

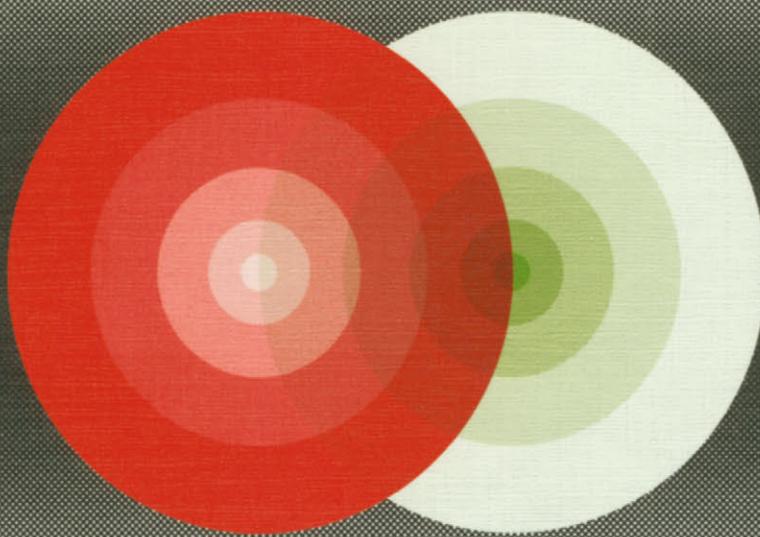
Nonequilibrium Statistical Mechanics

Ensemble Method

by

Byung Chan Eu

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Fundamental Theories of Physics

Nonequilibrium Statistical Mechanics

Fundamental Theories of Physics

*An International Book Series on The Fundamental Theories of Physics:
Their Clarification, Development and Application*

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**This is for Hui Young
and
my children**

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Preface

The statistical mechanics of J. C. Maxwell and L. Boltzmann is for dynamical processes in dilute monatomic gases and is based on the evolution equation—kinetic equation—for the singlet distribution function. Starting from the basic ideas of Maxwell and Boltzmann on the statistical treatment of systems of many particles, J. W. Gibbs synthesized a general formal theory of statistical mechanics, at least, for equilibrium phenomena which covers all states of aggregation of matter. This equilibrium ensemble theory of Gibbs—statistical thermodynamics—is a deductive approach based on a set of postulates which aims to give the thermodynamics of reversible processes—equilibrium thermodynamics—a molecular representation. It does succeed in the attempt because the mathematical structure of the phenomenological theory of reversible thermodynamic processes is well founded on the thermodynamic laws through the concept of entropy enunciated by R. Clausius. The generalization achieved by the Gibbs theory, however, came with a cost since the theory, with no kinetic equation, is limited to equilibrium phenomena and the underlying thermodynamics is necessarily that of reversible processes.

The Chapman–Enskog method and the Maxwell–Grad moment method for the Boltzmann kinetic equation are, in one aspect, theories attempting to generalize the Gibbsian ensemble theory to nonequilibrium theory, albeit for dilute gases. On the other hand, the theory of linear irreversible processes represents the phenomenological line of efforts to generalize equilibrium thermodynamics and receives statistical foundations through the first-order Chapman–Enskog solution of the Boltzmann equation. It makes the local equilibrium assumption to begin the development, but the assumption made for the basic structure of thermodynamics of irreversible processes has been troubling the subject field as it had J. Meixner, who may be regarded as one of founders of the linear theory of irreversible processes, simply because the Clausius entropy is a concept which is valid for reversible processes only. Therefore, the conclusion can be drawn that efforts toward a rational formulation of extended Gibbsian ensemble theory must first of all establish a rigorous thermodynamical theory of irreversible processes, albeit formal by necessity, firmly grounded in the laws of thermodynamics.

The realization of this essential point has come late in my winding course of study on kinetic theory and irreversible thermodynamics since 1975. This had a lot to do with the unfortunate fact that we often do not know exactly what shape our object of scientific inquiry will eventually take and even what we are looking for. The prevailing thoughts and modes of thinking in the community in which we found ourselves did not help in the matter, and if they turned out to be misleading they only detained progress. In the last few years it has been possible to acquire a mathematical representation of the second law of thermodynamics, as originally stated by

Clausius and Kelvin, which appears to be capable of serving the role for a nonequilibrium theory that the equilibrium thermodynamics does for the Gibbsian equilibrium ensemble theory. Another important piece of the mosaic of the nonequilibrium ensemble theory presented in this work is the demonstration that it is not necessary to solve the Boltzmann equation before constructing a rigorous formal theory of nonequilibrium statistical thermodynamics and a similarly rigorous formal theory of irreversible processes. It has been found sufficient to exploit the irreversibility and collision invariants of the Boltzmann kinetic equation and treat the equation formally, but exactly, for the purpose. In this manner the Boltzmann equation at long last is given a well deserved exact treatment so as to serve as the statistical mechanical foundations of irreversible thermodynamics. It turns out that what we have learned with the Boltzmann equation serves as a paradigm for other kinds of fluid, including dense fluids, since, after all, thermodynamics is a universal theory holding for all states of aggregation of matter, and different substances and states of aggregation are distinguished only by the constitutive equations which will have to be described by appropriate kinetic equations, if the processes are dynamic. The work presented in this monograph is in essence a set of examples showing that the aforementioned paradigm is capable of delivering nonequilibrium ensemble methods parallel with the equilibrium ensemble method of Gibbs. As is the Gibbsian theory based on postulates on the distribution function, the kinetic equations used are postulates that should satisfy a set of conditions on them. Therefore, practical applications of the theory should start with modelling kinetic equations meeting the conditions stated, and the justification of the theory is *a posteriori*, as is the case for the equilibrium ensemble theory. The modelling should be implemented on the collision term in the kinetic equation and its goodness will be determined by its ability to give transport properties experimentally studied. Our journey in the realm of science is personal in its essence, and one mode of journey, delightful to one, may be an intense discomfort to another. The modes are indeed diverse, and let them be. The solitary journey in the course of this work has been often lightened by the distant echoes which seem to reverberate from the depth of the Old Master Boltzmann's soul: "Alas, without me for eternity, the sun will rise in the east and will set in the west. Why suffer the pains but for just even a glimpse of Nirvana?" One still hopes for the day of the ultimate privilege.

This monograph has been written and prepared without a typesetter's assistance, thanks to the modern word processing softwares. The sophisticated word processing softwares, as powerful and versatile they are, can be heartbreaking to a novice. Much valuable technical assistance has been unstintingly given to me by my graduate student Mazen Al-Ghoul, who has also drawn many of the figures, and by Dr. Juan Gallego. I am grateful for their assistance. I would also like to thank Ms Margaret Deignan of Kluwer Academic Publishers for the interest in this work.

Finally, I would like to express my gratitudes to my wife Hui Young who has patiently carried with me the mental burden of writing a book throughout the course of this work. Without her constant and generous encouragements and understanding and her seeing to it that there is sufficient time for me to devote to this work, this monograph could not have been realized, incomplete as it seems, now that it is in a form to present.

Montreal
February 1997

B.C.E.

1

Introduction

Science is a collective human enterprise in which we continuously strive to achieve some coherent and rational understandings of how nature, our environs, and ourselves function. A collective effort implies that there is a system of rules and procedures according to which the individuals of the group endeavor to contribute to the general aim, and although such rules and procedures are ever refined and continuously reformulated over time so that they are better suited for the new questions to be answered, their evolution is such that the new ones are inclusive of the old in some manner and form whereas some of the old are simply discarded. The science of statistical mechanics is one of such strands of thoughts and methodologies known to serve the aforementioned aim.

Given the new atomic picture of the physical world emerging in the early part of the nineteenth century and the success of the Newtonian mechanics in accounting for macroscopic phenomena known at the time, the statistical mechanics of J. C. Maxwell [1] and L. Boltzmann [2] was an inevitable but revolutionary way of building a general theory of mechanical systems made up of an enormous number of subunits on the ideas of probability and Newtonian mechanics that was used to describe isolated collision events between the constituent subunits or dynamical events in the system. The word inevitable must be understood with suitable qualification since one might have had another way, although we have no idea even now what it might have been if it were different at all. The Maxwell–Boltzmann view was limited to the macroscopic phenomena in dilute gases, but the scope was widened, at least, for equilibrium phenomena in any state of aggregation of matter by the hands of J. W. Gibbs [3] some thirty years after Boltzmann published the work on his kinetic equation. The Gibbsian ensemble theory provides molecular pictures of physical systems consisting of an astronomically large number of constituent particles in a manner consistent with equilibrium thermodynamics which was formulated as a continuum theory devoid of the molecular concept for the system. Much of our current molecular understandings of macroscopic phenomena is achieved through the Maxwell–Boltzmann–Gibbs program of molecular theory for macroscopic phenomena, especially, in the case of equilibrium phenomena where the ideas of statistical mechanics of Maxwell, Boltzmann, and Gibbs are put into practice. The equilibrium theory is on firm foundations. The status of the theory of nonequilibrium phenomena, however, cannot be said

to be as firm and well established as is the Gibbsian ensemble theory of equilibrium phenomena, although there has been a great deal of work done by numerous authors in all directions of inquiry in the last five decades. The works of Chapman [4] and Enskog [5] on transport phenomena in dilute gases, based on theories of Maxwell and Boltzmann, were followed for dense fluids, especially after World War II, by new creative efforts of Bogoliubov [6], Born and Green [7], Kirkwood [8], and Yvon [9] and the theorists following their schools of thought. In parallel to this Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) line of work, the linear response theory was formulated by Green [10], Kubo [11], and Mori [12] and their followers from the early 1950s. The linear response theory aims to calculate transport properties of a system when the processes occur near equilibrium. It is a general theory with no restriction on the density of matter and the state of aggregation. The number of papers along the two lines of research is too numerous to cite them all here.

The evolution equation for the basic N -body probability distribution function in the aforementioned approaches is the Liouville equation, which is invariant with respect to time reversal. Since macroscopic thermodynamic processes are irreversible there is a troublesome aspect to the Liouville equation when one attempts to use it for description of systems exhibiting an irreversible behavior, and various stratagems have been used to introduce an element of irreversibility into the theories formulated. They appear implicitly in the guise of approximations, or by the device of coarse graining, or through the molecular chaos assumption, and so on. The efforts made along the lines of approach by the schools mentioned have so far not produced an ensemble theory for nonequilibrium phenomena in macroscopic systems which is comparable to the equilibrium Gibbs ensemble theory in generality and in the range of applicability. *The message to get across in this work, if the lengthy mathematical discourse necessary to develop the ideas underlying the theories is stripped away, is that the Liouville equation, whether for one particle or many particles, must have a collision term satisfying a set of conditions assuring its irreversibility and the existence of conservation laws if the Gibbs equilibrium ensemble theory is to be generalized to the nonequilibrium case.* We will find that the presence of such a collision term even sharpens the Gibbs equilibrium ensemble theory with regard to the uniqueness of equilibrium distribution function.

The work presented in this monograph is the fruit of efforts since 1980 [13] by the present author toward the general goal of the Maxwell–Boltzmann–Gibbs program for statistical mechanics of macroscopic systems consisting of molecules and particles. The evolutionary path taken by the present theory has been tortuous, since it has been inevitable to continuously revise the thoughts and directions of inquiry as we learn more with time and efforts made over the course of inquiry. The results of the early efforts for the goal can be found in my monograph [14] where I was not able to develop the nonequilibrium ensemble theory presented in this work.

The aforementioned program is, in essence, aimed at providing a general molecular theory of irreversible processes in macroscopic systems which obey the laws of thermodynamics. In other words, we wish to give molecular theory foundations to the thermodynamics of irreversible processes in systems at arbitrary degree of departure from equilibrium. A critical survey of the efforts made on the subject in the past will show that this program was made illusive from the start by the unfortunate fact that the mathematical representation of the second law of thermodynamics was historically limited to reversible or equilibrium phenomena and there has not been a mathematical representation of the second law of thermodynamics which maintains the same mathematical rigor for irreversible processes as for reversible processes. It is fair to say that the molecular theory of irreversible processes, namely, nonequilibrium statistical thermodynamics, has been missing its macroscopic and phenomenological counterpart to which the former aims to give molecular and statistical mechanical representation. Therefore the first task in nonequilibrium statistical thermodynamics lies in giving the second law of thermodynamics a rigorous mathematical representation and studying its continuum theoretical consequences [15] on the basis of which the description of irreversible processes can be carried out in sufficient generality and in a way consistent with the laws of thermodynamics. This task is performed in Chapter 2 of this monograph. The continuum theory of irreversible processes presented in Chapter 2 is minimal in the sense that only the essential aspects of irreversible thermodynamics necessary for nonequilibrium statistical thermodynamics that we aim to formulate in the later part of this work are presented. However, the theory of irreversible processes presented, albeit minimal in content, is new and contains what it takes to build a more encompassing theory which is reserved for a future exposition dedicated to the subject.

Equilibrium thermodynamics is an axiomatic formal theory of macroscopic reversible processes which gives a theoretical framework for relating diverse observable macroscopic properties to each other in a rigorous manner consistent with the laws of thermodynamics, which are empirical universal laws that are believed to axiomatically govern all dissipative macroscopic processes. Approximations in the theory appear only at the level of constitutive equations describing material properties to some approximations which stem from the limitations on measurements of the observables or our approximate or often inaccurate understanding of the processes of interest. Likewise, as a molecular theory underlying thermodynamics, the Gibbs equilibrium ensemble theory is also a formal theory which expresses thermodynamic quantities in terms of molecular models via the partition function and relates the observables to each other also in a rigorous manner. The theory generalizing the Gibbs equilibrium ensemble theory will be called the nonequilibrium ensemble theory in this work. Nonequilibrium generalizations of the aforementioned thermodynamic and statistical theories to macroscopic irreversible processes cannot be anything other than

formal theories in similar vein to their equilibrium counterparts, if such generalizations are to be sufficiently broad in coverage. It has been shown [16] that a formal treatment of the Boltzmann kinetic equation gives rise to a formal statistical theory of irreversible processes in dilute gases.

Equipped therewith and the thermodynamic theory of irreversible processes formulated on the basis of the laws of thermodynamics in a previous work [15], we have formulated a nonequilibrium ensemble theory for dilute gases on the basis of the Boltzmann equation in a previous work [17]. This method, at least in the case of dilute gases, generalizes the Gibbs equilibrium ensemble method to nonequilibrium to the desired degree of generality. The studies in the dilute gas theories have provided us with valuable and indispensable lessons, and thus a *paradigm* that can be tested for quantum gases and dense fluids. It turns out that the paradigm guides us to formulate a nonequilibrium ensemble theory not only for quantum gases but also for dense simple fluids so that the Gibbs equilibrium ensemble theory is generalized to a nonequilibrium simple fluid at arbitrary density and degree of removal from equilibrium.

Basically, the most important of the aforementioned lessons from the Boltzmann kinetic theory is that a formal thermodynamically consistent theory of irreversible processes can be constructed if the collision term in a kinetic equation satisfies a set of rather general conditions: (1) *existence of collision invariants*, (2) *satisfaction of the H theorem*, and (3) *invariance under canonical transformations*. The first condition guarantees the existence of the conservation laws of mass, momentum, and internal energy, whereas the second furnishes the Boltzmann entropy and its balance equation which has a positive source term—namely, the H theorem. The third condition is necessary for analytical dynamics purposes. Equipped with these formal properties and treated formally but exactly, the kinetic equation can be shown to provide a theory of irreversible processes in systems at arbitrary degree of removal from equilibrium and the accompanying statistical theory is the nonequilibrium ensemble method. It makes it possible to perform statistical mechanical computations of various macroscopic nonequilibrium quantities in terms of molecular parameters through the nonequilibrium partition function. We test this paradigm embodied by the aforementioned conditions and show its validity for the cases of classical monatomic gases, quantum gases, and dense simple fluids in this work. Only at the level of explicitly calculating the transport properties do we need an explicit model for the collision term in the kinetic equation. The transport properties are therefore the touchstone for assessing the validity of the models for the collision terms, since they are the link between the macroscopic phenomena and the molecular world. In the aforementioned monograph by the present author [14], some examples are shown for the collision term for dense fluids satisfying the conditions mentioned earlier. Therefore the present formal theory can be implemented for experimental comparisons by using such examples. For this reason we do not discuss such models in

this work. Only simple gases and liquids are discussed in this work since generalizations of the theories presented can be made straightforwardly to more complex fluids with internal degrees of freedom. The dense fluid theory is formulated by means of a nonequilibrium grand canonical ensemble distribution function expressed in local densities of energy, mass, and so on. This also adds a new aspect to the nonequilibrium ensemble method based on the nonequilibrium canonical form used in Chapter 7.

In Chapter 2 a mathematical representation of the second law of thermodynamics is presented for irreversible processes at arbitrary degree of removal from equilibrium by making use of the Clausius inequality. It must be remembered that Clausius in his pioneering work [18] in 1865 took the special case of a reversible process for his inequality and formulated the form of equilibrium thermodynamics known and practiced to this day. The case of irreversible processes was left barely touched, perhaps, for the future generations to resolve. Here we consider the inequality for the case left out by Clausius, namely, irreversible processes, and formulate a continuum theory of irreversible processes. The continuum theory formulated is the object to which the statistical mechanical theory is aimed to give molecular foundations by means of kinetic equations satisfying the set of conditions on them. The nonequilibrium generalization of the Clausius entropy for a reversible process appears in the form of calortropy¹ [15,17] which is a state function in the thermodynamic space spanned by the conserved and nonconserved variables characteristic of the irreversible processes occurring in the system. Therefore the calortropy differential is an exact differential in the thermodynamic space. Evolution of the thermodynamic variables appearing in the calortropy differential is described by a set of partial differential equations which we call the generalized hydrodynamics equations. (The terminology stems from the fact that they reduce to the classical hydrodynamics equations if the irreversible processes occur near equilibrium.) As a consequence, generalized hydrodynamics is an integral part of the theory of irreversible processes formulated in this work. Therefore it is not out of line to state that, as a molecular representation for the continuum theory of irreversible processes, the nonequilibrium ensemble theory is a nonequilibrium statistical thermodynamic theory of hydrodynamic processes in matter. It sets as its important aim the calculation of chemical potentials, pressure, and so on in terms of the nonequilibrium partition function and therewith the material functions of matter in hand.

Because of the prominent position which the Boltzmann equation occupies in the present work and the lessons to acquire therefrom, particular attention is paid to various aspects of the Boltzmann kinetic theory, including the functional hypothesis underlying the Chapman–Enskog method [19]

¹It means heat (*calor*) evolution (*tropy*). A similar coinage of a term made up of roots of Latin and Greek origins can be found in calorimetry.

and Maxwell–Grad moment method [20] which have been used for ‘solving the Boltzmann equation’. They are discussed in Chapters 3–6. In particular, some detailed discussions about the Chapman–Enskog first approximations for transport coefficients are given in Chapter 6 since the material functions for dilute gases in the present theory appear in terms of them. They are in fact the only material functions necessary for studying processes far from equilibrium if the theory is limited to the first-order cumulant approximation for the dissipation terms in the evolution equations for nonconserved variables. The reader well versed in Boltzmann kinetic theory may skip these chapters and directly proceed to Chapter 7 where the nonequilibrium ensemble method is treated in depth. The theories are developed in such a way that they immediately reduce to the first-order Chapman–Enskog theory as the system approaches a near-equilibrium state and, in the case of dense fluids, as the density becomes sufficiently low. In this sense the present theories are inclusive of the near-equilibrium and dilute gas theory of Chapman and Enskog. In Chapter 7 a noneqilibrium ensemble theory is developed for dilute gases by using a nonequilibrium canonical ensemble distribution function, and nonequilibrium macroscopic variables are expressed in terms of the nonequilibrium partition function. It is remarkable that such a theory along the line of Gibbs’s original idea of equilibrium ensemble theory can be developed by just exploiting only a set of general properties of the Boltzmann kinetic equation and, especially, of the Boltzmann collision term without having to find the solution of the kinetic equation. The realization that it is sufficient to exploit such general properties of the kinetic equation is the crucial key to the nonequilibrium ensemble theory formulated completely parallel with the Gibbs equilibrium ensemble theory. If one tries to achieve this objective by first solving the kinetic equation, then the task drowns in the flood of mathematical complications, since the solution can never be in a simple, let alone analytic, form and it is hard to see it all through. Working with such properties of the kinetic equation at the formal level, we have been able to discern the subtle difference, usually missed, between the Boltzmann entropy and the statistically defined calortropy, and therefore the importance of the role played by the relative Boltzmann entropy making up the difference between them. The relative Boltzmann entropy, as shown in Chapter 7, is not a state function in the thermodynamic space spanned by thermodynamic variables. Therefore any statistical theory of irreversible processes formulated on the premise of the Boltzmann entropy being a state function in such a space is invalid. It should be emphasized that *the Boltzmann entropy is not a state function in the thermodynamic space*. Associated with this point is the conclusion that *the H theorem is not the statistical mechanical equivalent of the second law of thermodynamics, but a theorem for the asymptotic stability of the steady state solution of the Boltzmann equation*.

The relative Boltzmann entropy can be expressed in terms of fluctuations

in temperature, pressure, chemical potentials, and generalized potentials. The evolution of these fluctuations can be deterministically described by their evolution equations derived from the kinetic equation. All these topics are discussed in detail in Chapter 7. If deterministic predictions of the fluctuations in temperature, chemical potentials, and so on are abandoned and a probabilistic description is sought for them, the Boltzmann relative entropy provides a means of generalizing the Einstein fluctuation theory [21]. This is also shown. In fact, a stochastic treatment of fluctuations gives rise to a concept of thermodynamic quantization, thermodynamic commutation relations, and eventually thermodynamic uncertainty (complementarity) relations for systems removed from equilibrium. Complementarity relations in thermodynamics were thought to be possible by Bohr [22], Heisenberg [23], and others. It is shown in Chapter 7 that such complementarity relations indeed hold for nonequilibrium systems [24] if the fluctuations are treated stochastically by generalizing to nonequilibrium the method used by Schlögl [25] to discuss thermodynamic complementarity relations for equilibrium systems.

A new theory must be inclusive of the well established old theories as special cases. Therefore it is important to demonstrate that this is the case for the present nonequilibrium ensemble theory. Moreover, it is equally important to show the capability of the new theory and its range of validity if possible. In the present theory the generalized forms of the classical hydrodynamics equations such as Navier–Stokes', Fourier's, and Fick's equations are the evolution equations for macroscopic variables underlying the irreversible processes of interest. The recovery of the latter from the former is discussed in Chapter 8. The theory then is applied to some fluid dynamics problems involving steep gradients or for systems far removed from equilibrium where the traditional linear constitutive laws such as Newton's law of viscosity and Fourier's law of heat conduction are incapable of properly describing fluid dynamic flow processes. Generalized hydrodynamics is thus demonstrated to have capabilities of yielding correct results for flow problems of practical interest. In particular, it has been successful in giving shock structures in gases which are in excellent agreement with experiment. Since the Navier–Stokes theory has not been useful for shock structures and there has not been a continuum hydrodynamics theory that can substitute for the Navier–Stokes theory, the success with the shock structures of the present generalized hydrodynamics within the framework of the theory of irreversible processes is very encouraging and even exciting; it is, in fact, a resolution of a long-standing problem in the continuum theory of shock structures in a rather simple form.

The nonequilibrium ensemble theory for the classical gases can be generalized to include quantum gases. This generalization can be approached by means of either the density matrix or the corresponding Wigner distribution function [26] obeying a suitable kinetic equation, provided that the kinetic equation again satisfies the set of conditions mentioned ear-

lier. We have implemented such a generalization by using a modification of the Boltzmann–Nordheim–Uehling–Uhlenbeck (BNUU) kinetic equation [27,28] in Chapter 9. The same results are demonstrated to arise from the density matrix version of the modified BNUU kinetic equation for a Wigner distribution function. A similar generalization should be possible for relativistic Boltzmann equations, but the subject is not discussed for lack of space and is left for the reader as an exercise since the necessary ingredients for a relativistic nonequilibrium ensemble theory are already available in [14].

The theories described for dilute gases can be generalized in the direction of dense fluids. The dense fluid kinetic theory has been a vexing subject, and the interest in it has considerably waned in recent years, probably because of inherent difficulties of the subject on the one hand and the advent of computational statistical mechanics [29,30] on the other. Even though numerical simulations can yield sensible looking results for macroscopic properties and they are the methods on which we will heavily depend in the future, they nevertheless need formal theories of irreversible processes and nonequilibrium statistical mechanics to equip them with sound conceptual frameworks within which one can carry out numerical simulations at arbitrary degree of removal from equilibrium. We study the nonequilibrium ensemble theory for dense fluids with that aim in mind. It is hoped that the formal theory presented in Chapter 10 will be the starting point of numerical simulation studies after the formulas have been cast in forms more suitable for numerical computations. Regardless of whatever use one might have for the results obtained, it is shown that a nonequilibrium ensemble theory can be formulated with a kinetic equation satisfying the same set of conditions as for the case of dilute and quantum gases. Such a kinetic equation allows the formulation of a statistical theory of irreversible processes underlying the nonequilibrium ensemble method for a dense simple fluid, and we find that the structures of the evolution equations for conserved and nonconserved variables constituting the generalized hydrodynamics remain the same as for those of the dilute gas counterparts. This suggests the generality of the generalized hydrodynamics which is derived from the kinetic equation and in the basis of the theory of irreversible processes in this work. This is as it should be, since irreversible thermodynamics is a formal theory which axiomatically satisfies the laws of thermodynamics and in which different matters are distinguished only by different constitutive equations. The nonequilibrium partition functions in principle will facilitate calculations of such constitutive equations, and there lies hard work in store for us since nonequilibrium partition functions are not trivial to calculate satisfactorily.

The nonequilibrium ensemble methods for dilute gases, both classical and quantum, can be implemented explicitly for practical systems if the collision bracket integrals appearing in the Chapman–Enskog first approximation can be calculated for a given potential model. The collision bracket

integrals are cast in such forms readily calculable from the results available in the literature. The formal expressions for the collision bracket integrals and the constitutive equations for nonconserved variables for dense simple fluids are available in [14]. However, there is a great deal of work to be done before the formal expressions for the collision bracket integrals for dense fluids are put into forms comparable in explicitness to the dilute gas counterparts in the Boltzmann kinetic theory. The present nonequilibrium ensemble theory provides the theoretical framework and the mathematical apparatus consistent with the thermodynamic principles for nonequilibrium phenomena in dense fluids.

In summary, we now have in the nonequilibrium ensemble methods presented in this work formal statistical mechanical theories of irreversible processes which extend the Gibbs equilibrium ensemble theory to the nonequilibrium regime for gases and liquids. Such theories have been made realizable by the kinetic equations assumed to satisfy a set of general conditions guaranteeing the conservation laws and the H theorem. Construction of the collision term of such a kinetic equation is an important task before us. Since we know what is required of the collision term, it is not impossible to find it, as is usually the case when we know what we are looking for, and some examples discussed in [14] should provide insight, if not an answer to the question. Except for the presence of generalized hydrodynamics equations which are essential components of the attendant irreversible thermodynamics, the structure of the nonequilibrium theory is completely parallel with Gibbs's equilibrium ensemble theory, and there is thus a hope for the Maxwell–Boltzmann–Gibbs program to be completed for nonequilibrium along the line of the theories presented.

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2

Thermodynamics of Irreversible Processes

The thermodynamics of irreversible processes is a continuum theory of processes in matter with no reference to its molecular constitution. The reductionist tradition of natural philosophy, however, inevitably requires molecular theoretical foundations in the form of a particulate theory of matter based on the concept of particles (*e.g.*, atoms and molecules) currently held in science. The kinetic theory of fluids has been primarily developed to provide macroscopic phenomena and thermodynamics of reversible and irreversible processes in continuum matter with molecular theoretical foundations. In such a theory a suitable kinetic equation is used for the distribution function of the system in the phase space or the Hilbert space, but in practice the solution of the kinetic equation is sought in such a way as to help understand at the thermodynamic level of description the macroscopic phenomena which we experience or observe in nature and in the laboratory. Therefore the solution is a particular solution corresponding to our thermodynamic level of understanding of the natural phenomena of interest. It is then inevitable that we examine what is really meant by the thermodynamic level of description in the first place. In the course of our scientific training we have been taught thermodynamics of reversible processes, and a great deal of our scientific reasoning and thinking processes is molded and influenced by equilibrium thermodynamics, especially when we are concerned with macroscopic phenomena in continuum matter, but the subject is not very useful for us when we face irreversible macroscopic processes. Consequently our first task in attempting to study the kinetic theory of matter is in establishing a theoretical formalism for macroscopic phenomena in continuum matter on the foundations of the laws of thermodynamics as we know of at present in the forms proposed by their formulators. We then develop a solution procedure for the kinetic equation for the distribution function of matter in the phase space or the Hilbert space depending on whether the classical or quantum mode of description is adopted for the development of the theory, in such a way that the thermodynamics of irreversible processes is described from the molecular viewpoint. We are thus motivated to develop first a thermodynamic theory of irreversible processes without using the molecular picture of matter. In this endeavor we take the position that the first task is to develop

a logical structure within the framework of the original form of the laws of thermodynamics as phrased by their formulators. Since the most difficult and unsettled part of the theory is concerned with the mathematical representation of the second law of thermodynamics, we will devote close attention to it, but will be brief with the representation of the first law of thermodynamics and other conservation laws as well as the zeroth law regarding the temperature, since there is nothing new for us to add to them at present. Applications of the theory developed for irreversible processes will be deferred to a later chapter. We will assume 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, but it is easy to modify the theory to include the case of chemical reactions. After completing the formulation of the theory under the assumptions taken, we will point out where the necessary modifications must be made to include chemical reactions. Since the kinetic theory part of this work does not deal with fluids with an angular momentum, we will not consider the irreversible thermodynamics of such fluids.

2.1 The Zeroth Law of Thermodynamics

If two bodies of different degrees of hotness are put into contact, they eventually reach thermal equilibrium. This phenomenon can be exploited to quantify the measure of hotness or coldness of systems. The following statement of the zeroth law of thermodynamics [1,2] provides a general procedure for quantification of temperature as a measure of hotness of a system.

The Zeroth Law of Thermodynamics *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.*

In other words, if there exists thermal equilibrium between A and C, there is a property called temperature θ such that

$$\theta_a = \theta_c \quad (2.1)$$

and similarly for systems B and C

$$\theta_b = \theta_c. \quad (2.2)$$

Therefore there follows the equality

$$\theta_a = \theta_b. \quad (2.3)$$

This relation supplies a means of devising thermometers and therewith quantify temperature. The details are to be found in the literature on

measurements of temperature [3]. In this work we will use the absolute temperature scale throughout.

The parameter θ requires thermal equilibrium between a body A and a thermometer B if it is to be quantified to a well defined value, but the term thermal equilibrium does not necessarily mean that body A is internally in thermodynamic equilibrium by itself. It may be a system where a number of irreversible processes are in progress at a value of θ . 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. Another example is a metallic bar subjected to different temperatures at two ends. It is well known that the temperature has a distribution between the two endpoints. By this we mean that if infinitesimally thin imaginary slices of the metal are taken perpendicular to the direction of heat flow and put into thermal equilibrium with a thermometer, the temperature values recorded along the direction of heat flow show different values 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. 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. 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 are 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 for a local elementary volume of the body at time t if the body is in a nonequilibrium condition.

2.2 The First Law of Thermodynamics

The first law of thermodynamics was formulated as a culmination of the understanding of what is meant by heat and its relation to energy. Without going into a discussion on its historical account [4–6] of how it came into being, we will simply state it. Before doing so it is necessary to establish sign conventions on heat transfer and work performed.

Sign convention on heat transfer *Heat transfer is counted negative if heat is given up by the system to the surroundings and as positive if heat is taken up by the system from the surroundings.*

Sign convention on work *Work is counted as positive if it is done on the system by the surroundings and as negative if it is done on the surroundings by the system.*

We state the first law of thermodynamics in the following two equivalent forms:

The First Law of Thermodynamics

(1) *The energy of an isolated system is constant.*

Equivalently:

(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 was made by Clausius [7]. It is a little obtuse. 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 statement in essence is ascribed to Planck [8]. These equivalent statements can be given a mathematical representation as follows. Let us denote a differential heat change by dQ and a differential work by dW . Then, under the sign conventions adopted earlier for heat and work the differential of the internal energy dE , regardless of whether the process is reversible or irreversible, is given by

$$dE = dQ + dW, \quad (2.4)$$

and for a cyclic process¹ the first law of thermodynamics is traditionally expressed by the vanishing closed contour integral for a cyclic process

$$\oint dE = 0, \quad (2.5)$$

where the contour integral is to be performed over the cycle in the space of macroscopic variables characterizing the thermodynamic state of the system; the cyclic process involved can be reversible or irreversible. We will later be more specific about what is really meant by the thermodynamic space. For now it means a space of macroscopic observables in which the thermodynamic state of the system is described. The vanishing closed contour integral (2.5) means that dE is an exact differential in the aforementioned thermodynamic space. We also remark that (2.5) is equivalent to the statement that heat is a form of energy, as mentioned earlier, since on substitution of (2.4) into (2.5) we obtain

$$Q = \oint dQ = - \oint dW = -W. \quad (2.6)$$

¹A 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 contour (or, alternatively, cyclic) integrals consequently play important roles in the formulation of the thermodynamics of irreversible processes.

If time is used as a parameter for E , then the closed contour integral in (2.5) may be written as an integral over a period τ of the cyclic motion

$$\int_0^\tau dt \frac{dE}{dt} = 0. \quad (2.7)$$

It must be noted here that this mathematical representation is for the global system comprising the cycle, namely, the working substance in the whole system which goes through the cyclic process in question.

However, many macroscopic processes in nature are described from the local theory viewpoint. Typical examples will be various flow processes in fluid dynamics where local field variables of fluids are assumed to obey partial differential equations. Since flow phenomena in fluids must obviously be subjected to the laws of thermodynamics 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. This is easily done by following the method of continuum mechanics [9]. We will simply present the results without going through the details of derivation for local conservations laws.

2.3 Local Forms of the Conservation Laws

In addition to the first law of thermodynamics the system must obey the mass conservation law and the momentum conservation law as a continuum extension of Newton's law of motion. Here we present them as a proposition.

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

mass:

$$\rho d_t v = \nabla \cdot \mathbf{u} \quad \text{or} \quad \frac{\partial \rho}{\partial t} = -\nabla \cdot \rho \mathbf{u}, \quad (2.8)$$

mass fractions:

$$\rho d_t c_a = -\nabla \cdot \mathbf{J}_a, \quad (2.9)$$

momentum:

$$\rho d_t \mathbf{u} = -\nabla \cdot \mathbf{P} - \rho \mathbf{F}, \quad (2.10)$$

energy:

$$\rho d_t \mathcal{E} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{F}_a \cdot \mathbf{J}_a. \quad (2.11)$$

The absence of a rotational angular momentum implies that the stress tensor is symmetric by virtue of the angular momentum conservation law: $\mathbf{P} = \mathbf{P}^\dagger$. These conservation laws can be easily derived [10] from the global

conservation laws by using the method of continuum mechanics. Here ρ is the mass density; v is the specific volume $v = \rho^{-1}$; \mathbf{u} is the fluid velocity; c_a is the mass fraction of species a defined by $c_a = \rho_a / \rho$ where ρ_a is the mass density of species a ; \mathcal{E} is the energy density defined by $E = \rho\mathcal{E}$ where E is the internal energy per volume; $\mathbf{J}_a = \rho_a(\mathbf{u}_a - \mathbf{u})$ is the mass diffusion flux where \mathbf{u}_a is the mean velocity of species a ; \mathbf{P} is the total pressure tensor (stress tensor) of the fluid which can be decomposed into species pressure tensors \mathbf{P}_a :

$$\mathbf{P} = \sum_{a=1}^r \mathbf{P}_a;$$

\mathbf{F} is the external force density which can be also decomposed into species contributions

$$\mathbf{F} = \sum_{a=1}^r c_a \mathbf{F}_a,$$

where \mathbf{F}_a denotes the external force on species a at position \mathbf{r} ; and \mathbf{Q} is the heat flux which can be decomposed into species contributions

$$\mathbf{Q} = \sum_{a=1}^r \mathbf{Q}_a.$$

Finally, d_t is the substantial time derivative defined by

$$d_t = \frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla.$$

This symbol is reserved for the substantial time derivative throughout this work unless stated otherwise. Eqs. (2.8)–(2.11) 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 ρ , c_a , \mathbf{u} , and \mathcal{E} . We notice that these field equations contain the variables \mathbf{J}_a , \mathbf{P} , and \mathbf{Q} in addition to the aforementioned variables, which are called the conserved variables since they obey the conservation laws. The additional variables \mathbf{J}_a , \mathbf{P} , and \mathbf{Q} are examples of nonconserved variables, and in the theory of linear irreversible processes or in the conventional classical hydrodynamics they are specified by means of constitutive relations characterizing the substance of interest. These traditionally used constitutive relations are not necessarily the most general forms to describe the evolution of the nonconserved variables in question. There is a considerable body of experimental and kinetic theory evidence that they require suitable generalizations. Examples for such necessity can be found in rheology [11], and nonlinear phenomena in semiconductor physics, heat transport [10], and so on. To make the theory we have in mind as general as possible we will introduce a new set of symbols for the nonconserved variables. We will denote the nonconserved variables by $\Phi_{ka} = \rho \hat{\Phi}_{ka}$ where

$1 \leq a \leq r$ and $k \geq 1$. The set of nonconserved variables will be suitably ordered:

$$\Phi_{1a} \equiv \boldsymbol{\Pi}_a = \frac{1}{2}(\mathbf{P}_a + \mathbf{P}_a^t) - \frac{1}{3}\boldsymbol{\delta}\text{Tr}\mathbf{P}_a,$$

$$\Phi_{2a} \equiv \Delta_a = \frac{1}{3}\text{Tr}\mathbf{P}_a - p_a,$$

$$\Phi_{3a} \equiv \mathbf{Q}'_a = \mathbf{Q}_a - \hat{h}_a \mathbf{J}_a,$$

$$\Phi_{4a} \equiv \mathbf{J}_a, \quad \text{etc.,}$$

where the boldface $\boldsymbol{\delta}$ denotes the unit second rank tensor, p_a the hydrostatic pressure of species a , and \hat{h}_a the enthalpy per unit mass of species a . The set of nonconserved variables can include as many nonconserved variables as necessary for the proper description of the process in hand. These nonconserved variables are regarded as field variables as the conserved variables are. In some cases, they may be changing on different, usually faster, time scales and shorter spatial scales than the conserved variables, but, in some other cases, they may be changing on time and spatial scales comparable to those for 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 an equal footing with regard to the time and spatial scales. 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. This turns out usually to be the case in practice. Having formed this viewpoint we now make the following proposition for the evolution equations for nonconserved variables Φ_{ka} . Since the nonconserved variables are field variables they obey partial differential equations. These equations take the form of a balance equation with a source term because the nonconserved variables are not conserved in time. It will be found convenient to assume a general form for the evolution equation for the nonconserved variables as below.

Proposition 2 *The nonconserved variables $\hat{\Phi}_{ka}$ ($k \geq 1$; $1 \leq a \leq r$) obey the evolution equation*

$$\rho d_t \hat{\Phi}_{ka} = -\nabla \cdot \boldsymbol{\psi}_{ka} + \mathcal{Z}_{ka} + \Lambda_{ka}, \quad (2.12)$$

where $\boldsymbol{\psi}_{ka}$ is the flux of Φ_{ka} , \mathcal{Z}_{ka} is called the kinematic term, which contains a term driving the process Φ_{ka} among other terms nonlinearly depending on nonconserved variables and gradients of the conserved variables, and Λ_{ka} is called the dissipation term, which is responsible for energy dissipation arising from the process Φ_{ka} .

The dissipation terms are generally algebraic functions of conserved and nonconserved variables. They also depend on material parameters such as

transport coefficients, density, pressure, and so on. Since the kinematic and dissipation terms have different physical origins and characteristics, we have put them as separate terms in the evolution equation (2.12). However, they could have been combined as a single term. It is possible to give statistical definitions for the kinematic and dissipation terms as will be shown in a later chapter on kinetic theory and their examples are given in Table 2.1. However, their explicit forms in terms of conserved and nonconserved variables are not necessary for the formal theory of irreversible processes we have in mind in this chapter. As will be seen, they will be subject to the constraint of the second law of thermodynamics, and in this sense the theory developed here is fully consistent with the second law of thermodynamics. It is remarked that the linearized versions of the evolution equations for the stress tensor and heat flux were known to Maxwell [12] as the transfer equations, on which he based his calculation of transport coefficients under the steady state assumption, and Chapman [13] later used them in his theory of linear transport processes in gases.

2.4 The Second Law of Thermodynamics

Unlike the first law of thermodynamics which cannot dictate the direction in which a reversible or irreversible macroscopic process proceeds, the second law of thermodynamics endows spontaneous natural processes with a quality progressing in one direction in time. This law is a summary of inviolable experimental facts of the unidirectional temporal evolution which spontaneous macroscopic processes in nature possess, and that is presented as an axiom. Historically it is rooted in the theorem of Carnot [14] which can be stated as follows:

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 η_{rev} and that of an irreversible cycle by η_{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 η_{rev} is a function of only the temperatures of the heat reservoirs of the Carnot cycle and the prime denotes another reversible cycle.

Consider two cycles 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 work² W_{rev} whereas the irreversible cycle does work W , both having re-

²The absolute value of work is used in this part of discussion.

ceived 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 [10] as a corollary of 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 available to the irreversible cycle.

If that amount of unavailable work is denoted by W_{ua} , then the reversible work W_{rev} may be decomposable into the form

$$W_{\text{rev}} = W + W_{\text{ua}} \quad (2.13)$$

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 [7].

This theorem of Carnot led Clausius [15] and Lord Kelvin (William Thomson) [16] 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 equivalent³ 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 development, it must be the goal for the theory of irreversible processes before an alternative or amended form of the second law is proposed or formulated.

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

³It 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.

reversible cycles operating between two heat reservoirs of temperatures T_1 and T_2 where $T_1 > T_2$. These temperatures are in the absolute scale. 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_{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

$$1 - \frac{Q_2}{Q_1} \leq 1 - \frac{T_2}{T_1}. \quad (2.14)$$

Clausius [7] rearranges (2.14) to the form

$$-\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \geq 0 \quad (2.15)$$

and argues that this inequality can be cast in an integral form by imagining a series of infinitesimal Carnot cycles:

$$-\oint \frac{dQ}{T} \geq 0 \quad (2.16)$$

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 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 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 which 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 elucidated⁴ in order to formulate

⁴In this connection I would like to quote a passage in an article by Prigogine

a thermodynamic theory of irreversible processes. Following Clausius, we denote it by N and express the Clausius inequality (2.14) as

$$N = - \oint \frac{dQ}{T} \geq 0. \quad (2.17)$$

Note that 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 [7] suggested calculating N by using (2.17) where the contour integral of the cycle must be performed along an irreversible path which includes at least one irreversible step. *Here we interpret the Clausius equation (2.17) differently, and recognize the compensated and uncompensated heats as two independent entities that must be elucidated in terms of the system properties for irreversible processes.* It is easy to see that there are such two independent physical entities if the aforementioned corollary to the Carnot theorem is recalled. First, by 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 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:

$$\frac{T_2}{T_1} = \frac{Q_2}{Q_1} - \frac{W_{\text{ua}}}{Q_1}. \quad (2.18)$$

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

$$\frac{Q_2}{T_2} = \frac{Q_1}{T_1} + N. \quad (2.19)$$

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

$$N = - \left(\frac{Q_1}{T_1} - \frac{Q_2}{T_2} \right) = - \sum_i \frac{Q_i}{T_i}, \quad (2.20)$$

which gives rise to (2.17) when passage is made from the sum to the contour 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

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 the S production here as being meant for the uncompensated heat, despite the notation S used for entropy in the aforementioned paper.

when the work is compared with the work of the reversible cycle. It is evidently intrinsic to the system, namely, the irreversible cycle in hand, and should be treated as a separate entity from the compensated heat.

Since a precise mathematical representation for the uncompensated heat was not known at the time of Clausius except that there should exist such a quantity, Clausius specialized to reversible processes for which $N = 0$ and developed the theory of equilibrium thermodynamics, namely, thermostatics, with which we are all familiar at present. If N is set equal to zero for a reversible cyclic process⁵, then there holds the equality

$$\oint \frac{dQ}{T} = 0, \quad (2.21)$$

which implies that there exists a state function S_e which Clausius called the entropy [6] of the system and defined by the differential relation

$$dS_e = \left(\frac{dQ}{T} \right)_{\text{rev}} \quad (2.22)$$

such that

$$\oint dS_e = 0. \quad (2.23)$$

In other words, 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 (2.4) for the first law of thermodynamics is called the equilibrium Gibbs relation. It is the basis of equilibrium thermodynamics. Keep it in mind that the Clausius entropy is defined for reversible processes only.

Before proceeding further to consider irreversible processes in a general context, we briefly examine the gist of the theory of linear irreversible processes as formulated by Onsager [17], Meixner [18], Prigogine [19], and so on. First, by interpreting the differentials of macroscopic observables to mean their substantial time derivatives, the equilibrium Gibbs relation for the Clausius entropy

$$dS_e = T^{-1} (dE - dW) \quad (2.24)$$

is cast into a local form which may be written as

$$d_t S_e = T^{-1} (d_t \mathcal{E} - d_t \mathcal{W}), \quad (2.25)$$

where d_t is the substantial time derivative introduced earlier and S_e , \mathcal{E} , and \mathcal{W} are local densities of the Clausius entropy, internal energy, and work,

⁵Reversible processes are traditionally defined as those of quasi-static processes which are in continuous equilibrium with the surroundings, but it is more precise to define them as quasi-static processes for which $N = 0$. This will be the definition used throughout in this work.

respectively. It is important to recognize that the derivatives in (2.24) are interpreted as substantial time derivatives in the local form (2.25). The theory of linear irreversible processes [20] assume the validity of the local equilibrium Gibbs formula which is combined with the conservation laws presented earlier for the conserved variables appearing in the right hand side of (2.25). This assumption is called the local equilibrium hypothesis. On combining this assumption with a set of linear thermodynamic force—flux relations as the constitutive relations for fluxes appearing in the conservation laws, we obtain in essence the theory of linear irreversible processes. The resulting field equations are the classical hydrodynamics equations, namely, the Navier–Stokes, the Fourier, and the Fick equation in the conventional hydrodynamics [21]. It must be remembered that 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 (2.25) when the process in question is not reversible. The theory 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 [22] who was also one of the formulators of the theory of linear irreversible processes. His attempt to resolve this vexing question was not successful. Since the early 1960s there have appeared propositions [8,23–30] that extend the thermodynamic space for systems undergoing irreversible processes to include nonconserved variables as a generalization of the local equilibrium hypothesis to nonequilibrium system. The differential form for the nonequilibrium entropy *which these theories postulate* is called the extended Gibbs relation and forms the starting equation for the subject field of extended irreversible thermodynamics⁶. This postulate for the extended

⁶There are basically two different versions of extended irreversible thermodynamics: one class of versions can be found in [23]–[30] and the other in [10] 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, for example, the information entropy for dynamical systems. In the latter class (*i.e.*, in [10]) it is shown from the second law of thermodynamics that there exists a quantity called the compensation function (renamed calentropy in this 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 the thermodynamics of irreversible processes must be securely founded on the laws of thermodynamics, it is crucial to show that the basic equations are consistent with the laws of thermodynamics 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 laws of thermodynamics in accounting for macroscopic processes in nature. Neither can the laws of thermodynamics afford approximate representations. The basic thermodynamic equation in the formulation made in [10] and in this work is a rigorous consequence of the second law of thermodynamics which mathematically extends equilibrium ther-

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 [27–32] to provide its kinetic theory basis in terms of the well known H theorem of Boltzmann. However, it must be recognized that Boltzmann's H theorem itself should not simply be taken as an equivalent of the second law of thermodynamics as is often and uncritically done in kinetic theory and irreversible thermodynamics. This statement will be shown to be true in a later chapter of this work when we discuss the kinetic theory foundations of the thermodynamics of irreversible processes. Besides this point just mentioned, 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 extended irreversible thermodynamics, 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. The theory presented below is addressed to resolve these questions and put the formalism on firmer foundations of the laws of thermodynamics. It is 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 proved inadequate on application to irreversible processes in nature.

To proceed further from the Clausius inequality (2.16), which is not the most useful mathematical form of representation for the second law, we observe that the uncompensated heat in (2.17) may be written as a contour integral over the cycle in hand:

$$N = \oint dN \geq 0, \quad (2.26)$$

where dN , or more precisely, dN/dt should be always positive except for reversible processes, for which it vanishes. Otherwise it would be possible to devise⁷ a cyclic process in such a way that it vanishes or is negative, violating the second law of thermodynamics.

By combining (2.26) with (2.17) we obtain the equation [10,33]

$$\oint \left(\frac{dQ}{T} + dN \right) = 0. \quad (2.27)$$

modynamics that is certainly endowed with a physical basis supported by the second law; it is not an assumption as in [23]–[30].

⁷A simple, albeit somewhat ideal, example would be a cycle consisting of the irreversible segment where $dN < 0$ and a reversible segment for the remainder of the cycle. This cycle, if possible to construct, would violate the second law.

This vanishing contour integral implies that there exists a state function Ψ in the thermodynamic space such that

$$d\Psi = \frac{dQ}{T} + dN \quad (2.28)$$

and

$$\oint d\Psi = 0. \quad (2.29)$$

Note that the differential form (2.28) and the contour integral (2.29) 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 result: namely,

$$d\Psi|_{\text{rev}} = \left. \frac{dQ}{T} \right|_{\text{rev}} = dS_e \quad (2.30)$$

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

$$\Psi_{\text{rev}} = S_e. \quad (2.31)$$

This quantity Ψ was previously called the compensation function. 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 chapter it is different from the Boltzmann entropy or the information entropy [34] for nonequilibrium processes. Since the Boltzmann entropy for a nonequilibrium system is often called the nonequilibrium entropy, it will be preferable to call Ψ by another term. Henceforth it will be called by the new term *calortropy* which means heat (*calor*) evolution (*tropy*).

With (2.5) and (2.29), the first and the second law of thermodynamics are expressed by a pair of vanishing contour integrals of internal energy and calortropy in the case of a cyclic process. This pair of vanishing contour integrals, equivalently, the corresponding differential forms (2.4) and (2.28), provides us with the starting point of a mathematical theory of thermodynamics of irreversible processes.

Let us now examine the relation of (2.29) to the Clausius–Duhem inequality. Clausius [7] considered a cyclic process consisting of a segment of irreversible process which starts from state A and ends at state B that are embedded⁸ in the equilibrium part of the thermodynamic space, and

⁸In his work Clausius made no mention of embedding the states A and B in the equilibrium part of the thermodynamic space. 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 space. It now is well recognized that there was no clear notion of thermodynamic space in the Clausius formulation of the second law of thermodynamics.

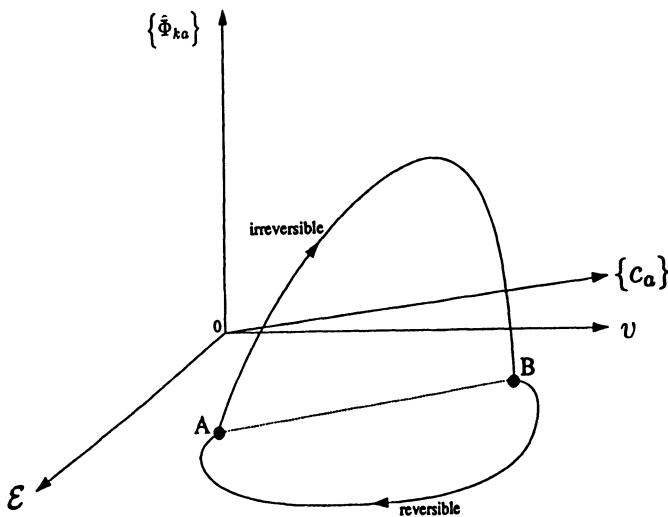


FIGURE 2.1 A cycle consisting of an irreversible and an reversible segment. This figure is a rendering in the thermodynamic space of the irreversible cycle from which Clausius deduced the Clausius–Duhem inequality. In the formulation of Clausius the concept of thermodynamic space is absent. The reversible segment is embedded in the equilibrium part of the thermodynamic space. This cycle is a special, somewhat ideal, case because of the presence of a reversible segment.

another segment of reversible process which reversibly restores the system at state B to its original thermodynamic state A ; see Fig. 2.1. In the sense of the condition imposed on states A and B this cyclic process is rather special, since the system must start from an equilibrium state and end at an equilibrium state but through a nonequilibrium path in the thermodynamic state space. For this cyclic process the vanishing contour integral (2.29) can be written as

$$\int_{A(\text{rev})}^B d\Psi = \int_{A(\text{irr})}^B d\Psi, \quad (2.32)$$

where the subscripts attached to the integrals, rev and 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

$$\int_{A(\text{rev})}^B d\Psi = \int_{A(\text{rev})}^B dS_e = S_e(B) - S_e(A) = \Delta S_e. \quad (2.33)$$

On use of (2.28) the right hand side of (2.32) can be written as

$$\int_{A(\text{irr})}^B d\Psi = \int_{A(\text{irr})}^B \left(\frac{dQ}{T} + dN \right). \quad (2.34)$$

Furthermore, by the second law of thermodynamics

$$\int_{A(\text{irr})}^B dN \geq 0. \quad (2.35)$$

Since by virtue of Ψ being a state function in the thermodynamic space

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

the following inequality holds:

$$\Delta\Psi \geq \int_{A(\text{irr})}^B \frac{dQ}{T}. \quad (2.36)$$

The differential form for this is

$$d\Psi \geq \frac{dQ}{T}, \quad (2.37)$$

which follows from (2.28) since $dN \geq 0$. Therefore it is concluded that $\Delta\Psi \geq 0$ always holds for an isolated system. Eqs. (2.32) and (2.36) also imply the Clausius–Duhem inequality

$$\Delta S_e \geq \int_{A(\text{irr})}^B \frac{dQ}{T} \quad (2.38)$$

under the sign convention adopted for heat transfer. Thus the Clausius–Duhem inequality⁹ is contained in the present expression for the second law of thermodynamics (2.29).

⁹The inequality (2.38), together with (2.32) and (2.33), seems to mean 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 ΔS_e is for the reversible segment complementary to the irreversible step making up the cycle in question, and the inequality (2.38) simply means that $\Delta S_e = \int_{A(\text{rev})}^B dQ/T$ for the reversible segment is always larger than that of the irreversible compensated heat change. If the system is isolated during the irreversible process only, the compensated heat $dQ = 0$ everywhere in the interval of integration, and hence $\Delta S_e \geq 0$. If the system is isolated during the entire cycle, it is clearly appropriate to think in terms of $\Delta\Psi \geq 0$ instead of $\Delta S_e \geq 0$ since the system cannot reversibly return to state A from state B without a compensation from the surroundings, but there are no surroundings for an isolated system to compensate for the system to return to state A from state B .

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, namely, the integral, 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. 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 Ψ defined by (2.28) or (2.29), which is the properly generalized form for a mathematical representation of the second law of thermodynamics. Instead of looking for an inequality like (2.38), by using the fact that $d\Psi$ is an exact differential we may simply write (2.32) in the form

$$\Delta S_e = \Delta\Psi = \Psi(B) - \Psi(A) \quad (2.39)$$

for the cyclic process considered by Clausius. Therefore for such a special process starting from an equilibrium state and ending at an 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. 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. Eq. (2.39) 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 (2.39) is for global changes, but not for local changes in a system not isolated. In the case of a local irreversible process it is not possible to transcribe (2.39) into the equality

$$d\Psi = dS_e, \quad (2.40)$$

since

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

Pursuing this discussion a little further, we remark that in the linear theory of irreversible processes [17–20] the entropy density change dS in a system is written as $dS = dQ/T + dN$ in the present notation. In the light that (2.40) 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 $d\Psi$.

The differential forms for the first and second law of thermodynamics (2.4) and (2.28) can be combined to the form

$$d\Psi = T^{-1}(dE - dW) + dN. \quad (2.41)$$

If dN is suitably represented in terms of global thermodynamic variables this differential form can be made the basis of thermodynamics of irreversible processes in the global scale. However, the precise meaning of the calortropy Ψ will not be known until the meaning of the uncompensated heat is clarified, and vice versa. Therefore the subject of irreversible thermodynamics may be said to be centered around the meaning of uncompensated heat. We will address our study to this task in the following.

2.5 Local Intensive Quantities: Temperature, Pressure, etc.

Since the thermodynamics of irreversible processes is intimately connected with fluid dynamics, which is a local field theory, it is preferable to carry the global differential forms (2.4), (2.28), and (2.41) over to local forms. This localization of equations, however, requires the concept of local temperature, pressure, and so forth for intensive variables. We will first deal with these latter¹⁰.

2.5.1 Local Temperature

The temperature appearing in the global differential form (2.28) is the temperature in the absolute scale of the heat reservoir of the infinitesimal Carnot cycle at the point in the contour integral (2.29) for the cyclic process. Therefore it is appropriate to consider a Carnot cycle between two heat reservoirs of infinitesimally different temperatures, $T + \epsilon$ and T , where $\epsilon > 0$. Let us imagine a piston which contains a gaseous working substance and is connected to the heat reservoirs of temperatures $T + \epsilon$ and T . The substance in this piston goes through a Carnot cycle. The system is macroscopic in size and the process spans over the entire length of the piston. We now imagine that this piston consists of a sequence of infinitesimally small

¹⁰The material presented in this chapter appears in a much condensed form in a recent commentary article by the present author and García-Colín on the status of temperature in a nonequilibrium system undergoing irreversible processes; see *Phys. Rev. E* **54**, 2501 (1996). This chapter chronologically precedes the aforementioned paper.

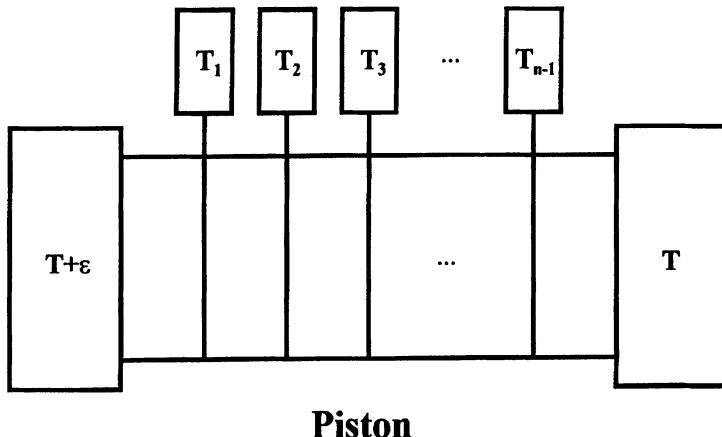


FIGURE 2.2 Division of a piston operating between two heat reservoirs of temperatures $T+\epsilon$ and T , where ϵ is infinitesimally small. The temperatures of the intermediate heat reservoirs are T_1, T_2, \dots, T_{n-1} at positions x_1, x_2, \dots, x_{n-1} . The intervals between these positions do not have to be equal. If the temperature profile is linear then it is convenient to make the intervals equal. The temperatures of the intermediate heat reservoirs define the local temperature in the piston

pistons which are in thermal contact with hypothetical heat reservoirs of temperatures $T_0, T_1, T_2, \dots, T_{n-1}, T_n$ where $T_0 = T + \epsilon$, $T_n = T$, and T_1, T_2, \dots, T_{n-1} are the temperatures of the heat reservoirs at positions x_1, x_2, \dots, x_{n-1} . For example, if the temperature distribution is linear and an equal interval δ is taken, then $T_0 = T + \epsilon, T_1 = T + \epsilon - \delta, T_2 = T + \epsilon - 2\delta, \dots, T_i = T + \epsilon - i\delta, \dots, T_{n-1} = T + \epsilon - (n-1)\delta, T_n = T$ where $\delta = \epsilon/n$ and n can be as large as necessary; see Fig. 2.2. Here the term ‘infinitesimally small piston’ means a piston infinitesimally small in physical size, but still large enough so that a continuum mechanical treatment is valid for the assembly of particles contained therein. The word ‘infinitesimal’ used in connection with the piston means a small size, whereas its use in connection with the Carnot cycle means a small temperature difference, even though the physical size of the piston may be large. In view of δ being sufficiently small, the temperature of the working substance in the i th piston may be taken as the mean temperature $T(i) \equiv \frac{1}{2}(T_{i-1} + T_i)$, and, for example, $T(i) = T + \frac{1}{n}(n-i+\frac{1}{2})\epsilon$ in the case of equal intervals taken earlier. This is the local temperature of the substance in the piston of the original global scale. This local temperature can be quantified by the following means. A thermometer is inserted in the heat reservoirs in contact with the i th piston and let into thermal equilibrium with them so that the temperature T_{i-1}

or T_i is registered on the thermometer. These temperatures of the heat reservoirs with which the infinitesimal piston is in thermal contact define the local temperature $T(i)$ of the system.

Now, the index i in $T(i)$ may be replaced with the position vector \mathbf{r} and time t in a suitable coordinate system in space-time so that $T(i)$ may be replaced by $T(\mathbf{r}, t)$. The local temperature used in the discussion below has the operational meaning as described above. It must be emphasized that the thermometer inserted is in thermal equilibrium with the hypothetical heat reservoirs of the infinitesimal piston that is undergoing a step of the irreversible Carnot cycle apportioned to the i th piston at time t . It is important to remember that the working substance in the piston is still undergoing an irreversible process, and this local temperature characterizes the thermal state of the nonequilibrium system at position i or \mathbf{r} and time t . For a typical example for temperature measurement discussed here we may take measurement of the temperature of an animate body with a thermometer. The animate body undergoes various irreversible processes to keep it functioning as a living system, yet it is possible to quantify its temperature and even establish the temperature distribution over the body. The temperature of the animate body also depends on what is going on inside the body, namely, the inevitable irreversible processes occurring in it. For example, the body may be locally inflamed and the temperature of the part or the whole body may be higher than normal. Therefore the body temperature is a function of the (irreversible) processes associated with the inflammation. We also recognize on empirical grounds that if there is a spatial inhomogeneity in temperature, that is, if there is a difference in temperatures between two points in space, there is flow of heat or an exchange of energy induced between the two points in question. Yet it is possible to quantify the temperature distribution between the two points. Such a temperature distribution is a set of local temperatures at a given time.

2.5.2 Local Pressure and Local Chemical Potentials

The pressure of a system can be gauged by means of a manometer, for example. For this purpose a pressure gauge of the same temperature as the local temperature of an infinitesimal piston is inserted into the aforementioned infinitesimal piston of interest and its value is read off the gauge when the system comes into mechanical equilibrium with the gauge. This procedure can be applied in principle to all the infinitesimal pistons considered in connection with the measurement of local temperature in Section 2.5.1. The mechanical equilibrium between the system and the gauge, however, does not mean that the system itself as a whole is mechanically in equilibrium, but that it is possible to define a mean local pressure in the infinitesimal piston which is in mechanical equilibrium with the pressure gauge. Therefore if the pressure gauge is sufficiently small and of sufficiently

good resolution the pressure distribution can be experimentally established in the system in the sense compatible with notions of field variables in continuum mechanics. The notion of local pressure has this kind of operational meaning in the local theory presented below. A pressure difference between two points in the system induces a volume change in the local elementary volumes involving the said points.

In the same manner as for temperature and pressure, local chemical potentials can be introduced by means of a gauge which is fitted with a semi-permeable membrane through which only one species is passed. The temperature and pressure of the gauge can be maintained at the same temperature and pressure as the temperature and pressure gauges used earlier to measure local temperature and pressure of an infinitesimal piston. Such measurements can, in principle, be made throughout the series of infinitesimal pistons in Fig. 2.2 and for all species in the system, and a distribution of chemical potentials can be established over all positions in the system at time t even if there are irreversible processes in progress. In this manner, the operational meaning of a local chemical potential can be given. A difference in chemical potentials for a species at two spatial points induces a change in the composition of matter in the elementary volumes around the said points in the system .

2.5.3 Local Generalized Potentials

The aforementioned local quantities we have considered in the previous two subsections are intimately related to the conserved variables of the system, namely, energy, volume, and mass fractions or concentrations of species. However, these are not the only macroscopic variables possible, as has been already pointed out in connection with Proposition 2. There are nonconserved variables to consider, and they may be induced by spatial inhomogeneities in certain potentials akin to the chemical potentials considered earlier. We will call these potentials generalized potentials. We will denote by X_{ka} the generalized potential conjugate to the nonconserved variable Φ_{ka} . Therefore there are as many generalized potentials as there are nonconserved variables taken in the theory. This plurality of generalized potentials is akin to that of chemical potentials. How are the generalized potentials quantified, at least in principle? To devise a scheme to make them operational let us recall how the temperature is quantified. It is done by putting two bodies in thermal equilibrium across a diathermal contact boundary and the state at which there is no longer a heat flow is characterized by a common temperature of the two bodies. Pressure is similarly made operational by putting two bodies in mechanical equilibrium across a deformable contact boundary and by the state where volume changes cease to occur in the two bodies involved. Therefore a local generalized potential can be determined in principle if the system of a given local temperature, pressure, and chemical potentials in the infinitesimal piston at the point of

interest is locally balanced with the measuring device with respect to the nonconserved variable Φ_{ka} across the contact boundary that is ‘permeable’ to Φ_{ka} . The word ‘permeable’ is used in the sense the words diathermal, deformable, and semi-permeable are used in connection with temperature, pressure, and chemical potentials. It means that the contact boundary let the system and the measuring device adjust themselves with regard to a difference in Φ_{ka} across the boundary and X_{ka} is defined by the state of the system where the flux of Φ_{ka} vanishes across the contact boundary. Operationally feasible methods of determining them will be realizable when a thermodynamic theory of irreversible processes is properly formulated in a way consistent with the laws of thermodynamics. Note that such is the case for chemical potentials which are defined by the state where the fluxes of the species vanish across the contact boundary. However, they are not directly measured in practice, but determined in terms of osmotic pressure, freezing point changes, and so forth in the case of equilibrium systems. Here our task is to define quantities in a logically and thermodynamically self-consistent manner so that they can be measured at least in principle. The present definition of generalized potentials should do for formulating a thermodynamic theory of irreversible processes.

As a summary for the discussions on measurements of temperature, pressure, chemical potentials, and generalized potentials in the previous three subsections, we make the following proposition.

Proposition 3 *There exists a set of measurable local intensive variables, namely, temperature T , pressure p , chemical potentials $\hat{\mu}_a$ ($1 \leq a \leq r$), and generalized potentials X_{ka} , which are conjugate to the internal energy \mathcal{E} , specific volume v , mass fractions c_a ($1 \leq a \leq r$), and nonconserved variables $\hat{\Phi}_{ka}$ ($k \geq 1$, $1 \leq a \leq r$), respectively. These intensive local variables are amenable to measurements at least in principle.*

The thermodynamics of irreversible processes developed below will provide theories of measurements for $\hat{\mu}_a$ and X_{ka} as well as other intensive variables just as equilibrium thermodynamics gives theories of measurements of equilibrium chemical potentials and so on. These intensive variables are basically the constitutive parameters which must be determined as functions of the 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_{ka} that can be used for studies of experimental data is $X_{ka} = -\rho g_{ka} \hat{\Phi}_{ka}$ where g_{ka} is independent of $\hat{\Phi}_{ka}$ but depends on ρ , T , and p only.

2.6 Local Differential Form for Calortropy

With the preparations made in the previous sections regarding the mathematical representation of the second law of thermodynamics and oper-

ational definitions of temperature, pressure, and so on for the intensive quantities conjugate to various thermodynamic variables, we now formulate in local form a thermodynamic theory of irreversible processes. To make the terminology uncluttered we will first define some necessary and recurring terms.

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

$$\Psi = \int_V d\mathbf{r} \rho \widehat{\Psi}(\mathbf{r}, t). \quad (2.42)$$

Here the integration is over the volume enclosing the system. Since thermodynamic descriptions of macroscopic processes involve a set of macroscopic variables subject to the thermodynamic laws, we will give names to the sets of variables and spaces spanned by the macroscopic variables.

Definition A space spanned by internal energy \mathcal{E} , specific volume v , mass fractions c_a ($1 \leq a \leq r$), nonconserved variables (generically, fluxes) $\widehat{\Phi}_{ka}$ ($1 \leq a \leq r$, $k \geq 1$) is called the thermodynamic space \mathfrak{P} . The union of this set with $\widehat{\Psi}$ is called the Gibbs space: $\mathfrak{G} = (\widehat{\Psi}, \mathcal{E}, v, c_a, \widehat{\Phi}_{ka} : k \geq 1; 1 \leq a \leq r)$.

The vanishing contour integral (2.29) may be written in a form similar to (2.7):

$$\int_0^\tau dt \frac{d\Psi}{dt} = 0 \quad (2.43)$$

and thus the differential form (2.28) can be cast into a derivative form:

$$\frac{d\Psi}{dt} = T^{-1} \frac{dQ}{dt} + \frac{dN}{dt}. \quad (2.44)$$

Since the time derivatives in (2.44) are the global rates of change, by using the well known procedure in continuum mechanics it is possible to express the time derivatives as volume integrals of the following forms [8]:

$$\frac{d\Psi}{dt} = \int_V d\mathbf{r} \left[\frac{\partial}{\partial t} \rho \widehat{\Psi} + \nabla \cdot (\mathbf{u} \rho \widehat{\Psi}) \right], \quad (2.45)$$

$$\begin{aligned} T^{-1} \frac{dQ}{dt} &= - \int_{\mathcal{B}} d\mathbf{B} \cdot \frac{\mathbf{Q}^c}{T} \\ &= - \int_V d\mathbf{r} \nabla \cdot \left[\frac{\mathbf{Q}^c}{T(\mathbf{r}, t)} \right], \end{aligned} \quad (2.46)$$

$$\frac{dN}{dt} = \int_V d\mathbf{r} \rho \widehat{\Xi}_c(\mathbf{r}, t). \quad (2.47)$$

Here \mathbf{u} is the fluid velocity and it is assumed in the derivation of (2.45) that the fluid sticks with the boundary. The subscript \mathcal{B} to the integral in (2.46) stands for the surface of the enclosing volume whose outward

normal direction is counted positive. The vector \mathbf{Q}^c is counted positive in the direction normal to the surface. First, it must be recalled that the differential form (2.44) 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 (2.17) 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 . Except for the terminal infinitesimal Carnot cycles this heat reservoir of temperature T is not one of 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 (2.16). The first equality in (2.46) 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 (2.20)], $T^{-1}dQ/dt$ 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

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

where $\mathcal{B} = \cup_i \mathcal{B}_i$. The second equality in (2.46) follows easily. In this connection the reader should recall the argument used for the meaning of local temperature in Sec. 2.5.1. The same argument underlies the discussion on the meaning of T as given above. The vector \mathbf{Q}^c is the net heat flux at the surface; it is the compensated heat flux. The quantity $\rho \hat{\Xi}_c(\mathbf{r}, t)$ is the local rate of uncompensated heat per volume. Use of (2.45)–(2.47) in (2.44) implies, by virtue of continuity, the balance equation for the calortropy density [35]:

$$\rho \frac{d\hat{\Psi}}{dt} = -\nabla \cdot \left[\frac{\mathbf{Q}^c}{T(\mathbf{r}, t)} \right] + \rho \hat{\Xi}_c(\mathbf{r}, t). \quad (2.48)$$

We will call $\mathbf{J}_c \equiv \mathbf{Q}^c/T$ and $\rho \hat{\Xi}_c$ the calortropy flux and the calortropy production, respectively. Except that $\rho \hat{\Xi}_c$ must be always positive and vanishes for reversible processes by virtue of $dN/dt \geq 0$, the precise forms for these quantities \mathbf{Q}^c and $\hat{\Xi}_c$ are not known at this point that would permit deductions on the properties of calortropy. To this end we reason as follows. First of all, since a macroscopic system must evolve in conformation with the conservation laws, the relevant variables for characterizing 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 thermodynamic space \mathfrak{P} . The desired deductions of the properties of the calortropy will be possible if the calortropy flux and the calortropy production are elucidated in the space \mathfrak{P} . We make the following proposition for them.

Proposition 4 *The calortropy flux $\mathbf{J}_c \equiv \mathbf{Q}^c/T$ is given by the bilinear form of the intensive variables T^{-1} , $\hat{\mu}_a T^{-1}$, and $X_{ka} T^{-1}$ ($k \geq 1$, $1 \leq a \leq r$) paired, respectively, with \mathbf{Q}_a , \mathbf{J}_a , and ψ_{ka} (flux of Φ_{ka}) as follows:*

$$\mathbf{J}_c \equiv \sum_{a=1}^r \frac{\mathbf{Q}_a^c}{T} = \sum_{a=1}^r T^{-1} \left(\mathbf{Q}_a - \hat{\mu}_a \mathbf{J}_a + \sum_{k \geq 1} X_{ka} \psi_{ka} \right), \quad (2.49)$$

and the calortropy production $\Xi_c \equiv \rho \hat{\Xi}_c$ is given by the bilinear form

$$\begin{aligned} \Xi_c &\equiv \rho \hat{\Xi}_c \\ &= -T^{-1} \sum_{a=1}^r [(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q}_a^c \cdot \nabla \ln T + \mathbf{J}_a \cdot (\nabla \hat{\mu}_a - \mathbf{F}_a) \\ &\quad - \sum_{k \geq 1} \psi_{ka} \cdot \nabla X_{ka}] + T^{-1} \sum_{a=1}^r \sum_{k \geq 1} X_{ka} (\mathcal{Z}_{ka} + \Lambda_{ka}). \end{aligned} \quad (2.50)$$

By the second law of thermodynamics $\Xi_c \geq 0$ always, the equality holding for reversible processes only.

The inequality for the calortropy production imposes the positivity condition that the kinematic and dissipation terms \mathcal{Z}_{ka} and Λ_{ka} in the evolution equation for $\hat{\Phi}_{ka}$ must satisfy, and thus dictates the acceptable forms for them. Therefore the evolution equations for nonconserved variables are not free but must conform to the second law of thermodynamics represented by $\Xi_c \geq 0$ in local theory. It must be noted that the terms in the square brackets in (2.50) except for the last term involving ∇X_{ka} are those making up the entropy production in the theory of linear irreversible processes [19,20]. The last term mentioned is a bilinear product of the gradient of the generalized potential and the flux ψ_{ka} of the nonconserved variable Φ_{ka} 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 ∇X_{ka} induces the flux ψ_{ka} of nonconserved variable Φ_{ka} 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 ψ_{ka} , there are contributions to the uncompensated heat from the kinematic and dissipation terms—the last group of terms in (2.50)—in the evolution

equations for the nonconserved variables in the present generalized theory. The calortropy flux proposed is also seen to include the classical terms as well as nonclassical terms—the last group of terms in (2.49)—attributable to the nonconserved variables. The calortropy flux and the calortropy production proposed in Proposition 4 are mutually compatible in the sense that they give rise to a differential form for $d_t \hat{\Psi}$ as will be shown¹¹.

Use of (2.49) and (2.50) in the calortropy balance equation (2.48) makes it possible to determine $\hat{\Psi}$ in the space \mathfrak{P} if the conservation laws in Proposition 1 and the evolution equations in Proposition 2 are used. In particular, if the fluxes \mathbf{Q}_a , \mathbf{J}_a , and ψ_{ka} are either eliminated or rearranged by means of generalized hydrodynamics equations (2.8)–(2.12) then it is possible to put the balance equation for $\hat{\Psi}$ in a Pfaffian differential form (one-form):

$$d_t \hat{\Psi} = T^{-1} \left(d_t \mathcal{E} + pd_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} d_t \hat{\Phi}_{ka} \right). \quad (2.51)$$

Inasmuch as the calortropy balance equation (2.48) is the local equivalent of the second law of thermodynamics, the Pfaffian differential form¹² (2.51) is an equivalent of the second law in the thermodynamic space \mathfrak{P} under Proposition 4. *This differential form is exact in the space \mathfrak{P} by virtue of the vanishing contour integral (2.29).* This can be shown as follows. From (2.43) and (2.45) we obtain

$$\begin{aligned} \int_0^\tau dt \frac{d\Psi}{dt} &= \int_0^\tau dt \int_V d\mathbf{r} \left(\frac{\partial}{\partial t} \rho \hat{\Psi} + \nabla \cdot \mathbf{u} \rho \hat{\Psi} \right) \\ &= \int_V d\mathbf{r} \int_0^\tau dt \rho \frac{d\hat{\Psi}}{dt} = 0, \end{aligned} \quad (2.52)$$

from which, by continuity, follows the vanishing local integral

$$\int_0^\tau dt \rho \frac{d\hat{\Psi}}{dt} = 0. \quad (2.53)$$

¹¹Although (2.49) and (2.50) are sufficient for \mathbf{J}_c and Ξ_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 Ξ_c , respectively, with no effect at all on the one-form that can be obtained from the balance equation for the calortropy. 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 Chapter 7. The formulas for \mathbf{J}_c and Ξ_c proposed in Proposition 4 therefore are minimal in the sense that they are sufficient to produce a one-form for $d_t \hat{\Psi}$.

¹²It must be noted that a Pfaffian differential form is not necessarily an exact differential unless it satisfies a set of integrability conditions. In the case of thermodynamics the second law of thermodynamics pre-empts the integrability conditions which are partial differential equations not easy to solve in general.

This implies that $d_t \hat{\Psi}$ is an exact differential in the space \mathfrak{P} since $\rho(d\hat{\Psi}/dt)$ may be replaced by $(d\rho\hat{\Psi}/dt)$. It is not simple to prove the exactness of a differential form like (2.51) if a purely mathematical approach is taken for the proof, but in the present case the differential form $d_t \hat{\Psi}$ is exact by the requirement 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 $d_t \hat{\Psi}$ and there exists a hypersurface in the space $\mathfrak{G} = \mathfrak{P} \cup \hat{\Psi}$. 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 the space \mathfrak{P}*

$$d_t \hat{\Psi} = T^{-1} \left(d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} d_t \hat{\Phi}_{ka} \right). \quad (2.54)$$

This differential form is integrable and there exists a state function $\hat{\Psi}$ in the space \mathfrak{P} . This function may be regarded as a hypersurface in the space \mathfrak{G} by the requirement of the second law of thermodynamics.

This theorem provides the foundation for the thermodynamics of irreversible processes in a fairly general form which we will develop with it later. Before doing so we examine how the present theory connects with the existing theories of thermodynamics. First of all, we see that as the X_{ka} vanish for all k and a equilibrium thermodynamics is recovered, since $\hat{\Psi}$ tends to its equilibrium limit $\hat{\Psi}_e$ which coincides with the Clausius entropy density S_e :

$$\begin{aligned} d_t \hat{\Psi}_e &= T_e^{-1} \left(d_t \mathcal{E} + p_e d_t v - \sum_{a=1}^r \hat{\mu}_a^e d_t c_a \right) \\ &= d_t S_e, \end{aligned} \quad (2.55)$$

where

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

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

$$\mu_a^e = \lim_{X \rightarrow 0} \mu_a = \lim_{\Phi \rightarrow 0} \mu_a.$$

Since we are not interested in equilibrium thermodynamics here, we will not dwell on this aspect.

In the versions of extended irreversible thermodynamics proposed in [23–26] and [28–30] it is assumed that there exists a nonequilibrium entropy which is a state function in the space \mathfrak{P} , consequently it has a differential form similar to that for $\hat{\Psi}$ in (2.51), and yet it can be given by the Boltzmann entropy or the information entropy for dynamical processes. The assumption of such a nonequilibrium entropy has no foundation in the laws of thermodynamics. Moreover, the assumption that the phenomenological nonequilibrium entropy is given by the Boltzmann entropy is incorrect, since $\hat{\Psi}$ is not the same as the Boltzmann entropy as will be shown in kinetic theory chapters of this work. The versions of extended irreversible thermodynamics in [23–26] and [28–30] can be given thermodynamic foundations, only if the nonequilibrium entropy postulated therein is replaced by $\hat{\Psi}$ and its equivalence with the Boltzmann entropy is abandoned. Therefore the aforementioned theories of irreversible processes based on the assumption on a nonequilibrium entropy and its differential form are unfounded from the viewpoint of the second law of thermodynamics.

2.7 Irreversible Thermodynamics in the space \mathfrak{P}

Thermodynamics of irreversible processes in the extended thermodynamic space \mathfrak{P} can be developed on the basis of the extended Gibbs relation for calortropy (2.51). Our aim here is not to delve into the subject in depth, but to sketch out the basic framework of the theory which will round it out and enable us to effectively use it for nonequilibrium statistical mechanics later in this work. A fuller exposition of the subject will be reserved for another work where the thermodynamics of irreversible processes will be treated independently of the attendant kinetic theory of matter.

2.7.1 The Inverse Temperature as an Integrating Factor

The inverse temperature factor appearing in the extended Gibbs relation for calortropy (2.51) has a special meaning, as has the inverse temperature in the equilibrium Gibbs relation in the equilibrium theory. When (2.51) is looked at from the viewpoint of differential forms the inverse temperature emerges as an integrating factor for the differential form

$$\omega = d\mathcal{E} + pdv - \sum_{a=1}^r \hat{\mu}_a dc_a + \sum_{a=1}^r \sum_{k \geq 1}^m X_{ka} d\hat{\Phi}_{ka}, \quad (2.56)$$

where the substantial time derivative $d_t x$ is replaced by the differential dx . To be definite, the set of nonconserved variables is made finite; there are m nonconserved variables. Therefore the dimension of the space \mathfrak{P} is

$l = (m + 1)r + 2$. The differential form (2.56) will be written as

$$\omega = \sum_{i=1}^l \omega_i dx_i, \quad (2.57)$$

where $(\omega_i : 1 \leq i \leq l) \equiv (1, p, -\hat{\mu}_a, X_{ka} : 1 \leq a \leq r, 1 \leq k \leq m)$ and $x = (x_i : 1 \leq i \leq l) \equiv (\mathcal{E}, v, c_a, \hat{\Phi}_{ka} : 1 \leq a \leq r, 1 \leq k \leq m) = \mathfrak{P}$. According to the second law of thermodynamics the differential form $\omega = 0$ is integrable and there exists a function $\hat{\Psi}$ such that $\omega = f(x)d\hat{\Psi}$, where $f(x)$ is an integrating factor. Comparison of this result with (2.51) implies that $f(x) = T(x)$. That is, the inverse temperature T^{-1} is an integrating factor for ω . This shows that although T^{-1} may be regarded as an intensive variable, it has a special status among the intensive variables ω_i . Starting from the integrability [36–39] of ω we can show that the integrating factor indeed can be chosen to be the inverse absolute temperature of the system. The details of this analysis can be found in the literature [40].

2.7.2 Integrability Conditions and Generalized Maxwell Relations

Since $d\hat{\Psi}$ is exact in the space \mathfrak{P} , generalized forms of the Maxwell relations are expected of the differential form (2.51). Thus we obtain the relations

$$\frac{\partial}{\partial x_j} \varpi_i = \frac{\partial}{\partial x_i} \varpi_j \quad (i, j = 1, 2, \dots, l), \quad (2.58)$$

where $\varpi = (\varpi_i : 1 \leq i \leq l) = (T^{-1}\omega_i : 1 \leq i \leq l)$. Since the integrability condition [36–39] for ω is

$$\omega \wedge d\omega = 0 \quad (2.59)$$

and for a function $h \neq 0$ in open domain $\subset \mathfrak{P}$ there also holds the condition

$$(h\omega) \wedge d(h\omega) = 0, \quad (2.60)$$

the integrability condition may be written as

$$\varpi \wedge d\varpi = 0 \quad (2.61)$$

if we choose $h = T^{-1}$. By using the rules of exterior calculus [36–39], this condition can be explicitly written out:

$$\begin{aligned} \varpi \wedge d\varpi &= \frac{1}{6} \sum_{ijk} [\varpi_i(\partial_j \varpi_k - \partial_k \varpi_j) + \varpi_j(\partial_k \varpi_i - \partial_i \varpi_k) \\ &\quad + \varpi_k(\partial_i \varpi_j - \partial_j \varpi_i)] dx_i \wedge dx_j \wedge dx_k \\ &= 0, \end{aligned} \quad (2.62)$$

where $\partial_i = \partial/\partial x_i$. From this follow the necessary and sufficient conditions for the integrability of ϖ

$$\varpi_i(\partial_j \varpi_k - \partial_k \varpi_j) + \varpi_j(\partial_k \varpi_i - \partial_i \varpi_k) + \varpi_k(\partial_i \varpi_j - \partial_j \varpi_i) = 0 \quad (2.63)$$

for $i, j, k = 1, 2, \dots, l$. These conditions are satisfied by the generalized Maxwell relations (2.58). This shows the intimate relation of the integrating factor to the generalized Maxwell relations for ϖ .

Now that we know that there exists a state function $\hat{\Psi}$ in the space \mathfrak{P} we may treat it as a primitive independent variable while treating \mathcal{E} as the dependent variable. In other words, we may use the energy representation and write¹³

$$\begin{aligned} d\mathcal{E} &= Td\hat{\Psi} - pdv + \sum_{a=1}^r \hat{\mu}_a dc_a - \sum_{a=1}^r \sum_{k \geq 1}^m X_{ka} d\hat{\Phi}_{ka} \\ &= \sum_{i=1}^l W_i dy_i, \end{aligned} \quad (2.64)$$

where $W = (W_i : 1 \leq i \leq l) = (T, -p, \hat{\mu}_a, -X_{ka} : 1 \leq a \leq r, 1 \leq k \leq m)$ and $y = (y_i : 1 \leq i \leq l) = (\hat{\Psi}, v, c_a, \hat{\Phi}_{ka} : 1 \leq a \leq r, 1 \leq k \leq m)$. The generalized Maxwell relations are then given by

$$\frac{\partial}{\partial y_j} W_i = \frac{\partial}{\partial y_i} W_j \quad (i, j = 1, 2, \dots, l). \quad (2.65)$$

These generalized Maxwell relations, especially those involving the generalized potentials X_{ka} , provide symmetry relations for phenomenological coupling constants appearing in the representations of X_{ka} in the space \mathfrak{P} in the linear regime as well as in the nonlinear regime where various nonconserved variables of different symmetry groups can couple nonlinearly. This subject should be further investigated because of its practical importance.

As in equilibrium thermodynamics, other thermodynamic functions can be defined. For example, we may define the generalized work function \mathcal{A} and the generalized Gibbs free energy \mathcal{G} [10]:

$$\mathcal{A} = \mathcal{E} - T\hat{\Psi}, \quad (2.66)$$

¹³This is known as the energy representation in the literature. See, for example, Sieniutycz and Berry, *Phys. Rev. A* **46**, 6359 (1992). This energy representation gives the impression that there is an exact differential form in the Gibbs space even if the system is in nonequilibrium. However, it masks the fact that there is a non-mechanical variable, namely, $\hat{\Psi}$ in the present notation, or ‘the entropy density’ in the notation of the aforementioned paper by Sieniutycz and Berry, among the variables, and this non-mechanical variable must be deduced from the second law. Therefore the energy representation must be used with this point clearly understood. It does not deliver us from facing up to the question of $\hat{\Psi}$ and its thermodynamic nature.

$$\mathcal{G} = \mathcal{H} - T\hat{\Psi}, \quad (2.67)$$

$$\begin{aligned}\hat{\Omega} &= \mathcal{G} + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \hat{\Phi}_{ka} \\ &= \mathcal{E} + pv - T\hat{\Psi} + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \hat{\Phi}_{ka},\end{aligned}\quad (2.68)$$

where \mathcal{H} is the enthalpy density

$$\mathcal{H} = \mathcal{E} + pv. \quad (2.69)$$

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} . Since the properties of the functions \mathcal{A} and \mathcal{G} can be discussed in complete parallel with the equilibrium thermodynamics by using the fundamental equation (2.51) or (2.64) we will not dwell on them further. The new function $\hat{\Omega}$ is a nonequilibrium thermodynamic potential which also may be written as

$$\hat{\Omega} = \sum_{a=1}^r \hat{\mu}_a c_a. \quad (2.70)$$

The Legendre transform (2.68) gives rise to the extended Gibbs relation for $d_t \hat{\Omega}$:

$$d_t \hat{\Omega} = -\hat{\Psi} d_t T + v d_t p + \sum_{a=1}^r \hat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{k \geq 1} \hat{\Phi}_{ka} d_t X_{ka}. \quad (2.71)$$

Let us define the extensive variables

$$\begin{aligned}\Omega &= V\rho\hat{\Omega}, \quad \Psi_v = V\rho\hat{\Psi}, \quad E = V\rho\mathcal{E}, \\ V &= V\rho v, \quad N_a = V\rho c_a/m_a, \quad \Phi_{ka}^v = V\rho\hat{\Phi}_{ka},\end{aligned}\quad (2.72)$$

where V is the volume of the system. With the help of (2.67) the differential form (2.71) can be written as

$$d_t \Omega = -\Psi_v d_t T + V d_t p + \sum_{a=1}^r \mu_a d_t N_a + \sum_{a=1}^r \sum_{k \geq 1} \Phi_{ka}^v d_t X_{ka}. \quad (2.73)$$

The differential form (2.71) will be found useful in connection with the nonequilibrium ensemble method discussed in later chapters. The function

$\hat{\Omega}$ also gives rise to the integrability condition for the differential form for $d_t \hat{\Psi}$:

$$\sum_{a=1}^r c_a d_t \left(\frac{\hat{\mu}_a}{T} \right) = \mathcal{E} d_t \left(\frac{1}{T} \right) + v d_t \left(\frac{p}{T} \right) + \sum_{a=1}^r \sum_{k \geq 1} \hat{\Phi}_{ka} d_t \left(\frac{X_{ka}}{T} \right), \quad (2.74)$$

or, alternatively, in the case of (2.73)

$$\sum_{a=1}^r N_a d_t \mu_a = -\Psi_v d_t T + V d_t p + \sum_{a=1}^r \sum_{k \geq 1} \Phi_{ka}^v d_t X_{ka}. \quad (2.75)$$

These integrability conditions are generalizations of the Gibbs–Duhem equation in equilibrium thermodynamics and useful for applying the present theory to nonequilibrium phenomena.

2.8 Irreversible Thermodynamics of Steady States

Experiments are often performed in steady state conditions where fluxes remain stationary in time. Such examples [41,42] can be seen in many transport processes in fluids and solids and many rheological experiments [12]. In fact, linear irreversible thermodynamics deals with such situations. Therefore it is useful to consider them and relate the present general theory to such special cases. Here we will examine cases where the nonconserved variables do not change in time in the frame of reference moving with the fluid's velocity. That is, we consider the cases of $d_t \hat{\Phi}_{ka} = 0$. However, the kinematic and dissipation terms in the evolution equations for $\hat{\Phi}_{ka}$ can be nonlinear. We will separately consider the case of linear evolution equations for Φ_{ka} in the next section.

If $d_t \hat{\Phi}_{ka} = 0$ for all k and a then the extended Gibbs relation for calortropy becomes

$$d_t \hat{\Psi}_{ss} = T^{-1} \left(d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a \right), \quad (2.76)$$

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 right hand side of (2.76) is simply the same as the local equilibrium entropy change in the steady state, the calortropy at the steady state coincides with the local equilibrium entropy S_e given by the same differential form as in (2.76) or (2.55) except for the meanings of the coefficients to the differentials since they

now depend on $\widehat{\Phi}_{ka}$:

$$d_t \widehat{\Psi}_{ss} = d_t \mathcal{S}_e = T^{-1} \left(d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \widehat{\mu}_a d_t c_a \right). \quad (2.77)$$

In this case the local equilibrium hypothesis is a perfectly acceptable differential form for a thermodynamic description of the process in hand, provided that the steady state evolution equations are given by¹⁴

$$-\nabla \cdot \psi_{ka} + \mathcal{Z}_{ka} + \Lambda_{ka} = 0 \quad (2.78)$$

for all k and a . See the examples for the kinematic and dissipation terms given in Table 2.1. In fact, the steady state evolution equations (2.78) give nonlinear thermodynamic force–flux relations, namely, the constitutive equations for fluxes whose solutions yield nonlinear transport coefficients. At this point, the nature of (2.77) can be put in a better light if (2.77) is compared with (2.39) 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 (2.77) and (2.78).

The solutions of (2.78) give Φ_{ka} , for example, the stress tensor, heat flux, and diffusion fluxes, and so on as functions of thermodynamic forces, temperature, density, and so on:

$$\mathbf{P} = \sum_{a=1}^r \mathbf{P}_a = F_p(T, \rho | \nabla \mathbf{u}, \nabla \ln T, \dots), \quad (2.79)$$

$$\mathbf{Q} = \sum_{a=1}^r \mathbf{Q}_a = F_q(T, \rho | \nabla \mathbf{u}, \nabla \ln T, \dots), \quad (2.80)$$

$$\mathbf{J}_a = F_a(T, \rho | \nabla \mathbf{u}, \nabla \ln T, \dots) \quad (1 \leq a \leq r), \quad (2.81)$$

and in general

$$\Phi_{ka} = F_{ka}(T, \rho | \nabla \mathbf{u}, \nabla \ln T, \dots). \quad (2.82)$$

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 $(\nabla \widehat{\mu}_a - \mathbf{F}_a)$, because the constitutive equations (2.78) are generally nonlinear with respect to the nonconserved variables or the thermodynamic forces. On substitution of, for example, (2.79)–(2.81) into (2.9)–(2.11), we obtain hydrodynamics

¹⁴In 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 as macroscopic variables and then assume the closure relations for higher order moments $\psi_{1a} = \psi_{3a} = 0$. Applications discussed in Chapter 8 take this kind of closure relations.

equations which generalize the classical hydrodynamics equations such as the Navier–Stokes, Fourier, and Fick equations. It must be noted that in the present theory the steady state constitutive equations (2.78) are still subject to the second law of thermodynamics since they must satisfy the inequality $\Xi_c \geq 0$ demanded by the second law.

The deduction made here from the general theory, therefore, shows that the theory of nonlinear steady state irreversible phenomena can be put in the framework of the present extended theory 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 [41,42], 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 as it does in the present theory. Some examples of steady state irreversible phenomena will be discussed in Chapter 8 dealing with applications of the theory. Finally, we point out that the steady state description will be appropriate for nonconserved 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 decayed 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. In fact, the steady state constitutive equations coincide with those in the adiabatic approximation, as will be seen in Chapter 8.

2.9 Thermodynamics of Linear Irreversible Processes

The theory of linear irreversible processes we discuss here is a special case of the thermodynamics of steady state irreversible processes examined in the previous section. Since the important position which the theory of linear irreversible processes [17–20] occupies historically and practically in irreversible thermodynamics warrants a more careful consideration, we devote this section to the subject. In this discussion we will consider a single component dilute monatomic gas and limit the set of nonconserved variables to stress tensor and heat flux which are traditionally the nonconserved parts in the set of Grad’s thirteen moments [43]. This assumption will make the present discussion compatible with the kinetic theory of dilute gases we will present in later chapters. However, the theory presented here being phenomenological, this restriction is not mandatory and can be easily removed without altering the conclusion. The theory can be made valid for dense gases and liquids, provided appropriate material functions, such as viscosity and thermal conductivity, are used in the constitutive equations.

The evolution equations for the stress tensor and heat flux for the system in hand are the linear equations [10]

$$\rho d_t \hat{\Pi} = -2p[\nabla \mathbf{u}]^{(2)} - \frac{p}{\eta_0} \Pi, \quad (2.83)$$

$$\rho d_t \hat{\mathbf{Q}} = -\hat{C}_p T p \nabla \ln T - \frac{\hat{C}_p T p}{\lambda_0} \mathbf{Q}, \quad (2.84)$$

where $\Pi = \rho \hat{\Pi}$ is the shear stress tensor, namely, the traceless symmetric part of the stress tensor \mathbf{P} , $\mathbf{Q} = \rho \hat{\mathbf{Q}}$ is the heat flux, \hat{C}_p is the specific heat per mass at constant pressure, \hat{h} is the enthalpy per mass, η_0 is the viscosity and λ_0 is the thermal conductivity of the gas. These equations were originally obtained by Maxwell [12] as transfer equations which he used in his kinetic theory. The molecular expressions for the viscosity and thermal conductivity can be found in Chapter 6 of this work. These equations are examples for linearized versions of the evolution equation (2.12). We will also take X_{ka} for the problem in hand in the following forms [10]:

$$X_p = -\frac{\Pi}{2p}, \quad X_q = -\frac{\mathbf{Q}}{\hat{C}_p T p}. \quad (2.85)$$

This is an approximation for X_{ka} which can be generally nonlinear functions of Φ_{ka} , derivable from the nonequilibrium partition function presented in later chapters on nonequilibrium ensemble methods. Note that there is no bulk viscosity in the case of dilute monatomic gases. Therefore $\Delta = \frac{1}{3} \text{Tr} \mathbf{P} - p = 0$ and there does not appear the equation for $\Delta = \rho \hat{\Delta}$. Unless the system is forced by an oscillating velocity or temperature field, Π and \mathbf{Q} relax to their steady state values on the time scale of the order of $10^{-10} s$ or shorter in the case of simple fluids. At the steady state of Π and \mathbf{Q} in the reference frame moving at \mathbf{u} the constitutive equations—the evolution equations—reduces to the Newtonian law of viscosity and the Fourier law of heat conduction:

$$\Pi = -2\eta_0 [\nabla \mathbf{u}]^{(2)}, \quad (2.86)$$

$$\mathbf{Q} = -\lambda_0 \nabla \ln T. \quad (2.87)$$

Thus the theory of linear irreversible processes is easily recovered from the general theory presented if the fluxes are steady in the moving reference frame and the constitutive equations are linearized with respect to fluxes and thermodynamic forces. With the approximation (2.85) and the evolution equations (2.83) and (2.84) the calortropy production Ξ_c takes the form

$$\Xi_c = T^{-1} \left(\frac{1}{2\eta_0} \Pi : \Pi + \frac{1}{\lambda_0} \mathbf{Q} \cdot \mathbf{Q} \right), \quad (2.88)$$

which is simply the Rayleigh dissipation function [44]. The positivity of Ξ_c demands that the transport coefficients be positive. Note that this is also the entropy production in the theory of linear irreversible processes. Therefore under the approximations made to recover the linear theory in this section the calortropy production Ξ_c coincides with the entropy production in the theory of linear irreversible processes, just as does $d_t \Psi_{ss}$ coincide with $d_t S_e$, the local equilibrium hypothesis for S_e . This conclusion should be compared with the conclusion suggested by (2.39) for insight into the nature of linear irreversible thermodynamics within the framework of the present theory.

2.10 Inclusion of Chemical Reactions

We now would like to take chemical reactions into consideration. Let us denote by R_k the rate of reaction k and by ν_{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 reaction is written in the form

$$\sum_{a=1}^r \nu_{al} B_a = 0, \quad (2.89)$$

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 (2.12) although the dissipation terms contain reactive contributions, but they do not have to be written out explicitly for our purpose here. The mass fraction balance equation reads

$$\rho d_t c_a = -\nabla \cdot \mathbf{J}_a + \sum_{l=1}^m \nu_{al} R_l. \quad (2.90)$$

The calortropy balance equation remains invariant. Let us define the affinity A_l by the expression

$$A_l = \sum_{a=1}^r \nu_{al} \hat{\mu}_a. \quad (2.91)$$

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

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 $\mathbf{J}_c \equiv \mathbf{Q}^c/T$ is given by the bilinear form of the intensive variables T^{-1} , $\hat{\mu}_a T^{-1}$, and $X_{ka} T^{-1}$ ($k \geq 1, 1 \leq a \leq r$) paired, respectively, with \mathbf{Q}_a , \mathbf{J}_a , and ψ_{ka} (flux of Φ_{ka}) as follows:*

$$\mathbf{J}_c \equiv \sum_{a=1}^r \frac{\mathbf{Q}_a^c}{T} = \sum_{a=1}^r T^{-1} \left(\mathbf{Q}_a - \hat{\mu}_a \mathbf{J}_a + \sum_{k \geq 1} X_{ka} \boldsymbol{\psi}_{ka} \right), \quad (2.92)$$

and the calortropy production $\Xi_c \equiv \rho \hat{\Xi}_c$ is given by the bilinear form

$$\begin{aligned} \Xi_c &\equiv \rho \hat{\Xi}_c \\ &= -T^{-1} \sum_{a=1}^r [(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q}_a^c \cdot \nabla \ln T + \mathbf{J}_a \cdot (\nabla \hat{\mu}_a - \mathbf{F}_a)] \\ &\quad - T^{-1} \sum_{a=1}^r \left[\sum_{l=1}^m \nu_{al} \hat{\mu}_a R_l - \sum_{k \geq 1} \boldsymbol{\psi}_{ka} \cdot \nabla X_{ka} \right] \\ &\quad + T^{-1} \sum_{a=1}^r \sum_{k \geq 1} X_{ka} (\mathcal{Z}_{ka} + \Lambda_{ka}). \end{aligned} \quad (2.93)$$

By the second law of thermodynamics the inequality $\Xi_c \geq 0$ always holds, the equality holding for reversible processes only.

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

$$\Xi_c^{\text{chem}} \equiv -T^{-1} \sum_{a=1}^r \sum_{l=1}^m \nu_{al} \hat{\mu}_a R_l = -T^{-1} \sum_{l=1}^m A_l R_l, \quad (2.94)$$

where A_l is the affinity defined by

$$A_l = \sum_{a=1}^r \nu_{al} \hat{\mu}_a. \quad (2.95)$$

This is the familiar looking form for the entropy production in the linear theory 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 $d_t \hat{\Psi}$ as (2.54) in Theorem 1. Therefore the differential form for $d_t \hat{\Psi}$ 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 Φ_{ak} ($k \geq 1$) whose evolution equations are also modified

in the dissipation terms. Thus the hydrodynamics equations are modified, but the basic thermodynamic structure remains 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 $d_t \hat{\Psi}$ becomes the local equilibrium formula for $d_t S_e$. The local equilibrium formula also arises if the nonconserved variables are in the steady state in the moving frame of reference.

Table 2.1 Examples for \mathcal{Z}_{qa} and Λ_{qa}

$$\mathcal{Z}_{1a} = -2[\mathbf{J}_a(d_t \mathbf{u} - \mathbf{F}_a)]^{(2)} - 2[\boldsymbol{\Pi}_a \cdot \nabla \mathbf{u}]^{(2)} - 2\Delta_a [\nabla \mathbf{u}]^{(2)}$$

$$- \frac{2}{3}\boldsymbol{\Pi}_a \nabla \cdot \mathbf{u} - 2p_a [\nabla \mathbf{u}]^{(2)}$$

$$\mathcal{Z}_{2a} = -\frac{2}{3}\mathbf{J}_a \cdot (d_t \mathbf{u} - \mathbf{F}_a) - \frac{2}{3}\boldsymbol{\Pi}_a : \nabla \mathbf{u} - \frac{2}{3}\Delta_a \nabla \cdot \mathbf{u}$$

$$- p_a d_t \ln(p_a v^{5/3}) - \nabla \cdot (\mathbf{J}_a p_a / \rho_a)$$

$$\mathcal{Z}_{3a} = -(d_t \mathbf{u} - \mathbf{F}_a) \cdot (\mathbf{P}_a - p_a \boldsymbol{\delta}) - \mathbf{Q}'_a \cdot \nabla \mathbf{u} - \boldsymbol{\varphi}_a^{(3)} : \nabla \mathbf{u}$$

$$- \mathbf{J}_a d_t \hat{h}_a - \mathbf{P}_a \cdot \nabla \hat{h}_a$$

$$\mathcal{Z}_{4a} = -\rho_a (d_t \mathbf{u} - \mathbf{F}_a) - \mathbf{J}_a \cdot \nabla \mathbf{u}$$

$$\Lambda_{qa} = (\beta g)^{-1} \sum_{k \geq 1} \sum_{b=1}^r R_{ab}^{(qk)} X_{kb} q(X)$$

The symbols in this table are as follows: $\boldsymbol{\varphi}_a^{(3)}$ is a third-rank tensor; $g = (m/2k_B T)^{1/2}/n^2 d^2$, n being the number density, d the size parameter, m the mean mass; $q(X)$ is a positive nonlinear function of $\{X_{qa}\}$, e.g., $q(X) = \sinh \kappa(X)/\kappa(X)$ with $\kappa(X)$ denoting a non-dimensional Rayleigh dissipation function; and $R_{ab}^{(qk)}$ are phenomenological coefficients. See Chapters 7 and 9 for the kinetic theory expressions for these quantities.

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3

Boltzmann Equation

Evolution of macroscopic processes in dilute classical monatomic gases can be described by means of the Boltzmann kinetic equation or equivalent kinetic equations. In the kinetic theory of gases it is conventional to justify the kinetic equation by showing its derivation from the Newtonian or quantum equations of motion for the many-particle system in hand under suitable assumptions of a statistical nature. Although such justification is useful in clarifying microscopic dynamics underlying the macroscopic process of interest, it does not enhance our understanding of the cause of irreversibility, which is generally investigated with the Newtonian or quantum mechanics of many particles, because of the presence of the statistical assumptions made for the derivation of the kinetic equation. This approach amounts to replacing one set of nonmechanical assumptions with another basically equivalent to the former. We therefore forego taking the approach of deriving a kinetic equation from the Newtonian or quantum equations of motion for the many-particle system in hand. Instead, we take a postulate approach in which the kinetic equation is taken as a postulate for the dilute gas of interest and its justification is *a posteriori* sought in comparison with experimental data measured in the laboratory or observed in nature. The reason for this approach is that the purported derivation of such a kinetic equation from the Newtonian or quantum dynamical equations of motion is not really a derivation in the true sense of the word because of the assumptions of a statistical nature which are necessary but take ‘the derivation’ out of the realm of pure dynamics. The kinetic equations are, in general, of broken time reversal symmetry, and a derivation of an irreversible kinetic equation of broken time reversal symmetry from the equations of motion which preserve the time reversal symmetry is at best a misnomer. The kinetic equations should better be regarded as postulates on the mesoscopic description of macroscopic systems which the dilute gases of interest here are. This way, our viewpoint toward kinetic equations becomes simplified and unencumbered by many conceptual questions arising from the claim of derivation of a kinetic equation. We take the viewpoint that dynamical systems consisting of 10^{23} particles require dynamical equations of broken time reversal symmetry which are not derivable from the time reversal invariant Newtonian or quantum equations of motion for the systems; for example, the Boltzmann equation is a fundamental equation for dilute classical gases in which the dynamics of binary collisions between the particles in the gas

is described by the dynamical laws of few-particle systems, namely, Newtonian mechanics or quantum mechanics, but the equation is not derivable from the latter in the true sense of the word.

3.1 Boltzmann Equation

If a gas mixture is so diluted that particles in the gas are to a good approximation not statistically correlated, then singlet distribution functions are sufficient for description of the macroscopic behavior of the gas. The singlet distribution function of species a , denoted by $f_a(\mathbf{v}_a, \mathbf{r}; t)$, is the probability of finding a particle of species a in the velocity and position intervals $\mathbf{v}_a \sim \mathbf{v}_a + d\mathbf{v}_a$ and $\mathbf{r} \sim \mathbf{r} + d\mathbf{r}$. Therefore the distribution function for the total system of independent uncorrelated particles is the product of singlet distribution functions. Boltzmann [1] obtained a kinetic equation for such a singlet distribution function under the *stosszahl ansatz*, and since his work numerous authors attempted a derivation of his equation from the Newtonian or quantum mechanical equations of motion for the system. Here we will not repeat the attempt, since we are treating his equation as a fundamental equation for dilute many-particle systems. In this viewpoint, such singlet distribution functions are, without ado, assumed to obey the Boltzmann equation [1]:

$$\partial_t f_a + \mathbf{v}_a \cdot \nabla f_a + \mathbf{F}_a \cdot \nabla_{\mathbf{v}_a} f_a = R[f_a], \quad (3.1)$$

where the collision integral $R[f_a]$ is given by

$$R[f_a] = \sum_{a=1}^r C(f_a f_b), \quad (3.2)$$

$$C(f_a f_b) = \int d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty db \, b g_{ab} [f_a^*(\mathbf{v}_a^*, \mathbf{r}, t) f_b^*(\mathbf{v}_b^*, \mathbf{r}, t) - f_a(\mathbf{v}_a, \mathbf{r}, t) f_b(\mathbf{v}_b, \mathbf{r}, t)]. \quad (3.3)$$

In these equations $\partial_t = \partial/\partial t$, $\nabla_{\mathbf{v}_a} = \partial/\partial \mathbf{v}_a$, $g_{ab} = |\mathbf{v}_a - \mathbf{v}_b|$, \mathbf{F}_a is the external force on unit mass of species a , b is the impact parameter, φ is the azimuthal angle of scattering, and the asterisk denotes the post-collision value. Here the subscripts a and b play a dual role of simultaneously indicating the species and a particle of that species. The external force is assumed to be changing slowly over the distance of the intermolecular force range, so the molecular collisions are not significantly affected by the presence of the external force. The singlet distribution functions are spatially coarse grained over the collision volume of the order of the intermolecular force range. Therefore they remain unchanged over the collision volume. This is

the reason why the singlet distribution functions in the Boltzmann collision integral (3.3) have the same position dependence. The collision integral given in (3.3) accounts for the net change in the number density owing to the collisions of particles in the collision volume. The first term on the right hand side of (3.3) accounts for the increase in the number density arising from the reverse collision, and the second term accounts for the depletion in the number density arising from the forward collision. The collision term was originally given by Ludwig Boltzmann [1]. Eq. (3.1) with (3.3) for the collision integral is called the Boltzmann equation, after its discoverer. If the right hand side of (3.1) were absent then the equation is simply the Liouville equation for a single particle distribution function and is equivalent to the equations of motion of Hamilton. The latter are symmetric with respect to time reversal and so is the single particle Liouville equation. However, as will be seen later, the collision integral breaks the time reversal symmetry and thereby renders the kinetic equation irreversible. Although the discovery of such an equation placed Boltzmann in a serious difficulty with his contemporaries, it should be regarded as his everlasting achievement in statistical mechanics and natural science.

There are many variations known for the Boltzmann collision integral which are designed to describe some specific aspects of gases in hand. For this reason we will generically denote the collisional effect by $R[f_a]$, and the kinetic equation with $R[f_a]$ as the collision term will be called the generic Boltzmann equation. This collision term must fulfill some requirements necessary for the generic Boltzmann equation to be useful for our study here. They are: (1) *it should have collisional invariants so that conservation laws are derivable from the generic Boltzmann equation;* (2) *it should satisfy the H theorem so that the state of equilibrium is stable;* (3) *it is invariant under canonical transformations.* We will elaborate on these conditions later. These requirements are fully satisfied by the Boltzmann collision integral given in (3.2) and (3.3).

Two-particle collision dynamics associated with the Boltzmann collision integral is such that

$$g_{ab} = g_{ab}^* \quad (3.4)$$

and

$$d\mathbf{v}_a d\mathbf{v}_b d\Omega = d\mathbf{v}_a^* d\mathbf{v}_b^* d\Omega^*, \quad (3.5)$$

where $d\Omega$ denotes the solid angle of scattering $d\Omega = \sin\theta d\theta d\varphi$, with θ standing for the scattering angle. If the scattering cross section $\sigma(g_{ab}^*|g_{ab})$ is defined by the relation [2,3]

$$\mathfrak{b} d\mathfrak{b} d\varphi = \sigma(g_{ab}^*|g_{ab}) d\Omega, \quad (3.6)$$

the microscopic reversibility and (3.4) imply the relation

$$\sigma(g_{ab}^*|g_{ab}) = \sigma(g_{ab}|g_{ab}^*). \quad (3.7)$$

These relations, which are consequences of the invariance properties of the dynamical equations of motion, will prove useful for deriving the conservation equations and proving the H theorem later.

3.2 Mean Macroscopic Variables

The distribution function may be normalized to number density n_a as follows:

$$n_a(\mathbf{r}, t) = \int d\mathbf{v}_a f_a(\mathbf{v}_a, \mathbf{r}; t). \quad (3.8)$$

Then the total number density of the mixture is given by

$$n(\mathbf{r}, t) = \sum_{a=1}^r n_a(\mathbf{r}, t). \quad (3.9)$$

Henceforth we will abbreviate the integral over velocity space with angular brackets; for example,

$$n_a(\mathbf{r}, t) = \int d\mathbf{v}_a f_a(\mathbf{v}_a, \mathbf{r}; t) = \langle f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle.$$

The mass densities are defined by

$$\rho_a(\mathbf{r}, t) = \langle m_a f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle \quad (3.10)$$

and thus the total mass density is given by

$$\rho(\mathbf{r}, t) = \sum_{a=1}^r \rho_a(\mathbf{r}, t). \quad (3.11)$$

The mean velocity $\mathbf{u}_a(\mathbf{r}, t)$ of species a is then defined by the formula

$$\rho_a(\mathbf{r}, t) \mathbf{u}_a(\mathbf{r}, t) = \langle m_a \mathbf{v}_a f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle \quad (3.12)$$

and the total mean velocity $\mathbf{u}(\mathbf{r}, t)$ by the expression

$$\mathbf{u}(\mathbf{r}, t) = \rho^{-1} \sum_{a=1}^r \rho_a(\mathbf{r}, t) \mathbf{u}_a(\mathbf{r}, t). \quad (3.13)$$

This total mean velocity will be simply called the fluid velocity or the mean velocity. It is now convenient to introduce the peculiar velocity of a particle which we define by

$$\mathbf{C}_a = \mathbf{v}_a - \mathbf{u}. \quad (3.14)$$

The internal energy density \mathcal{E} of the fluid is then defined by the statistical formula

$$\rho \mathcal{E}(\mathbf{r}, t) = \sum_{a=1}^r \left\langle \frac{1}{2} m_a C_a^2 f_a(\mathbf{v}_a, \mathbf{r}; t) \right\rangle. \quad (3.15)$$

Therefore $\rho\mathcal{E}$ is the internal energy per unit volume of the fluid. In general, moments of a peculiar velocity are defined by the statistical formula

$$\mathcal{M}_a^{(s)} = \langle \mathbf{C}_a^{s_1} \mathbf{C}_a^{s_2} \cdots \mathbf{C}_a^{s_m} f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle, \quad (3.16)$$

where $(s) = (s_1, s_2, \dots, s_m)$. Temporal and spatial evolutions of these macroscopic variables are important objects of study in the kinetic theory pursued in this work.

3.3 Collisional Invariants

The Boltzmann collision integral (3.2) has the special property that it gives rise to a vanishing integral of a collisionally invariant quantity. Let us denote by ψ_a a function of \mathbf{v}_a and \mathbf{r} and consider the integral [4,5]

$$I[\psi] \equiv \sum_{a=1}^r \sum_{b=1}^r \int d\mathbf{v}_a \psi_a(\mathbf{v}_a, \mathbf{r}) C(f_a f_b). \quad (3.17)$$

On substitution of the explicit expression for $C(f_a f_b)$, there follows

$$\begin{aligned} I[\psi] = & \sum_{a=1}^r \sum_{b=1}^r \iint d\mathbf{v}_a d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} \mathbf{b} g_{ab} \psi_a \\ & \times [f_a^*(\mathbf{v}_a^*, \mathbf{r}; t) f_b^*(\mathbf{v}_b^*, \mathbf{r}; t) - f_a(\mathbf{v}_a, \mathbf{r}; t) f_b(\mathbf{v}_b, \mathbf{r}; t)]. \end{aligned} \quad (3.18)$$

On exchanging the subscripts a and b , adding the result to (3.18), and dividing by 2, we obtain

$$\begin{aligned} I[\psi] = & \frac{1}{2} \sum_{a=1}^r \sum_{b=1}^r \iint d\mathbf{v}_a d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} \mathbf{b} g_{ab} (\psi_a + \psi_b) \\ & \times [f_a^*(\mathbf{v}_a^*, \mathbf{r}; t) f_b^*(\mathbf{v}_b^*, \mathbf{r}; t) - f_a(\mathbf{v}_a, \mathbf{r}; t) f_b(\mathbf{v}_b, \mathbf{r}; t)]. \end{aligned} \quad (3.19)$$

The collision process involved in (3.19) is $(\mathbf{v}_a, \mathbf{v}_b) \rightarrow (\mathbf{v}_a^*, \mathbf{v}_b^*)$. On reversal of this collision process the integral in (3.19) takes the form

$$\begin{aligned} I[\psi] = & \frac{1}{2} \sum_{a=1}^r \sum_{b=1}^r \iint d\mathbf{v}_a^* d\mathbf{v}_b^* \int_0^{2\pi} d\varphi^* \int_0^\infty d\mathbf{b}^* \mathbf{b}^* g_{ab} (\psi_a^* + \psi_b^*) \\ & \times [f_a(\mathbf{v}_a, \mathbf{r}; t) f_b(\mathbf{v}_b, \mathbf{r}; t) - f_a^*(\mathbf{v}_a^*, \mathbf{r}; t) f_b^*(\mathbf{v}_b^*, \mathbf{r}; t)]. \end{aligned} \quad (3.20)$$

However, since the symmetry properties (3.4)–(3.7) hold, (3.20) may be written as

$$\begin{aligned} I[\psi] = & \frac{1}{2} \sum_{a=1}^r \sum_{b=1}^r \iint d\mathbf{v}_a d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} \mathbf{b} g_{ab} (\psi_a^* + \psi_b^*) \\ & \times [f_a(\mathbf{v}_a, \mathbf{r}; t) f_b(\mathbf{v}_b, \mathbf{r}; t) - f_a^*(\mathbf{v}_a^*, \mathbf{r}; t) f_b^*(\mathbf{v}_b^*, \mathbf{r}; t)]. \end{aligned} \quad (3.21)$$

On adding this to (3.19) side by side and dividing the result by 2, we obtain

$$I[\psi] = -\frac{1}{4} \sum_{a=1}^r \sum_{b=1}^r \iint d\mathbf{v}_a d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} \, \mathbf{b} g_{ab} (\psi_a^* + \psi_b^* - \psi_a - \psi_b) \\ \times [f_a^*(\mathbf{v}_a^*, \mathbf{r}; t) f_b^*(\mathbf{v}_b^*, \mathbf{r}; t) - f_a(\mathbf{v}_a, \mathbf{r}; t) f_b(\mathbf{v}_b, \mathbf{r}; t)]. \quad (3.22)$$

If the quantity ψ_a is conserved in a collision, namely, if ψ_a is a collisionally invariant quantity, then

$$\psi_a^* + \psi_b^* - \psi_a - \psi_b = 0 \quad (3.23)$$

and the integral $I[\psi]$ vanishes identically:

$$I[\psi] = 0. \quad (3.24)$$

Such a quantity is called a collisional invariant. Mass, momentum, and kinetic energy are examples. As will be shown later, they give rise to mass, momentum, and energy conservation laws.

3.4 Broken Time Reversal Symmetry

Unlike the Newtonian equations of motion or quantum equations of motion, the Boltzmann equation is not invariant under the reversal of the directions of time and velocity, indicating the inherent unidirectionality of natural phenomena, namely, the irreversibility of macroscopic natural (spontaneous) processes which proceed only in one direction. To show this feature of the Boltzmann equation we reverse the direction of time, $t \rightarrow -t$, in the equation. Since the velocities must also be reversed with time reversal, the Boltzmann equation takes the form

$$[\partial_{-t} + (-\mathbf{v}_a) \cdot \nabla + \mathbf{F}_a \cdot \nabla_{-\mathbf{v}_a}] f_a(-\mathbf{v}_a, \mathbf{r}; -t) = - \sum_{b=1}^r \vartheta C(f_a f_b), \quad (3.25)$$

where ϑ is the time reversal operator and

$$\begin{aligned} \vartheta C(f_a f_b) &\equiv C[f_a(-\mathbf{v}_a, \mathbf{r}; -t) f_b(-\mathbf{v}_b, \mathbf{r}; -t)] \\ &= \int d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} \, \mathbf{b} g_{ab} [f_a^*(-\mathbf{v}_a^*, \mathbf{r}, -t) f_b^*(-\mathbf{v}_b^*, \mathbf{r}, -t) \\ &\quad - f_a(-\mathbf{v}_a, \mathbf{r}; -t) f_b(-\mathbf{v}_b, \mathbf{r}; -t)]. \end{aligned} \quad (3.26)$$

Because of the appearance of the negative sign in front of the collision integral in (3.25), the time reversed distribution function $f_a(-\mathbf{v}_a, \mathbf{r}; -t)$

does not obey the same Boltzmann equation (3.1) as the one obeyed by $f_a(\mathbf{v}_a, \mathbf{r}; t)$. This means that the Boltzmann equation is not invariant under time reversal, in contrast to the single particle Liouville equation

$$[\partial_t + \mathbf{v}_a \cdot \nabla + \mathbf{F}_a \cdot \nabla_{\mathbf{v}a}] f_a = 0,$$

which is invariant under time reversal, as are the Newtonian equations of motion. The broken time reversal symmetry is attributable to the presence of the Boltzmann collision integral, and the latter makes the kinetic equation irreversible. This is the most distinguishing feature of the Boltzmann equation which must be shared by any other kinetic equations one may assume for description of macroscopic processes in fluids; it is also the feature that makes the Boltzmann equation capable of describing irreversible phenomena in a way consistent with the second law of thermodynamics. Since the Boltzmann equation and any irreversible kinetic equations cannot be derived from the principles of classical or quantum mechanics alone in the strict sense of the word derivation, we raise it to the status of postulate and *a posteriori* seek its validity. We remark that, as will be shown in a later chapter, despite the inequality of the time derivative of the H function that reminds us of the Clausius–Duhem inequality, the H theorem of Boltzmann is not the second law of thermodynamics as commonly thought in kinetic theory and statistical mechanics. At least, their equivalence has by no means been demonstrated in a convincing and unequivocal manner.

3.5 Generic Boltzmann Equation

The Boltzmann equation, although it is a prototype of kinetic equations, is not unique in describing irreversible phenomena. The precise form of the time reversal symmetry breaking collision term can vary depending on our understanding of irreversible phenomena in fluids. However, as mentioned earlier, the irreversible collision integral must satisfy some stringent requirements in order for the kinetic equation, containing the collision integral as a part, to be useful for describing irreversible phenomena in fluids, since irreversible phenomena must obey the laws of thermodynamics. Here we elaborate on the aforementioned requirements. The irreversible collision integral is generically denoted by $R[f_a]$. We thus assume the kinetic equation in the form¹

$$[\partial_t + \mathbf{v}_a \cdot \nabla + \mathbf{F}_a \cdot \nabla_{\mathbf{v}a}] f_a(\mathbf{v}_a, \mathbf{r}; t) = R[f_a], \quad (3.27)$$

¹In the semigroup theory of irreversibility a similar approach is taken, where, for example, the Pauli master equation is postulated and then its consequences are formally investigated. See G. Lindblad, *Nonequilibrium Entropy and Irreversibility* (Reidel, Dordrecht, 1983) and other references cited therein. In the literature of semigroup theory transport processes and irreversible thermodynamics are not studied in any manner resembling the present work.

where $R[f_a]$ is assumed to be decomposable into components as follows:

$$R[f_a] \equiv \sum_{b=1}^r R[f_a f_b] \equiv \sum_{b=1}^r R(f_a f_b | f_a^* f_b^*) \quad (3.28)$$

with the requirements that $R(f_a f_b | f_a^* f_b^*)$ are symmetric with respect to interchange of indices a and b and change their sign under the reversal of the collision process which results in interchange of the post-collision values with the pre-collision values: $(f_a, f_b) \rightarrow (f_a^*, f_b^*)$, that is,

$$R(f_a f_b | f_a^* f_b^*) = R(f_b f_a | f_b^* f_a^*), \quad (3.29)$$

$$R(f_a f_b | f_a^* f_b^*) = -R(f_a^* f_b^* | f_a f_b). \quad (3.30)$$

Since the distribution function must be independent of time and position if the system is at equilibrium, the collision term $R(f_a f_b | f_a^* f_b^*)$ must vanish at equilibrium:

$$R(f_a^{\text{eq}} f_b^{\text{eq}} | f_a^{\text{eq}*} f_b^{\text{eq}*}) = 0, \quad (3.31)$$

where f_a^{eq} and so on are equilibrium solutions of the kinetic equation (3.27). The distribution functions $f_a(\mathbf{v}_a, \mathbf{r}; t)$ vanish at the boundaries of the phase space; namely, $f_a(\pm\infty, \mathbf{r}; t) = 0$ and $f_a(\mathbf{v}_a, \mathbf{r}; t) = 0$ at the boundaries of the container of the gas. The kinetic equation (3.27) implicitly assumes that the evolution of the gas is not affected by the boundaries of the system or by the surroundings. Removal of this assumption would require a reformulation of the theory, but would widen the scope of the theory to a new dimension. Formulation of such a theory will be deferred to a future work.

Let us define the following integral involving $R[f_a]$:

$$I_r[\psi] = \sum_{a=1}^r \langle \psi_a R[f_a] \rangle, \quad (3.32)$$

where ψ_a is a function of \mathbf{v}_a and \mathbf{r} . Integral (3.17) is a special case of this integral. The following conditions are required for $R[f_a]$ to satisfy.

Condition 1 *If ψ_a is a collisional invariant then*

$$I_r[\psi] = 0. \quad (3.33)$$

Condition 2 *For f_a obeying the kinetic equation (3.27) and $\psi_a = -\ln f_a$,*

$$I_r[-\ln f_a] \geq 0, \quad (3.34)$$

where the equality applies to equilibrium only.

Condition 3 *The collision term is invariant under canonical transformations.*

The first condition is for the conservation laws of mass, momentum, and energy, and the second condition, namely, the inequality, is related to the H theorem to be discussed later. When these conditions are met by $R[f_a]$, the kinetic equation (3.27) will be called the generic Boltzmann equation. The Boltzmann equation is a particular case or, more correctly put, a prototype of this class of kinetic equations. The linearized Boltzmann equation, the Bhatnagar–Krook–Gross kinetic equation [6], the Boltzmann–Nordheim–Uehling–Uhlenbeck (BNUU) equations [7,8] for Fermi–Dirac and Bose–Einstein gases, and the generalized Boltzmann equation [9] for singlet distribution functions of dense gases all belong to this class of generic Boltzmann equation. We first develop the theory in terms of the generic Boltzmann equation in this work.

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4

Equilibrium Solution and Local Variables

Boltzmann was interested in showing that the distribution function obeying his kinetic equation approaches equilibrium as time progresses and that the equilibrium solution is unique. He achieved this aim with the help of the H function, which may be regarded as a Lyapounov function. He preceded Lyapounov in introducing such a function, although the context was somewhat different from Lyapounov's, which is about ordinary differential equations. Boltzmann also showed that the equilibrium H function has the same qualities as the entropy of a dilute gas which was introduced by Clausius [1] about seven years earlier in thermodynamics. Furthermore, the H theorem makes it possible to construct a unique equilibrium solution for the Boltzmann equation. This will be shown. It will be also shown that the kinetic equation gives rise to the mass, momentum, and internal energy balance equations in conformity with the conservation laws that must be obeyed by macroscopic processes. The entropy balance equation will be also presented.

4.1 The H Theorem and Boltzmann Entropy

We define the Boltzmann entropy S of the gas by the statistical mechanical formula

$$S(t) = -k_B \sum_{a=1}^r \int_V d\mathbf{r} \langle [\ln f_a(\mathbf{v}_a, \mathbf{r}; t) - 1] f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle. \quad (4.1)$$

The integration in the configuration space is over the volume of the container of the gas. There are some important points which we must notice in this Boltzmann entropy that distinguish it from the thermodynamic entropy, namely, the Clausius entropy: the Boltzmann entropy $S(t)$ is defined in terms of distribution functions in the phase space. It is the negative of the average of information in the currently used terminology of information theory [2,3]. Since the distribution functions in the phase space describe the microscopic states of the particles in the system of the order of 10^{23} in number, the information content of $S(t)$ is enormous. Secondly, the Boltzmann entropy in (4.1) is defined for a system which is not neces-

sarily in equilibrium. In fact, it is in a nonequilibrium state at time t . Since the entropy introduced originally by Clausius [1] was defined for systems at equilibrium or, more precisely put, systems undergoing a reversible process, the Boltzmann entropy defined statistically in (4.1) generalizes the notion of Clausius' entropy defined for equilibrium and coincides with the latter only at equilibrium or for reversible processes where energy dissipation, which Clausius called uncompensated heat, is absent. This distinction between Clausius' entropy and the Boltzmann entropy should be clearly kept in mind to avoid possible conceptual difficulties that might arise in the course of the study of irreversible processes. Since there is a necessity of distinguishing them, the statistical entropy defined by (4.1) will be called the Boltzmann entropy.

By differentiating $S(t)$ with time and using the kinetic equation (3.27) and the boundary conditions on the distribution functions, we obtain

$$\begin{aligned} \frac{dS}{dt} &= k_B \sum_{a=1}^r \int_V d\mathbf{r} I_r[-\ln f_a] \\ &= -k_B \sum_{a=1}^r \int_V d\mathbf{r} \langle \ln f_a R[f_a] \rangle \geq 0 \end{aligned} \quad (4.2)$$

by Condition 2 on $R[f_a]$, namely, (3.34). Here we emphasize that the boundary effects on the gas properties are neglected, and hence there is no boundary contribution present in (4.2). This is permissible in the normal density range, but may require a correction in the rarefied density regime where the boundary effects become pronounced. In the case of the Boltzmann equation (3.1) the inequality (4.2) holds because

$$\begin{aligned} \frac{dS}{dt} &= \frac{1}{4} k_B \sum_{a=1}^r \sum_{b=1}^r \int_V d\mathbf{r} \int d\mathbf{v}_a \int d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} \mathfrak{b} g_{ab} \\ &\quad \times \ln \left(\frac{f_a^* f_b^*}{f_a f_b} \right) [f_a^* f_b^* - f_a f_b] \\ &\geq 0. \end{aligned} \quad (4.3)$$

Here the inequality $\ln(x/y)(x - y) \geq 0$ is used. The equality holds only at equilibrium, where

$$f_a^{\text{eq}*}(\mathbf{v}_a, \mathbf{r}) f_b^{\text{eq}*}(\mathbf{v}_b, \mathbf{r}) = f_a^{\text{eq}}(\mathbf{v}_a, \mathbf{r}) f_b^{\text{eq}}(\mathbf{v}_b, \mathbf{r}). \quad (4.4)$$

Here $f_a^{\text{eq}}(\mathbf{v}_a, \mathbf{r})$ and so on are the equilibrium distribution functions which are either independent of \mathbf{r} in the absence of an external force or depend on \mathbf{r} through the external force with a potential. *The equilibrium is asymptotically reached after a long time.* The equilibrium condition (4.4) is also

obtained from (4.2) on applying the symmetry properties of $R(f_a f_b | f_a^* f_b^*)$ in (3.29), which gives rise to the inequality

$$\frac{1}{4} k_B \sum_{a=1}^r \sum_{b=1}^r \int_V dr \left\langle \ln \left(\frac{f_a^* f_b^*}{f_a f_b} \right) R(f_a f_b | f_a^* f_b^*) \right\rangle \geq 0.$$

Since, as required by the condition on the collision term, the equality applies to equilibrium only, and Condition 1, namely, (3.33) implies that $\ln f_a$ must be a collision invariant at equilibrium, the equilibrium condition (4.4) is obtained for the generic collision term $R[f_a]$. Inequality (4.2) or (4.3) is called the H theorem of Boltzmann who first discovered it with his kinetic equation. In statistical mechanics and kinetic theory in particular this theorem is regarded as a statistical representation of the second law of thermodynamics. However, at this point in the development of theory it is no more than a plausible assertion, the validity of which must be demonstrated. Without such a demonstration the kinetic theory of matter remains detached from the laws of thermodynamics. It is an important aim of this work to investigate the manner of their mutual connection.

4.2 Equilibrium Solution

Since the equilibrium distribution functions are independent of time and position, and the collision integral is identically equal to zero at equilibrium

$$R(f_a^{\text{eq}} f_b^{\text{eq}} | f_a^{\text{eq}*} f_b^{\text{eq}*}) = 0, \quad (4.5)$$

f_a^{eq} is an equilibrium solution of the generic Boltzmann equation. It can be shown that it, moreover, is a unique solution of the kinetic equation except for the meaning of a parameter. We now construct the equilibrium solution f_a^{eq} and show that it has a unique mathematical form.

On taking the logarithm there follows from (4.4) the equation

$$\ln f_a^{\text{eq}*}(\mathbf{v}_a, \mathbf{r}) + \ln f_b^{\text{eq}*}(\mathbf{v}_b, \mathbf{r}) = \ln f_a^{\text{eq}}(\mathbf{v}_a, \mathbf{r}) + \ln f_b^{\text{eq}}(\mathbf{v}_b, \mathbf{r}). \quad (4.6)$$

This equation implies that $\ln f_a^{\text{eq}}(\mathbf{v}_a, \mathbf{r})$ and so on are collision invariants. Since there are only five basic collision invariants, $\ln f_a^{\text{eq}}(\mathbf{v}_a, \mathbf{r})$ must be a linear combination of the five collision invariants. Therefore, we may write

$$\ln f_a^{\text{eq}}(\mathbf{v}_a, \mathbf{r}) = m_a \alpha_0 + m_a \mathbf{v}_a \cdot \boldsymbol{\alpha}_1 - [\frac{1}{2} m_a v_a^2 + m_a U_a(\mathbf{r})] \alpha_2, \quad (4.7)$$

where α_0 , $\boldsymbol{\alpha}_1 = (\alpha_{11}, \alpha_{12}, \alpha_{13})$, and α_2 are five coefficients associated with the five collision invariants, and $U_a(\mathbf{r})$ is the external potential per unit mass of species a of the force \mathbf{F}_a , which is assumed to be a slowly changing function of \mathbf{r} in the collision volume. Therefore the Hamiltonian $H_a = \frac{1}{2} m_a v_a^2 + m_a U_a(\mathbf{r})$ is a collision invariant. By making the transformation

$\mathbf{C}_a = \mathbf{v}_a - \boldsymbol{\alpha}_1/\alpha_2$ it is possible to rewrite the equilibrium distribution function in the form

$$f_a^{\text{eq}}(\mathbf{v}_a, \mathbf{r}) = \exp \left\{ \alpha_3 - \left(\frac{1}{2} m_a C_a^2 + m_a U_a(\mathbf{r}) \right) \alpha_2 \right\}, \quad (4.8)$$

where $\alpha_3 = m_a(\alpha_0 + \boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_1/\alpha_2)$. To determine the coefficient α_3 , the distribution function is normalized to the number density n_a^e in the presence of the external field:

$$n_a^e = \langle f_a^{\text{eq}}(\mathbf{v}_a, \mathbf{r}) \rangle, \quad (4.9)$$

which yields

$$\exp(-\alpha_3) = n_a^e^{-1} \langle \exp \left[- \left(\frac{1}{2} m_a C_a^2 + m_a U_a(\mathbf{r}) \right) \alpha_2 \right] \rangle. \quad (4.10)$$

Here the angular brackets denote integration over the \mathbf{C}_a space. Since the potential is not involved in the integration over \mathbf{C}_a , it is convenient to factor out the potential term and define n_a^o such that

$$n_a^e = n_a^o \exp(-m_a U_a \alpha_2). \quad (4.11)$$

In this definition n_a^o is interpreted as the density of species a at the point where $U_a = 0$. Evaluating the velocity integral in (4.10), we find

$$\exp(-\alpha_3) = (n_a^o)^{-1} \left(\frac{2\pi}{m_a \alpha_2} \right)^{3/2}. \quad (4.12)$$

Since f_a^{eq} in (4.8) is an even function of \mathbf{C}_a , the mean value of $m_a \mathbf{C}_a$ is equal to zero. Therefore, we obtain

$$\frac{\boldsymbol{\alpha}_1}{\alpha_2} = \frac{\sum_{a=1}^r \langle m_a \mathbf{v}_a f_a^{\text{eq}} \rangle}{\sum_{a=1}^r \langle m_a f_a^{\text{eq}} \rangle}. \quad (4.13)$$

We now determine f_a^{eq} such that

$$\rho_e = \sum_{a=1}^r \langle m_a f_a^{\text{eq}} \rangle, \quad (4.14)$$

and

$$\rho_e \mathbf{u} = \sum_{a=1}^r \langle m_a \mathbf{v}_a f_a^{\text{eq}} \rangle. \quad (4.15)$$

The meanings of these definitions will be discussed later. With (4.14) and (4.15), we find

$$\frac{\boldsymbol{\alpha}_1}{\alpha_2} = \mathbf{u} \quad (4.16)$$

and \mathbf{C}_a is found to be the peculiar velocity introduced earlier. To determine the coefficient α_2 we proceed as follows. First, we define the mean kinetic energy by the statistical formula

$$\bar{E}_e = \sum_{a=1}^r \langle \frac{1}{2} m_a C_a^2 f_a^{\text{eq}} \rangle, \quad (4.17)$$

which we will recast in the form

$$\bar{E}_e \equiv \frac{3}{2} n_e k_B T_e. \quad (4.18)$$

Here $n_e = \sum_a^r n_a^e$. The right hand side of (4.18) at this point is merely a symbolic shorthand representation of the mean kinetic energy and no special meaning is to be read into the symbol T_e at this point. It will be bestowed with its thermodynamic meaning when the ensemble method of Gibbs is fully implemented presently. Evaluation of the term on the right hand side of (4.17) yields

$$\alpha_2 = \frac{1}{k_B T_e}, \quad (4.19)$$

which may be rewritten as

$$T_e = \frac{1}{\alpha_2 k_B} = \frac{2\bar{E}_e}{3n_e k_B}. \quad (4.20)$$

Thus the physical meanings of all the coefficients (4.7) are elucidated at the statistical mechanics level; in particular, α_2 is inversely proportional to the mean energy \bar{E}_e . The equilibrium distribution function is now found to be in the form

$$\begin{aligned} f_a^{\text{eq}}(\mathbf{v}_a, \mathbf{r}) &= n_a^0 \left(\frac{m_a}{2\pi k_B T_e} \right)^{3/2} \exp \left[-\frac{1}{k_B T_e} \left(\frac{1}{2} m_a C_a^2 + m_a U_a(\mathbf{r}) \right) \right] \\ &= n_a^0 \left(\frac{m_a}{2\pi k_B T_e} \right)^{3/2} \exp \left(-\frac{m_a C_a^2}{2k_B T_e} \right). \end{aligned} \quad (4.21)$$

This form of equilibrium distribution function is unique, since there is only one way of forming the linear combination of collision invariants, as in (4.7).

We have defined the symbol T_e by the statistical formula in (4.17), but nothing is said as to its thermodynamical operational meaning since, as it stands, T_e in (4.18) is just an abbreviation for the statistical average of the kinetic energy on the right hand side of (4.17) and is just a number. To clarify the meaning of the symbol T_e in terms of a physically more transparent concept in thermodynamics, it is necessary to invoke thermodynamics. In order to make connection with the phenomenological theory of thermodynamics the Gibbsian statistical mechanics in the tradition of Maxwell and Boltzmann claims that statistically computed mechanical variables, such as mean kinetic energy, pressure, density, and so on, can be made to correspond to their thermodynamic and phenomenological counterparts and also the statistical, equilibrium Boltzmann entropy to the Clausius entropy in thermodynamics. This correspondence principle for the statistical mean observables and the thermodynamic observables in essence selects a particular equilibrium solution of the Boltzmann equation that produces the structure of the equilibrium thermodynamics of Clausius. This correspondence

principle is the conceptual bedrock of the Gibbsian statistical mechanics [4]. By using this principle we can determine the precise thermodynamical meaning of the symbol T_e introduced earlier and, more generally, the constants α_1 , α_2 , and α_3 which are then selected to be a particular set of thermodynamically relevant variables. To this stated end we first calculate the equilibrium Boltzmann entropy S_e by substituting (4.21) into (4.1):

$$S_e = T_e^{-1} \left\{ E_e + N k_B T_e - k_B T_e \sum_{a=1}^r N_a \ln \left[\left(\frac{m_a}{2\pi k_B T_e} \right)^{3/2} n_a^e \right] \right\}, \quad (4.22)$$

where

$$N = \sum_{a=1}^r N_a = \sum_{a=1}^r \int_V d\mathbf{r} \langle f_a^{\text{eq}}(\mathbf{v}_a, \mathbf{r}) \rangle, \quad (4.23)$$

$$E_e = \sum_{a=1}^r \int_V d\mathbf{r} \left\langle \frac{1}{2} m_a C_a^2 f_a^{\text{eq}}(\mathbf{v}_a, \mathbf{r}) \right\rangle. \quad (4.24)$$

The preservation of normalization for the distribution functions means that $N_a^e = n_a^e V = n_a V = N_a$. The hydrostatic pressure p_e is defined by the statistical formula

$$p_e = \frac{1}{3} \langle m_a C_a^2 f_a^{\text{eq}} \rangle, \quad (4.25)$$

which on evaluation of the integral on the right hand side gives the equation of state

$$p_e = n_e k_B T_e. \quad (4.26)$$

Note that

$$p_e = \frac{2E_e}{3V}. \quad (4.27)$$

Together with this, one may identify the chemical potential from (4.12):

$$\mu_a^e = k_B T_e \ln \left[\left(\frac{m_a}{2\pi k_B T_e} \right)^{3/2} n_a^e \right]. \quad (4.28)$$

By substituting the equilibrium distribution function into (4.1) for S_e and taking its differential, we obtain the Gibbs relation for the Boltzmann entropy

$$dS_e = T_e^{-1} \left(dE_e + p_e dV - \sum_{a=1}^r \mu_a^e dN_a^e \right). \quad (4.29)$$

This differential form can be also derived from (4.22) by differentiating it and using the Gibbs–Duhem equation that can be derived from (4.28). This statistically derived formula is now compared with the equilibrium thermodynamic Gibbs relation[5]

$$dS = T^{-1} \left(dE + pdV - \sum_{a=1}^r \mu_a dN_a \right). \quad (4.30)$$

To be more specific, the following correspondences are made for extensive mechanical variables and the thermal variable S_e and S :

$$\begin{aligned} S_e|_{st} &\Leftrightarrow S|_{th}; & E_e|_{st} &\Leftrightarrow E|_{th}; \\ V|_{st} &\Leftrightarrow V|_{th}; & N_a^e|_{st} &\Leftrightarrow N_a|_{th}. \end{aligned} \quad (4.31)$$

The subscripts st and th on the variables in (4.31) indicate the quantities statistically computed by integration over the phase space and the thermodynamic extensive variables. The correspondence (4.31) suggests that the following correspondence must be made for the coefficients in (4.29) and (4.30):

$$T_e|_{st} \Leftrightarrow T|_{th}; \quad p_e|_{st} \Leftrightarrow p|_{th}; \quad \mu_a^e|_{st} \Leftrightarrow \mu_a|_{th}. \quad (4.32)$$

In this manner the symbol T_e is identified with the thermodynamic temperature T :

$$T_e = T. \quad (4.33)$$

We also conclude that

$$T_e^{-1} = \frac{\partial S_e}{\partial E_e}. \quad (4.34)$$

By this correspondence and by the second law of thermodynamics, as applied to reversible processes, the statistical Boltzmann entropy differential can be seen to be an exact differential in the thermodynamic space spanned by E , V , and n_a . It is of course unnecessary to resort to the second law to show that (4.29) is an exact differential in the thermodynamic space, since it is directly demonstrable from the statistical formulas (4.22) and (4.28) for S_e and μ_a^e , but the present way of looking at the problem is not only insightful but also necessary for more difficult situations such as nonequilibrium. The salient point of the construction of the equilibrium solution (distribution function) described earlier is that: the H theorem provides a unique equilibrium solution in a canonical form, but this canonical form can be made the thermodynamic branch of a solution for the kinetic equation, only if the equilibrium Gibbs relation (the second law of thermodynamics¹) is brought into correspondence with the statistically derived differential form for the Boltzmann entropy, so that the parameters T_e and μ_a^e together with p_e , or equivalently α_2 and α_3 with the equation of state, can be identified with their thermodynamic counterparts, as in (4.32). This summary of the points provides a valuable clue for developing a nonequilibrium theory later in this work.

The determination of the equilibrium distribution function in the form given in (4.21) requires a remark in connection with the determination of

¹In the case of reversible processes the equilibrium Gibbs relation is equivalent to the combination of the first and second laws of thermodynamics.

α_1 . This parameter was determined by demanding that f_a^{eq} also gives rise to the mean velocity \mathbf{u} , as does the nonequilibrium distribution function; see (3.12) and (3.13). This requirement was made for later convenience in theoretical development, but it would have been equally acceptable if it was demanded that f_a^{eq} be determined such that $\langle m_a \mathbf{v}_a f_a^{\text{eq}} \rangle = 0$ in which case α_1 would have been found to be equal to zero. In this event, f_a^{eq} would be given as follows:

$$f_a^{\text{eq}}(\mathbf{v}_a, \mathbf{r}) = n_a^0 \left(\frac{m_a}{2\pi k_B T_e} \right)^{3/2} \exp \left[-\frac{1}{k_B T_e} \left(\frac{1}{2} m_a v_a^2 + m_a U_a(\mathbf{r}) \right) \right]. \quad (4.35)$$

Note that the peculiar velocity in (4.21) is replaced by \mathbf{v}_a in this form.

In conclusion, at equilibrium the Boltzmann entropy is made to coincide with the Clausius entropy by the thermodynamic correspondence principle and the thermodynamic branch of the phase space distribution function is determined for equilibrium. Since the Clausius entropy is defined for equilibrium or reversible processes only, their coincidence at equilibrium is all we can hope for. In this sense the Boltzmann entropy is an extension of the Clausius entropy concept. However, the concept of Boltzmann entropy contains more than thermodynamics needs for the thermodynamic description of irreversible processes, as will be shown in later chapters.

4.3 Local Variables and Matching Conditions

Since the equilibrium fluid is uniform in density, concentrations, and temperature, the variables appearing in the equilibrium Gibbs relation are global. However, since the fluid is, in general, no longer uniform in density, concentrations, and temperature if the fluid is displaced from equilibrium, the fluid properties cannot be properly described in terms of global macroscopic variables; they must be given in terms of time- and space-dependent local macroscopic variables defined in an elementary volume of the fluid at a position and time. We have introduced their statistical definitions given in terms of distribution functions $f_a(\mathbf{v}_a, \mathbf{r}; t)$ in Sec. 4.2. In determining the equilibrium distribution functions we have required that the equilibrium distribution functions are such that the local fluid velocity, namely, the mean fluid velocity \mathbf{u} , is still given as the average over the distribution function f_a^{eq} . The consequence of this demand is that the peculiar velocity appears in f_a^{eq} which is thereby made dependent on \mathbf{r} and t through \mathbf{u} , inasmuch as \mathbf{u} is dependent on \mathbf{r} and t . This type of local-variable-dependent distribution functions, which are called local equilibrium distribution functions, are used in kinetic theory in constructing nonequilibrium distribution functions. Chapman and Cowling [6] state that they are preferred, but provide no other reason for the choice. However, such distribution functions

are a practical necessity if a local theory of hydrodynamics is sought. Therefore it is worthwhile paying closer attention to the procedure of constructing such distribution functions and, if necessary, to formalize the procedure.

If f_a^{eq} as given in (4.21) is a part of the nonequilibrium distribution function, as will be the case in this work and is in any other approaches in the kinetic theory of gases, the parameters such as T_e and the equilibrium density n_a^e would be at best inconvenient and inappropriate to use. Furthermore, it is necessary to embed the thermodynamic description of an equilibrium system in the nonequilibrium Gibbs space spanned by conserved and nonconserved macroscopic variables if the equilibrium theory is a special case of a nonequilibrium theory. Since from this viewpoint a canonical form (4.21) is convenient to have as a part of the distribution function, a reference distribution function is constructed in a mathematically identical form to (4.21) given in terms of local variables—namely, the local equilibrium distribution function. Use of such a distribution function is permissible since it still satisfies the equilibrium condition (4.5). Then the nonequilibrium distribution function is determined such that relative to this reference distribution function there hold the following matching conditions on conserved variables. To elaborate on them we construct the reference distribution function f_a^0 given by the form

$$\begin{aligned} f_a^0 &= n_a^0 \exp \left[-\frac{1}{k_B T} \left(\frac{1}{2} m_a C_a^2 + m_a U_a(\mathbf{r}) \right) \right] \\ &= n_a \left(\frac{m_a}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{m_a C_a^2}{2k_B T} \right). \end{aligned} \quad (4.36)$$

Here n_a is the number density to which the distribution function f_a is normalized, and by the matching condition on density f_a^0 is also normalized to it, as will be shown. The statistical meaning of T is fixed by the matching conditions for the distribution functions.

If the system is spatially homogeneous, by multiplying the collision invariant ψ_a with the generic Boltzmann equation (3.27) and integrating the resulting equation over the velocity and position we obtain [7,8]

$$\frac{d}{dt} V \sum_{a=1}^r \langle \psi_a (f_a - f_a^0) \rangle = 0. \quad (4.37)$$

Integrating it over time we obtain

$$\sum_{a=1}^r \langle \psi_a f_a \rangle = \sum_{a=1}^r \langle \psi_a f_a^0 \rangle. \quad (4.38)$$

This is the necessary and sufficient condition for (4.37) to hold. The nonequilibrium distribution function must rigorously satisfy (4.38).

For spatially inhomogeneous systems (4.38) is replaced by

$$\int_V d\mathbf{r} \sum_{a=1}^r \langle \psi_a (f_a - f_a^0) \rangle = 0. \quad (4.39)$$

Therefore (4.38) is only a sufficient condition for (4.39) to hold. Nevertheless, we determine the nonequilibrium distribution function and the parameters T and n_a in f_a^0 such that (4.38) remains valid. Eq. (4.38) provides the aforementioned matching conditions, which take the forms

$$\rho = \sum_{a=1}^r \langle m_a f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle = \sum_{a=1}^r \langle m_a f_a^0(\mathbf{v}_a, \mathbf{r}; t) \rangle = \rho_e, \quad (4.40)$$

$$\rho \mathbf{u} = \sum_{a=1}^r \langle m_a \mathbf{v}_a f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle = \sum_{a=1}^r \langle m_a \mathbf{v}_a f_a^0(\mathbf{v}_a, \mathbf{r}; t) \rangle = \rho_e \mathbf{u}, \quad (4.41)$$

$$\rho \mathcal{E} = \sum_{a=1}^r \langle \frac{1}{2} m_a C_a^2 f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle = \sum_{a=1}^r \langle \frac{1}{2} m_a C_a^2 f_a^0(\mathbf{v}_a, \mathbf{r}; t) \rangle = \rho_e \mathcal{E}_e. \quad (4.42)$$

By explicit evaluation of the right hand side of (4.42), the mean kinetic energy of the nonequilibrium system can be written as

$$\sum_{a=1}^r \langle \frac{1}{2} m_a C_a^2 f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle = \frac{3}{2} n k_B T, \quad (4.43)$$

which is traditionally taken as the definition of the temperature of the nonequilibrium system. However, as in the case of the equilibrium situation, this relation is no more than the definition of the symbol T and has no thermodynamic operational basis until thermodynamics of the nonequilibrium system is drawn in to play a role in determining the nonequilibrium distribution function f_a as has been the case for the equilibrium system considered in the previous section.

Since in view of the fact that $R(f_a^0 f_b^0 | f_a^{0*} f_b^{0*}) = 0$ and f_a^0 may therefore be replaced by f_a^{eq} and so on, we find $\rho_e \mathcal{E}_e = \frac{3}{2} n_e k_B T_e$, where T_e is the thermodynamic temperature, as has already been established in connection with (4.17). Consequently if (4.43) is taken for the definition of temperature, with the help of the matching conditions, it implies that T is the local temperature at \mathbf{r} and t :

$$T = T_e(\mathbf{r}, t) \quad (4.44)$$

with T_e in the absolute temperature scale. This way the parameter T in f_a^0 may be tentatively interpreted as a quantity with a thermodynamic operational meaning. The complete and final meaning of T will be determined when the nonequilibrium ensemble method is developed in Chapter 7.

Condition (4.40) is equivalent to the condition on the number density:

$$n = \sum_{a=1}^r \langle f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle = \sum_{a=1}^r \langle f_a^0(\mathbf{v}_a, \mathbf{r}; t) \rangle. \quad (4.45)$$

It gives the thermodynamic operational meaning to the statistical mechanical density n_a in f_a^0 . Thus these matching conditions provide correspondence between the equilibrium thermodynamic quantities that have thermodynamically well defined meanings and the statistically defined nonequilibrium quantities that have not as yet taken thermodynamic roots and thus lack operational meanings:

$$\rho \Leftrightarrow \rho_e; \quad T \Leftrightarrow T_e \quad \text{or} \quad \rho\mathcal{E} \Leftrightarrow \rho_e\mathcal{E}_e. \quad (4.46)$$

Here ρ_e and T_e or \mathcal{E}_e are quantities that are determined with f_a^{eq} in (4.21) and from thermodynamics as the equilibrium mass density and the equilibrium temperature or the equilibrium internal energy density. Nevertheless, the correspondence (4.46) is not enough for the purpose of irreversible thermodynamics we have in mind, although these matching conditions play an important role in constructing a theory of irreversible processes in reference to the equilibrium state on the basis of the kinetic equation postulated. We have already discussed in detail the phenomenological meanings of temperature, pressure, chemical potentials or, alternatively, densities of species when the system is away from equilibrium in a previous chapter. These matching conditions should be understood in the light of the discussion on local temperature, pressure, and so on, given in Chapter 2.

We examine the statistical definitions of temperature in more detail to furnish us with better insights that will serve in more complicated situations than the Boltzmann gases. Therefore we return to (4.43), which has been often taken as a statistical definition of temperature. Let us define the reduced peculiar velocity

$$z_a = \left(\frac{1}{2} \beta_e m_a \right)^{1/2} \mathbf{C}_a \quad (4.47)$$

and reduced chemical potential

$$\bar{\mu}_a^e = \frac{\beta_e \mu_a^e}{m_a}. \quad (4.48)$$

The energy per mass then may be written as

$$\begin{aligned} \mathcal{E}_e &= \frac{\sum_{a=1}^r \left\langle \frac{1}{2} m_a C_a^2 f_a^{\text{eq}} \right\rangle}{\sum_{a=1}^r \langle m_a f_a^{\text{eq}} \rangle} \\ &= \beta_e^{-1} \frac{\sum_{a=1}^r \left\langle z_a^2 f_a^{\text{eq}}(z_a, \bar{\mu}_a^e) \right\rangle_{\text{red}}}{\sum_{a=1}^r \langle m_a f_a^{\text{eq}}(z_a, \bar{\mu}_a^e) \rangle_{\text{red}}}, \end{aligned} \quad (4.49)$$

where the subscript red means integration with reduced variables:

$$\langle \cdots f_a^{\text{eq}}(z_a, \bar{\mu}_a^e) \rangle_{\text{red}} = \int dz_a \cdots f_a^{\text{eq}}(z_a, \bar{\mu}_a^e).$$

Such integrals are therefore dimensionless. The reduced mean values

$$\langle z_a^2 f_a^{\text{eq}}(z_a, \bar{\mu}_a^e) \rangle_{\text{red}} \quad \text{and} \quad \sum_{a=1}^r \langle m_a f_a^{\text{eq}}(z_a, \bar{\mu}_a^e) \rangle_{\text{red}}$$

are zero-order homogeneous functions of $(\beta_e m_a)^{-1}$ and μ_a^e/m_a , whereas the mean energy per mass \mathcal{E}_e is a first-order homogeneous function of $(\beta_e m_a)^{-1} = k_B T_e/m_a$:

$$\mathcal{E}_e = \frac{k_B T_e}{\sum_{a=1}^r m_a} O_h(\bar{\mu}^e). \quad (4.50)$$

Here $O_h(\bar{\mu}^e)$ is Euler's zero-order homogeneous function of $(\beta_e m_a)^{-1}$ and μ_a^e/m_a , namely, a function of $\bar{\mu}_a^e$ which is zero-order in the aforementioned variables. In fact, it is simply a constant in the case of Boltzmann gases, namely, the present case. As will be shown later, the mean energy per mass of a dilute gas is always first-order homogeneous in $(k_B T_e/m_a)$ with the coefficient being a zero-order homogeneous function of $(\beta_e m_a)^{-1}$ and μ_a^e/m_a . The temperature may be statistically defined in terms of mean kinetic energy in that sense, and it turns out to be consistent with the resulting thermodynamics theory in the case of dilute Boltzmann gases when the aforementioned thermodynamic correspondence is made.

Tolman [9] examined the equipartition law and showed that suitable generalizations of it can serve as statistical definitions of temperature for relativistic gases and photon gases. In the case of monatomic Boltzmann gases Tolman's definition of temperature coincides with the statistical definition of temperature presented earlier in this work. According to Tolman, the equipartition law can be generalized to the form

$$k_B T_e = \frac{1}{3} \langle (\mathbf{p}_a \cdot \nabla_{\mathbf{p}_a} E_a) f_a^{\text{eq}} \rangle, \quad (4.51)$$

where $\mathbf{p}_a = m_a \mathbf{v}_a$, $\nabla_{\mathbf{p}_a} = \partial/\partial \mathbf{p}_a$, and E_a is the energy (Hamiltonian) of particle a . This formula of Tolman was restated as a means of statistically defining temperature in the literature [10]. Tolman's formula, however, follows from the normalization condition (4.9) on performing integration by parts. Therefore it is simply a rearrangement of the normalization condition and, as such, does not offer a physical interpretation for temperature which is a measure of mean kinetic energy. Therefore it does not appear to be an appropriate definition of temperature, because if the right hand side of (4.51) is explicitly evaluated in the case of particles obeying statistics other than the Boltzmann statistics, namely, Bose-Einstein or Fermi-Dirac statistics, it turns out to be a rather complicated function of T_e related to

the number density. The equipartition approach to statistical definition of temperature breaks down completely in the case of liquids or solids. The Gibbs ensemble theory makes it clear that temperature is not determined statistically in statistical mechanics. It is the continuum, phenomenological, thermodynamical quantity in terms of which mean molecular properties are computed and reckoned in statistical mechanics.

4.4 Stability of Equilibrium

The conclusion from the H theorem examined earlier is that the time derivative of the Boltzmann entropy vanishes at equilibrium which will be reached some time in the future. However, nothing in the proof given indicates in an obvious manner that equilibrium is reached after a long time. Having constructed and examined closely the equilibrium distribution function that yields the structure of the equilibrium thermodynamics of Clausius, we are now prepared to take up for examination the question of when equilibrium is reached. The basic idea to use is that equilibrium is an asymptotically stable fixed point of the solution of the kinetic equation. This asymptotic stability can be shown by constructing a Lyapounov function.

For this proof we confine the discussion to the case where the external force is absent. In this case the equilibrium distribution function is a function of the velocity only. The Boltzmann entropy can be recast in the form

$$S(t) = S_e + S_n(t), \quad (4.52)$$

where

$$S_e = -k_B \sum_{a=1}^r \int d\mathbf{r} \langle [\ln f_a^{\text{eq}}(\mathbf{v}_a) - 1] f_a^{\text{eq}}(\mathbf{v}_a) \rangle, \quad (4.53)$$

$$S_n(t) = -k_B \sum_{a=1}^r \int d\mathbf{r} \left\langle f_a \ln \left[\frac{f_a(\mathbf{v}_a, \mathbf{r}; t)}{f_a^{\text{eq}}(\mathbf{v}_a)} \right] - f_a(\mathbf{v}_a, \mathbf{r}; t) + f_a^{\text{eq}}(\mathbf{v}_a) \right\rangle. \quad (4.54)$$

Since according to the H theorem the Boltzmann entropy $S(t)$ increases towards a maximum at equilibrium, it is clear that

$$\delta S(t) = S(t) - S_e \leq 0. \quad (4.55)$$

This is easy to see from (4.54), since there holds the inequality $x \ln(x/y) - x + y \geq 0$. By differentiating (4.55) and using the same procedure as for proving the H theorem we find

$$\frac{d}{dt} \delta S \geq 0. \quad (4.56)$$

We have used the fact that the time derivative of S_e is equal to zero. Therefore δS is seen to be a Lyapounov function, and according to the stability theory of Lyapounov [11] the equilibrium state where $\delta S(t) = 0$ is asymptotically stable. Thus the fluid asymptotically approaches equilibrium over a long time. This proves the second part of the H theorem. This puts the restriction on the nonequilibrium distribution function that any approximate form for f_a must asymptotically tend to the equilibrium distribution function in the course of time.

4.5 Conservation Laws and Balance Equations

4.5.1 Conservation Laws

Since the ultimate aim of the study made here is in formulating a local theory of irreversible processes, it is necessary to show that the kinetic equation postulated, (3.1), is consistent with the conservation laws of mass, momentum, and energy. By differentiating with respect to time the statistical formulas for mass density, momentum density, and internal energy density given in (3.10), (3.13) and (3.15), respectively, and using the kinetic equation together with the condition (3.33) on the collision integral, we can derive the mass, momentum, and internal energy balance equations. We list them below:

mass:

$$\frac{\partial}{\partial t} \rho = -\nabla \cdot \rho \mathbf{u}, \quad (4.57)$$

$$\frac{\partial}{\partial t} \rho_a = -\nabla \cdot (\mathbf{J}_a + \rho_a \mathbf{u}), \quad (4.58)$$

momentum:

$$\frac{\partial}{\partial t} \rho \mathbf{u} = -\nabla \cdot (\mathbf{P} + \rho \mathbf{u} \mathbf{u}) + \sum_{a=1}^r \rho_a \mathbf{F}_a, \quad (4.59)$$

energy:

$$\frac{\partial}{\partial t} \rho \mathcal{E} = -\nabla \cdot (\mathbf{Q} + \rho \mathcal{E} \mathbf{u}) - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a, \quad (4.60)$$

where \mathbf{P} , \mathbf{Q} , and \mathbf{J}_a are the stress tensor, heat flux, and diffusion flux of species a which will be presently defined statistically. If the substantial time derivative defined by $d/dt = \partial/\partial t + \mathbf{u} \cdot \nabla$ is used, then these balance equations can be written in the forms

$$\rho \frac{dv}{dt} = \nabla \cdot \mathbf{u}, \quad (4.61)$$

$$\rho \frac{d}{dt} c_a = -\nabla \cdot \mathbf{J}_a, \quad (4.62)$$

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla \cdot \mathbf{P} + \sum_{a=1}^r \rho_a \mathbf{F}_a, \quad (4.63)$$

$$\rho \frac{d\mathcal{E}}{dt} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a. \quad (4.64)$$

In these equations the stress tensor, heat flux, and diffusion fluxes are defined, respectively, by the statistical formulas

$$\mathbf{P} = \sum_{a=1}^r \mathbf{P}_a = \sum_{a=1}^r \langle m_a \mathbf{C}_a \mathbf{C}_a f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle, \quad (4.65)$$

$$\mathbf{Q} = \sum_{a=1}^r \mathbf{Q}_a = \sum_{a=1}^r \langle \frac{1}{2} m_a C_a^2 \mathbf{C}_a f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle, \quad (4.66)$$

$$\mathbf{J}_a = \langle m_a \mathbf{C}_a f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle. \quad (4.67)$$

The statistical formula for the stress tensor reflects the fact that stress is a mean momentum flux; the statistical formula for the heat flux stems from the interpretation that energy flux is responsible for heat flow²; and the formula for the diffusion flux clearly indicates that it is a mass flux. If the statistical definitions of mass density and mean velocity are used, the diffusion flux may be written as

$$\mathbf{J}_a = \rho_a (\mathbf{u}_a - \mathbf{u}) \quad (4.68)$$

in agreement with the diffusion flux commonly defined in continuum theory. Eq. (4.57) is the equation of continuity, the momentum balance equation (4.59) is Newton's law of motion generalized to systems subject to a stress, and the internal energy balance equation (4.60) is a representation of the energy conservation law. It is, in fact, a local representation of the first law of thermodynamics. We will return to these equations later when we develop theories of transport processes and irreversible thermodynamics.

4.5.2 Boltzmann Entropy Balance Equation

Evolution of macroscopic variables is subject to the second law of thermodynamics. In order to make this law manifestly satisfied by the macroscopic

²The meaning of heat in irreversible thermodynamics is rather delicate. The heat associated with the internal energy balance equation is not generally the same as that which is meant by the heat associated with the second law of thermodynamics. This subtle distinction between them is clearly made use of in connection with a restricted variational principle formulated by Eu and Ichianagi, *Fortschr. Phys.* **44** (1), 41 (1996).

variables, it is necessary to investigate how the second law of thermodynamics controls the evolution of the system. Since the Boltzmann entropy can be taken as corresponding to the Clausius entropy if the system is at equilibrium, the former is a generalized form of the latter and must have something to do with the second law of thermodynamics and the calortropy that has been found to be directly related to the second law of thermodynamics. To prepare for this line of investigation to be made later, we first develop a formal theory for the Boltzmann entropy in this section.

Since macroscopic irreversible processes are described by local field equations, it is necessary to have a local evolution equation for the Boltzmann entropy. To find the Boltzmann entropy balance equation we first define local Boltzmann entropy density $\mathcal{S}(\mathbf{r}, t)$ by the statistical formula

$$\rho\mathcal{S}(\mathbf{r}, t) = -k_B \sum_{a=1}^r \langle [\ln f_a(\mathbf{v}_a, \mathbf{r}; t) - 1] f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle. \quad (4.69)$$

We also define the Boltzmann entropy flux \mathbf{J}_s and the Boltzmann entropy production σ_{ent} by the statistical formulas, respectively,

$$\mathbf{J}_s(\mathbf{r}, t) = -k_B \sum_{a=1}^r \langle \mathbf{C}_a [\ln f_a(\mathbf{v}_a, \mathbf{r}; t) - 1] f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle, \quad (4.70)$$

$$\sigma_{\text{ent}}(\mathbf{r}, t) = -k_B \sum_{a=1}^r \langle \ln f_a(\mathbf{v}_a, \mathbf{r}; t) R[f_a] \rangle, \quad (4.71)$$

where the collision integral $R[f_a]$ satisfies the requirements mentioned earlier in connection with the generic Boltzmann equation (3.27). The entropy production is positive semidefinite. In the case of the Boltzmann equation, $\sigma_{\text{ent}}(\mathbf{r}, t) \geq 0$ because of the H theorem. Now, by differentiating (4.69) with time and using the kinetic equation (3.27) and the definitions (4.70) and (4.71) we obtain the balance equation for Boltzmann entropy density:

$$\frac{\partial}{\partial t} \rho\mathcal{S}(\mathbf{r}, t) = -\nabla \cdot [\mathbf{J}_s(\mathbf{r}, t) + \rho\mathbf{S}\mathbf{u}] + \sigma_{\text{ent}}(\mathbf{r}, t). \quad (4.72)$$

By using the substantial derivative, we may cast this equation in the form

$$\rho \frac{d\mathcal{S}}{dt} = -\nabla \cdot \mathbf{J}_s + \sigma_{\text{ent}}. \quad (4.73)$$

This Boltzmann entropy balance equation will be one of important objects of attention in this work. As it stands, it is rather formal and does not reveal its connection with macroscopic variables for the fluid and their evolution.

Eq. (4.73) describes the Boltzmann entropy change in an elementary volume located at position \mathbf{r} in a reference frame moving at the fluid velocity \mathbf{u} . This elementary volume is open and hence exchanges heat and matter with its surroundings. If we denote the rate of Boltzmann entropy flow

per unit volume per unit mass between the system (*i.e.*, the elementary volume) and its surroundings by (dQ_s/dt) , then we may write

$$\rho \frac{dQ_s}{dt} = -\nabla \cdot \mathbf{J}_s \quad (4.74)$$

with the outward direction of Q_s taken for the positive direction. Furthermore, if we set

$$\sigma_{\text{ent}} = \rho \hat{\sigma}_{\text{ent}}, \quad (4.75)$$

then the Boltzmann entropy balance equation may be written as

$$\frac{dS}{dt} = \frac{dQ_s}{dt} + \hat{\sigma}_{\text{ent}}. \quad (4.76)$$

Therefore, by the inequality $\hat{\sigma}_{\text{ent}} \geq 0$ implied by the H theorem there follows the inequality

$$\frac{dS}{dt} \geq \frac{dQ_s}{dt}, \quad (4.77)$$

which is reminiscent of the Clausius–Duhem inequality [1]. Note, however, that (dS/dt) is not the derivative of the Clausius entropy for a reversible process which appears in the Clausius–Duhem inequality, but a quantity for an irreversible process as is apparent from the fact that nothing is said about the process being reversible when the Boltzmann entropy balance equation is derived from the kinetic equation. We will investigate in detail in Chapter 7 what connection, if any, (4.73) or (4.76) has to the second law of thermodynamics. For now we will simply make use of the H theorem to construct a local field theory of irreversible processes in the next few chapters. We close this chapter with the following general observation regarding the Boltzmann entropy and the Boltzmann entropy balance equation.

The distribution function f_a obeying the kinetic equation (*i.e.*, the Boltzmann equation) is defined in the phase space appropriate for the system of particles of the order of 10^{23} in number. Thus the information content contained in the phase space distribution function f_a , or more precisely the product $\prod f_a$ for 10^{23} particles, is enormous and much beyond what is necessary for description of macroscopic processes at the thermodynamic level. The latter description requires a much smaller number of variables which are statistical averages of dynamical phase space variables over a large number of particles. We have seen in the discussion on the equilibrium solution of the kinetic equation that the statistical averages such as mean energy, pressure, and so on can be endowed with the status of thermodynamic variables if the thermodynamic correspondence is applied. Under such a correspondence the undetermined parameters in the distribution function acquire thermodynamic meanings. *The distribution function that gives such a description of the macroscopic processes in the system at the thermodynamic level will be called the thermodynamic branch.* The

equilibrium solution we have constructed earlier is one particular equilibrium solution, and it gives rise to a mathematical structure of equilibrium thermodynamics when the parameters, such as β_e , are so chosen as to yield statistically the desired structure of thermodynamics. One can conceive that there are such distribution functions for nonequilibrium.

Let us assume that f_a^c is a thermodynamic branch of the distribution function for the system in nonequilibrium. Its mathematical detail is not necessary for us to know for our purpose in the present discussion, since we look for a general and formal consequence. An important example for f_a^c will be studied in a later chapter. Define the thermodynamic branch of Boltzmann entropy S^c by the statistical formula [12]

$$\rho S^c = -k_B \sum_{a=1}^r \langle [\ln f_a^c(\mathbf{v}_a, \mathbf{r}; t) - 1] f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle. \quad (4.78)$$

We also define the relative Boltzmann entropy³ similarly to (4.54):

$$\begin{aligned} \rho S_r[f|f^c] &= k_B \sum_{a=1}^r \{ \langle [\ln f_a(\mathbf{v}_a, \mathbf{r}; t) - 1] f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle \\ &\quad - \langle [\ln f_a^c(\mathbf{v}_a, \mathbf{r}; t) - 1] f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle \} \\ &= k_B \sum_{a=1}^r \{ \langle [\ln f_a(\mathbf{v}_a, \mathbf{r}; t) - \ln f_a^c(\mathbf{v}_a, \mathbf{r}; t)] f_a \rangle \}. \end{aligned} \quad (4.79)$$

Therefore the Boltzmann entropy density is given by

$$S = S^c - S_r[f|f^c]. \quad (4.80)$$

By Klein's inequality $x \ln x - x + 1 \geq 0$, the relative Boltzmann entropy is positive:

$$S_r[f|f^c] \geq 0, \quad (4.81)$$

the equality holding only if $f = f^c$. It implies that

$$S \leq S^c. \quad (4.82)$$

From (4.80) follows the equation

$$\frac{d}{dt} S = \frac{d}{dt} S^c - \frac{d}{dt} S_r[f|f^c]. \quad (4.83)$$

³The notion of relative Boltzmann entropy appears in the literature on the semigroup theory of irreversibility [16–18] where f_a^c is usually taken for the equilibrium distribution function (solution). In the literature related to the information theory it is called the conditional entropy and sometimes the Kullback entropy. See [3] and [19].

Let us define the following statistical formulas:

$$\mathbf{J}_c(\mathbf{r}, t) = -k_B \sum_{a=1}^r \langle \mathbf{C}_a [\ln f_a^c(\mathbf{v}_a, \mathbf{r}; t) - 1] f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle, \quad (4.84)$$

$$\mathbf{J}_r[f|f^c] = k_B \sum_{a=1}^r \langle \mathbf{C}_a (\ln f_a - \ln f_a^c) f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle, \quad (4.85)$$

$$\sigma_c(\mathbf{r}, t) = -k_B \sum_{a=1}^r \langle \ln f_a^c(\mathbf{v}_a, \mathbf{r}; t) R[f_a] \rangle, \quad (4.86)$$

$$\sigma_r[f|f^c] = k_B \sum_{a=1}^r \langle (\ln f_a - \ln f_a^c) R[f_a] \rangle. \quad (4.87)$$

Therefore, by the H theorem

$$\sigma_{\text{ent}}(\mathbf{r}, t) = \sigma_c(\mathbf{r}, t) - \sigma_r[f|f^c] \geq 0 \quad (4.88)$$

and in the case of the Boltzmann entropy flux

$$\mathbf{J}_s = \mathbf{J}_c - \mathbf{J}_r[f|f^c]. \quad (4.89)$$

We will call $\mathbf{J}_r[f|f^c]$ and $\sigma_r[f|f^c]$ the relative Boltzmann entropy flux and the relative Boltzmann entropy production, respectively. Use of definitions in the Boltzmann entropy balance equation yields the equation

$$\rho \frac{dS}{dt} = -\nabla \cdot \mathbf{J}_c + \sigma_c - (-\nabla \cdot \mathbf{J}_r[f|f^c] + \sigma_r[f|f^c]). \quad (4.90)$$

From the statistical definitions of S^c and $S_r[f|f^c]$ and the kinetic equation (3.27) follows the balance equation for S^c and $S_r[f|f^c]$

$$\rho \frac{dS^c}{dt} = -\nabla \cdot \mathbf{J}_c + \sigma_c - k_B \sum_{a=1}^r \langle f_a \mathcal{D}_t \ln f_a^c \rangle, \quad (4.91)$$

$$\rho \frac{d}{dt} S_r[f|f^c] = -\nabla \cdot \mathbf{J}_r[f|f^c] + \sigma_r[f|f^c] - k_B \sum_{a=1}^r \langle f_a \mathcal{D}_t \ln f_a^c \rangle, \quad (4.92)$$

where

$$\mathcal{D}_t = d_t + \mathbf{C}_a \cdot \nabla + \mathbf{F}_a \cdot \nabla_{\mathbf{v}_a}. \quad (4.93)$$

It is important to recognize that since f_a^c is not necessarily a solution of the kinetic equation, in general

$$\langle f_a \mathcal{D}_t \ln f_a^c \rangle \neq 0. \quad (4.94)$$

These balance equations (4.91) and (4.92) will be the basic equations on which the nonequilibrium ensemble method will be built with an appropriate representation for f_a^c given later in this work.

We would like to discuss the physical significance of the formalism developed here. It was mentioned that the thermodynamic branch of the equilibrium solution was selected for the kinetic equation. Such a solution in the thermodynamic branch is, in essence, an outcome of projecting the phase space distribution function onto the thermodynamic space, and the projection is accompanied by a contraction in information since the description of macroscopic processes in the thermodynamic space requires a much smaller number of degrees of freedom than the description of the same processes in the phase space of, say, 10^{23} particles. Furthermore, a hydrodynamic description of matter inherently and inevitably implies some sort of approximation to the phase space description, since in the former approach we are, first of all, not interested in the molecular details which the kinetic theory is able to provide, but instead often carry on an incomplete description of the macroscopic system even at the macroscopic level, since some macroscopic variables are deemed unimportant and ignored. Thus if we have selected a finite set of macroscopic observables and projected the phase space distribution function onto the thermodynamic space spanned by the macroscopic observables chosen, then the distribution function f_a^c so constructed, rigorously speaking, is not necessarily the solution of the kinetic equation for f_a . Therefore the relative Boltzmann entropy complements our ignorance incurred by our particular choice of thermodynamic observables when f_a^c is constructed to statistically represent our knowledge of thermodynamics of the system in hand. This means that only if our knowledge for the system is without any reference to thermodynamics and to the fullest as required by f_a as a solution of the kinetic equation in the phase space, will the relative Boltzmann entropy and its time derivative then vanish. Otherwise, they do not, and we therefore conclude that in general

$$\frac{d}{dt} S \neq \frac{d}{dt} S^c. \quad (4.95)$$

This inequality has an important significance to the utility of the Boltzmann entropy for thermodynamics of irreversible processes in nonequilibrium systems. We will see that f_a and f_a^c coincide if the fluctuations in macroscopic intensive parameters in f_a^c vanish. We will discuss this point and related aspects in depth in later chapters in this work.

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5

Mathematical Preparation

The Boltzmann equation is a nonlinear integro-differential equation not solvable in a closed analytical form for realistic potential models. Therefore the Boltzmann equation and the generic Boltzmann equation in general must be solved by an approximation method. To prepare ourselves for approximate solutions, for a class of approximation methods, and for the nonequilibrium ensemble method we discuss some mathematical tools used in developing the theory intended in this work. The discussion will be confined only to what is needed for our aim.

5.1 Reduced Kinetic Equation

Since we are compelled to use some kinds of approximation in solving the kinetic equation, it is useful to identify a characteristic ordering parameter to be used in developing approximation methods. Since the left hand side of the kinetic equation (3.27) or the Boltzmann equation represents a change in density arising from collisionless streaming motions of the particles in a volume $V = L^3$, where L is the linear dimension of the container, the characteristic time scale for such motions is

$$L^{-1} \sqrt{\frac{2k_B T}{m}},$$

where T is the temperature and m is the mass of the gas molecule. The distribution function clearly scales like

$$n \left(\frac{m}{2k_B T} \right)^{3/2}$$

with n denoting the number density. Therefore the left hand side of the kinetic equation scales like

$$nL^{-1} \sqrt{\frac{m}{2k_B T}}. \quad (5.1)$$

On the other hand, if we examine the Boltzmann collision integral (3.3) it scales as

$$n^2 \sigma_{\text{el}} \sqrt{\frac{m}{2k_B T}}, \quad (5.2)$$

where σ_{el} is the elastic cross section. To arrive at this scaling factor, we observe that since g_{ij} scales like $(2k_B T/m)^{1/2}$ and the impact parameter is of the order of $\sqrt{\sigma_{\text{el}}}$ the Boltzmann collision integral scales as in (5.2) when the scale factors of the distribution functions are taken into account. Therefore division of the scale factor (5.2) with the scale factor (5.1) yields

$$\frac{n^2 \sigma_{\text{el}} \sqrt{m/2k_B T}}{nL^{-1} \sqrt{m/2k_B T}} = n\sigma_{\text{el}} L.$$

Since the mean free path l may be defined by $l = (n\sigma_{\text{el}})^{-1}$, this ratio is seen to be the inverse of the Knudsen number defined by

$$N_{Kn} = \frac{l}{L}. \quad (5.3)$$

Therefore if we define the following reduced quantities

$$\tau = tL^{-1} \sqrt{\frac{2k_B T}{m}}, \quad \bar{\mathbf{v}}_a = \mathbf{v}_a \sqrt{\frac{m}{2k_B T}},$$

$$\bar{\mathbf{r}} = \mathbf{r}L^{-1}, \quad \hat{\mathfrak{b}} = \mathfrak{b} \sigma_{\text{el}}^{-1/2},$$

$$\bar{\mathbf{F}}_a = \mathbf{F}_a m L (2k_B T)^{-1}, \quad \bar{g}_{ab} = g_{ab} \sqrt{\frac{m}{2k_B T}},$$

$$\hat{f}_a = f_a n^{-1} \left(\frac{2k_B T}{m} \right)^{3/2},$$

then the reduced Boltzmann equation takes the form

$$(\partial_\tau + \bar{\mathbf{v}}_a \cdot \bar{\nabla} + \bar{\mathbf{F}}_a \cdot \bar{\nabla}_{\mathbf{v}a}) \hat{f}_a(\bar{\mathbf{v}}_a, \bar{\mathbf{r}}; \tau) = \epsilon^{-1} \sum_{b=1}^r C(\hat{f}_a \hat{f}_b), \quad (5.4)$$

where ϵ is an abbreviation of the Knudsen number N_{Kn} and

$$\begin{aligned} C(\hat{f}_a \hat{f}_b) &= \int d\bar{\mathbf{v}}_b \int_0^{2\pi} d\varphi \int_0^\infty d\hat{\mathfrak{b}} \hat{\mathfrak{b}} g_{ab} \\ &\times \left[\hat{f}_a^*(\bar{\mathbf{v}}_a^*, \bar{\mathbf{r}}; \tau) \hat{f}_b^*(\bar{\mathbf{v}}_b^*, \bar{\mathbf{r}}; \tau) - \hat{f}_a(\bar{\mathbf{v}}_a, \bar{\mathbf{r}}; t) \hat{f}_b(\bar{\mathbf{v}}_b, \bar{\mathbf{r}}; \tau) \right]. \end{aligned} \quad (5.5)$$

With the understanding that reduced quantities are involved when the Boltzmann collision integral is multiplied by the inverse Knudsen number, we will henceforth drop the overbar from the quantities appearing in the reduced Boltzmann equation for brevity of notation. The generic Boltzmann equation can be reduced similarly, and the reduced generic Boltzmann equation has the form

$$(\partial_\tau + \bar{\mathbf{v}}_a \cdot \bar{\nabla} + \bar{\mathbf{F}}_a \cdot \bar{\nabla}_{\mathbf{v}a}) \hat{f}_a(\bar{\mathbf{v}}_a, \bar{\mathbf{r}}; \tau) = \epsilon^{-1} R[\hat{f}_a]. \quad (5.6)$$

The overbars will be dropped from this reduced kinetic equation under the same understanding as for the Boltzmann equation (5.4) when the reduced collision integral is multiplied by the inverse Knudsen number. It is remarkable that the Knudsen number appears as a parameter that gives the measure of relative importance between the streaming term and the collision integral in the kinetic equation. As the Knudsen number increases, the relative importance of the collision term diminishes and the kinetic equation increasingly approaches that of free streaming particles, namely, the Liouville equation for a particle—the collisionless Boltzmann equation. However, it is important to take into account the collision effect arising from the collision integral if the system of interest is in the transition regime between the normal and rarefied gases and the limiting behavior in the collisionless regime is desired for macroscopic properties. The transition regime is where approximation methods consistent with the H theorem and with the second law of thermodynamics become useful and often crucial to have.

5.2 Tensor Hermite Polynomials

The nonequilibrium distribution functions obeying the kinetic equation are determined in terms of tensor products of peculiar velocities. Since the equilibrium distribution function is Gaussian in the peculiar velocity it is convenient to use it as the weighting function for the tensor polynomials of peculiar velocities. This naturally motivates the use of tensor Hermite polynomials of Cartesian velocity components. Since the tensors and formulas involved can be rather unwieldy it is convenient to introduce a special system of notation. We follow the system of notation devised by Grad [1] and in [2].

In this notational system the d -dimensional vector x_i ($i = 1, 2, \dots, d$) is denoted by boldface \mathbf{x} . The second-rank tensor $x_i x_j$ is denoted by \mathbf{x}^2 . Similarly, \mathbf{x}^n stands for the rank n tensor $x_{i_1} x_{i_2} \dots x_{i_n}$. The scalar product of \mathbf{x} is denoted by the lightface x^2 :

$$x^2 = \sum_{i=1}^d x_i^2. \quad (5.7)$$

The differential operator $\partial/\partial x_i$ is abbreviated to ∇_i and its vector form to boldface ∇ . Similarly to the ordinary vectors, higher rank tensors made up of the differential operators are denoted by ∇^2 for $\nabla_i \nabla_j$ and so on. Whenever convenient the Kronecker delta δ_{ij} will be used in boldface $\boldsymbol{\delta}$ without the subscripts. The second order product $\boldsymbol{\delta}^2$ of the Kronecker deltas stands for the sum of all non-redundant terms obtained by permuting the indices:

$$\boldsymbol{\delta}^2 = \delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}. \quad (5.8)$$

This is a tensor of rank 4. Higher order products, namely, tensors of higher ranks may be built up similarly. In particular, the tensor of rank $2n$, δ^n , is formed by summing all distinct products of n Kronecker deltas which arise when the $2n$ indices are permuted. There are $(2n)!/2^n n!$ terms in the sum. There occur products of unit tensors (*i.e.*, Kronecker deltas) and vectors. For example, the product $\mathbf{x}^s \delta^n$ is a tensor of rank $(s + 2n)$, and it is the sum of all distinct terms obtained by permuting the $(s + 2n)$ subscripts, each term consisting of s \mathbf{x} and n δ . There are $(2n + s)!/2^n n! s!$ terms in the sum. Note that these products $\mathbf{x}^s \delta^n$, δ^n , and so on are symmetrized products. If such a symmetrized product contains a boldface \mathbf{x} or δ with a subscript then it means that only those terms should be included in the sum which are allowed by the restriction indicated by the subscript. For example, given four indices i , j , k , and l , the product $\mathbf{x}^2 \delta$ has 6 terms in the sum whereas $\mathbf{x}^2 \delta_l$ has three terms in which the index l is attached to the delta. This notational device makes the formulas concise and economical to remember. It is worthwhile giving some more examples of this notation since they will be used extensively later in this section. Given an index set $(i, j_1, j_2, \dots, j_n, j_{n+1})$ the product $\mathbf{x}^n \delta$ may be written as

$$\mathbf{x}^n \delta = \mathbf{x}^n \delta_i + x_i \mathbf{x}^{n-1} \delta, \quad (5.9)$$

where the product $\mathbf{x}^n \delta_i$ is the sum of all terms in which i is attached to δ and the subscripts $(j_1, j_2, \dots, j_n, j_{n+1})$ are symmetrically distributed among \mathbf{x}^n and the remaining subscript of δ , and the product $x_i \mathbf{x}^{n-1} \delta$ is the sum of all distinct terms formed with the subscripts $(j_1, j_2, \dots, j_n, j_{n+1})$. This identity is easily verified with the example of $\mathbf{x}^2 \delta$, given the subscript set (i, j, k, l) . If i is an element of the index set (i_1, i_2, \dots, i_n) and j is an element of the set (j_1, j_2, \dots, j_n) the product δ_{ij}^n is the sum of products of n deltas, each delta formed with one subscript from the set i and the other from the set j :

$$\delta_{ij}^n = \delta_{i_1 j_1} \delta_{i_2 j_2} \cdots \delta_{i_n j_n} + \text{all terms of distinct permutations of subscripts.} \quad (5.10)$$

This sum clearly has $n!$ terms in it. For example,

$$\delta_{ij}^2 = \delta_{i_1 j_1} \delta_{i_2 j_2} + \delta_{i_1 j_2} \delta_{i_2 j_1}.$$

It must be noted that δ_{ij}^2 is not the same as δ^2 where the subscripts are not designated to two different sets but simply permuted in a set of four elements. Similarly to (5.9), the product δ^n may be written as

$$\delta^n = \delta_i \delta^{n-1}, \quad (5.11)$$

where i is an element of the set $(i_1, i_2, \dots, i_{2n})$. The identity (5.11) suggests that δ_{ij}^n can be written as

$$\delta_{ij}^n = \delta_{i_1 j}^1 \delta_{ij}^{n-1}, \quad (5.12)$$

where we have affixed the superscript 1 to distinguish $\delta_{i_1 j}^1$ from $\delta_{i_1 j}$. Note that i_1 is attached to the Kronecker delta. Similarly to (5.12) $\mathbf{x}^m \delta_{ij}^n$ is defined as the sum of all terms where each δ draws one subscript from the set $(i_1, i_2, \dots, i_{n+s})$ and the other subscript from the set $(j_1, j_2, \dots, j_{n+r})$ where $r+s = m$. There are $(n+r)!(n+s)!/n!r!s!$ such terms. For example, the subscripts involved are i_1, i_2, j_1 , and j_2 , then the following four products are possible in the system of notation used here:

$$\mathbf{x}^2 \delta = x_{i_1} x_{i_2} \delta_{j_1 j_2} + x_{i_1} x_{j_1} \delta_{i_2 j_2} + x_{i_1} x_{j_2} \delta_{i_2 j_1}$$

$$+ x_{i_2} x_{j_1} \delta_{i_1 j_2} + x_{i_2} x_{j_2} \delta_{i_1 j_1} + x_{j_1} x_{i_2} \delta_{i_1 j_2},$$

$$\mathbf{x}^2 \delta_{i_1} = x_{j_1} x_{j_2} \delta_{i_1 i_2} + x_{i_2} x_{j_2} \delta_{i_1 j_1} + x_{i_2} x_{j_1} \delta_{i_1 j_2},$$

$$\mathbf{x}^2 \delta_{ij}^1 = x_{i_1} x_{j_1} \delta_{i_2 j_2} + x_{i_1} x_{j_2} \delta_{i_2 j_1} + x_{i_2} x_{j_1} \delta_{i_1 j_2} + x_{i_2} x_{j_2} \delta_{i_1 j_1},$$

$$\mathbf{x}^2 \delta_{i_1 j}^1 = x_{i_2} x_{j_1} \delta_{i_1 j_2} + x_{i_2} x_{j_2} \delta_{i_1 j_1}.$$

The weight function for tensor Hermite polynomials formed with d dimensional vectors is given by

$$\omega(\mathbf{x}) = (2\pi)^{-d/2} \exp\left(-\frac{1}{2}\mathbf{x}^2\right). \quad (5.13)$$

It is normalized:

$$\int d\mathbf{x} \omega(\mathbf{x}) = 1, \quad (5.14)$$

with $d\mathbf{x}$ denoting $dx_1 dx_2 \cdots dx_d$, the volume element of the space. These Hermite polynomials of d dimensional \mathbf{x} are defined by the generating function [3]

$$\exp\left[\frac{1}{2}\mathbf{x}^2 - \frac{1}{2}(\mathbf{x} - \mathbf{a}) \cdot (\mathbf{x} - \mathbf{a})\right] = \sum_{\{n_k\}} \prod_{k=1}^d \frac{a_k^{n_k}}{n_k!} \mathcal{H}^{(n_k)}(\mathbf{x}), \quad (5.15)$$

where

$$\mathbf{a} = (a_1, a_2, \dots, a_d)$$

and thus

$$(\mathbf{x} - \mathbf{a}) \cdot (\mathbf{x} - \mathbf{a}) = \sum_{k=1}^d (x_k - a_k)^2.$$

The sum over $\{n_k\}$ means summing over all possible distributions of n_k such that $n = \sum_{k=1}^d n_k$. The polynomials obey the partial differential equation

$$\nabla^2 \mathcal{H}^{(n)} - \mathbf{x} \cdot \nabla \mathcal{H}^{(n)} + n \mathcal{H}^{(n)} = 0, \quad (5.16)$$

where $n = \sum_{k=1}^d n_k$. The tensor Hermite polynomial $\mathcal{H}^{(m)}$ of order m can be also generated by using the Rodrigues formula

$$\mathcal{H}^{(m)}(\mathbf{x}) = (-1)^m \omega^{-1} \nabla^m \omega(\mathbf{x}). \quad (5.17)$$

By differentiating the generating function and using the system of notation introduced, we obtain the recurrence relation [1]

$$\nabla_i \mathcal{H}^{(m)} = \delta_i \mathcal{H}^{(m-1)}. \quad (5.18)$$

This is the multi-variable generalization of the well known recurrence relation for single-variable Hermite polynomials:

$$\frac{d}{d\mathbf{x}} \mathcal{H}^{(k)} = k \mathcal{H}^{(k-1)} \quad (k \geq 0).$$

The recurrence relation (5.18), when applied to the Rodrigues formula (5.17), yields the following recurrence relation

$$x_i \mathcal{H}^{(m)} = \mathcal{H}^{(m+1)} + \delta_i \mathcal{H}^{(m-1)}. \quad (5.19)$$

This recurrence relation can be used to generate all the tensor Hermite polynomials. Note that we take $\mathcal{H}^{(-1)} = 0$ and $\mathcal{H}^{(0)} = 1$. The leading examples of the tensor Hermite polynomials $\mathcal{H}^{(m)}$ of variable \mathbf{x} are:

$$\begin{aligned} \mathcal{H}^{(0)} &= 1, \\ \mathcal{H}_i^{(1)} &= x_i, \\ \mathcal{H}_{ij}^{(2)} &= (\mathbf{x}^2 - \boldsymbol{\delta})_{ij} = x_i x_j - \delta_{ij}, \\ \mathcal{H}_{ijk}^{(3)} &= (\mathbf{x}^3 - \mathbf{x}\boldsymbol{\delta})_{ijk} = x_i x_j x_k - x_i \delta_{jk} - x_j \delta_{ik} - x_k \delta_{ij}, \text{ etc.} \end{aligned} \quad (5.20)$$

For example, in the case of dimension one these polynomials take the form

$$\mathcal{H}^{(0)} = 1, \quad \mathcal{H}^{(1)} = x, \quad \mathcal{H}^{(2)} = x^2 - 1, \quad \mathcal{H}^{(3)} = x^3 - 3, \quad \text{etc.,}$$

which on multiplication of $2^{k/2}$ ($k \geq 0$) become the conventional Hermite polynomials $H_k(x)$ ($k \geq 0$) defined by, for example, Morse and Feshbach [4]:

$$H_k(x) = 2^{k/2} \mathcal{H}^{(k)}(x) \quad (k \geq 0).$$

The polynomials $\mathcal{H}_{i_1 \dots i_n}^{(n)}$ are symmetric with respect to interchanges of the subscripts. The moments of vector \mathbf{x} have the following values:

$$\int d\mathbf{x} \omega(\mathbf{x}) \mathbf{x}^{2n} = \boldsymbol{\delta}^n, \quad (5.21)$$

$$\int d\mathbf{x} \omega(\mathbf{x}) \mathbf{x}^{2n+1} = 0. \quad (5.22)$$

By using this result and the Rodrigues formula (5.17) it is possible to prove the orthogonality relation between the tensor polynomials

$$\int d\mathbf{x} \omega(\mathbf{x}) \mathcal{H}_{i_1 \dots i_n}^{(n)}(\mathbf{x}) \mathcal{H}_{j_1 \dots j_m}^{(m)}(\mathbf{x}) = \delta_{nm} \delta_{ij}^n, \quad (5.23)$$

where $i = (i_1, i_2, \dots, i_n)$ and $j = (j_1, j_2, \dots, j_m)$.

Since the tensor Hermite polynomials form a complete set, products of tensor Hermite polynomials also must be in the set. In other words the products may be given as linear combinations of tensor Hermite polynomials. Indeed, the following addition theorem holds: for $n < m$

$$\begin{aligned} \mathcal{H}_{i_1 \dots i_n}^{(n)} \mathcal{H}_{j_1 \dots j_m}^{(m)} &= \mathcal{H}_{ij}^{(n+m)} + \delta_{ij}^1 \mathcal{H}^{(n+m-2)} + \delta_{ij}^2 \mathcal{H}^{(n+m-4)} \\ &\quad + \dots + \delta_{ij}^{n-1} \mathcal{H}^{(m-n+2)} + \delta_{ij}^n \mathcal{H}^{(m-n)}. \end{aligned} \quad (5.24)$$

This addition theorem is the tensor analog of the addition theorem of scalar Hermite polynomials. In (5.24) the subscripts on $\mathcal{H}^{(n+m-2)}$ consist of the subsets of the sets i and j excluding those making up the subscripts on δ_{ij}^1 . For example,

$$\begin{aligned} \delta_{ij}^1 \mathcal{H}^{(n+m-2)} &= \delta_{i_1 j_1}^1 \mathcal{H}_{i_2 \dots i_n j_2 \dots j_m}^{(n+m-2)} + \delta_{i_1 j_2}^1 \mathcal{H}_{i_2 \dots i_n j_1 j_3 \dots j_m}^{(n+m-2)} \\ &\quad + \text{other permutation terms.} \end{aligned}$$

In Appendix A examples of the addition theorems are given for some leading tensor Hermite polynomials often appearing in the calculations in this work.

Any multi-variable function $f(\mathbf{x})$ now can be expanded in terms of the complete set of tensor Hermite polynomials constructed earlier:

$$f(\mathbf{x}) = \sum_{n=0}^{\infty} \sum_{i_1=1}^d \sum_{i_2=1}^d \dots \sum_{i_d=1}^d A_{i_1 \dots i_d}^{(n)} \mathcal{H}_{i_1 \dots i_d}^{(n)}(\mathbf{x}), \quad (5.25)$$

where the coefficients are determined by the integral

$$A_{i_1 \dots i_d}^{(n)} = (n!)^{-1} \int d\mathbf{x} \omega(\mathbf{x}) \mathcal{H}_{i_1 \dots i_d}^{(n)}(\mathbf{x}) f(\mathbf{x}), \quad (5.26)$$

for which the orthogonality relation (5.23) is used.

Since the expansion in (5.25) is a projection, the projection operator can be defined by

$$P_{i_1 \dots i_d}^{(n)} f(\mathbf{x}) = (n!)^{-1} \mathcal{H}_{i_1 \dots i_d}^{(n)}(\mathbf{x}) \int d\mathbf{x} \omega(\mathbf{x}) \mathcal{H}_{i_1 \dots i_d}^{(n)}(\mathbf{x}) f(\mathbf{x}). \quad (5.27)$$

This allows to write (5.25) in a more compact form

$$f(\mathbf{x}) = \sum_{n=0}^{\infty} P^{(n)} f(\mathbf{x}). \quad (5.28)$$

The formulas presented in this chapter will be used in the studies made in the subsequent chapters.

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6

The Chapman–Enskog and Moment Methods

The kinetic equation postulated in this work is not amenable to methods of closed analytical solutions in the case of physically realistic interaction potential models. It is, therefore, necessary to resort to an approximate method of solution. The most frequently used approximate methods of solution are the Chapman–Enskog method [1] and the Maxwell–Grad moment method [2,3]. Hilbert [4] developed a solution method for the Boltzmann equation as an application of his theory of linear integral equations. This Hilbert method was modified by Enskog [5]. Enskog’s method was later shown to yield the results identical with the Chapman method [6]. The Chapman method was based on the Maxwell transfer equations, which are related to the moment evolution equations originally proposed by James Clerk Maxwell [7]. The Enskog method is now known as the Chapman–Enskog method in the literature. The second method was later developed further by Grad [2], in particular, for the Boltzmann equation. The Chapman–Enskog method and the moment method give rise to identical linear transport coefficients although higher order results are not necessarily the same. The linear transport coefficients so calculated are extensively verified to be completely consistent with experimental results, and it is correct to state that the theory of linear transport processes in monatomic gases are well established and understood. However, nonlinear transport processes are a different matter, and it is necessary to investigate them in a thermodynamically consistent manner. Since the theory of nonlinear transport processes, which is an important point of interest in this work, can be built on the Chapman–Enskog solution for linear transport processes, it is useful to have some discussions on the method. We will also discuss the moment method since it is directly related to the nonequilibrium ensemble method which we would like to present in this work.

6.1 The Chapman–Enskog Method and Irreversible Processes

Since this method has been described in a number of excellent monographs [1,8], we will simply give only a brief summary of the results, deferring

detailed discussions on the method to the literature. Our review of this method will be confined to those aspects relevant to the nonequilibrium ensemble method, which we are going to develop later, and the question of thermodynamics of irreversible processes.

6.1.1 First-Order Solutions

We have shown that when the kinetic equation is reduced, there appears the Knudsen number in the reduced kinetic equation, which may be written in the form

$$Df_a = \epsilon^{-1} R[f_a]. \quad (6.1)$$

Here the operator D stands for the streaming term

$$D = \partial_\tau + \bar{\mathbf{v}}_a \cdot \bar{\nabla} + \bar{\mathbf{F}}_a \cdot \bar{\nabla}_{\mathbf{v}_a}, \quad (6.2)$$

where the overbars may be dropped and τ replaced with t in accordance with the remark made on the use of the reduced kinetic equation and the parameter ϵ in Sec. 5.1. The parameter ϵ in this work is an abbreviation for the Knudsen number. In the literature on kinetic theory this parameter is called the nonuniformity parameter, which is not necessarily taken to be the Knudsen number but a parameter characterizing the displacement of the system from equilibrium. The Knudsen number is a natural choice for the parameter. It is convenient to collectively represent the balance equations (4.57)–(4.60) in the form

$$\frac{\partial \mathbf{M}}{\partial t} = \mathbf{E}(\mathbf{r}, t), \quad (6.3)$$

where \mathbf{M} is a column vector consisting of conserved variables

$$\mathbf{M} = (\rho, \rho_a, \rho \mathbf{u}, \rho \mathcal{E}) \quad (6.4)$$

and $\mathbf{E}(\mathbf{r}, t)$ is a column vector whose elements are made up of terms corresponding to the balance equations

$$\mathbf{E}(\mathbf{r}, t) = \begin{bmatrix} -\nabla \cdot \rho \mathbf{u} \\ -\nabla \cdot (\mathbf{J}_a + \rho \mathbf{u}) \\ -\nabla \cdot (\mathbf{P} + \rho \mathbf{u} \mathbf{u}) + \sum_{a=1}^r \rho_a \mathbf{F}_a \\ -\nabla \cdot (\mathbf{Q} + \rho \mathbf{u} \mathcal{E}) - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a \end{bmatrix}. \quad (6.5)$$

The distribution functions $f_a(\mathbf{v}_a, \mathbf{r}; t)$ contain more information than necessary for the description of gross macroscopic behavior of the system which can be accomplished with a finite number of macroscopic variables. This

information reduction implied by the finite number of macroscopic variables is called the contraction of description. In line with this notion, in the Chapman–Enskog method the distribution functions are assumed to be functionals of the conserved variables and their spatial derivatives through which the evolution of the distribution functions in space–time is determined. Thus

$$f_a = f_a(\mathbf{v}_a | \mathbf{M}, \nabla \mathbf{M}, \nabla^2 \mathbf{M}, \dots). \quad (6.6)$$

In addition to this assumption the right hand side of the conservation equations \mathbf{E} is also regarded as a functional of $\mathbf{M}, \nabla \mathbf{M}, \nabla^2 \mathbf{M}, \dots$; that is, the quantities \mathbf{J}_a , \mathbf{P} , and \mathbf{Q} in \mathbf{E} are functionals of conserved variables and their spatial derivatives. Therefore the balance equations may be written as

$$\frac{\partial \mathbf{M}}{\partial t} = \mathbf{E}(\mathbf{r} | \mathbf{M}, \nabla \mathbf{M}, \nabla^2 \mathbf{M}, \dots). \quad (6.7)$$

These assumptions will be simply called the functional hypothesis. A noteworthy point in this functional hypothesis is that the spatial derivatives of the conserved variables \mathbf{M} of all orders are regarded as independent variables on the same footing as the conserved variables themselves. This is to be contrasted with the viewpoint that takes \mathbf{M} and nonconserved variables (*e.g.*, \mathbf{J}_a , \mathbf{P} , and \mathbf{Q}) as independent variables, which is the viewpoint taken in Chapter 2 and in the Maxwell–Grad moment method discussed in Sec. 6.2 below. The choice between the two viewpoints can be made on the basis of mathematical convenience and the efficacy and practicability of the theory constructed thereon.

Now, the temporal variation of f_a is calculated in terms of those of \mathbf{M} and its spatial derivatives as follows:

$$\begin{aligned} \frac{\partial f_a}{\partial t} &= \frac{\partial f_a}{\partial \mathbf{M}} \cdot \frac{\partial \mathbf{M}}{\partial t} + \frac{\partial f_a}{\partial \nabla \mathbf{M}} \cdot \frac{\partial \nabla \mathbf{M}}{\partial t} + \dots \\ &= \frac{\partial f_a}{\partial \mathbf{M}} \cdot \mathbf{E} + \frac{\partial f_a}{\partial \nabla \mathbf{M}} \cdot \nabla \mathbf{E} + \dots \end{aligned} \quad (6.8)$$

It is also assumed that f_a and \mathbf{E} are expandable in a series of the parameter ϵ :

$$f_a = f_a^{(0)} + \epsilon f_a^{(1)} + \epsilon^2 f_a^{(2)} + \dots, \quad (6.9)$$

$$\mathbf{E} = \mathbf{E}^{(0)} + \epsilon \mathbf{E}^{(1)} + \epsilon^2 \mathbf{E}^{(2)} + \dots. \quad (6.10)$$

Substitution of (6.9) and (6.10) into (6.8) yields the series in ϵ

$$\frac{\partial f_a}{\partial t} = \partial_0 f_a^{(0)} + \epsilon \left(\partial_1 f_a^{(0)} + \partial_0 f_a^{(1)} \right) + \epsilon^2 \left(\partial_2 f_a^{(0)} + \partial_1 f_a^{(1)} + \partial_0 f_a^{(2)} \right) + \dots, \quad (6.11)$$

where

$$\partial_k f_a^{(s)} = \frac{\partial f_a^{(s)}}{\partial \mathbf{M}} \cdot \mathbf{E}^{(k)} + \frac{\partial f_a^{(s)}}{\partial \nabla \mathbf{M}} \cdot \nabla \mathbf{E}^{(k)} + \dots \quad (6.12)$$

for $k, s \geq 0$. On substitution of the series (6.11) and (6.9) into the kinetic equation (6.1) and setting the coefficients in the ϵ series equal to zero, we obtain a hierarchy of linear integral equations for $f_a^{(s)}$, $s \geq 1$:

$$\sum_{b=1}^r R(f_a^{(0)} f_b^{(0)} | f_a^{(0)*} f_b^{(0)*}) = 0, \quad (6.13)$$

$$\sum_{b=1}^r \left[R(f_a^{(0)} f_b^{(1)} | f_a^{(0)*} f_b^{(1)*}) + R(f_a^{(1)} f_b^{(0)} | f_a^{(1)*} f_b^{(0)*}) \right] = (Df_a)^{(0)}, \quad (6.14)$$

$$\begin{aligned} & \sum_{b=1}^r \left[R(f_a^{(0)} f_b^{(s)} | f_a^{(0)*} f_b^{(s)*}) + R(f_a^{(s)} f_b^{(0)} | f_a^{(s)*} f_b^{(0)*}) \right] = (Df_a)^{(s-1)} \\ & - \sum_{k=1}^{s-1} \sum_{b=1}^r R(f_a^{(k)} f_b^{(s-k)} | f_a^{(k)*} f_b^{(s-k)*}), \end{aligned} \quad (6.15)$$

where $s \geq 2$, the collision integral $R[f_a]$ is decomposed into components $R(f_a f_b | f_a^* f_b^*)$ as indicated in (3.28), and

$$\begin{aligned} (Df_a)^{(s)} = & \partial_0 f_a^{(s)} + \partial_1 f_a^{(s-1)} + \partial_2 f_a^{(s-2)} + \dots + \partial_s f_a^{(0)} \\ & + (\mathbf{v}_a \cdot \nabla + \mathbf{F}_a \cdot \nabla \mathbf{v}_a) f_a^{(s)}. \end{aligned} \quad (6.16)$$

This method of linearizing the kinetic equation was first used by Enskog [5]; it is a variation of the linearization method originally used by Hilbert [4].

Eq. (6.13) is simply the equilibrium condition and appeared when the H theorem and the equilibrium solution were considered in Chapter 4. Its solution under the matching conditions (4.40)–(4.42) is the local equilibrium distribution function f_a^0 already constructed

$$\begin{aligned} f_a^{(0)} &= f_a^0 \\ &= n_a^0 \left(\frac{m_a}{2\pi k_B T} \right)^{3/2} \exp \left\{ -\frac{1}{k_B T} \left[\frac{1}{2} m_a C_a^2 + m_a U_a(\mathbf{r}) \right] \right\} \\ &= n_a \left(\frac{m_a}{2\pi k_B T} \right)^{3/2} \exp \left[-\frac{m_a C_a^2}{2k_B T} \right], \end{aligned} \quad (6.17)$$

where

$$n_a = n_a^0 \exp \left[-\frac{m_a U_a(\mathbf{r})}{k_B T} \right]. \quad (6.18)$$

The matching conditions and the local equilibrium distribution function constructed consistently therewith imply that the nonequilibrium correction for the distribution function Δf_a must be such that

$$\langle m_a \Delta f_a \rangle = 0, \quad (6.19)$$

$$\sum_{a=1}^r \langle m_a \mathbf{v}_a \Delta f_a \rangle = 0, \quad (6.20)$$

$$\sum_{a=1}^r \langle \frac{1}{2} m_a C_a^2 \Delta f_a \rangle = 0. \quad (6.21)$$

Specifically, in the case of the expansion (6.9), since every term in the ϵ expansion must satisfy the matching conditions, there hold for all $s \geq 1$ the conditions

$$\langle m_a f_a^{(s)} \rangle = 0, \quad (6.22)$$

$$\sum_{a=1}^r \langle m_a \mathbf{v}_a f_a^{(s)} \rangle = 0, \quad (6.23)$$

$$\sum_{a=1}^r \langle \frac{1}{2} m_a C_a^2 f_a^{(s)} \rangle = 0. \quad (6.24)$$

Since five conserved variables—collision invariants—are the eigenfunctions with null eigenvalue, (6.22)–(6.24) imply that $f_a^{(s)}$ are determined so as to be orthogonal to the null eigenfunctions.

The first-order correction $f_a^{(1)}$ is determined from (6.14), which is a linear integral equation for $f_a^{(1)}$. In the case of a mixture, (6.14) in fact represents coupled linear integral equations. They can be solved by applying the Hilbert–Schmidt theory [9] of solution of linear integral equations. According to the Hilbert–Schmidt theory, an inhomogeneous linear integral equation is solvable if and only if the inhomogeneous term is orthogonal to the solutions of the homogeneous integral equation. In the present case the homogeneous linear integral equations may be written in the form

$$\sum_{b=1}^r \left[R(f_a^{(0)} f_b^{(0)} \phi_b | f_a^{(0)*} f_b^{(0)*} \phi_b^*) + R(f_a^{(0)} \phi_a f_b^{(0)} | f_a^{(0)*} \phi_a^* f_b^{(0)*}) \right] = 0 \quad (6.25)$$

if the solution of the homogeneous integral equation is expressed as $f_a^{(0)} \phi_a$. The solutions of this integral equation are clearly the collision invariants:

$$\phi_a = \left(m_a, \sum_{a=1}^r m_a \mathbf{v}_a, \sum_{a=1}^r \frac{1}{2} m_a v_a^2 \right). \quad (6.26)$$

Therefore the solvability conditions for the linearized integral equations of the Chapman–Enskog hierarchy (6.16) are:

$$\langle m_a (Df_a)^{(s-1)} \rangle = 0, \quad (6.27)$$

$$\sum_{a=1}^r \langle m_a \mathbf{v}_a (Df_a)^{(s-1)} \rangle = 0, \quad (6.28)$$

$$\sum_{a=1}^r \left\langle \frac{1}{2} m_a v_a^2 (Df_a)^{(s-1)} \right\rangle = 0 \quad (6.29)$$

for $s \geq 1$ and $a = 1, 2, \dots, r$.

If the expansion (6.9) for f_a is substituted into the statistical formulas for \mathbf{P} , \mathbf{Q} , and \mathbf{J}_a given in (4.65)–(4.67), the following series in ϵ result for \mathbf{P} , \mathbf{Q} , and \mathbf{J}_a :

$$\mathbf{P} = \sum_{s=0}^{\infty} \epsilon^s \mathbf{P}^{(s)}, \quad (6.30)$$

$$\mathbf{Q} = \sum_{s=1}^{\infty} \epsilon^s \mathbf{Q}^{(s)}, \quad (6.31)$$

$$\mathbf{J}_a = \sum_{s=1}^{\infty} \epsilon^s \mathbf{J}_a^{(s)}, \quad (6.32)$$

where the sum over s for \mathbf{Q} and \mathbf{J}_a starts from $s = 1$ since the heat flux and the diffusion fluxes vanish at equilibrium whereas in the case of \mathbf{P} the sum begins from $s = 0$ since \mathbf{P} becomes the pressure at equilibrium. This latter point will be further elaborated later. The statistical formulas for $\mathbf{P}^{(s)}$, $\mathbf{Q}^{(s)}$, and $\mathbf{J}_a^{(s)}$ are easily deduced to be:

$$\mathbf{P}^{(s)} = \sum_{a=1}^r \langle m_a \mathbf{C}_a \mathbf{C}_a f_a^{(s)} \rangle, \quad (6.33)$$

$$\mathbf{Q}^{(s)} = \sum_{a=1}^r \langle \frac{1}{2} m_a C_a^2 \mathbf{C}_a f_a^{(s)} \rangle, \quad (6.34)$$

$$\mathbf{J}_a^{(s)} = \sum_{a=1}^r \langle m_a \mathbf{C}_a f_a^{(s)} \rangle. \quad (6.35)$$

On substitution of (6.11) into the solvability conditions (6.27)–(6.29) and use of the matching conditions (4.40)–(4.42) and their subsidiary conditions (6.22)–(6.24) on $f_a^{(s)}$, there follow the solvability conditions in the forms

$$\mathbf{E}_a^{(s-1)} = -\nabla \cdot \mathbf{J}_a^{(s-1)} - \delta_{s1} \nabla \cdot (\rho_a \mathbf{u}), \quad (6.36)$$

$$\mathbf{E}_p^{(s-1)} = -\nabla \cdot \mathbf{P}^{(s-1)} - \delta_{s1} \nabla \cdot (\rho \mathbf{u} \mathbf{u}) + \delta_{s1} \sum_{a=1}^r \rho_a \mathbf{F}_a, \quad (6.37)$$

$$\begin{aligned} \mathbf{E}_\epsilon^{(s-1)} &= -\nabla \cdot \mathbf{Q}^{(s-1)} - \delta_{s1} \nabla \cdot (\rho \mathcal{E} \mathbf{u}) - \mathbf{P}^{(s-1)} : \nabla \mathbf{u} \\ &\quad + \delta_{s1} \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a, \end{aligned} \quad (6.38)$$

where $\mathbf{E}_a^{(s-1)}$, $\mathbf{E}_p^{(s-1)}$, and $\mathbf{E}_\epsilon^{(s-1)}$ are, respectively, the mass, momentum and energy component of column vector \mathbf{E} , that is, $\partial \mathbf{M} / \partial t$. Since the equation of continuity consists of conserved variables only, there is only one components for it corresponding to $s = 0$. That is,

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \rho \mathbf{u}. \quad (6.39)$$

On substitution of (6.36)–(6.38) into (6.10) and the resulting series into the balance equations (6.7) and then setting $\epsilon = 1$, which is tantamount to reverting back to dimensionalized variables, we obtain the various balance equations in the forms

$$\rho \frac{dc_a}{dt} = -\nabla \cdot \sum_{s=1}^{\infty} \mathbf{J}_a^{(s)}, \quad (6.40)$$

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla \cdot \sum_{s=0}^{\infty} \mathbf{P}^{(s)} + \sum_{a=1}^r \rho_a \mathbf{F}_a, \quad (6.41)$$

$$\rho \frac{d\mathcal{E}}{dt} = -\nabla \cdot \sum_{s=1}^{\infty} \mathbf{Q}^{(s)} - \sum_{s=0}^{\infty} \mathbf{P}^{(s)} : \nabla \mathbf{u} + \sum_{a=1}^r \sum_{s=1}^{\infty} \mathbf{F}_a \cdot \mathbf{J}_a^{(s)}. \quad (6.42)$$

The point to emphasize here is that the balance equations of mass, concentrations (mass fractions), momentum, and energy result from the solvability conditions of the Chapman–Enskog hierarchy of linear integral equations. And, in particular, to the first order, namely, if $s = 1$, the balance equations become the diffusion equation, the Navier–Stokes equation, and the Fourier equation, respectively,

$$\rho \frac{dc_a}{dt} = -\nabla \cdot \mathbf{J}_a^{(1)}, \quad (6.43)$$

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla \cdot (\mathbf{P}^{(0)} + \mathbf{P}^{(1)}) + \sum_{a=1}^r \rho_a \mathbf{F}_a, \quad (6.44)$$

$$\rho \frac{d\mathcal{E}}{dt} = -\nabla \cdot \mathbf{Q}^{(1)} - (\mathbf{P}^{(0)} + \mathbf{P}^{(1)}) : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{F}_a \cdot \mathbf{J}_a^{(1)}, \quad (6.45)$$

since it can be shown that $\mathbf{P}^{(0)} = p\boldsymbol{\delta}$ and

$$\mathbf{J}_a^{(1)} = - \sum_{b=1}^r D_{ab} \mathbf{d}_b - D_{ta} \nabla \ln T, \quad (6.46)$$

$$\mathbf{P}^{(1)} = -2\eta_0 [\nabla \mathbf{u}]^{(2)}, \quad (6.47)$$

$$\mathbf{Q}^{(1)} = -\lambda_0 \nabla \ln T + \sum_{a=1}^r p \left(k_{ta} + \frac{5n_a}{2n} \right) \frac{\mathbf{J}_a^{(1)}}{m_a}. \quad (6.48)$$

Here

$$\mathbf{d}_a = \nabla \left(\frac{n_a}{n} \right) + \left(\frac{n_a}{n} - \frac{\rho_a}{\rho} \right) \nabla \ln p - \frac{\rho_a}{p} \left(\mathbf{F}_a - \sum_{b=1}^r c_b \mathbf{F}_b \right) \quad (6.49)$$

and D_{ab} , D_{ta} , η_0 , λ_0 , and k_{ta} are diffusion coefficients, thermal diffusion coefficients, viscosity, thermal conductivity, and thermal diffusion ratios, respectively, whose statistical expressions will be given later. Substitution of (6.46)–(6.48) into (6.43)–(6.45) gives the diffusion, Navier–Stokes, and Fourier equation, namely, the classical hydrodynamic equations. Therefore the first-order Chapman–Enskog solution gives rise to the classical hydrodynamics equations. We remark that the classical hydrodynamics equations do not arise in the Hilbert method and the merits of the Enskog modification of the Hilbert method lies in the derivation of the classical hydrodynamics equations which are thereby given the molecular theory foundations.

It is easy to verify that under the matching conditions mentioned earlier the lowest order approximation for the stress tensor is simply the pressure p :

$$\begin{aligned} \mathbf{P}^{(0)} &= \sum_{a=1}^r \langle m_a f_a^{(0)} \rangle = \sum_{a=1}^r \langle m_a \mathbf{C}_a \mathbf{C}_a f_a^0 \rangle \\ &= \frac{1}{3} \sum_{a=1}^r \langle m_a \mathbf{C}_a \cdot \mathbf{C}_a f_a^0 \rangle \boldsymbol{\delta} \\ &= \frac{2}{3} \sum_{a=1}^r \langle \frac{1}{2} m_a C_a^2 f_a \rangle \boldsymbol{\delta} \\ &= n k_B T \boldsymbol{\delta} \\ &= p \boldsymbol{\delta}. \end{aligned} \quad (6.50)$$

That is, the trace of the zeroth-order solution for the stress tensor gives rise to the equation of state.

The mathematical structures of the classical hydrodynamics equations presented and irreversible thermodynamics corresponding to the classical hydrodynamics, as will be discussed later in detail, do not depend on the details of the collision integral $R[f_a]$ as long as the collision integral satisfies the conditions mentioned earlier. However, to calculate the constitutive relations (6.46)–(6.48) and, in particular, the transport coefficients therein, it is now necessary to specify explicitly the collision integral $R[f_i]$, since the transport coefficients intimately reflect the molecularity of the substance of interest and the collision integral must be so modeled as to indicate the molecularity and the density or the state of aggregation of the substance of interest. The formal theory developed up to this point by means of the generic Boltzmann equation (3.27) is a statistical mechanics analog of analytical dynamics in mechanics which can be developed without explicitly stating the form of the potential energy or the force except for some general conditions on it. When the details of dynamical aspects of the problem, such as collision cross sections, trajectories, and so on, are required, it is necessary to explicitly model the interaction force. The situation is similar with the generic Boltzmann equation, and when we are interested in material functions, such as transport coefficients, we are compelled to model explicitly the collision integral in order to account for the behavior of the material functions, which thus sharpen our knowledge of the collision integral $R[f_a]$.

To calculate the transport coefficients we now choose the collision integral $R[f_a]$ to be the Boltzmann collision integral:

$$R[f_a] = \sum_{b=1}^r C(f_a, f_b) \quad (6.51)$$

and calculate the transport coefficients in terms of collision bracket integrals arising from the Boltzmann collision integral.

Setting the first-order correction $f_a^{(1)}$ to the distribution function in the form

$$f_a^{(1)} = f_a^0 \phi_a \quad (6.52)$$

and defining the integral operator $I_{ab}(\phi)$ by

$$I_{ab}(\phi) = -\frac{1}{n_a n_b} \int d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty db b g_{ab} f_a^0 f_b^0 (\phi_a^* + \phi_b^* - \phi_a - \phi_b), \quad (6.53)$$

we can put the integral equation for the first-order correction (6.14) into the form

$$\begin{aligned} \sum_{b=1}^r n_a n_b I_{ab}(\phi) &= -f_a^0 \left\{ [\mathbf{w}_a \mathbf{w}_a]^{(2)} : \nabla \mathbf{u} + \frac{n}{n_a} \sqrt{\frac{2k_B T}{m_a}} \mathbf{w}_a \cdot \mathbf{d}_a \right. \\ &\quad \left. + \sqrt{\frac{2k_B T}{m_a}} (w_a^2 - \frac{5}{2}) \mathbf{w}_a \cdot \nabla \ln T \right\}. \quad (6.54) \end{aligned}$$

Here the reduced peculiar velocity \mathbf{w}_a is defined by

$$\mathbf{w}_a = \sqrt{\frac{m_a}{2k_B T}} \mathbf{C}_a. \quad (6.55)$$

For (6.54) we have used the result

$$\begin{aligned} (Df_a)^{(0)} &= (\partial_0 + \mathbf{v}_a \cdot \nabla + \mathbf{F}_a \cdot \nabla_{\mathbf{v}_a}) f_a^0 \\ &= f_a^0 \left\{ [\mathbf{w}_a \mathbf{w}_a]^{(2)} : \nabla \mathbf{u} + \frac{n}{n_a} \sqrt{\frac{2k_B T}{m_a}} \mathbf{w}_a \cdot \mathbf{d}_a \right. \\ &\quad \left. + \sqrt{\frac{2k_B T}{m_a}} (w_a^2 - \frac{5}{2}) \mathbf{w}_a \cdot \nabla \ln T \right\}. \end{aligned} \quad (6.56)$$

Since the thermodynamic forces \mathbf{d}_a are linearly dependent owing to the relation

$$\sum_{a=1}^r \mathbf{d}_a = 0 \quad (6.57)$$

by definition, it is necessary to use a linearly independent set. Such a set can be prepared by taking a linear combination of \mathbf{d}_a . Let $\{\mathbf{d}_a^* : 1 \leq a \leq r\}$ be such a set. It may be taken to be such that [10]

$$\mathbf{d}_a = \sum_{b=1}^r \left(\delta_{ab} - \frac{\rho_a}{\rho} \right) \mathbf{d}_b^*. \quad (6.58)$$

This relation and (6.54) suggest that ϕ_a may be looked for in the form

$$n\phi_a = - \sum_{b=1}^r \mathbf{D}_a^{(b)} \cdot \mathbf{d}_b^* - \mathbf{A}_a \cdot \nabla \ln T - \mathbf{B}_a : \nabla \mathbf{u}, \quad (6.59)$$

where $\mathbf{D}_a^{(b)}$ and \mathbf{A}_a are vector functions of \mathbf{w}_a and \mathbf{B}_a is a second-rank tensor function of \mathbf{w}_a . Since the thermodynamic forces \mathbf{d}_b^* , $\nabla \ln T$, and $[\nabla \mathbf{u}]^{(2)}$ are independent, the linear integral equation (6.54) with (6.59) for ϕ_a separates into three integral equations for $\mathbf{D}_a^{(b)}(\mathbf{C})$, $\mathbf{A}_a(\mathbf{C})$, and $\mathbf{B}_a(\mathbf{C})$:

$$\begin{aligned} \sum_{b=1}^r \frac{n_a n_b}{n^2} I_{ab}(\mathbf{D}^{(k)}) &= n_a^{-1} f_a^0 \left(\delta_{ak} - \frac{\rho_a}{\rho} \right) \sqrt{\frac{2k_B T}{m_a}} \mathbf{w}_a, \\ (1 \leq a, k \leq r), \end{aligned} \quad (6.60)$$

$$\begin{aligned} \sum_{b=1}^r \frac{n_a n_b}{n^2} I_{ab}(\mathbf{A}) &= n^{-1} f_a^0 \sqrt{\frac{2k_B T}{m_a}} (w_a^2 - \frac{5}{2}) \mathbf{w}_a, \\ (1 \leq a \leq r), \end{aligned} \quad (6.61)$$

$$\sum_{b=1}^r \frac{n_a n_b}{n^2} I_{ab}(\mathbf{B}) = 2n^{-1} f_a^0 [\mathbf{w}_a \mathbf{w}_a]^{(2)},$$

$$(1 \leq a \leq r). \quad (6.62)$$

The solutions of these linear integral equations provide functions $\mathbf{D}_a^{(b)}$, \mathbf{A}_a , and \mathbf{B}_a in terms of \mathbf{C} .

6.1.2 Formal Expansions for Transport Coefficients

The Chapman–Enskog first-order solution ϕ_a yields linear transport coefficients. The latter can be formally expressed in terms of $\mathbf{D}_a^{(b)}(\mathbf{C})$, $\mathbf{A}_a(\mathbf{C})$, and $\mathbf{B}_a(\mathbf{C})$, even though the explicit forms of the latter are not known. For this purpose we first define the bracket integrals

$$[F, G] = \sum_{a=1}^r \sum_{b=1}^r \frac{1}{4n^2} \int d\Gamma_{ab} f_a^0 f_b^0 (F_a^* + F_b^* - F_a - F_b) \times (G_a^* + G_b^* - G_a - G_b), \quad (6.63)$$

where

$$\int d\Gamma_{ab} \dots = \int d\mathbf{v}_a \int d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} \mathbf{b} g_{ab} \dots \quad (6.64)$$

and F and G can be vectors or tensors. It is also useful to define the partial bracket integrals

$$[F_a, G_a]_{ab} = \frac{1}{2n_a n_b} \int d\Gamma_{ab} f_a^0 f_b^0 (F_a^* - F_a) (G_a^* - G_a), \quad (6.65)$$

$$[F_a, G_b]_{ab} = \frac{1}{2n_a n_b} \int d\Gamma_{ab} f_a^0 f_b^0 (F_a^* - F_a) (G_b^* - G_b). \quad (6.66)$$

Therefore,

$$[F, G] = \sum_{a=1}^r \sum_{b=1}^r \frac{n_a n_b}{2n^2} ([F_a, G_a] + [F_b, G_b] + [F_a, G_b] + [F_b, G_a]). \quad (6.67)$$

Since the matching conditions (6.22)–(6.24) must be satisfied at every order of approximation and furthermore the three components of ϕ_a in (6.59) must satisfy them separately, there follow the equations

$$\sum_{a=1}^r \langle \psi_a \mathbf{D}_a^{(b)} f_a^0 \rangle = 0, \quad (6.68)$$

$$\sum_{a=1}^r \langle \psi_a \mathbf{A}_a f_a^0 \rangle = 0, \quad (6.69)$$

$$\sum_{a=1}^r \langle \psi_a \mathbf{B}_a f_a^0 \rangle = 0, \quad (6.70)$$

where $\psi_a = m_a, m_a \mathbf{C}_a, \frac{1}{2} m_a C_a^2$. Because of symmetry, (6.70) is automatically satisfied and for the same reason, in the case of (6.68) and (6.69) there are only two conditions for $\mathbf{D}_a^{(b)}$ and \mathbf{A}_a to be satisfied:

$$\sum_{a=1}^r \sqrt{m_a} \langle \mathbf{w}_a \cdot \mathbf{D}_a^{(b)} f_a^0 \rangle = 0 \quad (1 \leq b \leq r), \quad (6.71)$$

$$\sum_{a=1}^r \sqrt{m_a} \langle \mathbf{w}_a \cdot \mathbf{A}_a f_a^0 \rangle = 0. \quad (6.72)$$

These equations become constraints for the linear integral equations (6.60) and (6.61). Various molecular expression for transport coefficients can be extracted from linear integral equations (6.60)–(6.62).

We first consider diffusion. The first-order diffusion flux $\mathbf{J}_a^{(1)}$ is given by

$$\begin{aligned} \mathcal{J}_a &\equiv \frac{\mathbf{J}_a^{(1)}}{\rho_a} = (nn_a)^{-1} \langle \mathbf{C}_a \phi_a f_a^0 \rangle \\ &= -\frac{1}{3nn_a} \sum_{b=1}^r \sqrt{\frac{2k_B T}{m_a}} \langle \mathbf{w}_a \cdot \mathbf{D}_a^{(b)} f_a^0 \rangle \mathbf{d}_b^* \\ &\quad - \frac{1}{3nn_a} \sqrt{\frac{2k_B T}{m_a}} \langle \mathbf{w}_a \cdot \mathbf{A}_a f_a^0 \rangle \nabla \ln T. \end{aligned} \quad (6.73)$$

The diffusion coefficient D_{ab} and thermal diffusion coefficient D_{ta} are defined by the linear constitutive relation (*i.e.*, linear force–flux relation)

$$\mathcal{J}_a = - \sum_{b=1}^r D_{ab} \mathbf{d}_b^* - D_{ta} \nabla \ln T. \quad (6.74)$$

By comparing (6.73) and (6.74), we now identify the diffusion and thermal diffusion coefficients

$$D_{ab} = \frac{1}{3nn_a} \sqrt{\frac{2k_B T}{m_a}} \langle \mathbf{w}_a \cdot \mathbf{D}_a^{(b)} f_a^0 \rangle, \quad (6.75)$$

$$D_{ta} = \frac{1}{3nn_a} \sqrt{\frac{2k_B T}{m_a}} \langle \mathbf{w}_a \cdot \mathbf{A}_a f_a^0 \rangle. \quad (6.76)$$

These transport coefficients may be expressed in terms of bracket integrals. To this end, we take scalar product of (6.60) with $\mathbf{D}_a^{(l)}$, integrate over \mathbf{v}_a , and then sum the result over a to obtain

$$n_k^{-1} \sqrt{\frac{2k_B T}{m_k}} \langle \mathbf{w}_k \cdot \mathbf{D}_k^{(l)} f_k^0 \rangle = [\mathbf{D}^{(l)}, \mathbf{D}^{(k)}], \quad (6.77)$$

for which (6.71) is used. Similarly, with \mathbf{A}_a instead of $\mathbf{D}_a^{(l)}$ we obtain

$$n_k^{-1} \sqrt{\frac{2k_B T}{m_k}} \langle \mathbf{w}_k \cdot \mathbf{A}_k f_k^0 \rangle = [\mathbf{A}, \mathbf{D}^{(k)}]. \quad (6.78)$$

Substitution of (6.77) and (6.78) into (6.75) and (6.76), respectively, yields

$$D_{ab} = \frac{1}{3n} [\mathbf{D}^{(b)}, \mathbf{D}^{(a)}], \quad (6.79)$$

$$D_{ta} = \frac{1}{3n} [\mathbf{A}, \mathbf{D}^{(a)}]. \quad (6.80)$$

Thermal diffusion ratios R_{ta} are defined by the relation

$$\sum_b D_{ab} R_{tb} = D_{ta} \quad (1 \leq a \leq r). \quad (6.81)$$

In matrix form

$$\mathbf{R}_t = \mathbf{D}^{-1} \mathbf{D}_t. \quad (6.82)$$

The thermal diffusion ratios will become useful later.

The first-order heat flux is given by the formula

$$\begin{aligned} \mathbf{Q}^{(1)} &= \sum_{a=1}^r \left\langle \left(\frac{1}{2} m_a C_a^2 - \frac{5}{2} k_B T \right) \mathbf{C}_a \phi_a f_a^0 \right\rangle + \frac{5k_B T}{2} \sum_{a=1}^r n_a \mathcal{J}_a \\ &= \frac{5k_B T}{2} \sum_{a=1}^r n_a \mathcal{J}_a - \frac{k_B T}{3n} \sum_{a=1}^r \left\langle \left(\frac{m_a C_a^2}{2k_B T} - \frac{5}{2} \right) \mathbf{C}_a \cdot \mathbf{A}_a f_a^0 \right\rangle \nabla \ln T \\ &\quad - \frac{k_B T}{3n} \sum_{a,b=1}^r \left\langle \left(\frac{m_a C_a^2}{2k_B T} - \frac{5}{2} \right) \mathbf{C}_a \cdot \mathbf{D}_a^{(b)} f_a^0 \right\rangle \mathbf{d}_b^*. \end{aligned} \quad (6.83)$$

To express the right hand side with bracket integrals, we follow the same procedure as for the diffusion flux already considered. We thereby find from (6.61) the following relations:

$$n^{-1} \sum_{a=1}^r \left\langle \left(\frac{m_a C_a^2}{2k_B T} - \frac{5}{2} \right) \mathbf{C}_a \cdot \mathbf{A}_a f_a^0 \right\rangle = [\mathbf{A}, \mathbf{A}], \quad (6.84)$$

$$n^{-1} \sum_{a=1}^r \left\langle \left(\frac{m_a C_a^2}{2k_B T} - \frac{5}{2} \right) \mathbf{C}_a \cdot \mathbf{D}_a^{(b)} f_a^0 \right\rangle = [\mathbf{D}^{(b)}, \mathbf{A}]. \quad (6.85)$$

Substitution of these results into (6.83) yields the first-order heat flux

$$\mathbf{Q}^{(1)} = \frac{5k_B T}{2} \sum_{a=1}^r n_a \mathcal{J}_a - \frac{k_B T}{3} [\mathbf{A}, \mathbf{A}] \nabla \ln T - \frac{k_B T}{3} \sum_{b=1}^r [\mathbf{D}^{(b)}, \mathbf{A}] \mathbf{d}_b^*$$

$$\begin{aligned}
&= \frac{5k_B T}{2} \sum_{a=1}^r n_a \mathcal{J}_a - \frac{k_B T}{3} [\mathbf{A}, \mathbf{A}] \nabla \ln T - nk_B T \sum_{b=1}^r D_{tb} \mathbf{d}_b^* \\
&= \frac{5k_B T}{2} \sum_{a=1}^r n_a \mathcal{J}_a - \frac{k_B T}{3} [\mathbf{A}, \mathbf{A}] \nabla \ln T - p \sum_{a,b=1}^r D_{ab} R_{ta} \mathbf{d}_b^*.
\end{aligned} \tag{6.86}$$

Note that $D_{ab} = D_{ba}$ in accord with the Onsager reciprocal relations. Eliminating \mathbf{d}_b^* by means of (6.74) and rearranging the terms, we obtain

$$\mathbf{Q}^{(1)} = -\lambda \nabla \ln T + p \sum_{a=1}^r \left(R_{ta} + \frac{5n_a}{2n} \right) \mathcal{J}_a, \tag{6.87}$$

where the thermal conductivity λ is given by

$$\lambda = \lambda' - p \sum_{a=1}^r R_{ta} D_{ta}, \tag{6.88}$$

$$\lambda' = \frac{k_B T}{3} [\mathbf{A}, \mathbf{A}] = \frac{k_B T}{3n} \sum_{a=1}^r \left\langle \left(w_a^2 - \frac{5}{2} \right) \mathbf{C}_a \cdot \mathbf{A}_a f_a^0 \right\rangle. \tag{6.89}$$

This is the thermal conductivity for a mixture given in terms of bracket integrals.

The first-order stress tensor consists of a traceless symmetric tensor. It is given by the formula

$$\begin{aligned}
\mathbf{P}^{(1)} &= \sum_{a=1}^r \left\langle m_a [\mathbf{C}_a \mathbf{C}_a]^{(2)} \phi_a f_a^0 \right\rangle \\
&= -\frac{1}{5n} \sum_{a=1}^r \left\langle m_a [\mathbf{C}_a \mathbf{C}_a]^{(2)} : \mathbf{B}_a f_a^0 \right\rangle [\nabla \mathbf{u}]^{(2)}.
\end{aligned} \tag{6.90}$$

The average on the right hand side of (6.90) can be expressed in terms of a bracket integral of \mathbf{B}_a by applying the same procedure as used earlier for the diffusion and heat fluxes. We thereby obtain from (6.62)

$$n^{-1} \sum_{a=1}^r \left\langle m_a [\mathbf{C}_a \mathbf{C}_a]^{(2)} : \mathbf{B}_a f_a^0 \right\rangle = k_B T [\mathbf{B}, \mathbf{B}]. \tag{6.91}$$

Substitution of this into (6.90) and comparison of the result with the phenomenological force–flux relation

$$\mathbf{P}^{(1)} = -2\eta_0 [\nabla \mathbf{u}]^{(2)} \tag{6.92}$$

yield the viscosity in terms of the bracket integral:

$$\eta_0 = \frac{k_B T}{10} [\mathbf{B}, \mathbf{B}] = \frac{1}{10n} \sum_{a=1}^r \langle m_a [\mathbf{C}_a \mathbf{C}_a]^{(2)} : \mathbf{B}_a f_a^0 \rangle. \quad (6.93)$$

In practice the functions $\mathbf{D}_a^{(k)}(\mathbf{C})$, $\mathbf{A}_a(\mathbf{C})$, and $\mathbf{B}_a(\mathbf{C})$ are expanded in series in Sonine polynomials [10,11] and the expansion coefficients are determined by solving the linear algebraic sets for the coefficients obtained from the linear integral equations (6.60)–(6.62). When the Sonine polynomial series are limited to a single term, the approximations are called the first Chapman–Enskog approximations for the transport coefficients. To make this part of the discussion self-contained, we would like to elaborate on the solution method for the integral equations (6.60)–(6.62). These integral equations are usually solved by means of the Fredholm alternative [9] using Sonine polynomials which are closely related to associated Laguerre polynomials [12]. Sonine polynomials [10,11] are defined by the generating function¹

$$(1-t)^{-m-1} \exp\left(-\frac{xt}{1-t}\right) = \sum_{n=0}^{\infty} t^n S_m^{(n)}(x). \quad (6.94)$$

From this expansion $S_m^{(n)}(x)$ is found to be a polynomial of order n in x :

$$S_m^{(n)}(x) = \sum_{q=0}^n \frac{\Gamma(m+n+1)}{(n-q)!q!\Gamma(q+m)} (-x)^q. \quad (6.95)$$

For example, for any value of index m

$$S_m^{(0)}(x) = 1, \quad S_m^{(1)}(x) = m + 1 - x. \quad (6.96)$$

These polynomials are orthogonal:

$$\int_0^\infty dx e^{-x} x^m S_m^{(q)}(x) S_m^{(p)}(x) = \delta_{qp} \frac{\Gamma(m+q+1)}{\Gamma(q+1)}. \quad (6.97)$$

Therefore by (6.97) the normalized Sonine polynomials are

$$\phi_m^{(q)} = \sqrt{\frac{\Gamma(q+1)}{m+q+1}} S_m^{(q)}(x). \quad (6.98)$$

¹This generating function for Sonine polynomials $S_m^{(n)}(x)$ is the same as for associated Laguerre polynomials $L_n^m(x)$. In fact, these two polynomials are related to each other by the relation

$$L_n^m(x) = \Gamma(m+n+1) S_m^{(n)}(x).$$

For associated Laguerre polynomials and their properties, see P. M. Morse and H. Feshbach, *Methods of Mathematical Physics* (McGraw-Hill, New York, 1953).

We now expand $\mathbf{D}_a^{(k)}$, \mathbf{A}_a , and \mathbf{B}_a in series of Sonine polynomials:

$$\mathbf{D}_a^{(k)} = \sum_{p=0}^M d_p^{(ka)} S_{3/2}^{(p)}(w_a^2) \mathbf{w}_a, \quad (6.99)$$

$$\mathbf{A}_a = \sum_{p=0}^M a_p^{(a)} S_{3/2}^{(p)}(w_a^2) \mathbf{w}_a, \quad (6.100)$$

$$\mathbf{B}_a = \sum_{p=0}^M b_p^{(a)} S_{5/2}^{(p)}(w_a^2) [\mathbf{w}_a \mathbf{w}_a], \quad (6.101)$$

where $1 \leq k \leq r$ and the upper index for the sum over p is in principle infinite, but in practice taken with a finite value. The matching conditions (6.71) and (6.72) demand that

$$\sum_{a=1}^r \sqrt{m_a} n_a d_0^{(ka)} = 0, \quad (6.102)$$

$$\sum_{a=1}^r \sqrt{m_a} n_a a_0^{(a)} = 0. \quad (6.103)$$

It is convenient to define the following:

$$\begin{aligned} C_{ab}^{(qp)} &= \sqrt{\frac{m_a}{2k_B T}} \delta_{ab} \sum_{l=1}^r \frac{n_b n_l}{n^2} [S_{3/2}^{(q)}(w_b^2) \mathbf{w}_b, S_{3/2}^{(p)}(w_b^2) \mathbf{w}_b]_{ab} \\ &\quad + \sqrt{\frac{m_a}{2k_B T}} \frac{n_a n_b}{n^2} [S_{3/2}^{(q)}(w_a^2) \mathbf{w}_a, S_{3/2}^{(p)}(w_a^2) \mathbf{w}_a]_{ab}, \end{aligned} \quad (6.104)$$

$$\begin{aligned} B_{ab}^{(qp)} &= \frac{2}{5k_B T} \delta_{ab} \sum_{l=1}^r \frac{n_b n_l}{n^2} [S_{5/2}^{(q)}(w_b^2) [\mathbf{w}_b \mathbf{w}_b]^{(2)}, S_{5/2}^{(p)}(w_b^2) [\mathbf{w}_b \mathbf{w}_b]^{(2)}]_{ab} \\ &\quad + \frac{2}{5k_B T} \frac{n_a n_b}{n^2} [S_{5/2}^{(q)}(w_a^2) [\mathbf{w}_a \mathbf{w}_a]^{(2)}, S_{5/2}^{(p)}(w_a^2) [\mathbf{w}_a \mathbf{w}_a]^{(2)}]_{ab}. \end{aligned} \quad (6.105)$$

The integral equations (6.99)–(6.101) then become the following algebraic equations:

$$\begin{aligned} \sum_{p=0}^M \sum_{b=1}^r C_{ab}^{(qp)} d_p^{(kb)} &= \frac{2}{3} \left(\delta_{ak} - \frac{\rho_a}{\rho} \right) \delta_{q0}, \\ (1 \leq a, k \leq r; 0 \leq q \leq M), \end{aligned} \quad (6.106)$$

$$\sum_{p=0}^M \sum_{b=1}^r C_{ab}^{(qp)} a_p^{(b)} = \frac{15n_a}{4n} \delta_{q1},$$

$$(1 \leq a \leq r; 0 \leq q \leq M), \quad (6.107)$$

$$\sum_{p=0}^M \sum_{b=1}^r B_{ab}^{(qp)} b_p^{(b)} = \frac{2n_a}{nk_B T} \delta_{q0},$$

$$(1 \leq a \leq r; 0 \leq q \leq M). \quad (6.108)$$

For a single-component gas (6.103) suggests $a_0^{(b)} = 0$ for every b . Therefore, by linear independence it is possible to take $a_0^{(b)} = 0$ for all b in (6.103). Consequently for \mathbf{A}_a the expansion may start from $p = 1$ in (6.100), in which case the matching condition is automatically satisfied for all p . Then (6.107) takes the form

$$\sum_{p=1}^M \sum_{b=1}^r C_{ab}^{(qp)} a_p^{(b)} = \frac{15n_a}{4n} \delta_{q1}. \quad (6.109)$$

In practice the algebraic equations (6.106), (6.108), and (6.109) are solved approximately with $p = 0$ for (6.106) and (6.108) and $p = 1$ for (6.109)—a one-term approximation. In that case the algebraic equations are:

$$\sum_{b=1}^r C_{ab}^{(00)} d_0^{(kb)} = \frac{3}{2} \left(\delta_{ak} - \frac{\rho_a}{\rho} \right) (1 \leq a, k \leq r), \quad (6.110)$$

$$\sum_{b=1}^r C_{ab}^{(11)} a_1^{(b)} = \frac{15n_a}{4n} (1 \leq a \leq r), \quad (6.111)$$

$$\sum_{b=1}^r B_{ab}^{(00)} b_0^{(b)} = \frac{2n_a}{nk_B T} (1 \leq a \leq r). \quad (6.112)$$

The solutions of these linear algebraic sets provide transport coefficients, when the former are used in the formulas obtained from (6.75), (6.76), (6.89), and (6.93), which then take the forms

$$D_{ab} = n^{-1} \sqrt{\frac{k_B T}{2m_a}} d_0^{(ab)}, \quad (6.113)$$

$$D_{ta} = n^{-1} \sqrt{\frac{k_B T}{2m_a}} a_0^{(a)} = 0, \quad (6.114)$$

$$\lambda' = \sum_{a=1}^r \frac{5n_a}{2n} \sqrt{\frac{k_B T}{m_a}} a_1^{(a)}, \quad (6.115)$$

$$\eta_0 = \sum_{a=1}^r \frac{n_a k_B T}{2n} b_0^{(a)}. \quad (6.116)$$

These approximate transport coefficients are called the Chapman–Enskog first approximations for transport coefficients. Since the thermal diffusion coefficients identically vanish in the one-term approximation owing to $a_0^{(a)} = 0$, they require an approximation beyond the lowest order (one-term) approximation.

6.1.3 The Chapman–Enskog Method and Irreversible Thermodynamics

Since one of the important motivations for this work is in understanding the thermodynamics of irreversible processes, it is useful to examine to what extent the Chapman–Enskog method yields a mathematical structure for theory of irreversible processes consistent with the H theorem and also with the second law of thermodynamics. This line of study was first made by Prigogine [13] in 1949. In his study he examined to what order of solution by the Chapman–Enskog method the Gibbs relation for entropy in thermodynamics is compatible with those provided by the leading order Chapman–Enskog solutions of the Boltzmann kinetic theory. We follow a similar line of investigation in this section. This study will also make it possible to assess the irreversible thermodynamic utility of the Boltzmann entropy within the framework of the Chapman–Enskog method.

Before we take it up we examine the Chapman–Enskog solution in the light of the thermodynamic branch of solution we have discussed at the end of Sec. 4.5.2. The Chapman–Enskog method is commonly thought to solve the kinetic equation, since the solution satisfies the kinetic equation under the functional hypothesis taken for f_a . However, it must be recognized that the functional hypothesis in effect allows us to select a thermodynamic branch of the solution for the kinetic equation when the parameters in the equilibrium canonical form for the solution are determined with the help of thermodynamics. Therefore the solution so constructed, even if the perturbation expansion used converges, can be only a particular solution of the kinetic equation whose general solution can be obtained by directly solving it subject to the initial and boundary conditions on f_a in the phase space but without the help of thermodynamics. In the viewpoint we take, in so constructing the solution as to yield a thermodynamic description of irreversible processes the Chapman–Enskog solution should be regarded as a way of obtaining a representation of f_a^c , but not f_a . If $f_a \neq f_a^c$ in the phase space then there will be a nonvanishing relative entropy and its time derivative. It must be inferred that the Chapman–Enskog method tacitly presumes that they are equal to zero. We will use the Chapman–Enskog solution under this understanding in the discussion on thermodynamics of irreversible processes below.

Since the distribution functions are expanded in a series in ϵ in the Chapman–Enskog method, the entropy, entropy flux, and entropy production must be accordingly expanded:

$$\mathcal{S} = \mathcal{S}^{(0)} + \epsilon \mathcal{S}^{(1)} + \epsilon^2 \mathcal{S}^{(2)} + \dots, \quad (6.117)$$

$$\mathbf{J}_s = \epsilon \mathbf{J}_s^{(1)} + \epsilon^2 \mathbf{J}_s^{(2)} + \dots, \quad (6.118)$$

$$\sigma_{\text{ent}} = \epsilon^2 \sigma^{(1)} + \epsilon^3 \sigma^{(2)} + \dots. \quad (6.119)$$

Here various terms are given by the statistical formulas

$$\mathcal{S}^{(0)} = T^{-1} \left(\mathcal{E} + k_B T - \sum_{a=1}^r c_a \hat{\mu}_a \right), \quad (6.120)$$

$$\mathcal{S}^{(1)} = -k_B \rho^{-1} \sum_{a=1}^r \left\langle f_a^{(1)} \ln f_a^0 \right\rangle, \quad (6.121)$$

$$\mathbf{J}_s^{(1)} = T^{-1} \left(\mathbf{Q}^{(1)} - \sum_{a=1}^r \hat{\mu}_a \mathbf{J}_a^{(1)} \right), \quad (6.122)$$

$$\mathbf{J}_s^{(2)} = T^{-1} \left(\mathbf{Q}^{(2)} - \sum_{a=1}^r \hat{\mu}_a \mathbf{J}_a^{(2)} \right) + \frac{1}{2} \sum_{a=1}^r \left\langle \mathbf{C}_a \phi_a^{(1)2} f_a^0 \right\rangle, \quad (6.123)$$

$$\sigma^{(1)} = -k_B \sum_{a,b=1}^r \left\langle \phi_a^{(1)} \ln f_a^0 \left[C(f_a^0 f_b^{(1)}) + C(f_a^{(1)} f_b^0) \right] \right\rangle, \quad (6.124)$$

$$\begin{aligned} \sigma^{(2)} &= -k_B \sum_{a,b=1}^r \left\{ \left\langle \ln f_a^0 \left(\phi_a^{(2)} - \frac{1}{2} \phi_a^{(1)2} \right) \left[C(f_a^0 f_b^{(1)}) + C(f_a^{(1)} f_b^0) \right] \right\rangle \right. \\ &\quad \left. + \left\langle \phi_a^{(1)} \left[C(f_a^0 f_b^{(2)}) + C(f_a^{(2)} f_b^0) \right] \right\rangle \right\}, \end{aligned} \quad (6.125)$$

with the definitions

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

$$\phi_a^{(s)} = \frac{f_a^{(s)}}{f_a^0}.$$

This definition of $\hat{\mu}_a$ is used in this and next sections only.

If the expansions (6.117)–(6.119) for S , \mathbf{J}_s , and σ_{ent} are substituted into the entropy balance equation (4.72) and terms of like power of ϵ are compared, then there arises the hierarchy of equations

$$\frac{dS^{(0)}}{dt} = 0, \quad (6.126)$$

$$\rho \frac{dS^{(1)}}{dt} = -\nabla \cdot \left[\left(\mathbf{Q}^{(1)} - \sum_{a=1}^r \hat{\mu}_a \mathbf{J}_a^{(1)} \right) T^{-1} \right], \quad (6.127)$$

$$\rho \frac{dS^{(2)}}{dt} = -\nabla \cdot \left[\left(\mathbf{Q}^{(2)} - \sum_{a=1}^r \hat{\mu}_a \mathbf{J}_a^{(2)} \right) T^{-1} \right] - \nabla \cdot \sum_{a=1}^r \left\langle \frac{\mathbf{C}_a}{2} \phi_a^{(1)2} f_a^0 \right\rangle + \sigma^{(1)}. \quad (6.128)$$

Eq. (6.126) is nothing but the equilibrium condition obtained from the H theorem stated in local form, since there should not be an entropy flux and an entropy production in a local volume if it is in equilibrium and cannot exchange matter and energy with its surroundings. It is convenient to consider the first and second order contributions together. For this purpose we define

$$\delta S = S - S^{(0)}. \quad (6.129)$$

Then by adding (6.127) and (6.128) side by side and using the balance equations of the conserved variables computed up to the second order

$$\rho \frac{dc_a}{dt} = -\nabla \cdot \left(\epsilon \mathbf{J}_a^{(1)} + \epsilon^2 \mathbf{J}_a^{(2)} \right), \quad (6.130)$$

$$\begin{aligned} \rho \frac{d\mathcal{E}}{dt} &= -\nabla \cdot \left(\epsilon \mathbf{Q}^{(1)} + \epsilon^2 \mathbf{Q}^{(2)} \right) - \left(p\delta + \epsilon \mathbf{P}^{(1)} + \epsilon^2 \mathbf{P}^{(2)} \right) : \nabla \mathbf{u} \\ &\quad + \sum_{a=1}^r \mathbf{F}_a \cdot \left(\epsilon \mathbf{J}_a^{(1)} + \epsilon^2 \mathbf{J}_a^{(2)} \right), \end{aligned} \quad (6.131)$$

we obtain the equation

$$\frac{d}{dt} \delta S = T^{-1} \left(\frac{d\mathcal{E}}{dt} + p \frac{dv}{dt} - \sum_{a=1}^r \hat{\mu}_a \frac{d}{dt} c_a \right) + \Delta_t S, \quad (6.132)$$

where

$$\begin{aligned} \Delta_t S &= (\rho T)^{-1} \left[\delta \mathbf{P} : \nabla \mathbf{u} + \delta \mathbf{Q} \cdot \nabla \ln T + \sum_{a=1}^r \delta \mathbf{J}_a \cdot \left(T \nabla \frac{\hat{\mu}_a}{T} - \mathbf{F}_a \right) \right] \\ &\quad + \epsilon^2 \rho^{-1} \sigma^{(1)} - \epsilon^2 \rho^{-1} \nabla \cdot \frac{1}{2} \sum_{a=1}^r \left\langle \mathbf{C}_a \phi_a^{(1)2} f_a^0 \right\rangle. \end{aligned} \quad (6.133)$$

The following definitions are made for the symbols in this equation:

$$\delta \mathbf{P} = \epsilon \mathbf{P}^{(1)} + \epsilon^2 \mathbf{P}^{(2)}, \quad (6.134)$$

$$\delta \mathbf{Q} = \epsilon \mathbf{Q}^{(1)} + \epsilon^2 \mathbf{Q}^{(2)}, \quad (6.135)$$

$$\delta \mathbf{J}_a = \epsilon \mathbf{J}_a^{(1)} + \epsilon^2 \mathbf{J}_a^{(2)}. \quad (6.136)$$

Since (6.126) can be added to (6.132) without any effect on the right hand side of the latter, the entropy derivative with respect to time is given, to the second order in ϵ , by the equation

$$\frac{dS}{dt} = T^{-1} \left(\frac{dE}{dt} + p \frac{dv}{dt} - \sum_{a=1}^r \hat{\mu}_a \frac{dc_a}{dt} \right) + \Delta_t S. \quad (6.137)$$

This is the entropy balance equation up to the second order in ϵ . In this equation $\Delta_t S \neq 0$ in general, since, first of all, the first two terms on the right hand side of (6.133) do not cancel and the third term is not equal to zero. The term $\Delta_t S$ does not vanish to the first order in ϵ either. In fact, it has the form

$$\Delta_t S = \epsilon (\rho T)^{-1} \left[\mathbf{P}^{(1)} : \nabla \mathbf{u} + \mathbf{Q}^{(1)} \cdot \nabla \ln T + \sum_{a=1}^r \mathbf{J}_a^{(1)} \cdot \left(T \nabla \frac{\hat{\mu}_a}{T} - \mathbf{F}_a \right) \right]. \quad (6.138)$$

Notice that this is the negative of the entropy production in the theory of linear irreversible thermodynamics. Therefore it is possible to conclude that in the Chapman–Enskog method the entropy balance equation gives rise to a form of (dS/dt) which is not compatible with the same derivative taken under the local equilibrium hypothesis in the theory of linear irreversible processes

$$\frac{dS}{dt} = T^{-1} \left(\frac{dE}{dt} + p \frac{dv}{dt} - \sum_{a=1}^r \hat{\mu}_a \frac{dc_a}{dt} \right). \quad (6.139)$$

They become compatible, only if $\Delta_t S$ is arbitrarily set equal to zero. However, $\Delta_t S \neq 0$ if there are irreversible processes present. It must be kept in mind that the assumption (6.139) presumes that (dE/dt) , (dv/dt) and (dc_a/dt) are governed by the full balance equations, not the lowest order corresponding to local equilibrium. Therefore a better way of phrasing the local equilibrium hypothesis is that the entropy density is a functional of conserved variables E , v , and c_a which are governed by their balance equations.

It is important to make the following remark in connection with the Gibbs relation (6.139) and its derivation from the statistical formula for $S^{(0)}$. Since the temperature and density appearing in f_a^0 in the Chapman–Enskog expansion for f_a are regarded as dependent on position and time

through the matching conditions—and this is the conventional viewpoint taken in the literature—it seems possible to calculate $(dS^{(0)}/dt)$ from (6.120) by performing differentiation. We thereby obtain

$$\frac{dS^{(0)}}{dt} = T^{-1} \left(\frac{d\mathcal{E}}{dt} + p \frac{dv}{dt} - \sum_{a=1}^r \hat{\mu}_a \frac{d}{dt} c_a \right), \quad (6.140)$$

since, by using the statistical formula for $\hat{\mu}_a$ and the matching conditions, it is possible to show

$$\mathcal{E} \frac{d}{dt} \left(\frac{1}{T} \right) + v \frac{d}{dt} \left(\frac{p}{T} \right) - \sum_{a=1}^r c_a \frac{d}{dt} \left(\frac{\hat{\mu}_a}{T} \right) = 0, \quad (6.141)$$

which is another form of the Gibbs–Duhem equation. Since in the order of ϵ^0 the right hand side of (6.140) vanishes, $(dS^{(0)}/dt)$ in (6.140) is consistent with the result (6.126) obtained by applying the Chapman–Enskog method to the entropy balance equation.

The most salient part of the conclusion we can draw from the consideration presented for the Chapman–Enskog method concerning irreversible processes is that the local equilibrium hypothesis (6.139) for the time variation of entropy does not hold and the entropy differential to the second or higher order in ϵ is not in a Pfaffian form in the thermodynamic space. Therefore the Boltzmann entropy differential computed by the Chapman–Enskog method hardly corresponds, in its essential aspect, to the calortropy differential deduced from the second law of thermodynamics in Chapter 2. In the conventional wisdom in kinetic theory, the entropy variation is thought to be intimately related to the second law of thermodynamics, which cannot be approximated in any way if it is going to be useful for macroscopic thermal physics, but the Boltzmann entropy differential is not in even a Pfaffian form in the thermodynamic space unless some terms therein are simply neglected. However, an approximate relation for (dS/dt) cannot be used to construct a theory of irreversible processes thereon. Therefore, based on the facts presented, we draw the conclusion that the Chapman–Enskog method cannot be applied for the purpose of constructing a thermodynamic theory of irreversible processes in the space \mathfrak{P} .

6.2 The Moment Method and Irreversible Processes

The Chapman–Enskog method determines the distribution functions as functionals of conserved macroscopic variables and their spatial derivatives under the functional hypothesis. In a way similar to this hypothesis the distribution functions may be regarded as functionals of conserved variables as well as other nonconserved macroscopic variables which are, in

the language of probability theory, nothing but moments of the distribution function. In other words, the distribution function is expanded into a complete set of moments, and the evolution of the former is determined by the evolution of the latter in space–time. Since the tensor Hermite polynomials form a complete orthonormal set the distribution functions may be expanded in them. As in the Chapman–Enskog method, the Maxwell–Grad moment method presumes that the moment expansion of the distribution function solves the kinetic equation in the phase space, but in effect it constructs a thermodynamic branch of the solution for the kinetic equation, namely, f_a^c since the moments are regarded as giving macroscopic thermodynamic observables. As we will see in Chapter 7, the moment expansion of the thermodynamic branch f_a^c is equal to f_a only if the fluctuations in intensive thermodynamic variables vanish. Nevertheless, in the discussion of the Maxwell–Grad moment method in this section this subtlety will be ignored and the spirit of the original formulators of the method will be simply followed. Therefore, as in the original version of the method, there are no relative entropy and its time derivative in the discussion presented below. The Boltzmann entropy is also presumed to be the nonequilibrium extension of the Clausius entropy and hence the Boltzmann entropy differential will be compared with the calortropy differential as a representative of the second law of thermodynamics.

6.2.1 The Maxwell–Grad Moment Method

Let us define reduced peculiar velocity² \mathbf{w}_a by

$$\mathbf{w}_a = \sqrt{\frac{m_a}{k_B T}} \mathbf{C}_a. \quad (6.142)$$

We also define the weight function

$$\omega_a(\mathbf{w}_a) = (2\pi)^{-3/2} \exp\left(-\frac{1}{2} w_a^2\right), \quad (6.143)$$

where \mathbf{w}_a is a three-dimensional vector. A complete set of tensor Hermite polynomials can be constructed with \mathbf{w}_a as described in Chapter 5. The local equilibrium distribution function f_a^0 is then given by

$$f_a^0 = n_a \left(\frac{m_a}{k_B T} \right)^{3/2} \omega_a(\mathbf{w}_a). \quad (6.144)$$

The nonequilibrium distribution function f_a now can be expanded into the complete set of tensor Hermite polynomials

$$f_a(\mathbf{w}_a) = n_a \left(\frac{m_a}{k_B T} \right)^{3/2} \omega_a(\mathbf{w}_a) g_a(\mathbf{w}_a), \quad (6.145)$$

²The reduced peculiar velocity defined by (6.142) is $\sqrt{2}$ times the reduced velocity in the Chapman–Enskog theory; see (6.55).

$$g_a(\mathbf{w}_a) = 1 + \sum_{q=1}^{\infty} \mathcal{H}^{(q)}(\mathbf{w}_a) \odot A_a^{(q)}, \quad (6.146)$$

where $A_a^{(q)}$ will turn out to be mean values of the tensor Hermite polynomials and the symbol \odot means an appropriate scalar product of the tensors involved. This symbol henceforth will be omitted for notational brevity. Let us define the mean value of $\mathcal{H}_a^{(q)}$ by $\Theta_a^{(q)}$:

$$\begin{aligned} \Theta_a^{(q)} &= \rho \widehat{\Theta}_a^{(q)} = n_a \int d\mathbf{w}_a \mathcal{H}^{(q)}(\mathbf{w}_a) \omega_a(\mathbf{w}_a) g_a(\mathbf{w}_a) \\ &= \langle \mathcal{H}^{(q)}(\mathbf{w}_a) f_a \rangle, \end{aligned} \quad (6.147)$$

where the angular brackets mean integration over the reduced peculiar velocity. For example, the diffusion flux \mathbf{J}_a , $\boldsymbol{\Pi}_a$, and \mathbf{Q}'_a are given by the expressions below:

$$\mathbf{J}_a = \sqrt{m_a k_B T} \Theta_a^{(1)}, \quad (6.148)$$

$$\boldsymbol{\Pi}_a = k_B T \left[\Theta_a^{(2)} - \frac{1}{3} \delta \text{Tr} \Theta_a^{(2)} \right], \quad (6.149)$$

$$\mathbf{Q}'_a = \mathbf{Q}_a - \frac{5k_B T}{2m_a} \mathbf{J}_a = \frac{1}{2} k_B T \sqrt{\frac{k_B T}{m_a}} \Theta_{a\gamma\gamma}^{(3)}, \quad (6.150)$$

where the repeated subscripts $\gamma\gamma$ on $\Theta_a^{(3)}$ mean taking the trace over two subscripts of the rank 3 tensor. We are using the Einstein convention for the repeated indices of a tensor.

Now, multiplying $\mathcal{H}_a^{(p)}$ to (6.145) and integrating over velocity and using the orthogonality relations (5.23), we find

$$\Theta_{a\alpha}^{(q)} = n_a A_{a\gamma}^{(q)} \delta_{\alpha\gamma}^q, \quad (6.151)$$

where α and γ stand for the sets $\boldsymbol{\alpha} = (a_1, \dots, a_q)$ and $\boldsymbol{\gamma} = (\gamma_1, \dots, \gamma_q)$, respectively, and the notation developed in Chapter 5 applies to the product of the Kronecker deltas. Thus the coefficient tensors $A_a^{(q)}$ in (6.146) are directly related to the macroscopic moment $\Theta_a^{(q)}$ which is taken to be the same as its macroscopic equivalent. The evolution equation for $\Theta_a^{(q)}$ is easily derived from the kinetic equation. By differentiating (6.147) with time and using the kinetic equation, we obtain the equation

$$\rho \frac{d\widehat{\Theta}_a^{(q)}}{dt} = -\nabla \cdot \langle \mathbf{C}_a \mathcal{H}^{(q)} f_a \rangle + \langle f_a \mathcal{D}_t \mathcal{H}^{(q)} \rangle + \langle \mathcal{H}^{(q)} R(f_a) \rangle, \quad (6.152)$$

where \mathcal{D}_t is defined by (4.93). The right hand side of this equation can be explicitly worked out in terms of macroscopic variables. Since the explicit

forms for the moment evolution equations in (6.152) will be given in a chapter dealing with the nonequilibrium ensemble method [14,15], they will be omitted here. The moment evolution equation (6.152) is in fact a general form of the Maxwell transfer equations and has been used by Grad [2] in his study of gas dynamics. When these moment evolution equations are solved by a perturbation method, in the first order we obtain linear constitutive equations, namely, linear thermodynamic force–flux relations, and the transport coefficients in agreement with the Chapman–Enskog first approximation. We will have an opportunity of discussing these aspects when the nonequilibrium ensemble method is discussed in the next chapter. Therefore the discussion on this topic will be deferred until later. Instead, we will pay closer attention to the possibility of constructing a thermodynamically consistent theory of irreversible processes by means of the moment method.

6.2.2 The Moment Method and Irreversible Thermodynamics

To be more specific, for this discussion we will consider the Boltzmann collision integral for $R[f_a]$. The angular brackets used in this section mean integration over the velocity \mathbf{v}_a . The entropy, entropy flux, and entropy production can be calculated by means of the moment expansion (6.146) for f_a as follows:

$$\mathcal{S} = \mathcal{S}^{(0)} - k_B \rho^{-1} \sum_{a=1}^r \langle f_a^0 g_a \ln g_a \rangle, \quad (6.153)$$

$$\mathbf{J}_s = \left(\mathbf{Q} - \sum_{a=1}^r \hat{\mu}_a \mathbf{J}_a \right) T^{-1} - k_B \sum_{a=1}^r \langle f_a \mathbf{C}_a (\ln g_a - 1) \rangle, \quad (6.154)$$

$$\sigma_{\text{ent}} = -k_B \sum_{a=1}^r \sum_{b=1}^r \langle \ln g_a C(f_a^0 g_a f_b^0 g_b) \rangle. \quad (6.155)$$

Here $\mathcal{S}^{(0)}$ is given by (6.120). Now, on substitution of the entropy flux given by (6.154) into the entropy balance equation and use of the balance equations for the conserved variables in the same manner as for (6.132), we obtain the equivalent form for the entropy balance equation

$$\begin{aligned} \frac{d\mathcal{S}}{dt} &= T^{-1} \left(\frac{d\mathcal{E}}{dt} + p \frac{dv}{dt} - \sum_{a=1}^r \hat{\mu}_a \frac{d}{dt} c_a - \sum_{q=1}^{\infty} \frac{k_B T}{m_a} A_a^{(q)} \frac{d}{dt} \hat{\Theta}_a^{(q)} \right) \\ &\quad - \hat{\Xi}_l + \Delta_{ms}, \end{aligned} \quad (6.156)$$

where

$$\hat{\Xi}_l = -(\rho T)^{-1} [(\mathbf{P} - p\boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q} \cdot \nabla \ln T]$$

$$- (\rho T)^{-1} \sum_{a=1}^r \mathbf{J}_a \cdot \left[T \nabla \left(\frac{\hat{\mu}_a}{T} \right) - \mathbf{F}_a \right], \quad (6.157)$$

$$\begin{aligned} \Delta_{ms} = & \rho^{-1} \nabla \cdot \left[k_B \sum_{a=1}^r \langle f_a^0 g_a \mathbf{C}_a \ln g_a \rangle \right] \\ & - \rho^{-1} k_B \sum_{a=1}^r \sum_{b=1}^r \langle (\ln g_a - g_a + 1) C(f_a^0 g_a f_b^0 g_b) \rangle \\ & + \sum_{q \geq 1} \sum_{a=1}^r \frac{k_B T}{m_a} A_a^{(q)} \nabla \cdot \langle f_a^0 g_a \mathbf{C}_a g_a \rangle \\ & - \rho^{-1} k_B \sum_{q \geq 1} \sum_{a=1}^r \langle f_a^0 \mathcal{D}_t \mathcal{H}_a^{(q)} \rangle. \end{aligned} \quad (6.158)$$

The term $\widehat{\Xi}_l$ is essentially the negative of the $\Delta_t S$ in (6.138) summed over all orders in the nonuniformity parameter ϵ . It does not vanish if the system is away from equilibrium. Neither does Δ_{ms} vanish within the framework of the moment method, in particular, as the form for Δ_{ms} stands. Therefore the Boltzmann entropy differential in (6.156) cannot be compared with the calortropy differential in Chapter 2, which is a phenomenological representation of the second law of thermodynamics, and hence cannot be given that crucial connection with the second law necessary to establish it as the basic equation for the thermodynamics of irreversible processes. In connection with this point we remark that Garcia-Colin *et al.* [16] show that $(\Delta_{ms} - \widehat{\Xi}_l)$ vanishes, to an approximation in which the lowest order term in the expansion of $\ln g_a$ is retained. Such an approximation for dS/dt cannot serve as the basis of the thermodynamics of irreversible processes since thermodynamics and its laws are axiomatic and cannot and should not be satisfied approximately. Such a theory loses the usefulness and the sole motivation for thermodynamics which, together with its consequences, guides us in formulating theories of macroscopic irreversible processes. Clearly, (6.158) is not compatible with the extended Gibbs relation for the calortropy even if g_a is set equal to unity. Since Δ_{ms} cannot be put into a differential form by any rigorous method if the moment expansion (6.146) for f_a is used, we conclude that the Maxwell-Grad moment method is impotent as a method of investigating the mathematical structure of irreversible thermodynamics. To make further progress in that direction it is necessary to devise a way of performing calculations rigorously, since any equation concerning the entropy variation should be an exact relation; the second law of thermodynamics does not leave room for an approximation. Either it is satisfied or it is not. There is no such thing as an axiom or a law being satisfied approximately.

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Classical Nonequilibrium Ensemble Method

In the Gibbs ensemble theory [1–3] of equilibrium statistical mechanics, aided by the Liouville equation for a uniform ensemble, we assume an equilibrium ensemble distribution function such as the canonical ensemble distribution function. Mean values are then computed for macroscopic observables therewith. By corresponding the mean values so computed of the mechanical variables such as energy, pressure, and the number of particles to the thermodynamically determined variables obeying the equilibrium Gibbs relation for the Clausius entropy, we not only identify the temperature with the parameter β appearing in the canonical distribution function [*i.e.*, $\exp(-\beta H)/\langle \exp(-\beta H) \rangle$] but also obtain the statistical mechanical expression for the equilibrium entropy (Clausius entropy) of the system in terms of the distribution function assumed. When such correspondences have been made between the thermodynamic variables and the statistical mechanical mean values for the variables, all the statistical mechanical mean values are expressible in terms of the canonical partition function, and it is possible to implement equilibrium statistical thermodynamics by means of the distribution function alone, which provides a molecular picture of the system of interest. In the Gibbs ensemble theory the burden of the required computation is shifted to the partition function, calculation of which constitutes the main task in statistical thermodynamics.

The nonequilibrium counterpart of the equilibrium Gibbs ensemble theory has been impeded in its development because there is absent the knowledge of nonequilibrium distribution functions that can be as simple and theoretically well grounded as equilibrium canonical distribution functions or their equivalents. There are various reasons for this situation: first of all, a nonequilibrium system requires the description of temporal and spatial evolutions of the distribution function for the system consisting of a large number of particles. The evolution equations for distribution functions are difficult to find in forms consistent with the irreversible phenomena in hand. Even if an evolution equation, namely, the kinetic equation, is known for such a distribution function, it is usually nonlinear and rather difficult to solve in a form that is sufficiently precise to make any attempt at constructing a theory of irreversible processes worthwhile, since the laws of thermodynamics are axiomatic and exacting in precision, and an ill-defined

approximation is insufficient for the purpose. In this regard it must be recalled that in the currently accepted natural philosophy all macroscopic phenomena are subject to the first and second laws of thermodynamics, and, therefore, to be thermodynamically consistent, a nonequilibrium distribution function, whether it is exact or approximate, must give rise to a theory of irreversible processes which exactly conforms to the laws of thermodynamics. In particular, since an exact solution of a physically realistic kinetic equation is usually not possible to obtain, the aforementioned thermodynamic consistency is an important criterion for a theory of irreversible processes to be acceptable. The nonequilibrium ensemble method described in this chapter enforces the stringent condition of thermodynamic consistency on the basis of an irreversible kinetic equation. In the major part of this work we have chosen to work with the Boltzmann equation for the historical prominence and theoretical acceptability it has enjoyed in statistical mechanics. Therefore the theory developed below applies in principle to dilute classical gases only and the kinetic equation (3.27) is the governing equation for the distribution function f_a in this chapter. We mean this equation by the kinetic equation in this chapter. The general idea of the nonequilibrium ensemble method can be applied to any irreversible kinetic equation satisfying a certain set of conditions, as will be shown in Chapters 9 and 10.

Nonequilibrium ensemble methods have been proposed by other authors in the past. McLennan [4,5] and Zubarev [6] constructed exponential forms for the distribution function in terms of fluxes and thermodynamic forces, but the evolution equation for the distribution function was essentially the Liouville equation or the von Neumann equation. Since the Liouville equation is reversible their methods require some kind of projection onto a reduced space if a theory of irreversible processes is to be constructed with it. In any case, their theories lack the evolution equations for nonconserved variables that we will present and make use of in the present nonequilibrium ensemble method. The lack of such evolution equations for nonconserved variables is traceable to the absence of an irreversible kinetic equation in their theories. The absence of an irreversible kinetic equation also deprives their theories of a possibility to formulate a thermodynamic theory of irreversible processes for systems removed far from equilibrium and spawns other secondary difficulties. These features are important points of departure between the methods of McLennan and Zubarev and the present nonequilibrium ensemble method.

We have seen that the Chapman–Enskog method and the Maxwell–Grad method give rise to a theory of linear transport processes which is found to be correct in comparison with experiments in the linear regime, but do not prove to be useful mathematical tools for studying a possible mathematical structure for a general theory of irreversible processes in the regime of nonlinear transport processes which would require nonlinear constitutive equations. The studies made in the previous chapter provide us with some

valuable lessons for achieving the goal; they point out that the Chapman–Enskog expansion method should be avoided and also that the conventional moment expansion is not better suited than the Chapman–Enskog expansion in that regard. Since the entropy production must be positive semidefinite for any process consistent with the H theorem, it is essential that the positivity of the entropy production is preserved regardless of the approximation used to calculate the distribution function and the entropy production itself. Therefore it is useful to look for a form for the entropy production that remains positive no matter what approximation is used for the distribution function, and yet is relatively simple in its mathematical form. It appears that the moment method is more suitable for the study of irreversible processes than the Chapman–Enskog method, since the former does not yield high order spatial gradients which would require a larger number of boundary conditions than normally available in experiments. For this reason we choose to follow the general strategy and spirit provided by the Maxwell–Grad moment method. Nevertheless, since the moment expansion (6.146) has a weakness as indicated in Sec. 6.2.2, it is necessary to find a way of modifying the method such that the weakness mentioned is removed. The form for the thermodynamic branch of the distribution function we take in this chapter is motivated by such a necessity. This form is obtained by suitably resumming the moment expansion (6.146) so that Δ_{ms} defined by (6.158) become a well-behaved quantity in the thermodynamic space spanned by $\mathfrak{P}_h = (\mathcal{E}, v, c_a, \hat{\Theta}_a^{(q)} : q \geq 1, 1 \leq a \leq r)$. Based on the form for the distribution function, we develop a theory of irreversible processes [7–9] and a theory of nonlinear transport processes in gases in this chapter¹.

¹The method described in this chapter was originally called the modified moment method when it was first proposed in a 1980 paper [7] of this author. Since then the method has been revised several times in significant ways in [8] and [9] and in this work. Each revision has been induced by reassessments and the revised viewpoint toward irreversible thermodynamics and its kinetic basis on the part of this author. Such revisions reflect the difficulty associated with the notion of the Boltzmann entropy and its connection with the second law of thermodynamics and how the force of the prevailing misplaced notion about the thermodynamic status of the Boltzmann entropy in the subject field can exert influence on our efforts to extend the classical thermodynamics. Although this nonequilibrium ensemble method descends from the modified moment method, it has an important difference of viewpoint from the latter, in particular, with regard to the meaning of the term ‘solution’ of a kinetic equation used in studying the kinetic foundation of thermodynamics. That which we conventionally call a solution of a kinetic equation, such as the Chapman–Enskog solution or the Maxwell–Grad moment expansion, is probably not a genuine solution of the kinetic equation in the strict mathematical sense of the term solution. They are mathematical forms which are systematically deduced from the kinetic equation in such a way, at least in the lower orders of approximation, to connect thermodynamic macroscopic phenomena with a molecular picture underlying the kinetic equation. Therefore, they

Despite this strategy for obtaining the distribution function such that the thermodynamics of irreversible processes is constructed in a form resembling the structure obtained in Chapter 2 as closely as possible, there is a need for reassessing the so called solution procedures of the kinetic equation, for example, the Boltzmann equation as we have had the glimpse of it in Sec. 4.5.2. To amplify what was discussed there we re-examine [10] the solution methods.

Although the Boltzmann equation necessarily implies the H theorem which suggests the existence of Lyapounov function in the form of δS as shown in Sec. 4.4 and a positive semidefinite local quantity termed the entropy production, the distribution function f_a defined in the phase space has no reference to thermodynamics. Therefore, for example, the parameters α_0 , α_1 , and α_2 in the equilibrium solution in (4.7) are simply quantities related to the normalization factor, the mean velocity, and the mean energy, respectively, which the underlying probability theory does not require to be thermodynamic quantities such as a chemical potential, the temperature of the system, and so on. They have been endowed the status of thermodynamic observables by corresponding them to the thermodynamic observables since we wish to obtain a molecular model for equilibrium thermodynamics. Therefore the assignment of thermodynamic meanings, such as temperature and chemical potential, to α_2 and α_3 in (4.8) is a particular choice made from a set of a wider range so as to connect the statistical theory with thermodynamics, namely, they are a subset of a larger set of the parameters that the probability theory and the boundary and initial conditions on the distribution function may allow. That subset is the one that gives rise to equilibrium thermodynamics, since the parameters in question have been chosen in correspondence with phenomenological equilibrium thermodynamics in the spirit of the Gibbs ensemble method [1–3]. The recognition of this subset is the basis of the idea of fluctuations in intensive variables discussed later. The Chapman–Enskog method, the Maxwell–Grad method, and the nonequilibrium ensemble method discussed below construct the distribution functions by taking a particular set for the parameters therein, since they are so chosen as to achieve the desired correspondence with thermodynamics one way or another. Therefore the distribution function determined as the solution of the kinetic equation in the aforementioned methods is in the class of thermodynamic branch f_a^c of f_a which was introduced in Sec. 4.5.2. The Chapman–Enskog and Maxwell–Grad moment methods do not explicitly acknowledge this fact,

are thermodynamic branches of the solution of the kinetic equation which are obtained by projecting the phase space solution onto the thermodynamic space of interest. Moreover, for example, the Chapman–Enskog solution is probably an asymptotic solution constructed by an *ad hoc* procedure that calculates the time derivatives in a rather special way so that the first-order approximation yields the Navier–Stokes and Fourier equations of hydrodynamics.

but it is clear that the Chapman–Enskog solution and the Grad moment expansion are thermodynamic branches of the distribution function since they are, if nothing else, built around the equilibrium solution which was shown to be the thermodynamic branch of the equilibrium solution of the kinetic equation. In these methods the thermodynamic branches are simply taken to be approximations to f_a , but the nature of approximations used for f_a is of a rather special kind. The notion of thermodynamic branch is rather subtle and at first glance seems unnecessary to introduce, but it is very important, especially when the status of the Boltzmann entropy is examined with respect to thermodynamics. As will be shown, the Boltzmann entropy is more than a nonequilibrium extension in the thermodynamic space of the Clausius entropy, and the H theorem is not exactly the second law of thermodynamics; it is something more than the second law and puts a constraint on the evolution of the distribution function in the phase space. It must be recalled that traditionally in kinetic theory the H theorem is thought to be a statistical mechanical representation of the second law of thermodynamics and the Boltzmann entropy is a nonequilibrium extension of the Clausius entropy in the thermodynamic space spanned by the conserved and nonconserved variables—an extension to which the Clausius inequality directly applies. This belief, however, has not been based on careful analysis but is a result of uncritical acceptance and elevation of a theorem of a mathematical nature in the probability theory to the status of a physical law.

7.1 Thermodynamic Branch of f_a

In order to implement the nonequilibrium ensemble method in the spirit and strategy described in the introduction of this chapter it is necessary to construct a suitable thermodynamic branch f_a^c of the distribution function, a notion introduced in Chapter 4. To this end we examine the Maxwell–Grad moment expansion because of its close relevance to the nonequilibrium ensemble method which we would like to formulate in this chapter. The discussion made with the expansion (7.1) below, however, is not essential for the nonequilibrium ensemble method envisaged, but presented in the hope of maintaining continuity to the more traditional manner of thinking which the firmly entrenched Maxwell–Grad moment method represents. Another aim is in pointing out that the Maxwell–Grad moment expansion is also a thermodynamic branch, albeit ill suited for irreversible thermodynamics.

First, let us define $f_a^c(m)$ by the expansion

$$f_a^c(m) = f_a^0 \left[1 + \sum_{q=1}^m A_a^{(q)} \mathcal{H}^{(q)}(\mathbf{w}_a) \right], \quad (7.1)$$

where f_a^0 and $\mathcal{H}^{(q)}(\mathbf{w}_a)$ have already been defined ; see Sec. 6.2.1. Note that by choosing f_a^0 to take a form similar to the thermodynamic branch of the equilibrium solution we already have a special kind of distribution function in mind with the expansion in (7.1). Here a finite upper limit m is taken for the sum in (7.1); the upper limit will be eventually taken to infinity. The meanings of the coefficients in (7.1) must be clarified. To this end, let us define the mean values

$$\Theta_a^{(q)} = \rho \widehat{\Theta}_a^{(q)} = \left\langle \mathcal{H}^{(q)}(\mathbf{w}_a) f_a \right\rangle \quad (q \geq 1). \quad (7.2)$$

The full distribution function f_a is used in this definition. The evolution equation for $\widehat{\Theta}_a^{(q)}$ can be easily obtained from the kinetic equation (3.27) and (7.1):

$$\rho \frac{d}{dt} \widehat{\Theta}_a^{(q)} = K_a^{(q)} + \mathcal{D}_a^{(q)} \quad (q \geq 1), \quad (7.3)$$

where the kinematic term $K_a^{(q)}$ and the dissipation term $\mathcal{D}_a^{(q)}$ are, respectively, given by the statistical formulas

$$K_a^{(q)} = -\nabla \cdot \psi_a^{(q)} + \left\langle f_a \mathcal{D}_t \mathcal{H}^{(q)}(\mathbf{w}_a) \right\rangle, \quad (7.4)$$

$$\mathcal{D}_a^{(q)} = \left\langle \mathcal{H}^{(q)}(\mathbf{w}_a) R[f_a] \right\rangle, \quad (7.5)$$

with the definition

$$\psi_a^{(q)} = \left\langle \mathbf{C}_a \mathcal{H}^{(q)}(\mathbf{w}_a) f_a \right\rangle. \quad (7.6)$$

Therefore $\psi_a^{(q)}$ is the flux of $\Theta_a^{(q)}$ in crude physical terminology. The \mathcal{D}_t is the streaming operator of the Boltzmann equation; see (4.93) for the definition of \mathcal{D}_t . The kinematic term is clearly seen to arise from the streaming term, namely, the kinematic term, in the kinetic equation and hence the designation used for it. It is useful to recall that the streaming term in the kinetic equation is also reversible, as was pointed out in the discussion of irreversibility and the kinetic equation in Chapter 3. This observation is useful for understanding the significance of the differential form obtained later for the time derivative of the quantities related to the Boltzmann entropy. Some examples for $\Theta_a^{(q)}$ are:

$$\begin{aligned} \Theta_a^{(0)} &= n_a, \\ \Theta_a^{(1)} &= \sqrt{\frac{\beta}{m_a}} \mathbf{J}_a, \\ \Theta_a^{(2)} &= \beta (\mathbf{P}_a - p_a \boldsymbol{\delta}), \\ \Theta_{a\gamma\gamma}^{(3)} &= 2\sqrt{\beta m_a} \beta \left(\mathbf{Q}_a - \widehat{h}_a \mathbf{J}_a \right), \quad etc., \end{aligned} \quad (7.7)$$

where $\beta = 1/k_B T$, p_a is the partial pressure of species a , \hat{h}_a is the enthalpy per mass of species a , and the subscript $\gamma\gamma$ denotes taking trace over two indices of Cartesian components of the third-rank tensor $\Theta_a^{(3)}$. The Einstein convention is used for repeated indices. These examples show the relations to $\Theta_a^{(q)}$ of macroscopic observables such as n_a , \mathbf{J}_a , \mathbf{P}_a , \mathbf{Q}_a , and so on; the former are linear combinations of the latter.

Expansion (7.1) is a finite term Grad expansion [11], and it is convergent to f_a only in the sense of means, namely, weakly convergent to f_a in the following sense:

$$\lim_{m \rightarrow \infty} \left\langle [f_a - f_a^c(m)] \mathcal{H}^{(q)}(\mathbf{w}_a) \right\rangle = 0. \quad (7.8)$$

Therefore, the moments may be defined by

$$\Theta_a^{(q)} = \lim_{m \rightarrow \infty} \left\langle f_a^c(m) \mathcal{H}^{(q)}(\mathbf{w}_a) \right\rangle. \quad (7.9)$$

By using this and the orthogonality properties of $\mathcal{H}^{(q)}(\mathbf{w}_a)$ the expansion coefficients $A_a^{(q)}$ can be determined in terms of the moments $\Theta_a^{(q)}$. Since it was discussed in Chapter 6, we will not repeat the determination of these coefficients. With $A_a^{(q)}$ thus determined in terms of $\Theta_a^{(q)}$, the thermodynamic branch is given by the expansion

$$f_a^c = f_a^0 \left[1 + \sum_{q \geq 1} A_a^{(q)} \mathcal{H}^{(q)}(\mathbf{w}_a) \right]. \quad (7.10)$$

Here the expansion now is over the complete set of $\mathcal{H}^{(q)}(\mathbf{w}_a)$. This is not an ordinary expansion in the phase space of the particle if the coefficients $A_a^{(q)}$ are given in terms of a thermodynamically identified set \mathfrak{P}_h made up of variables $(\mathcal{E}, v, c_a, \hat{\Theta}_a^{(q)} : q \geq 1, 1 \leq a \leq r)$; it is a projection of f_a onto the space \mathfrak{P}_h of variables identified with thermodynamic variables. The functional hypothesis and the thermodynamic correspondence underlie this projection method.

We have seen in the previous chapter that this form (7.10) of expansion for f_a is not very useful for developing a statistical theory of thermodynamics. The reason is that the (Boltzmann) entropy production is the seat of irreversibility in the system and σ_c is closely related to the former, as is clear from (4.84) and (4.86), but the expansion (7.10) does not give rise to a form for σ_c that is useful for erecting a mathematical structure of irreversible thermodynamics compatible with the laws of thermodynamics. For example, the chemical potential of the gas represented by the expansion (7.10) is simply the same as the equilibrium chemical potential. This is unrealistic. Nevertheless, (7.10) is conceptually relevant to the present theory since it readily shows the nature of the thermodynamic branch of the distribution function.

To remedy the weaknesses mentioned, the expansion (7.10) may be resummed to an exponential form [7–10]

$$\begin{aligned} f_a^c &= f_a^0 \exp \left[-\beta \sum_{q=1}^{\infty} Y_a^{(q)} \mathcal{H}^{(q)}(\mathbf{w}_a) + \gamma_a \right] \\ &= \exp \left\{ -\beta \left[\frac{1}{2} m_a C_a^2 + \sum_{q=1}^{\infty} Y_a^{(q)} \mathcal{H}^{(q)}(\mathbf{w}_a) - \mu_a \right] \right\}, \end{aligned} \quad (7.11)$$

where with the definitions

$$\begin{aligned} \mu_a &= m_a \hat{\mu}_a \\ &= -k_B T \ln \left[\frac{1}{n_a} \left\langle \exp -\beta \left(\frac{1}{2} m_a C_a^2 + \sum_{q=1}^{\infty} \mathcal{H}^{(q)} Y_a^{(q)} \right) \right\rangle \right], \end{aligned} \quad (7.12)$$

$$\begin{aligned} \hat{\mu}_a^0 &= \frac{\mu_a^0}{m_a} \\ &= \frac{k_B T}{m_a} \ln \left[n_a \left(\frac{m_a}{2\pi k_B T} \right)^{3/2} \right], \end{aligned} \quad (7.13)$$

the normalization factor γ_a is given by

$$\gamma_a = \frac{m_a}{k_B T} (\hat{\mu}_a - \hat{\mu}_a^0). \quad (7.14)$$

The coefficients $Y_a^{(q)}$ can be related to $A_a^{(p)}$ in (7.10) by the relation obtained by equating (7.10) and (7.11):

$$-\beta \sum_{q=1}^{\infty} \mathcal{H}^{(q)}(\mathbf{w}_a) Y_a^{(q)} + \gamma_a = \ln \left[1 + \sum_{q=1}^{\infty} \mathcal{H}^{(q)}(\mathbf{w}_a) A_a^{(q)} \right]. \quad (7.15)$$

We will return later in this chapter to the computational algorithm for $Y_a^{(q)}$ which is based on this relation. Therefore, inasmuch as $A_a^{(q)}$ are uniquely known in terms of the moments $\Theta_a^{(q)}$, the coefficients $Y_a^{(q)}$ are determinable from (7.15). We will find, however, that it is not necessary to relate the exponential form (7.11) to the Maxwell–Grad expansion (7.10) in the nonequilibrium ensemble method in the manner shown in (7.15) since we can simply take (7.11) for the thermodynamic branch of f_a and therefore dispose of the procedure of relating $Y_a^{(q)}$ to $A_a^{(q)}$ as described earlier, if we calculate the nonequilibrium partition function. For $Y_a^{(q)}$ is related to the nonequilibrium partition function in the nonequilibrium ensemble method which we aim to achieve in this chapter. The distribution function f_a^c in (7.11) is called the nonequilibrium canonical form. The external potential energy is absorbed into the density in the normalization factor. Here it must be

emphasized that the parameters n_a , T , and \mathbf{u} are determined such that the matching conditions (4.40)–(4.42) are satisfied. These matching conditions enable us to treat n_a and T as quantities related to equilibrium observables n_a^0 and T_e which are made space–time dependent and thus quantities of nonequilibrium. Therefore the same measuring procedures apply to n_a and T as for n_a^0 and T_e , as discussed in Sec. 4.3. The parameters T and n_a appearing in f_a in (7.11) are given the same meanings as those in (7.10). Nevertheless, in the development of the nonequilibrium ensemble method it is sufficient for now that they are independent of molecular velocities and may be simply regarded as parameters whose meanings are as yet to be elucidated. The thermodynamic significance of these parameters in the context of nonequilibrium will be completely elucidated when the nonequilibrium ensemble method has run its full course of development. In this regard the reader should recall the equilibrium ensemble method of statistical thermodynamics where the temperature and chemical potential in the distribution function are identified with their thermodynamic counterparts by means of correspondence between thermodynamics and statistical mechanics. Once the nonequilibrium canonical form is taken for the thermodynamic branch of the distribution function subject to the matching conditions, the expansion (7.10) retains only a seminal significance but no practical utility in the development of nonequilibrium ensemble method.

7.2 Thermodynamics of Irreversible Processes

The thermodynamic branch of the distribution function is a special form of distribution function that gives rise to a thermodynamic formalism consistent with the phenomenological theory of thermodynamics of irreversible processes developed in Chapter 2. Since the nonequilibrium canonical form f_a^c is explicitly given as in (7.11) we are now able to calculate S^c , \mathbf{J}_c , and σ_c defined by (4.78), (4.84), and (4.86), respectively. The nonequilibrium canonical form is essential for this line of calculation to construct a mathematical structure suitable for the study of irreversible processes and for the nonequilibrium ensemble method.

7.2.1 Calortropy Differential

Since S^c is eventually going to be compared with its phenomenological counterpart $\hat{\Psi}$, namely, the calortropy, introduced in Chapter 2, we make the following proposition as a way of defining $\hat{\Psi}$ statistically².

²In the previous articles [8,9] on the nonequilibrium ensemble method and irreversible thermodynamics the term compensation function was used for Ψ ,

Proposition 5 *The statistical definition of the calortropy density $\widehat{\Psi}$ is that of \mathcal{S}^c with f_a^c given by the nonequilibrium canonical form (7.11):*

$$\rho\widehat{\Psi} = -k_B \sum_{a=1}^r \langle f_a (\ln f_a^c - 1) \rangle \quad (7.16)$$

and the statistical definitions of calortropy flux and calortropy production are respectively

$$\mathbf{J}_c = -k_B \sum_{a=1}^r \langle f_a \mathbf{C}_a (\ln f_a^c - 1) \rangle, \quad (7.17)$$

$$\sigma_c = -k_B \sum_{a=1}^r \langle \ln f_a^c R[f_a] \rangle. \quad (7.18)$$

The balance equation for $\widehat{\Psi}$ therefore can be derived [10] from the kinetic equation (3.27) and (7.16) with the definitions (7.17) and (7.18):

$$\rho \frac{d\widehat{\Psi}}{dt} = -\nabla \cdot \mathbf{J}_c + \sigma_c - k_B \sum_{a=1}^r \langle f_a \mathcal{D}_t \ln f_a^c \rangle. \quad (7.19)$$

This balance equation, which will be the working equation for the kinetic formulation of thermodynamics of irreversible processes in this work, is accompanied by the balance equation [10] for the relative Boltzmann entropy $S_r[f|f_a^c]$

$$\rho \frac{d}{dt} S_r[f|f_a^c] = -\nabla \cdot \mathbf{J}_r[f|f_a^c] + \sigma_r[f|f_a^c] - k_B \sum_{a=1}^r \langle f_a \mathcal{D}_t \ln f_a^c \rangle \quad (7.20)$$

with the statistical definitions

$$\rho S_r[f|f_a^c] = k_B \sum_{a=1}^r \langle f_a (\ln f_a - \ln f_a^c) \rangle, \quad (7.21)$$

$$\mathbf{J}_r[f|f_a^c] = k_B \sum_{a=1}^r \langle f_a \mathbf{C}_a (\ln f_a - \ln f_a^c) \rangle, \quad (7.22)$$

$$\sigma_r[f|f_a^c] = k_B \sum_{a=1}^r \langle (\ln f_a - \ln f_a^c) R[f_a] \rangle. \quad (7.23)$$

but because of its potential importance in the theory of irreversible processes, its property which is obviously different from that of the Boltzmann entropy, and often indiscriminate use of the term entropy in the literature, we propose to coin a new terminology for the quantity. Since it is clearly related to heat (*calor*) and its evolution (*tropy*), the new compound term *calortropy* to mean heat evolution appears to be sufficiently simple and apt in view of its relation to entropy which should be reserved for reversible processes or equilibrium only, as it was originally defined for such processes by Clausius.

Subtracting (7.20) from (7.19) yields the Boltzmann entropy balance equation which can be also written as

$$\frac{dS}{dt} = \frac{d\hat{\Psi}}{dt} - \frac{d}{dt} S_r[f|f_a^c]. \quad (7.24)$$

The Boltzmann entropy is then given by the formula

$$S = \hat{\Psi} - S_r[f|f_a^c]. \quad (7.25)$$

In addition to this, there hold the relations

$$\mathbf{J}_s = \mathbf{J}_c - \mathbf{J}_r[f|f_a^c], \quad (7.26)$$

$$\sigma_{\text{ent}} = \sigma_c - \sigma_r[f|f_a^c]. \quad (7.27)$$

The relative Boltzmann entropy vanishes, only if $f_a = f_a^c$. The presence of the relative Boltzmann entropy [10] implies that whatever information deficiency f_a^c and thus $\hat{\Psi}$ might carry is corrected by the relative Boltzmann entropy to provide the full information content carried by f_a and S in the phase space. In this regard, we remark that by the Klein inequality

$$S_r[f|f_a^c] \geq 0,$$

which implies that

$$S \leq \hat{\Psi}.$$

Therefore, put in simple terms, this inequality means that the calortropy $\hat{\Psi}$ describes a state of the system reduced in the information content, compared with the state represented by the Boltzmann entropy S . This is consistent with the fact that $\hat{\Psi}$ gives rise to a thermodynamic description of the system and thermodynamics is a description of the system at a level of information content much contracted from the phase space description. The aforementioned inequality by no means implies that $\hat{\Psi} = \max S$ since $\hat{\Psi}$ is not of equilibrium. The definitions and balance equations of calortropy and relative Boltzmann entropy will be the objects of examination in this chapter.

Proposition 5 and comparison of (7.19) with the phenomenological equation for calortropy (2.48) suggest that the statistical formulas for \mathbf{J}_c and $\Xi_c = \rho\hat{\Xi}_c$ in (2.48) have now been found. The assertion that the formulas (7.17) and (7.18) for \mathbf{J}_c and σ_c indeed are the statistical formulas for \mathbf{J}_c and Ξ_c in (2.48) is formalized by the following theorem.

Theorem 2 *The calortropy flux \mathbf{J}_c and the calortropy production Ξ_c are statistically given by the formulas*

$$\mathbf{J}_c = -k_B \sum_{a=1}^r \langle f_a \mathbf{C}_a (\ln f_a^c - 1) \rangle, \quad (7.28)$$

$$\Xi_c = -k_B \sum_{a=1}^r \langle \ln f_a^c R[f_a] \rangle - k_B \sum_{a=1}^r \langle f_a D_t \ln f_a^c \rangle. \quad (7.29)$$

This theorem makes it possible to establish a Pfaffian differential form for $d_t \hat{\Psi}$ in the space \mathfrak{P}_h . This result is stated by the following theorem [10].

Theorem 3 *The statistical calortropy $\hat{\Psi}$ has the Pfaffian differential form*

$$d_t \hat{\Psi} = T^{-1} \left(d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{q \geq 1} Y_a^{(q)} d_t \hat{\Theta}_a^{(q)} \right), \quad (7.30)$$

which is an exact differential in the thermodynamic space \mathfrak{P}_h .

These theorems will be proved in the following, and their proofs will ultimately establish the basic procedure of the nonequilibrium ensemble method. It must be noted that the nonequilibrium canonical form³ is indispensable for proving this theorem.

The effect on $\hat{\mu}_a$ of variations in macroscopic parameters T^{-1} , n_a , and $Y_a^{(q)}$ can be calculated by taking the substantial time derivative of (7.12) with the kinetic energy and $\mathcal{H}^{(q)}(\mathbf{w}_a)$ kept fixed. On summing over the species after a suitable rearrangement of the terms we obtain

$$\sum_{a=1}^r c_a d_t \left(\frac{\hat{\mu}_a}{T} \right) = \mathcal{E} d_t T^{-1} + v d_t \left(\frac{p}{T} \right) + \sum_{a=1}^r \sum_{q \geq 1} \hat{\Theta}_a^{(q)} d_t \left(\frac{Y_a^{(q)}}{T} \right). \quad (7.31)$$

We have used $p = n k_B T$ for this result, which describes how the local variable $\hat{\mu}_a/T$ changes as other local macroscopic parameters $1/T$, p/T , and $Y_a^{(q)}/T$ are varied. We remark that $p = n k_B T$ is a result of the matching conditions (4.40)–(4.42) and holds even for nonequilibrium; see (6.50) and the discussion on the notion of temperature for nonequilibrium in Chapter 2.

If the nonequilibrium canonical form for f_a^c is substituted into (7.16) and use is made of the statistical definitions of macroscopic variables, we obtain the expression

$$\hat{\Psi} = T^{-1} \left(\mathcal{E} + p v - \sum_{a=1}^r \hat{\mu}_a c_a + \sum_{a=1}^r \sum_{q \geq 1} Y_a^{(q)} \hat{\Theta}_a^{(q)} \right). \quad (7.32)$$

³In the literature some authors [12–14] resort to the method of maximum entropy to obtain a nonequilibrium canonical form. However, it must be recognized that the Boltzmann entropy has no maximum away from equilibrium. Therefore the maximum entropy method has no mathematical and physical basis to be applied away from equilibrium. Given the statistical definition of $\hat{\Psi}$ in (7.16) and the fact that $\hat{\Psi}$ must be extensive and Ξ_c must be bilinear in the space \mathfrak{P} or \mathfrak{P}_h , it is clear that f_a^c must be an exponential form.

This means that $\widehat{\Psi}$ is a function in the space \mathfrak{P}_h and (7.32) represents a surface in the Gibbs space \mathfrak{G}_h spanned by the variables $(\widehat{\Psi}, \mathcal{E}, v, c_a, \widehat{\Theta}_a^{(q)} : q \geq 1, 1 \leq a \leq r)$. On taking the substantial time derivative of (7.32) and using (7.31) we obtain

$$d_t \widehat{\Psi} = T^{-1} \left(d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \widehat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{q \geq 1} Y_a^{(q)} d_t \widehat{\Theta}_a^{(q)} \right),$$

which is simply (7.30). Since the differential form (7.31) means that (7.30) integrates to a function $\widehat{\Psi}$ as given by (7.32) in the thermodynamic space \mathfrak{P}_h , it is seen to be the integrability condition [15] of (7.30). Indeed, if (7.31) and (7.32) are added side by side and integrated, (7.32) follows, apart from an integration constant. We will show that (7.30) also follows from the balance equation (7.19) for $\widehat{\Psi}$ if the nonequilibrium canonical form is used in (7.28) and (7.29) and the conservation laws are used for the conserved variables. To this end, we first calculate \mathbf{J}_c .

Substitution of the nonequilibrium canonical form f_a^c into (7.28) yields the formula⁴ for \mathbf{J}_c in space \mathfrak{P}_h

$$\mathbf{J}_c = \sum_{a=1}^r T^{-1} \left(\mathbf{Q}_a - \widehat{\mu}_a \mathbf{J}_a + \sum_{q \geq 1} Y_a^{(q)} \psi_a^{(q)} \right) + \sum_{a=1}^r \frac{k_B}{m_a} \mathbf{J}_a. \quad (7.33)$$

The same procedure as for \mathbf{J}_c can be used for σ_c , which then takes the form

$$\sigma_c = T^{-1} \sum_{a=1}^r \sum_{q \geq 1} Y_a^{(q)} \mathcal{D}_a^{(q)}. \quad (7.34)$$

⁴This expression can be cast into another form with more insight in its meaning. To this end we observe that by the recursion relation (5.19) of the tensor Hermite polynomials the higher order moments $\psi_a^{(q)}$ can be written as

$$\psi_a^{(q)} = (m_a \beta)^{-1/2} [\Theta_a^{(q+1)} + \Theta_a^{(q-1)} \delta]. \quad (\text{A})$$

By using this relation and the sum rule

$$\mathbf{J}_a = (m_a \beta)^{-1/2} \sum_{q \geq 1} Y_a^{(q)} \Theta_a^{(q-1)} \delta, \quad (\text{B})$$

it is possible to put (7.33) in the form

$$\mathbf{J}_c = \sum_{a=1}^r T^{-1} (\mathbf{Q}_a - \widehat{\mu}_a \mathbf{J}_a + \sum_{q \geq 1} Y_a^{(q)} \Theta_a^{(q+1)}), \quad (\text{C})$$

where $\Theta_a^{(q+1)}$ clearly is the reduced flux of $\Theta_a^{(q)}$.

For brevity of notation the following abbreviations will be useful:

$$\bar{Y}_a^{(q)} = \frac{Y_a^{(q)}}{T}, \quad \bar{\mu}_a = \frac{\hat{\mu}_a}{T}, \quad \bar{\mu}_a^0 = \frac{\hat{\mu}_a^0}{T}.$$

To calculate the third term on the right hand side of (7.19), it is useful to develop some identities. First, it is straightforward to show the identity

$$k_B \sum_{a=1}^r \langle f_a \mathcal{D}_t \ln f_a^0 \rangle = -\sigma_l + \rho d_t \left(\frac{pv}{T} \right), \quad (7.35)$$

where σ_l has the same form as the entropy production appearing in the theory of linear irreversible processes [16]:

$$\sigma_l = -T^{-1} \sum_{a=1}^r [(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q}_a \cdot \nabla \ln T + \mathbf{J}_a \cdot (T \nabla \bar{\mu}_a^0 - \mathbf{F}_a)]. \quad (7.36)$$

For derivation of this identity we have used the local Gibbs–Duhem relation

$$\sum_{a=1}^r c_a d_t \bar{\mu}_a^0 = \mathcal{E} d_t T^{-1} + v d_t \left(\frac{p}{T} \right), \quad (7.37)$$

which follows from (7.13) on differentiation and on use of the density and energy matching conditions (4.40) and (4.42). The statistical formula (7.4) for the kinematic term $K_a^{(q)}$ can be used to show the relation [10]

$$\begin{aligned} \sum_{q \geq 1} \langle f_a \mathcal{D}_t \bar{Y}_a^{(q)} \mathcal{H}^{(q)}(\mathbf{w}_a) \rangle &= \sum_{q \geq 1} [\bar{Y}_a^{(q)} K_a^{(q)} + \nabla \cdot (\psi_a^{(q)} \bar{Y}_a^{(q)})] \\ &\quad + \sum_{q \geq 1} \rho \hat{\Theta}_a^{(q)} d_t \bar{Y}_a^{(q)}. \end{aligned} \quad (7.38)$$

This relation follows if $\bar{Y}_a^{(q)}$ is multiplied to $K_a^{(q)}$ in (7.4), summed over q , and then the terms are rearranged. Since by definition

$$\ln \left(\frac{f_a^c}{f_a^0} \right) = -k_B^{-1} \sum_{q \geq 1} \bar{Y}_a^{(q)} \mathcal{H}^{(q)}(\mathbf{w}_a) + \gamma_a, \quad (7.39)$$

on use of the identities (7.35) and (7.38), the second term on the right hand side of (7.29) for Ξ_c can be written as

$$\begin{aligned} \mathcal{L}_f^c &\equiv -k_B \sum_{a=1}^r \langle f_a \mathcal{D}_t \ln f_a^c \rangle \\ &= -k_B \sum_{a=1}^r \left\langle f_a \mathcal{D}_t \left[\ln \left(\frac{f_a^c}{f_a^0} \right) + \ln f_a^0 \right] \right\rangle \end{aligned}$$

$$\begin{aligned}
&= \rho \left[\mathcal{E} d_t T^{-1} + v d_t \left(\frac{p}{T} \right) - \sum_{a=1}^r c_a d_t \bar{\mu}_a + \sum_{a=1}^r \sum_{q \geq 1} \hat{\Theta}_a^{(q)} d_t \bar{Y}_a^{(q)} \right] \\
&\quad - \rho d_t \left(\frac{pv}{T} \right) + \Xi_l + \sum_{a=1}^r \sum_{q \geq 1} \bar{Y}_a^{(q)} \hat{K}_a^{(q)}. \tag{7.40}
\end{aligned}$$

This is an important identity. Here the symbols are defined by the formulas

$$\begin{aligned}
\hat{K}_a^{(q)} &= \langle f_a \mathcal{D}_t \mathcal{H}^{(q)}(\mathbf{w}_a) \rangle \\
&= K_a^{(q)} + \nabla \cdot \psi_a^{(q)}, \tag{7.41}
\end{aligned}$$

$$\begin{aligned}
\Xi_l &= \sigma_l - \sum_{a=1}^r \mathbf{J}_a \cdot \nabla (\bar{\mu}_a - \bar{\mu}_a^0) + \sum_{a=1}^r \sum_{q \geq 1} \psi_a^{(q)} \cdot \nabla \bar{Y}_a^{(q)} \\
&= -T^{-1} \sum_{a=1}^r [(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q}_a \cdot \nabla \ln T + \mathbf{J}_a \cdot (T \nabla \bar{\mu}_a - \mathbf{F}_a)] \\
&\quad + \sum_{a=1}^r \sum_{q \geq 1} \psi_a^{(q)} \cdot \nabla \bar{Y}_a^{(q)}. \tag{7.42}
\end{aligned}$$

For the derivation of (7.42) we have used (7.31) and (7.37) as well as $p = nk_B T$. On application of (7.31) the crucial identity (7.40) can be written in the form

$$\begin{aligned}
\mathcal{L}_f^c &= -k_B \sum_{a=1}^r \langle f_a \mathcal{D}_t \ln f_a^c \rangle \\
&= \Xi_l + \sum_{a=1}^r \sum_{q \geq 1} \bar{Y}_a^{(q)} \hat{K}_a^{(q)} - \rho d_t \left(\frac{pv}{T} \right), \tag{7.43}
\end{aligned}$$

which plays an important role in the present theory. With the definition of the new heat flux

$$\mathbf{Q}_a^{\text{ch}} = \mathbf{Q}_a - \hat{\mu}_a \mathbf{J}_a + \sum_{q \geq 1} \psi_a^{(q)} Y_a^{(q)}, \tag{7.44}$$

Ξ_l in (7.42) can be rearranged to the more insightful form

$$\begin{aligned}
\Xi_l &= -T^{-1} \sum_{a=1}^r [(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q}_a^{\text{ch}} \cdot \nabla \ln T + \mathbf{J}_a \cdot (\nabla \hat{\mu}_a - \mathbf{F}_a)] \\
&\quad + T^{-1} \sum_{a=1}^r \sum_{q \geq 1} \psi_a^{(q)} \cdot \nabla Y_a^{(q)}. \tag{7.45}
\end{aligned}$$

This form is rather suggestive and should be compared with σ_l , the entropy production in the theory of linear irreversible processes [16]. In this formula the gradients of generalized potentials $Y_a^{(q)}$ appear on the equal footing as other gradients such as $\nabla \mathbf{u}$, $\nabla \ln T$, and $\nabla \hat{\mu}_a$, namely, thermodynamic gradients. Notice in this regard that $\psi_a^{(q)}$ are higher order fluxes. We also note that the notion of heat flux is generalized by addition of the bilinear form of $\psi_a^{(q)}$ and $Y_a^{(q)}$ in (7.44).

Substitution of (7.34) and (7.43) into (7.29) finally yields Ξ_c in the form

$$\Xi_c = \Xi_l + \sum_{a=1}^r \sum_{q \geq 1} \bar{Y}_a^{(q)} \left(\hat{K}_a^{(q)} + \mathcal{D}_a^{(q)} \right) + \sum_{a=1}^r \frac{k_B}{m_a} \nabla \cdot \mathbf{J}_a. \quad (7.46)$$

Note that

$$\sum_{a=1}^r \left(\frac{k_B}{m_a} \right) \nabla \cdot \mathbf{J}_a = -\rho d_t \left(\frac{pv}{T} \right).$$

This formula for Ξ_c constitutes the source term in the calortropy balance equation (7.19). If this formula and the formula for \mathbf{J}_c in (7.33) are substituted into the (7.19), the last term in (7.33) cancels the last term in (7.46). Therefore the mathematical structure of the calortropy balance equation remains unchanged if the last terms in (7.33) and (7.46) are ignored and the statistically derived formulas for \mathbf{J}_c and Ξ_c are written as

$$\mathbf{J}_c = \sum_{a=1}^r T^{-1} \mathbf{Q}_a^{ch}, \quad (7.47)$$

$$\Xi_c = \Xi_l + \sum_{a=1}^r \sum_{q \geq 1} \bar{Y}_a^{(q)} \left(\hat{K}_a^{(q)} + \mathcal{D}_a^{(q)} \right). \quad (7.48)$$

In this connection we remark that the last term in (7.33) would not have arisen if \mathbf{J}_c were defined by the statistical formula

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

without the factor 1, since then there would arise the expression⁵

$$\mathbf{J}_c = \sum_{a=1}^r T^{-1} \mathbf{Q}_a^{ch}.$$

⁵The additional term $\sum_{a=1}^r k_B \mathbf{J}_a / m_a$ appearing in (7.33) originates from the $k_B \sum_{a=1}^r \langle f_a \rangle$ term in the Boltzmann entropy formula (4.69). In the literature this latter factor is added to the original definition of the H function by Boltzmann, since with the factor the Boltzmann entropy formula readily gives rise to, e.g., the equilibrium Gibbs relation for the Clausius entropy for an open system. To remain as consistent with the literature as possible we have taken the same definition in this work of the Boltzmann entropy as in the literature. However, the aforementioned factor is not mandatory for erecting a thermodynamically

The expressions for \mathbf{J}_c and Ξ_c in (7.33) and (7.46) will be the statistical formulas we will use below. They have the same mathematical structures and physical interpretations as the calortropy flux and calortropy production given in Proposition 4 in Chapter 2 if $\Theta_a^{(q)}$ is corresponded to Φ_{qa} ; $\bar{Y}_a^{(q)}$ to \bar{X}_{qa} ; $\hat{K}_a^{(q)}$ to Z_{qa} ; $\mathcal{D}_a^{(q)}$ to Λ_{qa} ; and $\psi_a^{(q)}$ to ψ_{qa} , respectively. Since each term has a matching physical status in the phenomenological and statistically derived equations where they appear, these correspondences can be seen as the statistical definitions of the phenomenological quantities appearing in Proposition 4. We will make more precise correspondences presently by making transformation to the more physically motivated non-conserved variable set $\{\Phi_{ka} : k \geq 1, 1 \leq a \leq r\}$, but for now will accept these correspondences tentatively. We have taken this seemingly clumsy approach because the set $\{\Phi_{qa}\}$ is mathematically less convenient than the set $\{\Theta_a^{(q)}\}$, although more directly measurable than the latter. Since the latter set is based on an irreducible tensorial set, $\{\mathcal{H}^{(q)}(\mathbf{w}_a) : q \geq 0\}$, it allows us to perform calculations more efficiently, unambiguously, and in generality. With (7.33) and (7.46) or (7.47) and (7.48) we have essentially proved Theorem 2.

On comparison with (2.50) the local form in the space \mathfrak{P}_h of the second law of thermodynamics is given by

$$\Xi_c = \Xi_l + \sum_{a=1}^r \sum_{q \geq 1} \bar{Y}_a^{(q)} \left(\hat{K}_a^{(q)} + \mathcal{D}_a^{(q)} \right) \geq 0, \quad (2.50_1)$$

which imposes conditions on permissible approximate forms for $\bar{Y}_a^{(q)}$ and $\mathcal{D}_a^{(q)}$.

To prove Theorem 3 we now substitute (7.33) and (7.46) into the balance equation for $\hat{\Psi}$ (7.19) and eliminate the heat and diffusion fluxes therein by means of the conservation laws. The procedure is the same as used in the phenomenological theory formulated in Chapter 2. There then follows the Pfaffian differential form for $d_t \hat{\Psi}$

$$d_t \hat{\Psi} = T^{-1} \left(d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{q \geq 1} Y_a^{(q)} d_t \hat{\Theta}_a^{(q)} \right),$$

which proves the first part of Theorem 3 via the route using the balance equation for $\hat{\Psi}$. The second part of the theorem is readily proved by adding

consistent theory of irreversible processes. In fact, the term does not appear in the case of the nonequilibrium grand canonical ensemble, as will be discussed at the end of this chapter. It will be found that the term $\rho d_t (pv/T)$ originates from the normalization factor of the nonequilibrium grand canonical distribution function. In this case the ideal gas equation of state does not play a role in the formulation of the nonequilibrium ensemble method.

the integrability condition (7.31), since then $d_t \hat{\Psi}$ integrates to a state function in the space \mathfrak{P}_h .

To make the tentative correspondences of the variables earlier asserted in the proofs of Theorems 2 and 3 conclusive, we now observe that the set $\{\Theta_a^{(q)} : q \geq 1, 1 \leq a \leq r\}$ is linearly related to the set $\{\Phi_{qa} : q \geq 1, 1 \leq a \leq r\}$ as we have already shown some examples for the relations in (7.7). Therefore f_a^c may be expanded in the complete set of tensor polynomials $\{h_a^{(q)} : q \geq 1, 1 \leq a \leq r\}$ where some of the leading examples are:

$$\begin{aligned} h_a^{(1)} &= m_a [\mathbf{C}_a \mathbf{C}_a]^{(2)} = m_a \mathbf{C}_a \mathbf{C}_a - \frac{1}{3} m_a (\mathbf{C}_a \cdot \mathbf{C}_a) \boldsymbol{\delta}, \\ h_a^{(2)} &= \frac{1}{3} m_a \mathbf{C}_a \cdot \mathbf{C}_a - \frac{m_a p_a}{\rho_a}, \\ h_a^{(3)} &= m_a \left(\frac{1}{2} \mathbf{C}_a \cdot \mathbf{C}_a - \hat{h}_a \right) \mathbf{C}_a, \\ h_a^{(4)} &= m_a \mathbf{C}_a, \text{ etc..} \end{aligned} \tag{7.49}$$

The statistical averages of these quantities are Π_a , Δ_a , \mathbf{Q}'_a , \mathbf{J}_a , and so on or in general

$$\Phi_{qa} = \langle h_a^{(q)} f_a \rangle. \tag{7.50}$$

Since the set $\{h_a^{(q)} : q \geq 1; 1 \leq a \leq r\}$ can be given as a linear combination of the set $\{\mathcal{H}^{(q)}(\mathbf{w}_a) : q \geq 1; 1 \leq a \leq r\}$, the average of the former will be the same linear combination of the latter set. Eq. (7.7) gives examples for the linear combinations. Therefore f_a^c can be expanded in terms of the set $\{h_a^{(q)} : q \geq 1; 1 \leq a \leq r\}$:

$$f_a^c = f_a^0 \exp \left[-\beta \left(\sum_{q \geq 1} X_{qa} h_a^{(q)} - \gamma_a \right) \right], \tag{7.51}$$

This mode of expressing f_a^c will be called the h -representation of f_a^c . The nonequilibrium canonical form (7.51) implies that

$$\sum_{q \geq 1} X_{qa} h_a^{(q)}(\mathbf{C}_a) = \sum_{q \geq 1} Y_{qa} \mathcal{H}^{(q)}(\mathbf{w}_a). \tag{7.52}$$

This, when its average is taken, yields the linear relation

$$\sum_{q \geq 1} X_{qa} \Phi_{qa} = \sum_{q \geq 1} Y_{qa} \Theta_a^{(q)}, \tag{7.53}$$

which can be solved for X_{qa} or $Y_a^{(q)}$. The normalization factors for the distribution functions in the two modes of expansion are the same, since

the normalization is preserved regardless of the modes of expansion used. Therefore the same γ_a appears in both modes of expansion (7.11), and (7.51). If the nonequilibrium canonical form f_a^c in (7.51) is used instead of (7.11) then it is possible to obtain (7.30), (7.33), and (7.46) where $Y_a^{(q)}$ and $\Theta_a^{(q)}$ are replaced, respectively, by X_{qa} and Φ_{qa} whereas $\psi_a^{(q)}$, $\hat{K}_a^{(q)}$, and $\mathcal{D}_a^{(q)}$ are replaced, respectively, by the statistical formulas

$$\psi_{qa} = \langle \mathbf{C}_a h_a^{(q)} f_a \rangle, \quad (7.54)$$

$$\mathcal{Z}_{qa} = \langle f_a \mathcal{D}_t h_a^{(q)} \rangle, \quad (7.55)$$

$$\Lambda_{qa} = \langle h_a^{(q)} R[f_a] \rangle. \quad (7.56)$$

These terms form the evolution equation for $\hat{\Phi}_{qa} = \Phi_{qa}/\rho$:

$$\rho d_t \hat{\Phi}_{qa} = -\nabla \cdot \psi_{qa} + \mathcal{Z}_{qa} + \Lambda_{qa} \quad (q \geq 1). \quad (7.57)$$

This statement regarding the replacement of $(Y_a^{(q)}, \Theta_a^{(q)})$ with (X_{qa}, Φ_{qa}) is straightforward to verify if the kinetic equation (3.27) and the definitions in (7.54)–(7.56) are used and the same procedure is followed as for the expansion in the set $\{\mathcal{H}^{(q)}(\mathbf{w}_a)\}$. We simply present the final results in the h -representation for f_a^c :

$$\mathbf{J}_c = \sum_{a=1}^r T^{-1} \mathbf{Q}_a^c + \sum_{a=1}^r \frac{k_B}{m_a} \mathbf{J}_a, \quad (7.58)$$

$$\Xi_c = \Xi_l^x + \sum_{a=1}^r \sum_{q \geq 1} \bar{X}_{qa} (\mathcal{Z}_{qa} + \Lambda_{qa}) + \sum_{a=1}^r \frac{k_B}{m_a} \nabla \cdot \mathbf{J}_a, \quad (7.59)$$

$$d_t \hat{\Psi} = T^{-1} \left(d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{q \geq 1} X_{qa} d_t \hat{\Phi}_{qa} \right), \quad (7.60)$$

where $\bar{X}_{qa} = X_{qa}/T$ and

$$\mathbf{Q}_a^c = \mathbf{Q}_a - \hat{\mu}_a \mathbf{J}_a + \sum_{q \geq 1} \psi_{qa} X_{qa}, \quad (7.61)$$

$$\begin{aligned} \Xi_l^x &= -T^{-1} \sum_{a=1}^r [(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q}_a^c \cdot \nabla \ln T + \mathbf{J}_a \cdot (\nabla \hat{\mu}_a - \mathbf{F}_a)] \\ &\quad + T^{-1} \sum_{a=1}^r \sum_{q \geq 1} \psi_{qa} \cdot \nabla X_{qa}. \end{aligned} \quad (7.62)$$

Since the last terms in (7.58) and (7.59) cancel each other in the balance equation, they may be ignored with no consequence. They do not appear in the grand ensemble theory as will be seen later. We remark that the thermodynamic space is now the space \mathfrak{P} , not the space \mathfrak{P}_h . On comparison of (7.58)–(7.60) with their counterparts (2.49)–(2.51) in Chapter 2 we obtain the local second law of thermodynamics, which imposes a condition on its statistical counterpart, in the form of inequality

$$\Xi_c = \Xi_l^x + \sum_{a=1}^r \sum_{q \geq 1} \bar{X}_{qa} (\mathcal{Z}_{qa} + \Lambda_{qa}) \geq 0. \quad (7.50_2)$$

Theorems 2 and 3 are now proved.

7.2.2 Thermodynamic Correspondence

The nonequilibrium ensemble method will be completed if the statistically derived Pfaffian differential form (7.60) is made to correspond to the phenomenological Pfaffian differential form (2.51) which descends from the second law of thermodynamics. This correspondence therefore accords the statistically derived Pfaffian form (7.60) with the thermodynamic lineage and thus the desired thermodynamic foundations. We make the following proposition.

Proposition 6 *The statistically defined macroscopic extensive variables (st) are corresponded with their phenomenological thermodynamic counterparts (th) as follows:*

$$\begin{aligned} \hat{\Psi}|_{\text{st}} &\Leftrightarrow \hat{\Psi}|_{\text{th}}, & \mathcal{E}|_{\text{st}} &\Leftrightarrow \mathcal{E}|_{\text{th}}, & v|_{\text{st}} &\Leftrightarrow v|_{\text{th}}, \\ c_a|_{\text{st}} &\Leftrightarrow c_a|_{\text{th}}, & \hat{\Phi}_{qa}|_{\text{st}} &\Leftrightarrow \hat{\Phi}_{qa}|_{\text{th}}. \end{aligned} \quad . \quad (7.63)$$

This set of correspondences fixes the thermodynamic meanings of the intensive variables as follows:

$$\begin{aligned} T|_{\text{st}} &\Leftrightarrow T|_{\text{th}}, & p|_{\text{st}} &\Leftrightarrow p|_{\text{th}}, \\ \hat{\mu}_a|_{\text{st}} &\Leftrightarrow \hat{\mu}_a|_{\text{th}}, & X_{qa}|_{\text{st}} &\Leftrightarrow X_{qa}|_{\text{th}}. \end{aligned} \quad (7.64)$$

Therefore the thermodynamic meanings of the parameters in the statistical formula for the Pfaffian differential form (7.60) are completely and operationally fixed. This kind of correspondence between thermodynamic and statistically computed quantities is an essential and indispensable step

in the Gibbsian statistical mechanics and here we have simply formalized it with Proposition 6. In retrospect the correspondences (7.63) and (7.65) not only are consistent with the matching conditions for the conserved variables, but also give considerable insights for the meanings of the matching conditions. The results obtained so far for the dilute gases obeying the generic Boltzmann equation can be summarized as a theorem.

Theorem 4 *The statistically derived calortropy differential in (7.60) is the statistical representation of the calortropy differential (2.51) deduced from the second law of thermodynamics. It has the same mathematical properties as the latter in the thermodynamic space \mathfrak{P} .*

The situation with nonequilibrium phenomena is parallel with that of the equilibrium Gibbs ensemble theory in that there are phenomenological and statistical mechanical differential forms for the nonequilibrium version of Clausius entropy, namely, calortropy, to compare and the program of the nonequilibrium ensemble method will run its course to the full if the statistical quantities are expressed in terms of the nonequilibrium partition function.

7.3 Nonequilibrium Statistical Thermodynamics

Now that the differential form (7.60) for the calortropy and the parameters therein are given the required thermodynamic connections by Proposition 6, we are ready to formulate an algorithm to compute macroscopic observables in terms of the nonequilibrium partition function given in the space \mathfrak{P} . To this end, by using the nonequilibrium canonical form (7.51) we define the nonequilibrium partition function Z_a by the relation

$$\hat{\mu}_a = -(m_a \beta_a)^{-1} \ln Z_a. \quad (7.65)$$

That is⁶,

$$Z_a = n_a^{-1} \left\langle \exp \left[-\beta \left(H_a + \sum_{q \geq 1} X_{qa} h_a^{(q)} \right) \right] \right\rangle. \quad (7.66)$$

The density factor n_a appears in this definition owing to the particular normalization to density in deference to the conventional normalization of the distribution function used in kinetic theory. As we have done in Chapter

⁶To make the nonequilibrium partition function dimensionless, preferably, the following formula must be divided by h^3 , where h is the Planck constant. However, since this is not essential for the discussion in the present section we will use the formula as it stands.

2, we define a new function $\widehat{\Omega}$ by the Legendre transformation

$$\widehat{\Omega} = \mathcal{E} + pv + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \widehat{\Phi}_{ka} - T\widehat{\Psi}. \quad (7.67)$$

This transformation gives rise to the differential form for $\widehat{\Omega}$:

$$d_t \widehat{\Omega} = -\widehat{\Psi} d_t T + vd_tp + \sum_{a=1}^r \widehat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{k \geq 1} \widehat{\Phi}_{ka} d_t X_{ka}. \quad (7.68)$$

In addition to (7.67), we introduce the following extensive variables

$$\begin{aligned} \Psi_v &= V\rho\widehat{\Psi}, & E &= V\rho\mathcal{E}, & V &= V\rho v, \\ N_a &= V\rho c_a/m_a, & \Phi_{ka}^v &= V\rho\widehat{\Phi}_{ka}. \end{aligned} \quad (7.69)$$

Despite the appearance of volume V of the system the quantities in (7.69) are not global but local variables. The differential form (7.68) and the Legendre transform (7.67) suggest that

$$\widehat{\Omega} = \sum_{a=1}^r \widehat{\mu}_a c_a, \quad (7.70)$$

which may be written as

$$\Omega = \sum_{a=1}^r \mu_a N_a \quad (7.71)$$

with the definition

$$\Omega = V\rho\widehat{\Omega}. \quad (7.72)$$

On use of (7.67), (7.70), and the definitions given in (7.69) and (7.71), there follows from (7.68) the differential form for $d_t\Omega$:

$$d_t\Omega = -\Psi_v d_t T + V d_tp + \sum_{a=1}^r \mu_a d_t N_a + \sum_{a=1}^r \sum_{k \geq 1} \Phi_{ka}^v d_t X_{ka}. \quad (7.73)$$

The differential form (7.73) is not global, but local. The nonequilibrium thermodynamic potential Ω can be expressed in terms of nonequilibrium partition functions Z_a :

$$\Omega = -k_B T \ln Z, \quad (7.74)$$

where the total nonequilibrium partition function Z is given by

$$Z = \prod Z_a^{N_a}. \quad (7.75)$$

It is now easy to express various macroscopic variables in (7.73) in terms of \mathbb{Z} as follows:

$$\Psi_v = k_B \ln \mathbb{Z} + k_B T \left(\frac{\partial}{\partial T} \ln \mathbb{Z} \right)_{p,c,X}, \quad (7.76)$$

$$V = -k_B T \left(\frac{\partial}{\partial p} \ln \mathbb{Z} \right)_{T,N,X}, \quad (7.77)$$

$$\mu_a = -k_B T \left(\frac{\partial}{\partial N_a} \ln \mathbb{Z} \right)_{T,p,N',X} \quad (1 \leq a \leq r), \quad (7.78)$$

$$\Phi_{ka}^v = -k_B T \left(\frac{\partial}{\partial X_{ka}} \ln \mathbb{Z} \right)_{T,p,N,X'} \quad (1 \leq a \leq r; k \geq 1), \quad (7.79)$$

where the prime on the subscripts means exclusion of the variable in the derivative. These formulas are nonequilibrium generalizations of those in the equilibrium Gibbs ensemble theory except for the last one which does not appear in the equilibrium ensemble theory. If the nonequilibrium partition function \mathbb{Z} is defined by

$$\mathbb{Z} = \prod_{a=1}^r \mathbb{Z}_a^{c_a/m_a} \quad (7.80)$$

instead of (7.75), it is related to the nonequilibrium thermodynamic potential $\widehat{\Omega}$ by the formula

$$\widehat{\Omega} = -k_B T \ln \mathbb{Z}$$

and there will follow the expressions

$$\widehat{\Psi} = k_B \ln \mathbb{Z} + k_B T \left(\frac{\partial}{\partial T} \ln \mathbb{Z} \right)_{p,c,X}, \quad (7.81)$$

$$v = -k_B T \left(\frac{\partial}{\partial p} \ln \mathbb{Z} \right)_{T,c,X}, \quad (7.82)$$

$$\widehat{\mu}_a = -k_B T \left(\frac{\partial}{\partial c_a} \ln \mathbb{Z} \right)_{T,p,c',X} \quad (1 \leq a \leq r), \quad (7.83)$$

$$\widehat{\Phi}_{ka} = -k_B T \left(\frac{\partial}{\partial X_{ka}} \ln \mathbb{Z} \right)_{T,p,c,X'} \quad (1 \leq a \leq r; k \geq 1), \quad (7.84)$$

in place of (7.76)–(7.79). The two sets (7.76)–(7.79) and (7.81)–(7.84) can be easily shown to be equivalent.

There now remains the task of computing the nonequilibrium partition function \mathbb{Z} . Its calculation in terms of boundary and initial conditions of the system generally requires solutions of the generalized hydrodynamics equations together with the evaluation of X_{ka} in terms of macroscopic variables in the space \mathfrak{G} . Calculation of \mathbb{Z} in terms of X_{ka} therefore is an

important task of the present nonequilibrium ensemble method just as the calculation of the equilibrium partition function is in the equilibrium Gibbs ensemble method. It will be discussed in a later section. Finally, we note that the present ensemble theory results (7.81)–(7.84) can be transformed to those better reminding us of the grand ensemble theory results for a mixture, if the nonequilibrium grand partition function Ξ_a is defined for the mixture in the form

$$\begin{aligned}\beta p_a v &= \ln \Xi_a \\ &= n_a v \mathbb{Z}_a \exp(\beta m_a \hat{\mu}_a)\end{aligned}$$

and if the Legendre transformation

$$pv = \sum_{a=1}^r c_a \hat{\mu}_a - \mathcal{E} + T \hat{\Psi} - \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \hat{\Phi}_{ka}$$

is taken. The total nonequilibrium partition function in this case is given by the product $\Xi = \prod_{a=1}^r \Xi_a$. We will return to this aspect in Sec. 7.11 of this chapter.

7.4 Relative Boltzmann Entropy

We have now shown that the calortropy and its differential form can be calculated in terms of variables in the space \mathfrak{P}_h by using the nonequilibrium canonical form where the parameters are corresponded to the phenomenological thermodynamic parameters. However, such a nonequilibrium canonical form is not enough for us to calculate the relative Boltzmann entropy and its evolution, since it is also given in terms of the distribution function satisfying the Boltzmann equation which must be solved before it is calculated. We now examine the relative Boltzmann entropy and, in particular, its balance equation. This examination will further elucidate under what condition the nonequilibrium canonical form should be regarded as approximating the solution of the Boltzmann equation even in the sense of means as alluded to in Sec. 7.1.

7.4.1 Relative Boltzmann Entropy and Fluctuations

The balance equation (7.20) for $S_r[f|f^c]$, upon use of (7.43), can be written as

$$\rho \frac{d}{dt} S_r[f|f^c] = -\nabla \cdot \mathbf{J}_r[f|f^c] + \sigma_r[f|f^c]$$

$$+ \Xi_l + \sum_{a=1}^r \sum_{q \geq 1} \widehat{Y}_a^{(q)} \widehat{K}_a^{(q)} - \rho d_t \left(\frac{pv}{T} \right). \quad (7.85)$$

If the full distribution function f_a is not known, this is as far as calculation can proceed. However, even if f_a is not completely known, it is possible to cast the relative Boltzmann entropy and its balance equation into a more suggestive form and gain a new insight into the relative Boltzmann entropy. This will be discussed below. To facilitate the intended discussion a new notation will be introduced; a superscript t will be affixed on the parameters T^{-1} , $\bar{\mu}_a$, and $Y_a^{(q)}$ in f_a^c :

$$T^{-1} \Rightarrow T^{t-1} \equiv \bar{I}^t, \quad \frac{\bar{\mu}_a}{T} \Rightarrow \frac{\bar{\mu}_a^t}{T^t} \equiv \bar{\mu}_a^t,$$

$$\frac{Y_a^{(q)}}{T} \Rightarrow \frac{Y_a^{(q)t}}{T^t} \equiv \bar{Y}_a^{(q)t}.$$

Here the superscript t stands for the thermodynamically determined value since *the parameters \bar{I}^t , $\bar{\mu}_a^t$, and $\bar{Y}_a^{(q)t}$ are thermodynamic in the sense that they are determined by the thermodynamic correspondences in (7.63) and (7.65)*. The motivation for the adoption of this distinction for the parameters will become self-evident later. Similarly, p/T associated with f_a^c will be denoted in the new notation as follows:

$$\frac{p}{T} \Rightarrow \frac{p^t}{T^t} \equiv \bar{p}^t.$$

Therefore, for this part of discussion on the relative Boltzmann entropy f_a^c will be written as

$$f_a^c = \exp \left\{ -k_B^{-1} \left[\bar{I}^t H_a + \sum_{q \geq 1} \bar{Y}_a^{(q)t} \mathcal{H}^{(q)}(\mathbf{w}_a) - m_a \bar{\mu}_a^t \right] \right\}, \quad (7.86)$$

$$e^{-k_B^{-1} m_a \bar{\mu}_a^t} = n_a^{-1} \left\langle \exp \left\{ -k_B^{-1} \left[\bar{I}^t H_a + \sum_{q \geq 1} \bar{Y}_a^{(q)t} \mathcal{H}^{(q)}(\mathbf{w}_a) \right] \right\} \right\rangle. \quad (7.87)$$

The distribution function f_a that must be directly obtained from the kinetic equation is now written in the form

$$f_a = \exp \left\{ -k_B^{-1} \left[\bar{I} H_a + \sum_{q \geq 1} \bar{Y}_a^{(q)} \mathcal{H}^{(q)}(\mathbf{w}_a) - m_a \bar{\mu}_a \right] \right\}, \quad (7.88)$$

$$e^{-k_B^{-1} m_a \bar{\mu}_a} = n_a^{-1} \left\langle \exp \left\{ -k_B^{-1} \left[\bar{I} H_a + \sum_{q \geq 1} \bar{Y}_a^{(q)} \mathcal{H}^{(q)}(\mathbf{w}_a) \right] \right\} \right\rangle. \quad (7.89)$$

The phenomenological thermodynamics has already been used to determine the parameters \bar{I}^t , $\bar{\mu}_a^t$, and $\bar{Y}_a^{(q)t}$ in f_a^c ; they can also be expressed in terms of the nonequilibrium partition function, as is shown earlier. On the other hand, the parameters \bar{I} , $\bar{Y}_a^{(q)}$, and $\bar{\mu}_a$ must be determined such that (7.88) satisfies the kinetic equation, subject to the given initial and boundary conditions on f_a in the phase space. They cannot be determined in correspondence with their phenomenological thermodynamic counterpart as have been the case for \bar{I}^t and so on, since there is no such thing as phenomenological thermodynamics for f_a , principally because the Boltzmann entropy does not have an exact differential form in the space \mathfrak{P}_h . Since the parameters \bar{I} and so on therefore are not thermodynamic and generally not equal to the thermodynamically determined parameters \bar{I}^t and so on, their differences (fluctuations) are nonvanishing in general:

$$\begin{aligned}\delta\bar{I} &= \bar{I} - \bar{I}^t \neq 0, & \bar{p} = \bar{p} - \bar{p}^t \neq 0, \\ \delta\bar{\mu}_a &= \bar{\mu}_a - \bar{\mu}_a^t \neq 0, & \delta\bar{Y}_a^{(q)} = \bar{Y}_a^{(q)} - \bar{Y}_a^{(q)t} \neq 0.\end{aligned}\quad (7.90)$$

In this manner of looking for the solution of the kinetic equation the burden of the difference between f_a and its thermodynamic branch f_a^c is carried by the parameters \bar{I} , $\bar{\mu}_a$, and $\bar{Y}_a^{(q)}$. In this respect we note that with the form for f_a in (7.88) the kinetic equation can be converted into a set of coupled partial differential equations for parameters \bar{I} , $\bar{Y}_a^{(q)}$, and $\bar{\mu}_a$ which will, when solved subject to the initial and boundary conditions on the parameters, provide the solution of the kinetic equation itself.

By varying (7.87) with respect to \bar{I}^t , $\bar{\mu}_a^t$, and $\bar{Y}_a^{(q)t}$ while H_a and $\mathcal{H}^{(q)}(\mathbf{w}_a)$ are kept fixed as was for (7.31), namely, by replacing T^{-1} and so on in (7.31) with \bar{I}^t and so on, we obtain the form

$$\mathcal{E} dt \bar{I}^t + vd_t \bar{p}^t - \sum_{a=1}^r c_a d_t \bar{\mu}_a^t + \sum_{a=1}^r \sum_{q \geq 1} \hat{\Theta}_a^{(q)} d_t \bar{Y}_a^{(q)t} = 0. \quad (7.91)$$

It is easy to calculate $\mathbf{J}_r[f|f^c]$ and $\sigma_r[f|f^c]$ with (7.86) and (7.88) from (7.22) and (7.23):

$$\mathbf{J}_r[f|f^c] = - \sum_{a=1}^r \left(\mathbf{Q}_a \delta \bar{I} - \delta \bar{\mu}_a \mathbf{J}_a + \sum_{q \geq 1} \delta \bar{Y}_a^{(q)} \boldsymbol{\psi}_{qa} \right), \quad (7.92)$$

$$\sigma_r[f|f^c] = - \sum_{a=1}^r \sum_{q \geq 1} \delta \bar{Y}_a^{(q)} \mathcal{D}_a^{(q)}. \quad (7.93)$$

In the new system of notation the identity (7.43) reads

$$\mathcal{L}_f^c = -k_B \sum_{a=1}^r \langle f_a \mathcal{D}_t \ln f_a^c \rangle$$

$$= \Xi_l^t + \sum_{a=1}^r \sum_{q \geq 1} \bar{Y}_a^{(q)t} \hat{K}_a^{(q)} - \rho d_t (\bar{p}^t v), \quad (7.94)$$

where

$$\begin{aligned} \Xi_l^t &= \sum_{a=1}^r [\mathbf{Q}_a \cdot \nabla \bar{I}^t - \bar{I}^t (\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} - \mathbf{J}_a \cdot (\nabla \bar{\mu}_a^t - \bar{I}^t \mathbf{F}_a)] \\ &\quad + \sum_{a=1}^r \sum_{q \geq 1} \psi_a^{(q)} \cdot \nabla \bar{Y}_a^{(q)t}. \end{aligned} \quad (7.95)$$

On substitution of (7.92)–(7.95) into the balance equation (7.20) for $S_r[f|f^c]$ and eliminating the heat flux and diffusion flux by means of the energy and mass fraction balance equations in the same manner as for the calortropy balance equation, we obtain the following equation

$$\begin{aligned} d_t S_r[f|f^c] &= - \left[\delta \bar{I} d_t \mathcal{E} + \delta \bar{p} d_t v - \sum_{a=1}^r \delta \bar{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{q \geq 1} \delta \bar{Y}_a^{(q)} d_t \hat{\Theta}_a^{(q)} \right] \\ &\quad + \hat{\Sigma}_l - \rho d_t (\bar{p} v) + \rho^{-1} \sum_{a=1}^r \sum_{q \geq 1} \bar{Y}_a^{(q)} \hat{K}_a^{(q)}, \end{aligned} \quad (7.96)$$

where

$$\begin{aligned} \rho \hat{\Sigma}_l &= -T^{-1} \sum_{a=1}^r [(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q}_a^{\text{ch}} \cdot \nabla \ln T + \mathbf{J}_a \cdot (\nabla \bar{\mu}_a - \mathbf{F}_a)] \\ &\quad + T^{-1} \sum_{a=1}^r \sum_{q \geq 1} \psi_a^{(q)} \cdot \nabla Y_a^{(q)}. \end{aligned} \quad (7.97)$$

Here $T = 1/\bar{I}$, $\bar{\mu}_a = \bar{\mu}_a/\bar{I}$, and $Y_a^{(q)} = \bar{Y}_a^{(q)}/\bar{I}$. This form for $\rho \hat{\Sigma}_l$ is identical in form with that for $\rho \hat{\Xi}_l$ defined in (7.42), but recall the difference between the local parameters $(T^{-1}, \bar{\mu}_a/T, Y_a^{(q)}/T) \equiv (\bar{I}, \bar{\mu}_a, \bar{Y}_a^{(q)})$ and $(\bar{I}^t, \bar{\mu}_a^t, \bar{Y}_a^{(q)t})$; the former set is determined directly from the solution of the kinetic equation subject to the initial and boundary conditions and the latter from the thermodynamic correspondence for the calortropy. Eq. (7.96) for the time derivative of the relative Boltzmann entropy suggests that it is closely related to the fluctuations in the local parameters $(T^{-1}, \bar{\mu}_a/T, Y_a^{(q)}/T)$ from their thermodynamic values and the spatial gradients of the parameters. If the nonequilibrium canonical form in (7.86) and the distribution function in (7.88) are used in the statistical formula (7.21)

for the relative Boltzmann entropy, then there follows the formula

$$S_r[f|f^c] = - \left(\mathcal{E} \delta \bar{I} + v \delta \bar{p} - \sum_{a=1}^r c_a \delta \bar{\mu}_a + \sum_{a=1}^r \sum_{k \geq 1} \hat{\Theta}_{ka} \delta \bar{Y}_{ka} \right), \quad (7.98)$$

which indicates that the relative Boltzmann entropy at time t is a consequence of the fluctuations in the intensive variables $\delta \bar{I}$, $\delta \bar{p}$, $\delta \bar{\mu}_a$, and $\delta \bar{Y}_{ka}$. Although this result provides an insight into the nature of the relative Boltzmann entropy, the temporal behavior of the relative Boltzmann entropy given in (7.98) is misleading, since it does not specify the initial state and its manner of evolution. In fact, the temporal behavior of the relative Boltzmann entropy is rather subtle since it is not a state function in the space \mathfrak{P}_h and consequently depends on the path of evolution in the space \mathfrak{P}_h . The following discussion illustrates this point in an approximation where the fluctuations are neglected.

As an approximation for $d_t S_r[f|f^c]$, suppose the fluctuations $\delta \bar{I}$, $\delta \bar{p}$, $\delta \bar{\mu}_a$, and $\delta \bar{Y}_a^{(q)}$ vanish. Even in this situation the last three terms in (7.96) do not generally vanish if the system is away from equilibrium. The approximate relative entropy can be computed from the equation

$$d_t S_r[f|f^c] = \hat{\Xi}_{\text{rel}}(Y), \quad (7.99)$$

where

$$\hat{\Xi}_{\text{rel}}(Y) = \hat{\Sigma}_l + \rho^{-1} \sum_{a=1}^r \sum_{q \geq 1} \bar{Y}_a^{(q)} \hat{K}_a^{(q)} - d_t(\bar{p}v). \quad (7.100)$$

The relative entropy so computed can be used together with $\hat{\Psi}$ for computation of the (Boltzmann) entropy itself in the space \mathfrak{P}_h . If the h -representation is taken for f_a^c , then $\hat{\Xi}_{\text{rel}}$ is given by

$$\hat{\Xi}_{\text{rel}} = \hat{\Sigma}_l(X) + \rho^{-1} \sum_{a=1}^r \sum_{q \geq 1} \bar{X}_{qa} \mathcal{Z}_{qa} - d_t(\bar{p}v), \quad (7.101)$$

where $\hat{\Sigma}_l(X)$ stands for $\hat{\Sigma}_l$ defined in terms of X_{qa} and ψ_{qa} in place of $Y_a^{(q)}$ and $\psi_a^{(q)}$. This $\hat{\Xi}_{\text{rel}}$ does not generally vanish if the system is away from equilibrium. Therefore we finally conclude that in the aforementioned approximation

$$\frac{dS}{dt} = \frac{d\hat{\Psi}}{dt} - \hat{\Xi}_{\text{rel}}. \quad (7.102)$$

Associated with this result there holds the inequality

$$\sigma_c = T^{-1} \sum_{a=1}^r \sum_{q \geq 1} Y_a^{(q)} \mathcal{D}_a^{(q)} \geq 0 \quad (7.103)$$

or

$$\sigma_c = T^{-1} \sum_{a=1}^r \sum_{q \geq 1} X_{qa} \Lambda_{qa} \geq 0 \text{ (in the } h\text{-representation).} \quad (7.104)$$

These inequalities for the calortropy production arise because by the assumption of vanishing fluctuations in the parameters $(T^{-1}, \hat{\mu}_a/T, Y_a^{(q)}/T)$ the relative Boltzmann entropy production $\sigma_r[f|f^c]$ may be set equal to zero, and this implies that

$$\sigma_{\text{ent}} = \sigma_c - \sigma_r[f|f^c] = \sigma_c \geq 0. \quad (7.105)$$

Since $\widehat{\Xi}_{\text{rel}}$ is in general dependent on the path of the irreversible process taken in the thermodynamic space \mathfrak{P}_h by the system, $d_t S$ is not an exact differential in the space \mathfrak{P}_h whereas $d_t \widehat{\Psi}$ is clearly an exact differential in the space \mathfrak{P}_h . This point is clearly brought out if (7.102) is integrated in time. Eqs. (7.102) and the integrability [15,17,18] of (7.30) implies, owing to (7.31), that in the coordinate system moving at fluid velocity \mathbf{u} the Boltzmann entropy density $S(t)$ under the approximation (7.99) is given by

$$S = T^{-1} \left[\mathcal{E} + pv - \sum_{a=1}^r \hat{\mu}_a c_a + \sum_{a=1}^r \sum_{q \geq 1} Y_a^{(q)} \widehat{\Theta}_a^{(q)} \right] - \int_0^t dt \widehat{\Xi}_{\text{rel}}(t) \quad (7.106)$$

for which we arbitrarily set $S_r[f|f^c] = 0$ at $t = 0$. The time integral, which is a line integral and thus path-dependent, gives the measure of the relative Boltzmann entropy accompanying the irreversible process in the system. This result is consistent with (7.25). Eq. (7.106) is a time integral in the space \mathfrak{P}_h of the Boltzmann entropy balance equation for a dissipative system under the assumption of vanishing fluctuations, namely, $\delta \bar{I} = 0$ and so on. The results on the relative Boltzmann entropy up to this point may be summarized as a theorem on the Boltzmann entropy as follows:

Theorem 5 *The Boltzmann entropy differential dS for classical dilute gases obeying the generic Boltzmann equation is not an exact differential in the space \mathfrak{P}_h if the processes are irreversible and therefore the system is away from equilibrium, whereas $d\widehat{\Psi}$ is an exact differential in the space \mathfrak{P}_h . The derivative $d_t S_r[f|f^c]$ is path-dependent if the process is irreversible.*

Therefore the evolution of S in the space \mathfrak{P}_h is path-dependent and determined by the history of the system.

If one is interested in a thermodynamic formalism for irreversible processes which is parallel with equilibrium thermodynamics, and there is a great deal of advantage in having one such, then the Boltzmann entropy is not useful for the purpose; however, being defined in the phase space of the molecules in the system, it certainly contains more information on the

system than the calortropy given in the thermodynamic space \mathfrak{P}_h . Since Ξ_c is a local form of the second law of thermodynamics and the inequality (7.105), namely, the H theorem, is different from the positivity of Ξ_c , it is possible to conclude that the H theorem is not necessarily synonymous to the second law of thermodynamics as we have alluded to this point in the previous chapters. The H theorem simply dictates probabilistic processes in the phase space to obey the inequality imposed by it. Thus the Boltzmann H theorem has something more to tell about the distribution function of the system than the second law of thermodynamics. On reflection upon this point we see that the aforementioned fluctuations may take the molecular and statistical behavior of the system into a regime of states in the phase space where the second law of thermodynamics is no longer obeyed but the statistical (probabilistic) evolution of the system nevertheless is subject to the constraint of the H theorem in the sense that the Boltzmann entropy production is bounded from below—namely, non-negative.

In the literature [12] on information theory, the maximum entropy method is proposed for nonequilibrium processes. In this line of theories it is concluded [13] on the basis of the maximized information (or Boltzmann) entropy that the information entropy itself has a differential form which is exact in the space of variables chosen as the constraints imposed in maximizing the information entropy. This is at variance with the conclusion we have arrived at for the Boltzmann entropy in this work and the source of variance lies in the neglect of the relative Boltzmann entropy. The distribution function corresponding to the maximum information entropy is in fact an example of the thermodynamic branch f_a^c of the phase space distribution function f_a if the thermodynamic correspondences are imposed on the Lagrange parameters and, therefore, the maximized information entropy must correspond to $\hat{\Psi}$. The fluctuations of f_a from f_a^c contributes to the relative Boltzmann entropy. This important point is not recognized in the information theory applied to irreversible processes. If this recognition is made and Proposition 6 is applied to the maximized information entropy which now should be identified with the calortropy, the maximum entropy method can be given the desired thermodynamic foundations. It must be noted, however, that since there is no kinetic equation in information theory the description of dynamical variables such as $\Theta_a^{(q)}(\mathbf{r}, t)$ is not possible, and, consequently, the goal of the thermodynamics of irreversible processes cannot be achieved with the maximum entropy method. This shows that the maximum entropy method for nonequilibrium is not only superfluous and hardly necessary, but also is compelled to take extraneously the evolution equations for the nonconserved variables from another source of information. In a work [14] on the maximum entropy method the Boltzmann equation was postulated for the distribution function, but such a kinetic equation makes the maximization of entropy redundant and the attendant constraints of fixed fluxes unwarranted, because the macroscopic variables are not fixed in space-time, but field variables obeying partial

differential equations subject to initial and boundary conditions. It must also be pointed out that the differential form of Boltzmann entropy that arises disconnected from the second law of thermodynamics in the maximum entropy method is not appropriate for formulating irreversible thermodynamics, since such a lack of connection does not allow the constitutive equations to be consistent with the second law of thermodynamics. Such constitutive equations are not provided by the maximum entropy method, in any case, as mentioned earlier.

Finally, we remark that the notion of relative Boltzmann entropy is present even in the case of equilibrium if the fluctuations in the intensive variables are not negligible. This point is essential for distinguishing the general equilibrium solution of the Boltzmann equation and its thermodynamic branch, namely, the Maxwell distribution function which gives rise to the equilibrium thermodynamics of Clausius. To elaborate this point we return to (4.7) for the equilibrium solution of the Boltzmann equation. For a field-free case the equilibrium solution is given by a linear combination of the collision invariants in the manner

$$\ln f_a^{\text{eq}} = m_a \alpha_0 + m_a \mathbf{v}_a \cdot \boldsymbol{\alpha}_1 - \frac{1}{2} m_a v_a^2 \alpha_2. \quad (7.107)$$

The coefficients α_0 , $\boldsymbol{\alpha}_1$, α_2 of the linear combination are arbitrary except for the normalization condition and the Boltzmann equation cannot determine, in particular, α_2 beyond the fact that it is related to the mean energy, and any positive value taken for it makes f_a^{eq} in (7.107) an equilibrium solution of the Boltzmann equation. (In this regard it must be realized that the probabilistic theory mean value by itself is not necessarily equal to the thermodynamic observable.) In the Gibbs ensemble method this arbitrary parameter is chosen, by means of the thermodynamic correspondences (7.63) and (7.65) specialized to equilibrium, such that the equilibrium distribution function f_a^{eq} , with the help of the equilibrium Boltzmann entropy, gives rise to the Clausius entropy for a reversible process in the system under consideration. When the parameter is so chosen, the distribution function f_a^{eq} becomes the thermodynamic branch f_a^{eqc} of the equilibrium distribution function obtained from the form for f_a^{eq} in (7.107). Therefore we see that the parameter α_2 in the general equilibrium solution of the Boltzmann equation is not necessarily the same as the parameter β (inverse temperature) in the thermodynamic branch of f_a^{eq} —*the Maxwell distribution function corresponding to the Clausius entropy, if the fluctuation of α_2 from β is significant*. The qualification attached to the Maxwell distribution function as noted here is very important for discerning its subtle meaning. An aspect of this subtlety with more insight will be examined when the fluctuations $\delta \bar{I}$ and so on are given a probabilistic treatment in a later section which should be contrasted with the deterministic treatment based on the fluctuation evolution equations derived from the kinetic equation in the next subsection.

7.4.2 Evolution of Fluctuations

We now look for a way of describing the fluctuations which we have found involved in the evolution of the relative Boltzmann entropy and thus the Boltzmann entropy itself, when the system is away from equilibrium. Here we give a brief description of their derivation and then present the results without showing the details of the derivation.

By using the distribution functions in (7.86) and (7.88), we obtain

$$\ln \left(\frac{f_a}{f_a^c} \right) = -k_B^{-1} \left[\delta \bar{I} H_a + \sum_{k \geq 1} \delta \bar{y}_{ka} \mathcal{H}^{(k)}(\mathbf{w}_a) - m_a \delta \bar{\mu}_a \right], \quad (7.108)$$

where we have set $\bar{y}_{ka} \equiv \bar{Y}_a^{(k)}$. Its substantial time derivative is given by

$$\begin{aligned} d_t \ln \left(\frac{f_a}{f_a^c} \right) &= -k_B^{-1} \left[H_a d_t \delta \bar{I} + \sum_{k \geq 1} \mathcal{H}^{(k)}(\mathbf{w}_a) d_t \delta \bar{y}_{ka} - m_a d_t \delta \bar{\mu}_a \right] \\ &\quad - k_B^{-1} \left[\delta \bar{I} d_t H_a + \sum_{k \geq 1} \delta \bar{y}_{ka} d_t \mathcal{H}^{(k)}(\mathbf{w}_a) \right]. \end{aligned} \quad (7.109)$$

The weight function $\omega(\mathbf{w}_a)$ for the tensor Hermite polynomials $\mathcal{H}^{(k)}(\mathbf{w}_a)$ is

$$\omega(\mathbf{w}_a) = (2\pi)^{-3/2} \exp(-\frac{1}{2} w_a^2).$$

Multiplication of $n_a \omega(\mathbf{w}_a)$ or $n_a \omega(\mathbf{w}_a) H_a$ to (7.109) and integrating over \mathbf{w}_a yield the equations

$$\begin{aligned} \sum_{a=1}^r n_a \left\langle \omega d_t \ln \left(\frac{f_a}{f_a^c} \right) \right\rangle &= -\frac{3n}{2\bar{I}^t} d_t \delta \bar{I} + k_B^{-1} \sum_{a=1}^r \rho_a d_t \delta \bar{\mu}_a \\ &\quad - k_B^{-1} \sum_{a=1}^r \sum_{k \geq 1} n_a \left\langle \omega d_t \mathcal{H}^{(k)}(\mathbf{w}_a) \right\rangle \delta \bar{y}_{ka}, \end{aligned} \quad (7.110)$$

$$\begin{aligned} n_a \left\langle \omega H_a d_t \ln \left(\frac{f_a}{f_a^c} \right) \right\rangle &= -\frac{15k_B n_a}{4\bar{I}^{t2}} d_t \delta \bar{I} + \frac{3\rho}{2\bar{I}^t} c_a d_t \delta \bar{\mu}_a \\ &\quad - k_B^{-1} n_a \sum_{k \geq 1} \left\langle \omega H_a d_t \mathcal{H}^{(k)}(\mathbf{w}_a) \right\rangle \delta \bar{y}_{ka}. \end{aligned} \quad (7.111)$$

Solving these equations for $d_t \delta \bar{I}$ and $d_t \delta \bar{\mu}_a$, we obtain the equations

$$nd_t \delta \bar{I} = -\sum_{a=1}^r n_a \bar{I}^t \left\langle \omega \left(\frac{1}{3} w_a^2 - 1 \right) d_t \ln \left(\frac{f_a}{f_a^c} \right) \right\rangle$$

$$-k_B^{-1}\bar{I}^t \sum_{a=1}^r \sum_{k \geq 1} n_a \left\langle \omega \left(\frac{1}{3}w_a^2 - 1 \right) d_t \mathcal{H}^{(k)}(\mathbf{w}_a) \right\rangle \delta \bar{y}_{ka}, \quad (7.112)$$

$$\begin{aligned} m_a d_t \delta \bar{\mu}_a &= -k_B \left\langle \omega \left(\frac{1}{2}w_a^2 - \frac{5}{2} \right) d_t \ln \left(\frac{f_a}{f_a^c} \right) \right\rangle \\ &\quad - \frac{5k_B}{2} \sum_{b \neq a}^r \frac{n_b}{n} \left\langle \omega \left(\frac{1}{3}w_b^2 - 1 \right) d_t \ln \left(\frac{f_b}{f_b^c} \right) \right\rangle \\ &\quad - \sum_{k \geq 1} \left\langle \omega \left(\frac{1}{2}w_a^2 - \frac{5}{2} \right) d_t \mathcal{H}^{(k)}(\mathbf{w}_a) \right\rangle \delta \bar{y}_{ka} \\ &\quad - \frac{5k_B}{2} \sum_{b \neq a}^r \sum_{k \geq 1} \frac{n_b}{n} \left\langle \omega \left(\frac{1}{3}w_b^2 - 1 \right) d_t \mathcal{H}^{(k)}(\mathbf{w}_b) \right\rangle \delta \bar{y}_{ka}. \end{aligned} \quad (7.113)$$

Multiplication of $n_a \omega(\mathbf{w}_a) \mathcal{H}^{(k)}(\mathbf{w}_a)$ to (7.109) and integration over \mathbf{w}_a yield the equation

$$\begin{aligned} k! d_t \delta \bar{y}_{ka} &= -k_B \left\langle \omega \mathcal{H}^{(k)}(\mathbf{w}_a) d_t \ln \left(\frac{f_a}{f_a^c} \right) \right\rangle \\ &\quad - \left\langle \omega \mathcal{H}^{(k)}(\mathbf{w}_a) H_a \right\rangle d_t \delta \bar{I} - \left\langle \omega \mathcal{H}^{(k)}(\mathbf{w}_a) d_t H_a \right\rangle \delta \bar{I} \\ &\quad - \sum_{l \geq 1} \left\langle \omega \mathcal{H}^{(k)}(\mathbf{w}_a) d_t \mathcal{H}^{(l)}(\mathbf{w}_a) \right\rangle \delta \bar{y}_{la}. \end{aligned} \quad (7.114)$$

These three equations describe the evolution of the fluctuations $\delta \bar{I}$, $\delta \bar{\mu}_a$, and $\delta \bar{y}_{ka}$ in the intensive variables. The pressure fluctuations can be deduced from $\delta \bar{I}$ by virtue of the equation of state and the matching condition (4.40) on the density. These are deterministic equations⁷ for $\delta \bar{I}$ and so on.

Since it is necessary to know the dependence on fluctuations of the terms on the right hand side, the evolution equations in (7.112)–(7.114) must be more explicitly worked out. On use of the Boltzmann equation which can

⁷These equations, together with the balance equation for the calortropy density $\hat{\Psi}$ and the generalized hydrodynamic equations for conserved and nonconserved variables, form a set of evolution equations for the system, which are odd in number. Such an odd numbered set of variables may be considered to form a contact space. See Edelen, *Applied Exterior Calculus* (Wiley, New York, 1985) for the notion of contact space.

be rearranged to the form

$$d_t \ln \left(\frac{f_a}{f_a^c} \right) = -(\mathbf{C}_a \cdot \nabla + \mathbf{F}_a \cdot \nabla_{\mathbf{v}_a}) \ln \left(\frac{f_a}{f_a^c} \right) + f_a^{-1} R[f_a] - \mathcal{D}_t \ln f_a^c,$$

the evolution equations for $\delta \bar{I}$, $\delta \bar{\mu}_a$, and $\delta \bar{y}_{ka}$ take the following forms:

$$\begin{aligned} d_t \delta \bar{I} &= -A_I \delta \bar{I} - \sum_{a=1}^r \sum_{k \geq 1} \mathbf{A}_d^{(ka)} \cdot \nabla \delta \bar{y}_{ka} - \sum_{a=1}^r \sum_{k \geq 1} A_{ka} \delta \bar{y}_{ka} \\ &\quad - \frac{\bar{I}^t}{3n} \sum_{a=1}^r n_a \left\langle \omega f_a^{-1} \text{Tr} \mathcal{H}^{(2)} R[f_a] \right\rangle + \mathcal{S}_I, \end{aligned} \quad (7.115)$$

$$\begin{aligned} d_t \delta \bar{\mu}_a &= -B_{Ia} \delta \bar{I} - \sum_{b=1}^r \sum_{k \geq 1} B_{kb}^{(a)} \delta \bar{y}_{kb} - \sum_{b=1}^r \sum_{k \geq 1} \mathbf{B}_{dkb}^{(a)} \cdot \nabla \delta \bar{y}_{kb} \\ &\quad - \frac{5k_B}{6m_a} \sum_{b \neq a}^r \frac{n_b}{n} \left\langle \omega f_b^{-1} \text{Tr} \mathcal{H}^{(2)} (\mathbf{w}_b) R[f_b] \right\rangle \\ &\quad - \frac{k_B}{2m_a} \left\langle \omega f_a^{-1} \left(\text{Tr} \mathcal{H}^{(2)} - 2 \right) R[f_a] \right\rangle + \mathcal{S}_\mu^a, \end{aligned} \quad (7.116)$$

$$\begin{aligned} d_t \delta \bar{y}_{ka} &= -C_{ka}^{(I)} \delta \bar{I} - \mathbf{C}_{ka}^{(d)} \cdot \nabla \delta \bar{I} - \sum_{l \geq 1} \mathbf{C}_{dla}^{(k)} \cdot \nabla \delta \bar{y}_{la} \\ &\quad - \sum_{l \geq 1} C_{la}^{(k)} \delta \bar{y}_{la} - \mathbf{C}_{ka}^{(\mu)} \cdot \nabla \delta \bar{\mu}_a - \frac{k_B}{\bar{I}^t} \delta \delta_{k2} d_t \delta \bar{I} \\ &\quad - \frac{k_B}{k!} \left\langle \omega (\mathbf{w}_a) f_a^{-1} \mathcal{H}^{(k)} R[f_a] \right\rangle + \mathcal{S}_{Ha}^{(k)}, \end{aligned} \quad (7.117)$$

Here various coefficients are defined as follows:

Coefficients in the equation for the temperature fluctuation:

$$\begin{aligned} A_I &= \frac{n_a}{3n} \left[\left\langle \omega \text{Tr} \mathcal{H}^{(2)} \mathbf{C}_a \cdot \nabla H_a \right\rangle + \left\langle \omega \text{Tr} \mathcal{H}^{(2)} \nabla_{\mathbf{v}_a} H_a \right\rangle \cdot \mathbf{F}_a \right], \\ A_{ka} &= \frac{n_a \bar{I}^t}{3nk_B} \left\langle \omega \text{Tr} \mathcal{H}^{(2)} \mathbf{C}_a \cdot \nabla \mathcal{H}^{(k)} \right\rangle \\ &\quad + \frac{n_a \bar{I}^t}{3nk_B} \left\langle \omega \text{Tr} \mathcal{H}^{(2)} \nabla_{\mathbf{v}_a} \mathcal{H}^{(k)} \right\rangle \cdot \mathbf{F}_a \\ &\quad + \frac{n_a \bar{I}^t}{3nk_B} \left\langle \omega \text{Tr} \mathcal{H}^{(2)} d_t \mathcal{H}^{(k)} \right\rangle, \\ \mathbf{A}_d^{(ka)} &= \frac{n_a \bar{I}^t}{3nk_B} \left\langle \omega \text{Tr} \mathcal{H}^{(2)} \mathcal{H}^{(k)} \mathbf{C}_a \right\rangle, \end{aligned} \quad (7.118)$$

Coefficients in the equation for the fluctuation in the chemical potential:

$$\begin{aligned}
 B_a^{(I)} &= \frac{1}{2m_a} \left[\left\langle \omega (\text{Tr} \mathcal{H}^{(2)} - 2) [\mathbf{C}_a \cdot \nabla H_a + \mathbf{F}_a \cdot \nabla_{\mathbf{v}a} H_a] \right\rangle \right] \\
 &\quad + \frac{5}{6m_a} \sum_{b \neq a}^r \frac{n_b}{n} \left\langle \omega \text{Tr} \mathcal{H}^{(2)} [\mathbf{C}_b \cdot \nabla H_b + \mathbf{F}_b \cdot \nabla_{\mathbf{v}b} H_b] \right\rangle, \\
 B_{ab}^{(k)} &= \frac{\delta_{ab}}{2m_a} \left\langle \omega (\text{Tr} \mathcal{H}^{(2)} - 2) \mathcal{D}_t \mathcal{H}^{(k)} \right\rangle \\
 &\quad + \frac{5n_b(1 - \delta_{ab})}{6m_a n} \left\langle \omega \text{Tr} \mathcal{H}^{(2)} [\mathbf{C}_b \cdot \nabla \mathcal{H}^{(k)} + \nabla_{\mathbf{v}b} \mathcal{H}^{(k)} \cdot \mathbf{F}_b] \right\rangle \\
 &\quad + \frac{5n_b(1 - \delta_{ab})}{6m_a n} \left\langle \omega \text{Tr} \mathcal{H}^{(2)} d_t \mathcal{H}^{(k)} \right\rangle, \\
 \mathbf{B}_{dab}^{(k)} &= \frac{\delta_{ab}}{2m_a} \left\langle \omega (\text{Tr} \mathcal{H}^{(2)} - 2) \mathcal{H}^{(k)} \mathbf{C}_b \right\rangle \\
 &\quad + \frac{5n_b(1 - \delta_{ab})}{6m_a n} \left\langle \omega \text{Tr} \mathcal{H}^{(2)} \mathcal{H}^{(k)} \mathbf{C}_b \right\rangle,
 \end{aligned} \tag{7.119}$$

Coefficients in the equation for the fluctuation in the generalized potential:

$$\begin{aligned}
 \mathbf{C}_{ka}^{(I)} &= \frac{1}{k!} \left\langle \omega \mathcal{H}^{(k)} [H_a \mathbf{C}_a + \mathbf{F}_a \cdot \nabla_{\mathbf{v}a} H_a + d_t H_a] \right\rangle, \\
 \mathbf{C}_{la}^{(k)} &= \frac{1}{k!} \left\langle \omega \mathcal{H}^{(k)} \mathcal{D}_t \mathcal{H}^{(l)} \right\rangle, \\
 \mathbf{C}_{ka}^{(d)} &= \frac{1}{k!} \langle \omega H_a \mathbf{C}_a \rangle, \\
 \mathbf{C}_{ka}^{(\mu)} &= -\frac{1}{k!} \left\langle \omega \mathcal{H}^{(k)} m_a \mathbf{C}_a \right\rangle, \\
 \mathbf{C}_{dla}^{(k)} &= \frac{1}{k!} \left\langle \omega \mathcal{H}^{(k)} \mathcal{H}^{(l)} \mathbf{C}_a \right\rangle,
 \end{aligned} \tag{7.120}$$

The source terms are defined by the formulas

$$\begin{aligned}
 \mathcal{S}_I &= \frac{n_a \bar{I}^t}{3n} \sum_{a=1}^r \left\langle \omega \text{Tr} \mathcal{H}^{(2)} \mathcal{D}_t \ln f_a^c \right\rangle, \\
 \mathcal{S}_\mu^a &= \frac{k_B}{2m_a} \left\langle \omega (\text{Tr} \mathcal{H}^{(2)} - 2) \mathcal{D}_t \ln f_a^c \right\rangle
 \end{aligned}$$

$$\begin{aligned}
& + \frac{5k_B}{6m_a} \sum_{b \neq a}^r \frac{n_b}{n} \left\langle \omega \text{Tr} \mathcal{H}^{(2)} \mathcal{D}_t \ln f_b^c \right\rangle, \\
S_{Ha}^{(k)} & = \frac{k_B}{k!} \left\langle \omega \mathcal{H}^{(k)} \mathcal{D}_t \ln f_a^c \right\rangle.
\end{aligned} \tag{7.121}$$

The source terms S_I , S_μ^a , and $S_{Ha}^{(k)}$ are dependent on thermodynamic intensive variables \bar{I}^t , \bar{y}_{ka}^t , and $\bar{\mu}_a^t$ as well as their spatial gradients, time derivatives, and $\nabla \mathbf{u}$, namely,

$$S_I = S_I(\bar{I}^t, \dots, \nabla \bar{I}^t, \dots, d_t \bar{I}^t, \dots, \nabla \mathbf{u}), \quad \text{etc.}$$

Having calculated the kinematic contributions to the evolution equations for fluctuations, we consider the dissipative contributions associated with the Boltzmann collision integral. We will consider the following form for the dissipative contribution in the evolution equation for $\delta \bar{I}$ and so on:

$$D_{qa} = n_a \left\langle \omega(\mathbf{w}_a) f_a^{-1} G_{qa} R[f_a] \right\rangle, \tag{7.122}$$

where $q = I, \mu, H$ and:

$$\begin{aligned}
G_{Ia} &= \text{Tr} \mathcal{H}^{(2)}(\mathbf{w}_a); & G_{\mu a} &= \text{Tr} \mathcal{H}^{(2)}(\mathbf{w}_a) - 2; \\
G_{Ha} &= \mathcal{H}^{(k)}(\mathbf{w}_a).
\end{aligned} \tag{7.123}$$

Then, with the definitions

$$m_a \bar{\mu}_a^{0t} = k_B \ln \left[n_a \left(m_a \bar{I}^t / 2\pi k_B \right)^{3/2} \right], \tag{7.124}$$

$$f_a^0 = \exp \left[-\bar{I}^t H_a + m_a \bar{\mu}_a^{0t} \right], \tag{7.125}$$

we may write (7.122) in the form

$$\begin{aligned}
D_{qa} &= \left(\frac{k_B}{m_a \bar{I}^t} \right)^{3/2} \\
&\times \left\langle \frac{f_a^0}{f_a^c} \exp \left[\delta \bar{I} H_a + \sum_{k \geq 1} \delta \bar{y}_{ka} \mathcal{H}^{(k)}(\mathbf{w}_a) - m_a \delta \bar{\mu}_a \right] G_{qa} R[f_a] \right\rangle.
\end{aligned} \tag{7.126}$$

This form accounts for the energy dissipation arising from fluctuations $\delta \bar{I}$ and so on. To see this effect to the first order in fluctuations, take the approximation $f_a^c/f_a^0 \approx 1$ and expand the exponential factor retaining up

to the first order to obtain the following:

$$\begin{aligned}
 D_{qa} = & \left(\frac{k_B}{m_a \bar{I}^t} \right)^{3/2} [\langle G_{qa} R[f_a f_b] \rangle + \delta \bar{I} \langle H_a G_{qa} R[f_a] \rangle] \\
 & + \left(\frac{k_B}{m_a \bar{I}^t} \right)^{3/2} \sum_{k \geq 1} \delta \bar{y}_{ka} \langle \mathcal{H}^{(k)}(\mathbf{w}_a) G_{qa} R[f_a] \rangle \\
 & - \left(\frac{k_B}{m_a \bar{I}^t} \right)^{3/2} \delta \bar{\mu}_a \langle m_a G_{qa} R[f_a] \rangle. \tag{7.127}
 \end{aligned}$$

These results may be used in the dissipation terms in the evolution equations (7.115)–(7.117) to study the evolution of fluctuations $\delta \bar{I}$, $\delta \bar{\mu}_a$, and $\delta \bar{y}_{ka}$. The terms in the angular brackets are the dissipation terms for the nonconserved variables therein, and such dissipation terms contribute to the evolution of fluctuations which are all coupled with each other. Especially, in the case of the evolution equations for $\delta \bar{I}$ the dissipation term

$$\langle G_{Ia} R[f_a] \rangle = \langle \text{Tr} \mathcal{H}^{(2)} R[f_a] \rangle$$

does not contribute since $\text{Tr} \mathcal{H}^{(2)} = w_a^2 - 3$ is a collision invariant. Note that $(w_a^2 - 3)/2$ is the fluctuation of the particle kinetic energy from the mean value expressed in temperature, that is, the thermodynamic kinetic energy per particle. It is important to distinguish the mean value of kinetic energy computed from the distribution function f_a from the thermodynamic kinetic energy per particle. The former is simply a probabilistic mean value and the latter is a thermodynamic quantity onto which the former projects in the thermodynamic variable space. Such a fluctuation of mean kinetic energy from the mean thermal energy has to do with, for example, the fluctuation $\delta \bar{I}$ according to the analysis made here. In the case of linearized evolution equations for fluctuations which can be obtained from (7.115)–(7.117) the coefficients of $\delta \bar{I}$ and so on in (7.127) give a measure of relaxation time for the fluctuations since the aforementioned evolution equations are the regression equations for fluctuations.

7.5 Statistical Treatment of Fluctuations

The evolution equations derived for fluctuations $\delta \bar{I}$, $\delta \bar{\mu}$, and $\delta \bar{Y}_k$ in the previous section are deterministic equations on a par with the generalized hydrodynamic equations attendant on the differential form for $d_t \hat{\Psi}$. These evolution equations make it possible to determine the fluctuations, given suitable initial and boundary conditions at the boundaries of the volume. For example, the fluctuations may be assumed to vanish at the boundaries. It must be noted that such determinations of fluctuations are not possible in

the conventional fluctuation theories, but the present theory makes it possible to determine them because of the kinetic equation, namely, the Boltzmann equation, which is absent in the conventional fluctuation theories. Despite this advantage the evolution equations are rather complicated partial differential equations—hydrodynamic equations of some sort—which are not easy to solve. One may get around this handicap and learn more about the nature of fluctuations if a statistical treatment is sought for them. Schlögl [19] developed a statistical method of treatment for equilibrium fluctuations in his work on thermodynamic complementarity. We take a similar line of approach in this work.

7.5.1 Probability of Fluctuations

For the end we have in mind it is convenient to divide the phase space into small cells so that the integration over the velocity can be discretized. For the present section we will assume, for the sake of notational brevity, a single-component gas without loss of generality. It is easy to generalize it to the case of a mixture. The cells in the phase space will be denoted by the index i . Therefore, for example, the distribution function f_i will denote the probability distribution function for the event corresponding to the velocity and position values of cell i . This probability distribution function can be measured by repeatedly performing observations of events in the phase space.

We now imagine the system fluctuates from the state characterized by the thermodynamic intensive variables $(\bar{I}^t, \bar{p}^t, \bar{Y}_k^t : k \geq 1)$ conjugate to the extensive variables $(\mathcal{E}, v, \hat{\Theta}_k : k \geq 1)$. It must be recalled that the intensive variables mentioned appear in the probability distribution function f_i^c , namely, the nonequilibrium canonical form, as conjugate variables to the Hamiltonian, the tensor Hermite polynomials, and so on. This nonequilibrium canonical form is taken as an *a priori* probability distribution function and as a reference distribution function from which the system fluctuates. In the kinetic theory approach presented in the previous sections, the distribution function f_i is not necessarily the same as the nonequilibrium canonical form f_i^c since the latter is not necessarily the solution of the Boltzmann equation satisfying the initial and boundary conditions in the phase space, owing to the fact that the thermodynamic space represents a contraction of information from the phase space. In the probabilistic theory of fluctuations in this section, since the nonequilibrium canonical form underlies the thermodynamic state of the system and the fluctuations in question are away from the thermodynamic state inherent to f_i^c , it follows that $f_i^c \neq f_i$. This distribution function is not a solution of the Boltzmann equation, but is endowed with some other probabilistic properties. On performing a large number of observations of events in the system one finds the events occur with relative frequencies N_i/N . We look for the probability of this relative

frequency to be precisely equal to f_i , namely,

$$f_i = \frac{N_i}{NV}. \quad (7.128)$$

We have inserted the volume factor in order to have the dimension of f_i coincide with that of the distribution functions used in the earlier sections. The desired probability W of the events to occur with such relative frequencies is then given by

$$W = N! \prod_i \frac{(V f_i^c)^{N_i}}{N_i!}. \quad (7.129)$$

The use of Stirling's approximation puts (7.129) in the form

$$W = C \mathcal{P}^N, \quad (7.130)$$

where

$$\mathcal{P} = \exp(-k_B^{-1} S_r[f|f^c]), \quad (7.131)$$

$$S_r[f|f^c] = k_B \sum_i f_i \ln \left(\frac{f_i}{f_i^c} \right) = k_B \sum_i \left[f_i \ln \left(\frac{f_i}{f_i^c} \right) - f_i + f_i^c \right]. \quad (7.132)$$

The second equality in (7.132) follows from the preservation of normalization for f_i and f_i^c . In (7.130), C is the normalization factor for W . The relative Boltzmann entropy, therefore, is seen to define the probability distribution function for fluctuations. Eq. (7.131) is a nonequilibrium canonical ensemble generalization of the Einstein fluctuation formula since \mathcal{P} may be written as

$$\mathcal{P} = \exp \left[k_B^{-1} (S - \hat{\Psi}) \right], \quad (7.133)$$

and $\hat{\Psi}$ does not appear in the Einstein formula; it is a correction to the Einstein formula.

7.5.2 Thermodynamic Complementarity

If f_i is sought in a form mathematically identical with f_i^c except for the different conjugate parameters \bar{I} , \bar{p} , $\bar{\mu}$, and \bar{Y}_k , then for a single-component system the relative Boltzmann entropy is given by the formula

$$S_r[f|f^c] = - \left[\mathcal{E} \delta \bar{I} + v \delta \bar{p} + \sum_{k \geq 1} \widehat{\Theta}_k \delta \bar{Y}_k - \delta \bar{\mu} \right]. \quad (7.134)$$

Unlike the case of a deterministic treatment of fluctuations and the relative Boltzmann entropy deterministically treated in the previous sections, there

is no evolution equation for $S_r[f|f^c]$ in the present statistical treatment of fluctuations and no basis for inferring the kind of mathematical property giving rise to Theorem 5 in the earlier section. Under the circumstances, it is reasonable to consider the relative Boltzmann entropy in (7.134) as an integral surface of a differential form $S_r[f|f^c]$ in the space $(\mathcal{E}, v, \hat{\Theta}_k : k \geq 1)$. Consequently, there follow the relations

$$\frac{\partial}{\partial \mathcal{E}} S_r[f|f^c] = -\delta \bar{I}, \quad \frac{\partial}{\partial v} S_r[f|f^c] = -\delta \bar{p}, \quad \frac{\partial}{\partial \hat{\Theta}_k} S_r[f|f^c] = -\delta \bar{Y}_k. \quad (7.135)$$

Recast with the help of (7.131), these relations may be given the forms

$$k_B \frac{\partial \mathcal{P}}{\partial \mathcal{E}} = \delta \bar{I} \mathcal{P}, \quad k_B \frac{\partial \mathcal{P}}{\partial v} = \delta \bar{p} \mathcal{P}, \quad k_B \frac{\partial \mathcal{P}}{\partial \hat{\Theta}_k} = \delta \bar{Y}_k \mathcal{P}. \quad (7.136)$$

Mathematically these relations are eigenvalue problems for the differential operators appearing in the equations. They also may be interpreted as ‘thermodynamic quantization rules’ for the conjugate intensive variables (*i.e.*, fluctuations of intensive variables):

$$\delta \bar{I} \Rightarrow k_B \frac{\partial}{\partial \mathcal{E}}, \quad \delta \bar{p} \Rightarrow k_B \frac{\partial}{\partial v}, \quad \delta \bar{Y}_k \Rightarrow k_B \frac{\partial}{\partial \hat{\Theta}_k}, \quad (7.137)$$

with the Boltzmann constant playing the role of ‘the quantum of thermodynamic action’ as was observed by the present author in connection with a path integral solution [20] of a Fokker–Planck equation. These thermodynamic quantization rules suggest the following attendant ‘thermodynamic commutators’

$$[\delta \bar{I}, \mathcal{E}] = \delta \bar{I} \mathcal{E} - \mathcal{E} \delta \bar{I} = k_B, \quad etc.. \quad (7.138)$$

Relations (7.136) can be used to evaluate the mean values involving fluctuations. If we define such mean values by, for example,

$$\langle \delta \bar{I} \mathcal{E} \rangle = \int d\Gamma \delta \bar{I} \mathcal{E} \mathcal{P}(\mathcal{E}, v, \hat{\Theta}), \quad (7.139)$$

where $d\Gamma = d\mathcal{E} dv \prod_k d\hat{\Theta}_k$ is the volume element in the space \mathfrak{P}_h , then use of relations (7.136) yields

$$\langle \delta \bar{I} \mathcal{E} \rangle = -k_B, \quad \langle \delta \bar{p} v \rangle = -k_B, \quad \langle \delta \bar{Y}_k \hat{\Theta}_k \rangle = -k_B. \quad (7.140)$$

Therefore it can be concluded that

$$\langle S_r[f|f^c] \rangle = - \left[\langle \delta \bar{I} \mathcal{E} \rangle + \langle \delta \bar{p} v \rangle + \sum_{k \geq 1} \langle \delta \bar{Y}_k \hat{\Theta}_k \rangle \right] \geq 0. \quad (7.141)$$

This inequality is consistent with the Klein inequality for $S_r[f|f^c]$ itself. Since by the thermodynamic quantization rules

$$\langle \delta \bar{I} \rangle = 0, \quad \langle \delta \bar{p} \rangle = 0, \quad \langle \delta \bar{Y}_k \rangle = 0,$$

with the definitions of fluctuations in the extensive variables

$$\delta \mathcal{E} = \mathcal{E} - \langle \mathcal{E} \rangle, \quad \delta v = v - \langle v \rangle, \quad \delta \hat{\Theta}_k = \hat{\Theta}_k - \langle \hat{\Theta}_k \rangle, \quad (7.142)$$

it is possible to cast (7.141) in the form

$$\langle \delta \bar{I} \delta \mathcal{E} \rangle + \langle \delta \bar{p} \delta v \rangle + \sum_{k \geq 1} \langle \delta \bar{Y}_k \delta \hat{\Theta}_k \rangle \geq 0. \quad (7.143)$$

Furthermore, since by the Schwartz inequality

$$\langle \delta \bar{I} \delta \mathcal{E} \rangle^2 \leq \langle (\delta \bar{I})^2 \rangle \langle (\delta \mathcal{E})^2 \rangle, \quad \text{etc.,}$$

we find

$$\langle (\delta \bar{I})^2 \rangle^{1/2} \langle (\delta \mathcal{E})^2 \rangle^{1/2} \geq -\langle \delta \bar{I} \delta \mathcal{E} \rangle = k_B, \quad \text{etc..} \quad (7.144)$$

Therefore with the definitions of uncertainties

$$\Delta \bar{I} = \langle (\delta \bar{I})^2 \rangle^{1/2}, \quad \Delta \mathcal{E} = \langle (\delta \mathcal{E})^2 \rangle^{1/2}, \quad \text{etc.,}$$

we obtain the thermodynamic uncertainty relations for nonequilibrium systems:

$$\Delta \bar{I} \Delta \mathcal{E} \geq k_B, \quad \Delta \bar{p} \Delta v \geq k_B, \quad \Delta \bar{Y}_k \Delta \hat{\Theta}_k \geq k_B. \quad (7.145)$$

These inequalities are thermodynamic analogs of uncertainty relations in quantum mechanics. Such relations in thermodynamics were considered possible by Bohr [21], Heisenberg [22], and others. Later Lindhard [24] made an attempt at their derivation but did not quite obtain them. Schlogl eventually obtained them for the case of equilibrium [19]. Here we have derived thermodynamic complementarity relations for nonequilibrium. It is interesting to see that the relative Boltzmann entropy plays an essential role in the statistical treatment of fluctuations in intensive variables. The probability distribution function \mathcal{P} is expected to be in the basis of a thermodynamic fluctuation theory for nonequilibrium systems. We will not discuss such a theory in this work for lack of space.

7.6 Resummation of the Moment Expansion

It was indicated that the Maxwell–Grad expansion must be cast in an exponential form to construct a theory of irreversible processes in a way

consistent with the thermodynamic laws. Such a recasting of the moment expansion is in essence a resummation of the series. This resummation requires the determination of the generalized potentials $Y_a^{(q)}$ in terms of the coefficients $A_a^{(q)}$ in the moment expansion. Since they are formally related through (7.15), it is required to solve it for $Y_a^{(q)}$. Before we proceed further, we remark that the methods presented in this section are relevant only to the case where one builds a theory of irreversible processes via the Maxwell–Grad moment expansion augmented with its resummation to a nonequilibrium canonical form. As has been shown, the nonequilibrium ensemble method needs not proceed via the Maxwell–Grad expansion method.

The relation (7.15) is nonlinear since a logarithmic function is involved. A naive approach to relate $Y_a^{(q)}$ and $A_a^{(p)}$ is to expand the logarithmic function in a series and use the orthogonality property of the tensor Hermite polynomials, but the resulting series is not adequate except for the cases of $A_a^{(p)}$ small in magnitude, namely, near equilibrium. Therefore it is useful to develop a better method. We derive a set of linear integral equations for the generalized potentials [25]. By deriving such integral equations we are in fact converting a nonlinear problem into a linear problem. Therefore it is, by itself, an interesting example for such a conversion.

7.6.1 Algebraic Method

Differentiation of (7.11) with a component of \mathbf{w}_a , say, $w_{a\gamma}$ yields

$$f_a^c \left[w_{a\gamma} + \beta \sum_{q \geq 1} Y_a^{(q)} \delta_\gamma \mathcal{H}^{(q-1)}(\mathbf{w}_a) \right] = - \frac{\partial}{\partial w_{a\gamma}} f_a^c, \quad (7.146)$$

for which the recursion relation (5.18) is used. Multiply $\mathcal{H}^{(p)}(\mathbf{w}_a)$ and integrate over \mathbf{w}_a . Then, by using once again the recursion relation (5.19), we obtain the equation

$$\begin{aligned} \delta_\gamma \left\langle f_a^c \mathcal{H}^{(p-1)}(\mathbf{w}_a) \right\rangle &= \beta \sum_{q \geq 1} Y_a^{(q)} \delta_\gamma \left\langle f_a^c \mathcal{H}^{(p)}(\mathbf{w}_a) \mathcal{H}^{(q-1)}(\mathbf{w}_a) \right\rangle \\ &\quad + \left\langle f_a^c \left[\mathcal{H}_\gamma^{(p+1)}(\mathbf{w}_a) + \delta_\gamma \mathcal{H}^{(p-1)}(\mathbf{w}_a) \right] \right\rangle. \end{aligned} \quad (7.147)$$

The weak convergence (7.8) and the limit (7.9) put this equation in the form

$$\Theta_{a\gamma\alpha_1\dots\alpha_p}^{(p+1)} = -\beta \sum_{q \geq 1} Y_{a\epsilon_1\dots\epsilon_q}^{(q)} \delta_{\gamma\epsilon_k} \left\langle f_a \mathcal{H}_{\epsilon_1\dots\epsilon_{k-1}, \epsilon_{k+1}\dots\epsilon_q}^{(q-1)} \mathcal{H}_{\alpha_1\dots\alpha_p}^{(p)} \right\rangle \quad (p \geq 1), \quad (7.148)$$

where f_a^c is replaced with f_a by virtue of (7.8) and the Einstein convention is used for tensor products. By using the addition theorem for the tensor Hermite polynomials, the right hand side of (7.148) can be computed in terms of $\Theta_a^{(k)}$ ($k \geq 0$). We list the leading examples below:

$$\begin{aligned} -\beta^{-1}\Theta_{a\gamma}^{(1)} &= n_a Y_{a\gamma}^{(1)} + 2\{Y_a^{(2)}\}_{\gamma\alpha}\Theta_{a\alpha}^{(1)} \\ &\quad + 3\{Y_a^{(3)}\}_{\gamma\alpha_1\alpha_2}(\Theta_{a\alpha_1\alpha_2}^{(2)} + n_a\delta_{\alpha_1\alpha_2}) + \dots, \end{aligned} \tag{7.149}$$

$$\begin{aligned} -\beta^{-1}\Theta_{a\gamma\alpha_1}^{(2)} &= \Theta_{a\alpha_1}^{(1)} Y_{a\gamma}^{(1)} + 2\{Y_a^{(2)}\}_{\gamma\alpha_2}(\Theta_{a\alpha_1\alpha_2}^{(2)} + n_a\delta_{\alpha_1\alpha_2}) \\ &\quad + 3\{Y_a^{(3)}\}_{\gamma\alpha_2\alpha_3}(\Theta_{a\alpha_1\alpha_2\alpha_3}^{(2)} + \delta_{\alpha_1\alpha_2}\Theta_{a\alpha_3}^{(1)} + \delta_{\alpha_1\alpha_3}\Theta_{a\alpha_2}^{(1)}) \\ &\quad + \dots, \end{aligned} \tag{7.150}$$

$$\begin{aligned} -\beta^{-1}\Theta_{a\alpha\epsilon\gamma}^{(3)} &= \Theta_{a\alpha\epsilon}^{(2)} Y_{a\gamma}^{(1)} \\ &\quad + 2\{Y_a^{(2)}\}_{\gamma\beta_1}(\Theta_{a\beta_1\alpha\epsilon}^{(2)} + \delta_{\beta_1\alpha}\Theta_{a\epsilon}^{(1)} + \delta_{\beta_1\epsilon}\Theta_{a\alpha}^{(1)}) \\ &\quad + 3\{Y_a^{(3)}\}_{\gamma\beta_1\beta_2}(\Theta_{a\beta_1\beta_2\alpha\epsilon}^{(4)} + \delta_{\beta_1\alpha}\Theta_{a\beta_2\epsilon}^{(2)} + \delta_{\beta_1\epsilon}\Theta_{a\beta_2\alpha}^{(2)} \\ &\quad + \delta_{\beta_2\alpha}\Theta_{a\beta_1\epsilon}^{(2)} + \delta_{\beta_2\epsilon}\Theta_{a\beta_1\alpha}^{(2)} + \delta_{\alpha\beta_1}\delta_{\epsilon\beta_2} + \delta_{\alpha\beta_2}\delta_{\epsilon\beta_1}) \\ &\quad + \dots. \end{aligned} \tag{7.151}$$

These equations are supplemented by the formula for γ_a which may be calculated by means of applying a cumulant expansion to the equation

$$\gamma_a = \left\langle \omega(\mathbf{w}_a) \ln \left(1 + \zeta \sum_{p \geq 1} \mathcal{H}^{(p)}(\mathbf{w}_a) A_a^{(p)} \right) \right\rangle \tag{7.152}$$

or by the method described in Sec. 7.3.2 below. Here $\{Y_a^{(k)}\}$ denotes the symmetrized tensor:

$$\left\{ Y_a^{(2)} \right\}_{\gamma\epsilon} = \frac{1}{2} \left(Y_{a\gamma\epsilon}^{(2)} + Y_{a\epsilon\gamma}^{(2)} \right), \tag{7.153}$$

$$\left\{ Y_a^{(3)} \right\}_{\alpha\gamma\epsilon} = \frac{1}{3} \left(Y_{a\alpha\gamma\epsilon}^{(3)} + Y_{a\gamma\alpha\epsilon}^{(3)} + Y_{a\gamma\epsilon\alpha}^{(3)} \right). \tag{7.154}$$

The linear set (7.149)–(7.151) must be in practice truncated to solve for $Y_a^{(q)}$ in terms of $\Theta_a^{(k)}$ ($k \geq 1$).

7.6.2 Linear Integral Equations for Generalized Potentials

To derive the desired integral equations for generalized potentials, we first introduce a parameter, say, ζ into (7.15) and write it in the form

$$-\beta \sum_{q=1}^{\infty} \mathcal{H}^{(q)} Y_a^{(q)}(\zeta) + \gamma_a(\zeta) = \ln \left(1 + \zeta \sum_{q=1}^{\infty} \mathcal{H}^{(q)} A_a^{(q)} \right), \quad (7.155)$$

where $Y_a^{(q)}$ is now regarded as a function of ζ . The procedure used here is an analytical extension of $Y_a^{(q)}$ from the value at $\zeta = 1$ to the neighborhood of $\zeta = 1$. The interval of ζ is taken to be $\zeta = [0, 1]$. It is clear that

$$Y_a^{(q)} = Y_a^{(q)}(1), \quad Y_a^{(q)}(0) = 0. \quad (7.156)$$

For simplicity of notation we will drop the subscript a distinguishing the species from $Y_a^{(q)}$, $A_a^{(p)}$, and so forth, since there is no confusion arising thereby. When the derivation of the desired integral equation is completed, the subscript for species may be restored in the equations if it is desired. Thus we work with the equation

$$-\beta \sum_{q=1}^{\infty} \mathcal{H}^{(q)} Y^{(q)}(\zeta) + \gamma(\zeta) = \ln \left(1 + \zeta \sum_{q=1}^{\infty} \mathcal{H}^{(q)} A^{(q)} \right). \quad (7.157)$$

The conditions (7.156) still apply to this equation.

If the orthogonality relations of polynomials $\mathcal{H}^{(p)}$ are used in (7.155), the following equations can be easily obtained:

$$-Y_j^{(q)}(\zeta) \delta_{ij}^q = \langle \omega(\mathbf{w}) \mathcal{H}_i^{(q)} L(\zeta, A, \mathbf{w}) \rangle, \quad (7.158)$$

$$\gamma(\zeta) = \langle \omega(\mathbf{w}) L(\zeta, A, \mathbf{w}) \rangle, \quad (7.159)$$

where the subscripts i , j , and k are the abbreviations of the sets of indices (i_1, i_2, \dots, i_q) and so forth used in Chapter 5, and

$$L(\zeta, A, \mathbf{w}) = \ln \left(1 + \zeta \sum_{p \geq 1} \mathcal{H}_k^{(p)} A_k^{(p)} \right).$$

The sum over p in $L(\zeta, A, \mathbf{w})$, as a matter of fact, starts from 2 since $A^{(1)} = 0$. Now, by differentiating (7.158) with respect to ζ and rearranging the terms on the right hand side, we obtain

$$\delta_{ij}^q \frac{\partial}{\partial \zeta} Y_j^{(q)}(\zeta) = -A_j^{(q)} \delta_{ij}^q + \sum_{m \geq 1} A_k^{(m)} \zeta \frac{\partial}{\partial \zeta} \langle \omega \mathcal{H}_k^{(m)} \mathcal{H}_i^{(q)} L(\zeta, A, \mathbf{w}) \rangle. \quad (7.160)$$

Table 7.1 Leading Examples for $B_{ik}^{(qs)}$

$B_{ik}^{(1s)} = A_k^{(s+1)} \delta_{ik}^1 + A_k^{(s-1)} (s \geq 0)$
$B_{ik}^{(2s)} = A_k^{(s+2)} \delta_{ik}^2 + A_k^{(s)} \delta_{ik}^1 + A_k^{(s-2)} (s \geq 0)$
$B_{ik}^{(3s)} = A_k^{(s+3)} \delta_{ik}^3 + A_k^{(s+1)} \delta_{ik}^2 + A_k^{(s-1)} \delta_{ik}^1 + A_k^{(s-3)} (s \geq 0)$
$A_k^{(0)} = A_k^{(1)} = A_k^{(s)} = 0$ for $s < 0$

On using the addition theorem (5.24) of the tensor Hermite polynomials, the products of the tensor Hermite polynomials in the second term on the right hand side of (7.160) can be written as a linear combination of tensor Hermite polynomials in the form

$$\sum_{m \geq 1} A_k^{(m)} \mathcal{H}_k^{(m)} \mathcal{H}_i^{(q)} = \sum_{s \geq 0} B_{ik}^{(qs)} \mathcal{H}_k^{(s)} \quad (7.161)$$

where $B_{ik}^{(qs)}$ are given in terms of $A_k^{(q)}$ and δ_{ik} only. The explicit examples for $B_{ik}^{(qs)}$ are given for some leading terms necessary for practical applications in Table 7.1. The point to recognize here is the fact that the left hand side of (7.161) is expandable in a linear combination of tensor Hermite polynomials since they form a complete set. Substitution of (7.161) and integration of the resulting equation with regard to ζ yield the equation

$$\begin{aligned} \delta_{ij}^q Y_j^{(q)}(\zeta) &= \zeta A_j^{(q)} \delta_{ij}^q - \sum_{s \geq 0} B_{ik}^{(qs)} \left\langle \omega(\mathbf{w}) \mathcal{H}_k^{(s)} L(\zeta, A, \mathbf{w}) \right\rangle \\ &\quad + \sum_{s \geq 0} B_{ik}^{(qs)} \int_0^\zeta d\zeta' \left\langle \omega(\mathbf{w}) \mathcal{H}_k^{(s)} L(\zeta', A, \mathbf{w}) \right\rangle. \end{aligned} \quad (7.162)$$

The case of $s = 0$ must be considered separately since the terms corresponding to $s = 0$ are related to $\gamma(\zeta)$ owing to the fact $\mathcal{H}^{(0)} = 1$ and by the definition of the normalization factor $\gamma(\zeta)$, (7.159). Note that $\gamma = \gamma(1)$ and $\gamma(0) = 0$. By applying the same method as for (7.162), it is easy to cast (7.159) in the form

$$\gamma(\zeta) = -\zeta \sum_{s \geq 1} A_j^{(s)} \delta_{ij}^s Y_i^{(s)} + \sum_{s \geq 1} A_j^{(s)} \delta_{jk}^s \int_0^\zeta d\zeta' Y_k^{(s)}(\zeta'). \quad (7.163)$$

This result makes it possible to write the terms corresponding to $s = 0$ in (7.162) as follows:

$$\begin{aligned} B_{ik}^{(q0)} \gamma(\zeta) &= B_{ik}^{(q0)} \langle \omega(\mathbf{w}) L(\zeta, A, \mathbf{w}) \rangle \\ &= -\zeta \sum_{s \geq 1} B_i^{(q0)} A_j^{(s)} \delta_{ij}^s Y_i^{(s)}(\zeta) \\ &\quad + \sum_{s \geq 1} B_i^{(q0)} A_j^{(s)} \delta_{jk}^s \int_0^\zeta d\zeta' Y_k^{(s)}(\zeta'), \end{aligned} \quad (7.164)$$

$$\begin{aligned} B_{ik}^{(q0)} \int_0^\zeta d\zeta' \gamma(\zeta') &= B_{ik}^{(q0)} \int_0^\zeta d\zeta' \left\langle \omega(\mathbf{w}) \mathcal{H}_k^{(0)} L(\zeta', A, \mathbf{w}) \right\rangle \\ &= -\sum_{s \geq 1} B_i^{(q0)} A_j^{(s)} \delta_{ij}^s \int_0^\zeta d\zeta' \zeta' Y_i^{(s)}(\zeta') \\ &\quad + \sum_{s \geq 1} B_i^{(q0)} A_j^{(s)} \delta_{ij}^s \int_0^\zeta d\zeta' \int_0^{\zeta'} d\xi Y_i^{(s)}(\xi). \end{aligned} \quad (7.165)$$

Here we have dropped the subscript k from $B_{ik}^{(q0)}$ on the right hand side of (7.164) and (7.165) since it is not involved in the case of $s = 0$. Performing integrations over ζ' and ξ in the last integral in (7.165) and substituting (7.164) and (7.165) thus obtained into (7.162), we obtain the integral equation for $Y_j^{(q)}(\zeta)$:

$$\begin{aligned} \delta_{ij}^q Y_j^{(q)}(\zeta) &= -\zeta A_j^{(q)} \delta_{ij}^q - \zeta \sum_{s \geq 1} E_{il}^{(qs)} Y_l^{(s)}(\zeta) + \sum_{s \geq 1} E_{il}^{(qs)} \int_0^\zeta d\zeta' Y_l^{(s)}(\zeta') \\ &\quad - \zeta^2 \sum_{s \geq 1} N_{il}^{(qs)} Y_l^{(s)}(\zeta) + 2 \sum_{s \geq 1} N_{il}^{(qs)} \int_0^\zeta d\zeta' \zeta' Y_l^{(s)}(\zeta'). \end{aligned} \quad (7.166)$$

Here various new symbols are:

$$E_{il}^{(qs)} = B_{il}^{(qs)} \delta_{kl}^s, \quad (7.167)$$

$$N_{il}^{(qs)} = B_i^{(q0)} A_k^{(s)} \delta_{kl}^s, \quad (7.168)$$

$$N_{il}^{(q1)} = 0. \quad (7.169)$$

Eq. (7.166) is the set of integral equations for $Y_j^{(q)}$ earlier alluded to. The integral equations are linear and of Volterra type, and can be solved by a

variety of methods known for linear integral equations. When the solution process is completed, the value of ζ is set to unity and we obtain in terms of $\{A_j^{(q)}\}$ the desired $\{Y_j^{(s)}\}$ to be used in the nonequilibrium canonical form, the calortropy differential, the calortropy production, and so on.

To help implement the solution procedure for (7.166), it is useful to rearrange the equation in the following form. First, we define the matrix

$$M_{il}^{(qs)}(\zeta) = \delta_{il}^s \delta_{qs} + \zeta E_{il}^{(qs)} + \zeta^2 N_{il}^{(qs)}. \quad (7.170)$$

With this definition, the integral equation (7.166) can be written as

$$\begin{aligned} \sum_{s \geq 1} M_{il}^{(qs)}(\zeta) Y_l^{(s)}(\zeta) &= -\zeta A_j^{(q)} \delta_{ij}^q + \sum_{s \geq 1} E_{il}^{(qs)} \int_0^\zeta d\zeta' Y_l^{(s)}(\zeta') \\ &\quad + 2 \sum_{s \geq 1} N_{il}^{(qs)} \int_0^\zeta d\zeta' \zeta' Y_l^{(s)}(\zeta'). \end{aligned} \quad (7.171)$$

Since the unknowns in this integral equation are tensors, it is convenient to arrange the tensors involved in a one-dimensional array (a column vector), denoted by $y_s(\zeta)$, and construct the corresponding coefficient matrices, say, \mathcal{M}_{qs} , \mathcal{E}_{qs} , and \mathcal{N}_{qs} from the coefficients $M_{il}^{(qs)}$, $E_{il}^{(qs)}$, and $N_{il}^{(qs)}$, respectively, in a way consistent with the column vector $y_s(\zeta)$ constructed. Then the integral equation (7.171) may be written in the form

$$\sum_{s \geq 1} \mathcal{M}_{qs} y_s(\zeta) = -\zeta \mathcal{A}_q + \sum_{s \geq 1} \mathcal{E}_{qs} \int_0^\zeta d\zeta' y_s(\zeta') + 2 \sum_{s \geq 1} \mathcal{N}_{qs} \int_0^\zeta d\zeta' \zeta' y_s(\zeta'), \quad (7.172)$$

where \mathcal{A}_q is the element of the column vector corresponding to $A_j^{(q)} \delta_{ij}^q$ which is constructed in the same order as for $y_s(\zeta)$. Under the assumption that the matrix $\mathcal{M}(\zeta)$ is invertible, we may rewrite the integral equation in the form

$$y_q(\zeta) = -\phi_q(\zeta) + \sum_{s \geq 1} \int_0^\zeta d\zeta' K_{qs}(\zeta, \zeta') y_s(\zeta'), \quad (7.173)$$

where $q \geq 1$, $\zeta = [0, 1]$, and

$$\phi_q(\zeta) = \zeta \sum_{s \geq 1} (\mathcal{M}^{-1})_{qs} \mathcal{A}_s, \quad (7.174)$$

$$K_{qs}(\zeta, \zeta') = (\mathcal{M}^{-1} \mathcal{E})_{qs}(\zeta) + 2\zeta' (\mathcal{M}^{-1} \mathcal{N})_{qs}(\zeta). \quad (7.175)$$

Approximate solutions of the integral equation for $Y_j^{(s)}$ presented can be obtained by an iteration method. First of all, the lowest order solution for

$Y_j^{(s)}$ is easily obtained by simply neglecting all other terms except for the first term on the right hand side of (7.171):

$$Y_j^{(q)} = -A_j^{(q)} \quad (q \geq 2). \quad (7.176)$$

Note that $A_j^{(1)} = 0$. This agrees with the lowest order perturbation solution obtained from (7.158) with $\zeta = 1$. Improved solutions which correspond to resummations of the perturbation solution of (7.158) can be obtained from (7.173). For example, the integral term on the right hand side of (7.173) can be ignored to obtain

$$y_q(\zeta) = -\phi_q(\zeta), \quad (7.177)$$

which is in fact the solution of the linear algebraic set

$$\sum_{s \geq 1} \mathcal{M}_{qs} y_s(\zeta) = -\zeta \mathcal{A}_q \quad (7.178)$$

or, more explicitly, the set

$$\delta_{ij}^q Y_j^{(q)}(\zeta) = -\zeta A_j^{(q)} \delta_{ij}^q - \zeta \sum_{s \geq 1} E_{il}^{(qs)} Y_l^{(s)}(\zeta) - \zeta^2 \sum_{s \geq 1} N_{il}^{(qs)} Y_l^{(s)}(\zeta). \quad (7.179)$$

The lowest order solution for $Y_j^{(q)}$ in (7.176) is obtained from this set if the second and third terms on the right hand side are ignored. When this algebraic equation is iteratively solved, a perturbation solution similar to the one directly obtained from (7.158) by expanding the logarithmic function. As a matter of fact, the solution of the linear algebraic set (7.178) is equivalent to a resummation of the perturbation solution. The first iterative solution $y_q^{(1)}(\zeta)$ of (7.173) is obtained if (7.177) is substituted into the integral term in (7.173):

$$y_q^{(1)}(\zeta) = -\phi_q(\zeta) - \sum_{s \geq 1} \int_0^\zeta d\zeta' K_{qs}(\zeta, \zeta') \phi_s(\zeta'). \quad (7.180)$$

In this manner it is possible to obtain in terms of the moments $A_i^{(q)}$ the generalized potentials $Y_i^{(q)}$ and γ_a appearing in the nonequilibrium canonical form and also in the calortropy differential and thereby to make the Maxwell–Grad expansion method produce a theory of irreversible processes consistent with the laws of thermodynamics. We emphasize here that although this procedure is not essential for the nonequilibrium ensemble method, because we can simply start with the nonequilibrium canonical form, it is necessary if we aim to make the Maxwell–Grad moment method thermodynamically consistent.

7.7 Constitutive Equations for Fluxes

Constitutive equations for nonconserved variables can be derived from the kinetic equation if the statistical definitions are given for the nonconserved variables such as fluxes. Since nonconserved variables are in principle observable in the laboratory, their statistical definitions must be motivated by laboratory measurements based on the physics of the irreversible processes of interest. However, measurement-based statistical definitions of the nonconserved variables are not necessarily the most suitable from the mathematical standpoint. For this reason we first formulate the evolution equations for nonconserved variables by using a mathematically convenient complete set of functions of velocity and then relate them to the evolution equations for the statistical definitions of observable nonconserved variables. This is the main aim of this section.

7.7.1 Relation between Two Representations of f_a

The tensor Hermite polynomials $\mathcal{H}^{(q)}$ and their conjugate generalized potentials $Y_a^{(q)}$ are not only most convenient from the mathematical viewpoint but also most suitable from the viewpoint of the nonequilibrium ensemble method. However, the mean value $\Theta_a^{(q)}$ of $\mathcal{H}^{(q)}$ is not always directly related to an observable measured in the laboratory. For this reason it is useful to construct moments such that their mean values are the directly measurable observables as presented in (7.49). Here we will work out the transformation from the set $\{\Theta_a^{(q)}\}$ to the set $\{\Phi_{qa}\}$. The leading examples for the relations of the two sets are:

$$\begin{aligned}\Phi_{1a} &= n_a k_B T \left(\Theta_a^{(2)} - \frac{1}{3} \delta \text{Tr} \Theta_a^{(2)} \right), \\ \Phi_{2a} &= \frac{1}{3} n_a k_B T \text{Tr} \Theta_a^{(2)}, \\ \Phi_{3a} &= \frac{1}{2} n_a k_B T \sqrt{\frac{k_B T}{m_a}} \left(\Theta_a^{(3)} \right)_{kk}, \\ \Phi_{4a} &= n_a \sqrt{m_a k_B T} \Theta_a^{(1)}, \quad \text{etc.,}\end{aligned}\tag{7.181}$$

where the subscript k denotes the Cartesian components of the tensor. The Einstein convention is used for repeated indices of tensors. Therefore $\left(\Theta_a^{(3)} \right)_{kk}$ means a third-rank tensor with trace taken over two indices.

Thus the result is a vector. The relation between X_{qa} and $Y_a^{(q)}$ can be easily found if a tensor Hermite polynomial is multiplied with (7.52) and the orthogonality property of the tensor Hermite polynomials are used.

Thus we find

$$Y_a^{(q)} \left\langle f_a^0 \mathcal{H}^{(q)}(\mathbf{w}_a) \mathcal{H}^{(q)}(\mathbf{w}_a) \right\rangle = \sum_{p \geq 1} X_{pa} \left\langle f_a^0 \mathcal{H}^{(q)}(\mathbf{w}_a) h_a^{(p)}(\mathbf{C}_a) \right\rangle. \quad (7.182)$$

Since

$$\begin{aligned} h_a^{(1)} &= k_B T \left[\mathcal{H}^{(2)}(\mathbf{w}_a) - \frac{1}{3} \delta \text{Tr} \mathcal{H}^{(2)}(\mathbf{w}_a) \right], \\ h_a^{(2)} &= \frac{1}{3} k_B T \text{Tr} \mathcal{H}^{(2)}(\mathbf{w}_a), \\ h_a^{(3)} &= \frac{1}{2} k_B T \sqrt{\frac{k_B T}{m_a}} \left[\mathcal{H}^{(3)}(\mathbf{w}_a) \right]_{kk}, \\ h_a^{(4)} &= \sqrt{m_a k_B T} \mathcal{H}^{(1)}(\mathbf{w}_a), \quad \text{etc.}, \end{aligned} \quad (7.183)$$

the following examples can be easily worked out:

$$X_{1a} = Y_a^{(2)} - \frac{1}{3} \delta \text{Tr} Y_a^{(2)},$$

$$X_{2a} = \text{Tr} Y_a^{(2)}, \quad (7.184)$$

$$X_{3a} = \frac{6}{5} \sqrt{\frac{m_a}{k_B T}} (Y_a^{(3)})_{kk},$$

$$X_{4a} = \sqrt{\frac{k_B T}{m_a}} Y_a^{(1)}.$$

These relations make it unnecessary to develop a separate method of determining the h -representation generalized potentials X_{ka} ($k \geq 1$), since the latter may be computed from the set $\{Y_i^{(q)} : q \geq 1\}$ by means of the relations just given. If the lowest order approximation is used for $Y_a^{(q)}$ in (7.184) which is obtained from the algebraic equations in Sec. 7.3.1 or the integral equation given earlier in this section, the lowest order approximation for $X_{\alpha a}$ is obtained in terms of the corresponding flux as follows:

$$\begin{aligned} X_{1a} &= -\frac{\Pi_a}{2p_a}, \\ X_{2a} &= -\frac{3\Delta_a}{2p_a} = 0, \\ X_{3a} &= -\frac{\mathbf{Q}'_a}{p_a \hat{C}_p T}, \\ X_{4a} &= -\frac{\mathbf{J}_a}{\rho_a}. \end{aligned} \quad (7.185)$$

Since $\text{Tr} A_a^{(2)} = 0$ and $Y_a^{(2)}$ is proportional to $A_a^{(2)}$ the second equation for X_{2a} follows. These results will be used in the study of transport processes presented later and found sufficient for many cases according to the studies made so far [9, 26–36].

7.7.2 Kinematic Terms in the h -Representation

The kinematic term Z_{qa} appearing in the evolution equation for $\hat{\Phi}_{qa}$ (7.57) can be explicitly worked out without an approximation. Since $h_a^{(q)}$ is a function of peculiar velocity \mathbf{C}_a as well as ρ , c_a , and T , by using the chain rule we obtain from (7.55)

$$\begin{aligned} Z_{qa} = & -d_t \mathbf{u} \cdot \left\langle f_a \frac{\partial}{\partial \mathbf{C}_a} h_a^{(q)} \right\rangle - (\nabla \mathbf{u})^t : \left\langle \mathbf{C}_a \left(\frac{\partial}{\partial \mathbf{C}_a} h_a^{(q)} \right) f_a \right\rangle \\ & + \mathbf{F}_a \cdot \left\langle \left(\frac{\partial}{\partial \mathbf{C}_a} h_a^{(q)} \right) f_a \right\rangle + d_t T \left\langle f_a \frac{\partial}{\partial T} h_a^{(q)} \right\rangle \\ & + \left\langle f_a \left(\frac{\partial}{\partial T} h_a^{(q)} \right) \mathbf{C}_a \right\rangle \cdot \nabla T + d_t \rho \left\langle f_a \frac{\partial}{\partial \rho} h_a^{(q)} \right\rangle \\ & + \left\langle f_a \left(\frac{\partial}{\partial \rho} h_a^{(q)} \right) \mathbf{C}_a \right\rangle \cdot \nabla \rho + d_t c_a \left\langle f_a \frac{\partial}{\partial c_a} h_a^{(q)} \right\rangle \\ & + \left\langle f_a \left(\frac{\partial}{\partial c_a} h_a^{(q)} \right) \mathbf{C}_a \right\rangle \cdot \nabla c_a, \end{aligned} \quad (7.186)$$

where the superscript t means the transpose of the tensor. In conjunction with these formulas we also note

$$\psi_{4a} = \mathbf{P}_a. \quad (7.187)$$

The examples for the kinematic terms Z_{qa} ($q \geq 1$) of the leading members of the set $\{\Phi_{1a}, \dots, \Phi_{4a}, \dots\}$ are as follows:

$$\begin{aligned} Z_{1a} = & -2 [\mathbf{J}_a (d_t \mathbf{u} - \mathbf{F}_a)]^{(2)} - 2[\Pi_a \cdot \nabla \mathbf{u}]^{(2)} - 2\Delta_a [\nabla \mathbf{u}]^{(2)} \\ & - \frac{2}{3} \Pi_a \nabla \cdot \mathbf{u} - 2p_a [\nabla \mathbf{u}]^{(2)}, \\ Z_{2a} = & -\frac{2}{3} \mathbf{J}_a \cdot (d_t \mathbf{u} - \mathbf{F}_a) - \frac{2}{3} \Pi_a : \nabla \mathbf{u} - \frac{2}{3} \Delta_a \nabla \cdot \mathbf{u} \\ & - p_a d_t \ln(p_a v^{5/3}) - \nabla \cdot \left(\frac{p_a}{\rho_a} \mathbf{J}_a \right), \\ Z_{3a} = & -(d_t \mathbf{u} - \mathbf{F}_a) \cdot (\mathbf{P}_a - p_a \boldsymbol{\delta}) - \mathbf{Q}'_a \cdot \nabla \mathbf{u} - \boldsymbol{\varphi}_a^{(3)} : \nabla \mathbf{u} \end{aligned} \quad (7.188)$$

$$-\mathbf{J}_a d_t \hat{h}_a - \mathbf{P}_a \cdot \nabla \hat{h}_a,$$

$$\mathcal{Z}_{4a} = -\rho_a(d_t \mathbf{u} - \mathbf{F}_a) - \mathbf{J}_a \cdot \nabla \mathbf{u},$$

where

$$\varphi_a^{(3)} = \langle \mathbf{C}_a \mathbf{C}_a \mathbf{C}_a f_a \rangle. \quad (7.189)$$

Other symbols have been defined before. When these kinematic terms are combined with the dissipation terms Λ_{qa} which will be explicitly calculated shortly, the constitutive equations are obtained explicitly in terms of macroscopic variables in the space \mathfrak{P} . The constitutive equations so obtained, together with the balance equations for mass, momentum and energy, form the generalized hydrodynamics equations, which are one of important objects we wish to derive in this work. Finally, we remark that these constitutive equations, when linearized with regard to thermodynamic forces and nonconserved variables, become the Maxwell–Cattaneo–Vernotte equations [37–39] for the leading members corresponding to what is traditionally called the 13 moment approximation, or the equivalent.

7.7.3 Cumulant Approximations for Λ_{qa}

Calculation of the dissipation terms requires caution since, as we have seen before, the dissipation terms are intimately related to the calortropy production in the system. A suitable method of calculating the calortropy production must be devised. The method of cumulant expansion [40,41] appears to be most suitable for the purpose. In calculating the dissipation terms the distribution function f_a is replaced by its nonequilibrium canonical form. This replacement is tantamount to the neglect of fluctuations of distribution functions from the thermodynamic branch f_a^c of the distribution functions, namely, it is assumed that the fluctuations $\delta \bar{I}$ and so forth vanish. It is important to keep this in mind. If this assumption is removed there appear fluctuation terms in the evolution equations for nonconserved variables Φ_{ka} , giving rise to generalized hydrodynamics of fluctuating variables.

To be specific about the calculation performed, we will assume that the collision integral $R[f_a]$ is given by the Boltzmann collision integral:

$$R[f_a] = \sum_{b=1}^r C(f_a f_b), \quad (7.190)$$

where $C(f_a f_b)$ has been already defined in a previous chapter; see (3.3). It is convenient to introduce some abbreviations for various quantities involved to make the calculation and formulas as concise as possible. With the definition

$$x_a = \beta \left(H_a^{(1)} - \mu_a + \mu_a^0 \right) \quad (7.191)$$

the distribution function f_a will be written as

$$f_a = f_a^0 \exp(-x_a). \quad (7.192)$$

We also define

$$x_{ab} = x_a + x_b, \quad y_{ab} = y_a + y_b = x_{ab}^*. \quad (7.193)$$

Thus, y_a is the post-collision value of x_a and so on. It is also convenient to define reduced parameters as follows:

impact parameter:

$$\bar{b} = \frac{b}{d},$$

relative speed:

$$\bar{g}_{ab} = g_{ab} \sqrt{\frac{m}{2k_B T}},$$

where d and m are a mean diameter and a mean mass of the molecules, respectively. This manner of reducing the variables is not unique and depends on the physical circumstances. For example, the impact parameter b may be reduced with $\sqrt{\sigma(E)}$ where $\sigma(E)$ is a collision cross section, and g_{ab} with a suitable speed characteristic of the system in hand. However, the material functions computed will remain invariant to the manners of reduction. We also define parameter g by the expression

$$g = \frac{1}{n^2 d^2} \sqrt{\frac{m}{2k_B T}}. \quad (7.194)$$

In addition, we define reduced equilibrium distribution functions

$$\omega_a(\mathbf{w}_a) = (2\pi)^{-3/2} \exp(-\frac{1}{2} w_a^2), \quad (7.195)$$

$$\omega_{ab}(\mathbf{w}_a, \mathbf{w}_b) = (2\pi)^{-3} \exp(-\frac{1}{2} w_a^2 - \frac{1}{2} w_b^2) \quad (7.196)$$

with $\mathbf{w}_a = \mathbf{C}_a(m_a/k_B T)^{1/2}$ and similarly for \mathbf{w}_b . The reduced collision integral is then defined by

$$\langle A \rangle_c = \int d\hat{\Gamma}_{ab} \omega_{ab}(\mathbf{w}_a, \mathbf{w}_b) A(\mathbf{w}_a, \mathbf{w}_b), \quad (7.197)$$

where the reduced volume element $d\hat{\Gamma}_{ab}$ is defined by

$$\int d\hat{\Gamma}_{ab} \dots = \int d\mathbf{w}_a \int d\mathbf{w}_b \int_0^{2\pi} d\varphi \int_0^\infty d\bar{b} \bar{b} \bar{g}_{ab} \dots \quad (7.198)$$

See (6.64) for the definition of volume element $d\Gamma_{ab}$. Since the calortropy production can be written in the form:

$$\begin{aligned}\sigma_c &= T^{-1} \sum_{a,b=1}^r \left\langle \left(H_a + H_a^{(1)} - \mu_a \right) C [f_a^0 \exp(-x_a), f_b^0 \exp(-x_b)] \right\rangle \\ &= \frac{1}{4T} \sum_{a,b=1}^r \int d\Gamma_{ab} f_a^0 f_b^0 (x_{ab} - y_{ab}) [\exp(-y_{ab}) - \exp(-x_{ab})],\end{aligned}\quad (7.199)$$

the reduced calortropy production takes the form

$$\begin{aligned}\bar{\sigma}_c &= gk_B^{-1} \sigma_c \\ &= \frac{1}{4} \sum_{a,b=1}^r \langle (x_{ab} - y_{ab}) [\exp(-y_{ab}) - \exp(-x_{ab})] \rangle_c.\end{aligned}\quad (7.200)$$

The integral on the right hand side is dimensionless. It is convenient to consider the following dimensionless quantities:

$$\mathcal{R}^{(+)}(\lambda) = \sum_{a,b=1}^r \langle (x_{ab} - y_{ab}) [\exp(-\lambda y_{ab}) - 1] \rangle_c, \quad (7.201)$$

$$\mathcal{R}^{(-)}(\lambda) = \sum_{a,b=1}^r \langle (x_{ab} - y_{ab}) [\exp(-\lambda x_{ab}) - 1] \rangle_c. \quad (7.202)$$

The parameter λ is introduced as a bookkeeping index, but it may be related to the Knudsen number introduced in Chapter 5. This parameter will be put equal to unity when the series for the integral has been appropriately resummed. The reduced calortropy production in (7.200) is cast into the form

$$\bar{\sigma}_c = \frac{1}{4} [\mathcal{R}^{(+)}(\lambda) - \mathcal{R}^{(-)}(\lambda)]_{\lambda=1}. \quad (7.203)$$

This form is now ready for expansion. The factors $\mathcal{R}^{(\pm)}(\lambda)$ can be expanded in a cumulant series as follows:

$$\mathcal{R}^{(\pm)}(\lambda) = \left(\left\langle \sum_{a,b=1}^r (x_{ab} - y_{ab})^2 \right\rangle_c \right)^{1/2} \left\{ \exp \left[\sum_{l=1}^{\infty} \frac{(-\lambda)^l}{l!} \kappa_l^{(\pm)} \right] - 1 \right\}, \quad (7.204)$$

where the leading cumulants $\kappa_l^{(\pm)}$ are given by the formulas

$$\kappa_1^{(\pm)} = \mp \kappa, \quad (7.205)$$

$$\kappa_2^{(\pm)} = \mp \frac{\kappa_2}{\kappa} - \kappa^2, \quad (7.206)$$

$$\kappa_3^{(\pm)} = \mp \frac{\kappa_3}{\kappa} - 3\kappa_2 \mp 2\kappa^3, \quad etc.. \quad (7.207)$$

Here κ , κ_2 , and κ_3 are defined, respectively, by the reduced collision integrals

$$\kappa = \frac{1}{2} \left(\left\langle \sum_{a,b=1}^r (x_{ab} - y_{ab})^2 \right\rangle_c \right)^{1/2}, \quad (7.208)$$

$$\kappa_2 = \frac{1}{4} \left\langle \sum_{a,b=1}^r (x_{ab} - y_{ab}) (x_{ab}^2 - y_{ab}^2) \right\rangle_c, \quad (7.209)$$

$$\kappa_3 = \frac{1}{4} \left\langle \sum_{a,b=1}^r (x_{ab} - y_{ab}) (x_{ab}^3 - y_{ab}^3) \right\rangle_c. \quad (7.210)$$

If these cumulant expansions are used in (7.203), there follows the reduced calortropy production in the form

$$\begin{aligned} \bar{\sigma}_c &= \frac{\kappa}{2} \left\{ \exp \left[\kappa - \frac{1}{2} \left(\frac{\kappa_2}{\kappa} + \kappa^2 \right) + \frac{1}{3!} \left(\frac{\kappa_3}{\kappa} + 3\kappa_2 + 2\kappa^3 \right) + \dots \right] \right. \\ &\quad \left. - \exp \left[-\kappa + \frac{1}{2} \left(\frac{\kappa_2}{\kappa} - \kappa^2 \right) - \frac{1}{3!} \left(\frac{\kappa_3}{\kappa} - 3\kappa_2 + 2\kappa^3 \right) + \dots \right] \right\}. \end{aligned} \quad (7.211)$$

If the cumulants of second or higher orders, namely, κ_2 , κ_3 , \dots , are neglected, the reduced calortropy production in the first-order cumulant approximation is obtained:

$$\bar{\sigma}_c = \kappa \sinh \kappa. \quad (7.212)$$

This approximate calortropy production is always positive semidefinite regardless of the approximation made for X_{qa} as will be shown later.

To the third-order cumulant approximation [9,42] which takes the terms up to κ_3 inclusive, the reduced calortropy production is given by the formula

$$\bar{\sigma}_c = \kappa \exp \left[\frac{1}{2} (\kappa_2 - \kappa^2) \right] \sinh \left(\kappa - \frac{\kappa_2}{2\kappa} + \frac{\kappa_3}{6\kappa} + \frac{\kappa^3}{3} \right). \quad (7.213)$$

It is easy to show by using (7.208)–(7.210) that

$$\kappa - \frac{\kappa_2}{2\kappa} + \frac{\kappa_3}{6\kappa} + \frac{\kappa^3}{3} \geq 0 \quad (7.214)$$

and thus the calortropy production in the third-order cumulant approximation is also positive semidefinite⁸. It is not possible to show that the calortropy production in the second-order cumulant approximation is positive.

To deduce a form of the dissipation term Λ_{qa} which is consistent with the positivity of $\bar{\sigma}_c$, we must calculate κ a little more explicitly in terms of X_{qa} . We will first show that κ can be written in the quadratic form of X_{qa}

$$\kappa^2 = \sum_{a,b=1}^r \sum_{\alpha,\gamma \geq 1} X_{\alpha a} \mathbf{R}_{ab}^{(\alpha\gamma)} X_{\gamma b}, \quad (7.215)$$

where $\mathbf{R}_{ab}^{(\alpha\gamma)}$ are coefficients which are made up of collision bracket integrals of $h_a^{(\alpha)}$ and $h_b^{(\gamma)}$. These coefficients will be worked out explicitly later, but (7.215) is sufficient for our purpose here to calculate the dissipation term Λ_{qa} . Now, by substituting (7.215) into (7.212) and (7.213) and comparing the resulting equation with the formula for the calortropy production given in terms of the dissipation terms

$$\sigma_c = T^{-1} \sum_{a=1}^r \sum_{\alpha \geq 1} X_{\alpha a} \Lambda_{\alpha a}, \quad (7.216)$$

we identify the dissipation term:

$$\Lambda_{\alpha a} = (\beta g)^{-1} \sum_{b=1}^r \sum_{\gamma \geq 1} \mathbf{R}_{ab}^{(\alpha\gamma)} X_{\gamma b} q(X), \quad (7.217)$$

where

$$q(X) = \begin{cases} \kappa^{-1} \sinh \kappa \\ \kappa^{-1} \exp \left[\frac{1}{2} (\kappa_2 - \kappa^2) \right] \sinh \left(\kappa - \frac{1}{2} \kappa_2 \kappa^{-1} + \frac{1}{6} \kappa_3 \kappa^{-1} + \frac{1}{3} \kappa^3 \right). \end{cases} \quad (7.218)$$

⁸To prove the positivity it is sufficient to show

$$6\kappa^2 + \kappa_3 - 3\kappa_2 \geq 0.$$

We show the integrand of the left-hand side is positive. It is a sum of the following form

$$(x - y)^2 (6 + x^2 + y^2 + xy - 3x - 3y).$$

The second factor can be rearranged to the form

$$\frac{1}{2} (X^2 + Y^2) + \frac{1}{2} (X + Y)^2 + 3 \geq 0,$$

where $X = x - 1$ and $Y = y - 1$. This proves the desired inequality.

The first of (7.218) is for the first-order cumulant approximation, whereas the second is for the third-order cumulant approximation. Except for the calculation of the collision bracket integrals $\mathbf{R}_{ab}^{(\alpha\gamma)}$ and the nonequilibrium partition function, the nonequilibrium ensemble method is now complete, in that it has provided balance equations for conserved variables and thermodynamically consistent constitutive equations for fluxes since $\mathcal{Z}_{\alpha a}$ and $\Lambda_{\alpha a}$ are now given in terms of the variables in the space \mathfrak{P} and the generalized potentials.

7.8 Generalized Hydrodynamics Equations

We now summarize approximate, but thermodynamically consistent, generalized hydrodynamics equations [9] which consist of the balance equations for conserved variables and the constitutive equations (evolution equations) for nonconserved variables. They are:

$$\rho \frac{dv}{dt} = \nabla \cdot \mathbf{u}, \quad (7.219)$$

$$\rho \frac{dc_a}{dt} = -\nabla \cdot \mathbf{J}_a, \quad (7.220)$$

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla \cdot \mathbf{P} + \sum_{a=1}^r \rho_a \mathbf{F}_a, \quad (7.221)$$

$$\rho \frac{d\mathcal{E}}{dt} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a, \quad (7.222)$$

$$\begin{aligned} \rho \frac{d\hat{\Phi}_{1a}}{dt} &= -\nabla \cdot \psi_{1a} - 2[\mathbf{J}_a(d_t \mathbf{u} - \mathbf{F}_a)]^{(2)} - 2[\boldsymbol{\Pi}_a \cdot \nabla \mathbf{u}]^{(2)} \\ &\quad - 2\Delta_a [\nabla \mathbf{u}]^{(2)} - \frac{2}{3}\boldsymbol{\Pi}_a \nabla \cdot \mathbf{u} - 2p_a [\nabla \mathbf{u}]^{(2)} \\ &\quad + (\beta g)^{-1} \sum_{\gamma \geq 1} \sum_{b=1}^r \mathbf{R}_{ab}^{(1\gamma)} X_{\gamma b} q(X), \end{aligned} \quad (7.223)$$

$$\begin{aligned} \rho \frac{d\hat{\Phi}_{2a}}{dt} &= -\nabla \cdot \psi_{2a} - \frac{2}{3}\mathbf{J}_a \cdot (d_t \mathbf{u} - \mathbf{F}_a) - \frac{2}{3}\boldsymbol{\Pi}_a : \nabla \mathbf{u} \\ &\quad - \frac{2}{3}\Delta_a \nabla \cdot \mathbf{u} - p_a d_t \ln(p_a v^{5/3}) - \nabla \cdot \left(\frac{p_a}{\rho_a} \mathbf{J}_a \right) \end{aligned}$$

$$+ (\beta g)^{-1} \sum_{\gamma \geq 1} \sum_{b=1}^r \mathbf{R}_{ab}^{(2\gamma)} X_{\gamma b} q(X), \quad (7.224)$$

$$\begin{aligned} \rho \frac{d\hat{\Phi}_{3a}}{dt} = & - \nabla \cdot \psi_{3a} - (d_t \mathbf{u} - \mathbf{F}_a) \cdot (\mathbf{P}_a - p_a \boldsymbol{\delta}) - \varphi_a^{(3)} : \nabla \mathbf{u} \\ & - \mathbf{Q}'_a \cdot \nabla \mathbf{u} - \mathbf{J}_a d_t \hat{h}_a - \mathbf{P}_a \cdot \nabla \hat{h}_a \end{aligned}$$

$$+ (\beta g)^{-1} \sum_{\gamma \geq 1} \sum_{b=1}^r \mathbf{R}_{ab}^{(3\gamma)} X_{\gamma b} q(X), \quad (7.225)$$

$$\begin{aligned} \rho \frac{d\hat{\Phi}_{4a}}{dt} = & - \nabla \cdot \mathbf{P}_a - \rho_a (d_t \mathbf{u} - \mathbf{F}_a) - \mathbf{J}_a \cdot \nabla \mathbf{u} \\ & + (\beta g)^{-1} \sum_{\gamma \geq 1} \sum_{b=1}^r \mathbf{R}_{ab}^{(4\gamma)} X_{\gamma b} q(X), \quad etc.. \end{aligned} \quad (7.226)$$

Here it must be recalled that $X_{\gamma a}$ are functions of $\{\Phi_{qa} : q \geq 1\}$ as shown in the previous section. The parameter g is defined in (7.194). These equations unfortunately form an open set since they are coupled to the evolution equations for higher order moments. For this reason this set must be suitably closed by means of closure relations. However, a general method of closure is not available at present. This is closely related to the absence of the rate of convergence of the moment expansion or the expansion in the nonequilibrium canonical form. Under the circumstances, it is only possible to resort to an empirical method in which the utility of a truncation of the expansion is tested by its ability to account for experimental data available at present. The conventional way of closing the open hierarchy of evolution equations is to limit the number of moments to thirteen in the case of a single component system and 13 plus the number of independent diffusion fluxes in the case of a mixture and then use the Grad thirteen moment expansion—*i.e.*, (7.10) limited to the first thirteen moments plus the diffusion fluxes—to compute the higher-order moments. These closures have difficulty when the theory is applied to shock wave problems, for example. In this work we take the closures

$$\psi_{qa} = 0 \quad (q \geq 1, q \neq 4). \quad (7.227)$$

We will further examine the closure problem when the theory of transport processes based on the generalized hydrodynamics equations is discussed later. If the results given in (7.185) are used in the constitutive equations in (7.223)–(7.226) and if the nonlinear factor $q(X)$ is set equal to unity in the limit of sufficiently small Φ_{qa} , the constitutive equations become linear with respect to Φ_{qa} :

$$\Phi_{1a} = \Pi_a; \quad \Phi_{2a} = \Delta_a; \quad \Phi_{3a} = \mathbf{Q}'_a; \quad \Phi_{4a} = \mathbf{J}_a,$$

for the leading moments. In view of the linearization introduced into the dissipation terms, it is reasonable to drop the nonlinear terms in the constitutive equations and, at the level of the 13 moment approximation, to neglect the higher order moments. We then obtain the constitutive equations in easily recognizable forms:

$$\rho \frac{d\hat{\Phi}_{1a}}{dt} = -2p_a[\nabla \mathbf{u}]^{(2)} - (\beta g)^{-1} \sum_{\gamma \geq 1} \sum_{b=1}^r \mathbf{R}_{ab}^{(1\gamma)} \Phi_{\gamma b} g_b^{(\gamma)}, \quad (7.228)$$

$$\rho \frac{d\hat{\Phi}_{2a}}{dt} = -p_a d_t \ln(p_a v^{5/3}) - (\beta g)^{-1} \sum_{\gamma \geq 1} \sum_{b=1}^r \mathbf{R}_{ab}^{(2\gamma)} \Phi_{\gamma b} g_b^{(\gamma)}, \quad (7.229)$$

$$\rho \frac{d\hat{\Phi}_{3a}}{dt} = -p_a \hat{C}_p T \nabla \ln T - (\beta g)^{-1} \sum_{\gamma \geq 1} \sum_{b=1}^r \mathbf{R}_{ab}^{(3\gamma)} \Phi_{\gamma a} g_b^{(\gamma)}, \quad (7.230)$$

$$\begin{aligned} \rho \frac{d\hat{\Phi}_{4a}}{dt} &= -p \mathbf{d}_a + \rho_a (\mathbf{F}_a - \mathbf{F}) \\ &\quad - (\beta g)^{-1} \sum_{\gamma \geq 1} \sum_{b=1}^r \mathbf{R}_{ab}^{(4\gamma)} \Phi_{\gamma b} g_b^{(\gamma)}, \end{aligned} \quad (7.231)$$

where $\mathbf{F} = \sum_{a=1}^r c_a \mathbf{F}_a$ and

$$\mathbf{d}_a = \nabla \left(\frac{n_a}{n} \right) + \left(\frac{n_a}{n} - \frac{\rho_a}{\rho} \right) \nabla \ln p, \quad (7.232)$$

$$g_a^{(1)} = \frac{1}{2p_a}; \quad g_a^{(2)} = \frac{3}{2p_a}; \quad g_a^{(3)} = \frac{1}{p_a \hat{C}_p T}; \quad g_a^{(4)} = \frac{1}{\rho_a}, \quad (7.233)$$

with \hat{C}_p denoting the specific heat per molecule at constant pressure. The stress tensor evolution equation (7.228) is the multi-component version of the Maxwell equation for the stress tensor originally obtained by Maxwell [37] in his kinetic theory. The evolution equation for the heat flux \mathbf{Q}'_a is the multi-component and molecular version of the Cattaneo–Vernotte equation phenomenologically postulated by Cattaneo [38] and Vernotte [39], but it must be recognized that it was also a transfer equation used by Maxwell in his kinetic theory which gives rise to heat conductivity. We remark that the first terms on the right hand side of the constitutive equations (7.228)–(7.231) are thermodynamic forces that drive the respective fluxes and thus the irreversible processes. They appear in the linear theory of irreversible processes. Therefore we see that the constitutive equations presented earlier are intimately related to the transport processes in gases since they are driven by the same thermodynamic forces. In the case of dilute monatomic

gases the excess trace of the normal stress $\Phi_{2a} = \Delta_a$ vanishes since $p_a = \frac{1}{3}\text{Tr}\mathbf{P}_a$. In this case there also holds the relation $pv^{5/3} = \text{constant}$ (for an adiabatic process) as is well known. Therefore the constitutive equation for Φ_{2a} can be ignored. The vanishing Δ_a means that there is no bulk viscosity. We remark that the bulk viscosity is intimately related to the notion of temperature in kinetic theory of matter.

7.9 Collision Bracket Integrals

In kinetic theory the molecular information, and especially the information on molecular constitutions and interactions, is contained in the collision integral $R[f_a]$ and consequently in the collision bracket integrals. Since the latter serve as the bridge between the microscopic world of molecules and the macroscopic processes occurring in the fluid, a kinetic theory investigation necessarily gives rise to the question of how the collision bracket integrals may be calculated. Since their calculations in terms of molecular interaction potentials are well described in the existing monographs on kinetic theory of gases in the literature, we will not delve into the question here. In this work we simply connect the collision bracket integrals to transport coefficients measured in the laboratory and thereby set up generalized hydrodynamics equations in terms of such observables. This way, we will be able to obtain molecular theoretical hydrodynamic equations which can be used for hydrodynamic computations. Under this motivation we now return to $\mathbf{R}_{ab}^{(\alpha\gamma)}$ introduced earlier.

Since x_a appearing in κ consists of a sum of various moments

$$x_a = \beta \sum_{\alpha \geq 1} X_{\alpha a} h_a^{(\alpha)} - \gamma_a, \quad (7.234)$$

$$\gamma_a = \beta (\mu_a - \mu_a^0), \quad (7.235)$$

κ^2 may be written as

$$\kappa^2 = \frac{1}{4} \sum_{a,b=1}^r \sum_{\alpha,\gamma \geq 1} \left\langle \left(X_{\alpha a} \Delta h_a^{(\alpha)} + X_{\alpha b} \Delta h_b^{(\alpha)} \right) \left(X_{\gamma a} \Delta h_a^{(\gamma)} + X_{\gamma b} \Delta h_b^{(\gamma)} \right) \right\rangle_c \quad (7.236)$$

with the definition

$$\Delta h_a^{(\alpha)} = h_a^{(\alpha)} - h_a^{(\alpha)*}, \quad \text{etc.}$$

This is a quadratic form of $X_{\alpha a}$ and $X_{\gamma b}$ which on rearrangement of the terms may be written as in (7.215). It is convenient to define abbreviations for the collision bracket integrals as follows: with the definition

$$\Delta A_a = A_a - A_a^*, \quad \text{etc.},$$

$$[A_a B_a]_{ab} = \frac{n_a n_b}{4n^2} \int d\hat{\Gamma}_{ab} \omega_{ab}(\mathbf{w}_a, \mathbf{w}_b) (\Delta A_a + \Delta A_b)(\Delta B_a + \Delta B_b), \quad (7.237)$$

$$[A_a B_a]'_{ab} = \frac{n_a n_b}{2n^2} \int d\hat{\Gamma}_{ab} \omega_{ab}(\mathbf{w}_a, \mathbf{w}_b) \Delta A_a \Delta B_a, \quad (7.238)$$

$$[A_a B_b]''_{ab} = \frac{n_a n_b}{2n^2} \int d\hat{\Gamma}_{ab} \omega_{ab}(\mathbf{w}_a, \mathbf{w}_b) \Delta A_a \Delta B_b, \quad (7.239)$$

With these abbreviations for the collision bracket integrals, one can then show that for an isotropic system the tensor $\mathbf{R}_{ab}^{(\alpha\gamma)}$ reduces to a scalar coefficient $R_{ab}^{(\alpha\gamma)}$. We may thus write

$$\mathbf{R}_{ab}^{(\alpha\gamma)} X_{\gamma b} = R_{ab}^{(\alpha\gamma)} X_{\gamma b}. \quad (7.240)$$

Here scalar coefficients $R_{ab}^{(\alpha\gamma)}$ are given by the collision bracket integrals

$$R_{aa}^{(11)} = \frac{1}{5} \beta^2 \left[h_a^{(1)} : h_a^{(1)} \right]_{aa'} + \sum_{a \neq b}^r \left[h_a^{(1)} : h_a^{(1)} \right]_{ab}', \quad (7.241)$$

$$R_{ab}^{(11)} = \frac{1}{5} \beta^2 \left[h_a^{(1)} : h_b^{(1)} \right]_{ab}'' \quad (a \neq b), \quad (7.242)$$

$$R_{aa}^{(22)} = \beta^2 \left[h_a^{(2)} h_a^{(2)} \right]_{aa'} + \sum_{a \neq b}^r \left[h_a^{(2)} h_a^{(2)} \right]_{ab}', \quad (7.243)$$

$$R_{ab}^{(22)} = \beta^2 \left[h_a^{(2)} h_b^{(2)} \right]_{ab}'' \quad (a \neq b), \quad (7.244)$$

$$R_{aa}^{(\alpha\gamma)} = \frac{1}{3} \beta^2 \left[h_a^{(\alpha)} \cdot h_a^{(\gamma)} \right]_{aa'} + \sum_{a \neq b}^r \left[h_a^{(\alpha)} \cdot h_a^{(\gamma)} \right]_{ab}', \quad (7.245)$$

$$R_{ab}^{(\alpha\gamma)} = \frac{1}{3} \beta^2 \left[h_a^{(\alpha)} \cdot h_b^{(\gamma)} \right]_{ab}'' \quad (a \neq b; \alpha, \gamma = 3, 4). \quad (7.246)$$

In these expressions the prime on the subscript a means another particle of the species a . The collision bracket integrals for other moments may be written similarly, but they are omitted because they will not be used in this work. The collision bracket integrals appearing in (7.241)–(7.246) are sufficient for studying transport coefficients, linear and nonlinear, in this work. These coefficients $R_{ab}^{(\alpha\gamma)}$ satisfy the Onsager reciprocal relations [43]:

$$R_{ab}^{(\alpha\gamma)} = R_{ba}^{(\alpha\gamma)}, \quad R_{ab}^{(\alpha\gamma)} = R_{ab}^{(\gamma\alpha)}. \quad (7.247)$$

These symmetry relations are a direct consequence of the symmetry properties of the Boltzmann collision integral, the most important being the

microscopic reversibility. On using (7.240) in the expression for the dissipation term (7.217) we obtain the dissipation term for an isotropic system

$$\Lambda_{\alpha a} = (\beta g)^{-1} \sum_{b=1}^r \sum_{\gamma \geq 1} R_{ab}^{(\alpha\gamma)} X_{\gamma b} q(X), \quad (7.248)$$

which replaces the dissipation terms in the constitutive equations for fluxes (7.223)–(7.226) and (7.228)–(7.231). The resulting constitutive equations are for an isotropic system of dilute gases.

One thing remarkable at this point is that although the collision bracket integrals presented here are basically those appearing in the Chapman–Enskog first approximation [44,45] and therefore related to linear transport coefficients as will be shown later, the constitutive equations with (7.248) as their dissipation term are capable of describing nonlinear transport processes occurring in systems far removed from equilibrium. This will be shown in Chapter 8. Therefore the information provided by linear transport processes enables us to construct a theory of nonlinear transport processes even in the absence of the collision bracket integrals for the higher order approximations such as the Burnett solutions in the Chapman–Enskog method [44,45]. This is because of the cumulant approximation used for the calortropy production, which provides a resummation procedure for an expansion in the Knudsen number series of the Boltzmann collision integral. As a resummation of such a series, the dissipation term in (7.248) is expected to hold in the regime of Knudsen numbers higher than those for the Chapman–Enskog first approximation. We will have further discussions on this point in Chapter 8.

The formal expressions for the collision bracket integrals presented earlier should be worked out in more detail if one desires to relate the transport coefficients given in terms of them to intermolecular forces. Actual explicit integrations of the collision bracket integrals in terms of temperature and molecular parameters would require information on the collision cross section involved in the dynamical process. Since there are excellent treatments available for this aspect in the literature [46,47], we will not dwell on them. Instead we will put the collision bracket integrals presented in (7.241)–(7.246) in forms readily comparable with those in the literature so that the results available for them can be directly used in the present context. To this end we scale the reduced velocity \mathbf{w}_a with $\sqrt{2}$ so that $\boldsymbol{\tau}_a = \mathbf{w}_a/\sqrt{2}$. We then express the set $\{h_a^{(k)} : k \geq 1\}$ in terms of $\boldsymbol{\tau}_a$ as follows:

$$h_a^{(1)} = \frac{2}{\beta} [\boldsymbol{\tau}_a \boldsymbol{\tau}_a]^{(2)}, \quad (7.249)$$

$$h_a^{(2)} = \frac{2}{\beta} (\boldsymbol{\tau}_a^2 - \frac{3}{2}), \quad (7.250)$$

$$\begin{aligned} h_a^{(3)} &= \beta^{-1} \sqrt{\frac{2}{\beta m_a}} (\tau_a^2 - \frac{5}{2}) \boldsymbol{\tau}_a \\ &= -\beta^{-1} \sqrt{\frac{2}{\beta m_a}} S_{3/2}^{(1)}(\tau_a^2) \boldsymbol{\tau}_a, \end{aligned} \quad (7.251)$$

$$h_a^{(4)} = \sqrt{\frac{2m_a}{\beta}} \boldsymbol{\tau}_a, \quad (7.252)$$

where $S_{3/2}^{(1)}(\boldsymbol{\tau}_a)$ is a Sonine polynomial defined earlier. Substitution of $h_a^{(q)}$ given in (7.249)–(7.252) yields the collision bracket integrals in more familiar forms in Table 7.2. We now see that these collision bracket integrals are basically those appearing in the Chapman–Cowling first approximations for linear transport coefficients in Chapter 6. Therefore it is expected that the steady state solutions of the constitutive equations (7.228)–(7.231) would yield the linear transport coefficients in the Chapman–Cowling first approximation. This will be discussed in the next chapter.

Table 7.2 Collision Bracket Integrals for the Leading Moments

$$\begin{aligned} R_{aa}^{(11)} &= \frac{4}{5} \{ [[\boldsymbol{\tau}_a \boldsymbol{\tau}_a]^{(2)} : [\boldsymbol{\tau}_a \boldsymbol{\tau}_a]^{(2)}]_{aa'} + \sum_{a \neq b} [[\boldsymbol{\tau}_a \boldsymbol{\tau}_a]^{(2)} : [\boldsymbol{\tau}_a \boldsymbol{\tau}_a]^{(2)}]_{ab}' \} \\ R_{ab}^{(11)} &= \frac{4}{5} [[\boldsymbol{\tau}_a \boldsymbol{\tau}_a]^{(2)} : [\boldsymbol{\tau}_b \boldsymbol{\tau}_b]^{(2)}]_{ab}'' \quad (a \neq b) \\ R_{aa}^{(33)} &= \frac{2}{3} (\beta m_a)^{-1} \{ [S_{3/2}^{(1)}(\tau_a^2) \boldsymbol{\tau}_a \cdot S_{3/2}^{(1)}(\tau_a^2) \boldsymbol{\tau}_a]_{aa'} \\ &\quad + \sum_{a \neq b} [S_{3/2}^{(1)}(\tau_a^2) \boldsymbol{\tau}_a \cdot S_{3/2}^{(1)}(\tau_a^2) \boldsymbol{\tau}_a]_{ab}' \} \\ R_{ab}^{(33)} &= \frac{2}{3} (\beta \sqrt{m_a m_b})^{-1} [S_{3/2}^{(1)}(\tau_a^2) \boldsymbol{\tau}_a \cdot S_{3/2}^{(1)}(\tau_b^2) \boldsymbol{\tau}_b]_{ab}'' \\ R_{aa}^{(44)} &= \frac{2}{3} \sqrt{m_a m_b} \beta \{ [\boldsymbol{\tau}_a \cdot \boldsymbol{\tau}_a]_{aa'} + \sum_{a \neq b} [\boldsymbol{\tau}_a \cdot \boldsymbol{\tau}_a]_{ab}' \} \\ R_{ab}^{(44)} &= \frac{2}{3} \sqrt{m_a m_b} \beta [\boldsymbol{\tau}_a \cdot \boldsymbol{\tau}_a]_{ab}'' \\ R_{aa}^{(34)} &= R_{aa}^{(43)} = -\frac{2}{3} \{ [S_{3/2}^{(1)}(\tau_a^2) \boldsymbol{\tau}_a \cdot \boldsymbol{\tau}_a]_{aa'} + \sum_{a \neq b} [S_{3/2}^{(1)}(\tau_a^2) \boldsymbol{\tau}_a \cdot \boldsymbol{\tau}_a]_{ab}' \} \\ R_{ab}^{(34)} &= R_{ba}^{(43)} = -\frac{2}{3} [S_{3/2}^{(1)}(\tau_a^2) \boldsymbol{\tau}_a \cdot \boldsymbol{\tau}_b]_{ab}'' \end{aligned}$$

7.10 Nonequilibrium Partition Function

Formulation of an ensemble method for nonequilibrium systems has now been achieved. Various nonequilibrium thermodynamic variables are expressed in terms of the nonequilibrium partition function in a way completely parallel with the statistical formulas for equilibrium thermodynamic variables in the equilibrium Gibbs ensemble method [2,3]. There now remains the task of calculating the nonequilibrium partition function in a sufficiently general context so that it may be used to calculate various nonequilibrium thermodynamic functions for systems in nonequilibrium conditions. As is the case for equilibrium partition functions of interacting particle systems, the nonequilibrium partition function, however, cannot be calculated exactly in a closed form in a general situation even if the gases are ideal. This situation is in contrast to the case of equilibrium ideal gases for which the partition function can be calculated in a closed form. Consequently one must resort to an approximate method to calculate the nonequilibrium partition function. It is the purpose in this section to present some approximation methods and show that in the lowest order approximation they reduce to the previously used generalized potentials which were deduced by a less precise method, namely, the so-called consistency condition, or its variation used in the early versions of the modified moment method [7–10]. To prepare for the discussion we first define some notations and necessary quantities. First of all, we use the tensor Hermite polynomial representation for the moments taken and consequently the nonequilibrium part in the nonequilibrium canonical form will be expressed in terms of them, since a mathematically more precise procedure can be devised thereby. The macroscopic nonconserved variables $\Theta_a^{(k)}$ will be changed to the symbol $\Theta_{ka} \equiv \rho\hat{\Theta}_{ka}$ for notational brevity and the corresponding variables multiplied by V will be denoted by $\Theta_a^v \equiv V\rho\hat{\Theta}_{ka}$. The thermodynamic variable set will then be denoted by $\mathfrak{P}_h \equiv (\mathcal{E}, v, c_a, \hat{\Theta}_{ka} : k \geq 1, r \geq a \geq 1)$ and the space corresponding to Θ_a^v by $\mathfrak{P}_g \equiv (E, V, N_a, \Theta_a^v : k \geq 1, r \geq a \geq 1)$ which is obtained by multiplying the former with $V\rho$. Here the subscript a denotes the species as before. The subscript k denotes the tensorial rank of the variable. The nonequilibrium partition function Z_a is then defined by

$$Z_a = n_a^{-1} \left\langle \exp \left\{ -\beta \left[H_a + \sum_{k \geq 1} Y_{ka} \mathcal{H}^{(k)}(\mathbf{w}_a) \right] \right\} \right\rangle \quad (7.253)$$

in the notation familiar by now. The Y_{ka} are the generalized potentials conjugate to the nonconserved variables Θ_{ka}^v (e.g., fluxes) and generally functions of the nonconserved variables as well as the conserved variables. Note that we have used the symbol $Y_a^{(k)}$ for Y_{ka} in the previous sections, but the notation is changed to make it consistent with the change just made for $\Theta_a^{(k)}$. In the case of noninteracting and field-free dilute gases considered here, the Hamiltonian is simply the kinetic energy of a particle: $H_a =$

$\frac{1}{2}m_a C_a^2$. Eq. (7.253) suggests that the nonequilibrium chemical potential (the normalization factor of the nonequilibrium canonical form) μ_a can be written as

$$\mu_a = m_a \hat{\mu}_a = -\beta^{-1} \ln \mathbb{Z}_a. \quad (7.254)$$

The total nonequilibrium partition function for the r -component mixture is then given by the product of nonequilibrium partition functions of r species

$$\mathbb{Z} = \prod_{a=1}^r \mathbb{Z}_a^{N_a}, \quad (7.255)$$

which gives the various thermodynamic quantities given in (7.76)–(7.79).

Since the aforementioned formal expressions for nonequilibrium thermodynamic variables are given in terms of the nonequilibrium partition function \mathbb{Z} and the aim of the ensemble theory is to express thermodynamic functions in terms of the variables in the set \mathfrak{P}_h , the calculation of \mathbb{Z} becomes an important task. As mentioned earlier, since it cannot be calculated exactly in a closed form it is necessary to develop approximation methods for it. In this section a few methods of approximation are discussed which recover the lowest order approximation for the generalized potentials obtained by a different route in the formulation of theory of irreversible processes and used in various studies [7–10] of transport processes we have made previously.

If the integral in the nonequilibrium partition function \mathbb{Z}_a is cast in nondimensional reduced variables, it takes the form

$$\mathbb{Z}_a = \left(\frac{2\pi k_B T}{m_a} \right)^{3/2} n_a^{-1} \mathbb{K}_a, \quad (7.256)$$

where \mathbb{K}_a is given by the integral

$$\mathbb{K}_a = (2\pi)^{-3/2} \int dw_a \exp(-\frac{1}{2}w_a^2) \exp \left[- \sum_{k \geq 1} \bar{Y}_{ka} \mathcal{H}^{(k)}(\mathbf{w}_a) \right] \quad (7.257)$$

with $\bar{Y}_{ka} = Y_{ka}/k_B T$. This integral is dimensionless. The tensor Hermite polynomials are also dimensionless and so are \bar{Y}_{ka} . Henceforth the integral over the reduced velocity \mathbf{w}_a will be abbreviated by angular brackets $\langle \dots \rangle$. Thus we write

$$\mathbb{K}_a = \left\langle \omega(\mathbf{w}_a) \exp \left[- \sum_{k \geq 1} \bar{Y}_{ka} \mathcal{H}^{(k)}(\mathbf{w}_a) \right] \right\rangle. \quad (7.258)$$

Since the equilibrium partition function, or more precisely, the equilibrium

partition function divided by N_a , is⁹

$$\mathbb{Z}_a^0 = \left(\frac{2\pi k_B T}{m_a} \right)^{3/2} n_a^{-1}, \quad (7.259)$$

\mathbb{K}_a clearly is the nonequilibrium part of the partition function in question.

7.10.1 Expansion Method

The nonequilibrium part \mathbb{K}_a of the partition function in (7.258) can be calculated by expanding the exponential into a series, repeatedly applying the addition theorem (5.24) of the tensor Hermite polynomials, and using their orthogonality relations presented in Chapter 5. The general formula is rather complicated and lacks insight even if it is obtained after a tedious process of calculation. This expansion method would not be suitable in practice if the series does not converge sufficiently fast, but gives the lower order results rather quickly in agreement with the approximate result used in the previous work [25–35] on irreversible processes and also given in (7.185). By expanding the right hand side of (7.258), we obtain

$$\begin{aligned} \mathbb{K}_a &= 1 + \sum_{m=1}^{\infty} \frac{(-1)^m}{m!} \sum_{k_1 \geq 1} \cdots \sum_{k_m \geq 1} \bar{Y}_{k_1 a} \cdots \bar{Y}_{k_m a} \langle \mathcal{H}^{(k_1)} \cdots \mathcal{H}^{(k_m)} \omega(\mathbf{w}_a) \rangle \\ &= 1 + \frac{1}{2} \sum_{k \geq 1} \bar{Y}_{ka} \bar{Y}_{ka} \delta^2 + \text{third and higher order terms.} \end{aligned} \quad (7.260)$$

Therefore, to first order in the expansion, the nonequilibrium partition function is given by

$$\mathbb{Z}_a \approx \mathbb{Z}_a^0 \left(1 + \frac{1}{2} \sum_{k \geq 1} \bar{Y}_{ka} \bar{Y}_{ka} \delta^2 \right). \quad (7.261)$$

To this order of approximation we therefore obtain

$$\Theta_{ka}^v = - \left(1 + \frac{1}{2} \sum_{k \geq 1} \bar{Y}_{ka} \bar{Y}_{ka} \delta^2 \right)^{-1} \frac{\partial}{\partial \bar{Y}_{ka}} \frac{1}{2} \sum_{k \geq 1} \bar{Y}_{ka} \bar{Y}_{ka} \delta^2. \quad (7.262)$$

from which we can recover the linear relation between Θ_{ka}^v and \bar{Y}_{ka} used in (7.185), for example, if the second term in the denominator in (7.262)

⁹To make \mathbb{Z}_a^0 dimensionless and coincide with the partition function of the equilibrium ideal gas, it is necessary to insert h^2 in the denominator within the radical in (7.256) and (7.259). However, we will leave them as they stand because the factor h^2 is of no consequence to the question addressed in this work.

is neglected. In fact, to be consistent with the approximation taken for the nonequilibrium partition function in (7.261) it is appropriate to neglect the aforementioned second term in the denominator since $\|\bar{Y}_{ka}\|$ should be small for (7.262) to be sufficiently accurate. Thus we obtain

$$\Theta_{ka}^v = - \frac{\partial}{\partial \bar{Y}_{ka}} \frac{1}{2} \sum_{k \geq 1} \bar{Y}_{ka} \bar{Y}_{ka} \delta^2. \quad (7.263)$$

The generalized potentials are linear in \bar{Y}_{ka} in this approximation. To be more explicit, we write out the leading terms in the second and third order terms below:

$$\frac{1}{2} \sum_{k \geq 1} \bar{Y}_{ka} \bar{Y}_{ka} \delta^2 = \frac{1}{2} \bar{Y}_{1a} \cdot \bar{Y}_{1a} + \bar{Y}_{2a} : \bar{Y}_{2a} + \frac{9}{2} \bar{Y}_{3ajj} \cdot \bar{Y}_{3akk} + \dots,$$

$$\begin{aligned} \text{third order term} = & - [\bar{Y}_{1a} \bar{Y}_{1a} : \bar{Y}_{2a} + 7(\bar{Y}_{1a} \cdot \bar{Y}_{2a}) \cdot \bar{Y}_{3akk} \\ & + 3(\bar{Y}_{1a} \bar{Y}_{2a}) \odot^3 \bar{Y}_{3a} + \frac{4}{3}(\bar{Y}_{2a} \cdot \bar{Y}_{2a}) \odot^2 \bar{Y}_{2a} \\ & + c_1(\bar{Y}_{2a} \cdot \bar{Y}_{3a}) \odot^3 \bar{Y}_{3a} + c_2(\bar{Y}_{2a} \bar{Y}_{3akk}) \odot^3 \bar{Y}_{3a} + \dots]. \end{aligned}$$

Here the repeated subscripts such as jj and kk mean the trace in the Einstein convention and c_1 and c_2 are certain numerical coefficients. The symbol \odot^3 means the triple scalar product of third rank tensors. The higher order terms can be evaluated similarly, but become progressively more complicated.

7.10.2 Cumulant Method

We can try to improve the simple expansion method discussed in the previous subsection by performing a suitable resummation. The cumulant expansion method [40,41] appears to be suitable for the purpose. The nonequilibrium part \mathbb{K}_a in (7.258) can be expressed in terms of cumulants κ_m as follows:

$$\begin{aligned} \mathbb{K}_a &= \left\langle \omega(\mathbf{w}_a) \exp \left[- \sum_{k \geq 1} \bar{Y}_{ka} \mathcal{H}^{(k)}(\mathbf{w}_a) \right] \right\rangle \\ &= \exp \left(\sum_{m=1}^{\infty} \frac{(-1)^m}{m!} \kappa_m \right). \end{aligned} \quad (7.264)$$

The leading cumulants are easily found to be in the forms

$$\kappa_1 = 0,$$

$$\begin{aligned}\kappa_2 &= \sum_{q \geq 1} \sum_{p \geq 1} \bar{Y}_{qa} \bar{Y}_{pa} \left\langle \omega(\mathbf{w}_a) \mathcal{H}^{(q)} \mathcal{H}^{(p)} \right\rangle, \\ \kappa_3 &= \sum_{q \geq 1} \sum_{p \geq 1} \sum_{r \geq 1} \bar{Y}_{qa} \bar{Y}_{pa} \bar{Y}_{ra} \left\langle \omega(\mathbf{w}_a) \mathcal{H}^{(q)} \mathcal{H}^{(p)} \mathcal{H}^{(r)} \right\rangle, \quad \text{etc..}\end{aligned}\quad (7.265)$$

Working out these cumulants by using the orthogonality and addition theorem of the polynomials, we find that they are the same as the second and third order terms appearing in the expansion method, namely,

$$\begin{aligned}\frac{1}{2} \kappa_2 &= \frac{1}{2} \bar{Y}_{1a} \cdot \bar{Y}_{1a} + \bar{Y}_{2a} : \bar{Y}_{2a} + \frac{9}{2} \bar{Y}_{3ajj} \cdot \bar{Y}_{3akk} \\ &\quad + 3 \bar{Y}_{3a} \odot^3 \bar{Y}_{3a} + \dots\end{aligned}\quad (7.266)$$

$$\begin{aligned}\frac{1}{3!} \kappa_3 &= - [\bar{Y}_{1a} \bar{Y}_{1a} : \bar{Y}_{2a} + 7(\bar{Y}_{1a} \cdot \bar{Y}_{2a}) \cdot \bar{Y}_{3akk} \\ &\quad + 3(\bar{Y}_{1a} \bar{Y}_{2a}) \odot^3 \bar{Y}_{3a} + \frac{4}{3}(\bar{Y}_{2a} \cdot \bar{Y}_{2a}) \odot^2 \bar{Y}_{2a} \\ &\quad + c_1(\bar{Y}_{2a} \cdot \bar{Y}_{3a}) \odot^3 \bar{Y}_{3a} + c_2(\bar{Y}_{2a} \bar{Y}_{3akk}) \odot^3 \bar{Y}_{3a} + \dots].\end{aligned}\quad (7.267)$$

Therefore the cumulant sum is simply an exponentiation of the expansion (7.260), and we find

$$\Theta_{ka}^v = - \frac{\partial}{\partial \bar{Y}_{ka}} \sum_{m=2}^{\infty} \frac{(-1)^m}{m!} \kappa_m. \quad (7.268)$$

To the order of κ_2 this result agrees with the previously used approximation for the generalized potentials and with (7.263). Consequently we see that at a low order approximation the expansion method or the method of cumulants does not yield results for the generalized potentials which appear to be sufficient in the regime of states removed far from equilibrium.

7.10.3 Method of Differential Equations for \mathbb{K}_a

The previous two methods suggest that it would be preferable to avoid a straightforward expansion method. Since the nonequilibrium partition function is a function of generalized potentials \bar{Y}_{ka} , we examine the equation it obeys. It turns out that this method provides an exact formal result for the relations between Θ_{ka}^v and generalized potentials, but since the set of relations is open it is in practice necessary to truncate it and obtain suitable approximations for the relations.

To make the analysis simpler in notation we define $y^{(m)} \equiv \bar{Y}_{ma}$ and regard it as an element of a column vector suitably ordered. Thus various vector and tensor components for \bar{Y}_{ma} are the elements of the vector $\mathbf{y} = \{y^{(m)}\}$. This set of elements will be denoted by \mathfrak{V} . Therefore \mathbb{K}_a can be written in the form

$$\mathbb{K}_a = \left\langle \omega(\mathbf{w}_a) \exp \left(- \sum_{m \in \mathfrak{V}} y^{(m)} \mathcal{H}^{(m)} \right) \right\rangle, \quad (7.269)$$

where the tensors $\mathcal{H}^{(m)}$ are ordered in the same manner as their conjugates $y^{(m)}$. The superscript m of $\mathcal{H}^{(m)}$ and $y^{(m)}$ simultaneously indicates the rank and the component of the tensor or the vector. We will henceforth drop the subscript a denoting the species, for brevity of notation, and restore it after completing the calculation.

Differentiation of \mathbb{K} with $y^{(k)}$ yields the equation

$$\frac{\partial \mathbb{K}}{\partial y^{(k)}} = - \left\langle \omega \exp \left(- \sum_{m \in \mathfrak{V}} y^{(m)} \mathcal{H}^{(m)} \right) \mathcal{H}^{(k)} \right\rangle \quad (k \in \mathfrak{V}). \quad (7.270)$$

On using the recurrence relations for the tensor Hermite polynomials we obtain

$$\begin{aligned} \frac{\partial \mathbb{K}}{\partial y^{(k)}} &= \left\langle (\nabla_\alpha \omega) \exp \left(- \sum_{m \in \mathfrak{V}} y^{(m)} \mathcal{H}^{(m)} \right) \mathcal{H}^{(k-1)} \right\rangle \\ &\quad + \left\langle \omega \exp \left(- \sum_{m \in \mathfrak{V}} y^{(m)} \mathcal{H}^{(m)} \right) \nabla_\alpha \mathcal{H}^{(k-1)} \right\rangle. \end{aligned} \quad (7.271)$$

Here $\nabla_\alpha = \partial/\partial w_\alpha$ with α denoting a Cartesian component of \mathbf{w} . By performing integration by parts in the first term on the right, applying the recurrence relations of the polynomials, and using their addition theorem, we obtain the following:

$$\begin{aligned} \frac{\partial \mathbb{K}}{\partial y^{(k)}} &= \sum_{m \in \mathfrak{V}} y^{(m)} \delta_\alpha \left\langle \omega e^{- \sum_{n \in \mathfrak{V}} y^{(n)} \mathcal{H}^{(n)}} \mathcal{H}^{(k+m-2)} \right\rangle \\ &\quad + \sum_{m \in \mathfrak{V}} y^{(m)} \delta_\alpha \delta^1 \left\langle \omega e^{- \sum_{n \in \mathfrak{V}} y^{(n)} \mathcal{H}^{(n)}} \mathcal{H}^{(k+m-4)} \right\rangle + \dots \\ &\quad + y^{(k)} \delta_\alpha \left\langle \omega e^{- \sum_{n \in \mathfrak{V}} y^{(n)} \mathcal{H}^{(n)}} (\mathcal{H}^{(2k-2)} + \delta^1 \mathcal{H}^{(2k-4)}) \right\rangle \\ &\quad + \dots + y^{(k)} \delta_\alpha \delta^{2k-2} \left\langle \omega e^{- \sum_{n \in \mathfrak{V}} y^{(n)} \mathcal{H}^{(n)}} \right\rangle. \end{aligned} \quad (7.272)$$

The terms on the right hand side of (7.272) give either \mathbb{K} or its derivatives

multiplied by a y -dependent factor. The result can be expressed in the form

$$\frac{\partial \ln \mathbb{K}}{\partial y_{\alpha_1 \dots \alpha_k}^{(k)}} = (k-1)! y_{\alpha_1 \dots \alpha_k}^{(k)} + \sum_{m \in \mathfrak{V}} C_{\alpha_1 \dots \alpha_k \beta_1 \dots \beta_m}^{(k)} \frac{\partial \ln \mathbb{K}}{\partial y_{\beta_1 \dots \beta_m}^{(m)}}, \quad (7.273)$$

where $k \in \mathfrak{V}$ and $C_{\alpha_1 \dots \alpha_k \beta_1 \dots \beta_m}^{(k)}$ are coefficients depending on $\{\mathbf{y}^{(k)}\}$ and $\{\mathbf{y}^{(m)}\}$. This set of differential equations for $\ln \mathbb{K}$ is exact and linear with regard to the derivatives of $\ln \mathbb{K}$ since the coefficients $C_{\alpha_1 \dots \alpha_k \beta_1 \dots \beta_m}^{(k)}$ can be exactly evaluated, but the set is infinite. The leading examples are explicitly worked out and listed below:

$$\frac{\partial \ln \mathbb{K}}{\partial y_{\alpha_1}^{(1)}} = y_{\alpha_1}^{(1)} - y_{\alpha_1 \beta_1}^{(2)} \frac{\partial \ln \mathbb{K}}{\partial y_{\beta_1}^{(1)}} - y_{\alpha_1 \beta_1 \beta_2}^{(3)} \frac{\partial \ln \mathbb{K}}{\partial y_{\beta_1 \beta_2}^{(2)}} - \dots, \quad (7.274)$$

$$\begin{aligned} \frac{\partial \ln \mathbb{K}}{\partial y_{\alpha_1 \alpha_2}^{(2)}} &= y_{\alpha_1 \alpha_2}^{(2)} - y_{\alpha_2}^{(1)} \frac{\partial \ln \mathbb{K}}{\partial y_{\alpha_1}^{(1)}} \\ &\quad - \left(y_{\alpha_1 \beta_1 \alpha_2}^{(3)} + y_{\beta_1 \alpha_1 \alpha_2}^{(3)} + \dots \right) \frac{\partial \ln \mathbb{K}}{\partial y_{\beta_1}^{(1)}} \\ &\quad - \left(y_{\beta_1 \alpha_2}^{(2)} + \dots \right) \frac{\partial \ln \mathbb{K}}{\partial y_{\alpha_1 \beta_1}^{(2)}} \\ &\quad + \left(y_{\beta_1 \beta_2 \alpha_2}^{(3)} + \dots \right) \frac{\partial \ln \mathbb{K}}{\partial y_{\alpha_1 \beta_1 \beta_2}^{(3)}} - \dots, \end{aligned} \quad (7.275)$$

$$\begin{aligned} \frac{\partial \ln \mathbb{K}}{\partial y_{\alpha_1 \alpha_2 \alpha_3}^{(3)}} &= 2y_{\alpha_1 \alpha_2 \alpha_3}^{(3)} - \left(y_{\alpha_1 \alpha_3}^{(2)} \delta_{\alpha_2 \beta_1} + y_{\alpha_2 \alpha_3}^{(2)} \delta_{\alpha_1 \beta_1} + \dots \right) \frac{\partial \ln \mathbb{K}}{\partial y_{\beta_1}^{(1)}} \\ &\quad - \left(y_{\alpha_1 \beta_2 \alpha_3}^{(3)} \delta_{\alpha_2 \beta_1} + y_{\beta_1 \alpha_1 \alpha_3}^{(3)} \delta_{\alpha_2 \beta_2} + \dots \right) \frac{\partial \ln \mathbb{K}}{\partial y_{\beta_1 \beta_2}^{(2)}} \\ &\quad - y_{\alpha_3}^{(1)} \delta_{\alpha_1 \beta_1} \delta_{\alpha_2 \beta_2} \frac{\partial \ln \mathbb{K}}{\partial y_{\beta_1 \beta_2}^{(2)}} \\ &\quad - y_{\beta_1 \alpha_3}^{(2)} \delta_{\alpha_1 \beta_2} \delta_{\alpha_2 \beta_3} \frac{\partial \ln \mathbb{K}}{\partial y_{\beta_1 \beta_2 \beta_3}^{(3)}} + \dots. \end{aligned} \quad (7.276)$$

Here the Einstein convention is used for the repeated indices.

By inverting the matrix of the linear system in (7.273) under the assumption of invertibility of the matrix, we obtain the differential equations in the space $\mathfrak{T} \equiv (\mathbf{y}^{(k)})$

$$\frac{\partial \ln \mathbb{K}}{\partial \mathbf{y}^{(k)}} = F_k(\mathbf{y}) \quad (k \in \mathfrak{V}). \quad (7.277)$$

Here

$$F_k(\mathbf{y}) = \sum_{j \in \mathfrak{V}} (\mathbf{M}^{-1})_{kj} (j-1)! \mathbf{y}^{(j)} \quad (7.278)$$

with \mathbf{M} denoting the matrix of the linear system (7.273). The differential equations in (7.277) can be written as a differential form

$$d \ln \mathbb{K} = \sum_{k \in \mathfrak{V}} F_k(\mathbf{y}) d\mathbf{y}^{(k)}, \quad (7.279)$$

which can be integrated in the space \mathfrak{T} :

$$\ln \mathbb{K} = \sum_{k \in \mathfrak{V}} \int_0^{\mathbf{y}^{(k)}} F_k(\mathbf{x}) d\mathbf{x}^{(k)} \quad (7.280)$$

under the initial condition $\mathbb{K}(0) = 1$. The integral in (7.280) is a line integral in the space \mathfrak{T} . This result can also be obtained from (7.273) by using the method [48] of characteristics for first-order partial differential equations. An example will be considered for this result in the case where only the first thirteen moments plus the moments for diffusion are taken into account.

At this point we restore the species subscript a to the quantities in (7.277)–(7.280). Thus we write

$$\frac{\partial \ln \mathbb{K}_a}{\partial \mathbf{y}_a^{(k)}} = F_k^{(a)}(\mathbf{y}) \quad (k \in \mathfrak{V}), \quad (7.281)$$

where

$$F_k^{(a)}(\mathbf{y}_a) = \sum_{j \in \mathfrak{V}} (j-1)! (\mathbf{M}_a^{-1})_{kj} \mathbf{y}_a^{(j)} \quad (7.282)$$

with \mathbf{M}_a denoting the matrix of the linear system for the species a . Likewise,

$$\ln \mathbb{K}_a = \sum_{k \in \mathfrak{V}} \int_0^{\mathbf{y}_a^{(k)}} F_k^{(a)}(\mathbf{x}) d\mathbf{x}^{(k)}. \quad (7.283)$$

In view of (7.255) and (7.79) we find that (7.281) directly gives the nonconserved variable Θ_{ka}^v in the form

$$\Theta_{ka}^v = -N_a F_k^{(a)}(\mathbf{y}_a) \quad (k \in \mathfrak{V}). \quad (7.284)$$

This result is exact, but calculation of the right hand side requires inversion of an infinite matrix. Such a matrix in practice must be truncated, and the result obtained thereby will be approximate. Since Θ_{ka}^v is defined by $\Theta_{ka}^v = V\rho\widehat{\Theta}_{ka}$, it now is possible to deduce from (7.284) the local nonconserved variable $\Theta_{ka} \equiv \rho\widehat{\Theta}_{ka}$ which is simply given by the formula

$$\Theta_{ka} = -n_a F_k^{(a)}(\mathbf{y}_a) \quad (k \in \mathfrak{V}). \quad (7.285)$$

We now calculate the other thermodynamic quantities listed in (7.76)–(7.78) which the nonequilibrium ensemble method provides. To perform this calculation we first recall that in the nonequilibrium ensemble method the matching conditions (4.40)–(4.42) are used for the densities, momentum, and internal energy which give rise to the equation of state

$$p = nk_B T \quad (7.286)$$

even for the nonequilibrium system¹⁰. Therefore the nonequilibrium partition function \mathbb{Z} can be written in the form

$$\mathbb{Z} = \prod_{a=1}^r \left\{ \left[\left(\frac{2\pi}{m_a} \right)^{3/2} \frac{(k_B T)^{5/2}}{p} \right] \mathbb{K}_a \right\}^{N_a}. \quad (7.287)$$

Note also that \mathbb{K}_a is a function of temperature T and $\{y_a^{(k)}\}$ only. Thus by inserting this result into (7.77) we obtain the equation of state in the form of (7.286) which shows that the present theory is internally self-consistent with regard to the equation of state. Similarly we can also calculate from (7.78) the chemical potential in the form

$$\mu_a = -k_B T \ln \left\{ \left[\left(\frac{2\pi}{m_a} \right)^{3/2} \frac{(k_B T)^{5/2}}{p} \right] \exp \left(\sum_{k \in \mathfrak{V}} \int_0^{y_a^{(k)}} F_k^{(a)}(\mathbf{x}) d\mathbf{x}^{(k)} \right) \right\}. \quad (7.288)$$

Therefore the nonequilibrium contribution appears in a manner reminiscent of the fugacity [9,49] of a real gas in the nonequilibrium chemical potential. The calortropy is similarly obtained from (7.76) and (7.287). It is given by the formula

$$\begin{aligned} \Psi_v &= k_B \sum_{a=1}^r N_a \ln \left[\left(\frac{2\pi}{m_a} \right)^{3/2} \frac{(k_B T e)^{5/2}}{p} \right] \\ &\quad + k_B \sum_{a=1}^r \sum_{k \in \mathfrak{V}} N_a \int_0^{y_a^{(k)}} F_k^{(a)}(\mathbf{x}) d\mathbf{x}^{(k)} \\ &\quad + k_B T \sum_{a=1}^r \sum_{k \in \mathfrak{V}} N_a \left(\frac{\partial}{\partial T} \int_0^{y_a^{(k)}} F_k^{(a)}(\mathbf{x}) d\mathbf{x}^{(k)} \right)_{p, N_a, y_a^{(k)}}. \end{aligned} \quad (7.289)$$

¹⁰The T in this equation of state is the thermodynamic temperature which was discussed in the context of nonequilibrium in Chapter 2 and appears in the differential form for $d_t \hat{\Psi}$. This equation of state is internally consistent, for ideal gases, with the nonequilibrium thermodynamic expressions in (7.76)–(7.79).

Clearly the calortropy reduces to the equilibrium ideal gas entropy (*i.e.*, the Clausius entropy) as the system tends to equilibrium where the generalized potentials $y_a^{(k)}$ vanish. This completes the formal part of the calculation of nonequilibrium thermodynamic quantities, and there now remains the task of obtaining approximate $F_k^{(a)}(\mathbf{y}_a)$ to use for various purposes in irreversible thermodynamics. In this work we will consider a simple lower order case to indicate a possible mathematical structure of $F_k^{(a)}(\mathbf{y}_a)$.

7.10.4 The Case of Diffusion, Heat Flow, and Shear Only

We consider a lower order set for (7.273) which is obtained from (7.274)–(7.276) by discarding the generalized potentials beyond $k = 3$ and also retaining only the vectorial components of $y^{(3)}$ obtained by taking trace over two indices. Such vectorial components correspond to heat fluxes. In this approximation we are therefore limiting the number of moments to the first thirteen moments plus diffusion fluxes and thus have the equations

$$\frac{\partial \ln \mathbb{K}}{\partial y_{\alpha_1}^{(1)}} = y_{\alpha_1}^{(1)} - y_{\alpha_1 \beta_1}^{(2)} \frac{\partial \ln \mathbb{K}}{\partial y_{\beta_1}^{(1)}} - y_{\alpha_1 \beta_1 \beta_2}^{(3)} \frac{\partial \ln \mathbb{K}}{\partial y_{\beta_1 \beta_2}^{(2)}}, \quad (7.290)$$

$$\begin{aligned} \frac{\partial \ln \mathbb{K}}{\partial y_{\alpha_1 \alpha_2}^{(2)}} &= y_{\alpha_1 \alpha_2}^{(2)} - y_{\alpha_2}^{(1)} \frac{\partial \ln \mathbb{K}}{\partial y_{\alpha_1}^{(1)}} - \left(y_{\alpha_1 \beta_1 \alpha_2}^{(3)} + y_{\beta_1 \alpha_1 \alpha_2}^{(3)} \right) \frac{\partial \ln \mathbb{K}}{\partial y_{\beta_1}^{(1)}} \\ &\quad - y_{\beta_1 \alpha_2}^{(2)} \frac{\partial \ln \mathbb{K}}{\partial y_{\alpha_1}^{(2)}} + y_{\beta_1 \beta_2 \alpha_2}^{(3)} \frac{\partial \ln \mathbb{K}}{\partial y_{\alpha_1 \beta_1 \beta_2}^{(3)}}, \end{aligned} \quad (7.291)$$

$$\begin{aligned} \frac{\partial \ln \mathbb{K}}{\partial y_{\alpha_1 \beta_1 \beta_1}^{(3)}} &= 2y_{\alpha_1 \beta_1 \beta_1}^{(3)} - \left(y_{\alpha_1 \beta_1}^{(2)} \delta_{\beta_2 \beta_1} + y_{\beta_1 \beta_1}^{(2)} \delta_{\alpha_1 \beta_2} \right) \frac{\partial \ln \mathbb{K}}{\partial y_{\beta_2}^{(1)}} \\ &\quad - \left(y_{\alpha_1 \beta_3 \beta_1}^{(3)} \delta_{\beta_2 \beta_1} + y_{\beta_2 \alpha_1 \beta_1}^{(3)} \delta_{\beta_1 \beta_3} \right) \frac{\partial \ln \mathbb{K}}{\partial y_{\beta_2 \beta_3}^{(2)}} \\ &\quad - y_{\beta_1}^{(1)} \delta_{\alpha_1 \beta_2} \delta_{\beta_1 \beta_3} \frac{\partial \ln \mathbb{K}}{\partial y_{\beta_2 \beta_3}^{(2)}} - y_{\beta_1 \beta_2}^{(2)} \frac{\partial \ln \mathbb{K}}{\partial y_{\alpha_1 \beta_1 \beta_2}^{(3)}}. \end{aligned} \quad (7.292)$$

Therefore the coefficients $C_{\alpha_1 \dots \alpha_k \beta_1 \dots \beta_m}^{(k)}$ are linear in $y_a^{(m)}$. That is, the elements of the matrix \mathbf{M}_a are linear in $\mathbf{y}_a^{(m)}$ where

$$\mathbf{M}_a = (\mathbf{1} - \mathbb{C}_a) \quad (7.293)$$

with \mathbb{C}_a denoting the coefficient matrix in (7.273): $\mathbb{C}_a \equiv \left(C_{\alpha_1 \dots \alpha_k \beta_1 \dots \beta_m}^{(k)} \right)$. For the future reference we list the leading elements of \mathbb{C}_a in the following:

$$C_{\alpha_1 \beta_1}^{(1)} = -y_{\alpha_1 \beta_1}^{(2)},$$

$$C_{\alpha_1 \beta_1 \beta_1}^{(1)} = -y_{\alpha_1 \beta_1 \beta_1}^{(3)},$$

$$C_{\alpha_1 \alpha_2 \beta_1}^{(2)} = -y_{\alpha_2}^{(1)} \delta_{\alpha_1 \beta_1},$$

$$C_{\alpha_1 \alpha_2 \beta_1 \beta_1}^{(2)} = -(y_{\alpha_1 \alpha_2 \beta_1}^{(3)} + y_{\beta_1 \alpha_1 \alpha_2}^{(3)}),$$

$$C_{\alpha_1 \alpha_2 \beta_1 \beta_2}^{(2)} = -y_{\beta_1 \alpha_2}^{(2)} \delta_{\alpha_1 \beta_2},$$

$$C_{\alpha_1 \alpha_2 \beta_1 \beta_2 \beta_3}^{(2)} = y_{\beta_1 \beta_2 \alpha_2}^{(3)} \delta_{\alpha_1 \beta_3},$$

$$C_{\alpha_1 \alpha_2 \alpha_3 \beta_1 \beta_2}^{(3)} = -(y_{\alpha_1 \beta_1}^{(2)} \delta_{\beta_1 \beta_2} + y_{\beta_1 \beta_1}^{(2)} \delta_{\alpha_1 \beta_2}),$$

$$C_{\alpha_1 \alpha_2 \alpha_3 \beta_1 \beta_2}^{(3)} = -(y_{\alpha_3}^{(1)} \delta_{\alpha_1 \beta_1} \delta_{\alpha_2 \beta_2} + y_{\alpha_3 \beta_2 \alpha_3}^{(3)} \delta_{\alpha_2 \beta_1} + y_{\beta_1 \alpha_1 \alpha_3}^{(3)} \delta_{\alpha_2 \beta_2}),$$

$$C_{\alpha_1 \alpha_2 \alpha_3 \beta_1 \beta_1 \beta_2 \beta_3}^{(3)} = -y_{\beta_1 \alpha_3}^{(2)} \delta_{\alpha_1 \beta_2} \delta_{\alpha_2 \beta_3}.$$

Note that the repeated subscripts pertain to the trace of the tensor over the pair of the subscripts. It is easy to see the structure of the matrix \mathbf{M}_a from the table for the matrices \mathbb{C}_a given earlier. It has the form where the block diagonal matrices correspond to the diffusion, stress, heat flow, and so on and the off-diagonal matrices represent couplings between diffusion and stress, heat flow and stress, and so on. The matrix can be written in the following form:

$$\mathbf{M} = \begin{bmatrix} \mathbf{1} - \mathbb{C}^{(11)} & -\mathbb{C}^{(12)} & & & & \\ -\mathbb{C}^{(21)} & \mathbf{1} - \mathbb{C}^{(22)} & -\mathbb{C}^{(23)} & & & \\ & -\mathbb{C}^{(32)} & \mathbf{1} - \mathbb{C}^{(33)} & & & \\ & & & \ddots & & \\ & & & & \ddots & \\ & & & & & \ddots \end{bmatrix}. \quad (7.294)$$

Here the first block diagonal matrix is for diffusion, the second is for stress, and the third is for heat flow, and so on. The subscript a is omitted from the matrices for brevity of notation.

By using the result in (7.285) we find the relation

$$\mathbf{y}_a^{(k)} = -\{[\mathbf{1} - \mathbf{L}_a(\widehat{\Theta}_a)]^{-1} \widehat{\Theta}_a\}_k. \quad (7.295)$$

Here the subscript k denotes the k th component of set \mathfrak{V} , $\widehat{\Theta}_a = \Theta_a/n_a$.

The coefficient matrix $\mathbf{L}_a(\widehat{\Theta}_a)$ is defined such that

$$\mathbb{C}_a(\mathbf{y}_a)\widehat{\Theta}_a = \mathbf{L}_a(\widehat{\Theta}_a)\mathbf{y}_a$$

since \mathbb{C}_a is linear in \mathbf{y}_a as is clear from the table for \mathbb{C}_a presented. From this it is readily verified that to the first order in Θ_{ka}

$$\mathbf{y}_a^{(k)} = -n_a^{-1}\Theta_{ka}, \quad (7.296)$$

which agrees with the previous approximate result for the generalized potentials. Eq. (7.295) enables us to investigate the behavior of the generalized potentials as $\|\Theta_{ka}\| \rightarrow \infty$, if the right hand side of (7.295) is more explicitly examined. We will return to it when we discuss a specific example later. A point we would like to make in general terms is that the present nonequilibrium ensemble method provides us with a means to discuss some aspects of convergence of the expansion for the nonequilibrium term in the nonequilibrium canonical form. In contrast to this, the conventional moment method [11,37] does not even give rise to a nonequilibrium partition function and hence is incapable of yielding the statistical formulas such as (7.76)–(7.79).

This result for $\mathbf{y}_a^{(k)}$ can be used in the generalized hydrodynamics equations [9,10,50] which arise in the nonequilibrium ensemble method as a generalization of the classical hydrodynamic equations. The generalized hydrodynamic equations describe the space-time evolution of the hydrodynamic variables including Θ_{ka} and the distribution function through the latter variables under the functional hypothesis used in the nonequilibrium ensemble method.

7.10.5 The Case of Shear Only

To be more explicit about the structure of the matrix \mathbf{M}_a , we assume that the concentrations and temperature are uniform over the system. Consequently there are no diffusion and heat flow in the system. This assumption, within the framework of the thirteen moment approximation, makes the aforementioned matrix relatively simple since there is only $\mathbf{y}_a^{(2)}$ to consider. It is convenient to simplify the notation involved. Let us denote the components of the symmetric second-rank tensor $\mathbf{y}_a^{(2)}$ as follows:

$$y_1 = y_{xx}^{(2)}, \quad y_2 = y_{yy}^{(2)}, \quad y_3 = y_{zz}^{(2)},$$

$$y_4 = y_{xy}^{(2)}, \quad y_5 = y_{yz}^{(2)}, \quad y_6 = y_{zx}^{(2)}.$$

Here we have omitted the species index from $\mathbf{y}_a^{(2)}$. Then it is easy to construct the matrix \mathbf{M} from the table given earlier for the matrix \mathbb{C}_a :

$$\mathbf{M} = \begin{bmatrix} 1 + y_1 & 0 & 0 & y_4 & 0 & 0 \\ 0 & 1 + y_2 & 0 & 0 & y_5 & 0 \\ 0 & 0 & 1 + y_3 & 0 & 0 & y_6 \\ y_4 & 0 & 0 & 1 + y_1 & 0 & 0 \\ 0 & y_5 & 0 & 0 & 1 + y_2 & 0 \\ 0 & 0 & y_6 & 0 & 0 & 1 + y_3 \end{bmatrix}. \quad (7.297)$$

This matrix is easily inverted and we find

$$\mathbf{M}^{-1} = \begin{bmatrix} -\frac{1+y_1}{\Delta_1} & 0 & 0 & \frac{y_4}{\Delta_1} & 0 & 0 \\ 0 & -\frac{1+y_2}{\Delta_2} & 0 & 0 & \frac{y_5}{\Delta_2} & 0 \\ 0 & 0 & \frac{1+y_3}{\Delta_3} & 0 & 0 & -\frac{y_6}{\Delta_3} \\ \frac{y_4}{\Delta_1} & 0 & 0 & -\frac{1+y_1}{\Delta_1} & 0 & 0 \\ 0 & \frac{y_5}{\Delta_2} & 0 & 0 & -\frac{1+y_2}{\Delta_2} & 0 \\ 0 & 0 & -\frac{y_6}{\Delta_3} & 0 & 0 & \frac{1+y_3}{\Delta_3} \end{bmatrix}, \quad (7.298)$$

where the denominators are given by

$$\begin{aligned} \Delta_1 &= -(1 + y_1)^2 + y_4^2, \\ \Delta_2 &= -(1 + y_2)^2 + y_5^2, \\ \Delta_3 &= (1 + y_3)^2 - y_6^2. \end{aligned} \quad (7.299)$$

The determinant of the matrix \mathbf{M} is given by

$$\det \mathbf{M} = [(1 + y_1)^2 - y_4^2] [(1 + y_2)^2 - y_5^2] [(1 + y_3)^2 - y_6^2]. \quad (7.300)$$

Substitution of this result into (7.282) yields $F_k^{(a)}(\mathbf{y}_a)$ and the nonequilibrium partition function is obtained therewith from (7.283). The stress tensor can be easily calculated from this result by using (7.285). Since the generalized potential $\mathbf{y}^{(2)}$ is a quantity of interest in rheology, we present $\mathbf{y}^{(2)}$ which is obtained in terms of the stress by using (7.295). The matrix $\mathbf{L}_a(\hat{\Theta})$ is easily obtained from $\mathbb{C}^{(2)}$ by simply replacing $\mathbf{y}^{(2)}$ with $\hat{\Theta}$ in the elements of $\mathbb{C}^{(2)}$:

$$\mathbf{L}_a(\hat{\Theta}) = \mathbb{C}^{(2)} \left(\mathbf{y}^{(2)} = \hat{\Theta} \right).$$

Thus, if we set

$$\theta_1 = \hat{\Theta}_{2xx}, \quad \theta_2 = \hat{\Theta}_{2yy}, \quad \theta_3 = \hat{\Theta}_{2zz},$$

$$\theta_4 = \hat{\Theta}_{2xy}, \quad \theta_5 = \hat{\Theta}_{2yz}, \quad \theta_6 = \hat{\Theta}_{2zx}$$

in the same order as for y_1 , y_2 , and so on, then $[1 - L_a(\hat{\Theta})]^{-1}$ is given as follows:

$$(1 - L)^{-1} = \begin{bmatrix} -\frac{1+\theta_1}{D_1} & 0 & 0 & \frac{\theta_4}{D_1} & 0 & 0 \\ 0 & -\frac{1+\theta_2}{D_2} & 0 & 0 & \frac{\theta_5}{D_2} & 0 \\ 0 & 0 & \frac{1+\theta_3}{D_3} & 0 & 0 & -\frac{\theta_6}{D_3} \\ \frac{\theta_4}{D_1} & 0 & 0 & -\frac{1+\theta_1}{D_1} & 0 & 0 \\ 0 & \frac{\theta_5}{D_2} & 0 & 0 & -\frac{1+\theta_2}{D_2} & 0 \\ 0 & 0 & -\frac{\theta_6}{D_3} & 0 & 0 & \frac{1+\theta_3}{D_3} \end{bmatrix}, \quad (7.301)$$

where

$$D_1 = -(1 + \theta_1)^2 + \theta_4^2,$$

$$D_2 = -(1 + \theta_2)^2 + \theta_5^2, \quad (7.302)$$

$$D_3 = (1 + \theta_3)^2 - \theta_6^2.$$

Substitution of this result into (7.295) yields the desired generalized potential in terms of the stress tensor Θ_2 . For example, for the y_4 component which describes the shearing mode we find the following:

$$y_4 = -\frac{\theta_4}{(1 + \theta_1)^2 - \theta_4^2}. \quad (7.303)$$

This agrees with the result obtained by the expansion method in the limit of small θ_1 and θ_4 , but y_4 decreases as θ_4^{-1} when θ_4 increases in magnitude. In this connection we note that in the high shear (θ_4) regime it will be necessary to include the heat flux if we wish to obtain a more precise behavior of y_4 , since there will be thermoviscous couplings that cannot be neglected. Therefore the large shear limit behavior will require a more careful investigation than made here, and the present conclusion is subject to

the condition of no thermoviscous effect. Since the generalized potentials obtained by the nonequilibrium ensemble method has some unusual features not known hitherto and are worth further investigation, they should be an object of study, in particular, in connection with rheology in the future. We conclude this section by presenting the result for the nonequilibrium partition function corresponding to the inverse matrix \mathbf{M}^{-1} given in (7.298) for the shearing problem considered here. It is easy to find $F_k^{(a)}$ ($k = 1, 2, \dots, 6$) from (7.282) and (7.298):

$$\begin{aligned} F_1^{(a)} &= 1 + (1 + y_1) \Delta_1^{-1}, & F_2^{(a)} &= 1 + (1 + y_2) \Delta_2^{-1}, \\ F_3^{(a)} &= 1 - (1 + y_3) \Delta_3^{-1}, & F_4^{(a)} &= -y_4 \Delta_1^{-1}, \\ F_5^{(a)} &= -y_5 \Delta_2^{-1}, & F_6^{(a)} &= y_6 \Delta_3^{-1}. \end{aligned} \quad (7.304)$$

Here Δ_1 , Δ_2 , and Δ_3 are given in (7.299). By using these results, it is easy to verify that $F_k^{(a)}$ ($k = 1, 2, \dots, 6$) satisfy the integrability conditions [15,17,18,48], namely, that the differential form

$$d \ln \mathbb{K}_a = \sum_{k=1}^6 F_k^{(a)} dy_k \quad (7.305)$$

is an exact differential, so

$$\frac{\partial F_k^{(a)}}{\partial y_j} = \frac{\partial F_j^{(a)}}{\partial y_k}. \quad (7.306)$$

In view of the exactness of the differential form (7.305), the line integral of the terms on the right hand side of (7.305) from $(0, 0, 0, 0, 0, 0)$ to $(y_1, y_2, y_3, y_4, y_5, y_6)$ in the six-dimensional space spanned by the elements of $\mathbf{y}^{(2)}$ can be distorted to the following path:

$$\begin{aligned} (0, 0, 0, 0, 0, 0) &\xrightarrow{1} (y_1, 0, 0, 0, 0, 0) &&\xrightarrow{2} (y_1, y_2, 0, 0, 0, 0) \\ &\xrightarrow{3} (y_1, y_2, y_3, 0, 0, 0) &&\xrightarrow{4} (y_1, y_2, y_3, y_4, 0, 0) \\ &\xrightarrow{5} (y_1, \dots, y_4, y_5, 0) &&\xrightarrow{6} (y_1, \dots, y_4, y_5, y_6). \end{aligned} \quad (7.307)$$

The line integral for $\ln \mathbb{K}_a$ is then given by the sum of integrals as follows:

$$\ln \mathbb{K}_a = \int_0^{y_1} dx_1 \left[1 + \frac{1 + x_1}{y_4^2 - (1 + x_1)^2} \right]_{y_4=0} + \int_0^{y_4} dx_4 \frac{x_4}{(1 + y_1)^2 - x_4^2}$$

$$\begin{aligned}
& + \int_0^{y_2} dx_2 \left[1 + \frac{1+x_2}{y_5^2 - (1+x_2)^2} \right]_{y_5=0} + \int_0^{y_5} dx_5 \frac{x_5}{(1+y_2)^2 - x_5^2} \\
& + \int_0^{y_3} dx_3 \left[1 + \frac{1+x_3}{y_6^2 - (1+x_3)^2} \right]_{y_6=0} + \int_0^{y_6} dx_6 \frac{x_6}{(1+y_3)^2 - x_6^2}.
\end{aligned} \tag{7.308}$$

The first two integrals in this equation are for the first and fourth steps in the path described in (7.307); the third and fourth integrals are for the second and fifth steps; and the fifth and sixth integrals are for the third and sixth steps, respectively. These integrals are easily performed to yield the nonequilibrium part of the partition function

$$\mathbb{K}_a = \prod_{i=1}^3 \frac{e^{y_i}}{\sqrt{(1+y_i)^2 - y_{i+3}^2}}. \tag{7.309}$$

The correctness of this result can be easily checked by showing that, when differentiated with y_i ($i = 1, \dots, 6$), \mathbb{K}_a in (7.309) reproduces (7.304). There are singularities in this expression and the range of y_{i+3} must be less than $(1+y_i)$. Since y_i are normal stresses which are usually larger than the shear components, the singularities are not reached in practice. As mentioned earlier, the large y_{i+3} regime must be considered together with the heat flux contributions since there are thermoviscous couplings which are not negligible in the high shear regime and may prevent the singularities from appearing in the physical domain of $y^{(2)}$.

One unexpected byproduct of the present calculation is an indication of the convergence of the set \mathfrak{V} which can be deduced from (7.285) or (7.295). If the magnitudes of the moments in, for example, (7.295) are roughly of the same order, then the inverse matrix therein is $O(D^{-1} \|\Theta\|^{-1})$ and thus $\|\mathbf{y}_a^{(k)}\|$ is $O(D^{-1})$ where D is the dimension of the matrix, namely, the number of moments taken. With a more explicit calculation it is possible to sharpen this result, as we have shown earlier with the example for the case of shear. This estimate indicates the rate of convergence of the moment expansion in the nonequilibrium canonical form or in the exponent in (7.258) for the nonequilibrium partition function.

7.11 Nonequilibrium Grand Canonical Ensemble

We would like to close this chapter with a remark regarding the nonequilibrium grand canonical ensemble distribution function which may be used to formulate [51] the nonequilibrium ensemble method. To this end we introduce the singlet distribution function $F_a(\mathbf{r}_{ai}, \mathbf{p}_{ai}; t)$ in the phase space

$x_{ai} \equiv (\mathbf{r}_{ai}, \mathbf{p}_{ai})$ of particle i of species a ($i \in a$). The N particle phase will be abbreviated by $x^{(N)} = (\mathbf{r}_{a1}, \mathbf{p}_{a1}, \dots, \mathbf{r}_{aN}, \mathbf{p}_{aN})$. This singlet distribution function is a reduced distribution function obeying the kinetic equation (3.27) and is normalized as follows:

$$V^{-1} \int dx_{ai} F_a(x_{ai}; t) = 1. \quad (7.310)$$

Now, imagine an open dilute system consisting of N particles where $N = \sum_{a=1}^r N_a$. A grand ensemble can be constructed which consists of petit ensembles made up of representative systems of a varying number N of particles in a fixed volume V . The distribution function for the system to have N and $x^{(N)}$ will be denoted by $F^{(N)}(x^{(N)}; t)$. Since particles are not statistically correlated, the N -particle distribution function is given by the product of singlet distribution functions

$$F^{(N)}(x^{(N)}; t) = \prod_{a=1}^r \prod_{i=1}^{N_a} V^{-1} F_a(x_{ai}; t). \quad (7.311)$$

It normalizes to unity:

$$\int dx^{(N)} F^{(N)}(x^{(N)}; t) = 1, \quad (7.312)$$

where

$$dx^{(N)} = \prod_{a=1}^r \prod_{i=1}^{N_a} dx_{ai}.$$

Let the density of observable $M(x^{(N)})$ be denoted by

$$M(x^{(N)}) = \sum_{a=1}^r \sum_{i=1}^{N_a} M_{ai} \delta(\mathbf{r}_{ai} - \mathbf{r}). \quad (7.313)$$

The grand canonical ensemble average of $M(x^{(N)})$ at position \mathbf{r} and time t is then defined by

$$\langle M \rangle(\mathbf{r}, t) = \sum_{N \geq 0} \int dx^{(N)} M(x^{(N)}) F^{(N)}(x^{(N)}; t). \quad (7.314)$$

The nonequilibrium grand canonical form may be taken as

$$F_c^{(N)}(x^{(N)}; t) = c^{-1} \exp \left[- \int_V d\mathbf{r} \beta(\mathbf{r}, t) \sum_{a=1}^r \sum_{i=1}^{N_a} \mathcal{H}_{ai} \delta(\mathbf{r}_{ai} - \mathbf{r}) - \ln \Xi \right], \quad (7.315)$$

where $c = h^{3N} \prod_{a=1}^r N_a!$ with h denoting the Planck constant, $\beta(\mathbf{r}, t)$ and μ_a are parameters to be determined with the help of the second law of thermodynamics, and

$$\mathcal{H}_{ai} = H_{ai} + H_{ai}^1 - m_a \hat{\mu}_a,$$

$$H_{ai} = \frac{1}{2} m_a C_{ai}^2,$$

$$H_{ai}^1 = \sum_{q \geq 1} Y_{aq} \mathcal{H}^{(q)}(\mathbf{w}_{ai}),$$

$$\Xi = c^{-1} \sum_{N \geq 0} \int dx^{(N)} \exp \left[- \int_V d\mathbf{r} \beta(\mathbf{r}, t) \sum_{a=1}^r \sum_{i=1}^{N_a} \mathcal{H}_{ai} \delta(\mathbf{r}_{ai} - \mathbf{r}) \right]. \quad (7.316)$$

We remark that it will be convenient to express Ξ in the form

$$k_B \ln \Xi = k_B \int_V d\mathbf{r} \rho \ln \Gamma(\mathbf{r}, t) = \int_V d\mathbf{r} \frac{p}{T}, \quad (7.317)$$

where $\ln \Gamma(\mathbf{r}, t)$ is the density of $\ln \Xi$ and p and T ($T = 1/k_B \beta$) are parameters to be determined by the thermodynamic correspondence. They will turn out to be pressure and temperature, respectively. Since the nonequilibrium grand canonical ensemble theory which can be developed with this form of $F^{(N)}$ will be a special case for dilute gases of the dense fluid theory presented in Chapter 10, we will simply list the essential results [51], leaving their derivations to the reader as an exercise. From the differential form for $d_t \hat{\Psi}$ and its integrability condition follows the fundamental equation

$$\begin{aligned} d_t(pv) &= \hat{\Psi} d_t T + p d_t v + \sum_{a=1}^r c_a d_t \hat{\mu}_a - \sum_{a=1}^r \sum_{q \geq 1} \hat{\Phi}_{qa} d_t Y_{qa} \\ &= d_t [k_B T \ln \Gamma(\mathbf{r}, t)], \end{aligned} \quad (7.318)$$

where the second equality arises from (7.317). This differential form is the extended Gibbs relation for pv . From this differential form follow the statistical formulas desired:

$$\hat{\Psi} = k_B \ln \Gamma + k_B T \frac{\partial \ln \Gamma}{\partial T}, \quad (7.319)$$

$$p = k_B T \frac{\partial \ln \Gamma}{\partial v}, \quad (7.320)$$

$$c_a = k_B T \frac{\partial \ln \Gamma}{\partial \hat{\mu}_a}, \quad (7.321)$$

$$\hat{\Phi}_{qa} = -k_B T \frac{\partial \ln \Gamma}{\partial Y_{qa}}. \quad (7.322)$$

If the phase space is divided into small volumes $\Omega(\mathbf{r}_k)$ located at \mathbf{r}_k which contain a sufficiently large number of particles to assure the validity of the statistical method used, then Ξ may be written as

$$\Xi = \prod_k \Xi_k(\mathbf{r}_k, t), \quad (7.323)$$

where

$$\Xi_k(\mathbf{r}_k, t) = c^{-1} \sum_{\bar{N} \geq 0} \int dx^{(\bar{N})} \exp \left[-\Omega(\mathbf{r}_k) \beta(\mathbf{r}_k, t) \sum_{a=1}^r \sum_{i=1}^{\bar{N}_a} \mathcal{H}_{ai} \right]_{\mathbf{r}_{ai} \in \Omega(\mathbf{r}_k)}. \quad (7.324)$$

Here \bar{N}_a is the total number of particles of species a in $\Omega(\mathbf{r}_k)$ and $\bar{N} = \sum_{a=1}^r \bar{N}_a$. The total mass in $\Omega(\mathbf{r}_k)$ is then given by

$$\bar{M}_k = \sum_{a=1}^r \sum_{i=1}^{\bar{N}_a} m_a = \rho(\mathbf{r}_k) \Omega(\mathbf{r}_k) \quad (7.325)$$

and it is possible to write

$$\int_V d\mathbf{r} \rho \ln \Gamma(\mathbf{r}, t) = \ln \prod_k \Gamma_k^{\bar{M}_k}(\mathbf{r}_k, t). \quad (7.326)$$

We therefore find

$$\Gamma_k^{\bar{M}_k}(\mathbf{r}_k, t) = \Xi_k(\mathbf{r}_k, t). \quad (7.327)$$

This gives a way to compute $\Gamma(\mathbf{r}, t)$ and thus various thermodynamic functions in (7.319)–(7.322) in terms of $\Xi_k(\mathbf{r}_k, t)$ which is the nonequilibrium grand partition function of the system in the cell of volume $\Omega(\mathbf{r}_k)$ located at \mathbf{r}_k .

7.12 Synopsis

The synergetic and formal treatment of irreversible thermodynamics deduced from the laws of thermodynamics and the irreversible Boltzmann equation (3.27) has culminated in the formulation of nonequilibrium ensemble method in this chapter, which is a generalization of the equilibrium ensemble theory of Gibbs. The basic result of this method is contained in Sec. 7.3. The theory formulated is completely parallel with the equilibrium ensemble theory. We have thus achieved the long sought ensemble theory for nonequilibrium in the spirit of Gibbs, at least, for dilute classical gases obeying the Boltzmann equation or the kinetic equation (3.27) satisfying

the three conditions listed in Chapter 3. As will be shown in Chapters 9 and 10, this theory is generalizable to quantum gases and dense fluids. The indispensable components of the theory are the phenomenological differential form for the calortropy which is deduced from the laws of thermodynamics and the nonequilibrium canonical form which gives rise to the statistically derived calortropy differential form with the attendant evolution equations for the macroscopic variables derived from the Boltzmann equation. Since these evolution equations for macroscopic variables spanning the thermodynamic space are subjected to the thermodynamic laws in the present nonequilibrium ensemble method, the theory of irreversible processes described by the evolution equations are thermodynamically consistent. This is of course a much desired feature in a theory of macroscopic irreversible processes. The thermodynamically consistent set of evolution equations for macroscopic variables constitutes generalized hydrodynamics which systematically reduces to the classical hydrodynamics of Navier, Stokes, Fourier, and Fick as the transport processes become linear with respect to fluxes when the system is near equilibrium. We have shown that fluctuations in intensive macroscopic variables conjugate to the variables spanning the thermodynamic space play an important conceptual role in the nonequilibrium ensemble theory and also in understanding the meaning of the nonequilibrium canonical ensemble distribution function. We have seen that *the relative Boltzmann entropy does not vanish because of the non-vanishing path-dependent dissipative contribution, even if the fluctuations vanish. Nevertheless, in the limit of vanishing fluctuations the distribution function f_a may be well represented by the nonequilibrium canonical form f_a^c .* The evolution equations for fluctuations of the intensive variables follow linear equations to the lowest order approximation. Equipped with these evolution equations, we are now well posed to study the effects of fluctuations from the kinetic theory standpoint. Study of this aspect is deferred to the future since we have not had time to investigate them. It is significant that the deterministic evolution of fluctuations $\delta\bar{I}$, $\delta\bar{p}$, $\delta\bar{\mu}$, and $\delta\bar{Y}_k$ of thermodynamic intensive variables is governed by the kinetic equation subject to the H theorem whereas the extensive thermodynamic variables are governed by the evolution equations which are subject to the constraint of the calortropy and its production—the second law of thermodynamics.

The nonequilibrium partition function and its result give rise to the concept of generalized fugacity for nonequilibrium systems in a way akin to the fugacity concept originally introduced for equilibrium real fluids. This concept of generalized fugacity and the nonequilibrium chemical potentials now greatly elucidate the concept of nonequilibrium free energy which has been used in the literature without a question asked regarding its basic meaning from the standpoint of the thermodynamic principles. An example for such nonequilibrium free energy may be the Ginzburg–Landau free energy functional. The present nonequilibrium ensemble theory furnishes us with the necessary theoretical tools to carve out such an important and

useful concept and put it in the framework of a truly thermodynamic theory for irreversible processes in nonequilibrium systems.

Despite the terminology that sounds familiar, the nonequilibrium partition function is a recent entry in nonequilibrium statistical mechanics which provides us with various statistical formulas for nonequilibrium thermodynamic variables. It rests on the support of the generalized hydrodynamics equations accompanying the nonequilibrium ensemble method. The statistical expressions (7.76)–(7.79) for nonequilibrium thermodynamic variables and the attendant generalized hydrodynamics equations are not available in the nonequilibrium ensemble methods by McLennan [4,5] and Zubarev [6] extant in the literature. We have already indicated in the introduction the reason for the absence of such statistical formulas in the theories of McLennan and Zubarev.

It must be remembered that an irreversible kinetic equation is an essential ingredient of the nonequilibrium ensemble theory, and here in this chapter the venerable Boltzmann equation has finally seen its ultimate utility in elucidation of thermodynamics from the statistical and molecular viewpoints. This viewpoint and the results presented in this chapter once again underline the fact that the Boltzmann equation is a fundamental equation for many-particle systems of weak statistical correlations between the particles. The present nonequilibrium ensemble method can provide the nonequilibrium partition function with the help of the method of differential equations for K_a and the constitutive relations can be calculated therewith. This feature is something that is not available in the conventional moment method which does not even have a nonequilibrium partition function or the nonequilibrium chemical potential. It in fact assures us that the exponential representation of the nonequilibrium distribution function is mathematically appropriate and useful, at least, in the case of dilute gases. We have also shown an example for the nonequilibrium part K_a of Z_a which can be used for studies of irreversible processes within the bounds of the thirteen moment approximation. This approximation is in practice the most commonly used and relevant to experiments. The generalized potentials obtained from the nonequilibrium partition function computed are nonlinear with respect to nonconserved variables and present some interesting features the implication of which should be investigated in connection with nonlinear dynamics, pattern formation, and so on. Some examples for applications will be considered in the following chapter, but the utility of the theoretical results obtained is wide. It is hoped that the theory will see many applications in study of nonlinear transport processes in fluids in the future.

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Transport Processes in Fluids

The generalized hydrodynamics equations derived in the previous chapter include the flux evolution equations which are the constitutive equations for the fluxes in the system. As such, they contain the information on the material properties and, in particular, the transport processes occurring in the system. In this chapter we first show how to extract such information and under what condition the conventional theory of linear transport processes, such as the Chapman–Enskog first approximation for linear transport processes, arises from the more general viewpoint of the present nonequilibrium ensemble method and the generalized hydrodynamics equations underlying it. We then will formulate a theory of steady state nonlinear transport processes which extends the linear theory into regimes where nonlinear couplings between fluxes are required for the proper description of the processes in question. Some applications of the steady state constitutive equations and the nonlinear transport coefficients obtained therefrom will be discussed in the remainder of the chapter.

8.1 Approximate Constitutive Equations

Since constitutive equations derived in Chapter 7 form an open hierarchy of partial differential equations for nonconserved moments, it must be suitably closed. The consideration made in the previous chapter suggests that limiting the number of moments to Φ_{qa} , $1 \leq q \leq 4$, is a possible approximation. This, however, is more of an appeal to the physics of the situation in hand than based on an inescapable mathematical reason. Mathematically this question of closure is an open problem at present. Since higher order fluxes, namely, Φ_{qa} for $q > 4$, are not measured in the laboratory, our attention is confined only to the measurable which turn out to be the first thirteen moments in the case of a single-component gas. The suggested approximation which takes Φ_{qa} for $q \leq 4$ is the multicomponent equivalent of the 13 moment approximation for a single-component fluid in the Maxwell–Grad moment method. In the latter method the moments higher than the first 13 moments can be expressed in terms of the moments retained if the former are computed with the 13-moment expansion for the distribution function. This closure is no more justifiable than other plausible closures whose ultimate justification lies in the efficacy of the constitutive equa-

tions thus obtained to explain the experimental data. We will find that the closure

$$\psi_{qa} = 0 \quad (q \geq 1; q \neq 4) \quad (8.1)$$

yields reasonable results for transport properties and hydrodynamics equations that enable us to comprehend experimental data qualitatively and quantitatively as shown in rheological studies reported earlier and as will be demonstrated presently in the examples discussed in the subsequent sections. This closure gives rise to mathematically simpler constitutive equations than otherwise without sacrificing the physics of transport processes, as will be seen. We will find that when used at the steady state in the moving coordinate system where $d_t \hat{\Phi}_{qa} = 0$ the aforementioned closure becomes indispensable for the steady generalized hydrodynamics equations that adequately account for the behavior of, for example, steady shock waves which remain an outstanding unsolved problem in continuum hydrodynamic theory. In addition to this closure relation the generalized potentials X_{qa} are approximated by

$$X_{qa} = -\Phi_{qa} g_a^{(q)}, \quad (8.2)$$

where

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

as defined previously; see Eq. (7.233). The approximations in (8.2) are the lowest order solutions for the generalized potentials which can be obtained from the nonequilibrium partition function calculated in Sec. 7.10 of Chapter 7. These approximations for X_{qa} motivates us to define a new set of collision bracket integrals

$$\mathfrak{R}_{ab}^{(qk)} = (\beta g)^{-1} g_a^{(q)} R_{ab}^{(qk)} g_b^{(k)}, \quad (8.3)$$

where g and $R_{ab}^{(qk)}$ are defined in Secs. 7.7 and 7.9; see (7.194) and (7.241)–(7.246), respectively.

At this point we note that the constitutive equations presented here are the fixed frame version which is inappropriate¹ for investigating transport processes [1]. They must be cast into the corotating frame version [2]. The latter can be derived by following the method described in a paper by this author [3]. Since the derivation is lengthy, albeit essential, but the final results of the derivation can be rather simply related to the fixed frame results, a set of rules has been formulated for constructing corotating frame evolution equations from the fixed frame version in the paper cited. According to these rules the corotating frame evolution equations can be easily

¹A cogent argument in favor of the corotating frame can be found in [1].

obtained from the fixed-frame counterparts if the following replacements are made:

$$\begin{aligned} -[\boldsymbol{\Pi}_a, \boldsymbol{\omega}] &\Rightarrow [\boldsymbol{\Pi}_a, \boldsymbol{\omega}], \\ -\mathbf{Q}'_a \cdot \boldsymbol{\omega} &\Rightarrow \mathbf{Q}'_a \cdot \boldsymbol{\omega}, \\ -\mathbf{J}_a \cdot \boldsymbol{\omega} &\Rightarrow \mathbf{J}_a \cdot \boldsymbol{\omega}, \end{aligned} \quad (8.4)$$

in the fixed frame constitutive equations. Here $\boldsymbol{\omega}$ is the vorticity tensor, namely, the antisymmetric part of $\nabla \mathbf{u}$ defined explicitly later. That is, in terms like $[\boldsymbol{\Pi}_a \cdot \nabla \mathbf{u}]^{(2)}$, $\mathbf{Q}'_a \cdot \nabla \mathbf{u}$, and $\mathbf{J}_a \cdot \nabla \mathbf{u}$ the antisymmetric part of the tensor $\nabla \mathbf{u}$ must be changed in its sign. With such a modification the aforementioned approximation for X_{qa} , and the closure relation for ψ_{qa} ($q \geq 1$) mentioned earlier, the generalized hydrodynamics equations take the forms

$$\rho \frac{dv}{dt} = \nabla \cdot \mathbf{u}, \quad (8.5)$$

$$\rho \frac{d}{dt} c_a = -\nabla \cdot \mathbf{J}_a, \quad (8.6)$$

$$\rho \frac{d}{dt} \mathbf{u} = -\nabla \cdot \mathbf{P} + \sum_{a=1}^r \rho_a \mathbf{F}_a, \quad (8.7)$$

$$\rho \frac{d}{dt} \mathcal{E} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a, \quad (8.8)$$

$$\begin{aligned} \rho \frac{d}{dt} \hat{\boldsymbol{\Pi}}_a &= -2p_a \gamma - 2[\mathbf{J}_a (d_t \mathbf{u} - \mathbf{F}_a)]^{(2)} - 2[\boldsymbol{\Pi}_a \cdot \boldsymbol{\gamma}]^{(2)} - [\boldsymbol{\omega}, \boldsymbol{\Pi}_a] \\ &\quad - 2\Delta_a \boldsymbol{\gamma} - \frac{2}{3} \boldsymbol{\Pi}_a \nabla \cdot \mathbf{u} - 2p_a \sum_{b=1}^r \mathfrak{R}_{ab}^{(11)} \boldsymbol{\Pi}_b q(\Phi), \end{aligned} \quad (8.9)$$

$$\begin{aligned} \rho \frac{d}{dt} \hat{\boldsymbol{\Delta}}_a &= -p_a d_t \ln(p_a v^{5/3}) + p_a d_t \ln c_a - \frac{2}{3} \boldsymbol{\Pi}_a : \nabla \mathbf{u} \\ &\quad - \frac{2}{3} \Delta_a \nabla \cdot \mathbf{u} - \mathbf{J}_a \cdot \nabla \left(\frac{p_a}{\rho_a} \right) - \frac{2}{3} \mathbf{J}_a \cdot (d_t \mathbf{u} - \mathbf{F}_a) \\ &\quad - \frac{2p_a}{3} \sum_{b=1}^r \mathfrak{R}_{ab}^{(22)} \boldsymbol{\Pi}_b q(\Phi), \end{aligned} \quad (8.10)$$

$$\rho \frac{d}{dt} \hat{\mathbf{Q}}'_a = -p_a \hat{C}_{pa} T \nabla \ln T - \mathbf{Q}'_a \cdot (\boldsymbol{\gamma} + \frac{1}{3} \boldsymbol{\delta} \nabla \cdot \mathbf{u}) + \mathbf{Q}'_a \cdot \boldsymbol{\omega} - \mathbf{J}_a d_t \hat{h}_a$$

$$\begin{aligned}
& -(\boldsymbol{\Pi}_a + \Delta_a \boldsymbol{\delta}) \cdot \nabla \hat{h}_a - (d_t \mathbf{u} - \mathbf{F}_a) \cdot (\boldsymbol{\Pi}_a + \Delta_a \boldsymbol{\delta}) \\
& - p_a \hat{C}_{pa} T \sum_{b=1}^r \left(\mathfrak{R}_{ab}^{(33)} \mathbf{Q}'_b + \mathfrak{R}_{ab}^{(34)} \mathbf{J}_b \right) q(\Phi), \tag{8.11}
\end{aligned}$$

$$\begin{aligned}
\rho \frac{d}{dt} \hat{\mathbf{J}}_a &= -p \mathbf{d}_a - \nabla \cdot (\boldsymbol{\Pi}_a + \Delta_a \boldsymbol{\delta}) + c_a \nabla \cdot (\boldsymbol{\Pi} + \Delta \boldsymbol{\delta}) \\
& - \mathbf{J}_a \cdot \left(\gamma + \frac{1}{3} \boldsymbol{\delta} \nabla \cdot \mathbf{u} \right) + \mathbf{J}_a \cdot \boldsymbol{\omega} \\
& - \rho_a \sum_{b=1}^r \left(\mathfrak{R}_{ab}^{(43)} \mathbf{Q}'_b + \mathfrak{R}_{ab}^{(44)} \mathbf{J}_b \right) q(\Phi). \tag{8.12}
\end{aligned}$$

The various symbols in these equations are defined by

$$\mathbf{d}_a = \nabla \left(\frac{n_a}{n} \right) + \left(\frac{n_a}{n} - \frac{\rho_a}{\rho} \right) \nabla \ln p + \frac{\rho}{p} (\mathbf{F} - c_a \mathbf{F}_a), \tag{8.13}$$

$$\gamma = \frac{1}{2} [\nabla \mathbf{u} + (\nabla \mathbf{u})^t] - \frac{1}{3} \boldsymbol{\delta} \nabla \cdot \mathbf{u}, \tag{8.14}$$

$$\boldsymbol{\omega} = \frac{1}{2} [\nabla \mathbf{u} - (\nabla \mathbf{u})^t], \tag{8.15}$$

$$[\boldsymbol{\omega}, \boldsymbol{\Pi}_a] = \boldsymbol{\omega} \boldsymbol{\Pi}_a - \boldsymbol{\Pi}_a \boldsymbol{\omega}, \tag{8.16}$$

$$q(\Phi) = \frac{\sinh \kappa(\Phi)}{\kappa(\Phi)}, \tag{8.17}$$

$$\kappa(\Phi) = \left(\sum_{a,b=1}^r \sum_{\alpha,\gamma \geq 1} \Phi_{\alpha a} \mathfrak{R}_{ab}^{(44)} \Phi_{\gamma b} \right)^{1/2}, \tag{8.18}$$

and we have used the fact that by symmetry the collision bracket integrals of $h_a^{(\gamma)}$ of different tensorial ranks do not couple. It is emphasized that only the terms, such as $[\boldsymbol{\omega}, \boldsymbol{\Pi}_a]$, $\mathbf{Q}'_a \cdot \boldsymbol{\omega}$, and $\mathbf{J}_a \cdot \boldsymbol{\omega}$, involving the vorticity tensor $\boldsymbol{\omega}$ have changed their signs in the equations (8.9)–(8.12). Since these terms are products of the flux and the vorticity tensor, namely, nonlinear, they do not appear in the linear theory, and the question of Jaumann derivatives becomes irrelevant in the theory of linear irreversible processes. The terms $-2p_a [\nabla \mathbf{u}]^{(2)}$, $[-p_a d_t \ln(p_a v^{5/3}) + p_a d_t \ln c_a]$, $-p_a \hat{C}_{pa} T \nabla \ln T$, and $-p \mathbf{d}_a$ in (8.9)–(8.12) may be regarded as the driving forces of the associated fluxes. This interpretation of them becomes more cogent and transparent as we examine linear transport processes. In the case of dilute gases the excess

trace part of the stress Δ_a vanishes identically, as discussed in Chapter 7. Therefore the evolution equation for Δ_a is not necessary, and we will drop (8.10) from the set when dilute monatomic gases are considered.

Since one of the aims of this section is to show that the present theory contains the Chapman–Enskog theory and it is simpler to consider a single component system for the purpose, we will examine the generalized hydrodynamics equations for such a system. The case of mixtures can be examined in the same manner; since it is rather straightforward to consider a mixture, it is left to the reader as an exercise. Since $\Delta_a = 0$ and there are no diffusion fluxes, the generalized hydrodynamics equations consist of the partial differential equations

$$\rho \frac{dv}{dt} = \nabla \cdot \mathbf{u}, \quad (8.19)$$

$$\rho \frac{d}{dt} \mathbf{u} = -\nabla \cdot \mathbf{P} + \rho \mathbf{F}, \quad (8.20)$$

$$\rho \frac{d}{dt} \mathcal{E} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u}, \quad (8.21)$$

$$\begin{aligned} \rho \frac{d}{dt} \hat{\mathbf{\Pi}} &= -2p\gamma - 2[\mathbf{\Pi} \cdot \boldsymbol{\gamma}]^{(2)} - [\boldsymbol{\omega}, \mathbf{\Pi}] - \frac{2}{3}\mathbf{\Pi} \nabla \cdot \mathbf{u} \\ &\quad - \frac{p}{\eta_0} \mathbf{\Pi} q(\Phi), \end{aligned} \quad (8.22)$$

$$\begin{aligned} \rho \frac{d}{dt} \hat{\mathbf{Q}} &= -p\hat{C}_p T \nabla \ln T - \mathbf{\Pi} \cdot \nabla \hat{h} - (d_t \mathbf{u} - \mathbf{F}) \cdot \mathbf{\Pi} \\ &\quad - \mathbf{Q} \cdot (\boldsymbol{\gamma} + \frac{1}{3} \boldsymbol{\delta} \nabla \cdot \mathbf{u}) + \mathbf{Q} \cdot \boldsymbol{\omega} \\ &\quad - \frac{p\hat{C}_p T}{\lambda_0} \mathbf{Q} q(\Phi). \end{aligned} \quad (8.23)$$

These equations are Galileian invariant, as are the original equations before the closure relations are imposed. The transport coefficients η_0 and λ_0 are given by the kinetic theory expressions

$$\eta_0 = \frac{2p^2 g}{k_B T R^{(11)}}, \quad (8.24)$$

$$\lambda_0 = \frac{(\hat{C}_p T p)^2 g}{k_B T R^{(33)}}.$$

We have dropped the subscripts referring to the species in the collision bracket integrals $R^{(11)}$ and $R^{(33)}$. The κ in the nonlinear parameter $q(\Phi)$

can be written in the form

$$\kappa = \left[\left(\frac{\tau_p}{2\eta_0} \right)^2 \boldsymbol{\Pi} : \boldsymbol{\Pi} + \left(\frac{\tau_q}{\lambda_0} \right)^2 \mathbf{Q} \cdot \mathbf{Q} \right]^{1/2}, \quad (8.25)$$

$$\tau_p = \left[2\eta_0 \left(\frac{m_r k_B T}{2} \right)^{1/2} \right]^{1/2} (nk_B T d)^{-1}, \quad (8.26)$$

$$\tau_q = \left[\lambda_0 \left(\frac{m_r k_B T}{2} \right)^{1/2} \right]^{1/2} (nk_B T d)^{-1}, \quad (8.27)$$

with m_r and d denoting the reduced mass and the size parameter of the molecule. As will be shown later, η_0 and λ_0 will turn out to be the Newtonian viscosity and the Fourier thermal conductivity of the gas. These quantities, together with the specific heat \hat{C}_p , m_r , and d , are the only material parameters in the generalized hydrodynamics equations. The situation is similar to the Navier–Stokes and Fourier equations where only the aforementioned material parameters occur. In view of the fact that such classical hydrodynamics equations [5]—Navier–Stokes and Fourier equations—are applicable to both liquids and gases, it is plausible to conjecture that the generalized hydrodynamics equations (8.19)–(8.23) presented here applies to liquids as well. Indeed, they are applicable to condensed phases, as have been shown elsewhere [4], although we limit most of application of (8.19)–(8.23) to gases in this chapter.

8.2 Reduced Generalized Hydrodynamics Equations

To investigate how the generalized hydrodynamics equations give rise to the linear theory of transport processes obtained by the Chapman–Cowling first approximation [6], we cast them into dimensionless differential equations. These reduced equations are required to develop approximation procedures for the generalized hydrodynamics equations and also to make connection with other existing kinetic theory methods and particularly the Chapman–Enskog method.

The characteristic length and time of the system are respectively denoted by L and τ_r ; the characteristic velocity will be either the mean molecular speed or the mean velocity of the fluid; and other reference values will be denoted by the quantity affixed with the subscript r . There are more than one characteristic time scales for the generalized hydrodynamics equations, since the conserved variables and flux variables evolve generally on different time scales. Such a separation of the time scales motivates different approximation schemes, which will be examined in order to obtain approximate

results for constitutive relations suitable for different time scale regimes.

Here we reduce the variables by scaling them with appropriate reference variables in the following manner. The choice of reference variables depends on the phenomenon of interest.

$$\begin{aligned}\boldsymbol{\xi} &= \mathbf{r} L^{-1}, & \mathbf{u}^* &= \mathbf{u} U_r^{-1}, & \zeta &= t \tau_r^{-1}, \\ T^* &= T T_r^{-1}, & \rho^* &= \rho \rho_r^{-1}, & \mathcal{E}^* &= \mathcal{E} \mathcal{E}_r^{-1}, \\ p^* &= p p_r^{-1}, & \eta^* &= \eta_0 \eta_r^{-1}, & \lambda^* &= \lambda_0 \lambda_r^{-1}, \\ \gamma^* &= [\nabla \mathbf{u}]^{(2)} L U_r^{-1}, & \omega^* &= \boldsymbol{\omega} L U_r^{-1}, \\ \boldsymbol{\Pi}^* &= \boldsymbol{\Pi} L (\eta_r U_r)^{-1}, & \mathbf{Q}^* &= \mathbf{Q} L T_r (\lambda_r \Delta_r)^{-1},\end{aligned}$$

where U_r is the reference velocity, $\Delta_r = T_2 - T_1$ is the temperature difference between two characteristic points 1 and 2 in space and T_r may be taken as $\frac{1}{2}(T_1 + T_2)$. The rest of the symbols are self-explanatory. With the reference variables used here, we can define various dimensionless fluid dynamic numbers as follows²:

Mach:

$$N_M = \frac{U_r}{\sqrt{\gamma_0 \mathcal{R} T_r}},$$

Reynolds:

$$N_{Re} = \frac{\rho_r U_r L}{\eta_r},$$

Eckert:

$$N_E = \frac{U_r^2}{\widehat{C}_{pr} \Delta_r},$$

Prandtl:

$$N_{Pr} = \frac{\widehat{C}_{pr} T_r \eta_r}{\lambda_r},$$

Knudsen:

$$N_{Kn} = \frac{l}{L},$$

where l is the mean free path and \mathcal{R} is the gas constant per mass, and γ_0 is the polytropic ratio: $\gamma_0 = \widehat{C}_p / \widehat{C}_v$. These fluid dynamic numbers are not

²Since in the present work the thermodynamic force for heat flow is taken to be $\nabla \ln T$ instead of ∇T , the thermal conductivities λ_0 or λ_r differ by the factor T^{-1} from the one appearing in the conventional theory, e.g., the Chapman–Enskog theory: namely, $\lambda_0 = \lambda_{\text{Chapman-Enskog}} T$. For this reason there appears the extra T_r factor in the Prandtl number defined in this work.

all independent of each other, since some of them are related to others. For example, there holds the relation

$$N_{\text{Re}} = \sqrt{\frac{\pi \gamma_0}{2}} \frac{N_M}{N_{Kn}}.$$

It is useful to define the following composite fluid dynamic number

$$N_\delta = \frac{\eta_r U_r}{p_r L} = \gamma_0 N_M^2 N_{\text{Re}}^{-1} = \sqrt{\frac{2\pi}{\gamma_0}} N_M N_{Kn}. \quad (8.28)$$

Notice that this number is basically the ratio of shear stress to pressure, that is, a dimensionless shear stress. This number plays an important role in the present discussion. There are other dimensionless numbers characterizing flow problems associated with the generalized hydrodynamics equations. One is the Deborah number associated with shear flow. It is defined by the ratio of the characteristic time τ_s of stress relaxation to the characteristic time τ_h of flow:

$$N_{De} = \frac{\tau_s}{\tau_h} = \frac{(\eta_r/\Pi_r)}{(L/U_r)} = \frac{(\eta_r U_r/L)}{\Pi_r}, \quad (8.29)$$

which may be also regarded as the ratio of the stress in the linear theory to the stress at arbitrary shear rate. Another number often used in rheology is the Weissenberg number, which is defined as the product of characteristic time for stress and shear rate

$$N_{We} = \tau_s \frac{U_r}{L}. \quad (8.30)$$

Since the shear rate has the dimension of inverse time, the Weissenberg number is also seen as a dimensionless shear rate. This number may be expressed as the ratio of the first normal stress difference to the shear stress. It thus indicates the relative importance of first normal stress difference and shear stress. It is useful to define a dimensionless number associated with the heat flux in a similar manner to the Deborah number. We will call it the Q number, which is the ratio of the characteristic time τ_q of the heat flow to the characteristic hydrodynamic time τ_h :

$$N_Q = \frac{\tau_q}{\tau_h} = \frac{(h_r U_r / L^3)}{Q_r}, \quad (8.31)$$

where h_r is the reference enthalpy. This number may be interpreted as the ratio of ballistic heat flow ($h_r U_r / L^3$) to diffusive heat flow; we also note that $N_Q = N_{Pr}/N_\delta$ if we take $p_r = \rho_r U_r^2$. These dimensionless numbers are useful for examining the adiabatic approximation, in which the fluxes evolve on the time scale where the fluid velocity and temperature remain

constant. The meaning of steady fluxes in such a time scale will be discussed later.

When the reduction scheme presented is implemented on the generalized hydrodynamics equations, the reduced generalized hydrodynamics equations are all expressed in the reduced variables and the dimensionless fluid dynamic numbers appear in the equations. In the following set of reduced generalized hydrodynamics equations we drop the asterisk for the reduced quantities for brevity of notation. The reduced generalized hydrodynamics equations will be readily recognizable, since there will appear the dimensionless fluid dynamic numbers in them. If the dimensionless fluid dynamic numbers and the polytropic ratio are set equal to unity in these reduced equations, they will become the original unreduced generalized hydrodynamics equations (8.19)–(8.23). We have also set $\mathbf{F} = 0$ since we are going to consider the case of no external force. Inclusion of the external force will require an additional dimensionless number, for example, the Rayleigh number in the case of gravitational force. The reduced equations are:

$$\rho \frac{dv}{dt} = \nabla \cdot \mathbf{u}, \quad (8.32)$$

$$\gamma_0 N_M^2 \rho \frac{d}{dt} \mathbf{u} = -\nabla p - N_\delta \nabla \cdot \boldsymbol{\Pi}, \quad (8.33)$$

$$\frac{\gamma_0 N_M^2}{N_E} \rho \frac{d}{dt} \mathcal{E} = -\frac{N_\delta}{N_{Pr} N_E} \nabla \cdot \mathbf{Q} - p \nabla \cdot \mathbf{u} - N_\delta \boldsymbol{\Pi} : \nabla \mathbf{u}, \quad (8.34)$$

$$\begin{aligned} N_\delta \rho \frac{d}{dt} \hat{\boldsymbol{\Pi}} &= -2p\gamma - N_\delta \left(2[\boldsymbol{\Pi} \cdot \boldsymbol{\gamma}]^{(2)} - [\boldsymbol{\omega}, \boldsymbol{\Pi}] + \frac{2}{3} \boldsymbol{\Pi} \nabla \cdot \mathbf{u} \right) \\ &\quad - \frac{p}{\eta_0} \boldsymbol{\Pi} \mathbf{q}(N_\delta \kappa^*), \end{aligned} \quad (8.35)$$

$$\begin{aligned} \frac{N_\delta}{N_{Pr}} \rho \frac{d}{dt} \hat{\mathbf{Q}} &= -p \hat{C}_p T \nabla \ln T - N_\delta \boldsymbol{\Pi} \cdot \nabla \hat{h} \\ &\quad + \frac{N_\delta N_E}{\gamma_0 N_M^2} \nabla \cdot (p \boldsymbol{\delta} + N_\delta \boldsymbol{\Pi}) \cdot \hat{\boldsymbol{\Pi}} \\ &\quad - \frac{N_\delta}{N_{Pr}} \mathbf{Q} \cdot (\boldsymbol{\gamma} - \boldsymbol{\omega} + \frac{1}{3} \boldsymbol{\delta} \nabla \cdot \mathbf{u}) \\ &\quad - \frac{p \hat{C}_p T}{\lambda_0} \mathbf{Q} q(N_\delta \kappa^*). \end{aligned} \quad (8.36)$$

Here κ^* is the reduced Rayleigh dissipation function:

$$\kappa^* = \frac{\kappa}{N_\delta}$$

$$= \frac{1}{2} \sqrt{\frac{\pi^{3/2}}{\gamma_0}} \frac{T^{*1/4}}{p^* \sqrt{\eta^*}} \left[\boldsymbol{\Pi} : \boldsymbol{\Pi} + 2\epsilon \frac{\eta^*}{\lambda^*} \mathbf{Q} \cdot \mathbf{Q} \right]^{1/2} \quad (8.37)$$

with ϵ defined by

$$\epsilon = \frac{\Delta_r}{T_r N_{Pr} N_E}. \quad (8.38)$$

We recall the following point about κ^* : the nonlinear factor $q(\Phi)$ is a result of resumming the expansion of the Boltzmann collision integral in the Knudsen number. The scaling behavior of κ given in (8.37) indeed shows that such is the case. We also note that κ can be written as

$$\kappa = g_0 \left(\frac{1}{2\eta_0} \boldsymbol{\Pi} : \boldsymbol{\Pi} + \frac{1}{\lambda_0} \mathbf{Q} \cdot \mathbf{Q} \right)^{1/2} \quad (8.39)$$

with $g_0 = (mk_B T)^{1/4}/\sqrt{2}pd$ (m = molecular mass). We have kept the asterisks in (8.37) to distinguish κ^* from κ in (8.39), where the quantities are un-reduced. If the factor $(\pi^{3/2}/\gamma_0)^{1/2}$ in (8.37) is replaced by $(mk_B T)^{1/4}/d$, then κ^* becomes κ , provided that ϵ and N_δ in (8.37) are set equal to unity, and vice versa. With this understanding we may drop the asterisks from the reduced variables in (8.37) and write it in the form consistent with the reduced generalized hydrodynamics equations (8.32)–(8.36):

$$\kappa^* = \frac{1}{2} \sqrt{\frac{\pi^{3/2}}{\gamma_0}} \frac{T^{1/4}}{\sqrt{\eta_0 p}} \left[\boldsymbol{\Pi} : \boldsymbol{\Pi} + 2\epsilon \frac{\eta_0}{\lambda_0} \mathbf{Q} \cdot \mathbf{Q} \right]^{1/2}. \quad (8.40)$$

It is quite clear that κ^2 as given in (8.39) is related to the Rayleigh dissipation function for the gas subjected to a stress and heat flow.

8.3 Chapman–Cowling First-Order Theory

We now notice that the composite fluid dynamic number N_δ may be used as an expansion parameter for $\boldsymbol{\Pi}$ and \mathbf{Q} since it appears in both constitutive equations (8.35) and (8.36) for $\boldsymbol{\Pi}$ and \mathbf{Q} . On the strength of this observation, we expand $\boldsymbol{\Pi}$ and \mathbf{Q} as follows:

$$\boldsymbol{\Pi} = \boldsymbol{\Pi}_0 + \boldsymbol{\Pi}_1 N_\delta + \boldsymbol{\Pi}_2 N_\delta^2 + \dots, \quad (8.41)$$

$$\mathbf{Q} = \mathbf{Q}_0 + \mathbf{Q}_1 N_\delta + \mathbf{Q}_2 N_\delta^2 + \dots \quad (8.42)$$

Substitution of these expansions into (8.35) and (8.36) yields the equations for the coefficients $\boldsymbol{\Pi}_0$, $\boldsymbol{\Pi}_1$, \mathbf{Q}_0 , \mathbf{Q}_1 , and so forth when the terms of like

power in N_δ are equated:

$$\boldsymbol{\Pi}_0 = -2\eta_0[\nabla \mathbf{u}]^{(2)}, \quad (8.43)$$

$$\mathbf{Q}_0 = -\lambda_0 \nabla \ln T, \quad (8.44)$$

$$\begin{aligned} \boldsymbol{\Pi}_1 &= \frac{\eta_0}{p} \left\{ -\rho \frac{d}{dt} \widehat{\boldsymbol{\Pi}}_0 - 2[\boldsymbol{\Pi}_0 \cdot \boldsymbol{\gamma}]^{(2)} - [\boldsymbol{\omega}, \boldsymbol{\Pi}_0] \right\} \\ &\quad - \frac{2\eta_0}{3p} \boldsymbol{\Pi}_0 \nabla \cdot \mathbf{u}, \end{aligned} \quad (8.45)$$

$$\begin{aligned} \mathbf{Q}_1 &= \frac{\lambda_0}{T \widehat{C}_p p} \left\{ -N_{\text{Pr}}^{-1} \rho \frac{d}{dt} \widehat{\mathbf{Q}}_0 - \boldsymbol{\Pi}_0 \cdot \nabla \widehat{h} + \frac{N_E}{\gamma_0 N_M^2} \widehat{\boldsymbol{\Pi}}_0 \cdot \nabla p \right\} \\ &\quad - \frac{\lambda_0}{T \widehat{C}_p p N_{\text{Pr}}} \mathbf{Q}_0 \cdot (\boldsymbol{\gamma} + \frac{1}{3} \boldsymbol{\delta} \nabla \cdot \mathbf{u}) \\ &\quad + \frac{\lambda_0}{T \widehat{C}_p p N_{\text{Pr}}} \mathbf{Q}_0 \cdot \boldsymbol{\omega}, \end{aligned} \quad (8.46)$$

The nonlinear factor $q(N_\delta \kappa^*)$ does not contribute to the zero- and first-order solutions since

$$q(N_\delta \kappa^*) = 1 + \frac{1}{6} \kappa_0^{*2} N_\delta^2 + \dots \quad (8.47)$$

Here

$$\kappa_0^* = \frac{1}{2} \sqrt{\frac{\pi^{3/2}}{\gamma_0}} \frac{T^{1/4}}{\sqrt{\eta_0 p}} \left[\boldsymbol{\Pi}_0 : \boldsymbol{\Pi}_0 + 2\epsilon \frac{\eta_0}{\lambda_0} \mathbf{Q}_0 \cdot \mathbf{Q}_0 \right]^{1/2}. \quad (8.48)$$

The second order term in (8.47) contributes to $\boldsymbol{\Pi}_2$ and \mathbf{Q}_2 . The first-order solutions $\boldsymbol{\Pi}_1$ and \mathbf{Q}_1 correspond to the Burnett-order solutions in the Chapman–Enskog method.

The classical hydrodynamics equations follow when (8.43) and (8.44) are substituted into the balance equations:

$$\rho \frac{dv}{dt} = \nabla \cdot \mathbf{u}, \quad (8.49)$$

$$N_M^2 \rho \frac{d}{dt} \mathbf{u} = -\nabla p + 2N_\delta \nabla \cdot \eta_0 [\nabla \mathbf{u}]^{(2)}, \quad (8.50)$$

$$\begin{aligned} \frac{\gamma_0 N_M^2}{N_E} \rho \frac{d}{dt} \mathcal{E} &= \frac{N_\delta}{N_{\text{Pr}} N_E} \nabla \cdot \lambda_0 \nabla \ln T - p \nabla \cdot \mathbf{u} \\ &\quad + 2N_\delta \eta_0 [\nabla \mathbf{u}]^{(2)} : \nabla \mathbf{u}, \end{aligned} \quad (8.51)$$

which are the Navier–Stokes and Fourier equations. The last term in (8.51) represents a thermoviscous coupling. It must be noted that the bulk dilatation term does not appear in the Navier–Stokes equation since the bulk viscosity η_b does not exist in the case of dilute monatomic gases under consideration. This is related to the fact that the excess normal stress Δ vanishes for dilute monatomic gases.

If the first-order solutions for Π and \mathbf{Q} are substituted into the balance equations then the Burnett-order hydrodynamics equations are obtained:

$$\rho \frac{dv}{dt} = \nabla \cdot \mathbf{u}, \quad (8.52)$$

$$\gamma_0 N_M^2 \rho \frac{d}{dt} \mathbf{u} = -\nabla p - N_\delta \nabla \cdot (\Pi_0 + N_\delta \Pi_1), \quad (8.53)$$

$$\begin{aligned} \frac{\gamma_0 N_M^2}{N_E} \rho \frac{d}{dt} \mathcal{E} &= -\frac{N_\delta}{N_{Pr} N_E} \nabla \cdot (\mathbf{Q}_0 + \mathbf{Q}_1 N_\delta) - p \nabla \cdot \mathbf{u} \\ &\quad + N_\delta \Pi_0 : \nabla \mathbf{u} + N_\delta^2 \Pi_1 : \nabla \mathbf{u}. \end{aligned} \quad (8.54)$$

These Burnett-order equations contain third-order spatial derivatives of \mathbf{u} and T and hence require boundary conditions on the spatial derivatives of velocity and temperature, which are not generally available experimentally. Moreover, their solution is much more difficult to obtain numerically. Since not only their practical application is rather limited but also the H theorem is not generally satisfied by them, we will not consider the Burnett-order solutions in this work. Recall in this connection that according to the conclusion drawn in Sec. 6.1.3 of Chapter 6 the Chapman–Enskog solutions are not thermodynamically consistent.

The lowest order solutions for the stress and heat flux given in (8.43) and (8.44) are in exactly the same forms as those obtained by the Chapman–Enskog method, namely, the Chapman–Cowling first approximations for the stress tensor and the heat flux. Therefore the present theory contains the Chapman–Cowling first approximations for the transport coefficients η_0 and λ_0 . We have thus verified the statement made earlier to that effect. The analysis presented here indicates that the classical hydrodynamics equations simply correspond to the lowest order solutions for the constitutive equations, that is, the flux evolution equations and, consequently, their range of validity should be limited to the processes occurring near equilibrium. One might then be tempted to use the next order solutions, but the higher order solutions for the constitutive equations do not assure us of the positivity of the Boltzmann entropy production computed to the order in question. In other words, they are not consistent with the H theorem as discussed in Chapter 6. Therefore we would like to have an alternative method of approximation which will make it possible to extend

the theory into nonlinear regimes and at the same time keep the solutions thermodynamically consistent.

We now examine the thermodynamic aspect of the approximate solutions (8.41) and (8.42). To the order of $N_\delta^0 = 1$ for which (8.43) and (8.44) are the solutions of (8.35) and (8.36), Π and \mathbf{Q} are steady in time in the moving coordinate system and therefore there hold the relations

$$\frac{d\hat{\Pi}}{dt} = \frac{d\hat{\mathbf{Q}}}{dt} = 0. \quad (8.55)$$

Consequently the calortropy differential is then

$$d_t \hat{\Psi} = T^{-1} (d_t \mathcal{E} + p d_t v), \quad (8.56)$$

which is simply the local equilibrium formula for the Clausius entropy \mathcal{S}_e . Therefore to the order of N_δ^0 the calortropy coincides with the Clausius entropy and

$$d_t \hat{\Psi} = d_t \mathcal{S}_e. \quad (8.57)$$

Since the Navier–Stokes and Fourier equations (8.50) and (8.51) correspond to the lowest order (zeroth order in N_δ) solutions (8.43) and (8.44), *it can be concluded that the underlying thermodynamics of the classical hydrodynamics, namely, the Navier–Stokes–Fourier theory, is the local equilibrium formula (8.56)*. This is in agreement with the conclusion drawn from the usual Chapman–Enskog method presented in Chapter 6. In fact, if the substantial time derivatives of Π and \mathbf{Q} are calculated to the first order in N_δ they also vanish, that is, (8.55) holds. Continuing in this manner it is possible to show that (8.55) holds to all orders in N_δ . In other words the Chapman–Enskog method corresponds to the local equilibrium formula (8.56) to all orders in N_δ at the thermodynamic level. This is in contrast to the behavior exhibited by the statistical formula for $d_t \mathcal{S}$ as we have shown in Chapter 6, since there appear additional terms beyond the local equilibrium formula for $d_t \mathcal{S}_e$. These additional terms are in fact the terms related to the relative Boltzmann entropy. Therefore we can conclude that at the thermodynamic level the Chapman–Enskog method corresponds to the differential form for the calortropy that coincides with the local equilibrium formula for $d_t \mathcal{S}_e$. This must be so because the fluxes are, in essence, considered to be steady in the Chapman–Enskog method.

8.4 Steady Nonlinear Transport Processes

We now look for an alternative to the series solution method used for the constitutive equations in the previous section. For this purpose the generalized hydrodynamics equations are reduced somewhat differently from the reduced forms in the previous section. Let us compare the rates of change

in Π and \mathbf{u} . Relative to the rate of change in \mathbf{u} , the rate of change in Π has the following magnitude:

$$\left(\frac{d\hat{\Pi}}{dt} \right) / \eta_r \left(\frac{d\mathbf{u}}{dt} \right) L^{-1} \sim \left(\frac{\Pi_r}{\eta_r} \right) / \left(\frac{U_r}{L} \right) \sim \frac{\tau_h}{\tau_s} = N_{De}^{-1}, \quad (8.58)$$

where Π_r , η_r , U_r , and L are suitable reference values for the stress, viscosity, velocity, and length characteristic of the system. These reference values may be taken differently from those presented in the previous section. The ratio in (8.58) suggests that the time evolution rate of the stress tensor is N_{De}^{-1} times that of the velocity evolution rate in the scale of the hydrodynamic evolution of the velocity. Therefore if the temporal evolution of the stress tensor is reckoned in the hydrodynamic time scale τ_h characteristic of the velocity evolution, the factor N_{De}^{-1} must then be multiplied with the derivative $(d\hat{\Pi}/dt)$, with the understanding that the time variable is reduced relative to τ_h . A similar consideration can be made for the heat flux evolution, and the derivative $(d\hat{\mathbf{Q}}/dt)$ must be multiplied by the factor N_Q^{-1} in the reduced time scale mentioned earlier. Thus the constitutive equations (8.22) and (8.23) of the generalized hydrodynamics equations may be written in the forms

$$\begin{aligned} N_{De}^{-1} \rho \frac{d\hat{\Pi}}{dt} &= -2p\gamma - 2[\Pi \cdot \gamma]^{(2)} - [\omega, \Pi] - \frac{2}{3}\Pi \nabla \cdot \mathbf{u} \\ &\quad - \frac{p}{\eta_0} \Pi q(\kappa), \end{aligned} \quad (8.59)$$

$$\begin{aligned} N_Q^{-1} \rho \frac{d\hat{\mathbf{Q}}}{dt} &= -p\hat{C}_p T \nabla \ln T - \Pi \cdot \nabla \hat{h} + \nabla \cdot (p\delta + \Pi) \cdot \hat{\Pi} \\ &\quad - \mathbf{Q} \cdot (\gamma - \omega + \frac{1}{3}\delta \nabla \cdot \mathbf{u}) - \frac{p\hat{C}_p T}{\lambda_0} \mathbf{Q} q(\kappa). \end{aligned} \quad (8.60)$$

Coupled to these constitutive equations are the balance equations (8.19)–(8.21) for the conserved variables. The Deborah and Q numbers are much larger than unity in the cases where the stress and the heat flux relax fast, unless transient processes are important because the stress and the heat flux are driven by shearing or a temperature gradient, for example, oscillating on the same time scale as τ_h . In the limit of large N_{De} and N_Q the time derivatives on the left hand sides of (8.59) and (8.60) can be neglected and there follow steady state equations

$$\begin{aligned} q(\kappa)\Pi &= -2\eta_0\gamma - \frac{2\eta_0}{p}[\Pi \cdot \gamma]^{(2)} - \frac{\eta_0}{p}[\omega, \Pi] \\ &\quad - \frac{2\eta_0}{3p}\Pi \nabla \cdot \mathbf{u}, \end{aligned} \quad (8.61)$$

$$\begin{aligned} q(\kappa)\mathbf{Q} &= -\lambda_0 \nabla \ln T - \frac{\lambda_0}{p\hat{C}_p T} [\mathbf{\Pi} \cdot \nabla \hat{h} - \nabla \cdot (p\delta + \mathbf{\Pi}) \cdot \hat{\mathbf{\Pi}}] \\ &\quad - \frac{\lambda_0}{p\hat{C}_p T} \mathbf{Q} \cdot (\gamma - \omega + \frac{1}{3}\delta \nabla \cdot \mathbf{u}). \end{aligned} \quad (8.62)$$

These results are brought about because $\mathbf{\Pi}$ and \mathbf{Q} change much faster than \mathbf{u} and T , which evolve in a slower time scale of τ_h . Therefore on the time scale of conserved variables \mathbf{u} and T the nonconserved variables $\mathbf{\Pi}$ and \mathbf{Q} have reached a steady state condition. This idea is rather akin to the center-manifold approximation [8] and forms the basic concept of the adiabatic approximation underlying the steady state constitutive equations used for nonlinear transport processes in the present work. The right hand side of the equation (8.61) or (8.62) consists of the thermodynamic force term driving the particular irreversible process and the nonlinear terms. Eqs. (8.61) and (8.62) will be applied to the study of steady shock waves in a later section.

By using the same reasoning as for the series expansion, the equations (8.61) and (8.62) may be further ‘linearized’ if the nonlinear terms on the right hand side are neglected. Such a linearization in fact amounts to neglecting the normal stress differences and we thus obtain the equations

$$\mathbf{\Pi} = -\frac{2\eta_0}{q(\kappa)} [\nabla \mathbf{u}]^{(2)}, \quad (8.63)$$

$$\mathbf{Q} = -\frac{\lambda_0}{q(\kappa)} \nabla \ln T, \quad (8.64)$$

which are quasi-linear owing to the presence of the nonlinear factor $q(\kappa)$. Because of this factor, $\mathbf{\Pi}$ and \mathbf{Q} are still coupled with each other in contrast to the case of the linear constitutive relations (8.43) and (8.44) which are independent of each other in accordance with the Curie principle—a symmetry principle.

Here again it is useful to consider the thermodynamic implication of this level of approximation. Since in the hydrodynamic time scale the fluxes are steady in the present order of approximation, the calortropy differential $d_t \hat{\Psi}$ becomes the same as the local equilibrium formula for the Clausius entropy:

$$d_t \hat{\Psi} = T^{-1} [d_t \mathcal{E} + p d_t v] = d_t S_e,$$

where the chemical potential term does not appear because the gas consists of a single component. Therefore as in the case of the first-order Chapman–Enskog result considered in Sec. 6.1, at the thermodynamic level the system is described by the local equilibrium differential form for the calortropy differential $d_t \hat{\Psi}$, which coincides with $d_t S_e$, but the constitutive equations for the fluxes are nonlinear. These steady state constitutive equations are

still subject to the positivity condition of the calortropy production Ξ_c ; see, for example, (7.46) or (7.59) for the definition of Ξ_c . This steady state theory shares the same local equilibrium formula for $d_t S_e$ with the theory of linear irreversible processes, although there is a basic difference in the constitutive equations for fluxes, since the constitutive equations are linear with regard to the fluxes in the theory of linear irreversible processes, but nonlinear in the nonlinear steady state theory under discussion here.

The quasi-linear relations (8.61) and (8.62) can be solved as described below. Substitution of (8.63) and (8.64) into (8.39) yields the Rayleigh dissipation function in the form

$$\kappa = \frac{1}{q(\kappa)} g_0 \left(2\eta_0 [\nabla \mathbf{u}]^{(2)} : [\nabla \mathbf{u}]^{(2)} + \lambda_0 \nabla \ln T \cdot \nabla \ln T \right)^{1/2}. \quad (8.65)$$

With the definition

$$\kappa_l = g_0 \left(2\eta_0 [\nabla \mathbf{u}]^{(2)} : [\nabla \mathbf{u}]^{(2)} + \lambda_0 \nabla \ln T \cdot \nabla \ln T \right)^{1/2} \quad (8.66)$$

and recalling the definition of the nonlinear factor $q(\kappa)$, we find from (8.65)

$$\sinh \kappa = \kappa_l \quad \text{or} \quad \kappa = \sinh^{-1} \kappa_l.$$

Substitution of this result into (8.63) and (8.64) yields the steady state stress and heat flux in the form

$$\Pi = -2\eta_0 \left(\frac{\sinh^{-1} \kappa_l}{\kappa_l} \right) [\nabla \mathbf{u}]^{(2)}, \quad (8.67)$$

$$\mathbf{Q} = -\lambda_0 \left(\frac{\sinh^{-1} \kappa_l}{\kappa_l} \right) \nabla \ln T. \quad (8.68)$$

These solutions supply non-Newtonian viscosity and non-Fourier thermal conductivity

$$\eta_e = \eta_0 \left(\frac{\sinh^{-1} \kappa_l}{\kappa_l} \right), \quad (8.69)$$

$$\lambda_e = \lambda_0 \left(\frac{\sinh^{-1} \kappa_l}{\kappa_l} \right). \quad (8.70)$$

These effective transport coefficients depend on velocity and temperature gradients. If (8.61) and (8.62) are used, a little more complicated solutions are obtained and, perhaps, more intriguing constitutive relations follow for the material functions of the nonlinear fluid than the nonlinear material functions (8.69) and (8.70). This topic is left to the reader to consider.

On substitution of the approximate solutions (8.67) and (8.68) or the approximate solutions of (8.61) and (8.62) into the balance equations (8.20)

and (8.21), we obtain nonclassical hydrodynamic equations which extend the Navier–Stokes and Fourier equations. Such nonclassical hydrodynamic equations would not require more boundary conditions than the classical hydrodynamic equations in contrast to the Burnett-order hydrodynamic equations which involves third-order derivatives of velocity and temperature. Note that these third order derivatives originate from the time derivatives of Π_0 and \mathbf{Q}_0 in (8.45) and (8.46).

Since κ_l depends on both the velocity and temperature gradients the effective transport coefficients η_e and λ_e in (8.69) and (8.70) are affected by shearing and heat flow. These effective transport coefficients reduce to the linear transport coefficients as the velocity and temperature gradients diminish in magnitude since the nonlinear factor, $\sinh^{-1} \kappa_l / \kappa_l$, tends to unity in the limit of vanishing gradients. To verify this statement we return to the definition of η_0 and λ_0 given in (8.24). Since the system consists of a single component the relevant collision bracket integrals $R^{(11)}$ and $R^{(33)}$ are easily obtained from (7.241) and (7.245) in the forms

$$R^{(11)} = \frac{4}{5} [[\boldsymbol{\tau}\boldsymbol{\tau}]^{(2)} : [\boldsymbol{\tau}\boldsymbol{\tau}]^{(2)}]_{aa'}, \quad (8.71)$$

$$R^{(33)} = \frac{2}{3m\beta} [S_{3/2}^{(1)}(\tau^2)\boldsymbol{\tau} \cdot S_{3/2}^{(1)}(\tau^2)\boldsymbol{\tau}]_{aa'}, \quad (8.72)$$

where the subscripts aa' to the collision bracket integral mean that the collision bracket integral is for particles of the same species; see Table 7.2 and also (7.237) where $b = a'$, another particle of the species a . By using these formulas in (8.24) (with the subscript a replaced with 1), we obtain the transport coefficients in the forms

$$\eta_0 = \frac{5\sqrt{2mk_B T}}{4d^2} \left([[\boldsymbol{\tau}\boldsymbol{\tau}]^{(2)} : [\boldsymbol{\tau}\boldsymbol{\tau}]^{(2)}]_{11'} \right)^{-1}, \quad (8.73)$$

$$\lambda_0 = \frac{75k_B T}{8d^2} \sqrt{\frac{k_B T}{2m}} \left([S_{3/2}^{(1)}(\tau^2)\boldsymbol{\tau} \cdot S_{3/2}^{(1)}(\tau^2)\boldsymbol{\tau}]_{11'} \right)^{-1}. \quad (8.74)$$

These are Chapman–Cowling first approximations [6] for viscosity and thermal conductivity of a single-component gas, respectively. In the case of the hard sphere the collision bracket integrals in (8.73) and (8.74) are analytically computable. The hard sphere viscosity and thermal conductivity are [6], respectively, given by

$$\eta_0 = \frac{5}{16d^2} \sqrt{\frac{mk_B T}{\pi}}, \quad (8.75)$$

$$\lambda_0 = \frac{75k_B T}{64d^2} \sqrt{\frac{k_B T}{\pi m}}. \quad (8.76)$$

This completely verifies that the present theory recovers the well established Chapman–Enskog results for viscosity and heat conductivity in the

case of a single component gas, and it is straightforward to show that the same conclusion can be drawn for multicomponent gases. The verification of this statement is left to the reader as an exercise.

The effective viscosity and thermal conductivity in (8.69) and (8.70) decrease from their Chapman–Enskog value and vanish as κ_l increases, that is, as either both the shear rate and the temperature gradient increase or one of them increases. One prominent property of the Chapman–Enskog transport coefficients η_0 and λ_0 is their independence of the gas density or pressure. However, the effective transport coefficients in (8.69) and (8.70) vanish like $p \ln p^{-1}$ with the pressure of the gas since κ_l is inversely proportional to the pressure. Thus they vanish as the gas rarefies, and this behavior is in accord with experimental observation [9] on rarefied gases. We will return to some topics of rarefied gases later in this chapter when the present theory is applied to practical problems.

8.5 Applications

The steady state constitutive relations obtained in the adiabatic approximation have some interesting features which are worthwhile investigating in more detail. The constitutive relations suggest that the shear stress and the heat flux are generally coupled nonlinearly. Therefore the Curie principle [10] is broken in the nonlinear regime. The broken Curie principle implies that the fluxes that are decoupled and thus independent of each other in the linear regime induce each other in the nonlinear regime. We would like to study an example of such a coupling phenomenon. Eqs. (8.61) and (8.62) provide a mathematical basis for examining such a phenomenon. There are other phenomena which we can study with some further approximations of the constitutive equations presented or special cases thereof that are beyond the reach of the classical Navier–Stokes equation. We would like to investigate them in this and subsequent sections.

8.5.1 Plane Couette Flow

We consider a parallel flow as an example in this section. A flow is called parallel if the velocity is parallel to an axis of coordinates. The plane Couette flow is an example for such flows. We will consider the case of flow being parallel to the x axis. In this case, the velocity has the u_x component only and the equation of continuity is given by

$$\partial_x \rho u_x = 0. \quad (8.77)$$

This means that ρu_x is independent of x , but a function of y only, if the flow is extended to infinite in the direction of z coordinate. The boundary conditions on u_x at $y = \pm D/2$ are $u_x(\pm \frac{1}{2}D) = \pm \frac{1}{2}u_d$. The steady momentum balance equation for the flow subjected to a pressure gradient

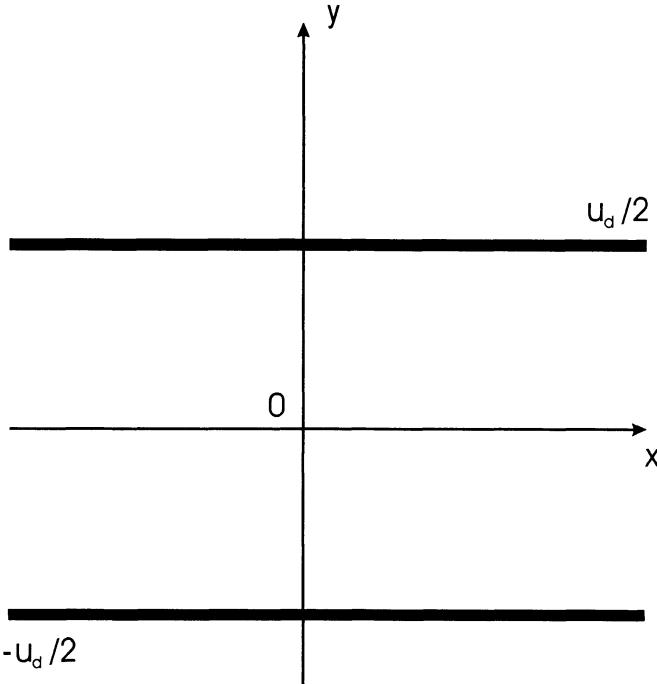


FIGURE 8.1 Plane Couette flow. The thick lines represent the plates moving in opposite directions at speed $u_d/2$.

$p_x = \partial_x p$ in the x direction is

$$\partial_y \Pi_{xy} + p_x = 0. \quad (8.78)$$

It is assumed that there are no normal stress differences. Then for the flow considered we have

$$\Pi_{xz} = \Pi_{xx} = 0.$$

Since there are no normal stress differences, (8.67) for Π implies that

$$\Pi_{xy} = -2\eta\gamma \quad (8.79)$$

with the viscosity given by the non-Newtonian formula

$$\eta = \eta_0 \frac{\sinh^{-1} \tau' \gamma}{\tau' \gamma}, \quad (8.80)$$

where

$$\gamma = \frac{1}{2} \frac{\partial u_x}{\partial y}, \quad (8.81)$$

$$\tau' = \sqrt{2}\tau = \frac{\sqrt{2}}{nk_B T d^2} \left[\eta_0 \sqrt{2m_r k_B T} \right]^{1/2} \quad (8.82)$$

with n , m_r , and d denoting the density, reduced mass, and radius of the molecule, respectively. The τ' may be treated as a phenomenological parameter in the present discussion.

A. The case of $p_x = 0$

Since $p_x = 0$ there follows from the momentum balance equation (8.78) the equation

$$\Pi_{xy} = \text{constant}.$$

On substitution of (8.79) into this equation and use of the boundary conditions on integration, there follows the velocity profile

$$u_x = \frac{u_d}{D} y, \quad (8.83)$$

where D is the width of the channel; see Fig. 8.1. Despite the non-Newtonian viscosity, the velocity profile is linear in y as is the case for the Newtonian viscosity. Substitution of this velocity profile into (8.80) gives rise to the viscosity formula and shear stress in the forms

$$\eta = \eta_0 \frac{\sinh^{-1}(\tau' u_d / 2D)}{(\tau' u_d / 2D)} \quad (8.84)$$

and

$$\Pi_{xy} = -\frac{4\eta_0}{\tau'} \ln \left(\frac{\tau' u_d}{2D} + \sqrt{1 + \left(\frac{\tau' u_d}{2D} \right)^2} \right). \quad (8.85)$$

These results indicate the shear-thinning behavior of the fluid. In particular, (8.84) is known as the Ree–Eyring viscosity formula, which was originally derived from the absolute reaction rate theory [11]. The present formula is derived from the kinetic equation and gives the molecular expression for the parameter τ' which in the absolute reaction rate theory appears as an empirical parameter. Formula (8.84) can be shown to account for the shear rate dependence of molecular dynamics simulation data on the viscosity of a Lennard-Jones fluid [12].

The result obtained here seems to be useful for examining the molecular dynamics algorithm. The molecular dynamics methods for sheared fluids [13] are usually implemented with a linear velocity profile even though the fluid is non-Newtonian. At first glance it looks odd that such a profile should be taken, even if the flow were non-Newtonian, but the calculation presented here supports the position that it is permissible to take such a profile. However, this conclusion applies only to parallel one-dimensional flows. For example, in the case of a Taylor–Couette flow the velocity profile is no longer linear with respect to the radial distance if the fluid is non-Newtonian [14].

B. The case of $p_x \neq 0$

In this case, the momentum balance equation (8.78) can be integrated to yield the velocity profile

$$u_x = \alpha u_d \left[\cosh \frac{\delta}{2} - \cosh \left(\frac{\delta y}{D} \right) \right], \quad (8.86)$$

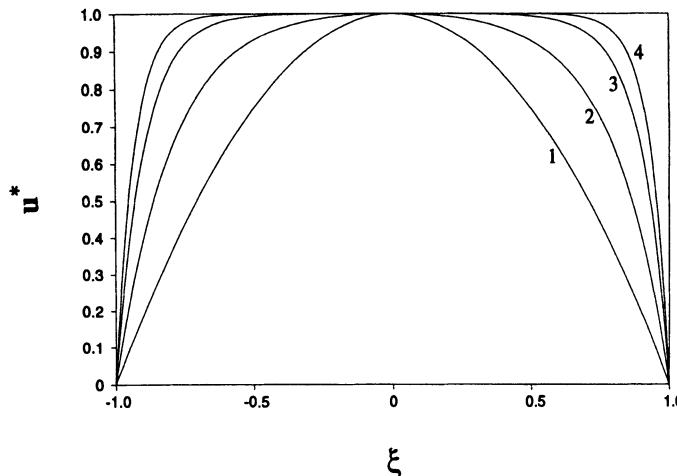


FIGURE 8.2 Velocity profiles of a channel flow in a non-Newtonian fluid for different values of the parameter δ : $\delta = 0.01$ for 1; $\delta = 5$ for 2; $\delta = 10$ for 3; $\delta = 15$ for 4. They become rectangular and behave like a plug flow at large values of δ . (Reprinted with permission from *Am. J. Phys.* **58**, 86 (1990). © 1989 American Association of Physics Teachers.)

where

$$\alpha = -\frac{4\eta_0}{\tau' p_x u_d}, \quad \delta = -\frac{\tau' p_x D}{2\eta_0}. \quad (8.87)$$

The velocity profile in (8.86) reduces to the Newtonian form as the parameter δ becomes small in magnitude. The flow profile is plotted in Fig. 8.2 where $u_m = u_x/u_{\max}$. As δ increases, the boundary layer decreases and the flow behaves like a plug flow. We remark that the parameter δ is proportional to $N_M N_{Kn}$ or $N_M^2 N_{Re}$. Therefore as N_{Kn} or N_{Re} increases, the boundary layer thickness decreases, and flow appears to be slipping at the boundary under observation at low resolution. Another quantity of physical interest here is the volume flow rate, namely, the volume of the fluid passing through unit area in unit time. It is given by the formula

$$\begin{aligned} Q_v &= \int_{-D/2}^{D/2} dz \int_{-D/2}^{D/2} dy \rho u_x(y) \\ &= \rho \alpha u D^2 \left[\cosh\left(\frac{\delta}{2}\right) - \frac{2}{\delta} \sinh\left(\frac{\delta}{2}\right) \right]. \end{aligned} \quad (8.88)$$

This may be cast in the form

$$Q_v = \frac{\rho D^4 \Delta p}{12\eta_0 L} F(\delta), \quad (8.89)$$

where $p_x = -\Delta p/L$ with L denoting the length of the channel, and Δp the pressure difference, and

$$F(\delta) = \frac{12}{\delta^2} \left[\cosh\left(\frac{\delta}{2}\right) - \frac{2}{\delta} \sinh\left(\frac{\delta}{2}\right) \right]. \quad (8.90)$$

This function, which reduces to unity as δ tends to zero, gives the non-Newtonian correction to the Hagen–Poiseuille volume flow rate [5] which is given by the coefficient factor in (8.89).

8.5.2 Tube Flow

The non-Newtonian viscosity used for the calculations in the previous subsection can be applied to a flow in cylindrical geometry. We consider it here since it can have a number of useful applications in connection with non-Newtonian fluids. The point to remember is that although we are considering it in the context of gases the same results as obtained in this subsection can be produced for liquids obeying the same viscosity formula, as is shown in [4] and [15].

Let us assume that a fluid obeying the shear stress constitutive equation (8.67) flows in a cylinder of radius R and length L which is much larger than R . We assume that the flow is parallel to the axis of the cylinder, which is taken to be parallel to the z axis, and the temperature is uniform throughout the cylinder. Because of the cylindrical symmetry, flow variables do not depend on the angle θ of the coordinates, and there is only the z component of the velocity to consider if L is so long as to make the translational symmetry sufficiently valid. In this case we have $\mathbf{u} = (0, 0, u_z)$ for the velocity since the equation of continuity and the boundary condition demand that the radial velocity $u_r = 0$. Note that $\rho \neq 0$. We also assume that there are no normal stress differences. Thus

$$N_1 = \Pi_{zz} - \Pi_{rr} = 0, \quad N_2 = \Pi_{rr} - \Pi_{\theta\theta} = 0,$$

and there is only the shear component non-vanishing:

$$\Pi = \Pi_{rz} = \Pi_{rz}.$$

The momentum balance equation then is given by

$$\frac{1}{r} \frac{\partial}{\partial r} r\Pi = -p_z. \quad (8.91)$$

In this connection it must be noted that the assumption of the vanishing normal stress differences implies a pressure which is independent of r . The

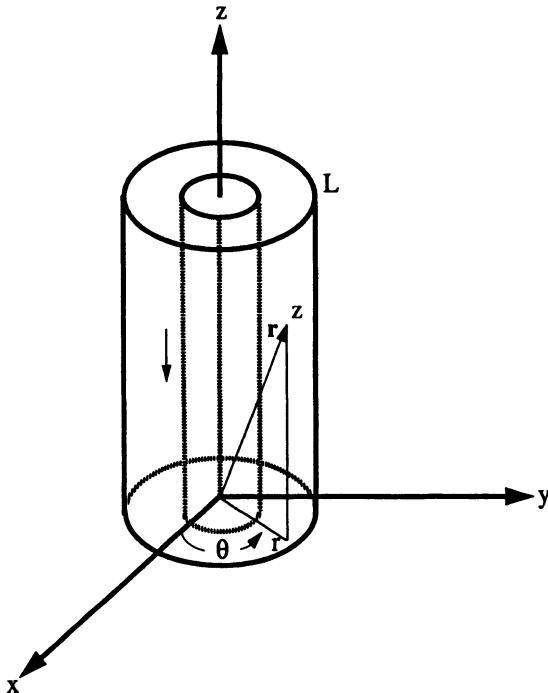


FIGURE 8.3 Cylindrical flow geometry. The inner cylinder represents an imaginary layer of the fluid.

pressure gradient along the z direction is assumed independent of z . Under this set of assumptions the relevant constitutive equation is given by

$$\Pi q(\kappa) = -2\eta_0 \gamma, \quad (8.92)$$

where

$$\gamma = \frac{1}{2} \frac{\partial u_z}{\partial r}, \quad (8.93)$$

and

$$\begin{aligned} q(\kappa) &= \frac{\sinh \kappa}{\kappa}, \\ \kappa &= \frac{\tau}{\sqrt{2}\eta_0} \Pi. \end{aligned} \quad (8.94)$$

Solving the momentum balance equation subject to the boundary conditions

$$u_z(R) = 0, \quad \left(\frac{\partial u_z}{\partial r} \right)_{r=0} = 0,$$

the velocity profile is found:

$$u_z = \frac{2R}{\tau' \bar{\delta}} \left[\cosh \bar{\delta} - \cosh \left(\bar{\delta} \frac{r}{R} \right) \right], \quad (8.95)$$

where

$$\bar{\delta} = \frac{\tau' R \Delta p}{4\eta_0 L}. \quad (8.96)$$

Defining the Hagen–Poiseuille formula [5] in the cylindrical geometry by

$$Q_{HP}^c = \frac{R^4 \Delta p}{8\eta_0 L N k_B T} \quad (N = \text{Avogadro's number}), \quad (8.97)$$

the volume flow rate can be calculated as follows:

$$\begin{aligned} Q_v^c &= 2\pi n \int_0^R dr r u_z(r) \\ &= Q_{HP}^c [1 + F_c(\bar{\delta})] p, \end{aligned} \quad (8.98)$$

where

$$F_c(\bar{\delta}) = \frac{8}{\bar{\delta}^2} \left[\frac{1}{2} \cosh \bar{\delta} - \frac{\sinh \bar{\delta}}{\bar{\delta}} + \frac{\cosh \bar{\delta} - 1}{\bar{\delta}^2} \right] - 1. \quad (8.99)$$

As in the case of plane Couette flow, the flow profile increasingly deviates from the parabolic behavior characteristic of a Newtonian fluid, becoming like a plug flow, since the boundary layer gets thinner as $\bar{\delta}$ increases. Again this parameter is proportional to $N_M N_{Kn}$ or $N_M^2 N_{Re}$.

The calortropy production for the flow is given by

$$\begin{aligned} \sigma_c &= k_B g^{-1} \kappa \sinh \kappa \\ &= \frac{k_B R^2 \Delta p^2}{4L^2 \eta_0 k_B T} \bar{\delta}^{-1} \frac{r}{R} \sinh \left(\bar{\delta} \frac{r}{R} \right), \end{aligned} \quad (8.100)$$

which on substitution of κ from (8.94) and integration over r gives the mean value

$$\begin{aligned} \Xi &= \frac{1}{\pi R^2} \int_0^R dr 2\pi r \sigma_c(r) \\ &= \frac{k_B R^2 \Delta p^2}{L^2 \eta_0 k_B T} \bar{\delta}^{-2} \left[\frac{1}{2} \cosh \bar{\delta} - \frac{\sinh \bar{\delta}}{\bar{\delta}} + \frac{\cosh \bar{\delta} - 1}{\bar{\delta}^2} \right] \\ &= \frac{N k_B \Delta p}{R^2 L p} Q_v^c. \end{aligned} \quad (8.101)$$

This indicates that the calortropy production increases linearly with the volume flow rate Q_v^c . That is, the energy dissipation increases in direct

proportion to the volume flow rate. This is an example for a possibility of direct measurement of calortropy production.

The drag coefficient gives a measure of friction by the flow past the body and is defined by the friction energy relative to the mean kinetic energy of the flow:

$$C_d = \frac{2\pi RL\Pi(R)}{2\pi RL \times \frac{1}{2}\rho \langle u_z \rangle^2}, \quad (8.102)$$

where

$$\langle u_z \rangle = \frac{1}{\pi R^2} \int_0^R dr 2\pi r u_z(r).$$

By using the result obtained earlier, we find

$$C_d = \frac{\Gamma(\bar{\delta})}{N_{Re}}, \quad (8.103)$$

where

$$N_{Re} = \frac{\rho u_z(0) R}{\eta_0} = \frac{2R}{\tau' \bar{\delta} (\cosh \bar{\delta} - 1)}, \quad (8.104)$$

$$\Gamma(\bar{\delta}) = \frac{4(\cosh \bar{\delta} - 1)}{[1 + F_c(\bar{\delta})]^2}. \quad (8.105)$$

The drag coefficient reduces to the Newtonian flow value $16/N_{Re}$ in the limit of $\delta \rightarrow 0$.

We remark that the volume flow rate formula derived here can be used to explain the Knudsen problem (paradox) observed by Knudsen [16] in 1909. The reader is referred to [4] and [17] cited therein. It can also be used to explain the laser-induced drift of gases in a capillary tube [18].

8.5.3 Boundary Layer and the Question of Slip

Maxwell's kinetic theory and the Chapman–Enskog first approximation for the transport coefficients predict the density independence of linear transport coefficients [6,19]. Maxwell's prediction led Kundt and Warburg [20] to perform an experiment on the flow behavior as a function of the gas density for a number of gases. They found that the prediction did not hold as the density was reduced to the rarefied gas regime. To account for such flow behavior as observed by Kundt and Warburg, Maxwell [21] introduced the notion of slip. This notion asserts that the tangential component of the flow velocity slips as the gas density becomes so low that the mean free path becomes comparable to the width of the channel. The slip velocity was expressed in terms of what is now known as the accommodation coefficient [9,22] which was often treated as an adjustable parameter. Even to these days the accommodation coefficient is regarded as an adjustable parameter, although calculable in principle if the surface–atom scattering problem is solved [23].

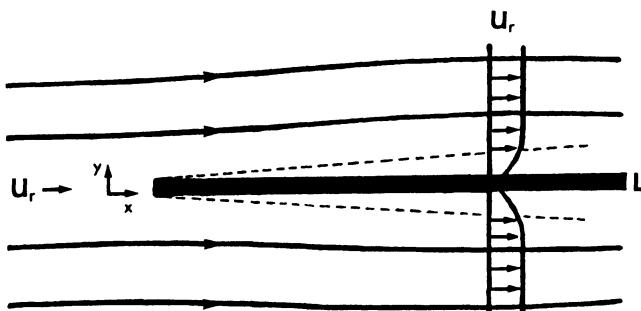


FIGURE 8.4 Flow incident onto a flat plate of length L . The region inside the broken curves is the boundary layer. Schematic flow profiles are shown by the arrows and their envelopes.

Maxwell's kinetic theory is basically for linear transport processes, and as such it provides the constitutive equations which are valid in the linear regime. We have seen in the previous subsections that such a constitutive equation for the shear stress provides the Navier-Stokes theory and is thus incapable of predicting any flow behavior beyond its regime of validity. In this subsection we show that the nonlinear constitutive equation for the shear stress used for various calculations in the previous subsections can provide an alternative viewpoint to the notion of slip. In other words an appropriate treatment of flow problems can be made without invoking the notion of slip velocity. We have seen in particular the flow velocity profile for a non-Newtonian fluid, which becomes almost like a plug flow and exhibits a narrow boundary layer as the parameter δ becomes large or the density of the fluid becomes low. We elaborate on this behavior from the viewpoint of the Prandtl boundary layer theory and show that, indeed, the velocity profile in the boundary layer becomes thinner as the gas density is reduced to a sufficiently low value. Therefore the present subsection is for an application of the non-Newtonian constitutive equation for the shear stress to the Prandtl boundary layer theory.

To illustrate that the aforementioned constitutive equation can be applied to the class of flow problems within the framework of the Prandtl boundary layer theory we consider a flow incident upon a flat plate of length L . Denote the reference flow variables by ρ_r for the mass density, p_r for the pressure, and u_r for the velocity which may be taken as the mainstream velocity. The reference viscosity will be taken with the non-Newtonian viscosity computed in terms of reference variables mentioned:

$$\eta_r = \eta_0 \frac{\sinh^{-1}(\tau_0 u_r / L)}{(\tau_0 u_r / L)}, \quad (8.106)$$

where

$$\tau_0 = \frac{1}{\sqrt{2}} \tau(n = n_r)$$

with τ defined as before but with n_r denoting the reference density. The non-Newtonian viscosity is then reduced by η_r :

$$\eta^* = \frac{\eta_0}{\eta_r} \frac{\sinh^{-1}(\tau\gamma)}{\tau\gamma}, \quad (8.107)$$

where τ and γ were defined previously. We assume that flow is in the x direction. The following reduced variables will be used:

$$\begin{aligned} \xi &= xL^{-1}, & \zeta &= yL^{-1}, & u &= u_x u_r^{-1}, \\ v &= u_y u_r^{-1}, & \rho^* &= \rho \rho_r^{-1} & p^* &= p p_r^{-1}. \end{aligned}$$

The Reynolds number is defined by

$$N_{\text{Re}} = \frac{\rho_r u_r L}{\eta_r}. \quad (8.108)$$

We remark that unlike the Reynolds number defined for a Newtonian fluid for which the viscosity remains invariant with regard to the shear rate u_r/L , the present N_{Re} varies with the shear rate. We will see that the variable viscosity is essentially responsible for the variable boundary layer thickness in a non-Newtonian flow. The boundary layer equations according to Prandtl [24] are then given by

$$\frac{\partial}{\partial \xi} \rho^* u + \frac{\partial}{\partial \zeta} \rho^* v = 0, \quad (8.109)$$

$$\rho^* \left(u \frac{\partial u}{\partial \xi} + v \frac{\partial u}{\partial \zeta} \right) = - \frac{\partial p^*}{\partial \xi} + N_{\text{Re}}^{-1} \frac{\partial}{\partial \zeta} \eta^* \frac{\partial u}{\partial \zeta}. \quad (8.110)$$

The reduced pressure is given by the equation of state $p^* = p/p_r = \rho \mathcal{R}T/p_r = \rho^* T^*$ where $T^* = T/T_r$. In the present discussion we will only consider the case of $\partial p^*/\partial \xi = 0$. If so, under the assumption that p is uniform in the boundary layer, which excludes the case of boundary layer separation, ρ^* becomes uniform and may be eliminated from the equations by setting $\rho^* = 1$. That is, we may choose $\rho = \rho_r$. Therefore the boundary layer equations to consider here are

$$\frac{\partial}{\partial \xi} u + \frac{\partial}{\partial \zeta} v = 0, \quad (8.111)$$

$$u \frac{\partial u}{\partial \xi} + v \frac{\partial u}{\partial \zeta} = N_{\text{Re}}^{-1} \frac{\partial}{\partial \zeta} \eta^* \frac{\partial u}{\partial \zeta}. \quad (8.112)$$

The boundary conditions are

$$u = v = 0 \text{ at } \zeta = 0, \quad u = 1 \text{ at } \zeta = \infty. \quad (8.113)$$

The boundary condition at $\zeta = \infty$ means that the velocity becomes that of the mainstream sufficiently far from the boundary. Note that η^* is a nonlinear function of $\partial u / \partial \zeta$:

$$\begin{aligned}\eta^* &= \eta^* \left(\frac{\partial u}{\partial \zeta} \right) \\ &= \frac{\sqrt{2}\tau_0}{\tau} \cdot \frac{\sinh^{-1} \left[\frac{1}{\sqrt{2}L} \tau u_r (\partial u / \partial \zeta) \right]}{(\partial u / \partial \zeta) \sinh^{-1} \left(\frac{1}{L} \tau_0 u_r \right)}.\end{aligned}\quad (8.114)$$

It is convenient to introduce the stream function ψ such that

$$u = \frac{\partial \psi}{\partial \zeta}, \quad v = -\frac{\partial \psi}{\partial \xi}.\quad (8.115)$$

It is also useful to express $\tau_0 u_r / L$ in terms of dimensionless numbers. For the purpose we define the mean free path l by the relation

$$\eta_0 = \frac{1}{2} m_r \sqrt{\frac{8k_B T}{\pi m_r}} l\quad (8.116)$$

and a number λ by the relation

$$\lambda = \sqrt{2} \pi d^2 n_r l,\quad (8.117)$$

which gives the measure of deviation that the mean free path l makes from that of hard spheres. Then, we find

$$\frac{\tau_0 u_r}{L} = k N_M N_{Kn} \equiv \chi,\quad (8.118)$$

where

$$k = \sqrt{\frac{2\pi\gamma_0}{\lambda}}, \quad N_M = \sqrt{\frac{\gamma_0 k_B T}{m_r}}, \quad N_{Kn} = \frac{l}{L}.\quad (8.119)$$

The momentum balance equation (8.112) then can be written as

$$\frac{\partial \psi}{\partial \zeta} \frac{\partial^2 \psi}{\partial \xi \partial \zeta} - \frac{\partial \psi}{\partial \xi} \frac{\partial^2 \psi}{\partial \zeta^2} = N_{Re}^{-1} \frac{\partial}{\partial \zeta} L_g,\quad (8.120)$$

where

$$L_g = \epsilon^{-1} \sinh^{-1} \left(\chi \frac{\partial^2 \psi}{\partial \zeta^2} \right)\quad (8.121)$$

with the definition

$$\epsilon = \sinh^{-1} \chi.\quad (8.122)$$

In order to cast the boundary layer equation (8.120) into an ordinary differential equation we introduce the transformations of variables (ξ, ζ, ψ) to (q, s, f) :

$$q = \xi,$$

$$\begin{aligned} s &= \left(\frac{N_{\text{Re}}}{3\xi} \right)^{1/3} \zeta, \\ \psi &= \left(\frac{3\xi}{N_{\text{Re}}} \right)^{2/3} f(s). \end{aligned} \quad (8.123)$$

These transformations put the boundary layer equation into a single non-linear ordinary differential equation

$$\left(\frac{df}{ds} \right)^2 - 2f \frac{d^2 f}{ds^2} = \frac{d}{ds} L_g \left(\frac{d^2 f}{ds^2} \right). \quad (8.124)$$

This is a similarity equation which is free from the system parameters except for the dimensionless number χ consisting of $N_M N_{Kn}$ or $N_M^2 N_{\text{Re}}$. It must be noted that the function $L_g (d^2 f / ds^2)$ does not involve the variable q :

$$L_g \left(\frac{d^2 f}{ds^2} \right) = \epsilon^{-1} \sinh^{-1} \left(\chi \frac{d^2 f}{ds^2} \right). \quad (8.125)$$

The boundary conditions for f are deduced to be as follows:

$$\begin{aligned} f(0) &= 0, \quad f'(0) = \left(\frac{df}{ds} \right)_{s=0} = 0 \quad \text{at } s = 0, \\ f'(\infty) &= \left(\frac{df}{ds} \right)_{s=\infty} = 1 \quad \text{at } s = \infty. \end{aligned} \quad (8.126)$$

To solve (8.124) in a power series in ϵ we introduce a new dependent variable

$$g = f' \text{ or } f = \int_0^s ds' g(s'). \quad (8.127)$$

This transformation applied to the boundary layer equation (8.124) yields the equation

$$\begin{aligned} \chi^2 g'^2 &= \chi^2 g_0'^2 + 2\epsilon\chi (1 + \chi^2 g_0'^2)^{1/2} \left[\frac{1}{3} g^3 - 2 \int_0^s ds' f(s') g'^2(s') \right] \\ &\quad + (\epsilon\chi)^2 \left[\frac{1}{3} g^3 - 2 \int_0^s ds' f(s') g'^2(s') \right]^2, \end{aligned} \quad (8.128)$$

where

$$g'_0 = g'(s)|_{s=0}. \quad (8.129)$$

This equation can be numerically integrated to yield the velocity profile in the boundary layer. We solve this equation in a series of variable

$$\phi = \tanh(\epsilon s). \quad (8.130)$$

By setting

$$g = \sum_{i=1}^{\infty} \frac{\phi^i a_i}{i!} \quad (8.131)$$

and determining the coefficients a_i , we find

$$g = a_1 \phi \left(1 + \frac{1}{3} \phi^2 + \frac{1}{5} \phi^4 \right) + O(\phi^6). \quad (8.132)$$

We resum this series to the [1,1] Padé approximant [25]:

$$g(\phi) = a_1 \phi [1, 1] = \frac{1}{3} a_1 \phi \frac{15 - 4\phi^2}{5 - 3\phi^2}. \quad (8.133)$$

Imposing the boundary condition $\phi = 1$, we find $a_1 = 6/11$. Finally, the velocity profile f' is given by the formula

$$f' = g = \frac{6}{11} \tanh(\epsilon s) \left[1 + \frac{5 \tanh^2(\epsilon s)}{15 - 9 \tanh^2(\epsilon s)} \right] \quad (8.134)$$

and the velocity components u_x and u_y by

$$\begin{aligned} u_x &= \left(\frac{3\xi}{N_{\text{Re}}} \right)^{1/3} f'(s), \\ u_y &= (3N_{\text{Re}}^2 \xi)^{-1/3} (s f' - 2f). \end{aligned} \quad (8.135)$$

The velocity profiles of u_x are plotted for various values of ϵ in Fig. 8.5. From the figure it is clear that as the Knudsen number increases, that is, as ϵ increases, the boundary layer becomes thinner and the flow becomes like a plug flow whose velocity may appear to slip if a low resolution experiment is performed. This result is consistent with the flow profile computed for the one-dimensional flows considered in the previous subsections. On the other hand, the linear (Navier–Stokes) theory, indicated by the broken curve, predicts an ϵ -independent boundary layer thickness. The present calculation indicates that it is not necessary to invoke a slip boundary condition in order to account for some experiments on flow variables in fluids obeying nonlinear constitutive equations for the shear stress. Appropriate constitutive equations should be sufficient to account for the observations made in experiments even if a slip boundary condition was not used.

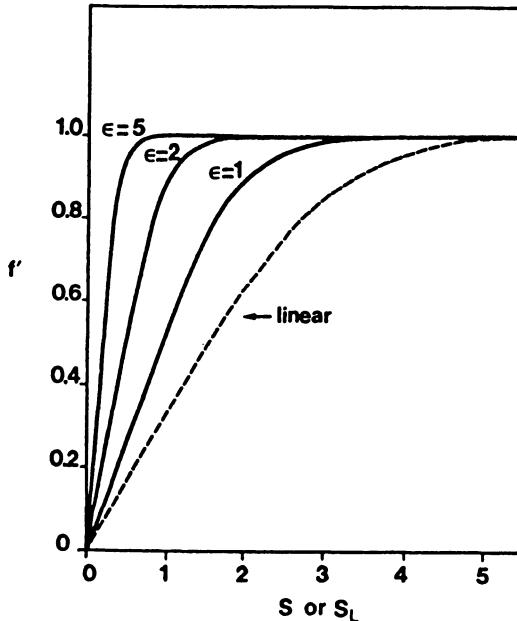


FIGURE 8.5 The velocity profiles in the boundary layer are plotted against the distance from the wall for a number of values of ϵ . This parameter increases with the Knudsen number of the system. (Reprinted with permission from *Phys. Rev. A* **36**, 400 (1987). Copyright 1987 The American Physical Society.)

8.5.4 Thermoviscous Coupling

Let us consider a flow in plane Couette flow geometry where a temperature gradient is applied in the direction transversal to the flow direction. We assume that the fluid confined in an infinitely long channel of width D between two plates is sheared in the xy plane in the Cartesian coordinate system. See Fig. 8.6. The flow is generated in the direction of x axis by the two plates oppositely moving at speed $u_d/2$ and the velocity gradient is in the direction of the y axis. Therefore the z direction is neutral. The temperature gradient is applied in the y direction. The coordinate system is such that the plates are located at $y = \pm \frac{1}{2}D$ and $T = T^\pm$ at $y = \pm \frac{1}{2}D$ ($T^- > T^+$). Let us denote by δ_x , δ_y , and δ_z the unit vectors along the Cartesian coordinate axes x , y , and z , respectively. Since $\mathbf{u} = (u_x, u_y, u_z) = (u_x, 0, 0)$ and $u_x = u_x(y)$ in such geometry, we have $\nabla \mathbf{u} = \delta_x \delta_y \nabla_y u_x(y)$ and $\nabla \cdot \mathbf{u} = 0$ identically. Therefore,

$$[\nabla \mathbf{u}]^{(2)} = \frac{1}{2} \partial_y u_x(y) \delta_x \delta_y \equiv \gamma \delta_x \delta_y \quad (8.136)$$

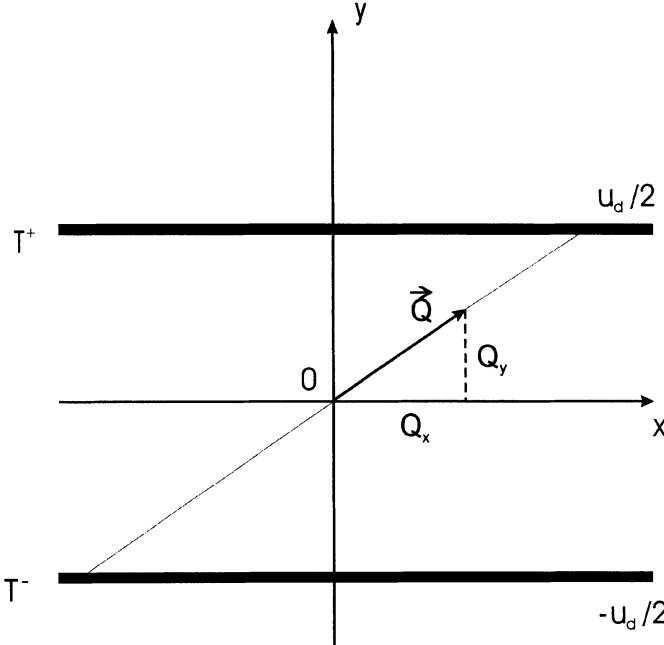


FIGURE 8.6 Flow geometry of plane Couette flow under a transversal temperature gradient. The upper and lower plates move in opposite directions at speed $u_d/2$. The plates are parallel to the x coordinate axis and the fluid flows in the x direction whereas the velocity gradient is in the y direction. The z axis is parallel to the neutral direction of the flow. $T^- > T^+$.

with γ denoting the velocity gradient

$$\gamma = \frac{1}{2} \partial_y u_x(y). \quad (8.137)$$

The temperature gradient is abbreviated by

$$\Omega = \partial_y \ln T. \quad (8.138)$$

The stress tensor Π has the following form:

$$\Pi = \delta_x \delta_x \Pi_{xx} + 2\delta_x \delta_y \Pi_{xy} + \delta_y \delta_y \Pi_{yy} + \delta_z \delta_z \Pi_{zz}, \quad (8.139)$$

since $\Pi_{xz} = \Pi_{yz} = \Pi_{zx} = \Pi_{zy} = 0$ for the flow geometry under consideration. Since the shear stress Π is traceless, there are only two independent normal stresses. In these circumstances it is convenient to define primary and secondary normal stress differences N_1 and N_2 , respectively, by

$$N_1 = \Pi_{xx} - \Pi_{yy}, \quad N_2 = \Pi_{yy} - \Pi_{zz}. \quad (8.140)$$

The shear component Π_{xy} of the tensor Π is abbreviated by $\Pi \equiv \Pi_{xy}$. Since Π is traceless symmetric the normal stress components Π_{xx} , Π_{yy} , and Π_{zz} then can be expressed in terms of N_1 and N_2 :

$$\Pi_{xx} = \frac{1}{3}(2N_1 + N_2), \quad \Pi_{yy} = \frac{1}{3}(N_2 - N_1), \quad \Pi_{zz} = -\frac{1}{3}(N_1 + 2N_2).$$

The heat flux is decomposed as follows:

$$Q = \delta_x Q_x + \delta_y Q_y + \delta_z Q_z. \quad (8.141)$$

We determine Π , N_1 , N_2 , Q_x , Q_y , and Q_z from the constitutive relations (8.61) and (8.62) which, when written in components, take the forms

$$N_1 q(\kappa) = \frac{4\eta_0}{p} \gamma \Pi, \quad (8.142)$$

$$N_2 q(\kappa) = -\frac{4\eta_0}{p} \gamma \Pi, \quad (8.143)$$

$$\Pi q(\kappa) = -2\eta_0 \gamma - \frac{2\eta_0}{3p} \gamma N_1, \quad (8.144)$$

$$Q_x q(\kappa) = -\frac{\lambda_0}{p} \Pi \Omega, \quad (8.145)$$

$$Q_y q(\kappa) = -\lambda_0 \Omega + \frac{2\lambda_0}{3p} N_1 \Omega - \frac{2\lambda_0}{p \hat{C}_p T} \gamma Q_x, \quad (8.146)$$

$$Q_z = 0. \quad (8.147)$$

Notice that if $q(\kappa)$ [(8.17) and (8.39)] is absent the heat fluxes will not influence the shear stress and normal stress differences, but Q_x and Q_y are nonlinearly dependent on the stresses, reflecting the physical fact that stress generates heat. Since $N_1 = -N_2$, there are four equations to solve for four variables Π , N_1 , Q_x , and Q_y . Eqs. (8.142) and (8.144) are formally solved first and then the results are substituted into (8.145) and (8.146) to obtain Q_x and Q_y . The formal solutions for (8.142) and (8.144) are:

$$\Pi = -\frac{2\eta_0 \gamma q(\kappa)}{[q^2(\kappa) + 6s^2]}, \quad (8.148)$$

$$N_1 = -\frac{8\eta_0^2 \gamma^2}{p[q^2(\kappa) + 6s^2]}. \quad (8.149)$$

These formal solutions, on substitution into (8.145) and (8.146), yield

$$Q_x = \frac{2\lambda_0 \eta_0 \Omega \gamma}{p[q^2(\kappa) + 6s^2]}, \quad (8.150)$$

$$\begin{aligned} Q_y &= -\lambda_0 \Omega q^{-1}(\kappa) \left\{ 1 + \frac{16\eta_0^2 \gamma^2 q(\kappa)}{3p^2[q^2(\kappa) + 6s^2]} \right\} \\ &\quad - \frac{4\lambda_0^2 \eta_0 \gamma^2 \Omega}{p^2 \widehat{C}_p T [q^2(\kappa) + 6s^2]}, \end{aligned} \quad (8.151)$$

where

$$s = \frac{2\eta_0 \gamma}{3p}. \quad (8.152)$$

Before attempting to solve these equations, we observe the following feature of (8.142) and (8.144). On eliminating $q(\kappa)$, the following equation is obtained from them

$$\Pi^2 + \frac{1}{6}N^2 = \frac{3}{8}p^2, \quad (8.153)$$

where $N = N_1 + \frac{3}{2}p$. This equation suggests that Π and N are confined to an ellipse centered at $\Pi = 0$ and $N = 0$ or $N_1 = -\frac{3}{2}p$ in the (Π, N) plane. This implies that the shear stress Π and the primary normal stress difference N_1 must approach the origin and thus vanish as $p \rightarrow 0$. The solution of (8.153) for N_1 is

$$N_1 = -\frac{3}{2}p \pm (\frac{9}{4}p^2 - 6\Pi^2)^{1/2}. \quad (8.154)$$

Now, if p is such that $p \leq -\sqrt{\frac{8}{3}}\Pi$, then N_1 becomes complex and thus inadmissible. When this happens, the only way to satisfy the ellipse is to set

$$\Pi = N_1 = 0 \quad (8.155)$$

at the critical pressure $p_c = -\sqrt{\frac{8}{3}}\Pi_c$. In other words, there is a critical pressure at and beyond which Π and N_1 simultaneously vanish. Note that the vanishing Π and N_1 do not violate the ellipse condition (8.153). The approximate solutions for Π and N_1 obtained from (8.142)–(8.144) should be consistent with the aforementioned properties related to the ellipse condition (8.153) and (8.154).

Eqs. (8.148)–(8.151) can be solved iteratively by starting with the zeroth iterative solutions

$$\Pi_0 = -\frac{2\eta_0 \gamma}{1 + 6s^2}, \quad (8.156)$$

$$N_{10} = -\frac{8\eta_0 \gamma^2}{1 + 6s^2}, \quad (8.157)$$

$$Q_{x_0} = \frac{2\lambda_0 \eta_0 \Omega \gamma}{p(1 + 6s^2)}, \quad (8.158)$$

$$Q_{y_0} = -\lambda_0 \Omega \left[1 + \frac{16\eta_0 \gamma^2}{3p^2(1 + 6s^2)} \right] - \frac{4\lambda_0^2 \eta_0 \gamma^2 \Omega}{p^2 \widehat{C}_p T (1 + 6s^2)}. \quad (8.159)$$

The first-order iterative solutions are obtained by substituting the zeroth-order iterative solutions into the factor $q(\kappa)$ on the right hand side of (8.148) and (8.151), and so on. These results imply that as the fluid is sheared, the heat flux vector $\mathbf{Q} = (0, Q_y, 0)$ in the quiescent fluid is rotated by shearing and aligns along the direction of the velocity gradient, namely, $\mathbf{Q} \rightarrow (Q_x, Q_y, 0)$ where Q_x is proportional to the velocity gradient γ , as in (8.158). It is a second-order effect which vanishes with γ . An interesting conclusion is that the stress is not generated by a heat flux and neither is a mechanical motion necessarily generated spontaneously by heat whereas heat is generated by a mechanical motion. Another interesting implication of the results for the heat fluxes is that heat flow is enhanced by the presence of shearing. We see that here again the second law of thermodynamics is in action. The result of this calculation may have some significance to molecular dynamic simulation methods.

The zeroth-order iterative solutions (8.156)–(8.158) imply that the transport coefficients are non-Newtonian and non-Fourier since the effective viscosity, normal stress coefficient, and heat conductivity are dependent on the shear rate and temperature gradient:

$$\eta_e = \frac{\eta_0}{1 + 6s^2}, \quad (8.160)$$

$$\Psi_e = \frac{8\eta_0}{1 + 6s^2}, \quad (8.161)$$

$$\lambda_e = \lambda_0 \left[1 + \frac{16\eta_0\gamma^2}{3p(1 + 6s^2)} \right] + \frac{4\lambda_0^2\eta_0\gamma^2}{p^2\hat{C}_p T(1 + 6s^2)}, \quad (8.162)$$

and the heat conductivity coefficient associated with Q_x is negative

$$\zeta_e = -\frac{2\lambda_0\eta_0\gamma}{p(1 + 6s^2)}, \quad (8.163)$$

if it is defined by the relation $Q_{x_0} = -\zeta_e\Omega$. The primary normal stress coefficient Ψ_e is defined such that $N_1 = -\Psi_e\gamma^2$.

We now examine the implication of the ellipse condition on Π_0 and N_{10} . The condition that p must be larger than p_c suggests that for Π_0 to be nonzero the shear rate γ must be such that

$$2\sqrt{\frac{8}{3}} \frac{\eta_0\gamma}{1 + 6s^2} \leq p_c. \quad (8.164)$$

Since $s_c = 2\eta_0\gamma_c/3p_c$ at the critical point, the value of γ at a given pressure must be such that

$$\gamma_c \equiv \sqrt{\frac{3}{8}} \frac{p_c}{\eta_0} \geq \gamma \quad (8.165)$$

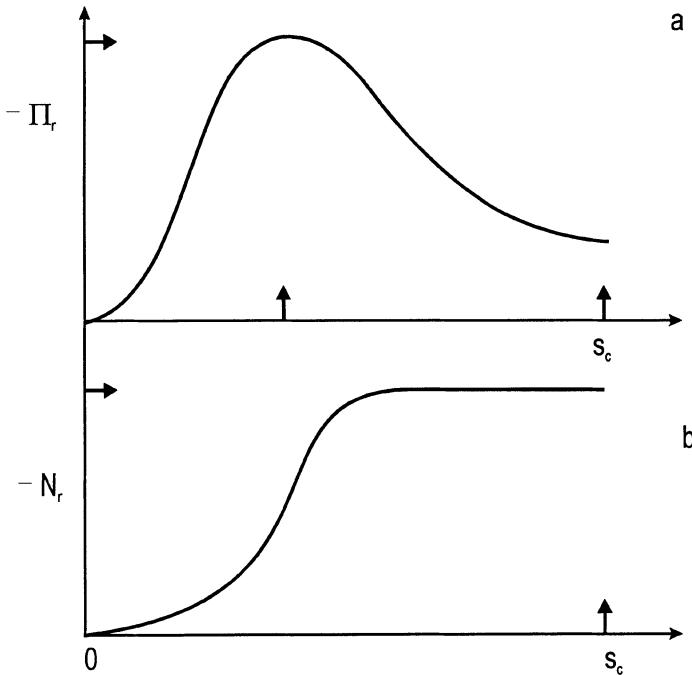


Figure 8.7 Qualitative s -dependence of $-\Pi_r = -\Pi_0/3p$ and $-N_r = -N_{10}/18p^2$ in the case of plane Couette flow. (a)— Π_r vs. s . (b)— N_r vs. s . Π_0 reaches a maximum at $s = 1/\sqrt{6}$ at which point N_{10} has an inflection point. They both vanish beyond s_c to satisfy the ellipse condition. $\max(-\Pi_r) = 1/(2\sqrt{6})$ and the plateau value of $-N_r$ is $1/6$.

for Π_0 and N_{10} to be nonzero. For the values of γ larger than γ_c the shear stress Π_0 and the primary normal stress difference N_{10} must be zero. Thus even the first-order iterative solutions Π_0 and N_{10} has a singular behavior. Their singular behavior also gives rise to a discontinuous behavior of Q_{x_0} and Q_{y_0} which take the values

$$Q_{x_0} = 0, \quad (8.166)$$

$$Q_{y_0} = -\lambda_0 \Omega \quad (8.167)$$

in the range of $\gamma \geq \gamma_c$ where Π_0 and N_{10} vanish. The s -dependence of Π_0 and N_{10} is plotted in Fig. 8.7 a and b. The fluid dynamic implication of vanishing Π_0 and N_{10} at $s \geq s_c$ is that the fluid becomes ideal and thus nondissipative with respect to shearing, giving rise to the Euler equation for the momentum conservation law. This means that the fluid motion no longer satisfies the boundary conditions for the velocity $u_x = \pm u_d/2$ at the boundaries and in fact the boundaries do not affect the fluid motion. This

means there is a slip in velocity which becomes equal to zero. The velocity profiles then have qualitatively the shapes as shown in Fig. 8.8 at different values of s . When the shear stress and normal stress difference vanish and thus the slip occurs, the velocity profile becomes horizontal.

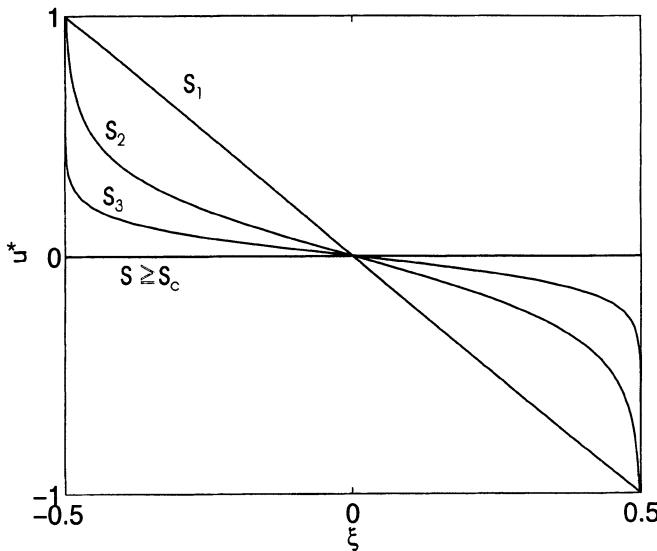


FIGURE 8.8 Schematic velocity profiles for various values of $s : s_1 < s_2 < s_3 < \dots < s_c$.

8.6 Shock Wave

Another important example of applications of the present theory is the study³ of shock waves. Shock waves have been conventionally studied by means of Navier–Stokes theory, but the theory does not quantitatively predict the shock wave structure. To remedy the situation the Burnett solutions of the Boltzmann equation have been explored [26,27] as a way to extend the Navier–Stokes theory, but they have so far not yielded reliable solutions to the problem. The Grad moment method [28] has been also used to the objective, but it has encountered a difficulty in that the theory predicts that there is no shock solution⁴ beyond the critical Mach number which, contrary to experiments, appears at $N_M = 1.65$ according to

³This section was completed in June, 1996 and preceded the later writings by the author and his collaborator on the subject.

⁴A shock wave is described by a set of variables, say, $\{\phi_i\}$, which satisfy the upstream and downstream boundary conditions $\{\phi_{i1}\}$ and $\{\phi_{i2}\}$, respectively. It

Grad's own investigation, at $N_M = 1.851$ according to Holway [29], and $N_M = 2.09$ according to Anile and Majorana [30]. These authors used a truncated set of Grad's moment equations where the moments beyond the first thirteen are expressed in terms of the lower order moments to study the existence of shock solutions. The precise values for the upper limit of the Mach number appear to depend on how the moment series is truncated. But one common feature is that there is an upper limit in the Mach number beyond which there is no shock solution. Therefore the shock wave still poses a theoretical challenge to kinetic theory of gases. In this section we take up this subject and study it from the viewpoint of the generalized hydrodynamics formulated in the previous chapter. Since the generalized hydrodynamics equations presented are basically the moment evolution equations, one can wonder if there is any basis to believe that they will provide us with an adequate solution to the problem. There is, however, reason to believe that they will, since the closure relations used for the constitutive equations in this work are different from those used by Grad and others in [28] and [29]. Furthermore, the applications of the steady constitutive equations subjected to the closure relations used in this work—*i.e.*, (8.61) and (8.62)—have produced some results [31–35] which are in quantitative agreement with experimental rheological data. Such agreement is rather encouraging and we would like to see if one can obtain similarly encouraging results for shock wave problems. In this section we will only consider a one-dimensional steady shock wave problem.

We assume that flow is in the direction of the x coordinate. Since we are interested in a steady shock wave, the governing balance equations are time-independent. They are in the form

$$\frac{d}{dx} \rho u = 0, \quad (8.168)$$

$$\frac{d}{dx} (\rho u^2 + p + \Pi_{xx}) = 0, \quad (8.169)$$

$$\frac{d}{dx} [\rho u (\mathcal{E} + \frac{1}{2} u^2) + u (p + \Pi_{xx}) + Q_x] = 0, \quad (8.170)$$

where the notation is standard and obvious by now. It, however, is useful to note that

$$[\nabla \mathbf{u}]_{xx} = \frac{2}{3} \partial_x u. \quad (8.171)$$

These balance equations are supplemented by the evolution equations for Π_{xx} and Q_x . For their evolution equations we take the closure relations in

is said that there exists a shock solution if for $\{\phi_i\} = \{\phi_{i1}\}$ at $x = -\infty$

$$\lim_{x \rightarrow -\infty} \{\phi_i\} = \{\phi_{i2}\}.$$

(8.1) which assume that the higher order moments ψ_1 and ψ_3 appearing in the moment evolution equations for Π and \mathbf{Q} are set equal to zero:

$$\psi_1 = 0, \quad \psi_3 = 0. \quad (8.172)$$

This set of closure relations is different from those taken in Grad's theory of solution for the Boltzmann equation, but there is no *a priori* reason to disfavor the present closure relations over those of Grad's theory where ψ_1 is expressed in terms of \mathbf{Q} and ψ_3 in terms of Π as follows:

$$\psi_1 = \frac{4}{5} \mathbf{T} \cdot \mathbf{Q}, \quad \psi_3 = \frac{5p^2}{2\rho} \boldsymbol{\delta} + \frac{7p}{2\rho} \Pi,$$

where \mathbf{T} is an isotropic fourth-rank tensor defined by

$$T_{ijkl} = \frac{1}{2} (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) - \frac{1}{3} \delta_{ij}\delta_{kl}.$$

This Grad closure is tantamount to truncating the moment expansion at the thirteenth moment. It is no more justifiable than the closures in (8.172). It is useful to compare the Grad closure with the closures (8.172). If the tensor Hermite polynomials $\mathcal{H}^{(q)}(\mathbf{w})$ are used to calculate the moments such as ψ_1 and ψ_3 as in Footnote 4 in Chapter 7, we then find

$$\begin{aligned} \psi_1 &= (m\beta)^{-1/2} [\Theta^{(3)} + \Theta^{(1)}\boldsymbol{\delta}] = (m\beta)^{-1/2} \Theta^{(3)}, \\ \psi_3 &= (m\beta)^{-1/2} [\Theta^{(4)} + \Theta^{(2)}\boldsymbol{\delta}]. \end{aligned}$$

Therefore, the present closure relations (8.172) mean that

$$\Theta^{(3)} = 0, \quad \Theta^{(4)} = -\Theta^{(2)}\boldsymbol{\delta} = -\Pi\boldsymbol{\delta}. \quad (8.173)$$

It must be noted that ψ_1 and ψ_3 are the moments beyond Π and \mathbf{Q} , and \mathbf{Q} must not be regarded as part of $\Theta^{(3)}$. The Grad closure takes $\Theta^{(3)} = 0$ since moments of higher orders than Π and \mathbf{Q} are ignored, that is, set equal to zero. The difference between the two methods of closure is simply in the manners of taking linear combinations for the higher order moments in terms of lower order moments. As we will see, this difference in the manners is crucial for the success of the theory when applied to shock waves. The closures (8.173) give rise to approximations for $\Theta^{(q)}$ ($q > 4$) which may be used in the distribution function so that the convergence of integrals involving the distribution function may be assured. We have shown in a number of studies [4,12,15,31–35] on nonlinear transport coefficients that the closure relations in (8.172), together with the adiabatic approximation described in Sec. 8.4, give rise to sufficiently accurate nonlinear transport coefficients and particularly non-Newtonian viscosities in comparison with experiments. On the strength of this finding, we take the closure relations in (8.172) and show their utility for the problem in hand.

With the closures (8.173) the constitutive equations for Π and \mathbf{Q} are given by (8.59) and (8.60). These equations suggest that if the shear stress and heat flux relax on faster time scales than the conserved variables, namely, if the Deborah number N_{De} and the Q number N_Q are large, then the time derivatives of Π and \mathbf{Q} may be neglected. This is the content of the adiabatic approximation for the constitutive equations (8.59) and (8.60). Equivalently, in this approximation we may set

$$\frac{d\hat{\Pi}}{dt} = \frac{d\hat{\mathbf{Q}}}{dt} = 0$$

in the constitutive equations for Π and \mathbf{Q} in the moving coordinate system. Thus we use the steady state constitutive equations (8.61) and (8.62) for steady shock waves of interest here. For the present one-dimensional problem the constitutive equations for Π_{xx} and Q_x are given by the equations

$$\frac{p}{\eta_0} \Pi_{xx} q(\kappa) + \frac{4}{3} \Pi_{xx} \partial_x u + \frac{4}{3} p \partial_x u = 0, \quad (8.174)$$

$$\frac{\hat{h}p}{\lambda_0} Q_x q(\kappa) + Q_x \partial_x u + \Pi_{xx} u \partial_x u + \hat{h}(p + \Pi_{xx}) \partial_x \ln T = 0, \quad (8.175)$$

where the nonlinear factor was defined before $q(\kappa) = \sinh \kappa / \kappa$ with κ defined by (8.25) and $\hat{h} = \hat{C}_p T$. These are partial differential equations for velocity component u and temperature T .

We note that these equations could have been obtained without resorting to the closure relations used earlier. To elaborate on this point we rearrange the evolution equations for Π and \mathbf{Q} as follows:

$$\begin{aligned} \rho \frac{d}{dt} \hat{\Pi} + \nabla \cdot \psi_1 &= -2p\gamma - 2[\Pi \cdot \gamma]^{(2)} - [\omega, \Pi] \\ &\quad - \frac{2}{3} \Pi \nabla \cdot \mathbf{u} - \frac{p}{\eta_0} \Pi q(\Phi), \end{aligned} \quad (8.176)$$

$$\rho \frac{d}{dt} \hat{\mathbf{Q}} + \nabla \cdot \psi_3 = -p\hat{C}_p T \nabla \ln T - \Pi \cdot \nabla \hat{h} - (d_t \mathbf{u} - \mathbf{F}) \cdot \Pi \quad (8.177)$$

$$- \mathbf{Q} \cdot (\gamma + \frac{1}{3} \delta \nabla \cdot \mathbf{u}) + \mathbf{Q} \cdot \omega - \frac{p\hat{C}_p T}{\lambda_0} \mathbf{Q} q(\Phi),$$

and treat the left hand side as a perturbation. This procedure will produce the steady state constitutive equations presented earlier in the lowest order of approximation.

Integration of the balance equations (8.168)–(8.170) yields the Rankine-Hugoniot relations

$$\rho u = M, \quad (8.178)$$

$$\rho u^2 + p + \Pi_{xx} = P, \quad (8.179)$$

$$\rho u (\mathcal{E} + \frac{1}{2} u^2) + u(p + \Pi_{xx}) + Q_x = Q, \quad (8.180)$$

where M , P , and Q are integration constants with the dimension of momentum per volume, momentum flux per volume, and energy flow per volume, respectively. These equations are also supplemented by the equation of state and the caloric equation of state

$$\begin{aligned} p &= \rho \mathcal{R}T, \\ \mathcal{E} &= \frac{3}{2} \mathcal{R}T. \end{aligned} \quad (8.181)$$

Let us define dimensionless variables

$$\begin{aligned} v &= MuP^{-1}, & \theta &= M^2 \mathcal{R}TP^{-2}, \\ \sigma &= \Pi_{xx}P^{-1}, & \phi &= pP^{-1}, \\ r &= P\rho M^{-2}, & \varphi &= Q_x Q^{-1}, \\ \xi &= xl^{-1}, & \alpha &= MQP^{-2}. \end{aligned} \quad (8.182)$$

The length scale is provided by the mean free path defined with the upstream momentum per volume, $M = \rho_1 u_1$ where the subscript 1 denotes the upstream. The downstream will be designated by subscript 2. The upstream mean free path is defined by

$$l = \frac{\eta_{01}}{M}, \quad (8.183)$$

where η_{01} is the upstream Newtonian viscosity at the upstream temperature T_1 . The transport coefficients are reduced with respect to the upstream transport coefficients:

$$\eta^* = \frac{\eta_0}{\eta_{01}}, \quad \lambda^* = \frac{\lambda_0}{\lambda_{01}}. \quad (8.184)$$

With this reduced variables we cast (8.178)–(8.181) in the forms

$$\begin{aligned} \phi &= r\theta, \\ rv &= 1, \\ rv^2 + \phi + \sigma &= 1, \\ rv^3 + 5\phi v + 2\sigma v + 2\alpha\varphi &= \alpha. \end{aligned} \quad (8.185)$$

From these equations and reduced constitutive equations obtained from (8.174) and (8.175) follow the five governing equations for the shock wave of interest

$$\phi v = \theta, \quad (8.186)$$

$$v + \phi + \sigma = 1, \quad (8.187)$$

$$v^2 + 5\theta + 2\sigma v + 2\alpha\varphi = \alpha, \quad (8.188)$$

$$\frac{1}{\eta^*} \phi \sigma q(\kappa) + \frac{4}{3} \sigma \partial_\xi v + \frac{4}{3} \phi \partial_\xi v = 0, \quad (8.189)$$

$$\frac{\alpha\beta}{\lambda^*} \theta \varphi q(\kappa) + \alpha\varphi \partial_\xi v + v\sigma \partial_\xi v + \frac{5}{2}\theta (\phi + \sigma) \partial_\xi \ln \theta = 0. \quad (8.190)$$

Here the new dimensionless parameter β is defined by

$$\beta = \frac{5}{3\theta_1} N_{\text{Pr}} \quad (8.191)$$

with θ_1 denoting the reduced upstream temperature and the Prandtl number defined with the upstream quantities: $N_{\text{Pr}} = \hat{C}_p T_1 \eta_{01} / \lambda_{01}$. Since the reduction scheme used here is slightly different from that in the literature [28], it is useful to explain it, especially, with regard to the appearance of the dimensionless number β in (8.190). On multiplication of the mean free path l , the first term in (8.175), apart from the nonlinear factor $q(\kappa)$, can be reduced as follows:

$$l \frac{\hat{h}p}{\lambda_0} Q_x = \frac{5\tau\phi\varphi}{2\lambda^*} \cdot \frac{lP^3Q}{\lambda_{01}M^2},$$

where the second factor on the right can be written as

$$\frac{lP^3Q}{\lambda_{01}M^2} = \frac{\eta_{01}}{\lambda_{01}} \cdot \frac{P^3Q}{M^3} = \frac{2N_{\text{Pr}}}{5\theta_1} \cdot \alpha \cdot \frac{P^2}{M^2}.$$

The second equality in this equation follows on making use of the definition of the Prandtl number and the reduced temperature. Finally, we obtain

$$l \frac{\hat{h}p}{\lambda_0} Q_x = \frac{\alpha\beta\tau\phi\varphi}{\lambda^*} \cdot \frac{P^2}{M^2}$$

and (8.190) follows on dividing the equation with $P^2 M^{-2}$ and use of the definition of β in (8.191). The argument κ in the nonlinear factor $q(\kappa)$ is given by the formula

$$\kappa = 4(2\gamma_0)^{-1/4} (5cN_M)^{-1/2} \left(\frac{\theta}{\theta_1} \right)^{1/4} \frac{1}{\phi\sqrt{\eta^*}} \left[\sigma^2 + \frac{8}{15f\theta} \alpha^2 \varphi^2 \right]^{1/2}, \quad (8.192)$$

where

$$\begin{aligned} c &= \frac{l}{l_h}, \\ f &= \frac{\lambda_{01}}{\frac{3}{2}\hat{C}_p T_1 \eta_{01}} \end{aligned} \quad (8.193)$$

with l_h denoting the hard sphere mean free path: $l_h = (\sqrt{2\pi}d^2n)^{-1}$. Therefore, for hard spheres, $c = 1$, $f = 1$ and $\eta^* = \sqrt{\theta/\theta_1}$. For a Maxwell gas $f = 1$, $\eta^* = \theta/\theta_1$, and

$$c = \frac{16}{15\sqrt{2\pi}A_2(5)} \sqrt{\frac{\theta_1}{E_d}},$$

where $A_2(5) = 0.432 \dots$ and $E_d = V_m M^2 / 4md^4 P^2$ with V_m denoting the potential parameter of the Maxwell model of interaction. The E_d is a dimensionless Maxwell potential energy at the hypothetical contact point of two hard spheres of radius $d/2$. The dimensionless potential energy E_d is set equal to unity by an appropriate choice of parameters M and P . With such a choice of reduction parameters which are arbitrary, we obtain

$$\kappa = \left(\frac{3\pi}{5}\right)^{1/4} \frac{[3A_2(5)]^{1/2}}{\sqrt{N_M}} \cdot \frac{1}{\phi\theta^{1/4}} \left[\sigma^2 + \frac{8}{15\theta} \alpha^2 \varphi^2\right]^{1/2}. \quad (8.194)$$

We note that the parameter α is related to the upstream Mach number as follows:

$$N_M = \sqrt{\frac{1 + \frac{1}{5}\mu}{1 - \frac{1}{3}\mu}}, \quad (8.195)$$

where

$$\mu = \sqrt{25 - 16\alpha}. \quad (8.196)$$

Therefore, expressed in terms of the upstream Mach number defined by the usual formula

$$N_M = \frac{v_1}{\sqrt{\gamma_0\theta_1}},$$

the parameter μ is given by

$$\mu = \frac{3(N_M^2 - 1)}{N_M^2 + \frac{3}{5}}.$$

It ranges⁵ from 0 to 3 which occurs at $N_M = \infty$.

⁵This range of μ also follows from the values of v and θ in (8.201) and (8.203) given below. If $\alpha = 25/16$, clearly $\mu = 0$ and there is no shock wave. For an infinitely strong shock, ϕ at one end must be equal to zero. Therefore $\mu = 3$ for which $\alpha = 1$. It is not possible to have $v = 0$ instead of $\phi = 0$ at one end, since then $\mu = 5$ which implies a negative pressure.

To determine the boundary conditions on v , ϕ , and θ , we observe that $\sigma \rightarrow 0$ and $\varphi \rightarrow 0$ as $\xi \rightarrow \pm\infty$. Eqs. (8.189) and (8.190) are identically satisfied in the limits if v and θ become independent of ξ at the boundaries. Therefore, as $\xi \rightarrow \pm\infty$,

$$\sigma, \phi \rightarrow 0, \quad (8.197)$$

$$\theta = \phi v, \quad (8.198)$$

$$v + \phi = 1, \quad (8.199)$$

$$v^2 + 5\theta = \alpha. \quad (8.200)$$

The solutions of (8.198)–(8.200) are

$$v = \frac{1}{8}(5 \pm \mu), \quad (8.201)$$

$$\phi = \frac{1}{8}(3 \mp \mu), \quad (8.202)$$

$$\theta = \frac{1}{64}(15 \mp 2\mu - \mu^2). \quad (8.203)$$

The upper sign is for the upstream and the lower sign is for the downstream. These solutions provide the boundary conditions at the upstream and downstream. They also imply

$$r = \frac{8}{5 \pm \mu}. \quad (8.204)$$

With the help of (8.186)–(8.188) the differential equations (8.189) and (8.190) may be cast into the following forms

$$\frac{dv}{d\xi} = \frac{3\theta(v^2 - v + \theta)}{4\eta^* v^2 (1 - v)} q(\kappa), \quad (8.205)$$

$$\begin{aligned} \frac{d\theta}{d\xi} = & -\frac{\theta}{5v^2(1-v)^2} \left[\frac{\beta\theta v(1-v)(\alpha + v^2 - 2v - 3\theta)}{\lambda^*} \right. \\ & \left. + \frac{3(v^2 - v + \theta)(\alpha - v^2 - 5\theta)}{4\eta^*} \right] q(\kappa). \end{aligned} \quad (8.206)$$

Here the argument κ in the nonlinear factor $q(\kappa)$ can be expressed in terms of v and θ by using (8.186)–(8.188). These equations are solved subject to the boundary conditions in (8.201)–(8.203). The second term on the right hand side of (8.206) stems from the thermoviscous effect involving the

second and third terms as well as the term $\hat{h}\Pi_{xx}\partial_x \ln T$ in (8.175). These, together with the second term in (8.174), are the terms that do not appear in the Navier–Stokes–Fourier theory. To indicate the difference between the governing equations in the classical Navier–Stokes–Fourier theory and the present theory and to facilitate the solution procedure for (8.205) and (8.206), the governing equations are presented for shock wave in the Navier–Stokes–Fourier theory

$$\frac{dv}{d\xi} = \frac{3(v^2 - v + \theta)}{4\eta^*v}, \quad (8.207)$$

$$\frac{d\theta}{d\xi} = -\frac{\theta\beta(\alpha + v^2 - 2v - 3\theta)}{5\lambda^*}. \quad (8.208)$$

These equations follow from (8.205) and (8.206) if $1 - v$ is replaced by ϕ , (8.198) is made use of, and the second term on the right hand side of (8.206) is omitted (since it arises from the thermoviscous coupling term that must vanish in the linear order). We note that in the case of a hard sphere gas the reduced transport coefficients η^* and λ^* depend on θ only:

$$\eta^* = \theta^{1/2}, \quad \lambda^* = \theta^{3/2}. \quad (8.209)$$

The governing equations (8.205) and (8.206) are quite different from the evolution equations for σ and φ appearing in the moment equation approach of Grad. The governing equations in the latter approach were found to fail to produce shock solutions for $N_M \geq 1.65$. The differential equations for σ and φ arise in the Grad theory, primarily because of the particular closure relations for ψ_1 and ψ_3 taken, which inevitably involve the spatial derivatives of ψ_1 and ψ_3 . In the following we first examine the governing equations (8.205) and (8.206) and the existence of shock solutions.

Here we will examine the governing equations in the case of the transport coefficients satisfying (8.209). In the Navier–Stokes–Fourier (NSF) theory the equation for direction fields is given by

$$\frac{dv}{d\theta} = \frac{\omega(v^2 - v + \theta)}{v(3\theta + 2v - v^2 - \alpha)}, \quad (8.210)$$

where

$$\omega = \frac{15\lambda^*}{4\beta\eta^*\theta}. \quad (8.211)$$

It is independent of θ for the transport coefficients obeying (8.209). The singularities of the direction field of the governing equations in the NSF theory are given by

$$v^2 - v + \theta = 0,$$

$$v^2 - 2v - 3\theta + \alpha = 0, \quad (8.212)$$

$$v = 0.$$

There are three singular points:

$$P_0 : v = \frac{1}{8}(5 + \mu), \quad \theta = \frac{1}{64}(15 - 2\mu - \mu^2)$$

$$P_1 : v = \frac{1}{8}(5 - \mu), \quad \theta = \frac{1}{64}(15 + 2\mu - \mu^2)$$

$$P_2 : v = 0, \quad \theta = 0$$

Points P_0 and P_1 coincide with the boundary values given in (8.201) and (8.203). By making linear stability analysis of the governing equations, one can show that P_0 is a saddle, P_1 is a node, and P_2 is a spiral. The shock solution is a curve connecting P_0 and P_1 as $\xi \rightarrow \infty$ from $\xi = -\infty$. The shock solution lies in the domain bounded by the two parabolas in (8.212) that intersect at P_0 and P_1 . It is possible to show that there exists such a solution for every value of α [28]. Therefore the NSF theory admits shock solutions for all values of Mach number. We will find that P_0 , P_1 , and P_2 are also the singular points of the governing equations (8.205) and (8.206) for the present theory.

We now examine the governing equations (8.205) and (8.206) by using the equation for direction fields:

$$\frac{dv}{d\theta} = -\frac{\omega(1-v)(v^2-v+\theta)}{[v(1-v)(v^2-2v-3\theta+\alpha)+(3/4\beta)(v^2-v+\theta)(\alpha-v^2-5\theta)]}. \quad (8.213)$$

The singularities of the direction field are given by the equations

$$1 - v = 0, \quad (8.214)$$

$$v^2 - v + \theta = 0, \quad (8.215)$$

$$v(1-v)(v^2-2v-3\theta+\alpha)+\frac{3}{4\beta}(v^2-v+\theta)(\alpha-v^2-5\theta)=0. \quad (8.216)$$

The first two equations are for the loci of zero slopes whereas the last equation is for the loci of infinite slopes. Eq. (8.216) factorizes to the form

$$\frac{15}{4\beta}(\theta - B + \sqrt{B^2 + A})(\theta - B - \sqrt{B^2 + A}) = 0, \quad (8.217)$$

where

$$A = \frac{4\beta}{15}v(v-1)\left[\left(1-\frac{3}{4\beta}\right)\alpha + \left(1+\frac{3}{4\beta}\right)v^2 - 2v\right], \quad (8.218)$$

$$B = \frac{2\beta}{5}\left[\left(1-\frac{1}{\beta}\right)v^2 - \left(1-\frac{5}{4\beta}\right)v - \frac{3}{4\beta}\alpha\right]. \quad (8.219)$$

There is an interval of v where the discriminant $B^2 + A$ becomes negative and thus (8.217) represents an ellipse or rather a loop whereas it represents a pair of parabolas in the intervals where the discriminant is positive. The intersections of the five curves arising from (8.214)–(8.216) are the following five points:

$$\begin{aligned} P_0 : \quad v &= \frac{1}{8}(5 + \mu), & \theta &= \frac{1}{64}(15 - 2\mu - \mu^2) \\ P_1 : \quad v &= \frac{1}{8}(5 - \mu), & \theta &= \frac{1}{64}(15 + 2\mu - \mu^2) \\ P_2 : \quad v &= 0 & \theta &= 0 \\ P_3 : \quad v &= 1, & \theta &= 0 \\ P_4 : \quad v &= 1, & \theta &= \frac{1}{5}(\alpha - 1). \end{aligned}$$

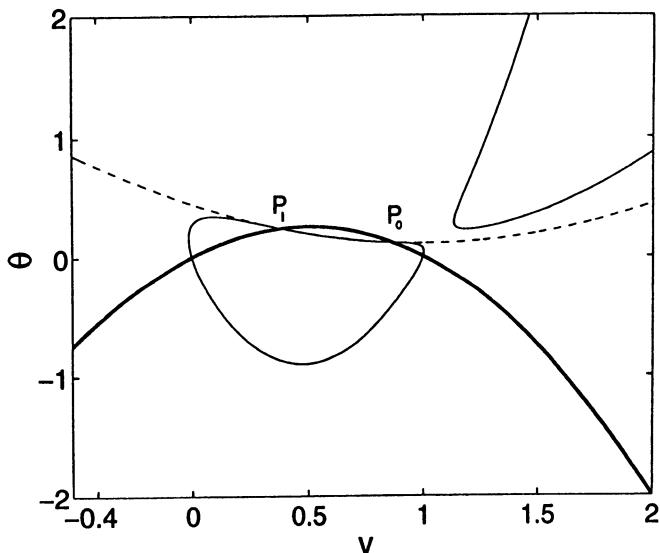


FIGURE 8.9 Loci of zero and infinite slopes in the direction field for the NSF and generalized hydrodynamics theories. The broken curve is for the NSF theory whereas the light curves are for the generalized hydrodynamics theory. The bold curve is shared by both theories. Both theories also share the same points of intersection P_0 and P_1 . There is a parabola in the upper left hand corner which does not show up in the scale used for the figure. (Reproduced with permission from M. Al-Ghoul, Ph.D. thesis, McGill University, 1997.)

Notice P_0 , P_1 , and P_2 are exactly the same as for the NSF theory. An example of the loci of zero and infinite slopes for both the NSF and present theories are plotted in the case of $N_M = 1.5$ in Fig. 8.9. The broken curve is the locus in the NSF theory whereas the solid curves are the loci in the present generalized hydrodynamics theory. Both theories share the same parabola in the bold line which intersects the parabola in the broken line and the ellipse at the same points P_0 and P_1 . This means that both theories share the same boundary conditions at the upstream and downstream. In the case of the direction field equation for the present theory there appear additional singularities P_3 and P_4 . It must be noted that line $v = 0$ is neither the locus of zero slopes nor the locus of infinite slopes. Linear analysis shows that P_3 is neutral in one direction and unstable in the other whereas P_4 is an unstable focus. As the Mach number increases, the intersections P_0 , P_3 , and P_4 coalesce at $v = 1$, which corresponds to the boundary value for velocity at infinite Mach number. This situation already is almost achieved at $N_M = 10$ as shown in Fig. 8.10. The shock

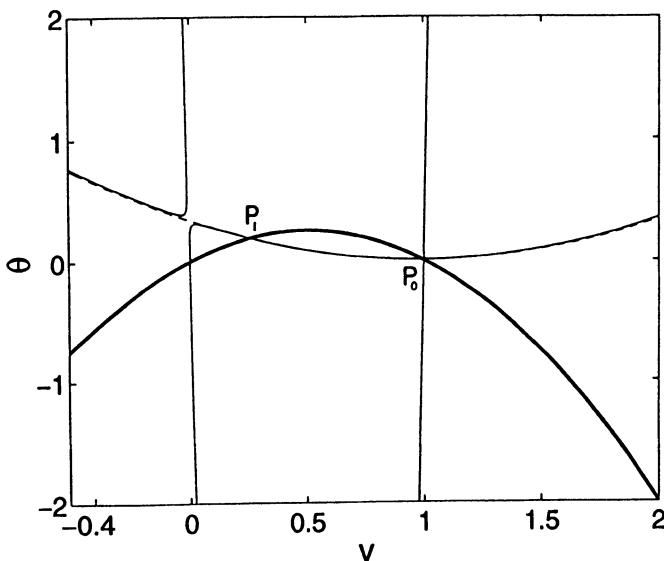


FIGURE 8.10 Same as FIGURE 8.9 except for $N_M = 10$. The curve $(0P_1P_01)$ is a part of a closed loop which does not fully show up in the scale used for the figure. (Reproduced with permission from M. Al-Ghoul, Ph.D. thesis, McGill University, 1997.)

solution must connect P_0 and P_1 . The fact that the intersections P_0 and P_1 are shared by both theories and there is an intersection of domain where the slopes are negative strongly indicates that a shock solution must exist for the governing equations (8.205) and (8.206). Such solutions can be demonstrated for all the cases of Mach number studied. Examples of density profile are shown in Fig. 8.11 where the reduced distance z is related to the reduced distance ξ used for the governing equations by the relation $\xi = zB\sqrt{5\pi/6}N_M$ where $B = 1$ for the Maxwell model and $B = (7 - 2s)(5 - 2s)/24$ for a variable hard sphere mode [36] for which the viscosity may be taken in the form $\eta_0 = \mu_0(T/T_0)^s$. In this formula μ_0 , T_0 , and s are parameters depending on the substance.

In shock wave experiments reported in the literature the shock structures are characterized by the shock width δ defined by the formula

$$\delta = \frac{n_2 - n_1}{(dn/dz)_{\max}}, \quad (8.220)$$

where $(dn/dz)_{\max}$ is the maximum value of the derivative which occurs at the shock transition point. This definition of shock width does not most effectively characterize the structure of a shock wave, but is widely used to present experimental data. Examples with the density are given in Fig. 8.12

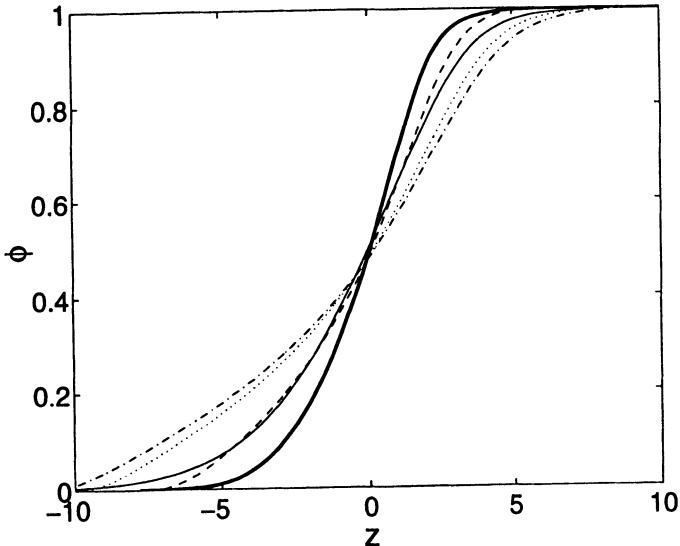


FIGURE 8.11 Density profiles in a one-dimensional shock for various cases of Mach number in the case of a variable hard sphere ($s = 0.75$). Solid line: $N_M = 1.5$; bold solid line: $N = 2$; dashed line: $N_M = 5$; dotted line: $N_M = 8$; dash-dotted line: $N_M = 10$. (Reproduced with permission from M. Al-Ghoul, Ph.D. thesis, McGill University, 1997.)

where the theoretical shock widths calculated by the governing equations (8.205) and (8.206) for argon are compared with experimental data [39–41]. A line is drawn through the theoretical results to guide the eyes. A variable hard sphere model mentioned earlier was used for the calculation with $s = 0.75$. Clearly the generalized hydrodynamics theory is capable of accounting for the experimental data for the entire range of Mach number studied.

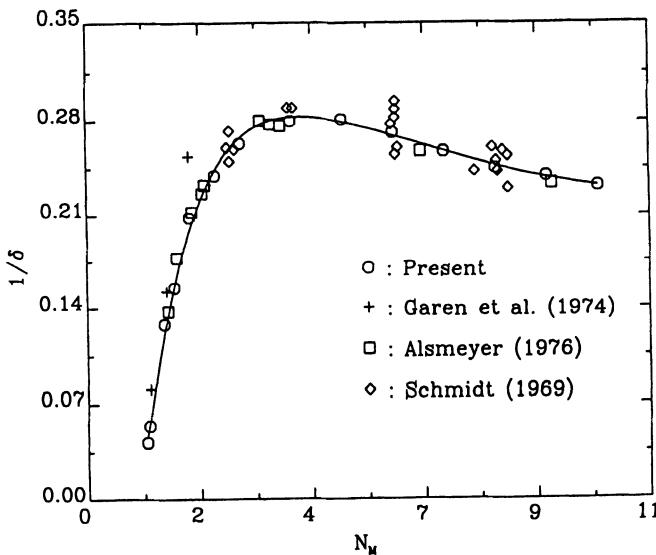


FIGURE 8.12 Theoretical inverse shock width vs. Mach number in the case of argon (a variable hard sphere model with $s = 0.75$). The experimental data are from [39]–[41]. (Reproduced with permission from M. Al-Ghoul, Ph.D. thesis, McGill University, 1997.)

One can also calculate the calortropy production associated with a shock wave. Since the calortropy production for the present problem is given by

$$\sigma_c = k_B g \kappa(\Pi, Q) \sinh \kappa(\Pi, Q), \quad (8.221)$$

where $g = \sqrt{m/k_B T}/2n^2 d^2$, we use the reduced calortropy production which may be written

$$\hat{\sigma}_c = \sqrt{\frac{\theta}{\theta_1}} \left(\frac{r_1}{r} \right)^2 \kappa(\sigma, \varphi) \sinh \kappa(\sigma, \varphi). \quad (8.222)$$

If this reduced calortropy production is plotted as a function of z , it is peaked around the shock transition point as the reduced stress and heat

flux are. Since the calortropy production is a measure of energy dissipation from a useful to a less useful in an irreversible process, the behavior of reduced calortropy production indicates how the shock wave dissipates its energy and deteriorates. An equally interesting quantity to consider is the global calortropy production which is the sum total of the measure of energy dissipation. It is defined as a reduced integral calortropy production

$$\langle \hat{\sigma}_c \rangle = \int_{-\infty}^{\infty} d\xi \sqrt{\frac{\theta}{\theta_1}} \left(\frac{r_1}{r} \right)^2 \kappa(\sigma, \varphi) \sinh \kappa(\sigma, \varphi). \quad (8.223)$$

In the case of the Maxwell model $\langle \hat{\sigma}_c \rangle$ increases with the Mach number in the following manner:

$$\langle \hat{\sigma}_c \rangle = \langle \hat{\sigma}_c \rangle_0 (N_M - a)^\epsilon, \quad (8.224)$$

where $\langle \hat{\sigma}_c \rangle_0$, a , and ϵ are constants. In the case of the variable hard sphere model used for argon earlier, $a = 0.87$ and $\epsilon = 2.98$, whereas $a = 0.85$ and $\epsilon = 3.14$ for the Maxwell model. This is shown in Fig. 8.13.

It may now be concluded that the generalized hydrodynamics equations presented represent a continuum hydrodynamics theory of shock waves and

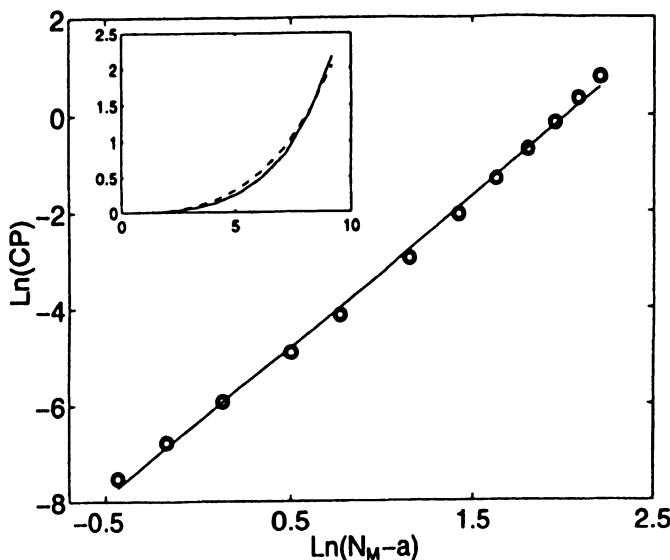


FIGURE 8.13 Reduced integral calortropy production CP vs. $(N_M - a)$ in the case of a Maxwell model of potential. (Reproduced with permission from M. Al-Ghoul, Ph.D. thesis, McGill University, 1997.)

structures beyond the range of validity of the Navier–Stokes–Fourier theory. An extension of the Navier–Stokes–Fourier theory has been long sought in the field of shock wave phenomena, and the present generalized hydrodynamics theory provides it. It thus in fact resolves one of the outstanding problems in gas dynamics and displays its power in treating nonlinear fluid dynamics problems in the regime far removed from equilibrium.

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9

Quantum Nonequilibrium Ensemble Method

The systems considered in the previous chapters were classical gases obeying the Boltzmann statistics and the Boltzmann kinetic equation, but transport phenomena in semiconductors and small quantum devices at low temperatures, radiation interacting with particles, quantum gases at low temperatures, and so on usually require quantum mechanical treatments. The questions then arise of whether quantum systems can be described in a macroscopic formalism similar to the one developed for the classical gases, whether the nonequilibrium ensemble method is still applicable, and whether there is a mathematical structure for a theory of irreversible processes in such quantum systems. The answers to these questions are in the affirmative. In this chapter we apply the nonequilibrium ensemble method to a quantum kinetic equation and develop a theory of irreversible processes in quantum gases. When faced with the task of statistically treating a quantum system, the obvious strategy to take is to use a kinetic equation governing the density matrix or a kinetic equation for the Wigner distribution function [1] of the system. Another method, a little more *ad hoc*, would be to assume a semiclassical kinetic equation such as the Boltzmann–Nordheim–Uehling–Uhlenbeck (BNUU) kinetic equation [2,3] as a generalization of the classical Boltzmann equation. However, since the latter can be derived from the former under some approximations [4–6] of the collision term, it is not as semiclassical and *ad hoc* as the words might give the impression. In Appendix B we will establish that the density matrix approach gives rise to generalized hydrodynamics equations which have the same mathematical structures as their classical counterparts, except that the macroscopic variables therein are quantum mechanical averages of dynamical observables (operators). However, the same aim can be more simply achieved if the density matrix and its governing equation—the kinetic equation—are represented by the Wigner distribution function and its governing equation derived from the quantum kinetic equation for the density matrix. Since the generalized hydrodynamics equations thus derived are subjected to the restriction of the second law of thermodynamics in the nonequilibrium ensemble method, the transport properties computed therefrom will be thermodynamically consistent. The thermodynamic compatibility of transport properties is a useful criterion to judge the quality of

the results because it is not obvious that nonlinear transport properties calculated are acceptable thermodynamically if the system is in the nonlinear regime. For example, many of the phenomena [7–9] in semiconductors and small quantum devices at high field gradients are essentially nonlinear, but a thermodynamically consistent theory of nonlinear transport processes will not be assured unless special care is exercised to satisfy the requirements of the laws of thermodynamics. The nonequilibrium ensemble method will ensure it even for quantum systems, as will be shown.

We will assume that the density of the system is sufficiently low so that the statistical correlations arising from the interactions between the particles are negligible. On this ground we will assume that the singlet density matrices are sufficient for the statistical description of the system, for example, consisting of dilute quantum gases, charges, phonons, or photons. We will also assume that the singlet density matrices obey a set of irreversible (time reversal symmetry breaking) kinetic equations. These kinetic equations may be approximately justified from the quantum Liouville (von Neumann) equation as is traditionally done [4–6] in statistical mechanics or simply postulated as is done, for example, in the quantum semigroup theory [10] of irreversible processes. In either one of these approaches it is necessary to formulate a theory of transport processes in a way consistent with the laws of thermodynamics, and the end results would be the same. Here we will take the same approach as for the classical theory that we have considered in the earlier chapters, namely, postulate suitable kinetic equations for the singlet density matrices for a gaseous mixture of quantum particles. We then show that a theory of irreversible thermodynamics can be erected with the kinetic equations postulated for the density matrices of the mixture. Generalized hydrodynamics is an integral part of the theory of irreversible processes formulated in the present nonequilibrium ensemble method. A theory of transport processes will be presented and applied to mass and heat transport phenomena later in this chapter.

9.1 Kinetic Equations for Density Matrices

The system is assumed to consist of r components. There are N_a particles of species a in volume V . The global number density of the species a then is N_a/V and the total number density is N/V where $N = N_1 + N_2 + \dots + N_r$. The system is assumed to be subjected to an external field \mathbf{F} which is uniform in space at least over the distance of interparticle interaction but may change in time with a characteristic frequency. The external force per mass of species a acting on a particle will be denoted by \mathbf{F}_a . The potential energy operator corresponding to this force will be denoted by \mathfrak{V}_a . It will be assumed that this potential energy varies very slowly over the range of interparticle interactions so that it does not affect particle collisions. The

Hamiltonian operator \mathbf{H}_a for a particle of species a thus may be written as

$$\mathbf{H}_a = \mathbf{H}_a^0 + m_a \mathfrak{V}_a, \quad (9.1)$$

where H_a^0 is the kinetic energy operator for the whole system:

$$\mathbf{H}_a^0 = \frac{p_a^2}{2m_a}, \quad (9.2)$$

with $p_a^2 \equiv \mathbf{p}_a \cdot \mathbf{p}_a$ and m_a denoting the mass of species a . This assumption should be taken with the understanding that although the interparticle correlations are absent at the statistical level, so that the statistical correlation functions are neglected since the density is low, the particles do collide with each other through interparticle interaction forces at the few-particle dynamical level. This few-particle dynamics is relevant to the collision term in the kinetic equations presented later, and numerous such molecular collisions are the ultimate cause for the irreversible behavior exhibited by many-particle systems.

Let us denote by boldface roman \mathbf{f}_a the singlet density matrix for a particle of species a in the system. If the density is sufficiently low so that the statistical correlations are negligible between the particles, the density matrix for the whole system composed of the r components is given by the product of the singlet density matrices \mathbf{f}_a :

$$\mathbf{f} = \prod_{a=1}^r \mathbf{f}_a. \quad (9.3)$$

The density matrix \mathbf{f}_a is assumed to normalize to N_a :

$$\text{Tr} \mathbf{f}_a = N_a, \quad (9.4)$$

where Tr is taken over the states of a particle of species a . The local number density of the species a is then given by

$$\text{Tr} [\delta(\mathbf{r}_a - \mathbf{r}) \mathbf{f}_a] = n_a. \quad (9.5)$$

Statistical averages (expectation values) of dynamical observables (operators) at position \mathbf{r} and time t can be computed by means of the singlet density matrix \mathbf{f}_a :

$$\bar{A}_a(\mathbf{r}, t) = \text{Tr} [\mathbf{A}_a \delta(\mathbf{r}_a - \mathbf{r}) \mathbf{f}_a(t)] \equiv \langle \mathbf{A}_a \delta(\mathbf{r}_a - \mathbf{r}) \mathbf{f}_a(t) \rangle, \quad (9.6)$$

where \mathbf{A}_a is the microscopic expression for a dynamical operator pertaining to a particle of species a . Vector \mathbf{r}_a is the position vector of a particle of species a and \mathbf{r} is a position vector in a suitable fixed coordinate system.

We now assume a nonlinear kinetic equation for the density matrix with time reversal symmetry breaking built into it. A well known example for

such a nonlinear evolution equation would be the quantum version of the Boltzmann equation. This kinetic equation is postulated to satisfy a set of conditions, such as the existence of conservation laws of mass, momentum, and energy, in addition to the H theorem which is necessary for the stability of equilibrium and constructing a theory of irreversible processes. As is the case for the classical kinetic equation used in the previous chapters, such a kinetic equation will be found to be sufficient for formulating a theory of irreversible processes. In this approach the precise form for the collision term in the kinetic equation is not required until transport processes are investigated case by case, which then will require a more explicit form for the collision term in the kinetic equation in question. To elaborate on what is said here we may assume that the density matrix \mathbf{f}_a obeys the irreversible kinetic equation

$$\partial_t \mathbf{f}_a - (i\hbar)^{-1} [\mathbf{H}_a, \mathbf{f}_a] = \mathbf{R}[\mathbf{f}_a], \quad (9.7)$$

where $[\mathbf{H}_a, \mathbf{f}_a]$ is the commutator of \mathbf{H}_a and \mathbf{f}_a and $\mathbf{R}[\mathbf{f}_a]$ stands for the collision term which has the properties: (1) its collision invariants are mass, momentum, and energy; (2) it breaks the time reversal symmetry. Therefore the kinetic equation is assumed to be irreversible and to satisfy the H theorem. The first condition gives rise to the conservation laws of mass, momentum, and energy. The second condition puts a constraint on the evolution of the density matrix toward equilibrium and the evolution equations of macroscopic variables through the H theorem. The collision term $\mathbf{R}[\mathbf{f}_a]$ is the replaceable part of the evolution equation for \mathbf{f}_a which can be modeled depending on the system of interest. Explicit models for the collision term should be constructed such that they meet the aforementioned requirements on it and yield an accurate interpretation of the experimental data for transport properties of interest. Therefore, as in the classical theory, the theory of transport processes plays the role of elucidating the collision term in the kinetic equation in this approach.

If the collision term is set equal to zero, then (9.7) becomes the Liouville–von Neumann equation for the singlet density matrix \mathbf{f}_a , which is nondissipative and time reversal invariant. The presence of the dissipative and time reversal symmetry breaking collision term in the kinetic equation is essential for describing irreversible processes in macroscopic systems, and by postulating such a kinetic equation we are elevating it to the status of a fundamental evolution equation for mesoscopic description of macroscopic systems, as in the classical theory. The question of the origin of irreversibility therefore is not asked in this approach. The principal aim of this chapter is to formulate the nonequilibrium ensemble method and a thermodynamically consistent theory of macroscopic processes for a class of quantum systems, which would facilitate our understanding of macroscopic irreversible processes and their molecular basis and provide us with a thermodynamically consistent statistical theory for such systems.

9.2 Wigner Representations for Operators

The density matrix and quantum mechanical operators are much more complicated and laborious to compute in practice than their classical counterparts. For this reason, and to show the correspondence between the quantum and classical theories, the Wigner distribution function has been used since 1932 when Wigner [1] introduced it. We will find it useful to approach our subject from the viewpoint of the Wigner distribution function. To prepare the reader for the study intended we will briefly review some basic aspects of Wigner distribution function.

In the coordinate representation the density matrix is defined for a pure state as

$$f^{(n)}(\mathbf{r}^{(n)}, \mathbf{r}^{(n)\prime}; t) = \Psi^*(\mathbf{r}^{(n)\prime}; t) \Psi(\mathbf{r}^{(n)}; t), \quad (9.8)$$

where $\Psi(\mathbf{r}^{(n)}; t)$ is the wave function for the state of the system at position $\mathbf{r}^{(n)} \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$. For a system in a mixed state the density matrix has the form

$$f^{(n)}(\mathbf{r}^{(n)}, \mathbf{r}^{(n)\prime}; t) = \sum_j A_j \Psi_j^*(\mathbf{r}^{(n)\prime}; t) \Psi_j(\mathbf{r}^{(n)}; t), \quad (9.9)$$

where Ψ_j and A_j are the wave function and the statistical weight of the j th state in the ensemble, respectively. The average (expectation value) for a macroscopic observable [11,12] is calculated by taking trace of the quantum mechanical operator weighted by the density matrix. If the quantum mechanical operator corresponding to a classical observable $g(\mathbf{p}^{(n)}, \mathbf{r}^{(n)})$ is denoted by \mathbf{G} , then the expectation value of \mathbf{G} is computed with the formula

$$\begin{aligned} \langle g \rangle &= \text{Tr}(\mathbf{G} f^{(n)}) \\ &= \iint d\mathbf{r}^{(n)} d\mathbf{r}^{(n)\prime} G(\mathbf{r}^{(n)}, \mathbf{r}^{(n)\prime}) f^{(n)}(\mathbf{r}^{(n)\prime}, \mathbf{r}^{(n)}; t). \end{aligned} \quad (9.10)$$

Here the trace is given in coordinate representation, and $f^{(n)}(\mathbf{r}^{(n)\prime}, \mathbf{r}^{(n)}; t)$ and $G(\mathbf{r}^{(n)}, \mathbf{r}^{(n)\prime})$ are the matrix elements of quantum operators $\mathbf{f}^{(n)}$ and \mathbf{G} , respectively. The quantum mechanical operator \mathbf{G} corresponding to the classical variable $g(\mathbf{p}^{(n)}, \mathbf{r}^{(n)})$ is obtained by quantizing the latter by means of the Weyl correspondence [13,14]. The matrices are constructed for the basic observables in the following manner:

coordinates:

$$g(\mathbf{r}^{(n)}) \rightarrow g(\mathbf{r}^{(n)}) \prod_k \delta(\mathbf{r}_k - \mathbf{r}'_k), \quad (9.11)$$

momenta:

$$\mathbf{p}_i \rightarrow -i\hbar \nabla_{\mathbf{r}_i} \prod_k \delta(\mathbf{r}_k - \mathbf{r}'_k). \quad (9.12)$$

For example, the Hamiltonian operator has the matrix element

$$\mathbf{H}^{(n)}(\mathbf{r}^{(n)}, \mathbf{r}^{(n)\prime}) = \left[-\sum_i \left(\frac{\hbar^2}{2m_i} \right) \nabla_{\mathbf{r}_i}^2 + V(\mathbf{r}^{(n)}) \right] \prod_k \delta(\mathbf{r}_k - \mathbf{r}'_k). \quad (9.13)$$

Reduced density matrices can be defined in a manner similar to the classical theory by integrating the n -particle density matrix over the configuration space of a subset of the n particles. Here we are particularly interested in the single-particle density matrix $f(\mathbf{r}, \mathbf{r}'; t)$ which is defined by

$$f(\mathbf{r}, \mathbf{r}'; t) = \iint d\mathbf{r}^{(n-1)} d\mathbf{r}^{(n-1)\prime} f^{(n)}(\mathbf{r}^{(n)\prime}, \mathbf{r}^{(n)}; t). \quad (9.14)$$

The integrals are over the configuration space of $n - 1$ particles.

The Wigner distribution function corresponding to the density matrix $f^{(n)}$ is defined by

$$\begin{aligned} f^{(n)}(\mathbf{p}^{(n)}, \mathbf{r}^{(n)}; t) &= \pi^{-3n} \int d\mathbf{y}^{(n)} \exp \left(i \frac{2}{\hbar} \mathbf{p}^{(n)} \cdot \mathbf{y}^{(n)} \right) \\ &\times f^{(n)}(\mathbf{r}^{(n)} - \mathbf{y}^{(n)}, \mathbf{r}^{(n)} + \mathbf{y}^{(n)}; t) \end{aligned} \quad (9.15)$$

and the corresponding von Neumann equation takes the form [15]

$$\left[\partial_t + \sum_{i=1}^n \frac{\mathbf{p}_i}{m_i} \cdot \nabla_{\mathbf{r}_i} - \frac{2}{\hbar} \sin \left(\frac{1}{2} \hbar \nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{p}} \right) V(\mathbf{r}^{(n)}) \right] f^{(n)}(\mathbf{p}^{(n)}, \mathbf{r}^{(n)}; t) = 0, \quad (9.16)$$

where $\nabla_{\mathbf{r}} = \sum_i^n \partial/\partial \mathbf{r}_i$ and $\nabla_{\mathbf{p}} = \sum_i^n \partial/\partial \mathbf{p}_i$. The operators $\nabla_{\mathbf{r}}$ and $\nabla_{\mathbf{p}}$ act only on $V(\mathbf{r}^{(n)})$ and $f^{(n)}$, respectively. Eq. (9.16) reduces to the classical Liouville equation as $\hbar \rightarrow 0$.

Kinetic theory and thermodynamics of irreversible processes of quantum fluids can be developed in terms of the density matrices. The governing equation (9.16) for the Wigner distribution function suggests the underlying parallelism between the classical and quantum theories. In fact, the theories turn out to be simpler if the Wigner distribution functions are used instead of the density matrices. We illustrate how the Wigner distribution function enters into the theory and how its definition given in (9.15) is motivated. We will do it, for the sake of simplicity, with the singlet density matrix in which case only one set of coordinate variables is involved.

Let us denote a classical observable by $g(\mathbf{p}, \mathbf{r})$. Then its operator form is obtained as follows. First, $g(\mathbf{p}, \mathbf{r})$ is decomposed into its Fourier components $\xi(\boldsymbol{\sigma}, \boldsymbol{\tau})$:

$$g(\mathbf{p}, \mathbf{r}) = \iint d\boldsymbol{\sigma} d\boldsymbol{\tau} \exp[i(\boldsymbol{\sigma} \cdot \mathbf{p} + \boldsymbol{\tau} \cdot \mathbf{r})] \xi(\boldsymbol{\sigma}, \boldsymbol{\tau}). \quad (9.17)$$

The quantum mechanical operator corresponding to $g(\mathbf{p}, \mathbf{r})$ is defined as

$$\mathbf{G}(\mathbf{r}, \mathbf{r}') = \iint d\boldsymbol{\sigma} d\boldsymbol{\tau} \exp[i(\boldsymbol{\sigma} \cdot \mathbf{P} + \boldsymbol{\tau} \cdot \mathbf{Q})] \xi(\boldsymbol{\sigma}, \boldsymbol{\tau}), \quad (9.18)$$

where $\mathbf{P}(\mathbf{r}, \mathbf{r}')$ and $\mathbf{Q}(\mathbf{r}, \mathbf{r}')$ are the operators corresponding to momentum and position and defined as in (9.11):

$$\begin{aligned} \mathbf{P}(\mathbf{r}, \mathbf{r}') &= -i\hbar \nabla \delta(\mathbf{r} - \mathbf{r}'), \\ \mathbf{P}^n(\mathbf{r}, \mathbf{r}') &= (-i\hbar \nabla)^n \delta(\mathbf{r} - \mathbf{r}'), \\ \mathbf{Q}(\mathbf{r}, \mathbf{r}') &= \mathbf{r} \delta(\mathbf{r} - \mathbf{r}'), \\ \mathbf{Q}^n(\mathbf{r}, \mathbf{r}') &= \mathbf{r}^n \delta(\mathbf{r} - \mathbf{r}'), \end{aligned} \quad (9.19)$$

where $\nabla = \partial/\partial\mathbf{r}$. The expectation value of operator \mathbf{G} may be written as

$$\langle \mathbf{G} \rangle = \iint d\mathbf{r} d\mathbf{r}'' \left[\int d\mathbf{r}' \mathbf{G}(\mathbf{r}, \mathbf{r}') f(\mathbf{r}', \mathbf{r}''; t) \right] \delta(\mathbf{r} - \mathbf{r}''). \quad (9.20)$$

We remark that $\langle \mathbf{G} \rangle \equiv \text{Tr}(\mathbf{G}f)$. On substitution of the Fourier decomposition (9.18) for \mathbf{G} and use of the identity for the exponential operator

$$e^{i[\boldsymbol{\sigma} \cdot \mathbf{P}(\mathbf{r}, \mathbf{r}') + \boldsymbol{\tau} \cdot \mathbf{Q}(\mathbf{r}, \mathbf{r}')] } = e^{i\frac{1}{2}\hbar \boldsymbol{\sigma} \cdot \boldsymbol{\tau}} e^{i\boldsymbol{\tau} \cdot \mathbf{Q}(\mathbf{r}, \mathbf{r}') } e^{i\boldsymbol{\sigma} \cdot \mathbf{P}(\mathbf{r}, \mathbf{r}') }, \quad (9.21)$$

(9.20) can be put in the form

$$\begin{aligned} \langle \mathbf{G} \rangle &= \int \cdots \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' d\boldsymbol{\sigma} d\boldsymbol{\tau} e^{i\frac{1}{2}\hbar \boldsymbol{\sigma} \cdot \boldsymbol{\tau}} e^{i\boldsymbol{\tau} \cdot \mathbf{Q}(\mathbf{r}, \mathbf{r}') } e^{i\boldsymbol{\sigma} \cdot \mathbf{P}(\mathbf{r}, \mathbf{r}') } \\ &\quad \times f(\mathbf{r}', \mathbf{r}''; t) \xi(\boldsymbol{\sigma}, \boldsymbol{\tau}) \delta(\mathbf{r} - \mathbf{r}''). \end{aligned} \quad (9.22)$$

Since there holds the identity

$$e^{i\boldsymbol{\sigma} \cdot \mathbf{P}(\mathbf{r}, \mathbf{r}') } f(\mathbf{r}', \mathbf{r}''; t) = f(\mathbf{r}' + \boldsymbol{\sigma} \hbar, \mathbf{r}''; t) \delta(\mathbf{r} - \mathbf{r}'), \quad (9.23)$$

which can be shown if (9.19) is used, there follows from (9.22)

$$\begin{aligned} \langle \mathbf{G} \rangle &= \int \cdots \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' d\boldsymbol{\sigma} d\boldsymbol{\tau} e^{i\frac{1}{2}\hbar \boldsymbol{\sigma} \cdot \boldsymbol{\tau}} e^{i\boldsymbol{\tau} \cdot \mathbf{Q}(\mathbf{r}, \mathbf{r}') } \\ &\quad \times f(\mathbf{r}' + \boldsymbol{\sigma} \hbar, \mathbf{r}''; t) \xi(\boldsymbol{\sigma}, \boldsymbol{\tau}) \delta(\mathbf{r} - \mathbf{r}') \delta(\mathbf{r} - \mathbf{r}''). \end{aligned} \quad (9.24)$$

Before the integral over \mathbf{r}' is performed, the following replacement of the operator product $\exp[i\boldsymbol{\tau} \cdot \mathbf{Q}(\mathbf{r}, \mathbf{r}')]\delta(\mathbf{r} - \mathbf{r}')$ must be made:

$$e^{i\boldsymbol{\tau} \cdot \mathbf{Q}(\mathbf{r}, \mathbf{r}') } \delta(\mathbf{r} - \mathbf{r}') \Rightarrow e^{i\boldsymbol{\tau} \cdot \mathbf{r}} \delta(\mathbf{r} - \mathbf{r}').$$

The reason for this is that the matrix element $\mathbf{Q}(\mathbf{r}, \mathbf{r}')$ on the left also contains the delta function $\delta(\mathbf{r} - \mathbf{r}')$, and since the delta function must be used in the sense of a distribution function the replacement suggested is appropriate. In fact, if it is not made, a divergent result arises¹. Eq. (9.24), on integration over \mathbf{r}' and \mathbf{r}'' , gives rise to the integral

$$\langle \mathbf{G} \rangle = \iiint d\mathbf{r} d\boldsymbol{\sigma} d\boldsymbol{\tau} e^{i\frac{1}{2}\hbar\boldsymbol{\sigma}\cdot\boldsymbol{\tau}} e^{i\boldsymbol{\tau}\cdot\mathbf{Q}} f(\mathbf{r} + \boldsymbol{\sigma}\hbar, \mathbf{r}; t) \xi(\boldsymbol{\sigma}, \boldsymbol{\tau}). \quad (9.25)$$

On substitution of the inverse Fourier transform for $\xi(\boldsymbol{\sigma}, \boldsymbol{\tau})$ from (9.18), the average $\langle \mathbf{G} \rangle$ can be written as

$$\begin{aligned} \langle \mathbf{G} \rangle = (2\pi)^{-6} & \int \dots \int d\mathbf{p} d\mathbf{q} d\mathbf{r} d\boldsymbol{\sigma} d\boldsymbol{\tau} e^{i\frac{1}{2}\hbar\boldsymbol{\sigma}\cdot\boldsymbol{\tau}} e^{i\boldsymbol{\tau}\cdot\mathbf{r}} \\ & \times f(\mathbf{r} + \boldsymbol{\sigma}\hbar, \mathbf{r}; t) g(\mathbf{p}, \mathbf{q}) e^{-i(\boldsymbol{\sigma}\cdot\mathbf{p} + \boldsymbol{\tau}\cdot\mathbf{q})}. \end{aligned} \quad (9.26)$$

Integration over $\boldsymbol{\tau}$ yields a delta function $\delta(\mathbf{r} - \mathbf{q} + \frac{1}{2}\hbar\boldsymbol{\sigma})$. By performing integration over \mathbf{r} , we obtain

$$\langle \mathbf{G} \rangle = (2\pi)^{-3} \iiint d\mathbf{p} d\mathbf{q} d\boldsymbol{\sigma} e^{-i\boldsymbol{\sigma}\cdot\mathbf{p}} g(\mathbf{p}, \mathbf{q}) f(\mathbf{q} + \frac{1}{2}\hbar\boldsymbol{\sigma}, \mathbf{q} - \frac{1}{2}\hbar\boldsymbol{\sigma}; t). \quad (9.27)$$

We now define the Wigner distribution function for f by the Fourier transform

$$f(\mathbf{p}, \mathbf{r}; t) = \pi^{-3} \int d\mathbf{y} e^{i2\mathbf{p}\cdot\mathbf{y}/\hbar} f(\mathbf{r} - \mathbf{y}, \mathbf{r} + \mathbf{y}; t). \quad (9.28)$$

With the transformation $\mathbf{y} = -\frac{1}{2}\hbar\boldsymbol{\sigma}$, the average $\langle \mathbf{G} \rangle$ in (9.27) may then be given in terms of the Wigner distribution function $f(\mathbf{p}, \mathbf{r}; t)$ and the classical observable $g(\mathbf{p}, \mathbf{q})$ as follows:

$$\langle \mathbf{G} \rangle = \text{Tr}(\mathbf{G}f) = \hbar^{-3} \iint d\mathbf{p} d\mathbf{q} g(\mathbf{p}, \mathbf{q}) f(\mathbf{p}, \mathbf{q}; t). \quad (9.29)$$

This relation is exact and shows that the quantum mechanical expectation value—average—can be computed as the average of the classical observable $g(\mathbf{p}, \mathbf{q})$, provided that the Wigner distribution function is used as the distribution function. Since the Wigner distribution function clearly is not a classical phase space distribution function, the average in (9.29) is a quantum mechanical mean value for $g(\mathbf{p}, \mathbf{q})$. It is now required to develop the governing equation for the Wigner distribution function $f(\mathbf{p}, \mathbf{r}; t)$ and compute the integral in the phase space instead of the quantum mechanical trace for the average.

¹For the subtleties and treatments of multiple products of Dirac delta functions, see W. Güttinger, *Prog. Theor. Phys.* **13**, 612 (1955).

9.3 Kinetic Equation for f_a

Given the kinetic equation (9.7) for the density matrix, it is possible to derive the kinetic equation for the Wigner distribution function. The procedure of deriving the governing equation for an N -particle Wigner distribution function from the von Neumann equation for the density matrix is well documented in the literature [12,15]. On application of the same method to the kinetic equation (9.7) we obtain the kinetic equation for the Wigner distribution function $f_a(\mathbf{r}, \mathbf{v}_a; t)$

$$(\partial_t + \mathbf{v}_a \cdot \nabla) f_a(\mathbf{r}, \mathbf{v}_a; t) - \frac{2m_a}{\hbar} \sin\left(\frac{1}{2}\hbar \nabla \cdot \nabla_{\mathbf{p}_a}\right) \mathfrak{V}_a f_a(\mathbf{r}, \mathbf{v}_a; t) = R[f_a], \quad (9.30)$$

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

$$R[f_a] = \pi^{-3} \int d\mathbf{y} \exp\left(i \frac{2}{\hbar} \mathbf{p} \cdot \mathbf{y}\right) \mathbf{R}[f_a](\mathbf{r} - \mathbf{y}, \mathbf{r} + \mathbf{y}), \quad (9.31)$$

$\nabla_{\mathbf{p}_a} = \partial/\partial \mathbf{p}_a$, and \mathfrak{V}_a is the external potential per mass of species a at position \mathbf{r} , and the gradient operators ∇ and $\nabla_{\mathbf{p}_a}$ operate only on \mathfrak{V}_a and $f_a(\mathbf{r}, \mathbf{v}_a; t)$, respectively. As in the classical theory, the subscript a is used dually to distinguish the species and at the same time to denote a particle of that species in order to keep the notation as simple as possible. In the case of dilute gases this notational device does not cause confusion. If the external force is homogeneous in space, as it is in many cases of interest in kinetic theory, then the potential energy term in (9.30) reduces to the usual classical form seen in the Boltzmann equation, and we obtain the kinetic equation in the form

$$(\partial_t + \mathbf{v}_a \cdot \nabla + \mathbf{F}_a \cdot \nabla_{\mathbf{v}_a}) f_a(\mathbf{r}, \mathbf{v}_a; t) = R[f_a], \quad (9.32)$$

where $\mathbf{F}_a = -\nabla \mathfrak{V}_a$. The collision integral $R[f_a]$ may be decomposed into species components

$$R[f_a] = \sum_{b=1}^r R[f_a f_b]. \quad (9.33)$$

To be more concrete, we will assume that the Wigner representation of $\mathbf{R}[f_a]$ is given by the BNUU collision integral [2–6]:

$$\begin{aligned} R[f_a f_b] &= G_b \frac{m_a^3}{\hbar^3} \int d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin\theta W^{(\epsilon)}(\mathbf{v}_a \mathbf{v}_b | \mathbf{v}_a^* \mathbf{v}_b^*) \\ &\times \{ f_a^*(\mathbf{v}_a, \mathbf{r}, t) f_b^*(\mathbf{v}_b, \mathbf{r}, t) [1 + \epsilon_a f_a(\mathbf{v}_a, \mathbf{r}, t)] [1 + \epsilon_b f_b(\mathbf{v}_b, \mathbf{r}, t)] \\ &- f_a(\mathbf{v}_a, \mathbf{r}, t) f_b(\mathbf{v}_b, \mathbf{r}, t) [1 + \epsilon_a f_a^*(\mathbf{v}_a, \mathbf{r}, t)] [1 + \epsilon_b f_b^*(\mathbf{v}_b, \mathbf{r}, t)] \} . \end{aligned} \quad (9.34)$$

Here $\epsilon_a = +1$ for bosons; -1 for fermions; and 0 for Boltzmann particles. The asterisk denotes the post-collision value and $W^{(\epsilon)}(\mathbf{v}_a \mathbf{v}_b | \mathbf{v}_a^* \mathbf{v}_b^*)$ is the transition probability given in terms of the differential cross section $\sigma(ab; a^*b^*|\theta, \varphi)$ for process $(\mathbf{v}_a, \mathbf{v}_b) \rightarrow (\mathbf{v}_a^*, \mathbf{v}_b^*)$:

$$W^{(\epsilon)}(\mathbf{v}_a \mathbf{v}_b | \mathbf{v}_a^* \mathbf{v}_b^*) = g_{ab} \sigma(ab; a'b'|\theta, \varphi), \quad (9.35)$$

$$\sigma(ab; a'b'|\theta, \varphi) = |\mathbf{T}(\mathbf{v}_a \mathbf{v}_b | \mathbf{v}_a^* \mathbf{v}_b^* : \theta, \varphi) + \epsilon_a \mathbf{T}(\mathbf{v}_a \mathbf{v}_b | \mathbf{v}_a^* \mathbf{v}_b^* : \pi - \theta, \varphi + \pi)|^2 \quad (9.36)$$

with $\mathbf{T}(\mathbf{v}_a \mathbf{v}_b | \mathbf{v}_a^* \mathbf{v}_b^* : \theta, \varphi)$ denoting the scattering operator describing the collision of particles a and b . In (9.35) g_{ab} is the relative speed of a and b . The scattering operator \mathbf{T} may be calculated quantum mechanically. It is assumed to be known in this work. The collision cross section is symmetrized in accordance with the statistics of the particles involved, namely, the Fermi–Dirac or Bose–Einstein statistics. The transition probabilities obey symmetry relations:

$$W_{ab}^{(\epsilon)} = W_{ba}^{(\epsilon)}$$

and

$$W^{(\epsilon)}(\mathbf{v}_a \mathbf{v}_b | \mathbf{v}_a^* \mathbf{v}_b^*) = W^{(\epsilon)}(\mathbf{v}_a^* \mathbf{v}_b^* | \mathbf{v}_a \mathbf{v}_b).$$

The first relation is for the symmetry with respect to the interchange of particle species and the second expresses the microscopic reversibility of the collision events under the reversal of the processes $(\mathbf{v}, \mathbf{v}_b) \rightarrow (\mathbf{v}_a^*, \mathbf{v}_b^*)$ to $(\mathbf{v}_a^*, \mathbf{v}_b^*) \rightarrow (\mathbf{v}_a, \mathbf{v}_b)$ and vice versa. These two symmetry properties of $W_{ab}^{(\epsilon)}$ are sufficient for a thermodynamically consistent theory of irreversible processes in dilute quantum systems since they are required for fulfilling Condition 2 mentioned earlier. More detailed forms will be required for $W_{ab}^{(\epsilon)}$ for elucidation of transport processes in comparison with experiment, but our main interest in this work is not in this topic, which is beyond the scope of this work and therefore is deferred to a future work on transport properties. Owing to the symmetry properties of the transition probability the collision integral $R[f_a f_b]$ is symmetric with respect to interchange of species subscripts a and b :

$$R[f_a f_b] = R[f_b f_a] \quad (9.37)$$

and breaks the time reversal symmetry by changing its sign when the collision process is reversed. These properties are necessary for the conditions for the collision term to satisfy:

Condition 1 *The collision term is such that the conservation laws of mass, momentum, and energy follow from the quantum kinetic equation (9.30) or (9.32).*

Condition 2 *The H theorem is satisfied by the quantum kinetic equation postulated.*

The kinetic theory foundations of (9.32), which with $R[f_a]$ given by (9.34) is the BNUU equation, have been studied by various authors [4–6]. The equation has also been applied to some aspects of carrier mobilities [16–18] and to kinetic processes related to radiation interacting with matter [19,20]. The model has a wide ranging applicability to phenomena of recent interests, but the theory of transport processes based thereon has not been fully developed. Kinetic equation (9.30) is a slight generalization of the BNUU equation. Eq. (9.30) or (9.32) is then seen as the kinetic equation for the Wigner distribution function, the latter being a special case of the former. Therefore the term semiclassical often attached to the BNUU kinetic equation does not appear to be an accurate description of the status of the kinetic equation from the viewpoint of the origin of the kinetic equation (9.32). The kinetic equation (9.30) will find applications [21] in the fields of quantum transport processes in systems far removed from equilibrium in the later part of this chapter.

It is helpful, for insight into the kinetic theory of quantum fluids in general, to observe that the factors $(1 + \epsilon_a f_a)(1 + \epsilon_b f_b)$ and $(1 + \epsilon_a f_a^*)(1 + \epsilon_b f_b^*)$ appearing in (9.34) may be regarded as approximate forms for the pair correlation functions for the quantum particles in the post-collision and the pre-collision state, respectively. Such particle correlations arise at the level of momentum distribution from the quantum effect, namely, the quantum attraction in the case of bosons and the quantum repulsion (Pauli exclusion principle) in the case of fermions, which are inherent to quantum particles. Such correlations are absent in the case of classical Boltzmann particles for which the doublet distribution function is simply a product of two singlet distribution functions in the low density limit. In this sense a gas of quantum particles is not ideal in the manner a gas of Boltzmann particles is. Note in this connection that the equations of state for quantum gases are not in the form of the ideal gas equation of state holding for the Boltzmann gas. In fact, the quantum gases have virial coefficients [22] owing to the correlations arising from the quantum mechanical effects.

In the case of (9.32), which arises if the external force is uniform in space, the quantum feature can appear only in the collision term. Since the collision term is related to the transport properties of the system and the energy dissipation, quantum effects will appear only in the material functions (*i.e.*, transport coefficients such as viscosity, thermal conductivity, *etc.*) and in the energy dissipation mechanism. Consequently, the mathematical structure of the theory of irreversible processes is expected to be little affected by the quantum aspect of the system. If the external force is inhomogeneous in space, then the quantum effect also appears in the streaming term in the kinetic equation. This quantum effect term gives rise to a component of the thermodynamic forces that drive heat and mass transports as will

be seen in a later section.

To simplify the notation we will abbreviate integration over velocity by angular brackets:

$$\langle A(\mathbf{v}_a) f_a(\mathbf{v}_a, \mathbf{r}, t) \rangle \equiv G_a \frac{m_a^3}{h^3} \int d\mathbf{v}_a A(\mathbf{v}_a) f_a(\mathbf{v}_a, \mathbf{r}, t), \quad (9.38)$$

where G_a is the statistical weight of the species a . The average value of an observable $A(\mathbf{v}_a)$ is then obtained by the formula

$$\bar{A}(\mathbf{r}, t) = \langle A(\mathbf{v}_a) f_a(\mathbf{v}_a, \mathbf{r}, t) \rangle. \quad (9.39)$$

This is in fact a shortcut in the way of calculating the average. More precisely, it should read as the phase space average

$$\bar{A}(\mathbf{r}, t) = \int_V d\mathbf{r}_a \langle A(\mathbf{v}_a) \delta(\mathbf{r}_a - \mathbf{r}) f_a(\mathbf{v}_a, \mathbf{r}_a, t) \rangle, \quad (9.40)$$

which readily reduces to the formula in (9.39). For example, the mass density $\rho_a(\mathbf{r}, t)$ and the total mass density $\rho(\mathbf{r}, t)$ are respectively given by

$$\rho_a(\mathbf{r}, t) = \langle m_a f_a(\mathbf{v}_a, \mathbf{r}_a, t) \rangle \quad (9.41)$$

and

$$\rho(\mathbf{r}, t) = \sum_{a=1}^r \rho_a(\mathbf{r}, t). \quad (9.42)$$

The barycentric velocity (or fluid velocity) \mathbf{u} is defined by

$$\rho \mathbf{u}(\mathbf{r}, t) = \sum_{a=1}^r \rho_a(\mathbf{r}, t) \mathbf{u}_a(\mathbf{r}, t) = \sum_{a=1}^r \langle m_a \mathbf{v}_a f_a(\mathbf{v}_a, \mathbf{r}_a, t) \rangle. \quad (9.43)$$

With the definition of peculiar velocity $\mathbf{C}_a = \mathbf{v}_a - \mathbf{u}$, the internal energy density \mathcal{E} is then defined by

$$\rho \mathcal{E}(\mathbf{r}, t) = \sum_{a=1}^r \left\langle \frac{1}{2} m_a C_a^2 f_a(\mathbf{v}_a, \mathbf{r}_a, t) \right\rangle. \quad (9.44)$$

The observables ρ , $\rho \mathbf{u}$, and \mathcal{E} are conserved variables as in the classical theory since they obey the conservation laws of mass, momentum, and energy. Condition 1 states that these conserved variables have vanishing values when averaged with the collision term $R[f_a]$ as the statistical weight. Namely, if ϕ_a is one of the conserved variables then

$$\sum_{a=1}^r \langle \phi_a R[f_a] \rangle = 0 \quad (9.45)$$

since

$$\sum_{a=1}^r \langle \phi_a R[f_a] \rangle = \frac{1}{4} \sum_{a=1}^r \sum_{b=1}^r \langle (\phi_a + \phi_b - \phi_a^* - \phi_b^*) R[f_a f_b] \rangle = 0 \quad (9.46)$$

by the condition $\phi_a + \phi_b - \phi_a^* - \phi_b^* = 0$ for collision invariants

$$\phi_a = m_a, m_a \mathbf{v}_a, \frac{1}{2} m_a C_a^2.$$

The asterisk denotes the post-collision value. If there is an external potential energy \mathfrak{V}_a which does not change over the distance of collision between two particles so that it does not affect two-particle collisions, then the Hamiltonian $H_a = m_a (\frac{1}{2} C_a^2 + \mathfrak{V}_a)$ is also a collision invariant. This implies that if the external force is inhomogeneous its spatial scale of variation is macroscopic. It will be assumed that this is the case in the present theory.

Condition 2 means that there holds the inequality

$$\sum_{a=1}^r \langle \ln(\epsilon_a + f_a^{-1})] R[f_a] \rangle \geq 0, \quad (9.47)$$

the equality holding only at equilibrium. The origin of this particular form of inequality will be presently clarified further when the Boltzmann entropy is defined for the system. The equilibrium solution f_a^{eq} to the kinetic equation is defined by

$$\sum_{a=1}^r \langle \ln(\epsilon_a + f_a^{\text{eq}-1})] R[f_a^{\text{eq}}] \rangle = 0. \quad (9.48)$$

We will return to this equation and obtain the explicit form for f_a^{eq} .

We employ the kinetic equation (9.30) to generalize the nonequilibrium ensemble method developed for dilute classical gases in Chapter 7. The kinetic equation is irreversible by virtue of Condition 2, and so is the BNUU kinetic equation which breaks the time reversal symmetry, as does the Boltzmann equation. That is, if the direction of time and velocity is reversed they do not remain invariant, indicating that they will be capable of describing macroscopic phenomena occurring irreversibly along a unidirectional time axis. This historically controversial property of the Boltzmann, BNUU, and postulated kinetic equations is exactly what we need to describe irreversible phenomena. This property is closely associated with the H theorem phrased in terms of the statistical mechanical expression for the Boltzmann entropy

$$S(t) = \int_V d\mathbf{r} \rho S(\mathbf{r}, t). \quad (9.49)$$

Here the Boltzmann entropy density $\mathcal{S}(\mathbf{r}, t)$ is defined by

$$\begin{aligned}\rho\mathcal{S}(\mathbf{r}, t) &= -k_B \sum_{a=1}^r \langle [f_a \ln f_a - \epsilon_a(1 + \epsilon_a f_a) \ln(1 + \epsilon_a f_a)] \rangle \\ &= k_B \sum_{a=1}^r \langle [f_a \ln(\epsilon_a + f_a^{-1}) + \epsilon_a \ln(1 + \epsilon_a f_a)] \rangle.\end{aligned}\quad (9.50)$$

It should be emphasized that this particular form for $\rho\mathcal{S}$, necessary for proving the H theorem, is suggested by the collision integral (9.34) taken for $R[f_a]$.

With the Boltzmann entropy defined as in (9.50), on differentiation with time and use of the kinetic equation (9.30) the H theorem can be easily proved. Namely, there holds the inequality

$$\frac{dS}{dt} = k_B \sum_{a=1}^r \int_V d\mathbf{r} \langle \ln(\epsilon_a + f_a^{-1}) R[f_a] \rangle \geq 0,\quad (9.51)$$

with the equality applying only to equilibrium reached in long time. This form of the H theorem is the motivation for Condition 2 as expressed by (9.47). The local form of this H theorem may be expressed in the same form as the Boltzmann entropy balance equation for the classical gases

$$\rho d_t \mathcal{S} = -\nabla \cdot \mathbf{J}_s + \sigma_{\text{ent}}\quad (9.52)$$

with the inequality

$$\sigma_{\text{ent}} \geq 0,\quad (9.53)$$

provided that the Boltzmann entropy flux \mathbf{J}_s and the Boltzmann entropy production σ_{ent} are defined by the statistical formulas

$$\begin{aligned}\mathbf{J}_s &= -k_B \sum_{a=1}^r \langle \mathbf{C}_a [f_a \ln f_a - \epsilon_a(1 + \epsilon_a f_a) \ln(1 + \epsilon_a f_a)] \rangle \\ &= k_B \sum_{a=1}^r \langle \mathbf{C}_a [f_a \ln(\epsilon_a + f_a^{-1}) + \epsilon_a \ln(1 + \epsilon_a f_a)] \rangle,\end{aligned}\quad (9.54)$$

$$\sigma_{\text{ent}} = k_B \sum_{a=1}^r \sum_{b=1}^r \langle \ln(\epsilon_a + f_a^{-1}) R[f_a f_b] \rangle \geq 0.\quad (9.55)$$

The equality in (9.53) holds valid at equilibrium only. Therefore equilibrium is the state of the system where the Boltzmann entropy production vanishes. Since the Boltzmann entropy production is seen, as will be shown, as a measure of energy dissipation from a useful form to one less useful, if the system is at equilibrium or the process is reversible, then one form of energy is entirely converted to another without dissipation. The inequality

(9.53) is commonly considered to be a local representation of the second law of thermodynamics. In view of the discussion presented in connection with the Boltzmann entropy in Chapter 7, this interpretation is questionable and in fact misleading. With the nonequilibrium ensemble method we answer this question in the negative also for the quantum system under consideration.

To prepare for the investigation of this question and to implement the nonequilibrium ensemble method, we introduce a distribution function f_a^c which is representative of the thermodynamic behavior of the system and define therewith the statistical calortropy density $\hat{\Psi}$ and the relative Boltzmann entropy $S_r[f|f^c]$:

$$\begin{aligned}\rho\hat{\Psi} &= -k_B \sum_{a=1}^r \langle [f_a \ln f_a^c - \epsilon_a (1 + \epsilon_a f_a) \ln (1 + \epsilon_a f_a^c)] \rangle \\ &= k_B \sum_{a=1}^r \langle [f_a \ln (\epsilon_a + f_a^{c-1}) + \epsilon_a \ln (1 + \epsilon_a f_a^c)] \rangle, \quad (9.56) \\ S_r[f|f^c] &= k_B \sum_{a=1}^r \left\langle \left\{ f_a \ln \left(\frac{f_a}{f_a^c} \right) - \epsilon_a (1 + \epsilon_a f_a) \ln \left(\frac{1 + \epsilon_a f_a}{1 + \epsilon_a f_a^c} \right) \right\} \right\rangle \\ &= k_B \sum_{a=1}^r \left\langle \left\{ f_a \ln \left(\frac{(1 + \epsilon_a f_a^c) f_a}{(1 + \epsilon_a f_a) f_a^c} \right) + \epsilon_a \ln \left(\frac{1 + \epsilon_a f_a^c}{1 + \epsilon_a f_a} \right) \right\} \right\rangle. \quad (9.57)\end{aligned}$$

The thermodynamic branch f_a^c of the distribution function f_a , which is called the nonequilibrium canonical form, will be explicitly specified later when we are better prepared for it. Regardless of the explicit form that f_a^c may assume, definitions (9.56) and (9.57) imply that

$$S = \hat{\Psi} - S_r[f|f^c], \quad (9.58)$$

$$d_t S = d_t \hat{\Psi} - d_t S_r[f|f^c]. \quad (9.59)$$

The explicit form for the calortropy in thermodynamic space basically reflects our understanding of macroscopic phenomena in the system, the description of which often involves an enormous contraction of information on the system at the molecular level. Since the Boltzmann entropy is a measure of the molecular information of the system, the decomposition of S into $\hat{\Psi}$ and the relative Boltzmann entropy $S_r[f|f^c]$ reflects the necessity to complement for the contracted information contained in $\hat{\Psi}$ when one opts out to describe the system thermodynamically by means of $\hat{\Psi}$.

The balance equations for $\hat{\Psi}$ and $S_r[f|f^c]$ are easily derived from their statistical definitions and the quantum kinetic equation (9.30):

$$\rho d_t \hat{\Psi} = -\nabla \cdot \mathbf{J}_c + \sigma_c + \Upsilon_c, \quad (9.60)$$

$$\rho dt S_r[f|f^c] = -\nabla \cdot \mathbf{J}_r[f|f^c] + \sigma_r[f|f^c] + \Upsilon_c, \quad (9.61)$$

where the statistical definitions of the various quantities involved are

$$\mathbf{J}_c = k_B \sum_{a=1}^r \left\langle \mathbf{C}_a [f_a \ln (\epsilon_a + f_a^{c-1}) + \epsilon_a \ln (1 + \epsilon_a f_a^c)] \right\rangle, \quad (9.62)$$

$$\sigma_c = k_B \sum_{a=1}^r \left\langle \ln (\epsilon_a + f_a^{c-1}) R[f_a] \right\rangle, \quad (9.63)$$

$$\begin{aligned} \mathbf{J}_r[f|f^c] &= -k_B \sum_{a=1}^r \left\langle \mathbf{C}_a f_a \ln \left(\frac{(1 + \epsilon_a f_a) f_a^c}{(1 + \epsilon_a f_a^c) f_a} \right) \right\rangle \\ &\quad - k_B \sum_{a=1}^r \epsilon_a \left\langle \mathbf{C}_a \ln \left(\frac{1 + \epsilon_a f_a}{1 + \epsilon_a f_a^c} \right) \right\rangle, \end{aligned} \quad (9.64)$$

$$\sigma_r[f|f^c] = -k_B \sum_{a=1}^r \left\langle \ln \left(\frac{(1 + \epsilon_a f_a) f_a^c}{(1 + \epsilon_a f_a^c) f_a} \right) R[f_a] \right\rangle, \quad (9.65)$$

$$\begin{aligned} \Upsilon_c &= k_B \sum_{a=1}^r \left\langle f_a \mathcal{D}_w \ln (\epsilon_a + f_a^{c-1}) \right\rangle \\ &\quad + k_B \sum_{a=1}^r \epsilon_a \langle \mathcal{D}_w \ln (1 + \epsilon_a f_a^c) \rangle, \end{aligned} \quad (9.66)$$

with the definition of the operator \mathcal{D}_w

$$\mathcal{D}_w = \partial_t + \mathbf{v}_a \cdot \nabla - \frac{2m_a}{\hbar} \sin \left(\frac{1}{2} \hbar \nabla \cdot \mathbf{v}_{pa} \right) \mathfrak{V}_a. \quad (9.67)$$

If f_a^c were equal to f_a in the strong sense of convergence, as discussed for the classical theory in Sec. 7.1, then Υ_c would vanish, but, as mentioned earlier, f_a^c is simply a thermodynamic branch of f_a which represents the latter under the functional hypothesis and thus is not the solution of the kinetic equation (9.30) that satisfies the initial and boundary conditions in the phase space, but rather a ‘solution’ that evolves through the macroscopic variables satisfying their own initial and boundary conditions. As in the classical theory, it is important to keep this subtle distinction in mind. The statistical definitions of \mathbf{J}_c , σ_c , and so on in (9.62)–(9.65) mean that the Boltzmann entropy flux and the Boltzmann entropy production can be decomposed into two components corresponding to the calortropy and the relative Boltzmann entropy, respectively:

$$\mathbf{J}_s = \mathbf{J}_c - \mathbf{J}_r[f|f^c], \quad (9.68)$$

$$\sigma_{\text{ent}} = \sigma_c - \sigma_r[f|f^c] \geq 0 \quad (9.69)$$

in a way much similar to the decomposition of the Boltzmann entropy density in (9.58). The balance equations for calortropy $\hat{\Psi}$ and relative Boltzmann entropy $S_r[f|f^c]$ will be the basic equations on which the present nonequilibrium ensemble method is founded.

9.4 Evolution Equations for Observables

The description of a macroscopic system in kinetic theory is made in terms of the positions and momenta of all particles in the phase space. Since the kinetic equation taken gives a singlet distribution function as in the classical Boltzmann kinetic theory, the kinetic theory description of a many-particle system just mentioned is achieved by calculating the total distribution function as the product of the singlet distribution functions obeying the kinetic equations:

$$f^{(N)}(\mathbf{x}^{(N)}; t) = \prod_{a=1}^r \prod_{i=1}^{N_a} f_a(\mathbf{r}_i, \mathbf{v}_i, t),$$

since it is assumed that the particles are not statistically correlated at the level of density considered. This N particle distribution function contains the necessary information about the system with which to compute all of its mean properties. However, since the number of particles in the system is of the order of 10^{23} and hence the number of degrees of freedom is correspondingly large, the information content carried by the distribution function for the system in the phase space is enormous. In contrast, in thermodynamics, only a small number of macroscopic observables are required for the description of macroscopic processes in bulk matter. Therefore when an attempt is made to construct a theory of thermodynamic processes from the statistical mechanical viewpoint there is an enormous contraction in the information content of the distribution function. This required shedding of the unnecessary part of the information is also a focal point of the present quantum kinetic theory of irreversible thermodynamics, since it must be done in such a way that the theory acquired thereby must not only be as rigorous as possible, but also be consistent with the laws of thermodynamics. As in the classical theory a theory will be said to be thermodynamically consistent when its mathematical formalism is consistent with the laws of thermodynamics. The nonequilibrium ensemble method used here is again designed to meet these requirements.

As a first step to achieving such a theory we need the evolution equations for various macroscopic observables, conserved or nonconserved. These evolution equations can also be derived from (9.7) instead of (9.30). See Appendix B. It was noted earlier that there are collisional invariants associ-

ated with the quantum kinetic equation (9.30). They in fact give rise to the conservation laws in the forms of balance equation for mass, momentum, and energy. The derivations of the balance equations proceed in the same manner as for the classical theory by using the quantum kinetic equation and the statistical mechanical formulas (9.41)–(9.44) for conserved variables. Before listing them here it is convenient to define some additional macroscopic variables:

concentration:

$$c_a = \frac{\rho_a}{\rho}, \quad (9.70)$$

diffusion flux:

$$\mathbf{J}_a = \langle m_a \mathbf{C}_a f_a \rangle, \quad (9.71)$$

stress tensor:

$$\mathbf{P} = \sum_{a=1}^r \mathbf{P}_a = \sum_{a=1}^r \langle m_a \mathbf{C}_a \mathbf{C}_a f_a \rangle, \quad (9.72)$$

heat flux:

$$\mathbf{Q} = \sum_{a=1}^r \mathbf{Q}_a = \sum_{a=1}^r \left\langle \frac{1}{2} m_a C_a^2 \mathbf{C}_a f_a \right\rangle, \quad (9.73)$$

total force density:

$$\mathbf{F} = \sum_{a=1}^r c_a \mathbf{F}_a. \quad (9.74)$$

Notice that these definitions are in the same forms as their classical analogs, thanks to the fact that $f_a(\mathbf{r}, \mathbf{v}_a; t)$ is a Wigner distribution function, but they are quantum mechanical, inasmuch as the Wigner distribution function is quantum mechanical. It is useful to compare these definitions with the quantum operator listed in Appendix B. The conservation laws then take the forms:

mass:

$$\partial_t \rho = - \nabla \cdot \rho \mathbf{u}, \quad (9.75)$$

mass fraction:

$$\rho d_t c_a = - \nabla \cdot \mathbf{J}_a, \quad (9.76)$$

momentum:

$$\rho d_t \mathbf{u} = - \nabla \cdot \mathbf{P} + \rho \mathbf{F}, \quad (9.77)$$

energy:

$$\rho d_t \mathcal{E} = - \nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_a^r \mathbf{F}_a \cdot \mathbf{J}_a. \quad (9.78)$$

These conservation laws also are exactly in the same forms as the classical equations derived from the Boltzmann equation for classical dilute gases. A note of clarification is in order here in connection with the derivations

of these equations, in particular, with regard to the external force term in the quantum kinetic equation (9.30). Let us consider the following integral of an observable ϕ_a associated with the external force term:

$$\langle \phi_a \sin\left(\frac{1}{2}\hbar\boldsymbol{\nabla} \cdot \boldsymbol{\nabla}_{\mathbf{p}a}\right) \mathfrak{V}_a f_a \rangle.$$

This can be calculated by expanding the sine function in an operator series and by repeatedly performing integration by parts for the terms in the said series:

$$\begin{aligned} I_a &= \frac{2m_a}{\hbar} \langle \phi_a \sin\left(\frac{1}{2}\hbar\boldsymbol{\nabla} \cdot \boldsymbol{\nabla}_{\mathbf{p}a}\right) \mathfrak{V}_a f_a \rangle \\ &= -\frac{2m_a}{\hbar} \langle f_a \sin\left(\frac{1}{2}\hbar\boldsymbol{\nabla} \cdot \boldsymbol{\nabla}_{\mathbf{p}a}\right) \mathfrak{V}_a \phi_a \rangle. \end{aligned} \quad (9.79)$$

If $\phi_a = m_a$, then $I_a = 0$; if $\phi_a = m_a \mathbf{v}_a$ or $m_a \mathbf{C}_a$, then $I_a = \rho_a \mathbf{F}_a$; if $\phi_a = \frac{1}{2}m_a C_a^2$, then $I_a = \mathbf{F}_a \cdot \mathbf{J}_a$ and so on. These results have been used for the balance equations presented earlier.

In addition to these equations the evolution equations for nonconserved variables can be derived from their statistical definitions and the quantum kinetic equation (9.30). We will compactly denote them by the form

$$\rho d_t \hat{\Phi}_{ka} = -\boldsymbol{\nabla} \cdot \boldsymbol{\psi}_{ka} + \mathcal{Z}_{ka} + \Lambda_{ka}, \quad (9.80)$$

where

$$\Phi_{ka} = \rho \hat{\Phi}_{ka} = \left\langle h_a^{(k)} f_a \right\rangle \quad (k \geq 1), \quad (9.81)$$

with $h_a^{(k)}$ defined by

$$\begin{aligned} h_a^{(1)} &= m_a \mathbf{C}_a \mathbf{C}_a - \frac{1}{3} m_a C_a^2 \delta \equiv m_a [\mathbf{C}_a \mathbf{C}_a]^{(2)}, \\ h_a^{(2)} &= \frac{1}{3} m_a C_a^2 - \frac{p_a}{n_a}, \\ h_a^{(3)} &= \frac{1}{2} m_a C_a^2 \mathbf{C}_a - \hat{h}_a m_a \mathbf{C}_a, \\ h_a^{(4)} &= m_a \mathbf{C}_a, \quad etc.. \end{aligned} \quad (9.82)$$

Here δ is the unit Cartesian tensor of rank 2, p_a is the pressure, which will be given a statistical definition later at a more appropriate stage, n_a is the number density, and \hat{h}_a is the enthalpy per unit mass of species a . These definitions are the same as for the classical systems considered in the previous chapters. Other symbols in (9.80) are

$$\mathcal{Z}_{ka} = \left\langle f_a \mathcal{D}_w h_a^{(k)} \right\rangle, \quad (9.83)$$

$$\Lambda_{ka} = \left\langle h_a^{(k)} R[f_a] \right\rangle = \sum_{b=1}^r \left\langle h_a^{(k)} R[f_a f_b] \right\rangle, \quad (9.84)$$

$$\psi_{ka} = \left\langle \mathbf{C}_a h_a^{(k)} f_a \right\rangle. \quad (9.85)$$

As in the classical theory, the physical meaning of ψ_{ka} is the flux of Φ_{ka} which is evident from its statistical formula in (9.85). The Z_{ka} is the kinematic term and Λ_{ka} the dissipation term, since the former is related to the streaming (kinematic) term of the quantum kinetic equation and the latter is related to its collision term which is intimately associated with the energy dissipation in the system. The dissipation term does not vanish since $h_a^{(k)}$ is not a conserved variable. The explicit forms for Z_{ka} for $k \leq 4$ will be presented later when transport processes are considered.

It is clear that the following relationships hold for the nonconserved variables as in the case of classical gases:

$$\begin{aligned} \Phi_{1a} &= [\mathbf{P}_a]^{(2)} = \frac{1}{2}(\mathbf{P}_a + \mathbf{P}_a^t) - \frac{1}{3}\delta \text{Tr} \mathbf{P}_a \equiv \Pi_a, \\ \Phi_{2a} &= \frac{1}{3}\text{Tr} \mathbf{P}_a - p_a \equiv \Delta_a, \\ \Phi_{3a} &= \mathbf{Q}_a - \hat{h}_a \mathbf{J}_a \equiv \mathbf{Q}'_a, \\ \Phi_{4a} &= \mathbf{J}_a, \quad etc. \end{aligned} \quad (9.86)$$

For ease of comparison with the classical theory the nonconserved variables in the set $\{\Phi_{ka} : k \geq 1\}$ are ordered in the same manner as in the classical counterpart. As do the conservation laws (9.75)–(9.78) presented earlier, the flux evolution equations (9.80) have formally the mathematical forms similar to their classical counterparts, except for the quantum effect implicitly contained in Λ_{ka} and the quantum correction present in the kinematic term Z_{ka} which consists of third or higher order derivatives of the external potential. As a matter of fact, the kinematic terms for Z_{1a} , Z_{2a} , and Z_{4a} are the same as the classical counterparts, but Z_{3a} contains a quantum correction term of the order of \hbar^2 . This, however, does not mean that the material parameters appearing in the evolution equations for Φ_{ka} are the same for both quantum and classical fluids; they are different by the quantum effects, which are contained in the collision term as will be discussed later. The evolution equations presented form an open hierarchy of differential equations for observables and in practice must be closed by means of a suitable closure relation. This aspect is also the same as in the classical theory. When experiments are performed on macroscopic systems, only a few of the variables are measured. Thus the experimental unavailability of information about them usually compels us to truncate the set one way or

another. For the moment we do not worry about the closure and assume that the set is complete. For the purpose of constructing a formal theory of irreversible processes we follow the same strategy as for the classical theory in Chapter 7. The explicit forms for the kinematic and dissipation terms therefore are not necessary for the formal theory that will be discussed. We first examine the equilibrium solution of the quantum kinetic equation and build thereon the nonequilibrium distribution function.

9.5 Equilibrium Distribution Function

The equilibrium solution for the quantum kinetic equation can be uniquely obtained by means of the H theorem. The H theorem requires the equilibrium distribution functions f_a^{eq} to satisfy the equation

$$\sum_{a=1}^r \langle \ln(\epsilon_a + f_a^{\text{eq}-1}) R[f_a^{\text{eq}} f_b^{\text{eq}}] \rangle = 0. \quad (9.87)$$

This equation suggests that since $\ln(\epsilon_a + f_a^{\text{eq}-1})$ must be collision invariant and there are only five basic collision invariants (mass, momentum and energy) it must be a linear combination of them. In fact, it is sufficient to have the following form for it:

$$\ln(\epsilon_a + f_a^{\text{eq}-1}) = \beta_e (H_a - \mu_a^e), \quad (9.88)$$

where β_e is a parameter whose physical meaning is not fixed as yet and μ_a^e is the normalization factor of the distribution function. When the equilibrium Boltzmann entropy calculated with f_a^{eq} is made to correspond to the Clausius entropy, the physical meanings of these parameters can be fixed and the distribution function can be given a thermodynamical basis. The normalization factor μ_a^e will turn out to be the chemical potential of species a . Eq. (9.88) can be rearranged to yield the equilibrium distribution function:

$$f_a^{\text{eq}} = [\exp \beta_e (H_a - \mu_a^e) - \epsilon_a]^{-1}. \quad (9.89)$$

This well known distribution function is a unique equilibrium solution of the quantum kinetic equation. Here the term equilibrium is used to mean that $\sigma_{\text{ent}} = 0$ as in (9.87). It does not as yet have the same meaning as the equilibrium used in thermodynamics, although it will turn out to mean just that when the statistical theory has been brought into correspondence with thermodynamics, as will be done shortly; for now it means a solution of the kinetic equation which is independent of space and time. If $\epsilon_a = 0$, f_a^{eq} becomes the equilibrium distribution function for the Boltzmann gas.

On use of this equilibrium solution in the statistical formula for the Boltzmann entropy density to calculate $d_t S_e$ and comparison of the resulting differential form with the equilibrium Gibbs relation for thermodynamic

(Clausius) entropy density S_e as prescribed by the Gibbs ensemble method [23–25] and as was done in Chapter 7, the parameter β_e is identified with the inverse of the absolute temperature times the Boltzmann constant:

$$\beta_e = \frac{1}{k_B T_e}, \quad (9.90)$$

where T_e denotes the absolute temperature. Thus with the definition of equilibrium pressure by the statistical formula [22]

$$p_e = \beta_e^{-1} \sum_{a=1}^r \langle \epsilon_a \ln(1 + \epsilon_a f_a^{\text{eq}}) \rangle, \quad (9.91)$$

we obtain, by using the equilibrium solution f_a^{eq} , a statistical mechanics-based Gibbs relation

$$dS_e = T_e^{-1} \left[d\mathcal{E}_e + p_e dv - \sum_{a=1}^r \hat{\mu}_a^e dc_a \right], \quad (9.92)$$

where $\hat{\mu}_a^e = \mu_a^e/m_a$. The theory up to this point in this section constitutes, in essence, the Gibbs ensemble method applied to the equilibrium solution of the kinetic equation taken. It must be emphasized that only in the case of equilibrium does the Boltzmann entropy coincide with the Clausius entropy if the identification in (9.90) is made between β_e and T_e and fluctuations in the intensive variables are absent. The inverse of the temperature T_e is known as the integrating factor for the differential form

$$\varpi_e \equiv d\mathcal{E}_e + p_e dv - \sum_{a=1}^r \hat{\mu}_a^e dc_a$$

in equilibrium thermodynamics. An equivalent integrability condition [26–29] of the differential form (9.92) is

$$\sum_{a=1}^r c_a d\bar{\mu}_a^e = \mathcal{E}_e d\left(\frac{1}{T_e}\right) + v d\left(\frac{p_e}{T_e}\right), \quad (9.93)$$

which is the equilibrium Gibbs–Duhem relation. Comparison of the statistical mechanical equations (9.92) and (9.93) with the equilibrium thermodynamics equations clearly identify the meaning of $\hat{\mu}_a^e$ as the chemical potential, and all the parameters in the equilibrium solution are now identified with the thermodynamic parameters. In achieving this conclusion we have already made use of the correspondence between the phenomenological thermodynamic Gibbs relation and its kinetic theory counterpart. To avoid repetition we have omitted the discussion on this aspect. Nevertheless, it is worthwhile adding the following remark on the integrability conditions for the entropy differential: the conclusion that T_e^{-1} is an integrating factor is drawn on the basis of a physical principle, namely, the

second law of thermodynamics, but not from the solution of the integrability conditions for the differential form ϖ_e , which are a set of coupled partial differential equations not readily solvable. Even if they are solved, the solutions do not necessarily give rise to the interpretation of T_e as the absolute temperature, since statistical mechanics, which is a probability theory, is not by itself able to endow the parameters such as β_e , p_e , and $\hat{\mu}_a^e$ with thermodynamical meanings. The bestowal on them of such thermodynamical meanings is accomplished by the thermodynamic correspondence made in the Gibbs ensemble method. This situation is the same as for the classical theory. We also emphasize that the role of the Carnot theorem in the physical interpretation of T_e should not be forgotten in equilibrium thermodynamics and in developing a theory of irreversible processes. Since the temperature of a nonequilibrium system must be measured in a universal scale, the absolute temperature scale is the most logical one on which to base the measure of heat and therewith erect a theory of irreversible processes. Nonequilibrium thermodynamic functions, whatever forms they may be found to take, are then constructed on the basis of such a temperature scale as well as the pressure and chemical potentials as identified earlier. This was basically the conclusion drawn in the case of the classical gases studied in Chapter 7 and the same conclusion holds for quantum gases studied here.

9.6 Nonequilibrium Distribution Function

As was done for the Boltzmann equation, the nonequilibrium distribution function can be constructed on the basis of the equilibrium solution. Since the parameters T_e and $\hat{\mu}_a^e$ are uniform in space and time, the equilibrium distribution function with the uniform parameters T_e and $\hat{\mu}_a^e$ therein cannot be part of the nonequilibrium distribution function. Instead, position- and time-dependent parameters corresponding to T_e and $\hat{\mu}_a^e$ must be used in the nonequilibrium distribution function. In the case of classical gases we have seen that the equilibrium distribution function is the thermodynamic branch of the solution which is constructed in such a way that the statistical Boltzmann entropy of the system at equilibrium coincides with the Clausius entropy which is defined only for the equilibrium system or for reversible processes. We will use the same procedure as for the classical gases in constructing the thermodynamic branch of the nonequilibrium distribution function, and there is again a parallelism in the manner the equilibrium distribution functions are determined in the classical and quantum theories.

9.6.1 Matching Conditions

Let ϕ_a denote the collision invariants of the quantum kinetic equation (9.30). It then is easy to show [30,31] by using the kinetic equation that

$$\int_V dr \sum_{a=1}^r \langle \phi_a (f_a - f_a^{\text{eq}}) \rangle = 0. \quad (9.94)$$

This implies that there exists a scalar function $G(\mathbf{r}, t)$ which vanishes at the boundaries and is such that

$$\sum_{a=1}^r \langle \phi_a (f_a - f_a^{\text{eq}}) \rangle = \nabla G(\mathbf{r}, t). \quad (9.95)$$

Differentiate this with time and use the kinetic equation. Since the balance equations must hold, it is concluded that $\nabla(\partial_t G) = 0$. This implies that G is a function of \mathbf{r} only. If the system is homogeneous this function is a constant and we find

$$\sum_{a=1}^r \langle \phi_a (f_a - f_a^{\text{eq}}) \rangle = 0. \quad (9.96)$$

This is also a sufficient condition for (9.94) to hold even for a spatially inhomogeneous system. We look for f_a such that (9.96) is satisfied even if the system is spatially inhomogeneous. These are called the matching conditions. Explicitly written out, they are as follows:

$$\rho = \sum_a^r \langle m_a f_a \rangle = \sum_a^r \langle m_a f_a^{\text{eq}} \rangle = \rho_e, \quad (9.97)$$

$$\rho \mathbf{u} = \sum_a^r \langle m_a \mathbf{v}_a f_a \rangle = \sum_a^r \langle m_a \mathbf{v}_a f_a^{\text{eq}} \rangle = \rho_e \mathbf{u}, \quad (9.98)$$

$$\rho \mathcal{E} = \sum_a^r \left\langle \frac{1}{2} m_a C_a^2 f_a \right\rangle = \sum_a^r \left\langle \frac{1}{2} m_a C_a^2 f_a^{\text{eq}} \right\rangle = \rho_e \mathcal{E}_e. \quad (9.99)$$

To better understand, especially, the energy matching condition, we observe that $\rho_e \mathcal{E}_e$ may be written in the form²

$$\rho_e \mathcal{E}_e = \frac{3}{2} n_e \zeta_e k_B T_e, \quad (9.100)$$

²It must be understood that this is not a formula defining the temperature. Here $T_e = 1/k_B \beta_e$ and in the Gibbs ensemble method this parameter T_e is identified with thermodynamic temperature by making the correspondence of (9.92) with the thermodynamic counterpart. As has already been shown, the statistical derivation of (9.92) does not require T_e to be defined through (9.100) which, however, shows the physical significance of T_e . Note that $\zeta_e \neq 1$, which implies that the equipartition law of energy is broken in the case of quantum particles and the energy–temperature relation is not so simple as for the classical theory. There is

where

$$\zeta_e = \frac{2}{3} \frac{\sum_{a=1}^r G_a m_a^{3/2} \langle \frac{1}{2} z_a^2 f_a^{eq}(\mathbf{z}_a, \bar{\mu}_a^e) \rangle_{red}}{\sum_{a=1}^r G_a m_a^{3/2} \langle f_a^{eq}(\mathbf{z}_a, \bar{\mu}_a^e) \rangle_{red}}, \quad (9.101)$$

$$\mathbf{z}_a = \sqrt{m_a \beta_e} \mathbf{C}_a, \quad (9.102)$$

$$\bar{\mu}_a^e = \left(\frac{\mu_a^e}{m_a} \right) m_a \beta_e \equiv \hat{\mu}_a^e m_a \beta_e. \quad (9.103)$$

Here the angular brackets with the subscript red mean the integration over the reduced velocity z_a :

$$\langle \dots \rangle_{red} = \int d\mathbf{z}_a \dots$$

It therefore is possible to conclude that the right hand side of (9.100) is *first-order homogeneous* in $(k_B T_e / m_a)$, for ζ_e is a function of reduced variables \mathbf{z}_a and $\bar{\mu}_a^e$ and thus is zero-order homogeneous in $(k_B T_e / m_a)$ and $\hat{\mu}_a^e$. Note that $\bar{\mu}_a^e$ itself may be regarded as being a homogeneous function of order zero with respect to $\hat{\mu}_a^e$ and $(k_B T_e / m_a)$. Therefore the temperature may still be regarded as a measure, albeit a fuzzy one compared to the classical case, of the local mean kinetic energy, since the latter is proportional to T_e and so is the local temperature of the nonequilibrium system by virtue of the matching conditions. A similar interpretation holds for the mass density ρ_e . For this reason the subscript e will be dropped from temperature and density, and the equilibrium Gibbs relation which we have obtained from the equilibrium thermodynamic branch f_a^{eq} now reads

$$dS_e = T^{-1} \left(dE + p_e dv - \sum_{a=1}^r \hat{\mu}_a^e dc_a \right). \quad (9.104)$$

The accompanying Gibbs–Duhem equation reads

$$\sum_{a=1}^r c_a d\bar{\mu}_a^e = E d\left(\frac{1}{T}\right) + v d\left(\frac{p_e}{T}\right). \quad (9.105)$$

These are the local equilibrium equations and f_a^{eq} , on replacement of T_e therein, becomes the local equilibrium distribution function³ which will be

no temperature operator whose statistical average will give the temperature of the system. Any allusion to this effect in the literature is incorrect, since temperature cannot be defined detached from the zeroth law of thermodynamics. Neither is it useful to define temperature approximately since it is the yardstick against which all thermal properties, equilibrium and nonequilibrium, are reckoned.

³The meaning of local equilibrium was discussed in Chapter 7 and the same remains applicable in the case of quantum systems. See Chapter 7.

denoted by f_a^0 :

$$f_a^0 = [\exp \beta (H_a - \mu_a^0) - \epsilon_a]^{-1}, \quad (9.106)$$

where μ_a^0 is the normalization factor defined by

$$n_a = \langle [\exp \beta (H_a - \mu_a^0) - \epsilon_a]^{-1} \rangle \quad (9.107)$$

and

$$\beta = \frac{1}{k_B T}. \quad (9.108)$$

It is possible to show that the kinetic energy in (9.106) can be given in terms of the peculiar velocity: $\frac{1}{2}m_a C_a^2$ instead of $\frac{1}{2}m_a v_a^2$. Note that $n_a = \rho_a/m_a$ and the matching condition holds for ρ_a or n_a individually. We reiterate that the local temperature T in (9.108) is in the absolute scale and statistically related to the mean kinetic energy at position \mathbf{r} and time t by virtue of the energy matching condition. However, its status as a parameter in the nonequilibrium theory is not fully established as yet. In the nonequilibrium ensemble method this parameter will be eventually identified with the temperature of the nonequilibrium system, as will be shown. At the moment it is simply an abbreviation for a quantity related to the mean kinetic energy of the nonequilibrium system at \mathbf{r} and time t . A similar comment applies to p_e and the parameter μ_a^0 is simply a normalization factor which does not appear in the final thermodynamic result for nonequilibrium as will be seen.

The matching conditions imply that the nonequilibrium part of distribution function f_a is orthogonal to the conserved variables:

$$\sum_{a=1}^r \langle \phi_a (f_a - f_a^0) \rangle = 0 \quad (9.109)$$

for $\phi_a = m_a, m_a \mathbf{v}_a, \frac{1}{2}m_a C_a^2$. Therefore the conditions in (9.109) imply that the equilibrium thermodynamic space spanned by the conserved variables $\mathfrak{P}_e \equiv (\rho_e, \mathcal{E}_e, c_a : 1 \leq a \leq r)$ is embedded in the nonequilibrium thermodynamic space spanned by $\mathfrak{P} \equiv (\rho, \mathcal{E}, c_a, \hat{\Phi}_{ka} : 1 \leq a \leq r; k \geq 1)$ where $v = \rho^{-1}$ and that all macroscopic variables, thermodynamic functions included, are determined in reference to the parameters T, p_a , and $\hat{\mu}_a$ which the nonequilibrium ensemble method will identify with the local thermodynamic intensive parameters as will be seen. The aforementioned matching conditions are necessary for constructing a thermodynamically consistent theory of irreversible processes presented later in this section.

9.6.2 Nonequilibrium Canonical Form

We now use a complete set of orthogonal tensor Hermite polynomials $\mathcal{H}^{(k)}(\mathbf{w}_a)$ ($k \geq 0$) [32,33] of reduced peculiar velocity $\mathbf{w}_a = \sqrt{m_a \beta} \mathbf{C}_a$,

which are defined in Chapters 5 and 6, and express the thermodynamic branch f_a^c therewith. The weighting function of the Hermite polynomials will be denoted by

$$\omega(\mathbf{w}) = (2\pi)^{-3/2} \exp(-\frac{1}{2}w^2)$$

in the same notation as in the classical theory. The mean value of $\mathcal{H}^{(k)}$ yields the macroscopic variable

$$\Theta_a^{(k)} = \langle \mathcal{H}^{(k)}(\mathbf{w}_a) f_a \rangle \quad (k \geq 1). \quad (9.110)$$

As in the case of the classical Boltzmann gases, this operation is a projection onto the space of macroscopic variables. Moreover, this projection is non-bijective since there is a contraction in information accompanying the projection operation. In fact, this averaging operation may be regarded as part of a dual projection of f_a onto the ' $\mathcal{H}^{(k)}$ axis' in the velocity space on the one hand and onto the ' $\Theta_a^{(k)}$ axis' in the macroscopic variable space on the other. However, the words 'projection of f_a ' should not be taken literally since it must be performed with a logarithmic function of f_a if a nonequilibrium canonical form is used for quantum distribution functions.

The macroscopic variables $\Theta_a^{(k)}$ obey their own evolution equations which can be derived from the quantum kinetic equation in the same manner as for Φ_{ka} . There is, however, no necessity for deriving once again such evolution equations since $\Theta_a^{(k)}$ can be related to Φ_{ka} according to Table 9.1. Therefore we will assume that $\Theta_a^{(k)}$ are given in terms of Φ_{ka} for all k . Since the Boltzmann entropy and the calortropy must be extensive and thus additive, given their statistical forms dictated by the kinetic equation, it is unavoidable to take f_a^c in the form

$$f_a^c = \left\{ \exp \beta \left[H_a + \sum_{k \geq 1} Y_a^{(k)} \mathcal{H}^{(k)}(\mathbf{w}_a) - \mu_a \right] - \epsilon_a \right\}^{-1} \quad (9.111)$$

with μ_a defined by the normalization condition

$$n_a = \left\langle \left\{ \exp \beta \left[H_a + \sum_{k \geq 1} Y_a^{(k)} \mathcal{H}^{(k)}(\mathbf{w}_a) - \mu_a \right] - \epsilon_a \right\}^{-1} \right\rangle. \quad (9.112)$$

The thermodynamic meanings of the parameters β , μ_a , and $Y_a^{(k)}$ will be fixed by thermodynamic correspondence as in the classical theory and their statistical expressions will be obtained in terms of the nonequilibrium partition function. In particular, the intensive parameters $Y_a^{(k)}$ may be approximately determined in terms of $\Theta_a^{(k)}$ by suitably modifying the procedure developed in Sec. 7.6.

Table 9.1. Relation of $h_a^{(k)}$ to $\mathcal{H}^{(k)}$ and Φ_{ka} to $\Theta_a^{(k)}$ for $k \leq 4$

$h_a^{(1)}(\mathbf{C}_a) = k_B T \left[\mathcal{H}^{(2)}(\mathbf{w}_a) - \frac{1}{3} \mathcal{H}_{\gamma\gamma}^{(2)}(\mathbf{w}_a) \delta \right]$
$h_a^{(2)}(\mathbf{C}_a) = k_B T \left[\frac{1}{3} \mathcal{H}_{\gamma\gamma}^{(2)}(\mathbf{w}_a) - (p_a/n_a k_B T - 1) \right]$
$h_a^{(3)}(\mathbf{C}_a) = \frac{5}{2} k_B T \sqrt{k_B T/m_a}$
$\times \left[\frac{1}{5} \mathcal{H}_{\gamma\gamma}^{(3)}(\mathbf{w}_a) - \left(2m_a \hat{h}_a / 5k_B T - 1 \right) \mathcal{H}^{(1)}(\mathbf{w}_a) \right]$
$h_a^{(4)}(\mathbf{C}_a) = \sqrt{m_a k_B T} \mathcal{H}^{(1)}(\mathbf{w}_a)$
<hr/>
$\Phi_{1a} = k_B T \left(\Theta_a^{(2)} - \frac{1}{3} \delta \text{Tr} \Theta_a^{(2)} \right)$
$\Phi_{2a} = k_B T \left[\frac{1}{3} \text{Tr} \Theta_a^{(2)} - (p_a/n_a k_B T - 1) \right]$
$\Phi_{3a} = \frac{1}{2} k_B T \sqrt{k_B T/m_a} \left(\Theta_{a\gamma\gamma}^{(3)} - \hat{h}_a \Theta_a^{(1)} \right)$
$\Phi_{4a} = \sqrt{m_a k_B T} \Theta_a^{(1)}$
<hr/>

* The repeated Greek subscripts $\gamma\gamma$ mean a sum over γ .

Since $\Theta_a^{(k)}$ are generally measurable indirectly, it is convenient in practice to use a set of nonconserved variables directly accessible experimentally. The leading elements of such a set is summarized in Table 9.1. The nonequilibrium quantum canonical form may then be written in terms of such a set as follows:

$$f_a^c = [\exp \beta (H_a + H_a^1 - \mu_a) - \epsilon_a]^{-1}, \quad (9.113)$$

$$H_a^1 = \sum_{k \geq 1} X_{ka} h_a^{(k)}(\mathbf{C}_a). \quad (9.114)$$

Here the expansion coefficients X_{ka} are now related to $Y_a^{(k)}$ by the equation

$$\sum_{k \geq 1} \left\langle \omega(\mathbf{w}_a) \mathcal{H}_i^{(l)}(\mathbf{w}_a) h_a^{(k)}(\mathbf{C}_a) \right\rangle_{\text{red}} X_{ka} = Y_{aj}^{(l)} \delta_{ij}^l. \quad (9.115)$$

This is a set of linear algebraic relations between X_{ka} and $Y_a^{(l)}$ since $h_a^{(k)}$ is a linear combination of $\mathcal{H}^{(l)}(\mathbf{w}_a)$. See Table 9.1 for examples of such linear combinations for $k \leq 4$. The approximate relation between $Y_a^{(k)}$ and X_{ka} can be obtained if only the term matching the value of l is retained on the left hand side of (9.115). Calculation of $Y_a^{(k)}$ and μ_a in (9.111) and (9.112) is comparable to the calculation of the partition function in equilibrium statistical mechanics. We now look for a general formalism⁴ for calculating $Y_a^{(k)}$ by making a quantum generalization of the nonequilibrium ensemble method formulated for classical gases in Chapter 7. We will use the nonequilibrium canonical form (9.113) for the purpose.

9.7 Quantum Nonequilibrium Ensemble Method

With the nonequilibrium quantum canonical form (9.113) for the thermodynamic branch f_a^c of the distribution function f_a , we are now ready to examine the calortropy and relative Boltzmann entropy balance equations (9.60) and (9.61). In particular, the calortropy balance equation will be put into an equivalent Pfaffian differential form so that it can be made to correspond with its phenomenological counterpart presented in Chapter 2 in a manner similar to the correspondence made in Chapter 7. With the differential form so derived the nonequilibrium ensemble method can be implemented for quantum gases.

9.7.1 Calortropy Differential and the Second Law of Thermodynamics

On use of the nonequilibrium canonical form (9.113) in (9.62) and (9.63) the calortropy flux and the calortropy production can be put into the forms

$$\mathbf{J}_c = T^{-1} \sum_{a=1}^r \left[\mathbf{Q}_a - \hat{\mu}_a \mathbf{J}_a + \sum_{k \geq 1} X_{ka} \boldsymbol{\psi}_{ka} \right] + \mathbf{J}_{cq}, \quad (9.116)$$

$$\mathbf{J}_{cq} = k_B \sum_{a=1}^r \langle \mathbf{C}_a \epsilon_a \ln (1 + \epsilon_a f_a^c) \rangle, \quad (9.117)$$

⁴For a method of calculating approximate $Y_a^{(k)}$ by using a generalization of the Maxwell–Grad moment expansion, see Eu, Nonequilibrium Ensemble Method and Irreversible Thermodynamics in *Lectures on Thermodynamics and Statistical Mechanics*, eds., M. Costas, R. Rodriguez, and A. L. Benavides (World Scientific, Singapore, 1994), pp. 205–234.

$$\sigma_c = T^{-1} \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \Lambda_{ka}, \quad (9.118)$$

where Λ_{ka} is defined by (9.84). Although J_{cq} appears to be a quantum contribution to J_c because it appears to vanish if $\epsilon_a = 0$, it in fact has a nonvanishing limit at $\epsilon_a = 0$, indicating that it has the classical analog, $\sum_{a=1}^r p_a J_a / \rho_a$; see Chapter 7 for this term.

After substituting the calortropy flux and the calortropy production given in (9.116) and (9.118) into the calortropy balance equation (9.60), we follow the same procedure as for the one used for classical Boltzmann gases in Chapter 7 and eliminate the heat flux, diffusion flux, and the dissipation term by means of the evolution equations for conserved and nonconserved variables. The calortropy balance equation can thereby be put into a Pfaffian differential form in the thermodynamic space \mathfrak{P} . To achieve this aim we use the following identities:

$$\mathcal{E} dt \left(\frac{1}{T} \right) + v dt \left(\frac{p}{T} \right) - \sum_{a=1}^r c_a dt \left(\frac{\hat{\mu}_a}{T} \right) + \sum_{a=1}^r \sum_{k \geq 1} \hat{\Phi}_{ka} dt \left(\frac{X_{ka}}{T} \right) = 0, \quad (9.119)$$

and

$$\begin{aligned} \mathcal{L}_c &\equiv k_B \sum_{a=1}^r \langle f_a \mathcal{D}_w \ln (\epsilon_a + f_a^{c-1}) \rangle \\ &= \rho \hat{\Xi}_l + T^{-1} \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \mathcal{Z}_{ka} - \rho dt \left(\frac{pv}{T} \right), \end{aligned} \quad (9.120)$$

where the statistical definition of p is

$$\begin{aligned} p &= k_B T \sum_{a=1}^r \langle \epsilon_a \ln (1 + \epsilon_a f_a) \rangle \\ &= -k_B T \sum_{a=1}^r \langle \epsilon_a \ln [1 - \epsilon_a \exp -\beta (H_a + H_a^1 - \mu_a)] \rangle, \end{aligned} \quad (9.121)$$

and $\hat{\Xi}_l$ has the same form as the classical expression for the energy dissipation defined in Chapter 7, namely,

$$\begin{aligned} \rho \hat{\Xi}_l &= -T^{-1} \sum_{a=1}^r [(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q}_a^c \cdot \nabla \ln T + \mathbf{J}_a \cdot (\nabla \hat{\mu}_a - \mathbf{F}_a)] \\ &\quad + T^{-1} \sum_{a=1}^r \sum_{k \geq 1} \psi_{ka} \cdot \nabla X_{ka} \end{aligned} \quad (9.122)$$

with \mathbf{Q}_a^c defined by

$$\mathbf{Q}_a^c = \mathbf{Q}_a - \hat{\mu}_a \mathbf{J}_a + \sum_{k \geq 1} \psi_{ka} X_{ka}. \quad (9.123)$$

The identity (9.119) is derived from the normalization factor for f_a^c by varying the macroscopic parameters. It is equivalent to the integrability condition [28] for the Pfaffian differential form for the calortropy. The identity (9.120) is the most crucial for the derivation of the Pfaffian form for $d_t \hat{\Psi}$. This identity is a generalization of the classical identity we have used in Chapter 7. Related to this identity is the relation

$$\Upsilon_c = \rho \hat{\Xi}_l + T^{-1} \sum_{a=1}^r \sum_{k \geq 1} X_{ka} Z_{ka} + \nabla \cdot \sum_{a=1}^r k_B \epsilon_a \langle \mathbf{C}_a \ln(1 + \epsilon_a f_a^c) \rangle. \quad (9.124)$$

For the identities (9.120) and (9.124) the statistical formula for Z_{ka} is used instead of the explicit forms for which examples will be given in the subsequent section. The explicit forms for Z_{ka} are not useful for the purpose deriving the identities given here. With the help of the aforementioned identities it is straightforward to obtain the differential form

$$d_t \hat{\Psi} = T^{-1} \left[d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} d_t \hat{\Phi}_{ka} \right]. \quad (9.125)$$

This is a differential form in the thermodynamic space which is equivalent to the calortropy balance equation (9.60). The parameters T , p , $\hat{\mu}_a$, and X_{ka} , however, are not as yet fully fixed of their thermodynamic meanings despite their statistical mechanical definitions of the last three parameters. To endow them with thermodynamic meanings, we now compare the statistically derived formula for $d_t \hat{\Psi}$ with the phenomenological differential form (2.54). More specifically, in the spirit of the Gibbs ensemble method the mechanical variables \mathcal{E} , v , c_a , and $\hat{\Phi}_{ka}$ in the statistical formula (9.125) and the phenomenological formula (2.54) are brought into correspondence with each other together with the correspondence of the statistical $\hat{\Psi}$ with the phenomenological $\hat{\Psi}$:

$$\begin{aligned} \hat{\Psi}|_{st} &\Leftrightarrow \hat{\Psi}|_{th}, & \mathcal{E}|_{st} &\Leftrightarrow \mathcal{E}|_{th}, & v|_{st} &\Leftrightarrow v|_{th}, \\ c_a|_{st} &\Leftrightarrow c_a|_{th}, & \hat{\Phi}_{ka}|_{st} &\Leftrightarrow \hat{\Phi}_{ka}|_{th}. \end{aligned} \quad (9.126)$$

As in the case of the classical theory, this correspondence makes it possible to identify the parameters T , p , $\hat{\mu}_a$, and X_{ka} in (9.125) with the phenomenological parameters in (2.54):

$$T|_{st} \Leftrightarrow T|_{th}, \quad p|_{st} \Leftrightarrow p|_{th},$$

$$\hat{\mu}_a|_{\text{st}} \Leftrightarrow \hat{\mu}_a|_{\text{th}}, \quad X_{ka}|_{\text{st}} \Leftrightarrow X_{ka}|_{\text{th}}, \quad (9.127)$$

which completely fixes the meanings of the parameters appearing in the nonequilibrium canonical form f_a^c . With this result it is possible to conclude that the structure of thermodynamics of irreversible processes in the quantum system considered is the same as for the classical system examined in Chapter 7. This result is summarized as a theorem.

Theorem 6 *The calortropy differential for the quantum dilute gases described by the kinetic equation (9.30) is the statistical representation of the calortropy differential (2.51) deduced from the second law of thermodynamics. It has the same mathematical properties as for the latter in the thermodynamic space \mathfrak{P} . It also has the same mathematical form as the calortropy differential for the classical gases.*

Therefore, except for the statistical definitions for the constitutive variables, the thermodynamics of irreversible processes is the same for both quantum and classical gases. However, the quantum effects will manifest themselves when the constitutive relations are explicitly computed in terms of temperature, volume, concentrations, their spatial gradients, and non-conserved variables.

The mathematical structure of the theory of irreversible processes is remarkably the same for both quantum and classical systems since irreversible thermodynamics is a continuum macroscopic description of many-particle systems and macroscopic variables *per se* are not quantum mechanical although they are the statistical averages of quantum mechanical operators computed with a quantum mechanical density matrix or equivalently by means of the Wigner distribution function.

If the external force is more explicitly taken into account, the differential form in (9.125) can be recast into the form

$$d_t \hat{\Psi} = T^{-1} \left(d_t \mathcal{E}_{\text{ex}} + p d_t v - \sum_{a=1}^r \hat{\mu}_a^{\text{ex}} d_t c_a + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} d_t \hat{\Phi}_{ka} \right), \quad (9.128)$$

where

$$\begin{aligned} \mathcal{E}_{\text{ex}} &= \mathcal{E} + \sum_{a=1}^r c_a \mathfrak{V}_a, \\ \hat{\mu}_a^{\text{ex}} &= \hat{\mu}_a + \mathfrak{V}_a. \end{aligned} \quad (9.129)$$

Therefore $\hat{\mu}_a^{\text{ex}}$ is seen as the chemical potential of species a subject to the external field. Thus, if the external field is electrical, then $\hat{\mu}_a^{\text{ex}}$ is the electrochemical potential.

Finally, we remark that on using the identity \mathcal{L}_c and \mathbf{J}_c in the balance equation for $\hat{\Psi}$ and comparing the result with its phenomenological counterpart presented in Chapter 2 (see (2.48)–(2.50)) the local statistical form

of the second law of thermodynamics can be found to take the inequality

$$\rho \widehat{\Xi}_l + T^{-1} \sum_{a=1}^r \sum_{k \geq 1} X_{ka} (\mathcal{Z}_{ka} + \Lambda_{ka}) \geq 0. \quad (9.130)$$

This inequality puts a constraint on the constitutive equations for the non-conserved variables used for description of irreversible processes, namely, the generalized hydrodynamic equations.

9.7.2 Nonequilibrium Statistical Thermodynamics for Quantum Gases

Theorem 5 summarizes the correspondences in (9.126) and (9.127) for the macroscopic variables appearing in the differential form (9.125) for the calortropy. It makes it possible to obtain statistical expressions for various macroscopic variables in terms of the nonequilibrium partition function. This nonequilibrium partition function is a function of temperature, volume, and generalized potentials X_{ka} . Since the procedure of calculation for them is similar to that for the classical gases considered in Chapter 7, only the final results will be presented.

The normalization factor $\mu_a = m_a \widehat{\mu}_a$ is related to the nonequilibrium partition function since μ_a is defined by (9.112). In the case of quantum gases this normalization integral cannot be calculated in a closed form regardless of whether the system is in equilibrium or nonequilibrium. In any case, it is not necessary to dwell on explicit evaluation of the integral for the formal relations we have in mind here. It is sufficient for the purpose here to define the nonequilibrium partition function \mathbb{Z}_a by the relation

$$\widehat{\mu}_a = - (m_a \beta)^{-1} \ln \mathbb{Z}_a, \quad (9.131)$$

We also take the Legendre transformation

$$\widehat{\Omega} = \mathcal{E} + pv - T\widehat{\Psi} + \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \widehat{\Phi}_{ka}. \quad (9.132)$$

This transformation and (9.125) give rise to the differential form

$$d_t \widehat{\Omega} = - \widehat{\Psi} d_t T + v d_t p + \sum_{a=1}^r \widehat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{k \geq 1} \widehat{\Phi}_{ka} d_t X_{ka}. \quad (9.133)$$

The Legendre transformation (9.132) and the differential form (9.133) mean that the nonequilibrium thermodynamic potential $\widehat{\Omega}$ is given by the sum

$$\widehat{\Omega} = \sum_{a=1}^r \widehat{\mu}_a c_a. \quad (9.134)$$

It is convenient to use the following variables for the purpose of calculating the total partition function and its derivatives:

$$\begin{aligned}\Omega &= V\rho\widehat{\Omega}, \quad \Psi_v = V\rho\widehat{\Psi}, \quad E = V\rho\mathcal{E}, \\ N_a &= \frac{V\rho c_a}{m_a}, \quad \Phi_{ka}^v = V\rho\widehat{\Phi}_{ka},\end{aligned}\quad (9.135)$$

where V is the volume. Despite the appearance of the volume V of the system in them these variables are not global, but local. Using these new variables, we write the differential form (9.133) as

$$d_t\Omega = -\Psi d_t T + V d_t p + \sum_{a=1}^r \mu_a d_t N_a + \sum_{a=1}^r \sum_{k \geq 1} \Phi_{ka}^v d_t X_{ka}. \quad (9.136)$$

With the definition of the total partition function \mathbb{Z}

$$\mathbb{Z} = \prod_{a=1}^r \mathbb{Z}_a^{N_a}, \quad (9.137)$$

the thermodynamic potential Ω can be obtained from (9.134) and (9.132) in the form

$$\Omega = -k_B T \ln \mathbb{Z}. \quad (9.138)$$

This total partition function \mathbb{Z} for the mixture can be used to calculate various macroscopic variables with the help of the differential form (9.136):

$$\Psi_v = k_B \ln \mathbb{Z} + k_B T \left(\frac{\partial}{\partial T} \ln \mathbb{Z} \right)_{p,N,X}, \quad (9.139)$$

$$V = -k_B T \left(\frac{\partial}{\partial p} \ln \mathbb{Z} \right)_{T,N,X}, \quad (9.140)$$

$$\mu_a = -k_B T \left(\frac{\partial}{\partial N_a} \ln \mathbb{Z} \right)_{T,p,N',X}, \quad (9.141)$$

$$\Phi_{ka}^v = -k_B T \left(\frac{\partial}{\partial X_{ka}} \ln \mathbb{Z} \right)_{T,p,N,X'}, \quad (9.142)$$

where the prime on the subscripts mean exclusion of the variable in the derivative. These are nonequilibrium generalizations of the equilibrium ensemble theory results for the quantum gas mixture. If the nonequilibrium partition function is defined by

$$\mathbb{Z} = \prod_{a=1}^r \mathbb{Z}_a^{c_a/m_a},$$

which implies the relation to the thermodynamic potential $\hat{\Omega}$

$$\hat{\Omega} = -k_B T \ln Z,$$

then (7.81)–(7.84) will result in place of (9.139)–(9.142). However, both sets are completely equivalent. Calculation of the nonequilibrium partition function remains the task of the present nonequilibrium ensemble method. This is left for applications of the theory in the future.

9.8 Relative Boltzmann Entropy and Fluctuations

We now examine the relative Boltzmann entropy and its rate of change in time. Rigorously speaking, the relative Boltzmann entropy and its time derivative cannot be calculated explicitly unless the quantum kinetic equation (9.30) is solved under the initial and boundary conditions for the Wigner distribution function in the phase space. Nevertheless, it is possible to put them into forms giving more insight by following the approach taken for the classical theory. Since the basic procedure is the same as for the classical theory except for the distribution functions used, we simply present the key equations which are different from the equations in the classical theory. For the purpose in hand we change the notation for the intensive parameters in (9.113) as follows:

$$\begin{aligned} T^{-1} &\Rightarrow T^{t-1} \equiv \bar{T}^t, & pT^{-1} &\Rightarrow p^t T^{t-1} \equiv \bar{p}^t, \\ \hat{\mu}_a T^{-1} &\Rightarrow \hat{\mu}_a^t T^{t-1} \equiv \bar{\mu}_a^t, & X_{ka} T^{-1} &\Rightarrow X_{ka}^t T^{t-1} \equiv \bar{X}_{ka}^t. \end{aligned} \quad (9.143)$$

It must be recognized that these parameters have been determined by the thermodynamic correspondence as in (9.127), not from the kinetic equation (9.30). The reason is that the nonequilibrium canonical form is not constructed as a solution of the kinetic equation, but as a form that puts the calortropy balance equation (9.60) into a Pfaffian differential form (9.128) so that it can be computed from the evolution equations (9.76)–(9.80) of the macroscopic variables on the one hand and compared with its phenomenological thermodynamic counterpart (2.54) on the other hand. Strictly speaking, the nonequilibrium canonical form is not a solution of the kinetic equation that satisfies the initial and boundary conditions in the phase space or the Hilbert space. In the notation of (9.143), the nonequilibrium canonical form may be written as

$$f_a^c = \left\{ \exp \left[k_B^{-1} \left(\bar{T}^t H_a + \sum_{k \geq 1} \bar{X}_{ka}^t h_a^{(k)} - m_a \bar{\mu}_a^t \right) \right] - \epsilon_a \right\}^{-1}. \quad (9.144)$$

Now, let us seek f_a in the form

$$f_a = \left\{ \exp \left[k_B^{-1} \left(\bar{I} H_a + \sum_{k \geq 1} \bar{X}_{ka} h_a^{(k)} - m_a \bar{\mu}_a \right) \right] - \epsilon_a \right\}^{-1}, \quad (9.145)$$

where the parameters \bar{I} , $\bar{\mu}_a$, and \bar{X}_{ka} are independent of the momentum and to be determined such that (9.145) is the solution of the kinetic equation (9.30) which satisfies the initial and boundary conditions on f_a in the phase space or the Hilbert space. It is therefore clear that they are not the same as \bar{I}^t , $\bar{\mu}_a^t$, and \bar{X}_{ka}^t . Substitution of (9.144) and (9.145) into the statistical formula for the relative Boltzmann entropy (9.57) yields it in the form

$$S_r[f|f^c] = - \left(\mathcal{E} \delta \bar{I} + v \delta \bar{p} - \sum_{a=1}^r c_a \delta \bar{\mu}_a + \sum_{a=1}^r \sum_{k \geq 1} \hat{\Phi}_{ka} \delta \bar{X}_{ka} \right), \quad (9.146)$$

where

$$\begin{aligned} \delta \bar{I} &= \bar{I} - \bar{I}^t, & \delta \bar{p} &= \bar{p} - \bar{p}^t, \\ \delta \bar{\mu}_a &= \bar{\mu}_a - \bar{\mu}_a^t, & \delta \bar{X}_{ka} &= \bar{X}_{ka} - \bar{X}_{ka}^t. \end{aligned} \quad (9.147)$$

Note that the relative Boltzmann entropy is in exactly the same form as for the classical gases. Written in the form of (9.146) the relative Boltzmann entropy is seen related to the fluctuations of the intensive parameters from their thermodynamically determined values as in the case of the classical theory. This is easy to understand, since the relative Boltzmann entropy, by definition, is the excess part of the Boltzmann entropy over and above the calortropy which is determined with the help of thermodynamics. After all, thermodynamics is not only anthropomorphic in the sense that with it we try to understand the macroscopic behavior under consideration as we perceive it, but, from the statistical viewpoint, is also an approximation—owing to the functional hypothesis—obtained after contracting an enormous amount of molecular information contained in the distribution function f_a into that contained in the thermodynamic space.

The relative Boltzmann entropy flux and relative Boltzmann entropy production can be similarly calculated with (9.144) and (9.145). With the help of the identity (9.124), the relative Boltzmann entropy balance equation can be written as

$$\begin{aligned} \rho d_t S_r[f|f^c] &= - \left(\delta \bar{I} d_t \mathcal{E} + \delta \bar{p} d_t v - \sum_{a=1}^r \delta \bar{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{k \geq 1} \delta \bar{X}_{ka} d_t \hat{\Phi}_{ka} \right) \\ &\quad + \rho \hat{\Xi}_l + \sum_{a=1}^r \sum_{k \geq 1} \bar{X}_{ka} \mathcal{Z}_{ka} + \nabla \cdot \sum_{a=1}^r k_B \langle \mathbf{C}_a \epsilon_a \ln(1 + \epsilon_a f_a) \rangle. \end{aligned} \quad (9.148)$$

This form of the balance equation for the relative Boltzmann entropy is rather perspicacious and suggestive since it is isomorphic to the structure of the equation we will obtain for $d_t S$ if the form (9.145) of f_a is used in the statistical formulas (9.54) and (9.55) for the Boltzmann entropy flux \mathbf{J}_s and the Boltzmann entropy production σ_{ent} , together with the mass fraction and energy balance equations. The point of difference, however, lies in the fluctuations $\delta \bar{I}$, $\delta \bar{p}$, $\delta \bar{\mu}_a$, and $\delta \bar{X}_{ka}$ appearing in place of \bar{I} , \bar{p} , $\bar{\mu}_a$, and \bar{X}_{ka} in the differential form which would appear in the differential equation for $d_t S$ if the time derivative of the Boltzmann entropy were so calculated as mentioned earlier. Therefore the relative Boltzmann entropy may be regarded as a quantity made up of fluctuations in the intensive variables conjugate to the thermodynamic variables and their spatial gradients. Recall in this regard that $\widehat{\Xi}_l$ and \mathcal{Z}_{ka} consist of spatial gradients of \bar{I} , \bar{p} , $\bar{\mu}_a$, and \bar{X}_{ka} . Since the last three terms in (9.148) do not generally vanish if the processes are nonlinear, the time derivative of the relative Boltzmann entropy does not have a one-form [27,28], and there is no chance for it to become an exact differential in the space \mathfrak{P} . The relative Boltzmann entropy is generally path-dependent in the space \mathfrak{P} . Recall that this was also the case in the classical theory.

If we set $\delta \bar{I} = \delta \bar{p} = \delta \bar{\mu}_a = \delta \bar{X}_{ka} = 0$ as an approximation, then the rate of relative Boltzmann entropy change is given by

$$\rho d_t S_r[f|f^c] = \rho \widehat{\Xi}_l + \sum_{a=1}^r \sum_{k \geq 1} \bar{X}_{ka} \mathcal{Z}_{ka} + \nabla \cdot \sum_{a=1}^r k_B \langle \mathbf{C}_a \epsilon_a \ln(1 + \epsilon_a f_a) \rangle. \quad (9.149)$$

Both (9.148) and (9.149) indicate that $d_t S_r[f|f^c]$ does not generally vanish if the system is away from equilibrium. If the processes are linear with respect to the thermodynamic forces and \bar{X}_{ka} are given by the approximate formulas in Table 9.2, then the right hand side of (9.149) reduces to $\rho \widehat{\sigma}_l$, the Boltzmann entropy production in the linear theory of irreversible processes,

$$\rho \widehat{\sigma}_l = -T^{-1} \sum_{a=1}^r [(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q}_a^c \cdot \nabla \ln T + \mathbf{J}_a \cdot (\nabla \widehat{\mu}_a - \mathbf{F}_a)], \quad (9.150)$$

where $\mathbf{Q}_a^c = \mathbf{Q}_a - \widehat{\mu}_a \mathbf{J}_a$ since ψ_{ka} must be set equal to zero for linear irreversible processes. In this case, $d_t S_r[f|f^c]$ clearly does not vanish and is dependent on the path of irreversible processes. We are therefore able to conclude that generally

$$d_t S_r[f|f^c] \neq 0 \quad (9.151)$$

and consequently

$$d_t S \neq d_t \widehat{\Psi}. \quad (9.152)$$

This means that whereas $d_t \widehat{\Psi}$ is an exact differential in the thermodynamic space \mathfrak{P} , the differential $d_t S$ cannot be an exact differential in the space

\mathfrak{P} since $d_t S_r[f|f^c]$ is not an exact differential owing to the fact that it is path-dependent in the thermodynamic space. This result is summarized as a theorem.

Theorem 7 *The Boltzmann entropy differential dS for the quantum gases described by the kinetic equation (9.30) is not an exact differential in the thermodynamic space \mathfrak{P} whereas the calortropy differential $d\hat{\Psi}$ is exact in the space \mathfrak{P} . The rate of change in the relative Boltzmann entropy depends on the path of irreversible processes in the space \mathfrak{P} .*

The same conclusion could be drawn for classical systems and was summarized as Theorem 5 in Chapter 7. The evolution equations for fluctuations $\delta\bar{I}$, $\delta\bar{\mu}_a$, and $\delta\bar{X}_{ka}$ can be derived from the kinetic equation (9.30) by following the same procedure as for their classical counterparts presented in Chapter 7. This completes the description of the nonequilibrium ensemble method for the kinetic equation (9.7) or, equivalently, (9.30) except for the calculation of the dissipation terms Λ_{ka} in terms of macroscopic variables so that the constitutive equations for Φ_{ka} become more explicit.

9.9 Cumulant Approximations for Λ_{ka}

To implement the scheme of the nonequilibrium ensemble method for transport processes it is necessary to solve the evolution equations for the nonconserved variables, namely, the constitutive equations, together with the balance equations for the conserved variables. This means that the dissipation terms in the constitutive equations must be explicitly calculated in terms of nonconserved variables as well as the conserved variables, namely, temperature and density, and so on. We now calculate the dissipation term by following the same procedure as for the Boltzmann equation. Since we do not wish to repeat the calculation, only the result will be presented for the first-order cumulant approximation. The higher order approximants can be obtained by following the method developed in Chapter 7. The dissipation term in the first-order cumulant approximation has the same form as the classical counterpart:

$$\Lambda_{ka} = (\beta g)^{-1} \sum_{b=1}^r \sum_{l \geq 1} R_{ab}^{(kl)} X_{lb} \left(\frac{\sinh \kappa}{\kappa} \right), \quad (9.153)$$

where κ is the quadratic form given by

$$\kappa^2 = \sum_{a=1}^r \sum_{b=1}^r \sum_{k \geq 1} \sum_{l \geq 1} X_{ka} R_{ab}^{(kl)} X_{lb} \quad (9.154)$$

and $R_{ab}^{(kl)}$ are quantum collision bracket integrals of tensor polynomials $h_a^{(k)}$ which may be expressed in terms of tensor Hermite polynomials. The quantum feature appears in the distribution functions and κ^2 is a generalized

form of the Rayleigh dissipation function [34]. The collision bracket integrals are such that κ is dimensionless. The dissipation term in (9.153) is obtained as follows. The procedure is the same as for the classical theory in Chapter 7. With the definition of the parameter $g = \sqrt{m\beta/2}/(nd)^2$ where m is the mean mass and d is the mean size parameter of the molecules, the first-order cumulant approximation for the calortropy production is given by the formula

$$\sigma_c = k_B g^{-1} \kappa \sinh \kappa. \quad (9.155)$$

We remark that the dimension of g is *volumex time* and therefore the dimension of calortropy production is [$k_B/volume \times time$] and that f_a in Λ_{ka} in (9.118) must be replaced by the nonequilibrium canonical form under the assumption that the fluctuations in \bar{I} , \bar{p} , and so on vanish, namely, $\delta\bar{I} = \delta\bar{p} = \dots = 0$. Since the calortropy production is given by (9.118), by comparing it with (9.155) with the help of (9.154), we obtain the dissipation term given in (9.153). Since X_{ka} can be determined in terms of Φ_{ka} through the nonequilibrium partition function or by approximate relations given in Table 9.2, the evolution equations for Φ_{ka} are now closed with respect to Φ_{ka} , if the closure relations $\psi_{ka} = 0$ ($k \neq 4$) are taken:

$$\rho d_t \hat{\Phi}_{ka} = \mathcal{Z}_{ka} + (\beta g)^{-1} \sum_{b=1}^r \sum_{l \geq 1} R_{ab}^{(kl)} X_{lb} \left(\frac{\sinh \kappa}{\kappa} \right). \quad (9.156)$$

These evolution equations are coupled to the balance equations for the conserved variables (9.75)–(9.78). This set of partial differential equations constitutes generalized hydrodynamics equations which reduce to the classical hydrodynamics equations: Navier–Stokes, Fourier and Fick’s equations under certain approximations valid near equilibrium. The kinematic terms can be easily calculated explicitly in terms of macroscopic variables as will be shown later. For some nonlinear transport processes the first-order cumulant approximation for the calortropy production and the dissipation

Table 9.2. Approximate Relations* of X_{ka} to Φ_{ka} for $k \leq 4$

$$X_{1a} = - (2n_a k_B T)^{-1} \Phi_{1a}$$

$$X_{2a} = - 3 (2n_a k_B)^{-1} [\Phi_{2a} - \frac{1}{3} \text{Tr} \langle \mathcal{H}^{(2)} f_a^0 \rangle]$$

$$X_{3a} = - 2 (5n_a k_B^2 T^2)^{-1} \Phi_{3a}$$

$$X_{4a} = - \rho_a^{-1} \Phi_{4a}$$

* See the reference cited in Footnote 4.

terms may be inadequate and a higher order approximation may be required. See Chapter 7 for higher order cumulant approximations.

The collision bracket integrals $R_{ab}^{(kl)}$ in (9.154) are given by the integrals given below. They clearly satisfy the Onsager reciprocal relations [35]. Some quantities involved must be abbreviated for brevity of notation. We therefore define the following:

$$f_a^m = \exp[-\beta(H_a - \mu_a^0)], \text{ etc.}, \quad (9.157)$$

$$Q_{ab} = [(1 - \epsilon_a f_a^m)(1 - \epsilon_b f_b^m)]^{-2}, \quad (9.158)$$

$$g = \frac{\sqrt{m\beta}}{\sqrt{2}(nd)^2}, \quad (9.159)$$

$$[AB]_{ab} = \frac{G_a G_b m_a^3 m_b^3}{h^6 (k_B T)^2} g \int d\Gamma_{ab} f_a^m(\mathbf{v}_a) f_b^m(\mathbf{v}_b) Q_{ab}(\mathbf{v}_a, \mathbf{v}_b) AB, \quad (9.160)$$

where

$$\int d\Gamma_{ab} \dots = \iint d\mathbf{v}_a d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta W^{(\epsilon)}(\mathbf{v}_a \mathbf{v}_b | \mathbf{v}_a^* \mathbf{v}_b^*) \dots \quad (9.161)$$

The quantum nature of the distribution functions in this integral can be better seen by the relation

$$f_a^m f_b^m Q_{ab} = f_a^0 (1 + \epsilon_a f_a^0) f_b^0 (1 + \epsilon_b f_b^0). \quad (9.162)$$

The collision bracket integrals then are given by the formulas:

$$\begin{aligned} R_{aa}^{(kl)} &= \frac{1}{4} \left[\left(h_a^{(k)} + h_{a'}^{(k)} - h_a^{(k)*} - h_{a'}^{(k)*} \right) \left(h_a^{(l)} + h_{a'}^{(l)} - h_a^{(l)*} - h_{a'}^{(l)*} \right) \right]_{aa} \\ &\quad + \frac{1}{2} \sum_{b \neq a}^r \left[\left(h_a^{(k)} - h_a^{(k)*} \right) \left(h_a^{(l)} - h_a^{(l)*} \right) \right]_{ab}, \end{aligned} \quad (9.163)$$

$$R_{ab}^{(kl)} = \left[\left(h_a^{(k)} - h_a^{(k)*} \right) \left(h_b^{(l)} - h_b^{(l)*} \right) \right]_{ab} \quad (a \neq b). \quad (9.164)$$

In these formulas the primed subscript, for example, a' means another particle of species a . These collision bracket integrals require a remark in connection with the factor Q_{ab} defined by (9.158). This factor originates from the term in the collision integral

$$Q_{ab}^n \equiv \prod_{c=a}^b \left[1 - \epsilon_c e^{-\beta(H_c + H_c^1 - \mu_c)} \right]^{-1} \left[1 - \epsilon_c e^{-\beta(H_c + H_c^1 - \mu_c)^*} \right]^{-1}. \quad (9.165)$$

The Q_{ab} is the leading term in the expansion of Q_{ab}^n in powers of

$$\epsilon_c [\exp -\beta(H_c^1 - \Delta\mu_c) - 1] f_c^0,$$

which represents the quantum correction as well as, partially, a nonequilibrium correction to f_c^0 .

When explicitly worked out, the kinematic terms \mathcal{Z}_{ka} for $k \leq 4$ are as follows:

$$\mathcal{Z}_{1a} = -2[(d_t \mathbf{u} - \mathbf{F}_a) \mathbf{J}_a]^{(2)} - 2[\Pi_a \cdot \nabla \mathbf{u}]^{(2)} - 2p_a [\nabla \mathbf{u}]^{(2)}, \quad (9.166)$$

$$\begin{aligned} \mathcal{Z}_{2a} = & -\frac{2}{3}(d_t \mathbf{u} - \mathbf{F}_a) \cdot \mathbf{J}_a - \frac{2}{3}[\Pi_a \cdot \nabla \mathbf{u}]^{(2)} - \frac{2}{3}\Delta_a \nabla \cdot \mathbf{u} \\ & - p_a d_t \ln(p_a v^{5/3}) - \nabla \cdot \left(\frac{\mathbf{J}_a p_a}{\rho_a} \right), \end{aligned} \quad (9.167)$$

$$\begin{aligned} \mathcal{Z}_{3a} = & -(d_t \mathbf{u} - \mathbf{F}_a) \cdot (\mathbf{P}_a - p_a \boldsymbol{\delta}) - \mathbf{Q}'_a \cdot \nabla \mathbf{u} - \varphi_a^{(3)} : \nabla \mathbf{u} - \mathbf{J}_a d_t \hat{h}_a \\ & - \mathbf{P}_a \cdot \nabla \hat{h}_a - \frac{\rho_a \hbar^2}{24m_a^2} [\nabla^2 \mathbf{F}_a + 2\nabla(\nabla \cdot \mathbf{F}_a)], \end{aligned} \quad (9.168)$$

$$\mathcal{Z}_{4a} = -\rho_a(d_t \mathbf{u} - \mathbf{F}_a) - \mathbf{J}_a \cdot \nabla \mathbf{u}, \quad (9.169)$$

where $\varphi_a^{(3)} = \langle m_a \mathbf{C}_a \mathbf{C}_a \mathbf{C}_a f_a \rangle$. In particular, we note that the flux of diffusion flux is the pressure tensor:

$$\psi_{4a} = \mathbf{P}_a, \quad (9.170)$$

and this is not part of the closure relations mentioned earlier. The generalized hydrodynamics equations presented here form the basis to study transport processes in quantum fluids and hydrodynamic flow problems associated with them. Within the framework of the first thirteen moment approximation where higher order moments are neglected, the quantum effect appears only in the kinematic term for the heat flux [36]:

$$\mathcal{Z}_{3a}^{\text{quan}} \equiv -\frac{\rho_a \hbar^2}{24m_a^2} [\nabla^2 \mathbf{F}_a + 2\nabla(\nabla \cdot \mathbf{F}_a)], \quad (9.171)$$

which is of the order of \hbar^2 . This term implies that the heat flux is driven also by the spatial derivatives, in fact the curvatures, of the external force even if there is absent a temperature or concentration gradient. This quantum effect term should be compared with the thermodynamic force term (*i.e.*, the temperature gradient term) in \mathcal{Z}_{3a} :

$$\chi_a^{(3)} \equiv -\hat{C}_{pa} T p_a \nabla \ln T, \quad (9.172)$$

where \hat{C}_{pa} is the specific heat per mass of species a . By expressing the external force in terms of $\mathcal{F}_a = m_a \mathbf{F}_a$ instead of \mathbf{F}_a defined for unit mass of species a and calculating the mass in the units of the electron mass m_e ,

the ratio of the quantum effect term to the thermodynamic force term can be estimated:

$$\frac{\|\mathcal{Z}_{3a}^{\text{quan}}\|}{\|\chi_a^{(3)}\|} = 1.068 \times 10^6 \frac{m_e}{m_a} T^{-2} \frac{\|\nabla^2 \mathcal{F}_a + 2\nabla(\nabla \cdot \mathcal{F}_a)\|}{\|\nabla \ln T\|}. \quad (9.173)$$

Therefore, if the external force has a second derivative comparable with the temperature gradient in the system, then the quantum effect in heat flux should be noticeable. In particular, if the external force is electric, then $\nabla \cdot \mathcal{F}_a = \rho_e$ where ρ_e is the charge density. And if the charge density variation $\nabla \rho_e$ is comparable to $\nabla \ln T$ in magnitude, then the quantum effect in question should be noticeable.

9.10 Transport Processes in Quantum Fluids

Transport processes taking place in a fluid can be studied by means of the generalized hydrodynamics equations presented earlier. To be rigorous the generalized hydrodynamics equations must be solved subject to the initial and boundary conditions appropriate for a given flow problem. This would mean solving the partial differential equations. It would be not only rather laborious and difficult but also often unnecessary if the transport coefficients are the quantities desired. A general theory of transport processes for quantum gases [36] can be developed according to the procedure described in Chapter 7. As a preparation for studies in transport processes such as charge conductivity and thermal conductivity related to the charge carriers in the context of solid state phenomena [7–9], we will tailor the theory to the aim. Thus we will assume that there are no stresses applied to the system. This leaves only the diffusion and heat fluxes to consider.

The diffusion and heat flux evolution equations to the first-order cumulant approximation, written out explicitly, have the following general forms:

$$\begin{aligned} \rho d_t \hat{\mathbf{J}}_a &= -\nabla \cdot \mathbf{P}_a - \rho_a (d_t \mathbf{u} - \mathbf{F}_a) - \mathbf{J}_a \cdot \nabla \mathbf{u} \\ &\quad + (\beta g)^{-1} \sum_{b=1}^r \left[R_{ab}^{(43)} X_{3b} + R_{ab}^{(44)} X_{4b} \right] \frac{\sinh \kappa}{\kappa}, \end{aligned} \quad (9.174)$$

$$\begin{aligned} \rho d_t \hat{\mathbf{Q}}'_a &= - (d_t \mathbf{u} - \mathbf{F}_a) \cdot (\mathbf{P}_a - p_a \boldsymbol{\delta}) - \mathbf{Q}'_a \cdot \nabla \mathbf{u} - \mathbf{J}_a d_t \hat{h}_a \\ &\quad - \mathbf{P}_a \cdot \nabla \hat{h}_a - \frac{\rho_a \hbar^2}{24 m_a^2} [\nabla^2 \mathbf{F}_a + 2\nabla(\nabla \cdot \mathbf{F}_a)] \\ &\quad + (\beta g)^{-1} \sum_{b=1}^r \left[R_{ab}^{(33)} X_{3b} + R_{ab}^{(34)} X_{4b} \right] \frac{\sinh \kappa}{\kappa}, \end{aligned} \quad (9.175)$$

where the flux of \mathbf{Q}'_a , namely ψ_{3a} , is set equal to zero by virtue of the closure relations. The $\varphi_a^{(3)}$ term is also neglected since it is a third rank tensor which is one of higher order moments set equal to zero. This is consistent with the fact that the nonconserved variables beyond \mathbf{Q}'_a are truncated away. The X_{3b} and X_{4b} may be given by the approximate formulas in Table 9.2. They may be written in the forms

$$X_{3a} = -\frac{\mathbf{Q}'_a}{\hat{C}_{pa} T p_a}, \quad (9.176)$$

$$X_{4a} = -\frac{\mathbf{J}_a}{\rho_a}. \quad (9.177)$$

Eqs. (9.174) and (9.175) are coupled to the conservation equations (9.75)–(9.78).

Before discussing further approximations for these equations in accordance with the assumptions mentioned earlier, we examine the diffusion flux evolution equation a little more closely. For this discussion we set $R_{ab}^{(43)} = 0$ temporarily. Since $\mathbf{J}_a = \rho_a(\mathbf{u}_a - \mathbf{u})$, (9.174) can be recast as follows:

$$\rho_a d_t \mathbf{u}_a = \rho_a \mathbf{F}_a - \nabla p_a - \mathbf{J}_a d_t \ln c_a - \rho_a \sum_{b=1}^r \zeta_{ab} \mathbf{J}_b \frac{\sinh \kappa}{\kappa}, \quad (9.178)$$

where we have set $\Pi_a = \mathbf{P}_a - p_a \boldsymbol{\delta} = 0$ and $\nabla \mathbf{u} = 0$ according to the assumption of no stress, and the friction tensor ζ_{ab} is given in terms of collision bracket integral $R_{ab}^{(44)}$ by the formula

$$\zeta_{ab} = (\beta g)^{-1} \rho_a^{-1} R_{ab}^{(44)} \rho_b^{-1}. \quad (9.179)$$

Eq. (9.178), a drift velocity evolution equation, is reminiscent of the Langevin equation for the center of mass of species a subjected to an external force \mathbf{F}_a and frictional forces represented by the last term in (9.179). The additional terms therein are thermal driving forces brought about by concentration changes in space and time. Notice that the friction term is highly nonlinear with respect to the diffusion fluxes owing to the presence of the nonlinear factor $q = \sinh \kappa / \kappa$. If the process occurs sufficiently near equilibrium, then this nonlinear factor q may be put equal to unity and the friction term becomes linear with respect to the diffusion fluxes. We observe that the diffusion flux may be regarded as a fluctuation of the velocity of the center of mass of species a from the mean velocity \mathbf{u} . A response theory was used to derive an equation for \mathbf{u}_a in the literature [37] and for studying hot electron problems, but it is considerably different from (9.179) in important aspects.

To discuss transport processes with (9.174) and (9.175) it is convenient to rearrange the kinematic terms in them, since they contain the thermodynamic driving forces. We define the thermodynamic driving forces \mathbf{d}_a

and χ_a for diffusion and heat flow, respectively, by the formulas

$$\mathbf{d}_a = \nabla \left(\frac{n_a}{n} \right) + \left(\frac{n_a}{n} - \frac{\rho_a}{\rho} \right) \nabla \ln p, \quad (9.180)$$

$$\chi_a = \nabla \ln T. \quad (9.181)$$

Then, on linearization of the kinematic terms with regard to fluxes, the diffusion and heat flux evolution equations (9.174) and (9.175) under the aforementioned assumptions may be written as

$$\begin{aligned} \rho d_t \hat{\mathbf{J}}_a &= -[p \mathbf{d}_a + \rho_a (\mathbf{F} - \mathbf{F}_a)] \\ &\quad - \rho_a \sum_{b=1}^r (\zeta_{ab} \mathbf{J}_b + L_{ab} \mathbf{Q}'_b) \frac{\sinh \kappa}{\kappa}, \end{aligned} \quad (9.182)$$

$$\begin{aligned} \rho d_t \hat{\mathbf{Q}}'_a &= -\hat{C}_{pa} T p_a \chi_a - \frac{\rho_a \hbar^2}{24 m_a^2} [\nabla^2 \mathbf{F}_a + 2 \nabla (\nabla \cdot \mathbf{F}_a)] \\ &\quad - \hat{C}_{pa} T p_a \sum_{b=1}^r (K_{ab} \mathbf{Q}'_b + L_{ab} \mathbf{J}_b) \frac{\sinh \kappa}{\kappa}, \end{aligned} \quad (9.183)$$

where coefficients K_{ab} and L_{ab} are defined by collision bracket integrals as follows:

$$K_{ab} = (\beta g)^{-1} \left(\hat{C}_{pa} T p_a \right)^{-1} R_{ab}^{(33)} \left(\hat{C}_{pb} T p_b \right)^{-1}, \quad (9.184)$$

$$\begin{aligned} L_{ab} &= (\beta g)^{-1} \rho_a^{-1} R_{ab}^{(43)} \left(\hat{C}_{pb} T p_b \right)^{-1} \\ &= (\beta g)^{-1} \left(\hat{C}_{pb} T p_b \right)^{-1} R_{ba}^{(34)} \rho_a^{-1} = L_{ba}. \end{aligned} \quad (9.185)$$

The matrix $\mathbf{K} = (K_{ab})$ is related to the inverse of the thermal conductivity whereas the matrix $\mathbf{L} = (L_{ab})$ is related to the inverse of the thermal diffusion coefficient. Eqs. (9.182) and (9.183) are obtained from (9.174) and (9.175) on applying the assumptions of no stress and velocity gradient made for the transport processes under consideration and retaining the terms involving linear thermodynamic forces in the kinematic terms of the evolution equations.

The transport coefficients may be determined from (9.184) and (9.185) if the steady state is considered in the coordinate system moving at the fluid velocity \mathbf{u} . Recall that this is basically the adiabatic approximation discussed in Sec. 8.4, Chapter 8. In this case we obtain the steady constitutive equations

$$q(\kappa) \sum_{b=1}^r (\zeta_{ab} \mathbf{J}_b + L_{ab} \mathbf{Q}'_b) = -p \rho^{-1} \mathbf{d}_a - (\mathbf{F} - \mathbf{F}_a), \quad (9.186)$$

$$q(\kappa) \sum_{b=1}^r (K_{ab} \mathbf{Q}'_b + L_{ab} \mathbf{J}_b) = -\chi_a - \frac{\rho_a \hbar^2}{24m_a^2 \widehat{C}_{pa} T p_a} [\nabla^2 \mathbf{F}_a + 2\nabla(\nabla \cdot \mathbf{F}_a)], \quad (9.187)$$

where the nonlinear factor $q(\kappa)$ is given by

$$q(\kappa) = \frac{\sinh \kappa}{\kappa} \quad (9.188)$$

with κ defined by the quadratic form in (9.154). If $q(\kappa)$ is set equal to unity as is the case for near-equilibrium phenomena where the magnitude of fluxes is small, then (9.186) and (9.187) become the linear thermodynamic force-flux relations. If only the diffusion processes are considered without the heat fluxes, then the dependent diffusion flux, say, \mathbf{J}_r must be eliminated in favor of independent fluxes \mathbf{J}_a ($1 \leq a \leq r-1$). However, this procedure is not necessary if heat fluxes are present and coupled to the diffusion fluxes since then the matrix of the linear system on the left of (9.186) and (9.187) is no longer singular. It is convenient to define the matrix \mathbf{M} of dimension $2r \times 2r$ by

$$\mathbf{M} = \begin{bmatrix} \zeta & \mathbf{L} \\ \mathbf{L} & \mathbf{K} \end{bmatrix}, \quad (9.189)$$

where $\zeta = (\zeta_{ab})$, \mathbf{L} , and \mathbf{K} are $r \times r$ matrices. Define also the column vectors

$$\mathbf{V} = (\mathbf{J}_1, \dots, \mathbf{J}_r, \mathbf{Q}'_1, \dots, \mathbf{Q}'_r), \quad (9.190)$$

$$\mathbf{X} = (\bar{\mathbf{d}}_1, \dots, \bar{\mathbf{d}}_r, \bar{\chi}_1, \dots, \bar{\chi}_r), \quad (9.191)$$

where

$$\bar{\mathbf{d}}_a = p\rho^{-1} \mathbf{d}_a + (\mathbf{F} - \mathbf{F}_a), \quad (9.192)$$

$$\bar{\chi}_a = \chi_a + \frac{\rho_a \hbar^2}{24m_a^2 \widehat{C}_{pa} T p_a} [\nabla^2 \mathbf{F}_a + 2\nabla(\nabla \cdot \mathbf{F}_a)]. \quad (9.193)$$

By inverting the quasi-linear system (9.186) and (9.187) for \mathbf{V} , we obtain

$$\mathbf{V} = \frac{\mathbf{M}^{-1} \mathbf{X}}{q(\kappa)}. \quad (9.194)$$

This is a quasi-linear system because of the presence of the nonlinear factor $q(\kappa)$. To calculate nonlinear transport coefficients, (9.194) must be solved. Before solving (9.194) we would like to calculate linear transport coefficients so that the quantum effects can be clearly identified. For this purpose we

consider processes occurring near equilibrium where the nonlinear factor $q(\kappa)$ may be set equal to unity. Then we have

$$\mathbf{V} = \mathbf{M}^{-1} \mathbf{X}. \quad (9.195)$$

Define the following transport coefficients:

$$D_{ab} = p\rho_b^{-1}\mu_{ab} \quad (1 \leq a, b \leq r), \quad (9.196)$$

$$\mu_{ab} = (\mathbf{M}^{-1})_{ab} \quad (1 \leq a, b \leq r), \quad (9.197)$$

$$\vartheta_{ab} = (\mathbf{M}^{-1})_{ab} \quad (1 \leq a \leq r; r+1 \leq b \leq 2r), \quad (9.198)$$

$$\varphi_{ab} = \frac{\rho_a \hbar^2}{24m_a^2 \hat{C}_{pa} T p_a} \vartheta_{ab} \quad (1 \leq a \leq r; r+1 \leq b \leq 2r), \quad (9.199)$$

$$\lambda_{ab} = (\mathbf{M}^{-1})_{ab} \quad (r+1 \leq a, b \leq 2r), \quad (9.200)$$

$$\phi_{ab} = \lambda_{ab} \quad (r+1 \leq a, b \leq 2r). \quad (9.201)$$

The D_{ab} , λ_{ab} , μ_{ab} , and ϑ_{ab} are, respectively, the diffusion coefficients, thermal conductivities, ‘mobilities’, and thermal diffusion coefficients, whereas φ_{ab} and ϕ_{ab} are mechanico-diffusion and mechanico-thermal conduction coefficients, respectively, which are the quantum effects we have set out to show. It is helpful to mention that to the approximation neglecting the matrix \mathbf{L}

$$D_{ab} \approx p\rho_b^{-1}(\boldsymbol{\zeta}^{-1})_{ab} \quad (1 \leq a, b \leq r), \quad (9.202)$$

$$\lambda_{ab} \approx (\mathbf{K}^{-1})_{ab} \quad (r+1 \leq a, b \leq 2r), \quad (9.203)$$

whereas to the first order in \mathbf{L}

$$\vartheta_{ab} \approx (\mathbf{K}^{-1} \mathbf{L} \boldsymbol{\zeta}^{-1})_{ab} \quad (1 \leq a \leq r; r+1 \leq b \leq 2r). \quad (9.204)$$

With the definitions in (9.196)–(9.201) the linear force–flux relations can be written as

$$\begin{aligned} \mathbf{J}_a = & - \sum_{b=1}^r [D_{ab} \mathbf{d}_b + \mu_{ab} (\mathbf{F} - \mathbf{F}_b)] \\ & - \sum_{b=r+1}^{2r} [\vartheta_{ab} \boldsymbol{\chi}_a + \varphi_{ab} (\nabla^2 \mathbf{F}_b + 2\boldsymbol{\nabla} \boldsymbol{\nabla} \cdot \mathbf{F}_b)], \\ & \quad (1 \leq a \leq r), \end{aligned} \quad (9.205)$$

$$\begin{aligned}
\mathbf{Q}'_a &= - \sum_{b=1}^r [p\vartheta_{ab}\rho_b^{-1}\mathbf{d}_b + \vartheta_{ab}(\mathbf{F} - \mathbf{F}_b)] \\
&\quad - \sum_{b=r+1}^{2r} [\lambda_{ab}\chi_a + \phi_{ab}(\nabla^2\mathbf{F}_b + 2\nabla\mathbf{V}\cdot\mathbf{F}_b)], \\
&\quad (r+1 \leq a \leq 2r).
\end{aligned} \tag{9.206}$$

If the processes occur far removed from equilibrium, by restoring the non-linear factor $q(\kappa)$ we then obtain the quasi-linear constitutive relations

$$\begin{aligned}
\mathbf{J}_a q(\kappa) &= - \sum_{b=1}^r [D_{ab}\mathbf{d}_b + \mu_{ab}(\mathbf{F} - \mathbf{F}_b)] \\
&\quad - \sum_{b=r+1}^{2r} [\vartheta_{ab}\chi_a + \varphi_{ab}(\nabla^2\mathbf{F}_b + 2\nabla\mathbf{V}\cdot\mathbf{F}_b)], \\
&\quad (1 \leq a \leq r),
\end{aligned} \tag{9.207}$$

$$\begin{aligned}
\mathbf{Q}'_a q(\kappa) &= - \sum_{b=1}^r [p\vartheta_{ab}\rho_b^{-1}\mathbf{d}_b + \vartheta_{ab}(\mathbf{F} - \mathbf{F}_b)] \\
&\quad - \sum_{b=r+1}^{2r} [\lambda_{ab}\chi_a + \phi_{ab}(\nabla^2\mathbf{F}_b + 2\nabla\mathbf{V}\cdot\mathbf{F}_b)], \\
&\quad (r+1 \leq a \leq 2r).
\end{aligned} \tag{9.208}$$

These transport coefficients satisfy the Onsager reciprocal relations [35] as is clear from their definitions given in terms of the collision bracket integrals. Such symmetry relations essentially originate from the microscopic reversibility of the BNUU collision integral (9.34) in the kinetic equation. We reiterate that the evolution equations considered here keep the calortropy production σ_c in (9.155) positive. To prepare for the derivation of the nonlinear transport coefficients, we first recast the dissipation function κ^2 by using the definitions (9.179), (9.184), and (9.185) together with the approximations for X_{ka} in Table 9.2. It is given by the quadratic form

$$\kappa^2 = \beta g \sum_{a=1}^r \sum_{b=1}^r (K_{ab}\mathbf{Q}'_a \cdot \mathbf{Q}'_b + 2L_{ab}\mathbf{J}_a \cdot \mathbf{Q}'_b + \zeta_{ab}\mathbf{J}_a \cdot \mathbf{J}_b). \tag{9.209}$$

This is in essence the Rayleigh dissipation function [34] for the processes under consideration. In matrix form, it may be written as

$$\kappa^2 = \beta g \mathbf{V}^t \mathbf{M} \mathbf{V}. \tag{9.210}$$

In this notation the quasi-linear set (9.207) and (9.208) can be written as

$$\mathbf{M} \mathbf{V} = q(\kappa)^{-1} \mathbf{X}. \tag{9.211}$$

To solve this quasi-linear system for \mathbf{V} , multiplying $\beta g \mathbf{V}^t$ to this equation from left and using (9.211) again, we obtain the Rayleigh dissipation function in the form

$$\kappa^2 = q(\kappa)^{-1} \beta g \mathbf{V}^t \mathbf{X} = q(\kappa)^{-2} \beta g \mathbf{X}^t \mathbf{M}^{-1} \mathbf{X}. \quad (9.212)$$

Note that $\mathbf{M}^t = \mathbf{M}$ by the Onsager reciprocal relations satisfied by \mathbf{K} , \mathbf{L} , and ζ . By using the definition of $q(\kappa)$, (9.212) can be rearranged into the form

$$\sinh^2 \kappa = \beta g \mathbf{X}^t \mathbf{M}^{-1} \mathbf{X}. \quad (9.213)$$

This means that the dissipation function may be written in terms of the quadratic form $\mathbf{X}^t \mathbf{M}^{-1} \mathbf{X}$ as

$$\kappa = \sinh^{-1} \sqrt{\beta g \mathbf{X}^t \mathbf{M}^{-1} \mathbf{X}}. \quad (9.214)$$

Therefore the solution to the quasi-linear set (9.207) and (9.208) is

$$\mathbf{V} = \mathbf{M}^{-1} \mathbf{X} q_e, \quad (9.215)$$

where q_e is the abbreviation for the nonlinear factor

$$q_e = \frac{\sinh^{-1} \sqrt{\beta g \mathbf{X}^t \mathbf{M}^{-1} \mathbf{X}}}{\sqrt{\beta g \mathbf{X}^t \mathbf{M}^{-1} \mathbf{X}}}. \quad (9.216)$$

Here \mathbf{M}^{-1} is basically a matrix of linear transport coefficients. With this nonlinear factor and in view of the linear transport coefficients defined in (9.196)–(9.201), nonlinear transport coefficients can be naturally defined from (9.168) as follows:

$$\begin{aligned} D_{ab}^n &= D_{ab} q_e, & \mu_{ab}^n &= \mu_{ab} q_e, \\ \vartheta_{ab}^n &= \vartheta_{ab} q_e, & \lambda_{ab}^n &= \lambda_{ab} q_e, \\ \varphi_{ab}^n &= \varphi_{ab} q_e, & \phi_{ab}^n &= \phi_{ab} q_e. \end{aligned} \quad (9.217)$$

These nonlinear transport coefficients depend on the thermodynamic forces through the nonlinear factor q_e . It must be noted that as $\|\mathbf{X}\| \rightarrow \infty$, the nonlinear transport coefficients D_{ab}^n and so on vanish as $\|\mathbf{X}\|^{-1+\epsilon}$ ($\epsilon > 0$).

9.11 Collision Bracket Integrals for Heat and Mass Transports

The quantum collision bracket integrals presented in the previous section can be cast into readily calculable forms for the case of heat and mass transports once the collision cross section is given for the system. In these

collision bracket integrals the quantum effects are also contained in the Fermi–Dirac or Bose–Einstein distribution functions appearing in them; see (9.106) and (9.162). Since it will be convenient to use reduced variables, the transition rate is reduced to a dimensionless form as follows:

$$\bar{W}_{ab}^{(\epsilon)} = \left[\frac{m_a m_b \beta}{m_a + m_b} \right]^{1/2} (\pi \sigma^2)^{-1} W^{(\epsilon)}(\mathbf{v}_a \mathbf{v}_b | \mathbf{v}_a^* \mathbf{v}_b^*), \quad (9.218)$$

where $\pi \sigma^2$ represents a mean cross section. It is useful to define the quantity

$$S_{ab} = G_a G_b \frac{\sigma^2 g \beta^{3/2}}{8\pi^2} \left(\frac{2\pi m_a}{\beta h^2} \right)^{3/2} \left(\frac{2\pi m_b}{\beta h^2} \right)^{3/2}. \quad (9.219)$$

Observe that there holds the collision invariant

$$m_a \mathbf{C}_a + m_b \mathbf{C}_b - m_a \mathbf{C}_a^* - m_b \mathbf{C}_b^* = 0.$$

Then, with the abbreviation for reduced enthalpy $\bar{e}_a = \hat{h}_a m_a \beta$ and the reduced integrals

$$\int d\hat{\Gamma}_{ab} \dots = \int d\mathbf{w}_a \int d\mathbf{w}_{a'} \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta \bar{W}_{ab}^{(\epsilon)}(\mathbf{w}_a, \mathbf{w}_b) \dots, \quad (9.220)$$

the quantum collision bracket integrals associated with heat and mass transports are given as follows:

$$\begin{aligned} R_{aa}^{(33)} &= \frac{k_B T}{24m_a} S_{aa} \int d\hat{\Gamma}_{aa'} f_a^0 (1 + \epsilon_a f_a^0) f_{a'}^0 (1 + \epsilon_{a'} f_{a'}^0) \\ &\quad \times \Delta(w^2 \mathbf{w})_{aa'} \cdot \Delta(w^2 \mathbf{w})_{aa'} \\ &+ \frac{k_B T}{6m_a} \sum_{a \neq b}^r S_{ab} \int d\hat{\Gamma}_{ab} f_a^0 (1 + \epsilon_a f_a^0) f_b^0 (1 + \epsilon_b f_b^0) \\ &\quad \times \Delta\left[\left(\frac{w^2}{2} - \bar{e}\right) \mathbf{w}\right]_a \cdot \Delta\left[\left(\frac{w^2}{2} - \bar{e}\right) \mathbf{w}\right]_b, \end{aligned} \quad (9.221)$$

$$\begin{aligned} R_{ab}^{(33)} &= \frac{(k_B T)^3}{3\sqrt{m_a m_b}} S_{ab} \int d\hat{\Gamma}_{ab} f_a^0 (1 + \epsilon_a f_a^0) f_b^0 (1 + \epsilon_b f_b^0) \\ &\quad \times \Delta\left[\left(\frac{w^2}{2} - \bar{e}\right) \mathbf{w}\right]_a \cdot \Delta\left[\left(\frac{w^2}{2} - \bar{e}\right) \mathbf{w}\right]_b, \end{aligned} \quad (9.222)$$

$$R_{ab}^{(43)} = \frac{\sqrt{m_a} (k_B T)^2}{3\sqrt{m_b}} S_{ab} \int d\hat{\Gamma}_{ab} f_a^0 (1 + \epsilon_a f_a^0) f_b^0 (1 + \epsilon_b f_b^0)$$

$$\times (\mathbf{w}_a - \mathbf{w}_a^*) \cdot \Delta \left[\left(\frac{w^2}{2} - \bar{e} \right) \mathbf{w} \right]_b, \quad (9.223)$$

$$R_{aa}^{(44)} = \frac{m_a k_B T}{6} \sum_{a \neq b} S_{ab} \int d\hat{\Gamma}_{ab} f_a^0 (1 + \epsilon_a f_a^0) f_b^0 (1 + \epsilon_b f_b^0) \\ \times (\mathbf{w}_a - \mathbf{w}_a^*) \cdot (\mathbf{w}_a - \mathbf{w}_a^*), \quad (9.224)$$

$$R_{ab}^{(44)} = \frac{k_B T}{3} (m_a m_b)^{1/2} S_{ab} \int d\hat{\Gamma}_{ab} f_a^0 (1 + \epsilon_a f_a^0) f_b^0 (1 + \epsilon_b f_b^0) \\ \times (\mathbf{w}_a - \mathbf{w}_a^*) \cdot (\mathbf{w}_b - \mathbf{w}_b^*). \quad (9.225)$$

In these expressions the following abbreviations are used:

$$\Delta(w^2 \mathbf{w})_{aa'} = w_a^2 \mathbf{w}_a + w_{a'}^2 \mathbf{w}_{a'} - w_a^{*2} \mathbf{w}_a^* - w_{a'}^{*2} \mathbf{w}_{a'}^*, \quad (9.226)$$

$$\Delta \left[\left(\frac{w^2}{2} - \bar{e} \right) \mathbf{w} \right]_a = \left(\frac{w_a^2}{2} - \bar{e}_a \right) \mathbf{w}_a - \left(\frac{w_a^{*2}}{2} - \bar{e}_a \right) \mathbf{w}_a^*. \quad (9.227)$$

In (9.221) the prime on subscript a means another particle of species a . These collision bracket integrals can be readily calculated numerically when the collision cross section is supplied. This part of calculation requires a suitable modeling of the collision process of interest and will be left to specific applications of the theory.

9.12 Applicability to Radiation Kinetic Theory

The theory developed here can be readily applied to a system consisting of matter and radiation (photons) in nonequilibrium, if photons are treated as non-interacting particles obeying the Bose-Einstein statistics. If photons are in nonequilibrium as in many practically interesting cases, then a kinetic equation for nonequilibrium photons can be assumed to obey the kinetic equation postulated in this work, and it is possible to derive radiation hydrodynamics equations as in [19] and [20]. Since they can be obtained by transcribing the generalized hydrodynamics equations already presented to the case of radiation we will not pursue the derivation here.

It is also possible to apply the theory to a system of electrons (or holes) and phonons in a manner similar to the matter-radiation system mentioned. This line of applications is rather interesting since much of semiconductor physics or solid state physics in general falls into this category. The theory developed here can be applied quite successfully as shown in

[16] since transport processes in such systems are often nonlinear and the present theory provides thermodynamically consistent descriptions of such nonlinear processes. For lack of space such theories are not developed here. Applications of the present theory to radiation and semiconductor transport processes are left to the reader and future works.

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10

Nonequilibrium Ensemble Method for Dense Fluids

The Boltzmann kinetic theory for dilute gases which we have used to develop the nonequilibrium ensemble method in the previous chapters has taught us a lesson about the kinetic theory of irreversible processes and provided us with a paradigm for the treatment of such processes in dense and complex fluids. The Boltzmann kinetic theory is based on a time reversal symmetry breaking irreversible kinetic equation. It is an evolution equation for singlet distribution functions for a system which consists of statistically uncorrelated subunits made up of a single particle and evolves through binary encounters of the subunits in phase space. The crucial point of the theory is that the kinetic equation is irreversible, in sharp contrast to the Newtonian dynamics or the quantum dynamics on which the underlying particulate evolution of the subunits is based. We consider this feature essential to any kinetic theory aspiring to transcend the level of density to which the Boltzmann kinetic theory is limited. There are two basic premises that have to do with the density limitation of the Boltzmann kinetic theory. They are the statistically uncorrelated subunits of a single particle and binary encounters of subunits. Of these two basic premises the former has a deeper physical significance than the latter from the statistical viewpoint; it suggests that a subunit consisting of a single particle with which the subunit—the particle—in question is interacting via a binary collision can serve as a model for the rest of the system which may double as a heat reservoir. This picture, when the second premise regarding the binary encounters is removed so as to include encounters involving many subunits, can be readily generalized to a situation where the subunits no longer consist of a single particle, but may contain many particles. We have also learned that when a formal theory of irreversible processes is the principal aim the details of the collision term in the Boltzmann kinetic equation are not all that crucial to have at the stage of structuring such a formal theory. All that is necessary for the purpose is that the collision term satisfies a set of conditions which guarantee the conservation laws of mass, momentum, and energy and the H theorem for the Boltzmann entropy. In the case of dilute gases, with a kinetic equation satisfying such conditions and with the help of the phenomenological theory of irreversible processes constructed on the basis of the thermodynamic laws, it was pos-

sible to develop a nonequilibrium ensemble method in parallel with the Gibbs equilibrium ensemble method [1–4]. The details of the collision term in the kinetic equation become important when the transport processes in the nonequilibrium system are studied and compared with experiments. Transport processes are those on which experimental measurements are made and hence the testing ground for the quality of the collision terms representing dynamical mechanisms in the system at the molecular level. In this chapter the paradigm acquired from the aforementioned lessons is shown to remain valid for dense fluids since a formal theory of irreversible processes and an accompanying nonequilibrium ensemble method can be formulated in the same form as for the case of dilute gases. For the sake of simplicity we will confine the discussion to the case of simple dense fluids consisting of monatomic molecules. The generalization of the results presented in this chapter can be straightforwardly made to more complex fluids with internal degrees of freedom, if the techniques described for simple dense fluids can be made use of in treating the internal degrees of freedom. Such generalizations therefore are left to the reader as exercises.

10.1 Irreversible Kinetic Equation

We consider a fluid composed of a non-reacting mixture of N_1, N_2, \dots, N_r monatomic molecules in volume V . This volume exchanges matter as well as energy with its surroundings. Therefore the numbers mentioned are not fixed and hence the system is open. The species will be distinguished by subscripts a, b, \dots , and the particles of species will be denoted by subscripts i, j, \dots . For example, the composite subscript ja denotes particle $j \in a$. The position and conjugate momentum vectors of particle ja will be denoted by \mathbf{r}_{ja} and \mathbf{p}_{ja} , respectively. It will be convenient to abbreviate the phases by $x_{ja} = (\mathbf{p}_{ja}, \mathbf{r}_{ja})$ and so on and the total phase by $x^{(N)} = (x_1^{(N_1)}, \dots, x_r^{(N_r)})$ where $N = (N_1, N_2, \dots, N_r)$ and $x_a^{(N_a)} = (x_{1a}, \dots, x_{N_aa})$. The Liouville operator for the system consisting of N particles is then defined by

$$\begin{aligned} L^{(N)} &= \sum_{a=1}^r \sum_{ja=1}^{N_a} \left[\mathbf{v}_{ja} \cdot \nabla_{ja} + \frac{1}{2} \sum_{b=1}^r \sum_{kb=1}^{N_b} \mathbf{F}_{jakb}(\mathbf{r}_{jakb}) \cdot (\nabla_{\mathbf{p}_{ja}} - \nabla_{\mathbf{p}_{kb}}) \right] \\ &\quad + \sum_{a=1}^r \sum_{ja=1}^{N_a} m_a \mathbf{F}_a(\mathbf{r}_{ja}) \cdot \nabla_{\mathbf{p}_{ja}}, \end{aligned} \tag{10.1}$$

where $\mathbf{v}_{ja} = \mathbf{p}_{ja}/m_a$, m_a being the mass of species a ,

$$\mathbf{r}_{jakb} = \mathbf{r}_{ja} - \mathbf{r}_{kb},$$

$$\begin{aligned}
\nabla_{ja} &= \frac{\partial}{\partial \mathbf{r}_{ja}}, \\
\nabla_{\mathbf{p}_{ja}} &= \frac{\partial}{\partial \mathbf{p}_{ja}}, \\
\mathbf{F}_{jakb}(\mathbf{r}_{jakb}) &= -\frac{\partial}{\partial \mathbf{r}_{jakb}} V_{jakb}(\mathbf{r}_{jakb})
\end{aligned} \tag{10.2}$$

with $V_{jakb}(\mathbf{r}_{jakb})$ denoting the intermolecular potential energy of particle pair (ja, kb) and $\mathbf{F}_a(\mathbf{r}_{ja})$ the external force on a unit mass of particle ja at \mathbf{r}_{ja} . The external forces are assumed to be varying slowly over the range of intermolecular interaction. It will be convenient to abbreviate the Hamiltonian of molecule ja by H'_{ja} :

$$H'_{ja} = \frac{1}{2} m_a C_{ja}^2 + \frac{1}{2} \sum_{b=1}^r \sum_{\substack{k=1 \\ (kb \neq ja)}}^{N_b} V_{jakb} \tag{10.3}$$

with \mathbf{C}_{ja} denoting the peculiar velocity of particle ja defined by

$$\mathbf{C}_{ja} = \mathbf{v}_{ja} - \mathbf{u}. \tag{10.4}$$

The kinetic energy is defined relative to the frame of reference moving at fluid velocity \mathbf{u} .

Since the number of particles in the system changes as it interacts with the surroundings, it is not even possible to describe the dynamical evolution of the system in a single phase space of a fixed dimension. This difficulty is overcome if an ensemble is constructed which is made up of representative systems distributed over all possible values of N . There are \mathcal{N} representative systems in the ensemble ($\mathcal{N} \rightarrow \infty$). The ensemble is an isolated supersystem consisting of the representative systems. It is called a grand ensemble in the sense of the term originally used by Gibbs [1]. It consists of petit ensembles of fixed values of N and V which are therefore closed. The members of a petit ensemble are now equipped with the phase space of a fixed dimension corresponding to the value of N . The members of various petit ensembles weakly interact among themselves and with the members belonging to other petit ensembles in the grand ensemble. It is now appropriate to consider the distribution function for a representative system (subsystem) to acquire a value of N and phase $x^{(N)}$ corresponding to N . The N particle distribution function will be denoted by $F^{(N)}(x^{(N)}; t)$.

To help us see the required structure of the kinetic equation for the distribution function, it is useful to examine the Boltzmann equation or, more generally, (3.27). In the notation used in Sec. 7.11 the kinetic equation (3.27), specialized to a single-component gas for the simplicity of discussion,

can be written in the form

$$(\partial_t + \mathbf{v}_j \cdot \nabla + \mathbf{F}_j \cdot \nabla_{\mathbf{v}_j}) F_j(x_j; t) = \sum_k C_{jk} (F_j F_k), \quad (10.5)$$

where

$$C_{jk} (F_j F_k) = V^{-1} \int d\mathbf{v}_k \int_0^{2\pi} d\varphi \int_0^\infty db \, b g_{jk} (F_j^* F_k^* - F_j F_k). \quad (10.6)$$

The notation used is standard¹. It is convenient to cast this Boltzmann collision integral in an equivalent form

$$C_{jk} (F_j F_k) = V^{-1} \int dx_k (-i) T_{jk} F_j F_k, \quad (10.7)$$

where $i = \sqrt{-1}$ and T_{jk} is the classical two-body collision operator obeying the classical Lippmann–Schwinger equation. See [5] for the details of the classical collision operator. Let us imagine a set of particles that includes particle j , but not particle k with which particle j collides. This set contains N particles and will be designated as set N . Also imagine another set of N' particles which includes particle k . This set will be designated as set N' . The two sets do not intersect, that is, do not share a particle. The distribution functions of sets N and N' will be denoted respectively by $F_0^{(N)}(x^{(N)}; t)$ and $F_0^{(N')}(x^{(N')}; t)$ which are products of singlet distribution functions:

$$F_0^{(N)}(x^{(N)}; t) = \prod_{l=1}^N V^{-1} F_l(x_l; t), \quad F_0^{(N')}(x^{(N')}; t) = \prod_{m=1}^{N'} V^{-1} F_m(x_m; t). \quad (10.8)$$

Note that the phases of these two distribution functions are not the same. The kinetic equation for $F_0^{(N)}(x^{(N)}; t)$ can be easily obtained from (10.5):

$$\left(\partial_t + L_0^{(N)} \right) F_0^{(N)}(x^{(N)}; t) = \sum_{j,k} R_{jk} \left[F_0^{(N)} F_k \right], \quad (10.9)$$

where $L_0^{(N)}$ is the Liouville operator for noninteracting particles, namely, $L^{(N)}$ with all intermolecular forces \mathbf{F}_{jk} in (10.1) set equal to zero and $R_{jk} \left[F_0^{(N)} F_k \right]$ is the Boltzmann collision integral recast in the form

$$R_{jk} \left[F_0^{(N)} F_k \right] = V^{-1} \int dx_k (-i) T_{jk} F_0^{(N)}(x^{(N)}; t) F_k(x_k; t). \quad (10.10)$$

¹When the Boltzmann equation is written in this form in the phase space, it is presumed that distribution functions are coarse-grained over the collision volume.

Written as in (10.9), the kinetic equation (3.27) can be regarded as an evolution equation for a subsystem made up of N statistically uncorrelated particles interacting with another subsystem consisting of a single particle. This latter subsystem may be replaced with a larger system consisting of more than one particle, say, the set N' mentioned earlier. With this set taken into consideration, it is easy to cast (10.10) in the form

$$R_{jk} \left[F_0^{(N)} F_0^{(N')} \right] = \int dx^{(N')} (-i) T_{jk} F_0^{(N)}(x^{(N)}; t) F_0^{(N')}(x_k^{(N')}; t), \quad (10.11)$$

where

$$dx^{(N')} = dx_k \prod_{m \neq k}^{N'} dx_m.$$

Written in this form, $R_{jk} \left[F_0^{(N)} F_0^{(N')} \right]$ describes the collisional evolution of two sets N and N' (subsystems) where the interaction between them is via the two-body collision operator T_{jk} of particles j and k . These two-body collision operators T_{jk} now may be regarded as the leading terms in the cluster expansion [5] of a many-body collision operator for a supersystem consisting of \mathcal{N} subsystems distributed over various values of N . Then we may write (10.9) in a more general form

$$\left(\partial_t + L_0^{(N)} \right) F_0^{(N)}(x^{(N)}; t) = R \left[F_0^{(N)} F_0^{(N')} \dots \right], \quad (10.12)$$

where

$$R \left[F_0^{(N)} F_0^{(N')} \dots \right] = \int dx^{(\mathcal{N}-N)} (-i) T^{(\mathcal{N})} F_0^{(N)} F_0^{(N')} \dots \quad (10.13)$$

with $T^{(\mathcal{N})}$ denoting the collision operator for the supersystem of \mathcal{N} subsystems, and $dx^{(\mathcal{N}-N)}$ is the phase volume element of the supersystem excluding the set N . This kinetic equation reduces to the Boltzmann equation if the cluster expansion of $T^{(\mathcal{N})}$ in a series of density is truncated at the leading order. Therefore the Boltzmann equation is seen as a special case of (10.12) holding at low densities. This kinetic equation (10.12) is very suggestive for kinetic theory of dense fluids.

On the basis of the clues provided by the Boltzmann kinetic theory and of the argument given above, we now assume that the dense fluid kinetic equation is given by the equation

$$\left(\partial_t + L^{(N)} \right) F^{(N)}(x^{(N)}; t) = \mathfrak{R} \left[F^{(N)} \right], \quad (10.14)$$

where $\mathfrak{R} \left[F^{(N)} \right]$ is the collision term. It may depend on the distribution functions for other values of N but only $F^{(N)}$ is made explicit for brevity of notation. We furthermore require that $\mathfrak{R} \left[F^{(N)} \right]$ is such that the kinetic

equation (10.14) has a broken time reversal symmetry. That is, if the directions of time and velocity are reversed, namely, if the time reversal operator ϑ is applied, the collision term is such that the kinetic equation becomes

$$\left[\partial_{-t} + \vartheta L^{(N)} \right] F^{(N)}(\vartheta x^{(N)}; -t) = -\Re \left[F^{(N)} \left(\vartheta x^{(N)}; -t \right) \right]. \quad (10.15)$$

Note that $\vartheta L^{(N)}(\mathbf{p}^{(N)}) = L^{(N)}(-\mathbf{p}^{(N)})$ and $\vartheta x^{(N)} = (-\mathbf{p}^{(N)}, \mathbf{r}^{(N)})$. This property is also shared by the Boltzmann kinetic equation which is irreversible; see (3.25). The collision term also must satisfy additional conditions regarding the conservation laws. To state these conditions explicitly in mathematical form, we denote collectively the mass, momentum, and energy densities by

$$I(x^{(N)}; \mathbf{r}) = \sum_{a=1}^r \sum_{ja=1}^{N_a} I_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \quad (10.16)$$

and then demand the collision term to satisfy:

Condition 1

$$\int_V d\mathbf{r} \sum_{\{N\} \geq 0} \int dx^{(N)} \sum_{a=1}^r \sum_{ja=1}^{N_a} I_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \Re \left[F^{(N)} \right] = 0. \quad (10.17)$$

Condition 2

$$-\sum_{\{N\} \geq 0} \int dx^{(N)} \ln F^{(N)}(x^{(N)}; t) \Re \left[F^{(N)} \right] \geq 0 \quad (10.18)$$

with the equality holding for equilibrium only. At equilibrium

$$\Re \left[F_{\text{eq}}^{(N)} \right] = 0. \quad (10.19)$$

Condition 3 It is invariant under canonical transformations.

Here $\{N\}$ denotes the set (N_1, N_2, \dots, N_r) , the sum over $\{N\}$ is over all possible values of the elements of the set, and $dx^{(N)}$ stands for the phase volume element:

$$dx^{(N)} = d\mathbf{p}^{(N)} d\mathbf{r}^{(N)} = \prod_{a=1}^r \prod_{ja=1}^{N_a} d\mathbf{p}_{ja} d\mathbf{r}_{ja}.$$

The first condition guarantees the conservation laws of mass, momentum, and energy. Note that I_{ja} can be equal to unity. The second condition assures the existence of the Boltzmann entropy satisfying the H theorem and consequently the asymptotic stability of equilibrium characterized by $F_{\text{eq}}^{(N)}$. The third condition facilitates use of analytical dynamics techniques when

the dynamics of collision is considered for the collision term. Recall that these conditions are also met by the Boltzmann kinetic equation and many variants of it known in the literature. We reiterate that the Boltzmann equation is a fundamental evolution equation for the probability distribution function of a system consisting of statistically uncorrelated subunits each of which is made up of a single particle. It is not derivable from the basically time reversal invariant Newtonian dynamical equations of motion for the system consisting of the same subunits mentioned if one takes the strict sense of word for the term derivation. The kinetic equation (10.14) is a fundamental postulate in the same spirit as taken for the Boltzmann equation in the present work. If the collision term is set equal to zero, then the kinetic equation becomes the time reversal invariant Liouville equation. In the Gibbs ensemble theory [1–4], the Liouville equation is considered at the stationary state and an equilibrium distribution function is constructed to satisfy the stationary Liouville equation. The kinetic equation (10.14) is inclusive of the equilibrium Gibbs ensemble theory in which only equilibrium is of interest since at equilibrium (10.19) holds and

$$\frac{\partial F_{\text{eq}}^{(N)}}{\partial t} = 0.$$

The phase space average henceforth will be abbreviated by angular brackets:

$$\left\langle F^{(N)} M \left(x^{(N)}; t \right) \right\rangle = \sum_{\{N\} \geq 0} \int_V dx^{(N)} F^{(N)} \left(x^{(N)}; t \right) M \left(x^{(N)}; t \right). \quad (10.20)$$

We define various conserved and nonconserved variables which will be used in the development of theory in this chapter:

mass density:

$$\begin{aligned} \rho(\mathbf{r}, t) &= \sum_{a=1}^r \rho_a(\mathbf{r}, t) \\ &= \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} m_a \delta(\mathbf{r}_{ja} - \mathbf{r}) F^{(N)} \right\rangle, \end{aligned} \quad (10.21)$$

momentum density:

$$\begin{aligned} \rho \mathbf{u}(\mathbf{r}, t) &= \sum_{a=1}^r \rho_a \mathbf{u}_a(\mathbf{r}, t) \\ &= \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} m_a \mathbf{v}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) F^{(N)} \right\rangle, \end{aligned} \quad (10.22)$$

energy density:

$$\rho \mathcal{E}(\mathbf{r}, t) = \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} H'_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) F^{(N)} \right\rangle. \quad (10.23)$$

It is also convenient to define a generalized virial tensor operator \mathbf{W}_{jakb} by the formula

$$\mathbf{W}_{jakb} = \int_0^1 d\lambda \mathbf{r}_{jakb} \mathbf{F}_{jakb} \exp(-\lambda \mathbf{r}_{jakb} \cdot \nabla). \quad (10.24)$$

This tensor operator acts on delta function $\delta(\mathbf{r}_{kb} - \mathbf{r})$. We then define the diffusion fluxes, stress (pressure) tensor, and heat flux as follows:

diffusion fluxes:

$$\mathbf{J}_a = \left\langle \sum_{ja=1}^{N_a} m_a \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) F^{(N)} \right\rangle, \quad (10.25)$$

stress tensor:

$$\begin{aligned} \mathbf{P} &= \mathbf{P}_k + \mathbf{P}_v \\ &= \sum_{a=1}^r \left(\mathbf{P}_a^{(k)} + \mathbf{P}_a^{(v)} \right), \end{aligned} \quad (10.26)$$

$$\begin{aligned} \mathbf{P}_k &= \sum_{a=1}^r \mathbf{P}_a^{(k)} \\ &= \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} m_a \mathbf{C}_{ja} \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) F^{(N)} \right\rangle, \end{aligned} \quad (10.27)$$

$$\begin{aligned} \mathbf{P}_v &= \sum_{a=1}^r \mathbf{P}_a^{(v)} \\ &= \left\langle \frac{1}{2} \sum_{a,b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) F^{(N)} \right\rangle_{(ja \neq kb)}, \end{aligned} \quad (10.28)$$

heat flux:

$$\begin{aligned} \mathbf{Q} &= \mathbf{Q}_h + \mathbf{Q}_v \\ &= \sum_{a=1}^r \left(\mathbf{Q}_a^{(h)} + \mathbf{Q}_a^{(v)} \right), \end{aligned} \quad (10.29)$$

$$\begin{aligned} \mathbf{Q}_h &= \sum_{a=1}^r \mathbf{Q}_a^{(h)} \\ &= \left\langle \sum_{a=1}^r \sum_{j=1}^{N_a} H'_{ja} \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) F^{(N)} \right\rangle, \end{aligned} \quad (10.30)$$

$$\begin{aligned} \mathbf{Q}_v &= \sum_{a=1}^r \mathbf{Q}_a^{(v)} \\ &= \left\langle \frac{1}{2} \sum_{a,b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \mathbf{W}_{jakb} \cdot \mathbf{C}_{ja} \delta(\mathbf{r}_{kb} - \mathbf{r}) F^{(N)} \right\rangle_{(ja \neq kb)}. \end{aligned} \quad (10.31)$$

The intermolecular interaction energy part \mathbf{P}_v of stress tensor \mathbf{P} did not appear in the case of dilute gases. The virial tensor contribution \mathbf{Q}_v of heat flux \mathbf{Q} represents a flow of energy in excess of the potential energy flow contained in \mathbf{Q}_h and accounts for the flow of energy arising from the work of the intermolecular forces. This component is not obvious in the phenomenological theory. It is possible to derive the balance equations for the conserved variables from the kinetic equation (10.1) by using the statistical definitions (10.21)–(10.31) and the method of Irving and Kirkwood [6]. We will show their derivations in the subsequent section, but the results are collected as a set in the following:

$$\partial_t \rho = -\nabla \cdot \rho \mathbf{u} \quad or \quad \rho d_t v = \nabla \cdot \mathbf{u}, \quad (10.32)$$

$$\rho d_t c_a = -\nabla \cdot \mathbf{J}_a, \quad (10.33)$$

$$\rho d_t \mathbf{u} = -\nabla \cdot \mathbf{P} + \rho \mathbf{F}, \quad (10.34)$$

$$\rho d_t \mathcal{E} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a, \quad (10.35)$$

where v is the specific volume defined by $v = \rho^{-1}$, d_t is an abbreviation for the substantial time derivative, c_a is the mass fraction of a defined by $c_a = \rho_a / \rho$, and

$$\rho \mathbf{F} = \sum_{a=1}^r \rho_a \mathbf{F}_a. \quad (10.36)$$

We remark that the conservation laws (10.32)–(10.35) are in exactly the same forms as for dilute gases despite the fact that the fluid under consideration is dense. Of course, the statistical definitions for macroscopic variables involved appear appropriately generalized in them. We collectively denote nonconserved moment densities such as the stress tensors, heat fluxes, diffusion fluxes, and so on of various species by

$$\bar{h}_a^{(q)} = \sum_{ja=1}^{N_a} h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \quad (q \geq 1) \quad (10.37)$$

and its mean value by

$$\Phi_{qa} = \rho \hat{\Phi}_{qa} = \left\langle \sum_{ja=1}^{N_a} h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) F^{(N)} \right\rangle. \quad (10.38)$$

Here the symbols Φ_{qa} have the same meaning and are ordered in the same manner as in the previous chapters; see, for example, Sec. 2.3. The evolution equations for Φ_{qa} can be derived from the kinetic equation and the statistical formula (10.38):

$$\rho d_t \hat{\Phi}_{qa} = -\nabla \cdot \psi_{qa} + \mathcal{Z}_{qa} + \Lambda_{qa}, \quad (10.39)$$

where the dissipation term Λ_{qa} is defined by

$$\Lambda_{qa} = \left\langle \sum_{ja=1}^{N_a} h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \Re[F^{(N)}] \right\rangle, \quad (10.40)$$

the kinematic term \mathcal{Z}_{qa} by

$$\mathcal{Z}_{qa} = \left\langle \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathcal{D}_t^{(N)} h_{ja}^{(q)} \right\rangle, \quad (10.41)$$

with operator $\mathcal{D}_t^{(N)}$ denoting the operator sum

$$\mathcal{D}_t^{(N)} = d_t + L^{(N)} + \mathbf{C}_{ja} \cdot \nabla, \quad (10.42)$$

and the higher order moment ψ_{qa} by the statistical formula

$$\psi_{qa} = \left\langle \sum_{ja=1}^{N_a} \mathbf{C}_{ja} h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) F^{(N)} \right\rangle. \quad (10.43)$$

The leading examples are: for the traceless part $\Phi_{1a} = \Pi_a$ of the stress tensor of species a

$$\begin{aligned} h_{ja}^{(1)} \delta(\mathbf{r}_{ja} - \mathbf{r}) &= [m_a \mathbf{C}_{ja} \mathbf{C}_{ja}]^{(2)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \\ &+ \frac{1}{2} \sum_{b=1}^r \sum_{\substack{kb=1 \\ (ja \neq kb)}}^{N_b} [\mathbf{W}_{jakb}]^{(2)} \delta(\mathbf{r}_{kb} - \mathbf{r}); \end{aligned} \quad (10.44)$$

for the excess normal stress $\Phi_{2a} = \Delta_a$

$$\begin{aligned} h_{ja}^{(2)} \delta(\mathbf{r}_{ja} - \mathbf{r}) &= \left(\frac{1}{3} m_a C_{ja}^2 - m_a p_a \rho_a^{-1} \right) \delta(\mathbf{r}_{ja} - \mathbf{r}) \\ &+ \frac{1}{6} \sum_{b=1}^r \sum_{\substack{k=1 \\ (ja \neq kb)}}^{N_b} \text{Tr} \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}); \end{aligned} \quad (10.45)$$

for the heat flux $\Phi_{3a} = \mathbf{Q}'_a = \mathbf{Q}_a - \hat{h}_a \mathbf{J}_a$

$$\begin{aligned} h_{ja}^{(3)} \delta(\mathbf{r}_{ja} - \mathbf{r}) &= (H'_{ja} - m_a \hat{h}_a) \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \\ &+ \frac{1}{2} \sum_{b=1}^r \sum_{\substack{j=1 \\ (ja \neq kb)}}^{N_a} \sum_{k=1}^{N_b} \mathbf{W}_{jakb} \cdot \mathbf{C}_{ja} \delta(\mathbf{r}_{kb} - \mathbf{r}); \end{aligned} \quad (10.46)$$

and for the diffusion flux $\Phi_{3a} = \mathbf{J}_a$

$$h_{ja}^{(4)} \delta(\mathbf{r}_{ja} - \mathbf{r}) = m_a \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}). \quad (10.47)$$

Here p_a and \hat{h}_a denote the partial pressure and enthalpy per mass of a molecule of species a , respectively, and Tr stands for trace. We assume that there is a complete set of functions $h_{ja}^{(q)}$, $q \geq 1$, which are molecular expressions² for various nonconserved macroscopic observables. For the purpose of the formal theory of irreversible processes which we aim to construct in this chapter it is not necessary to explicitly work out these statistical formulas for ψ_{qa} , Z_{qa} , and Λ_{qa} in terms of macroscopic variables. In fact, it is counterproductive to work with a more explicit form for the evolution equation for $\hat{\Phi}_{qa}$ because they are very complicated in form and would defy the construction of a general theory out of them if they were more explicitly given in terms of conserved and nonconserved variables. Since the evolution equation for $\hat{\Phi}_{qa}$ is a constitutive equation, if transport properties of the fluid is desired, then explicit forms for the constitutive

²The simplest and most straightforward method of constructing the set of $h_{ja}^{(q)}$ is to start from the derivation of the conservation laws, which naturally suggest the statistical definitions for \mathbf{P} , \mathbf{Q} , and \mathbf{J}_a , and derive the evolution equations for \mathbf{P} , \mathbf{Q} , and \mathbf{J}_a which, in turn, naturally suggest the statistical expressions for the moments one order higher than their orders. With thus obtained statistical expressions for the high order moments, their evolution equations can be derived and so on. This process can be continued until a complete set of statistical expressions for moments is constructed. This procedure is mathematically naive, but practical if a small incomplete set of $h_{ja}^{(q)}$ is desired.

equations will be required. The examples for them are available in the literature; see, for example, [5]. Transport processes can be studied after the formal structure of irreversible thermodynamics is erected in a way consistent with the laws of thermodynamics. We would like to add the following remark regarding the evolution equations for the nonconserved variables (10.39). If the Irving–Kirkwood procedure [6] is used to derive the evolution equations for Φ_{qa} with the Liouville equation instead of the kinetic equation (10.14), then the dissipation term Λ_{qa} will be missing and there will be no energy dissipation mechanism in the theory formulated therewith. Of course, this also has to do with the absence of irreversibility in the Liouville equation.

It will be useful to work with an exponential form for the distribution function $F^{(N)}$

$$k_B \ln F^{(N)} = - \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} G_{ja}(x^{(N)}; t) \delta(\mathbf{r}_{ja} - \mathbf{r}), \quad (10.48)$$

where $G_{ja}(x^{(N)}; t)$ are well behaved phase functions representing the distribution function. This representation for $F^{(N)}$ makes it possible to cast the kinetic equation (10.14) in the following form:

$$- \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathcal{D}_t^{(N)} G_{ja} = k_B \mathfrak{R}[F^{(N)}]. \quad (10.49)$$

For this we have used the property of the Dirac delta function with regard to differentiation

$$\nabla_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) = -\nabla \delta(\mathbf{r}_{ja} - \mathbf{r}). \quad (10.50)$$

There appears a divergence term in the course of transforming the kinetic equation (10.14) into (10.49), but this term vanishes by virtue of the boundary condition on the distribution function that it vanishes at the boundaries:

$$\int_V d\mathbf{r} \nabla \cdot \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) G_{ja}(x^{(N)}; t) = 0. \quad (10.51)$$

This condition implies that there is no accumulation of particles at the boundaries. It is consistent with the implicit assumption made for the theory. This condition must be amended if the system of interest is finite and has an interface where particles get adsorbed. We remark that the condition does not mean that there are no fluxes at the boundaries.

Clearly, on integration over the phase space the kinetic equation vanishes on account of Condition 1 for the collision term $\mathfrak{R}[F^{(N)}]$:

$$\int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathcal{D}_t^{(N)} G_{ja} \right\rangle = k_B \langle \mathfrak{R}[F^{(N)}] \rangle = 0. \quad (10.52)$$

This property will be useful in discussions in this chapter. The phase space functions $G_{ja}(x^{(N)}; t)$ solve the kinetic equation subject to the boundary and initial conditions in the phase space.

10.2 Boltzmann Entropy and the H Theorem

The kinetic equation admits the Boltzmann entropy for which the H theorem is assured by Condition 2. The H theorem makes it possible to show the stability of the equilibrium solution $F_{\text{eq}}^{(N)}$ defined by (10.19). We will return to this question later. First, we define the Boltzmann entropy by the formula

$$S(t) = -k_B \left\langle F^{(N)}(x^{(N)}; t) \ln F^{(N)}(x^{(N)}; t) \right\rangle. \quad (10.53)$$

The Boltzmann entropy density $\mathcal{S}(\mathbf{r}, t)$ is defined by the integral relation

$$S(t) = \int_V d\mathbf{r} \rho \mathcal{S}(\mathbf{r}, t). \quad (10.54)$$

By using this relation and the exponential representation for $F^{(N)}$ in (10.48) we find the statistical formula for the Boltzmann entropy density

$$\rho \mathcal{S}(\mathbf{r}, t) = \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) G_{ja}(x^{(N)}; t) \right\rangle. \quad (10.55)$$

Differentiation of (10.53) with time and use of the kinetic equation (10.14) yield

$$\begin{aligned} \frac{dS}{dt} &= \int_V d\mathbf{r} \frac{\partial}{\partial t} \rho \mathcal{S}(\mathbf{r}, t) \\ &= \int_V d\mathbf{r} [-\nabla \cdot (\mathbf{J}_s + \mathbf{u} \rho \mathcal{S}) + \sigma_{\text{ent}}(\mathbf{r}, t)] \\ &\quad + \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathcal{D}_t^{(N)} G_{ja} \right\rangle, \end{aligned} \quad (10.56)$$

where the last term vanishes by virtue of (10.52) and the Boltzmann entropy flux \mathbf{J}_s and the Boltzmann entropy production σ_{ent} are respectively defined by the statistical formulas

$$\mathbf{J}_s(\mathbf{r}, t) = \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathbf{C}_{ja} G_{ja} \right\rangle, \quad (10.57)$$

$$\sigma_{\text{ent}}(\mathbf{r}, t) = \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} \delta(\mathbf{r}_{ja} - \mathbf{r}) G_{ja} \Re[F^{(N)}] \right\rangle. \quad (10.58)$$

Therefore we finally obtain the local balance equation for the Boltzmann entropy density

$$\rho d_t \mathcal{S}(\mathbf{r}, t) = -\nabla \cdot \mathbf{J}_s + \sigma_{\text{ent}}(\mathbf{r}, t). \quad (10.59)$$

Furthermore, by Condition 2 for $\Re[F^{(N)}]$ and by continuity in space there holds the inequality

$$\sigma_{\text{ent}}(\mathbf{r}, t) \geq 0. \quad (10.60)$$

This is the local form of the H theorem. The global Boltzmann entropy balance equation corresponding to (10.59) may be written in the form

$$\begin{aligned} \frac{dS}{dt} &= \frac{d_e S}{dt} + \frac{d_i S}{dt} \\ &\geq \frac{d_e S}{dt}, \end{aligned} \quad (10.61)$$

where

$$\frac{d_e S}{dt} = - \int_V d\mathbf{r} \nabla \cdot (\mathbf{J}_s + \mathbf{u} \rho \mathcal{S}), \quad (10.62)$$

$$\frac{d_i S}{dt} = \int_V d\mathbf{r} \sigma_{\text{ent}}(\mathbf{r}, t) \geq 0. \quad (10.63)$$

It must be noted, as in the case of dilute gas kinetic theories, that (10.61), despite the similarity in form to the Clausius inequality, does not represent the second law of thermodynamics in thermodynamic space. We will return to this aspect later in this chapter.

Since at equilibrium

$$\Re[F_{\text{eq}}^{(N)}] = 0$$

and, furthermore, by Condition 1 for $\Re[F^{(N)}]$, there holds the equation

$$\int_V d\mathbf{r} \sum_{\{N\} \geq 0} \int dx^{(N)} \sum_{a=1}^r \sum_{ja=1}^{N_a} I_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \Re[F_{\text{eq}}^{(N)}] = 0, \quad (10.64)$$

where

$$I_{ja} = m_a, \mathbf{p}_{ja}, \text{ or } H'_{ja}, \quad (10.65)$$

the vanishing Boltzmann entropy production at equilibrium $\sigma_{\text{ent}}(\mathbf{r}, t) = 0$ implies that $\ln F_{\text{eq}}^{(N)}$ must be a linear combination of the collision invariants listed above. Furthermore, this linear combination is unique since there are no other linearly independent linear combinations. This is a feature absent in the Gibbs equilibrium ensemble theory; in his theory $F_{\text{eq}}^{(N)}$ is a solution of $L^{(N)} F_{\text{eq}}^{(N)} = 0$ which only suggests that there are an infinite number of functions of constants of motion for $F_{\text{eq}}^{(N)}$. Since the external force is assumed to remain unchanged over the elementary volume around position \mathbf{r} , the external potential energy $U_a^{(\text{ex})}$ per molecule may be added to the

energy invariant. We thus write the equilibrium distribution function in the form

$$F_{\text{eq}}^{(N)} = c^{-1} \exp \left\{ - \int_V d\mathbf{r} \beta [H^{(N)}(\mathbf{r}) - \rho \mathcal{G}_e] - \ln \Xi_e \right\}. \quad (10.66)$$

Here, with N denoting $N = \sum_{a=1}^r N_a$ and h the Planck constant,

$$c = h^{3N} \prod_a N_a!, \quad (10.67)$$

$H^{(N)}(\mathbf{r})$ is the energy density defined by

$$\begin{aligned} H^{(N)}(\mathbf{r}) &= \sum_{a=1}^r \sum_{ja=1}^{N_a} H_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \\ &\equiv \sum_{a=1}^r \sum_{ja=1}^{N_a} \left(H'_{ja} + U_a^{(\text{ex})} \right) \delta(\mathbf{r}_{ja} - \mathbf{r}), \end{aligned} \quad (10.68)$$

$\mathcal{G}_e(\mathbf{r})$ may be written as

$$\mathcal{G}_e = \sum_{a=1}^r c_a \hat{\mu}_a^e, \quad (10.69)$$

and Ξ_e is the normalization factor defined by

$$\begin{aligned} \Xi_e &= \sum_{\{N\} \geq 0} c^{-1} \int dx^{(N)} \exp \left\{ - \int_V d\mathbf{r} \beta [H^{(N)}(\mathbf{r}) - \rho \mathcal{G}_e] \right\} \\ &\equiv \left\langle \exp \left\{ - \int_V d\mathbf{r} \beta [H^{(N)}(\mathbf{r}) - \rho \mathcal{G}_e] \right\} \right\rangle \\ &= \left\langle \exp \left[- \int_V d\mathbf{r} \beta \sum_{a=1}^r \sum_{ja=1}^{N_a} (H_{ja} - m_a \hat{\mu}_a^e) \delta(\mathbf{r}_{ja} - \mathbf{r}) \right] \right\rangle. \end{aligned} \quad (10.70)$$

The meaning of the angular brackets in (10.70) has slightly changed from their meaning in the previous chapters since the multiplication of the factor c^{-1} is implied this time. Henceforth, angular brackets associated with an exponential form for the distribution function should be understood in this sense. Since the variables such as β and $\hat{\mu}_a^e$ must be spatially uniform if the system is in equilibrium, the volume integral in (10.70) may be simply replaced by $V \beta (H^{(N)} - N \mathcal{G}_e)$ in that case.

The equilibrium state defined by $F_{\text{eq}}^{(N)}$ is stable and the variation of the Boltzmann entropy from $F_{\text{eq}}^{(N)}$ is a Lyapounov function [7] in the following sense. First, we define

$$\delta S = S(t) - S_e, \quad (10.71)$$

where S_e is defined by

$$S_e = -k_B \left\langle F^{(N)}(x^{(N)}; t) \ln F_{eq}^{(N)}(x^{(N)}) \right\rangle. \quad (10.72)$$

It then is possible to show that

$$\delta S \leq 0 \quad (10.73)$$

by Klein's inequality whereas by virtue of the H theorem and under the assumption that there is no contribution from the boundary term (see (10.62))

$$\frac{d\delta S}{dt} \geq 0. \quad (10.74)$$

This implies that δS may be regarded as a Lyapounov function and the state characterized by $F_{eq}^{(N)}$ is a stable stationary state³ asymptotically approached in time from a nonequilibrium state.

10.3 Evolution Equations

It is possible to derive evolution equations for various macroscopic variables such as mass, momentum, internal energy, and flux densities which will make it possible to describe irreversible processes in the fluid. We will describe the derivations of conservation equations for mass, momentum, and energy to illustrate the basic procedures necessary to obtain them from the kinetic equation. The procedure used is basically that of Irving and Kirkwood [6] who derived conservation equations from the Liouville equation. Similar procedures can then be applied to derive flux density evolution equations from the kinetic equation, when their explicit forms are necessary in their applications to study various macroscopic irreversible processes.

10.3.1 Equation of Continuity

Since the volume integral of the expression (10.21) for the mass density ρ gives the total mass M_V in the volume, its rate of change in time can be

³In the Gibbs ensemble theory this stable stationary state (*i.e.*, the statistical equilibrium state) is made coincide with the thermodynamic equilibrium state characterized by the Clausius entropy when thermodynamic correspondence is made between the statistical and thermodynamic equilibrium states in the limit of vanishing fluctuations in the intensive macroscopic variables (conjugate to energy, volume, and mass fractions) as will be elaborated in later sections, 10.4.4 and 10.5. This subtle distinction between the statistical and thermodynamic equilibrium states is important in understanding fluctuations.

calculated as follows:

$$\begin{aligned}\frac{dM_V}{dt} &= \int_V d\mathbf{r} \frac{\partial}{\partial t} \rho(\mathbf{r}, t) \\ &= \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} m_a \delta(\mathbf{r}_{ja} - \mathbf{r}) \frac{\partial}{\partial t} F^{(N)}(x^{(N)}; t) \right\rangle.\end{aligned}$$

On substituting the kinetic equation (10.14), integrating by parts, and using Condition 1 for $\Re[F^{(N)}]$, we obtain

$$\begin{aligned}\int_V d\mathbf{r} \frac{\partial}{\partial t} \rho(\mathbf{r}, t) &= \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} L^{(N)} m_a \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle \\ &= \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \mathbf{v}_{ja} \cdot \nabla_{ja} m_a \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle \\ &= - \int_V d\mathbf{r} \nabla \cdot \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \mathbf{v}_{ja} m_a \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle \\ &= - \int_V d\mathbf{r} \nabla \cdot \rho \mathbf{u},\end{aligned}\tag{10.75}$$

for which we have made use of the property (10.50) of the delta function under differentiation and the fact that by definition of diffusion fluxes

$$\sum_{a=1}^r \mathbf{J}_a = 0.\tag{10.76}$$

Since the velocity is assumed to vanish at the boundaries, the right hand side of (10.75) is equal to zero and

$$\frac{dM_V}{dt} = 0\tag{10.77}$$

indicating the mass conservation law. If there is a material flux at a boundary, then there will be a nonvanishing boundary term and (10.77) no longer holds. By virtue of continuity of macroscopic variables in space, we obtain the equation of continuity (10.32) from (10.75). The mass fraction balance equations (10.33) can be derived in exactly the same manner as for the equation of continuity.

10.3.2 Momentum Conservation Law

Let us denote the total momentum of the mass in volume V by \mathfrak{P}_V . Its rate of change in time is then given by

$$\frac{d\mathfrak{P}_V}{dt} = \int_V d\mathbf{r} \frac{\partial}{\partial t} \rho \mathbf{u}(\mathbf{r}, t)$$

$$= \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} m_a \mathbf{v}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \frac{\partial}{\partial t} F^{(N)}(x^{(N)}; t) \right\rangle. \quad (10.78)$$

On substituting the kinetic equation (10.14), integrating by parts, and using Condition 1 for $\Re[F^{(N)}]$, we obtain

$$\begin{aligned} RHS &= \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} L^{(N)} m_a \mathbf{v}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle \\ &= \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} m_a \mathbf{v}_{ja} \mathbf{v}_{ja} \cdot \nabla_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle \\ &\quad + \int_V d\mathbf{r} \left\langle \frac{1}{2} \sum_{a,b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} F^{(N)} \mathbf{F}_{jakb} [\delta(\mathbf{r}_{ja} - \mathbf{r}) - \delta(\mathbf{r}_{kb} - \mathbf{r})] \right\rangle_{(ja \neq kb)} \\ &\quad + \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} m_a \mathbf{F}_a(\mathbf{r}) \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle. \end{aligned}$$

To proceed further, we note the identity:

$$\delta(\mathbf{r}_j - \mathbf{r}) - \delta(\mathbf{r}_k - \mathbf{r}) = -\nabla \cdot \int_0^1 d\lambda \mathbf{r}_{jk} \exp(-\lambda \mathbf{r}_{jk} \cdot \nabla) \delta(\mathbf{r}_k - \mathbf{r}). \quad (10.79)$$

This identity is derived as follows:

$$\begin{aligned} \delta(\mathbf{r}_j - \mathbf{r}) - \delta(\mathbf{r}_k - \mathbf{r}) &= [\exp(-\mathbf{r}_{jk} \cdot \nabla) - 1] \delta(\mathbf{r}_k - \mathbf{r}) \\ &= \int_0^1 d\lambda \frac{d}{d\lambda} \exp(-\lambda \mathbf{r}_{jk} \cdot \nabla) \delta(\mathbf{r}_k - \mathbf{r}) \\ &= -\nabla \cdot \int_0^1 d\lambda \mathbf{r}_{jk} \exp(-\lambda \mathbf{r}_{jk} \cdot \nabla) \delta(\mathbf{r}_k - \mathbf{r}), \end{aligned}$$

where $\mathbf{r}_{jk} = \mathbf{r}_j - \mathbf{r}_k$. By using this identity and the property (10.50) together with the definition of generalized virial tensor operator \mathbf{W}_{jakb} in (10.24), we obtain the equation

$$\int_V d\mathbf{r} \frac{\partial}{\partial t} \rho \mathbf{u}(\mathbf{r}, t) = \int_V d\mathbf{r} [-\nabla \cdot (\mathbf{P} + \rho \mathbf{u} \mathbf{u}) + \rho \mathbf{F}(\mathbf{r})], \quad (10.80)$$

where \mathbf{P} is defined by (10.26). As noted earlier, the stress tensor \mathbf{P} may be decomposed into two components: $\mathbf{P} = \mathbf{P}_k + \mathbf{P}_v$. This manner of expressing the stress tensor of a dense fluid implies the physical notion that it consists of a component \mathbf{P}_k arising from the fluidity and the other \mathbf{P}_v arising from the rigidity (elasticity) of the fluid. That is, the liquid may be viewed partly as a solid, and the relative importance of the two components is determined by their relaxation times. From (10.80) follows the momentum balance equation (10.34). If a stress is absent and the momentum flux vanishes at the boundaries, the total momentum balance is given by the equation

$$\frac{d\mathfrak{P}_V}{dt} = \int_V d\mathbf{r} \rho \mathbf{F}(\mathbf{r}), \quad (10.81)$$

where the right hand side represents the body force on matter in the volume V . This is Newton's equation of motion for a body free from stress.

10.3.3 Internal Energy Conservation Law

The internal energy change over time can be calculated by using the statistical definition for the internal energy and the kinetic equation. Although the basic procedure of derivation is similar to those for other balance equations discussed earlier, it entails the definition of heat flux which is not merely a flux of internal energy, if the particles are interacting. For this reason and since it serves as a heuristic example for derivations of flux evolution equations appearing in the present theory, we illustrate the derivation in detail. Let us denote the total internal energy of matter in the volume V by E . We then obtain

$$\begin{aligned} \frac{dE}{dt} &= \int_V d\mathbf{r} \frac{\partial}{\partial t} \rho \mathcal{E}(\mathbf{r}, t) \\ &= \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} H'_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \frac{\partial}{\partial t} F^{(N)}(x^{(N)}; t) \right\rangle \\ &\quad + \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} \frac{\partial H'_{ja}}{\partial \mathbf{u}} \delta(\mathbf{r}_{ja} - \mathbf{r}) F^{(N)} \right\rangle \cdot \frac{\partial \mathbf{u}}{\partial t}. \end{aligned}$$

Since only the kinetic energy part of H'_{ja} depends on \mathbf{u} , the second term on the right hand side of this equation vanishes identically by virtue of (10.76). On substitution of the kinetic equation (10.14), use of (10.50) and Condition 1 on $\mathfrak{R}[F^{(N)}]$, and integration by parts, we obtain

$$\begin{aligned} \int_V d\mathbf{r} \frac{\partial}{\partial t} \rho \mathcal{E}(\mathbf{r}, t) &= - \int_V d\mathbf{r} [\nabla \cdot (\mathbf{Q}_h + \mathbf{u} \rho \mathcal{E}) + \mathbf{P}_k : \nabla \mathbf{u}] \\ &\quad + \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) L^{(N)} H'_{ja} \right\rangle, \end{aligned} \quad (10.82)$$

where \mathbf{Q}_h is the heat flow associated with H'_{ja} and defined in (10.30). The second integral on the right hand side of (10.83) will be denoted by I_e and examined in detail. On substitution of the Liouville operator, it can be written as

$$\begin{aligned} I_e = & \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) m_a \mathbf{C}_{ja} \cdot \mathbf{F}_a(\mathbf{r}) \right\rangle \\ & - \int_V d\mathbf{r} \left\langle \frac{1}{2} \sum_{a,b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} F^{(N)} \mathbf{v}_{ja} \mathbf{F}_{jakb} [\delta(\mathbf{r}_{ja} - \mathbf{r}) + \delta(\mathbf{r}_{kb} - \mathbf{r})] \right\rangle \\ & + \int_V d\mathbf{r} \left\langle \sum_{a,b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} F^{(N)} \mathbf{C}_{ja} \mathbf{F}_{jakb} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle. \end{aligned} \quad (10.83)$$

Since the forces \mathbf{F}_{jakb} have the property that $\mathbf{F}_{jakb} = -\mathbf{F}_{kbja}$, it follows that

$$\sum_{a,b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \mathbf{F}_{jakb} [\delta(\mathbf{r}_{ja} - \mathbf{r}) + \delta(\mathbf{r}_{kb} - \mathbf{r})] = 0$$

and the last two terms in (10.83) may be written as

$$- \int_V d\mathbf{r} \left[\nabla \cdot \left\langle \frac{1}{2} \sum_{a,b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} F^{(N)} \mathbf{W}_{jakb} \cdot \mathbf{C}_{ja} \delta(\mathbf{r}_k - \mathbf{r}) \right\rangle + \nabla \mathbf{u} : \mathbf{P}_v \right].$$

Combining this term with the rest of the terms on the right hand side of (10.83), we obtain the internal energy balance in the volume V :

$$\int_V d\mathbf{r} \frac{\partial}{\partial t} \rho \mathcal{E}(\mathbf{r}, t) = \int_V d\mathbf{r} \left[-\nabla \cdot (\mathbf{Q} + \rho \mathcal{E} \mathbf{u}) - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a \right], \quad (10.84)$$

where the heat flux \mathbf{Q} is defined by (10.29) and the stress tensor \mathbf{P} by (10.26). By virtue of continuity, this equation gives rise to the internal energy balance equation (10.35). If the heat flux \mathbf{Q} and the velocity \mathbf{u} vanish at the boundaries then the total internal energy in the volume V is balanced as follows:

$$\frac{dE}{dt} = \int_V d\mathbf{r} \left(-\mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a \right). \quad (10.85)$$

This form of global energy balance can be cast into another more suitable form if global processes are of interest. For example, if the mean pressure

of the volume is defined by

$$p_m = V^{-1} \int_V d\mathbf{r} p(\mathbf{r}, t),$$

(10.85) may be written as

$$\frac{dE}{dt} = -p_m \frac{dV}{dt} + \frac{dW_{\text{int}}}{dt}, \quad (10.86)$$

where

$$\frac{dW_{\text{int}}}{dt} = - \int_V d\mathbf{r} \left[(\mathbf{P} - p_m \boldsymbol{\delta}) : \nabla \mathbf{u} - \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a \right]. \quad (10.87)$$

It represents an internal work per unit time whereas the first term on the right hand side of (10.86) is the mean pressure–volume work per unit time. The internal work W_{int} consists of that arising from the stress and the other from the external force. For discussions on global irreversible processes, the reader is referred to [5]. If the pressure is uniform in V , then $p_m = p$ and the first term on the right hand side of (10.86) is the usual pressure–volume work per unit time, well known in thermodynamics.

10.3.4 Evolution Equations for Nonconserved Variables

Let us denote the global nonconserved variables by Γ_{qa} :

$$\Gamma_{qa} = \int_V d\mathbf{r} \rho \hat{\Phi}_{qa}.$$

The rate of change in Γ_{qa} can then be calculated from the kinetic equation and the statistical formula for the nonconserved variables Φ_{qa} . Since we will need only their formal expressions in the development of a formal theory of irreversible processes in this work, the statistical formulas for them will not be calculated explicitly in terms of macroscopic variables as for the conservation laws presented earlier. The rate of change in Γ_{qa} is given by

$$\begin{aligned} \frac{d\Gamma_{qa}}{dt} &= \int_V d\mathbf{r} \frac{\partial}{\partial t} \rho \hat{\Phi}_{qa} \\ &= \int_V d\mathbf{r} \left\langle \sum_{ja=1}^{N_a} h_{ja}^{(q)}(x^{(N)}; t) \delta(\mathbf{r}_{ja} - \mathbf{r}) \frac{\partial}{\partial t} F^{(N)} \right\rangle \\ &\quad + \int_V d\mathbf{r} \left\langle \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \frac{\partial h_{ja}^{(q)}}{\partial t} \right\rangle. \end{aligned}$$

On substitution of the kinetic equation and integration by parts we obtain

$$\begin{aligned} \int_V d\mathbf{r} \frac{\partial}{\partial t} \rho \hat{\Phi}_{qa} &= \int_V d\mathbf{r} \left\langle \sum_{ja=1}^{N_a} F^{(N)} h_{ja}^{(q)}(x^{(N)}; t) L^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle \\ &\quad + \int_V d\mathbf{r} \left\langle \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \frac{\partial}{\partial t} h_{ja}^{(q)}(x^{(N)}; t) \right\rangle \\ &\quad + \int_V d\mathbf{r} \left\langle \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) L^{(N)} h_{ja}^{(q)} \right\rangle \\ &\quad + \int_V d\mathbf{r} \Lambda_{aq}(\mathbf{r}, t). \end{aligned}$$

On use of (10.50) the first term on the right hand side of this equation can be written as

$$\int_V d\mathbf{r} \left[-\nabla \cdot (\psi_{aq} + \mathbf{u} \rho \hat{\Phi}_{aq}) + \left\langle \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathbf{v}_{ja} \cdot \nabla h_{ja}^{(q)} \right\rangle \right]. \quad (10.88)$$

Substitution of this result into the previous equation yields the balance equation for Φ_{qa} :

$$\int_V d\mathbf{r} \frac{\partial}{\partial t} \rho \hat{\Phi}_{qa} = \int_V d\mathbf{r} \left[-\nabla \cdot (\psi_{aq} + \mathbf{u} \rho \hat{\Phi}_{aq}) + \mathcal{Z}_{qa} + \Lambda_{aq} \right],$$

which, by continuity, implies the evolution equation (10.39) for Φ_{qa} . If the boundary conditions are such that ψ_{aq} and \mathbf{u} vanish at the boundaries, then the global balance of Γ_{qa} is given by the equation

$$\frac{d\Gamma_{qa}}{dt} = \int_V d\mathbf{r} (\mathcal{Z}_{qa} + \Lambda_{aq}). \quad (10.89)$$

This statistical mechanical formula for the global rate of change in nonconserved variables can be used in studying irreversible processes in discrete systems. The right hand side of (10.89) is seen to be a measure of energy dissipation arising from the irreversible nonconservative processes in the system.

This section is closed with a brief mention of the matching conditions for the conserved variables. By using the kinetic equation (10.14) together with Conditions 1–3 on the collision term we can obtain the local matching conditions for the density, momentum, and internal energy in the same forms as for classical dilute gases and quantum gases, (4.40)–(4.42) and (9.97)–(9.99). These matching conditions again allow us to embed the equilibrium thermodynamic states in the space \mathfrak{P} in which the thermodynamics of irreversible processes is constructed by means of the nonequilibrium ensemble method described below for dense simple fluids.

10.4 Nonequilibrium Ensemble Method

The macroscopic variables statistically defined for dense fluids in the previous section may be regarded as spanning the thermodynamic space $\mathfrak{P} \equiv (\mathcal{E}, v, c_a, \hat{\Phi}_{qa} : 1 \leq a \leq r; q \geq 1)$ for the system and evolution equations derived for macroscopic variables can be used to describe macroscopic irreversible processes in the system. The variables of the thermodynamic space \mathfrak{P} have conjugate variables representative of the system which provide constitutive relations for matter comprising the system. In statistical mechanics such constitutive relations for the conjugate variables to the thermodynamic variables of \mathfrak{P} are looked for in terms of molecular parameters. The connection with the molecular world for such macroscopic nonequilibrium constitutive variables is sought in the nonequilibrium ensemble method in a way parallel with that in the equilibrium Gibbs ensemble theory. We have accomplished such a connection for nonequilibrium dilute gases in the previous chapters and thereby made the theory thermodynamically consistent. In this section we formulate a dense fluid extension of the theory for dilute gases. To achieve the desired aim it is necessary to develop a statistical formula for the phenomenological calortropy introduced in Chapter 2 since it is a mathematical representation of the second law of thermodynamics.

10.4.1 Nonequilibrium Grand Canonical Form

It is necessary to introduce a thermodynamic branch of the distribution function which gives rise to the same mathematical structure of thermodynamics of irreversible processes as the continuum theory version formulated on the basis of the laws of thermodynamics in Chapter 2. Such a distribution function for an open system, which will be called the nonequilibrium grand canonical form, is given by the form

$$k_B \ln F_c^{(N)} = - \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} \mathcal{H}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) - k_B \ln(c \Xi). \quad (10.90)$$

Here

$$\mathcal{H}_{ja} = \bar{H}_{ja} + \bar{H}_{ja}^1 - m_a \bar{\mu}_a \quad (10.91)$$

with various symbols defined by

$$\bar{H}_{ja} = \frac{H_{ja}}{T}, \quad \bar{H}_{ja}^1 = \frac{H_{ja}^1}{T}, \quad \bar{\mu}_a = \frac{\hat{\mu}_a}{T}. \quad (10.92)$$

The parameter T in this expression is as yet undetermined. It depends on the position \mathbf{r} and the time t , but not on molecular positions and momenta. It is a macroscopic parameter whose meaning will be determined with the help of the laws of thermodynamics and thus, in particular, the thermodynamically constructed calortropy, namely, by means of thermodynamic

correspondence made as for the dilute gas theories presented in Chapters 7 and 9. It is convenient to use parameter β related to T as follows:

$$\beta(\mathbf{r}, t) = \frac{1}{k_B T(\mathbf{r}, t)}. \quad (10.93)$$

The quantity $k_B \ln \Xi$ in (10.90) is the normalization factor defined by

$$\Xi = \left\langle \exp \left\{ -k_B^{-1} \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} \mathcal{H}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\} \right\rangle. \quad (10.94)$$

It will be convenient to define a macroscopic parameter Υ such that

$$-k_B \ln \Xi = \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} m_a \delta(\mathbf{r}_{ja} - \mathbf{r}) \Upsilon(\mathbf{r}, t) \right\rangle \quad (10.95)$$

with Υ to be determined with the help of phenomenological thermodynamics and in particular the calortropy for the system of interest. This relation may be written as

$$-k_B \ln \Xi = \int_V d\mathbf{r} \rho \Upsilon(\mathbf{r}, t). \quad (10.96)$$

Therefore, if the volume average of $\rho \Upsilon(\mathbf{r}, t)$ is denoted by $\bar{\Upsilon}$, namely,

$$\bar{\Upsilon} = V^{-1} \int_V d\mathbf{r} \rho \Upsilon(\mathbf{r}, t),$$

then

$$\bar{\Upsilon}V = -k_B \ln \Xi. \quad (10.97)$$

With the normalization factor expressed as in (10.95) the distribution function $F_c^{(N)}$ can be written as

$$F_c^{(N)} = c^{-1} \exp \left\{ -k_B^{-1} \int_V d\mathbf{r} \left[\sum_{a=1}^r \sum_{ja=1}^{N_a} \mathcal{H}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) - \rho \bar{\Upsilon} \right] \right\}. \quad (10.98)$$

This form for the distribution function will be used in the subsequent discussions.

10.4.2 Statistical Calortropy and its Balance Equation

The thermodynamic calortropy introduced as a mathematical representation of the laws of thermodynamics in Chapter 2 can be statistically expressed in terms of $F_c^{(N)}$ given in (10.98). It has the form

$$\Psi(t) = -k_B \left\langle F^{(N)}(x^{(N)}; t) \ln F_c^{(N)}(x^{(N)}; t) \right\rangle. \quad (10.99)$$

The global calortropy $\Psi(t)$ can be expressed in terms of local calortropy density $\widehat{\Psi}(\mathbf{r}, t)$:

$$\Psi(t) = \int_V d\mathbf{r} \rho \widehat{\Psi}(\mathbf{r}, t), \quad (10.100)$$

which implies the statistical formula for the calortropy density:

$$\rho \widehat{\Psi}(\mathbf{r}, t) = \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) (\mathcal{H}_{ja} - m_a \Upsilon) \right\rangle. \quad (10.101)$$

The balance equation for calortropy can be derived from this statistical formula by using the kinetic equation (10.14). To this end we calculate the rate of change in $\Psi(t)$. By using the statistical formula (10.99) and the kinetic equation we find

$$\begin{aligned} \frac{d\Psi}{dt} &= \int_V d\mathbf{r} \frac{\partial}{\partial t} \rho \widehat{\Psi}(\mathbf{r}, t) \\ &= \int_V d\mathbf{r} \left[-\nabla \cdot (\mathbf{J}_c + \mathbf{u} \rho \widehat{\Psi}) + \sigma_c \right] \\ &\quad + \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathcal{D}_t^{(N)} (\mathcal{H}_{ja} - m_a \Upsilon) \right\rangle, \end{aligned} \quad (10.102)$$

where the calortropy flux \mathbf{J}_c and the calortropy production σ_c are respectively defined by the statistical formulas

$$\mathbf{J}_c(\mathbf{r}, t) = \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathcal{H}_{ja} \mathbf{C}_{ja} \right\rangle, \quad (10.103)$$

$$\sigma_c(\mathbf{r}, t) = \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathcal{H}_{ja} \Re [F^{(N)}] \right\rangle. \quad (10.104)$$

The derivation of (10.102) can be made by following the procedure used for the evolution equations for macroscopic variables presented in the previous section. It must be emphasized that, contrary to the belief held in [5], the last term on the right hand side of (10.102) does not vanish if the macroscopic parameters in the exponent of $F_c^{(N)}$ are determined by thermodynamic correspondence with the help of the continuum theoretical irreversible thermodynamics presented in Chapter 2. It is the term that makes it possible to remove the assumption made in [5] in connection with \mathbf{Q}_v/T which was added to \mathbf{Q}_h/T so that \mathbf{Q}/T appears in the expression for \mathbf{J}_c . (See Footnote 4 below for further elaboration.) The assumption became necessary because the term in question was thought to vanish identically.

But this is not true. Eq.(10.102) implies the local balance equation for calortropy density:

$$\rho \frac{d}{dt} \hat{\Psi}(\mathbf{r}, t) = -\nabla \cdot \mathbf{J}_c + \sigma_c(\mathbf{r}, t) + \mathbb{D}, \quad (10.105)$$

where

$$\mathbb{D} = \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathcal{D}_t^{(N)} (\mathcal{H}_{ja} - m_a \Upsilon) \right\rangle. \quad (10.106)$$

We have used the substantial time derivative in (10.105). The calortropy balance equation (10.105) is the starting point of the investigation into the statistical foundations of irreversible processes in dense fluids as is its dilute gas counterpart used in Chapter 7.

10.4.3 Pfaffian Form for Calortropy

To derive a Pfaffian form for calortropy from the calortropy balance equation (10.105) we first calculate the calortropy flux \mathbf{J}_c and the calortropy production σ_c . To this end we write the nonequilibrium contribution \bar{H}_{ja}^1 in (10.91) in terms of a complete set of functions $h_{ja}^{(q)}$ which are led by the moments for the stress tensor, heat flux, and so on, as given in (10.44)–(10.47):

$$\bar{H}_{ja}^1 = \sum_{q \geq 1} \bar{X}_{qa} h_{ja}^{(q)}, \quad (10.107)$$

where $\bar{X}_{qa} = X_{qa}/T$ are as yet undetermined macroscopic parameters whose meanings will be determined with the help of phenomenological thermodynamics. The present nonequilibrium ensemble method also aims to ultimately determine them in terms of the nonequilibrium partition function. The calortropy flux and calortropy production can be easily calculated from their statistical expressions and are given by the formulas

$$\mathbf{J}_c = T^{-1} \sum_{a=1}^r \mathbf{Q}_a^{(h)} + \sum_{a=1}^r \sum_{q \geq 1} \bar{X}_{qa} \psi_{qa} - \sum_{a=1}^r \bar{\mu}_a \mathbf{J}_a, \quad (10.108)$$

$$\sigma_c = \sum_{a=1}^r \sum_{q \geq 1} \bar{X}_{qa} \Lambda_{qa}. \quad (10.109)$$

Here $\mathbf{Q}_a^{(h)}$ is the component of \mathbf{Q}_h for species a defined in (10.30). The term \mathbb{D} in (10.106) can be calculated by using the procedures used for the Liouville operator in connection with the derivations of various macroscopic equations presented earlier. We first present the result for \mathbb{D} :

$$\mathbb{D} = \rho \left[\mathcal{E} \frac{d}{dt} \frac{1}{T} + \sum_{a=1}^r \sum_{q \geq 1} \widehat{\Phi}_{qa} \frac{d\bar{X}_{qa}}{dt} - \sum_{a=1}^r c_a \frac{d\bar{\mu}_a}{dt} - \frac{d\Upsilon}{dt} \right]$$

$$\begin{aligned}
& -T^{-1} \left[\mathbf{Q} \cdot \nabla \ln T + \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot (T \nabla \bar{\mu}_a - \mathbf{F}_a) \right] \\
& - \nabla \cdot \left(\frac{\mathbf{Q}_v}{T} \right) + \sum_{a=1}^r \sum_{q \geq 1} \bar{X}_{qa} \frac{d\hat{\Phi}_{qa}}{dt} \\
& + \sum_{a=1}^r \sum_{q \geq 1} \nabla \cdot (\psi_{qa} \bar{X}_{qa}) - \sum_{a=1}^r \sum_{q \geq 1} \bar{X}_{qa} \Lambda_{qa} \quad (10.110)
\end{aligned}$$

and then illustrate its derivation at the end of this subsection. On substitution of (10.108), (10.109), and (10.110) into the calortropy balance equation (10.105) and making use of the internal energy balance equation (10.35), we finally obtain

$$\begin{aligned}
\frac{d\hat{\Psi}}{dt} &= T^{-1} \left[\frac{d\mathcal{E}}{dt} + \sum_{a=1}^r \sum_{q \geq 1} X_{qa} \frac{d\hat{\Phi}_{qa}}{dt} - \sum_{a=1}^r \hat{\mu}_a \frac{dc_a}{dt} \right] \\
&+ \left[\mathcal{E} \frac{dT^{-1}}{dt} + \sum_{a=1}^r \sum_{q \geq 1} \hat{\Phi}_{qa} \frac{d}{dt} \bar{X}_{qa} - \sum_{a=1}^r c_a \frac{d\bar{\mu}_a}{dt} \right] \\
&- \frac{d\Upsilon}{dt}. \quad (10.111)
\end{aligned}$$

To proceed further, we now set

$$\Upsilon = -\frac{pv}{T} = -\bar{p}v, \quad (10.112)$$

which implies that

$$k_B \ln \Xi = \int_V d\mathbf{r} \frac{p}{T}. \quad (10.113)$$

This is the statistical definition of parameter p . We will return to this formula later. On use of the identification for Υ made in (10.112) and on varying the normalization condition (10.94) for $F_c^{(N)}$, the integrability condition follows for the differential form for $\hat{\Psi}$

$$\mathcal{E} \frac{dT^{-1}}{dt} + v \frac{d\bar{p}}{dt} - \sum_{a=1}^r c_a \frac{d\bar{\mu}_a}{dt} + \sum_{a=1}^r \sum_{q \geq 1} \hat{\Phi}_{qa} \frac{d}{dt} \bar{X}_{qa} = 0, \quad (10.114)$$

and therewith we finally obtain the Pfaffian form for $\hat{\Psi}$

$$\frac{d\hat{\Psi}}{dt} = T^{-1} \left[\frac{d\mathcal{E}}{dt} + p \frac{dv}{dt} - \sum_{a=1}^r \hat{\mu}_a \frac{dc_a}{dt} + \sum_{a=1}^r \sum_{q \geq 1} X_{qa} \frac{d\hat{\Phi}_{qa}}{dt} \right]. \quad (10.115)$$

Clearly, (10.114) is the integrability condition for the Pfaffian form $d\hat{\Psi}$ in (10.115) since on addition of (10.114) and (10.115) there follows the calortropy density in the thermodynamic space \mathfrak{P} . It has the form

$$\hat{\Psi} = T^{-1} \left(\mathcal{E} + pv - \sum_{a=1}^r c_a \hat{\mu}_a + \sum_{a=1}^r \sum_{q \geq 1} X_{qa} \hat{\Phi}_{qa} \right), \quad (10.116)$$

which is an integral of (10.111) with (10.112) for Υ . It also follows from the statistical expression (10.101) for $\hat{\Psi}$ on substitution of $F_c^{(N)}$. Therefore the statistical formula (10.101) for $\hat{\Psi}$ and its balance equation are consistent with each other, and the Pfaffian form (10.115) for $d\hat{\Psi}$ is an exact differential in the space \mathfrak{P} under the integrability condition (10.114). We reiterate that, when looked at from the purely mathematical standpoint, it is not easy to show the exactness of the Pfaffian form (10.115), since its integrability conditions are coupled partial differential equations which are generally nonlinear, but the second law of thermodynamics provides a physical means of proof for its exactness in a simple way.

On substitution of (10.108), (10.109), and (10.110) and use of the integrability condition (10.114) the calortropy balance equation (10.105) takes the form

$$\begin{aligned} \rho \frac{d\hat{\Psi}}{dt} &= -\nabla \cdot T^{-1} \left(\mathbf{Q} - \sum_{a=1}^r \hat{\mu}_a \mathbf{J}_a + \sum_{a=1}^r \sum_{q \geq 1} X_{qa} \boldsymbol{\psi}_{qa} \right) \\ &\quad + \rho \hat{\Sigma}_l + \sum_{a=1}^r \sum_{q \geq 1} X_{qa} (\mathcal{Z}_{qa} + \Lambda_{qa}) \end{aligned} \quad (10.117)$$

where $\hat{\Sigma}_l$ has the same mathematical form as (7.97) except that \mathbf{P} , \mathbf{Q} , and \mathbf{J}_a therein now are for the dense fluid. The local form of the second law of thermodynamics is then given by the inequality

$$\Xi_c \equiv \rho \hat{\Sigma}_l + T^{-1} \sum_{a=1}^r \sum_{q \geq 1} X_{qa} (\mathcal{Z}_{qa} + \Lambda_{qa}) \geq 0. \quad (10.118)$$

This inequality should be compared with (2.50) for Ξ_c deduced from the second law of thermodynamics. The inequality (10.118) is the local statistical representation of the latter.

We now derive the identity for \mathbb{D} in (10.110). To this end we split (10.106) into three parts and consider them separately to alleviate the labor of calculating the unwieldy formula:

$$\mathbb{D} = \mathbb{D}_1 + \mathbb{D}_2 + \mathbb{D}_3, \quad (10.119)$$

where

$$\begin{aligned} \mathbb{D}_1 &= \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \frac{d}{dt} \left(\bar{H}'_{ja} + \sum_{q \geq 1} \bar{X}_{qa} h_{ja}^{(q)} \right) \right\rangle \\ &\quad - \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) m_a \frac{d}{dt} (\bar{\mu}_a + \Upsilon) \right\rangle, \end{aligned} \quad (10.120)$$

$$\begin{aligned} \mathbb{D}_2 &= \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) L^{(N)} \left(\bar{H}'_{ja} + \sum_{q \geq 1} \bar{X}_{qa} h_{ja}^{(q)} \right) \right\rangle \\ &\quad - \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) L^{(N)} m_a (\bar{\mu}_a + \Upsilon) \right\rangle, \end{aligned} \quad (10.121)$$

$$\begin{aligned} \mathbb{D}_3 &= \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathbf{C}_{ja} \cdot \nabla \left(\bar{H}'_{ja} + \sum_{q \geq 1} \bar{X}_{qa} h_{ja}^{(q)} \right) \right\rangle \\ &\quad - \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathbf{C}_{ja} \cdot \nabla m_a (\bar{\mu}_a + \Upsilon) \right\rangle, \end{aligned} \quad (10.122)$$

It is easy to show that with the help of definitions of macroscopic variables

$$\begin{aligned} \mathbb{D}_1 &= \rho \left[\mathcal{E} \frac{dT^{-1}}{dt} + \sum_{a=1}^r \sum_{q \geq 1} \hat{\Phi}_{qa} \frac{d\bar{X}_{qa}}{dt} - \sum_{a=1}^r c_a \frac{d\bar{\mu}_a}{dt} - \frac{d\Upsilon}{dt} \right] \\ &\quad + \sum_{a=1}^r \sum_{q \geq 1} \bar{X}_{qa} \left\langle F^{(N)} \sum_{ja=1}^{N_a} \delta(\mathbf{r}_{ja} - \mathbf{r}) \frac{d}{dt} h_{ja}^{(q)} \right\rangle. \end{aligned} \quad (10.123)$$

By using the procedures used for the Liouville operator in connection with the derivations of various evolution equations and noting that the last two terms in \mathbb{D}_2 do not contribute, we obtain the following result⁴:

$$\begin{aligned} \mathbb{D}_2 &= -\nabla \cdot \left(\frac{\mathbf{Q}_v}{T} \right) - T^{-1} \sum_{a=1}^r \left(\mathbf{Q}_a^{(v)} \cdot \nabla \ln T + \mathbf{P}_a^{(v)} : \nabla \mathbf{u} - \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a \right) \\ &\quad + \sum_{a=1}^r \sum_{q \geq 1} \bar{X}_{qa} \left\langle F^{(N)} \sum_{ja=1}^{N_a} \delta(\mathbf{r}_{ja} - \mathbf{r}) L^{(N)} h_{ja}^{(q)} \right\rangle. \end{aligned} \quad (10.124)$$

⁴In the derivation of the extended Gibbs relation for $\widehat{\Psi}$ in [5], $\nabla \cdot \mathbf{Q}_v$ was added to the calortropy flux term by arguing that its boundary value vanishes. In the present derivation the virial contribution \mathbf{Q}_v to the heat flux appears without such an argument. The derivation made in [5] was therefore deficient in the sense that the divergence term was put in with the force of a weak argument.

Similarly, we obtain for \mathbb{D}_3 the equation

$$\begin{aligned} \mathbb{D}_3 = & -T^{-1} \sum_{a=1}^r \left(\mathbf{Q}_a^{(h)} \cdot \nabla \ln T + \mathbf{P}_a^{(k)} : \nabla \mathbf{u} \right) \\ & - \sum_{a=1}^r \mathbf{J}_a \cdot \nabla \bar{\mu}_a + \sum_{a=1}^r \sum_{q \geq 1} \psi_{qa} \nabla \bar{X}_{qa} \\ & + \sum_{a=1}^r \sum_{q \geq 1} \bar{X}_{qa} \left\langle F^{(N)} \sum_{ja=1}^{N_a} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathbf{C}_{ja} \cdot \nabla h_{ja}^{(q)} \right\rangle. \end{aligned} \quad (10.125)$$

Combining these three terms into \mathbb{D} and making use of the statistical formula (10.41) for \mathcal{Z}_{qa} together with the evolution equation (10.39) for $\hat{\Phi}_{qa}$, we obtain the form of \mathbb{D} given in (10.110).

10.4.4 Nonequilibrium Statistical Thermodynamics for Dense Fluids

The differential form (10.115) contains undetermined macroscopic parameters T , p , $\hat{\mu}_a$, and X_{qa} —variables conjugate to the extensive thermodynamic variables \mathcal{E} , v , c_a , $\hat{\Phi}_{qa}$ spanning the space \mathfrak{P} —and thermodynamical meanings of the parameters can be fixed by making correspondence with the phenomenological differential form for $\hat{\Psi}$ derived from the laws of thermodynamics. That is, by corresponding the statistically computed extensive variables \mathcal{E} , v , c_a , and $\hat{\Phi}_{qa}$ to their thermodynamic counterparts, we identify the conjugate intensive variables in the nonequilibrium grand canonical form $F_c^{(N)}$ in (10.98) in which \tilde{H}_{ja}^1 is given as in (10.107) in terms of the thermodynamic intensive variables. More precisely stated, by making correspondence between the extensive variables calculated statistically and their phenomenological counterparts

$$\begin{aligned} \mathcal{E}|_{st} &\Leftrightarrow \mathcal{E}|_{th}, & v|_{st} &\Leftrightarrow v|_{th}, & c_a|_{st} &\Leftrightarrow c_a|_{th}, \\ \hat{\Phi}_{qa}|_{st} &\Leftrightarrow \hat{\Phi}_{qa}|_{th}, & \hat{\Psi}|_{st} &\Leftrightarrow \hat{\Psi}|_{th}, \end{aligned} \quad (10.126)$$

we identify the conjugate variables of the statistical extensive variables in space \mathfrak{P} with phenomenological thermodynamic intensive variables:

$$\begin{aligned} T|_{st} &\Leftrightarrow T|_{th}, & p|_{st} &\Leftrightarrow p|_{th}, \\ \hat{\mu}_a|_{st} &\Leftrightarrow \hat{\mu}_a|_{th}, & X_{qa}|_{st} &\Leftrightarrow X_{qa}|_{th}, \end{aligned} \quad (10.127)$$

where the subscripts st and th denote the statistically and thermodynamically determined quantities, respectively. The set of correspondences in

(10.126) and (10.127) is referred to as the thermodynamic correspondence. It is for the dense fluid under consideration, but has exactly the same form as for its dilute gas counterparts obtained in Chapters 7 and 9. This thermodynamic correspondence means that the calortropy deduced from the Clausius inequality, namely, the second law of thermodynamics, can be given the statistical mechanical foundations by means of the kinetic equation (10.14) and the statistical definition of $\hat{\Psi}$ given earlier. This conclusion is summarized as a theorem below.

Theorem 8 *The calortropy differential (10.115) for the dense simple fluid described by (10.14) is the statistical representation of the calortropy differential (2.51) deduced from the second law of thermodynamics. It has the same mathematical properties in the thermodynamic space \mathfrak{P} as the latter.*

This conclusion suggests that the formal thermodynamic theory of irreversible processes has the same mathematical structure for classical and quantum dilute gases and for dense simple fluids. It is expected to remain the same for dense complex fluids. It in fact is not difficult to show it, but we omit it for lack of space.

We now examine the statistical meaning of the composite parameter p/T . Returning to (10.113), we first write

$$\ln \Xi = \int_V d\mathbf{r} \rho \ln \Gamma(\mathbf{r}, t). \quad (10.128)$$

Comparing this formula with the definition of Ξ , we find

$$\exp \left[\int_V d\mathbf{r} \rho \ln \Gamma(\mathbf{r}, t) \right] = \left\langle \exp \left\{ -k_B^{-1} \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} \mathcal{H}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\} \right\rangle. \quad (10.129)$$

This relation gives a way to compute $\ln \Gamma(\mathbf{r}, t)$ from Ξ . A way to compute $\Gamma(\mathbf{r}, t)$ in terms of local nonequilibrium grand partition function was indicated in Sec. 7.11, Chapter 7, and a similar method may be used here. Eq. (10.128) implies that

$$\Upsilon = -\frac{pv}{T} = -k_B \ln \Gamma(\mathbf{r}, t). \quad (10.130)$$

That is,

$$pv = k_B T \ln \Gamma(\mathbf{r}, t), \quad (10.131)$$

which supplies the statistical meaning of the parameter p in terms of the local quantity $\Gamma(\mathbf{r}, t)$. It will turn out to be pressure. To grasp the meaning of this parameter more clearly and in the sense akin to the equilibrium theory, we define the volume average of p/T :

$$\left\langle \frac{p}{T} \right\rangle_V = V^{-1} \int_V d\mathbf{r} \frac{p}{T}. \quad (10.132)$$

Since the local properties are of interest, the volume may be reduced to an infinitesimally small magnitude such that p/T is uniform over the volume V , yet this volume still contains a sufficiently large number of particles so as to validate the statistical method used. Thus the following procedure is legitimate:

$$\int_V d\mathbf{r} \frac{p}{T} = \frac{pV}{T}, \quad (10.133)$$

where V is the magnitude of the infinitesimal elementary volume. Therefore in the limit of validity of (10.133)

$$pV = k_B T \ln \Xi, \quad (10.134)$$

which has the same form as for p in the equilibrium theory. The partition function Ξ in this expression is to be evaluated for a system with a sufficiently small volume, which of course contains a sufficiently large number of particles to make the present statistical formalism remain valid. By virtue of the parameters such as T , p , $\hat{\mu}_a$, and X_{qa} in the distribution function $F_c^{(N)}$ being local and dependent on time, the partition function Ξ evaluated in such a volume around the position \mathbf{r} is a function of position as well as time. Eq. (10.134) is a more easily comprehensible form since it gives the equation of state at \mathbf{r} and t .

On recasting the integrability condition (10.114)—the extended Gibbs–Duhem relation—by using (10.116) derived from the statistical formula for the calortropy density, we obtain

$$\begin{aligned} d(pv) &= \hat{\Psi}dT + pdv - \sum_{a=1}^r \sum_{q \geq 1} \hat{\Phi}_{qa} dX_{qa} + \sum_{a=1}^r c_a d\hat{\mu}_a \\ &= d[k_B T \ln \Gamma(\mathbf{r}, t)]. \end{aligned} \quad (10.135)$$

Here pv is the nonequilibrium thermodynamic potential in the grand ensemble theory. From the differential form (10.135) follow the statistical formulas for the macroscopic variables:

$$\hat{\Psi} = k_B \ln \Gamma + k_B T \frac{\partial \ln \Gamma}{\partial T}, \quad (10.136)$$

$$p = k_B T \frac{\partial \ln \Gamma}{\partial v}, \quad (10.137)$$

$$c_a = k_B T \frac{\partial \ln \Gamma}{\partial \hat{\mu}_a}, \quad (10.138)$$

$$\hat{\Phi}_{qa} = -k_B T \frac{\partial \ln \Gamma}{\partial X_{qa}}. \quad (10.139)$$

Except for the formula for $\hat{\Phi}_{qa}$, these statistical expressions are in the same forms as for their equilibrium counterparts. These expressions are also the

dense fluid grand canonical ensemble versions of the relations obtained for dilute gases with a nonequilibrium canonical ensemble distribution function and of the relations (7.319)–(7.322) formulated with the nonequilibrium grand ensemble distribution function for a classical dilute gas mixture. Thus we now have acquired an ensemble theory for nonequilibrium dense simple fluids which is completely parallel with the equilibrium ensemble theory of Gibbs. The evolution of macroscopic variables appearing in this theory is described by the various balance equations presented in the previous sections. There now remains the task of evaluating the nonequilibrium partition function Ξ or Γ and the attendant generalized hydrodynamics equations consisting of the evolution equations for macroscopic variables spanning the thermodynamic space for the system.

We close this section with a remark on the differences of the present theory from the linear response theory [9–11] and, particularly, Mori's version [11] of it. In this latter version, a canonical or grand canonical distribution function with a bilinear form of thermodynamic forces and molecular fluxes in the exponent is assumed and the entropy production is calculated therewith. In the sense that such a bilinear form is added to the exponent of the distribution function, there is a similarity with regard to the distribution function between the linear response theory and the present theory. However, apart from the differences in the details of the bilinear forms in the two theories, there is a crucial difference in that there is no kinetic equation governing the evolution of the distribution function and giving rise to the evolution equations (constitutive equations) for nonconserved variables in the linear response theory. The absence of an irreversible kinetic equation and the constitutive equations derived therefrom confines the linear response theory to near-equilibrium regimes of processes since one is forced to assume a local equilibrium formula for the entropy and to consider linear constitutive equations only. It must be pointed out that it is not enough to have a nonequilibrium canonical or grand canonical form for the distribution function if the constitutive equations for nonconserved variables are the objects of derivation. The reason is that the techniques used for deriving the conservation equations for mass, momentum, and internal energy in linear response theory would not yield correct evolution equations for nonconserved variables since there would be missing a dissipation term in them which is responsible for energy dissipation in the system arising from irreversible processes. The dissipation terms are the seats of energy dissipation in the nonequilibrium system where one form of energy is converted into a less useful form when a given mechanical task is performed by the system. The local equilibrium entropy formula used in the linear response theory also forecloses the possibility of developing a nonequilibrium ensemble theory, as is done in the present theory. The same comment applies to Kubo's version [10] of linear response theory. In the case of Green's theory [9] the situation is somewhat different, since there is a kinetic equation in the form of Fokker–Planck equation which is irre-

versible and can be possibly exploited to develop a more general theory of irreversible processes. Such a development has not been attempted as far as this author is aware.

10.5 Relative Boltzmann Entropy and Fluctuations

As for dilute gases, the Boltzmann entropy is not the same as the calortropy, and the difference between them is called the relative Boltzmann entropy. It is defined by the statistical formula

$$S_r[F^{(N)}|F_c^{(N)}](t) = k_B \left\langle F^{(N)}(x^{(N)}; t) \ln \left(\frac{F^{(N)}}{F_c^{(N)}} \right) \right\rangle. \quad (10.140)$$

The relative Boltzmann entropy density may be defined by the integral relation

$$S_r[F^{(N)}|F_c^{(N)}] = \int_V d\mathbf{r} \rho S_r[F^{(N)} | F_c^{(N)}](\mathbf{r}, t), \quad (10.141)$$

which implies the formula for the relative Boltzmann entropy density

$$\begin{aligned} \rho S_r[F^{(N)}|F_c^{(N)}] &= - \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) (G_{ja} - \mathcal{H}_{ja}) \right\rangle \\ &\quad - \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) m_a \Upsilon \right\rangle. \end{aligned} \quad (10.142)$$

Use of this statistical formula and the kinetic equation yields the balance equation for the relative Boltzmann entropy:

$$\begin{aligned} \rho \frac{d}{dt} S_r[F^{(N)}|F_c^{(N)}] &= -\nabla \cdot \mathbf{J}_r[F^{(N)}|F_c^{(N)}] + \sigma_r[F^{(N)}|F_c^{(N)}] \\ &\quad + \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathcal{D}_t^{(N)} (\mathcal{H}_{ja} - m_a \Upsilon) \right\rangle, \end{aligned} \quad (10.143)$$

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 formulas

$$\mathbf{J}_r[F^{(N)}|F_c^{(N)}] = - \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} F^{(N)} \delta(\mathbf{r}_{ja} - \mathbf{r}) (G_{ja} - \mathcal{H}_{ja}) \mathbf{C}_{ja} \right\rangle, \quad (10.144)$$

$$\sigma_r[F^{(N)}|F_c^{(N)}] = - \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} \delta(\mathbf{r}_{ja} - \mathbf{r}) (G_{ja} - \mathcal{H}_{ja}) \Re [F^{(N)}] \right\rangle. \quad (10.145)$$

To evaluate the right hand side of (10.143), we write G_{ja} and \mathcal{H}_{ja} in the forms

$$G_{ja} = T^{-1} H'_{ja} + \sum_{q \geq 1} \bar{X}_{qa} h_{ja}^{(q)} - m_a \bar{\mu}_a + m_a \bar{p} v + N^{-1} \ln c, \quad (10.146)$$

$$\mathcal{H}_{ja} = T^{t-1} H'_{ja} + \sum_{q \geq 1} \bar{X}_{qa}^t h_{ja}^{(q)} - m_a \bar{\mu}_a^t, \quad (10.147)$$

and

$$\Upsilon = -\bar{p}^t v. \quad (10.148)$$

The factor $N^{-1} \ln c$ in (10.146) is for the c^{-1} factor in the exponential form for $F^{(N)}$ which renders the phase integral dimensionless. In other words, we write the distribution functions $F^{(N)}$ and $F_c^{(N)}$ in the forms

$$\begin{aligned} k_B \ln c F^{(N)} &= - \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} \left(T^{-1} H'_{ja} + \sum_{q \geq 1} \bar{X}_{qa} h_{ja}^{(q)} \right) \delta(\mathbf{r}_{ja} - \mathbf{r}) \\ &\quad + \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} (m_a \bar{\mu}_a - m_a \bar{p} v) \delta(\mathbf{r}_{ja} - \mathbf{r}), \end{aligned} \quad (10.149)$$

$$\begin{aligned} k_B \ln c F_c^{(N)} &= - \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} \left(T^{t-1} H'_{ja} + \sum_{q \geq 1} \bar{X}_{qa}^t h_{ja}^{(q)} \right) \delta(\mathbf{r}_{ja} - \mathbf{r}) \\ &\quad + \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} (m_a \bar{\mu}_a^t - m_a \bar{p}^t v) \delta(\mathbf{r}_{ja} - \mathbf{r}). \end{aligned} \quad (10.150)$$

Therefore the distribution functions are sought in mathematical forms isomorphic to each other except for the meanings of the parameters such as T^{-1} , T^{t-1} , and so on. The parameter \bar{p}^t is thermodynamically determined by the thermodynamic correspondence (10.127) as are T^{t-1} , \bar{X}_{qa}^t , and $\bar{\mu}_a^t$ whereas T^{-1} , \bar{X}_{qa} , $\bar{\mu}_a$, and \bar{p} are simply parameters (mean values) which must be determined from the solution of the kinetic equation for G_{ja} . We emphasize that these latter parameters are purely statistically determined from the phase space distribution function $F^{(N)}(x^{(N)}; t)$ obeying the kinetic equation (10.14) and in fact are solutions of the fluctuation evolution equations derived from the kinetic equation as shown later; they should not be confused with the parameters T^{t-1} , \bar{X}_{qa}^t , $\bar{\mu}_a^t$, and \bar{p}^t appearing in $F_c^{(N)}(x^{(N)}; t)$ which are determined by thermodynamic correspondence and expressed in terms of the nonequilibrium partition function as in (10.136)–(10.139) in the nonequilibrium ensemble method. We define

fluctuations in the parameters T^{-1} , \bar{X}_{qa} , $\bar{\mu}_a$, and \bar{p} from those thermodynamically determined, T^{t-1} , \bar{X}_{qa}^t , $\bar{\mu}_a^t$, and \bar{p}^t :

$$\begin{aligned}\delta\bar{I} &= T^{-1} - T^{t-1}, & \delta\bar{X}_{qa} &= \bar{X}_{qa} - \bar{X}_{qa}^t, \\ \delta\bar{\mu}_a &= \bar{\mu}_a - \bar{\mu}_a^t, & \delta\bar{p} &= \bar{p} - \bar{p}^t.\end{aligned}\quad (10.151)$$

These definitions are exactly the same as for the case of dilute gases discussed in Chapters 7 and 9.

By using the forms for G_{ja} and \mathcal{H}_{ja} as given in (10.146) and (10.147) together with the definitions in (10.151), we find the relative Boltzmann entropy in the form

$$\mathcal{S}_r[F^{(N)}|F_c^{(N)}] = \mathcal{E}\delta\bar{I} + v\delta\bar{p} - \sum_{a=1}^r c_a \delta\bar{\mu}_a + \sum_{a=1}^r \sum_{q \geq 1} \hat{\Phi}_{qa} \delta\bar{X}_{qa}. \quad (10.152)$$

This also is in exactly the same form as for the dilute gases. By the Klein inequality $\ln x \geq 1 - x^{-1}$ applied to the statistical definition of relative Boltzmann entropy, there holds the inequality

$$\mathcal{S}_r[F^{(N)}|F_c^{(N)}] \geq 0, \quad (10.153)$$

the equality holding only if $F^{(N)} = F_c^{(N)}$. The equality implies the vanishing fluctuations, when looked at from the viewpoint of (10.152). In general, from inequality (10.153) follows the inequality between the Boltzmann entropy and the calortropy:

$$\mathcal{S} \leq \hat{\Psi}, \quad (10.154)$$

which suggests a loss of information content when the thermodynamic branch $F_c^{(N)}$ is constructed from $F^{(N)}$ as prescribed in the nonequilibrium ensemble theory. We also see that the fluctuations are such that

$$\mathcal{E}\delta\bar{I} + v\delta\bar{p} - \sum_{a=1}^r c_a \delta\bar{\mu}_a + \sum_{a=1}^r \sum_{q \geq 1} \hat{\Phi}_{qa} \delta\bar{X}_{qa} \geq 0. \quad (10.155)$$

By applying the same method as for the calortropy balance equation, we can express the relative Boltzmann entropy balance equation in the form

$$\begin{aligned}\frac{d}{dt} \mathcal{S}_r[F^{(N)}|F_c^{(N)}] &= -\frac{d\mathcal{E}}{dt} \delta\bar{I} - \frac{dv}{dt} \delta\bar{p} + \sum_{a=1}^r \frac{dc_a}{dt} \delta\bar{\mu}_a - \sum_{a=1}^r \sum_{q \geq 1} \frac{d\hat{\Phi}_{qa}}{dt} \delta\bar{X}_{qa} \\ &\quad + \hat{\Sigma}_l + \rho^{-1} \sum_{a=1}^r \sum_{q \geq 1} \bar{X}_{qa} Z_{qa},\end{aligned}\quad (10.156)$$

where $\widehat{\Sigma}_l$ is defined in (7.97). This equation is also in the same form as for the dilute gases described in Chapters 7 and 9. If the fluctuations all vanish then the relative Boltzmann entropy evolves according to the equation

$$\frac{d}{dt} \mathcal{S}_r[F^{(N)}|F_c^{(N)}] = \widehat{\Sigma}_l + \rho^{-1} \sum_{a=1}^r \sum_{q \geq 1} \bar{X}_{qa} Z_{qa}. \quad (10.157)$$

The right hand side of this equation generally does not vanish if there are irreversible processes in the system. Moreover, these irreversible processes depend on the path in the thermodynamic space \mathfrak{P} . Therefore, as in the case of dilute gases, we can conclude that the Boltzmann entropy is not a state function in the thermodynamic space mentioned since

$$\frac{dS}{dt} = \frac{d\widehat{\Psi}}{dt} - \frac{d}{dt} \mathcal{S}_r[F^{(N)}|F_c^{(N)}], \quad (10.158)$$

which depends on the path of evolution of the irreversible process on account of the time derivative of the relative Boltzmann entropy. Therefore, as for the classical and quantum dilute gases considered in the previous chapters, it is possible to summarize this conclusion as a theorem.

Theorem 9 *The Boltzmann entropy differential dS for dense simple fluids described by the kinetic equation (10.14) is not an exact differential in the thermodynamic space \mathfrak{P} whereas $d\widehat{\Psi}$ is an exact differential in the same space. The rate of change in the relative Boltzmann entropy depends on the path of irreversible processes in the space \mathfrak{P} .*

The same conclusion was drawn for classical and quantum dilute gases on the basis of the Boltzmann equation and the kinetic equation for the singlet Wigner distribution function. It was the content of Theorem 5 and 7, which we see remains valid for dense fluids. It is as it should be, since thermodynamics is a general theory for macroscopic irreversible processes that should hold regardless of the state of aggregation of matter. The nonequilibrium ensemble method developed here then makes it possible to compute thermodynamic variables for nonequilibrium systems made up of liquids or dense gases in terms of the nonequilibrium partition function and, ultimately, in terms of molecular parameters and temperature. Therefore we have now acquired a theory of nonequilibrium liquids and dense gases which is completely parallel with the equilibrium Gibbs ensemble theory.

The evolution equations for fluctuations $\delta\bar{I}$ and so on alluded to earlier can be derived from the kinetic equation and the nonequilibrium distribution functions $F^{(N)}$ and $F_c^{(N)}$ which together may be written as

$$\begin{aligned} k_B \ln \left(\frac{F^{(N)}}{F_c^{(N)}} \right) &= - \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} \left(H_{ja} \delta\bar{I} + \sum_{q \geq 1} h_{ja}^{(q)} \delta\bar{X}_{qa} \right) \delta(\mathbf{r}_{ja} - \mathbf{r}) \\ &+ \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} m_a (\delta\bar{\mu}_a - v\delta\bar{p}) \delta(\mathbf{r}_{ja} - \mathbf{r}). \end{aligned} \quad (10.159)$$

Let M_{kb} represent phase functions such as H_{kb} , $h_{kb}^{(l)}$, or m_b . Multiply $M_{kb} (\partial/\partial t + L^{(N)})$ to (10.159) from left and integrate the resulting equation over the phase space to obtain,

$$\mathfrak{M}_k \equiv k_B \left\langle M_{kb} \left(\frac{\partial}{\partial t} + L^{(N)} \right) \ln \left(\frac{F^{(N)}}{F_c^{(N)}} \right) \right\rangle. \quad (10.160)$$

On substitution of (10.159) into this equation we obtain

$$\begin{aligned} \mathfrak{M}_k = & - \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} M_{kb} \left(\frac{\partial}{\partial t} + L^{(N)} \right) H_{ja} \delta \bar{I} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle \\ & - \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} M_{kb} \left(\frac{\partial}{\partial t} + L^{(N)} \right) \sum_{q \geq 1} \delta \bar{X}_{qa} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle \\ & + \int_V d\mathbf{r} \left\langle \sum_{a=1}^r \sum_{ja=1}^{N_a} M_{kb} \left(\frac{\partial}{\partial t} + L^{(N)} \right) m_a (\delta \bar{\mu}_a - v \delta \bar{p}) \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle. \end{aligned} \quad (10.161)$$

This equation, when evaluated explicitly, gives rise to a linear combination of time derivatives of $\delta \bar{I}$, $\delta \bar{X}_{qa}$, $\delta \bar{\mu}_a$, and $\delta \bar{p}$. On the other hand, use of the kinetic equation in (10.160) puts \mathfrak{M}_k in the form

$$\mathfrak{M}_k = k_B \left\langle M_{kb} \Re[F^{(N)}] \right\rangle - k_B \left\langle M_{kb} \left(\frac{\partial}{\partial t} + L^{(N)} \right) \ln F_c^{(N)} \right\rangle \quad (10.162)$$

With (10.161) substituted into the left hand side, this equation becomes a set of coupled equations which determine fluctuations $\delta \bar{I}$, $\delta \bar{X}_{qa}$, $\delta \bar{\mu}_a$, and $\delta \bar{p}$. They are deterministic equations for $\delta \bar{I}$, $\delta \bar{X}_{qa}$, $\delta \bar{\mu}_a$, and $\delta \bar{p}$ generalizing to dense fluids the fluctuation evolution equations presented in Chapter 7. The second term on the right hand side of (10.162) does not vanish and can be explicitly worked out with the form for $F_c^{(N)}$ given earlier. Since the ensemble method in practice assumes vanishing fluctuations, the deterministic evolution of fluctuations is not an object of study in irreversible thermodynamics except for investigations on the question of the fundamental basis of the ensemble theory. For this reason we will not dwell on the details of the evolution equations for fluctuations in this work, although a theory of fluctuations is of intrinsic interest in statistical mechanics and we have briefly touched on this subject in Chapter 7.

10.6 Summing up

The thermodynamics of irreversible processes, as is the thermodynamics of reversible processes, is a formal and general theory structured on the

laws of thermodynamics. When supplemented with suitable constitutive equations, the formal theory takes a more concrete form which makes it possible to interpret macroscopic phenomena without reference to molecular models of substances. The nonequilibrium ensemble method developed here is a formal theory which can be formulated on the basis of a postulate for the existence of a collision term satisfying the three conditions listed early in the development, but it nevertheless provides the molecular theoretic foundations of such a theory of irreversible processes. Formulation of such a formal theory does not require a detailed model for the collision term. Such a model becomes necessary when the details of the constitutive equations are required in order to interpret experimental data on transport processes and material functions for the fluid in terms of molecular properties. Boltzmann's kinetic theory has provided us with a paradigm for our study in irreversible thermodynamics and nonequilibrium ensemble methods for dense fluids, and the two subjects are synergistically studied throughout this work under the paradigm. The lesson learned from the Boltzmann kinetic theory should also guide us in inventing suitable collision terms which will be adequate for appropriate understandings of nonequilibrium phenomena in dense fluids. We have seen in the discussion leading to (10.12) an example of how one might model a suitable collision term. Since the main aim of this work is to put in place a formal theoretical structure for nonequilibrium ensemble methods for fluids of all densities and some examples for such collision term are already available in [5], they are not discussed here. When such a collision term is explicitly postulated in one form or another, one will be able to calculate the dissipation terms in the evolution equations for nonconserved variables spanning the nonequilibrium part of the thermodynamic space and therewith transport processes and transport coefficients. Physical insights into nonequilibrium processes and proper understandings of collision processes at the molecular level will aid us in finding such collision terms, and detailed and hard calculations in comparison with experiments will make us refine them well enough to account for irreversible processes in sufficient generality. We owe it to Boltzmann [12], who provided us with the lasting insights into the nature of irreversible phenomena and the basic theoretical framework, albeit for dilute gases, that we have been able to come up with the theoretical structures of nonequilibrium ensemble methods in the present work. *The important point is that one does not have to solve the Boltzmann equation before erecting a theory of irreversible processes with the solution. We only need to use the kinetic equation and exploit the properties of the collision term therein which are embodied by Conditions 1-3 mentioned earlier.* In other words, irreversible thermodynamics for dilute gases is an exact formal consequence of the Boltzmann equation and the attendant nonequilibrium canonical or grand canonical form of distribution function. The same point applies to the case of dense fluids, as has been shown. Thus, I believe that we now have theoretical tools to effectively treat irreversible phenom-

ena in fluids in a way that is consistent with the laws of thermodynamics and parallel with the Gibbsian ensemble theory for equilibrium which has been so powerful in treating equilibrium phenomena in terms of molecular models. The fundamental object of attention here is the nonequilibrium partition function, but this quantity demands the knowledge of generalized hydrodynamic processes if we desire to acquire a complete interpretation of experimental data on nonequilibrium processes. We have repeatedly shown the importance of the relative Boltzmann entropy in relating the thermodynamics of irreversible processes and the phase space evolution of macroscopic variables. The evolutions of these two sets of macroscopic variables are not necessarily the same, if there are fluctuations in the intensive variables. Such fluctuations are important in understanding the mutual relation of the second law of thermodynamics and the H theorem. Further studies of such fluctuations will be quite useful and beneficial, but it is clear from the study made in this work that the second law of thermodynamics can be violated if the fluctuations are large, even if the H theorem is strictly satisfied. This is an interesting and useful piece of result of the present work.

The theories, macroscopic and microscopic, presented in this work appear to be labyrinthine at a quick glance, but after all we have made an attempt to put irreversible thermodynamics, kinetic theory, and nonequilibrium ensemble methods under the umbrella of the laws of thermodynamics, and the unified development of such theories cannot be expected to be simple. Nevertheless, the overall strategy can be summarized in the flowchart of Fig. 10.1 which I believe presents basic skeletal features of the theories and their mutual relationships in a single glance. Viewed from this chart, generalized hydrodynamics, embodied, for example, by the evolution equations (10.32)–(10.35) and (10.39), is an integral part of nonequilibrium statistical mechanics and irreversible thermodynamics in the present theory. Generalized hydrodynamics, more complicated than the classical hydrodynamics of Navier, Stokes, and Fourier, poses difficult mathematical tasks but offers considerable promises for understanding nonlinear irreversible phenomena not amenable by the classical hydrodynamics, as shown by the examples of application presented in Chapter 8. Despite the daunting tasks, with the promises held out by the theory we now are given motivations to exert ourselves more strenuously toward the goal, and there is much work to do.

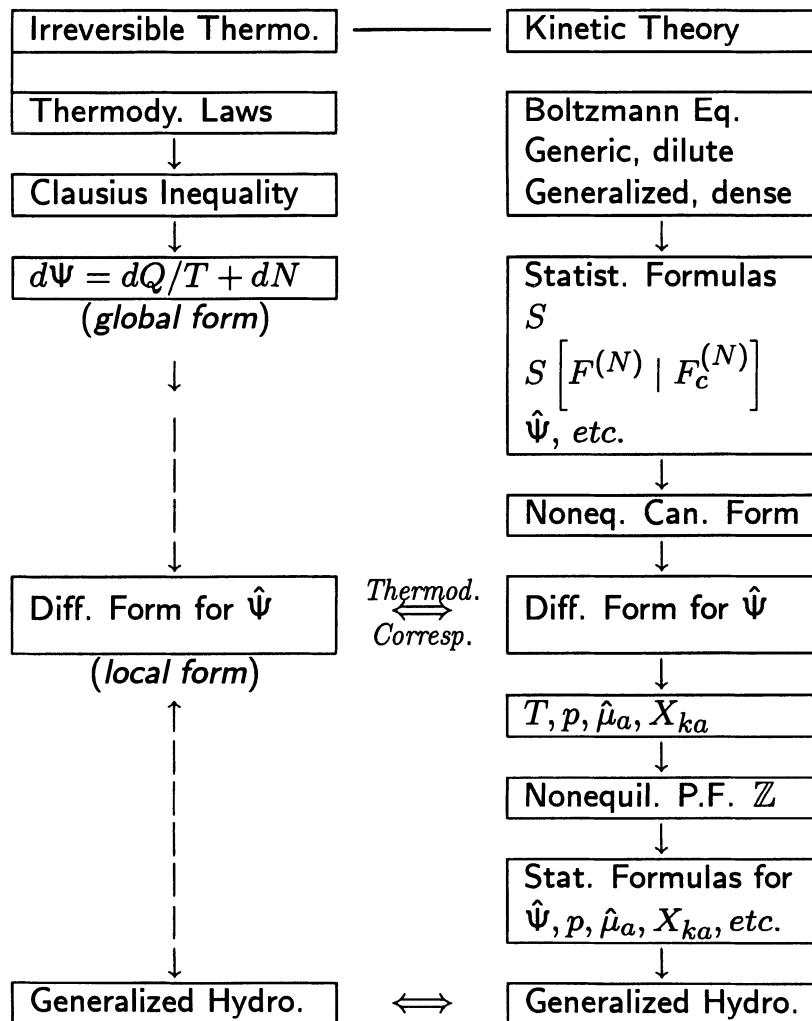


FIGURE 10.1 Flowchart for irreversible thermodynamics, nonequilibrium statistical thermodynamics, and their relationship.

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Appendix A

Addition Theorem of Tensor Hermite Polynomials

Here we list some of examples for the addition theorem for leading tensor Hermite polynomials. Hermite polynomial $\mathcal{H}^{(q)}(\mathbf{w})$ is a Cartesian tensor of rank q and its product with another polynomial $\mathcal{H}^{(p)}(\mathbf{w})$ is a linear combination of tensor Hermite polynomials $\mathcal{H}^{(k)}(\mathbf{w})$ whose maximum rank is $(p+q)$. These examples become handy later when some approximation methods are discussed.

$$\mathcal{H}_{i_1}^{(1)} \mathcal{H}_{j_1}^{(1)} = \mathcal{H}_{i_1 j_1}^{(2)} + \delta_{i_1 j_1}, \quad (\text{A.1})$$

$$\mathcal{H}_{i_1}^{(1)} \mathcal{H}_{j_1 j_2}^{(2)} = \mathcal{H}_{i_1 j_1 j_2}^{(3)} + \delta_{i_1 j_1} \mathcal{H}_{j_2}^{(1)} + \delta_{i_1 j_2} \mathcal{H}_{j_1}^{(1)}, \quad (\text{A.2})$$

$$\begin{aligned} \mathcal{H}_{i_1 i_2}^{(2)} \mathcal{H}_{j_1 j_2}^{(2)} &= \mathcal{H}_{i_1 i_2 j_1 j_2}^{(4)} + \delta_{i_1 j_1} \mathcal{H}_{i_2 j_2}^{(2)} + \delta_{i_1 j_2} \mathcal{H}_{i_2 j_1}^{(2)} + \delta_{i_2 j_1} \mathcal{H}_{i_1 j_2}^{(2)} \\ &\quad + \delta_{i_2 j_2} \mathcal{H}_{i_1 j_1}^{(2)} + \delta_{i_1 j_1} \delta_{i_2 j_2} + \delta_{i_1 j_2} \delta_{i_2 j_1}. \end{aligned} \quad (\text{A.3})$$

The subsequent examples are given with some of subscripts omitted for brevity of the expressions:

$$\mathcal{H}_{i_1}^{(2)} \mathcal{H}^{(3)} = \mathcal{H}^{(4)} + \delta_i \mathcal{H}^{(2)}, \quad \text{etc.,} \quad (\text{A.4})$$

$$\mathcal{H}_{ij}^{(2)} \mathcal{H}^{(2)} = \mathcal{H}^{(4)} + \delta_i \mathcal{H}_j^{(2)} + \delta_j \mathcal{H}_i^{(2)} + \delta_i \delta_j, \quad (\text{A.5})$$

$$\mathcal{H}_{ij}^{(2)} \mathcal{H}^{(3)} = \mathcal{H}^{(5)} + \delta_i \mathcal{H}_j^{(3)} + \delta_j \mathcal{H}_i^{(3)} + \delta_i \delta_j \mathcal{H}^{(1)}, \quad (\text{A.6})$$

$$\mathcal{H}_{ij}^{(2)} \mathcal{H}^{(4)} = \mathcal{H}^{(6)} + \delta_i \mathcal{H}_j^{(4)} + \delta_j \mathcal{H}_i^{(4)} + \delta_i \delta_j \mathcal{H}^{(2)}, \quad (\text{A.7})$$

$$\mathcal{H}_{ij}^{(2)} \mathcal{H}^{(5)} = \mathcal{H}^{(7)} + \delta_i \mathcal{H}_j^{(5)} + \delta_j \mathcal{H}_i^{(5)} + \delta_i \delta_j \mathcal{H}^{(3)}, \quad \text{etc.,} \quad (\text{A.8})$$

$$\begin{aligned} \mathcal{H}_{ijk}^{(3)} \mathcal{H}^{(3)} &= \mathcal{H}^{(6)} + \delta_i \mathcal{H}_{jk}^{(4)} + \delta_j \mathcal{H}_{ik}^{(4)} + \delta_k \mathcal{H}_{ij}^{(4)} + \delta_i \delta_j \mathcal{H}_k^{(2)} \\ &\quad + \delta_i \delta_k \mathcal{H}_j^{(2)} + \delta_j \delta_k \mathcal{H}_i^{(2)} + \delta_i \delta_k \mathcal{H}_{jk}^{(2)} + \delta_j \delta_k \mathcal{H}_{ik}^{(2)} \end{aligned}$$

$$+ \delta_k \delta \mathcal{H}_{ij}^{(2)} + \delta_i \delta_j \delta_k, \quad (\text{A.9})$$

$$\begin{aligned} \mathcal{H}_{ijk}^{(3)} \mathcal{H}^{(4)} = & \mathcal{H}^{(7)} + \delta_i \mathcal{H}_{jk}^{(5)} + \delta_j \mathcal{H}_{ik}^{(5)} + \delta_k \mathcal{H}_{ij}^{(5)} + \delta_i \delta_j \mathcal{H}_k^{(3)} \\ & + \delta_i \delta_k \mathcal{H}_j^{(3)} + \delta_j \delta_k \mathcal{H}_i^{(3)} + \delta_i \delta \mathcal{H}_{jk}^{(3)} + \delta_j \delta \mathcal{H}_{ik}^{(3)} \\ & + \delta_k \delta \mathcal{H}_{ij}^{(3)} + \delta_i \delta_j \delta_k \mathcal{H}^{(1)}, \quad \text{etc..} \end{aligned} \quad (\text{A.10})$$

These expansion formulas are used in computing various moments in this work.

Appendix B

Density Matrix and Evolution Equations

In this appendix the density matrix version (9.7) of the BNUU kinetic equation in Chapter 9 is used to derive the evolution equations for conserved and nonconserved variables spanning the thermodynamic space. It is possible to show that these evolution equations form a theory of irreversible processes. For the formulation of such a theory the reader is referred to [1] listed at the end of this appendix.

B.1 Quantum Operator Calculus

It is necessary to establish the evolution equation for $\ln \mathbf{f}_a$ and $\ln(1 + \epsilon_a \mathbf{f}_a)$ since the density matrix is a quantum operator. For this purpose we first review some of the mathematical identities [2] for operators and their time derivatives in quantum mechanics.

Let us consider two quantum mechanical operators x and y which do not commute. If operator z is such that

$$e^x e^y = e^z, \quad (\text{B.1})$$

then

$$z = x + y + \frac{1}{2}[x, y] + \frac{1}{3}[[x, y], y] + \dots \quad (\text{B.2})$$

If the l nested commutators $[[\dots [x, y], y] \overbrace{\dots, y}]^{l \text{ times}}, y]$ where the y factors appear l times within the commutators are abbreviated by $\{x, y^l\} \equiv [[\dots$

$[x, y], y] \overbrace{\dots, y}, y]$ then z may be expressed as a series in nested commutators:

$$z = x + y + \frac{1}{2}[x, y] + \frac{1}{2} \sum_{l \geq 2} \frac{1}{(l+1)!} (\{x, y^l\} + \{y, (-x)^l\}). \quad (\text{B.3})$$

This is the Baker–Hausdorff formula [3,4]. The curly braces are reserved for the nested commutators in this and other calculations associated with

commutators in this appendix. In addition to this relation, the following well known operator relation will be useful for our calculations:

$$e^{-x}ye^x = \sum_{l=0}^{\infty} \frac{1}{l!} \{y, x^l\}. \quad (\text{B.4})$$

Applying this relation, we obtain

$$e^{-x} \left(y \frac{\partial}{\partial x} \right) e^x = \sum_{l=0}^{\infty} \frac{1}{l!} \left\{ \left(y \frac{\partial}{\partial x} \right), x^l \right\}. \quad (\text{B.5})$$

Since

$$\left\{ \left(y \frac{\partial}{\partial x} \right), x^0 \right\} = 0, \quad \{y, x^0\} = y,$$

and

$$\left\{ \left(y \frac{\partial}{\partial x} \right), x^l \right\} = \{y, x^{l-1}\}$$

for $l \geq 1$, we find the series in (B.5) in the form

$$e^{-x} \left(y \frac{\partial}{\partial x} \right) e^x = \sum_{l=1}^{\infty} \frac{1}{l!} \{y, x^{l-1}\} = \left\{ y, \frac{e^x - 1}{x} \right\}. \quad (\text{B.6})$$

By using the identity $\{\{y, x^l\}, x^m\} = \{y, x^{l+m}\}$, it is easy to show

$$\left[\left(y \frac{\partial}{\partial x} \right) e^x \right] e^{-x} = e^x \left\{ y, \frac{e^x - 1}{x} \right\} e^{-x} = \left\{ y, \frac{1 - e^{-x}}{x} \right\}. \quad (\text{B.7})$$

According to Magnus [1] there holds the following lemma:

Lemma *Let P and Q such that $PQ = 1$ and $\{y, P\} = z$. Then $y = \{z, Q\}$ and vice versa.*

This lemma obviously enables us to solve a commutator relation in terms of the inverse of the operator with which the operator in question forms a (nested) commutator. This and the aforementioned mathematical identities are useful in the calculations performed below.

Let operator \mathbf{F} be defined such that

$$\mathbf{f}_a = e^{\mathbf{F}}. \quad (\text{B.8})$$

The evolution equation for \mathbf{F} is then obtained by using the identities given earlier. First, we note

$$\begin{aligned} \frac{\partial}{\partial t} e^{\mathbf{F}} &= \left(\frac{\partial \mathbf{F}}{\partial t} \frac{\partial}{\partial \mathbf{F}} \right) e^{\mathbf{F}} \\ &= \left\{ \frac{\partial \mathbf{F}}{\partial t}, \frac{1 - e^{-\mathbf{F}}}{\mathbf{F}} \right\} e^{\mathbf{F}} \\ &= (i\hbar)^{-1} [\mathbf{H}_a, \mathbf{f}_a] + \mathbf{R}[\mathbf{f}_a]. \end{aligned} \quad (\text{B.9})$$

Applying the Magnus lemma to this equation we obtain

$$\frac{\partial \mathbf{F}}{\partial t} e^{\mathbf{F}} = \left\{ (i\hbar)^{-1} [\mathbf{H}_a, \mathbf{f}_a], \frac{\mathbf{F}}{1 - e^{-\mathbf{F}}} \right\} + \left\{ \mathbf{R}[\mathbf{f}_a], \frac{\mathbf{F}}{1 - e^{-\mathbf{F}}} \right\}. \quad (\text{B.10})$$

That is, written in terms of \mathbf{f}_a ,

$$\begin{aligned} \left(\frac{\partial}{\partial t} \ln \mathbf{f}_a \right) \mathbf{f}_a &= \left\{ (i\hbar)^{-1} [\mathbf{H}_a, \mathbf{f}_a], \frac{\ln \mathbf{f}_a}{1 - e^{-\ln \mathbf{f}_a}} \right\} \\ &\quad + \left\{ \mathbf{R}[\mathbf{f}_a], \frac{\ln \mathbf{f}_a}{1 - e^{-\ln \mathbf{f}_a}} \right\}. \end{aligned} \quad (\text{B.11})$$

By applying to this formula the Bernoulli expansion [5]

$$\frac{\tau}{e^\tau - 1} = \sum_{l=0}^{\infty} \frac{B_l}{l!} \tau^l$$

where B_l are the Bernoulli numbers, $B_0 = 1$, $B_1 = -\frac{1}{2}$, $B_2 = \frac{1}{6}$, $B_4 = -\frac{1}{30}$, $B_6 = \frac{1}{42}$, and so on, and $B_{2l+1} = 0$ ($l \geq 1$), we obtain

$$\begin{aligned} \left(\frac{\partial}{\partial t} \ln \mathbf{f}_a \right) \mathbf{f}_a &= (i\hbar)^{-1} [\mathbf{H}_a, \mathbf{f}_a] + \mathbf{R}[\mathbf{f}_a] \\ &\quad + \sum_{l=1}^{\infty} \frac{B_l}{l!} \left\{ (i\hbar)^{-1} [\mathbf{H}_a, \mathbf{f}_a] + \mathbf{R}[\mathbf{f}_a], (-\ln \mathbf{f}_a)^l \right\}. \end{aligned} \quad (\text{B.12})$$

A similar calculation can be made for $\ln(1 + \epsilon_a \mathbf{f}_a)$ to obtain the equation

$$\begin{aligned} \left[\frac{\partial}{\partial t} \ln(1 + \epsilon_a \mathbf{f}_a) \right] &= (i\hbar)^{-1} \left\{ [\mathbf{H}_a, (1 + \epsilon_a \mathbf{f}_a)], \frac{\ln(1 + \epsilon_a \mathbf{f}_a)}{1 - e^{-\ln(1 + \epsilon_a \mathbf{f}_a)}} \right\} \\ &\quad + \left\{ \mathbf{R}[\mathbf{f}_a], \frac{\ln(1 + \epsilon_a \mathbf{f}_a)}{1 - e^{-\ln(1 + \epsilon_a \mathbf{f}_a)}} \right\}. \end{aligned} \quad (\text{B.13})$$

These results are useful for calculating evolutions of quantum mechanical operators.

B.2 The H theorem

To be concrete, we will assume

$$\mathbf{R}[\mathbf{f}_a] = \sum_{b=1}^r \text{Tr}_{(b)} W_{ab}^{(\epsilon)} [\mathbf{f}'_a \mathbf{f}'_b (1 + \epsilon_a \mathbf{f}_a) (1 + \epsilon_b \mathbf{f}_b) - \mathbf{f}_a \mathbf{f}_b (1 + \epsilon_a \mathbf{f}'_a) (1 + \epsilon_b \mathbf{f}'_b)], \quad (\text{B.14})$$

the prime denoting the post-collision density operator. This form suggests the Boltzmann entropy in the form

$$S = -k_B \sum_{a=1}^r \text{Tr} (\ln \mathbf{f}_a - \epsilon_a (1 + \epsilon_a \mathbf{f}_a) \ln(1 + \epsilon_a \mathbf{f}_a)). \quad (\text{B.15})$$

By differentiating this Boltzmann entropy formula and using the quantum kinetic equation (9.7), we obtain

$$\begin{aligned} \frac{dS}{dt} &= -\frac{k_B}{i\hbar} \sum_{a=1}^r \text{Tr} (\ln \mathbf{f}_a [\mathbf{H}_a, \mathbf{f}_a] - \epsilon_a \ln(1 + \epsilon_a \mathbf{f}_a) [\mathbf{H}_a, (1 + \epsilon_a \mathbf{f}_a)]) \\ &\quad - k_B \sum_{a=1}^r \text{Tr} ([\ln \mathbf{f}_a - \ln(1 + \epsilon_a \mathbf{f}_a)] \mathbf{R}[\mathbf{f}_a]) \\ &\quad - \frac{k_B}{i\hbar} \sum_{a=1}^r \text{Tr} \left\{ [\mathbf{H}_a, \mathbf{f}_a], \frac{\ln \mathbf{f}_a}{1 - e^{-\ln \mathbf{f}_a}} \right\} \\ &\quad + \frac{k_B}{i\hbar} \sum_{a=1}^r \text{Tr} \left\{ [\mathbf{H}_a, (1 + \epsilon_a \mathbf{f}_a)], \frac{\epsilon_a \ln(1 + \epsilon_a \mathbf{f}_a)}{1 - e^{-\ln(1 + \epsilon_a \mathbf{f}_a)}} \right\} \\ &\quad - k_B \sum_{a=1}^r \text{Tr} \left\{ \mathbf{R}[\mathbf{f}_a], \frac{\ln \mathbf{f}_a}{1 - e^{-\ln \mathbf{f}_a}} \right\} \\ &\quad + k_B \sum_{a=1}^r \text{Tr} \left\{ \mathbf{R}[\mathbf{f}_a], \frac{\epsilon_a \ln(1 + \epsilon_a \mathbf{f}_a)}{1 - e^{-\ln(1 + \epsilon_a \mathbf{f}_a)}} \right\}. \end{aligned} \quad (\text{B.16})$$

The last four terms on the right hand side can be shown to vanish and the first term also vanishes at the boundary of the system. Therefore we have

$$\begin{aligned} \frac{dS}{dt} &= -k_B \sum_a^r \text{Tr} ([\ln \mathbf{f}_a - \ln(1 + \epsilon_a \mathbf{f}_a)] \mathbf{R}[\mathbf{f}_a]) \\ &= k_B \sum_a^r \text{Tr} (\ln(\epsilon_a + \mathbf{f}_a^{-1}) \mathbf{R}[\mathbf{f}_a]) \geq 0, \end{aligned} \quad (\text{B.17})$$

since $\mathbf{R}[\mathbf{f}_a]$ satisfies Condition 2 imposed on the collision term in Chapter 9. This inequality is satisfied by the collision term given in (B.14). We note that

$$\text{Tr}[\mathbf{H}_a, \mathbf{f}_a] = \text{Tr}(\mathbf{R}[\mathbf{f}_a]) = 0,$$

$$\text{Tr}\{[\mathbf{H}_a, \mathbf{f}_a], P(\ln \mathbf{f}_a)\} = \text{Tr}\{\mathbf{R}[\mathbf{f}_a], P(\ln \mathbf{f}_a)\} = 0,$$

where $P(\ln \mathbf{f}_a)$ is a function of $\ln \mathbf{f}_a$. These identities have been used to obtain (B.17) from (B.16). We now observe that because of these identities

the time derivative of the Boltzmann entropy could have been calculated without taking into account the noncommutativity of the quantum operators involved, and thus by simply taking the time derivative of $\ln \mathbf{f}_a$ as if it is a classical object. However, this conclusion was not known at the beginning.

B.3 Evolution Equations for Macroscopic Variables

Here we present evolution equations for macroscopic variables which have been obtained by using the density matrix method. The balance equations for mass, momentum, and energy have been derived by a number of authors [6–9] in the past. Here the evolution equations for nonconserved variables are also derived. However, we will not describe the details of the derivations, but present the results only.

The local mass density $\rho(\mathbf{r}, t)$ at position \mathbf{r} and time t is defined by

$$\rho(\mathbf{r}, t) = \sum_{a=1}^r \text{Tr}[m_a \delta(\mathbf{r}_a - \mathbf{r}) \mathbf{f}_a(t)]. \quad (\text{B.18})$$

The mass density of species a may also be defined by

$$\rho_a(\mathbf{r}, t) = \text{Tr}[m_a \delta(\mathbf{r}_a - \mathbf{r}) \mathbf{f}_a(t)]. \quad (\text{B.19})$$

Therefore, the total mass density is

$$\rho(\mathbf{r}, t) = \sum_{a=1}^r \rho_a(\mathbf{r}, t). \quad (\text{B.20})$$

The mass fraction c_a is then defined, as in the classical theory, by the formula

$$c_a = \frac{\rho_a(\mathbf{r}, t)}{\rho(\mathbf{r}, t)}, \quad (\text{B.21})$$

which normalizes to unity by definition. By differentiating (B.18) with time and using the kinetic equation (9.7) and the conditions on the collision term, we obtain the equation of continuity. Since other evolution equations can be derived similarly to this equation, we illustrate the method of derivation with this example. The time derivative of (B.18) is given by

$$\begin{aligned} \partial_t \rho &= \text{Tr} \left(\sum_{a=1}^r m_a \delta(\mathbf{r}_a - \mathbf{r}) \partial_t \mathbf{f}_a \right) \\ &= (i\hbar)^{-1} \text{Tr} \left(\sum_{a=1}^r m_a \delta(\mathbf{r}_a - \mathbf{r}) [\mathbf{H}_a, \mathbf{f}_a] \right) \end{aligned}$$

$$+ \text{Tr} \left(\sum_{a=1}^r m_a \delta(\mathbf{r}_a - \mathbf{r}) \mathbf{R}[\mathbf{f}_a] \right). \quad (\text{B.22})$$

The second term on the right hand side vanishes by virtue of the condition on the collision term $\mathbf{R}[\mathbf{f}_a]$. For brevity of notation the delta function $\delta(\mathbf{r}_a - \mathbf{r})$ will be abbreviated with δ_a . By using the cyclic property of the trace of operator products, $\text{Tr}(\mathbf{ABC}) = \text{Tr}(\mathbf{BCA}) = \text{Tr}(\mathbf{CAB})$, the first term of the right hand side of (B.22) can be written as

$$\begin{aligned} \text{Tr}(m_a \delta(\mathbf{r}_a - \mathbf{r}) [\mathbf{H}_a, \mathbf{f}_a]) &= -\text{Tr}([\mathbf{H}_a, m_a \delta_a] \mathbf{f}_a) \\ &= -\frac{1}{2} i \hbar \nabla \cdot \text{Tr}[(\mathbf{p}_a \delta_a + \delta_a \mathbf{p}_a) \mathbf{f}_a]. \end{aligned} \quad (\text{B.23})$$

To obtain the second equality we first observe that by the commutation relation $[\mathbf{r}_a, \mathbf{p}_a] = -(\mathbf{p}_a \mathbf{r}_a)$, where the parentheses mean that \mathbf{p}_a operates on \mathbf{r}_a only, the commutator in the first line can be calculated as follows:

$$\begin{aligned} 2m_a [\mathbf{H}_a, \delta_a] \mathbf{f}_a &= [p_a^2, \delta_a] \mathbf{f}_a \\ &= (\mathbf{p}_a \cdot [\mathbf{p}_a, \delta_a] + [\mathbf{p}_a, \delta_a] \cdot \mathbf{p}_a) \mathbf{f}_a \\ &= [\mathbf{p}_a \cdot (\mathbf{p}_a \delta_a) + (\mathbf{p}_a \delta_a) \cdot \mathbf{p}_a] \mathbf{f}_a. \end{aligned}$$

Then, by using the property of the delta function

$$\nabla_i \delta(\mathbf{r}_i - \mathbf{r}) = -\nabla \delta(\mathbf{r}_i - \mathbf{r})$$

where $\nabla_i = \partial/\partial r_i$ and $\nabla = \partial/\partial \mathbf{r}$, we arrive at the second equality in (B.23). Therefore, with the definition of mean velocities \mathbf{u}_a and \mathbf{u} by the formulas

$$\rho_a \mathbf{u}_a(\mathbf{r}, t) = \text{Tr}[\frac{1}{2} (\mathbf{p}_a \delta_a + \delta_a \mathbf{p}_a) \mathbf{f}_a], \quad (\text{B.24})$$

and

$$\rho \mathbf{u}(\mathbf{r}, t) = \sum_{a=1}^r \rho_a \mathbf{u}_a(\mathbf{r}, t), \quad (\text{B.25})$$

we obtain the equation of continuity (mass balance equation)

$$\partial_t \rho = -\nabla \cdot \rho \mathbf{u}. \quad (\text{B.26})$$

It must be noted that the definition of the average velocity \mathbf{u}_a involves a symmetrized product of \mathbf{p}_a and δ_a , and this appearance of a symmetrized product is a natural consequence of quantum mechanics. As will be seen, various symmetrized products of momenta and a delta function appears

naturally when the evolution equations for macroscopic variables are sequentially derived step by step starting from the equation of continuity.

We now define the peculiar velocity operator \mathbf{C}_a by

$$\mathbf{C}_a = m_a^{-1} \mathbf{p}_a - \mathbf{u}. \quad (\text{B.27})$$

The diffusion flux \mathbf{J}_a of species a can then be defined by the symmetrized product

$$\mathbf{J}_a = \text{Tr} \left[\frac{1}{2} m_a (\mathbf{C}_a \delta_a + \delta_a \mathbf{C}_a) \mathbf{f}_a \right]. \quad (\text{B.28})$$

Here the velocity \mathbf{u} is a classical variable as any other macroscopic averaged variables are, and thus commutes with the delta function δ_a and other quantum mechanical operators. All other mean continuum macroscopic variables are classical in that sense. Similar calculation can be made for the time derivative of the mass density ρ_a as for ρ , and we obtain

$$\partial_t \rho_a = -\nabla \cdot \rho_a \mathbf{u}_a. \quad (\text{B.29})$$

This can be put into the form

$$\rho d_t c_a = -\nabla \cdot \mathbf{J}_a. \quad (\text{B.30})$$

By differentiating (B.25) with time, using the kinetic equation (9.7), and applying the same procedure as for the equation of continuity, we obtain the momentum balance equation

$$\rho d_t \mathbf{u} = -\nabla \cdot \mathbf{P} + \rho \mathbf{F}(\mathbf{r}, t), \quad (\text{B.31})$$

where \mathbf{P} is the stress tensor defined by

$$\begin{aligned} P_{\beta\gamma} &= \sum_{a=1}^r (\mathbf{P}_a)_{\beta\gamma} \\ &= \frac{1}{4} \sum_{a=1}^r \text{Tr} [m_a (C_{a\beta} C_{a\gamma} \delta_a + C_{a\beta} \delta_a C_{a\gamma} \\ &\quad + C_{a\gamma} \delta_a C_{a\beta} + \delta_a C_{a\beta} C_{a\gamma}) \mathbf{f}_a] \end{aligned} \quad (\text{B.32})$$

$$\begin{aligned} \rho \mathbf{F} &= \sum_a^r \rho_a \mathbf{F}_a \\ &= - \sum_{a=1}^r \text{Tr} [\delta_a (\nabla_a \mathfrak{V}) \mathbf{f}_a] \equiv \sum_{a=1}^r \text{Tr} (\delta_a \mathcal{F}_a \mathbf{f}_a). \end{aligned} \quad (\text{B.33})$$

Note that $\mathcal{F}_a = -\nabla_a \mathfrak{V}$ is the force on a particle of species a located at \mathbf{r}_a . The Greek subscripts β and γ in (B.33) refer to the Cartesian components

of the vectors and the tensors involved. The peculiar velocity product in (B.33) is symmetrized owing to the noncommutativity of the operators involved.

The internal energy can be defined by the formula

$$\rho\mathcal{E}(\mathbf{r}, t) = \frac{1}{8} \sum_{a=1}^r \text{Tr} [m_a (\mathbf{C}_a \cdot \mathbf{C}_a \delta_a + 2\mathbf{C}_a \delta_a \cdot \mathbf{C}_a + \delta_a \mathbf{C}_a \cdot \mathbf{C}_a) \mathbf{f}_a]. \quad (\text{B.34})$$

On application of the procedure used for deriving the aforementioned balance equations for mass and momentum, this definition gives rise to the energy balance equation as follows:

$$\rho d_t \mathcal{E} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a. \quad (\text{B.35})$$

Here \mathbf{Q} is the heat flux defined by

$$\begin{aligned} \mathbf{Q} &= \sum_{a=1}^r \mathbf{Q}_a \\ &= \frac{1}{16} \sum_{a=1}^r \text{Tr} [m_a (C_a^2 \mathbf{C}_a \delta_a + C_a^2 \delta_a \mathbf{C}_a + 2\mathbf{C}_a \mathbf{C}_a \delta_a \cdot \mathbf{C}_a \\ &\quad + 2\mathbf{C}_a \cdot \delta_a \mathbf{C}_a \mathbf{C}_a + \mathbf{C}_a \delta_a C_a^2 + \delta_a C_a^2 \mathbf{C}_a) \mathbf{f}_a]. \end{aligned} \quad (\text{B.36})$$

If the statistical formulas (B.28), (B.33), and (B.36) are differentiated with time and the kinetic equation (9.7) is used, the evolution equations for \mathbf{J}_a , \mathbf{P} , and \mathbf{Q} will follow. Since a mixture is under consideration, it is more appropriate to derive evolution equations for species components \mathbf{P}_a and \mathbf{Q}_a from their statistical definitions:

$$\begin{aligned} P_{\alpha\beta\gamma} &= \frac{1}{4} \text{Tr} [m_a (C_{\alpha\beta} C_{\alpha\gamma} \delta_a + C_{\alpha\beta} \delta_a C_{\alpha\gamma} \\ &\quad + C_{\alpha\gamma} \delta_a C_{\alpha\beta} + \delta_a C_{\alpha\beta} C_{\alpha\gamma}) \mathbf{f}_a], \end{aligned} \quad (\text{B.37})$$

$$\begin{aligned} \mathbf{Q}_a &= \frac{1}{16} \text{Tr} [m_a (C_a^2 \mathbf{C}_a \delta_a + C_a^2 \delta_a \mathbf{C}_a + 2\mathbf{C}_a \mathbf{C}_a \delta_a \cdot \mathbf{C}_a \\ &\quad + 2\mathbf{C}_a \cdot \delta_a \mathbf{C}_a \mathbf{C}_a + \mathbf{C}_a \delta_a C_a^2 + \delta_a C_a^2 \mathbf{C}_a) \mathbf{f}_a]. \end{aligned} \quad (\text{B.38})$$

The calculations required are rather tedious but straightforward. With the definitions $\widehat{\mathbf{P}}_a = \mathbf{P}_a / \rho$, $\widehat{\mathbf{Q}}_{aa} = \mathbf{Q}_a / \rho$, and $\widehat{\mathbf{J}}_a = \mathbf{J}_a / \rho$, they are given by the equations

$$\rho d_t \widehat{\mathbf{P}}_a = -\nabla \cdot \bar{\psi}_{1a} - [(d_t \mathbf{u} - \mathbf{F}_a) \mathbf{J}_a + \mathbf{J}_a (d_t \mathbf{u} - \mathbf{F}_a)]$$

$$-[\mathbf{P}_a \cdot \nabla \mathbf{u} + (\nabla \mathbf{u})^t \cdot \mathbf{P}_a^t] + \Lambda_a^{(s)}, \quad (\text{B.39})$$

$$\rho d_t \hat{\mathbf{Q}}_a = -\nabla \cdot \bar{\psi}_{3a} - (\mathbf{P}_a - p_a \delta) \cdot (d_t \mathbf{u} - \mathbf{F}_a) - \varphi_a^{(3)} : \nabla \mathbf{u} - \mathbf{Q}_a \cdot \nabla \mathbf{u}$$

$$-\frac{\rho_a \hbar^2}{24m_a^2} [\nabla^2 \mathbf{F}_a + 2\nabla(\nabla \cdot \mathbf{F}_a)] + O(\hbar^4) + \Lambda_a^{(h)}, \quad (\text{B.40})$$

$$\rho d_t \hat{\mathbf{J}}_a = -\nabla \cdot \mathbf{P}_a - \rho_a (d_t \mathbf{u} - \mathbf{F}_a) - \mathbf{J}_a \cdot \nabla \mathbf{u} + \Lambda_a^{(d)}. \quad (\text{B.41})$$

Here, the superscript t means the transpose of the tensor, δ denotes the unit second rank tensor, and various other symbols are defined by the statistical expressions

$$\begin{aligned} \bar{\psi}_{a\beta\gamma\epsilon}^{(1)} &= \frac{1}{8} \text{Tr} [m_a (C_{a\beta} C_{a\gamma} C_{a\epsilon} \delta_a + C_{a\beta} C_{a\gamma} \delta_a C_{a\epsilon} \\ &\quad + C_{a\beta} \delta_a C_{a\gamma} C_{a\epsilon} + \delta_a C_{a\beta} C_{a\gamma} C_{a\epsilon} \\ &\quad + C_{a\beta} C_{a\epsilon} \delta_a C_{a\gamma} + C_{a\epsilon} C_{a\gamma} \delta_a C_{a\beta} \\ &\quad + C_{a\gamma} \delta_a C_{a\beta} \delta_a C_{a\epsilon} + C_{a\epsilon} \delta_a C_{a\gamma} C_{a\beta}) \mathbf{f}_a], \quad (\text{B.42}) \end{aligned}$$

$$\begin{aligned} \bar{\psi}_{a\beta\gamma}^{(3)} &= \frac{1}{32} \text{Tr} [m_a (C_{a\beta} C_{a\gamma} C_{a\epsilon}^2 \delta_a + C_{a\beta} C_{a\gamma} \delta_a C_{a\epsilon}^2 \\ &\quad + C_{a\beta} \delta_a C_{a\gamma} C_{a\epsilon}^2 + C_{a\beta} \delta_a C_{a\gamma} C_{a\epsilon}^2 \\ &\quad + \delta_a C_{a\beta} C_{a\gamma} C_{a\epsilon}^2 + C_{a\beta} C_{a\epsilon}^2 \delta_a C_{a\gamma} \\ &\quad + C_{a\gamma} \beta C_{a\epsilon}^2 \delta_a C_{a\beta} + C_a^2 \delta_a C_{a\beta} C_{a\gamma} \\ &\quad + C_{a\gamma} \delta_a C_{a\beta} C_{a\epsilon}^2 + 2C_{a\beta} C_{a\gamma} C_{a\epsilon} \delta_a C_{a\epsilon} \\ &\quad + 2C_{a\beta} C_{a\epsilon} \delta_a C_{a\epsilon} C_{a\gamma} + 2C_{a\gamma} C_{a\epsilon} \delta_a C_{a\epsilon} C_{a\beta} \\ &\quad + 2C_{a\epsilon} \delta_a C_{a\epsilon} C_{a\beta} C_{a\gamma}) \mathbf{f}_a], \quad (\text{B.43}) \end{aligned}$$

$$\varphi_{a\beta\gamma\epsilon}^{(3)} = \bar{\psi}_{a\beta\gamma\epsilon}^{(1)}. \quad (\text{B.44})$$

$$\Lambda_{a\alpha\beta}^{(s)} = \frac{1}{4} \text{Tr} [m_a (C_{a\alpha} C_{a\beta} \delta_a + C_{a\alpha} \delta_a C_{a\beta}),$$

$$+ C_{\alpha\beta}\delta_a C_{a\alpha} + \delta_a C_{aa}C_{\alpha\beta})\mathbf{R}[\mathbf{f}_a]] \quad (\text{B.45})$$

$$\begin{aligned} \Lambda_a^{(h)} = & \frac{1}{16}\text{Tr}[m_a(C_a^2\mathbf{C}_a\delta_a + C_a^2\delta_a\mathbf{C}_a + 2\mathbf{C}_a\mathbf{C}_a\delta_a \cdot \mathbf{C}_a \\ & + 2\mathbf{C}_a \cdot \delta_a\mathbf{C}_a\mathbf{C}_a + \mathbf{C}_a\delta_aC_a^2 + \delta_aC_a^2\mathbf{C}_a)\mathbf{R}[\mathbf{f}_a]], \end{aligned} \quad (\text{B.46})$$

$$\Lambda_a^{(d)} = \frac{1}{2}\text{Tr}[m_a(\mathbf{C}_a\delta_a + \delta_a\mathbf{C}_a)\mathbf{R}[\mathbf{f}_a]], \quad (\text{B.47})$$

Calculation of these evolution equations will be elaborated on later.

It is convenient to define the following abbreviations for the symmetrized molecular expressions appearing in the stress tensor and the heat flux:

$$\begin{aligned} \bar{h}_{a\beta\gamma}^{(1)} = & \frac{m_a}{4}(C_{\alpha\beta}C_{a\gamma}\delta_a + C_{\alpha\beta}\delta_aC_{a\gamma} + C_{a\gamma}\delta_aC_{\alpha\beta} + \delta_aC_{\alpha\beta}C_{a\gamma}) \\ & - \frac{m_a}{12}(C_{a\epsilon}^2\delta_a + C_{a\epsilon}\delta_aC_{a\epsilon} + C_{a\epsilon}\delta_aC_{a\epsilon} + \delta_aC_{a\epsilon}^2)\delta_{\beta\gamma}, \end{aligned} \quad (\text{B.48})$$

$$\begin{aligned} \bar{h}_a^{(2)} = & \frac{m_a}{12}(C_a^2\delta_a + \mathbf{C}_a\delta_a \cdot \mathbf{C}_a + \mathbf{C}_a\delta_a \cdot \mathbf{C}_a + \delta_aC_a^2) - \frac{p_a m_a}{\rho_a}\delta_a \end{aligned} \quad (\text{B.49})$$

$$\begin{aligned} \bar{h}_a^{(3)} = & \frac{m_a}{16}(C_a^2\mathbf{C}_a\delta_a + C_a^2\delta_a\mathbf{C}_a + 2\mathbf{C}_a\mathbf{C}_a\delta_a \cdot \mathbf{C}_a + 2\mathbf{C}_a\delta_a \cdot \mathbf{C}_a\mathbf{C}_a \\ & + \mathbf{C}_a\delta_aC_a^2 + \delta_aC_a^2\mathbf{C}_a) - \frac{1}{2}\hat{h}_a m_a(\mathbf{C}_a\delta_a + \delta_a\mathbf{C}_a), \end{aligned} \quad (\text{B.50})$$

$$\bar{h}_a^{(4)} = \frac{m_a}{2}(\mathbf{C}_a\delta_a + \delta_a\mathbf{C}_a), \quad (\text{B.51})$$

where $\delta_{\beta\gamma}$ is a Kronecker delta and the Einstein summation convention is used for repeated Greek indices. The average of $\bar{h}_a^{(k)}$ is denoted by

$$\Phi_{ka} = \rho\widehat{\Phi}_{ka} = \text{Tr}\left(\bar{h}_a^{(k)}\mathbf{f}_a\right). \quad (\text{B.52})$$

These definitions of moments also motivate us to define the quantities:

$$\begin{aligned} \psi_{1a\beta\gamma\epsilon} &= \bar{\psi}_{1a\beta\gamma\epsilon} - \frac{1}{3}\bar{\psi}_{a\sigma\sigma\epsilon}^{(1)}\delta_{\beta\gamma} \\ &= \frac{1}{2}\text{Tr}\left[\left(\bar{h}_{a\beta\gamma}^{(1)}C_{a\epsilon} + C_{a\epsilon}\bar{h}_{a\beta\gamma}^{(1)}\right)\mathbf{f}_a\right], \end{aligned} \quad (\text{B.53})$$

$$\begin{aligned} \psi_{2a\epsilon} &= \frac{1}{3}\bar{\psi}_{1a\beta\beta\epsilon} - \frac{p_a}{\rho_a}J_{a\epsilon} \\ &= \frac{1}{2}\text{Tr}\left[\left(\bar{h}_a^{(2)}C_{a\epsilon} + C_{a\epsilon}\bar{h}_a^{(2)}\right)\mathbf{f}_a\right], \end{aligned} \quad (\text{B.54})$$

$$\begin{aligned}\psi_{3a\beta\gamma} &= \bar{\psi}_{3a\beta\gamma} - \hat{h}_a P_{a\beta\gamma} \\ &= \frac{1}{2} \text{Tr} \left[\left(\bar{h}_{a\beta}^{(3)} C_{a\gamma} + C_{a\gamma} \bar{h}_{a\beta}^{(3)} \right) \mathbf{f}_a \right].\end{aligned}\quad (\text{B.55})$$

With the molecular moments $\bar{h}_a^{(1)}$ and so on defined earlier we define the dissipative terms

$$\Lambda_{ka} = \text{Tr} \left(\bar{h}_a^{(k)} \mathbf{R}[\mathbf{f}_a] \right) \quad (k = 1, 2, 3, 4, \dots), \quad (\text{B.56})$$

and the corresponding kinematic terms

$$\begin{aligned}\mathcal{Z}_{ka} &= (i\hbar)^{-1} \text{Tr} \left[\frac{1}{2} m_a C_a^2, \mathbf{f}_a \bar{h}_a^{(k)} \right] \\ &\quad + \text{Tr} \left[\mathbf{f}_a \left(\frac{\partial}{\partial t} \bar{h}_a^{(k)} - (i\hbar)^{-1} [\mathbf{H}_a, \bar{h}_a^{(k)}] \right) \right]\end{aligned}\quad (\text{B.57})$$

where $k = 1, 2, 3, 4, \dots$. When the first term on the right hand side of (B.57) is calculated a little further, the kinematic term may be written as

$$\mathcal{Z}_{ka} = -\nabla \cdot \psi_{ka} + \text{Tr} \left[\mathbf{f}_a \left(\frac{\partial}{\partial t} \bar{h}_a^{(k)} - (i\hbar)^{-1} [\mathbf{H}_a, \bar{h}_a^{(k)}] \right) \right]. \quad (\text{B.58})$$

Calculated explicitly in terms of macroscopic variables, these kinematic terms are as follows:

$$\begin{aligned}\mathcal{Z}_{1a} &= -\nabla \cdot \psi_{1a} - [(d_t \mathbf{u} - \mathbf{F}_a) \mathbf{J}_a]^{(2)} - 2[\mathbf{\Pi}_a \cdot \boldsymbol{\gamma}]^{(2)} \\ &\quad - [\mathbf{\Pi}_a, \boldsymbol{\omega}] - \frac{2}{3} \mathbf{\Pi}_a \nabla \cdot \mathbf{u},\end{aligned}\quad (\text{B.59})$$

$$\begin{aligned}\mathcal{Z}_{2a} &= -\nabla \cdot \psi_{2a} - \frac{2}{3} (d_t \mathbf{u} - \mathbf{F}_a) \cdot \mathbf{J}_a - p_a d_t \ln(p_a v^{5/3}) \\ &\quad - \frac{2}{3} \mathbf{\Pi}_a \cdot \boldsymbol{\gamma} - \frac{2}{3} \Delta_a \nabla \cdot \mathbf{u} - \nabla \cdot \left(\frac{p_a}{\rho_a} \mathbf{J}_a \right),\end{aligned}\quad (\text{B.60})$$

$$\begin{aligned}\mathcal{Z}_{3a} &= -\nabla \cdot \psi_{3a} - (\mathbf{P}_a - p_a \boldsymbol{\delta}) \cdot (d_t \mathbf{u} - \mathbf{F}_a) - \boldsymbol{\varphi}_a^{(3)} : \nabla \mathbf{u} \\ &\quad - \mathbf{Q}'_a \cdot \nabla \mathbf{u} - \mathbf{J}_a d_t \hat{h}_a - \mathbf{P}_a \cdot \nabla \hat{h}_a \\ &\quad - \frac{\rho_a \hbar^2}{24 m_a^2} [\nabla^2 \mathbf{F}_a + 2\nabla(\nabla \cdot \mathbf{F}_a)] + O(\hbar^4),\end{aligned}\quad (\text{B.61})$$

$$\mathcal{Z}_{4a} = -\nabla \cdot \mathbf{P}_a - \rho_a (d_t \mathbf{u} - \mathbf{F}_a) - \mathbf{J}_a \cdot \nabla \mathbf{u}. \quad (\text{B.62})$$

These are exactly the same kinematic terms appearing in the evolution equations in (9.166)–(9.169) which were obtained from the kinetic equation for the Wigner distribution function. Here various symbols are defined by

$$\gamma = \frac{1}{2}[\nabla \mathbf{u} + (\nabla \mathbf{u})^t] - \frac{1}{3}\delta \nabla \cdot \mathbf{u},$$

$$\omega = \frac{1}{2}[\nabla \mathbf{u} - (\nabla \mathbf{u})^t],$$

$$[\Pi_a, \omega] = \Pi_a \omega - \omega \Pi_a.$$

These definitions also appeared in the previous chapters.

B.3.1 Boltzmann Entropy Balance Equation

The evolution equations for conserved and nonconserved variables presented earlier are subject to the constraint of the H theorem. Since the evolution equations are local, it is necessary to have the entropy constraint also in local form, and such a local form is the balance equation for the Boltzmann entropy. To derive it, it is first necessary to define the Boltzmann entropy density at position \mathbf{r} and time t . We define it by

$$S(t) = \int_V d\mathbf{r} \rho S(\mathbf{r}, t). \quad (\text{B.63})$$

Comparison of this with the statistical definition of $S(t)$ in (B.15) yields the statistical formula for the Boltzmann entropy density

$$\begin{aligned} \rho S(\mathbf{r}, t) &= -k_B \sum_{a=1}^r \text{Tr} [\mathbf{f}_a \{\delta_a \ln \mathbf{f}_a\} - \epsilon_a (1 + \epsilon_a \mathbf{f}_a) \{\delta_a \ln(1 + \epsilon_a \mathbf{f}_a)\}] \\ &= k_B \sum_{a=1}^r \text{Tr} [\mathbf{f}_a \{\delta_a \ln(\epsilon_a + \mathbf{f}_a^{-1})\} + \epsilon_a \{\delta_a \ln(1 + \epsilon_a \mathbf{f}_a)\}], \end{aligned} \quad (\text{B.64})$$

where the delta function δ_a is symmetrized with the logarithmic functions of \mathbf{f}_a since the distribution function is generally a function of momentum. It is convenient to define

$$\mathfrak{F}_a = \epsilon_a \mathbf{f}_a^{-1} \ln(1 + \epsilon_a \mathbf{f}_a) \quad (\text{B.65})$$

$$\mathfrak{G}_a = \ln(1 + \epsilon_a \mathbf{f}_a^{-1}) \quad (\text{B.66})$$

By differentiating the formula (B.64) for the Boltzmann entropy density and using the kinetic equation together with the mathematical identities

leading to (B.12) and (B.13), we obtain the Boltzmann entropy balance equation

$$\rho d_t \mathcal{S}(\mathbf{r}, t) = -\nabla \cdot \mathbf{J}_s(\mathbf{r}, t) + \sigma_{\text{ent}}(\mathbf{r}, t) \quad (\text{B.67})$$

where the Boltzmann entropy flux \mathbf{J}_s and the Boltzmann entropy production σ_{ent} are given respectively by

$$\mathbf{J}_s(\mathbf{r}, t) = \frac{1}{2} k_B \sum_{a=1}^r \text{Tr} ([\mathbf{C}_a \{(\mathfrak{G}_a + \mathfrak{F}_a) \delta_a\} + \{(\mathfrak{G}_a + \mathfrak{F}_a) \delta_a\} \mathbf{C}_a] f_a), \quad (\text{B.68})$$

$$\sigma_{\text{ent}}(\mathbf{r}, t) = -k_B \sum_{a=1}^r \text{Tr} (\{\mathfrak{G}_a \delta_a\} \mathbf{R}[\mathbf{f}_a]). \quad (\text{B.69})$$

The definition of the Boltzmann entropy production in (B.69) follows straightforwardly from the production term

$$k_B \sum_a^r \text{Tr}\{\ln(\epsilon_a + \mathbf{f}_a^{-1}) \mathbf{R}[\mathbf{f}_a]\},$$

which we recover on integrating (B.69) over the volume of the system. The definition of the Boltzmann entropy flux $\mathbf{J}_s(\mathbf{r}, t)$ in (B.68) arises as follows. First, observe that it stems from the first term on the right hand side of (B.11). After symmetrizing the logarithmic factors with δ_a , the said term can be manipulated into the divergence form

$$\begin{aligned} \mathfrak{D}_a &\equiv -\frac{k_B}{i\hbar} \text{Tr} (\{\delta_a \ln \mathbf{f}_a\} [\mathbf{H}_a, \mathbf{f}_a] - \epsilon_a \{\delta_a \ln(1 + \epsilon_a \mathbf{f}_a)\} [\mathbf{H}_a, (1 + \epsilon_a \mathbf{f}_a)]) \\ &= \frac{k_B}{i\hbar} \text{Tr} ([\mathbf{H}_a, \{\delta_a \ln \mathbf{f}_a\}] f_a - \epsilon_a [\mathbf{H}_a, \{\delta_a \ln(1 + \epsilon_a \mathbf{f}_a)\}] (1 + \epsilon_a \mathbf{f}_a)) \\ &= (i\hbar)^{-1} \text{Tr} \frac{1}{2m_a} [p_a^2, \{\delta_a \ln \mathbf{f}_a\}] \mathbf{f}_a \\ &\quad - (i\hbar)^{-1} \text{Tr} \frac{1}{2m_a} \epsilon_a [p_a^2, \{\delta_a \ln(1 + \epsilon_a \mathbf{f}_a)\}] (1 + \epsilon_a \mathbf{f}_a) \\ &= (i\hbar)^{-1} \text{Tr} \frac{1}{2m_a} [(\mathbf{p}_a \cdot [\mathbf{p}_a, \{\delta_a \ln \mathbf{f}_a\}] + [\mathbf{p}_a, \{\delta_a \ln \mathbf{f}_a\}] \cdot \mathbf{p}_a) \mathbf{f}_a \\ &\quad - \epsilon_a \mathbf{p}_a \cdot [\mathbf{p}_a, \{\delta_a \ln(1 + \epsilon_a \mathbf{f}_a)\}] (1 + \epsilon_a \mathbf{f}_a) \\ &\quad - \epsilon_a [\mathbf{p}_a, \{\delta_a \ln(1 + \epsilon_a \mathbf{f}_a)\}] \cdot \mathbf{p}_a (1 + \epsilon_a \mathbf{f}_a)] \\ &= (i\hbar)^{-1} \text{Tr} \frac{1}{2m_a} [(\mathbf{p}_a \cdot (\mathbf{p}_a \{\delta_a \ln \mathbf{f}_a\}) + (\mathbf{p}_a \{\delta_a \ln \mathbf{f}_a\}) \cdot \mathbf{p}_a) \mathbf{f}_a \end{aligned}$$

$$\begin{aligned}
& - \epsilon_a \mathbf{p}_a \cdot (\mathbf{p}_a \{\delta_a \ln(1 + \epsilon_a \mathbf{f}_a)\}) (1 + \epsilon_a \mathbf{f}_a) \\
& - \epsilon_a (\mathbf{p}_a \{\delta_a \ln(1 + \epsilon_a \mathbf{f}_a)\}) \cdot \mathbf{p}_a (1 + \epsilon_a \mathbf{f}_a) \\
= & \quad \nabla \cdot \text{Tr} \frac{1}{2m_a} (\mathbf{p}_a \{\delta_a \ln \mathbf{f}_a\} + \{\delta_a \ln \mathbf{f}_a\} \mathbf{p}_a) \mathbf{f}_a \\
& - \nabla \cdot \text{Tr} \frac{1}{2m_a} \epsilon_a \mathbf{p}_a \{\delta_a \ln(1 + \epsilon_a \mathbf{f}_a)\} (1 + \epsilon_a \mathbf{f}_a) \\
& + \nabla \cdot \text{Tr} \frac{1}{2m_a} \{\delta_a \ln(1 + \epsilon_a \mathbf{f}_a)\} \mathbf{p}_a (1 + \epsilon_a \mathbf{f}_a) \\
= & \quad - \nabla \cdot \sum_a^r k_B \text{Tr} \frac{1}{2} [(\mathbf{C}_a \{(\mathfrak{G}_a + \mathfrak{F}_a) \delta_a\} + \{(\mathfrak{G}_a + \mathfrak{F}_a) \delta_a \mathbf{C}_a\}) \mathbf{f}_a] \\
& - \nabla \cdot \sum_a^r \mathbf{u} k_B \text{Tr} [(\mathfrak{G}_a + \mathfrak{F}_a) \delta_a \mathbf{f}_a]. \tag{B.70}
\end{aligned}$$

Therefore summing this equation over species we obtain the divergence term in the Boltzmann entropy balance equation

$$\begin{aligned}
\nabla \cdot (\mathbf{J}_s + \rho \mathcal{S} \mathbf{u}) = & \quad \nabla \cdot \sum_{a=1}^r k_B \text{Tr} \frac{1}{2} \mathbf{C}_a \{(\mathfrak{G}_a + \mathfrak{F}_a) \delta_a\} \mathbf{f}_a \\
& + \nabla \cdot \sum_{a=1}^r k_B \text{Tr} \frac{1}{2} \{(\mathfrak{G}_a + \mathfrak{F}_a) \delta_a\} \mathbf{C}_a \mathbf{f}_a \\
& + \nabla \cdot \sum_{a=1}^r \mathbf{u} k_B \text{Tr} [(\mathfrak{G}_a + \mathfrak{F}_a) \delta_a \mathbf{f}_a]. \tag{B.71}
\end{aligned}$$

In the fourth equality of (B.70), $(\mathbf{p}_a \{\delta_a \ln \mathbf{f}_a\})$ means that \mathbf{p}_a operates on $\{\delta_a \ln \mathbf{f}_a\}$ only and similarly for $(\mathbf{p}_a \{\delta_a \ln(1 + \epsilon_a \mathbf{f}_a)\})$. For the fifth equality the property of the derivative of a delta function is used. Note that if the distribution function vanishes at the boundaries of the system then this divergence term, when integrated over the volume, does not contribute to the time derivative of the entropy (dS/dt). This was the result we used for (B.16).

B.3.2 The H theorem for the BNUU model

We now show the BNUU model satisfies the conditions required of the collision term $\mathbf{R}[\mathbf{f}_a]$. On multiplication of collision invariant operator \mathbf{A}_a

to $\mathbf{R}[\mathbf{f}_a]$, summation over species and taking trace, we find

$$\begin{aligned} \sum_{a=1}^r \text{Tr}_{(a)} \mathbf{A}_a \mathbf{R}[\mathbf{f}_a] &= \frac{1}{4} \sum_{a=1}^r \sum_{b=1}^r \text{Tr}_{(ab)} \left[(\mathbf{A}_a + \mathbf{A}_b - \mathbf{A}'_a - \mathbf{A}'_b) W_{ab}^{(\epsilon)} \right] \\ &\quad \times [\mathbf{f}'_a \mathbf{f}'_b (1 + \epsilon_a \mathbf{f}_a)(1 + \epsilon_b \mathbf{f}_b) - \mathbf{f}_a \mathbf{f}_b (1 + \epsilon_a \mathbf{f}'_a)(1 + \epsilon_b \mathbf{f}'_b)] \\ &= 0, \end{aligned} \tag{B.72}$$

since $\mathbf{A}_a + \mathbf{A}_b - \mathbf{A}'_a - \mathbf{A}'_b = 0$ by the fact that \mathbf{A}_a and so on are collision invariants. The prime denotes the post-collision value. Thus Condition 1 is satisfied by the collision term. Proceeding similarly with multiplication of $\ln(\epsilon_a + \mathbf{f}_a^{-1})$ to $\mathbf{R}[\mathbf{f}_a]$, we obtain

$$\begin{aligned} k_B^{-1} \sigma_{\text{ent}} &= \sum_{a=1}^r \text{Tr}_{(a)} [\ln(\epsilon_a + \mathbf{f}_a^{-1}) \mathbf{R}[\mathbf{f}_a]] \\ &= \frac{1}{4} \sum_{a=1}^r \sum_{b=1}^r \text{Tr}_{(ab)} \left[W_{ab}^{(\epsilon)} \ln \left(\frac{F_{ab}}{F'_{ab}} \right) (F_{ab} - F'_{ab}) \right] \\ &\geq 0, \end{aligned} \tag{B.73}$$

where

$$F_{ab} = \mathbf{f}'_a \mathbf{f}'_b (1 + \epsilon_a \mathbf{f}_a)(1 + \epsilon_b \mathbf{f}_b),$$

$$F'_{ab} = \mathbf{f}_a \mathbf{f}_b (1 + \epsilon_a \mathbf{f}'_a)(1 + \epsilon_b \mathbf{f}'_b).$$

This is the H theorem for the BNUU model.

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