}_a^* \cdot \nabla^* p^* + \Delta_a^* \nabla^* p^* - N_\delta \boldsymbol{\Pi}_a^* : (\nabla^* \boldsymbol{\Pi}_a^*) \\
& \quad - N_\delta \Delta_a^* \nabla^* \cdot \boldsymbol{\Pi}_a^* - N_\delta \boldsymbol{\Pi}_a^* \cdot \nabla^* \Delta_a^* - N_\delta \Delta_a^* \nabla^* \Delta_a^*] \\
& - \frac{N_\delta}{N_{\text{Pr}}} \nabla^* \cdot \psi_a^{(3)*} - N_{\text{E}} \varphi_a^* : \nabla^* \mathbf{u}^*, \tag{9.48}
\end{aligned}$$

$$\begin{aligned}
\frac{N_\delta}{N_{\text{S}}} \rho^* \frac{d\widehat{\mathbf{J}}_a^*}{d\zeta} = & -p^* \mathbf{d}_a^* - \epsilon_{QJ} \rho_a^* \sum_{b=1}^{r-1} \mathfrak{K}_{ab}^* \mathbf{Q}_b'^* q_n(\kappa) - \rho_a^* \sum_{b=1}^{r-1} \mathfrak{D}_{ab}^* \mathbf{J}_b^* q_n(\kappa) \\
& - N_\delta \nabla^* \cdot (\boldsymbol{\Pi}_a^* - \mathfrak{c}_a^* \boldsymbol{\Pi}_a^*) - N_\delta \left( \frac{\eta_{\text{Br}}}{\eta_r} \right) \nabla^* (\Delta_a^* - \mathfrak{c}_a^* \Delta_a^*) \\
& - N_\delta \left[ \boldsymbol{\Pi}^* + \left( \frac{\eta_{\text{Br}}}{\eta_r} \right) \Delta^* \boldsymbol{\delta} \right] \cdot \nabla^* \mathfrak{c}_a^* - \frac{N_\delta}{N_{\text{S}}} \mathbf{J}_a^* \cdot \nabla^* \mathbf{u}^*. \tag{9.49}
\end{aligned}$$

In the equations presented above,  $\psi_a^{(1)*}$ ,  $\psi_a^{(3)*}$ , and  $\varphi_a$  are reduced as follows:

$$\begin{aligned}
\psi_a^{(1)*} &= \psi_a^{(1)}/\left(\frac{\eta_r U_r^2}{L}\right), \\
\psi_a^{(3)*} &= \psi_a^{(3)}/\left(\frac{U_r \lambda_r \Delta T_r}{L}\right), \\
\varphi_a^* &= \varphi_a/(p_r U_r). \tag{9.50}
\end{aligned}$$

We observe that in (9.46)–(9.49) there are two different classes of terms, one multiplied by the critical number  $N_\delta$  and the other free from it. This distinction

suggests that the equations exhibit two distinctive behaviors in the range of  $N_\delta$ . Another point to observe is that, first of all, the conservation laws (9.42)–(9.45), although there still are two distinctive classes of terms, scale distinctively from the nonconserved variable evolution equations (9.46)–(9.49), since the time derivative terms in the former are not multiplied by the critical number  $N_\delta$ , but instead by  $\gamma_0 N_M^2$  or  $N_R N_S / \Delta c_r$  in the case of mass fraction balance equation. This characteristic behavior with regard to  $N_\delta$  by the conservation laws, in fact, portends the familiar scalings of the classical hydrodynamic equations in which the Reynolds, Mach, or Schmidt numbers play significant roles in studying flow problems.

Having cast the evolution equations for nonconserved variables in the forms presented above, we are now ready to examine various ways of approximating them and connecting with the known theories of transport processes and thereby to demonstrate the generalized hydrodynamics deserves the term “generalized” as a modifier.

In the evolution equations presented above, the nonlinear factor  $q_n(\kappa)$  arising from the first-order cumulant approximation for the dissipation term is now given in terms of  $N_\delta \kappa^*$

$$q_n(N_\delta \kappa^*) = \frac{\sinh(N_\delta \kappa^*)}{N_\delta \kappa^*}, \quad (9.51)$$

in which the dissipation function  $\kappa$  is scaled linearly with respect to  $N_\delta$ . The reduced dissipation function  $\kappa^*$  is given by a quadratic form of reduced shear stresses, normal stresses, heat fluxes, and diffusion fluxes:

$$\begin{aligned} \kappa^* = & \frac{\sqrt{\pi} \sqrt{2T^*}}{p^*} \left\{ \sum_{a,b=1}^r [\mathcal{B}_{ab} \boldsymbol{\Pi}_a^* : \boldsymbol{\Pi}_b^* + \mathcal{V}_{ab} \Delta_a^* \Delta_b^* + \mathcal{T}_{ab} \mathbf{Q}'_a^* \cdot \mathbf{Q}'_b^*] \right. \\ & + \left[ \sum_{a=1}^r \sum_{b=1}^{r-1} \mathcal{H}_{ab} \mathbf{Q}'_a^* \cdot \mathbf{J}_b^* + \sum_{a=1}^{r-1} \sum_{b=1}^r \mathcal{K}_{ab} \mathbf{J}_a^* \cdot \mathbf{Q}'_b^* \right] \\ & \left. + \sum_{a,b=1}^{r-1} \mathcal{D}_{ab} \mathbf{J}_a^* \cdot \mathbf{J}_b^* \right\}^{1/2}. \end{aligned} \quad (9.52)$$

The higher-order moments appearing in the nonconserved variable evolution equations are nondimensionalized as follows:

$$\psi_a^{(1)} = \frac{p_r U_r}{\sqrt{\gamma_0} N_M} \psi_a^{(1)*}, \quad (9.53)$$

$$\psi_a^{(3)} = \frac{2}{5} \widehat{C}_{pr} T_r p_r N_\delta \psi_a^{(3)*}, \quad (9.54)$$

$$\varphi_a = \frac{p_r U_r}{\sqrt{\gamma_0} N_M} \varphi_a^*. \quad (9.55)$$

In (9.52) we have defined various symbols

$$\begin{aligned}\mathcal{B}_{ab} &= \mathfrak{B}_{ab}^*, \quad \mathcal{V}_{ab} = \frac{\eta_{Br}}{3\eta_r} \mathfrak{V}_{ab}^*, \\ \mathcal{T}_{ab} &= 2\epsilon \mathfrak{T}_{ab}^*, \quad \mathcal{H}_{ab} = 2\epsilon \epsilon_n \epsilon_t \epsilon_{QJ} \mathfrak{H}_{ab}^*, \quad \mathcal{K}_{ab} = 2\epsilon \epsilon_n \epsilon_{JQ} \mathfrak{K}_{ab}^*, \\ \mathcal{D}_{ab} &= 2\epsilon \epsilon_n \mathfrak{D}_{ab}^*\end{aligned}\tag{9.56}$$

with  $\epsilon$ , etc. denoting the abbreviations defined by

$$\begin{aligned}\epsilon &= \frac{1}{N_E N_{Pr} \Delta T_r}, \\ \epsilon_{QJ} &= \frac{\mathfrak{D}_r D_r \rho_r}{\mathfrak{T}_r \lambda_r} \frac{T_r \Delta x_r}{\Delta T_r}, \quad \epsilon_{JQ} = \frac{\mathfrak{K}_r}{\mathfrak{D}_r D_r \rho_r} \frac{\lambda_r}{T_r \Delta x_r} \frac{\Delta T_r}{\Delta T_r}, \\ \epsilon_n &= \frac{p_r D_r \rho_r \Delta x_r}{\lambda_r}, \quad \epsilon_t = \frac{\mathfrak{H}_r^*}{\mathfrak{K}_r^*}.\end{aligned}\tag{9.57}$$

The coefficients listed in (9.56) are reduced transport coefficients.

The reduced generalized hydrodynamic equations are now ready for analysis and study of various flow problems, linear or nonlinear.

### 9.1.4 Quasilinear Transport Phenomena

In linear irreversible thermodynamics [12] the transport phenomena are formulated by means of linear constitutive relations describing linear transport processes. The classical hydrodynamics [9, 10, 20] of Navier, Stokes, Fourier, and Fick is founded on the aforementioned linear constitutive relations. Hence the classical hydrodynamics may be said to be attendant on linear irreversible thermodynamics. For this reason it is useful to examine in what manner the linear transport phenomena should be understood in the viewpoint of generalized hydrodynamics presented in this work. This objective is well served if we examine the reduced generalized hydrodynamic equations. We first note that  $N_\delta$  is a measure of time scale, for example, for stress relaxation relative to hydrodynamic relaxation. It may be also said to be a measure of displacement of the fluid system from the regime of linear irreversible processes. Since this fluid dynamic number appears in the constitutive evolution equations (9.46)–(9.49), there are two distinctive classes of terms in them; those in the small  $N_\delta$  regime, where the  $N_\delta$ -independent terms in (9.46)–(9.49) are dominant, and the other directly proportional to  $N_\delta$ . In fact, in small  $N_\delta$  regime or as  $N_\delta \rightarrow 0$  the constitutive equations become a steady-state set of quasilinear algebraic equations for fluxes ( $\boldsymbol{\Pi}_a^*$ ,  $\Delta_a^*$ ,  $\boldsymbol{Q}_a^*$ ,  $\boldsymbol{J}_a^*$ ):

$$\sum_{b=1}^r p_a^* \mathfrak{B}_{ab}^* \boldsymbol{\Pi}_b^* + q_n^{-1} p_a^* [\nabla^* \mathbf{u}^*]^{(2)} = 0, \quad (9.58)$$

$$\sum_{b=1}^r p_a^* \mathfrak{V}_{ab}^* \Delta_b^* + \frac{5}{2} q_n^{-1} p_a^* \nabla^* \cdot \mathbf{u}^* = 0, \quad (9.59)$$

$$\sum_{b=1}^r \widehat{C}_{pa}^* \mathfrak{T}_{ab}^* \mathbf{Q}_b'^* + \epsilon_{QJ} \sum_{b=1}^{r-1} \widehat{C}_{pa}^* \mathfrak{H}_{ab}^* \mathbf{J}_b^* + q_n^{-1} \widehat{C}_{pa}^* \nabla^* T^* = 0, \quad (9.60)$$

$$\sum_{b=1}^r \epsilon_{JQ} \mathfrak{K}_{ab}^* \mathbf{Q}_b^* + \sum_{b=1}^{r-1} \mathfrak{D}_{ab}^* \mathbf{J}_b^* + q_n^{-1} \frac{p_a^*}{\rho_a^*} \mathbf{d}_a^* = 0. \quad (9.61)$$

In fact, in the limit  $N_\delta \rightarrow 0$  the nonlinear factor  $q_n \rightarrow 1$ , strictly speaking, and in this sense (9.58)–(9.61) becomes steady-state equations of (9.46)–(9.49) in the limit of small  $N_\delta$ . Setting the left-hand side of (9.46)–(9.49) in the limit of  $N_\delta \rightarrow 0$  was previously termed the adiabatic approximation [5]. In (9.58)–(9.61), the nonlinear factor  $q_n^{-1}$  may be understood in the following sense:

$$\begin{aligned} q_n^{-1} &= \frac{\kappa}{\sinh \kappa} = \frac{\kappa + \ln \sqrt{1 - \kappa^2}}{\kappa} \\ &= \frac{N_\delta \kappa^* + \ln \sqrt{1 - N_\delta^2 \kappa^{*2}}}{N_\delta \kappa^*} = 1 + O(N_\delta^{1-\epsilon}) (\epsilon > 0) \end{aligned} \quad (9.62)$$

in the limit of  $N_\delta \rightarrow 0$ . Hence the  $N_\delta$ -dependent term is not quite  $O(N_\delta)$ , but  $O(N_\delta^{1-\epsilon})$ . Therefore this model may be regarded as  $O(N_\delta^{1-\epsilon})$ . The presence of this factor, therefore, renders the transport processes described by (9.58)–(9.61) quasilinear unlike the linear constitutive relations in which the factor is absent. Nevertheless, this set of quasilinear constitutive relations is not only solvable algebraically and exactly in terms of thermodynamic forces as will be shown later, but also is capable [15–17, 21–24] of describing transport processes subjected to steep thermodynamic gradients, namely, far removed from equilibrium. This is one of the attractive features of the generalized hydrodynamics formalism and, in particular, of the quasilinear model described in this work.

The first two equations for  $\boldsymbol{\Pi}_a^*$  and  $\Delta_a^*$  are uncoupled from each other and the remaining two equations if we disregard the dependence of  $\kappa^*$  on the fluxes  $(\boldsymbol{\Pi}_a^*, \Delta_a^*, \mathbf{Q}_a^*, \mathbf{J}_a^*)$ , whereas the last two equations for  $\mathbf{Q}_a'^*$  and  $\mathbf{J}_a^*$  are coupled to each other even without the  $q_n^{-1}$  factor. However, we can treat the  $q_n^{-1}$  factor as if it is a constant until the quasilinear equations are formally solved for  $(\boldsymbol{\Pi}_a^*, \Delta_a^*, \mathbf{Q}_a'^*, \mathbf{J}_a^*)$  as if the set were linear. After “the linear set” is algebraically solved we can express the dissipation functions in terms of the thermodynamic gradients and then the quasilinear model is solved in terms of thermodynamic forces, as will be shown presently. On this strategy, we solve the quasilinear set to obtain

$$\Pi_a^* = -q_n^{-1} \sum_{b=1}^r \|\mathfrak{B}^*\|_{ab}^{-1} [\nabla^* \mathbf{u}^*]^{(2)}, \quad (9.63)$$

$$\Delta_a^* = -\frac{5}{2} q_n^{-1} \sum_{b=1}^r \|\mathfrak{V}^*\|_{ab}^{-1} p_b^* \nabla^* \cdot \mathbf{u}^*, \quad (9.64)$$

$$\begin{aligned} \mathbf{Q}'_i^* &= -q_n^{-1} \sum_{j=1}^r \|\mathfrak{S}^*\|_{ij}^{-1} \nabla^* \ln T^* \\ &\quad - q_n^{-1} \sum_{j=r+1}^{2r-1} \|\mathfrak{S}^*\|_{ij}^{-1} \frac{p_j^*}{\rho_j^*} \mathbf{d}_j^* \quad (i = 1, \dots, r), \end{aligned} \quad (9.65)$$

$$\begin{aligned} \mathbf{J}_i^* &= -q_n^{-1} \sum_{j=1}^r \|\mathfrak{S}^*\|_{ij}^{-1} \nabla^* \ln T^* \\ &\quad - q_n^{-1} \sum_{j=r+1}^{2r-1} \|\mathfrak{S}^*\|_{ij}^{-1} \frac{p_j^*}{\rho_j^*} \mathbf{d}_j^* \quad (i = r+1, \dots, 2r-1), \end{aligned} \quad (9.66)$$

where matrix  $\mathfrak{S}^*$  is defined by  $(2r-1) \times (2r-1)$  square supermatrix made up of submatrices  $\mathfrak{T}^*$ ,  $\mathfrak{H}^*$ ,  $\mathfrak{K}^*$  and  $\mathfrak{D}^*$

$$\mathfrak{S}^* = \begin{pmatrix} \mathfrak{T}^* & \epsilon_{QJ} \mathfrak{H}^* \\ \epsilon_{JQ} \mathfrak{K}^* & \mathfrak{D}^* \end{pmatrix} \quad (9.67)$$

in the space of  $(r \oplus r-1) = (2r-1)$  dimensional column vector  $\mathfrak{F}^*$  consisting of thermodynamic forces  $\nabla^* \ln T^*$  and  $(p_j^*/\rho_j^*) \mathbf{d}_j^*$

$$\mathfrak{F}^* = (\nabla^* \ln T^*, \dots, \nabla^* \ln T^*, (p_1^*/\rho_1^*) \mathbf{d}_1^*, \dots, (p_{r-1}^*/\rho_{r-1}^*) \mathbf{d}_{r-1}^*)^t. \quad (9.68)$$

In (9.68), the first half of the column vector made up by  $\nabla^* \ln T^*$  is  $r$  dimensional while the second half made up by  $\mathbf{d}_1^*, \dots, \mathbf{d}_{r-1}^*$  is  $(r-1)$  dimensional. The superscript  $t$  on the vector means the transpose of the row vector shown, that is, the column vector.

We may define reduced linear transport coefficients for a mixture as follows:

$$\eta_{ab}^{0*} = \|\mathfrak{B}^*\|_{ab}^{-1}, \quad (9.69)$$

$$\eta_{Bab}^{0*} = \frac{5}{2} \|\mathfrak{V}^*\|_{ab}^{-1}, \quad (9.70)$$

$$\lambda_{ab}^{0*} = \|\mathfrak{S}^*\|_{ab}^{-1} \quad (1 \leq a, b \leq r), \quad (9.71)$$

$$D_{ab}^{(dh)0*} = \|\mathfrak{S}^*\|_{ij}^{-1} \frac{p_j^*}{\rho_j^*} \quad (r+1 \leq a \leq r; \quad r+1 \leq b \leq 2r-1), \quad (9.72)$$

$$D_{ab}^{(td)0*} = \|\mathfrak{S}^*\|_{ab}^{-1} \quad (1 \leq a \leq r; \quad r+1 \leq b \leq 2r-1), \quad (9.73)$$

$$D_{ab}^{0*} = \|\mathfrak{S}^*\|_{ij}^{-1} \frac{p_j^*}{\rho_j^*} \quad (r+1 \leq a, b \leq 2r-1), \quad (9.74)$$

where  $\eta_{ab}^{0*}$  is the viscosity;  $\eta_{Bab}^{0*}$  the bulk viscosity;  $\lambda_{ab}^{0*}$  the thermal conductivity;  $D_{ab}^{(dh)0*}$  the diffusive heat conductivity;  $D_{ab}^{(td)0*}$  the thermal diffusion coefficient; and  $\mathfrak{D}_{ab}^{0*}$  the diffusion coefficient defined on the basis of  $\mathbf{J}_a$ ; all of them are reduced transport coefficients. We emphasize the transport coefficients defined here are those of linear transport processes of the mixture [18, 19].

The constitutive relations (9.63)–(9.66) are now expressed in the forms<sup>3</sup>

$$\boldsymbol{\Pi}_a^* = - \sum_{b=1}^r \eta_{ab}^{0*} q_n^{-1} [\nabla^* \mathbf{u}^*]^{(2)} := -\eta_a^{0*} q_n^{-1} [\nabla^* \mathbf{u}^*]^{(2)}, \quad (9.75)$$

$$\Delta_a^* = - \sum_{b=1}^r \eta_{Bab}^{0*} q_n^{-1} \nabla^* \cdot \mathbf{u}^* := -\eta_{Ba}^{0*} q_n^{-1} \nabla^* \cdot \mathbf{u}^*, \quad (9.76)$$

$$\begin{aligned} \mathbf{Q}_a^* &= - \sum_{b=1}^r \lambda_{ab}^{0*} q_n^{-1} \nabla^* \ln T^* - \sum_{b=1}^{r-1} D_{ab}^{(dh)0*} q_n^{-1} \mathbf{d}_b^* \\ &:= -\lambda_a^{0*} q_n^{-1} \nabla^* \ln T^* - \sum_{b=1}^{r-1} D_{ab}^{(dh)0*} q_n^{-1} \mathbf{d}_b^*, \end{aligned} \quad (9.77)$$

$$\begin{aligned} \mathbf{J}_a^* &= - \sum_{b=1}^r D_{ab}^{(td)0*} q_n^{-1} \nabla^* \ln T^* - \sum_{b=1}^{r-1} D_{ab}^{0*} q_n^{-1} \mathbf{d}_b^* \\ &:= -D_a^{(td)0*} q_n^{-1} \nabla^* \ln T^* - \sum_{b=1}^{r-1} D_{ab}^{0*} q_n^{-1} \mathbf{d}_b^*. \end{aligned} \quad (9.78)$$

There are a couple of points we would like to reiterate about the definition of transport coefficients  $\lambda_{ab}^{0*}$  and diffusion coefficients  $D_{ab}^{0*}$  and  $D_{ab}^{(td)0*}$ . In the case of  $\lambda_{ab}^{0*}$ , if it is defined in reference to  $\nabla^* T^*$ , the thermal conductivity so defined is equal to  $\lambda_{ab}^{0*}/T^*$  and, in the case of the aforementioned diffusion coefficients, if they are defined with reference to  $\mathbf{J}_a^*$  instead of  $(\mathbf{u}_a^* - \mathbf{u}^*)$  then the diffusion coefficients so defined is equal to  $D_{ab}^{0*}/\rho_a^*$  and  $D_{ab}^{(td)0*}/\rho_a^*$ , respectively.

### 9.1.5 Dissipation Function and Thermodynamic Forces

To find the dissipation function  $\kappa$  in terms of thermodynamic forces we return to (9.52). Upon substitution of fluxes  $(\boldsymbol{\Pi}_a^*, \Delta_a^*, \mathbf{Q}_a^*, \mathbf{J}_a^*)$  given by (9.75)–(9.78) into (9.52), we obtain

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<sup>3</sup>The nonlinear factor  $q_n^{-1}$  can be replaced by the equivalent quantity  $q_L = \sinh^{-1} \Gamma / \Gamma$ , where  $\Gamma^2$  is a quadratic form of the thermodynamic gradients in (9.58)–(9.61). The details about this replacement procedure is discussed below; see the steps leading to (9.85)–(9.88) of this chapter.

$$\begin{aligned} q_n^2 \kappa^2 &= N_\delta^2 \frac{\pi \sqrt{2T^*}}{p^{*2}} \left[ C_{SV} [\nabla^* \mathbf{u}^*]^{(2)} : [\nabla^* \mathbf{u}^*]^{(2)} + C_{BV} (\nabla^* \cdot \mathbf{u}^*)^2 \right. \\ &\quad \left. + C_{TT} (\nabla^* T^* \cdot \nabla^* T^*) + C_{Td} \nabla^* T^* \cdot \mathbf{d}_k^* + C_{dd} \mathbf{d}_k^* \cdot \mathbf{d}_l^* \right] \\ &:= N_\delta^2 \kappa_L^{*2}, \end{aligned} \quad (9.79)$$

where the coefficients are defined by

$$C_{SV} = \sum_{a,b=1}^r \eta_a^{0*} \mathcal{B}_{ab} \eta_b^{0*}, \quad (9.80)$$

$$C_{BV} = \sum_{a,b=1}^r \eta_{Ba}^{0*} \mathcal{V}_{ab} \eta_{Bb}^{0*}, \quad (9.81)$$

$$\begin{aligned} C_{TT} &= \sum_{a,b=1}^r \lambda_a^{0*} \mathcal{T}_{ab} \lambda_b^{0*} + \sum_{a=1}^r \sum_{b=1}^{r-1} \lambda_a^{0*} \mathcal{H}_{ab} D_b^{(td)0*} \\ &\quad + \sum_{a=1}^{r-1} \sum_{b=1}^r \mathcal{K}_{ab} D_a^{(td)0*} \lambda_b^{0*} + \sum_{a,b=1}^{r-1} D_a^{(td)0*} \mathcal{D}_{ab} D_b^{(td)0*}, \end{aligned} \quad (9.82)$$

$$\begin{aligned} C_{dd} &= \sum_{a,b=1}^r \sum_{k,l=1}^{r-1} \bar{D}_{ak}^{(dh)0*} \mathcal{T}_{ab} \bar{D}_{bl}^{(dh)0*} + \sum_{a,k,l=1}^{r-1} \sum_{b=1}^r \bar{D}_{ak}^{0*} \mathcal{K}_{ab} \bar{D}_{bl}^{(dh)0*} \\ &\quad + \sum_{a=1}^r \sum_{b,k,l=1}^{r-1} \bar{D}_{ak}^{(dh)0*} \mathcal{H}_{ab} \bar{D}_{bl}^{0*} + \sum_{a,b,k,l=1}^{r-1} \bar{D}_{ak}^{0*} \mathcal{D}_{ab} \bar{D}_{bl}^{0*}, \end{aligned} \quad (9.83)$$

$$\begin{aligned} C_{Td} &= \sum_{a,b=1}^r \sum_{k=1}^{r-1} \mathcal{T}_{ab} \left( \lambda_a^{0*} \bar{D}_{bk}^{(dh)0*} + \bar{D}_{ak}^{(dh)0*} \lambda_b^{0*} \right) \\ &\quad + \sum_{a=1}^r \sum_{b,k=1}^{r-1} \mathcal{H}_{ab} \left( \lambda_a^{0*} \bar{D}_{bk}^{0*} + \bar{D}_{bk}^{(dh)0*} D_a^{(td)0*} \right) \\ &\quad + \sum_{a,k=1}^{r-1} \sum_{b=1}^r \mathcal{K}_{ab} \left( \bar{D}_{ak}^{0*} \lambda_b^{0*} + D_a^{(td)0*} \bar{D}_{bk}^{(dh)0*} \right) \\ &\quad + \sum_{a,b,k,l=1}^{r-1} \mathcal{D}_{ab} \left( D_a^{(td)0*} \bar{D}_{bk}^{0*} + \bar{D}_{ak}^{0*} D_b^{(td)0*} \right). \end{aligned} \quad (9.84)$$

Since by definition of  $q_n(\kappa)$

$$q_n^2 \kappa^2 = \sinh^2 \kappa,$$

the right-hand side of (9.79) is equal to  $\sinh \kappa$ , and inverting the equation  $\kappa$  we finally obtain the dissipation function in terms of the quadratic form of thermodynamic gradients:

$$\kappa = N_\delta \kappa^* = \sinh^{-1} (N_\delta \kappa_L^*) , \quad (9.85)$$

where  $\kappa_L^*$  defined in (9.79) is a quadratic form of reduced thermodynamic forces (gradients)

$$\begin{aligned} \kappa_L^* = \frac{\sqrt{\pi} \sqrt[4]{2T^*}}{p^*} & \left[ C_{SV} [\nabla^* \mathbf{u}^*]^{(2)} : [\nabla^* \mathbf{u}^*]^{(2)} + C_{BV} (\nabla^* \cdot \mathbf{u}^*)^2 \right. \\ & \left. + C_{TT} (\nabla^* T^* \cdot \nabla^* T^*) + C_{dd} \mathbf{d}_k^* \cdot \mathbf{d}_l^* + C_{Td} \nabla^* T^* \cdot \mathbf{d}_k^* \right]^{1/2} . \end{aligned} \quad (9.86)$$

Therefore  $\kappa$  is obtained in terms of  $\kappa_L$  in the form

$$\kappa = \sinh^{-1} (N_\delta \kappa_L^*) \quad (9.87)$$

and hence  $q_n^{-1}$  is given by

$$\begin{aligned} q_n^{-1} &= \frac{\kappa}{\sinh \kappa} \\ &= \frac{\sinh^{-1} (N_\delta \kappa_L^*)}{N_\delta \kappa_L^*} := q_L, \end{aligned} \quad (9.88)$$

where the second line is brought out on substituting  $\kappa$  given by (9.87) into the right of the first line. Now  $\kappa_L = N_\delta \kappa_L^*$  is seen as a dissipation function given in a quadratic form of thermodynamic gradients in contrast to  $\kappa^*$ , which was originally defined by a quadratic form of fluxes, i.e.,  $\Pi_a$ ,  $\mathbf{Q}'_a$ , etc. With this result inserted into (9.75)–(9.78) it can be said that the steady-state quasilinear constitutive relations are algebraically solved in terms of thermodynamic forces (gradients), thanks to the special algebraic feature of the quasilinear model. And the result obtained enables us to explore the highly nonlinear regime of transport processes by means of the information inherent to linear transport processes only. In this connection, it should be remembered that the present quasilinear model descends from the first-order cumulant approximation for the dissipation terms, which is a special class of resummation of an Chapman–Enskog expansion in thermodynamic forces of collision integrals or, more mathematically precisely, an expansion of the Boltzmann collision integral or the extended Boltzmann collision integral in series of the critical fluid dynamic number  $N_\delta$ . In this regard it is useful to recall the composite nature of  $N_\delta$ ; see (9.40). With  $q_n^{-1}$  replaced by  $q_L(\kappa_L)$  the quasilinear steady-state constitutive equations (9.75)–(9.78) are summarized below:

$$\boldsymbol{\Pi}_a^* = - \sum_{b=1}^r \eta_{ab}^{0*} q_L [\nabla^* \mathbf{u}^*]^{(2)} := -\eta_a^{0*} q_L [\nabla^* \mathbf{u}^*]^{(2)}, \quad (9.89)$$

$$\Delta_a^* = - \sum_{b=1}^r \eta_{Bab}^{0*} q_L \nabla^* \cdot \mathbf{u}^* := -\eta_{Ba}^{0*} q_L \nabla^* \cdot \mathbf{u}^*, \quad (9.90)$$

$$\begin{aligned} \mathbf{Q}'_a^* &= - \sum_{b=1}^r \lambda_{ab}^{0*} q_L \nabla^* \ln T^* - \sum_{b=1}^{r-1} D_{ab}^{(dh)0*} q_L \mathbf{d}_b^* \\ &:= -\lambda_a^{0*} q_L \nabla^* \ln T^* - \sum_{b=1}^{r-1} D_{ab}^{(dh)0*} q_L \mathbf{d}_b^*, \end{aligned} \quad (9.91)$$

$$\begin{aligned} \mathbf{J}_a^* &= - \sum_{b=1}^r D_{ab}^{(td)0*} q_L \nabla^* \ln T^* - \sum_{b=1}^{r-1} D_{ab}^{0*} q_L \mathbf{d}_b^* \\ &:= -D_a^{(td)0*} q_L \nabla^* \ln T^* - \sum_{b=1}^{r-1} D_{ab}^{0*} q_L \mathbf{d}_b^*. \end{aligned} \quad (9.92)$$

These quasilinear constitutive equations are given in terms of thermodynamic gradients only, which nonlinearly drive the fluxes on the left hand side. These constitutive relations no longer satisfy the Curie law owing to the nonlinear factor  $q_L$ .

### 9.1.6 Nonlinear Transport Coefficients

With  $q_n^{-1}$  so expressed as  $q_L$  in (9.88), the nonlinear transport coefficients may be readily obtained from steady-state quasilinear constitutive equations (9.89)–(9.92) in terms of thermodynamic forces (i.e., thermodynamic gradients). They are given by the formulas

$$\eta_a = \eta_a^0 q_L, \quad (9.93)$$

$$\eta_{Ba} = \eta_{Ba}^0 q_L, \quad (9.94)$$

$$\lambda_a = \lambda_a^0 q_L, \quad (9.95)$$

$$D_{ab}^{(dh)} = D_{ab}^{(dh)0} q_L, \quad (9.96)$$

$$D_{ab}^{(td)} = D_{ab}^{(td)0} q_L, \quad (9.97)$$

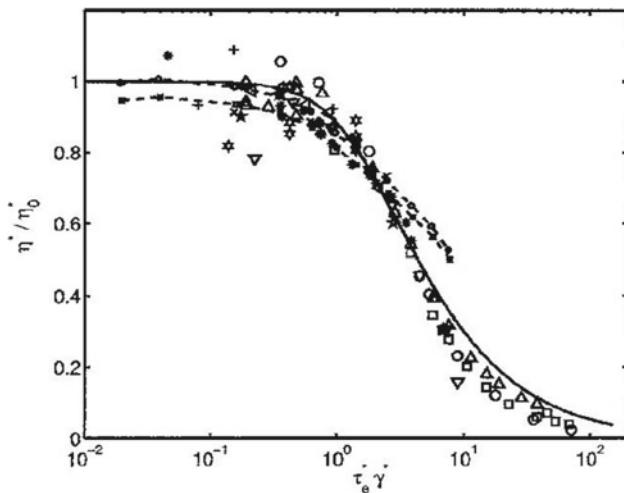
$$D_{ab} = D_{ab}^0 q_L, \quad (9.98)$$

where we have restored the transport coefficients in physical units.

Because of the presence of  $q_L$ , which is a quadratic form of all thermodynamic forces, the transport coefficients in (9.93)–(9.98) are nonlinear in the sense that they depend on the thermodynamic forces, namely, the thermodynamic gradients, unlike

the linear transport coefficients  $\eta_a^0$ ,  $\eta_{Ba}^0$ , etc. Therefore  $\eta_a$  may be called a non-Newtonian viscosity;  $\lambda_a$  non-Fourier thermal conductivity;  $D_{ab}$  non-Fickian diffusion coefficient, etc., which are influenced by all thermodynamic forces present in the fluid. This is in sharp contrast to linear transport coefficients, which would be independent of thermodynamic forces. It should be noted that the nonlinear transport coefficients in (9.93)–(9.98) are dependent on thermodynamic forces of symmetry different from the symmetry of the particular process for which the nonlinear transport coefficient is defined. In other words, for example, the nonlinear bulk viscosity coefficient is influenced by scalar processes as well as vectorial or tensorial transport processes present in the system through the  $q_L$  factor. Thus the Curie principle is broken by the afore-defined nonlinear transport processes because of the  $q_L$  factor—a rather intriguing feature.

Since the aforementioned linear transport coefficients are given in terms of collision bracket integrals which can be calculated in terms of molecular information on the fluid system the quasilinear transport coefficients can be computed from the dynamical information on the molecular system. Examples of such computations are available in Ref. [25] and references quoted therein. Particularly, the non-Newtonian viscosity formula (9.93) in the absence of all other thermodynamic forces except for the shear gradient has been tested against the nonequilibrium molecular dynamics simulation data on a simple fluid by Hoover and his collaborators [26, 27]. It is found [28] that the non-Newtonian shear viscosity predicted by the quasilinear generalized hydrodynamic theory formula (9.93) describes well the simulation data on the shear rate dependence of the viscosity of a simple fluid as shown in Fig. 9.1. In Ref. [28] the



**Fig. 9.1** Scaled non-Newtonian shear viscosity ( $\eta^*/\eta_0^*$ ) given in (9.93) is plotted against the scaled reduced shear rate  $\tau^*\gamma^*$  and compared with all available simulation data. The symbols and *broken curve* are by simulation results, whereas the *solid curve* is the prediction by (9.93) for which the Newtonian shear rate viscosity is calculated by the modified free volume theory of Eu and collaborators. Reprinted with permission from R. Laghae, A. E. Nasrabad, and B. C. Eu, J. Chem. Phys. **123**, 234507 (2005) © 2005 American Institute of Physics

diffusion coefficient and non-Newtonian viscosity have been calculated and tested in comparison with experiments. They are found to yield experimental transport coefficients in good accuracy within the bounds of uncertainty in simulation, especially, in the small shearing rate regime. Other nonlinear transport coefficients, being new, have not been tested as yet.

### 9.1.7 Linear Transport Coefficients and Classical Hydrodynamics

The linear transport coefficients of the Chapman–Enskog theory [18] can be recovered either from (9.93)–(9.98), or the quasilinear constitutive equations (9.75)–(9.78) if the limit  $N_\delta \rightarrow 0$  is taken, because this limit renders them linear with respect to the thermodynamic gradients. Therefore, the linear transport coefficients (9.69)–(9.74) can be recovered from (9.93)–(9.98). As has been shown in Chap. 3, since the linear transport coefficients obtained in the present theory are identical with the first-order Chapman–Enskog theory results, the comprehensiveness of the nonlinear theory of transport processes described above is now demonstrated. And it is a characteristic feature in the limit of vanishing critical number ( $N_\delta \rightarrow 0$ ) of the generalized hydrodynamic equations presented in the present work.

#### 9.1.7.1 Linear Transport Processes and Parabolic Partial Differential Equations

In the limit of  $N_\delta \rightarrow 0$  the constitutive relations for nonconserved variables (9.63)–(9.66) collapse to a set of steady-state linear equations for fluxes, which are readily obtained from (9.75)–(9.78) by setting  $q_L = 1$ . If the constitutive relations thus obtained are substituted into the conservation laws (9.42)–(9.45) there arises a set of coupled parabolic partial differential equations for conserved variables  $(v^*, c_a^*, \mathbf{u}^*, \mathcal{E})$ , which are first order in time derivative and second order in spatial derivatives. They are, as a matter of fact, the classical hydrodynamic equations [9] of Navier, Stokes, Fourier, and Fick.

Therefore such parabolic partial differential equations may be said to belong to the regime of vanishing  $N_\delta$ . They are collected below:

$$\rho^* \frac{dv^*}{d\zeta} = \nabla^* \cdot \mathbf{u}^*, \quad (9.99)$$

$$\frac{N_{\text{Re}} N_S}{\Delta c_r} \rho^* \frac{dc_a^*}{d\zeta} = \sum_{b=1}^r \nabla^* \cdot (\mathfrak{D}_{ab}^* \mathbf{d}_b^*) + \nabla^* \cdot (D_a^{(td)0*} \nabla^* T^*), \quad (9.100)$$

$$\begin{aligned} \gamma_0 N_M^2 \rho^* \frac{d\mathbf{u}^*}{d\zeta} = & - (\nabla^* p^* - \rho^* \widehat{\mathbf{F}}^*) + N_\delta \nabla^* \cdot \left( \eta^{0*} [\nabla^* \mathbf{u}^*]^{(2)} \right) \\ & + N_\delta \nabla^* (\eta_B^{0*} \nabla^* \cdot \mathbf{u}^*), \end{aligned} \quad (9.101)$$

$$\begin{aligned}
\gamma_0 N_M^2 \rho^* \frac{d\mathcal{E}}{d\zeta} = & -\frac{N_\delta}{N_{\text{Pr}} N_E} \left\{ \nabla^* \cdot (\lambda^{0*} \nabla^* T^*) + \sum_{a=1}^r \nabla^* \cdot \widehat{h}_a^* D_a^{(td)0*} \nabla^* T^* \right. \\
& + \sum_{a=1}^r \sum_{b=1}^{r-1} \left[ \nabla^* \cdot (D_{ab}^{(dh)0*} \mathbf{d}_b^*) + \nabla^* \cdot (\widehat{h}_a^* \mathfrak{D}_{ab}^* \mathbf{d}_b^*) \right] \Big\} \\
& + N_\delta \eta^{0*} \left( [\nabla^* \mathbf{u}^*]^{(2)} : [\nabla^* \mathbf{u}^*]^{(2)} \right) + N_\delta \eta_B^{0*} (\nabla^* \cdot \mathbf{u}^*)^2 \\
& - \left( p^* \nabla^* \cdot \mathbf{u}^* - \rho^* \sum_{a=1}^r \widehat{\mathbf{J}}_a^* \cdot \widehat{\mathbf{F}}_a^* \right). \tag{9.102}
\end{aligned}$$

These are the Navier–Stokes, Fourier, and Fick’s equations of classical hydrodynamics for a gas mixture. For a noninteracting collisionless molecular gases for which the transport coefficients vanish, they clearly reduce to the Euler equations [9].

It should be noted that the classical hydrodynamic equations (9.99)–(9.102) predict an infinite speed of disturbance propagation, and this feature is regarded by some as a liability in the study of hydrodynamic wave propagation phenomena. Despite the viewpoint held by some, the classical hydrodynamic equations successfully serve as principal and indispensable tools for study of flow phenomena in many branches of science and engineering [29]. There lies the mystique of the classical hydrodynamics of Navier, Stokes, and Fourier.

### 9.1.8 Quasilinear Transport Processes and Hyperbolic-Type Partial Differential Equations

As shown in the previous subsection, the generalized hydrodynamic equations tend to parabolic-type partial differential equations in the limit of  $N_\delta \rightarrow 0$ . In contrast to this, in the regime of the nonvanishing critical number  $N_\delta$ , namely, the full generalized hydrodynamic equations or if the portion of terms linear in  $N_\delta$  is kept therein, we find the evolution equations for the conserved and nonconserved variables become hyperbolic-type. For example, if the terms giving rise to quasilinear constitutive equations (9.58)–(9.61) are kept in the right hand side of nonconserved variable evolution equations (9.46)–(9.49), the generalized hydrodynamic equations become hyperbolic.

To show this feature it is convenient to cast the conservation laws (9.42)–(9.45) and the evolution equations (9.46)–(9.49) in simplified forms displaying only the most relevant parts of the equations explicitly. By the most relevant parts, we mean specifically the first derivative terms of the variables spanning the thermodynamic manifold. Under this guiding rule of casting equations, we include the spatial derivatives of  $v^*$ ,  $\mathbf{u}^*$ ,  $\widehat{\mathbf{J}}_a^*$ ,  $\widehat{\Pi}^*$ ,  $\widehat{\Delta}^*$ ,  $\widehat{\mathbf{Q}}'^*$ , and  $\widehat{\mathbf{J}}_a^*$  in (9.42)–(9.45) and only the thermodynamic forces in (9.46)–(9.49). The rest of the terms in the conservation laws and the flux evolution equations are lumped into terms, such as  $\mathfrak{S}_{ca}^*$ ,  $\dots$ ,  $\mathfrak{S}_h^*$ ,  $\mathfrak{L}_{\Pi a}^*$ ,  $\dots$ ,  $\mathfrak{L}_{Ja}^*$ , in the generalized hydrodynamic equations. They are defined below for completeness. Of course, some of the terms, such as those originating from the dissipation terms  $\Lambda_a^{(q)}$ ,

are crucially important for transport processes, but not for considering the hyperbolicity of the generalized hydrodynamic equations. Therefore, the first-order derivative parts of the equations are explicitly shown, but the rest of the terms containing non-linear terms are collected in single terms such as  $\mathfrak{S}_{ca}^*$ ,  $\mathfrak{L}_{\Pi a}^*$ , etc. mentioned earlier and defined below:

$$\frac{dv^*}{d\zeta} = v^* \nabla^* \cdot \mathbf{u}^*, \quad (9.103)$$

$$\frac{N_{\text{Re}} N_S}{\Delta \mathfrak{c}_r} \frac{dc_a^*}{d\zeta} = -\nabla^* \cdot \widehat{\mathbf{J}}_a^* + v^* \mathfrak{S}_{ca}^*, \quad (9.104)$$

$$\gamma_0 N_M^2 \frac{d\mathbf{u}^*}{d\zeta} = \frac{1}{\kappa_\Psi^*} \nabla^* v^* - N_\delta \nabla^* \cdot \widehat{\boldsymbol{\Pi}}^* - N_\delta \nabla^* \widehat{\Delta}^* + N_\delta v^* \mathfrak{S}_u^*, \quad (9.105)$$

$$\begin{aligned} \frac{\gamma_0 N_M^2}{N_E} \frac{dT^*}{d\zeta} &= -\frac{N_\delta}{N_{\text{Pr}} N_E} v^* \left[ \nabla^* \cdot \widehat{\mathbf{Q}}'^* + \left( \frac{T_r \Delta \mathfrak{c}_r}{\Delta T_r} \right) \sum_{a=1}^r T_a^* \nabla^* \cdot \widehat{\mathbf{J}}_a^* \right] \\ &\quad - v^* \frac{dp^*}{d\zeta} + N_\delta v^* \mathfrak{S}_h^*, \end{aligned} \quad (9.106)$$

$$N_\delta \frac{d\widehat{\boldsymbol{\Pi}}_a^*}{d\zeta} = -2p_a^* v^* [\nabla^* \mathbf{u}^*]^{(2)} + N_\delta v^* \mathfrak{L}_{\Pi a}^*, \quad (9.107)$$

$$N_\delta \frac{d\widehat{\Delta}_a^*}{d\zeta} = -\frac{5}{3} p_a^* v^* \nabla^* \cdot \mathbf{u}^* + N_\delta v^* \mathfrak{L}_{\Delta a}^*, \quad (9.108)$$

$$\frac{N_\delta}{N_{\text{Pr}}} \frac{d\widehat{\mathbf{Q}}_a'^*}{d\zeta} = -\widehat{C}_{pa}^* p_a^* v^* \nabla^* T^* + N_\delta v^* \mathfrak{L}_{\mathbf{Q}_a}^*, \quad (9.109)$$

$$\frac{N_\delta}{N_S} \frac{d\widehat{\mathbf{J}}_a^*}{d\zeta} = -p^* v^* \mathbf{d}_a^* + N_\delta v^* \mathfrak{L}_{Ja}^*, \quad (9.110)$$

where the so-far undefined symbols are as follows:  $\kappa_\Psi^*$  is the iso-calortropic compressibility<sup>4</sup>

$$\kappa_\Psi^* = -\frac{1}{v^*} \left( \frac{\partial v^*}{\partial p^*} \right)_\Psi = \kappa_T^*/\gamma_0, \quad (9.111)$$

namely, the compressibility at constant calortropy surface on which the present differential system evolves, and the remaining symbols are:

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<sup>4</sup>The compressibility  $\kappa_\Psi^*$  is defined for the system evolving on the constant calortropy surface  $\widehat{\Psi}$  because the generalized hydrodynamic equations used here are subject to the calortropy differential as shown in the kinetic theory chapter of this work. This compressibility tends to the usual adiabatic compressibility  $\kappa_S^*$  as the system tends to equilibrium in the limit of  $N_\delta \rightarrow 0$ . Equation (9.111) can be shown as follows: Since the calortropy density is described by an exact differential form in the thermodynamic space in the thermodynamic manifold for the present irreversible system, we find [30]

$$\mathfrak{S}_{ca}^* = \mathbf{J}_a^* \cdot \nabla^* \ln v^*, \quad (9.112)$$

$$\mathfrak{S}_{\mathbf{u}}^* = \boldsymbol{\Pi}^* \cdot \nabla^* \ln v^* + \Delta^* \nabla^* \ln v^*, \quad (9.113)$$

$$\begin{aligned} \mathfrak{S}_h^* &= -\boldsymbol{\Pi}^* : [\nabla^* \mathbf{u}^*]^{(2)} - \Delta^* \nabla^* \cdot \mathbf{u}^* + \frac{1}{N_{\text{Pr}} N_{\text{E}}} \mathbf{Q}'^* \cdot \nabla^* \ln v^* \\ &\quad - \frac{1}{N_{\text{Pr}} N_{\text{E}}} \left( \frac{T_r \Delta \mathfrak{c}_r}{\Delta T_r} \right) \sum_{a=1}^r T_a^* \mathbf{J}_a^* \cdot \nabla^* \ln v^*, \end{aligned} \quad (9.114)$$

$$\begin{aligned} \mathfrak{L}_{\boldsymbol{\Pi} a}^* &= -\nabla^* \cdot \psi_a^{(1)*} - 2 \frac{\Delta \mathfrak{c}_r}{N_{\text{S}}} \left[ \frac{d \mathbf{u}^*}{d \zeta} \mathbf{J}_a^* \right]^{(2)} - 2 [\boldsymbol{\Pi}_a^* \cdot \nabla^* \mathbf{u}^*]^{(2)} \\ &\quad - 2 \Delta_a^* [\nabla^* \mathbf{u}^*]^{(2)} - 2 p_a^* v^* \sum_{b=1}^r \mathfrak{B}_{ab}^* \boldsymbol{\Pi}_b^* q_\gamma, \end{aligned} \quad (9.115)$$

$$\begin{aligned} \mathfrak{L}_{\Delta a}^* &= -\frac{1}{N_{\text{Pr}} N_{\text{E}}} \nabla^* \cdot \left( \frac{2}{3} \mathbf{Q}_a^* - \frac{N_{\text{Pr}} N_{\text{E}} \Delta \mathfrak{c}_r}{\gamma_0 N_{\text{M}}^2 N_{\text{S}}} p_a^* v_a^* \mathbf{J}_a^* \right) \\ &\quad - \frac{2}{3} (\boldsymbol{\Pi}_a^* + \Delta_a^* \boldsymbol{\delta}) \odot \nabla^* \mathbf{u}^* - \frac{2 \Delta x_r}{3 N_{\text{S}}} (d_\zeta \mathbf{u}^*) \cdot \mathbf{J}_a^* \\ &\quad + \frac{\Delta x_r}{\gamma_0 N_{\text{M}} N_{\text{S}}} \frac{p_a^*}{\rho_a^*} \mathbf{J}_a^* \cdot \nabla^* \ln \rho_a^* - \frac{2}{3} p_a^* v^* \sum_{b=1}^r \mathfrak{V}_{ab}^* \Delta_b^* q_\gamma, \end{aligned} \quad (9.116)$$

$$\begin{aligned} \mathfrak{L}_{\mathbf{Q} a}^* &= -\frac{1}{N_{\text{Pr}}} \mathbf{Q}_a^* \cdot \nabla^* \mathbf{u}^* - \frac{N_{\text{E}}}{\gamma_0 N_{\text{M}}^2} [\boldsymbol{\Pi}_a^* \cdot \nabla^* p^* + \Delta_a^* \nabla^* p^*] \\ &\quad - \frac{N_\delta N_{\text{E}}}{\gamma_0 N_{\text{M}}^2} [\boldsymbol{\Pi}_a^* \cdot (\nabla^* \cdot \boldsymbol{\Pi}_a^*) + \Delta_a^* \nabla^* \cdot \boldsymbol{\Pi}_a^*] \\ &\quad - \frac{N_\delta N_{\text{E}}}{\gamma_0 N_{\text{M}}^2} [\boldsymbol{\Pi}_a^* \cdot \nabla^* \Delta_a^* + \Delta_a^* \nabla^* \Delta_a^*] \\ &\quad - \widehat{C}_{pa}^* (\boldsymbol{\Pi}_a^* + \Delta_a^* \boldsymbol{\delta}) \cdot \nabla^* T^* - \frac{1}{N_{\text{S}}} \Delta \mathfrak{c}_r \mathbf{J}_a^* d_\zeta \widehat{h}_a^* \\ &\quad - \frac{1}{N_{\text{Pr}}} \nabla^* \cdot \psi_a^{(3)*} - \frac{N_{\text{E}}}{N_\delta} (\boldsymbol{\varphi}_a^* : \nabla^* \mathbf{u}^*) \\ &\quad - \widehat{C}_{pa}^* p_a^* T^* v^* \left( \sum_{b=1}^r \mathfrak{T}_{ab}^* \mathbf{Q}_b'^* + \epsilon_{QJ} \sum_{b=1}^{r-1} \mathfrak{H}_{ab}^* \mathbf{J}_b^* \right) q_\gamma, \end{aligned} \quad (9.117)$$

(Footnote 4 continued)

$$\begin{aligned} \gamma_0 &= \left( \frac{\partial \widehat{\Psi}}{\partial T} \right)_p / \left( \frac{\partial \widehat{\Psi}}{\partial T} \right)_v = \frac{\partial(\widehat{\Psi}, p)}{\partial(T, p)} \frac{\partial(T, v)}{\partial(\widehat{\Psi}, v)} \\ &= \frac{\partial(v, p)}{\partial(T, p)} \frac{\partial(\widehat{\Psi}, p)}{\partial(\widehat{\Psi}, v)} = \left( \frac{\partial v}{\partial p} \right)_T / \left( \frac{\partial v}{\partial p} \right)_{\widehat{\Psi}}. \end{aligned}$$

This proves (9.111).

$$\begin{aligned}
\mathfrak{L}_{\mathbf{J}a}^* = & -\nabla^* \cdot (\boldsymbol{\Pi}_a^* - \mathfrak{c}_a^* \boldsymbol{\Pi}^*) - \left( \frac{\eta_{Br}}{\eta_r} \right) \nabla^* (\Delta_a^* - \mathfrak{c}_a^* \Delta^*) \\
& - \left[ \boldsymbol{\Pi}^* + \left( \frac{\eta_{Br}}{\eta_r} \right) \Delta^* \boldsymbol{\delta} \right] \cdot \nabla^* \mathfrak{c}_a^* - \frac{1}{N_S} \mathbf{J}_a^* \cdot \nabla^* \mathbf{u}^* \\
& - \frac{N_\delta}{N_{Pr} N_E} v^* \left( \frac{T_r \Delta c_r}{\Delta T_r} \right) \sum_{a=1}^r \widehat{\mathbf{J}}_a^* \cdot \nabla^* T_a^* \\
& - \sum_{b=1}^r \epsilon_{JQ} \mathfrak{c}_a^* \mathfrak{K}_{ab}^* \mathbf{Q}'_b^* q_\gamma - \sum_{b=1}^{r-1} \mathfrak{c}_a^* \mathfrak{D}_{ab}^* \mathbf{J}_b^* q_\gamma. \tag{9.118}
\end{aligned}$$

For this particular discussion we will approximate  $\mathbf{d}_a^*$  as below:

$$\mathbf{d}_a^* \simeq \nabla^* \mathfrak{c}_a^*, \tag{9.119}$$

assuming that the mass differences between the molecules of the mixture are small since  $x_a^* - \mathfrak{c}_a^* = O(m_a - m_b)$ . It should be noted that the energy conservation law is now written in terms of enthalpy, which is expressed in terms of reduced temperature, and the heat flux  $\widehat{\mathbf{Q}}_a^*$  is replaced with the modified heat flux  $\widehat{\mathbf{Q}}'_a^*$  because in the case of a mixture the heat flux evolution equation appears in terms of the latter.

### 9.1.8.1 Mathematical Formulation of Hyperbolicity

The general question of hyperbolicity of the quasilinear differential system (9.103)–(9.110) is of interest if it is desired to develop a numerical solution method and a computational algorithm for the method. To begin the analysis let us recall that the present differential system evolves on a *calortropy surface* in the extended Gibbs manifold, which is the union of calortropy and the thermodynamic manifold  $\mathfrak{P} \cup \mathfrak{T}$  spanned by variables of (9.103)–(9.110)—this union is called *the Gibbs manifold*.

For an  $r$ -component fluid mixture there are  $(12r + 3)$  dependent variables and independent space-time variables  $(\xi_1, \xi_2, \xi_3, \zeta)$ . Therefore we introduce a column vector  $\mathbf{U}$  of  $(12r + 3)$  elements and three accompanying  $(12r + 3) \times (12r + 3)$  square matrices  $\mathbf{M}_{\xi_1}$ ,  $\mathbf{M}_{\xi_2}$ , and  $\mathbf{M}_{\xi_3}$ . The column vector consisting of  $1, v^* \mathfrak{S}_{ca}^*, \dots, N_\delta v^* \mathfrak{S}_h^*, N_\delta v^* \mathfrak{L}_{\Pi a}^*, \dots, N_\delta v^* \mathfrak{L}_{Ja}^*$  will be denoted by

$$\mathbf{W} = \text{col} (1, v^* \mathfrak{S}_{ca}^*, \dots, N_\delta v^* \mathfrak{S}_h^*, N_\delta v^* \mathfrak{L}_{\Pi a}^*, \dots, N_\delta v^* \mathfrak{L}_{Ja}^*). \tag{9.120}$$

Then the differential system in question can be written in the form

$$\frac{\partial \mathbf{U}}{\partial \zeta} + \mathbf{M}_{\xi_1} \frac{\partial \mathbf{U}}{\partial \xi_1} + \mathbf{M}_{\xi_2} \frac{\partial \mathbf{U}}{\partial \xi_2} + \mathbf{M}_{\xi_3} \frac{\partial \mathbf{U}}{\partial \xi_3} = \mathbf{W}(\mathbf{U} | \xi_1, \xi_2, \xi_3). \tag{9.121}$$

Here the column vector  $\mathbf{U}$  has  $(12r + 3)$  elements

$$\mathbf{U} = \text{col}(v^*, c_1^*, \dots, c_{r-1}^*, u_{\xi_1}^*, \dots, u_{\xi_3}^*, \hat{h}^*, \hat{\Pi}_{1\xi_1\xi_1}^*, \dots, \hat{\Pi}_{r\xi_3\xi_3}^*, \hat{\Delta}_1^*, \dots, \hat{\Delta}_r^*, \hat{Q}_{1\xi_1}^*, \dots, \hat{Q}_{r\xi_3}^*, \hat{J}_{1\xi_1}^*, \dots, \hat{J}_{(r-1)\xi_3}^*), \quad (9.122)$$

and  $\xi$  is the position vector with three elements  $\xi = (\xi_1, \xi_2, \xi_3)$ . The position variables (coordinates)  $(\xi_1, \xi_2, \xi_3)$  are then transformed to

$$\varphi_i(\xi_1, \xi_2, \xi_3, t) = \text{constant} \quad (i = 1, 2, 3) \quad (9.123)$$

such that its Jacobian of transformation is not equal to 0:

$$J = \frac{\partial(\xi_1, \xi_2, \xi_3)}{\partial(\varphi_1, \varphi_2, \varphi_3)} \neq 0. \quad (9.124)$$

In the transformed coordinates, (9.121) then takes the form

$$\sum_{j=1}^3 \left( \frac{\partial \varphi_j}{\partial \zeta} + \sum_{i=1}^3 \mathbf{M}_{\xi_i} \frac{\partial \varphi_j}{\partial \xi_i} \right) \frac{\partial \mathbf{U}}{\partial \varphi_j} = \mathbf{W}. \quad (9.125)$$

If we define

$$-\lambda_j = \frac{\frac{\partial \varphi_j}{\partial \zeta}}{\sqrt{\sum_{k=1}^3 \left( \frac{\partial \varphi_j}{\partial \xi_k} \right)^2}}, \quad \nu_{ij} = \frac{\frac{\partial \varphi_j}{\partial \xi_i}}{\sqrt{\sum_{k=1}^3 \left( \frac{\partial \varphi_j}{\partial \xi_k} \right)^2}}, \quad (9.126)$$

then (9.125) becomes

$$\sum_{j=1}^3 \left( \sum_{i=1}^3 \mathbf{M}_{\xi_i} \nu_{ij} - \lambda_j \right) \frac{\partial \mathbf{U}}{\partial \varphi_j} = \mathbf{W}. \quad (9.127)$$

If a super-column vector spanned by  $(\partial \mathbf{U} / \partial \varphi_1, \partial \mathbf{U} / \partial \varphi_2, \partial \mathbf{U} / \partial \varphi_3)$  is constructed, then the matrix on the left forms a  $[3 \times (12r + 3)] \times [3 \times (12r + 3)]$  block diagonal supermatrix matrix. Therefore the eigenvalues of the supermatrix are determined by the eigenvalue problems of each  $(12r + 3) \times (12r + 3)$  matrix separately. The eigenvalues are thus determined by the characteristic determinants

$$\det \left| \sum_{i=1}^3 \mathbf{M}_{\xi_i} \nu_{ij} - \lambda_j \right| = 0 \quad (j = 1, 2, 3). \quad (9.128)$$

If the eigenvalues of the matrix, which are roots  $\lambda_j^\alpha$  ( $\alpha = 1, \dots, 12r + 3$ ) of the determinant, are all real, then the quasilinear differential system (9.121) of the generalized

hydrodynamic equations under consideration, are said to be *hyperbolic* according to the definition of hyperbolicity [31].

It would be impractical to demonstrate it for the general case. In the case of a system of arbitrary dimension the hyperbolicity can be demonstrated, perhaps, by numerical methods. Nevertheless, the consideration given here may be applied to develop a numerical algorithm to study transport processes based on the generalized hydrodynamic equations in a manner consistent with the laws of thermodynamics on which the present theory is founded as has been shown in the previous chapters in this work.

However, it is found possible to show that the differential system is indeed hyperbolic by using an alternative direct method, although the direct method employed for the purpose is seen pedestrian from the mathematical viewpoint. In the following we will present the results of tedious analysis on the question, leaving out the details. If one follows the method described below, hyperbolic wave equations can be obtained without fail.

To obtain the second-order substantial time derivatives of (9.103)–(9.106) we note the following commutation relation of substantial time derivative  $d_\zeta$  and spatial derivative  $\nabla^*$ :

$$[d_\zeta, \nabla^*] = d_\zeta \nabla^* - \nabla^* d_\zeta = -(\nabla^* \mathbf{u}^*) \cdot \nabla^*. \quad (9.129)$$

Operating  $d_\zeta$  on, namely, differentiating, (9.103)–(9.106) and making use of (9.107)–(9.110) to replace the derivatives of  $\widehat{\Pi}_a^*$ , etc. generated thereby in the former set, we obtain second-order partial differential equations of hyperbolic type in substantial time derivative form as follows:

$$\frac{1}{c_v^2} d_\zeta^2 v^* - \nabla^{*2} v^* = c_v^2 v^* \left[ (\nabla^* \cdot \mathbf{u}^*)^2 - (\nabla^* \mathbf{u}^*) : (\nabla^* \mathbf{u}^*) \right] + \mathfrak{N}_v(N_\delta), \quad (9.130)$$

$$\frac{1}{c_{ca}^2} d_\zeta^2 \mathfrak{c}_a^* - \nabla^{*2} \mathfrak{c}_a^* = (\nabla^* \mathfrak{c}_a^*) \cdot \nabla^* \ln(p^* v^*) + \mathfrak{N}_{ca}(N_\delta), \quad (9.131)$$

$$\frac{1}{c_u^2} d_\zeta^2 \mathbf{u}^* - \nabla^* \cdot [\nabla^* \mathbf{u}^*]^{(2)} = \frac{5}{6} \nabla^* (\nabla^* \cdot \mathbf{u}^*) + \mathfrak{N}_{vw}, \quad (9.132)$$

$$\frac{1}{c_{hw}^2} d_\zeta^2 T^* - \nabla^{*2} T^* = \frac{N_\delta}{2N_{Pr}\widehat{C}_p^* p^* v^*} \mathfrak{N}_{hw} \quad (9.133)$$

with various wave speeds to which we are led to define by the formulas:

$$c_v = \frac{1}{N_M} \sqrt{\frac{6v_0^*}{5\kappa_T^*}}, \quad (9.134)$$

$$c_{ca} = \frac{1}{N_M} \sqrt{\frac{6p^* v^* \Delta \mathfrak{c}_r}{5}} \simeq \sqrt{\frac{6\Delta \mathfrak{c}_r}{5}} \frac{1}{N_M}, \quad (9.135)$$

$$c_u = \frac{1}{N_M} \sqrt{\frac{4p^*v^*}{\gamma_0}} \simeq \sqrt{\frac{12}{5}} \frac{1}{N_M}, \quad (9.136)$$

$$c_{hw} = \frac{1}{N_M} \sqrt{\frac{2\widehat{C}_p^* p^* v^*}{\gamma_0}} \simeq \sqrt{\frac{6\widehat{C}_p^*}{5}} \frac{1}{N_M}. \quad (9.137)$$

Interestingly, the inverse Mach number essentially defines the wave speeds.

The terms  $\mathfrak{N}_v$ ,  $\mathfrak{N}_{ca}$ ,  $\mathfrak{N}_{vw}$ , and  $\mathfrak{N}_{hw}$  in the wave equations, which depend on  $N_\delta$ , are defined as follows:

$$\mathfrak{N}_v = -N_\delta \kappa_\Psi^* \left( \nabla^* \nabla^* : \widehat{\Pi}^* + \nabla^{*2} \widehat{\Delta}^* \right) + N_\delta \kappa_T^* \nabla^* \cdot (v^* \mathfrak{S}_u^*), \quad (9.138)$$

$$\begin{aligned} \mathfrak{N}_{ca} = & \frac{N_\delta}{2N_S p^* v^*} (\nabla^* \mathbf{u}) : \nabla^* \widehat{\mathbf{J}}_a^* + \frac{N_\delta}{2N_S p^* v^*} d_\zeta (v^* \mathfrak{S}_{ca}^*) \\ & - \frac{N_\delta}{p^* v^*} \nabla^* \cdot (v^* \mathfrak{L}_{Ja}^*), \end{aligned} \quad (9.139)$$

$$\begin{aligned} \mathfrak{N}_{vw} = & \frac{1}{4p^* v^*} \left[ (\nabla^* \mathbf{u}^*) : \nabla^* \widehat{\Pi}^* + (\nabla^* \mathbf{u}^*) \cdot \nabla^* \widehat{\Delta}^* \right] \\ & - \frac{1}{4p^*} \nabla^* (d_\zeta p^*) + [\nabla^* \mathbf{u}^*]^{(2)} \cdot \nabla^* \ln(p^* v^*) \\ & - \frac{1}{4} (\nabla^* \cdot \mathbf{u}^*) \left[ \nabla^* \ln p^* - \frac{10}{3} \nabla^* \ln(p^* v^*) \right] \\ & - \frac{N_\delta}{2p^* v^*} \nabla^* \cdot \left( \sum_{a=1}^r v^* \mathfrak{L}_{\Pi a}^* \right) - \frac{N_\delta}{2p^* v^*} \nabla^* \left( \sum_{a=1}^r v^* \mathfrak{L}_{\Delta a}^* \right) \\ & + \frac{N_\delta}{4p^* v^*} d_\zeta (v^* \mathfrak{S}_u^*), \end{aligned} \quad (9.140)$$

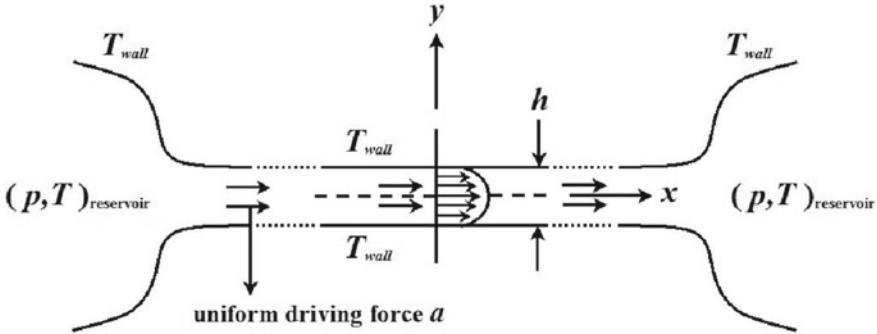
$$\begin{aligned} \mathfrak{N}_{hw} = & \frac{N_{\text{Re}} N_{\text{Pr}} N_E}{\gamma_0 N_M^2} \left[ (d_\zeta v^*) d_\zeta p^* + v^* d_\zeta^2 p^* \right] \\ & - 2 \left( \frac{T_r \Delta \mathfrak{c}_r}{\Delta T_r} \right) \sum_{a=1}^r \left[ (d_\zeta T_a^*) \nabla^* \cdot \widehat{\mathbf{J}}_a^* + \widehat{\mathbf{J}}_a^* \cdot \nabla^* (d_\zeta T_a^*) \right] \\ & + (\nabla^* \mathbf{u}^*) \odot \nabla^* \left[ \widehat{\mathbf{Q}}'^* + \left( \frac{T_r \Delta \mathfrak{c}_r}{\Delta T_r} \right) \sum_{a=1}^r T_a^* \widehat{\mathbf{J}}_a^* \right] \\ & + \frac{2T_r \Delta \mathfrak{c}_r p^* v^*}{\Delta T_r} (\nabla^* T^*) \cdot \nabla^* \ln(\widehat{C}_p^* p^* v^*) \end{aligned}$$

$$\begin{aligned}
& + \frac{2T_r \Delta c_r p^* v^*}{\Delta T_r} \sum_{a=1}^r T_a^* (\nabla^* c_a) \cdot \nabla^* \ln(p^* v^*) \\
& - \frac{2N_\delta N_{Pr}}{N_\delta} \nabla^* \cdot \left( v^* \sum_{a=1}^r \mathcal{L}_{Qa}^* \right) + 2N_\delta \left( \frac{T_r \Delta c_r}{\Delta T_r} \right) \sum_{a=1}^r \nabla^* \cdot (T_a^* v^* \mathcal{L}_{Ja}^*) \\
& - 2N_\delta \left( \frac{T_r \Delta c_r}{\Delta T_r} \right) \sum_{a=1}^r v^* (\nabla^* T_a^*) \cdot \mathcal{L}_{Ja}^* + N_{Pr} N_E d_\zeta (v^* \mathfrak{S}_h^*). \quad (9.141)
\end{aligned}$$

If one is willing to labor further to include the linear dissipation terms which are lumped into terms such as  $\mathcal{L}_{\Pi a}^*$ , etc., it is possible to make them explicit in the wave equations obtained earlier. They would then indicate and even compel us to modify the wave speed formulas because they would include the effects of dissipation processes on the transport coefficients. In this connection, we note that a special case of generalized hydrodynamics considered here was studied in Ref. [32] in the case of chemical reactions with a feedback loop—specifically, the Selkov model [33] for glycolysis—for which numerical solution methods were employed to obtain solutions. The evolution equations for such a case were also found hyperbolic—more precisely, nonlinear coupled telegraphist equations [32]—and produce a plethora of wave patterns including stable or unstable spirals, oscillatory waves, solitary waves, other types of complex patterns. When the dissipation terms and other nonlinear terms in  $\mathfrak{N}_v$ ,  $\mathfrak{N}_{ca}$ , etc. are explicitly taken into account in the equations presented earlier, it would appear reasonable to expect for such complex wave patterns to emerge if numerical solutions are sought for such evolution equations of generalized hydrodynamics.

## 9.2 Applications of Generalized Hydrodynamic Equations for Gases

The generalized hydrodynamic equations presented have been applied to study a number of flow problems appearing in rarefied gas dynamic phenomena [34, 35], semiconductor carrier mobility [36], and shock wave phenomena [15–17, 37, 38] in excellent accuracy. A computational fluid dynamic code [39] also has been developed for the quasilinear model presented earlier. Since the topics mentioned have been reported in the literature, the interested reader in the subject is referred to the literature cited. Nevertheless, before moving onto to the generalized hydrodynamics of liquids we would like to discuss a more recent study of application that has appeared in the literature.



**Fig. 9.2** Flow configuration for a unidirectional flow gas through a channel of width \$2 \times d\$. The channel is aligned to the \$x\$ direction of the coordinate system subject to a uniform driving force. The width of the channel is \$2 \times d\$ along the \$y\$ direction across which a thermal gradient is applied. Therefore the temperature of the walls are not the same as the gas temperature. The length of the channel is \$L\$, which is arbitrary. The figure is reprinted with permission from R. S. Myong, Phys. Fluids **23**, 012002 (2011) © 2011 American Institute of Physics

### 9.2.1 Compressible Poiseuille Gas Flow

Here we discuss application of the generalized hydrodynamic equations to formulate a hydrodynamic theory of unidirectional flow of a one-component gas at pressure \$p\$ and temperature \$T\$ described in Fig. 9.2. The channel is parallel to the \$x\$ direction of the coordinate system and the gas flows unidirectionally along the \$x\$ direction, driven by a uniform force aligned in the positive direction. The length of the channel, which is arbitrary, is \$L\$. The width of the channel is \$2 \times d\$ in the \$y\$ direction across which a thermal gradient is applied. \$T\_{wall}\$ denotes temperature at the walls located at \$y = \pm d\$ on the \$y\$ axis. The temperature of the walls are not the same as the gas temperature. Therefore there is present a steady temperature gradient in the \$y\$ direction.

The present flow configuration, originally studied by Myong [38], mimics cooling or heating by a pipe system in a reactor. In this one-dimensional model flow, the velocity vector \$\mathbf{u}\$ has no \$y\$ and \$z\$ components: \$u\_y = u\_z = 0\$. Therefore there are no \$x\$ and \$z\$ spatial derivatives of flow variables involved. Thus the dimensionless generalized hydrodynamic equations for the steady state of the flowing gas are as follows:

$$v^* \nabla_x^* u_x^* = 0, \quad (9.142)$$

$$N_\delta \nabla_y^* \Pi_{xy}^* = \rho^* a, \quad (9.143)$$

$$\nabla_y^* p^* + N_\delta \nabla_y^* \Pi_{yy}^* = 0, \quad (9.144)$$

$$N_\delta \nabla_y^* \Pi_{yz}^* = 0, \quad (9.145)$$

$$\frac{N_\delta}{N_{Pr} N_E} \nabla_y^* Q_y^* + N_\delta \nabla_y^* (\Pi_{xy}^* u_x^*) = a \rho^* u_x^*, \quad (9.146)$$

$$-\frac{p^*}{\eta_0^*} \Pi_{xx}^* q_L(\kappa_L) - \frac{4}{3} N_\delta \Pi_{xy}^* [\nabla^* \mathbf{u}^*]_{xy}^{(2)} = 0, \quad (9.147)$$

$$-\frac{p^*}{\eta_0^*} \Pi_{yy}^* q_L(\kappa_L) - \frac{2}{3} N_\delta \Pi_{xy}^* [\nabla^* \mathbf{u}^*]_{xy}^{(2)} = 0, \quad (9.148)$$

$$-\frac{p^*}{\eta_0^*} \Pi_{zz}^* q_L(\kappa_L) - \frac{2}{3} N_\delta \Pi_{xy}^* [\nabla^* \mathbf{u}^*]_{xy}^{(2)} = 0, \quad (9.149)$$

$$-\frac{p^*}{\eta_0^*} \Pi_{xy}^* q_L(\kappa_L) - 2 N_\delta \Pi_{xy}^* [\nabla^* \mathbf{u}^*]_{xy}^{(2)} - 2 p^* [\nabla^* \mathbf{u}^*]_{xy}^{(2)} = 0, \quad (9.150)$$

$$-\frac{p^*}{\eta_0^*} \Pi_{xz}^* q_L(\kappa_L) - 2 N_\delta \Pi_{xy}^* [\nabla^* \mathbf{u}^*]_{xy}^{(2)} = 0, \quad (9.151)$$

$$-\frac{p^*}{\eta_0^*} \Pi_{yz}^* q_L(\kappa_L) = 0, \quad (9.152)$$

$$\begin{aligned} & -\frac{\widehat{C}_p^* p^*}{\lambda_0^*} Q_x^* q_L(\kappa_L) - \frac{2 N_\delta}{N_{\text{Pr}}} Q_y [\nabla^* \mathbf{u}^*]_{xy}^{(2)} - N_\delta \widehat{C}_p^* \Pi_{xy}^* \nabla_y^* T^* \\ & - \frac{N_\delta N_E}{\gamma_0 N_M^2} \Pi_{xy}^* \nabla_y^* p^* - \frac{N_\delta^2 N_E}{\gamma_0 N_M^2} [\Pi_{xx}^* \nabla_y^* \Pi_{yx}^* + \Pi_{xy}^* \nabla_y^* \Pi_{yy}^* + \Pi_{xz}^* \nabla_y^* \Pi_{yz}^*] = 0, \end{aligned} \quad (9.153)$$

$$\begin{aligned} & -\frac{\widehat{C}_p^* p^*}{\lambda_0^*} Q_y^* q_L(\kappa_L) - \widehat{C}_p^* (p^* + N_\delta \Pi_{yy}^*) \nabla_y^* T^* - \frac{N_\delta N_E}{\gamma_0 N_M^2} \Pi_{yy}^* \nabla_y^* p^* \\ & - \frac{N_\delta^2 N_E}{\gamma_0 N_M^2} [\Pi_{yx}^* \nabla_y^* \Pi_{xy}^* + \Pi_{yy}^* \nabla_y^* \Pi_{yy}^* + \Pi_{yz}^* \nabla_y^* \Pi_{yz}^*] = 0, \end{aligned} \quad (9.154)$$

$$\begin{aligned} & -\frac{\widehat{C}_p^* p^*}{\lambda_0^*} Q_z^* q_L(\kappa_L) - N_\delta \widehat{C}_p^* \Pi_{yz}^* \nabla_y^* T^* - \frac{N_\delta N_E}{\gamma_0 N_M^2} \Pi_{yz}^* \nabla_y^* p^* \\ & - \frac{N_\delta^2 N_E}{\gamma_0 N_M^2} [\Pi_{xz}^* \nabla_y^* \Pi_{yx}^* + \Pi_{zy}^* \nabla_y^* \Pi_{yy}^* + \Pi_{zz}^* \nabla_y^* \Pi_{yz}^*] = 0, \end{aligned} \quad (9.155)$$

where we have replaced the collision bracket integrals  $\mathfrak{B}^*$  and  $\mathfrak{T}^*$  with the shear viscosity  $\eta_0^*$  and thermal conductivity  $\lambda_0^* T^*$  appearing in the linear theory of transport processes [see (9.69)–(9.71)], and lastly  $a := \widehat{F}_x$ . Also recall that  $\kappa_L = N_\delta \kappa_L^*$  in the nonlinear factor  $q_L(\kappa_L)$ . The asterisks stand for dimensionless reduced quantities. There are 14 equations in all to solve for flow profiles. We have ignored the bulk viscosity contribution. Therefore the excess normal stress  $\Delta = \frac{1}{3} \text{Tr} \mathbf{P} - p$  and its evolution equation do not appear in the set. In the case of a gas supporting bulk viscosity phenomena, it would be necessary to include the evolution equation for  $\Delta$  and the related. The evolution equations presented above differ from Myong's model equations [38] by the terms of  $N_\delta^2$  and the nonlinear factor  $q_L$ , which he set equal to unity when the equations are solved. Therefore the results of his model is valid

as well under the aforementioned conditions. The nonlinear factor  $q_L$  is important if one wishes to describe flow conditions far removed from equilibrium, although it is necessary to sacrifice it if analytic solutions are desired.

### 9.2.2 Integration of Conservation Laws

The conservation laws (9.142)–(9.146) are easily integrated over  $y$  to yield the expressions

$$\begin{aligned} u_x^*(y) &= C_1, \\ p^*(y) &= C_2 - N_\delta \Pi_{yy}^*(y), \\ N_\delta \Pi_{xy}^*(y) &= a\phi(y) + N_\delta b, \\ \phi(y) &= \int_d^y dy \rho^*(y) = \int_d^y dy \frac{p^*(y)}{k_B T^*(y)} \\ &= \int_d^y dy \frac{C_2 - N_\delta \Pi_{yy}^*(y)}{k_B T^*(y)}, \\ \Pi_{yz}^*(y) &= C_4, \\ N_\delta Q_y^*(y) &= N_{Pr} N_e [a\phi_u(y) - N_\delta [a\phi(y) + N_\delta b] u_x^*(y) + C_3], \\ \phi_u(y) &= \int_d^y \rho^*(y) u_x^*(y), \end{aligned} \quad (9.156)$$

where  $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$  and  $b$  are integration constants. In particular,  $b = \Pi_{xy}^*(d)$ , which is the value of the shear stress at  $y = d$ , the position of the upper wall. Here the density of the fluid is determined through the equation of state  $\rho^* = p^*/k_B T^*$ . Thus the function  $\phi(y)$  describes the reduced density distribution along the  $y$  direction. The function  $\phi_u(y)$  gives the mass flux induced by shearing. The results in (9.156) feed into the constitutive equations.

The integration constants can be determined from the boundary conditions on flow variables. The constant  $C_4$  will be found equal to zero owing to (9.17), and with  $Q_y^*(0) = 0$  the constant  $C_3$  is determined such that

$$a\phi_u(0) - N_\delta [a\phi(0) + N_\delta b] u_x^*(0) + C_3 = 0. \quad (9.157)$$

Therefore, there are two as yet undetermined constants in (9.156).

### 9.2.3 Reduction of Constitutive Relations to an Independent Set

The constitutive relations (9.147)–(9.155) are not all independent. They are eventually reduced to a pair of independent nonlinear ordinary differential equations for

velocity  $u_x^*$  and  $T^*$  whose solutions provide the velocity and temperature profiles characteristic of the flow model in hand.

### 9.2.3.1 Shear Stress Equations

The  $yz$  component  $\Pi_{yz}^*$  of the shear stress tensor  $\Pi$  is found equal to zero as in (9.156). The shear stress tensor is found traceless. This is indeed borne out by (9.147)–(9.149), which, upon adding side by side, result in

$$\Pi_{xx}^* + \Pi_{yy}^* + \Pi_{zz}^* = 0 \quad (9.158)$$

owing to the fact that  $q_L \geq 1$ . There also follow the relations between the normal stress components:

$$\Pi_{yy}^* = \Pi_{zz}^* = -\frac{1}{2}\Pi_{xx}^* = -\frac{C_2 - p^*}{2N_\delta}, \quad (9.159)$$

where the last equality follows from the second equation in (9.156). Equation (9.152) confirms that  $\Pi_{yz}^*$  is indeed equal to zero, which thus fixes the integration constant:  $C_4 = 0$ . From (9.150) and (9.151) follows the relation

$$\Pi_{xz}^* = \frac{N_\delta \Pi_{xy}^{*2}}{(p^* + N_\delta \Pi_{xy}^*)}. \quad (9.160)$$

This is a parabolic curve in the  $(\Pi_{xz}^*, \Pi_{xy}^*)$  plane, but  $O(N_\delta)$ . Thus  $\Pi_{xz}^*$  vanishes as  $N_\delta \rightarrow 0$ . Therefore there remains  $\Pi_{xy}^*$  as the independent shear stress component, which would be coupled to a heat flux component  $Q_y^*$  as will be shown. In fact, on substitution of  $\Pi_{xy}^*$  from the third equation in (9.156) we obtain (9.150) in the form

$$\nabla_y^* u_x^* = \frac{p^*[a\phi(y) + N_\delta b]}{N_\delta \eta_0^*[p^* + a\phi(y) + N_\delta b]} q_L(N_\delta \kappa_L^*). \quad (9.161)$$

This is one of the nonlinear ordinary differential equations for the flow problem under consideration. From this we already see that compressibility of the fluid (gas) plays an important role in determining the velocity profile of the flow.

### 9.2.3.2 Heat Flux Equations

On substituting the shear stress components shown in (9.156) into the heat flux equations in (9.153)–(9.155) we obtain the constitutive relations for heat flux components as follows:

$$Q_z^* q_L = S_z(y|b), \quad (9.162)$$

$$Q_x^* q_L = -\frac{N_\delta \lambda_0^*}{N_{\text{Pr}} \widehat{C}_p^* p^*} Q_y^* \nabla_y^* u_x^* + S_x(\nabla_y^* T^*|y, b), \quad (9.163)$$

$$Q_y^* q_L = -\lambda_{\text{eff}}^* \nabla_y^* T^* + S_y(y|b), \quad (9.164)$$

where  $\lambda_{\text{eff}}^*$  is given by an effective thermal conductivity defined by the formula

$$\lambda_{\text{eff}}^* = \lambda_0^* - \frac{1}{3} N_\delta^2 \lambda_0^* \left[ 1 + \frac{N_E \alpha_p}{\widehat{C}_p^* \gamma_0 N_M^2 \kappa_T} \right] \frac{[a\phi(y) + N_\delta b]^2}{p^* [p^* + a\phi(y) + N_\delta b]} \quad (9.165)$$

with  $\alpha_p$  and  $\kappa_T$  denoting isobaric expansion coefficient and isothermal compressibility, respectively, defined by

$$\alpha_p = \frac{1}{v^*} \left( \frac{\partial v^*}{\partial T^*} \right)_p, \quad \kappa_T = -\frac{1}{v^*} \left( \frac{\partial v^*}{\partial p^*} \right)_T, \quad (9.166)$$

and  $S_z(y|b)$ ,  $S_x(\nabla_y^* T^*|y, b)$ , and  $S_y(y|b)$  are given by the formulas

$$S_z(y|b) = \frac{N_E \lambda_0^*}{\gamma_0 N_M^2 \widehat{C}_p^*} \frac{(1 - N_\delta) a [a\phi(y) + N_\delta b]^2}{p^* [p^* + a\phi(y) + N_\delta b]}, \quad (9.167)$$

$$S_x(\nabla_y^* T^*|y, b) = -\frac{\lambda_0^*}{p^*} \left( 1 + \frac{2N_E \alpha_p}{\gamma_0 N_M^2 \widehat{C}_p^* \kappa_T} \right) [a\phi(y) + N_\delta b] \nabla_y^* T^* \\ + \frac{2N_E \lambda_0^*}{\gamma_0 N_M^2 \widehat{C}_p^*} a (1 - N_\delta) \left[ 1 - \frac{p_0^*}{p^*} + \frac{N_\delta^2 b^2}{3p^*(p_0^* + N_\delta b)} \right], \quad (9.168)$$

$$S_y(y|b) = \frac{N_E \lambda_0^*}{2\gamma_0 N_M^2 \widehat{C}_p^* p^*} \nabla_y^* [a\phi(y) + N_\delta b]^2 \\ + \frac{N_E \lambda_0^*}{2\gamma_0 N_M^2 \widehat{C}_p^* p^*} \nabla_y^* \frac{[a\phi(y) + N_\delta b]^4}{9 [p^* + a\phi(y) + N_\delta b]^2} \\ - \frac{N_\delta^2 N_E \lambda_0^*}{2\gamma_0 N_M^2 \widehat{C}_p^* p^*} a. \quad (9.169)$$

Therefore mentioned quantities are, most importantly, given by the shear stress  $\Pi_{xy}^*$  expressed by the third equation in (9.156)—an integral of the momentum conservation law. Therefore  $Q_z^*$  is determined by the shear stress  $\Pi_{xy}^*$  and hence not an independent quantity. From (9.163) and (9.164) is obtained a relation of  $Q_x^*$  to  $Q_y^*$ :

$$Q_x^* = \frac{\frac{N_\delta \lambda_0^*}{N_{\text{Pr}} \widehat{C}_p^* p^*} Q_y^* \nabla_y^* u_x^* - S_x(\nabla_y^* T^*|y, b)}{\lambda_{\text{eff}}^* \nabla_y^* T^* - S_y(y|b)} Q_y^*. \quad (9.170)$$

Therefore only  $Q_y^*$  is an independent heat flux component. On substituting  $Q_y^*$  from the sixth equation of (9.156) into (9.164) we finally obtain a nonlinear ordinary differential equation for reduced temperature  $T^*$ :

$$\begin{aligned}\nabla_y^* T^* &= \frac{1}{\lambda_{eff}^*} S_y(y|b) \\ &- \frac{N_{Pr} N_E}{N_\delta \lambda_{eff}^*} \left\{ C_3 + \int_0^y dy a u_x^*(y) - u_x^* [a\phi(y) + N_\delta b] \right\} q_L(N_\delta \kappa_L^*) .\end{aligned}\quad (9.171)$$

This equation together with (9.161) forms a pair of coupled nonlinear ordinary differential equations for profiles of  $u_x^*$  and  $T^*$  for the flow problem described in Fig. 9.2. The differential equations are coupled owing to the nonlinear factor  $q_L$  which is given by the quadratic dissipation function  $\kappa^*$ , which in turn is found to depend on  $\nabla_y^* u_x^*$  and  $\nabla_y^* T^*$  if the expressions obtained earlier for  $\Pi^*$  and  $\mathbf{Q}^*$  are substituted into the dissipation function  $\kappa^*$ . It is given by the expression

$$\kappa^* = \frac{\sqrt{\pi} \sqrt[4]{2T^*}}{p^* \sqrt{\eta_0^*}} \left[ \Pi^* : \Pi^* + \frac{2\epsilon\eta_0^*}{T^* \lambda_0^*} \mathbf{Q}^* \cdot \mathbf{Q}^* \right]^{1/2} \quad (9.172)$$

where

$$\epsilon = \frac{\Delta T_r}{T_r N_E N_{Pr}} . \quad (9.173)$$

With the formulas for  $\Pi^*$  and  $\mathbf{Q}^*$  substituted into (9.172), the explicit form for the dissipation function  $\kappa^*$  can be obtained in an algebraic expression depending on gradients of  $u_x^*$  and  $T^*$  as well as  $y$  and integration constants:

$$\kappa^* = \frac{\sqrt{\pi} \sqrt[4]{2T^*}}{p^* \sqrt{\eta_0^*}} K(\nabla_y^* u_x^*, \nabla_y^* T^* | y, b, C_2) , \quad (9.174)$$

where the factor  $K(\nabla_y^* u_x^*, \nabla_y^* T^* | y, b, C_2)$  represents the square root factor in (9.172). Recall that

$$q_L = \frac{\sinh(N_\delta \kappa_L^*)}{N_\delta \kappa_L^*} . \quad (9.175)$$

### 9.2.3.3 Summary of Nonlinear Ordinary Differential Equations for $u_x^*$ and $T^*$

As a summary, we collect the pair of nonlinear coupled differential equations below:

$$N_\delta \nabla_y^* u_x^* = \frac{p^* [a\phi(y) + N_\delta b]}{\eta_0^* [p^* + a\phi(y) + N_\delta b]} q_L(N_\delta \kappa_L^*) , \quad (9.176)$$

$$\begin{aligned} N_\delta \nabla_y^* T^* &= \frac{N_\delta}{\lambda_{eff}^*} S_y(y|b) \\ &\quad - \frac{N_{Pr} N_E}{\lambda_{eff}^*} \left\{ C_3 + \int_0^y dy a u_x^*(y) - u_x^* [a \phi(y) + N_\delta b] \right\} q_L(N_\delta \kappa_L^*) . \end{aligned} \quad (9.177)$$

This set is now seen to involve four integration constants  $b$  and  $C_2$  together with two arising from integration of (9.176) and (9.177). There are four boundary conditions on  $u_x^*$  and  $T^*$ :  $u_x^*(\pm d)$  and  $T^*(\pm d)$ . Therefore the problem is well-posed, and the conventional integration routines provide numerical solutions. For example, they may be solved by a shooting method as used in Ref. [21].

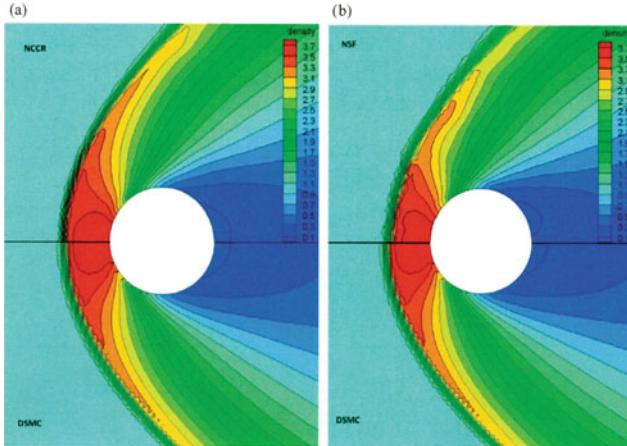
This type of coupled nonlinear ordinary differential equations was solved numerically for a cylindrical Couette flow configuration by Khayat in his Ph.D dissertation [21]. The summary of the results were reported in Refs. [22, 23], which well account for experimental results on cylindrical Couette flow. Although the flow configuration studied by Khayat is different from the present flow configuration, both his and the present set of equations are based on the generalized hydrodynamic equations, which are approximated similarly to those presented here. If the nonlinear factor  $q_L$  is set equal to unity and the nonlinear contributions in  $S_x(\nabla_y^* T^*|y, b)$  and  $S_y(y|b)$  are ignored, the two equations become not only decoupled and thus independent of each other, but also yield the classical hydrodynamic results for the one-dimensional channel flow. In that case, it is possible to recover Myong's results [38]. The set (9.176) and (9.177) should represent an extension of the classical theory for the one-dimensional (i.e., unidirectional) flow configuration in Fig. 9.2 in conditions far removed from equilibrium.

### 9.2.4 Rarefied Gas Flow Past a Circular Cylinder

The quasilinear evolution equation for shear stress and its role in rarefied gas flow has been recently studied by Myong and his collaborators [40, 41]. Their results have been reported in Ref. [38]. In this application the quasilinear generalized hydrodynamic equations for the flow configuration have been solved numerically and normalized density ( $\rho/\rho_\infty$ ) fields and contours of hypersonic flow at  $N_M = 5.48$  and  $N_{Kn} = 0.05$  are compared with the predictions by the direct simulation Monte Carlo (DSMC) method [42] and the classical hydrodynamic theory (NSF) predictions indirectly through comparison with DSMC predictions which are compared with the NSF predictions. An example of comparison is reproduced in Fig. 9.3.

They also calculated the time evolution of the enstrophy, defined by the surface integral of the square of the vorticity  $\Omega = \nabla \times \mathbf{u}$

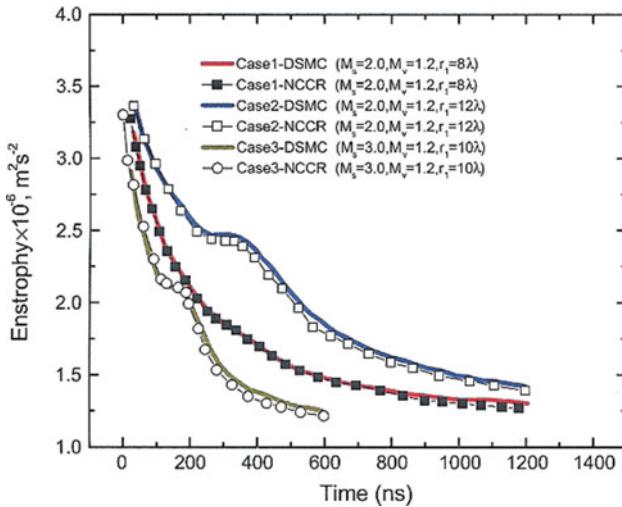
$$Enstropy = \int_V \Omega_z^2 dx dy = \int_A (\nabla \times \mathbf{u})_{xy} dx dy \quad (9.178)$$



**Fig. 9.3** Normalized density ( $\rho/\rho_\infty$ ) fields and contours of hypersonic flows around a cylinder at  $N_M = 5.48$  and  $N_{Kn} = 0.5$ . The *upper* and *lower* half of panel **(a)** are, respectively, the NCCR and DSMC predictions, and the *upper* and *lower* half of panel **(b)** are, respectively, the NSF and DSMC predictions (Ref. [54]). Reprinted with permission from N.T.P. Le, H. Xiao, and R.S. Myong, J. Comp. Phys. **273**, 160 (2014) Copyright, with permission from Elsevier

in the flow field and compared the results predicted by the DSMC method and by the quasilinear generalized hydrodynamic equations (NCCR) for the same flow configuration. Comparisons made in Fig. 9.4 reproduced from Ref. [41] show that the DSMC and NCCR methods yield virtually identical results for enstrophy versus time (ns).

In the figure NCCR (nonlinear coupled constitutive relation) stands for the quasilinear constitutive relation. Comparison made in Fig. 9.3 shows that the quasilinear constitutive model and DSMC in panel a gives virtually identical Mach number (velocity) contours, whereas the results by NSF in panel b display significantly different contours obtained by DSMC. The panel (a) of the figure shows that the quasilinear generalized hydrodynamic equations (NCCR) and the direct simulation Monte Carlo (DSMC) method predict virtually identical density profiles, whereas the Navier–Stokes–Fourier theory (NSF) predicts significantly different density profiles from the DSMC method predictions. This comparison again demonstrates the practical utility of the quasilinear generalized hydrodynamic model, which can substitute for the DSMC method. Flow parameters  $N_M$  and  $N_{Kn}$  chosen for the study of flow presented evidently represent the system far removed from equilibrium. This example, therefore, demonstrates the practical utility of the quasilinear generalized hydrodynamic equations for flows far removed from equilibrium.



**Fig. 9.4** Comparison of enstrophy versus time (ns) predicted by the DSMC method and the NCCR (quasilinear generalized hydrodynamic equations). Reproduced with permission from H. Xiao and R. S. Myong, Comput. Fluids **105**, 179 (2014) Copyright, with permission from Elsevier

### 9.2.5 The Knudsen Problem

Maxwell's 1867 paper [43] on kinetic theory of gases predicts a density independence of viscosity and thermal conductivity of normal state gas, and prompted by the contradictory experimental result by Kundt and Warburg [44] on rarefied gas viscosity, Maxwell [45] re-examined more deeply his kinetic theory of gas transport processes and, in order to repair his theory, invented the notion of velocity slip at the boundaries when a rarefied gas flows through a tube.

Influenced by the Kundt–Warburg experiment and Maxwell's kinetic theory of slip flow, Knudsen [46] performed various experiments and in 1909 reported an experimental investigation into the validity of Hagen–Poiseuille (HP) volume flow rate for rarefied gas flow through a long circular tube. According to the experiment, he found that although the volume flow rate follows the Hagen–Poiseuille flow rate if the mean pressure is in the range of normal gas pressure, it does not obey the HP flow rate, which predicts the flow rate should vanish as the pressure vanishes or the gas density vanishes. But he found it instead increases after reaching a minimum value as the pressure decreases toward zero.

In fact, he was able to fit his data for the volume flow rate per unit pressure difference  $Q_k$  to the empirical formula

$$Q_k = ap + b \frac{1 + c_1 p}{1 + c_2 p}, \quad (9.179)$$

where

$$a = \frac{\pi R^4}{8L\eta_0}, \quad (9.180)$$

$$b = \frac{4\sqrt{2\pi}}{3L\sqrt{\rho_1}}, \quad (9.181)$$

$c_1$  and  $c_2$  are numerical constants depending on the nature of gas molecule, and  $R$  and  $L$  denote the radius and length of the tube,  $\eta_0$  the shear viscosity of the gas,  $\rho_1$  the specific density of the gas at temperature  $T$  when the pressure is equal to 1 dyn/cm<sup>2</sup>, and  $p$  the mean gas pressure. The first term on the right of the empirical formula (9.179) represents the HP flow rate and the second term is responsible for giving the minimum of  $Q_k$  versus  $p$ . The ultimate validity of the second term as  $p$  tends to zero requires further investigation. His experiment induced other research workers to investigate the phenomenon observed by Knudsen. For example, Gaede [47] confirmed the presence of minimum in flow rate, but he also found that it does not tend to a finite value as  $p$  vanishes, but exhibit a logarithmic increase as  $p \rightarrow 0$ . Since Knudsen's experimental discovery contradicts the hydrodynamic prediction, it was referred to the Knudsen paradox in the literature. However, it seems more appropriate to call it the Knudsen problem because it may not be a paradox after all from a broader viewpoint in hydrodynamics extending the Navier–Stokes theory of hydrodynamics to flows in the rarefied gas regime.

In this subsection we investigate the Knudsen problem [48] from the viewpoint of generalized hydrodynamics described earlier in this work. This investigation, as a matter of fact, would be another example of applications of the generalized hydrodynamics. We assume that a gas flows laminarly in a circular tube of radius  $R$  and length  $L$ , subject to a longitudinal pressure gradient  $p$ . The pressure difference between the entrance and exit of the tube is denoted by  $\Delta p := p_i - p_f$  where  $p_i$  is the pressure at the entrance and  $p_f$  the pressure at the exit of the tube. The gas is maintained a constant uniform temperature. Therefore there is no heat flux involved. We also assume that there is no normal stress differences present.

Since there is axial symmetry present in the flow, the appropriate coordinates to take are of cylindrical coordinate system. We denote them by  $(r, \theta, z)$ , where the direction of flow is taken  $z$ ; that is, the axis of tube is parallel to the  $z$  axis of the coordinate system. Since the length of the tube is assumed sufficiently long so that the end effects of the tube is negligible, the flow properties and, in particular, the fluid velocity components are independent of  $z$ . They are also independent of polar angle  $\theta$  because of the axial symmetry of the flow. The flow is assumed to be in the positive direction of the axial coordinate  $z$ . The angular component of velocity  $\mathbf{u}$  is equal to zero owing to the absence of a rotary motion of the gas around the  $z$  axis. The radial velocity component  $u_r$  is equal to zero for the following reason.

Since we are interested in a steady flow, the steady-state equation of continuity is

$$\nabla \cdot (\rho \mathbf{u}) = 0. \quad (9.182)$$

In the cylindrical coordinate this equation takes form

$$\frac{1}{r} \frac{\partial}{\partial r} (\rho r u_r) + \frac{1}{r} \frac{\partial}{\partial \theta} (\rho u_\theta) + \frac{\partial}{\partial z} (\rho u_z) = 0. \quad (9.183)$$

Since the density  $\rho$  and the velocity components  $u_\theta$  and  $u_z$  do not depend on  $z$  and  $\theta$  for the reasons mentioned earlier, we obtain from (9.183)

$$\frac{\partial}{\partial r} (\rho r u_r) = 0,$$

which on integration yields

$$\rho r u_r = \text{constant}.$$

Since at the boundary  $r = R$  (i.e., tube wall)  $u_r = 0$ , we conclude that  $u_r = 0$  everywhere specially since  $\rho \neq 0$ . Since  $u_\theta = 0$  as noted earlier, we conclude

$$\mathbf{u} = (0, 0, u_z). \quad (9.184)$$

We define the normal stress difference  $N_1$  and  $N_2$  in terms of traceless symmetric shear stress tensor  $\Pi$ :

$$N_1 = \Pi_{zz} - \Pi_{rr}, \quad N_2 = \Pi_{rr} - \Pi_{\theta\theta}, \quad (9.185)$$

where  $\Pi_{rr}$ ,  $\Pi_{\theta\theta}$ , and  $\Pi_{zz}$  are the normal components of  $\Pi$ . We will denote the off-diagonal elements  $\Pi_{rz}$  and  $\Pi_{zr}$ , which are symmetric, by a scalar symbol  $\Pi$ :

$$\Pi := \Pi_{rz} = \Pi_{zr}. \quad (9.186)$$

The component  $\Pi$  is the only nonvanishing component of the flow configuration considered. Then the components of the momentum balance equation are:

$$-\frac{\partial p}{\partial r} - \frac{1}{3r} \frac{\partial}{\partial r} r(N_2 - N_1) - \frac{1}{3r} (2N_2 + N_1) = 0, \quad (9.187)$$

$$-\frac{\partial p}{\partial z} - \frac{1}{r} \frac{\partial}{\partial r} r\Pi = 0. \quad (9.188)$$

Note that these are exact balance equations.

Since the normal stress differences  $N_1$  and  $N_2$  are assumed to be absent for the present consideration, setting  $N_1 = N_2 = 0$ , we obtain from Eq. (9.187)

$$\frac{\partial p}{\partial r} = 0. \quad (9.189)$$

Therefore the pressure is seen independent of  $r$ ; that is, there is no pressure variation across the tube. Furthermore, since the pressure gradient in the  $z$  direction is assumed constant, we find

$$p = -\frac{\Delta p}{L}z + p_i. \quad (9.190)$$

In the adiabatic approximation the quasilinear evolution equation for the shear stress  $\Pi$  for the flow is given by

$$\Pi q(\kappa) = -2\eta_0\gamma, \quad (9.191)$$

where

$$\gamma = \frac{1}{2} \frac{\partial u_z}{\partial r}, \quad (9.192)$$

$$q(\kappa) = \frac{\sinh \kappa}{\kappa}, \quad (9.193)$$

$$\kappa = \frac{\tau \Pi}{\eta_0}, \quad (9.194)$$

$$\tau = \frac{\sqrt{2\eta_0(m_r k_B T/2)^{1/2}}}{\sqrt{2} n k_B T \sigma}. \quad (9.195)$$

Here  $\eta_0$  is the Newtonian shear viscosity of the gas. It may be calculated from the first-order Chapman–Enskog formula of the Boltzmann kinetic theory. The symbols  $n$ ,  $\sigma$ , and  $m_r$  stand for number density, size parameter, and reduced mass of the gas molecule.

It is useful to note that the constitutive equation (9.191) for  $\Pi$  was in fact shown in a previous section on non-Newtonian flow to give rise a non-Newtonian viscosity agreeing with experiment in which the normal stress effects are absent. Its experimental relevance has been already established. The present investigation based on the constitutive equation is therefore thought to be well founded. We have already shown that the constitutive equation (9.191) together with the momentum balance equation, subject to the boundary conditions

$$u_z(R) = 0, \quad \left( \frac{\partial u_z}{\partial r} \right)_{r=R} = 0, \quad (9.196)$$

gives rise to the velocity profile

$$u_z(r) = \frac{r}{\tau r} [\cosh \delta - \cosh (\delta r/R)], \quad (9.197)$$

where

$$\delta = \frac{\tau R \Delta p}{2 L \eta_0}. \quad (9.198)$$

We also find that by the boundary condition on the velocity derivative at  $r = R$

$$\Pi = \frac{r \Delta p}{2 L}. \quad (9.199)$$

The velocity profile (9.197) gives rise to the parabolic HP velocity profile as the parameter  $\delta$  gets small.

The number of particles flowing through the tube per unit time  $Q$  is given by the formula

$$Q = 2\pi n \int_0^R dr r u_z(r). \quad (9.200)$$

On substitution of the velocity profile (9.197) we obtain the flow rate  $Q$ :

$$Q = Q_{HP} \frac{n\pi R^4 \Delta p}{8L\eta_0} (1 + \Delta Q)p,$$

where  $Q_{HP}$  is the Hagen–Poiseuille flow rate

$$Q_{HP} = \frac{\pi R^4 \Delta p}{8L\eta_0 \mathcal{R}T} \quad (9.201)$$

and  $\Delta Q$  is a correction factor to  $Q_{HP}$  defined by the formula

$$\Delta Q = 4\delta^2 \left[ \sinh^2 \left( \frac{\delta}{2} \right) + \left[ \cosh \left( \frac{\delta}{2} \right) - \frac{2}{\delta} \sinh \left( \frac{\delta}{2} \right) \right]^2 \right] - 1. \quad (9.202)$$

It is a correction arising from the non-Newtonian flow behavior of the gas. It is a consequence of the constitutive equation assumed for the shear stress  $\Pi$  under the assumption of vanishing normal stress differences. Within the framework of the assumptions taken, it is an exact result for the correction factor to the flow rate.

Now, let us examine the limiting behavior the result obtained for the flow rate. Since  $\delta$  is proportional to the parameter  $\tau$ , which is in turn inversely proportional to pressure, it is easy to infer that as  $p \rightarrow 0$

$$Q \rightarrow p \exp(\delta_0/p), \quad (9.203)$$

where

$$\delta_0 = \frac{\tau_0 R \Delta p}{2L\eta_0}, \quad (9.204)$$

$$\tau_0 = \frac{\sqrt{\eta_0 (2m_r k_B T)^{1/2}}}{\sqrt{2}\sigma}. \quad (9.205)$$

Since  $Q$  is linear with respect  $p$  as  $p$  increases to the normal pressure, the limiting behavior implies that there exists a minimum in  $Q$  at some value of  $p$  in the neighborhood of  $p = 0$ . The location of the minimum is given by

$$\frac{d}{d\delta} \left\{ \delta^{-3} \left[ \frac{1}{2} \cosh \delta + \delta^{-2} (\cosh \delta - 1) - \delta^{-1} \sinh \delta \right] \right\} = 0, \quad (9.206)$$

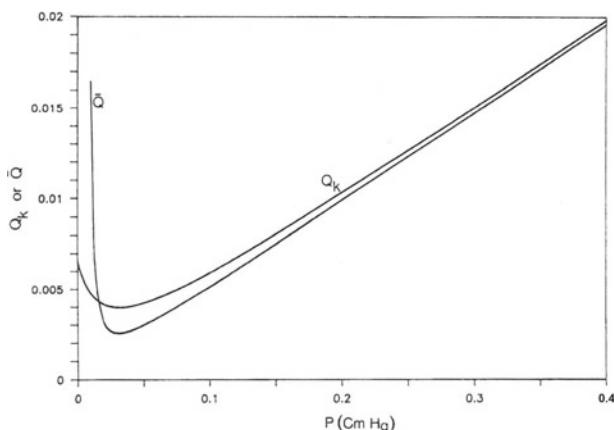
which yields a transcendental equation for  $\delta_m$  at the minimum:

$$\delta_m (10 + \delta_m^2) \sinh \delta_m - 5 (2 + \delta_m^2) \cosh \delta_m + 10 = 0. \quad (9.207)$$

Thus the pressure at the minimum is given by

$$p_m = \frac{\delta_0}{\delta_m}. \quad (9.208)$$

Despite the feature appearing qualitatively correct in comparison with Knudsen's experimental result, we are not able to make a quantitative comparison with his experimental result for the following reason: It is found the  $\Delta p$  dependence is quite significant since the flow rate depends on it sensitively. Knudsen, however, reduced the flow rate with  $\Delta p$  in presenting his data without stating the  $\Delta p$  values taken in his experiment. This would be acceptable if the flow depends linearly on  $\Delta p$  and the scaled result is independent of  $\Delta p$ , but in the present theory the flow rate is not linear with respect to  $\Delta p$ , but a rather complicated function of  $\Delta p$ . Therefore the scaled function cannot be calculated if  $\Delta p$  is not known. For this reason we can only make a qualitative numerical comparison of the present theoretical result with his experimental result only if  $\delta_0$  is suitably chosen. We find the present theoretical result predicts only the presence of a minimum in the flow rate versus pressure curves. Such a comparison is made in Fig. 9.5 for carbon dioxide gas. In this figure  $\bar{Q} := QRT/\Delta p$ . For this particular comparison the parameters  $a$ ,  $b$ ,  $c_1$ , and  $c_2$  of the Knudsen's empirical formula are as follows:



**Fig. 9.5** Comparison of theoretical flow rate  $\bar{Q}$  with  $Q_K$  for  $\delta_0 = 0.07$ . Reprinted with permission from B. C. Eu, Phys. Rev. A **40**, 6395 (1989) © 1989 American Physical Society

$$a = 0.04880/\text{cm Hg}, \quad b = 0.03489, \\ c_1 = 43.13/\text{cm Hg}, \quad c_2 = 53.10/\text{cm Hg}.$$

The figure shows that the present theory clearly predicts the presence of a minimum in flow rate, and we see it arises from the non-Newtonian behavior of the gas when the flow condition is such that the Knudsen number is large and consequently the gas is removed far from equilibrium.

The present theoretical result at zero pressure regime may be thought more comparable to the experimental result by Gaede mentioned earlier, since his result indicates a logarithmic divergence as  $p \rightarrow 0$ , whereas the present theory result predict an exponential divergence at the zero pressure limit. Further investigation seems to be necessary to take the excess normal stresses into consideration, which we find alter flow profiles and thus flow rate especially as the density diminishes. Because of limited time, we will not be able to delve into the question at present.

### ***9.2.6 Light-Induced Gas Flow in Rarefied Gas***

A number of experimental studies have been made in which atoms or molecules in a gas are successfully manipulated by light. In such experiments, a narrow-band laser is tuned within a Doppler-broadened absorption line of an atomic or molecular gas, thereby inducing velocity-selective excitation of atoms or molecules. Thus drifts of particles are produced to give rise to a number of interesting effects, such as an optical piston [49], light-induced viscous flow arising from collisions in the bulk flow of a gas [50] and with surface [51]. These effects must be distinguished from those originating from the photon pressure, since they are much smaller than the light-induced effects mentioned earlier since the collisions between the matter particles are intimately related to the light-induced effects and much larger than the effects due to the collisions with photons. In the following discussion, we would like to discuss specifically the experimental result by Hoogeveen et al. [52] who reported on an experiment on a gas flow induced in a capillary by a Doppler-broadened laser beam of radially distributed intensity. The flow generates a pressure difference and a stress in the capillary. By measuring the pressure difference that the flow produces in the capillary by means of a differential manometer and by plotting it against the gas pressure, they were able to show that the normal-pressure-regime behavior follows the classical Hagen–Poiseille flow rate as expected of gas flow in a capillary under the normal pressure regime. Therefore, light-induced flow can be described by the classical Navier–Stokes hydrodynamics in the normal pressure regime. However, as the gas pressure is decreased down to the rarefied gas density regime, the curves for the pressure difference versus pressure started to decrease in contrast to the Hagen–Poiseuille theory prediction, which, in fact, exhibits a maximum appearing in the curve at some low pressure value. This unexpected behavior of the pressure

difference versus pressure curve can be adequately accounted for by applying the generalized hydrodynamics for a non-Newtonian behavior of the gas. If we put the conclusion first, the observed behavior of the pressure difference versus pressure in question is a manifestation of the Knudsen effect in the case of a light-induced rarefied gas flow.

Since the experiment was done in a pure gas under a uniform constant temperature it is sufficient to consider only the stress evolution equation together with the momentum balance equation and mass balance equation. We assume that the molecule has only two internal states, and the molecules of the two different internal states are treated as two different species as far as their statistical (kinetic theory) treatment of the system goes. Therefore three species of particles involved—two matter species in two different internal states and photons—in the kinetic theory of the processes we are going to consider. With this model we can apply the kinetic theory [53] of radiation and matter we have developed elsewhere along the same line as we have treated in the previous chapters in this book. Then in the first-order cumulant approximation for the dissipation terms in the quasilinear nonconserved variable evolution equations the quasilinear stress tensor evolution equation for species  $a$  ( $a = \text{state 1}$ , state 2, and photon  $r$ ) is given by

$$\rho \frac{d}{dt} \widehat{\Pi}_a = -2p_a \gamma - \sum_{a=1}^r p_a \mathfrak{B}_{ab} \boldsymbol{\Pi}_b q(\kappa), \quad (9.209)$$

where, as in the previous sections,  $\widehat{\Pi}_a = \boldsymbol{\Pi}_a / \rho$  and  $\mathfrak{B}_{ab}$  are collision bracket integrals, which may be treated as empirical parameters characterizing linear transport coefficients of the system consisting of matter and radiation. The symbol  $\gamma$  stands for the traceless symmetric part of the velocity gradient defined by

$$\gamma = \frac{1}{2} [\nabla \mathbf{u} + (\nabla \mathbf{u})'] - \frac{1}{3} \mathbf{U} \nabla \cdot \mathbf{u}, \quad (9.210)$$

with  $\mathbf{u}$  denoting hydrodynamic velocity and  $\mathbf{U}$  the unit second rank tensor. The nonlinear factor  $q(\kappa)$  is defined by

$$q(\kappa) = \frac{\sinh \kappa}{\kappa} \quad (9.211)$$

with  $\kappa$  denoting a dissipation function defined by

$$\kappa = \frac{\sqrt{\eta_0 (2m_r k_B T)^{1/2}}}{nk_B T \sigma} \sqrt{|\boldsymbol{\Pi} : \boldsymbol{\Pi}|}. \quad (9.212)$$

Here  $m_r$  is the mean reduced mass and  $\sigma$  the mean size parameter of the molecules. The nonlinear factor is a result of the first-order cumulant approximation for the calortropy production defined in terms of the collision integral of the kinetic equation.

In any case, the nonlinear factor and the dissipation function  $\kappa$  may be taken as empirical inputs, but we stress that they have a firm kinetic theoretic foundations; see the paper [53] by Eu and Mao already cited.

In the experiment under consideration here, since the light is in equilibrium and acts as a driving force of the transitions in the internal state of molecules in interaction with it, the evolution equation for the shear stress of radiation is absent in the set of evolution equations (9.209). Therefore there are only two independent nonconserved variable evolution equations for the shear stress of matter to consider, and the index  $a$  in Eq. (9.209) is limited to  $a = 1$  and 2. Consequently, the  $\Pi_r$  term in (9.209) plays the role of the driving force for the internal state transition, being the stress generated by the light (laser), which is proportional to the light intensity distributed radially across the cross section of the capillary. The desired relation of  $\Pi_r$  to the light intensity is provided by a kinetic theory consideration [53]. As a matter of fact,  $\mathfrak{B}_{ab}$  are related to the gas viscosity  $\eta_0$  in the following sense:

$$\eta_0 = \frac{\mathfrak{B}_{11} + \mathfrak{B}_{22} - 2\mathfrak{B}_{12}}{\mathfrak{B}_{11}\mathfrak{B}_{22} - \mathfrak{B}_{12}^2} \quad (9.213)$$

and  $\mathfrak{B}_{rr}$ ,  $\mathfrak{B}_{1r}$ ,  $\mathfrak{B}_{2r}$  are related to the photon (radiation) viscosity. Since experiment was performed under steady-state conditions, it is sufficient to consider the steady-state equations (i.e., the adiabatic approximation)

$$2p_1 + p_1(\mathfrak{B}_{11}\Pi_1 + \mathfrak{B}_{12}\Pi_2 + \mathfrak{B}_{1r}\Pi_r)q(\kappa) = 0, \quad (9.214)$$

$$2p_2 + p_2(\mathfrak{B}_{21}\Pi_1 + \mathfrak{B}_{22}\Pi_2 + \mathfrak{B}_{rr}\Pi_r)q(\kappa) = 0. \quad (9.215)$$

Solving these equations for  $\Pi_1$  and  $\Pi_2$  and adding them, we obtain the total stress  $\Pi$  for matter

$$\begin{aligned} \Pi &= \Pi_1 + \Pi_2 \\ &= -2\eta_0\gamma + \Pi_L, \end{aligned} \quad (9.216)$$

where

$$\Pi_L = -\frac{[\mathfrak{B}_{1r}(\mathfrak{B}_{22} - \mathfrak{B}_{12}) + \mathfrak{B}_{2r}(\mathfrak{B}_{11} - \mathfrak{B}_{12})]}{\mathfrak{B}_{11}\mathfrak{B}_{22} - \mathfrak{B}_{12}^2}\Pi_r. \quad (9.217)$$

In the case of the flow geometry for the experiment, a cylindrical coordinate is appropriate to take for a circular tube with the gas flow direction taken parallel to the positive axial direction. If we further assume that the normal stress differences are absent to an approximation, then owing to the axial symmetry of flow the steady-state equation of continuity is trivially integrated and we find the flow velocity has only the  $z$  component:

$$\mathbf{u} = (0, 0, u_z), \quad (9.218)$$

where  $u_z$  is a function of  $r$ , the radial distance from the axis of flow.

Since the experiment is performed such that the flow generated by the pressure difference induced by the laser is exactly balanced by the opposing pressure difference in the differential manometer, the matter part  $\Pi$  of the shear stress is equal to zero. Therefore we obtain from (9.216) the equation

$$\Pi_L = 2\eta_0\gamma q^{-1}(\kappa), \quad (9.219)$$

where, in view of (9.218) for the flow velocity, the shear rate  $\gamma$  is now given by the derivative

$$\gamma = \frac{1}{2} \frac{\partial u_z}{\partial r} = \frac{1}{2} \frac{\partial u(r)}{\partial r}. \quad (9.220)$$

Equation (9.219) can be manipulated in the same manner as for one-dimensional non-Newtonian flow discussed earlier in the section for the non-Newtonian flow and solved for  $\Pi_L$  in terms of  $\gamma$  and the velocity profile of the non-Newtonian flow can be obtained subject to the boundary conditions on the velocity:

$$u(r) = \eta_0^{-1} \int_R^r dr \Pi_L(r). \quad (9.221)$$

With the velocity  $u(r)$  obtained from (9.221), the flow rate  $Q(I)$  defined by the integral

$$\begin{aligned} Q(I) &= 2\pi \int_0^R dr r u(r) \\ &= \pi \eta_0^{-1} \int_R^0 dr r^2 \Pi_L(r) \end{aligned} \quad (9.222)$$

is calculated. If  $Q/I$  is expressed alternatively, this integral may be written in the form

$$\frac{\pi R^3 \nu \bar{n}_e}{n} = \pi \eta_0^{-1} \int_R^0 dr r^2 \Pi_L(r), \quad (9.223)$$

where  $\bar{n}_e$  is the density of the excited state of the molecule,  $n$  is the total density, and  $\nu$  is a parameter of the dimension of inverse time related to the collision frequency, which, in the kinetic theory underlying the present theory, is identifiable by collision bracket integrals. As a matter of fact, this aim can be easily achieved if from (9.223) with the kinetic theory expression for  $\Pi_L$  in terms of collision bracket integrals. See the kinetic theory referenced cited earlier. Since we are interested in the pressure dependence of the flow rate, it will be sufficient to treat the parameter as a semiempirical parameter.

Balancing the light-induced flow with the pressure difference in the differential manometer is equivalent to opposing the flow with another flow generated by the same pressure difference in the absence of light. Therefore  $Q(I)$  may be equated to

the flow rate  $Q_0$  arising in the Knudsen flow in the absence of light. Since  $Q_0$  has been already calculated in the previous section we may simply use it here:

$$\begin{aligned} Q_0(\Delta p) &= \left( \frac{2\pi}{\tau\delta} \right) \left[ \frac{1}{2} \cosh \delta + \delta^{-2} (\cosh \delta - 1) - \delta^{-1} \sinh \delta \right] \\ &:= Q_{HP} (1 + \Delta Q), \end{aligned} \quad (9.224)$$

where various parameters are defined below:

$$\delta = \frac{\tau R \Delta p}{2L\eta_0}, \quad (9.225)$$

$$\tau = \frac{\sqrt{\eta_0 (mk_B T/2)^{1/2}}}{nk_B T \sigma}, \quad (9.226)$$

$$Q_{HP} = \frac{\pi R^4}{8L\eta_0} \Delta p, \quad (9.227)$$

$$\Delta Q = 8\delta^{-2} \left[ \frac{1}{2} \cosh \delta + \delta^{-2} (\cosh \delta - 1) - \delta^{-1} \sinh \delta \right] - 1. \quad (9.228)$$

Note that  $Q_{HP}$  is the Hagen–Poiseuille flow rate,  $\Delta p$  is the pressure difference,  $m$  is the reduced mass of the molecules,  $L$  is the length of the capillary, and  $\sigma$  is the size parameter of the molecule. It is clear that  $Q_0(\Delta p)$  tends to  $Q_{HP}$  as  $\delta$  vanishes; in other words, the Navier–Stokes theory limit.

Now equating  $Q_0(\Delta p)$  with  $Q(I)$ , we obtain

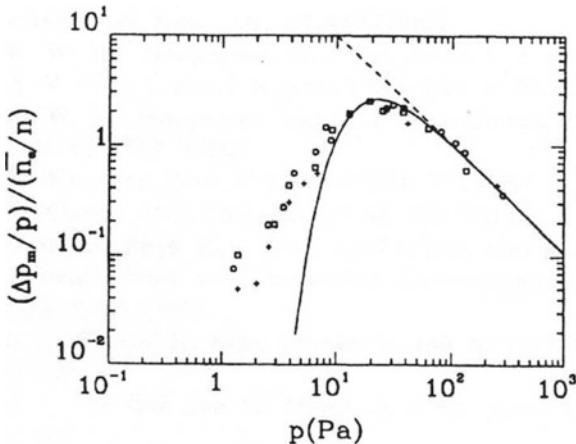
$$\begin{aligned} \frac{\pi R^3 \nu \bar{n}_e}{n} &= \left( \frac{2\pi}{\tau\delta} \right) \left[ \frac{1}{2} \cosh \delta + \delta^{-2} (\cosh \delta - 1) - \delta^{-1} \sinh \delta \right] \\ &= Q_{HP} (1 + \Delta Q). \end{aligned} \quad (9.229)$$

To compare with experiment this equation must be solved for  $\Delta p$ . It may be solved by an iterative method. By taking the lowest order approximation by setting  $\Delta Q = 0$ , we obtain

$$\left( \frac{\Delta p}{p} \right)_0 = \frac{8L\eta_0\nu}{R} \left( \frac{\bar{n}_e}{np} \right) := C \left( \frac{\bar{n}_e}{np} \right). \quad (9.230)$$

This is the classical hydrodynamic result and gives a linear relationship between  $(\Delta p/p)_0$  ( $\bar{n}_e/n$ ) and  $p^{-1}$  as observed in the experiment in the normal pressure regime. By using this as the zeroth iterate and substituting it into (9.229) we obtain the first-order iterate:

$$\left( \frac{\Delta p}{p} \right)_1 = \frac{1}{4} C b^4 \left\{ b^2 p^3 \sinh^2 \left( \frac{b}{2p} \right) + p^3 \left[ b \cosh \left( \frac{b}{2p} \right) - 2p \sinh \left( \frac{b}{2p} \right) \right]^2 \right\}^{-1}, \quad (9.231)$$



**Fig. 9.6** Scaled pressure difference versus pressure for light-induced Knudsen flow in a capillary. Gas flow is induced in a rarefied gas by laser and the Knudsen effect is observed  $\Delta p$  versus  $p$ . The broken line is the Navier–Stokes theory prediction and the solid curve is the prediction by the present theory. The squares, circles, crosses are the experimental data for the  $Q(12, 2)$ ,  $Q(12, 3)$ , and  $Q(12, 2)$  transitions, respectively. The  $Q(12, 2)$  data were obtained with a stainless steel capillary, whereas a quartz capillary was used for  $Q(12, 3)$  and  $Q(12, 2)$  data [Hoogeveen, et al., the reference cited earlier]. Reproduced with permission from K. Mao and B.C. Eu, Phys. Rev. A 48, 2471 (1993) © 1993 American Physical Society

where

$$b = \frac{\sqrt{\eta_0 (mk_B T/2)^{1/2}}}{nk_B T \sigma} \left( \frac{RC}{2L\eta_0 \sigma} \right). \quad (9.232)$$

The process of iteration can be continued, and the sequence is found converge rapidly. Therefore the first iterate is found sufficient in practice. Formula (9.232) is the main theoretical result of this section. The subscript 1 will be dropped with the understanding that the first iterative solution is meant for  $\left(\frac{\Delta p}{p}\right)$ .

The theoretical result obtained above is tested by using the experimental data of Hoogeveen et al. The parameter  $C$  is fixed with the data point in the high pressure regime and  $\Delta p$  is calculated with (9.231). The numerical result obtained is plotted in Fig. 9.6. In the normal pressure regime it gives the HP flow rate (the broken line), but as the  $\Delta p$  value decreases it starts to deviate from the linear relation and exhibits a maximum around  $p \approx 20$  Pa. The appearance of a maximum is intimately related to the non-Newtonian behavior of the gas as the Knudsen number increases and thereby the gas is increasingly removed from equilibrium; in other words, we are seeing another example of the Knudsen effect. However, the theory does not exactly agree with the experiment in the post-maximum region. There are a number of factors that may be attributed to the discrepancy. An important factor may be attributed to the neglect of normal stress differences, but inclusion of the normal stress differences leads to a mathematical complication which could be treated only by a numerical solution method, which we have tried to avoid in this investigation. A rough estimate

of the normal stress differences appears to give the value of pressure  $p$  appearing in the final expression modified. Therefore such a correction might improve the numerical results. Nevertheless, the present result should be sufficient because it enables us to basically understand in physical terms the light-induced flow studied. Further improvement may be left for future investigation eliminating some of the approximations and assumptions made for the present study made.

### 9.3 Generalized Hydrodynamics for Liquids

#### 9.3.1 Quasilinear Generalized Hydrodynamics and Transport Processes

Just as in the case of gases, the generalized hydrodynamic equations for liquids can be used to describe transport processes, linear or quasilinear. If the generalized potentials  $X_a^{(q)}$  are approximated by the linear approximation (7.311) of Chap. 7 and the dissipation functions  $\Lambda_a^{(q)}$  by (9.13), the quasilinear generalized hydrodynamic equations are given as follows.

#### 9.3.2 Balance Equations for Conserved Variables

The conservation laws for collision invariant quantities are formally in the same forms as for gases:

$$\partial_t \rho = -\nabla \cdot (\rho \mathbf{u}), \quad (9.233)$$

$$\rho d_t c_a = -\nabla \cdot \mathbf{J}_a, \quad (9.234)$$

$$\rho d_t \mathbf{u} = -\nabla \cdot \mathbf{P} + \rho \widehat{\mathbf{F}}, \quad (9.235)$$

$$\rho d_t \mathcal{E} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a. \quad (9.236)$$

The conservation laws superficially remain the same as their versions for gases. However,  $\mathbf{P}$  and  $\mathbf{Q}$  for liquids have their statistical expressions significantly different from their counterparts for gases as have been shown in previous chapters.

#### 9.3.3 Quasilinear Nonconserved Evolution Equations

The quasilinear evolution equations for nonconserved variables also retain formally the same mathematical structures as for gases in the sense that they consist of

kinematic terms made up of the same driving forces for transport processes and dissipation terms, although the presence of interactions of particles give rise to not only density-dependent collision bracket integrals and significantly different kinematic terms involving intermolecular force effects, but also correlations of particle distributions in space. The density dependence of the collision bracket integrals can be correctly obtained for liquid mixtures if the cluster expansion method is employed as discussed in Sect. 5.5.11 in Chap. 5, but the spatial particle correlation functions must be treated by applying various theories available in equilibrium statistical mechanics, such as the Percus-Yevick equation theory [55] or hypernetted chain equation theory [56] or their suitable variations. The quasilinear evolution equations for nonconserved variables are collected below:

$$\begin{aligned} \rho \frac{d}{dt} \widehat{\Phi}_a^{(0)} &= \beta \sum_{b=1}^r \left( \lambda_{ab}^{(01)} \cdot \Phi_b^{(1)} + \lambda_{ab}^{(02)} \cdot \Phi_b^{(2)} \right) \\ &\quad - \frac{\epsilon}{\beta g_a^{(0)}} \sum_{b=1}^r \sum_{s=0,5} \mathfrak{R}_{ab}^{(0s)} \Phi_b^{(s)} q_n(\kappa), \end{aligned} \quad (9.237)$$

$$\rho \frac{d\widehat{\Phi}_a^{(1)}}{dt} = -p \mathbf{d}_a - \frac{\epsilon}{\beta g_a^{(1)}} \sum_{b=1}^r \sum_{s=1,2,3} \mathfrak{R}_{ab}^{(1s)} \Phi_b^{(s)} q_n(\kappa), \quad (9.238)$$

$$\begin{aligned} \rho \frac{d\widehat{\Phi}_a^{(2)}}{dt} &= -\mathfrak{c}_a \alpha_a^{(2)} \nabla p - p_a \nabla \alpha_a^{(2)} - \alpha_a^{(2)} \rho_a \widehat{\mathbf{F}}_a \\ &\quad - \frac{\epsilon}{\beta g_a^{(2)}} \sum_{b=1}^r \sum_{s=1,2,3} \mathfrak{R}_{ab}^{(2s)} \Phi_b^{(s)} q_n(\kappa), \end{aligned} \quad (9.239)$$

$$\begin{aligned} \rho \frac{d\widehat{\Phi}_a^{(3)}}{dt} &= -C_{Ta}^{(3)} \nabla T + C_{pa}^{(3)} \nabla p - C_{da}^{(3)} \mathbf{d}_a \\ &\quad - \frac{\epsilon}{\beta g_a^{(3)}} \sum_{b=1}^r \sum_{s=1,2,3} \mathfrak{R}_{ab}^{(3s)} \Phi_b^{(s)} q_n(\kappa), \end{aligned} \quad (9.240)$$

$$\rho \frac{d\widehat{\Phi}_a^{(4)}}{dt} = -2p_a [\nabla \mathbf{u}]^{(2)} - \frac{\epsilon}{\beta g_a^{(4)}} \sum_{b=1}^r \mathfrak{R}_{ab}^{(44)} \Phi_b^{(4)} q_n(\kappa), \quad (9.241)$$

$$\begin{aligned} \rho \frac{d\widehat{\Phi}_a^{(5)}}{dt} &= - \left( \frac{5}{3} p_a + \alpha_a^{(5)} - \frac{1}{\kappa \widehat{\Psi}_a} \right) \nabla \cdot \mathbf{u} \\ &\quad - \frac{\epsilon}{\beta g_a^{(5)}} \sum_{b=1}^r \sum_{s=0,5} \mathfrak{R}_{ab}^{(5s)} \Phi_b^{(s)} q_n(\kappa), \end{aligned} \quad (9.242)$$

where various symbols are defined in Sect. 7.7.2 of Chap. 7 and, especially, (7.349) and (7.350) for collision bracket integrals  $\mathfrak{R}_{ab}^{(qs)}$ . Recall also (9.30) for  $q_n(\kappa)$  defined in terms of the first-order cumulant  $\kappa$ : namely,  $q_n(\kappa) := \sinh \kappa / \kappa$ . If this nonlinear factor  $q_n(\kappa)$  is approximated by unity, to which it tends as equilibrium is approached, and if the processes, moreover, are at steady state, then we obtain steady-state linear constitutive equations for liquids. For quasilinear transport processes  $q_n$  is kept and eventually replaced by equivalent nonlinear factor  $q_L = \sinh^{-1} \Gamma / \Gamma$  after the steady-state constitutive equations are solved for  $\Phi_a^{(q)}$  ( $q = 0, 1, \dots, 5$ ); for this step see Sect. 7.1.5. Then the quasilinear constitutive equations are given by the equations:

$$0 = -\frac{\epsilon}{\beta g_a^{(0)}} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(00)} \Phi_b^{(0)} + \mathfrak{R}_{ab}^{(05)} \Phi_b^{(5)} \right) q_n(\kappa), \quad (9.243)$$

$$0 = -p \mathbf{d}_a - \frac{\epsilon}{\beta g_a^{(1)}} \sum_{b=1}^r \sum_{s=1,2,3} \mathfrak{R}_{ab}^{(1s)} \Phi_b^{(s)} q_n(\kappa), \quad (9.244)$$

$$0 = -\alpha_a^{(2)} \mathbf{d}_a^{(2)} - \frac{\epsilon}{\beta g_a^{(2)}} \sum_{b=1}^r \sum_{s=1,2,3} \mathfrak{R}_{ab}^{(2s)} \Phi_b^{(s)} q_n(\kappa), \quad (9.245)$$

$$0 = -C_{Ta}^{(3)} \nabla T + C_{pa}^{(3)} \nabla p - C_{da}^{(3)} \mathbf{d}_a - \frac{\epsilon}{\beta g_a^{(3)}} \sum_{b=1}^r \sum_{s=1,2,3} \mathfrak{R}_{ab}^{(3s)} \Phi_b^{(s)} q_n(\kappa), \quad (9.246)$$

$$0 = -2p_a [\nabla \mathbf{u}]^{(2)} - \frac{\epsilon}{\beta g_a^{(4)}} \sum_{b=1}^r \mathfrak{R}_{ab}^{(44)} \Phi_b^{(4)} q_n(\kappa), \quad (9.247)$$

$$\begin{aligned} 0 = & - \left( \frac{5}{3} p_a + \alpha_a^{(5)} - \frac{1}{\kappa_{\Psi a}} \right) \nabla \cdot \mathbf{u} \\ & - \frac{\epsilon}{\beta g_a^{(5)}} \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(50)} \Phi_b^{(0)} + \mathfrak{R}_{ab}^{(55)} \Phi_b^{(5)} \right) q_n(\kappa). \end{aligned} \quad (9.248)$$

In (9.245)  $\mathbf{d}_a^{(2)}$  is the composite thermodynamic force for volume flux, defined by

$$\mathbf{d}_a^{(2)} = \mathfrak{c}_1 \nabla p + \rho_1 \widehat{\mathbf{F}}_1 + p_1 \nabla \ln \alpha_1^{(2)}. \quad (9.249)$$

Since  $\nabla \ln \alpha_a^{(2)}$  may be expanded in gradients of  $T, p$ , and  $\mathfrak{c}_a$  we find

$$\begin{aligned} \nabla \ln \alpha_a^{(2)} = & \left( \frac{\partial \ln \alpha_a^{(2)}}{\partial T} \right) \nabla T + \left[ \frac{\partial \ln \alpha_a^{(2)}}{\partial p} - \left( \frac{\partial \ln \alpha_a^{(2)}}{\partial \mathfrak{c}_a} \right) \frac{(x_a - \mathfrak{c}_a)}{p} \right] \nabla p \\ & + \left( \frac{\partial \ln \alpha_a^{(2)}}{\partial \mathfrak{c}_a} \right) \mathbf{d}_a - \left( \frac{\partial \ln \alpha_a^{(2)}}{\partial \mathfrak{c}_a} \right) \frac{\rho}{p} (\widehat{\mathbf{F}} - \widehat{\mathbf{F}}_a), \end{aligned}$$

for which we have made use of (9.38) for  $\mathbf{d}_a$ . Thus we may express  $\mathbf{d}_a^{(2)}$  in the form

$$\mathbf{d}_a^{(2)} = p_a C_{Ta}^{(2)} \nabla T + p_a C_{da}^{(2)} \mathbf{d}_a + p_a C_{pa}^{(2)} \nabla p + \rho_a \Delta \widehat{\mathbf{F}}_a. \quad (9.250)$$

Here the coefficients  $C_{Ta}^{(2)}$ , etc. are defined by the formulas below:

$$C_{Ta}^{(2)} = \frac{\partial \ln \alpha_a^{(2)}}{\partial T}, \quad (9.251)$$

$$C_{ca}^{(2)} = \frac{\partial \ln \alpha_a^{(2)}}{\partial c_a}, \quad (9.252)$$

$$C_{pa}^{(2)} = \frac{c_a}{p_a} + \frac{\partial \ln \alpha_a^{(2)}}{\partial p} - \frac{(x_a - c_a)}{p} \left( \frac{\partial \ln \alpha_a^{(2)}}{\partial c_a} \right), \quad (9.253)$$

$$\Delta \widehat{\mathbf{F}}_a = \widehat{\mathbf{F}}_a - \frac{p_a}{p c_a} \left( \frac{\partial \ln \alpha_a^{(2)}}{\partial c_a} \right) (\widehat{\mathbf{F}} - \widehat{\mathbf{F}}_a). \quad (9.254)$$

From the quasilinear constitutive equations (9.243)–(9.248) it is possible to determine kinetic theory formulas for quasilinear transport coefficients of irreversible processes in a liquid mixture. Inspection of the set of constitutive equations indicates that only the equation for shear stress tensor  $\Phi_b^{(4)}$  is uncoupled from others. On the other hand, (9.243) and (9.248) are coupled, while three vector equations (9.244)–(9.246) are coupled together. Solving these subsets of coupled equations, we will be able to find quasilinear and linear transport coefficients for various transport processes.

### 9.3.4 Volume Transport Phenomena

Equations (9.243) and (9.248) are coupled because they are linear constitutive equations for scalar fluxes  $\Phi_a^{(0)}$  and  $\Phi_a^{(5)}$ , which represent, respectively, a volume fluctuation and excess normal stress difference. To solve the coupled algebraic equations for the fluxes it would be convenient to cast them in matrix form

$$q_n(\kappa) \mathfrak{M} \mathbb{C}^{(05)} = -\mathfrak{F} \nabla \cdot \mathbf{u}, \quad (9.255)$$

where matrix  $\mathfrak{M}$  is defined by block matrices  $\mathfrak{M}^{(00)}$ , etc.

$$\mathfrak{M} := \begin{pmatrix} \mathfrak{M}^{(00)} & \mathfrak{M}^{(05)} \\ \mathfrak{M}^{(50)} & \mathfrak{M}^{(55)} \end{pmatrix}, \quad (9.256)$$

each block matrix consisting of square matrices

$$\begin{aligned}\mathfrak{M}^{(00)} &:= \begin{pmatrix} \frac{\epsilon \mathfrak{R}_{11}^{(00)}}{\beta g_1^{(0)}} & \cdots \\ \vdots & \ddots \end{pmatrix}, \quad \mathfrak{M}^{(55)} := \begin{pmatrix} \frac{\epsilon \mathfrak{R}_{11}^{(55)}}{\beta g_1^{(0)}} & \cdots \\ \vdots & \ddots \end{pmatrix}, \\ \mathfrak{M}^{(05)} &:= \begin{pmatrix} \frac{\epsilon \mathfrak{R}_{11}^{(05)}}{\beta g_1^{(0)}} & \cdots \\ \cdots & \ddots \end{pmatrix}, \quad etc.,\end{aligned}\tag{9.257}$$

and the column vectors by

$$\mathfrak{F}^{(05)} := \begin{pmatrix} \mathbf{0} \\ \mathfrak{F}^{(5)} \end{pmatrix} = \begin{pmatrix} 0 \\ \vdots \\ \frac{5}{3}p_1 + \alpha_1^{(5)} - \frac{1}{\kappa_{\Psi_1}} \\ \vdots \end{pmatrix},\tag{9.258}$$

$$\mathbb{C}^{(05)} := \begin{pmatrix} \Phi_1^{(0)} \\ \vdots \\ \Phi_1^{(5)} \\ \vdots \end{pmatrix}.\tag{9.259}$$

The solution of (9.255) is then given by

$$q_n(\kappa) \mathbb{C}^{(05)} = -\mathfrak{M}^{-1} \mathfrak{F} \nabla \cdot \mathbf{u}.\tag{9.260}$$

This means that volume transport is indirectly caused by  $\nabla \cdot \mathbf{u}$ , which is the rate of volume change that drives excess normal stress even if volume fluctuation is absent. *The volume transport is new to the theory of transport processes*, compelling us a suitable modification of the existent theory of transport processes. The required modification is investigated below.

### 9.3.5 Shear Viscous Transport

The shear stress tensor transport  $\Phi_a^{(4)}$  is not coupled to other vectorial or scalar transport processes. It is simply obtained by solving (9.247). We easily find the solution

$$q_n(\kappa) \Phi_a^{(4)} = -2\eta_a^0 [\nabla \mathbf{u}]^{(2)},\tag{9.261}$$

where the shear viscosity  $\eta_a^0$  of species  $a$  is given by a matrix consisting of collision bracket integrals  $\mathfrak{R}_{ab}^{(44)}$ :

$$\eta_a^0 := \sum_{b=1}^r \eta_{ab}^0 = \sum_{b=1}^r \left( \begin{array}{ccc} \frac{\epsilon}{\beta g_1^{(4)}} \mathfrak{R}_{11}^{(44)} & \cdots & \\ \vdots & \ddots & \\ \end{array} \right)_{ab}^{-1} \left( \begin{array}{c} p_1 \\ \vdots \end{array} \right)_b. \quad (9.262)$$

The coefficients  $\eta_a^0$  define the shear viscosity of species  $a$  in terms of collision bracket integrals  $\mathfrak{R}_{ab}^{(44)}$ . When summed over species, the shear viscosity of the liquid mixture is obtained.

### 9.3.6 Heat Conduction, Diffusion, Volume Flux

Vector transport processes, heat conduction, mass diffusion, and volume flux associated with the volume fluctuation, are determined by solving the coupled equations (9.244)–(9.246). For the purpose let us define the column vector

$$\mathbb{C}^{(123)} := \left( \Phi_1^{(1)} \cdots, \Phi_1^{(2)} \cdots, \Phi_1^{(3)} \cdots \right)^t, \quad (9.263)$$

where  $t$  denotes the transpose, namely, the column vector, and the column vector spanned by thermodynamic forces by

$$\mathfrak{F}^{(123)} := (\mathfrak{F}^{(1)}, \mathfrak{F}^{(2)}, \mathfrak{F}^{(3)})^t, \quad (9.264)$$

each subcolumn vector being spanned by column vectors

$$\begin{aligned} \mathfrak{F}^{(1)} &:= (p\mathbf{d}_1, \cdots)^t, \\ \mathfrak{F}^{(2)} &:= (\alpha_1^{(2)} \mathbf{d}_1^{(2)}, \cdots)^t, \\ \mathfrak{F}^{(3)} &:= \left\{ \left( C_{T1}^{(3)} \nabla T + C_{p1}^{(3)} \nabla p + C_{d1}^{(3)} \mathbf{d}_1 \right), \cdots \right\}^t \end{aligned} \quad (9.265)$$

driving the transport processes  $\Phi_a^{(1)}$ ,  $\Phi_a^{(2)}$ , and  $\Phi_a^{(3)}$ . We construct a compound matrix

$$\mathfrak{W} := \begin{pmatrix} \mathfrak{W}^{(11)} & \mathfrak{W}^{(12)} & \mathfrak{W}^{(13)} \\ \mathfrak{W}^{(21)} & \mathfrak{W}^{(22)} & \mathfrak{W}^{(23)} \\ \mathfrak{W}^{(31)} & \mathfrak{W}^{(32)} & \mathfrak{W}^{(33)} \end{pmatrix}, \quad (9.266)$$

where the submatrices  $\mathfrak{W}^{(qs)}$  are defined by matrices associated with the dissipation terms in (9.244)–(9.246):

$$\mathfrak{W}^{(qs)} = \begin{pmatrix} \frac{\epsilon \mathfrak{R}_{11}^{(qs)}}{\beta g_1^{(q)}} & \frac{\epsilon \mathfrak{R}_{12}^{(qs)}}{\beta g_2^{(q)}} & \dots \\ \frac{\epsilon \mathfrak{R}_{21}^{(qs)}}{\beta g_2^{(q)}} & \frac{\epsilon \mathfrak{R}_{22}^{(qs)}}{\beta g_2^{(q)}} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \quad (q, s = 1, 2, 3). \quad (9.267)$$

Then the three coupled equations can be cast into matrix form

$$q_n(\kappa) \mathfrak{W} \mathbb{C}^{(123)} = -\mathfrak{F}^{(123)}. \quad (9.268)$$

Inverting the matrix  $\mathfrak{W}$  the solution is obtained:

$$q_n(\kappa) \mathbb{C}^{(123)} = -\mathfrak{W}^{-1} \mathfrak{F}^{(123)}, \quad (9.269)$$

which gives  $\Phi_a^{(1)}, \Phi_a^{(2)}, \Phi_a^{(3)}$  ( $a = 1, 2, \dots$ ) in terms of thermodynamic forces (i.e., temperature, pressure, concentration gradients) driving the transport processes. The fluxes  $\Phi_a^{(q)}$  are therefore given by linear combinations of the thermodynamic forces, the coefficients of the linear combinations providing the statistical mechanical formulas for the linear transport coefficients.

The steady-state quasilinear equations for a single-component system were previously solved by first treating  $q_n(\kappa)$  as if it is a constant, and then substituting the results into the Rayleigh dissipation function  $\kappa$  and inverting  $\sinh \kappa$ , we obtain  $\kappa$  in terms of a quadratic form of thermodynamic gradients. We employ the same method for the case of multi-component mixture. We simply list the constitutive relations thus obtained below:

$$q_n(\kappa) \mathbb{C}^{(05)} = -\mathfrak{M}^{-1} \mathfrak{F} \nabla \cdot \mathbf{u}, \quad (9.270)$$

$$q_n(\kappa) \Phi_a^{(4)} = -2\eta_a^0 [\nabla \mathbf{u}]^{(2)}, \quad (9.271)$$

$$q_n(\kappa) \mathbb{C}^{(123)} = -\mathfrak{W}^{-1} \mathfrak{F}^{(123)}. \quad (9.272)$$

These are not complete solutions of the quasilinear constitutive equation since  $q_n(\kappa)$  still depends the fluxes. This particular step of the solution procedure is the same as the one used for a single-component system. Recall that we substitute (9.270)–(9.272) into the quadratic form for  $\kappa^2$

$$\kappa^2 = \sum_{a,b=1}^r \left[ \Phi_a^{(1)} \mathfrak{T}_{ab}^{(11)} \Phi_b^{(1)} + \sum_{q,s=0,5} \Phi_a^{(q)} \mathfrak{S}_{ab}^{(qs)} \Phi_b^{(s)} + \sum_{q,s=1,2,3} \Phi_a^{(q)} \mathfrak{V}_{ab}^{(qs)} \Phi_b^{(s)} \right] \quad (9.273)$$

to obtain the equation

$$\kappa^2 q_n^2 = \sum_{a,b=1}^r \left[ \mathfrak{B}_{ab} [\nabla \mathbf{u}]^{(2)} : [\nabla \mathbf{u}]^{(2)} + \sum_{q,s=0,5} \mathfrak{C}_{ab}^{(qs)} (\nabla \cdot \mathbf{u})^2 \right. \\ \left. + \sum_{q,s=1,2,3} \mathfrak{H}_{ab}^{(qs)} \mathfrak{F}_q^{(123)} \cdot \mathfrak{F}_s^{(123)} \right], \quad (9.274)$$

where  $\mathfrak{T}_{ab}^{(11)}$ ,  $\mathfrak{S}_{ab}^{(qs)}$ , and  $\mathfrak{V}_{ab}^{(qs)}$  are given by collision bracket integrals and  $\mathfrak{B}_{ab}$ ,  $\mathfrak{C}_{ab}^{(qs)}$ , and  $\mathfrak{H}_{ab}^{(qs)}$  are defined by

$$\mathfrak{B}_{ab} = 4\eta_a^0 \eta_b^0 \mathfrak{T}_{ab}^{(11)}, \quad (9.275)$$

$$\mathfrak{C}_{ab}^{(qs)} = [\mathfrak{M}^{-1} \mathfrak{F}^{(05)}]_a^{(q)} \mathfrak{S}_{ab}^{(qs)} [\mathfrak{M}^{-1} \mathfrak{F}^{(05)}]_b^{(s)}, \quad (9.276)$$

$$\mathfrak{H}_{ab}^{(qs)} = [\mathfrak{W}^{-1}]_a^{(q)} \mathfrak{V}_{ab}^{(qs)} [\mathfrak{W}^{-1}]_b^{(s)}. \quad (9.277)$$

The right-hand side of (9.274) is another form of the Rayleigh dissipation function, which is expressed in a quadratic form of thermodynamic gradients. We will denote it by  $\kappa_L$ :

$$\kappa_L = \left\{ \sum_{a,b=1}^r \left[ \mathfrak{B}_{ab} [\nabla \mathbf{u}]^{(2)} : [\nabla \mathbf{u}]^{(2)} + \sum_{q,s=0,5} \mathfrak{C}_{ab}^{(qs)} (\nabla \cdot \mathbf{u})^2 \right. \right. \\ \left. \left. + \sum_{q,s=1,2,3} \mathfrak{H}_{ab}^{(qs)} \mathfrak{F}_q^{(q)} \cdot \mathfrak{F}_s^{(s)} \right] \right\}^{1/2}. \quad (9.278)$$

See (9.86)–(9.88) for  $\kappa_L$  and the related. Since  $q_n(\kappa) = \sinh \kappa / \kappa$  by definition, the left-hand side of (9.274) is given by

$$\sinh^2 \kappa = \kappa_L^2.$$

Inverting the hyperbolic sine function yields the Rayleigh dissipation function  $\kappa$  is found in terms of a quadratic form of thermodynamic derivatives  $\kappa_L$ :

$$\kappa = \sinh^{-1} \kappa_L. \quad (9.279)$$

Thus we obtain  $q_n^{-1}$  in terms of  $\kappa_L$ :

$$q_n^{-1} = \frac{\kappa}{\sinh \kappa} = \frac{\sinh^{-1} \kappa_L}{\kappa_L} := q_L. \quad (9.280)$$

With this result for  $q_n^{-1}$  the quasilinear constitutive relations (9.270)–(9.272) are completely solved in terms of thermodynamic forces in exactly the same manner as for gases, and we obtain the constitutive relations as follows:

$$\mathbb{C}^{(05)} = -q_L \mathfrak{M}^{-1} \mathfrak{F} \nabla \cdot \mathbf{u}, \quad (9.281)$$

$$\Phi_a^{(4)} = -2\eta_a^0 q_L [\nabla \mathbf{u}]^{(2)}, \quad (9.282)$$

$$\mathbb{C}^{(123)} = -q_L \mathfrak{W}^{-1} \mathfrak{F}^{(123)}. \quad (9.283)$$

More explicitly written out, the quasilinear constitutive relations (9.281)–(9.283) take the forms

$$\Phi_a^{(0)} = -q_L [\mathfrak{M}^{-1} \mathfrak{F}^{(05)}]_a^{(0)} \nabla \cdot \mathbf{u}, \quad (9.284)$$

$$\Phi_a^{(4)} = -2q_L \eta_a^0 [\nabla \mathbf{u}]^{(2)}, \quad (9.285)$$

$$\Phi_a^{(5)} = -q_L [\mathfrak{M}^{-1} \mathfrak{F}^{(05)}]_a^{(5)} \nabla \cdot \mathbf{u}. \quad (9.286)$$

$$\begin{aligned} \Phi_a^{(s)} = & -q_L \sum_{b=1}^r \left[ (\mathfrak{W}^{-1})_{ab}^{(11)} p + (\mathfrak{W}^{-1})_{ab}^{(13)} C_{db}^{(3)} \right] \mathbf{d}_b \\ & - q_L \left[ (\mathfrak{W}^{-1})_{ab}^{(12)} \alpha_b^{(2)} \mathbf{d}_b^{(2)} + (\mathfrak{W}^{-1})_{ab}^{(13)} \left( C_{Tb}^{(3)} \nabla T + C_{pb}^{(3)} \nabla p \right) \right], \quad (9.287) \\ & (s = 1, 2, 3; a = 1, \dots, r). \end{aligned}$$

Using these constitutive relations, quasilinear and linear transport coefficients of transport processes considered are determined in terms of collision bracket integrals and their kinetic theory formulas are obtained thereby. They are quadratures involving collision dynamical events in many-particle systems. One may apply molecular dynamic simulation methods or Monte Carlo simulation methods to calculate them numerically after converting them into more computationally convenient forms as described in Sects. 8.5 and 8.6, Chap. 8.

### 9.3.7 Quasilinear and Linear Transport Coefficients

The quasilinear transport coefficients are easily identified from (9.270)–(9.272).

#### 9.3.7.1 Volume Transport Coefficient

The linear volume transport coefficient is given by

$$\lambda_{ab}^{(05)0} = [\mathfrak{M}^{-1} \mathfrak{F}^{(05)}]_a^{(0)}. \quad (9.288)$$

Then quasilinear volume transport coefficient is defined by

$$\lambda_{ab}^{(05)} = [\mathfrak{M}^{-1} \mathfrak{F}^{(05)}]_a^{(0)} q_L = \lambda_{ab}^{(05)0} q_L. \quad (9.289)$$

### 9.3.7.2 Bulk Viscosity Coefficient

The linear bulk viscosity  $\eta_{Ba}^0$  for species  $a$  is identified by the formula

$$\eta_{Ba}^0 = [\mathfrak{M}^{-1} \mathfrak{F}^{(05)}]_a^{(5)}. \quad (9.290)$$

The quasilinear bulk viscosity is then defined by

$$\eta_{Ba} = [\mathfrak{M}^{-1} \mathfrak{F}^{(05)}]_a^{(5)} q_L = \eta_{Ba}^0 q_L. \quad (9.291)$$

Summing this over species, we obtain the bulk viscosity of the mixture.

### 9.3.7.3 Shear Viscosity

The linear shear viscosity  $\eta_a^0$  has been already defined in terms of collision bracket integrals in (9.262). Therefore the quasilinear (non-Newtonian) shear viscosity for species  $a$  is defined by the formula

$$\eta_a = \eta_a^0 q_L. \quad (9.292)$$

This is an example of non-Newtonian viscosity which depends on shear rate, diminishing as the shear rate increases. The shear viscosity for the mixture is obtained on summing (9.292).

### 9.3.7.4 Vector Processes—Diffusion, Volume Flow, and Thermal Conduction

To identify various transport coefficients associated with vectorial transport processes it is necessary to more explicitly express  $\mathbf{d}_a^{(2)}$  in terms of thermodynamic forces as given in (9.250). Equation (9.287) can be rendered in the following form

$$\begin{aligned} \Phi_a^{(s)} = & -q_L \sum_{b=1}^r \left[ (\mathfrak{W}^{-1})_{ab}^{(11)} p + (\mathfrak{W}^{-1})_{ab}^{(13)} C_{db}^{(3)} + \alpha_b^{(2)} p_a (\mathfrak{W}^{-1})_{ab}^{(12)} C_{db}^{(2)} \right] \mathbf{d}_b \\ & - q_L \sum_{b=1}^r \left[ \alpha_b^{(2)} p_a (\mathfrak{W}^{-1})_{ab}^{(12)} C_{Tb}^{(2)} + (\mathfrak{W}^{-1})_{ab}^{(13)} C_{Tb}^{(3)} \right] \nabla T \end{aligned}$$

$$\begin{aligned}
& -q_L \sum_{b=1}^r \left[ \alpha_b^{(2)} p_a (\mathfrak{W}^{-1})_{ab}^{(12)} C_{pb}^{(2)} + (\mathfrak{W}^{-1})_{ab}^{(13)} C_{pb}^{(3)} \right] \nabla p \\
& - q_L \sum_{b=1}^r (\mathfrak{W}^{-1})_{ab}^{(12)} \alpha_b^{(2)} \rho_b \Delta \hat{\mathbf{F}}_b, \\
(s = 1, 2, 3; a = 1, \dots, r).
\end{aligned} \tag{9.293}$$

From these set of constitutive relations it is possible to identify the statistical mechanical formulas for various quasilinear and linear transport coefficients. We may identify the following linear transport coefficients with the coefficients of (9.293):

$$\lambda_a^{(sd)0} = \sum_{b=1}^r \left[ (\mathfrak{W}^{-1})_{ab}^{(s1)} p + (\mathfrak{W}^{-1})_{ab}^{(s3)} C_{db}^{(3)} + \alpha_b^{(2)} p_a (\mathfrak{W}^{-1})_{ab}^{(s2)} C_{da}^{(2)} \right], \tag{9.294}$$

$$\lambda_a^{(sT)0} = \sum_{b=1}^r \left[ \alpha_b^{(2)} p_a (\mathfrak{W}^{-1})_{ab}^{(s2)} C_{Tb}^{(2)} + (\mathfrak{W}^{-1})_{ab}^{(s3)} C_{Tb}^{(3)} \right], \tag{9.295}$$

$$\lambda_a^{(sp)0} = \sum_{b=1}^r \left[ \alpha_b^{(2)} p_a (\mathfrak{W}^{-1})_{ab}^{(s2)} C_{pb}^{(2)} + (\mathfrak{W}^{-1})_{ab}^{(s3)} C_{pb}^{(3)} \right], \tag{9.296}$$

$$\lambda_a^{(sf)0} = \sum_{b=1}^r (\mathfrak{W}^{-1})_{ab}^{(12)} \alpha_b^{(2)} \rho_b \quad (s = 1, 2, 3). \tag{9.297}$$

And the corresponding quasilinear transport coefficients for species  $a$  are defined by

$$\begin{aligned}
\lambda_a^{(sd)} &= \lambda_a^{(sd)0} q_L, & \lambda_a^{(sT)} &= \lambda_a^{(sT)0} q_L, \\
\lambda_a^{(sp)} &= \lambda_a^{(sp)0} q_L, & \lambda_a^{(sf)} &= \lambda_a^{(sf)0} q_L
\end{aligned} \tag{9.298}$$

All the quasilinear transport coefficients presented earlier depend on spatial gradients and, in fact, vanish as the thermodynamic forces increase in magnitude as alluded to for the case of non-Newtonian viscosity. For example, the non-Newtonian viscosity in fact shows how the thermodynamic forces other than the shear rate affect the viscosity because  $q_L$  depends on all the thermodynamic gradients present in the sheared fluid. More specifically, all the quasilinear transport coefficients in (9.289), (9.291), (9.292), and (9.298) vanish in the limit of  $\kappa_L \rightarrow \infty$ . On the other hand, as  $q_L \rightarrow 1$  at equilibrium, the quasilinear transport coefficients tend to the linear transport coefficients  $\lambda_{ab}^{(05)0}$ ,  $\eta_{Ba}^0$ ,  $\eta_a^0$ , and  $\lambda_a^{(sd)0}$  ( $s = 1, 2, 3$ ). We note that  $\lambda_a^{(1d)0}$  is the mass diffusion coefficients;  $\lambda_a^{(3T)0}$  the thermal conductivity,  $\lambda_a^{(3d)0}$  the thermal diffusion coefficients coupling temperature and diffusion processes; etc.

The points of distinction of the present theoretical results are: (1) appearance of the transport coefficients associated with volume transport phenomena, volume fluctuations and volume flux, which have not been taken into account in the

*conventional theory of transport processes in liquids; (2) the nonlinear transport coefficients for the quasilinear transport processes; (3) the thermodynamic consistency of the generalized hydrodynamic equations and, especially, of the quasilinear transport processes even if they are far removed from equilibrium. (4) In the case of quasilinear transport processes the Curie principle is broken because of the presence of the nonlinear factor  $q_L(\kappa_L)$ .*

There are only a few example for practical applications of the theory of generalized hydrodynamic equations for liquids that have been studied of the present theory to quote, although there were some studies reported [24, 57], which successfully explained the stability and shear rate dependences of normal stresses in polymeric systems and demonstrated the utility of the generalized hydrodynamic equations approach to flow problems in liquid systems. Such examples for application raise a hopeful expectation for the utility of theory discussed, when the theory is applied to problems related to nonlinear transport processes in dense fluids and monatomic liquids.

## 9.4 Concluding Remarks

In the previous chapters on kinetic theories we have shown the generalized hydrodynamics is an integral part of the thermodynamic theory of irreversible transport processes in macroscopic material systems. Inasmuch as the former conforms to the laws of phenomenological thermodynamics—the thermodynamic principles enunciated by Carnot, Clausius, and Thomson—the generalized hydrodynamic equations in support of the thermodynamic theory of irreversible phenomena are found consistent with the laws of thermodynamics. Described by such a hydrodynamics theory, irreversible phenomena theoretically studied therewith should be judged also to conform to the laws of thermodynamics. In this chapter, the generalized hydrodynamic formalism is shown capable of describing transport processes in gases and liquids, at least, formally recovering the well-established Chapman–Enskog theory results for dilute gases in the low density limit of the ensemble kinetic theory results and also near equilibrium, and in the case of hydrodynamic problems, by the examples of the theoretical results by the present theory reported in the literature.

On the basis of the examples and the demonstrated efficacy of the theoretical results to explain observed flow phenomena, we are assured that the generalized hydrodynamics formalism presented in this work holds up promises to be useful for comprehending flow phenomena occurring far removed from equilibrium beyond the realm of the classical hydrodynamic of Navier, Stokes, and Fourier. The thermodynamics of irreversible processes accompanying the generalized hydrodynamics also has an underlying theory of nonequilibrium statistical mechanics with which we are now able to carry on molecular theory investigations of macroscopic irreversible processes.

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# Epilogue: Non-Relativistic Theories

In this work, we have adhered to the tenet that a theory of transport processes in macroscopic matter should conform to the principles and laws of thermodynamics for it to remain a credible theoretical representation of natural macroscopic processes. Under this tenet we have formulated a theory of macroscopic processes from the molecular (particulate) theory standpoint on the basis of irreversible (time-reversal symmetry breaking) kinetic equations for dense gases and liquids. We have found that such kinetic equations are possible if J.W. Gibbs's ideas of ensemble theory in statistical mechanics are adopted for systems undergoing nonequilibrium irreversible processes. As a matter of fact, the Boltzmann kinetic equation is found to be a special case of such an irreversible kinetic equation that arises as a low density limit in gases which are not spatially correlated. The class of irreversible kinetic equations employed in this work is a postulate for the probabilistic distribution functions in the phase space of the ensemble members just as the Boltzmann kinetic equation should be regarded as such, but not as a strict derivation from the laws of mechanics. Therefore, this approach to kinetic theory of nonequilibrium phenomena in correlated systems (e.g., dense gases and liquids) radically different from the BBGKY hierarchy approach in kinetic theory based on the reversible Liouville equation.

Since the collision processes between the ensemble members (called subsystems) occur in a constant energy-momentum-mass plane of the phase space, the generalized Boltzmann equations postulated are irreversible and admit the  $H$  theorem. The  $H$  theorem, however, turns out to provide us with a stability criteria for solutions in the phase space of the irreversible kinetic equations, but remain a theorem broader than the second law of thermodynamics in the thermodynamic manifold of macroscopic variables since the macroscopic variables subject to the second law are projections of the phase space distribution function obeying the kinetic equation onto a space of much smaller dimension; put it in different words, the second law of thermodynamics is a stability theory of macroscopic processes in a manifold of macroscopic variables finite in number much smaller than the phase space dimension of an astronomical number of particles contained in a macroscopic

system of a fluid. This recognition has led us to conclude that there exists a quantity which we call calortropy  $\Psi$  controlling and governing evolutions of irreversible macroscopic observables in place of the Boltzmann entropy associated with the  $H$  theorem: The calortropy obeys an inequality descending from the  $H$  theorem and rightly deserves the position of a statistical mechanical representation of the second law of thermodynamics, since it has all the desired properties to qualify for a nonequilibrium version of Clausius's entropy for reversible processes that R. Clausius originally introduced for reversible thermodynamic processes in system at equilibrium.

The difference between the Boltzmann entropy  $S$  and the calortropy  $\Psi$  is borne by what we call the relative Boltzmann entropy, which describes the fluctuations of states from the thermodynamic states predicted by the calortropy. Such fluctuations are described by the solutions of the kinetic equation postulated for the system.

The calortropy  $\Psi$  gives rise to a thermodynamic theory of irreversible macroscopic processes consistent the thermodynamic laws, and therewith we have acquired a theory of irreversible thermodynamics of macroscopic irreversible processes for systems removed from equilibrium to arbitrary degree. And thus the linear theory of irreversible thermodynamics is now generalized to a general situation.

The most outstanding characteristics of the present irreversible thermodynamic theory are the existence of an exact Pfaffian form (i.e., extended Gibbs equation) for the calortropy density and its integrability condition (i.e., the nonequilibrium Gibbs–Duhem equation); a theory of irreversible thermodynamics for nonequilibrium transport processes and an accompanying structure of nonequilibrium statistical thermodynamics. This theory of irreversible thermodynamics supports the generalized hydrodynamic equations derived from the generalized Boltzmann equations, making the generalized hydrodynamic equations consistent with the laws of thermodynamics. Moreover, the classical hydrodynamics of Navier, Stokes, Fourier, and Fick is fully recovered from the generalized hydrodynamic equations in the limit of vanishing critical parameter  $N_\delta$ . In this limit it is also possible to show that the well-known Chapman–Enskog theory results for linear transport coefficients for gases are recovered. The aforementioned features all together demonstrates the comprehensive nature of the generalized hydrodynamic equations as well as the generalized Boltzmann equations from which the generalized hydrodynamic equations descend.

The following points that have been discussed or demonstrated:

1. *Boltzmann equation for the ensemble theory viewpoint—a product of deduction, but not a derivation from the mechanical laws alone;*
2. *Ensemble kinetic equation for members of an ensemble colliding with each other on the constant energy-mass surface for dilute gases and dense fluids and liquids;*
3. *Distinction between the solutions in the phase space of the ensemble and the thermodynamic branch of solution—nonequilibrium functional hypothesis for the distribution function;*

4. Appearance of the calortropy and the relative Boltzmann entropy and fluctuations;
5. Functional hypothesis and theory of irreversible thermodynamics;
6. Irreversible thermodynamics and generalized hydrodynamics and their intimate relation;
7. Generalized hydrodynamics and thermodynamically consistent quasi-linear constitutive equations;
8. Recovery of the classical hydrodynamics;
9. Recovery of the Chapman–Enskog-type solutions for the irreversible kinetic equations;
10. Linear transport coefficients for gases and liquids;
11. Comprehensiveness of the ensemble kinetic theory—the irreversible generalized Boltzmann equations employed—to encompass the wide density range of monatomic fluids.

**Part II**  
**Essays on Equilibrium Theories**

# Chapter 10

## Molecular Theory of Liquid Mixtures: Equilibrium Properties

The nonequilibrium thermophysical properties, typical examples being transport coefficients, of liquid mixtures are not only important as molecular properties of liquids but also essential for understanding nonequilibrium phenomena in physical, chemical, and biological systems in condensed phase. They are also indispensable in engineering applications of transport phenomena. Since a nonequilibrium molecular theory of transport processes necessarily requires a practicable knowledge of equilibrium properties of liquids, the first task of this chapter will be to discuss theoretical methods to calculate the equilibrium properties of mixtures and then therewith the transport properties for which molecular theories are developed in the previous chapters. The equilibrium theories, only requiring equilibrium distribution functions already available, have been reported in the literature well before the theories of transport properties were developed. Therefore the discussions on equilibrium properties are necessarily of the nature of review or rather essays on equilibrium properties, although we will endeavor to provide new aspect or perspective, wherever possible. The discussions of the equilibrium theories may then be followed by the development of a theory of transport coefficients of liquid mixtures that extends the density fluctuation theory of transport coefficients of pure liquids, which have been reported in the literature [1, 2] and validated by comparing with either experiment or simulation results in recent years.

The earliest work on equilibrium dense mixtures is the McMillan–Mayer theory [3], which was applied to some aspects [4] of liquid solution theory. Since it played a useful role in the development of liquid solution theory in statistical mechanics, closer attentions will be paid to the theory of Kirkwood and Buff [5], and we will also discuss the Ornstein–Zernike theory [12] that is generalized for solutions in this chapter because there is a necessity of calculating pair correlation functions and algorithms for pair correlation functions for mixtures.

Despite the fact that the theories mentioned and studies in equilibrium thermodynamic properties and, in particular, the equations of state of liquid mixtures are fairly extensive in the literature, the subject field is still in an underdeveloped state at present, because it is inherently difficult and complicated. Therefore, there are still numerous technical and practical problems remaining unresolved. It is our aim in these essays to contribute to the subjects of discussion. It thus may be regarded as the *raison d'être* for chapters in the monograph devoted to nonequilibrium statistical mechanics, irreversible thermodynamics, and hydrodynamics. We note that the notation of this and the following appendix has no correlation to the notations employed in the main text of this book.

## 10.1 Kirkwood–Buff Theory of Mixtures

The Kirkwood–Buff theory [5] of solutions in equilibrium appeared in 1951, but it was later reformulated by Pearson and Rushbrooke [6] and O'Connell [7]. Their reformulation has resulted in a form that requires direct correlation functions instead of total correlation functions, and it gives much simplified and transparent forms for thermodynamic quantities, compared with the original Kirkwood–Buff (KB) version. The Kirkwood–Buff (KB) version has been taken in Ben-Naim's work [8] on binary mixtures and more recently in Ruckenstein and coworker [9]. I believe that the direct correlation function version of Pearson and Rushbrooke (PR) can be more easily implemented and is more practical. We will begin with the KB version and then move on to the PR version.

The grand canonical ensemble distribution function is assumed for an  $r$  component mixture of simple liquids contained in volume  $V$  at temperature  $T$ . The numbers of species are  $N_1, N_2, \dots, N_r$ . This set of numbers will be abbreviated by the boldface symbol  $\mathbf{N} = (N_1, N_2, \dots, N_r)$  and, similarly, position vectors by  $\mathbf{r}^{(N)} = (\mathbf{r}_1^{(N_1)}, \mathbf{r}_2^{(N_2)}, \dots, \mathbf{r}_r^{(N_r)})$  and momentum vectors by  $\mathbf{p}^{(N)} = (\mathbf{p}_1^{(N_1)}, \mathbf{p}_2^{(N_2)}, \dots, \mathbf{p}_r^{(N_r)})$ . The particles are assumed to interact by pairwise additive potentials which sum up to the total potential energy  $U_{\mathbf{N}}(\mathbf{r}^{(N)})$ :

$$U_{\mathbf{N}}(\mathbf{r}^{(N)}) = \sum_{a,b=1}^r \sum_{i < j}^{N_a, N_b} u_{iabj}(\mathbf{r}_{ia}, \mathbf{r}_{bj}). \quad (10.1)$$

This pairwise additive potential assumption can be removed, but with a little more complication, without altering the important features of the theory. The subscripts  $i \in a$  and  $j \in b$  denote the particles of species  $a$  and  $b$ , respectively.

Then the grand canonical partition function [4] is given by

$$\Xi = \sum_{\mathbf{N} \geq 0} \left( \prod_{a=1}^r \frac{z_a^{N_a}}{N_a!} \right) Z_{\mathbf{N}}, \quad (10.2)$$

where

$$Z_N = \int d\mathbf{r}^{(N)} \exp(-\beta U_N), \quad (10.3)$$

$$z_a = \exp(\mu_a \beta) / \Lambda_a^3, \quad (10.4)$$

$$\Lambda_a = \frac{h}{\sqrt{2\pi m_a k_B T}} \quad (10.5)$$

with  $h$  denoting the Planck constant and  $m_a$  the mass of species  $a$ ;  $\beta = 1/k_B T$  with  $k_B$  denoting the Boltzmann constant and  $T$  the absolute temperature; and  $z_a$  the absolute activity ( $\mu_a$  = chemical potential of species  $a$ ). We note that the grand canonical partition function  $\Xi$  is related to the equation of state

$$pV = k_B T \ln \Xi. \quad (10.6)$$

The grand canonical probability may then be defined by

$$P_N = \left( \prod_{a=1}^r \frac{z_a^{N_a}}{N_a!} \right) \frac{Z_N}{\Xi}. \quad (10.7)$$

It is useful to define reduced canonical probability distribution functions

$$P_N^{(n)}(\mathbf{r}^{(n)}) = \frac{1}{Z_N} \int d\mathbf{r}^{(N-n)} \exp(-\beta U_N), \quad (10.8)$$

$$\rho_N^{(n)}(\mathbf{r}^{(n)}) = \left( \prod_{\alpha=1}^r \frac{N_\alpha!}{(N_\alpha - n_\alpha)!} \right) P_N^{(n)}(\mathbf{r}^{(n)}), \quad (10.9)$$

and with  $\rho_N^{(n)}(\mathbf{r}^{(n)})$  the grand canonical reduced distribution function

$$\rho^{(n)}(\mathbf{r}^{(n)}) = \sum_{N \geq 0} P_N \rho_N^{(n)}(\mathbf{r}^{(n)}). \quad (10.10)$$

This is the probability of finding  $\mathbf{n} = (n_1, n_2, \dots, n_r)$  particles at  $\mathbf{r}^{(n)}$  out of  $N$  particles in the system regardless of the distribution of the remaining  $(N - \mathbf{n})$  particles. Therefore integration of  $\rho_N^{(n)}(\mathbf{r}^{(n)})$  over  $\mathbf{r}^{(n)}$  yields the average value

$$\begin{aligned} \int d\mathbf{r}^{(n)} \rho^{(n)}(\mathbf{r}^{(n)}) &= \sum_{N \geq 0} P_N \prod_{\alpha=1}^r \frac{N_\alpha!}{(N_\alpha - n_\alpha)!} \\ &:= \left\langle \prod_{\alpha=1}^r \frac{N_\alpha!}{(N_\alpha - n_\alpha)!} \right\rangle_{av}. \end{aligned} \quad (10.11)$$

For example,

$$\int d\mathbf{r}_{a1} \rho_a^{(1)}(\mathbf{r}_{a1}) = \langle N_a \rangle_{av}, \quad (10.12)$$

$$\int d\mathbf{r}_{a1} \int d\mathbf{r}_{b2} \rho_{ab}^{(2)}(\mathbf{r}_{a1}, \mathbf{r}_{b2}) = \langle N_a N_b - N_a \delta_{ab} \rangle_{av}, \quad (10.13)$$

$$\int d\mathbf{r}_{a1} \int d\mathbf{r}_{a2} \rho_{aa}^{(2)}(\mathbf{r}_{a1}, \mathbf{r}_{a2}) = \langle N_a N_a - N_a \rangle_{av}. \quad (10.14)$$

Here the compound subscript  $ai$  means particle  $i \in$  species  $a$ .

It is convenient to define mean number densities by

$$n_a = \frac{\bar{N}_a}{V} = \frac{\langle N_a \rangle_{av}}{V}, \quad (10.15)$$

where

$$\bar{N}_a = \langle N_a \rangle_{av} = \sum_{\mathbf{N} \geq 0} N_a P_{\mathbf{N}}. \quad (10.16)$$

Therefore for uniform fluid mixtures the mean densities have the form

$$\rho_a^{(1)}(\mathbf{r}_{a1}) = n_a = \frac{\langle N_a \rangle_{av}}{V}, \quad (10.17)$$

$$\begin{aligned} \rho_{ab}^{(2)}(\mathbf{r}_{a1}, \mathbf{r}_{b2}) &= \rho_a^{(1)}(\mathbf{r}_{a1}) \rho_b^{(1)}(\mathbf{r}_{b2}) g_{ab}(\mathbf{r}_{ab}) \\ &= n_a n_b g_{ab}(\mathbf{r}_{ab}) \quad (\mathbf{r}_{ab} = \mathbf{r}_{a1} - \mathbf{r}_{b2}), \text{ etc.} \end{aligned} \quad (10.18)$$

Here  $g_{ab}(\mathbf{r}_{ab})$  is the pair distribution function at relative distance  $\mathbf{r}_{ab}$  of particle 1 and 2 of species  $a$  and  $b$ , respectively. It is convenient to introduce the total correlation function defined by

$$h_{ab}(\mathbf{r}_{ab}) = g_{ab}(\mathbf{r}_{ab}) - 1 \quad (10.19)$$

for the pair of particles  $1 \in a$  and  $2 \in b$ . All the molecular theory information is contained in the total correlation function  $h_{ab}(\mathbf{r}_{ab})$ . We will see that all thermodynamic functions can be expressed ultimately in terms of  $h_{ab}(\mathbf{r}_{ab})$ .

Upon using (10.18), the mean number fluctuation in (10.13) may be written in the form

$$\int d\mathbf{r}_{ab} h_{ab}(\mathbf{r}_{ab}) = V \frac{\langle N_a N_b \rangle_{av} - \langle N_a \rangle_{av} \langle N_b \rangle_{av}}{\langle N_a \rangle_{av} \langle N_b \rangle_{av}} - \frac{\delta_{ab}}{n_a}. \quad (10.20)$$

This formula shows that density fluctuations are related to the total correlation function.

Upon using the method of thermodynamics it can be shown that the density fluctuations are expressible in terms of the thermodynamic derivative

$$\begin{aligned} \frac{k_B T}{V n_a n_b} \left( \frac{\partial \bar{N}_a}{\partial \mu_b} \right)_{T, V, \mu'} &= \frac{k_B T}{n_a n_b} \left( \frac{\partial n_a}{\partial \mu_b} \right)_{T, V, \mu'} \\ &= \frac{\langle N_a N_b \rangle_{av} - \langle N_a \rangle_{av} \langle N_b \rangle_{av}}{\langle N_a \rangle_{av} \langle N_b \rangle_{av}}. \end{aligned} \quad (10.21)$$

This relation follows on differentiating the grand partition function  $\Xi_N$  with chemical potential  $\mu_b$ . Thus we obtain the integral relation connecting the thermodynamic derivative on the left of (10.21):

$$\begin{aligned} \frac{k_B T}{V} \left( \frac{\partial \bar{N}_a}{\partial \mu_b} \right)_{T, V, \mu'} &= k_B T \left( \frac{\partial n_a}{\partial \mu_b} \right)_{T, V, \mu'} \\ &= n_a \left[ \delta_{ab} + \int d\mathbf{r}_{ab} H_{ab}(\mathbf{r}_{ab}) \right], \end{aligned} \quad (10.22)$$

where

$$H_{ab}(\mathbf{r}_{ab}) = n_b h_{ab}(\mathbf{r}_{ab}). \quad (10.23)$$

Equation (10.22) is a key equation relating thermodynamic phenomenology to molecular theory. It will be convenient to define an analogous symbol for the direct correlation function  $c_{ab}(\mathbf{r}_{ab})$  appearing later:

$$C_{ab}(\mathbf{r}_{ab}) = n_b c_{ab}(\mathbf{r}_{ab}). \quad (10.24)$$

Relation (10.21) indicates that chemical potentials are intimately related to the pair correlation functions of the mixture. This relation is the generalization of the single (pure) fluid version. Equation (10.21), as a matter of fact, represents a matrix equation for the mixture, and the KB solution theory is basically about inverting this matrix equation and calculating thermodynamic quantities, such as chemical potentials, partial molar volumes, and so on, of solutions, at least, formally in terms of pair correlation functions, which are functions of temperature and densities.

For the purpose mentioned, it is convenient to define the matrix elements

$$\hat{B}_{ab} = \delta_{ab} + G_{ab}, \quad (10.25)$$

where  $G_{ab}$  is defined by the integral

$$G_{ab} = \int d\mathbf{r}_{ab} H_{ab}(\mathbf{r}_{ab}), \quad (10.26)$$

which would be determined if  $H_{ab}(\mathbf{r}_{ab})$  are obtained. From (10.22) follows the relation

$$\frac{1}{V} \left( \frac{\partial \bar{N}_a}{\partial \mu_b} \right)_{T, V, \mu'} = \frac{1}{k_B T} n_a \hat{B}_{ab} = \frac{1}{k_B T} (\mathbf{n} \cdot \hat{\mathbf{B}})_{ab}, \quad (10.27)$$

where  $N_a := \overline{N}_a$  and  $\mathbf{n}$  is a diagonal matrix

$$\mathbf{n} = \begin{pmatrix} n_1 & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & n_r \end{pmatrix}. \quad (10.28)$$

It should be noted that the matrices  $\widehat{\mathbf{B}}$  and  $\mathbf{G}$  are slightly different from those appearing in the KB theory of solutions by the density factor  $\mathbf{n}$ . As will be shown in a later section, matrix  $\widehat{\mathbf{B}}$  can be expressed in terms of direct correlation functions instead of the total correlation functions.

### 10.1.1 Chemical Potentials

Inverting this matrix equation yields the chemical potential derivative

$$\begin{aligned} V \left( \frac{\partial \mu_b}{\partial N_a} \right)_{T,V,N'} &= \left( \frac{\partial \mu_b}{\partial n_a} \right)_{T,V,n'} = k_B T (\mathbf{n} \cdot \widehat{\mathbf{B}})^{-1}_{ab} \\ &= \frac{V k_B T}{N_b} (\widehat{\mathbf{B}}^{-1})_{ab} = \frac{k_B T}{n_b} (\widehat{\mathbf{B}}^{-1})_{ab}. \end{aligned} \quad (10.29)$$

Here the inverse of matrix  $\widehat{\mathbf{B}}$  is expressible in the form

$$(\widehat{\mathbf{B}}^{-1})_{ab} = \frac{|\widehat{\mathbf{B}}|_{ab}}{|\widehat{\mathbf{B}}|} \quad (10.30)$$

with  $|\widehat{\mathbf{B}}|$  denoting the determinant of matrix  $\widehat{\mathbf{B}}$ , and  $|\widehat{\mathbf{B}}|_{ab}$  the  $ab$  cofactor of the determinant  $|\widehat{\mathbf{B}}|$ .

Relation (10.29) is at the heart of the KB theory of solutions, which gives rise to various thermodynamic relations when thermodynamics is made use of. It also indicates that the KB theory invariably yields statistical mechanical thermodynamic expressions made up of a group of formulas that include the compressibility equation of state instead of the virial equation of state. That is, the KB theory [5] of solutions may be regarded as a compressibility equation of state version if we may call the McMillan–Mayer (MM) theory [3] the virial equation of state version.

We also note that the KB theory of solutions has an advantage over the virial equation of state version in the sense that the chemical potentials do not involve the Kirkwood charging parameter [4] that appears in the virial equation of state approach (i.e., the MM theory) for thermodynamic quantities. This can be a rather useful feature.

### 10.1.2 Partial Molar Volumes and Isothermal Compressibility

The partial molar volumes can be expressed in terms of  $\widehat{\mathbf{B}}^{-1}$ . To obtain the desired expression we observe that

$$\left( \frac{\partial p}{\partial N_a} \right)_{T,N'} = - \left( \frac{\partial V}{\partial N_a} \right)_{T,p,N'} \left( \frac{\partial p}{\partial V} \right)_{T,N} = \frac{\bar{v}_a}{V\kappa}, \quad (10.31)$$

where  $v_a$  is the partial molar volume of species  $a$

$$\bar{v}_a = \left( \frac{\partial V}{\partial N_a} \right)_{T,p,N'} \quad (10.32)$$

and  $\kappa$  is the isothermal compressibility of the fluid

$$V \left( \frac{\partial p}{\partial V} \right)_{T,N} = -\kappa^{-1}, \quad (10.33)$$

which can be alternatively written as

$$V \left( \frac{\partial p}{\partial V} \right)_{T,N} = -N \left( \frac{\partial p}{\partial N} \right)_{T,V}. \quad (10.34)$$

The prime on the subscript  $N$  means omitting the variable of differentiation  $N_a$ . Henceforth, similar notation will be used for other derivatives. Relations (10.31)–(10.34) may be phrased in terms of specific volume  $v = 1/n$  of the fluid (solution). We will henceforth use this system of notation.

Since  $\mu_b = \mu_b(T, V, \{N_a\})$  according to the way the chemical potentials are related to correlation functions in the grand ensemble theory, its differential may be written as

$$d\mu_b = \sum_{c \geq a} \left( \frac{\partial \mu_b}{\partial N_c} \right)_{T,V,N'} dN_c + \left( \frac{\partial \mu_b}{\partial V} \right)_{T,N} dV,$$

which yields

$$\begin{aligned} \left( \frac{\partial \mu_b}{\partial N_a} \right)_{T,p,N'} &= \left( \frac{\partial \mu_b}{\partial N_a} \right)_{T,V,N'} + \left( \frac{\partial \mu_b}{\partial V} \right)_{T,N} \left( \frac{\partial V}{\partial N_a} \right)_{T,p,N'} \\ &= \left( \frac{\partial \mu_b}{\partial N_a} \right)_{T,V,N'} + \bar{v}_a \left( \frac{\partial \mu_b}{\partial p} \right)_{T,N} \left( \frac{\partial p}{\partial V} \right)_{T,N} \\ &= \left( \frac{\partial \mu_b}{\partial N_a} \right)_{T,V,N'} - \frac{\bar{v}_a \bar{v}_b}{V\kappa}, \end{aligned} \quad (10.35)$$

where

$$\left( \frac{\partial \mu_b}{\partial p} \right)_{T,N} = \bar{v}_b,$$

the partial molar volume of species  $b$ , when  $\mu_b$  is considered a function of its characteristic variables ( $T, p, \{N_a\}$ ). By virtue of the Gibbs–Duhem relation [10, 11] at constant  $T$  and  $p$  it follows that

$$\sum_b N_b \left( \frac{\partial \mu_b}{\partial N_a} \right)_{T,V,N'} - \sum_b N_b \frac{\bar{v}_a \bar{v}_b}{V \kappa} = 0,$$

that is,

$$\sum_b N_b \left( \frac{\partial \mu_b}{\partial N_a} \right)_{T,V,N'} = \frac{\bar{v}_a}{\kappa}, \quad (10.36)$$

since

$$\sum_a N_a \bar{v}_a = V. \quad (10.37)$$

Upon substitution of (10.29) into (10.36), there follows the partial molar volume in terms of  $\widehat{\mathbf{B}}^{-1}$ :

$$\bar{v}_a = k_B T \kappa \sum_b (\widehat{\mathbf{B}}^{-1})_{ab} = \frac{k_B T \kappa \sum_b |\widehat{\mathbf{B}}|_{ab}}{|\widehat{\mathbf{B}}|}. \quad (10.38)$$

Therefore we find the determinant  $|\widehat{\mathbf{B}}|$  in the form

$$\sum_{a=1}^r N_a \bar{v}_a = V = \frac{k_B T \kappa \sum_{a,b} N_a |\widehat{\mathbf{B}}|_{ab}}{|\widehat{\mathbf{B}}|}$$

or

$$|\widehat{\mathbf{B}}| = \frac{k_B T \kappa}{V} \sum_{a,b} N_a |\widehat{\mathbf{B}}|_{ab} = n k_B T \kappa \sum_{a,b} x_a |\widehat{\mathbf{B}}|_{ab}, \quad (10.39)$$

and the partial molar volume may be alternatively written as

$$n \bar{v}_a = \frac{\sum_b |\widehat{\mathbf{B}}|_{ab}}{\sum_{a,b} x_a |\widehat{\mathbf{B}}|_{ab}} = \frac{\sum_b (\widehat{\mathbf{B}}^{-1})_{ab}}{\sum_{l,b} x_l (\widehat{\mathbf{B}}^{-1})_{lb}}. \quad (10.40)$$

This is the molecular theory formula for partial molar volumes of the mixture in the KB theory. Furthermore, it also follows from (10.39) that the isothermal compressibility is given by

$$(n k_B T \kappa)^{-1} = \frac{\sum_{l,b} x_a |\widehat{\mathbf{B}}|_{lb}}{|\widehat{\mathbf{B}}|} = \sum_{l,b} x_l (\widehat{\mathbf{B}}^{-1})_{lb}. \quad (10.41)$$

These are the desired molecular theory formulas for partial molar volumes and the isothermal compressibility of mixtures, both expressed in terms of total correlation functions.

### 10.1.3 Equation of State

The equation of state by the compressibility route follows if (10.31) is integrated over concentration:

$$p = p_0 + k_B T \int_0^n dn \sum_{a,b} x_a |\hat{\mathbf{B}}|_{ab} |\hat{\mathbf{B}}|^{-1},$$

where  $p_0$  is the integration constant. Since the pressure must approach the ideal gas equation of state for the mixture as  $n_a \rightarrow 0$ , we may choose

$$p_0 = 0.$$

Thus we obtain

$$p = k_B T \int_0^n dn \sum_{a,b} x_a |\hat{\mathbf{B}}|_{ab} |\hat{\mathbf{B}}|^{-1} \quad (10.42)$$

for the equation of state.

This expression for  $p$  appears to be much different from that of a single-component fluid, which is given in terms of the direct correlation function of the fluid. Therefore, it appears to be less intuitive than that of a single-component fluid. However, it can be shown to be indeed expressible in term of direct correlation functions, if the Ornstein–Zernike (OZ) integral equations for the mixture [12] are made use of. We will discuss this aspect separately in a subsequent section. By this procedure, the KB theory of solutions can be put into formally much more simplified and intuitive form. But it can also be made rather practical and easily amenable to numerical methods, as will be shown later.

### 10.1.4 Chemical Potentials Revisited

Having obtained the density derivatives of chemical potentials, it is possible to calculate chemical potentials in the pressure-density plane. Regard  $\mu_b$  as a function of  $p$ ,  $T$ , and  $\{n_a\}$  and examine its variation in the  $(p, \{n_a\})$  subspace with  $T$  held fixed:

$$d\mu_b = \bar{v}_b dp + \sum_a \left( \frac{\partial \mu_b}{\partial n_a} \right)_{T,p,n'} dn_a. \quad (10.43)$$

This total derivative of chemical potential is integrated in the  $(p, \{n_a\})$  space to obtain an integral of chemical potential  $\mu_b(p, T, \{n_a\})$  in terms of total correlation functions without using the charging parameter. It is in contrast to the Kirkwood charging parameter method within the McMillan–Mayer theory [3].

#### 10.1.4.1 Density Dependence of Chemical Potentials

The density dependence of chemical potentials at constant  $p$  and  $T$  can be computed with the formula given below. Since variation of  $\mu_a$  at such a condition is given by

$$\begin{aligned} d\mu_b &= \sum_{ab} \left( \frac{\partial \mu_b}{\partial N_a} \right)_{T, p, N'} dN_a \\ &= \sum_a \left[ \left( \frac{\partial \mu_b}{\partial N_a} \right)_{T, V, N'} - \frac{\bar{v}_a \bar{v}_b}{V \kappa} \right] dN_a \end{aligned} \quad (10.44)$$

for which we have used Relation (10.35), upon substituting (10.29), (10.40), and (10.41) we obtain the equation

$$d\mu_b = k_B T \sum_a \left[ \frac{1}{n_b} (\widehat{\mathbf{B}}^{-1})_{ab} - \frac{\sum_{l,m} (\widehat{\mathbf{B}}^{-1})_{am} (\widehat{\mathbf{B}}^{-1})_{bl}}{\sum_{l,m} n_l (\widehat{\mathbf{B}}^{-1})_{lm}} \right] dn_a. \quad (10.45)$$

Integrating over  $\{n_l\}$ , there follows the statistical mechanical formula for  $\mu_a$  as a function of density at constant  $T$  and  $p$ :

$$\begin{aligned} \mu_b(T, p, \{n_l\}) &= \mu_b(T, p) + k_B T \sum_k \int^{n_k} dn_k \frac{1}{n_b} (\widehat{\mathbf{B}}^{-1})_{kb} \\ &\quad - k_B T \sum_k \int^{n_k} dn_k \frac{\sum_{l,m} (\widehat{\mathbf{B}}^{-1})_{bl} (\widehat{\mathbf{B}}^{-1})_{km}}{\sum_{l,m} n_l (\widehat{\mathbf{B}}^{-1})_{lm}}. \end{aligned} \quad (10.46)$$

Here  $\mu_b(T, p)$  is the integration constant, which depends on  $T$  and  $p$ . It is essentially the chemical potential of pure component  $b$  at  $T$ . It is determined by integrating the differential over  $p$  with  $\{n_l\}$  held fixed:

$$d\mu_b(T, p) = \bar{v}_b dp.$$

It thus follows from this equation the chemical potential  $\mu_b(T, p)$ :

$$\mu_b(T, p) = \mu_b^0(T) + k_B T \ln p + \int^p dp' \left( \bar{v}_b - \frac{k_B T}{p'} \right). \quad (10.47)$$

Therefore the overall chemical potential  $\mu_b(T, p, \{n_l\})$  in (10.46) is given by

$$\begin{aligned}\mu_b(T, p, \{n_l\}) &= \mu_b^0(T) + k_B T \ln p + \int^p dp' \left( \bar{v}_b - \frac{k_B T}{p'} \right) \\ &\quad + k_B T \sum_k \int^{n_k} dn_k \frac{1}{n_b} (\widehat{\mathbf{B}}^{-1})_{kb} \\ &\quad - k_B T \sum_k \int^{n_k} dn_k \frac{\sum_{l,m} (\widehat{\mathbf{B}}^{-1})_{bl} (\widehat{\mathbf{B}}^{-1})_{km}}{\sum_{l,m} n_l (\widehat{\mathbf{B}}^{-1})_{lm}}.\end{aligned}\quad (10.48)$$

Changing variable in the first integral on the right we obtain

$$\begin{aligned}I_p &= \int^p dp' \left( \bar{v}_b - \frac{k_B T}{p'} \right) \\ &= \int^n dn \frac{1}{n\kappa} \left( \bar{v}_b - \frac{k_B T}{p'} \right),\end{aligned}$$

which may be expressed as

$$\begin{aligned}I_p &= k_B T \int^n dn \frac{1}{n} \sum_m (\widehat{\mathbf{B}}^{-1})_{bm} - k_B T \int^n dn' \frac{\sum_{l,m} x_l (\widehat{\mathbf{B}}^{-1})_{lm}}{\int^{n'} dn'' \sum_{l,m} x_l (\widehat{\mathbf{B}}^{-1})_{lm}} \\ &= k_B T \int^n dn \frac{1}{n} \sum_m [(\widehat{\mathbf{B}}^{-1})_{bm} - \delta_{bm}] \\ &\quad - k_B T \ln \left[ \frac{1}{n} \int^{n'} dn'' \sum_{l,m} x_l (\widehat{\mathbf{B}}^{-1})_{lm} \right].\end{aligned}\quad (10.49)$$

Inserting this into (10.48), we obtain the overall chemical potential in the form

$$\mu_b(T, p, \{x_l\}) = \mu_b^0(T) + k_B T \ln(x_b \gamma_b). \quad (10.50)$$

Here the integration constant may be suitably chosen in the limits of dilute solutions and vanishing  $n$ . Thus  $\mu_b^0$  is now defined as the limiting value of  $\mu_b(T, p, \{n_l\})$  in the following sense

$$\mu_b^0(T) = \lim_{\substack{n \rightarrow 0 \\ \{x_l\} \rightarrow 0}} [\mu_b(T, p, \{n_l\}) - k_B T \ln(x_b n k_B T)] \quad (10.51)$$

with the activity coefficient  $\gamma_b$  now expressed as follows:

$$\begin{aligned}\ln \gamma_b = & \ln(nk_B T) + \int_0^n dn \frac{1}{n} \sum_m [(\widehat{\mathbf{B}}^{-1})_{bm} - \delta_{bm}] \\ & + \sum_k \int_0^{n_k} dx_k \frac{1}{x_b} [(\widehat{\mathbf{B}}^{-1})_{kb} - \delta_{kb}] \\ & + \sum_k \int_0^{n_k} dx_k \frac{\sum_{l,m} (\widehat{\mathbf{B}}^{-1})_{bl} (\widehat{\mathbf{B}}^{-1})_{km}}{\sum_{l,m} x_l (\widehat{\mathbf{B}}^{-1})_{lm}}.\end{aligned}\quad (10.52)$$

It is entirely expressed in terms of pair correlation function. It is therefore a statistical mechanical representation of activity coefficients for solutions.

The activity may be defined as

$$a_b = x_b \gamma_b \quad (10.53)$$

and the chemical potential written as

$$\mu_b(T, p, \{n_l\}) = \mu_b^0(T) + k_B T \ln a_b, \quad (10.54)$$

which may be compared with the chemical potential of species  $b$  measured in phenomenological thermodynamics.

The statistical mechanical activity  $a_b$  consists of two parts, one over the changes in composition and the other over the change in overall density of the solution in question. The composition dependence is an additional feature appearing in the case of solutions in contrast to pure liquids for which only the density change determines the thermodynamic properties in an isothermal condition.

### 10.1.5 Osmotic Pressure

The relation of osmotic pressure to the chemical potentials of the solutes can be obtained from the Gibbs–Duhem equation. If the pressure of the pure solvent is denoted by  $p$  the solvent chemical potential in equilibrium across a semipermeable membrane is related to the pure solvent chemical potential  $\mu_s$  at  $p$  by the relation

$$\mu_s(T, p + \Pi, \{n_a\}) = \mu_s(T, p, \{n_s, 0\}) + \int_p^{p+\Pi} dp' \bar{v}_a(T, p', \{n_a\}), \quad (10.55)$$

where  $\Pi$  is called the osmotic pressure. Therefore the solvent chemical potential of the solution is a function of  $\Pi$  as well. Then the total differential of the solvent chemical potential of the solution is given by

$$d\mu_s = \bar{v}_1 d\Pi + \sum_b \left( \frac{\partial \mu_s}{\partial N_b} \right)_{T,p,N'} dN_b, \quad (10.56)$$

if the temperature is held constant. If the solvent chemical potential is now held constant then we obtain

$$\left( \frac{\partial \Pi}{\partial N_a} \right)_{T,\mu_s,N'} = -\frac{1}{\bar{v}_s} \left( \frac{\partial \mu_s}{\partial N_a} \right)_{T,p,N'}. \quad (10.57)$$

Inserting Relation (10.35) and using (10.40) and (10.41), we obtain

$$\left( \frac{\partial \Pi}{\partial N_a} \right)_{T,\mu_s,N'} = -\frac{1}{\bar{v}_s} \left[ \left( \frac{\partial \mu_s}{\partial N_a} \right)_{T,V,n'} - \frac{\bar{v}_a \bar{v}_s}{V \kappa} \right], \quad (10.58)$$

which is now expressible in the form

$$\left( \frac{\partial \Pi}{\partial n_a} \right)_{T,\mu_s,N'} = k_B T \sum_l (\widehat{\mathbf{B}}^{-1})_{al} - \frac{k_B T}{x_s} \frac{\sum_{l,m} x_l (\widehat{\mathbf{B}}^{-1})_{lm} (\widehat{\mathbf{B}}^{-1})_{as}}{\sum_m (\widehat{\mathbf{B}}^{-1})_{sm}}. \quad (10.59)$$

Since variation with respect to solute densities of  $\Pi$  at constant  $T$  and  $p$  and with  $\mu_s$  held fixed is given by

$$d\Pi = \sum_{a \neq s} \left( \frac{\partial \Pi}{\partial n_a} \right)_{T,\mu_s,N'} dn_a, \quad (10.60)$$

the osmotic pressure is obtained by integrating this equation over solute densities<sup>1</sup>:

<sup>1</sup>Equation (10.59) is obtained from (10.58) upon insertion of the formulas for the chemical potential derivative and partial molar volumes:

$$\begin{aligned} \left( \frac{\partial \Pi}{\partial N_a} \right)_{T,\mu_s,N'} &= -\frac{k_B T}{N_s} (\widehat{\mathbf{B}}^{-1})_{as} \frac{\sum_{l,m} N_l (\widehat{\mathbf{B}}^{-1})_{lm}}{V \sum_m (\widehat{\mathbf{B}}^{-1})_{sm}} \\ &\quad + \frac{V \sum_l (\widehat{\mathbf{B}}^{-1})_{al}}{\sum_{l,m} N_l (\widehat{\mathbf{B}}^{-1})_{lm}} \frac{1}{V} \frac{k_B T}{V} \sum_{l,m} N_l (\widehat{\mathbf{B}}^{-1})_{lm}, \end{aligned}$$

which is simplified to the form

$$\begin{aligned} \left( \frac{\partial \Pi}{\partial N_a} \right)_{T,\mu_s,N'} &= \frac{k_B T}{V} \sum_l (\widehat{\mathbf{B}}^{-1})_{al} \\ &\quad - \frac{k_B T}{VN_s} \frac{\sum_{l,m} N_l (\widehat{\mathbf{B}}^{-1})_{lm} (\widehat{\mathbf{B}}^{-1})_{as}}{\sum_m (\widehat{\mathbf{B}}^{-1})_{sm}}. \end{aligned}$$

This is cast into the form given in (10.59).

$$\begin{aligned}\Pi(T, p, \{n_a : a \neq s\}) = & \Pi^0(T, p) + k_B T \sum_{a,l} \int_0^{n_a} dn_a (\widehat{\mathbf{B}}^{-1})_{al} \\ & - \frac{k_B T}{x_s} \sum_a \int_0^{n_a} dn_a \frac{\sum_{l,m} x_l (\widehat{\mathbf{B}}^{-1})_{as} (\widehat{\mathbf{B}}^{-1})_{lm}}{\sum_m (\widehat{\mathbf{B}}^{-1})_{sm}}.\end{aligned}\quad (10.61)$$

Here the integration constant  $\Pi^0$  is the osmotic pressure in the limit of infinitely dilute solution. The pressure dependence of  $\Pi^0$  can be determined from the information on the isothermal compressibility and the partial molar volume. It can be obtained in a manner similar to the determination of  $\mu_b(T, p)$  described in the previous section. Since it is not an overriding interest in the case of osmotic pressure, we will not dwell on it.

Now that we have shown all thermodynamic quantities are given in terms of matrix  $\widehat{\mathbf{B}}$  or its inverse it is necessary to devise a way to determine the matrix  $\mathbf{B}$  or the pair correlation functions comprising it.

## 10.2 Ornstein–Zernike Theory of Solutions

We have now seen that the KB theory of solutions needs a practicable theory of calculating pair correlation functions to obtain the thermodynamic quantities presented earlier. One method of calculating pair correlation functions is OZ integral equations [12] with a suitable closure such as the Percus–Yevick (PY) closure [13] or hypernetted chain closure [14] or the mean spherical approximation closure and its variant [15, 16]. The Kirkwood integral equation [18] may be used for the purpose. However, the PY integral equation is known to be more accurate than the Kirkwood integral equation, although the latter can be manipulated [19] to yield the PY integral equation.

For the discussion in this section there is no need as yet for considering a closure because we are interested in formal relations between the KB theory of solutions and the OZ theory of mixtures. Besides being generally a practical method for the purpose of computing thermodynamic properties, the OZ theory can give rise to particularly simple forms for thermodynamic quantities appearing in the KB theory of solutions that are rather insightful as has been shown by Pearson and Rushbrooke [6] and O’Connell [7].

The OZ equations for mixtures may be written in the form [21–23]

$$h_{ab}(\mathbf{r}_a, \mathbf{r}_b) = c_{ab}(\mathbf{r}_a, \mathbf{r}_b) + \sum_{c=1}^r \int d\mathbf{r}_c n_c c_{ac}(\mathbf{r}_a, \mathbf{r}_c) h_{cb}(\mathbf{r}_c, \mathbf{r}_b), \quad (10.62)$$

where  $c_{ab}(\mathbf{r}_a, \mathbf{r}_b)$  is the direct correlation function. This set of integral equations can be derived from the grand canonical ensemble distribution function by applying the functional derivative method [20]. The OZ equation (10.62) then can be written as

$$H_{ab}(\mathbf{r}_a, \mathbf{r}_b) = C_{ab}(\mathbf{r}_a, \mathbf{r}_b) + \sum_c \int d\mathbf{r}_c C_{ac}(\mathbf{r}_a, \mathbf{r}_c) H_{cb}(\mathbf{r}_c, \mathbf{r}_b). \quad (10.63)$$

The OZ equations are often solved by means of Fourier transform, on the assumption of a closure. There are a number of closures possible and available in the literature [13–16] as mentioned earlier. They are usually taken for the direct correlation functions. Quite apart from the question of closure, the OZ equations have a powerful significance to the solution theory of liquids, and in this lies the power of the OZ equations as applied to the KB theory of solutions because it puts the latter, at least formally, in a rather concise form facilitating analysis of the results.

Let us denote the Fourier transforms of  $H_{ab}(\mathbf{r}_a, \mathbf{r}_b)$  and  $C_{ab}(\mathbf{r}_a, \mathbf{r}_b)$  by  $\widehat{H}_{ab}(\mathbf{k})$  and  $\widehat{C}_{ab}(\mathbf{k})$ , respectively:

$$\begin{aligned} \widehat{H}_{ab}(\mathbf{k}) &= \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) H_{ab}(\mathbf{r}), \\ \widehat{C}_{ab}(\mathbf{k}) &= \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) C_{ab}(\mathbf{r}). \end{aligned} \quad (10.64)$$

Then owing to the convolution theorem the Fourier transform of the OZ equation is given by

$$\widehat{H}_{ab}(\mathbf{k}) = \widehat{C}_{ab}(\mathbf{k}) + \sum_{c \geq 1} \widehat{C}_{ac}(\mathbf{k}) \widehat{H}_{cb}(\mathbf{k}). \quad (10.65)$$

This set of equations may be put into matrix form:

$$\widehat{\mathbf{H}} = \widehat{\mathbf{C}} + \widehat{\mathbf{C}}\widehat{\mathbf{H}}. \quad (10.66)$$

Solving this set of coupled equations for  $\widehat{C}_{ab}(\mathbf{k})$ , we obtain

$$\widehat{C}_{ab}(\mathbf{k}) = \sum_{c \geq 1} \widehat{H}_{ac}(\mathbf{k}) [\mathbf{I} + \widehat{\mathbf{H}}(\mathbf{k})]_{cb}^{-1} = [\widehat{\mathbf{H}} (\mathbf{I} + \widehat{\mathbf{H}}(\mathbf{k}))^{-1}]_{ab}, \quad (10.67)$$

where  $\mathbf{I}$  is the unit matrix. With a suitable closure relation for the direct correlation functions this equation can be solved by means of an iterative method. Since this procedure is well known in the literature [13–17] we will not dwell on it here.

### 10.3 The KB Theory Recast

We now observe that there holds the relation

$$\widehat{B}_{ab} = \delta_{ab} + \widehat{H}_{ab}(0) \quad (10.68)$$

between  $\widehat{B}_{ab}$  and the Fourier transform of  $H_{ab}(r)$  at  $k = 0$ . This is easy to verify from (10.19) and (10.26). Note in this connection that

$$\widehat{H}_{ab}(0) = \left[ \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} H_{ab}(r) \right]_{\mathbf{k}=0} = G_{ab} \quad (10.69)$$

and similarly

$$\widehat{C}_{ab}(0) = \left[ \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} C_{ab}(r) \right]_{\mathbf{k}=0} := D_{ab}, \quad (10.70)$$

where

$$D_{ab} = \int d\mathbf{r} C_{ab}(r). \quad (10.71)$$

Therefore, since according to the OZ equation

$$[\mathbf{I} + \widehat{\mathbf{H}}(0)]^{-1} = \mathbf{I} - \widehat{\mathbf{H}}(0) [\mathbf{I} + \widehat{\mathbf{H}}(0)]^{-1} = \mathbf{I} - \widehat{\mathbf{C}}(0), \quad (10.72)$$

the matrix  $\widehat{\mathbf{B}}$  then is given by

$$\widehat{\mathbf{B}} = [\mathbf{I} + \widehat{\mathbf{H}}(0)]. \quad (10.73)$$

Therefore

$$(\widehat{\mathbf{B}})^{-1} = [\mathbf{I} + \widehat{\mathbf{H}}(0)]^{-1} = \mathbf{I} - \widehat{\mathbf{C}}(0). \quad (10.74)$$

In other words, we now see that the inverse of matrix  $\widehat{\mathbf{B}}$  can be directly calculated with the direct correlation functions. Thus we have

$$n_b \left( \frac{\partial \mu_b}{\partial n_a} \right)_{T,V,N'} = k_B T [\mathbf{I} - \widehat{\mathbf{C}}(0)]_{ab}. \quad (10.75)$$

With the help of the OZ equation the inversion problem of matrix  $\widehat{\mathbf{B}}$  inherent to the KB theory of solutions, therefore, is neatly avoided, and the KB theory of solutions can be reformulated in terms of direct correlation functions only, as will be seen presently. This is a considerable formal simplification and intuitively more easily comprehensible from the theory of pure liquids. Its advantage also becomes great in developing approximate theories, which must assume a suitable closure for the OZ equation that usually is taken for the direct correlation function. Moreover, for hard sphere fluids the direct correlation function is analytically known and a similar analytic form is also known for square well potential models. Therefore a thermodynamic theory can be easily developed for such liquid mixtures by means of such analytic results.

### 10.3.1 Partial Molar Volumes and Isothermal Compressibility

Partial molar volume and isothermal compressibility given in (10.40) and (10.41) can be expressed in terms of direct correlation functions. The isothermal compressibility

and partial molar volumes are, respectively, given by

$$(nk_B T \kappa)^{-1} = 1 - \sum_{l,m} x_l \widehat{C}_{lm}(0), \quad (10.76)$$

$$n\bar{v}_a = \frac{1 - \sum_l \widehat{C}_{al}(0)}{1 - \sum_{l,m} x_l \widehat{C}_{lm}(0)}. \quad (10.77)$$

Since

$$\widehat{C}_{ab}(0) = nx_b \int d\mathbf{r} c_{ab}(r), \quad (10.78)$$

we obtain<sup>2</sup>

$$(nk_B T \kappa)^{-1} = 1 - n \sum_{a,b} x_a x_b \int d\mathbf{r} c_{ab}(r), \quad (10.79)$$

$$n\bar{v}_a = \frac{1 - n \sum_b x_b \int d\mathbf{r} c_{ab}(r)}{1 - n \sum_{a,b} x_a x_b \int d\mathbf{r} c_{ab}(r)}. \quad (10.80)$$

Therefore, since

$$\frac{1}{\kappa} = n \left( \frac{\partial p}{\partial n} \right)_{T,V}, \quad (10.81)$$

the equation of state is obtained from the equation

$$\left( \frac{\partial p}{\partial n} \right)_{T,V} = k_B T - nk_B T \sum_{a,b} x_a x_b \int d\mathbf{r} c_{ab}(r) \quad (10.82)$$

which on integration yields

$$p = nk_B T - k_B T \int_0^n dn' n' \sum_{a,b} x_a x_b \int d\mathbf{r} c_{ab}(\mathbf{r}). \quad (10.83)$$

This is the generalization of the pure fluid compressibility equation of state to solutions we have alluded to earlier.

<sup>2</sup>In connection with these relations it appears useful to digress and make the following observation: For practical computation of thermodynamic quantities presented in the following, note that computation of the integral of direct correlation functions

$$\int d\mathbf{r} c_{ab}(r)$$

is more easily accomplished if the Fourier transform  $\widehat{C}_{ab}(0)$  is directly computed with the factorization functions or the integral equations obeyed by the factorization functions, for example, the integral equations for  $c_{ab}(r)$  in the Wiener–Hopf method [24–27].

In connection with (10.83) it is useful to note the following: The compressibility equation of state (10.83) may be recast in terms of the Fourier transform of the factorization function [24, 27]. Since

$$\left(\frac{\partial p}{\partial n}\right)_{T,V} = k_B T - k_B T \sum_{a,b} x_a \widehat{C}_{ab}(0), \quad (10.84)$$

if, for example,  $\widehat{C}_{ab}(0)$  is factorized into the form

$$\widehat{C}_{ab}(0) = \delta_{ab} - [\widehat{K}^t(-k) \widehat{K}(k)]_{ab,k=0}, \quad (10.85)$$

where  $\widehat{K}^t(-k)$  is the transpose of  $\widehat{K}(-k)$ , we obtain

$$\begin{aligned} \left(\frac{\partial p}{\partial n}\right)_{T,V} &= k_B T - k_B T \sum_{a,b} x_a \left\{ \delta_{ab} - [\widehat{K}^t(-k) \widehat{K}(k)]_{ab,k=0} \right\} \\ &= k_B T \sum_{a,b} x_a [\widehat{K}^t(-k) \widehat{K}(k)]_{ab,k=0}. \end{aligned} \quad (10.86)$$

As is the case for pure fluids, this form is simpler to evaluate than with the cavity function or the direct correlation function. It should be especially so for the case of mixtures because evaluation of the Fourier transform  $\widehat{K}(k)$  is rather straightforward. This line of approach may be used to implement a theory of mixtures.

### 10.3.2 Chemical Potentials Recast

Since

$$\left(\frac{\partial \mu_b}{\partial n_a}\right)_{T,V,n'} = \left(\frac{\partial \mu_b}{\partial n_a}\right)_{T,p,n'} + \frac{\bar{v}_a \bar{v}_b}{\kappa} \quad (10.87)$$

and by using (10.29) and (10.74) the left hand side of (10.87) can be written as

$$\left(\frac{\partial \mu_b}{\partial n_a}\right)_{T,V,n'} = \frac{k_B T}{n_b} [\delta_{ab} - \widehat{C}_{ab}(0)], \quad (10.88)$$

we obtain

$$\left(\frac{\partial \mu_b}{\partial n_a}\right)_{T,V,n'} = \frac{k_B T}{n_b} \left[ \delta_{ab} - n_b \int d\mathbf{r} c_{ab}(r) \right]. \quad (10.89)$$

Since at constant  $T$  and  $p$

$$d\mu_a = \sum_b \left( \frac{\partial \mu_a}{\partial n_b} \right)_{T,p,n'} dn_b, \quad (10.90)$$

it follows from the relations above

$$\begin{aligned} d\mu_a &= k_B T \sum_b \left[ \frac{\delta_{ab}}{n_b} - \int d\mathbf{r} c_{ab}(r) \right] dn_b - \sum_b \frac{\bar{v}_a \bar{v}_b}{\kappa} dn_b \\ &= k_B T d \ln x_a + k_B T \sum_b d \ln f_{ab}, \end{aligned} \quad (10.91)$$

where

$$\begin{aligned} d \ln f_{ab} &= -dn_b \int d\mathbf{r} c_{ab}(r) \\ &\quad - \frac{\left[ 1 - \sum_j x_j \int d\mathbf{r} c_{aj}(r) \right] \left[ 1 - \sum_i x_i \int d\mathbf{r} c_{bi}(r) \right]}{n \left[ 1 - n \sum_{i,j} x_i x_j \int d\mathbf{r} c_{ij}(r) \right]} dn_b. \end{aligned} \quad (10.92)$$

Therefore, the knowledge of the direct correlation function  $c_{ab}(r)$  provides us the chemical potential  $\mu_a$ , and this formally rather simple relation is a direct generalization of the single-component fluid result. It should be noted that this is obtained by means of the KB theory based on the grand canonical ensemble distribution function, which is now seen to be a theory yielding the thermodynamic quantities by the compressibility route. Integrating (10.91) along a constant  $(T, p)$  path yields the chemical potential

$$\mu_a(T, p, \{n_b\}) = \mu_a^0(T, p) + k_B T \ln x_a + k_B T \ln f_a, \quad (10.93)$$

where

$$f_a = \prod_{b=1}^r f_{ab} \quad (10.94)$$

with  $f_{ab}$  given by the formula

$$\begin{aligned} \ln f_{ab} &= - \int^{n_b} dn_b \int d\mathbf{r} c_{ab}(r) \\ &\quad - \int^{n_b} dn_b \frac{\left[ 1 - \sum_j x_j \int d\mathbf{r} c_{aj}(r) \right] \left[ 1 - \sum_i x_i \int d\mathbf{r} c_{bi}(r) \right]}{n \left[ 1 - n \sum_{i,j} x_i x_j \int d\mathbf{r} c_{ij}(r) \right]} dn_b, \end{aligned} \quad (10.95)$$

and the integration constant can be suitably chosen in the limit of  $n_a$  or  $x_a \rightarrow 0$  such that

$$\mu_a^0(T, p) = \lim_{n_a \rightarrow 0} [\mu_a(T, p, \{n_b\}) - k_B T \ln n_a]. \quad (10.96)$$

From the statistical mechanics viewpoint  $\mu_a^0(T, p)$  in this limit is simply the ideal gas (or solution) chemical potential minus  $k_B T \ln x_a$ . With this identification of the integration constant it is now possible to fix the lower end of the density integral at  $n_a = 0$ . Thus we have

$$\begin{aligned} \ln f_{ab} = & - \int_0^{n_b} dn_b \int d\mathbf{r} c_{ab}(r) \\ & - \int_0^{n_b} dn_b \frac{\left[1 - \sum_j x_j \int d\mathbf{r} c_{aj}(r)\right] \left[1 - \sum_i x_i \int d\mathbf{r} c_{bi}(r)\right]}{n \left[1 - n \sum_{i,j} x_i x_j \int d\mathbf{r} c_{ij}(r)\right]} dn_b. \end{aligned} \quad (10.97)$$

Therefore  $f_a$  is fully identified with the activity coefficient for component  $a$  in the convention using  $x_a \rightarrow 0$ .

The reference chemical potential  $\mu_a^0(T, p)$  must be also calculated at the low pressure limit. It is calculated in the following manner

$$\mu_a^0(T, p) = \mu_a^0(T) + k_B T \ln p + \int_0^p dp' \left( v_a - \frac{k_B T}{p'} \right), \quad (10.98)$$

where  $v_a$  is the molar volume of pure fluid  $a$ . The integral on the right can be replaced with its statistical mechanical expression in terms of correlation function. The integral over pressure—the last term on the right in (10.98)—can be expressed in terms of direct correlation function by using (10.20, 10.40), and the fugacity  $f_a$  is found given by the formula.

$$f_p = \int_0^n dn \left( -\frac{1}{n} \sum_m \widehat{C}_{am}(0) - \frac{\left[1 - \sum_{l,m} x_l \widehat{C}_{lm}(0)\right]}{\int_0^n dn' \left[1 - \sum_{l,m} x_l \widehat{C}_{lm}(0)\right]} \right). \quad (10.99)$$

We now have obtained a formal statistical mechanical expression for the fugacity (or activity coefficient) given in terms of direct correlation functions and densities alone at constant  $T$  and  $n$ .

### 10.3.3 Osmotic Pressure Recast

The osmotic pressure can be recast in terms of direct correlation functions in a manner similar to the equation of state. Upon substituting the chemical potential derivatives, partial molar volumes, and the isothermal compressibility into (10.58), we obtain from (10.60) the equation expressed in terms of direct correlation functions

$$d\Pi = k_B T \sum_{a \neq s}^r \sum_b^r (\delta_{ab} - \widehat{C}_{ab}(0)) dn_a \\ - k_B T \sum_{a \neq s}^r \frac{\sum_{l,m} x_l [\mathbf{I} - \widehat{\mathbf{C}}(0)]_{as} [\mathbf{I} - \widehat{\mathbf{C}}(0)]_{lm}}{x_s \sum_k [\mathbf{I} - \widehat{\mathbf{C}}(0)]_{sk}} dn_a. \quad (10.100)$$

This is the statistical mechanics expression for the differential form for osmotic pressure, which can be used for various investigations regarding osmotic phenomena of solutions.

Thus by integrating (10.100) over densities we finally obtain the statistical mechanics formula for osmotic pressure  $\Pi$  given in terms of direct correlation functions:

$$\Pi(T, p, \{n_a : a \neq s\}) \\ = \Pi^0 + k_B T \sum_{a \neq s}^r n_a - k_B T \sum_{a \neq s}^r \sum_b^r \int_0^{n_a} dn_a \widehat{C}_{ab}(0) \\ - k_B T \sum_{a \neq s}^r \int_0^{n_a} dn_a \frac{\sum_{l,m} x_l [\mathbf{I} - \widehat{\mathbf{C}}(0)]_{lm} [\mathbf{I} - \widehat{\mathbf{C}}(0)]_{as}}{x_s \sum_k [\mathbf{I} - \widehat{\mathbf{C}}(0)]_{sk}}, \quad (10.101)$$

where the second term on the right is the result of the integral

$$k_B T \sum_{a \neq s}^r \sum_b^r \int_0^{n_a} dn_a \delta_{ab} = k_B T \sum_{a \neq s}^r n_a, \quad (10.102)$$

which is the van't Hof limit of the osmotic pressure. Compare this result with (10.61), which requires inversion of matrix  $\widehat{\mathbf{B}}$ . Now, there is no need for such a cumbersome procedure necessary for the osmotic pressure.

It should be noted that the direct correlation functions depend on densities. Since

$$\lim_{n_a \rightarrow 0} \Pi(T, p, \{n_a; a \neq s\}) = 0, \quad (10.103)$$

it follows

$$\Pi^0(T, v) = 0 \quad (10.104)$$

and we finally obtain for the osmotic pressure the equation

$$\begin{aligned} & \Pi(T, p, \{n_a; a \neq s\}) \\ &= \sum_{a \neq s} n_a k_B T - k_B T \sum_{a \neq s}^r \int_0^{n_a} dn_a \sum_b^r \widehat{C}_{ab}(0) \\ & \quad - k_B T \sum_{a \neq s}^r \int_0^{n_a} dn_a \frac{\sum_{l,m} x_l [\mathbf{I} - \widehat{\mathbf{C}}(0)]_{lm} [\mathbf{I} - \widehat{\mathbf{C}}(0)]_{as}}{x_s \sum_k [\mathbf{I} - \widehat{\mathbf{C}}(0)]_{sk}}. \end{aligned} \quad (10.105)$$

This is the non-ideal solution version of the van't Hof equation for osmotic pressure of the solution expressed in terms of direct correlation functions. The second and third term on the right represent the non-ideal solution correction to the osmotic pressure expressed in terms of direct correlation functions.

### 10.3.4 Entropy of Mixing

The entropies of solutions have played an important role in the development of solution theories and thermodynamics [28] in particular. They are important quantities for understanding solution properties. We calculate them and associated quantities here. The partial molar entropy is obtained from the chemical potential presented:

$$\bar{s}_a = - \left( \frac{\partial \mu_a}{\partial T} \right)_{p,n}. \quad (10.106)$$

On use of (10.93) we obtain

$$\bar{s}_a(T, p, \{n_b\}) = \bar{s}_a^0(T, p) - k_B \ln(x_a f_a) - k_B T \sum_b \left( \frac{\partial}{\partial T} \ln f_{ab} \right)_{p,x}, \quad (10.107)$$

where we have used the mole fraction representation and the derivative of the activity coefficient is computed with (10.95). The reference partial molar entropy is given by

$$\bar{s}_a^0(T, p) = - \left( \frac{\partial \mu_a^0}{\partial T} \right)_p. \quad (10.108)$$

The pure liquid entropy is obtained from the corresponding chemical potential

$$\mu_a(T, p) = \mu_a^0(T) + k_B T \ln p + \int_0^p dp' \left( v_a - \frac{k_B T}{p'} \right), \quad (10.109)$$

where  $v$  is the molar volume. Therefore

$$\bar{s}_a(T, p) = s_a^0(T) + k_B \ln p + \int_0^p dp' \left[ \left( \frac{\partial v_a}{\partial T} \right)_p - \frac{k_B}{p'} \right]. \quad (10.110)$$

This is identical with the pure liquid molar entropy  $s_a(T, p)$  of species  $a$ . Therefore the entropy of mixing for the  $r$ -component solution is given by

$$\begin{aligned} \Delta S &= \sum_a^r x_a (\bar{s}_a - s_a) \\ &= -k_B \sum_a^r x_a \ln x_a - k_B \sum_a x_a \left[ \ln f_a + \left( \frac{\partial \ln f_a}{\partial \ln T} \right)_{p,x} \right]. \end{aligned} \quad (10.111)$$

The second term therefore makes up the real solution correction to the ideal solution entropy of mixing, for which  $f_a$  can be calculated with the knowledge of direct correlation functions as indicated earlier.

### 10.3.5 Enthalpy of Mixtures

Another kind of thermodynamic properties readily accessible by measurement is the heat of mixing for the solution. This is even used in a classification scheme of solutions in conjunction with the entropy of mixing. In any case, regardless of the classification scheme mentioned, the heat of mixing real fluids is practical interest experimentally. We therefore express it within the framework of the solution theory formulated here. As a matter of fact, we now have the necessary ingredients to calculate it: the chemical potential and entropy formulas. The partial molar enthalpy  $\bar{h}_a$  of species  $a$  is obtained from the relation

$$\bar{h}_a = \mu_a + T \bar{s}_a. \quad (10.112)$$

By using the formulas for  $\mu_a$  and  $\bar{s}_a$  presented earlier we can straightforwardly obtain the molecular expression for heat of mixing.

## 10.4 Monte Carlo Simulation Method for Pair Correlation Functions

The reformulated version of the KB theory of solutions requires pair distribution functions. Since real complex liquids cannot be, in general, studied by means of analytic methods, a numerical method must be employed one way or another. There are a number of methods available to obtain the pair distribution functions for liquids. The Ornstein-Zernike integral equation approach is quite practicable numerically

with the Percus-Yevick closure or the hypernetted chain closure. A thermodynamically consistent closure combined with the Wiener–Hopf method can be also feasible numerically. These will be discussed in the next chapter. In this section we will simply mention Monte Carlo (MC) simulation method [29, 30] to obtain correlation functions required for the theory of mixtures presented in this essay. The MC simulation method is an attractive option which provides pair correlation functions fairly accurately and fast on a personal computer at a minimum of cost.

The general procedure to be used for the theory of mixtures by the MC approach is first to compute the total correlation functions of the mixture of interest and then the OZ equations (10.67) may be used for the mixture to compute the direct correlation functions. The latter are then used to compute the thermodynamic quantities from the formulas presented in earlier sections. Therefore, the procedure is just the reverse to the one generally used to solve the OZ equations.

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# Chapter 11

## Equilibrium Pair Correlation Functions

This chapter consists of two separate sections: (1) Integral Equation Method for Pair Correlation Functions and (2) Pair Correlation Function in the Subcritical Regimes. The two sections discuss pair correlation functions on quite different aspects.

As is evident from the equilibrium theory of mixtures in the previous chapter, a statistical mechanical theory, equilibrium or nonequilibrium, requires a theory of pair correlation functions unless the system is sufficiently dilute as for correlation functions to be negligible. In the ensemble kinetic theories developed in Chaps. 5–7 the correlation functions do not appear to be present, but as soon as one wants to implement the theories in detail at the molecular level of particles all the quantities therein are bound to be expressed in terms of lower order correlation functions. Therefore the theories of equilibrium pair correlation functions presented in this chapter are essential for implementing the theories developed so far to a level in which the theoretical results are compared with experiments. This point also applies to the generalized hydrodynamics and irreversible thermodynamics when they are put into the level of development in which experimental comparison can be made with the theory. In the first section a method of determining pair correlation functions is discussed on the basis of the Ornstein–Zernike equation. In the next section, we discuss a problem of determining the pair correlation function in the subcritical regime in which two phases are present. We make use of the grand canonical ensemble distribution function.

### 11.1 Integral Equation Method for Pair Correlation Functions

There are a number of theories in the literature by which correlation functions can be computed for systems of interacting particles. In this section we will discuss a theory of integral equations based on the Ornstein–Zernike (OZ) equation [1].

The OZ equation is a circular relation between the total and direct correlation functions of a pair of particles, which may be regarded as a partial resummation of the Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy of reduced distribution functions. Being a circular relation between total and direct correlation functions it requires a closure relation between them. There are two well-known closure relations: Percus–Yevick (PY) [2] and hypernetted chain (HNC) [3] closures. There are other closures available in the literature [4–6]. The aforementioned are simplest closure relations, which give rise to integral equations that can be readily solved numerically on a computer. Their numerical results, however, are not sufficiently accurate, nor are they able to provide description of sufficient dynamical details of the systems, especially, near the regime of phase transitions, for example. Moreover, it is difficult make them thermodynamically consistent in the sense that the direct and indirect pair correlation functions related by the closure relation become numerically consistent with each other. This thermodynamic consistency question has been investigated by a number of authors in the literature [7–15]. Here we would like to discuss a new type of closure, which is first of all thermodynamically consistent, a feature absent in the case of the PY and HNC closures. With the new closure we would like to make an attempt at incorporating some important phenomenological aspects of the system, especially, in the regime of phase transition. This new feature can be made apparent if the Wiener–Hopf (WH) method in the theory of Fourier transforms [16–18] is applied.

The OZ integral equation will be put into an equivalent set of integral equations by using the Wiener–Hopf (WH) method in the theory of Fourier transforms. This method, first employed by Baxter [19] in connection with the Percus–Yevick integral equation for hard sphere fluids, has been employed by a number of authors in connection with OZ equations but with the same factorization function originally used by Baxter [20]. However, Baxter’s factorization is not the most general according to the WH factorization method. It in fact assumes a rather special analyticity property of the Fourier transform of the factorization function—that it has no zeros in the complex plane of the Fourier transform variable, say,  $k$ .

The WH method requires that the Fourier transform of the direct correlation functions should have no zeros on the real axis of  $k$ , but there is no mathematically valid reason why it should not have zeros in the complex plane off the real axis.<sup>1</sup> Indeed, if this possibility of zeros in the complex plane is allowed, the theory becomes more flexible, and some problems looking intractable in physics of liquids and condensed matter appears to naturally present themselves as something tractable. Therefore we will take this opportunity and pursue the idea more thoroughly.

This idea was initially discussed, couched in the language of hard sphere fluids, in the monograph “Transport Coefficients of Fluids” by the present author [22]. However, it is not necessary to confine it to hard sphere fluids. It, as a matter of

<sup>1</sup>In fact, from the viewpoint of the Yang–Lee theory of condensation [21], which examines the grand partition function  $\Xi$  in the complex absolute activity ( $z$ ) plane the zeros of complex roots in the  $z$  plane approach points  $t_s$  ( $s = 1, 2, \dots$ , finite) on real axis as  $V \rightarrow \infty$ , so that every neighborhood, however small, of some points on the real axis contains zero of  $\Xi$  and consequently  $\ln \Xi$  is not an analytic function. This nonanalyticity manifests itself in phase transition.

fact, requires removal of some restrictive conditions used in Ref. [22]. The theory formulated can apply to any potential model, for example, the LJ potential model.

### 11.1.1 The Wiener–Hopf Method of Solution for the OZ Equation

For simplicity of presentation we consider the OZ equation [23] for pure liquids obeying continuous potential functions such as the LJ potential:

$$h(\mathbf{r}) = c(\mathbf{r}) + n \int d\mathbf{r}' c(\mathbf{r}, \mathbf{r}') h(\mathbf{r}', \mathbf{r}). \quad (11.1)$$

Here we adopt the same notation as for a mixture used for correlation functions in Chap. 10. Thus, for example, the total and direct correlation functions are written without a subscript denoting the species: for example,

$$H(\mathbf{r}) = nh(\mathbf{r}), \quad C(\mathbf{r}) = nc(\mathbf{r}).$$

The OZ equation is then written as

$$H(\mathbf{r}) = C(\mathbf{r}) + \int d\mathbf{r}' C(\mathbf{r}, \mathbf{r}') H(\mathbf{r}', \mathbf{r}). \quad (11.2)$$

Let us denote the Fourier transforms of  $H(\mathbf{r})$  and  $C(\mathbf{r})$  by  $\widehat{H}(\mathbf{k})$  and  $\widehat{C}(\mathbf{k})$ , respectively:

$$\begin{aligned} \widehat{H}(\mathbf{k}) &= \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) H(\mathbf{r}), \\ \widehat{C}(\mathbf{k}) &= \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) C(\mathbf{r}). \end{aligned} \quad (11.3)$$

Then by the convolution theorem the Fourier transform of the OZ equation is given by

$$\widehat{H}(\mathbf{k}) = \widehat{C}(\mathbf{k}) + \widehat{C}(\mathbf{k}) \widehat{H}(\mathbf{k}). \quad (11.4)$$

For spherically symmetric interaction potentials the aforementioned Fourier transforms are reduced to one-dimensional Fourier transforms of real functions. The functions involved are therefore dependent on  $k$  only, the absolute value (radial component) of vector  $\mathbf{k}$ . Solving this set (11.4) of coupled equations for  $\widehat{H}(k)$  under the assumption that  $1 - \widehat{C}(k)$  is invertible, we obtain

$$\widehat{H}(k) = \frac{\widehat{C}(k)}{1 - \widehat{C}(k)}. \quad (11.5)$$

In a version<sup>2</sup> of the WH method [16, 17], the denominator is conventionally factorized into a product of two functions of  $k$

$$1 - \widehat{C}(k) = \widehat{K}(k)\widehat{K}(-k), \quad (11.6)$$

where  $\widehat{K}(k)$  is a real function of  $k$ , which fulfills the condition of no zeros on the real axis and certain asymptotic properties in the strip surrounding the real axis such that  $|1 - \widehat{K}(k)| \sim O(1/k)$  as  $k \rightarrow \infty$ . These conditions are necessary for the WH method to be applicable, and they are generally met by finite ranged potential functions such as the LJ potential or any potential mimicking it, such as a square well with a hard core. The conditions mentioned are still met even if the factorization functions contain zeros in the complex plane within the strip mentioned, as long as they are off the real axis. The presence of such zeros in the factorized form requires that they fulfill the necessary asymptotic condition of the overall factorized form as discussed subsequently.

Before proceeding further, we discuss a general property of the factorization function. Since  $K(k)$ , as  $|k| \rightarrow \infty$ , must be such that

$$|1 - \widehat{K}(k)| \sim O(1/k), \quad (11.7)$$

it is possible to define  $K(r)$  for  $r > 0$  such that

$$2\pi n K(r) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk [1 - \widehat{K}(k)] \exp(-ikr). \quad (11.8)$$

The inverse of this relation is

$$\widehat{K}(k) = 1 - 2\pi n \int_{-\infty}^{\infty} dr K(r) \exp(ikr). \quad (11.9)$$

Since  $K(k)$  is regular in the strip  $-\varepsilon < \text{Im } k < \varepsilon$  ( $\varepsilon > 0$ ) and as  $|k| \rightarrow \infty$   $|\widehat{K}(k)| \rightarrow 1$ , by closing the contour in the upper half in the  $k$  plane in the case of  $r < 0$ , we find

$$K(r) = 0 \quad (r < 0). \quad (11.10)$$

This is one of the important properties of the factorization function  $K(r)$ . Because of this property  $\widehat{K}(k)$  may be written as

$$\widehat{K}(k) = 1 - 2\pi n \int_0^{\infty} dr K(r) \exp(ikr). \quad (11.11)$$

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<sup>2</sup>This is the version used by Baxter [19].

The assumption that  $M(k) := 1 - \widehat{C}(k)$  is invertible, which is implicit in (11.5), does not hold in general. This can be seen if we recall that the inverse isothermal compressibility is related to the direct correlation function since it can be written as

$$(k_B T)^{-1} \left( \frac{\partial p}{\partial n} \right)_{T,V} = 1 - \widehat{C}(0). \quad (11.12)$$

Since the inverse isothermal compressibility tends to zero as the fluid undergoes the liquid–vapor phase transition,  $M(k)$  is not invertible everywhere in the  $k$  plane. Therefore, if the critical point is denoted by  $(T_c, n_c)$ , at which point  $\left( \frac{\partial p}{\partial n} \right)_{T,V} = 0$ , then clearly it follows

$$\lim_{T \rightarrow T_c \text{ or } n \rightarrow n_c} M(0) := \lim_{T \rightarrow T_c \text{ or } n \rightarrow n_c} [1 - \widehat{C}(0)] = 0. \quad (11.13)$$

Since in the neighborhood of the critical point we may thus take

$$\left( \frac{\partial p}{\partial n} \right)_{T,V} = c \left| 1 - \frac{T}{T_c} \right|^{\delta} \left| 1 - \frac{n}{n_c} \right|^{\gamma}, \quad (11.14)$$

where  $c$  is a constant, and  $\delta$  and  $\gamma$  are constant positive exponents, it follows

$$M(0) := 1 - \widehat{C}(0) = \frac{c}{k_B T} \left| 1 - \frac{T}{T_c} \right|^{\delta} \left| 1 - \frac{n}{n_c} \right|^{\gamma}. \quad (11.15)$$

The factorization in (11.6) therefore is a rather special case. As a matter of fact, there exists a mathematical theorem [16, 17] that the denominator  $1 - \widehat{C}(k)$  of (11.5) can be factorized in the form

$$1 - \widehat{C}(k) = \widehat{K}(k) \widehat{K}(-k) \prod_i \left[ \frac{(k - k_i)^2 + \kappa_i^2}{(k - k_i)^2 + \varepsilon_i^2} \right], \quad (11.16)$$

where  $k_i$  and  $\kappa_i$  are positive real numbers locating the zeros and  $\varepsilon_i$  are such that  $\varepsilon := \max \varepsilon_i > \max \kappa_i$  for all  $i$ , that is, the zeros are all within a bounded domain of an extent  $\varepsilon$ . [See pp. 119–121, Ref. [22] for a more detailed discussion on this particular form of factorization (11.16).] It is useful to recall that regular functions in a region in complex plane are finite according to one of the properties of regular functions (see Whittaker and Watson, Modern Analysis [24]). Therefore normalizing the function suitably, it is always possible to find the factorization function fulfilling the condition  $|\widehat{K}(k)| \rightarrow 1$ . This is the reason that the denominators are inserted in the factors under the product sign. It is assumed there are a finite number of zeros. This form of factorization in (11.16) allows a possibility of introducing dynamical aspects of the system into the factorization made. This can be seen by the following reasoning.

The physical meanings of zeros  $\kappa_i$  may be sought in the zeros of the grand partition function  $\Xi$  which may be factorized in zeros in complex activity plane  $z = \Lambda^{-3} \exp(\beta\mu)$ , where  $\beta = 1/k_B T$ ,  $\mu$  is the chemical potential and  $\Lambda = h/\sqrt{2\pi m k_B T}$  ( $m$  = mass,  $h$  = Planck constant). According to the Yang–Lee theory [21] the zeros of  $\Xi$  are arranged on a circle in the complex  $z$  plane—the circle theorem that indicates there exists a maximum value of zeros. Since  $pV = k_B T \ln \Xi$  and the inverse isothermal compressibility  $\kappa_T$  is related to  $(1 - \widehat{C}(0))$ , it is reasonable to imagine a close relation between the zeros of  $\Xi$  and the zeros of the inverse isothermal compressibility of the system. Since on the one hand

$$M(0) = \widehat{K}^2(0) \prod_i \frac{\kappa_i^2}{\varepsilon_i^2}, \quad (11.17)$$

and, on the other hand, if there is only one relevant zero, then that zero can be related to, for example, liquid–vapor phase transition and hence

$$\kappa_0^2 = c \left| 1 - \frac{T}{T_c} \right|^{\delta} \left| 1 - \frac{n}{n_c} \right|^{\gamma} \quad (c = \text{constant}). \quad (11.18)$$

Furthermore, since the equation of state is given by the grand canonical partition function  $\Xi$

$$pV = k_B T \ln \Xi, \quad (11.19)$$

and  $\Xi$  is factorizable

$$\Xi = B \prod_j (z - z_j) = B \prod_i (z^2 + z_i^2), \quad (11.20)$$

it is reasonable to associate the lowest lying zero  $\kappa_0$  of  $M(0)$  with the lowest zero of  $\Xi$  as is (11.18). The second equality in (11.20) is owing to the fact that the zeros of  $\Xi$  must be in pairs of complex conjugates. Thus we now see that  $\kappa_i$  must be intimately related to the zeros of the grand canonical partition function.

### 11.1.2 Integral Equation for the Direct Correlation Function

We now assume for simplicity of discussion that there is only one pair of zeros  $\kappa_c$  of  $[1 - \widehat{C}(k)]$  on the imaginary axis within the strip of  $k$  plane. Then it is factorized in the form

$$1 - \widehat{C}(k) = \widehat{K}(k) \widehat{K}(-k) \frac{(k^2 + \kappa_c^2)}{(k^2 + \varepsilon^2)}. \quad (11.21)$$

It was shown in Ref. [22] that the OZ equation in the PY closure can be put into the pair of integral equations. Since the theory is discussed in detail in the reference cited earlier, we will only briefly review the result here. Inserting (11.21) into the Fourier transform of the OZ equation yields the equation

$$[1 + \hat{H}(k)](k^2 + k_c^2)\hat{K}(k) = [\hat{K}(-k)]^{-1}(k - i\varepsilon)(k + i\varepsilon), \quad (11.22)$$

whereas (11.21) may be cast into the form

$$(k^2 + k_c^2)[\hat{C}(k) + \hat{K}(k)\hat{K}(-k) - 1] = (\varepsilon^2 - k_c^2)[1 - \hat{C}(k)]. \quad (11.23)$$

Upon inserting (11.11) into (11.22) and taking inverse Fourier transform, we obtain for  $r > 0$

$$\left(-\frac{\partial^2}{\partial r^2} + k_c^2\right)\phi(r) = \frac{(\varepsilon^2 - \kappa_c^2)}{2\pi n}[\delta(r) - 2\pi nC(r)], \quad (11.24)$$

where

$$C(r) = \int_r^\infty dssc(r) \quad (11.25)$$

and function  $\phi(r)$  is defined by

$$\phi(r) = C(r) - K(r) + 2\pi n \int_r^\infty dt K(t)K(t - r). \quad (11.26)$$

Equation (11.24) is an inhomogeneous wave equation for an evanescent wave of correlation. Physically, it is a kind of potential of mean force in the fluid. Since

$$C(r), K(r) \rightarrow 0 \text{ as } r \rightarrow \infty,$$

it follows that

$$\phi(r) \rightarrow 0 \text{ as } r \rightarrow \infty. \quad (11.27)$$

Differentiating (11.24) with respect to  $r$  yields the differential equation

$$\left(\frac{\partial^2}{\partial r^2} - \kappa_c^2\right)\frac{\partial\phi(r)}{\partial r} = -\frac{(\varepsilon^2 - \kappa_c^2)}{2\pi n}\left[\frac{\partial}{\partial r}\delta(r) + 2\pi nrc(r)\right], \quad (11.28)$$

for which we impose the boundary condition at  $r = 0$

$$\left[\frac{d\phi(r)}{dr}\right]_{r=0} = \text{finite}. \quad (11.29)$$

Equation (11.28) will be used to determine  $\phi(r)$  in the present theory.

Differentiation of (11.26) with respect to  $r$  yields the integral equation for the direct correlation function  $c(r)$

$$rc(r) = -K'(r) + 2\pi n \int_r^\infty dt K'(t)K(t-r) - \frac{\partial \phi}{\partial r}, \quad (11.30)$$

where the prime on  $K(r)$  denotes differentiation with respect to  $r$ , the variable of the factorization function  $K(r)$ . Equation (11.30) is one of the integral equations sought in the Wiener–Hopf method. The third term on the right of (11.30) arises from the presence of zeros in  $\widehat{C}(k)$ , and it is the point of departure from the integral equation for  $rc(r)$  obtained by Baxter [19, 20] and others for hard sphere fluids. This equation indicates that for a disordered system the direct correlation function decays exponentially as  $r \rightarrow \infty$ , as will be shown, and the correlation range of this function has to do with the zero of the inverse isothermal compressibility.

### 11.1.3 Integral Equation for the Total Correlation Function

Equation (11.22) can be rearranged similarly to the case of the direct correlation function:

$$(k^2 + \kappa_c^2) \left\{ [\widehat{K}(k) - 1] + \widehat{H}(k) + \widehat{H}(k)[\widehat{K}(k) - 1] - \left[ \frac{1}{\widehat{K}(-k)} - 1 \right] \right\} = \frac{(\varepsilon^2 - \kappa_c^2)}{\widehat{K}(-k)}. \quad (11.31)$$

Upon taking the inverse Fourier transform of this equation there follows the equation for  $H(r)$

$$H(r) = \int_r^\infty ds h(s). \quad (11.32)$$

The resulting equation may be written as

$$\left( \frac{\partial^2}{\partial r^2} - k_c^2 \right) \psi(r) = \frac{(k_c^2 - \varepsilon^2)}{2\pi n} \delta(r), \quad (11.33)$$

where  $\psi(r)$  is defined by

$$\psi(r) = H(r) - K(r) - 2\pi n \int_0^\infty dt K(t) H(|r-t|). \quad (11.34)$$

The boundary condition on  $\psi(r)$  at  $r = \infty$  and at  $r = 0$  are

$$\psi(\infty) = 0 \quad \psi'(0) = 0. \quad (11.35)$$

To obtain this result we have made use of the following

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} dk \exp(-ikr) [1/\widehat{K}(-k) - 1] = 0, \quad (11.36)$$

where the integral vanishes since  $\widehat{K}(-k)$  is regular and bounded in the strip  $-\varepsilon < \text{Im } k < \varepsilon$ , tending to unity as  $|k| \rightarrow \infty$ .

Equation (11.33) is solved with the help of Green's function defined by the differential equation [17]

$$\left( \frac{\partial^2}{\partial r^2} - k_c^2 \right) G(r, r') = -4\pi \delta(r - r'). \quad (11.37)$$

The Green's function is easily obtained by the method of Fourier transform and contour integration:

$$G(r, r') = \frac{\pi}{\kappa_c} \exp[-\kappa_c|r - r'|]. \quad (11.38)$$

Making use of the Green function method, the solution for (11.37) can be readily obtained:

$$\psi(r) = \left[ \psi_0 - \frac{(\kappa_c^2 - \varepsilon^2)}{8\pi n \kappa_c} \right] \exp(-\kappa_c r). \quad (11.39)$$

The boundary condition at  $r = 0$  implies that

$$\psi_0 - \frac{(\kappa_c^2 - \varepsilon^2)}{8\pi n \kappa_c} = 0. \quad (11.40)$$

Therefore  $\psi(r) = 0$  everywhere in  $r$ , and the integral equation (11.34) turns out to be simply the same equation as that for the case of the zeros of the isothermal compressibility being absent:

$$H(r) = K(r) + 2\pi n \int_0^{\infty} dt K(t) H(|r - t|). \quad (11.41)$$

This is the other of the integral equations in the Wiener–Hopf method; it is coupled to (11.26) for  $C(r)$ . Differentiating (11.41) with respect to  $r$  yields the equation for the total correlation function

$$rh(r) = -K'(r) - 2\pi n \int_0^{\infty} dt (t - r) K(t) h(|r - t|). \quad (11.42)$$

This equation is coupled to (11.30).

Equations (11.28), (11.30), and (11.42) are collected below for summary:

$$rh(r) = -K'(r) - 2\pi n \int_0^\infty dt (t-r) K(t) h(|r-t|), \quad (11.43)$$

$$rc(r) = -K'(r) + 2\pi n \int_r^\infty dt K'(t) K(t-r) - \frac{\partial \phi}{\partial r}, \quad (11.44)$$

$$\begin{aligned} \left( \frac{\partial^2}{\partial r^2} - \kappa_c^2 \right) \frac{\partial \phi(r)}{\partial r} &= -\frac{(\varepsilon^2 - \kappa_c^2)}{2\pi n} \frac{\partial}{\partial r} [\delta(r) - 2\pi n K(r)] \\ &\quad - 2\pi n (\varepsilon^2 - \kappa_c^2) \int_r^\infty dt K'(t) K(t-r), \end{aligned} \quad (11.45)$$

These equations are equivalent to the OZ equation. However, there are three equations for four functions  $h(r)$ ,  $c(r)$ ,  $K(r)$ , and  $\phi(r)$  to be determined. For this reason a closure relation must be imposed before the solution procedure is implemented for them. In this connection, recall that since Baxter [19] used the Percus–Yevick closure for  $c(r)$  from the outset, he had the equations for  $h(r)$  and  $K(r)$  to solve.

### 11.1.4 Thermodynamically Consistent Closure

We have two forms for the statistical mechanics formulas for the equation of state, one the virial and the other the compressibility form in the OZ theory approach. The virial form involves the total correlation function  $h(r)$  whereas the compressibility form is given in terms of the direct correlation function  $c(r)$ . As long as the OZ equation is exactly used, the two forms should give the identical result, but the OZ equation requires a closure relation to solve it unless either one of the correlation functions is exactly obtained by some other method. However, the partition function is not possible to calculate exactly in general. For this reason, to make progress in the integral equation theory a closure is usually assumed for the relation between the total and direct correlation functions. However, if the OZ equation is solved using an assumed closure, the two forms of the equation of state are liable to predict different numerical values and formal structures; in other words, they are numerically inconsistent. This is called the thermodynamic consistency problem.

There are a number of studies made in the literature [14], which are approximate in nature because the closure relation used turns out to be approximate in the end. We approach this thermodynamic consistency problem from a different viewpoint. By ensuring the thermodynamic consistency by equating the virial and compressibility equations of state, we derive an integral relation between the direct and total correlation function. This integral relation provides the desired fourth equation. This integral relation is found coupled to the OZ equation. By continuity, this integral relation gives rise to an equivalent differential equation within an arbitrary function  $q(r)$  which will be called the gauge function. The relation is

$$c(r) = \frac{1}{6nr^2} \frac{\partial}{\partial n} \left[ n^2 f(r) \frac{\partial}{\partial r} r^3 y(r, n) \right] + \frac{1}{nr^2} \frac{\partial q(r, n)}{\partial r}, \quad (11.46)$$

where  $f(r)$  is the Mayer function

$$f(r) = \exp[-\beta u(r)] - 1, \quad (11.47)$$

$y(r, n)$  is the cavity function defined by

$$y(r, n) = \exp[\beta u(r)] g(r, n) = \exp[\beta u(r)] [h(r, n) + 1] \quad (11.48)$$

with  $u(r)$  denoting the potential energy, and  $g(r, n)$  the pair correlation function. The gauge function  $q(r, n)$ , which is an arbitrary function of  $r$  and  $n$ , is such that

$$\int_0^\infty dr \frac{\partial q(r, n)}{\partial r} = 0. \quad (11.49)$$

This condition is fulfilled if there hold the boundary conditions

$$q(r, n) = 0 \text{ at } r = 0 \text{ and } \infty. \quad (11.50)$$

Inasmuch as the gauge function is arbitrary as long as it satisfies the boundary conditions, it is reasonable to take it equal to zero everywhere<sup>3</sup> in  $r \in [0, \infty]$ . Then (11.46) becomes

$$c(r) = \frac{1}{6nr^2} \frac{\partial}{\partial n} \left[ n^2 f(r) \frac{\partial}{\partial r} r^3 y(r, n) \right]. \quad (11.51)$$

This is the simplest possible form for the thermodynamic consistency, which we take in this work.

To implement a solution procedure for the set of integral equations (11.43)–(11.45) with (11.51) it is convenient to cast them in dimensionless reduced variables, so that we can work with dimensionless equations. Thus if we define the dimensionless quantities

$$\begin{aligned} x &= r/\sigma, & \eta &= \frac{\pi}{6} \sigma^3 \rho, & \xi &= \kappa_c \sigma, & \alpha &= \varepsilon \sigma, \\ p^* &= p v_0 / \epsilon, & T^* &= k_B T / \epsilon, & K^* &= K \sigma^{-2}, & \varphi &= \phi \sigma^{-2}, \end{aligned}$$

where  $\beta^* = 1/T^*$ ,  $v_0 = \pi \sigma^3 / 6$  is the volume of the hard core,  $\epsilon$  is the well depth (or interaction strength) of the potential (e.g., the Lennard-Jones potential), then the reduced integral equations in the WH method are

$$x h(x) = -K^{**}(x) - 12\eta \int_0^\infty dt (t - x) K^*(t) h(|x - t|), \quad (11.52)$$

---

<sup>3</sup>This gauge may be called the thermodynamic consistency gauge.

$$\frac{f(x)}{6\eta x} \frac{\partial^2}{\partial x \partial \eta} \eta^2 x^3 y(x, \eta) = -K^{*\prime}(x) + 12\eta \int_x^\infty dt K^{*\prime}(t) K(t-x) - \Psi(x), \quad (11.53)$$

$$\left( \frac{\partial^2}{\partial x^2} - \xi^2 \right) \Psi(x) = -\frac{(\alpha^2 - \xi^2)}{12\eta} R(x), \quad (11.54)$$

where

$$\Psi(x) = \frac{\partial \varphi(x)}{\partial x}, \quad (11.55)$$

$$R(x) = \frac{\partial}{\partial x} \delta(x) - 12\eta K^{*\prime}(x) + 144\eta^2 \int_x^\infty dt K^{*\prime}(t) K^*(t-x). \quad (11.56)$$

The set (11.52)–(11.56) is the main formal result of the present integral equation theory of correlation functions. Since  $h(x) = f(x)y(x) - 1$ , the set in question is now well posed. It should be emphasized that these integro-differential equations are valid for any finite ranged potential model in the case of a single pair of zeros for  $M(k)$ .

### 11.1.5 Function $\Psi(x)$

Inspection of (11.54) and (11.56) indicates that since  $\varphi(x)$  is indirectly coupled to  $h(x)$  through  $K^*(x)$  the three coupled equations (11.52)–(11.54) can be reduced to two coupled equations for  $h(x)$  or  $y(x)$  and  $K^*(x)$ , if (11.56) is formally solved. The formal solution of (11.56) is given by

$$\Psi(x) = c_1 e^{-\xi x} + \frac{(\alpha^2 - \xi^2)}{24\eta\alpha} \left[ e^{-\xi x} \int_0^x dt R(t) e^{\xi t} + e^{\xi x} \int_x^\infty dt R(t) e^{-\xi t} \right], \quad (11.57)$$

where  $c_1$  is an integration constant. This solution suggests that  $\Psi(x)$  is well behaved with respect to  $(\alpha^2 - \xi^2)$  and regular in  $(\alpha^2 - \xi^2)$ . With this result for  $\Psi(x)$  together with (11.56), the set (11.52)–(11.55) is reduced to a pair of integro-differential equations for  $y(x)$  and  $K^*(x)$ :

$$xh(x) = -K^{*\prime}(x) - 12\eta \int_0^\infty dt (t-x) K^*(t) h(|x-t|), \quad (11.58)$$

$$\begin{aligned} \frac{f(x)}{6\eta x} \frac{\partial^2}{\partial x \partial \eta} \eta^2 x^3 y(x, \eta) &= -K^{*\prime}(x) + 12\eta \int_x^\infty dt K^{*\prime}(t) K(t-x) \\ &\quad - c_1 e^{-\xi x} - \frac{(\alpha^2 - \xi^2)}{24\eta\alpha} \int_0^x dt R(t) e^{\xi(t-x)} \end{aligned}$$

$$-\frac{(\alpha^2 - \xi^2)}{24\eta\alpha} \int_x^\infty dt R(t) e^{-\xi(t-x)} \quad (11.59)$$

with  $R(x)$  given by (11.56). In this connection, recall (11.48) for the relation between  $h(x)$  and  $y(x)$ . Here the integration constant  $c_1$  can be determined by using the boundary condition on  $\Psi(x)$  or  $\varphi(x)$ .

To gain the idea of how to determine the constant  $c_1$  we take the following procedure for a hard sphere fluid as an example. In the Wiener-Hopf method  $\pm\alpha$  determine the width of the strip in complex  $k$  plane, but the width is arbitrary except that  $-\alpha < \xi < \alpha$ , since  $\alpha$  can be as close to  $\max \xi_i$  as can be. Therefore having obtained the general solution which evidently is regular with respect to  $(\alpha^2 - \xi^2)$  and well behaved, it now is appropriate to take the limit  $\alpha \rightarrow \xi + 0$  to make the determination of  $c_1$  as simple as possible. Then the solution in the limit is found to be

$$\Psi(x) = c_1 e^{-\xi x}. \quad (11.60)$$

This solution now evidently suggests that  $\varphi(x)$  is a correlation function decaying exponentially and  $\xi$  has to do with the inverse correlation range. Since we may assume that the particles have a hard repulsive core although the attractive tail is smooth and continuous, so that

$$\begin{aligned} u(x) &= \infty \quad \text{for } x < 1 \\ &= u_a(x) \quad \text{for } x > 1, \end{aligned}$$

then the total correlation function  $h(x)$  must be such that

$$\begin{aligned} h(x) &= -1 \quad \text{for } x < 1 \\ &= h_2(x) \neq 0 \quad \text{for } x > 1, \end{aligned}$$

where  $h_2(x)$  is to be determined in the range  $x > 1$  by the integro-differential equations (11.52)–(11.53). This property of  $h(x)$  suggests that  $\varphi(x)$  should be taken equal to zero for  $x < 1$  so as to make it consistent with the total correlation function for the hard core part of space. Since the behavior of  $\varphi(x)$  must be consistent with  $h(x)$  and its properties are also closely associated with those of  $K(x)$  for  $x > 1$  as will be seen later, it is appropriate to look for  $\varphi(x)$  such that

$$\varphi(x) = 0 \quad \text{for } x < 1, \quad (11.61)$$

$$\neq 0 \quad \text{for } x > 1. \quad (11.62)$$

This means that it is necessary to examine (11.54) in the range of  $1 < x < \infty$  only. It is emphasized that (11.61) is only for hard sphere fluids or fluids with a hard core.

Since  $\Psi(1)$  must be finite at  $x = 1$  and  $\Psi(\infty) = 0$  by the boundary conditions, it follows from the solution (11.60)

$$\varphi(x) - \varphi(1) = \int_1^x dx \Psi(x) = \xi^{-1} e^{-\xi} [1 - e^{-\xi(x-1)}] c_1,$$

and we find

$$\varphi(x) = \varphi(1) + \xi^{-1} e^{-\xi} [1 - e^{-(x-1)\xi}] c_1.$$

But since

$$\varphi(\infty) = 0,$$

it follows that

$$c_1 = -\xi e^\xi \varphi(1) \quad (11.63)$$

and consequently

$$\varphi(x) = \varphi(1) e^{-\xi(x-1)} \quad (x > 1), \quad (11.64)$$

$$\Psi(x) = -\xi \varphi(1) e^{-\xi x}. \quad (11.65)$$

Thus we see that in the case of fluids with a hard core the value of  $\varphi(1)$  would determine  $c_1$ , and  $\varphi(1)$  is determined from the knowledge of the direct correlation function and  $K(x)$  according to (11.26). This value of  $c_1$  should remain applicable even if the limit  $\alpha \rightarrow \xi + 0$  were not taken. This procedure can be extended to the general case to determine the integration constant.

The result presented for  $\varphi(x)$ , in fact, turns out to be independent of the potential energy models for fluids except that it is given only in the range of  $1 < x < \infty$  in the case of fluids with a hard core. For non-hard sphere potentials the range is  $0 \leq x < \infty$ , and  $\varphi(x)$  is determined from Eq. (11.60) in the whole range of  $x$  irrespective of the potential models. Consideration made for  $\varphi(x)$  and  $\Psi(x)$  up to this point implies that  $\varphi(x)$  is evidently a potential of mean force describing correlations of particles in the fluid. It is therefore a mean field in the fluid, but not an additional potential tail for hard spheres. Clearly, even hard spheres should create such a mean field if a multitude of them are confined in proximity to each other in a volume, and here lies one of obvious advantages of the Wiener–Hopf factorization (11.21) taken in the present theory.

With the so-determined  $c_1$  inserted into (11.59) two coupled equations (11.58) and (11.59) can be solved for  $y(x)$  and  $K(x)$ . They can be solved by means of a numerical solution method. Either a method of Fourier transforms or a method of Laguerre transforms in the case of a fluid with a hard core can be used. In the case of the latter method see Ref. [22], Sect. 6.8.6 for a description of the method.

### 11.1.6 Equation for Inverse Correlation Length

The parameter  $c$  appearing in (11.15) for  $\kappa_c$  may be fixed by using the relation

$$\left( \frac{\partial \beta^* p^*}{\partial \eta} \right)_T = 1 - \widehat{C}(0). \quad (11.66)$$

Since  $\widehat{K}(0)$  is related to the zeroth moment of  $K^*(x)$

$$\widehat{K}(0) = 1 - 12\eta \int_0^\infty dx K^*(x) := m_0, \quad (11.67)$$

we may write (11.66) as

$$m_0^2 = \left( \frac{\partial \beta^* p^*}{\partial \eta} \right)_T. \quad (11.68)$$

Furthermore, since the Fourier transform of the OZ equation at  $k = 0$  may be also written as

$$\left( \frac{\partial \beta^* p^*}{\partial \eta} \right)_T \left[ 1 + 24\eta \int_0^\infty dx x^2 h(x) \right] = 1, \quad (11.69)$$

it follows that

$$m_0^2 \left[ 1 + 24\eta \int_0^\infty dx x^2 h(x) \right] = 1. \quad (11.70)$$

This equation puts a constraint on the parameter in the factorized functions, for example, in (11.14).

This completes the framework of the solution procedure under the particular factorization (11.21) for the direct correlation function. Equations (11.58) and (11.59) may be solved numerically. They have been solved for the case of a hard sphere fluid, in which case a perturbation theory can be developed. This subject is discussed in Sects. 6.8.4 and 6.8.5, pp. 133–138, Ref. [22]. The results for the equation of state and the pair correlation function obtained are quite accurate compared with Monte Carlo simulation [25, 26] results. It should be noted that in the present theory there is no distinction between the virial and compressibility equations of state because of the thermodynamic consistency ensured in the formulation of the theory.

## 11.2 Pair Correlation Function in the Subcritical Regime

In Sect. 11.1 of this chapter we have dealt with the correlation functions for a simple fluid with the possibility of being in the neighborhood of the liquid–vapor critical point. This possibility gives rise to a question of what the correlation functions might look like if the state of the fluid is in the subcritical regime. Specifically, we would

like to investigate the behavior of the total correlation function in the density plane when there are two phases coexisting at a given temperature and chemical potential. We then derive an interpolation formula for the total correlation function in the two-phase region.

For this purpose it is useful to recast the grand canonical probability in a more suitable form. First let us define the work function  $A$  by the statistical mechanical formula

$$A(N, V, \beta) = -k_B T \ln Q(N, V, \beta) = -k_B T \ln \left[ \frac{Z_N}{N! \Lambda^{3N}} \right] \quad (11.71)$$

and

$$\overline{G}(N, V, \beta) = \beta G = \beta(A + pV). \quad (11.72)$$

It must be kept in mind that  $pV$  here is not only a function of  $N$ , but another way of writing the normalization factor, since it is related to the grand partition function [27, 28]

$$\Xi = \exp(\beta pV).$$

Then, with the definition

$$\phi(N) = \overline{G}(N, V, \beta) - N\overline{\mu}, \quad (11.73)$$

where  $\overline{\mu} = \beta\mu$ , the grand canonical probability can be written as

$$P_N = \exp[-\phi(N)]. \quad (11.74)$$

Similarly, with the definition

$$\varphi(N) = \beta A - N\overline{\mu} \quad (11.75)$$

the grand partition function can be written in the form

$$\Xi = \sum_{N \geq 0} \exp[-\varphi(N)]. \quad (11.76)$$

If the sum over  $N$  is replaced with the integral over  $N$  in the thermodynamic limit,  $P_N$  is normalized as follows:

$$\int_0^\infty dN \exp[-\phi(N)] = 1 \quad (11.77)$$

and the grand partition function may be written in the form

$$\Xi = \int_0^\infty dN \exp[-\varphi(N)]. \quad (11.78)$$

In this notation the reduced distribution function of  $n$  particles is given by

$$\rho^{(n)}(\mathbf{r}^{(n)}) = \sum_{N \geq 0} \exp[-\phi(N)] \rho_N^{(n)}(\mathbf{r}^{(n)}), \quad (11.79)$$

or

$$\rho^{(n)}(\mathbf{r}^{(n)}) = \int_0^\infty dN \exp[-\phi(N)] \rho_N^{(n)}(\mathbf{r}^{(n)}). \quad (11.80)$$

In a single phase regime sufficiently removed from the critical point there must exist a single stationary phase—that is, a minimum—for the exponent of the integral. Let the value of  $N$  where  $\phi(N)$  is minimum be  $N^*$ . Expanding  $\phi(N)$  around  $N^*$  we obtain

$$\phi(N) = \phi(N^*) + \frac{1}{2}\phi^{(2)}(N - N^*)^2 + \dots, \quad (11.81)$$

where  $\phi^{(2)} = (\partial^2 \phi / \partial N^2)_{N=N^*}$ . Since

$$\phi^{(1)} = \beta \left[ \left( \frac{\partial G}{\partial N} \right)_{V,T} - \mu \right]_{N=N^*} = \beta \left( \frac{\partial A}{\partial N^*} \right)_{V,T} - \mu = 0,$$

the parameter  $\mu$  is identified as

$$\mu = \left( \frac{\partial A}{\partial N^*} \right)_{V,T},$$

and hence

$$\phi(N^*) = \overline{G}(N^*, V, \beta) - N^* \overline{\mu} = 0,$$

that is,  $G(N^*, V, \beta)$  is the free energy of  $N^*$  particles. The series (11.81) is truncated at the second order. Then, since the truncation is an approximation, it is necessary to introduce a correction, and it can be done by inserting a constant so that the distribution is normalized. Thus we find

$$\exp[-\phi(N)] = \sqrt{\frac{\phi^{(2)}}{2\pi}} \exp \left[ -\frac{1}{2}\phi^{(2)}(N - N^*)^2 \right]. \quad (11.82)$$

Since, the mean value  $\overline{N}$  of  $N$  is equal to  $N^*$  in this approximation,

$$\phi^{(2)} = \left( \frac{\partial \overline{\mu}}{\partial N^*} \right)_{T,V} = \langle (N - \overline{N})^2 \rangle_{av}^{-1}. \quad (11.83)$$

In the limit of large  $N^*$ ,  $\phi^{(2)}$  tends to be very large because it is inversely proportional to fluctuations in  $N$ , and the right hand side of (11.82) and hence  $P_N$  may be approximated by a delta function:

$$\begin{aligned}
P_N &= \exp[-\phi(N)] \\
&= \sqrt{\frac{\phi^{(2)}}{2\pi}} \exp\left[-\frac{1}{2}\phi^{(2)}(N - N^*)^2\right] \\
&= \delta(N - N^*). \tag{11.84}
\end{aligned}$$

This is what is called the maximum term approximation for  $P_N$  where  $N^* = \bar{N}$ . By using this approximate Gaussian  $P_N$ , we may compute reduced distribution functions in the case of a single phase fluid:

$$\rho^{(n)}(\mathbf{r}^{(n)}) = \sqrt{\frac{\phi^{(2)}}{2\pi}} \int_{-\infty}^{\infty} dx \exp\left[-\frac{1}{2}\phi^{(2)}x^2\right] \rho_{N^*+x}^{(n)}(\mathbf{r}^{(n)}), \tag{11.85}$$

which in the limit of  $\phi^{(2)} \rightarrow \infty$  yields

$$\rho^{(n)}(\mathbf{r}^{(n)}) = \rho_{N^*}^{(n)}(\mathbf{r}^{(n)}) = \rho_{\bar{N}}^{(n)}(\mathbf{r}^{(n)}). \tag{11.86}$$

This means that the grand canonical reduced distribution function becomes identical with the canonical reduced distribution function in the limit of vanishing density fluctuations.

We now consider the case of two stationary phase points where  $\phi$  has a minimum at two different values of  $N$ , say,  $N_v^*$  and  $N_l^*$ . The states of these minima will be called phases. Therefore the grand canonical probability  $P_N$  can be approximated by a superposition of two Gaussian functions representative of the two phases:

$$\begin{aligned}
P_N &= \exp[-\phi(N)] \\
&= \frac{1}{1+R} \sqrt{\frac{\phi_v^{(2)}}{2\pi}} \exp\left[-\frac{1}{2}\phi_v^{(2)}(N - N_v^*)^2\right] \\
&\quad + \frac{R}{1+R} \sqrt{\frac{\phi_l^{(2)}}{2\pi}} \exp\left[-\frac{1}{2}\phi_l^{(2)}(N - N_l^*)^2\right] \tag{11.87}
\end{aligned}$$

where

$$\phi_k^{(2)} = \left(\frac{\partial^2 \phi}{\partial N^2}\right)_{N=N_k^*} = \left\langle (N - \bar{N})^2 \right\rangle_{avk}^{-1} \quad (k = v, l), \tag{11.88}$$

$$R = \sqrt{\frac{\phi_v^{(2)}}{\phi_l^{(2)}}} = \frac{\rho_l}{\rho_v} \sqrt{\frac{\kappa_l}{\kappa_v}}. \tag{11.89}$$

In (11.89)  $\kappa_l$  and  $\kappa_v$  are the compressibility coefficients [29] of liquid and vapor phases, respectively. For this, recall the fact that the inverse density fluctuation  $\langle (N - \bar{N})^2 \rangle_{avk}^{-1}$  is proportional to isothermal compressibility

$$\langle (N - \bar{N})^2 \rangle_{avk}^{-1} = \bar{N} \rho_k k_B T \kappa_k, \quad (11.90)$$

because

$$(\partial \mu / \partial \bar{N})_{V,T} V = - \left( V^3 / \bar{N}^2 \right) (\partial p / \partial V)_{N,T}. \quad (11.91)$$

If the system contains  $M$  particles in total in volume  $V$  and if the most probable values of  $N$  in the two phases are  $N_v^*$  and  $N_l^*$  respectively, there holds the relation

$$M = N_v^* + N_l^*.$$

If the maxima of  $P_N$  are well separated, then  $N_v^* = \bar{N}_v$  and  $N_l^* = \bar{N}_l$  where  $\bar{N}_v$  and  $\bar{N}_l$  are the mean values, and we have

$$M = \bar{N}_v + \bar{N}_l.$$

In the case of vanishing fluctuations in both phases we find  $R \rightarrow 1$  and the Gaussian functions in (11.87) become delta function. Hence we have

$$P_N = \frac{1}{2} \delta(N - N_v^*) + \frac{1}{2} \delta(N - N_l^*). \quad (11.92)$$

Within the validity of the approximation (11.92) we find the grand canonical reduced distribution function of  $n$  particles in the form

$$\rho^{(n)}(\mathbf{r}^{(n)}) = \frac{1}{2} \rho_{N_v^*}^{(n)}(\mathbf{r}^{(n)}) + \frac{1}{2} \rho_{N_l^*}^{(n)}. \quad (11.93)$$

This means that in the two phase region the grand canonical pair correlation function may be taken as an arithmetic mean of two canonical pair correlations for the two different phases:

$$g^{(2)}(\mathbf{r}^{(2)}) = \frac{1}{2} g_{N_v^*}^{(2)}(\mathbf{r}^{(2)}) + \frac{1}{2} g_{N_l^*}^{(2)}(\mathbf{r}^{(2)}). \quad (11.94)$$

Restoring the factor  $R$  for more general cases we may approximate the pair correlation function  $g^{(2)}(\mathbf{r}^{(2)})$  in the form

$$g^{(2)}(\mathbf{r}^{(2)}) = \frac{\rho_v \sqrt{\kappa_v}}{\rho_v \sqrt{\kappa_v} + \rho_l \sqrt{\kappa_l}} g_{N_v^*}^{(2)}(\mathbf{r}^{(2)}) + \frac{\rho_l \sqrt{\kappa_l}}{\rho_v \sqrt{\kappa_v} + \rho_l \sqrt{\kappa_l}} g_{N_l^*}^{(2)}(\mathbf{r}^{(2)}), \quad (11.95)$$

provided that

$$\frac{\rho_N^{(1)}(\mathbf{r}_1)\rho_N^{(1)}(\mathbf{r}_2)}{\rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)} \simeq 1. \quad (11.96)$$

This result for  $g^{(2)}(\mathbf{r}^{(2)})$  provides a way to interpolate the branches of pair correlation functions in the subcritical regime of a two-phase system.

We now examine the grand partition function for the cases considered for the reduced distribution function. Corresponding to the case of a single maximum in  $P_N$  we find

$$\Xi = \exp[-\varphi(N^*)] = \exp[\beta N^* \mu - \beta A(N^*, V, T)], \quad (11.97)$$

which means

$$N^* \mu = pV + A(N^*, V, T) \quad (11.98)$$

and

$$A(N^*, V, T) = -k_B T \ln\left(\frac{Z_{N^*}}{N^*! \Lambda^{3N^*}}\right). \quad (11.99)$$

In the case of two maxima, armed with formula (11.95) for  $g^{(2)}$  we can put  $\Xi$  in the following form. Since we have

$$\Xi = \exp\left[\overline{N} - \frac{\beta}{6} \int d\mathbf{r}_1 \int d\mathbf{r}_2 r_{12} u'(\mathbf{r}_{12}) \rho^{(2)}(\mathbf{r}^{(2)})\right], \quad (11.100)$$

on substitution of formula (11.95) we find

$$\begin{aligned} \Xi &= \exp(\overline{N}) \exp\left[-\frac{\beta \rho_v^2}{6} R_v \int d\mathbf{r}_1 \int d\mathbf{r}_2 r_{12} u'(\mathbf{r}_{12}) g_v^{(2)}(\mathbf{r}^{(2)})\right] \\ &\quad \times \exp\left[-\frac{\beta \rho_l^2}{6} R_l \int d\mathbf{r}_1 \int d\mathbf{r}_2 r_{12} u'(\mathbf{r}_{12}) g_l^{(2)}(\mathbf{r}^{(2)})\right], \end{aligned} \quad (11.101)$$

where

$$R_v = \frac{\rho_v \sqrt{\kappa_v}}{\rho_v \sqrt{\kappa_v} + \rho_l \sqrt{\kappa_l}}, \quad R_l = \frac{\rho_l \sqrt{\kappa_l}}{\rho_v \sqrt{\kappa_v} + \rho_l \sqrt{\kappa_l}}.$$

Since at equilibrium the pressures are equal in the two phases the expression for  $\Xi$  in (11.101) implies that

$$\overline{N} = R_v \overline{N}_v + R_l \overline{N}_l, \quad (11.102)$$

where  $\overline{N}_v = N_v^*$  and  $\overline{N}_l = N_l^*$  are such that

$$A(N_a^*, V, T) = -k_B T \ln\left(\frac{Z_{N_a^*}}{N_a^*! \Lambda^{3N_a^*}}\right) \quad (a = v, l). \quad (11.103)$$

Equation (11.102) is a generalized formula of the rectilinear law at the critical point to which it reduces:

$$\rho = R_v \rho_v + R_l \rho_l. \quad (11.104)$$

Since at the critical point  $R_v = R_l = 1/2$  because  $\kappa_v, \kappa_l \rightarrow \infty$ , this formula becomes the rectilinear law [29] for density:

$$\rho_c = \frac{1}{2}(\rho_v + \rho_l), \quad (11.105)$$

where  $\rho_c$  is the critical density. The temperature dependence of the combination rule (11.104) can be studied if pair correlation functions calculated in the previous section of this Chapter are made use of.

### 11.3 Concluding Remarks

As a concluding remark, it seems worthwhile to give a summarizing remark on the method described above. By applying the Wiener–Hopf factorization theorem to the OZ equation for fluids of interacting particles that admit phase transitions, we have developed a method to calculate pair correlation functions which not only are thermodynamically consistent, but also capable of good numerical accuracy comparable to numerical simulation results as demonstrated in the examples shown in Ref. [22]. Moreover, the factorization method used should be potentially capable of describing critical behavior of such fluids. It is believed that here lies the intriguing feature of the Wiener–Hopf factorization method, which displays a departure from the conventional methods employed in the integral equation theory for the pair correlation functions.

The topic discussed in Sect. 11.1.2 on the total pair correlation function in the subcritical regime would give a useful way to summarize, for example, computer simulation results on subcritical pair correlation functions of fluids. It also provides an interpolation formula for subcritical pair correlation functions near the liquid-vapor critical point.

Finally, we would like to add the following remark, which concerns the correlation functions of nonsimple fluids. Since the present work would not require such correlation functions, discussions on them are excluded here. Nevertheless, it seems appropriate to conclude the discussion on correlation functions by briefly making remarks on the lines of approach to calculating correlation functions for nonsimple fluids.

Unlike the Ornstein–Zernike equation and the Wiener–Hopf method described in the first section of this chapter, the correlation functions for nonsimple fluids require theories much more complicated in mathematical structures and demanding much more elaborate mathematical treatments. There are a number of articles dealing with the questions on correlation functions of polyatomic fluids. They deal with integral

equations for correlation functions in one form or another. A notable approach is the reference interaction site model (RISM) [30], which makes use of integral equations for correlation functions of rigid molecules. The method is basically a modification of the Ornstein–Zernike equation. The approach yields reasonably accurate correlation functions. Another approach [31] reported in the literature takes the Kirkwood hierarchy of integral equations for correlation functions, which is closed with closure relations taking the triple correlation functions into consideration and thereby explicitly taking into account internal pair correlation functions in the solution procedure. This manner of closure and the resulting coupled integral equations for correlation functions produces accuracy as comparable to or better than the RISM integral equations. This approach has been successfully applied to study thermodynamics and structures of polymeric liquids [32, 33].

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# Appendix A

## List of Symbols (Volume 1)

The mathematical symbols appearing infrequently or only in one section or a few pages are not included in this list. Such symbols are generally defined locally. The location of a symbol is given when it occurs for the first time either by the equation number or the page number or redefined in a slightly different context or equation.

### Italic and Roman Symbols

$A, \mathcal{A}$	Helmholtz free energy	p. 47, 147
$A_{\text{eq}}$	Equil. Helmholtz energy	p. 267
$\mathbf{C}_a$	Peculiar velocity of species $a$	p. 66
$\mathbf{C}_{ja}$	Peculiar velocity of $j \in$ species $\alpha$	p. 218, 325, 349
$\mathbf{d}_a$	Thermody. force for diffusion	p. 49, 118, 197, 377, 472, 473
$\mathbf{d}_a^*$	Red. diffu. thermody. force of $a$	p. 491
$D$	Einstein diffusion coefficient	p. 312
$D_{ab}$	Non-Fickian diff. coefficient	p. 205, 485
$D_{ab}^0$	Diffusion coefficient of $a$ and $b$	p. 202
$D_{ab}^{(dh)}$	Nonlin. diffusive heat coeff.	p. 485
$D_{ab}^{(td)}$	Nonl. thermal diffusion coeff.	p. 485
$\mathbb{D}$	Eq. (6.202)	p. 263, 271
$\mathbb{D}_{\text{rB}}$	Eq. (6.20)	p. 264
$E$	Internal energy	p. 22, 25, 77
$E_t$	Total energy	p. 324
$\mathcal{E}$	Internal energy density	p. 25, 82, 188, 236, 350
$\mathcal{E}_a^*$	Reduced internal energy of $a$	p. 473
$f_a$	Nonequil. distribution function	p. 89, 110, 123, 127
$f_a^c$	Nonequil. canon. distr. f. of $a$	p. 90, 93, 110, 123, 127, 130, 131
$f_a, f_a^{(1)}$	Singlet distr. function	p. 63, 162
$f^{(N)}$	$N$ particle distr. function	p. 139, 150, 221

$\overline{f}^{(1)}, \overline{f}^{(N)}$	Time-coarse-grained distrib. function	p. 163, 170, 222, 225, 232, 259, 301, 315
$\overline{f}_c^{(N)}$	Nonequil. grand canon. form	p. 282, 302, 388, 423
$f^{(N)}(x_1^{(N)}, t)$	Red. dist. f. of $N$ -particle petit ensemble	p. 327
$\overline{f}^{(N)}(x_1^{(N)}, t)$	Time-coarse-grained $f^{(N)}$	p. 328
$f_{\text{eq}}^{(N)}, f_{\text{eq}}$	Equilibrium distr. function	p. 151, 153, 266, 336
$f_a^{(N)}$	Equilibrium distr. function	p. 74
$\overline{f}^{(N)}$	Time-coarse-grained distr. function	p. 265, 266
$F_s(x^{(s)}, t)$	$s$ -particle red. distr. function	p. 161
$F^{(N)}$	Distribution function, $N$ particle	p. 63, 161
$\overline{F}_{\text{eq}}^{(N)}$	Equil. time coarse-grained distribution function, $F_{\text{eq}}^{(N)}$	p. 172, 184, 266
$\mathbb{F}^{(N)}$	Grand Ensemble distr. function	p. 219, 327
$\overline{\mathbb{F}}^{(N)}$	Time-coarse-grained ensemble distr. function	p. 225, 327
$\overline{F}^{(N)}$	Time coarse grained distribution function	p. 165, 170, 192
$\widehat{\mathbf{F}}$	Total external force density	p. 25
$\mathbf{F}_{12}$	Intermol. force of particles	p. 162, 173, 217
$\widehat{\mathbf{F}}_a, \mathbf{F}_a$	Ext. force density, force on a g factor (inverse collision time)	p. 25, 467, 51, 111, 191
$g$	Nonequil. spatial distr. func.	p. 240
$g^{(N)}(\mathbf{r}^{(N)}, t)$	Coeff. to generalized potentials	p. 48, 100, 116, 281, 400
$g_{ab}^{(sq)}, g_a^{(q)}$	Relative speed of particles $a$ and $b$	p. 63, 111
$g_{ab}$	Eq. (7.424)	p. 423
$G_{ja}^{(N)}$	Nonequil. Gibbs energy, density	p. 47, 99
$G, \mathcal{G}$	Planck constant, $\hbar = h/2\pi$	p. 138
$h, \hbar$	Moment of $s$ particle velocity	p. 67
$h_a^{(s)}$	Mol. moment of $a$ and order $q$	p. 84, 106, 181, 243, 247, 252, 254, 354-364
$h_a^{(q)}, \bar{h}_a^{(q)}$	Hamiltonian of $j \in$ species $\alpha$	p. 218, 236, 268, 270, 336
$H_{ja}, H'_{ja}$	Orthog. tensor Hermite polynom.	p. 127, 128, 130
$\mathcal{H}^{(k)}(\omega_a)$	Thermodynamic Hamiltonian	p. 389
$\mathcal{H}_{ja}^{(N)}$	Enthalpy density	p. 47, 99
$\mathcal{H}$	Inverse temperature	p. 123, 302
$I^t$	fluctuation of $\bar{I} = I/T$	p. 302, 425
$\delta\bar{I}$	Diffusion flux of species $a$	p. 25, 81, 84, 118, 202, 205, 357, 466
$J_a := \widehat{\mathbf{J}}_a$	Calortropy flux	p. 43, 55, 91, 180, 270, 390
$J_c$	Reduced diffusion flux of $a$	p. 473, 481, 482, 485
$J_a^*$	Boltzmann entropy flux	p. 79, 260, 333
$J_s(\mathbf{r}, t)$	Rel. Boltzmann entropy flux	p. 122, 124, 180, 424
$\mathbf{J}_r[f f^c], \mathbf{J}_{rB}$	Hermitean Liouville operator	p. 432, 433, 438, 441
$\mathcal{L}$	Hermit. Liouville operator of $N$	p. 164, 219
$\mathcal{L}^{(N)}$	Free Hermit. Liouville operator	p. 159, 220,
$\mathcal{L}_0, \mathcal{L}^{(N)}$	Hermit. Interac. Liouville operator	p. 159
$\mathcal{L}_{12}$	$\mathcal{L}_a^{(N)} = -i\mathbf{L}_a^{(N)}$	p. 324
$\mathcal{L}_a^{(N)}$	$\mathcal{L}_0^{(N)} = -i \sum_\alpha^\nu \mathbf{L}_\alpha^{(N)}$	p. 173, 219
$\mathcal{L}_0^{(N)}$	$\mathcal{L}_{\alpha\beta}^{(N,N')} = -i\mathbf{L}_{\alpha\beta}^{(N,N')}$	p. 219, 326
$\mathcal{L}_{\alpha\beta}^{(N,N')}$		

$\mathcal{L}_{\alpha\beta}^{(N,N')}$	$\mathcal{L}_{\alpha\beta}^{(N,N')} = -i\mathbf{L}_{\alpha\beta}^{(NN')}$	p. 325
$\mathcal{L}^{(N)}$	Liouville operator of grand ensem.	p. 219, 326
$\mathcal{L}_1^{(N)}$	Interac. Liouville operator of grand ensemble	p. 326
$\mathbf{L}^{(1)}$	One-particle Liouville operator	p. 67
$\mathbf{L}^{(N)}$	Liouville operator of $N$	p. 162, 217
$\mathbf{L}_{\alpha}^{(N)}$	Liouville operator of an ensemble	p. 324
$\mathbf{L}_0^{(N)}$	Free $N$ -particle Liouville oper.	p. 162
$\mathbf{L}_1^{(N)}$	$N$ -interaction Liouville oper.	p. 162
$\mathbf{L}_{ex}^{(N)}$	$N$ -external Liouville oper.	p. 162
$\mathbf{L}_{oi}$	One-particle Liouville oper.	p. 162
$\mathbf{L}_{\alpha\beta}^{(N,N')}$	Intersubsys. interac. Liouville oper.	p. 217
$\mathbf{L}_{\alpha\beta}^{(N,N')}$	Interac. Liouville operator of petit ensemble $\alpha, \beta$	p. 325
$N$	uncompensated heat	p. 35, 38, 41
$\mathcal{N}$	Particle number in the ensemble	p. 142, 150, 215
$N_{\delta}$	Critical number	p. 474
$N_{De}$	Deborah number	p. 118, 475
$N_E$	Eckert number	p. 474
$N_{Kn}$	Knudsen number	p. 474
$N_M$	Mach number	p. 474, 475
$N_{Pr}$	Prandtl number	p. 474
$N_Q$	Ratio of ballistic heat flow to diffusive heat flow	p. 476
$N_{Re}$	Reynolds number	p. 474
$N_S$	Schmidt number	p. 474
$N_{We}$	Weissenberg number	p. 475
$\mathbf{N}$	$\mathbf{N} := (N_1, N_2, \dots, N_r)$	p. 323
$N_a$	Number of particles of species $a$	p. 323
$\mathcal{N}$	Total particle No. of grand ensem.	p. 324
$\mathcal{P}$	Probability of fluctuations	p. 131, 132,
$\mathbf{P}$	Pressure tensor	p. 25, 181, 233, 250, 340, 352
$\mathbf{P}_k, \mathbf{P}^{(k)}$	Pressure tensor, kinetic part	p. 233, 340, 352, 369
$\mathbf{P}_v, \mathbf{P}^{(v)}$	Pressure tensor, potential part	p. 233, 340, 352
$\delta\bar{p}$	Fluctuation of $\bar{p} = p/T$	p. 124, 302
$p^*$	Reduced pressure (Table 9.1)	p. 473
$p, p_e$	Pressure	p. 18, 23, 103, 153, 279, 396
$q_n$	Nonlinear factor	p. 113, 119, 204, 205, 290, 478, 479, 484
$q_L (\kappa_L)$	Nonl. factor in thermod. grads.	p. 121, 205, 422, 484, 501
$Q(N, V, T)$	Equil. canon. part. func.	p. 144, 148
$Q_{eq}$	Equil. canon. part. func.	p. 266
$Q$	Heat	p. 20, 23
$\mathbf{Q}_h, \mathbf{Q}^{(h)}, \mathbf{Q}^{(k)}$	Heat flux due to energy $H'$	p. 236, 351, 391
$\mathbf{Q}_v, \mathbf{Q}^{(v)}$	Heat flux due to virial tensor $\mathbf{W}_{ij}$	p. 236, 371
$\mathbf{Q}$	Heat flux	p. 25, 82, 181, 236, 351, 371
$\mathbf{Q}', \mathbf{Q}'_a$	Heat flux in excess of mass flux	p. 87, 118, 121, 205, 254, 361
$\mathbf{Q}^c$	Calortropy flux $\times T$	p. 43, 55, 96
$\mathbf{Q}_a^{ch}$	Effective heat flux; (6.257)	p. 125, 275, 397
$\mathbf{Q}_a^*, \mathbf{Q}_a'^*$	Reduced heat flux of $a$ (Table 9.1)	p. 473, 477, 481, 482, 489

$\mathcal{R}_0(z)$	Free resolvent operator	p. 166, 173, 230
$\mathcal{R}_0^{(N)}$	$N$ -particle free resolvent operator	p. 170, 173, 230
$\mathcal{R}(z)$	Resolvent operator	p. 160, 230
$\mathcal{R}^{(N)}$	$N$ -particle resolvent operator	p. 164, 170
$\mathcal{R}^{(\pm)}$	Cumulant expansion; Eq. (3.233); (5.173)	p. 112, 193, 285
$R_{ab}^{(qs)}$	Collision bracket integral	p. 114
$\mathbb{R}_{ab}^{(qs)}$	Coll. brack. integrals of order $(q, s)$ of species $a$ and $b$	p. 195, 287, 406, p. 33, 36, 75, 76, 152, 153, 266, 337
$S, \mathcal{S}_e$	Equil. Boltzmann entropy	p. 72, 178, 259, 260, 332, 425
$\mathcal{S}(\mathbf{r}, t)$	Boltzmann entropy density	p. 121, 131, 179, 264, 303, 423, 426
$S_r[f f^c]$	Relative Boltzmann entropy	p. 17, 32, 92, 93, 269
$T$	Temperature	p. 165, 166, 446, 448
$\mathcal{T}, \mathcal{T}_{12}$	Classical collision operator	p. 174
$\mathcal{T}_{ij}^{(N)}$	Interaction collision operator of particles $i & j \in N$	p. 174, 175, 224, 229, 230
$\mathcal{T}^{(N)}$	$N$ -particle collision operator	p. 361, 363
$\mathbf{T}_{ja}$	Pressure tensor, molecular form	p. 469
$\mathbf{T}_{ijkl}^{(4,1)}$	Traceless symmetric isotropic fourth-rank tensor	p. 24, 66, 180, 232, 339, 349, 473
$\mathbf{u}$	Fluid velocity	p. 309, 311
$\mathbf{u}_d$	Diffusive barycentric velocity	p. 309, 311
$\mathbf{u}_c$	Center of mass barycen. vel.	p. 233, 236
$U_{ij}$	Potential energy of pair $(i, j)$	p. 16, 80, 233, 367, 465
$v, v_{sp}$	Specific volume	p. 239, 346,
$\bar{v}_{vo}, v$	Mean Voronoi volume	p. 346, 356
$\hat{v}$	Molar volume, nonequilibrium	p. 355
$\hat{v}^{(0)}$	Equilibrium molar volume	p. 242
$\bar{v}_a$	Partial molar volume of a	p. 19, 29
$W$	Work	p. 234, 247, 250, 340, 351
$\mathbf{W}_{ij}$	Virial tensor of particle pair $(i, j)$	p. 63, 138, 149, 322, 323
$\mathbf{x}^{(N)}$	Phase of $N$ particles	p. 327
$x^{(\mathcal{N})}$	Phase of a grand ensemble of $\mathcal{N}$	p. 123, 302, 424, 425
$\overline{X}_a^{(q)t}$	$:= T^{t-1} X_a^{(q)}$	p. 17, 22, 40, 45, 92, 95, 101, p. 106, 190, 291, 387, 467
$X_a^{(s)}$	Generalized potential of species $a$ and order $s$	p. 302, 425
$\delta\overline{X}^{(k)}$	fluctuation of $\overline{X}^{(k)} = X^{(k)}/T$	p. 128
$Y_a^{(q)}$	Generalized potentials in Hermite polynomial basis	p. 242
$Z$	Compressibility factor	p. 27, 49, 56, 84, 85-87, 188, 249, p. 343, 373, 373-385, 409-414
$\mathcal{Z}_a^{(s)}$	Kinematic term of species $a$ and order $s$	p. 269, 282, 395 401
$\mathbb{Z}^{(N)}$	Nonequil. canon. partit. func.	p. 266, 336
$\mathbb{Z}_e^{(N)}$	Equil. grand canon. partit. f.	

## German Symbols

$b$	Impact parameter of collision	p. 64
$\mathfrak{B}_{ab}$	$:= \mathfrak{R}_{ab}^{(11)} / \beta g$	p. 471
$c_a$	concentration of species $a$	p. 16, 25, 81, 339, 368
$\mathfrak{D}_r$	Red. diffus. coeff. of $r$ (Table 9.1)	p. 473
$\mathfrak{D}_{ab}$	$:= (\mathfrak{R}_{ab}^{(44)} + \mathfrak{R}_{rr}^{(44)} - \mathfrak{R}_{ar}^{(44)} - \mathfrak{R}_{rb}^{(44)}) / \beta g$	p. 471
$\mathfrak{G}$	Gibbs manifold	p. 41
$\mathfrak{H}_{ab}$	$:= (\mathfrak{R}_{ab}^{(34)} - \mathfrak{R}_{ar}^{(34)}) / \beta g$	p. 471
$\mathfrak{K}_{ab}$	$:= (\mathfrak{R}_{ab}^{(43)} - \mathfrak{R}_{rb}^{(43)}) / \beta g$	p. 471
$\mathfrak{M}$	Molecular moment set	p. 92
$\mathfrak{P}$	Thermodynamic manifold	p. 16, 92,
$\mathfrak{P}_{gl}$	Global thermodynamic manifold	p. 16
$\mathfrak{R}_{ab}^{(qs)}$	$:= g_a^{(q)} \mathbb{R}_{ab}^{(qs)} g_b^{(s)}$	p. 118, 121, 196, 197-203 206, 208, 291-298, 407, 408, 410-417, 419-422, 454, 455, 457-459, 467, 475, 517, 518
$\mathfrak{T}$	Tangent manifold	p. 17, 261, 387
$\mathfrak{Z}_a$	Cumulant of species $a$	p. 105, 106

## Greek Symbols

$\beta$	Inverse temperature $1 / (k_B T)$	p. 93
$\Gamma_a, \Gamma$	LocaL nonequil. grand canonical partition function of $a$ ,	p. 93, 94, 95, 105, 116, 186, p. 189, 192, 271, 279, 281, 395
$\Gamma_a^{(s)}$	Global nonconserved variable of species $a$ and order $s$	p. 16
$\Delta_a, \widehat{\Delta}_a$	Excess normal stress of $a$	p. 84, 88, 120, 201, 203, 342
$\Delta_a^*$	Reduced $\Delta_a$ : Table 9.1	p. 473, 477, 481, 482, 485
$\epsilon$	Scaling factor for collision	p. 284, 290, 404
$\zeta_{ab}^0$	Diffusive thermal conductivity of $a$ and $b$	p. 202, 205
$\zeta_{ab}$	Nonlinear diffusive thermal conductivity of $a$ and $b$	p. 205
$\zeta_v$	Volume transport coefficient	p. 295

$\eta_0, \eta_a^0$	Newtonian shear viscosity	p. 294, 417, 456, 485,
$\eta_a$	Non-Newtonian viscosity	p. 205, 485, 525
$\eta_{Ba}^0$	Linear bulk viscosity	p. 201, 458, 481, 525
$\eta_B, \eta_{Ba}$	Nonlinear bulk viscosity, of $a$	p. 205, 485, 525
$\eta^*$	Reduced viscosity (Table 9.1)	p. 473
$\theta, \theta_A, \theta_B, \theta_C$	Temperature	p. 14
$\kappa_i^a, \kappa_i^{(\pm)}$	The $i$ th order cumulant of $a$	p. 107, 112, 194, 285, 403
$\kappa_i$	The $i$ th order cumulant	p. 112, 285, 403
$\kappa$	Generalized dissipation function	p. 51, 112, 113, 194, 197,
	zeroth order cumulant	p. 285, 287, 289, 403, 404, 405, 407, 484, 522
$\kappa_L, \kappa_L^*$	Diss. f. in terms of thermo. grads.	p. 204, 484, 501
$\kappa_i$	The $i$ -th cumulant	p. 285
$\kappa^*$	Reduced dissipation function	p. 501
$\kappa_{\Psi}^*$	iso-calortropic compressibility	p. 489
$\lambda_a$	Non-Fourier heat conductivity	p. 205, 485
$\lambda^*$	Red. heat conductivity (Table 9.1)	p. 473
$\lambda^0, \lambda_{ab}^0$	Thermal conductivity of $a$ and $b$	p. 202, 485
$\lambda_{ab}^{(05)0}$	Volume transport coefficient	p. 524, 525
$\lambda_a^{(sT)0}$	Linear thermal-thermodiff. coeff.	p. 526
$\lambda_a^{(sT)}$	Nonlinear thermal-thermodiff. coeff.	p. 526
$\Lambda_a^{(s)}$	Dissipation term of species $a$ and of order $s$	p. 27, 49, 51, 56, 84, 87, 88, 113, p. 115, 182, 188, 195, 196, 249, 250-256, 271, 286, 289-291, 343, 373-385, 404, 408-415
$\mu_a, \widehat{\mu}_a$	Chemical potential of $a$ , chem. pot./ $m_a$	p. 17, 41, 104, 152
$\overline{\mu}_a^t$	$:= T^{t-1} \widehat{\mu}_a$	p. 123, 424
$\widehat{\mu}_a^e$	Equil. chem. potential/ $m_a$	p. 74
$\delta \overline{\mu}$	Fluctuation of $\overline{\mu} = \mu/T$	p. 302
$\xi_{ab}$	Nonlinear thermodiffusion coefficient of $a$ and $b$	p. 205
$\xi_{ab}^0$	Thermodiffu. coeff. of $a$ and $b$	p. 202
$\xi$	Reduced distance (Table 9.1)	p. 473
$\Xi_{cal}$	Local calortropy prod., (6.258)	p. 43, 275, 276, 397, 398
$\widehat{\Xi}_{cal}$	Local calortropy prod. density	p. 42, 43, 55, 91
$\Xi_{eq}$	Equil. grand part. f. of N	p. 151, 153
$\Pi_a = \rho \widehat{\Pi}_a$	Shear stress tensor of $a$	p. 84, 88, 117, 120, 121, 197, 201, 203, 250, 342, 466, 470

$\Pi_a^*$	<i>Red. <math>\Pi_a</math>: Table 9.1</i>	
$\rho, \rho_a$	Mass density, mass density of a	p. 473, 476, 481, 482, 485, 489, 497, 499
$\rho^*$	Reduced density (Table 9.1)	p. 16, 24, 50, 66, 81, 232, 308, 348
$\sigma_{\text{ent}}$	Boltzmann entropy production	p. 473
$\sigma_r[f f^c], \sigma_{rB}$	Rel. Boltzmann entropy prod.	p. 79, 178, 260, 333, 334
$\sigma_c, \hat{\sigma}_c$	Calortropy production	p. 122, 124, 180, 264, 424
$\sigma(g_{ab} g_{ab}^*)$	Differential cross section	p. 91, 111, 113, 180, 191, 271, 284, 285, 286, 391
$\Phi_a^{(q)}, \widehat{\Phi}_a^{(q)}$	Nonconserved variable of species $a$ and order $q$ ,	p. 64
$\Phi^{(0)}$	Fluctuation of Voronoi volume	p. 16, 26, 41, 44-50, 56, 84-87,
$\Phi^{(4)}$	Volume flux	92, 105, 107, 109, 116, 248-255,
$\Psi_a^{(s)}, \overline{\Psi}_a^{(S)}$	Flux of $\Phi_a^{(s)}$	342, 357-365, 372-385, 396,
$\Psi$	Global calortropy	400, 415-422, 466, 517-525
$\hat{\Psi}$	Calortropy density	p. 244
$\omega^*$	Reduced vorticity	p. 245
$\Omega, \Omega_t$	Total No. of states in ensem.	p. 27, 56, 84, 182, 249-255, 373-385, 466
$\Omega^{(N)}(0, \pm\infty)$	Møller operator	p. 35, 41, 45, 179, 261, 390
$\Omega_{\alpha\beta}^{(j)}$	Tetrahedral volume of vertices $\alpha, \beta \in j$	p. 40, 41, 42-48, 91-95, 98,
$\Omega_{\text{vo}}, \Omega_j$	Sum of $\Omega_{\alpha\beta}^{(j)}$ of the pyramid of base $p_j$	109, 121, 179, 180, 187,
$\Omega_{\text{vo}}, \Omega, \Omega_{\text{ja}}$	Sum of tetrahedral volumes	190, 263, 270, 273-279,
		390, 392, 396, 398
		p. 473
		p. xxx
		p. 165
		p. 239, 345, 346
		p. 240, 346
		p. 240, 243, 346

## Mathematical Operations

$[\mathbf{A}]^{(2)}$	Traceless symmetric part of tensor $\mathbf{A}$	p. 84
$[A_a B_a]_{ab}$	Collision bracket integral	p. 114
$[A_a B_a]_{ab}'$	Collision bracket integral	p. 114
$[A_a B_a]_{ab}''$	Collision bracket integral	p. 114
$\langle A f_a \rangle$	Mean value of $A$	p. 64
$C(f, f_2)$	Boltzmann collision integral	p. 63, 68
$d_t$	Substantial time derivative	p. 24, 79,
$\mathcal{D}_t$	$:= d_t + \mathbf{C}_a \cdot \nabla + \widehat{\mathbf{F}} \cdot \nabla_{\mathbf{v}_a}$	p. 85, 126, 182
$\mathcal{D}_t^{(N)}$	$:= \frac{d}{dt} + \mathbf{L}^{(N)} + \mathbf{C}_{ja} \cdot \nabla$	p. 249, 343
$\Delta\tau$	time interval	p. 14
$\mathbf{R}[f]$	$:= \sum_{b=1}^r C(f, f_b)$	p. 63, 159
$\Re \left[ \overline{\mathbb{F}}^{(N)} \right]$	Collision operator of an ensemble	p. 226, 260, 263, 328, 333
$\Re \left[ \overline{F}^{(N)} \right]$	Time-coarse grained	
	$N$ -particle ensemble collision integral	p. 167, 169, 170, 178
$\vartheta$	Time reversal operator	p. 71
$[\nabla \mathbf{u}]^{(2)*}$	$:= [\nabla \mathbf{u}]^{(2)} L U_r^{-1}$ , reduced $[\nabla \mathbf{u}]^{(2)}$	p. 473

## Eigenvalue Problem of Liouville Operator

$\mathcal{L}$	Hermit. Liouville operator	p. 432
$\mathcal{L}_0$	Hermit. free Liouville operator	p. 443
$\mathcal{L}_1$	Interaction Liouville operator	p. 444
$\tilde{\mathcal{L}}_1$	Interaction representation of $\mathcal{L}_1$	p. 444
$\mathcal{L}_g(\mathbf{p}, \mathbf{r}, s)$	Lagrangian	p. 435
$p_k$	Momentum of particle $k$	p. 434
$Q_k$	Gen. coordinate of particle $k$	p. 434
$\mathcal{R}(z)$	Classical resolvent operator	p. 446
$\mathcal{R}_0(z)$	Free classical resolvent operator	p. 446
$S$	Hamilton–Jacobi generating function	p. 435
$\mathbf{T}(z)$	Classical collision operator	p. 446, 449
$\Phi_\lambda$	Eigenfunction of $\mathcal{L}_0$	p. 443
$\psi_\lambda$	Eigenfunction of $\mathcal{L}$ of eigenvalue $\lambda$	p. 433, 435, 436, 437-442
$\psi_\lambda^{(+)}, \psi_\lambda^{(-)}$	Outgoing, incoming eigenfunc.	p. 445
$\Gamma(x)$	Phase function	p. 433, 434
$\omega_k$	Frequency	p. 434, 436

# Index

## A

- Abel-Tauber theorem, 164, 222, 444
- Activity coefficient, 556
  - in terms of total correlation functions, 548
- Adiabatic approximation, 480
- Affinity, 54
- Average
  - statistical mechanical formula for, 331
- Average value
  - of mechanical quantity, 139

## B

- Balance equation
  - for Boltzmann entropy, 178
- Barycentric velocity, 308, 309
  - constitutive relation for, 311
  - diffusive part of, 311
- Binary collision expansion, 174
- Body force, 25
- Body force density, 82, 340
- Boltzmann entropy, 5
  - global, 332
  - of liquids, 258
  - statistical mechanical formula for, 332
- Boltzmann entropy balance equation, 79, 334
- Boltzmann entropy density
  - local, 259
- Boltzmann entropy flux, 79, 334
  - for liquids, 260
  - statistical mechanical formula for, 178
- Boltzmann entropy for reversible processes and Clausius entropy, 75

Boltzmann entropy production, 79, 334

for liquids, 260

statistical formula for, 178

Boltzmann kinetic equation, 63, 158

alternative form for, 160

and Gibbs ensemble theory, 5

Boltzmann entropy balance equation, 260

Bra and ket vector, 448

Broken time reversal symmetry, 70

Bulk viscosity, 201, 295, 457

reduced, 482

Bulk viscosity law, 201

## C

- Calortropy, 2, 4, 36, 90, 389
  - vanishing circular path integral of, 41
  - and LambertW function, 109
  - bilinear form for, 46, 187, 392
  - global, 41
  - local density, 41
  - local density of, 93
  - Pfaffian differential form of (see extended Gibbs relation), 44
  - statistical mechanical formula for, 263
  - statistical mechanical representation of, 91
- Calortropy balance equation, 91, 263, 390
  - of liquids, 275
- Calortropy density
  - bilinear form of, 94, 273
  - local, 270
- Calortropy density balance equation, 42, 396
- Calortropy differential, 35, 40

- Calortropy flux, 42, 43, 55, 96, 270, 390  
 explicit form for, 43  
 statistical mechanical formula for, 180,  
   263  
 statistical mechanical representation of,  
   91
- Calortropy production, 42, 43, 96, 113, 282,  
   390  
 bilinear form of, 43  
 approximate (first order cumulant approximation) formula, 51  
 first-order cumulant approximation for,  
   285, 404  
 in the presence of a chemical reaction, 55  
 statistical mechanical formula for, 180,  
   263  
 statistical mechanical representation of,  
   91
- Calortropy production, local, 271
- Calortropy, liquid  
 statistical mechanical formula for, 261
- Calortropybalance equation, 179
- Canonical ensemble, 140
- Carnot theorem, 2, 28
- Cavity function, 571
- Chapman–Enskog collision bracket integral, 451
- Characteristic determinant  
 of the quasilinear differential system, 492
- Characteristic number  
 for ballistic heat flow, 476
- Chemical potential  
 density dependence for, 546  
 in the Kirkwood–Buff theory of solutions, 542  
 nonequilibrium, 104
- Chemical reaction, 54
- Circle theorem  
 of the Yang–Lee theory, 566
- Classical hydrodynamic equations, 487  
 Navier–Stokes, Fourier, and Fick's equations, 50, 120
- Classical hydrodynamics  
 as a limit of generalized hydrodynamics, 7
- Classical Lippmann–Schwinger equation, 224
- Clausius entropy, 146  
 statistical mechanical formula for, 152
- Clausius inequality, 2, 30, 31  
 and the second law of thermodynamics, 2
- Clausius principle, 29
- Clausius's virial, 352
- Clausius–Duhem inequality, 36, 38
- Cluster expansion  
 for a collision operator, 207  
 Collision bracket integral, 406, 448  
 alternative form for, 450  
 for shear viscosity, 456  
 for three-particle collision, 452  
 in the form of time-correlation function, 455
- Collision bracket integrals, 198, 200, 288, 454  
 basic, 407  
 for excesses normal stresses, 415  
 for heat flux, 413  
 for mass diffusion, 411  
 for moderately dense gases, 208  
 for shear stresses, 414  
 for the Boltzmann equation, 114  
 for volume flux, 412
- Collision integral  
 Boltzmann, 63  
 its relation to the collision operator, 160  
 of the generalized Boltzmann equation, 328
- Collision invariants, 69, 169, 228, 330  
 property of, 330
- Collision operator  
 and its relation to resolvent operator, 223  
 binary, 174  
 classical, 446  
 integral equation for, 160
- Compensated heat, 276, 398  
 exchange rate of calortropy, 398
- Compressibility  
 adiabatic, 103
- Compressibility equation of state, 553
- Connected cluster expansion  
 for collision bracket integrals of moderately dense gases, 210  
 for collision operator, 174, 175
- Conservation law, 50, 181, 232, 366, 465  
 continuum mechanics forms of, 24  
 for liquids, 516  
 local, 24  
 of conserved variables, 339
- Conserved moments, 85
- Conserved variables, 65
- Consistency condition  
 with the second law of thermodynamics, 43
- Convective kinetic energy, 67
- Convolution theorem

- for Fourier transforms, 563  
Correlation function  
  direct, 563  
  in the subcritical regime, 575  
  total, 563  
Coupled integral equations  
  for collision operators, 174  
Critical number, 474  
Cumulant, 106, 193, 285, 403  
  for calorropy production, 112  
Cumulant expansion  
  for calorropy, 193  
  for calorropy production, 110, 112, 282, 285  
  for macroscopic variables, 109  
  for nonequilibrium partition function, 106  
Cumulant series, 403  
Curie principle, 50, 101, 358
- D**
- Dahler–Hirschfelder collective coordinates, 313  
Deborah number, 118, 475  
Density  
  statistical mechanical formula for, 180  
Density fluctuations  
  equilibrium, 540  
  its relation to total correlation function, 541  
Derivatives  
  of the local nonequilibrium partition function, 396  
Diffusion coefficient  
  Einstein formula for, 312  
Differential equations  
  for fluctuations in intensive variables, 306  
Differential form  
  for the thermodynamic potential, 279  
  for calorropy, 392  
  for equilibrium Boltzmann entropy, 77  
  for nonequilibrium enthalpy, work function, and Gibbs free energy, 47  
  for nonequilibrium partition function, 96  
  for thermodynamic potential, 395  
  for work function, 148  
Diffusion coefficient, 202  
  reduced, 482  
Diffusion flux, 25, 84, 181, 340  
  statistical mechanical formula, 357  
  statistical mechanical formula for, 349
- Diffusion tensor, 311  
Diffusive heat conductivity  
  reduced, 482  
Diffusive thermal diffusivity, 202  
Dimensionless flow variables, 473  
Dirac delta function  
  an identity for, 234  
  properties of, 234  
Direct correlation function, 541  
Disconnected clusters, 174  
Displacement operator, 310, 341  
Dissipation function  
  reduced, 478  
  scaling behavior of, 478  
Dissipation term, 27, 182, 249  
  first-order cumulant approximation for, 404, 467  
  for diffusion, 377  
  for excess normal stress, 384  
  for heat flux, 379  
  for nonconserved variables, 85  
  for shear stress, 382  
  for volume flux, 378  
  linear, 49  
  of generic evolution equation, 343  
Distribution function  
  coarse-grained, 315  
  of  $s$  particles, 161  
  reduced, 162  
  singlet, 63  
Driving force  
  for mass flow, 118, 197
- E**
- Effective heat flux, 397  
Effective thermal conductivity  
  in one-dimensional tube flow, 500  
Eigenfunction  
  Fourier decomposition of, 432  
  in terms of phase functions, 435  
  in terms of phase integrals, 436  
  mathematical properties of, 437  
Eigenvalue problem  
  of the Liouville operator, 8, 220  
Einstein diffusion coefficient, 311  
Einstein probability  
  of fluctuations, 306  
Ensemble average  
  of mechanical quantity, 140  
Ensemble theory  
  of Gibbs for statistical mechanics, 138  
Enstrophy, 502

- Enthalpy  
  generalized (nonequilibrium), 47
- Entropy, 2, 90  
  Clausius, 33, 36, 73, 75  
  see information (Shannon) entropy, 73
- Entropy of mixing  
  in terms of direct correlation functions, 559
- Equal a priori hypothesis, 323
- Equal a priori probability hypothesis, 139, 214
- Equation of continuity, 232, 366
- Equation of state, 539  
  and grand canonical partition function, 566  
  via compressibility, 545
- Equilibrium average  
  of a mechanical observable, 145
- Equilibrium Boltzmann entropy, 266  
  Clausius entropy, 75
- Equilibrium condition, 169, 231  
  for generalized Boltzmann equation, 265, 330
- Equilibrium distribution function  
  for a mixture, 336  
  for liquids, 265  
  of a canonical ensemble, 144
- Equilibrium Gibbs relation, 33, 146
- Equilibrium partial molar volume  
  statistical mechanical formula for, 355
- Equilibrium partition function  
  grand canonical, 336
- Equilibrium pressure  
  statistical mechanical definition of, 76
- Equilibrium solution  
  of the Boltzmann equation, 70, 74  
  of the extended Boltzmann equation, 184  
  of the generalized Boltzmann equation, 228, 335
- Equilibrium thermodynamic potential  
  differential of, 267
- Ergodic hypothesis, 140
- Ergodic theory, 140
- Evolution equation  
  for a singlet distribution function, 163  
  for diffusion flux, 376  
  for excess normal stress, 253, 384  
  for heat flux, 255, 379  
  for partial molar volume, 374  
  for shear stress, 250, 381  
  for total excess normal stress, 385  
  for volume flux, 249, 378  
  of volume fluctuation, 244
- Evolution equation, fine grained  
  of a subsystem distribution function, 221
- Evolution equations  
  for fluctuations, 304  
  for linear transport processes, 119  
  for nonconserved variables, 469, 471
- Exact differential, 20, 45
- Excess normal stress  
  statistical mechanical formula for, 363
- Exponential form  
  for distribution function, 301
- Exponential representation  
  for reduced distribution function, 332
- Extended Boltzmann equation  
  for a gas mixture, 167
- Extended Gibbs relation, 6, 95, 187, 273, 393  
  for calortropy, 45  
  for Gibbs free energy, work function, and enthalpy, 99
- Extended irreversible thermodynamics, 35
- Extended zeroth law, 18
- Extensive macroscopic observable  
  density of, 78
- F**
- Factorization theorem  
  for the Wiener-Hopf method, 565
- Fick's law of diffusion, 201
- First degree homogeneous function, 395
- First law of thermodynamics, 19  
  circular integral representation of, 19  
  for a cyclic process, 277  
  mathematical statement of, 19  
  representation for a cyclic process, 399
- First-order cumulant approximation  
  for calortropy production, 113, 194, 403  
  for dissipation functions, 290  
  for dissipation term, 113, 115, 195, 286
- Fluid dynamic numbers  
  definitions for  
    Mach, Reynolds, Eckert, Prandtl, Knudsen, Schmidt, 473
- Fokker-Planck equation  
  of Kirkwood, 316
- Fourier's law of heat conductivity, 201
- Friction tensor, 316
- Fugacity  
  statistical mechanical expression for, 556
- Functional hypothesis, 89  
  for distribution functions, 387
- Fundamental postulates  
  of statistical mechanics, 139

**G**

- Gauge function, 570  
Generalized hydrodynamic equations, 289  
Generalized Boltzmann equation, 226  
  for a mixture, 328  
Generalized hydrodynamic equations, 85, 182, 188, 365, 495  
  for a mixture, 385  
  for compressible Poiseuille gas flow, 496  
  for linear transport processes, 50  
  quasilinear, 117, 196, 206  
  reduced (dimensionless), 476  
Generalized hydrodynamics, 6  
Generalized hydrodynamics equations  
  quasilinear, 117  
Generalized potential, 17, 100, 115, 190, 280, 399, 467  
  and its relation to nonconserved variables, 40  
  and LambertW function, 108  
  its relation to nonconserved variables, 48  
  linear, 291  
Generalized rectilinear law  
  for a two-phase fluid, 581  
Generating function  
  and action integral, 435  
  of canonical transformation, 433  
Generic evolution equation, 182  
  for nonconserved variables, 27, 84, 249, 342, 373, 466  
Generic evolution equations  
  quasilinear, 121  
G factor  
  the scaling factor for calortropy production, 51  
Gibbs free energy  
  generalized (nonequilibrium), 47  
Gibbs manifold, 41, 96  
Gibbs–Duhem equation, 45, 77  
  nonequilibrium, 6  
Global Boltzmann entropy  
  dissipation rate for, 335  
  exchange rate for, 335  
Global calortropy balance equation, 398  
Global calortropy change, 276  
Global nonequilibrium grand partition function, 278  
Global pressure  
  statistical mechanical representation of, 94  
Grand canonical distribution function, 151  
  reduced, 539  
Grand canonical ensemble, 141, 149

- nonequilibrium, 322  
Grand canonical ensemble average  
  of a mechanical quantity, 151  
Grand canonical partition function, 538, 576  
  and thermodynamic quantities, 153  
Grand canonical probability distribution function  
  bimodal form for, 578  
Grand ensemble average  
  of a mechanical quantity, 150  
Green's function, 569

**H**

- Hamilton–Jacobi characteristic function, 437  
Hamilton–Jacobi equation, 434  
Hamilton–Jacobi theory, 433  
Heat  
  compensated, 31  
  uncompensated, 2, 29, 31, 32, 35  
Heat flux, 25, 84, 181, 340, 391  
  statistical mechanical formula for, 236, 351, 360, 371  
  statistical mechanical formula for dilute gas, 82  
Heat of mixing, 559  
Heat transfer coefficient, 15  
Heat transfer rate, 22  
Helmholtz free energy, 147  
Helmholtz work function, 268  
Hermite tensors  
  orthogonal, 105  
H function  
  of the Boltzmann equation, 72  
Hierarchy  
  homologous, 3  
H theorem, 78  
  for extended Boltzmann equation, 169  
  for generalized Boltzmann equation, 229  
  for liquids, 259  
  for the generalized Boltzmann equation, 330, 331  
  global form for, 261  
  local, 334  
  of Boltzmann, 73  
  of the Boltzmann equation, 70  
Hydrodynamics  
  in the presence of chemical reactions, 54  
Hyperazimuthal angle, 452  
Hyperbolic differential equations  
  for hydrodynamic flow, 489  
Hyperbolicity  
  definition of, 493

- of quasilinear differential equations, 491
- Hyperpolar angles, 452
- Hypersonic flow contours, 503
- Hyperspherical coordinates
  - for a three-particle system, 452
  
- I**
- Information content
  - loss of, 426
- Information entropy, 36
- Integral equation
  - for resolvent operator, 169
  - of the Wiener–Hopf method, 571
- Intensive variable
  - local, 40
- Interaction representation, 444
- Internal energy
  - statistical mechanical formula for, 236
- Internal energy balance equation, 82, 236, 371
- Internal energy conservation law, 236
- Internal energy density, 25, 67, 339
  - statistical mechanical formula for, 180, 350
- Internal energy Hamiltonian, 350
- Internal rate of change, 21
- Interrelations
  - of fluid dynamic numbers, 474
- Inverse collision time, 290
- Irreversible cycle
  - efficiency of, 30
- Isobaric expansion coefficient, 500
- Isocalortropic compressibility, 489
- Isothermal compressibility, 296, 500, 543
  - and total correlation functions, 544
  - in terms of direct correlation functions, 552
- Isotropic tensor of rank 4
  - traceless symmetric, 469
  
- J**
- Jellyfish model
  - for barycentric velocity, 312
  
- K**
- Kelvin principle, 29
- Kinematic contribution
  - to the calortropy, 390
- Kinematic term, 27, 85, 249
  - for diffusion flux, 87
  - for excess normal stress, 86
- for gases, 467
- for heat flux, 86
- for shear stress, 382
- for shear stress tensor, 86
- for volume flux, 378
- list of, 182
- of generic evolution equation, 343
- Kinetic energy density, 67
- Kinetic equation
  - for time-coarse grained distribution function, 163, 224
  - for time-coarse grained singlet distribution function, 167
  - irreversible, 2
- Kirkwood–Buff theory
  - in terms of direct correlation functions, 552
- Kirkwood–Buff theory of solution, 538
  - the basic equation of, 542
- Klein inequality, 122, 262
- Knudsen flow, 514
- Knudsen problem (paradox)
  - of tube flow, 504
  
- L**
- Lagrange method of variation, 215
- LambertW function, 108
- Light-induced viscous flow
  - of gas, 510
- Linear constitutive equation
  - for excess normal stress, 293
  - for excess normal stresses, 415
  - for heat flux, 293
  - for heat fluxes, 413
  - for mass diffusion fluxes, 411
  - for nonconserved variables, 120, 200
  - for shear stress, 292
  - for shear stresses, 414
  - for volume fluctuations, 292
  - for volume flux, 294
  - for volume fluxes, 412
  - for volume transport, 410, 519
- Linear constitutive relation for heat and diffusion, 202
- Linear constitutive relations
  - for moderately dense gas, 453
- Linear dissipation term, 291, 408
- Linear transport coefficients
  - for vectorial processes, 526
  - reduced, 481
- Liouville equation, 220, 432, 443
  - for an isolated system (ensemble), 326

- of N particles, 162
- Liouville operator, 324, 432
  - a generator of hierarchy of moments, 68
  - eigenvalue problem of, 433
  - free particle, 159
  - Hermitean, 164
  - interaction, 159, 162
  - intersubsystem interaction, 325
  - noninteracting particle, 162
  - of intersubsystem interaction, 217
  - of N particle, 162
  - of subsystems, 217
  - one-particle, 67
  - self-adjoint, 219
- Lippmann–Schwinger equation
  - classical, 159, 169, 173, 446
- Local Boltzmann entropy
  - statistical mechanical formula for, 178
- Local Boltzmann entropy density, 332
- Local calorropy production, 275
  - local form of the second law of thermodynamics, 397
- Local equilibrium hypothesis, 33
- Local equilibrium pressure
  - statistical mechanical formula, 363
- Local H theorem, 80, 260
- Local mean observable
  - statistical mechanical definition of, 232
- Local momentum, 233
- Local nonequilibrium grand partition function, 279
- Local partition function
  - canonical, 266
- Local pressure
  - statistical mechanical representation of, 94
- Lyapounov function, 259, 337
  - and the H function, 72
- M**
- Mach number, 475
- Macroscopic variables
  - global, 16
  - local, 16
  - statistical thermodynamic formulas for, 98
- Manifold
  - of macroscopic variables, 92
  - of tangents to manifold of variables, 92
- Mass density
  - local, 66
  - statistical mechanical formula, 339, 348
- total, 66, 339
- Mass density balance equation, 80
- Mass density fraction, 272, 348
- Mass diffusion flux, 81
- Mass fraction, 25
  - of a species, 339
- Mass fraction balance equation, 81, 368
  - in the presence of a chemical reaction, 54
- Mass-normralized collective coordinates, 313
- Maximum work, 29
- Maxwell distribution function, 74
- Maxwell relations
  - generalized, 100
  - generalized (nonequilibrium), 47
- Mayer function, 571
- Mean collision time, 404
- Mean density, 232, 308
- Mean momentum, 4
- Mean momentum density
  - statistical formula for, 339
- Mean velocity, 66
  - statistical mechanical formula for, 367
- Mean Voronoi volume
  - statistical mechanical formula for, 243
- Mean work per unit volume, 146
- Microscopic reversibility, 64
- Molar volume, 237, 346, 354, 464
  - thermodynamic definition of, 241
- Molar volume fluctuation, 356
- Molecular moment
  - for excess normal stress, 383
  - for volume, 354
  - for volume flux, 357
- Møller operator, 165
- Momentum balance equation, 81, 233, 368
- Momentum density, 66
  - statistical mechanical formula for, 180, 349
  - total, 339
- N**
- Newton’s law of viscosity, 201, 294
- Newtonian law of viscosity, 416
- Newtonian shear viscosity, 294
- Nonconserved moment of rank q, 181
- Nonconserved variable, 26
  - statistical mechanical formula for, 84
- Nonconserved variable evolution equations, 87
- Nonconserved variable flux, 182
- Nonconserved variables, 466

- statistical mechanical formula for, 342, 347, 372
- Nonequilibrium canonical distribution function, 192
- Nonequilibrium canonical form, 262  
for distribution function, 92, 185, 268, 282  
for the thermodynamic branch of distribution function, 301
- Nonequilibrium entropy, 34
- Nonequilibrium flux  
and cumulants, 107
- Nonequilibrium Gibbs–Duhem equation, 46, 95, 187, 273, 393
- Nonequilibrium grand canonical form, 388
- Nonequilibrium partition function  
and macroscopic variables, 280  
canonical, 186  
grand, 104  
local form for, 395
- Non-Fickian diffusion coefficient, 205
- Non-Fourier heat conductivity, 205
- Nonlinear heat flux equations  
for one-dimensional flow, 499
- Nonlinear constitutive equations  
for non-Fickian mass flow, 119  
for non-Newtonian flow, 119  
for vectorial processes, 522  
non-Fourier heat conduction, 119
- Nonlinear factor, 113, 195, 290, 420, 470  
in terms of thermodynamic gradients, 205, 422, 484
- Nonlinear ordinary differential equation  
for one-dimensional flow velocity, 499  
for temperature in one-dimensional tube flow, 501
- Nonlinear shear viscosity  
for a liquid, 521
- Nonlinear transport coefficients, 485  
see non-Newtonian viscosity etc., 485
- Non-Newtonian bulk viscosity, 205
- Non-Newtonian viscosity, 205
- Normalization factor  
for nonequilibrium canonical form, 93
- Null eigenvalue class, 221
- Number density, 64
- Number of states  
of an isolated supersystem, 151
- O**
- Orbital angular momentum conservation law of a fluid, 343
- Ornstein–Zernike equation, 550, 563  
and convolution theorem, 551
- Osmotic pressure  
in terms of total correlation functions, 549
- P**
- Pair correlation function  
bimodal interpolation formula for in the subcritical regime, 579
- Partial mass density  
statistical mechanical formula for, 348
- Partial molar volume, 241  
in terms of direct correlation functions, 553  
in terms of total correlation functions, 544  
statistical mechanical formula for, 354, 355
- Partial velocity evolution equation, 87
- Particle phase, 215
- Partition function  
canonical, 144  
nonequilibrium grand canonical, 93
- Peculiar velocity, 66, 218, 325, 349, 455
- Petit ensemble, 149, 323
- Pfaffian differential  
of calortropy, 391
- Pfaffian differential  
of calortropy, 273
- Phase, 138
- Phase space, 138
- Phase vectors, 322
- Poisson brackets, 432
- Polytropic ratio, 474
- Positive semidefinite form  
for the relative Boltzmann entropy, 303
- Pressure  
nonequilibrium, 103
- Pressure tensor, 25, 181, 340  
statistical mechanical formula for, 233, 352  
statistical mechanical formula for dilute gas, 82
- Probability distribution function, 139  
for a grand ensemble, 327
- Probability of fluctuations  
and relative Boltzmann entropy, 306
- Proposition 1, 24
- Proposition 2, 27
- Proposition 2v, 56
- Proposition 3, 40

- Proposition 4, 43  
Proposition 4c, 55  
Proposition 5, 89  
Proposition 7, 97
- Q**  
Quasilinear bulk viscosity, 525  
Quasilinear constitutive equations  
  steady state, 479, 518  
Quasilinear constitutive relations, 205, 482,  
  524  
  reduced, 484  
Quasilinear differential system  
  of generalized hydrodynamic equations,  
  492  
Quasilinear evolution equations  
  for nonconserved variables, 420, 517  
Quasilinear generalized hydrodynamic  
  equations, 297  
  model for, 298  
Quasilinear shear viscosity  
  non-Newtonian shear viscosity, 525  
Quasilinear transport coefficients, 205  
  for vectorial processes, 526  
Quasilinear volume transport coefficient,  
  525
- R**  
Random distribution  
  number of, 215  
Random phase approximation, 225  
Rate of transfer, 21  
Rayleigh dissipation function, 51, 197, 203,  
  289, 405, 408  
  generalized, 118  
  generalized form for, 467  
  in terms of thermodynamic derivatives,  
  523  
Reciprocal relations  
  of Onsager, 406  
Rectilinear law, 581  
Reduced distribution function  
  for a petit ensemble, 327  
  of N particles, 221  
  time-coarse-grained, 328  
Relative Boltzmann entropy, 7, 121, 131,  
  179, 263, 301, 423  
  and fluctuation theory, 301  
  balance equation for, 303  
  bilinear form for, 303, 306, 425  
  for liquids, 262  
  inequality for, 425
- statistical mechanical formula for, 179  
Relative Boltzmann entropy balance equa-  
  tion, 122, 125, 264, 424  
  an alternative equation, 426  
  vanishing fluctuation limit of, 426  
Relative Boltzmann entropy flux, 122, 424  
  statistical mechanical formula for, 180,  
  264  
Relative Boltzmann entropy production, 122  
  statistical mechanical formula for, 180,  
  264  
Relative entropy balance equation, 179  
Relative entropy production, 424  
Renormalized kinematic term  
  for excess normal stress, 384  
  for heat flux, 380  
Resolvent operator, 164, 223  
  classical, 445  
  free particle, 159  
  full, 160  
  integral representation for, 170  
  integral representation of, 230  
  of N free particles, 166  
Reversible cycle  
  efficiency of, 30
- S**  
Sackur-Tetrode formula  
  for Clausius entropy, 75  
Scaling factor  
  for calortropy production, 111, 191  
Scaling factor for calortropy production, 284  
Scattering cross section, 64  
Schwartz inequality, 134  
Second fundamental postulate  
  of statistical mechanics, 140  
Second law of thermodynamics, 28  
  and positivity of uncompensated heat, 38  
  for a cyclic process, 277  
  local theory representation of, 43  
  representation for a cyclic process, 398  
  representation of a local process for, 398  
Seed element, 3  
Shear stress  
  statistical mechanical formula for, 362  
Shear stress evolution equation  
  total, 383  
Shear viscosity, 201, 417  
  reduced, 482  
Sign convention  
  for heat transfer, 18  
  for work, 18

Singlet distribution function, 161  
     time-coarse grained, 163  
 Specific heat, 102  
 Specific volume, 80, 233, 237, 241, 367  
     partial, of species a, 86  
 Speed of sound, 475  
 Statistical mean value, 64  
 Steady quasilinear constitutive relations, 203  
 Steady state evolution equations  
     for nonconserved variables, 52  
 Steady-state constitutive equation  
     quasilinear, 119, 480  
 Steady-state evolution equations  
     quasilinear, 199  
 Stirling approximation, 143  
 Stirling cycle number, 109  
 Stochastic evolution equations  
     for fluctuations of intensive variables,  
         307  
 Stochastic differential equations  
     for fluctuations, 307  
 Stress tensor, 84  
 Substantial time derivative, 24, 333, 367, 373  
 Summation invariants  
     see collision invariants, 69

**T**

Tangent manifold  
     of macroscopic variables, 17  
 Temperature  
     nonequilibrium, 102  
 Tetrahedron  
     volume of, 239  
 Theorem 1, 45  
 Theorem 2, 97  
 Thermal conductivity, 202, 296  
     reduced, 482  
 Thermal-diffusion coefficient  
     reduced, 482  
 Thermo-diffusion coefficient, 202  
 Thermodynamic branch  
     of distribution function, 89  
     of the distribution function, 123, 130  
 Thermodynamic commutators, 133  
 Thermodynamic complementarity relations,  
     134  
 Thermodynamic consistency, 3, 27  
     for pair correlation function, 570  
 Thermodynamic correspondence, 76, 77, 97,  
     189, 393  
     for the system at equilibrium, 267  
 Thermodynamic correspondences, 146, 274

Thermodynamic derivatives  
     and nonequilibrium partition function,  
         190  
 Thermodynamic driving forces, 49  
 Thermodynamic force  
     for diffusion, 376, 472  
     for mass diffusion, 49  
     for volume flux, 518  
 Thermodynamic manifold, 16, 92, 387  
 Thermodynamic potential, 77, 95, 98, 153  
     differential form for, 46  
     differential form of, 189  
     nonequilibrium, 279  
 Thermodynamic quantities  
     and canonical partition function, 147  
 Thermodynamic quantization rules, 132,  
     307  
 Thermodynamic uncertainty principle, 7  
 Thermodynamic uncertainty relations, 134  
 Time average  
     of mechanical quantity, 140  
 Time-coarse graining, 222  
 Total correlation function, 540  
     integral equation for, 569  
 Traceless symmetric part  
     of second rank tensor, 361  
 Traceless symmetric tensor  
     of rank 2, 84  
 Transfer coefficient, 18  
 Transport coefficient  
     for volume transport, 410  
 Transport coefficients  
     related to volume transport, 296

**U**

Unavailable work, 23  
 Uncompensated heat, 276, 398  
     global caltropy creation rate, 398  
 Unit second rank tensor, 469

**V**

Van't Hof equation for osmotic pressure  
     in terms of direct correlation functions,  
         558  
 Variational method  
     of undetermined multipliers, 143  
 Virial tensor, 234, 340  
     for a mixture, 351  
 Volume flux  
     statistical mechanical formula for, 358,  
         377  
 Volume transpiration, 296

- Volume transport  
and molar volume, 6
- Volume transport coefficient, 295
- Volume transport phenomena, 57
- Voronoi polyhedron, 238
- Voronoi tessellation, 238
- Voronoi volume, 6, 56, 238, 345, 353, 464  
statistical mechanical formula for, 240  
statistical mechanical representation of,  
346
- Weissenberg number, 474
- Wiener–Hopf (WH) method, 564
- Work, 20  
generalized form of, 21  
unavailable, 31, 32
- Work function  
generalized (nonequilibrium), 47
- Work of task, 22
- W**
- Wave speed, 493
- Z**
- Zeroth law of thermodynamics, 14, 15