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B.C. Eu

# Transport Coefficients of Fluids

With 65 Figures and 15 Tables



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## Preface

In this monograph, the density fluctuation theory of transport coefficients of simple and complex liquids is described together with the kinetic theory of liquids, the generic van der Waals equation of state, and the modified free volume theory. The latter two theories are integral parts of the density fluctuation theory, which enables us to calculate the density and temperature dependence of transport coefficients of liquids from intermolecular forces. The terms nanoscience and bioscience are the catch phrases currently in fashion in science. It seems that much of the fundamentals remaining unsolved or poorly understood in the science of condensed matter has been overshadowed by the frenzy over the more glamorous disciplines of the former, shunned by novices, and are on the verge of being forgotten. The transport coefficients of liquids and gases and related thermophysical properties of matter appear to be one such area in the science of macroscopic properties of molecular systems and statistical mechanics of condensed matter. Even nano- and bio materials, however, cannot be fully and appropriately understood without firm grounding and foundations in the macroscopic and molecular theories of transport properties and related thermophysical properties of matter in the condensed phase. One is still dealing with systems made up of not a few particles but a multitude of them, often too many to count, to call them few-body problems that can be understood without the help of statistical mechanics and macroscopic physics. In the density fluctuation theory of transport coefficients, the basic approach taken is quite different from the approaches taken in the conventional kinetic theories of gases and liquids. Yet, it provides us with a practical method of computing transport coefficients of fluids in the liquid density regime in terms of intermolecular and intramolecular forces.

As is well known, the trail of the molecular theory of transport processes in matter began with J. C. Maxwell closely followed by L. Boltzmann. It was Maxwell who obtained theoretical results for the transport coefficients of normal state gases, which were found independent of density. His theory set into motion the ever-widening frontiers of scientific investigation in the subject matter in many directions. We have seen in the literature numerous molecular

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and statistical mechanical theories of transport coefficients in dense gases and liquids that include the theory of D. Enskog, the theory of N. N. Bogoliubov, the theories of J. G. Kirkwood and his school, and the linear response theory. We have also seen developments in the opposite direction of decreasing density, namely, rarefied gas dynamics. These theories aim to account for the density and temperature dependence of transport coefficients of dense gases and liquids, first of all, in the linear regime near equilibrium. Except for the Enskog theory formulated for moderately dense gases, the aforementioned theories have not been fully demonstrated to qualitatively account even for the desired density and temperature dependence of the transport coefficients of liquids, which have been extensively measured by laboratory experiments and collated by many research workers in the fields. It is true that the desire to understand transport properties of matter is what has been a long running motivation for statistical mechanics and, especially, for kinetic theory, but the field has been stalled at numerous stumbling blocks that have been created by our difficulties in treating many-particle dynamic problems underlying the theories mentioned. If the subject matter related to the problem in question is examined in depth, it becomes clear that it will be difficult to make further progress unless our viewpoint is altered from the traditional one and different methodologies are employed.

The desired alternative viewpoint toward the problem in question is provided by recognizing the role of voids in liquids, which becomes important in creating density fluctuations in relatively high compaction of particles around a given point of observation in the liquid. Density fluctuations in such conditions are made possible by the creation of voids, and vice versa, and such density fluctuations drive diffusion of particles through the liquid. Therefore, diffusion of particles sets the time- and spatial scales for the transport of momentum and energy in liquids. This implies that the transport coefficients of the liquid depend on the self-diffusion coefficient of the liquid. This viewpoint has given rise to the density fluctuation theory of transport coefficients of liquids discussed in this work, in which all transport coefficients have been expressed in terms of a diffusion coefficient of one kind or another, in addition to the equilibrium pair correlation function and intermolecular force. Thus, we have a potentially completely molecular theory of transport coefficients of liquids and a semiempirical theory if the diffusion coefficient is treated as an empirical input. The modified free volume theory, developed subsequently to the density fluctuation theory, takes the theory steps closer to a completely ab initio molecular theory, thanks to the generic van der Waals equation of state, which enables us to quantify the mean free volume by the equilibrium statistical mechanics of the liquid. The combination of the density fluctuation theory, the modified free volume theory, and the generic van der Waals equation of state has been validated by comparison with experiment whenever possible.

I would like to acknowledge, particularly, the valuable contributions of Dr. Kyunil Rah, and those of Dr. Rozita Laghaei and Dr. Afshin Eskandari Nasrabad, in connection with the work presented in this monograph.

Finally, I would like to thank my wife Hui Young who has been generous in understanding and encouragement in the course of this work.

May 2005, Montreal

B.C.E.

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## **Part I**

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### **Transport Coefficients of Dilute Gases**

# 1

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## Introduction

The kinetic theories of James Clerk Maxwell [1] and Ludwig Boltzmann [2], formulated in the mid nineteenth century, were successful in giving atomistic theory accounts of the transport phenomena and thermal properties then known of dilute gases. Together with the theory of Willard Gibbs [3] for matter in equilibrium, which was developed subsequent to the kinetic theories of Maxwell and Boltzmann, statistical mechanics based on the particulate hypothesis of matter remains one of the principal theoretical tools for studying diverse natural phenomena in the macroscopic world of matter. Because the Maxwell–Boltzmann kinetic theory is for dilute gases in normal states, their theories have seen numerous theoretical efforts and studies to remove the limitations thereof in the latter half of the twentieth century. They have been made in the directions of rarefied gases, on the one hand, and of higher density gases and liquids, on the other hand, in addition to the efforts in rendering the theory capable of describing the thermophysical properties of complex molecular structures. Such efforts are still continuing, and this work constitutes a contribution to the kind of studies mentioned earlier in statistical mechanics.

In particular, in the post-World War II, era, we have seen the theories designed to generalize the Maxwell–Boltzmann kinetic theory to dense gases and liquids. The Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy theory [4–7], the linear response theory of Green [8], Kubo [9], and Mori [10], and the mode coupling theory [11] are important examples of such efforts toward the generalization mentioned. The basic ideas fundamental to the Boltzmann kinetic theory also have been taken in the formulation of generalized Boltzmann equations [12–14], which have been employed for studying irreversible thermodynamics and transport processes in condensed matter in recent years [15, 16]. The aims of these theories have been to enable us to calculate and account for thermophysical properties, such as transport coefficients and thermodynamic properties, of dense gases and matter in the condensed phase (e.g., liquids and solids) with regard to their density and temperature dependence as well as other thermophysical behavior of matter.

The aforementioned theories invariably require solutions of many-particle dynamics if the thermophysical properties are to be adequately studied in the density range of dense gases or liquids, but acquiring such solutions with good accuracy poses an enormous theoretical challenge.

For this practical reason, in recent years, they have been largely supplanted by computer simulation methods, which have become practicable with readily available computer resources. Computer simulation methods [17–19], however, have their own practical and theoretical limitations when they are applied to calculate, for example, transport coefficients of liquids (e.g., viscosity, thermal conductivity, diffusion coefficients) as functions of temperature and density.

For dynamic problems, such as transport coefficients, molecular dynamics (MD) simulation methods are used principally in conjunction with the linear response theory, whereas for equilibrium thermophysical properties Monte Carlo (MC) simulation methods [20, 21] are widely employed. MC simulation methods have fewer limitations than the former and yield robust results in many cases if, for example, large density fluctuations are not involved. However, the same cannot be said with assurance about MD simulation methods because there are some subtle questions regarding the definition of temperature and the use of constraints imposed on the system as external forces (e.g., shear). Nevertheless, computer simulation methods are akin to laboratory experiments on thermophysical properties, but still require numerous concepts and procedures to put them on firmer theoretical foundations of statistical mechanics and irreversible thermodynamics. Therefore, there is still considerable need to develop formal theories and practical, sometimes approximate, theories of nonequilibrium statistical mechanics to overcome the limitations posed by computer simulation methods and also by the aforementioned statistical mechanics theories for dense gases and liquids. At least, such practical theories would supplement computer simulation methods, if not serve as an alternative to MD simulation methods.

The aim of this work is to describe statistical mechanics theories for transport properties of dense gases and liquids in which the desired transport coefficients can be computed with sufficiently good accuracy if either equilibrium statistical mechanics methods or MC simulation methods are employed only for some equilibrium properties of the fluids. In other words, in the theories presented in this work, dynamic transport properties of dense gases and liquids are computed with acceptable accuracy as functions of density and temperature in terms of equilibrium quantities alone, which can be computed by either approximate equilibrium theories (e.g., integral equation theories for equilibrium correlation functions) or MC simulation methods. Monte Carlo simulation methods or integral equation theories for equilibrium properties enable us to get around the enormous difficulty posed by many-particle collision dynamics involved in the BBGKY hierarchy and linear response theory approaches.

Historically, all important concepts and basic principles have been formulated for transport processes in fluids by following the trails pioneered by Maxwell and Boltzmann and extending the theories of Chapman [22] and Enskog [23] based on the Boltzmann equation for dilute gases or the Enskog equation [24] for moderately dense gases. It is most natural to follow Maxwell and Boltzmann's lead and Chapman and Enskog after them because dilute gas transport processes are limiting phenomena at low density of the corresponding processes in dense gases or liquids. Therefore, it is important to have them firmly anchored in the Maxwell and Boltzmann kinetic theories for historical and heuristic reasons and also for the practical reason of obtaining a comprehensive theory of transport processes in fluids in general that includes dilute gas phenomena.

For this reason, we discuss the kinetic theory of transport processes in dilute gases by employing the Boltzmann kinetic equation for monatomic gases in Chap. 2. In Chap. 2, we quickly review the Chapman–Enskog theory of solution for the Boltzmann equation for monatomic gases and present formal expressions for various linear transport coefficients. The theory of nonlinear transport processes is also discussed within the framework of generalized hydrodynamics [15, 16, 25], which the present author has developed and applied to various flow problems in gases for a number of years. The transport coefficients associated with nonlinear transport processes can be calculated from generalized hydrodynamic equations, given the linear transport coefficients associated with them. Thus, we have a well-defined methodology for computing nonlinear transport coefficients, such as non-Newtonian viscosity, non-Fourier thermal conductivity, and non-Fickian diffusion coefficients, from knowledge of linear transport coefficients if related flow problems are solved with the generalized hydrodynamic equations mentioned. The formulas for transport coefficients are given for monatomic gases in Chap. 3, where some examples of nonlinear transport processes are also discussed to illustrate how the generalized hydrodynamic equations might be employed to study flows far removed from equilibrium. The results of these examples suggest a considerable potential for generalized hydrodynamics in the fields of gas dynamics in transient and hypersonic regimes of flow as demonstrated in the literature; see, for example, [15, 16, 25] and other references cited therein.

The kinetic theory of dilute gases discussed in Chaps. 2 and 3 applies to monatomic gases. The subject of dilute polyatomic gases is briefly discussed in Chaps. 4 and 5. The discussions are brief because the subject matter is less extensively developed in the literature and the development can be made parallel to those given in the previous chapters. Another important reason is that the present work is not principally for either monatomic or polyatomic gases, but for liquids. Therefore topics related to gases are discussed only to the extent they provide insights into the theories of transport processes in liquids and serve as the limiting theories of the more general theories developed for liquids. In these two chapters, we discuss some applications of dilute gas

transport processes, which may be employed for measuring the dilute gas transport coefficients of non monatomic gases.

In Part II, topics on gases discussed in Chaps. 2–5, are followed by chapters dealing with transport processes and, in particular, transport coefficients of liquids, the principal topics of this work. As intimated earlier, the basic approach taken for transport properties of liquids in this work is not that of the traditional one that extends the Chapman–Enskog line, in which the kinetic equation is solved, or that of the linear response theory, either one of which requires a solution of many-particle collision dynamics. Whereas the Chapman–Enskog approach builds the theory on the theory of gases and extends it, in the present approach, we begin from the liquid density end of the density spectrum and build the theory on the basis of what we believe the structure of liquids is while ensuring that the theory recovers the dilute gas results for the transport coefficients as the density is reduced to the state of dilute gases. This approach, which is diametrically opposite to that of the Chapman–Enskog theory based on the kinetic equation, requires accurate knowledge of equilibrium structures of liquids. This requires theories to handle equilibrium structure problems for liquids. For this important reason, we begin Part II with a chapter dealing with equilibrium structures of liquids under the title of equation of state and equilibrium properties of liquids.

The van der Waals equation of state has played an extremely important role in liquid physics, but it also has well known defects when the subcritical properties of liquids are studied with it. There have also been numerous attempts to derive it rigorously by statistical mechanics, but unsuccessfully. It is not an exact equation, and one does not derive an approximate equation rigorously. In Chapter 6, we discuss how to construct the canonical form of the equation of state and the statistical mechanical representation of free volume, which will occupy a central position in the theory of transport coefficients of liquids developed in later chapters. The canonical equation of state, also called the generic van der Waals (GvdW) equation of state, builds on the concept of mean free volume, first introduced by van der Waals himself. It is a statistical mechanics expression, which can be computed on the basis of only the intermolecular force at a given temperature and density of a liquid. The GvdW equation of state is the keystone in the density fluctuation theory of transport coefficients developed later in this work. In Chapter 6, an integral equation theory is also discussed, which ensures a thermodynamically consistent equation of state for liquids. Such a theory, it is hoped, will serve eventually as a computational means for pair distribution functions and the GvdW equation of state. Because the solution theory for the integral equation has not yet reached full maturity, only the general methodology will be discussed and only limited computational results will be presented for hard sphere fluids.

In the BBGKY hierarchy theory of dense gases and liquids, the goal is to achieve a systematic kinetic theory. It is based on the Liouville equation and aims to develop a theory of transport processes and other thermophysical

phenomena in dense gases and liquids. Because the Liouville equation is time-reversal invariant, the theory, viewed from the rigorous standpoint of irreversibility, is incapable of describing the irreversibility of thermal phenomena in liquids, although one may be able to achieve the goal by using suitable approximations. In this regard, it is important to observe the fundamental and qualitative difference between the Boltzmann equation and the Liouville equation. This difference should be regarded as something fundamental that cannot be derived from the equations of motion, either classical or quantum. Based on this important observation, a generalized Boltzmann equation was proposed for dense gases and liquids and applied to study irreversible phenomena in such fluids. The initial canonical ensemble formulation of the generalized Boltzmann equation was later further generalized to grand ensembles, and the meanings of the irreversible collision operator term in the kinetic equation were made more cogent. Because the generalized Boltzmann equation can be employed to formulate a theory of transport processes in dense gases and liquids, as shown in the literature, we provide a chapter summarizing the theory in Chapter 7 for simple fluids and in Chapter 8 for polyatomic fluids. Because of the difficulty of solving the many-particle collision dynamics problem required by this generalized Boltzmann equation approach, there are only limited results for transport coefficients of hard sphere fluids available in the literature. Nevertheless, this line of theory provides a theory of transport coefficients that recovers the transport coefficients by the traditional Boltzmann equation approach in the limit of low density. For this reason and because of the generalized hydrodynamic equations, which furnish the backdrop of the density fluctuation theory and rest on the support of the aforementioned kinetic equation, the kinetic theories based on the generalized Boltzmann equations are presented for simple and complex fluids, respectively, in Chaps. 7 and 8. The transport coefficients obtained by the generalized Boltzmann equations are given in terms of collision bracket integrals consisting only of equilibrium fluid attributes, although they involve many-particle collision dynamics. The subject matter is presented in the hope that computational algorithms will be developed for such collision bracket integrals in the future, so that the transport coefficients can be directly computed therewith.

The difficulty of solving the many-particle collision problem associated with the collision bracket integrals in the generalized Boltzmann equation approach provides motivations to seek an alternative approach. One alternative would be to take a viewpoint opposite to that in the traditional approach.

We observe that voids play an important role in thermal phenomena in liquids, and evidence for it can be seen in the early literature on the fluidity of liquids. For example, Batschinsky [26] proposed that the viscosity increases with third power of free volume, and later all phenomenological theories [27–30] of fluidity use the concept of free volume one way or another. This clearly suggests that the behavior of voids in liquids plays a central role in the transport of matter in the condensed phase. As the sizes

of void in liquids vary, the density fluctuates from position to position. Thus, we relate constitutive variables, such as stress tensors and heat fluxes, to density fluctuations by using the nonequilibrium ensemble distribution function provided by the generalized Boltzmann equation. The results are constitutive equations for transport coefficients. Comparing them with phenomenological constitutive equations, such as Newton's law of viscosity and Fourier's law of heat conduction, we derive statistical mechanical expressions for transport coefficients of liquids. This approach constitutes the density fluctuation theory of transport coefficients of liquids and dense gases described in Chapter 10 for simple liquids and in Chapter 11 for complex liquids, more specifically, for rigid diatomic liquids.

In this theory, the dynamic pair distribution functions appear in the constitutive equations. Because a general theory of treating the dynamic pair distribution functions is desirable, an integral equation for dynamic pair correlation functions that looks like the Ornstein–Zernike equation is derived, and its general properties are discussed in Chapter 9. The full potential of the dynamic Ornstein–Zernike equation has not yet been exploited for nonequilibrium statistical mechanics of transport processes. The topic is presented again in the hope that it will form the basis of a more comprehensive theory of transport processes in liquids in the future.

In the density fluctuation theory, transport coefficients consist of a kinetic part representative of the gas and a potential energy part representative of the liquid. The potential energy part is inversely proportional to the self-diffusion coefficient of the liquid. It resembles the well-known Stokes–Einstein relation between viscosity and the diffusion coefficient. However, the density fluctuation theory does not provide a readily computable theory for the self-diffusion coefficient. Thus the transport coefficients obtained need inputs from another source for the self-diffusion coefficient, and it renders the theory semiempirical if experimental data are used for the self-diffusion coefficient. Nevertheless, the theory is accurate and reliable in accounting for the density and temperature dependence of transport coefficients of the systems examined.

It is possible to remove the semiempiricism of the density fluctuation theory of transport coefficients mentioned if the modified free volume theory is used. As mentioned earlier, free volume theories have been around for many decades, but have not been successful as molecular theories of fluidity, primarily, because of the difficulty of quantifying the mean free volume in terms of statistical mechanical quantities and, secondarily, numerous other adjustable parameters. The free volume theory of Cohen and Turnbull [30] is in this category of theories, but it puts the essential point of free volume in a more lucid form than any other free volume theory in the literature. The modified free volume theory of diffusion mentioned reinterprets various parameters in the Cohen–Turnbull theory and provides a statistical mechanical representation of mean free volume with the help of the generic van der Waals equation of state. In Chap. 12, this modified free volume theory of diffusion is developed and applied to compute the transport coefficients obtained by the density

fluctuation theory in the previous chapters. The modified free volume theory contains two parameters, the free volume overlap factor  $\alpha$  and the minimum free volume  $v^*$ , which appear together as a product  $\alpha v^*$ . Therefore, this product may be interpreted as the critical free volume  $v_0$  that activates diffusion. The appearance of such a parameter is welcome because it is possible to comprehend diffusion in a physical term reflecting the molecular structure in the liquid. With such an interpretation, the self-diffusion coefficient sets time- and spatial scales for transport processes in a liquid. With thus calculated self-diffusion coefficient, various transport coefficients are computed according to the density fluctuation theory described in Chaps. 10 and 11. Although the range of validation is narrower than those in Chaps. 10 and 11 because there has not been much time for a more complete validation, it is clear from the results of validation made with empirical self-diffusion coefficients of various liquids in Chaps. 10 and 11 that the density fluctuation theory with the help of the modified free volume theory and the generic van der Waals equation of state is a reliable and robust molecular theory of transport coefficients of liquids. Albeit limited, the theory is successfully validated in comparison with experiment in Chap. 12. The implication of this limited validation is clear and resounding in the light of the successful semiempirical comparison of theory and experiment in Chaps. 10 and 11.

Therefore, it is fair to state that we now have a molecular theory of transport coefficients in the density range covering gases and liquids and in the temperature range including both supercritical and subcritical regimes. To achieve this goal, by providing the statistical mechanics expression for the mean free volume, the generic van der Waals equation of state holds together the density fluctuation theory and the modified free volume theory as a functioning and practical molecular theory structure, simply because it is capable of rigorously quantifying the notion of voids in liquids by statistical mechanics. In addition to this important role in the molecular theory of transport coefficients of liquids, the generic van der Waals equation of state holds up an alluring potential for fruitfully studying equilibrium thermodynamics of liquids that we can look forward to.

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## Boltzmann Equation for Dilute Monatomic Gases

Simple fluids consisting of monatomic molecules form a rather special class among the gases and liquids we encounter routinely in our daily life and in the laboratory. However, they occupy an important position in the statistical mechanics of fluids because they can be represented by the simplest model both mathematically and physically and, for this reason, they have been studied more in depth than other kinds of fluids. In many cases of more realistic nonmonatomic fluids, which may be termed complex fluids, some of their thermophysical properties can be fairly well approximated by the properties predicted by the theory of simple fluids. For example, there are diatomic or polyatomic molecules whose thermophysical properties can be rather close to those of monatomic fluids. In such cases, the theory of simple fluids can be a useful guide for understanding the macroscopic thermophysical behavior of such fluids. Of course, there are properties of such fluids which cannot be understood with a model good for monatomic fluids. Nevertheless, for the aforementioned reason, simple fluids are naturally the first subject to discuss in a kinetic theory of matter and statistical mechanics in general. In this work, the Boltzmann equation for monatomic gases will be discussed, especially, in relation to the predictions for both linear and nonlinear transport coefficients. By linear transport coefficients, we mean those associated with linear irreversible processes occurring near equilibrium and describable by linear constitutive equations for nonconserved variables such as the stress tensor, heat flux, and diffusion fluxes, whereas nonlinear transport coefficients mean those associated with the nonlinear constitutive equations for nonconserved variables mentioned earlier.

In their chapter, we will assume that the reader has a rudimentary understanding of the Boltzmann equation and its solution procedure for linear transport processes. So, we will simply proceed to a brief review of the procedures for acquiring linear transport coefficients and then a little more detailed discussion of nonlinear transport coefficients. Various technical details of obtaining linear transport coefficients are referred to in many excellent monographs [1–3] on the kinetic theory of gases.

## 2.1 Boltzmann Equation and Boltzmann Entropy

Assume that the fluid of interest is an  $r$ -component mixture of monatomic gases. Irreversible processes evolving in a macroscopic simple fluid mixture may be described by the well-known Boltzmann equation [4]. It is an evolution equation for the singlet distribution function of finding a monatomic molecule (particle) at a point in molecular phase space at time  $t$ . Let us denote the phase point of a particle by  $(\mathbf{r}, \mathbf{v}_a)$ , where  $\mathbf{r}$  is the position and  $\mathbf{v}_a$  is the velocity of molecule  $a$  in a suitably fixed coordinate system. Here, the subscript  $a$  plays a dual role of simultaneously indicating the species and a particle of that species, and the asterisk will be used to denote the postcollision value. Then the Boltzmann equation for the singlet distribution function  $f_a(\mathbf{r}, \mathbf{v}_a, t)$  for species  $a$  is given by

$$\partial_t f_a + \mathbf{v}_a \cdot \nabla f_a + \mathbf{F}_a \cdot \nabla_{\mathbf{v}_a} f_a = \mathfrak{R}_B[f_a], \quad (2.1)$$

where  $\mathbf{F}_a$  is the external force per mass on molecule  $a$  and the term  $\mathfrak{R}_B[f_a]$  stands for the collision integral defined by

$$\mathfrak{R}_B[f_a] = \sum_{b=1}^r C(f_a f_b) \quad (2.2)$$

with the definition

$$\begin{aligned} C(f_a f_b) = & \int d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} \, \mathbf{b} g_{ab} [f_a^*(\mathbf{v}_a^*, \mathbf{r}; t) f_b^*(\mathbf{v}_b^*, \mathbf{r}; t) \\ & - f_a(\mathbf{v}_a, \mathbf{r}; t) f_b(\mathbf{v}_b, \mathbf{r}; t)]. \end{aligned} \quad (2.3)$$

In these expressions, the operators for differentiations are abbreviated by the symbols  $\partial_t = \partial/\partial t$ ,  $\nabla = \partial/\partial \mathbf{r}$ , and  $\nabla_{\mathbf{v}_a} = \partial/\partial \mathbf{v}_a$ . Other symbols are  $g_{ab} = |\mathbf{v}_a - \mathbf{v}_b|$ , the relative speed of particles  $a$  and  $b$ ;  $\mathbf{F}_a$  is the external force on unit mass of species  $a$ ;  $\mathbf{b}$  is the impact parameter of collision; and  $\varphi$  is the azimuthal angle of scattering. The external force is assumed to be changing slowly over the distance of the intermolecular force range, so that the molecular collisions are not significantly affected by the external force. It is also assumed that there is no chemical reaction in the fluid. The singlet distribution functions are spatially coarse-grained over the collision volume on the order of the intermolecular force range. For this reason, they remain unchanged over the collision volume, and this is why the singlet distribution functions in the Boltzmann collision integral (2.3) have the same position dependence before and after collision. It is important to remember this spatial coarse-graining, especially, when one derives the Boltzmann equation from the Liouville equation, as often attempted in the kinetic theory of gases, and also when the Boltzmann equation is applied to macroscopic flow problems.

The mean local value of observable  $A(\mathbf{v}_a)$  is defined by the average of the observable over the velocity space

$$\langle A \rangle = \int d\mathbf{v}_a A(\mathbf{v}_a) f_a(\mathbf{v}_a, \mathbf{r}; t). \quad (2.4)$$

Therefore, the mass density  $\rho$  is defined by the average of mass  $m_a$  of species  $a$  summed over all species

$$\rho(\mathbf{r}, t) = \sum_{a=1}^r \langle m_a f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle = \sum_{a=1}^r \rho_a(\mathbf{r}, t), \quad (2.5)$$

where  $\rho_a$  denotes the mean mass density of species  $a$ . The mean velocity of the fluid is similarly given by the average

$$\rho\mathbf{u} = \sum_{a=1}^r \langle m_a \mathbf{v}_a f_a(\mathbf{v}_a, \mathbf{r}; t) \rangle = \sum_{a=1}^r \rho_a \mathbf{u}_a(\mathbf{r}, t). \quad (2.6)$$

Here,  $\mathbf{u}_a(\mathbf{r}, t)$  is the mean velocity of species  $a$ . Therefore  $\mathbf{u}$  is the barycentric velocity of all species. The internal energy is defined by

$$\rho\mathcal{E} = \sum_{a=1}^r \left\langle \frac{1}{2} m_a C_a^2 f_a(\mathbf{v}_a, \mathbf{r}; t) \right\rangle, \quad (2.7)$$

where  $\mathbf{C}_a$  is the peculiar velocity defined by

$$\mathbf{C}_a = \mathbf{v}_a - \mathbf{u}. \quad (2.8)$$

According to the definition here, the internal energy is the mean kinetic energy—in dilute gases—of the gas in the coordinate system moving at fluid velocity  $\mathbf{u}$ . The macroscopic variables  $\rho$ ,  $\rho\mathbf{u}$ , and  $\rho\mathcal{E}$  are the so-called conserved variables that occupy special status in the theory of macroscopic processes in matter because they obey the conservation laws of mass, momentum, and energy.

One of the most important properties of the Boltzmann equation is the  $H$  theorem. In local form, the Boltzmann entropy<sup>1</sup> is expressible as

$$\mathcal{S}(\mathbf{r}, t) = -k_B \sum_{a=1}^r \langle f_a(\mathbf{v}_a, \mathbf{r}; t) (\ln f_a - 1) \rangle, \quad (2.9)$$

where  $\mathcal{S}$  is the Boltzmann entropy per unit volume,  $k_B$  is the Boltzmann constant, and the angular brackets stand for integration in the velocity space. This local density of the Boltzmann entropy obeys the balance equation

$$\partial_t \mathcal{S}(\mathbf{r}, t) = -\nabla \cdot (\mathbf{J}_s + \mathbf{u}\mathcal{S}) + \sigma_{\text{ent}}(\mathbf{r}, t), \quad (2.10)$$

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<sup>1</sup> The Boltzmann entropy, apart from the factor  $-1$ , has the same form as information entropy in information theory. The important difference between the Boltzmann kinetic theory and the information theory of Shannon [5] and his followers [6, 7] is that the Boltzmann kinetic theory has a kinetic equation, whereas the latter does not. This difference has important consequences.

where  $\mathbf{J}_s$  is the Boltzmann entropy flux defined by the statistical mechanical formula

$$\mathbf{J}_s(\mathbf{r}, t) = -k_B \sum_{a=1}^r \langle \mathbf{C}_a f_a(\mathbf{v}_a, \mathbf{r}; t) (\ln f_a - 1) \rangle \quad (2.11)$$

and  $\sigma_{\text{ent}}$  is the Boltzmann entropy production defined by

$$\sigma_{\text{ent}}(\mathbf{r}, t) = -k_B \sum_{a=1}^r \langle \ln f_a \mathfrak{R}_B[f_a] \rangle. \quad (2.12)$$

The local form of the  $H$  theorem is then expressed by the inequality

$$\sigma_{\text{ent}}(\mathbf{r}, t) \geq 0. \quad (2.13)$$

The equality holds only for equilibrium reached in an infinitely long time. The term equilibrium should be understood to mean the state described by the steady-state solution of the Boltzmann equation. At this point of development in the theory, what that steady state means exactly is not clarified, but it can be shown that the steady state corresponds to an equilibrium state if the notion of temperature corresponds to the mean internal energy in a thermodynamically consistent manner. Here, the term thermodynamic consistency means that the formalism, constructed with the distribution function obeying the Boltzmann equation and the  $H$  theorem, is compatible with the laws of thermodynamics. For the details of this line of study, the reader is referred to the literature on the theory of irreversible thermodynamics formulated on the basis of the Boltzmann equation [8, 9].

## 2.2 Equilibrium Solution

At equilibrium, the distribution function is uniform in space and invariant with respect to time. If such a solution to the Boltzmann equation is denoted by  $f_a^{\text{eq}}$ , because the left-hand side of the Boltzmann equation (2.1) is evidently equal to zero, the following equation holds:

$$\mathfrak{R}_B[f_a^{\text{eq}}] = 0. \quad (2.14)$$

The equilibrium solution satisfying this equation is unique because it follows from the  $H$  theorem that, as a gas reaches equilibrium,

$$\sum_{a=1}^r \langle \ln f_a^{\text{eq}} \mathfrak{R}_B[f_a^{\text{eq}}] \rangle = 0. \quad (2.15)$$

By using the symmetry properties of the Boltzmann collision integral with respect to the dynamic reversal and interchange of species, (2.15) can be recast

in the form

$$\sum_{a=1}^r \sum_{b=1}^r \int d\Gamma \ln \left( \frac{f_a^{\text{eq}*} f_b^{\text{eq}*}}{f_a^{\text{eq}} f_b^{\text{eq}}} \right) [f_a^{\text{eq}*}(\mathbf{v}_a^*) f_b^{\text{eq}*}(\mathbf{v}_b^*) - f_a^{\text{eq}}(\mathbf{v}_a) f_b^{\text{eq}}(\mathbf{v}_b)] = 0. \quad (2.16)$$

Here the following abbreviation is used:

$$\int d\Gamma \dots \equiv \int d\mathbf{v}_a \int d\mathbf{v}_b \int_0^{2\pi} d\varphi \int_0^\infty d\mathbf{b} \, \mathbf{b} g_{ab} \dots$$

Equation (2.16) is then satisfied if and only if

$$f_a^{\text{eq}*}(\mathbf{v}_a^*) f_b^{\text{eq}*}(\mathbf{v}_b^*) = f_a^{\text{eq}}(\mathbf{v}_a) f_b^{\text{eq}}(\mathbf{v}_b). \quad (2.17)$$

This solution for (2.16) holds at equilibrium and implies that  $\ln f_i^{\text{eq}}$  ( $i = a, b$ ) is a linear combination of collision invariants of the Boltzmann collision integral, namely, mass, momentum, and energy. Because the collision invariants obey the conservation laws of mechanics, the solution (2.17) uniquely yields the equilibrium distribution function in terms of collisional invariants of the gas. It should be noted that this uniqueness could not be deduced if there were no collision term as defined by (2.3) in the kinetic equation because a vanishing streaming term of the kinetic equation would not be sufficient for the uniqueness.

As it stands, the condition (2.17) is for the global equilibrium, but it can be shown to hold even if the condition is relaxed to the situation in which the system is described in the coordinate system moving at the mean velocity of the fluid  $\mathbf{u}$ . Such equilibrium is the local equilibrium. The local equilibrium solution will be denoted by  $f_a^e$  and is given by the local equilibrium Maxwell–Boltzmann distribution function

$$f_a^e(\mathbf{v}_a, \mathbf{r}) = n_a \left( \frac{m_a}{2\pi k_B T} \right)^{2/3} \exp \left( -\frac{1}{2k_B T} m_a C_a^2 \right), \quad (2.18)$$

provided that  $n_a$  and  $T$  are, respectively, the local density and temperature, which are dependent on position and time and are determined so that these are relations hold:

$$\langle m_a f_a^e \rangle = \langle m_a f_a \rangle = \rho_a, \quad (2.19)$$

$$\sum_{a=1}^r \langle m_a \mathbf{v}_a f_a^e \rangle = \sum_{a=1}^r \langle m_a \mathbf{v}_a f_a \rangle = \rho \mathbf{u}, \quad (2.20)$$

$$\sum_{a=1}^r \left\langle \frac{1}{2} m_a C_a^2 f_a^e \right\rangle = \sum_{a=1}^r \left\langle \frac{1}{2} m_a C_a^2 f_a \right\rangle = \rho \mathcal{E}. \quad (2.21)$$

These conditions imply that the nonequilibrium parts of the distribution functions,  $f_a^{\text{ne}} = f_a - f_a^e$ , are orthogonal to the conserved variables for the system

in the sense that

$$\langle m_a f_a^{\text{ne}} \rangle = \sum_{a=1}^r \langle m_a \mathbf{v}_a f_a^{\text{ne}} \rangle = \sum_{a=1}^r \left\langle \frac{1}{2} m_a C_a^2 f_a^{\text{ne}} \right\rangle = 0. \quad (2.22)$$

It should be emphasized here that the local equilibrium distribution function  $f_a^e(\mathbf{v}_a, \mathbf{r})$  given in (2.18) is unique and the  $H$  theorem is essential for the uniqueness of  $f_a^e$ . Historically, Boltzmann [4] used his kinetic equation and the  $H$  theorem, first, to prove the uniqueness of the Maxwell distribution function. He then showed that the  $H$  function, with the help of the equilibrium (i.e., Maxwell) distribution function, could be related to the Clausius entropy with regard to its temperature and density dependence, which was introduced in equilibrium thermodynamics by Clausius [10] about seven years earlier.

The local equilibrium solution (2.18) is a solution in the phase space of a particle that gives rise to the equilibrium thermodynamic description of the system consistent with the laws of thermodynamics. Solutions giving rise to the thermodynamic description of the system will be called the thermodynamic branch of solutions that live in the phase space of molecules. It is important to distinguish the thermodynamic branch of a solution and a general solution in the phase space to understand thermodynamic fluctuations properly. For details of constructing the local equilibrium solution, see [8, 9], and for thermodynamic uncertainties associated with thermodynamic fluctuations see Sect. 7.5 of [9], where thermodynamic uncertainty relations are derived. The theory of transport processes in the gas phase discussed in this work is built on the local equilibrium distribution function.

### 2.3 Linear Transport Processes

If a system is slightly displaced from equilibrium, the distribution function can be obtained by applying a perturbation method of solution to the Boltzmann equation. If the perturbation solution is limited to the first order, then the corresponding transport processes are described to the linear order. Such non-equilibrium processes involve the transport of mass, momentum, and energy and are called linear transport processes. The perturbation solution method is built on and around the equilibrium solution. The Chapman–Enskog method of solution [1, 3] is the celebrated perturbation solution method developed for the Boltzmann equation that yields a theory of linear transport processes. It is fully confirmed to be reliable by experiments performed for near equilibrium processes. We will sketch the method here and present the formulas for transport coefficients of dilute monatomic gases because they serve as the dilute gas limits of the transport coefficients of dense gases and liquids. For the details of the theory, the reader is referred to [9]. The linear transport coefficients for dilute gases are in the foundations of the nonlinear transport coefficients of gases and the linear transport coefficients of dense gases and liquids that will be discussed in subsequent chapters in this work.

It is convenient to introduce the nonuniformity parameter, denoted by  $\epsilon$ , for the purpose of systematically developing the Chapman–Enskog method of solution. This parameter can be identified and given an explicit physical meaning if the Boltzmann equation is suitably nondimensionalized. It can be shown that this parameter is related to the Knudsen number defined as the ratio of the mean free path to the characteristic length of the system. Because of such an identification is not required for the discussion of linear transport processes, we will defer it to later sections where nonlinear transport processes are discussed. There, the identification of the aforementioned expansion parameter will be unavoidable for a systematic description.

To implement the perturbation solution method in mind, we multiply the collision term of the Boltzmann equation by  $\epsilon$ . Thus, it is written in the form

$$\partial_t f_a + \mathbf{v}_a \cdot \nabla f_a + \mathbf{F}_a \cdot \nabla_{va} f_a = \epsilon \mathfrak{R}_B [f_a], \quad (2.23)$$

and  $f_a$  is sought to first-order in  $\epsilon$  in the form

$$f_a = f_a^e (1 + \epsilon \phi_a), \quad (2.24)$$

where  $f_a^e$  is the local equilibrium Maxwell–Boltzmann distribution function defined earlier and  $f_a^{(1)} = f_a^e \phi_a$  is the first-order correction of  $f_a^e$ .

On the basis of the functional hypothesis which states that  $f_a$  is a function of the conserved variables and their derivatives of all orders, the Chapman–Enskog method requires a special way of computing time derivatives. To explain this rule of computing the time derivatives, first we express the conservation laws in matrix form

$$\frac{\partial \mathbf{M}}{\partial t} = \mathbf{E}(\mathbf{r}, t), \quad (2.25)$$

where  $\mathbf{M} = (\rho, \rho\mathbf{u}, E)$  with  $E$  denoting the internal energy and  $\mathbf{E}$  is the column vector made up of the right-hand sides of the mass, momentum, and energy conservation laws [11]:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \rho \mathbf{u}, \quad (2.26)$$

$$\frac{\partial \rho c_a}{\partial t} = -\nabla \cdot (\mathbf{J}_a + \rho \mathbf{u} c_a), \quad (2.27)$$

$$\frac{\partial \rho \mathbf{u}}{\partial t} = -\nabla \cdot (\mathbf{P} + \rho \mathbf{u} \mathbf{u}) + \rho \mathbf{F}, \quad (2.28)$$

$$\frac{\partial \rho \mathcal{E}}{\partial t} = -\nabla \cdot (\mathbf{Q} + \rho \mathcal{E} \mathbf{u}) - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a. \quad (2.29)$$

Here,  $\mathbf{P}$  is the stress tensor,  $\mathbf{Q}$  is the heat flux,  $\mathbf{J}_a$  is the diffusion flux of species  $a$ , and  $\mathbf{F}$  is the total external force density

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

where  $c_a$  is the mass fraction of species  $a$  defined by  $c_a = \rho_a / \rho$ .

Under the functional hypothesis, the time derivative of  $f_a$  is computed through  $\mathbf{M}$ ,  $\nabla \mathbf{M}$ , and so on, as in the formula

$$\frac{\partial f_a}{\partial t} = \mathbf{E} \cdot \frac{\partial f_a}{\partial \mathbf{M}} + \nabla \mathbf{E} \cdot \frac{\partial f_a}{\partial \nabla \mathbf{M}} + \dots . \quad (2.31)$$

If the distribution function  $f$  is expanded in the series

$$f = f^{(0)} + \epsilon f^{(1)} + \epsilon^2 f^{(2)} + \dots , \quad (2.32)$$

then according to the rule used by the Chapman–Enskog method, the time derivative of  $f$  is computed as follows:

$$\begin{aligned} \frac{\partial f}{\partial t} = \frac{\partial_0 f^{(0)}}{\partial t} + \epsilon \left( \frac{\partial_1 f^{(0)}}{\partial t} + \frac{\partial_0 f^{(1)}}{\partial t} \right) + \epsilon^2 \left( \frac{\partial_2 f^{(0)}}{\partial t} + \frac{\partial_1 f^{(1)}}{\partial t} + \frac{\partial_0 f^{(2)}}{\partial t} \right) \\ + \dots , \end{aligned} \quad (2.33)$$

where various derivatives are computed according to the rule

$$\frac{\partial_k f^{(j)}}{\partial t} = \mathbf{E}^{(k)} \cdot \frac{\partial f^{(j)}}{\partial \mathbf{M}} + \nabla \mathbf{E}^{(k)} \cdot \frac{\partial f^{(j)}}{\partial \nabla \mathbf{M}} + \dots \quad (2.34)$$

with  $\mathbf{E}^{(k)}$  denoting the  $k$ th-order coefficient in the expansion

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

The species subscript is omitted from the distribution function in (2.33) for notational brevity. This rule of computing the time derivatives stems from the aforementioned functional hypothesis underlying the Chapman–Enskog method. Note that the functional hypothesis is generally applicable to other solution methods for the kinetic equation, such as the moment method, because macroscopic variables evolve more slowly than the variables of molecules in the phase space.

Substituting  $f_a$  in (2.24) and using the aforementioned rule for calculating time derivatives, the Boltzmann equation yields the equations to first order in  $\epsilon$

$$\sum_{b=1}^r C(f_a^e f_b^e) = 0, \quad (2.35)$$

$$\sum_{b=1}^r [C(f_a^e f_b^e \phi_b) + C(f_a^e f_b^e \phi_a)] = (Df_a)^{(0)}, \quad (2.36)$$

where

$$(Df_a)^{(0)} = \frac{\partial_0 f_a^{(0)}}{\partial t} + \mathbf{v}_a \cdot \nabla f_a^e + \mathbf{F}_a \cdot \nabla_{\mathbf{v}_a} f_a^e. \quad (2.37)$$

Equation (2.35) is the zeroth-order equation, which yields the local equilibrium solution for the kinetic equation. We have already discussed the solution of this equation. Equation (2.36) is a first-order equation, which yields a first-order correction to the equilibrium distribution function. It is an inhomogeneous linear integral equation and can be solved by the standard method of solution for linear integral equations.

The first-order correction of the distribution function should satisfy the conditions arising from (2.19)–(2.21), that is,

$$\langle m_a f_a^{(1)} \rangle = 0, \quad (2.38)$$

$$\sum_{a=1}^r \langle m_a \mathbf{v}_a f_a^{(1)} \rangle = 0, \quad (2.39)$$

$$\sum_{a=1}^r \left\langle \frac{1}{2} m_a C_a^2 f_a^{(1)} \right\rangle = 0. \quad (2.40)$$

Similar conditions, of course, hold for higher order solutions of distribution functions.

The stress tensor, heat flux, and diffusion fluxes are computable in a series in  $\epsilon$  by using the expansion for  $f_a$ :

$$\begin{aligned} \mathbf{P} &= \sum_{a=1}^r \mathbf{P}_a = \sum_{a=1}^r [\langle m_a \mathbf{C}_a \mathbf{C}_a f_a^e \rangle + \epsilon \langle m_a \mathbf{C}_a \mathbf{C}_a f_a^e \phi_a \rangle + \dots] \\ &\equiv \mathbf{P}^{(0)} + \epsilon \mathbf{P}^{(1)} + \dots, \end{aligned} \quad (2.41)$$

$$\begin{aligned} \mathbf{Q} &= \sum_{a=1}^r \mathbf{Q}_a = \sum_{a=1}^r \left[ \left\langle \frac{1}{2} m_a C_a^2 \mathbf{C}_a f_a^e \right\rangle + \epsilon \left\langle \frac{1}{2} m_a C_a^2 \mathbf{C}_a f_a^e \phi_a \right\rangle + \dots \right] \\ &\equiv \mathbf{Q}^{(0)} + \epsilon \mathbf{Q}^{(1)} + \dots, \end{aligned} \quad (2.42)$$

$$\begin{aligned} \mathbf{J}_a &= \langle m_a \mathbf{C}_a f_a^e \rangle + \epsilon \langle m_a \mathbf{C}_a f_a^e \phi_a \rangle + \dots \\ &\equiv \mathbf{J}^{(0)} + \epsilon \mathbf{J}^{(1)} + \dots. \end{aligned} \quad (2.43)$$

The first terms  $\mathbf{Q}^{(0)}$  and  $\mathbf{J}^{(0)}$  in (2.42) and (2.43) vanish because of symmetry and

$$\mathbf{P}^{(0)} = \langle m_a \mathbf{C}_a \mathbf{C}_a f_a^e \rangle = \frac{2}{3} \rho \mathcal{E} \boldsymbol{\delta} = p \boldsymbol{\delta} \quad (2.44)$$

where  $p$  is the hydrostatic pressure and  $\boldsymbol{\delta}$  is the unit second-rank tensor.

The inhomogeneous integral equation must satisfy the solvability conditions [12]. The homogeneous integral equation has five eigenfunctions  $\varphi_a = (m_a, m_a \mathbf{v}_a, m_a C_a^2 / 2 : 1 < a < r)$  for each species. These eigenfunctions should be orthogonal to the inhomogeneous term of the integral equation for the

integral equation to be solvable. Therefore,

$$\begin{aligned} \left\langle m_a (Df_a)^{(0)} \right\rangle &= 0, \\ \sum_{a=1}^r \left\langle m_a \mathbf{v}_a (Df_a)^{(0)} \right\rangle &= 0, \\ \sum_{a=1}^r \left\langle \frac{1}{2} m_a C_a^2 (Df_a)^{(0)} \right\rangle &= 0 \end{aligned} \quad (2.45)$$

for every  $a$ . These are the solvability conditions and give rise to the conservation laws of mass, momentum, and internal energy for the first order in  $\epsilon$ ; they are the Navier–Stokes, Fourier, and Ficks equations of classical hydrodynamics [13] in which the transport coefficients are expressed in terms of the Boltzmann collision integral—collision bracket integrals. They will be presented later.

For the zeroth order the conservation laws are simply nondissipative Euler equations [13]

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0, \quad (2.46)$$

$$\frac{\partial \rho c_a}{\partial t} + \nabla \cdot (\rho \mathbf{u} c_a) = 0 \quad (1 \leq a \leq r), \quad (2.47)$$

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (p \boldsymbol{\delta} + \rho \mathbf{u} \mathbf{u}) = \rho \mathbf{F}, \quad (2.48)$$

$$\frac{\partial \rho \mathcal{E}}{\partial t} + \nabla \cdot (\rho \mathcal{E} \mathbf{u}) + p \nabla \cdot \mathbf{u} = 0. \quad (2.49)$$

The first-order solution of the Boltzmann equation gives rise to the classical hydrodynamic equations of Navier, Stokes, Fourier, and Fick [13]

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0, \quad (2.50)$$

$$\frac{\partial \rho c_a}{\partial t} + \nabla \cdot \left( \mathbf{J}_a^{(1)} + \rho \mathbf{u} c_a \right) = 0, \quad (2.51)$$

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot \left( p \boldsymbol{\delta} + \mathbf{P}^{(1)} + \rho \mathbf{u} \mathbf{u} \right) = \rho \mathbf{F}, \quad (2.52)$$

$$\frac{\partial \rho \mathcal{E}}{\partial t} + \nabla \cdot \left( \mathbf{Q}^{(1)} + \rho \mathcal{E} \mathbf{u} \right) + \left( p \boldsymbol{\delta} + \mathbf{P}^{(1)} \right) : \nabla \mathbf{u} - \sum_{a=1}^r \mathbf{J}_a^{(1)} \cdot \mathbf{F}_a = 0, \quad (2.53)$$

where we have set  $\epsilon = 1$ , as is the usual practice, when the solution is obtained for the Boltzmann equation because  $\epsilon$  is merely a bookkeeping parameter in the perturbation method employed. The first-order quantities  $\mathbf{P}^{(1)}$ ,  $\mathbf{Q}^{(1)}$ , and  $\mathbf{J}_a^{(1)}$  are obtained from the integral equation (2.36). They are proportional to

the first-order spatial gradients of  $\mathbf{u}$ ,  $T$ , and  $c_a$  or  $n_a$ , the number density of species  $a$ . Because of symmetry, the equation for the second-rank tensor  $\mathbf{P}^{(1)}$  is decoupled from those for the vectors  $\mathbf{Q}^{(1)}$  and  $\mathbf{J}_a^{(1)}$ , and we obtain them in the forms [8, 9, 11],

$$\mathbf{P}^{(1)} = -\eta_b^0 (\nabla \cdot \mathbf{u}) \boldsymbol{\delta} - 2\eta_0 [\nabla \mathbf{u}]^{(2)}, \quad (2.54)$$

$$\mathbf{Q}^{(1)} = -\lambda_0 \nabla \ln T - p \sum_{a=1}^r D_{Ta} \mathbf{d}_a + \frac{5}{2} k_B T \sum_{a=1}^r \frac{1}{m_a} \mathbf{J}_a^{(1)}, \quad (2.55)$$

$$\mathbf{J}_a^{(1)} = -\rho_a \sum_{b=1}^r D_{ab} (\mathbf{d}_b + k_{Tb} \nabla \ln T), \quad (2.56)$$

where  $\eta_b^0$ ,  $\eta_0$ ,  $\lambda_0$ ,  $D_{Ta}$ ,  $D_{ab}$ , and  $k_{Tb}$  are the bulk viscosity, shear viscosity, thermal conductivity, thermal diffusion coefficient, diffusion coefficient, and thermal diffusion ratio. Other symbols are defined by<sup>2</sup>

$$[\nabla \mathbf{u}]^{(2)} = \frac{1}{2} [\nabla \mathbf{u} + (\nabla \mathbf{u})^t] - \frac{1}{3} \boldsymbol{\delta} \nabla \cdot \mathbf{u}, \quad (2.57)$$

$$\mathbf{d}_a = \nabla \left( \frac{n_a}{n} \right) + \left( \frac{n_a}{n} - \frac{\rho_a}{\rho} \right) \nabla \ln p + \frac{\rho_a}{p} (\mathbf{F} - \mathbf{F}_a). \quad (2.58)$$

The notation  $[\nabla \mathbf{u}]^{(2)}$  stands for the traceless symmetric part of the second-rank tensor  $\nabla \mathbf{u}$ , and this notation will be used for the traceless symmetric part of the second-rank tensor  $\mathbf{A}$  throughout this work:

$$[\mathbf{A}]^{(2)} = \frac{1}{2} (\mathbf{A} + \mathbf{A}^t) - \frac{1}{3} \boldsymbol{\delta} \text{Tr} \mathbf{A},$$

where the superscript  $t$  denotes the transpose.

If the constitutive equations (2.54)–(2.56) are substituted in the first-order conservation laws (2.50)–(2.53) there arise the Navier–Stokes, Fourier, and Fick’s hydrodynamic equations, which constitute classical hydrodynamics. Therefore, it can be said that the classical hydrodynamics of gases corresponds to the first-order Chapman–Enskog solution of the Boltzmann equation at the kinetic theory level and to the linear constitutive equations for the stress tensor, heat flux, and diffusion fluxes at the level of irreversible thermodynamics because the linear constitutive equations are the linear thermodynamic force–flux relations in the linear theory of irreversible thermodynamics. Hydrodynamics describes macroscopic flow processes that must be subject to the laws

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<sup>2</sup> The external force term in the definition of thermodynamic force  $\mathbf{d}_a$  in (8.13) of [9] is in error. It should read

$$\frac{\rho_a}{p} (\mathbf{F} - \mathbf{F}_a).$$

of thermodynamics. If a theory describing such processes conforms fully with the laws of thermodynamics, then the theory is said to be thermodynamically consistent. The thermodynamic consistency of a macroscopic theory is an important criterion by which to judge the truthfulness of the theory. The classical hydrodynamic equations on the support of the linear constitutive equations presented earlier are completely thermodynamically consistent, although they are only applicable to near-equilibrium flow phenomena. Subjecting the constitutive equations for linear processes to the laws of thermodynamics the positivity conditions on linear transport coefficients follow.

The transport coefficients appearing in the constitutive equations (2.54)–(2.56) are obtained from (2.36) in terms of collision bracket integrals. Because the procedure is rather involved in the way it is described in monographs dealing with the subject matter, it is useful to give a sketch of it and present the usual results for the transport coefficients that we will employ later in this work, when nonlinear transport processes in gases and linear transport processes in liquids are discussed.

For the purpose in mind, it is convenient to define the abbreviation for the integral operator involved:

$$I_{ab}(G) = \frac{1}{n_a n_b} \int d\mathbf{v}_b \int_0^\infty d\mathbf{b} \int_0^{2\pi} d\varphi g_{ab} f_a^e f_b^e (G_a + G_b - G_a^* - G_b^*), \quad (2.59)$$

where  $G$  is a function of velocities, the impact parameter of collision, and the scattering angle. It is also convenient to define the bracket integral

$$\begin{aligned} [G, H] &= \sum_{a=1}^r \sum_{b=1}^r \int d\mathbf{v}_a I_{ab}(G) \\ &= \frac{1}{4n^2} \sum_{a=1}^r \sum_{b=1}^r \int d\mathbf{v}_a \int d\mathbf{v}_b \int_0^\infty d\mathbf{b} \int_0^{2\pi} d\varphi g_{ab} f_a^e f_b^e \\ &\quad \times (G_a + G_b - G_a^* - G_b^*) (H_a + H_b - H_a^* - H_b^*). \end{aligned} \quad (2.60)$$

The inhomogeneous term  $(Df_a)^{(0)}$  of the integral equation for the first-order solution, Eq. (2.36), is readily calculated by using the equilibrium solution (2.18) in Eq. (2.37):

$$\begin{aligned} (Df_a)^{(0)} &= f_a^e \left[ \frac{n}{n_a} \mathbf{C}_a \cdot \mathbf{d}_a + \left( \frac{m_a C_a^2}{2k_B T} - \frac{5}{2} \right) \mathbf{C}_a \cdot \nabla \ln T \right. \\ &\quad \left. + \frac{m_a}{k_B T} [\mathbf{C}_a \mathbf{C}_a]^{(2)} : \nabla \mathbf{u} \right]. \end{aligned} \quad (2.61)$$

Because the thermodynamic forces  $\mathbf{d}_1, \mathbf{d}_2, \dots, \mathbf{d}_r$  are linearly dependent vectors and because the following equation holds:

$$\sum_{a=1}^r \mathbf{d}_a = 0 \quad (2.62)$$

it is useful to construct linearly independent vectors. Let  $\mathbf{d}_1^*, \mathbf{d}_2^*, \dots, \mathbf{d}_r^*$  be a new set of linearly independent vectors for the thermodynamic gradients (or thermodynamic forces) for diffusion. An acceptable relation of  $\mathbf{d}_a$  to  $\mathbf{d}_a^*$  is [3]

$$\mathbf{d}_a = \mathbf{d}_a^* - \frac{\rho_a}{\rho} \sum_{b=1}^r \mathbf{d}_b^*, \quad (2.63)$$

because it satisfies the condition (2.62). Here, the precise expression for  $\mathbf{d}_a^*$  is not necessary because  $\mathbf{d}_a^*$  may be replaced with  $\mathbf{d}_a$  after linearly independent integral equations are obtained for the diffusion part of the first-order correction for the distribution function, as will be seen.

$(Df_a)^{(0)}$  is linear with respect to thermodynamic gradients, so the first-order solution  $\phi_a$  for  $f_a$  should also be linear with respect to  $\nabla \ln T$ ,  $\nabla \mathbf{u}$ , and  $\mathbf{d}_b^*$ . Therefore, it can be sought in the form,

$$\phi_a = -\frac{1}{n} \sum_{b=1}^r \mathbf{D}_a^b \cdot \mathbf{d}_b^* - \frac{1}{n} \mathbf{A}_a \cdot \nabla \ln T - \frac{1}{n} \mathbf{B}_a : \nabla \mathbf{u}, \quad (2.64)$$

where  $\mathbf{D}_a^b$ ,  $\mathbf{A}_a$ , and  $\mathbf{B}_a$  are functions of momentum, density, and temperature. Upon substituting this form of  $\phi_a$  in the integral equation (2.36), because the gradients  $\mathbf{d}_b^*$ ,  $\nabla \ln T$ , and  $\nabla \mathbf{u}$  are linearly independent, three independent linear integral equations follow:

$$\sum_{b=1}^r \frac{n_a n_b}{n^2} I_{ab}(\mathbf{D}^c) = \frac{1}{n_a} f_a^e \left( \delta_{ac} - \frac{\rho_a}{\rho} \right) \mathbf{C}_a \quad (1 \leq a, c \leq r), \quad (2.65)$$

$$\sum_{b=1}^r \frac{n_a n_b}{n^2} I_{ab}(\mathbf{A}) = \frac{1}{n_a} f_a^e \left( \frac{m_a}{2k_B T} C_a^2 - \frac{5}{2} \right) \mathbf{C}_a \quad (1 \leq a \leq r), \quad (2.66)$$

$$\sum_{b=1}^r \frac{n_a n_b}{n^2} I_{ab}(\mathbf{B}) = \frac{m_a}{nk_B T} f_a^e [\mathbf{C}_a \mathbf{C}_a]^{(2)} \quad (1 \leq a \leq r). \quad (2.67)$$

It is convenient to put these equations in scalar form. For the purpose let us introduce vector functions  $\bar{\mathbf{D}}_a^c$  and  $\bar{\mathbf{A}}_a$  and tensor function  $\bar{\mathbf{B}}_a$  and take the scalar product of the vector or tensor function with the integral equation of interest to obtain

$$\sum_{a=1}^r \sum_{b=1}^r \frac{n_a n_b}{n^2} I_{ab}(\mathbf{D}^c) \cdot \bar{\mathbf{D}}_a^k = [\mathbf{D}^c, \bar{\mathbf{D}}^k] \quad (1 \leq c, k \leq r), \quad (2.68)$$

$$\sum_{a=1}^r \sum_{b=1}^r \frac{n_a n_b}{n^2} I_{ab}(\mathbf{A}) \cdot \bar{\mathbf{A}}_a = [\mathbf{A}, \bar{\mathbf{A}}], \quad (2.69)$$

$$\sum_{a=1}^r \sum_{b=1}^r \frac{n_a n_b}{n^2} I_{ab}(\mathbf{B}) : \bar{\mathbf{B}}_a = [\mathbf{B}, \bar{\mathbf{B}}]. \quad (2.70)$$

Using these collision bracket integrals, the integral equations (2.65)–(2.67) can be written as

$$[\mathbf{D}^c, \bar{\mathbf{D}}^k] = \frac{1}{n_c} \left\langle f_c^e \mathbf{C}_c \cdot \bar{\mathbf{D}}_c^k \right\rangle - \frac{1}{\rho} \sum_{a=1}^r \left\langle f_a^e m_a \mathbf{C}_a \cdot \bar{\mathbf{D}}_a^k \right\rangle, \quad (2.71)$$

$$[\mathbf{A}, \bar{\mathbf{A}}] = \frac{1}{n} \sum_{a=1}^r \left\langle f_a^e \left( \frac{m_a}{2k_B T} C_a^2 - \frac{5}{2} \right) \cdot \bar{\mathbf{A}}_a \right\rangle, \quad (2.72)$$

$$[\mathbf{B}, \bar{\mathbf{B}}] = \frac{1}{nk_B T} \sum_{a=1}^r \left\langle f_a^e m_a [\mathbf{C}_a \mathbf{C}_a]^{(2)} : \bar{\mathbf{B}}_a \right\rangle. \quad (2.73)$$

Equations (2.71)–(2.73) are inhomogeneous linear integral equations for  $\mathbf{D}^c$ ,  $\mathbf{A}$ , and  $\mathbf{B}$ , respectively. The solvability conditions (2.45) for these linear integral equations are satisfied. These functions must also satisfy conditions (2.38)–(2.40). For diffusion components  $\mathbf{D}^c$ , these conditions do not determine  $\mathbf{D}^c$  uniquely because it can be shown that

$$\sum_{c=1}^r \frac{\rho_c}{\rho} \mathbf{D}^c = 0. \quad (2.74)$$

This follows since if  $\rho_c/\rho$  is multiplied by (2.65) and the resulting equation is summed over  $c$ , then the right-hand side is equal to zero, and it means that the sum on the left in (2.74) is a constant, which may be taken equal to zero. Therefore, (2.74) suggests that it is possible to replace  $\mathbf{d}_b^*$  in (2.64) with

$$\mathbf{d}_b^* - \frac{\rho_b}{\rho} \sum_{c=1}^r \mathbf{d}_c^*$$

with no effect on the outcome of the theory. This expression is simply  $\mathbf{d}_b$ , so the first-order solution  $\phi_a$  may be written as

$$\begin{aligned} \phi_a = & -\frac{1}{n} \sum_{b=1}^r \mathcal{D}_a^b(C) \mathbf{C}_a \cdot \mathbf{d}_b - \frac{1}{n} \mathcal{A}_a(C) \mathbf{C}_a \cdot \nabla \ln T \\ & - \frac{1}{n} \mathcal{B}_a(C) [\mathbf{C}_a \mathbf{C}_a]^{(2)} : \nabla \mathbf{u}. \end{aligned} \quad (2.75)$$

In this expression for  $\phi_a$  the unknowns are written in the forms

$$\begin{aligned} \mathbf{D}^b &= \mathbf{C} \mathcal{D}^b(C), \\ \mathbf{A} &= \mathbf{C} \mathcal{A}(C), \\ \mathbf{B} &= [\mathbf{C} \mathbf{C}]^{(2)} \mathcal{B}(C), \end{aligned} \quad (2.76)$$

where  $\mathcal{D}^b(C)$ ,  $\mathcal{A}(C)$ , and  $\mathcal{B}(C)$  denote scalar functions of  $C$  to be determined from (2.71)–(2.73).

The integral equations (2.71)–(2.73) may be solved, for example, by the Galerkin method in which the unknowns are expanded in Sonine polynomials<sup>3</sup> of the peculiar velocity. Because this aspect of the solution method is well documented, refer to the literature [1, 3, 9].

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<sup>3</sup> Sonine polynomials [14]  $S_m^{(n)}(x)$  are related to associated Laguerre polynomials  $L_n^m(x)$ . There are two different definitions of Laguerre polynomials in the literature, so caution is required when they are used. According to the definition of Laguerre polynomials by Morse and Feshbach in their book, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953),  $S_m^{(n)}(x)$  used in [1] differs from  $L_n^m(x)$  only by a constant factor

$$L_n^m(x) = \Gamma(n + m + 1) S_m^{(n)}(x),$$

whereas  $S_m^{(n)}(x)$  is the same as  $L_n^m(x)$  defined by Bateman [15]. Therefore, note that

$$[L_n^m(x)]_{\text{Morse-Feshbach}} = \Gamma(n + m + 1) [L_n^m(x)]_{\text{Bateman}}.$$

Hence the Sonine polynomials originally defined by Sonine are the same as those defined by Morse and Feshbach. The Sonine polynomials—used in [1]—are normalized as follows:

$$\int_0^\infty dx e^{-x} x^m S_m^{(q)}(x) S_m^{(p)}(x) = \delta_{pq} \frac{\Gamma(m + q + 1)}{\Gamma(q + 1)}.$$

Therefore, the normalization integral for the Laguerre polynomials  $L_n^m(x)$  defined by Bateman is the same as that for  $S_m^{(n)}(x)$ .

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# 3

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## Transport Processes in Monatomic Gases

Assuming that the solutions of (2.71)–(2.73) are obtained according to the method mentioned in Chap. 2, we present the formal expressions for the transport coefficients in this chapter. The theory of linear transport processes is abundantly discussed in the literature, so the description of the theory will be brief and confined to the essential points of the formal feature that will help us comprehend the parallel theory for dense gases and liquids treated in later chapters. It will be also helpful for understanding the theory of nonlinear transport processes discussed later because we build it on the foundations of linear transport processes.

### 3.1 Diffusion Processes

The first-order diffusion flux  $\mathbf{J}_a^{(1)}$  is given by

$$\mathbf{J}_a^{(1)} = \langle m_a C_a f_a^e \phi_a \rangle. \quad (3.1)$$

Therefore, inserting of the first-order solution (2.64) and using the symmetry of the integral, there follows the equation

$$\mathbf{J}_a^{(1)} = -\frac{1}{3n} \sum_{b=1}^r \langle f_a^e m_a C_a^2 \mathcal{D}_a^b(C) \rangle \mathbf{d}_b - \frac{1}{3n} \langle f_a^e m_a C_a^2 \mathcal{A}_a(C) \rangle \boldsymbol{\nabla} \ln T. \quad (3.2)$$

This is the linear constitutive equation for the diffusion flux of gaseous species  $a$  derived from the Boltzmann kinetic equation. On the other hand, the diffusion coefficients and the thermal diffusion coefficients are phenomenologically defined by the linear constitutive relation for velocity  $\mathbf{V}_a = \mathbf{J}_a^{(1)} / \rho_a$ :

$$\mathbf{V}_a = - \sum_{b=1}^r D_{ab} \mathbf{d}_b - D_{Ta} \boldsymbol{\nabla} \ln T, \quad (3.3)$$

where  $D_{ab}$  and  $D_{Ta}$  are the diffusion and thermal diffusion coefficients, respectively. Comparing (3.3) with (2.56), we find

$$D_{Ta} = \sum_{b=1}^r D_{ab} k_{Tb}. \quad (3.4)$$

On comparison of the kinetic theory relation (3.2) with the phenomenological relation (3.3), the phenomenological coefficients  $D_{ab}$  and  $D_{Ta}$  are identified with the kinetic theory expressions for them as follows:

$$D_{ab} = \frac{1}{3n} \langle f_a^e m_a C_a^2 \mathcal{D}_a^b(C) \rangle, \quad (3.5)$$

$$D_{Ta} = \frac{1}{3n} \langle f_a^e m_a C_a^2 \mathcal{A}_a(C) \rangle. \quad (3.6)$$

Because by the condition arising from (2.19)–(2.21), there hold the equations,

$$\begin{aligned} \sum_{a=1}^r \langle f_a^e m_a C_a^2 \mathcal{D}_a^b(C) \rangle &= 0, \\ \sum_{a=1}^r \left\langle f_a^e \frac{1}{2} m_a C_a^2 \mathcal{A}_a(C) \right\rangle &= 0, \end{aligned} \quad (3.7)$$

on replacing  $\bar{\mathbf{D}}^k$  in (2.71) with  $\mathbf{D}^k$ , it follows that

$$\langle f_a^e m_a C_a^2 \mathcal{D}_a^b(C) \rangle = [\mathbf{D}^a, \mathbf{D}^b]. \quad (3.8)$$

Similarly, on replacing  $\bar{\mathbf{D}}^k$  in (2.71) with  $\mathbf{A}$ , we obtain

$$\langle f_a^e m_a C_a^2 \mathcal{A}_a(C) \rangle = [\mathbf{D}^a, \mathbf{A}]. \quad (3.9)$$

Therefore,  $D_{ab}$  and  $D_{Ta}$  can be expressed in compact form as

$$D_{ab} = \frac{1}{3n} [\mathbf{D}^a, \mathbf{D}^b], \quad (3.10)$$

$$D_{Ta} = \frac{1}{3n} [\mathbf{D}^a, \mathbf{A}]. \quad (3.11)$$

With the solutions for the integral equations (2.71) and (2.72), the diffusion and thermal diffusion coefficients can be calculated in terms of collision bracket integrals. Because this work is not concerned with the evaluation of transport coefficients of gases and their formal expressions will be sufficient for our purpose, we will not dwell on the question here.

The constitutive equation for a diffusion flux can be expressed in terms of thermodiffusion ratios by using the ratio of  $D_{Ta}$  to  $D_{ab}$ :

$$\mathbf{V}_a = - \sum_{b=1}^r D_{ab} (\mathbf{d}_b + k_{Tb} \nabla \ln T). \quad (3.12)$$

In our later studies of transport processes in liquids, the self-diffusion and binary diffusion coefficients of hard sphere fluids will be of interest because hard repulsive forces play a dominant role in momentum and energy transport in liquids where particles are close to each other.

### 3.2 Thermal Conduction

The first-order heat flux in gases is given by

$$\mathbf{Q}^{(1)} = \sum_{a=1}^r \left\langle \frac{1}{2} m_a C_a^2 \mathbf{C}_a f_a^e \phi_a \right\rangle. \quad (3.13)$$

Substituting  $\phi_a$  in (2.75), rearranging terms, and employing the expression for  $\mathbf{J}_a^{(1)}$  in (3.2), there follows the expression

$$\begin{aligned} \mathbf{Q}^{(1)} = & -\frac{k_B T}{3n} \sum_{a=1}^r \sum_{b=1}^r \left\langle f_a^e \left( \frac{m_a C_a^2}{2k_B T} - \frac{5}{2} \right) C_a^2 \mathcal{D}_a^b(C) \right\rangle \mathbf{d}_b \\ & -\frac{k_B T}{3n} \sum_{a=1}^r \left\langle f_a^e \left( \frac{m_a C_a^2}{2k_B T} - \frac{5}{2} \right) C_a^2 \mathcal{A}_a(C) \right\rangle \nabla \ln T \\ & -\frac{5k_B T}{2} \sum_{a=1}^r \frac{1}{m_a} \mathbf{J}_a^{(1)}. \end{aligned} \quad (3.14)$$

Comparing it with the phenomenological constitutive equation for  $\mathbf{Q}^{(1)}$  in (2.55), the phenomenological coefficients  $\lambda_0$  and  $D_{Ta}$  are identified with their kinetic theory expressions

$$\lambda_0 = \frac{k_B T}{3n} \sum_{a=1}^r \left\langle f_a^e \left( \frac{m_a C_a^2}{2k_B T} - \frac{5}{2} \right) C_a^2 \mathcal{A}_a(C) \right\rangle, \quad (3.15)$$

$$pD_{Ta} = \frac{k_B T}{3n} \sum_{b=1}^r \left\langle f_b^e \left( \frac{m_b C_b^2}{2k_B T} - \frac{5}{2} \right) C_b^2 \mathcal{D}_b^a(C) \right\rangle. \quad (3.16)$$

Since the kinetic theory expression of  $D_{Ta}$  as in (3.16) has to be compatible with the expression in (3.6) it follows that there holds the relation

$$\frac{1}{n} \sum_{b=1}^r \left\langle f_b^e \left( \frac{m_b C_b^2}{2k_B T} - \frac{5}{2} \right) C_b^2 \mathcal{D}_b^a(C) \right\rangle = \langle f_a^e m_a C_a^2 \mathcal{A}_a(C) \rangle.$$

Moreover, in the light of (3.4) the kinetic theory expression for the thermal diffusion ratio may be expressed as

$$k_{Tb} = \frac{\left\langle f_b^e \left( \frac{m_b C_b^2}{2k_B T} - \frac{5}{2} \right) C_b^2 \mathcal{D}_b^a(C) \right\rangle}{n \langle f_a^e m_a C_a^2 \mathcal{D}_a^b(C) \rangle}. \quad (3.17)$$

If the bracket integral notation is used, the thermal conductivity  $\lambda_0$  and the thermal diffusion ratio  $k_{Tb}$  may be written as

$$\lambda_0 = \frac{k_B T}{3n} [\mathbf{A}, \mathbf{A}], \quad (3.18)$$

$$k_{Tb} = \frac{1}{n} \frac{[\mathbf{A}, \mathbf{D}^b]}{[\mathbf{D}^a, \mathbf{D}^b]}. \quad (3.19)$$

As is for diffusion coefficients, these formal expressions can be explicitly calculated as functions of temperature and density by using the solutions of the linear integral equations (2.65) and (2.66).

### 3.3 Viscous Phenomena

The first order correction to the stress tensor results in the shear viscosity coefficient of gases. The first order stress tensor is given by the kinetic theory expression

$$\mathbf{P}^{(1)} = \sum_{a=1}^r \langle m_a \mathbf{C}_a \mathbf{C}_a f_a^e \phi_a \rangle. \quad (3.20)$$

On substitution of  $\phi_a$  in (2.75) and exploiting the symmetry properties of integrands associated with the heat flow and diffusion we obtain

$$\mathbf{P}^{(1)} = -\frac{1}{5n} \sum_{a=1}^r \left\langle f_a^e m_a [\mathbf{C}_a \mathbf{C}_a]^{(2)} : [\mathbf{C}_a \mathbf{C}_a]^{(2)} \mathcal{B}_a(C) \right\rangle [\nabla \mathbf{u}]^{(2)}. \quad (3.21)$$

Comparing this expression with the phenomenological constitutive equation for the stress tensor (2.54) we find the first order kinetic theory results for the shear viscosity  $\eta_0$  and the bulk viscosity  $\eta_b^0$ :

$$\eta_0 = \frac{1}{10n} \sum_{a=1}^r \left\langle f_a^e m_a [\mathbf{C}_a \mathbf{C}_a]^{(2)} : [\mathbf{C}_a \mathbf{C}_a]^{(2)} \mathcal{B}_a(C) \right\rangle, \quad (3.22)$$

$$\eta_b^0 = 0. \quad (3.23)$$

It is remarkable that the bulk viscosity coefficient  $\eta_b^0$  is equal to zero for dilute monatomic gases for the solution of the kinetic equation at this order of approximation. The shear viscosity formula may be written in terms of a collision bracket integral as follows:

$$\eta_0 = \frac{k_B T}{10} [\mathbf{B}, \mathbf{B}]. \quad (3.24)$$

This collision bracket integral can be calculated by using the solution of the linear integral equation (2.70) or, equivalently, (2.73).

### 3.4 Nonlinear Transport Processes

We have reviewed in some detail the Chapman–Enskog first-order solution of the Boltzmann equation, which has been quite successful in accounting for linear transport processes that occur near equilibrium in gases. The theory provides the statistical mechanical expressions to compute all transport coefficients of dilute monatomic gases, given information on intermolecular forces. The reliability of the transport coefficients so obtained has been successfully verified [1–3] by laboratory experiments. Moreover, the first-order Chapman–Enskog solution furnishes the kinetic theory foundations [4–6] of linear irreversible processes, which are mathematically represented by the linear constitutive equations presented in the previous section for the stress tensor, heat flux, and diffusion fluxes. Therefore, the kinetic theory of linear irreversible thermodynamics [5, 6, 10] can be satisfactorily understood for monatomic gaseous mixtures with the help of the first-order solution of the Boltzmann equation.

As the system is increasingly displaced from equilibrium, it is not sufficient to use linear constitutive equations developed in the previous section because higher order thermodynamic gradients or thermodynamic forces must be taken into consideration if flow phenomena far removed from equilibrium are to be adequately explained from the standpoint of statistical mechanics. Efforts have been made to develop an extension of the Chapman–Enskog method of solution of the Boltzmann equation by including higher order perturbation terms in the solution. The solution in the second-order theory is called the Burnett solution [1, 3], and the third-order solution the super-Burnett solution [1, 3]. The second-order solution, the Burnett solution, involves second-order thermodynamic gradients, whereas the third-order (super-Burnett) solution involves third-order thermodynamic gradients among others. The corresponding hydrodynamic equations are called the Burnett equations and the super-Burnett equations, respectively. The Burnett and super-Burnett equations are not thermodynamically consistent [6] in the sense of the term defined earlier. Furthermore, they require additional boundary conditions on flow variables which are not available experimentally. For these reasons, we rule them out as an adequate theory of macroscopic flow processes in gases far removed from equilibrium. This is also why we have not considered the Chapman–Enskog method beyond first order.

In this section, we describe a thermodynamically consistent theory of nonlinear hydrodynamic processes and accompanying constitutive equations for the stress tensor, heat flux, and diffusion fluxes in monatomic gaseous mixtures. The constitutive equations will also provide nonlinear transport coefficients appropriate for flow processes. They will be generally nonclassical and dependent on thermodynamic gradients, unlike the linear transport coefficients that are independent of thermodynamic gradients, as we have seen earlier.

The basic strategy for developing such a theory is to avoid the Chapman–Enskog expansion for the distribution functions and macroscopic variables and the manner in which the time derivatives are calculated. Nevertheless, it is necessary to assume the functional hypothesis underlying the Chapman–Enskog method, namely, that the distribution functions evolve as functionals of macroscopic variables. If we wish to study macroscopic flow processes from the viewpoint of statistical mechanics, this hypothesis seems to be unavoidable to reduce the sheer amount of information contained in the phase space distribution function to a level compatible with the macroscopic description of systems consisting of many molecules. If the distribution functions evolve through macroscopic flow variables, then it is natural to look for their evolution equations, and the kinetic equation for the distribution functions should give the desired evolution equations for macroscopic flow variables.

### 3.4.1 Generalized Hydrodynamic Equations

Derivation of such evolution equations has been well described in the literature [5, 6], so we will present them without going into their derivation in this work. In the notation used in this work, they are made of the mass, momentum, and internal energy balance equations—conservation laws—in addition to the complete set of constitutive equations for nonconserved variables of the fluid of interest. In the absence of chemical reactions,

$$\rho \frac{dv}{dt} = \nabla \cdot \mathbf{u} \quad (v = \rho^{-1}), \quad (3.25)$$

$$\rho \frac{dc_a}{dt} = -\nabla \cdot \mathbf{J}_a \quad (1 \leq a \leq r), \quad (3.26)$$

$$\rho \frac{du}{dt} = -\nabla \cdot \mathbf{P} + \rho \mathbf{F}, \quad (3.27)$$

$$\rho \frac{d\mathcal{E}}{dt} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a, \quad (3.28)$$

$$\rho \frac{d\hat{\Phi}_{ka}}{dt} = -\nabla \cdot \psi_{ka} + \mathcal{Z}_{ka} + \Lambda_{ka} \quad (k \geq 1, r \geq a \geq 1), \quad (3.29)$$

where  $d/dt$  is the substantial time derivative defined by

$$\frac{d}{dt} = d_t = \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla, \quad (3.30)$$

$\Phi_{ka}$  represents the  $k$ th nonconserved variable of species  $a$ , and  $\hat{\Phi}_{ka}$  is the density of  $\Phi_{ka}$  defined by

$$\hat{\Phi}_{ka} = \Phi_{ka} \rho^{-1}.$$

The set of nonconserved variables includes the complete set of macroscopic nonconserved variables that are necessary for appropriate description of the

flow process of interest. It includes stress tensors, heat fluxes, diffusion fluxes of various species, and other higher order variables, if necessary.

To define  $\Phi_{ka}$  specifically, it is necessary to split the stress tensor  $\mathbf{P}$  into species components, which are then decomposed into trace and traceless symmetric parts:

$$\mathbf{P} = \sum_{a=1}^r \mathbf{P}_a = \sum_{a=1}^r (p_a \delta + \Delta_a \delta + \Pi_a), \quad (3.31)$$

where  $p_a$  is the partial hydrostatic pressure of species  $a$

$$\Delta_a = \frac{1}{3} \text{Tr} \mathbf{P}_a - p_a, \quad (3.32)$$

$$\Pi_a = [\mathbf{P}_a]^{(2)}. \quad (3.33)$$

The heat flux  $\mathbf{Q}$  is also decomposed into species components:

$$\mathbf{Q} = \sum_{a=1}^r \mathbf{Q}_a. \quad (3.34)$$

The set of nonconserved variables  $\Phi_{ka}$  is then arranged in the order

$$\Phi_{1a} = \Pi_a, \quad \Phi_{2a} = \Delta_a, \quad \Phi_{3a} = \mathbf{Q}'_a \equiv \mathbf{Q}_a - \hat{h}_a \mathbf{J}_a, \quad \Phi_{4a} = \mathbf{J}_a, \dots, \quad (3.35)$$

where  $\hat{h}_a = 5k_B T / 2m_a$ , the enthalpy density per unit mass of species  $a$ . Let us denote by  $h_a^{(k)}$  the molecular expression corresponding to the macroscopic variable  $\Phi_{ka}$ . The statistical mechanical expression for  $\Phi_{ka}$  then is given by

$$\Phi_{ka} = \langle f_a h_a^{(k)} \rangle \quad (k \geq 1). \quad (3.36)$$

Leading examples of the molecular expression for  $h_a^{(k)}$  are

$$\begin{aligned} h_a^{(1)} &= m_a [\mathbf{C}_a \mathbf{C}_a]^{(2)}, & h_a^{(2)} &= \frac{1}{3} \text{Tr} (m_a \mathbf{C}_a \mathbf{C}_a) - m_a p_a / \rho_a, \\ h_a^{(3)} &= m_a \left( \frac{1}{2} C_a^2 - \hat{h}_a \right) \mathbf{C}_a, & h_a^{(4)} &= m_a \mathbf{C}_a, \dots. \end{aligned} \quad (3.37)$$

With this notation, the various terms on the right-hand side of the constitutive equations (3.29) are defined by the statistical mechanical formulas

$$\psi_{ka} = \langle f_a \mathbf{C}_a h_a^{(k)} \rangle, \quad (3.38)$$

$$\mathcal{Z}_{ka} = \langle f_a \mathcal{D}_t h_a^{(k)} \rangle, \quad (3.39)$$

$$\Lambda_{ka} = \langle h_a^{(k)} \mathfrak{R}_B [f_a] \rangle, \quad (3.40)$$

where

$$\mathcal{D}_t = d_t + \mathbf{C}_a \cdot \nabla + \mathbf{F}_a \cdot \nabla_{\mathbf{v}_a}. \quad (3.41)$$

The physical meaning of  $\psi_{ka}$  is the flux of  $h_a^{(k)}$ , and mathematically it is a moment one order higher than  $\Phi_{ka}$ . However, it is generally a reducible moment, which is expressible as a combination of irreducible moments. Such combinations may be exploited to obtain closure of the open hierarchy of evolution equations for the nonconserved variables  $\Phi_{ka}$  presented.  $\mathcal{Z}_{ka}$  is called the kinematic term, which on explicit evaluation consists of nonlinear terms made up of gradients of velocity, density, and temperature.  $\Lambda_{ka}$  is called the dissipation term because it is closely associated with, and thus the seat of, energy dissipation arising from the process  $\Phi_{ka}$ . The dissipation terms  $\Lambda_{ka}$  do not vanish for nonconserved variables because  $h_a^{(k)}$  are not summational invariants of the kinetic equation, more specifically, the Boltzmann equation. The kinematic terms and  $\psi_{ka}$  can be explicitly calculated by substituting  $h_a^{(k)}$ , as given in (3.37), and examples of the kinematic terms are given in Table 3.1 for the constitutive equations for the stress tensors, heat fluxes, and diffusion fluxes.

In Table 3.1,  $\varphi_a^{(3)}$  is a third-rank tensor defined by

$$\varphi_a^{(3)} = \langle m_a C_a C_a C_a f_a \rangle.$$

Note that, when linearized with respect to the thermodynamic gradients, the kinematic terms  $\mathcal{Z}_{ka}$  are approximated by thermodynamic forces:

$$\begin{aligned} \mathcal{Z}_{1a} &\simeq -2p_a [\nabla \mathbf{u}]^{(2)}, & \mathcal{Z}_{2a} &\simeq -p_a d_t \ln(p_a v^{5/3}) + p_a d_t \ln c_a, \\ \mathcal{Z}_{3a} &\simeq -p_a \hat{C}_{pa} T \nabla \ln T, & \mathcal{Z}_{4a} &\simeq -p \mathbf{d}_a, \quad \text{etc.} \end{aligned} \quad (3.42)$$

These approximate forms of kinematic terms imply that nonconserved variables are primarily driven by thermodynamic forces stemming from a velocity gradient, volume change, temperature gradient, concentration gradients, and so on. Driven by these thermodynamic forces, the fluid evolves along the trajectory described by nonconserved and conserved variables while dissipating energy because the nonconserved variables are not collision invariant and

**Table 3.1.** Leading kinematic terms for dilute monatomic gases

$\mathcal{Z}_{1a} = -2[\mathbf{J}_a (d_t \mathbf{u} - \mathbf{F}_a)]^{(2)} - 2[\Pi_a \cdot [\nabla \mathbf{u}]^{(2)}]^{(2)} - 2\Delta_a [\nabla \mathbf{u}]^{(2)}$
$- \frac{2}{3}\Pi_a \nabla \cdot \mathbf{u} - 2p_a [\nabla \mathbf{u}]^{(2)}$
$\mathcal{Z}_{2a} = -\frac{2}{3}\mathbf{J}_a \cdot (d_t \mathbf{u} - \mathbf{F}_a) - \frac{2}{3}\Pi_a : \nabla \mathbf{u} - \frac{2}{3}\Delta_a \nabla \cdot \mathbf{u}$
$- \mathbf{J}_a \cdot \nabla (p_a / \rho_a) - p_a d_t \ln(p_a v^{5/3}) + p_a d_t \ln c_a$
$\mathcal{Z}_{3a} = -(d_t \mathbf{u} - \mathbf{F}_a) \cdot (\Pi_a + \Delta_a \delta) - \mathbf{Q}'_a \cdot \nabla \mathbf{u} - \varphi_a^{(3)} : \nabla \mathbf{u}$
$- \mathbf{J}_a d_t \hat{h}_a - (\Pi_a + \Delta_a \delta) \cdot \nabla \hat{h}_a - p_a \hat{C}_{pa} T \nabla \ln T$
$\mathcal{Z}_{4a} = \nabla \cdot \mathbf{P}_a + \frac{\rho_a}{\rho} \nabla \cdot (\Pi + \Delta \delta) - \nabla \cdot (\Pi_a + \Delta_a \delta)$
$- \mathbf{J}_a \cdot \nabla \mathbf{u} - p \mathbf{d}_a$

hence not conserved. Nonlinear transport processes can be understood by the generalized hydrodynamics equations (3.25)–(3.29).

The set of macroscopic evolution equations (3.25)–(3.29) is thermodynamically consistent because they satisfy the local form of the second law of thermodynamics, if exact solutions are used for the distribution functions obeying the Boltzmann equation. However, if an approximate solution is employed, there is no assurance that the second law of thermodynamics is rigorously satisfied. In the following, we will discuss an approximate solution that will yield thermodynamically consistent evolution equations. The point to emphasize here is that a careless approximation of the distribution function does not guarantee the desired thermodynamic consistency, and the inevitable approximation method must be developed to maintain thermodynamic consistency.

As the first step in developing a thermodynamically consistent approximation of the Boltzmann equation, we seek the distribution function in exponential form, the nonequilibrium canonical form,

$$f_a^c = \exp \left\{ \beta \mu_a - \beta \left[ \frac{1}{2} m_a C_a^2 + \sum_{k \geq 1} X_{ka} h_a^{(k)}(\mathbf{C}_a) \right] \right\}, \quad (3.43)$$

where  $X_{ka}$  is the macroscopic variable conjugate to  $\Phi_{ka}$ ; it does not depend on  $\mathbf{C}_a$  but may depend on  $\beta = 1/k_B T$  and density. It is called the generalized potential conjugate to  $\Phi_{ka}$  and it is akin to the chemical potential  $\mu_a$ . The distribution function is normalized to density  $n_a$

$$\langle f_a^c \rangle = n_a.$$

Therefore, the nonequilibrium chemical potential  $\mu_a$  is given by the normalization factor of  $f_a^c$  through the relation

$$\begin{aligned} \mu_a &= m_a \hat{\mu}_a \\ &= -k_B T \ln \left\{ n_a^{-1} \left\langle \exp \left[ -\beta \left( \frac{1}{2} m_a C_a^2 + \sum_{k \geq 1} X_{ka} h_a^{(k)} \right) \right] \right\rangle \right\}. \end{aligned} \quad (3.44)$$

If the Boltzmann entropy production,

$$\sigma_{\text{ent}} = -k_B \sum_{a=1}^r \langle \ln f_a \mathfrak{R}_B [f_a] \rangle \quad (3.45)$$

is calculated by substituting the nonequilibrium canonical form in  $\ln f_a$  in (3.45), then it follows that  $\sigma_{\text{ent}}$  takes a bilinear form:

$$\sigma_{\text{ent}} = T^{-1} \sum_{a=1}^r \sum_{k \geq 1} X_{ka} \Lambda_{ka} \geq 0. \quad (3.46)$$

This positive bilinear form further elucidates the significance of the dissipation term  $\Lambda_{ka}$  mentioned earlier. The dissipation terms  $\Lambda_{ka}$  must be approximated so that this inequality is preserved.

It has been found that if the cumulant expansion method [5, 6] is applied to the dissipation terms in (3.46), the first- or the third-order cumulant approximation produces thermodynamically consistent dissipation terms. In particular, the first-order cumulant approximation of  $\Lambda_{ka}$  is given by

$$\Lambda_{ka} = (\beta g)^{-1} q(X) \sum_{b=1}^r \sum_{l \geq 1} R_{ab}^{(kl)} X_{lb}, \quad (3.47)$$

where

$$g = \frac{1}{n^2 d^2} \sqrt{\frac{m}{2k_B T}}, \quad (3.48)$$

$$q(X) = \frac{\sinh \kappa}{\kappa} \quad (3.49)$$

with  $\kappa^2$  denoting the quadratic form

$$\kappa^2 = \sum_{a,b=1}^r \sum_{k,l \geq 1} X_{ka} R_{ab}^{(kl)} X_{lb}. \quad (3.50)$$

$R_{ab}^{(kl)}$  are given in terms of the collision bracket integrals and  $m$  denotes the reduced mass. They are listed in Table 3.2 for the leading nonconserved variables. In Table 3.2, collision bracket integrals are expressed in terms of the reduced variable

$$\boldsymbol{\tau}_a = \sqrt{\frac{m_a}{2k_B T}} \mathbf{C}_a = \frac{1}{\sqrt{2}} \mathbf{w}_a. \quad (3.51)$$

$S_{3/2}^{(1)}(\tau)$  denotes the Sonine polynomial  $S_{3/2}^{(1)}(\tau) = 5/2 - \tau$  of order  $(\frac{3}{2}, 1)$ ; see

**Table 3.2.** Collision bracket integrals for the leading moments

$R_{aa}^{(11)} = \frac{4}{5} \{ [[\boldsymbol{\tau}_a \boldsymbol{\tau}_a]^{(2)} : [\boldsymbol{\tau}_a \boldsymbol{\tau}_a]^{(2)}]_{aa'} + \sum_{a \neq b} [[\boldsymbol{\tau}_a \boldsymbol{\tau}_a]^{(2)} : [\boldsymbol{\tau}_a \boldsymbol{\tau}_a]^{(2)}]_{ab}' \}$
$R_{ab}^{(11)} = \frac{4}{5} [[\boldsymbol{\tau}_a \boldsymbol{\tau}_a]^{(2)} : [\boldsymbol{\tau}_b \boldsymbol{\tau}_b]^{(2)}]_{ab}'' \quad (a \neq b)$
$R_{aa}^{(33)} = \frac{2}{3} (\beta m_a)^{-1} \left\{ \left[ S_{3/2}^{(1)}(\tau_a^2) \boldsymbol{\tau}_a \cdot S_{3/2}^{(1)}(\tau_a^2) \boldsymbol{\tau}_a \right]_{aa'} \right.$
$\left. + \sum_{a \neq b} \left[ S_{3/2}^{(1)}(\tau_a^2) \boldsymbol{\tau}_a \cdot S_{3/2}^{(1)}(\tau_a^2) \boldsymbol{\tau}_a \right]_{ab}' \right\}$
$R_{ab}^{(33)} = \frac{2}{3} (\beta \sqrt{m_a m_b})^{-1} [S_{3/2}^{(1)}(\tau_a^2) \boldsymbol{\tau}_a \cdot S_{3/2}^{(1)}(\tau_b^2) \boldsymbol{\tau}_b]_{ab}''$
$R_{aa}^{(44)} = \frac{2}{3} \sqrt{m_a m_b} \beta \{ [\boldsymbol{\tau}_a \cdot \boldsymbol{\tau}_a]_{aa'} + \sum_{a \neq b} [\boldsymbol{\tau}_a \cdot \boldsymbol{\tau}_a]_{ab}' \}$
$R_{ab}^{(44)} = \frac{2}{3} \sqrt{m_a m_b} \beta [\boldsymbol{\tau}_a \cdot \boldsymbol{\tau}_a]_{ab}''$
$R_{aa}^{(34)} = R_{aa}^{(43)} = -\frac{2}{3} \left\{ \left[ S_{3/2}^{(1)}(\tau_a^2) \boldsymbol{\tau}_a \cdot \boldsymbol{\tau}_a \right]_{aa'} + \sum_{a \neq b} [S_{3/2}^{(1)}(\tau_a^2) \boldsymbol{\tau}_a \cdot \boldsymbol{\tau}_a]_{ab}' \right\}$
$R_{ab}^{(34)} = R_{ba}^{(43)} = -\frac{2}{3} [S_{3/2}^{(1)}(\tau_a^2) \boldsymbol{\tau}_a \cdot \boldsymbol{\tau}_b]_{ab}''$

Footnote 3 in Chap. 2 regarding Sonine polynomials. The following abbreviations are also used for collision bracket integrals:

$$\begin{aligned}[A_a, B_a]_{ab} &= \frac{n_a n_b}{4n^2} \left\langle (\Delta A_a + \Delta A_b) (\Delta B_a + \Delta B_b) \right\rangle_c, \\ [A_a, B_a]'_{ab} &= \frac{n_a n_b}{2n^2} \langle \Delta A_a \Delta B_a \rangle_c, \\ [A_a, B_a]''_{ab} &= \frac{n_a n_b}{2n^2} \langle \Delta A_a \Delta B_b \rangle_c,\end{aligned}$$

where

$$\Delta A_a = A_a - A_a^*,$$

etc.,

$$\langle \cdots \rangle_c = (2\pi)^{-3} d^{-2} \sqrt{\frac{m_a}{2k_B T}} \int d\mathbf{w}_a \int d\mathbf{w}_b \int_0^{2\pi} \int_0^\infty d\mathbf{b} \langle \cdots \rangle e^{-\frac{1}{2} w_a^2 - \frac{1}{2} w_b^2} \dots.$$

The quadratic form  $\kappa^2$  is the Rayleigh dissipation function [7], and the Boltzmann entropy production in the first cumulant approximation is given by

$$\sigma_{\text{ent}} = k_B \kappa \sinh \kappa. \quad (3.52)$$

It is positive and vanishes only if  $\kappa = 0$ , which occurs at equilibrium at which  $X_{ka} = 0$  for all  $k$  and  $a$ . If the hyperbolic sine function is approximated by  $\kappa$  to the lowest order, the Boltzmann entropy production is simply proportional to the Rayleigh dissipation function.

When the first-order cumulant approximation of the dissipation term  $\Lambda_{ka}$  given in (3.47) is used in (3.29), a thermodynamically consistent set of macroscopic evolution equations is obtained. Because the constitutive equations for the nonconserved variables thus arising from (3.29) generalize the linear constitutive equations (2.54)–(2.56), which we have seen give rise to the classical hydrodynamic equations, together with the balance equations for the conserved variables, they represent a generalization of the classical hydrodynamics to nonlinear transport processes. They are called the generalized hydrodynamic equations in the first-order cumulant approximation or simply *generalized hydrodynamic equations*.

The generalized potentials  $X_{ka}$  in the dissipation terms are not yet determined. They should be obtained in terms of variables  $\{\rho, \beta, \Phi_{ka}\}$  describing the processes of interest. For this purpose, we recall that the nonequilibrium canonical form gives rise to the nonequilibrium partition function [6]

$$\mathbb{Z}_a = n_a^{-1} \left\langle \exp \left[ -\beta \left( \frac{1}{2} m_a C_a^2 + \sum_{k \geq 1} X_{ka} h_a^{(k)} \right) \right] \right\rangle. \quad (3.53)$$

This nonequilibrium partition function gives the chemical potential of species  $a$  in the form

$$\hat{\mu}_a = -(m_a \beta)^{-1} \ln \mathbb{Z}_a.$$

If there are  $N_1, N_2, \dots, N_r$  molecules, respectively, for each species in the mixture, the total partition function is given by the product

$$\mathbb{Z} = \prod_a \mathbb{Z}_a^{N_a}, \quad (3.54)$$

and it can be shown that the nonconserved variables are related to the generalized potentials by the relation [6]

$$\Phi_{ka} = -\frac{k_B T}{V} \left( \frac{\partial}{\partial X_{ka}} \ln \mathbb{Z} \right)_{T,p,N,X} \quad (k \geq 1; r \geq a \geq 1). \quad (3.55)$$

Thus by calculating the nonequilibrium partition function and inverting this relation, the generalized potentials can be computed in terms of  $T, p, N_a$ , and  $\Phi_{ka}$ . However, it is not trivial to solve this problem because the nonequilibrium partition function is not known explicitly, although it is possible to implement the procedure precisely for some particular flow configurations. For this reason, rigorous forms for the generalized potentials are not known yet in generality. Therefore, we will discuss a general theory with approximate forms for the generalized potentials.

The generalized potentials  $X_{ka}$  may be written as [5, 6]

$$X_{ka} = -\Phi_{ka} g_a^{(k)}, \quad (3.56)$$

where the scalar function  $g_a^{(k)}$  generally depends on the nonconserved variables  $\{\Phi_{ka}\}$  in addition to temperature and density. In particular, to the lowest order approximation,  $g_a^{(k)}$  may be approximated as

$$g_a^{(1)} \simeq \frac{1}{2p_a}, \quad g_a^{(2)} \simeq \frac{3}{2p_a}, \quad g_a^{(3)} \simeq \frac{1}{p_a \hat{C}_{pa} T}, \quad g_a^{(4)} \simeq \frac{1}{\rho_a}. \quad (3.57)$$

Here  $\hat{C}_{pa}$  is the isobaric heat capacity per unit mass of species  $a$ . We will use these approximations for  $g_a^{(k)}$  in the dissipative terms of the constitutive equations. In these approximations for  $X_{ka}$ , the leading examples of the first-order cumulant approximation of  $\Lambda_{ka}$  are

$$\begin{aligned} \Lambda_{1a} &= -2p_a q(\Phi) \sum_{b=1}^r \mathfrak{R}_{ab}^{(11)} \Pi_b, \\ \Lambda_{2b} &= -\frac{2}{3} p_a q(\Phi) \sum_{b=1}^r \mathfrak{R}_{ab}^{(22)} \Delta_b, \\ \Lambda_{3a} &= -p_a \hat{C}_{pa} T q(\Phi) \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(33)} \mathbf{Q}'_b + \mathfrak{R}_{ab}^{(34)} \mathbf{J}_b \right), \\ \Lambda_{4a} &= -\rho_a q(\Phi) \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(43)} \mathbf{Q}'_b + \mathfrak{R}_{ab}^{(44)} \mathbf{J}_b \right), \end{aligned} \quad (3.58)$$

where the coefficients  $\mathfrak{R}_{ab}^{(qk)}$  are defined by

$$\mathfrak{R}_{ab}^{(qk)} = (\beta g)^{-1} g_a^{(q)} R_{ab}^{(qk)} g_b^{(k)} \quad (3.59)$$

and  $q(\Phi)$  is defined by (3.49) and (3.50), where the generalized potentials are approximated as in (3.57).

At this point, it is useful to examine the flux  $\psi_{ka}$  of nonconserved variable  $\Phi_{ka}$ , which when calculated explicitly may be expressible in a combination of irreducible moments. The leading examples corresponding to stress tensors, heat fluxes, and diffusion fluxes are

$$\psi_{1a} = \langle f_a m_a \mathbf{C}_a \mathbf{C}_a \mathbf{C}_a \rangle - \frac{2}{3} \delta \mathbf{Q}_a, \quad (3.60)$$

$$\psi_{2a} = \frac{2}{3} \mathbf{Q}_a - \frac{p_a}{\rho_a} \mathbf{J}_a, \quad (3.61)$$

$$\psi_{3a} = \frac{1}{2} \text{Tr}^{(2)} \langle f_a m_a \mathbf{C}_a \mathbf{C}_a \mathbf{C}_a \mathbf{C}_a \rangle - \hat{h}_a \mathbf{P}_a, \quad (3.62)$$

$$\psi_{4a} = \mathbf{P}_a, \quad \text{etc.,} \quad (3.63)$$

where  $\text{Tr}^{(2)}$  denotes taking the trace of the first two or the last two vectors of the fourth-rank tensor. Therefore, the flux tensor  $\psi_{ka}$  consists of the rank  $k$  Cartesian tensor made up of  $\mathbf{C}_a$  and lower rank tensors. The rank  $k$  tensor is irreducible unless the trace is taken.

The evolution equations for the nonconserved variables—the constitutive equations—form an open hierarchy of equations. To obtain a theory of irreversible processes, it is necessary to close the open hierarchy. Although the choice is not unique, we choose the closure so that the flux tensors  $\psi_{1a}$  and  $\psi_{3a}$  vanish identically [6, 8, 9]:

$$\langle f_a m_a \mathbf{C}_a \mathbf{C}_a \mathbf{C}_a \rangle = \frac{2}{3} \delta \mathbf{Q}_a, \quad (3.64)$$

$$\text{Tr}^{(2)} \langle f_a m_a \mathbf{C}_a \mathbf{C}_a \mathbf{C}_a \mathbf{C}_a \rangle = 2 \hat{h}_a \mathbf{P}_a.$$

Similarly, for higher order flux tensors. Then all the moments of orders higher than  $\mathbf{P}_a$  are expressible only in terms of  $\mathbf{P}_a$ ,  $\mathbf{Q}_a$ , and  $\mathbf{J}_a$ . Thus the theory is closed to the first thirteen moments or equivalent. The theory of nonlinear transport processes discussed below is formulated under this closure of the open hierarchy of evolution equations for nonconserved variables.

In summary, the evolution equations for nonconserved variables limited to  $\Phi_{ka}$  ( $k = 1, \dots, 4$ ) and under the closure just mentioned are [5, 6]

$$\rho d_t \hat{\Phi}_{1a} = \mathcal{Z}_{ka} - 2 p_a q(\Phi) \sum_{b=1}^r \mathfrak{R}_{ab}^{(11)} \Pi_b, \quad (3.65)$$

$$\rho d_t \hat{\Phi}_{2a} = \mathcal{Z}_{2a} - \frac{2}{3} p_a q(\Phi) \sum_{b=1}^r \mathfrak{R}_{ab}^{(22)} \Delta_b, \quad (3.66)$$

$$\rho d_t \hat{\Phi}_{3a} = \mathcal{Z}_{3a} - p_a \hat{C}_{pa} T q(\Phi) \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(33)} \mathbf{Q}'_b + \mathfrak{R}_{ab}^{(34)} \mathbf{J}_b \right), \quad (3.67)$$

$$\rho d_t \hat{\Phi}_{4a} = \mathcal{Z}_{4a} - \rho_a q(\Phi) \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(43)} \mathbf{Q}'_b + \mathfrak{R}_{ab}^{(44)} \mathbf{J}_b \right), \quad (3.68)$$

where the kinematic terms are summarized in Table 3.1. This set combined with the conservation laws (3.25)–(3.28) constitutes the generalized hydrodynamic equations for irreversible processes described by the macroscopic variable set  $(\rho, c_a, \mathbf{u}, \mathcal{E}, \Phi_{ka} : k = 1, \dots, 4; 1 \leq a \leq r)$ . This set represents the thermodynamic variables because a generalized theory of irreversible thermodynamics can be formulated on the manifold spanned by them.

It is convenient to introduce the composite hydrodynamic parameter  $N_\delta$ —the nonuniformity parameter—defined by [5, 6, 10]

$$N_\delta = \gamma_0 N_M^2 N_{Re}^{-1} = \sqrt{\frac{2\pi}{\gamma_0}} N_M N_K n, \quad (3.69)$$

where  $N_M$ ,  $N_K n$ , and  $N_{Re}$  are the Mach, Knudsen, and Reynolds number, respectively, defined by

$$\begin{aligned} N_M &= \frac{u_r}{\sqrt{\gamma_0 k_B T}}, \\ N_K n &= \frac{l}{L}, \\ N_{Re} &= \frac{\rho_r u_r L}{\eta}, \end{aligned}$$

$\gamma_0$  is the polytropic ratio,  $u_r$  is the reference flow velocity,  $l$  is the mean free path,  $L$  is the characteristic length, and  $\rho_r$  is the reference density. Then it can be shown that the generalized hydrodynamic equations reduce to the classical hydrodynamic equations in the limit of  $N_\delta$  tending to zero. This is the reason for the terminology of generalized hydrodynamics used here.

### 3.4.2 Nonlinear Constitutive Equations

The nonconserved variables  $\Phi_{ka}$  of the thermodynamic variable set generally evolve on a faster timescale than the conserved variables consisting of  $(\rho, c_a, \mathbf{u}, \mathcal{E} : 1 \leq a \leq r)$ . Therefore on the timescale of evolution for  $\Phi_{ka}$ , the conserved variables remain virtually constant. Therefore, the nonconserved variables reach their steady-state values before the conserved variables change significantly. On such timescales, we may then set the substantial time derivatives of  $\hat{\Phi}_{ka}$  equal to zero in the generalized hydrodynamic equations. Furthermore, it can be also shown [5, 6, 10] that in the limit of small  $N_\delta$ , the kinematic terms  $\mathcal{Z}_{ka}$  may be approximated by the forms given in (3.42). In such a limit of  $N_\delta$ , the constitutive equations for nonconserved variables become

$$-[\nabla \mathbf{u}]^{(2)} - q(\Phi) \sum_{b=1}^r \mathfrak{R}_{ab}^{(11)} \Pi_b = 0 \quad (3.70)$$

$$-\nabla \ln T - q(\Phi) \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(33)} \mathbf{Q}'_b + \mathfrak{R}_{ab}^{(34)} \mathbf{J}_b \right) = 0, \quad (3.71)$$

$$-\frac{p}{\rho_a} \mathbf{d}_a - q(\Phi) \sum_{b=1}^r \left( \mathfrak{R}_{ab}^{(43)} \mathbf{Q}'_b + \mathfrak{R}_{ab}^{(44)} \mathbf{J}_b \right) = 0, \quad (3.72)$$

where the constitutive equation for  $\Delta_a$  is not listed because  $\Delta_a = 0$  identically for dilute monatomic gases and there thus holds the relation

$$pv^{5/3} = \text{constant}, \quad (3.73)$$

a well known relation in the adiabatic expansion of an ideal gas. These nonlinear constitutive equations in the adiabatic approximation [5,6,10] at small  $N_\delta$  form the basis of a theory of nonlinear transport processes considered in this work. For large  $N_\delta$ , the full set of generalized hydrodynamic equations presented must be solved, but then the problem defies relatively simple treatment as done here and hence must be handled numerically.

### 3.4.3 Nonlinear Transport Coefficients

To calculate nonlinear transport coefficients from (3.70)–(3.72), it is necessary to solve them for  $\Pi_a$ ,  $\mathbf{Q}'_a$ , and  $\mathbf{J}_a$ . For the purpose, we examine the argument of the nonlinear factor  $q(\Phi)$ , the dissipation function  $\kappa^2$ , which is in the quadratic form,

$$\begin{aligned} \kappa^2 = g\beta \sum_{a=1}^r \sum_{b=1}^r & \left[ \mathbf{\Pi}_a : \mathfrak{R}_{ab}^{(11)} \mathbf{\Pi}_b + \mathbf{Q}'_a \cdot \left( \mathfrak{R}_{ab}^{(33)} \mathbf{Q}'_b + \mathfrak{R}_{ab}^{(34)} \mathbf{J}_b \right) \right. \\ & \left. + \mathbf{J}_a \cdot \left( \mathfrak{R}_{ab}^{(43)} \mathbf{Q}'_b + \mathfrak{R}_{ab}^{(44)} \mathbf{J}_b \right) \right]. \end{aligned} \quad (3.74)$$

It is useful to note that there follow from the definitions of the collision bracket integrals the symmetry relations

$$\mathfrak{R}_{ab}^{(lk)} = \mathfrak{R}_{ba}^{(kl)} \quad (3.75)$$

because the collision bracket integrals are symmetrical with respect to interchange of species indexes and concurrent interchange of indexes  $l$  and  $k$ . These symmetry properties underlie the Onsager reciprocal relations of the coefficients. On using the constitutive equations (3.70)–(3.72) in (3.74),  $\kappa^2$  can be written as

$$\kappa^2 = -q^{-1} g\beta \sum_{a=1}^r \left[ \mathbf{\Pi}_a : [\nabla \mathbf{u}]^{(2)} + \mathbf{Q}'_a \cdot \nabla \ln T + \mathbf{J}_a \cdot \frac{p}{\rho_a} \mathbf{d}_a \right]. \quad (3.76)$$

Equations (3.70)–(3.72), which are quasi-linear, can be solved for  $\Pi_a$ ,  $\mathbf{Q}'_a$ , and  $\mathbf{J}_a$ . The solutions may be written as

$$\Pi_a = -q^{-1} \sum_{b=1}^r (\mathbf{S}^{-1})_{ab} [\nabla \mathbf{u}]^{(2)}, \quad (3.77)$$

$$\mathbf{Q}'_a = -q^{-1} \sum_{b=1}^r (\mathbf{M}^{-1})_{ab}^{(33)} \nabla \ln T - q^{-1} \sum_{b=1}^r (\mathbf{M}^{-1})_{ab}^{(34)} \frac{p}{\rho_b} \mathbf{d}_b, \quad (3.78)$$

$$\mathbf{J}_a = -q^{-1} \sum_{b=1}^r (\mathbf{M}^{-1})_{ab}^{(43)} \nabla \ln T - q^{-1} \sum_{b=1}^r (\mathbf{M}^{-1})_{ab}^{(44)} \frac{p}{\rho_b} \mathbf{d}_b, \quad (3.79)$$

where  $\mathbf{S}$  is the matrix consisting of  $\mathfrak{R}_{ab}^{(11)}$

$$\mathbf{S} = \left( \mathfrak{R}_{ab}^{(11)} \right) \quad (3.80)$$

and similarly  $\mathbf{M}$  is a matrix defined by

$$\mathbf{M} = \begin{pmatrix} \mathfrak{R}^{(33)} & \mathfrak{R}^{(34)} \\ \mathfrak{R}^{(43)} & \mathfrak{R}^{(44)} \end{pmatrix}, \quad (3.81)$$

where the submatrices  $\mathfrak{R}^{(33)}$  and so on are matrices made up of  $\mathfrak{R}_{ab}^{(33)}$  and so on like matrix  $\mathbf{S}$ . If the nonlinear factor  $q(\Phi)$  were equal to unity, (3.77)–(3.79) would be the linear constitutive equations for  $\Pi_a$ ,  $\mathbf{Q}'_a$ , and  $\mathbf{J}_a$ . The nonlinear factor  $q(\Phi)$  now can be expressed in terms of thermodynamic forces. To this end, we substitute (3.77)–(3.79) in (3.76) to obtain  $\kappa^2$  in the form,

$$q^2(\kappa) \kappa^2 = \chi^2,$$

where

$$\begin{aligned} \chi = \sqrt{g\beta} & \left[ \sum_{a,b=1}^r (\mathbf{S}^{-1})_{ab} [\nabla \mathbf{u}]^{(2)} : [\nabla \mathbf{u}]^{(2)} \right. \\ & + \sum_{a,b=1}^r (\mathbf{M}^{-1})_{ab}^{(33)} \nabla \ln T \cdot \nabla \ln T + \sum_{a,b=1}^r \frac{p}{\rho_b} (\mathbf{M}^{-1})_{ab}^{(34)} \mathbf{d}_b \cdot \nabla \ln T \\ & \left. + \sum_{a,b=1}^r \frac{p}{\rho_a} (\mathbf{M}^{-1})_{ab}^{(43)} \mathbf{d}_a \cdot \nabla \ln T + \sum_{a,b=1}^r \frac{p^2}{\rho_a \rho_b} (\mathbf{M}^{-1})_{ab}^{(44)} \mathbf{d}_a \cdot \mathbf{d}_b \right]^{1/2}. \end{aligned} \quad (3.82)$$

Therefore the dissipation function  $\kappa$  is now given only in terms of thermodynamic forces and collision bracket integrals:

$$\kappa = \sinh^{-1} \chi.$$

Substituting this result in (3.77)–(3.79) and noting that

$$q^{-1}(\kappa) = \frac{\kappa}{\sinh \kappa} = \frac{\sinh^{-1} \chi}{\chi} \equiv q_\chi, \quad (3.83)$$

we obtain the solutions of the quasi-linear constitutive equations

$$\Pi_a = -q_\chi \sum_{b=1}^r (\mathbf{S}^{-1})_{ab} [\nabla \mathbf{u}]^{(2)}, \quad (3.84)$$

$$\mathbf{Q}'_a = -q_\chi \sum_{b=1}^r \left[ (\mathbf{M}^{-1})_{ab}^{(33)} \nabla \ln T + \frac{p}{\rho_b} (\mathbf{M}^{-1})_{ab}^{(34)} \mathbf{d}_b \right], \quad (3.85)$$

$$\mathbf{J}_a = -q_\chi \sum_{b=1}^r \left[ (\mathbf{M}^{-1})_{ab}^{(43)} \nabla \ln T + \frac{p}{\rho_b} (\mathbf{M}^{-1})_{ab}^{(44)} \mathbf{d}_b \right]. \quad (3.86)$$

These nonlinear constitutive equations suggest the following nonlinear transport coefficients<sup>1</sup>:

$$\eta = q_\chi \sum_{a,b=1}^r (\mathbf{S}^{-1})_{ab}, \quad (3.87)$$

$$\lambda = q_\chi \sum_{a,b=1}^r (\mathbf{M}^{-1})_{ab}^{(33)}, \quad (3.88)$$

$$D_{Ta} = q_\chi \sum_{b=1}^r \frac{1}{\rho_b} (\mathbf{M}^{-1})_{ab}^{(34)}, \quad (3.89)$$

$$D_{ab} = q_\chi \frac{p}{\rho_b} (\mathbf{M}^{-1})_{ab}^{(44)}, \quad (3.90)$$

$$k_{Tb} = \frac{\rho_b}{p} \frac{(\mathbf{M}^{-1})_{ab}^{(43)}}{(\mathbf{M}^{-1})_{ab}^{(44)}}. \quad (3.91)$$

These nonlinear transport coefficients, except for the thermal diffusion ratio  $k_{Tb}$ , depend on thermodynamic gradients (forces) and tend to the first-order Chapman–Enskog transport coefficients, as can be readily verified by using the definitions of matrices  $\mathbf{S}$  and  $\mathbf{M}$ . Thus,

$$\eta_0 = \sum_{a,b=1}^r (\mathbf{S}^{-1})_{ab}, \quad (3.92)$$

$$\lambda_0 = \sum_{a,b=1}^r (\mathbf{M}^{-1})_{ab}^{(33)}, \quad (3.93)$$

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<sup>1</sup> These nonlinear transport coefficients were derived by the present author in the early 1980s in connection with the theory of irreversible thermodynamics [11–15]. Especially, the non-Newtonian viscosity derived has been applied rather extensively to rarefied gas dynamics and the rheology of fluids. See [5, 6, 10] and the references cited therein.

$$D_{Ta}^0 = \sum_{b=1}^r \frac{1}{\rho_b} (\mathbf{M}^{-1})_{ab}^{(34)}, \quad (3.94)$$

$$D_{ab}^0 = \frac{p}{\rho_b} (\mathbf{M}^{-1})_{ab}^{(44)}. \quad (3.95)$$

Substituting these limiting values in the expressions for the nonlinear transport coefficients in (3.87)–(3.90), nonlinear transport coefficients can be expressed in insightful forms:

$$\eta = \eta_0 q_\chi, \quad (3.96)$$

$$\lambda = \lambda_0 q_\chi, \quad (3.97)$$

$$D_{Ta} = D_{Ta}^0 q_\chi, \quad (3.98)$$

$$D_{ab} = D_{ab}^0 q_\chi, \quad (3.99)$$

in which the  $\chi$  in the nonlinear factor  $q_\chi$  may be also expressed in terms of  $\eta_0$ ,  $\lambda_0$ ,  $D_{ab}$ , and so on as well as various gradients such as  $[\nabla \mathbf{u}]^{(2)}$  and so on. In this manner, we now have derived thermodynamic force dependent nonlinear transport coefficients, namely, non-Newtonian shear viscosity, non-Fourier thermal conductivity, non-Fickian diffusion coefficients, and so on. These nonlinear transport coefficients reduce to the first-order Chapman–Enskog transport coefficients as  $\chi \rightarrow 0$  and also require only linear transport coefficients to describe nonlinear transport processes. This is interesting because nonlinear transport coefficients are characterized only by linear transport coefficients and thermodynamic forces in addition to thermodynamic variables such as temperature and density. Some examples of the application of nonlinear transport coefficients will be shown.

### 3.5 Applications of Nonlinear Transport Coefficients

It is well known that the Chapman–Enskog viscosity and thermal conductivity do not depend on density. However, non-Newtonian viscosity and non-Fourier thermal conductivity depend on density because  $\chi$  is inversely proportional to  $n$  or pressure. Therefore we have the limiting behavior of  $\eta$  and  $\lambda$  as follows:

$$\begin{aligned} \eta &\sim n \ln n^{-1}, \\ \lambda &\sim n \ln n^{-1}, \end{aligned} \quad (3.100)$$

that is,  $\eta$  and  $\lambda$  vanish as the gas rarefies. This indicates that the regime of density in which transport coefficients are independent of density is rather limited in contrast to the prediction by Maxwell's kinetic theory [16]. Such a regime is confined to the rather narrow range around the normal density of fluids because transport coefficients also increase rapidly with density beyond normal density as the fluid becomes dense. The particular behavior indicated

by the density dependence in (3.101) has significance for rarefied gas dynamics, as demonstrated by various applications [17–21] of the generalized hydrodynamics equations from which the nonlinear transport coefficients presented here are derived. In the following, we give brief discussions of their applications to nonlinear flow processes in rarefied gases.

### 3.5.1 Non-Newtonian Flow in Rarefied Gases

It is generally known in rheology [22,23] that if a fluid is complex, that is, has an internal structure, its viscosity tends to be non-Newtonian and requires a constitutive equation other than the Newtonian law of viscosity for Newtonian flow. Dynamically, such behavior arises from complicated interactions between constituent components making up the molecules.

Even if the fluid is so dilute as to be regarded as rarefied, non-Newtonian behavior can also arise because of the nonlinear dynamics necessitated by a large value of the nonuniformity parameter  $N_\delta$ . This non-Newtonian behavior in viscous flow is clearly indicated by the viscosity formula presented earlier, (3.87). If the nonlinear viscosity  $\eta$  is plotted against

$$\gamma \equiv \|[\nabla \mathbf{u}]^{(2)}\| = \left[ [\nabla \mathbf{u}]^{(2)} : [\nabla \mathbf{u}]^{(2)} \right]^{1/2}, \quad (3.101)$$

which is the shear rate, then  $\eta$  decreases as the shear rate  $\gamma$  increases, that is, the fluid is thixotropic. Unfortunately, because such shear-thinning non-Newtonian viscosity is not directly measured for dilute gases, it is not directly verifiable in comparison with experimental data on  $\eta$ . However, it is possible to infer such shear-thinning behavior by examining gas flows in various flow configurations. Here we briefly discuss examples flow behavior exhibited by the non-Newtonian viscosity formula (3.87).

First, we plot  $\eta$  as a function of  $\gamma$  with a hard sphere gas as an example to show the shear-thinning behavior mentioned. It is preferable to use non-dimensionalized quantities, so we reduce relevant flow variables as follows:

$$\xi = \mathbf{r}L^{-1}, \quad \mathbf{u}^* = \mathbf{u}/u_r, \quad T^* = T/T_r,$$

$$p^* = p/p_r, \quad \rho^* = \rho/\rho_r, \quad \eta_0^* = \eta_0/\eta_r,$$

where the subscript  $r$  refers to the reference variable,  $L$  is a characteristic length of the flow, and the reference speed may be chosen with the gas kinetic mean speed at reference temperature  $T_r$

$$u_r = \sqrt{\frac{8k_B T_r}{\pi m}}. \quad (3.102)$$

For a hard sphere gas, the shear viscosity is given by

$$\eta_0 = \frac{5\sqrt{mk_B T}}{16\sqrt{\pi}\sigma^2}. \quad (3.103)$$

If we choose  $\eta_r$  as

$$\eta_r = \frac{5\sqrt{mk_B T_r}}{16\sqrt{\pi}\sigma^2},$$

then it follows that

$$\eta_0 = T^{*1/2} \eta_r.$$

Furthermore, because

$$\nabla \mathbf{u} = \frac{u_r}{L} \nabla_\xi \mathbf{u}^*,$$

if only the shear flow is considered, we obtain  $\chi$  in the reduced form

$$\chi = N_\delta \frac{4(2\pi)^{1/4}}{\sqrt{10}} \frac{T^{*1/2}}{\phi} \gamma^*, \quad (3.104)$$

where  $\gamma^*$  is the reduced shear rate defined by

$$\gamma^* = \left[ (\nabla_\xi \mathbf{u}^*)^{(2)} : (\nabla_\xi \mathbf{u}^*)^{(2)} \right]^{1/2}.$$

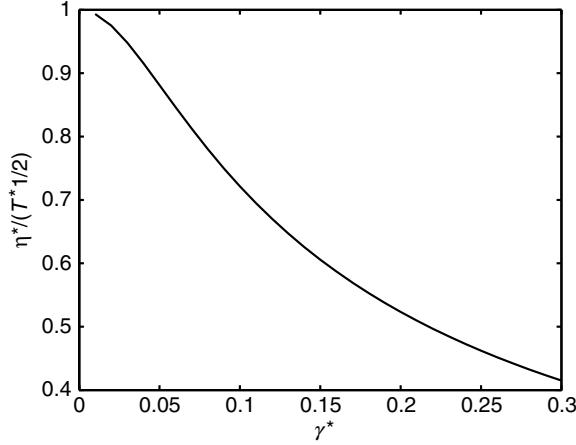
Therefore, the reduced non-Newtonian shear viscosity of a rarefied gas, defined by  $\eta^* = \eta/\eta_r$ , is given by the formula

$$\begin{aligned} \eta^* &= T^{*1/2} \frac{\sinh^{-1} \chi}{\chi} \\ &= \frac{\sqrt{10}\phi}{4(2\pi)^{1/4} N_\delta \gamma^*} \ln H(N_\delta, \phi, T^*), \end{aligned} \quad (3.105)$$

where

$$H(N_\delta, \phi, T^*) = \frac{4(2\pi)^{1/4} N_\delta T^{*1/2}}{\sqrt{10}\phi} \gamma^* + \sqrt{1 + \frac{8(2\pi)^{1/2} N_\delta^2 T^*}{5\phi^2} \gamma^{*2}}. \quad (3.106)$$

The reduced viscosity  $\eta^*/T^{*1/2}$  is plotted against the reduced shear rate  $\gamma^*$  in Fig. 3.1 when  $N_\delta T^{*1/2} \phi^{-1} = 10$ . Clearly, the reduced viscosity is shear rate dependent and therefore non-Newtonian, decreasing with increasing reduced shear rate  $\gamma^*$ . The non-Newtonian behavior is exhibited even by a hard sphere gas if either the nonuniformity number  $N_\delta$  is sufficiently large or  $\phi$  is small, namely, the gas is rarefied, although the shear rate is not too high. Unfortunately, such non-Newtonian behavior of rarefied gas viscosity is not measured directly. Therefore it is necessary to deduce it from other experimental evidence, such as the boundary layer structure [24], the flow rate through a duct, or the flow profile.



**Fig. 3.1.** Reduced non-Newtonian viscosity vs. reduced shear rate for a hard sphere fluid.  $N_\delta T^{*1/2} \phi^{-1} = 10$

### 3.5.2 Non-Poiseuille Flow in a Channel

Non-Newtonian flow behavior can manifest itself in the velocity profile of flow in a channel. By considering the steady-state flow in a rectangular channel of infinite length for a gas obeying the non-Newtonian viscosity formula (3.105), it is possible to derive a velocity profile formula. Since details of the analysis are available in the literature [5, 6, 25] and the present work is not aimed at fluid dynamics discussions, we do not repeat the derivation, but present only the result. We consider a rectangular channel of width  $D$  in the  $y$  direction in a suitably chosen coordinate system, which is aligned along the  $x$  axis. The channel length  $L$  is assumed to be sufficiently long compared with the width so that it may be regarded as infinitely long. Its extension in the  $z$  direction is also assumed to be infinite. The gas is subject to a pressure difference in the  $x$  direction. The gas flow is assumed to be laminar. Then flow is neutral in the  $z$  direction but subject to a velocity gradient in the  $y$  direction. In this flow configuration, the flow is reduced to one dimension, and it is necessary to determine the velocity component  $u_x$  of  $\mathbf{u}$  along the  $x$  axis. This component depends on  $y$ . The stick boundary conditions are assumed for  $u_x(y)$  at the channel walls at  $y = \pm D/2$ . This means that a steady velocity profile arises along the  $y$  axis, which is not necessarily the well-known Poiseuille type [26].

Upon substituting the non-Newtonian viscosity formula (3.105) in the constitutive equation for the stress tensor

$$\boldsymbol{\Pi} = -\eta [\nabla \mathbf{u}]^{(2)}, \quad (3.107)$$

which is in turn substituted in the steady momentum balance equation appropriate for the flow configuration, there follows the reduced differential equation for reduced velocity  $u = u_x/u_r$ :

$$\frac{\partial}{\partial \zeta} \left[ \frac{N_\delta}{\tau} \sinh^{-1} \left( \tau \frac{\partial u}{\partial \zeta} \right) \right] + \varepsilon \frac{\partial \phi}{\partial \xi} = 0. \quad (3.108)$$

In this equation,

$$\tau = \frac{2(2\pi)^{1/4} N_\delta}{\sqrt{5}\phi} \quad (3.109)$$

with  $\phi = p/p_r$  ( $p_r$  = reference pressure),  $\zeta = y/D$ ,  $\xi = x/L$ ,  $\varepsilon = D/L$ , and  $u_r = \sqrt{8k_B T_r / \pi m}$ . Also note that  $\partial \phi / \partial \xi < 0$ . Solving this differential equation subject to the stick boundary conditions  $u(\zeta) = 0$  at  $\zeta = \pm 1/2$  on the reduced velocity  $u$ , we obtain the formula for the velocity profile

$$u = u_m \frac{\left( \cosh \frac{\delta}{2} - \cosh \delta \zeta \right)}{\left( \cosh \frac{\delta}{2} - 1 \right)}, \quad (3.110)$$

where

$$u_m = \frac{1}{\tau \delta} \left( \cosh \frac{\delta}{2} - 1 \right) \quad (3.111)$$

with  $\delta$  defined by

$$\delta = \frac{2(2\pi)^{1/4} \varepsilon}{\sqrt{5}\phi} \left( -\frac{\partial \phi}{\partial \xi} \right). \quad (3.112)$$

Therefore it follows that

$$(\tau \delta)^{-1} = \frac{5\phi^2}{4(2\pi)^{1/2} \varepsilon N_\delta \left( -\frac{\partial \phi}{\partial \xi} \right)}.$$

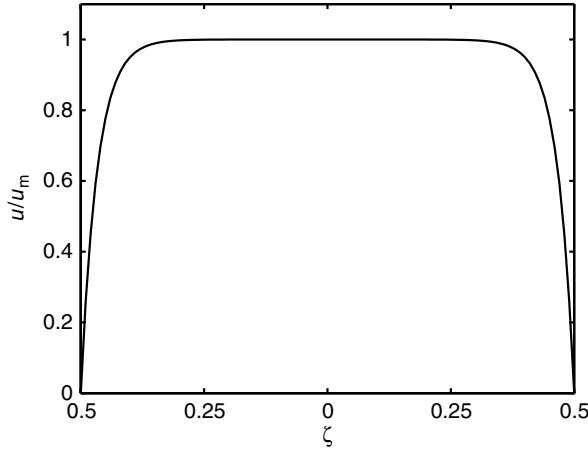
Note that  $u_m$  is the maximum velocity of flow in a channel and  $u$  reduces to a parabolic Poiseuille profile [26] as  $\delta$  becomes small

$$u = u_m (1 - 4\zeta^2). \quad (3.113)$$

In the rarefied gas limit, the velocity profile tends to be rectangular. For example, if  $\delta = 10$ , the reduced profile  $u/u_m$  has the form shown in Fig. 3.2. The tendency for the channel flow profile to become rectangular is therefore a manifestation of the non-Newtonian viscosity of the gas as it rarefies. In such a limit, the gas flow becomes ballistic, and a beam is formed.

### 3.5.3 Non-Poiseuille Flow in a Tube

The rectangular channel flow considered in the previous subsection is an idealization of channel flows in the laboratory or natural conditions. A more



**Fig. 3.2.** Reduced velocity profile for the flow of a dilute gas in a rectangular channel when  $\delta = 10$ . As  $\delta$  decreases, the flow profile tends to the Poiseuille profile of a Newtonian fluid

realistic flow configuration is achieved if tube flow is examined. Such a flow configuration was carefully studied by Knudsen [27] for rarefied gases. We consider a thin tube aligned along the  $z$  axis in the laboratory coordinate system in which a rarefied gas flows laminarly. The radius of the tube is assumed to be  $R$ , and its length is  $L$ , which is sufficiently long, so that the aspect ratio  $R/L$  is very small. The gas is subject to a pressure difference between the inlet and the outlet. In the approximation in which  $L$  may be regarded as being infinitely long, the flow variables do not depend on  $z$  or on the angle  $\theta$  of the cylindrical coordinates. Furthermore, if it is assumed that the normal stress differences are absent to an approximation, it is easy to find

$$r\rho u_r = \text{constant}, \quad (3.114)$$

where  $u_r$  is the radial velocity component. Since  $u_r = 0$  at the boundary—the tube wall—and the density  $\rho \neq 0$  everywhere, it follows that  $u_r = 0$ . The angular velocity component is also absent, so it follows that there exists only the  $z$  component  $u_z$  of velocity  $\mathbf{u}$  that is nonvanishing. The momentum balance equation is then decomposed into two equations

$$\begin{aligned} \frac{\partial p}{\partial r} &= 0, \\ -\frac{\partial p}{\partial z} - \frac{1}{r} \frac{\partial}{\partial r} r\Pi &= 0, \end{aligned} \quad (3.115)$$

where  $p$  is the pressure and  $\Pi = \Pi_{rz} = \Pi_{zr}$  is the  $rz$  or  $zr$  component of the stress tensor that is symmetrical. These momentum balance equations must

be supplemented by the constitutive equation for  $\Pi$

$$\Pi = -\eta \frac{\partial u_z}{\partial r}, \quad (3.116)$$

where  $\eta$  is the non-Newtonian viscosity, (3.87), in the cylindrical coordinate system used for the description of the flow in hand. Since the solution of these equations subject to the stick boundary condition  $u_z(r) = 0$  at  $r = R$  is well described in the literature [10, 20, 21, 28, 29], we present only the result. The flow velocity  $u_z(r)$  is given by

$$u_z(r) = \frac{R}{\tau\delta} \left[ \cosh \delta - \cosh \left( \frac{r\delta}{R} \right) \right], \quad (3.117)$$

where

$$\begin{aligned} \tau &= \left[ 2\eta_0 (mk_B T/2)^{1/2} \right]^{1/2} \left( \sqrt{2} n k_B T \sigma \right)^{-1}, \\ \delta &= \frac{\tau R \Delta p}{2 L \eta_0}. \end{aligned} \quad (3.118)$$

In the limit of small  $\delta$ , this flow velocity formula reduces to the well-known parabolic Poiseuille formula [26]

$$u_z(r) = \frac{\Delta p}{4L\eta_0} (R^2 - r^2). \quad (3.119)$$

Deviation from this velocity profile by the formula (3.117) therefore is a manifestation of the non-Newtonian viscosity of the gas.

It is more instructive to see this effect if we calculate the volume flow rate defined in the tube flow configuration by

$$f = 2\pi n \int_0^R dr r u_z(r)$$

which is easily evaluated by substituting  $u_z(r)$  given in (3.117)

$$f = \frac{\pi R^4 \Delta p}{8L\eta_0 \mathcal{R}T} (1 + \Delta f) p \quad (3.120)$$

where

$$\Delta f = 8\delta^{-2} \left[ \frac{1}{2} \cosh \delta + \delta^{-2} (\cosh \delta - 1) - \delta^{-1} \sinh \delta \right] - 1. \quad (3.121)$$

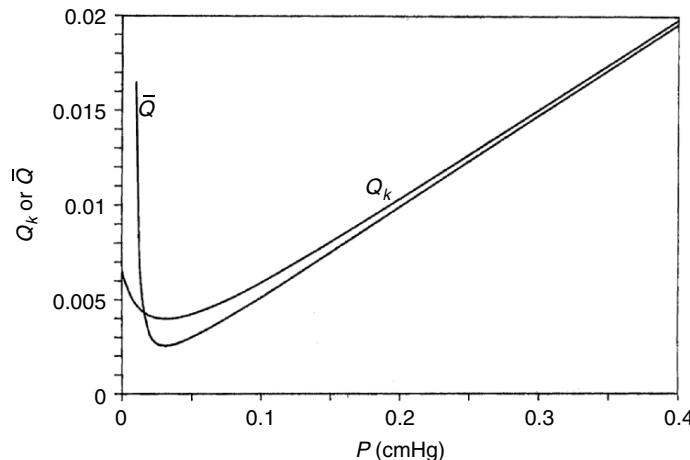
For the flow profile given in (3.119), the Hagen–Poiseuille volume flow rate [26] is obtained

$$f_{hp} = \frac{\pi R^4 \Delta p}{8L\eta_0 \mathcal{R}T} p. \quad (3.122)$$

Therefore  $\Delta f$  represents deviation from the Hagen–Poiseuille flow rate for a Newtonian gas. If the non-Newtonian gas flow rate  $f$  in (3.120) is plotted against pressure, a minimum appears in the low-pressure regime, the appearance of which is known as the Knudsen phenomenon —originally called the Knudsen paradox; see Fig. 3.3. The Knudsen phenomenon is a manifestation of the non-Newtonian viscosity of a gas in the rarefied density regime. The Ostwald viscometry is based on the measurement of  $f_{hp}$ . The formula for  $f$  can be employed for measuring non-Newtonian viscosity [28].

### 3.5.4 Shock Wave Width in Dilute Gases

Study of shock wave structures is important for practical engineering in aerodynamics and gas dynamics and also for developing the hydrodynamic theory of flows in general. The ability of a hydrodynamic theory to understand shock wave structures correctly can serve as a touchstone for testing the truthfulness of the hydrodynamic theory. From the standpoint of nonlinear transport processes, the study of shock structures in gases provides an indirect test of whether or not the nonlinear transport coefficients or the corresponding constitutive equations for the stress tensor, heat flux, and diffusion fluxes employed are useful. Studies of shock wave structures in the literature [6, 8–10] used the constitutive equations for the stress tensor and heat flux that give rise to the non-Newtonian and non-Fourier transport coefficients presented in



**Fig. 3.3.** Flow rate vs. pressure for a rarefied gas flow through a long thin tube.  $Q_k$  is the flow rate experimentally observed by Knudsen and  $\bar{Q} = f$  is the generalized hydrodynamics prediction. [Reproduced with permission from Byung Chan Eu, Phys. Rev. A **40**, 6395 (1989). Copyright 1989 American Physical Society.]

(3.84) and (3.85) for a single-component gas. Because the process of calculating shock wave structures is lengthy, we will describe the procedure and then present the most relevant result, the shock wave width as a function of Mach number, which is generally used as a gauge of the reliability of a hydrodynamic theory for shock waves. In the context of transport coefficients, it tests the correctness of the nonlinear transport coefficients employed.

For steady one-dimensional shock waves in monatomic gases, the steady-state balance equations for mass, momentum, and energy are employed. If the wave is taken in the direction of the  $x$  coordinate with velocity  $u$ , the steady mass, momentum, and energy balance equations are

$$\frac{d}{dx} \rho u = 0, \quad (3.123)$$

$$\frac{d}{dx} (\rho u^2 + p + \Pi_{xx}) = 0, \quad (3.124)$$

$$\frac{d}{dx} \left[ \rho u \left( \mathcal{E} + \frac{1}{2} u^2 \right) + u (p + \Pi_{xx}) + Q_x \right] = 0, \quad (3.125)$$

where  $\Pi_{xx}$  and  $Q_x$  are the  $xx$  component of the stress tensor and the  $x$  component of the heat flux, respectively, and  $\mathcal{E}$  is the internal energy density. These balance equations are supplemented by constitutive equations for  $\Pi_{xx}$  and  $Q_x$ , which we assume are non-Newtonian and non-Fourier:

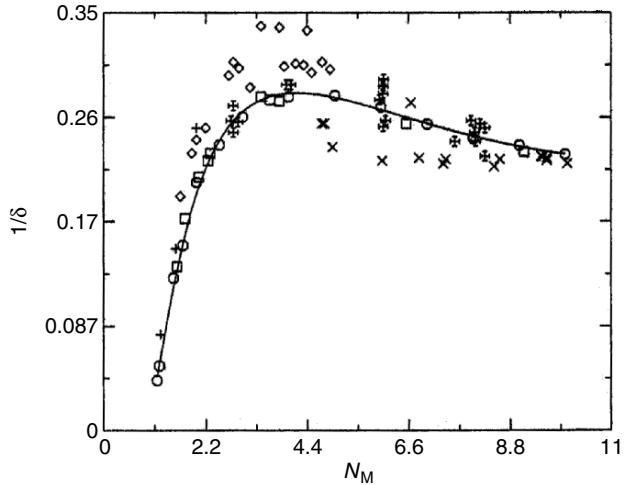
$$\frac{p}{\eta_0} \Pi_{xx} q(\kappa) = -\frac{4}{3} \Pi_{xx} - \frac{4}{3} p \frac{\partial u}{\partial x}, \quad (3.126)$$

$$\frac{\hat{h}p}{\lambda_0} Q_x q(\kappa) = -Q_x \frac{\partial u}{\partial x} - \Pi_{xx} u \frac{\partial u}{\partial x} - \hat{h} (p + \Pi_{xx}) \frac{\partial}{\partial x} \ln T, \quad (3.127)$$

where  $\hat{h}$  is the enthalpy per mass per molecule and other symbols have already been defined. Equations (3.126) and (3.127) are the one-dimensional versions of the steady-state constitutive equations for stress tensor  $\Pi$  and heat flux  $\mathbf{Q}$  in the adiabatic approximation [6, 10]. The set of equations (3.123)–(3.127) therefore is the steady-state one-dimensional version of the generalized hydrodynamic equations in the adiabatic approximation. These equations can be reduced to a pair of ordinary nonlinear differential equations for velocity and temperature [6, 8–10]. It can be shown that the shock solutions exist for the differential equations. The pair of differential equations can be solved numerically and flow profiles can be calculated from the solutions. If the upstream and downstream densities are denoted by  $n_1$  and  $n_2$ , respectively, the shock wave width  $\delta$  may be defined by

$$\delta = (n_2 - n_1) \left( \frac{dn}{d\zeta} \right)_{\max}^{-1} \quad (3.128)$$

where  $\zeta = \sqrt{6/5\pi}x / (lN_M)$  with  $l$  denoting the mean free path defined by  $l = (\eta_0/\rho u)_{\text{upstream}} = \eta_{01}/\rho_1 u_1$ . The maximum of  $dn/d\zeta$  occurs at the shock



**Fig. 3.4.** Inverse shock width vs. Mach number for argon (a variable hard sphere model with  $s = 0.75$ ). The experimental data are from [31–33]. [Reproduced with permission from Mazen Al-Ghoul and Byung Chan Eu, Phys. Rev. E **56**, 2981 (1997). Copyright 1997 American Physical Society.]

transition point. The inverse shock wave width has been measured in experiments by various authors. In Fig. 3.4, the theoretical prediction by the generalized hydrodynamic equations (3.123)–(3.127) is compared with experimental values. The symbols in Fig. 3.4 are experimental data and the *solid curve* is the theoretical prediction. The Navier–Stokes hydrodynamic equations have been applied to calculate shock structures in the literature, but they have been unsuccessful in correctly predicting the shock structures; most importantly, the inverse shock wave width predicted by the Navier–Stokes equation has been much too large, usually, by over a factor of 2, compared with the experimental value. The comparison in Fig. 3.4 indicates that the non-Newtonian and non-Fourier constitutive equations, namely, the generalized hydrodynamic equations, are correct for the constitutive equations for the stress tensor and heat flux of the gas studied. We can conclude that the successful comparison is another indicator of the correctness of the non-Newtonian viscosity and non-Fourier heat conductivity discussed in this subsection.

There are more examples of the effects of nonlinear transport coefficients, but we will not discuss them in this work for lack of space. We refer the reader to the literature [17–19, 30].

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## Boltzmann Equation for Dilute Polyatomic Gases

In the kinetic theory of polyatomic gases, internal degrees of freedom must be taken into account to describe the internal motions, such as rotational and vibrational motions, of the molecules in collision. For the desired aim, for example, the Boltzmann equation must be suitably generalized by including the internal degrees of freedom in the description. Internal degrees of freedom generally require a quantum mechanical description, but, if the conditions are appropriate, it is possible to treat them classically. For example, if the temperature is not so low as to warrant a quantum mechanical description, a classical theory is permissible except for vibrational degrees of freedom.

In practice, it is sufficient in many cases to blend a classical treatment of translational degrees of freedom with a quantum mechanical treatment of the internal degrees of freedom. Such a semiclassical generalization of the Boltzmann kinetic equation has been achieved by Waldmann [1] and Snider [2]. They derived a kinetic equation, now called the Waldmann–Snider (WS) kinetic equation [3], in which the translational distribution function is described by a phase space distribution function, whereas the distribution of internal states is given by the density matrices . When a complete classical treatment is permitted, it is possible to make the generalization fully classical by postulating a Boltzmann equation for polyatomic gases. In both cases, the kinetic theory of molecular gases at the formal theory level can be developed in a parallel manner because the kinetic equations in the two approaches have the same formal structure except for the details, most importantly, of the collision terms; the kinematic streaming terms of the kinetic equations are only slightly different because in the classical formalism, the internal motions are described with the classical Liouville operator, whereas in the quantum treatment, the quantum mechanical Liouville operator is used in place of the classical Liouville operator. For this reason and because the classical kinetic equations are sufficient for the topic discussed in this work, we will formulate the theory with a classical Boltzmann equation for nonsimple gases. There is a formal parallelism in the WS kinetic equation and the classical Boltzmann equation for polyatomic gases, as pointed out earlier, so the generalized hydrodynamics

equations obtained with the classical kinetic equation can be readily translated into the forms appropriate in the WS kinetic equation approach if the classical collision operator is replaced by the Waldmann–Snider collision operator. In this chapter, we will limit our discussion to the Boltzmann–Curtiss equation [4] after presenting the classical Boltzmann equation for polyatomic gases and the H theorem. The kinetic theory of polyatomic gases remains to be studied further in depth.

## 4.1 Kinetic Equation for Polyatomic Gases

Before presenting the kinetic equation for polyatomic gases, it is necessary to define some symbols and abbreviations for the set of position and momentum variables. The position and momentum variables of the polyatomic molecule consisting  $(c+1)$  atoms will be denoted, respectively, by  $\{\mathbf{R}, \mathbf{r}_l : l = 1, \dots, c\}$  and  $\{\mathbf{P}, \mathbf{p}_l : l = 1, \dots, c\}$ , where  $\mathbf{R}$  and  $\mathbf{P}$  are the center-of-mass position and momentum vectors, respectively, and  $\mathbf{r}_l$  and  $\mathbf{p}_l$  the coordinates and momenta of internal degrees of freedom, respectively. The center of mass and internal phases will be abbreviated, respectively, by  $X = (\mathbf{R}, \mathbf{P})$  and  $x(\mathbf{r}_l, \mathbf{p}_l : l = 1, \dots, c)$ . The combined phase of internal degrees of freedom for two particles will be abbreviated by  $x^{(2)} = (x_1, x_2)$  in which the subscripts refer to the molecules involved. It will be convenient to further abbreviate the phases in the following discussion, so we will also define the symbols

$$\xi = (\mathbf{P}, x) = (\mathbf{P}, \mathbf{r}_l, \mathbf{p}_l : l = 1, \dots, c),$$

so that the full phase of a molecule is denoted by

$$(X, x) = (\mathbf{R}, \xi),$$

that is,  $\xi$  stands for the dynamic variables of a molecule that include the center of mass momentum and the phase (i.e., coordinates and momenta) of internal motions of the molecule. The subscript 1 or 2 to  $\xi$  will refer to the molecule involved.

The Poisson brackets for internal degrees of freedom of a molecule, multiplied by  $-i = -\sqrt{-1}$ , will be denoted by

$$\mathcal{L} = -i[H_I]_{PB} = -i \sum_l \left( \frac{\partial H_I}{\partial p_l} \frac{\partial}{\partial r_l} - \frac{\partial H_I}{\partial r_l} \frac{\partial}{\partial p_l} \right), \quad (4.1)$$

where  $H_I$  denotes the classical Hamiltonian for the internal degrees of freedom. The operator  $\mathcal{L}$ , called the Liouville operator for the internal degrees of freedom, is the classical limit of its quantum analog, the Liouville–von Neumann operator.

The dilute gas of interest in this chapter will be described by the singlet distribution function  $f(X, x, t)$ , which is assumed to obey the classical Boltzmann equation

$$\left( \frac{\partial}{\partial t} + \frac{\mathbf{P}}{m} \cdot \nabla + m \mathbf{F} \cdot \nabla_{\mathbf{P}} + i\mathcal{L} \right) f(\mathbf{R}, \boldsymbol{\xi}, t) = \mathfrak{R}[f]. \quad (4.2)$$

In this Boltzmann equation for polyatomic gases,  $\mathfrak{R}[f]$  is the collision integral defined by [5]

$$\begin{aligned} \mathfrak{R}[f] = & \int d\boldsymbol{\xi}_2 \int d\boldsymbol{\xi}^{(2)*} \left[ W\left(\boldsymbol{\xi}^{(2)*}|\boldsymbol{\xi}^{(2)}\right) f^*(\mathbf{R}, \boldsymbol{\xi}_1^*, t) f^*(\mathbf{R}, \boldsymbol{\xi}_2^*, t) \right. \\ & \left. - W\left(\boldsymbol{\xi}^{(2)}|\boldsymbol{\xi}^{(2)*}\right) f(\mathbf{R}, \boldsymbol{\xi}_1, t) f(\mathbf{R}, \boldsymbol{\xi}_2, t) \right], \end{aligned} \quad (4.3)$$

where the asterisked quantities are postcollision variables and distribution functions

$$\boldsymbol{\xi}^{(2)} = (\boldsymbol{\xi}_1, \boldsymbol{\xi}_2),$$

and  $W\left(\boldsymbol{\xi}^{(2)}|\boldsymbol{\xi}^{(2)*}\right)$  is the transition probability of finding the final state  $\boldsymbol{\xi}^{(2)*}$  in the range  $\boldsymbol{\xi}^{(2)*} \sim \boldsymbol{\xi}^{(2)*} + d\boldsymbol{\xi}^{(2)*}$  at the end of the collision process, which transforms  $\boldsymbol{\xi}^{(2)}$  to  $\boldsymbol{\xi}^{(2)*}$ . In this mode of notation,  $W\left(\boldsymbol{\xi}^{(2)*}|\boldsymbol{\xi}^{(2)}\right)$  then is the transition probability of the reversed collision event.

It is important to keep in mind that the transition probability  $W$  includes the Dirac delta functions ensuring the conservation of energy and momentum in the course of collision. Note that the distribution functions for polyatomic gases remain uniform within the collision volume in the configuration space of the center of mass of the molecule, and this is the reason that the same  $\mathbf{R}$  is taken for both molecules 1 and 2 in the distribution functions in the collision integral  $\mathfrak{R}[f]$ . The kinetic equation is coarse-grained in space in the aforementioned sense.

When summed (integrated) over all final states, the transition probability then gives the total cross section  $\sigma_t$  multiplied by the flux of the collision process  $\boldsymbol{\xi}^{(2)} \rightarrow \boldsymbol{\xi}^{(2)*}$ :<sup>1</sup>

$$\int d\boldsymbol{\xi}^{(2)*} W\left(\boldsymbol{\xi}^{(2)}|\boldsymbol{\xi}^{(2)*}\right) = |\boldsymbol{\xi}_1 - \boldsymbol{\xi}_2| \sigma_t. \quad (4.4)$$

This total cross-section is invariant to variable transformations—canonical transformations. For the scattering theory foundation for this relation, see Sec. A.2 of Appendix A.

The transition probability should be invariant to time-reversal transformation because the equations of motion are invariant to time reversal. Let us distinguish the time-reversed variables by an overbar. Therefore, there holds

---

<sup>1</sup> Cercignani and Lampis in [5] define the total cross section times flux as the integral of  $W(\boldsymbol{\xi}^{(2)*}|\boldsymbol{\xi}^{(2)})$  over  $\boldsymbol{\xi}^{(2)*}$  in the collision process  $\boldsymbol{\xi}^{(2)*} \rightarrow \boldsymbol{\xi}^{(2)}$ , which is the reverse of the process  $\boldsymbol{\xi}^{(2)} \rightarrow \boldsymbol{\xi}^{(2)*}$  corresponding to  $W(\boldsymbol{\xi}^{(2)}|\boldsymbol{\xi}^{(2)*})$ . If  $W(\boldsymbol{\xi}^{(2)*}|\boldsymbol{\xi}^{(2)})$  is the transition probability for the collision process  $\boldsymbol{\xi}^{(2)*} \rightarrow \boldsymbol{\xi}^{(2)}$  in which  $\boldsymbol{\xi}^{(2)*}$  is the initial state, then integrating over the phase  $\boldsymbol{\xi}^{(2)*}$ , the initial phase, is inappropriate. Integration should be over the final phase, namely,  $\boldsymbol{\xi}^{(2)}$  of the particular collision process under consideration.

the relation between the transition probability of process  $\xi^{(2)} \rightarrow \xi^{(2)*}$  and that of the time-reversed process  $\bar{\xi}^{(2)*} \rightarrow \bar{\xi}^{(2)}$

$$W(\xi^{(2)}|\xi^{(2)*}) = W(\bar{\xi}^{(2)*}|\bar{\xi}^{(2)}). \quad (4.5)$$

Integrate this equation over  $\xi^{(2)}$  to obtain

$$\int d\xi^{(2)} W(\xi^{(2)}|\xi^{(2)*}) = \int d\xi^{(2)} W(\bar{\xi}^{(2)*}|\bar{\xi}^{(2)}), \quad (4.6)$$

but because the phase volume remains invariant:

$$\int d\xi^{(2)} = \int d\bar{\xi}^{(2)},$$

the dummy integration variable  $\bar{\xi}^{(2)}$  can be renamed  $\xi^{(2)}$  and hence it follows that

$$\int d\xi^{(2)} W(\bar{\xi}^{(2)*}|\bar{\xi}^{(2)}) = \int d\xi^{(2)} W(\bar{\xi}^{(2)*}|\xi^{(2)}). \quad (4.7)$$

The right-hand side of this equation is proportional to the total cross section, which is invariant to transformation  $\bar{\xi}^{(2)*} \rightarrow \xi^{(2)*}$ . Therefore, from (4.6) and (4.7) follows the relation

$$\int d\xi^{(2)} W(\xi^{(2)}|\xi^{(2)*}) = \int d\xi^{(2)} W(\xi^{(2)*}|\xi^{(2)}). \quad (4.8)$$

This relation is necessary to prove the H theorem for the kinetic equation (4.2) for polyatomic gases and deriving macroscopic evolution equations consistent with the laws of thermodynamics.

If the classical Liouville operator on the left side of the kinetic equation (4.2) is replaced by the quantum mechanical Liouville operator for the internal motion of the molecule

$$\mathcal{L}_q = -\hbar^{-1} [\mathcal{H}_I,], \quad (4.9)$$

where  $\mathcal{H}_I$  is the Hamiltonian operator for the internal degrees of freedom of the molecule and  $[\mathbf{A}, \mathbf{B}]$  is the commutator of operators  $\mathbf{A}$  and  $\mathbf{B}$ . If the collision integral  $\mathfrak{R}[f]$  is replaced by the WS collision integral, then (4.2) becomes the WS kinetic equation for diatomic gases, provided that the polyatomic molecule is assumed to be diatomic. The abstract operator form for the WS collision operator is given by [6]

$$T\rho_1\rho_2 \equiv \text{Tr}_2 [T\rho_1\rho_2 - \rho_1\rho_2 T^\dagger + 2\pi i T\rho_1\rho_2 \delta(\mathcal{K}) T^\dagger] \quad (4.10)$$

where  $\rho_i$  are the density matrix for molecule  $i$  ( $i = 1, 2$ ),  $T$  is the transition matrix which obeys the quantum mechanical Lippmann–Schwinger equation [7],  $\mathcal{K}$  is the free superoperator<sup>2</sup>—free quantum mechanical Liouville operator,

---

<sup>2</sup> In the notation of Appendix A, the superoperator  $\mathcal{K}$  can be written in terms of tetradic Hamiltonian operators as follows:

and the subscripted trace operator  $\text{Tr}_2$  means taking a trace over the Hilbert space of molecule 2; see Sect. A.2 of Appendix A for the scattering theory derivation of (4.10). When the Wigner transform [8] is taken to put the translational part of the density matrix into the Wigner distribution function, the abstract form of the collision operator (4.10) yields the WS collision operator in the WS kinetic equation [6]

$$T\rho_1\rho_2 \Rightarrow \mathfrak{R}_{\text{WS}}[f].$$

For details of the derivation, refer to the original literature. The point we emphasize here is that if  $\mathfrak{R}_{\text{WS}}[f]$  replaces  $\mathfrak{R}[f]$  and  $\mathcal{L}_q$  is used on the left side of (4.2), the WS kinetic equation is obtained. Thus the kinetic theory couched in (4.2) can be readily translated into the kinetic theory based on the WS kinetic equation.

We also note that, if a rigid rotator is assumed for the polyatomic molecule and the coordinate variables are appropriately chosen, the kinetic equation (4.2) becomes the kinetic equation derived by Curtiss [4], which will be used later, when transport coefficients of rigid diatomic fluids are considered.

## 4.2 The H Theorem

The kinetic equation for polyatomic gases (4.2) satisfies the H theorem, and this implies that it is possible to construct a thermodynamic theory of irreversible processes in polyatomic gases in a manner parallel to the thermodynamic theory for simple gases discussed in the previous chapter.

Define the Boltzmann entropy density for the polyatomic gas

$$\rho\mathcal{S} = -k_B \int d\xi (\ln f - 1) f. \quad (4.11)$$

We can then show

$$-\int d\xi (\ln f - 1) \mathfrak{R}[f] \geq 0. \quad (4.12)$$

Note here that

$$\int d\xi \mathfrak{R}[f] = 0. \quad (4.13)$$

Differentiating (4.11) with  $t$  and using the kinetic equation, we obtain the Boltzmann entropy balance equation for polyatomic gases,

$$\frac{\partial}{\partial t} \rho\mathcal{S} = -\nabla \cdot (\mathbf{J}_S + \rho\mathcal{S}\mathbf{u}) + \sigma_{\text{ent}}, \quad (4.14)$$

---


$$\mathcal{K} = \mathcal{H}_0 - \mathcal{H}_0^*,$$

where  $\mathcal{H}_0 = \mathbf{H}_0 \otimes \mathbf{I}$  with  $\mathbf{H}_0$  denoting the free Hamiltonian operator—dyadic—in the Hilbert space and  $\mathbf{I}$  is the unit (dyadic) diagonal operator.

where  $\rho$  and  $\mathbf{u}$  denote the mass density and the mean velocity, respectively, defined by

$$\rho = \int d\boldsymbol{\xi} m f(\mathbf{R}, \boldsymbol{\xi}, t), \quad (4.15)$$

$$\rho \mathbf{u} = \int d\boldsymbol{\xi} \frac{\mathbf{P}}{m} f(\mathbf{R}, \boldsymbol{\xi}, t), \quad (4.16)$$

whereas

$$\mathbf{J}_S = -k_B \int d\boldsymbol{\xi} \left( \frac{\mathbf{P}}{m} - \mathbf{u} \right) (\ln f - 1) f(\mathbf{R}, \boldsymbol{\xi}, t), \quad (4.17)$$

$$\sigma_{\text{ent}} = -k_B \int d\boldsymbol{\xi} \ln f(\mathbf{R}, \boldsymbol{\xi}, t) \Re[f]. \quad (4.18)$$

Here,  $\mathbf{J}_S$  is the statistical mechanics formula for the Boltzmann entropy flux, and the H theorem is about the positivity of Boltzmann entropy production  $\sigma_{\text{ent}}$ . By using the relation (4.8), it is easy to show that

$$\begin{aligned} \sigma_{\text{ent}} &= \frac{1}{4} k_B \int d\boldsymbol{\xi}^{(2)} \int d\boldsymbol{\xi}^{(2)*} W\left(\boldsymbol{\xi}^{(2)} | \boldsymbol{\xi}^{(2)*}\right) \ln \left( \frac{f_1^* f_2^*}{f_1 f_2} \right) (f_1^* f_2^* - f_1 f_2) \\ &\geq 0. \end{aligned} \quad (4.19)$$

The equality holds at equilibrium, reached as  $t \rightarrow \infty$ . The subscripts 1 and 2 on the distribution functions refer to molecules 1 and 2. The equality holds if and only if

$$f_1^{\text{eq}*} f_2^{\text{eq}*} = f_1^{\text{eq}} f_2^{\text{eq}}, \quad (4.20)$$

which holds at equilibrium reached as  $t \rightarrow \infty$ . The superscript eq on the distribution functions in (4.20) refers to equilibrium.

One important consequence of the H theorem is that by virtue of the equilibrium condition (4.20), the equilibrium solution for the kinetic equation (4.2) can be uniquely determined. The argument for the uniqueness of the equilibrium distribution function proceeds similarly to that for monatomic dilute gases described on the basis of the Boltzmann equation, which was presented in Chap. 2. Therefore we may simply present only the result. When normalized to density in the center-of-mass velocity space, the local equilibrium distribution function satisfying (4.20) and the conservation laws of mass, momentum, and energy are given by

$$f_i^{\text{eq}}(\mathbf{r}, \mathbf{p}_i) = \frac{n_i}{q_i^c} \left( \frac{m_i \beta}{2\pi} \right)^{3/2} \exp \left( -\frac{3}{2} \beta m_i C_i^2 \right) \exp(-\beta H_1), \quad (4.21)$$

where  $\beta = 1/k_B T$  and  $q_i^c$  is the classical internal molecular partition function

$$q_i^c = \int dx \exp(-\beta H_1). \quad (4.22)$$

If the WS kinetic equation is used, then the classical partition function  $q_i^c$  should be replaced by the quantum mechanical version.

Equation (4.14) is the Boltzmann entropy balance equation for polyatomic gases, which can be the starting point of a thermodynamic theory of irreversible processes in polyatomic gases. Such a theory can be formulated in a manner parallel to that of simple fluids described in [9] to which the interested reader is referred. The statistical mechanical definitions of  $\mathcal{S}$ ,  $\mathbf{J}_S$ , and  $\sigma_{\text{ent}}$  are formally identical with the monatomic gas versions except for the internal degrees of freedom implicit, so it is expected that the theory of irreversible thermodynamics should also be formally parallel to that for monatomic gases. In this connection, we note that the theory of irreversible processes consistent with the laws of thermodynamics is formulated in terms of calortropy, calortropy flux, and calortropy production instead of  $\mathcal{S}$ ,  $\mathbf{J}_S$ , and  $\sigma_{\text{ent}}$ ; see [9] on this subject.

### 4.3 Generalized Hydrodynamic Equations

The kinetic equation (4.2) can be employed to derive the evolution equations for macroscopic variables for polyatomic gases in general, which can also be made consistent with the laws of thermodynamics. The procedure is completely parallel to that employed for simple fluids based on the Boltzmann equation for simple gases [9]. Since such a theory of irreversible thermodynamics is not the aim in this work nor is the kinetic theory of general polyatomic gases going to be studied in comparison with experiment, the theory will be couched in a special case of polyatomic gases, namely, rigid linear diatomic molecular gases. It is the simplest example of nonsimple fluids, which allows us to explain the important basic differences between transport processes in simple and polyatomic gases. It also will provide the generalized hydrodynamic equations for hydrodynamic variables, namely, macroscopic variables, which are required to obtain transport coefficients of rigid diatomic gases that we are going to use in Chaps. 11 and 12. Therefore, we will describe their derivation with a particular form of the kinetic equation (4.2)—the Boltzmann–Curtiss equation—for such gases and show how the transport coefficients can be extracted from the generalized hydrodynamic equations derived.

The Boltzmann–Curtiss equation for rigid diatomic gases [4] can be expressed in terms of Euler angles  $\alpha$ ,  $\beta$ , and  $\gamma$  that specify the orientation of the rigid molecule. We choose  $\alpha$  and  $\beta$  as the polar angles of the angular momentum  $\mathbf{j}$  of the molecule, namely,  $\alpha = \theta$  and  $\beta = \phi$ . Then  $\gamma$  is the azimuth specifying the orientation of the molecule in the plane perpendicular to the  $\mathbf{j}$  vector. The unit vector of the body axis is denoted by  $\hat{\mathbf{R}}$ , whose polar angles will be denoted by  $\vartheta$  and  $\varphi$ . Therefore,

$$\hat{\mathbf{R}} = (\sin \vartheta \cos \varphi, \sin \vartheta \sin \varphi, \cos \vartheta).$$

The center-of-mass position vector will be denoted by  $\mathbf{r}$  and its conjugate momentum by  $\mathbf{p}$ . Therefore in the notation of kinetic equation (4.2), we have the correspondence  $(\mathbf{R}, \mathbf{P}) \Rightarrow (\mathbf{r}, \mathbf{p})$ . This notation puts the kinetic equation into a more readily recognizable form vis à vis the Boltzmann equation for simple gases. In this notation, the distribution function  $f$  is a function of variables  $(\mathbf{p}, \mathbf{r}, \mathbf{j}, \mathbf{c}, t)$ , and the kinetic equation (4.2) becomes the Boltzmann–Curtiss equation with the identification of the internal Liouville operator in the form

$$\mathcal{L} = -i[H_I]_{PB} = \frac{j}{I} \frac{\partial}{\partial \mathbf{c}} + (\boldsymbol{\omega}_B \times \mathbf{j}) \cdot \frac{\partial}{\partial \mathbf{j}} \quad (4.23)$$

and the collision integral with the expression

$$\begin{aligned} \mathfrak{R}[f] &= \iiint d\mathbf{p}_2 d\Omega_2 d\mathbf{p}_r^* d\Omega_2^* d\Omega^* \frac{p_r}{\mu_r} \\ &\quad \times \sigma(p_r^*, j^*, j_2^* | p_r, j, j_2) (f^* f_2^* - f f_2) \\ &\equiv \mathfrak{R}_{BC}[f], \end{aligned} \quad (4.24)$$

where

$$d\Omega = jdjdc \sin \theta d\theta d\phi,$$

$\mathbf{p}_r = \mathbf{p} - \mathbf{p}_2$ , and  $\mu_r$  is the reduced mass. The subscript 2 refers to the second molecule. For the rigid linear molecular gas considered in the following, the kinetic equation (4.2) is understood with the aforementioned meanings for the collision integral term and the internal Liouville operator with the meanings of coordinates mentioned earlier. We also identify  $\xi$  with  $(\mathbf{p}, \mathbf{j}, \mathbf{c})$  for the abbreviation of variables indicated.

With this preparation, the procedure for deriving generalized hydrodynamic equations for a molecular gas is completely parallel to that of simple dilute gases. Therefore, we will be as brief as possible but emphasize the points of difference from the simple fluid theory. For the aim we have in mind, we first observe that the collision integral  $\mathfrak{R}[f]$  given in (4.24) has the same collision invariants as those for the collision integral in (4.3). The collision invariants are the mass, momentum,<sup>3</sup> and energy of a molecule, which will be collectively denoted by  $\psi = (m, \mathbf{P}, E_{kin} + E_{rot})$ , where  $E_{kin}$  and  $E_{rot}$  are the center-of-mass energy and the rotational energy of a molecule, respectively. For such collisional invariants,

$$\int d\xi \psi \mathfrak{R}[f] = 0. \quad (4.25)$$

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<sup>3</sup> By the momentum in this connection is meant the center-of-mass momentum. The center-of-mass momentum, however, is not in general a collision invariant in collision processes of polyatomic molecules if there is a transfer of the center-of-mass momentum to the internal degrees of freedom of the molecule, that is, if the collision is inelastic. Inelastic collisions giving rise to a portion of the center-of-mass momentum transferred to internal degrees of freedom are excluded in the formulation here.

### 4.3.1 Conservation Equations

With the identity (4.25), the kinetic equation (4.2) gives rise to the equation of continuity, the momentum balance equation, and the energy balance equation

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \rho \mathbf{u}, \quad (4.26)$$

$$\frac{\partial \rho \mathbf{u}}{\partial t} = -\nabla \cdot (\mathbf{P} + \rho \mathbf{u} \mathbf{u}), \quad (4.27)$$

$$\frac{\partial \rho \mathcal{E}}{\partial t} = -\nabla \cdot (\mathbf{Q} + \rho \mathcal{E} \mathbf{u}) - \mathbf{P} : \nabla \mathbf{u}, \quad (4.28)$$

where various macroscopic variables are defined as follows:

$$\rho \mathcal{E}(\mathbf{r}, t) = \int d\xi \left( \frac{1}{2} m C^2 + H_I \right) f(\mathbf{r}, \xi, t), \quad (4.29)$$

$$\mathbf{P}(\mathbf{r}, t) = \int d\xi m \mathbf{C} \mathbf{C} f(\mathbf{r}, \xi, t), \quad (4.30)$$

$$\mathbf{Q}(\mathbf{r}, t) = \int d\xi \left( \frac{1}{2} m C^2 + H_I \right) \mathbf{C} f(\mathbf{r}, \xi, t). \quad (4.31)$$

In these expressions,  $\mathcal{E}$  is the internal energy density, which includes the contribution from the internal degrees of freedom;  $\mathbf{P}$  is the pressure (stress) tensor; and  $\mathbf{Q}$  is the energy flow, namely, the heat flux. It should be emphasized that the balance equations are for a single-component gas free of external fields. In addition to the balance equation for the energy density  $\mathcal{E}$ , it is useful to consider the evolution equation for the internal energy of the molecule. For this purpose, we first define the mean angular momentum and its deviation from the mean. If the molecule is rigid and has an angular momentum  $\mathbf{j}$ , the mean angular momentum  $\mathfrak{J}$  can be defined by

$$\mathfrak{J} = \int d\xi \mathbf{j} f(\mathbf{R}, \xi, t). \quad (4.32)$$

The deviation of  $\mathbf{j}$  from the mean is then denoted by

$$\mathbf{J} = \mathbf{j} - \mathfrak{J}. \quad (4.33)$$

The total angular momentum of the fluid is equal to the sum of the orbital and molecular angular momenta,

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} + \mathbf{j}. \quad (4.34)$$

Its mean value will be denoted by

$$\rho \mathfrak{L}(\mathbf{r}, t) = \int d\xi \mathbf{L} f(\mathbf{r}, \xi, t). \quad (4.35)$$

The mean rotational energy density is defined by

$$\rho \mathcal{E}_{\text{rot}}(\mathbf{r}, t) = \int d\boldsymbol{\xi} H_{\text{rot}} f(\mathbf{r}, \boldsymbol{\xi}, t), \quad (4.36)$$

where the rotational Hamiltonian  $H_{\text{rot}}$  is given by

$$H_{\text{rot}} = \frac{\mathbf{J} \cdot \mathbf{J}}{2I} \quad (4.37)$$

with  $I$  denoting the moment of inertia.

The evolution equations for  $\mathcal{E}_{\text{int}}$  and  $\mathfrak{J}$  can be readily derived by employing their definitions and the Boltzmann–Curtiss equation. They are, respectively, given by

$$\frac{\partial}{\partial t} \rho \mathcal{E}_{\text{rot}} = -\nabla \cdot (\mathbf{Q}_r + \mathbf{u} \rho \mathcal{E}_{\text{rot}}) + A_{\text{rot}}, \quad (4.38)$$

$$\frac{\partial}{\partial t} \rho \mathfrak{L} = -\nabla \cdot \mathbf{M}_L, \quad (4.39)$$

where

$$\mathbf{Q}_r = \int d\boldsymbol{\xi} \mathbf{C} (H_{\text{rot}} - m \mathcal{E}_{\text{rot}}) f(\mathbf{r}, \boldsymbol{\xi}, t), \quad (4.40)$$

$$\mathbf{M}_L = \int d\boldsymbol{\xi} \mathbf{C} \mathbf{L} f(\mathbf{r}, \boldsymbol{\xi}, t), \quad (4.41)$$

$$A_{\text{rot}} = \int d\boldsymbol{\xi} H_{\text{rot}} \mathfrak{R}_{\text{BC}}[f]. \quad (4.42)$$

The source term in the balance equation for  $\mathcal{E}_{\text{rot}}$  appears because  $H_{\text{rot}}$  is not a collisional invariant. The balance equations (4.38) and (4.39) are absent for simple fluids.

### 4.3.2 Evolution Equations for Nonconserved Variables

Nonconserved variables, such as the stress tensor and heat flux, appear in the conservation laws—the balance equations—presented earlier, so it is necessary to derive the evolution equations for nonconserved variables. To derive them, first we define molecular moments, which are arranged in the following manner:

$$\begin{aligned} h^{(1)} &= m [\mathbf{CC}]^{(2)}, & h^{(2)} &= \frac{1}{3} m C^2 - p/n, \\ h^{(3)} &= \left[ \frac{1}{2} m C^2 + H_{\text{rot}} - m \hat{h} \right] \mathbf{C}, & h^{(4)} &= [\mathbf{JJ}]^{(2)}, \quad \text{etc.,} \end{aligned} \quad (4.43)$$

where  $p$  is the hydrostatic pressure,  $\hat{h}$  is the enthalpy per mass, and  $n$  is the number density. For the dilute gas of interest here, the equation of state is given by

$$p = n k_B T,$$

and the enthalpy per mass by

$$\hat{h} = \frac{5k_B T}{2m} + \frac{\mathcal{E}_{\text{rot}}}{m}.$$

Mean values of the moments  $h^{(i)}$  defined are then given by the formula

$$\bar{\Phi}_i = \int d\xi h^{(i)} f(\mathbf{r}, \xi, t), \quad (4.44)$$

which are identified with the traceless part of the stress tensor and so on

$$\boldsymbol{\Pi} = \bar{\Phi}_1, \quad \Delta = \bar{\Phi}_2, \quad \mathbf{Q} = \bar{\Phi}_3, \quad \boldsymbol{\Theta} = \bar{\Phi}_4, \quad \text{etc.} \quad (4.45)$$

The evolution equation for  $\bar{\Phi}_i$  ( $i \geq 1$ ) is then easily derived if  $\bar{\Phi}_i$  is differentiated with time and the Boltzmann–Curtiss equation is used:

$$\rho \frac{d}{dt} \hat{\bar{\Phi}}_i = -\nabla \cdot \psi^{(i)} + \mathcal{Z}_i + \Lambda_i, \quad (4.46)$$

where  $\hat{\bar{\Phi}}_i = \bar{\Phi}_i / \rho$  and

$$\psi^{(i)} = \int d\xi \mathbf{C} h^{(i)} f(\mathbf{r}, \xi, t), \quad (4.47)$$

$$\mathcal{Z}_i = \int d\xi f(\mathbf{r}, \xi, t) \left( \frac{\partial}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla + i\mathcal{L} \right) h^{(i)}, \quad (4.48)$$

$$\Lambda_i = \int d\xi h^{(i)} \mathfrak{R}_{\text{BC}} [f]. \quad (4.49)$$

Equation (4.46) represents the constitutive equations for nonconserved variables for the rigid diatomic molecular fluid under consideration. By explicitly working out the kinematic terms  $\mathcal{Z}_i$ , we obtain the leading members of the constitutive equations for nonconserved variables:

$$\rho \frac{d\hat{\boldsymbol{\Pi}}}{dt} = -\nabla \cdot \psi^{(1)} - 2(p + \Delta) [\nabla \mathbf{u}]^{(2)} - 2[\boldsymbol{\Pi} \cdot \nabla \mathbf{u}]^{(2)} + \Lambda_1, \quad (4.50)$$

$$\begin{aligned} \rho \frac{d\hat{\Delta}}{dt} &= -\frac{2}{3} \nabla \cdot \left( \frac{C_{\text{rot}}}{C_v} \mathbf{Q} - \mathbf{Q}_r \right) - \frac{2C_{\text{rot}}}{3C_v} (\boldsymbol{\Pi} + \Delta \boldsymbol{\delta}) : \nabla \mathbf{u} \\ &\quad - \frac{2C_{\text{rot}}}{3C_v} p \nabla \cdot \mathbf{u} + \Lambda_2, \end{aligned} \quad (4.51)$$

$$\begin{aligned} \rho \frac{d\hat{\mathbf{Q}}}{dt} &= -\nabla \cdot \psi^{(3)} - \mathbf{Q} \cdot \nabla \mathbf{u} - \boldsymbol{\varphi}^{(3)} : \nabla \mathbf{u} - \boldsymbol{\varphi}^{(J)} : \nabla \mathfrak{J} \\ &\quad - (\boldsymbol{\Pi} + \Delta \boldsymbol{\delta}) \cdot \frac{d\mathbf{u}}{dt} - \frac{\mathbf{S}}{I} \cdot \frac{d\mathfrak{J}}{dt} - \mathbf{P} \cdot \nabla \hat{h} + \Lambda_3, \end{aligned} \quad (4.52)$$

$$\rho \frac{d\hat{\boldsymbol{\Theta}}}{dt} = -\nabla \cdot \psi^{(4)} - 2[\mathbf{S} \cdot \nabla \mathfrak{J}]^{(2)} + \Lambda_4, \quad (4.53)$$

where

$$\varphi^{(3)} = \int d\xi \mathbf{CCC} f(\mathbf{r}, \xi, t), \quad (4.54)$$

$$\varphi^{(4)} = \int d\xi \mathbf{CCJ} f(\mathbf{r}, \xi, t), \quad (4.55)$$

$$\mathbf{S} = \int d\xi \mathbf{CJ} f(\mathbf{r}, \xi, t), \quad (4.56)$$

and

$$C_v = \left( \frac{\partial \mathcal{E}}{\partial T} \right)_v, \quad C_{\text{rot}} = \left( \frac{\partial \mathcal{E}_{\text{rot}}}{\partial T} \right)_v. \quad (4.57)$$

Equation (4.53) for  $\hat{\Theta}$  was absent for simple fluids. It describes the evolution of the stress produced by the rotation of rigid molecules. The constitutive equations presented here are adequate for describing transport processes in the rigid diatomic gas under consideration. For the purpose in mind, it is necessary to close the set of nonconserved variables by suitably expressing the nonconserved variables  $\psi^{(i)}$  ( $i = 1, 3, 4$ ),  $\varphi^{(3)}$ , and  $\varphi^{(4)}$  in terms of the variables included and to calculate the dissipation terms  $A_i$  ( $i = 1, \dots, 4$ ) in a suitable approximation. The constitutive equations (4.50)–(4.53) together with (4.26)–(4.28), (4.38), and (4.39) constitute the generalized hydrodynamic equations for dilute rigid diatomic fluids, which are described by the Boltzmann–Curtiss equation.

To calculate the dissipation terms  $A_i$ , the distribution function  $f(\mathbf{r}, \xi, t)$  is first expressed by the nonequilibrium canonical form

$$f^c(\mathbf{r}, \xi, t) = \exp \left[ \beta \mu - \beta \left( \frac{1}{2} m C^2 + H_{\text{rot}} + \sum_{k \geq 1} X_k h^{(k)} \right) \right], \quad (4.58)$$

where  $\mu$  is the nonequilibrium chemical potential, which is the normalization factor

$$\begin{aligned} \mu &= m \hat{\mu} \\ &= -k_B T \ln Q, \end{aligned} \quad (4.59)$$

$$Q = n^{-1} \int d\xi \exp \left[ -\beta \left( \frac{1}{2} m C^2 + H_{\text{rot}} + \sum_{k \geq 1} X_k h^{(k)} \right) \right], \quad (4.60)$$

with  $X_k$  denoting generalized potentials characterizing the degree of displacement of the fluid from equilibrium. The generalized potentials were introduced in a similar context for simple fluids in Chap. 2. As  $X_k$  vanish, the fluid approaches local equilibrium. The theory of irreversible thermodynamics can be developed on the basis of the nonequilibrium canonical form  $f^c(\mathbf{r}, \xi, t)$  given in (4.58) in the same manner as for simple fluids. The details of the theory

of irreversible thermodynamics are not described here because the subject is not the aim of this work. The general method used for monatomic fluids is described in the literature [9]. By using the nonequilibrium canonical form  $f^c$  in the expression for  $\sigma_{\text{ent}}$ , it is possible to obtain a cumulant expansion [10,11]. The first-order cumulant approximation for  $\sigma_{\text{ent}}$  gives rise to the form for  $A_i$  in the form

$$A_i = (\beta g)^{-1} q(X) \sum_{k \geq 1} R^{(ik)} X_k, \quad (4.61)$$

where  $g$  and  $q(X)$  are defined by (2.120) and (2.121) of Chap. 2, but the dissipation function  $\kappa$  for the fluid of interest here is defined by

$$\kappa^2 = \sum_{k,l \geq 1} X_k R^{(kl)} X_l \quad (4.62)$$

where the coefficients  $R^{(kl)}$  are the collision bracket integrals given in terms of  $\mathfrak{R}_{\text{BC}}[f]$  defined by (4.24). With the abbreviation of the collision bracket integrals

$$[AB]_c = \frac{\beta g}{4(2s+1)} \int d\xi \int d\Gamma_2 f_{1\text{eq}} f_{2\text{eq}} (A_1 + A_2 - A_1^* - A_2^*) \times \odot^s (B_1 + B_2 - B_1^* - B_2^*), \quad (4.63)$$

where  $s$  is the rank of the tensors involved and

$$\int d\Gamma_2 \cdots = \iiint \int d\mathbf{p}_2 d\Omega_2 d\mathbf{p}_r^* d\Omega_r^* d\Omega_2^* d\Omega_r^* \frac{p_r}{\mu_r} \sigma(p_r^*, j^*, j_2^* | p_r, j, j_2) \cdots,$$

the coefficients  $R^{(kl)}$  are given by the collision bracket integrals

$$R^{(kl)} = \left[ h^{(k)} h^{(l)} \right]_c. \quad (4.64)$$

The generalized potentials  $X_k$  may be calculated if the nonequilibrium partition function  $\mathcal{Q}$  is calculated. To the lowest order approximation, it is found that

$$X_i = -g_i \Phi_i, \quad (4.65)$$

$$g_1 \simeq \frac{1}{2p}, \quad g_2 \simeq \frac{3C_{\text{rot}}\Delta}{2pC_v}, \quad g_3 \simeq \frac{1}{\widehat{C}_p T p}, \quad g_4 \simeq \frac{3}{2I}, \\ \text{etc.}, \quad (4.66)$$

where  $g_1$  and  $g_3$  are found in the same forms as those for simple fluids, whereas  $g_2$  differs from the simple fluid form by the factor  $C_{\text{rot}}/C_v$  and  $g_4$  is new. These results for the generalized potentials can be found if the nonequilibrium partition function  $\mathcal{Q}$  is calculated [12] to first order in  $X_i$ . It should be noted that  $\widehat{C}_p$  for a rigid diatomic fluid consists of translational and rotational

parts. With these approximations for  $X_i$  and  $\Lambda_i$ , the generalized hydrodynamic equations (4.26)–(4.28), (4.38), (4.39), and (4.50)–(4.53) presented here are closed, provided that closure relations are suitably taken for the nonconserved variables  $\psi^{(i)}$  ( $i = 1, 3, 4$ ),  $\varphi^{(3)}$ , and  $\varphi^{(4)}$ . These closure relations are not unique and appear to depend on the flow process under consideration according to the hydrodynamic flow problems examined so far [9, 13]. This aspect will be discussed later when specific flow problems are examined.

Because the collision bracket integrals for a single-component fluid are diagonal with regard to indexes  $k$  and  $l$  because the collision bracket integrals corresponding to nonconserved moments belonging to different tensorial ranks vanish owing to symmetry, the dissipation terms  $\Lambda_i$  are given by

$$\Lambda_i = -(\beta g)^{-1} g_i R^{(ii)} \Phi_i q(X). \quad (4.67)$$

It will be found convenient to define the material parameters  $\eta_0, \eta_b, \lambda_0$

$$\eta_0 = \frac{4p^2 \beta g}{R^{(11)}}, \quad (4.68)$$

$$\eta_b^0 = \frac{p^2 \beta g}{R^{(22)}}, \quad (4.69)$$

$$\lambda_0 = \frac{(C_p T p)^2 \beta g}{R^{(33)}}, \quad (4.70)$$

which will turn out to be the linear transport coefficients of the rigid diatomic gas of interest when we discuss linear transport processes within the context of the present theory:  $\eta_0$  will be identified with the shear viscosity,  $\eta_b^0$  with the bulk viscosity, and  $\lambda_0$  with the thermal conductivity. In this set of linear transport coefficients, the material parameter corresponding to the second-rank tensor  $[\mathbf{JJ}]^{(2)}$  does not appear owing to the absence of a linear thermodynamic driving force in the evolution equation for  $[\mathbf{JJ}]^{(2)}$  because the term  $[\mathbf{S} \cdot \nabla \mathfrak{J}]^{(2)}$  is nonlinear; see (4.53). For this reason, the theory of linear transport processes of rigid diatomic fluids and associated hydrodynamics can be discussed with the generalized hydrodynamic equations, excluding (4.53). In this connection, we note that the relaxation of  $\Theta$  in the linear approximation may be discussed with the evolution equation

$$\frac{d\widehat{\Theta}}{dt} = -\frac{1}{\tau_\Theta} \widehat{\Theta}, \quad (4.71)$$

where the relaxation time  $\tau_\Theta$  is given by the kinetic theory formula,

$$\tau_\Theta = \frac{2I\beta g\rho}{3R^{(44)}}. \quad (4.72)$$

This relaxation time should be of interest if the effects of rotational motions in the rigid diatomic fluid are desired. It is expected to be rather short for dilute gases.

## 4.4 Linear Transport Processes

As for the kinetic theory of simple fluids, the constitutive equations (4.50)–(4.53) contain the essence of most transport processes considered in the laboratory and observed in nature. This is rather evident if we compare them with their simple fluid counterpart from which we have extracted the information on linear transport processes in simple fluids. Therefore, we proceed to the subject in a manner similar to the theory of linear transport processes in simple fluids.

Upon linearization of the constitutive equations with respect to the non-conserved variables and gradients and closing the set with the closures

$$\psi^{(1)} = \psi^{(3)} = \varphi^{(3)} = \varphi^{(J)} = 0, \quad (4.73)$$

there follow the linearized constitutive equations

$$\rho \frac{d\hat{\Pi}}{dt} = -2p [\nabla \mathbf{u}]^{(2)} - \frac{2p}{\eta_0} \Pi, \quad (4.74)$$

$$\rho \frac{d\hat{\Delta}}{dt} = -\frac{2C_{\text{rot}}p}{3C_v} \nabla \cdot \mathbf{u} - \frac{2C_{\text{rot}}p}{3C_v \eta_b^0} \Delta, \quad (4.75)$$

$$\rho \frac{d\hat{\mathbf{Q}}}{dt} = -\hat{C}_p T p \nabla \ln T - \frac{\hat{C}_p T p}{\lambda_0} \mathbf{Q}, \quad (4.76)$$

$$\rho \frac{d\hat{\Theta}}{dt} = -\frac{\rho}{\tau_\Theta} \hat{\Theta}. \quad (4.77)$$

Noted that (4.74)–(4.76) are rigid diatomic fluid generalizations of the Maxwell equations [14] for  $\Pi$ ,  $\Delta$ , and  $\mathbf{Q}$  under consideration.

If the substantial time derivatives on the left side are neglected or at the steady state in the coordinate system moving at the fluid velocity  $\mathbf{u}$ —namely, the adiabatic approximation in effect—there arise the constitutive equations for linear transport processes from (4.74)–(4.76)

$$\Pi = -\eta_0 [\nabla \mathbf{u}]^{(2)}, \quad (4.78)$$

$$\Delta = -\eta_b^0 \nabla \cdot \mathbf{u}, \quad (4.79)$$

$$\mathbf{Q} = -\lambda_0 \nabla \ln T, \quad (4.80)$$

and we see that  $\eta_0$ ,  $\eta_b^0$ , and  $\lambda_0$  defined in (4.68)–(4.70) are, respectively, identified with the shear viscosity, bulk viscosity, and thermal conductivity of the fluid of interest.

## 4.5 Remarks

The theory presented here represents the simplest example of the classical kinetic theory of nonsimple fluids. Although only for the particular case of

Polyatomic fluids, rigid diatomic molecules, it is now quite clear that the kinetic theory of polyatomic fluids can be similarly developed, and generalized hydrodynamic equations can be derived for polyatomic fluids in general. It is also evident that the Waldmann–Snider equation for diatomic fluids can be used to derive the balance equations and the constitutive equations for the shear stress  $\Pi$ , excess normal stress  $\Delta$ , heat flux  $\mathbf{Q}$ , and so on, in the same manner as that for the Boltzmann–Curtiss equation. By linearizing the constitutive equations so derived, it is possible to extract the kinetic theory formulas for the transport coefficients of polyatomic fluids of interest from the constitutive equations so derived. Since the methodology is rather clear by now, we leave their derivations to the reader as exercises. The reader is also referred to the literature [3] on the subject.

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## Transport Processes in Dilute Polyatomic Gases

The kinetic theory of polyatomic gases presented in Chap. 4 indicates that once the collision cross section is calculated for collision between polyatomic molecules, the collision bracket integrals can be evaluated as functions of temperature and density. However, such calculations are technically not trivial because of, first of all, the time- and labor-consuming many-body collision problem to solve. Recent progress on the subject matter is described in the literature [1]. There is much theoretical work to be done on the topics. In this chapter, we will instead devote the space to discuss how flow processes in dilute nonsimple gases can be studied and transport coefficients of such gases may be empirically deduced. These are not subjects new to the kinetic theory of polyatomic gases. The subjects discussed may be regarded as methods for measuring transport coefficients in the laboratory through the flow processes discussed, although they may be also regarded as hydrodynamic applications of the constitutive equations of the nonsimple gases presented in Chap. 4. In this chapter, ultrasonic wave absorption in nonsimple gases will be discussed as well as shock wave propagation in them. The former phenomenon represents a practical method of measuring the bulk viscosity of nonsimple gases, which is the only practicable method of measuring bulk viscosity. The latter phenomenon is of practical importance in engineering problems in gas dynamics and aerodynamics, but their continuum mechanics treatment has posed an interesting challenge to theory.

### 5.1 Ultrasonic Absorption in Rigid Diatomic Gases

As a sound wave propagates through a fluid, the medium is longitudinally compressed and decompressed periodically. If an energy dissipation mechanism is present in the medium, the sound wave can be absorbed and dissipated. The subject of sound wave absorption and dispersion has been studied within the framework of the classical Navier–Stokes theory [2–4] or equivalent forms of kinetic theory [5–8]. In these theories, a local equilibrium assumption

is made for the entropy of the fluid. Because as we have seen throughout this work, the classical hydrodynamics of Navier and Stokes is a limiting theory of generalized hydrodynamics and the local equilibrium assumption can be removed, it is expected that the theory of sound wave absorption and dispersion should be suitably generalized so as to accommodate situations in which the aforementioned assumptions become too restricted. The generalized hydrodynamics presented in the previous chapter provides a theoretical tool for achieving the desired aim. Besides the inherent theoretical interest posed by the phenomena of sound wave absorption and dispersion, experimenters have found that the phenomena provide a practicable method of measurements [9–11] for bulk viscosity. Since our interest in this work lies in transport coefficients and theories of their measurements, we discuss a generalized hydrodynamic theory of sound wave absorption and dispersion in this section, by which the bulk viscosity of the fluid can be measured more generally than that in classical theory.

### 5.1.1 Linearized Generalized Hydrodynamic Equations

Since sound wave absorption and dispersion phenomena necessarily require an energy dissipation mechanism, it is necessary to consider a nonsimple fluid as a medium of wave propagation. For this reason, the generalized hydrodynamic equations (4.26)–(4.28) and (4.50)–(4.53) presented in Chap. 4 meet the minimum requirement. Because it is estimated that the relaxation time for  $\Theta$ , the mean value of  $[\mathbf{JJ}]^{(2)}$ , is rather short compared to those of the stress and heat flux, the evolution equation for  $\Theta$  may be ignored from the standpoint of timescale—the hydrodynamic timescale—appropriate for the phenomena of interest. For the phenomena under consideration, we will also assume the following closure relations:

$$\nabla \cdot \psi^{(1)} = -\frac{2p_0 v_0 \lambda_0}{T_0 \hat{C}_p} [\nabla \nabla T]^{(2)}, \quad (5.1)$$

$$\psi^{(2)} = \frac{2\rho_0 \hat{C}_{\text{rot}}}{3\hat{C}_v} \hat{\mathbf{Q}}, \quad (5.2)$$

$$\psi^{(3)} = -p_0 v_0 \left( 2\eta_0 [\nabla \mathbf{u}]^{(2)} + \eta_b^0 \delta \nabla \cdot \mathbf{u} \right), \quad (5.3)$$

where the subscript 0 for  $p$ ,  $v$ , and  $T$  denotes the equilibrium value for pressure, specific volume, and temperature, respectively, and the specific heat per mass  $\hat{C}_p = C_p/m$  and the rotational specific heat per mass  $\hat{C}_{\text{rot}} = C_{\text{rot}}/m$  are assumed constant. With these closure relations, the generalized hydrodynamic equations mentioned are closed. Their solutions, subject to suitable initial and boundary conditions, will provide the desired information on sound wave absorption and dispersion as well as other flow characteristics if the latter are of interest in the given flow configuration. For this discussion,

it is assumed that the external shear and temperature gradients are absent and the fluid is initially in equilibrium. To make the analysis as simple as possible, we will also assume that the sound wave does not displace the fluid too far from equilibrium, so that linearized generalized hydrodynamic equations are sufficient for the description of the process. Thus the relevant generalized hydrodynamic equations are for the set  $(v, \mathbf{u}, \mathcal{E}, \hat{\boldsymbol{\Pi}}, \hat{\Delta}, \hat{\mathbf{Q}})$  of macroscopic variables, and they are linearized as follows [12] :

$$\rho_0 \frac{\partial v}{\partial t} = \nabla \cdot \mathbf{u}, \quad (5.4)$$

$$\rho_0 \frac{\partial \mathbf{u}}{\partial t} = -\nabla(p + \Delta) - \nabla \cdot \boldsymbol{\Pi}, \quad (5.5)$$

$$\rho_0 \frac{\partial T}{\partial t} = -\frac{1}{\hat{C}_v} \nabla \cdot \mathbf{Q} - \frac{T_0 \alpha_p}{\kappa_T \hat{C}_v} \nabla \cdot \mathbf{u}, \quad (5.6)$$

$$\rho_0 \frac{\partial \hat{\boldsymbol{\Pi}}}{\partial t} = -\nabla \cdot \psi^{(1)} - 2p_0 [\nabla \mathbf{u}]^{(2)} - \frac{p_0 \rho_0}{\eta_0} \hat{\boldsymbol{\Pi}}, \quad (5.7)$$

$$\rho_0 \frac{\partial \hat{\mathbf{Q}}}{\partial t} = -\nabla \cdot \psi^{(3)} - p_0 \hat{C}_p \nabla T - \frac{p_0 \hat{C}_p \rho_0}{\lambda_0} \hat{\mathbf{Q}}, \quad (5.8)$$

$$\rho_0 \frac{\partial \hat{\Delta}}{\partial t} = -\nabla \cdot \psi^{(2)} - \frac{2\hat{C}_{\text{rot}}}{3\hat{C}_v} p_0 \nabla \cdot \mathbf{u} - \frac{2\hat{C}_{\text{rot}} p_0 \rho_0}{3\hat{C}_v \eta_b^0} \hat{\Delta}, \quad (5.9)$$

where the subscript 0 for quantities other than the transport coefficients denotes the equilibrium value,  $\kappa_T$  and  $\alpha_p$  are the equilibrium isothermal compressibility and isobaric expansion coefficient, respectively,

$$\begin{aligned} \kappa_T &= -v_0^{-1} \left( \frac{\partial v}{\partial p} \right)_T^0, \\ \alpha_p &= v_0^{-1} \left( \frac{\partial v}{\partial T} \right)_p^0, \end{aligned} \quad (5.10)$$

and the closure relations (5.1) and (5.3) are to be taken for  $\psi^{(1)}$  and  $\psi^{(3)}$ . The transport coefficients  $\eta_0, \eta_b^0$ , and  $\lambda_0$  are the Chapman–Enskog viscosity, bulk viscosity, and thermal conductivity of a rigid diatomic gas, given in terms of the collision bracket integrals in Chap. 4. These transport coefficients may be regarded as phenomenological coefficients, which may then be determined experimentally. Note that in the present set, the evolution of the internal rotational motion is ignored. Therefore  $\mathbf{Q}_r$ , which appear in (4.38) is neglected to be consistent with the approximation that does not explicitly take into account the rotational energy evolution. If the internal rotational motion is of interest, then the moments  $\mathcal{E}_{\text{rot}}, \hat{\mathfrak{L}}, \hat{\Theta}$  as well as  $\hat{\mathbf{Q}}_r$  must be chosen as independent variables. Also note that the evolution equations are still consistent with the constraints of the thermodynamic laws represented by the extended

Gibbs relation for calortropy and the positive calortropy production  $\Xi_c$ . This constraint appears as the positivity conditions for the transport coefficients because  $\Xi_c$  for a linear process is given by the expression

$$\Xi_c = \frac{1}{\eta_0 T_0} \mathbf{\Pi} : \mathbf{\Pi} + \frac{1}{\lambda_0 T_0} \mathbf{Q} \cdot \mathbf{Q} + \frac{1}{\eta_b^0 T_0} \frac{\hat{C}_{\text{rot}}}{\hat{C}_v} \Delta^2. \quad (5.11)$$

In this form, the positivity of  $\Xi_c$  implies that the transport coefficients are positive:  $\eta_0, \lambda_0, \eta_b^0 > 0$ .

### 5.1.2 Solution by Fourier Transform

The linearized evolution equations presented can be solved by the Fourier transform in time and space. Various variables are transformed as follows:

$$s(\mathbf{r}, t) = \left( \frac{1}{2\pi} \right)^4 \int d\mathbf{k} \int_{-\infty}^{\infty} d\omega \exp(-i\omega t + i\mathbf{k} \cdot \mathbf{r}) \tilde{s}(\mathbf{k}, \omega). \quad (5.12)$$

Inserting it in the linearized generalized hydrodynamic equations (5.4)–(5.9) and performing a Fourier transform, we obtain

$$\rho_0 \omega \tilde{v} = -\mathbf{k} \cdot \tilde{\mathbf{u}}, \quad (5.13)$$

$$\omega \mathbf{k} \cdot \tilde{\mathbf{u}} = v_0 k^2 + k^2 \tilde{\Delta} + \mathbf{k} \mathbf{k} : \tilde{\mathbf{\Pi}}, \quad (5.14)$$

$$\hat{C}_v \omega \tilde{T} + \frac{T_0 \alpha_p}{\kappa_T} \omega \tilde{v} = \mathbf{k} \cdot \tilde{\mathbf{Q}}, \quad (5.15)$$

$$(i\omega + \tau_s^{-1}) \mathbf{k} \mathbf{k} : \tilde{\mathbf{\Pi}} = iv_0 \mathbf{k} \mathbf{k} \mathbf{k} \odot^3 \tilde{\psi}^{(1)} - i \frac{4p_0}{3} k^2 \omega \tilde{v}, \quad (5.16)$$

$$(i\omega + \tau_q^{-1}) \mathbf{k} \cdot \tilde{\mathbf{Q}} = iv_0 \mathbf{k} \mathbf{k} : \tilde{\psi}^{(3)} + ip_0 v_0 \hat{C}_p k^2 \tilde{T}, \quad (5.17)$$

$$(i\omega + \tau_b^{-1}) \tilde{\Delta} = iv_0 \mathbf{k} \cdot \tilde{\psi}^{(2)} - i \frac{2\gamma' p_0}{3} \omega \tilde{v}, \quad (5.18)$$

where  $\odot^3$  denotes triple contraction, other symbols are defined by

$$\gamma' = \frac{\hat{C}_{\text{rot}}}{\hat{C}_v}, \quad \tau_s^{-1} = \frac{p_0}{\eta_0}, \quad \tau_b^{-1} = \frac{2\gamma' p_0}{3\eta_b^0}, \quad \tau_q^{-1} = \frac{p_0 \hat{C}_p}{\lambda_0}, \quad (5.19)$$

and a scalar product with  $\mathbf{k}$  and a double contraction with  $\mathbf{k} \mathbf{k}$  are formed, respectively, for vector equations and for second-rank tensor equations. The expressions are also simplified with the following abbreviations:

$$\Gamma_s = \frac{\eta_0}{1 + i\omega\tau_s}, \quad \Gamma_q = \frac{\lambda_0}{1 + i\omega\tau_q}, \quad \Gamma_b = \frac{\eta_b^0}{1 + i\omega\tau_b}. \quad (5.20)$$

Equations (5.13)–(5.18) can be reduced to a pair of algebraic equations for  $\tilde{v}$  and  $\tilde{T}$ , which may be written in the following forms:

$$\begin{aligned} A_{11}\tilde{v} + A_{12}\tilde{T} &= 0, \\ A_{21}\tilde{v} + A_{22}\tilde{T} &= 0 \end{aligned} \quad (5.21)$$

for which we have used

$$\tilde{p} = \frac{1}{v_0\kappa_T} (v_0\alpha_p\tilde{T} - \tilde{v}).$$

Here, the coefficients are defined by

$$\begin{aligned} A_{11} &= -\frac{\omega^2}{v_0} + k^2 \left( \frac{1}{\kappa_T} + i\omega\Gamma_b + \frac{4i}{3}\omega\Gamma_s \right), \\ A_{12} &= -\frac{v_0\alpha_p}{\kappa_T}k^2 + \frac{\lambda_0 v_0 k^4}{p_0} \left( \Gamma_b + \frac{4}{3} \frac{p_0 v_0}{T_0 \hat{C}_p} \Gamma_s \right), \\ A_{21} &= \frac{T_0 \alpha_p \omega}{\kappa_T} - \frac{v_0 \omega k^2}{\hat{C}_p} \left( \frac{4}{3} \eta_0 + \eta_b^0 \right) \Gamma_q, \\ A_{22} &= \hat{C}_v \omega - i v_0 k^2 \Gamma_q. \end{aligned} \quad (5.22)$$

Therefore the solvability condition is

$$A_{11}A_{22} - A_{12}A_{21} = 0 \quad (5.23)$$

from which the dispersion relation follows.

It is convenient to use the following dimensionless parameters:

$$c_0 = \sqrt{\frac{\gamma k_B T_0}{m}}, \quad \omega^* = \frac{\omega \eta_0 v_0}{c_0^2}, \quad r^* = \frac{1}{\gamma \omega^*}, \quad k^* = \frac{k c_0}{\omega}$$

and abbreviations

$$\xi_s = \left( 1 + \frac{7}{5}i\omega^* \right)^{-1}, \quad \xi_q = \left( 1 + \frac{19}{10}i\omega^* \right)^{-1}, \quad \xi_b = \left( 1 + \frac{21}{4}if_b\omega^* \right)^{-1}.$$

The two parameters  $r^*$  and  $k^*$  are introduced to compare the theoretical results with experimental data in the literature, where the sound wave absorption is given in terms of  $|\text{Im } k^*|$ , whereas the sound wave phase speed

is given in terms of  $|\text{Re } k^*|$ . The two quantities mentioned can be calculated from the dispersion relation (5.23). Because the gas is ideal, we use

$$p_0 = n_0 k_B T_0, \quad \hat{C}_v = \frac{5k_B}{2m}, \quad \alpha_p = \frac{1}{T_0}, \quad \kappa_T = \frac{1}{p_0},$$

$$\gamma = \frac{7}{5}, \quad \gamma' = \frac{2}{5}, \quad \hat{h}_0 = \gamma \hat{C}_v T_0.$$

We also define the Eucken number

$$f_E = \frac{9\gamma - 5}{4} \quad (5.24)$$

and denote the Eucken ratio [13] of the bulk viscosity to the shear viscosity by

$$f_b = \frac{\eta_b^0}{\eta_0}. \quad (5.25)$$

The dispersion relation then can be expressed as a polynomial of  $k^*$

$$B_6 k^{*6} + B_4 k^{*4} + B_2 k^{*2} + B_0 = 0, \quad (5.26)$$

where the coefficients are given by the formulas

$$\begin{aligned} B_0 &= -\frac{5}{2}, \\ B_2 &= \frac{5}{2} + i\omega^* \left( \frac{5}{2} f_b \xi_b + \frac{10}{3} \xi_s + \frac{19}{4} \xi_q \right), \\ B_4 &= -i \frac{95}{28} \omega^* \xi_q - \frac{19}{3} \omega^{*2} \left( \frac{2}{7} \xi_s + \frac{2}{7} \xi_q + \frac{3}{4} f_b \xi_b \right. \\ &\quad \left. + \frac{3}{14} f_b \xi_q - \xi_s \xi_q - \frac{3}{4} f_b \xi_q \xi_b \right), \\ B_6 &= \frac{361}{30} \omega^{*4} \xi_q \left( \frac{8}{21} \xi_s + f_b \xi_b \right) \left( 1 + \frac{3}{4} f_b \right). \end{aligned} \quad (5.27)$$

Although (5.26) can be solved in closed analytic form, the solutions are not in forms readily interpretable physically. It is therefore useful to consider the limiting case of low frequency before the equations are solved numerically.

Before proceeding to the question, it appears useful to note the relation of the present set of evolution equations to the result obtained on the basis of the Navier–Stokes theory in the literature. Clearly, the present set generalizes the classical Navier–Stokes theory [6, 7] because the latter is recovered from the former as the time derivatives of  $\widehat{\Pi}$ ,  $\widehat{\mathbf{Q}}$ , and  $\widehat{\Delta}$  and the higher order moments  $\psi^{(1)}$  and  $\psi^{(3)}$  are neglected.

Moraal and McCourt used a moment method in their work [5], in which approximations were made directly on the kinetic equation. They derived a set of evolution equations comparable to (5.4)–(5.9), although the details are different, including the closure relations for higher order moments. Because of the

differences in the details of the evolution equations, their dispersion relation [(4.10) in [5]] is different from the present dispersion relation (5.26). A salient difference between the Moraal–McCourt theory and the present theory is that their dispersion relation in the second-order approximation, which they use in their comparison with experiment, is quartic with respect to  $k$ , whereas the present theory predicts a dispersion relation of order six. This indicates that their kinetic theory treatment amounts to a further approximation with regard to the  $\omega\tau$  dependence. Therefore, the present method of generalized hydrodynamics, although using the same number of moments as the theory of Moraal and McCourt, differs from it in the way the kinetic equation is treated; in the present method, the generalized hydrodynamic equations are first derived and then suitably approximated, whereas the Moraal–McCourt method first approximates the kinetic equation and then derives the moment equations therefrom. The generalized hydrodynamics approach is more convenient for inevitable approximations in a thermodynamically consistent manner because the generalized hydrodynamic equations derived from the kinetic equation are exact within the framework of the kinetic theory used and thus allow us to see the macroscopic implications directly when they are approximated. The possibility of making the theory thermodynamically consistent at the order of approximation taken is another advantage of the generalized hydrodynamics approach.

In the low-frequency limit, that is, as  $\omega^* \rightarrow 0$ ,

$$\begin{aligned} B_6 &\rightarrow 0, \\ B_4 &\rightarrow -i \frac{95}{28} \omega^* - \left( \frac{205}{56} + \frac{19}{14} f_b \right) \omega^{*2}, \\ B_2 &\rightarrow \frac{5}{2} + i \left( \frac{97}{12} + \frac{5}{2} f_b \right) \omega^* + \left( \frac{1643}{120} + \frac{105}{8} f_b^2 \right) \omega^{*2}. \end{aligned} \quad (5.28)$$

This means that the solutions of the dispersion relation in this limit yield the sound modes,

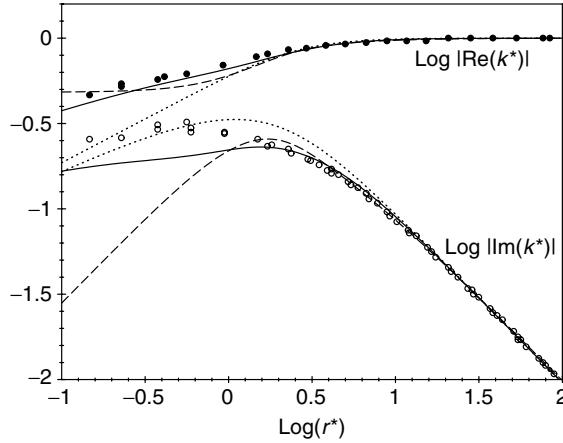
$$k^* = \pm \left[ 1 - i \frac{1}{2} \left( \frac{197}{105} + f_b \right) \omega^* - \left( \frac{8563}{4200} + \frac{16}{35} f_b + 3f_b^2 \right) \omega^{*2} \right], \quad (5.29)$$

and the thermal modes,

$$k^* = \pm (1 - i) \sqrt{\frac{7}{19\omega^*}}. \quad (5.30)$$

### 5.1.3 Application of the Theory

As a test of the theory presented, the sound wave absorption coefficient and dispersion calculated from the dispersion relation (5.26) have been compared with the experimental data on nitrogen gas by Greenspan [14] in Fig. 5.1. The temperature of nitrogen was  $T = 300$  K. For the figure, the value of  $f_b$  was



**Fig. 5.1.** Sound wave absorption coefficient  $\log |\text{Im } k^*|$  and dispersion  $\log |\text{Re } k^*|$  vs. reduced inverse frequency  $\log r^*$  for nitrogen at  $T = 300\text{ K}$ . The ordinate is for either  $\log |\text{Re } k^*|$  or  $\log |\text{Im } k^*|$  in the common scale as indicated. The *solid curve* is from generalized hydrodynamic theory, the dotted curve is from the Navier–Stokes theory, and the broken curve is from the Moraal–McCourt theory. The symbols are experimental values reported by Greenspan [14]. The value of  $f_b$  is 0.8. [Reproduced with permission from Byung Chan Eu and Young Gie Ohr, Phys. Fluids **13**, 744 (2001). Copyright 2001 American Institute of Physics.]

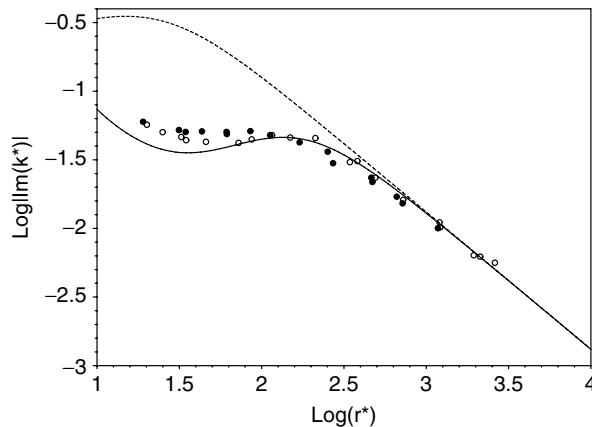
adjusted so that the classical theory and the generalized hydrodynamic theory coincide at the large  $r^* = 1/\gamma\omega^*$  limit, where the classical Navier–Stokes theory is adequate. It was found that  $f_b = 0.8$  is an adequate value for the purpose. This also means that the value of the bulk viscosity is  $\eta_b^0 = 0.8\eta_0$  according to the sound wave absorption measurement. In effect, it amounts to measurement of bulk viscosity. This is tantamount to treating the constitutive equations (5.7)–(5.9) as empirical constitutive equations where the transport coefficients are empirically determined. The *solid curve* is the result of the present theory and the symbols are the Greenspan data for sound wave absorption (*lower curve*) and sound wave dispersion (*upper curve*). The linearized generalized hydrodynamic theory is much improved over the Moraal–McCourt theory result in the small  $r^*$  (high-frequency) region. But there is still room for improvement, especially, for the sound wave absorption coefficient. Because a small  $r^*$  means a long relaxation time for nonconserved variables, the linear approximations for the dissipation terms  $\Lambda^{(k)}$  in the present linear analysis may be inadequate in the small  $r^*$  regime. However, because removal of the linear approximation produces nonlinear evolution equations, which require numerical solution of nonlinear evolution equations, the method of extracting the sound wave absorption and dispersion coefficients will differ [15] from the Fourier transform method used here.

The Navier–Stokes theory yields a qualitatively correct result for the absorption curve, whereas it is poor for the dispersion curve in the small  $r^*$  region. The comparison presented indicates that there is still room for improvement in the theory in some aspects of the phenomena, such as the role of internal energy relaxation and the effects of nonlinearity in the dissipation terms in the stress and heat flux evolution equations. These aspects can be readily included in the generalized hydrodynamic approach but will require numerical solution techniques different from that employed in the present theory.

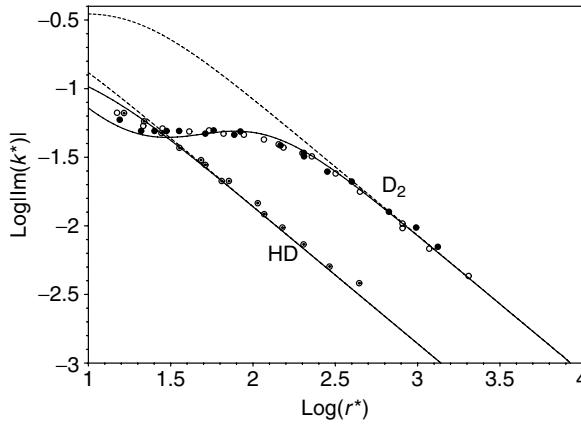
To show the utility of the theory for other gases, the sound wave absorption intensity of normal H<sub>2</sub>, para H<sub>2</sub>, normal D<sub>2</sub>, ortho D<sub>2</sub>, and HD gases have been calculated and the results have been compared with the data reported by Sluijter et al. [9].  $T = 293\text{ K}$  was chosen in the light of the high-temperature approximations for  $\gamma, \gamma', C_v$ , and so on, which were used in the derivation of the dispersion relation.

In Fig. 5.2, comparison is made between the experimental and theoretical values for  $|\text{Im}(k^*)|$ , plotted against  $r^* = 1/\gamma\omega^*$  for normal H<sub>2</sub> and para H<sub>2</sub> at  $T_0 = 293\text{ K}$ . The *open circles* denote the values for normal H<sub>2</sub> and the *filled circles* are for para H<sub>2</sub>. The *solid curve* is the prediction by the present theory and the *broken curve* is the prediction by the Navier–Stokes theory. The values of  $f_b$  for both curves were  $f_b = 35$ . The present theory is much better than the Navier–Stokes theory in the low-frequency regime.

In Fig. 5.3, a similar comparison is made for normal D<sub>2</sub>, ortho D<sub>2</sub>, and HD at  $T_0 = 293\text{ K}$ . The *open circles* are for normal D<sub>2</sub>, the *filled circles*



**Fig. 5.2.** Sound wave absorption coefficient  $\log |\text{Im } k^*|$  vs. inverse reduced frequency  $\log r^*$ . The *open circles* are for normal H<sub>2</sub> and the *filled circles* are for para H<sub>2</sub>. The *solid curve* is the prediction by the generalized hydrodynamic theory and the *broken curve* is the prediction by the Navier–Stokes theory.  $f_b = 3.5$  and  $\eta_0 = 88.2\text{ }\mu\text{P}$ . [Reproduced with permission from Byung Chan Eu and Young Gie Ohr, Phys. Fluids **13**, 744 (2001). Copyright 2001 American Institute of Physics.]



**Fig. 5.3.** Sound wave absorption coefficient  $\log|\text{Im } k^*|$  vs. inverse reduced frequency  $\log r^*$  for normal D<sub>2</sub>, ortho D<sub>2</sub>, and HD at  $T_0 = 293\text{ K}$ . The *open circles* are for normal D<sub>2</sub>, the *filled circles* are for ortho D<sub>2</sub>, and the *dotted circles* are for HD. The *solid curve* is the prediction by the generalized hydrodynamic theory and the *broken curves* are the predictions by the Navier–Stokes theory.  $f_b = 22$  for D<sub>2</sub> and  $\eta_0 = 123\text{ }\mu\text{P}$  for D<sub>2</sub>, whereas  $f_b = 2$  and  $\eta_0 = 108\text{ }\mu\text{P}$  for HD. [Reproduced with permission from Byung Chan Eu and Young Gie Ohr, Phys. Fluids **13**, 744 (2001). Copyright 2002 American Institute of Physics.]

are for ortho D<sub>2</sub>, and the *dotted circles* are for HD. The *solid curves* are from the present theory and the *broken curves* are the Navier–Stokes theory predictions. The following values were taken for  $f_b$  and  $\eta_0 : f_b = 22$  and  $\eta_0 = 123\text{ }\mu\text{P}$  for D<sub>2</sub>;  $f_b = 2$  and  $\eta_0 = 108\text{ }\mu\text{P}$  for HD, which indicate the values of the bulk viscosity. The shear viscosity values are from the paper of Sluijter et al. [9]. Again for the gases examined, the present theory predicts fairly accurate behavior of the sound wave absorption intensity.

In addition to being a measure of the bulk viscosity, the Eucken ratio  $f_b = \eta_b^0/\eta_0$  is related to the rotational relaxation time  $\tau_b$  defined by (5.19), which may be recast in the form

$$\tau_b = \frac{15f_b\eta_0}{4p_0}, \quad (5.31)$$

for which we have used  $\gamma' = 2/5$ . The numerical values of  $\tau_b$  corresponding to the values of  $f_b$ , the bulk viscosity, are summarized for N<sub>2</sub>, H<sub>2</sub>, D<sub>2</sub>, and HD in Table 5.1.

Prangsma et al. [10], for example, report  $\tau_b = 2.2 \times 10^{-8}\text{ s}$  at  $T = 293\text{ K}$  for ortho-hydrogen. Herzfeld and Litovitz [2] quote  $\tau_b = 2 \sim 2.8 \times 10^{-8}\text{ s}$  for hydrogen. Therefore, the aforementioned values are comparable with the literature values, and the difference may be attributed to the difference in the sound wave absorption formulas used because the present theory is a generalization of the classical theory that the authors in the literature use.

**Table 5.1.** Rotational relaxation times

molecule	$\tau_b$ (s)	$\eta_0$ ( $\mu P$ )	$f_b$
N <sub>2</sub>	$0.084 \times 10^{-8}$	178.6	0.8
H <sub>2</sub>	$1.2 \times 10^{-8}$	88.2	35
D <sub>2</sub>	$1.0 \times 10^{-8}$	123	22
HD	$0.08 \times 10^{-8}$	108	2

The point here is that the values chosen for  $f_b$  are not so strange as they might appear at first glance. This aspect may be examined from another direction. Chapman and Cowling [13] define a quantity  $\zeta_r = \tau_b/\tau_s$ , which is comparable with  $f_b$ . For the present cases,

$$\zeta_r = \frac{15}{4} f_b,$$

which yields the values  $\zeta_r = 3$  for N<sub>2</sub>, 131 for H<sub>2</sub>, 82.5 for D<sub>2</sub>, and 7.5 for HD. Generally, the value of  $\zeta_r$  ranges from 3 to 20, but Chapman and Cowling quote 300 for H<sub>2</sub> and 200 for D<sub>2</sub>. This again affirms that the values chosen for  $f_b$  do not differ greatly from the literature values. However, the cause for the noticeably smaller value for HD is not understood at present. It may have to do with the fact that the HD molecule acts as if it is a loaded sphere because the center of mass is significantly shifted toward deuterium owing to the large disparity in the masses of H and D. In any case, the present comparison indicates that, on the basis of the experimental data employed for the analysis, H<sub>2</sub> and D<sub>2</sub> have abnormally large bulk viscosities. To understand this property better, it is necessary to calculate the bulk viscosity on the basis of the kinetic theory formula, which would require computation of scattering cross sections for the molecules concerned. This remains to be done.

In summary, it is shown in this section that generalized hydrodynamic equations derived from the Boltzmann–Curtiss kinetic equation for dilute rigid diatomic gases can be employed in an experimental procedure to determine the bulk viscosities of rigid diatomic gases, such as nitrogen, hydrogen, deuterium, and deuterium hydride, from measurements of ultrasonic wave absorption and dispersion by the gases. The model set of generalized hydrodynamic equations is applied to study sound wave absorption and dispersion in nitrogen, normal H<sub>2</sub>, para H<sub>2</sub>, normal D<sub>2</sub>, ortho D<sub>2</sub>, and HD or nitrogen. In all the cases studied, the generalized hydrodynamic theory predicts better results for the absorption intensity as a function of frequency, although for nitrogen, the prediction of the absorption curve by the generalized hydrodynamic theory is poorer than that by the Navier–Stokes theory in the high-frequency regime. This feature is not yet fully understood, but the discrepancy may be attributed to neglecting the rotational energy relaxation effect. This aspect remains to be studied. The present generalized hydrodynamic theory may be applied without linearization to study sound wave absorption phenomena, but

then it will require numerical solutions of the nonlinear generalized hydrodynamic equations subject to oscillating velocity and temperature fields. Such a numerical solution method is not yet developed to determine bulk viscosities from ultrasound absorption and dispersion measurements.

## 5.2 Nonlinear Transport Coefficients and Shock Waves

Propagation of shock waves in fluids is influenced by the transport of energy and momentum in them and can be a source of information on transport properties of fluids and, in particular, their nonlinearity, as is ultrasonic wave propagation in fluids discussed in the previous subsection. In most engineering problems, the situation is reversed because given transport properties of fluids, one is interested in shock wave structures and their influence on the flow properties of fluids. In the history of chemical kinetics, shock waves were employed to study the rates of chemical reactions [16–20], which may be regarded as a kind of transport property, and to learn about molecular relaxation processes behind the shock front. To understand shock wave structures, it is necessary to have correct constitutive equations for the stress tensor and heat flux of the fluid of interest, and in this sense the study of shock waves is relevant to the investigation of transport properties of fluids and their nonlinear aspects. In this spirit, we discuss and show that the generalized hydrodynamic equations for diatomic gases presented in the previous chapter are quite relevant to the study of shock structures in the fluids, and the kinetic theory evaluation of transport coefficients can be valuable for such studies from the completely molecular theory standpoint. However, because there is only a limited number of results for computation of transport coefficients as a function of temperature and density by using the collision cross-section, which is a rather laborious task to achieve adequately, we can discuss only how shock structures can be calculated given the information on the transport coefficients at this point. The discussion is also limited to the cases in which chemical reactions are absent.

As is the case for ultrasonic wave absorption and dispersion, the generalized hydrodynamic equations presented in (4.26)–(4.28) and (4.50)–(4.53) in Chap. 4 are the basis of the theory of shock wave propagation in diatomic fluids. However, to study the topic of interest in this section, we assume the closure relations,

$$\begin{aligned}\psi^{(1)} &= \psi^{(2)} = 0, \\ \mathbf{Q}_r &= \frac{C_{\text{rot}}}{C_v} \mathbf{Q},\end{aligned}\tag{5.32}$$

and that the rotational angular momentum relaxes so fast that its evolution can be ignored. We will also employ the adiabatic approximation for nonconserved variables such as the stress tensor and heat flux—which is tantamount to the assumption that on the timescale for variation of conserved variables,

the nonconserved variables are at a steady state in the moving coordinate system. We consider a one-dimensional shock wave, which is directed along the  $x$  axis in the suitably fixed coordinate system.

### 5.2.1 Steady Generalized Hydrodynamic Equations

Under the aforementioned conditions, flow velocity has only the  $x$  component which is denoted by  $u$ . Then the generalized hydrodynamic equations for the steady shock wave are given by [21, 22]

$$\frac{d}{dx} \rho u = 0, \quad (5.33)$$

$$\frac{d}{dx} (\rho u^2 + p + \Delta + \Pi_{xx}) = 0, \quad (5.34)$$

$$\frac{d}{dx} \left[ \rho u \left( \mathcal{E} + \frac{1}{2} u^2 \right) + u (p + \Delta + \Pi_{xx}) + Q_x \right] = 0, \quad (5.35)$$

$$\frac{4}{3} p \partial_x u + \frac{4}{3} \Pi_{xx} \partial_x u + \frac{4}{3} \Pi_{xx} \partial_x u + \frac{p}{\eta_0} \Pi_{xx} q(\kappa) = 0, \quad (5.36)$$

$$\begin{aligned} Q_x \partial_x u + (\Pi_{xx} + \Delta) u \partial_x u + \hat{h} (\Pi_{xx} + \Delta) \partial_x \ln T \\ + \hat{h} p \partial_x \ln T + \frac{\hat{h} p}{\lambda_0} Q_x q(\kappa) = 0, \end{aligned} \quad (5.37)$$

$$\left( \Pi_{xx} + \Delta + \frac{1}{3} p \right) \partial_x u + \frac{p}{3 \eta_b} \Delta q(\kappa) = 0, \quad (5.38)$$

where for the flow configuration under consideration

$$\begin{aligned} q(\kappa) &= \frac{\sinh \kappa}{\kappa}, \\ \kappa &= \frac{(m k_B T)^{1/4}}{\sqrt{2} p d} \left( \frac{1}{2 \eta_0} \Pi_{xx}^2 + \frac{\hat{C}_{\text{rot}}}{C_v \eta_b} \Delta^2 + \frac{1}{\lambda_0} Q_x^2 \right)^{1/2}. \end{aligned} \quad (5.39)$$

Equations (5.33)–(5.35) are the steady-state balance equations for mass density, momentum, and energy, whereas (5.36)–(5.38) are the constitutive equations for shear stress, heat flux, and excess normal stress. Here, pressure is given by the ideal gas equation of state,

$$p = \rho \mathcal{R} T \quad (5.40)$$

and the internal energy by the caloric equation of state,

$$\mathcal{E} = \frac{5}{2} \mathcal{R} T, \quad (5.41)$$

where  $\mathcal{R}$  is the gas constant per unit mass. The linear transport coefficients  $\eta_0$ ,  $\lambda_0$ , and  $\eta_b^0$  can be calculated from the formulas in the previous chapter

[see (4.68)–(4.70)] if the scattering cross section is known as a function of energy and scattering angles. Because there is no analytic form for it known at present, to solve the shock wave equations (5.33)–(5.38) suitable forms must be assumed for them. One may pattern them after the Sutherland model for transport coefficients [13].

Integrating the balance equations (5.33)–(5.35), we obtain

$$\rho u = M, \quad (5.42)$$

$$\rho u^2 + p + \Delta + \Pi_{xx} = P, \quad (5.43)$$

$$2\rho u \left( \mathcal{E} + \frac{1}{2}u^2 \right) + 2u(p + \Delta + \Pi_{xx}) + 2Q_x = Q, \quad (5.44)$$

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. Since it is convenient to work with dimensionless equations the following dimensionless variables are defined:

$$\begin{aligned} v &= uMP^{-1}, \theta = \mathcal{R}TM^2P^{-2}, \phi = pP^{-1}, r = \rho PM^{-2}, \\ \sigma &= \Pi_{xx}P^{-1}, \varphi = Q_xQ^{-1}, \psi = \Delta P^{-1}, \alpha = MQP^{-2}. \end{aligned} \quad (5.45)$$

The reduced distance is given by  $\xi = xl^{-1}$  where the length scale is provided by the mean free path  $l$  defined by

$$l = \frac{\eta_{01}}{\rho_1 u_r}. \quad (5.46)$$

In this expression and henceforth, the subscript 1 refers to upstream, whereas downstream will be designated by subscript 2; therefore,  $\rho_1$  is the upstream density and  $\eta_{01}$  is the upstream Newtonian viscosity at the upstream temperature  $T_1$ ;  $u_r$  is the reference speed which is taken as the sound speed in the upstream, and so on. Therefore, if the constants  $M$  and  $P$  are specifically chosen so that  $M = \rho_1 u_r$  and  $P = \rho_1 u_r^2 \equiv p_r$ , then

$$r = \frac{\rho}{\rho_1}, \quad v = \frac{u}{u_r}, \quad \phi = \frac{p}{p_r}. \quad (5.47)$$

Furthermore, if we choose

$$Q = \frac{\lambda_{01}\Delta_r}{T_1 l} \quad (\Delta_r = T_r - T_1) \quad (5.48)$$

and

$$\lambda_{01} = \rho_1 u_r^3 l, \quad (5.49)$$

where  $T_r$  is a reference temperature which may be taken as the temperature at the transition point, then  $Q$  may be written as

$$Q = \rho_1 u_r^3 \frac{\Delta_r}{T_1}. \quad (5.50)$$

Thus  $Q$  may be regarded as ballistic energy transport under the temperature difference  $\Delta_r$ .

The transport coefficients  $\eta_0$ ,  $\eta_b^0$ , and  $\lambda_0$  are reduced with respect to the upstream transport coefficients  $\eta_{01}$  and  $\lambda_{01}$ , respectively

$$\eta^* = \frac{\eta_0}{\eta_{01}}, \quad \eta_b^* = \frac{\eta_b^0}{\eta_{01}}, \quad \lambda^* = \frac{\lambda_0}{\lambda_{01}}. \quad (5.51)$$

With the reduced variables, the equation of state, the balance equations (5.42)–(5.44), and the constitutive equations (5.36)–(5.38) may be cast into six equations with six variables  $\phi, \theta, v, \sigma, \varphi$ , and  $\psi$ :

$$\phi v = \theta, \quad (5.52)$$

$$v + \phi + \sigma + \psi = 1, \quad (5.53)$$

$$v^2 + 7\theta + 2\sigma v + 2\psi v + 2\alpha\varphi = \alpha, \quad (5.54)$$

$$\frac{1}{\eta^*} \phi \sigma q(\kappa) + \frac{4}{3} (\sigma + \psi + \phi) \partial_\xi v = 0, \quad (5.55)$$

$$\frac{\alpha\beta}{\lambda^*} \theta \varphi \phi q(\kappa) + (\alpha\varphi + v\sigma + v\psi) \partial_\xi v + \frac{7}{2} \theta (\phi + \sigma + \psi) \partial_\xi \ln \theta = 0, \quad (5.56)$$

$$\frac{1}{\eta_b^*} \phi \psi q(\kappa) + \left( \sigma + \psi + \frac{1}{3} \phi \right) \partial_\xi v = 0. \quad (5.57)$$

Here, the new dimensionless parameter  $\beta$  is defined by

$$\beta = \frac{N_{\text{Pr}}}{\theta_1} \quad (5.58)$$

with  $\theta_1$  denoting the reduced upstream temperature and  $N_{\text{Pr}}$  the Prandtl number defined with the upstream quantities

$$N_{\text{Pr}} = \left( \frac{C_p}{C_v} \right) f_{\text{E}}^{-1}. \quad (5.59)$$

In this formula  $f_{\text{E}}$  is the Eucken number [13] defined for a diatomic gas as

$$f_{\text{E}} = \frac{5}{2} \frac{C_{\text{tr}}}{C_v} + \frac{C_{\text{rot}}}{C_v}, \quad (5.60)$$

where  $C_{\text{tr}}$  is the translational part of  $C_v$ . The Eucken number is usually temperature and density dependent. However, we will assume that it is a constant. Therefore,  $N_{\text{Pr}} = 14/19$  for a rigid diatomic gas.

The Rayleigh dissipation function  $\kappa^2$  is reduced as follows:

$$\kappa = N_M \pi^{1/4} \sqrt{\frac{\gamma_0}{2}} \frac{\theta^{1/4}}{\phi \sqrt{\eta^*}} \left( \sigma^2 + \frac{4}{5} \frac{\eta^*}{\eta_b^*} \psi^2 + 2\varepsilon \frac{\eta^*}{\lambda^*} \varphi^2 \right)^{1/2}, \quad (5.61)$$

where

$$\varepsilon = \frac{49}{24} \sqrt{\frac{\pi \gamma_0}{2}} N_M \left[ 1 - 25 \left( \frac{N_M^2 - 1}{7N_M^2 + 5} \right)^2 \right], \quad (5.62)$$

$\gamma_0$  is the polytropic ratio defined by  $\gamma_0 = C_p/C_v$ , and  $N_M$  is the upstream Mach number defined by

$$N_M = \frac{u_1}{\sqrt{\frac{7}{5} \mathcal{R} T_1}}. \quad (5.63)$$

Therefore, the parameter  $\alpha$  is related to  $N_M$  as follows:

$$N_M = \sqrt{\frac{1 + \frac{1}{7}\mu}{1 - \frac{1}{5}\mu}}, \quad (5.64)$$

where

$$\mu = \sqrt{49 - 24\alpha}. \quad (5.65)$$

The parameter  $\mu$  ranges from 0 to 5 at which  $N_M = \infty$ . Therefore,  $\alpha = 1$  at  $N_M = \infty$ .

The boundary conditions for the differential equations (5.55)–(5.57) can be determined upon observing that  $\sigma \rightarrow 0$  and  $\varphi \rightarrow 0$  as  $\xi \rightarrow \pm\infty$ . Because (5.55) and (5.56) are identically satisfied in the limits if  $v$  and  $\theta$  become independent of  $\xi$  at the boundaries, as  $\xi \rightarrow \pm\infty$ ,

$$\sigma, \varphi, \psi \rightarrow 0, \quad (5.66)$$

$$\theta = \phi v, \quad (5.67)$$

$$v + \phi = 1, \quad (5.68)$$

$$v^2 + 7\theta = \alpha. \quad (5.69)$$

Solving these algebraic equations yields the boundary conditions

$$v = \frac{1}{12} (7 \pm \mu), \quad (5.70)$$

$$\phi = \frac{1}{12} (5 \mp \mu), \quad (5.71)$$

$$\theta = \frac{1}{144} (7 \pm \mu) (5 \mp \mu). \quad (5.72)$$

The upper sign is for upstream and the lower sign is for downstream. On account of the equation of state, the reduced densities at the boundaries are given by

$$r = \frac{12}{7 \pm \mu}. \quad (5.73)$$

With these boundary conditions, the differential equations (5.55)–(5.57) can be solved.

### 5.2.2 Differential Equations for Reduced Velocity and Temperature

With the help of (5.52)–(5.57), the reduced excess normal stress  $\psi$  can be calculated as a function of only  $v$  and  $\theta$ :

$$\psi = \frac{(1 - v - 2\theta/3v)(1 - v - \theta/v)}{\left[\frac{4}{3}(\eta^*/\eta_b^*)(1 - v) + (1 - v - 2\theta/3v)\right]}. \quad (5.74)$$

Eliminating variables other than  $v$  and  $\theta$ , the differential equations (5.55) and (5.56) may be cast into a pair of ordinary differential equations

$$\frac{dv}{d\xi} = \frac{3\theta}{4\eta^*v^2(1-v)}(v^2 - v + \theta + v\psi)q(\kappa), \quad (5.75)$$

$$\begin{aligned} \frac{d\theta}{d\xi} = & -\frac{\theta}{7v^2(1-v)^2} \left[ \frac{3(\alpha - v^2 - 7\theta)(v^2 - v + \theta)}{4\eta^*} \right. \\ & \left. + \frac{\beta\theta v(1-v)(\alpha + v^2 - 5\theta - 2v)}{\lambda^*} + \frac{3(\alpha - v^2 - 7\theta)v\psi}{4\eta^*} \right] q(\kappa). \end{aligned} \quad (5.76)$$

These evolution equations for reduced velocity and temperature can be solved for shock profiles, subject to the boundary conditions in (5.70)–(5.73). They generalize the evolution equations for  $v$  and  $\theta$  in the Navier–Stokes–Fourier theory [8, 23] of shock wave propagation and also those in the generalized hydrodynamic theory of one-dimensional shock waves for monatomic gases [22]. These equations for reduced velocity and temperature show that transport coefficients are directly related to the velocity and temperature, and hence the measurements of velocity and temperature profiles can yield information on the linear and nonlinear transport coefficients of the fluid. Examination of the directional fields of the pair of differential equations for  $v$  and  $\theta$  shows that shock solutions for the pair exist for all Mach numbers. Therefore, the generalized hydrodynamic equations employed are capable of describing shock wave propagation in the diatomic fluid under consideration over the entire regime of Mach number.

### 5.2.3 Shock Wave Structure

The shock wave structure can be effectively characterized by the shock width, which is defined by

$$\delta = \frac{n_2 - n_1}{(dn/dz)_{\max}}. \quad (5.77)$$

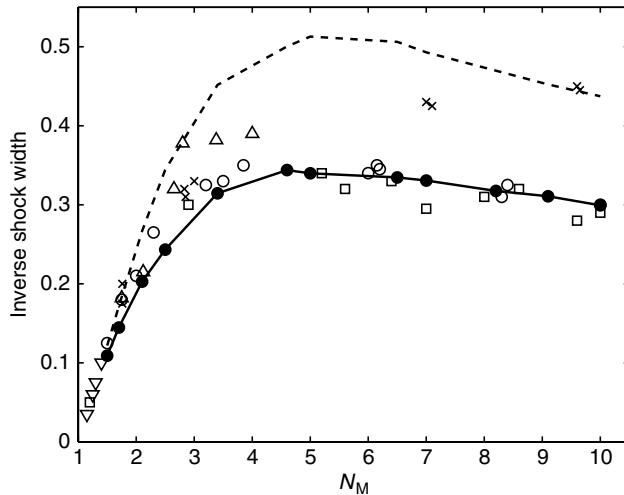
Here  $\delta$  is the inverse shock width;  $n_1$  and  $n_2$  refer to the upstream and downstream densities, respectively; and  $z = x/l_1$ , where  $l_1$  is the upstream mean free path defined with the upstream velocity instead of the upstream sound

speed. The origin of the coordinate system is fixed at the point where the density derivative is maximum. This point corresponds to the inflection point in the density profiles.

Solving the differential equations (5.75) and (5.76) numerically, subject to the boundary conditions mentioned earlier, the density profiles and the profiles of other flow variables can be computed as functions of the Mach number, and the inverse shock width in particular can be calculated. For this purpose, the linear transport coefficients are modeled after the Sutherland model [13] in the forms

$$\eta^* = \left( \frac{\theta}{\theta_1} \right)^{0.78}, \quad \eta_b^* = \frac{2}{3} \eta^*, \quad \lambda^* = \left( \frac{\theta}{\theta_1} \right)^{1.78}. \quad (5.78)$$

These forms facilitate the numerical solutions of the differential equations. Otherwise, the kinetic theory formulas for the transport coefficients (4.68)–(4.70) must be computed over a wide temperature range. Because of the complexity of computing the scattering cross sections involved, it becomes an extremely laborious procedure. For this reason, it has not been implemented for the present shock structure study. The model assumed for the transport coefficients makes it possible to avoid the practical difficulty mentioned. The present discussion, at least, illustrates how information on transport coefficients and relaxation processes in nonsimple fluids can be extracted from measurements of shock wave structures in such fluids. In Fig. 5.4, the inverse



**Fig. 5.4.** Inverse shock width vs. Mach number. The *solid curve* connects the theoretical values (*filled circles*) to guide the eyes, and the *broken curve* is the prediction by the Navier–Stokes theory. Other symbols are experimental data. [Reproduced with permission from Mazen Al-Ghoul and Byung Chan Eu, Phys. Rev. Lett. **86**, 4294 (2001). Copyright 2001 American Physical Society.]

shock width is plotted against the Mach number, and the theoretical results are compared with the experimental values for various diatomic fluids. The *filled circles* ( $\bullet$ ) are theoretical values for the inverse shock width predicted by the present generalized hydrodynamic theory, and the *broken curve* is the prediction by the Navier–Stokes theory, which yields values much too large if the Mach number  $N_M$  exceeds approximately 1.5. Other symbols are experimental data:  $\nabla$  by Greene and Hornig [16];  $\Delta$  by Linzer and Hornig [24];  $\square$  by Camac [25];  $\times$  by Robben and Talbot [26]; and  $\circ$  by Alsmeyer [27]. The present theory is capable of predicting the shock structures beyond  $N_M = 10$ , but because no experimental data are available for  $N_M \geq 10$ , a comparison of theory with experiment is not feasible in the region.

In summary of this chapter, we have seen how classical kinetic theory can give rise to generalized hydrodynamic equations, which have been made consistent with the laws of thermodynamics, and they can be used to extract information on transport coefficients from ultrasonic wave propagation and also shock wave propagation in nonsimple gases. Inversely, if transport coefficients are calculated from the kinetic theory formulas in generalized hydrodynamic equations, then ultrasonic and shock wave propagation phenomena in nonsimple fluids can be predicted on the basis of the kinetic theory. We note that the generalized hydrodynamic equations underlying the present theory can be numerically solved by the numerical code developed and available in the literature [28] and the flow characteristics can be computed with the solutions. Information on linear and nonlinear transport coefficients can be thereby extracted with the help of relevant experimental data.

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## **Part II**

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### **Transport Coefficients of Liquids**

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## Equation of State and Equilibrium Properties of Liquids

We have seen in the previous chapters devoted to dilute gases that transport properties are expressed in terms of collision bracket integrals, which are equilibrium ensemble averages of moments weighted by the collision cross section of bimolecular collisions. However, the equilibrium ensemble distribution function is Maxwellian because the gas is dilute, and also the equation of state involved is that of an equilibrium ideal fluid, the ideal gas equation of state. Therefore, we see that, although the transport coefficients, are physical quantities pertaining to systems in nonequilibrium states, they can be obtained if equilibrium ensemble averages of dynamic observables—the collision cross section and moments representative of dynamic events—are calculated with the help of the equation of state of the gas in equilibrium. This characteristic feature of using an equilibrium distribution function and the equilibrium equation of state remains unchanged, even if the fluid is not a dilute gas but a liquid. However, the equilibrium ensemble distribution function involved is no longer Maxwellian but that of interacting molecules. Neither is the equation of state that of an ideal gas made up of noninteracting molecules, but for molecules that are interacting and correlated in space. Therefore, we will find that the calculation of the transport coefficients of dense gases and liquids requires the equilibrium pair correlation functions and the equation of state of interacting molecules.

For this reason, if we are to implement a proper kinetic theory of transport processes in dense gases and liquids, it is essential to pay attention to and develop methods for calculating equilibrium properties of dense gases and liquids and, in particular, equilibrium pair correlation functions and the equation of state because they are indispensable components of the theory. They will be the subject of discussion in this chapter as an important preparation for calculating transport coefficients of dense gases and liquids. The discussion, however, will be limited to the topics that are indispensable for calculating transport coefficients because equilibrium statistical mechanics is wide in scope and therefore cannot be covered in a limited space which this monograph has for the subject.

## 6.1 Virial Equation of State

Consider a monatomic (simple) fluid consisting of  $N$  molecules contained in volume  $V$  at temperature  $T$ . The molecules are assumed to interact through pairwise additive potentials, such as the Lennard-Jones interaction potential. The pairwise additivity of potential energies is not essential for the present theory, but the formalism becomes simpler if it is assumed. The theory can be easily generalized to include three-body interaction potentials, for example.

The equation of state under the assumption is then given by the expression [1, 2]

$$\frac{p\beta}{n} = 1 - \frac{2\pi}{3}\beta n \int_0^\infty dr r^3 \frac{du(r)}{dr} \exp[-\beta u(r)] y(r, n, \beta), \quad (6.1)$$

where  $p$  is the pressure,  $n$  is the number density,  $\beta = 1/k_B T$ ,  $u(r)$  is the intermolecular potential, and  $y(r, n, \beta)$  is the cavity function defined by its relation to the pair correlation function  $g(r, n, \beta)$

$$y(r, n, \beta) = \exp[\beta u(r)] g(r, n, \beta). \quad (6.2)$$

This statistical mechanics formula for pressure is called the virial equation of state. It is exact for the pairwise additive potential assumed and often is the starting point for numerous theoretical studies in equilibrium statistical mechanics. Given the intermolecular potential, if the pair correlation function or the cavity function is known for a fluid, then the equation of state can be calculated at every value of  $n$  and  $\beta$ . For normal states of fluids, the pair correlation function is routinely computed by Monte Carlo simulation methods [3] at present. There are also some well-developed approximation methods based on integral equation theories [4] for the pair correlation function, which even give analytic equations of state [5, 6, 9, 10] if the interaction potential is of hard spheres. However accurately the virial equation of state may be computable by simulation methods, it is not suitable for developing a statistical mechanical theory of transport coefficients for liquids that takes the effects of excluded volume into consideration because then the excluded volume effects must be calculated as accurately as possible to achieve the desired aim. But the virial form (6.1) is unsuitable for calculating the excluded volume. It does not even enable us to define it properly if the form given in (6.1) is used.

## 6.2 Generic van der Waals Equation of State

Well before the virial expansion for the equation of state for real fluids was proposed by Kammerlingh-Onnes [11] and its statistical mechanical derivation from the virial equation of state (6.1) was given by later workers [12, 13] in statistical mechanics, van der Waals [14] in 1873 obtained the celebrated equation of state named after him on the basis of heuristic arguments:

$$(p + an^2)(1 - bn) = nk_B T, \quad (6.3)$$

where  $a$  and  $b$  are the van der Waals parameters, which are independent of density and temperature. In particular,  $nb$  is the measure of excluded volume attributable to the finite size of the molecule. Careful studies, however, have shown that  $b$  is not a reliable measure for the excluded volume of a fluid. The correct measure of excluded volume has been elusive in thermodynamics and statistical mechanics, although excluded volume plays an important role in understanding the structure of fluids at high density, as will be seen later in this work. Science historians [15, 16] report that van der Waals himself labored unsuccessfully for many years to calculate accurately the excluded volume. Despite this difficulty and some glaring defects in describing critical and subcritical behavior of fluids, the van der Waals equation of state has been a powerful influence in the thermodynamics of fluids ever since its inception. Much effort has been expended to derive it exactly by using methods of statistical mechanics, but it has not been possible to derive it rigorously from statistical mechanics. There cannot be an exact derivation of it by statistical mechanics, and there is an important reason for it, as will be shown shortly.

### 6.2.1 A Potential with a Hard Core

The van der Waals equation of state presumes the existence of a hard core for the molecule and an attractive potential operating in the range of distance beyond the hard core. To be consistent with this picture of intermolecular interaction potential, let us assume that the potential energy has the form

$$\begin{aligned} u(r) &= u_h(r) + u_a(r), \\ u_h(r) &= \infty \quad \text{for } r \leq \sigma \\ &= 0 \quad \text{for } r > \sigma, \\ u_a(r) &= 0 \quad \text{for } r \leq \sigma \\ &= w(r) \quad \text{for } r > \sigma, \end{aligned} \tag{6.4}$$

where  $w(r)$  is a negative function of  $r$  that vanishes as  $r^{-m}$  ( $m \geq 4$ ) as  $r \rightarrow \infty$ . The required asymptotic behavior of  $w(r)$  ensures convergence of the integral in the virial equation of state. Then the virial equation of state can be written in the form

$$\frac{\beta p}{n} = 1 + \frac{2\pi\sigma^3}{3} ny(\sigma, n, \beta) + \frac{2\pi}{3} n \int_{\sigma}^{\infty} dr r^3 y(r, n, \beta) \frac{d}{dr} f(r) \tag{6.5}$$

where  $f(r)$  is the Mayer function defined by

$$f(r) = \exp[-\beta u_a(r)] - 1. \tag{6.6}$$

In the integration range of the integral in (6.5), the potential energy  $u_a(r)$  in the Mayer function may be replaced by  $w(r)$ , the attractive potential, if the potential model (6.4) is employed.

Define the following functions of density and temperature

$$A(n, \beta) = -\frac{2\pi}{3\beta} \int_{\sigma}^{\infty} dr r^3 y(r, n, \beta) \frac{d}{dr} f(r), \quad (6.7)$$

$$B(n, \beta) = \frac{(2\pi/3) \int_0^{\sigma} dr r^3 y(r, n, \beta) \frac{d}{dr} f(r)}{1 + (2\pi/3) n \int_0^{\sigma} dr r^3 y(r, n, \beta) \frac{d}{dr} f(r)}. \quad (6.8)$$

Upon using these definitions of parameters  $A$  and  $B$ , the virial equation of state (6.5) can be rearranged to the form [17]

$$[p + A(n, \beta) n^2] [1 - B(n, \beta) n] = n k_B T, \quad (6.9)$$

which is formally isomorphic to the van der Waals equation of state (6.3). It must be emphasized that this form of the equation of state is as exact as the virial form (6.5). As will be shown shortly, if the density is sufficiently low and the temperature is sufficiently high, the parameters  $A$  and  $B$  approach the van der Waals parameters  $a$  and  $b$ , respectively, and hence the form in (6.9) tends to the van der Waals equation of state. For this reason, (6.9) is called the generic van der Waals (GvdW) equation of state,<sup>1</sup> and the parameters  $A$  and  $B$  are the generic van der Waals (GvdW) parameters. We now see clearly that the van der Waals equation of state cannot follow from the virial equation of state (6.5) unless some approximations are made for the derivation, and it explains why numerous previous attempts at exact derivation of the van der Waals equation of state have failed.

If the potential is simply hard instead of having a repulsive soft core for  $r < \sigma$ , then GvdW parameter  $B$  must be modified to the form

$$B(n, \beta) = \frac{(2\pi\sigma^3/3) y(\sigma, n, \beta)}{1 + (2\pi\sigma^3/3) ny(\sigma, n, \beta)}. \quad (6.10)$$

For a  $c$ -component mixture, the equation of state can be expressed in canonical form if the GvdW parameters are defined by [18]

$$A = \sum_{i,j=1}^c A_{ij}(n, \beta) X_i X_j, \quad (6.11)$$

$$B = \sum_{i,j=1}^c B_{ij}(n, \beta) X_i X_j \left[ 1 + n \sum_{i,j=1}^c B_{ij}(n, \beta) X_i X_j \right]^{-1}, \quad (6.12)$$

where  $X_{\alpha}$  ( $\alpha = i, j$ ) is the mole fraction of species  $\alpha$  and

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<sup>1</sup> Previously, it was proposed to call it the canonical equation of state because it is a canonical form. All equations of state for fluids that have attractive and repulsive parts in intermolecular potential energy can be put into the form of the GvdW equation of state. We propose to use this terminology henceforth for the brevity of the term.

$$A_{ij}(n, \beta) = -\frac{2\pi}{3\beta} \int_{\sigma_{ij}}^{\infty} dr r^3 y_{ij}(r, n, \beta) \frac{d}{dr} f_{ij}(r), \quad (6.13)$$

$$B_{ij}(n, \beta) = \frac{2\pi}{3} \int_0^{\sigma_{ij}} dr r^3 y_{ij}(r, n, \beta) \frac{d}{dr} f_{ij}(r), \quad (6.14)$$

with the definition of Mayer function

$$f_{ij}(r) = \exp[-\beta u_{ij}(r)] - 1 \quad (6.15)$$

and  $\sigma_{ij}$  denoting the contact distance between molecules of species  $i$  and  $j$ . This shows that the canonical equation of state (6.9) follows from the virial equation of state as long as the potential energy has positive repulsive and negative attractive parts. This further reinforces the notion that (6.9) is the canonical form for the equation of state of matter.

### 6.2.2 A Square-Well Potential

Square-well (SW) potentials are simple to use and sometime yield some insightful theoretical results, although they require care in application because of their inherent discontinuity. We will apply them to examine the canonical equation of state derived by using the potential model (6.4) given in the previous subsection. We assume the square-well potential

$$u(r) = u_h(r) + u_a(r)$$

with the hard core ( $u_h$ ) and attractive ( $u_a$ ) parts of the potential given by

$$\begin{aligned} u_h(r) &= \infty \quad \text{for } r \leq \sigma \\ &= 0 \quad \text{for } r > \sigma, \\ u_a(r) &= 0 \quad \text{for } r \leq \sigma \\ &= -\varepsilon \quad \text{for } \lambda > r > \sigma, \\ &= 0 \quad \text{for } r > \lambda, \end{aligned} \quad (6.16)$$

where  $\varepsilon$  and  $\lambda$  are the well depth and width of the attractive potential, respectively.

Because this potential model (6.16) yields the Mayer function in the form

$$\begin{aligned} f(r) &= -1 \quad \text{for } r < \sigma \\ &= \exp(\beta\varepsilon) - 1 \quad \text{for } \sigma < r < \lambda \\ &= 0 \quad \text{for } \lambda < r, \end{aligned} \quad (6.17)$$

it is convenient for performing computation to express this form of Mayer function in terms of Heaviside step functions

$$f(r) = 1 - \theta(r - \sigma) + [\exp(\beta\varepsilon) - 1] [\theta(r - \sigma) - \theta(r - \lambda)]. \quad (6.18)$$

Here,  $\theta(x)$  is the Heaviside step function defined by

$$\begin{aligned} \theta(x) &= 1 \quad \text{for } x > 0 \\ &= 0 \quad \text{for } x < 0. \end{aligned} \quad (6.19)$$

Because

$$\frac{d}{dr} f(r) = -\delta(r - \sigma) + [\exp(\beta\varepsilon) - 1] [\delta(r - \sigma) - \delta(r - \lambda)], \quad (6.20)$$

the virial equation of state for the SW potential is given by the expression

$$\begin{aligned} \frac{\beta p}{n} &= 1 + \frac{2\pi\sigma^3}{3} ny(\sigma, n, \beta) + \frac{2\pi\sigma^3}{3} n [\exp(\beta\varepsilon) - 1] \\ &\quad \times [y(\sigma, n, \beta) - \gamma^3 y(\lambda, n, \beta)], \end{aligned} \quad (6.21)$$

where  $\gamma = \lambda/\sigma$  is the range of the potential well reduced by the diameter  $\sigma$  of the hard core of the molecule. This form of equation of state may be easily put into the canonical form, and the GvdW parameters  $A$  and  $B$  are given by the expressions [17]

$$A(n, \beta) = \frac{2\pi\sigma^3}{3\beta} (\exp(\beta\varepsilon) - 1) [\gamma^3 y(\lambda, n, \beta) - y(\sigma, n, \beta)], \quad (6.22)$$

$$B(n, \beta) = \frac{(2\pi\sigma^3/3) y(\sigma, n, \beta)}{1 + (2\pi\sigma^3/3) ny(\sigma, n, \beta)}. \quad (6.23)$$

Because of the hard core, the GvdW parameter  $B$  has the same form as the expression in (6.8). These GvdW parameters for the SW potential model will be useful for studies of transport properties of liquids and, in particular, of supercooled liquids; see, for example, [19].

Because the GvdW parameters  $A$  and  $B$  in the SW potential model become fairly simple, they enable us to examine their limiting behavior in a definite manner. It is easy to deduce that the cavity function tends to unity as the density of the fluid decreases. Thus we obtain the limiting behavior of  $A$  and  $B$

$$\begin{aligned} \lim_{n \rightarrow 0} A(n, \beta) &= \frac{2\pi\sigma^3}{3\beta} (\exp(\beta\varepsilon) - 1) (\gamma^3 - 1) \\ &= \frac{2\pi\sigma^3}{3} (\gamma^3 - 1) \varepsilon [1 + O(\varepsilon\beta)], \end{aligned} \quad (6.24)$$

$$\lim_{n \rightarrow 0} B(n, \beta) = \frac{2\pi\sigma^3}{3}. \quad (6.25)$$

Because the volume of the hard sphere is

$$v_0 = \frac{\pi\sigma^3}{6},$$

the limiting value of  $B$  is easily identified with the van der Waals covolume

$$b = 4v_0, \quad (6.26)$$

whereas the limiting value of  $A$  to the lowest order in  $\varepsilon\beta$  may be identified with the van der Waals parameter  $a$ :

$$a = 4v_0 (\gamma^3 - 1) \varepsilon. \quad (6.27)$$

This clearly indicates that the van der Waals parameter  $a$  is directly related to the attractive potential energy. The identification here of the van der Waals parameters  $a$  and  $b$  clearly shows why rigorous derivation of the van der Waals equation of state from Gibbsian statistical mechanics has not been possible; the van der Waals equation of state is an approximate form that can be obtained only if suitable approximations are made to the canonical form of equation of state (6.9), which is a rigorous result of Gibbsian statistical mechanics for the potential model assumed. A rigorous derivation of an approximate equation is an oxymoron.

For completeness, we present the GvdW parameters for mixtures obeying the square-well models for interaction potentials

$$u_{ij}(r) = u_{ij}^{(h)}(r) + u_{ij}^{(a)}(r), \quad (6.28)$$

where the repulsive and attractive parts are defined by

$$\begin{aligned} u_{ij}^{(h)}(r) &= \infty \quad \text{for } r \leq \sigma_{ij} \\ &= 0 \quad \text{for } r > \sigma_{ij}, \end{aligned} \quad (6.29)$$

$$\begin{aligned} u_{ij}^{(a)}(r) &= 0 \quad \text{for } r \leq \sigma_{ij} \\ &= -\varepsilon_{ij} \quad \text{for } \lambda_{ij} > r > \sigma_{ij}, \\ &= 0 \quad \text{for } r > \lambda_{ij}. \end{aligned} \quad (6.30)$$

Then because

$$\frac{d}{dr} f_{ij}(r) = -\delta(r - \sigma_{ij}) + [\exp(\beta\varepsilon_{ij}) - 1] [\delta(r - \sigma_{ij}) - \delta(r - \lambda_{ij})],$$

the GvdW parameters for mixtures are easily shown to have the forms

$$A = \sum_{i,j=1}^c A_{ij}(n, \beta) X_i X_j, \quad (6.31)$$

$$B = \sum_{i,j=1}^c B_{ij}(n, \beta) X_i X_j \left[ 1 + n \sum_{i,j=1}^c B_{ij}(n, \beta) X_i X_j \right]^{-1}, \quad (6.32)$$

where

$$A_{ij}(n, \beta) = \frac{2\pi\sigma_{ij}^3}{3\beta} [\exp(\beta\varepsilon_{ij}) - 1] \\ \times [\gamma_{ij}^3 y_{ij}(\lambda_{ij}, n, \beta) - y_{ij}(\sigma_{ij}, n, \beta)], \quad (6.33)$$

$$B_{ij}(n, \beta) = \frac{2\pi\sigma_{ij}^3}{3} y_{ij}(\sigma_{ij}, n, \beta) \quad (6.34)$$

with  $\gamma_{ij} = \lambda_{ij}/\sigma_{ij}$ . If the cavity functions  $y_{ij}(\sigma_{ij}, n, \beta)$  and  $y_{ij}(\lambda_{ij}, n, \beta)$  are evaluated by either simulation methods or integral equations [10, 20, 21] for pair correlation functions, the equation of state given in terms of GvdW parameters may be used for studying the thermodynamics of mixtures in the square-well potential model.

### 6.3 Free Volume

For the first time in the history of science van der Waals [14] used the notion of excluded volume, which was attributed to the inherent molecular structure that results in the repulsive force exerted between molecules. This notion logically gave rise to the concept of free volume. In the van der Waals line of thought, the excluded volume of the fluid is given by  $nb$  in the van der Waals equation of state (6.3). Therefore the free volume is naturally defined by the formula,

$$v_f = v(1 - bn), \quad (6.35)$$

where  $v$  is the specific volume. This definition suggests that the free volume decreases linearly with density and vanishes altogether at a characteristic value of density given by  $b^{-1}$ . It is now well recognized that this behavior of free volume is unsatisfactory as are some other features of the van der Waals theory. According to Levelet-Sengers [16], van der Waals himself made considerable effort to remove the unsatisfactory feature of  $v_f$  but unsuccessfully.

Numerous authors [22–24] in the literature developed free volume theories of the macroscopic properties of matter, but free volume has been a rather elusive quantity to capture quantitatively from the viewpoint of statistical mechanics. For this reason, free volume theories have been reduced to theories laden with empirical parameters, which obscure the physics of liquids, and consequently they have fallen into disuse.

The isomorphism of the canonical equation of state to the van der Waals equation of state and the unambiguous association of the GvdW parameter  $B$  with the hard core of molecules and, more generally, the repulsive potential energy naturally suggests that the mean free volume per molecule of the fluid should be defined by [17]

$$v_f = v[1 - B(n, \beta)n], \quad (6.36)$$

where  $B(n, \beta)$  is defined by (6.8) for fluids with a hard core repulsive potential or by (6.10) for a soft sphere repulsive potential. Because either of the expressions for  $B$  is a rigorous statistical mechanical representation of the GvdW

parameter  $B$ , we now have a rigorous statistical mechanical representation of mean free volume per molecule :

$$v_f = v \left[ 1 + \frac{2\pi}{3} n \int_0^\sigma dr r^3 y(r, n, \beta) \frac{d}{dr} f(r) \right]^{-1} \quad (6.37)$$

for potentials that are repulsive where  $r < \sigma$ . Because the cavity function or the pair correlation function, given the intermolecular potential, can be computed as accurately as possible by computer simulation, the mean free volume of a fluid can be accordingly known accurately as a function of temperature and density. This statistical mechanical representation of the mean free volume per molecule has been made possible because of the canonical equation of state (6.9). Because  $B(n, \beta)$  is density and temperature dependent, the mean free volume is no longer linear with respect to  $n$  in contrast to the van der Waals theory. It can be also a discontinuous function [17, 25, 26] of density if the temperature is below the critical temperature. The statistical mechanical representation of  $v_f$  obtained here will be indispensable in calculating the transport properties of dense gases and liquids later in this work.

#### 6.4 Temperature and Density Dependence of $A$ and $B$

The van der Waals parameters  $a$  and  $b$  are constants independent of density and temperature, as is well known and shown earlier. Their constancy is the principal reason that makes the van der Waals equation of state defective in the critical and subcritical phenomena of fluids. Because it is unrealistic to hope to obtain rigorous closed forms for them by using statistical mechanics methods, it will be practical to develop some useful models for the GvdW parameters  $A$  and  $B$ . Given this motivation, it is logical to investigate their temperature and density dependence by integral equation methods or computer simulation methods, so that we gain some valuable insights into their behavior.

To perform such numerical studies, it is convenient to reduce the variables and equations involved to dimensionless forms. Thus we define reduced variables

$$\begin{aligned} \eta &= v_0 n, & \beta^* &= T^{*-1} = \beta \varepsilon, & p^* &= p v_0 / \varepsilon, \\ A^* &= A / \varepsilon v_0, & B^* &= B / v_0. \end{aligned} \quad (6.38)$$

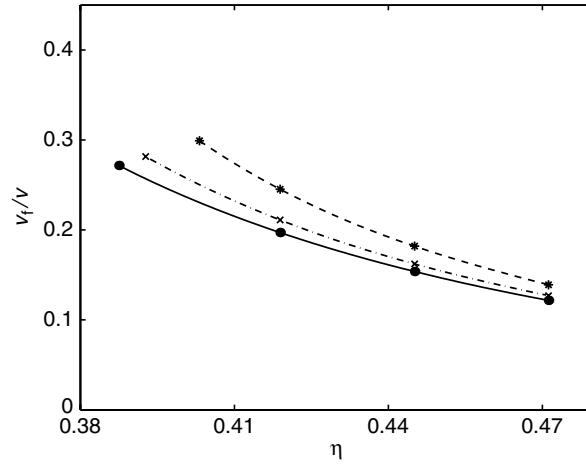
Then the canonical equation of state can be written in the reduced form:

$$(p^* + A^* \eta^2) (1 - B^* \eta) = \eta T^*. \quad (6.39)$$

For example, the GvdW parameters for the SW potential model have the reduced forms,

$$A^*(\eta, \beta^*) = 4\beta^{*-1} \left( e^{\beta^*} - 1 \right) [\gamma^3 y(\gamma, \eta, \beta^*) - y(1, \eta, \beta^*)], \quad (6.40)$$

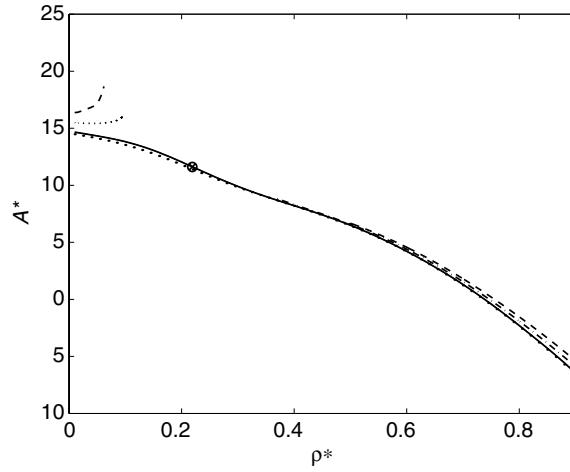
$$B^*(\eta, \beta^*) = \frac{4y(1, \eta, \beta^*)}{1 + 4\eta y(1, \eta, \beta^*)}. \quad (6.41)$$



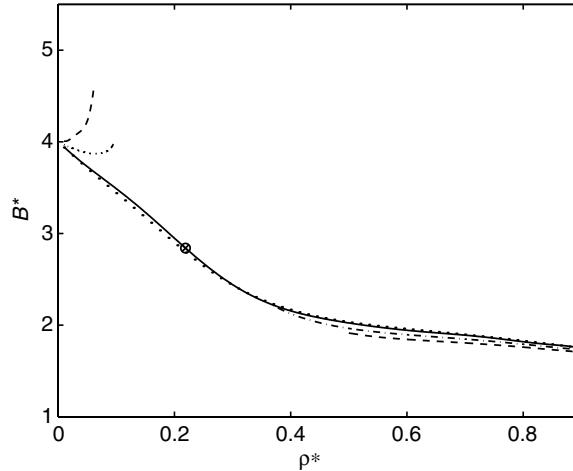
**Fig. 6.1.** Density dependence of mean free volume. The *solid curve* is for  $T^* = 1.25$ ; the *dash-dotted curve* is for  $T^* = 1.1$ ; and the *broken curve* is for  $T^* = 0.9$ . The *broken* and *dash-dotted* curves are for the subcritical regime. [Reproduced with permission from Byung Chan Eu and Kyunil Rah, Phys. Rev. E **63**, 031203 (2001). Copyright 2001 American Physical Society]

The cavity functions in these expressions for  $A^*$  and  $B^*$  can be calculated, for example, from the solutions of the Percus–Yevick (PY) integral equation [20] for the pair correlation function. Such solutions have been obtained for an SW potential, and the cavity functions computed therefrom. As expected, the free volume is nonlinear with respect to  $n$ . The density and temperature dependence of  $v_f/v$  is shown in Fig. 6.1 for  $\gamma = 1.5$  and three different temperatures. Because the critical point is located at  $T_c^* \approx 1.2$ ,  $\eta_c \approx 0.12$ , the free volume is for the liquid phase when  $T^* = 1.1$  and  $\eta_c = 0.9$ .

The calculated temperature and density dependence of  $A^*$  and  $B^*$  show interesting and rather insightful behavior, which can guide us in devising a semiempirical theory of canonical equation of state. The results for the same potential model as that for the free volume shown are given in Figs. 6.2 and 6.3. The numerical results for them indicate that  $A^*$  and  $B^*$  are continuous functions of temperature and density if  $T^* > T_c^*$ , but become discontinuous functions if  $T^* < T_c^*$ ; the GvdW parameters are discontinuous, nonanalytic functions in the subcritical regime of temperature. This is the reflection of the first-order liquid–vapor phase transition that the fluid must undergo as the density changes from the gas regime to the liquid regime, and vice versa, if  $T^* < T_c^*$ . This behavior should be contrasted with the van der Waals parameters  $a$  and  $b$  that remain constant regardless of changes in temperature and density. It is one of the glaring defects of the van der Waals theory.



**Fig. 6.2.**  $A^*$  vs.  $\rho^*$ . The dotted curve is for  $T^* = 1.25$ , the solid curve is for  $T^* = 1.218$ , the dash-dotted curve is for  $T^* = 1.1$ , and the broken curve is for  $T^* = 1.0$ . The last two curves are subcritical and undefined in the interval enclosing the critical point and hence are disjointed. This reflects the discontinuity of subcritical isotherms. The symbol represents the critical point and  $\rho^* = \rho\sigma^3$ . [Reproduced with permission from Byung Chan Eu and Kyunil Rah, Phys. Rev. E **63**, 031203 (2001). Copyright 2001 American Physical Society]



**Fig. 6.3.**  $B^*$  vs.  $\rho^*$ . The meanings of the symbol and curves are the same as those for Fig. 6.2. [Reproduced with permission from Byung Chan Eu and Kyunil Rah, Phys. Rev. E **63**, 031203 (2001). Copyright 2001 American Physical Society]

The points of discontinuity  $\eta_1$  and  $\eta_2$  ( $\eta_1 < \eta_2$ ) are, respectively, a little larger and smaller than the coexisting vapor and liquid density, which appear to be roughly of the same orders of magnitude as the spinodal densities. The appearance of discontinuity in  $A^*$  and  $B^*$  is not unique to the PY integral equation but is present in the other integral equation theories such as the hypernetted chain integral equation [21] and also in computer simulation methods [3]. Besides the discontinuities in  $A^*$  and  $B^*$ , there are some noticeable features present in them. For example, the  $B^*$  curves invariably tend to a nonvanishing asymptote as density increases, which is a manifestation of a hard core. Another feature is that  $A^*$  becomes negative as the density passes a threshold value, say,  $\rho_{\text{th}}^*$ , where  $\rho^* = \sigma^3 n$ . This means that, as molecules in the liquid are packed further and further, the attractive force is gradually overpowered by the repulsive force and eventually rendered impotent. As a consequence, the behavior of  $A^*$  is determined by the repulsive hard core. In such a density regime, the definition of free volume may have to be changed as follows:

$$v_f = v(1 - B_f^* \eta), \quad (6.42)$$

where

$$B_f^* = B^* \left[ \frac{1 + (1 - B^* \eta) \chi_{ab}}{1 + B^* \eta (1 - B^* \eta) \chi_{ab}} \right], \quad (6.43)$$

$$\chi_{ab} = -\frac{A^* \beta^*}{B^*} > 0. \quad (6.44)$$

The corresponding equation of state is then given by

$$p^* (1 - B_f^* \eta) = \eta T^*, \quad (6.45)$$

which is akin to the van der Waals equation of state for a hard sphere fluid.

## 6.5 Model Canonical Equation of State

The numerical study presented in Figs. 6.1–6.3 clearly indicates that the GvdW parameters  $A$  and  $B$  are nonanalytic functions of density and temperature at the critical point and in the subcritical regime of real fluids. Therefore, by incorporating the nonanalyticity into  $A$  and  $B$ , it should be possible to construct a model canonical equation of state that is capable of describing critical and subcritical phenomena. This line of investigation is in the early stage of development, but there is a development [26] well worth discussing here to bring it to the fore.

For the aim in mind, it is useful to employ reduced variables defined relative to the critical parameters  $(p_c^*, \eta_c, T_c^*)$ . Thus we define

$$\phi = \psi - 1, \quad x = y - 1, \quad t = \theta - 1, \quad (6.46)$$

where

$$\psi = \frac{p^*}{p_c^*} = \frac{p}{p_c}, \quad y = \frac{\eta}{\eta_c} = \frac{n}{n_c}, \quad \theta = \frac{T^*}{T_c^*} = \frac{T}{T_c}. \quad (6.47)$$

The relative reduced variables therefore vanish at the critical point by definition. It is also useful to define the dimensionless variables

$$\nu = B_c^* \eta_c, \quad \tau = \frac{A_c^* \eta_c^2}{p_c^*}, \quad \zeta = \frac{\eta_c T_c^*}{p_c^*}, \quad (6.48)$$

where

$$A_c^* = A^*(t = 0, x = 0), \quad B_c^* = B^*(t = 0, x = 0), \quad (6.49)$$

the values of  $A^*$  and  $B^*$  at the critical point. If the GvdW parameters are treated as empirical quantities,  $A_c^*$  and  $B_c^*$  may be chosen as empirical parameters. It is useful to observe that the reduced parameter  $\zeta$  is free of  $A_c^*$  and  $B_c^*$ . The relations in (6.48) may be cast into the forms

$$\eta_c = \frac{\nu}{B_c^*}, \quad p_c^* = \frac{\nu^2 A_c^*}{\tau B_c^{*2}}, \quad T_c^* = \frac{\zeta \nu A_c^*}{\tau B_c^*}, \quad (6.50)$$

which may be compared with the van der Waals theory counterparts

$$(\eta_c)_{\text{vdw}} = \frac{1}{3b^*}, \quad (p_c^*)_{\text{vdw}} = \frac{a^*}{27b^{*2}}, \quad (T_c^*)_{\text{vdw}} = \frac{8a^*}{27b^*}, \quad (6.51)$$

where  $a^* = a/\varepsilon v_0$  and  $b^* = b/v_0$ . According to the limiting behaviors of  $A$  and  $B$  discussed earlier, the constants  $A_c^*$  and  $B_c^*$  are qualitatively comparable to the van der Waals parameters  $a^*$  and  $b^*$ , and the dimensionless parameters  $(\nu, \nu^2/\tau, \zeta\nu/\tau)$  should correspond to the van der Waals theory values  $(1/3, 1/27, 8/27)$ . The former tend to the latter in a special case, as can be shown later. This correspondence suggests the advantage of building a model canonical equation of state on the van der Waals equation of state, which is successful in providing a qualitatively correct theory [27] of critical phenomena. It should be relatively easier to build an improved model on the van der Waals theory if the canonical form is used for the equation of state.

If the aforementioned reduced variables and parameters  $\nu$ ,  $\tau$ , and  $\zeta$  are used, the reduced canonical equation of state takes the reduced form,

$$\left[ 1 + \phi + \tau (1 + x)^2 \mathcal{A}(x, t) \right] \left[ 1 - \nu (1 + x) \mathcal{B}(x, t) \right] = \zeta (1 + x) (1 + t), \quad (6.52)$$

where

$$\mathcal{A} = \frac{A^*}{A_c^*}, \quad \mathcal{B} = \frac{B^*}{B_c^*}. \quad (6.53)$$

If  $\mathcal{A} = \mathcal{B} = 1$ ,  $\nu = 1/3$ ,  $\tau = 3$ , and  $\zeta = 8/3$ , then (6.52) becomes the nondimensionalized van der Waals equation of state

$$\left[ 1 - \frac{1}{3} (1 + x) \right] \left[ 1 + \phi + 3 (1 + x)^2 \right] = \frac{8}{3} (1 + x) (1 + t), \quad (6.54)$$

which is obviously in the corresponding state form.

The spinodal densities are denoted by  $\eta_{sl}$  and  $\eta_{sv}$ , where the subscripts  $l$  and  $v$ , respectively, refer to the liquid and vapor branch. These spinodal

densities are reduced with respect to the critical density  $\eta_c$ :

$$z_k = \frac{\eta_k}{\eta_c} \quad (k = \text{sl, sv}). \quad (6.55)$$

Because the spinodal curve shares the same tangent as the critical isotherm at the critical point, there holds the limit for  $z_k$

$$\lim_{t \rightarrow 0} z_k = 1 \quad (k = \text{sl, sv}). \quad (6.56)$$

Taking into account the discontinuity of  $A^*$  and  $B^*$  in the subcritical regime, the following forms may be assumed for the subcritical GvdW parameters:

$$\begin{aligned} \frac{A^*}{A_c^*} &= \sum_{i=0}^{l_a} a_i^{(\text{sl})}(t) (y - z_{\text{sl}})^i + A_{\text{na}}^{(\text{sl})}(t, y - z_{\text{sl}}) \\ &\quad \text{for } y > z_{\text{sl}}, t \leq 0 \end{aligned} \quad (6.57)$$

$$\begin{aligned} &= \sum_{i=0}^{l_a} a_i^{(\text{sv})}(t) (y - z_{\text{sv}})^i + A_{\text{na}}^{(\text{sv})}(t, z_{\text{sv}} - y) \\ &\quad \text{for } y < z_{\text{sv}}, t \leq 0, \end{aligned}$$

$$\begin{aligned} \frac{B^*}{B_c^*} &= \sum_{i=0}^{l_b} b_i^{(\text{sl})}(t) (y - z_{\text{sl}})^i + B_{\text{na}}^{(\text{sl})}(t, y - z_{\text{sl}}) \\ &\quad \text{for } y > z_{\text{sl}}, t \leq 0 \end{aligned} \quad (6.58)$$

$$\begin{aligned} &= \sum_{i=0}^{l_b} b_i^{(\text{sv})}(t) (y - z_{\text{sv}})^i + B_{\text{na}}^{(\text{sv})}(t, z_{\text{sv}} - y) \\ &\quad \text{for } y < z_{\text{sv}}, t \leq 0, \end{aligned}$$

where  $a_i^{(k)}$  and  $b_i^{(k)}$  ( $k = \text{sl, sv}$ ) are temperature-dependent parameters such that the liquid and vapor branches of the coefficients coincide with each other at the critical temperature:

$$\begin{aligned} a_i^{(\text{sl})}(0) &= a_i^{(\text{sv})}(0) \equiv a_i \neq 0, & b_i^{(\text{sl})}(0) &= b_i^{(\text{sv})}(0) \equiv b_i \neq 0, \\ \lim_{t \rightarrow 0} a_0^{(k)}(t) &= 1 \quad (k = \text{sl, sv}), & \lim_{t \rightarrow 0} b_0^{(k)}(t) &= 1 \quad (k = \text{sl, sv}). \end{aligned} \quad (6.59)$$

The terms  $A_{\text{na}}^{(k)}$  and  $B_{\text{na}}^{(k)}$  ( $k = \text{sl, sv}$ ) are nonanalytic parts that are responsible for the nonanalytic—discontinuous—behavior of the equation of state and the nonclassical critical exponents, which differ from the mean field theory values for the exponents. The presence of the non-analytic terms in  $A^*$  and  $B^*$  is essential for the equation of state to exhibit a discontinuity in the subcritical regime in sharp contrast to the van der Waals equation of state, which is continuous throughout the entire fluid density range. Therefore, the present model for  $A^*$  and  $B^*$  is expected to exhibit a liquid–vapor phase transition. Reasonable forms for the nonanalytic terms of  $A^*$  and  $B^*$  are

$$\begin{aligned} A_{\text{na}}^{(k)} &= a_{\text{na}}^{(k)}(t) (y - z_k)^3 |y - z_k|^{1+\delta}, \\ B_{\text{na}}^{(k)} &= b_{\text{na}}^{(k)}(t) (y - z_k)^3 |y - z_k|^{1+\delta} \quad (k = \text{sl, sv}), \end{aligned} \quad (6.60)$$

where  $a_{\text{na}}^{(k)}(t)$  and  $b_{\text{na}}^{(k)}(t)$  denote temperature-dependent coefficients, which become constants on the critical isotherm:

$$a_{\text{na}}^{(\text{sl})}(0) = a_{\text{na}}^{(\text{sv})}(0) \equiv \alpha_{\text{na}}, \quad b_{\text{na}}^{(\text{sl})}(0) = b_{\text{na}}^{(\text{sv})}(0) \equiv \beta_{\text{na}}, \quad (6.61)$$

and the exponent  $\delta$  is a fractional number less than unity, which is determined from the critical isotherm. This exponent is intimately related to the asymptotic behavior  $\phi \sim x^{4+\delta}$  experimentally observed near the critical point. If  $\delta = 0.3$ , then the critical exponent for  $\phi$  is 4.30, as experimentally observed [27, 28]. This indicates that the models for  $A^*$  and  $B^*$  can be constructed by employing the critical and subcritical data on the fluid of interest.

Because of the properties of the coefficients  $a_i^{(k)}$ ,  $b_i^{(k)}$ ,  $A_{\text{na}}^{(k)}$ , and  $B_{\text{na}}^{(k)}$ , the expressions for  $A^*$  and  $B^*$  on the critical isotherm ( $t = 0$ ) reduce to the forms

$$\frac{A^*}{A_c^*} = 1 + \sum_{i=1}^{l_a} a_i x^i + \alpha_{\text{na}} x^3 |x|^{1+\delta}, \quad (6.62)$$

$$\frac{B^*}{B_c^*} = 1 + \sum_{i=1}^{l_b} b_i x^i + \beta_{\text{na}} x^3 |x|^{1+\delta}. \quad (6.63)$$

By employing these forms for the GvdW parameters on the critical isotherm, it is possible to determine the coefficients in terms of critical parameters.

### 6.5.1 Quadratic Model

If  $a_i = b_i = 0$  and  $\alpha_{\text{na}} = \beta_{\text{na}} = 0$  in (6.62) and (6.63), then the model is reduced to the van der Waals parameters. Therefore, the model is expected to improve the van der Waals theory. It is useful to show how the coefficients can be determined from the critical data. For the purpose in hand, we assume that the sums in (6.62) and (6.63) are truncated at  $i = 2$ , that is,  $A^*$  and  $B^*$  are quadratic with respect to  $x$ , apart from the nonanalytic term. For this reason, the model is called the quadratic model [26].

To apply this quadratic model, it is necessary to generalize the conventional definition of the critical point, which requires that the first two density derivatives of pressure on the critical isotherm vanish. The generalization is such that the first four density derivatives vanish instead of the first two. This generalization of the definition of critical point was originally made by van Laar [29] and later used by Baehr [30] and Planck [31]. The thermodynamic stability of the system then requires that the fifth density derivative not vanish, which is in contrast to the conventional definition where the third density derivative does not vanish. In this generalized definition of the critical point,

there are five algebraic equations on the critical isotherm:

$$\begin{aligned} p_c^* \beta_c^* &= \frac{\eta_c}{1 - B_c^* \eta_c} - \beta_c^* A_c^* \eta_c^*, \\ \left( \frac{\partial^i p^*}{\partial \eta^i} \right)_{t=0, \phi=0} &= 0 \quad (i = 1, \dots, 4). \end{aligned} \quad (6.64)$$

To calculate the algebraic equations more explicitly, it is convenient to define the function  $P(x, t)$ :

$$P(x, t) = \phi [1 - \nu (1 + x) \mathcal{B}(x, t)]. \quad (6.65)$$

Then, the reduced canonical equation of state is rearranged to the form,

$$\begin{aligned} P(x, t) &= \zeta (1 + x) (1 + t) \\ &- [1 + \tau (1 + x)^2 \mathcal{A}(x, t)] [1 - \nu (1 + x) \mathcal{B}(x, t)]. \end{aligned} \quad (6.66)$$

The function  $P(x, t)$  is now sought in a power series,

$$P(x, t) = \sum_{i \geq 0} P_i x^i, \quad (6.67)$$

where the expansion coefficients can be readily identified by expanding  $P(x, t)$ . Then because  $\phi = 0$  at the critical point and

$$\left( \frac{\partial^i p^*}{\partial \eta^i} \right)_{t=0, \phi=0, x=0} = \left( \frac{\partial^i \phi}{\partial \eta^i} \right)_{t=0, x=0} \quad (i = 1, \dots, 4),$$

the conditions in (6.64) are equivalent to the conditions

$$\left( \frac{\partial^i P}{\partial x^i} \right)_{t=0, x=0} = 0 \quad (i = 1, \dots, 4). \quad (6.68)$$

The derivatives of  $P(x, t)$  are then evaluated with (6.66) by using the quadratic model for  $\mathcal{A}$  and  $\mathcal{B}$  on the critical isotherm. This procedure yields the following five algebraic equations:

$$\begin{aligned} \zeta - (1 + \tau) (1 - \nu) &= 0, \\ \nu + \zeta + \tau (\nu b_1 - a_1 + \nu a_1 + 3\nu - 2) + \nu b_1 &= 0, \\ \tau \nu (b_2 + 3b_1 + a_1 b_1 + 3a_1 + a_2 + 3) \\ - \tau (a_2 + 2a_1 + 1) + 2\nu (b_2 + b_1) &= 0, \\ \tau \nu (a_2 + 3a_1 + 3) b_1 + \tau \nu (3 + a_1) b_2 + \nu b_2 + 6\tau \nu \\ + 3\tau \nu (a_1 + a_2) - \tau (a_1 + 2a_2) &= 0, \\ \tau \nu (3a_1 + 3a_2 + 1) b_1 + \tau \nu (3a_1 + a_2 + 3) b_2 \\ + \tau \nu (a_1 + 3a_2) - \tau a_2 &= 0. \end{aligned} \quad (6.69)$$

The left-hand sides of these equations are, respectively,  $P_0$ ,  $P_1$ ,  $\dots$ , and  $P_4$ . Because there are seven variables  $a_1$ ,  $a_2$ ,  $b_1$ ,  $b_2$ ,  $\tau$ ,  $\nu$ , and  $\zeta$  for five equations, two variables remain undetermined and thus act as free variables. These free variables may be fixed with the help of experimental critical parameters  $(p_c, \eta_c, T_c)$  and the Monte Carlo simulation value for  $B_c^*$  determined for a potential, for example, an SW potential model.

It is worthwhile to elaborate on this procedure. We note that if (6.69) is solved for  $\tau$ ,  $\nu$ , and  $\zeta$ , then a pair of algebraic equations for  $a_1$ ,  $a_2$ ,  $b_1$ , and  $b_2$  is obtained, and  $a_2$  and  $b_2$  can be expressed in terms of  $a_1$  and  $b_1$ . To determine the latter, first, the Monte Carlo simulations are performed for the fluid obeying a potential model, say, the SW potential model on the critical isotherm. Then  $B_c^*$  is determined from its statistical mechanical formula. In the next step, (6.69) is iteratively solved so that  $B_c^* = \nu\eta_c$  is in agreement with  $B_c^*$  determined by the Monte Carlo simulations and also the critical compressibility factor  $\zeta^{-1}$  [see (6.48)] is in agreement with the experimental value. Thus the simulated  $B_c^*$  and the experimental critical compressibility factor provide a pair of equations for  $a_1$  and  $b_1$ . In this way,  $a_1$  and  $b_1$  are uniquely determined as

$$a_1 = -0.336, \quad b_1 = -0.618,$$

and, by using the aforementioned pair of algebraic equations for  $a_2$  and  $b_2$ , the values of  $a_2$  and  $b_2$  are determined

$$a_2 = -0.360, \quad b_2 = 0.0436.$$

This procedure, of course, simultaneously determines  $a_2$ ,  $b_2$ , and  $A_2^*$  as well as  $\tau$ ,  $\nu$ , and  $\zeta$  so that the critical parameters agree with experimental values. The values of  $\tau$ ,  $\nu$ , and  $\zeta$  thus determined are

$$\tau = 6.424, \quad \nu = 0.535, \quad \zeta = 3.448,$$

which in turn yield

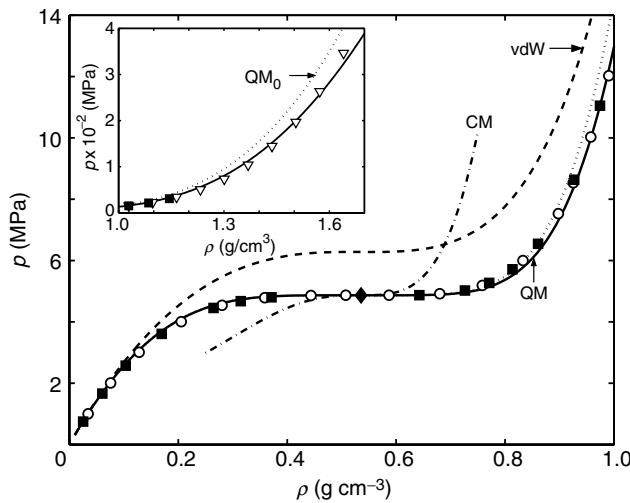
$$T_c^* = 0.287 \frac{A_c^*}{B_c^*}, \quad \eta_c = \frac{0.535}{B_c^*}, \quad \frac{p_c^*}{\eta_c T_c^*} = 0.290.$$

These results with the values for experimental  $T_c^*$  and  $\eta_c$  yield

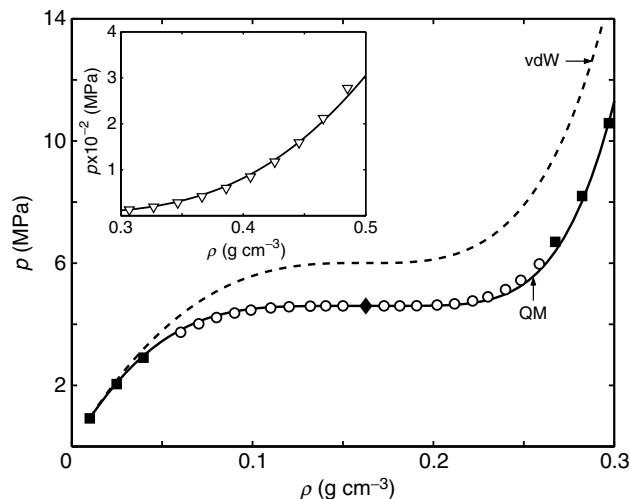
$$A_c^* = 30.25, \quad B_c^* = 4.01.$$

In this manner, the quadratic model for the GvdW parameters is determined except for the nonanalytic coefficients, which can be empirically fixed by fitting the experimental critical isotherm to the quadratic model.

The quadratic model was excellent for accuracy. We quote the numerical test made for argon by Rah and Eu in Fig. 6.4, where the prediction by the quadratic model is compared with the experimental data by Michels et al. [32]



**Fig. 6.4.** Critical isotherms for argon predicted by the quadratic model are compared with experiment, the van der Waals equation of state, and the cubic model. [Reproduced with permission from K. Rah and B. C. Eu, J. Phys. Chem. B **107**, 4382 (2003). Copyright American Chemical Society]



**Fig. 6.5.** The critical isotherm predicted by the quadratic model for methane. [Reproduced with permission from K. Rah and B. C. Eu, J. Phys. Chem. B **107**, 4382 (2003). Copyright 2003 American Chemical Society]

and Gilgen et al. [33]. The *filled diamond* represents the critical point. The *solid curve* is for the quadratic model with  $\alpha_{\text{na}} = 0.01$  and  $\beta_{\text{na}} = -0.015$ . The *dotted curve* ( $QM_0$ ) in the inset is the quadratic model without the

nonanalytic terms. The *dashed curve* is for the van der Waals theory and the *dash-dot curve* is for the cubic model [26] for which the same values of the nonanalytic coefficients are used. The symbols are the experimental data: ■ by Michels et al. [32] and ○ by Gilgen et al. [33]. The triangles ( $\nabla$ ) in the inset are experimental data computed by employing the empirical equation of state for argon proposed by Tegeler et al. [34]. The curve CM in Fig. 6.4 is the result predicted by the cubic model, which is obtained by setting  $a_2 = b_2 = 0$  and  $a_i = b_i = 0$  for  $i \geq 4$  in (6.62) and (6.63). Therefore it is cubic, apart from the nonanalytic terms. It is not good except near the critical point because the quadratic coefficients are absent.

The quadratic model is also excellent for methane, which may be approximated as a spherical fluid, according to the test in [26]. Figure 6.5 shows the prediction of the quadratic model in comparison with the experimental data by Händel et al. [35] and Kleinrahm et al. [36]. The parameter values for the critical isotherm of methane are as follows:

$$\begin{aligned} a_1 &= -0.336 & b_1 &= -0.618 \\ a_2 &= -0.360 & b_2 &= 0.0436 \\ \sigma_{\text{sw}} &= 0.345 \text{ nm} & \varepsilon_{\text{sw}} &= 115.0 k_{\text{B}} \\ A_{\text{c}}^* &= 23.5 & B_{\text{c}}^* &= 4.08 \\ T_{\text{c}} &= 190.56 \text{ K} & \rho_{\text{c}} &= 0.163 \text{ g cm}^{-3} \\ \zeta^{-1} &= 0.286 \end{aligned}$$

The comparison with experiments here indicates the robustness of the quadratic model, and the GvdW equation of state constructed as described extends the original van der Waals equation of state quite successfully. The quadratic model must be extended to account for experimental data on isotherms other than critical isotherms. Such a study is not available at present except for supercooled liquids discussed in [19]. It clearly is worth a study in the future.

### 6.5.2 Conclusion on the Canonical Form

It is shown in this section that the rearrangement of the virial equation of state to the canonical form engenders a powerful form for the equation of state that preserves all insightful aspects of the van der Waals equation of state, yet can be endowed with a form that can far exceed the latter in its capability, flexibility, and numerical precision with regard to critical phenomena. Phenomenological models for  $A$  and  $B$  can be expected to be very useful for studying the subcritical and supercritical behavior of real fluids and also dynamic thermophysical properties, such as transport coefficients of liquids, as will be seen. As will be shown in Chap. 12, the canonical equation of state plays a crucial and keystone role in the density fluctuation theory of transport coefficients of liquids. Therefore, it should be worth a serious study.

## 6.6 Integral Equations for Pair Correlation Functions

We have seen that the equilibrium pair correlation function or the cavity function related to it is an essential input to the GvdW parameters and the canonical equation of state. It is, of course, true for any theory of equilibrium statistical mechanics of dense gases and liquids. Therefore, computation of the pair correlation function is a central issue in the equilibrium theory of liquids. For this reason, it has been studied widely and in depth in the literature, and a considerable body of knowledge has been accumulated. Nevertheless, there are still many aspects to be investigated, especially, in the subcritical regime of temperature. This is the region of temperature where computer simulation methods become less and less effective as the temperature is lowered toward the melting point and below. In addition to the equilibrium theory mentioned, we will see that the equilibrium pair correlation function is also an input required in the theory of transport coefficients of liquids presented in Chaps. 10–12. With such problems in view and to provide general mathematical machinery to treat the problems in the future, we formulate an integral equation theory<sup>2</sup> more general than those available hitherto in the literature on equilibrium pair correlation functions of liquids and present some numerical results [10] to show its utility and potential.

### 6.6.1 Ornstein–Zernike Equation

Historically, the statistical mechanics approach to dense gases and liquids in its early stage has taken the Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy method [37–40]. Because the BBGKY hierarchy is open, it requires closure for the open hierarchy, and the Kirkwood superposition approximation has been the most popular closure conventionally taken in the literature. Any other closure gives rise to a complicated theory which is difficult to handle. The Kirkwood superposition approximation, however, does not yield sufficiently satisfactory values for the pair correlation function.

Many years before the advent of the BBGKY hierarchy, Ornstein and Zernike [41], in connection with their work on light scattering by liquids, introduced the concept of direct correlation function and, together with it, the Ornstein–Zernike (OZ) equation in which the direct correlation function is related to the total correlation function. It is a circular relation between the direct and total correlation functions, requiring a closure relation. However, because the direct correlation function was short ranged, by assuming a suitable form for it on physical grounds, they were able to derive from the equation a long-ranged total correlation function, which adequately accounted for the light scattering by the fluid in the critical regime. Since then, the OZ

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<sup>2</sup> The material presented in this and subsequent sections in this chapter is an outgrowth of the author's work initiated about 5 years ago before the numerical work was carried out to examine its potential in [10].

equation has been given statistical mechanical derivations by using a resummation method of the cluster expansion or a functional derivative method. The functional derivative method of Percus [42] gives an especially elegant derivation of the equation from the grand canonical ensemble distribution function. This derivation shows that the OZ equation may be regarded as a kind of resummation of the BBGKY hierarchy of correlation functions.

The OZ equation thus derived for a simple liquid has the form

$$h(r) = c(r) + n \int d\mathbf{r}' c(|\mathbf{r} - \mathbf{r}'|) h(r'), \quad (6.70)$$

where  $h(r)$  and  $c(r)$  are, respectively, the total and the direct correlation function for a particle pair at relative distance  $\mathbf{r}$ .

As for the BBGKY hierarchy theory, a closure must be assumed for the OZ equation, and it is usually done by assuming a suitable form for the direct correlation function. A closure frequently taken is the Percus–Yevick (PY) closure [2, 20, 43]

$$c(r) = f(r)y(r), \quad (6.71)$$

where  $f(r)$  is the Mayer function and  $y(r)$  is the cavity function. There is another well-known closure called the hypernetted chain closure [21]

$$c(r) = h(r) - \ln y(r). \quad (6.72)$$

For example, with the PY closure substituted in the OZ equation, we obtain the PY integral equation for  $h(r)$ :

$$h(r) = f(r)y(r) + n \int d\mathbf{r}' f(|\mathbf{r} - \mathbf{r}'|) y(|\mathbf{r} - \mathbf{r}'|) h(r'). \quad (6.73)$$

This was the integral equation for  $h(r)$  that was solved for an SW potential to compute the GvdW parameters  $A$  and  $B$  in [17]; see Figs. 6.2 and 6.3. The PY integral equation can be readily solved by Fourier transform combined with iteration. With the solution obtained for  $h(r)$ , the virial equation of state (6.1) can be computed numerically, but the results are not sufficiently satisfactory, especially, if the density is high. Another problem with the PY closure and also with the hypernetted chain closure is the lack of thermodynamic consistency.

The direct correlation function is related to the isothermal compressibility as follows:

$$(nk_B T \kappa)^{-1} = \beta \left( \frac{\partial p}{\partial n} \right)_T = 1 - n \int d\mathbf{r} c(r), \quad (6.74)$$

where  $\kappa$  is the isothermal compressibility. With knowledge of the direct correlation function, it is possible to compute the equation of state of the fluid. If, for example, the PY closure is used, the equation of state obtained thereby differs from the virial equation of state computed with the same closure. The same situation arises for the hypernetted chain closure. This kind of difference

in the equations of state computed by the two modes mentioned is called the thermodynamic consistency problem. There have been numerous articles [44] in the literature in which attempts have been made to resolve the thermodynamic consistency problem. In this backdrop of the integral equation approach to the equilibrium statistical mechanics of simple dense gases and liquids, we discuss an integral equation theory in a more general context than available in the recent literature.

### 6.6.2 Thermodynamic Consistency

In most of the approaches [44] taken to resolve the thermodynamic consistency for a closure assumed so far, a bridge function is introduced so that the desired thermodynamic consistency is achieved. Somewhat different in spirit from the bridge function approaches, the virial equation of state is used together with the energy equation [45] to obtain the closure preserving thermodynamic consistency.

Instead of these methods, we may directly impose thermodynamic consistency on the virial and isothermal compressibility equation of state. In other words, the direct correlation function is determined so that the two equations of state mentioned are equal to each other for all values of  $r$ . Upon integrating (6.74) with respect to  $n$ , there follows the isothermal compressibility (IC) equation of state

$$\frac{\beta p}{n} = 1 - n^{-1} \int_0^n dn' n' \int drc(r, n'). \quad (6.75)$$

Because the density is uniform in space, the two integrals on the right of (6.75) are interchangeable. The pressure calculated from this equation must be equal to the pressure calculated from the virial equation of state (6.1), so upon equating them there arises the local form of constraint on the direct correlation function [26]

$$c(r) = \frac{1}{6nr^2} \frac{\partial}{\partial n} n^2 f(r) \frac{\partial}{\partial r} r^3 y(r, n) + \frac{1}{nr^2} \frac{\partial q(r, n)}{\partial r}, \quad (6.76)$$

where  $q(r, n)$  is an arbitrary function of  $r$  and  $n$ , which vanishes at  $r = 0$  and  $r = \infty$ . It is called the gauge function, which must be suitably assumed or determined by another means. However, determining it exactly is tantamount to solving the liquid structure problem exactly, a task that is unlikely to be achieved in a sufficiently general form. A suitable assumption for the gauge function is tantamount to a closure for the OZ equation, and it is a more practical approach.

With the gauge function satisfying the boundary conditions at  $r = 0$  and  $r = \infty$ , the direct correlation function given in (6.76) ensures thermodynamic consistency. Therefore, it is a thermodynamically consistent closure. We will discuss a choice for the gauge function later in this chapter. With such a choice of  $q(r, n)$ , the OZ equation can be solved and the equation of state can be determined in a thermodynamically consistent manner.

Working out the first term on the right of (6.76), its relation to the PY closure is better exposed:

$$\begin{aligned} rc(r) &= rf(r)y(r) + rf(r)\left(\frac{1}{3}\frac{\partial y}{\partial \ln r} + \frac{1}{2}\frac{\partial y}{\partial \ln \eta} + \frac{1}{6}\frac{\partial^2 y}{\partial \ln \eta \partial \ln r}\right) \\ &\quad + \frac{1}{nr^2}\frac{\partial q(r, n)}{\partial r}, \end{aligned} \quad (6.77)$$

where the first term on the right is the PY closure.

As it is for pressure, the chemical potential can be calculated in two ways. If the grand canonical partition function is employed, the excess chemical potential can be obtained in the form [1],

$$\beta\mu_{\text{ex}} = n \int_0^1 d\lambda \int d\mathbf{r} \beta u(r) g^*(r, \lambda), \quad (6.78)$$

where  $\lambda$  is the charging parameter and  $g^*(r, \lambda)$  is the pair correlation function in the grand canonical ensemble theory, which is defined by

$$g^*(r, \lambda) = \frac{\langle N \rangle}{n^2 \Xi(z, \lambda)} \int_0^z dz' \frac{\Xi(z', \lambda) \rho^{(2)}(r, \lambda, z')}{z'}. \quad (6.79)$$

In this expression,  $\langle N \rangle$  denotes the grand canonical ensemble average [1] of  $N$ ,  $z$  is the (equilibrium) activity defined by

$$z = e^{\beta\mu} \Lambda^{-3} = e^{\beta\mu} (2\pi m k_B T)^{3/2} / h^3, \quad (6.80)$$

$\Xi(z, \lambda)$  is the grand canonical partition function at charging parameter  $\lambda$ ,

$$\Xi(z, \lambda) = \sum_{N \geq 0} \frac{z^N}{N!} \int d\mathbf{r}^{(N)} \exp \left[ -\beta U^{(N)}(\lambda) \right], \quad (6.81)$$

and the pair distribution function  $\rho^{(2)}(r, \lambda, z)$  is defined by

$$\rho^{(2)}(r, \lambda, z) = \frac{1}{\Xi(z, \lambda)} \sum_{N \geq 2} \frac{z^N}{(N-2)!} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N \exp \left[ -\beta U^{(N)}(\lambda) \right] \quad (6.82)$$

with  $U^{(N)}(\lambda)$  denoting the  $N$  particle potential energy at charging parameter  $\lambda$

$$U^{(N)}(\lambda) = \sum_{i=2}^N \lambda u_{1i}(r_{1i}) + \sum_{2 \leq i < j}^N u_{ij}(r_{ij}). \quad (6.83)$$

If the canonical ensemble theory is employed, the excess chemical potential is given by

$$\beta\mu_{\text{ex}} = n \int_0^1 d\lambda \int d\mathbf{r} \beta u(r) g(r, \lambda), \quad (6.84)$$

which is clearly seen as an approximation of the grand canonical ensemble excess chemical potential.

On the other hand, the thermodynamically derived excess chemical potential is given by

$$\beta\mu_{\text{ex}} = \left( \frac{\beta p}{n} - 1 \right) + \int_0^n dn' \frac{1}{n'} \left( \frac{\beta p}{n'} - 1 \right), \quad (6.85)$$

which by using of (6.75) can be written as

$$\beta\mu_{\text{ex}} = - \int_0^n dn' \int drc(r, n'). \quad (6.86)$$

The direct correlation function must be also such that the excess chemical potential calculated via (6.78) is identical with that calculated via (6.86). This constraint gives rise to the equation for  $c(r)$  as follows:

$$c(r) = \frac{\partial}{\partial n} n \int_0^1 d\lambda f(r, \lambda) \left[ y^*(r, \lambda) \delta(\lambda - 1) - \frac{\partial y^*(r, \lambda)}{\partial \lambda} \right] - r^{-2} \frac{\partial q_\mu(r, n)}{\partial r}, \quad (6.87)$$

where  $q_\mu(r)$  is another arbitrary gauge function that must satisfy the boundary conditions  $q_\mu(0, n) = 0$  and  $q_\mu(\infty, n) = 0$  and  $y^*(r, \lambda)$  is the cavity function defined by

$$y^*(r, \lambda) = \exp[\lambda\beta u(r)] g^*(r, \lambda). \quad (6.88)$$

This cavity function  $y^*(r, \lambda)$ , however, is much more complicated to calculate than  $y(r, \lambda)$  because the grand canonical ensemble pair correlation function  $g^*(r, \lambda)$  by definition requires a much more elaborate equation than that for  $g(r, \lambda)$ . Because the direct correlation function requires a closure, or the gauge function suitably postulated, it is permissible to assume that the direct correlation functions in both, grand and canonical ensembles, are identical. This is the viewpoint we have tacitly taken when (6.86) is obtained for the excess chemical potential from (6.85), which is a thermodynamical relation. After all, thermodynamical relations should be independent of the ensembles employed to derive them by statistical mechanics, if the fluctuations are negligible.

There consequently follows from (6.76) and (6.87) the relation

$$-\beta u(r) \frac{\partial}{\partial n} n \langle g^* \rangle = \frac{1}{r^2 n} \frac{\partial}{\partial r} (q + nq_\mu) + \frac{1}{6nr^2} \frac{\partial}{\partial n} \frac{1}{6} n^2 f(r) \frac{\partial}{\partial r} r^3 y(r, n), \quad (6.89)$$

where

$$\langle g^* \rangle = \int_0^1 d\lambda g^*(r, \lambda). \quad (6.90)$$

Therefore, (6.89) yields  $\langle g^* \rangle$ , the average of  $g^*(r, \lambda)$  over the charging parameter, from knowledge of  $y(r, n)$ , once the gauge functions  $q$  and  $q_\mu$  are known or suitably chosen. This, of course, means that the thermodynamically consistent excess chemical potential can be calculated from (6.86) by using the closure (6.76).

Thus, we have formally achieved a complete thermodynamic consistency for pressure and excess chemical potential, and there now remain the tasks of determining the cavity function and finding the gauge function.

### 6.6.3 Wiener–Hopf Method

The Wiener–Hopf method [46–48] is a procedure used for solving integral equations or differential equations by Fourier transform. This method is relevant to solving the OZ equation because the OZ equation is generally solved by a combination of Fourier transform and iteration. Use of Fourier transforms implies that the knowledge of analyticity in the Fourier space of the functions involved becomes indispensable for acquiring the solutions of the OZ equation by Fourier transform.

Let us define Fourier transforms of  $h(r)$  and  $c(r)$  by

$$\begin{aligned}\widehat{h}(k) &= \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) h(r), \\ \widehat{c}(k) &= \int d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) c(r).\end{aligned}\quad (6.91)$$

If the auxiliary functions  $H(r)$  and  $C(r)$  are defined by the integrals

$$\begin{aligned}H(r) &= \int_r^\infty dt t h(t), \\ C(r) &= \int_r^\infty dt t c(t),\end{aligned}\quad (6.92)$$

the Fourier transforms  $\widehat{h}(k)$  and  $\widehat{c}(k)$  for fluids of spherically symmetrical molecules can be expressed as one-dimensional Fourier transforms of  $H(r)$  and  $C(r)$  by suitably extending the latter into the negative axis of  $r$

$$\begin{aligned}\widehat{h}(k) &= 4\pi \int_0^\infty dr \cos(kr) H(r) = 2\pi \int_{-\infty}^\infty dr \exp(ikr) H(r), \\ \widehat{c}(k) &= 4\pi \int_0^\infty dr \cos(kr) C(r) = 2\pi \int_{-\infty}^\infty dr \exp(ikr) C(r).\end{aligned}\quad (6.93)$$

Using the Fourier transform, the OZ equation can be written, by virtue of the convolution theorem, as

$$[1 - n\widehat{c}(k)] [\widehat{1} + n\widehat{h}(k)] = 1. \quad (6.94)$$

Provided  $[1 - n\hat{c}(k)] \neq 0$ , it can be solved for  $\hat{h}(k)$  as follows:

$$n\hat{h}(k) = \frac{n\hat{c}(k)}{1 - n\hat{c}(k)}. \quad (6.95)$$

In the Wiener–Hopf method, the denominator of the right-hand side in (6.95) is factored into a product of two functions of  $k$  that should not have zeros in a strip of the  $k$  plane enclosing the real axis, but tend to a finite limit as  $\text{Re}(k) \rightarrow \pm\infty$ . These properties of the factorization functions are essential for the validity of the Wiener–Hopf method. When the factorization functions are suitably determined, the solution of the integral equation is obtained.

Baxter [9] applied the Wiener–Hopf method to the OZ equation subject to the PY closure, namely, the PY integral equation, for a hard sphere fluid and obtained a pair of integral equations for  $h(r)$  and the factorization function, which he was able to solve exactly. With the solution thus obtained, he derived an equation of state for a hard sphere fluid, which turned out to be the same as that Thiele [5] and Wertheim [6] previously obtained for a hard sphere fluid by using the Laplace transform method:

$$\frac{p\beta}{n} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3}. \quad (6.96)$$

Here  $\eta$  is the packing fraction defined by  $\eta = \pi\sigma^3n/6$  with  $\sigma$  denoting the hard sphere diameter. Thus established for hard sphere fluids, Baxter's factorization in the Wiener–Hopf method has become the starting point of solution methods based on the Wiener–Hopf method for the OZ equation under the assumption of closures other than the PY closure; for example, the mean spherical approximation (MSA) closure and the generalized mean spherical approximation (GSMA) closure [7, 8] for which the potential energy is assumed no longer to be of hard spheres but involves an attractive potential representative of real fluids. For the GSMA closure, an attractive Yukawa type potential function<sup>3</sup> is assumed without theoretical justification under the argument that hard spheres have an attractive potential tail. There is a considerable body of literature on the subject.

The factor  $M(k) \equiv 1 - n\hat{c}(k)$ , however, is not always invertible everywhere in the  $k$  plane if the fluid is real. Particles therein interact through an attractive force as well as a repulsive force, and consequently there exists a first-order liquid–vapor phase transition admissible. The reason for this can be easily seen by the following reasoning. Because the inverse isothermal compressibility can be written as

$$\left( \frac{\partial \beta p}{\partial n} \right)_T = 1 - n\hat{c}(0), \quad (6.97)$$

---

<sup>3</sup> The analysis made later on the basis of a generalized Wiener–Hopf theorem shows that the Yukawa type potential function in the GSMA is not a potential energy, but part of the correlation function that is related to the potential of mean force.

and if a liquid–vapor phase transition is possible for the fluid—this is possible for all real fluids—then as the state of the fluid tends toward the critical point, there holds the limit

$$\lim_{T \rightarrow T_c, n \rightarrow n_c} M(0) \equiv \lim_{T \rightarrow T_c, n \rightarrow n_c} [1 - n\hat{c}(0)] = 0. \quad (6.98)$$

This is an experimental fact for real fluids [49]. Therefore there appears, at least, a zero of  $M(k)$  at the origin of  $k$  plane as the critical state is approached. In other words, the zeros of  $M(k)$ , which might have been in the complex  $k$  plane, may tend to the origin as the critical state is approached by the fluid, and if that happens, then the mathematical operation leading to (6.95) from (6.94) is no longer valid. From the viewpoint of the Wiener–Hopf method, the factorization of  $M(k)$  into a product of functions of  $k$ , as done for hard sphere fluids, is no longer applicable. It must be suitably modified.

### Wiener–Hopf Factorization Theorem

A mathematical way of looking at the property (6.98) required of  $M(k)$  is that for a disordered fluid,  $M(k)$  has zeros in the complex  $k$  plane—for example, on the imaginary axis—which tend to the origin as the critical state is approached by the fluid. Because  $\hat{c}(k)$  must be real, the roots of  $M(k)$  must appear in conjugate pairs. Therefore, it is plausible to conjecture that  $M(k)$  may be written as

$$M(k) = 1 - n\hat{c}(k) = B(k) \prod_j (k^2 + k_j^2), \quad (6.99)$$

where  $\pm ik_j$  are zeros of  $M(k)$  on the imaginary axis<sup>4</sup> and  $B(k)$  is a nonvanishing function of  $k$  in a strip of  $k$  enclosing the real axis of the complex  $k$  plane. This function factorizes to a product of functions of  $k$ . There is at least a pair of  $k_j$ 's that vanishes at the critical point, that is,

$$\lim_{T \rightarrow T_c, n \rightarrow n_c} k_j(T, n) = 0$$

---

<sup>4</sup> The zeros need not be distributed on the imaginary axis, but we may instead have

$$M(k) = B(k) \prod_j [(k - \kappa_j)^2 + k_j^2],$$

where  $\kappa_j$  and  $k_j$  are, respectively, the real and imaginary parts of the  $j$ th zero. Moreover, the number of zeros need not be finite. The real parts of the zeros may remain constant, but the imaginary parts may tend to the real axis, as temperature and density vary. Such a situation may occur if the fluid makes a transition to a crystal with well-defined lattice spacing. We do not consider such cases in this work for simplicity of the formalism. In this generalized approach, the thermal properties of fluids and their behavior are turned into questions of the analyticity of both direct and total pair correlation functions in the Fourier space, and the thermal properties of matter may be classified according to the analyticity of  $M(k)$ .

and the phenomenology of first-order phase transition suggests that [49]

$$k_j^2(T, n) = c(n - n_c)^\delta (T - T_c)^\gamma$$

where  $\delta$  and  $\gamma$  are the critical exponents characteristic of the inverse isothermal compressibility. The discussion presented here clearly indicates that the form in (6.99) is plausible for  $M(k)$ . For the sake of simplicity of the formalism without sacrificing the essential physical consequences for  $M(k)$ , we will assume that there is only a pair of zeros of  $M(k)$  on the imaginary axis of the  $k$  plane. This assumption can be removed for nonhard sphere fluids by including more zeros and also real parts in the zeros.

The physics of matter in a disordered state requires that  $\hat{c}(k)$  vanish with increasing  $k$  along the real axis. According to the Wiener–Hopf factorization theorem [46–48], if  $M(k)$  has a pair of complex zeros within the strip  $-\epsilon < \text{Im}k < \epsilon$  and if

$$\begin{aligned} M(k) &\rightarrow \exp(i\mu) \quad \text{as } k \rightarrow +\infty \\ &\rightarrow \exp(-i\nu) \quad \text{as } k \rightarrow -\infty, \end{aligned} \tag{6.100}$$

where  $\mu$  and  $\nu$  are real constants, then there exist functions  $K_+(k)$  and  $K_-(k)$  such that

$$\begin{aligned} c_1|k|^{-1-\lambda} &< |K_+(k)| < c_2|k|^{-1-\lambda} \quad (\text{Im}k > c, c > -\varepsilon), \\ c_3|k|^{-1+\lambda} &< |K_-(k)| < c_4|k|^{-1+\lambda} \quad (\text{Im}k < d, d < \varepsilon) \end{aligned} \tag{6.101}$$

with  $c_1, c_2, c_3$ , and  $c_4$  denoting constants and

$$\lambda = (2\pi)^{-1}(\mu - \nu).$$

Then the function  $B(k)$  is factored into the product

$$B(k) = K_+(k) K_-(k) (k + i\varepsilon)^{-1} (k - i\varepsilon)^{-1}. \tag{6.102}$$

Here

$$\varepsilon > k_c,$$

where  $k_c$  is the absolute value of the zeros of  $M(k)$  taken for the present discussion. For more than one pair of complex zeros,  $\varepsilon$  must be taken such that  $\varepsilon > \max |\text{Im}k_n|$  with  $k_n$  denoting the complex zeros. In the present case,  $\lambda = 0$  because  $\hat{c}(k)$  is even in  $k$  and hence  $\mu$  and  $\nu$  should be equal.

Functions  $K_+(k)$  and  $K_-(k)$  are regular and free from zeros, respectively, in the half plane  $\text{Im}k > -\varepsilon$  and  $\text{Im}k < \varepsilon$ , and by virtue of inequalities (6.101)

$$1 - K_\pm(k) \rightarrow 0 \quad \text{as } \text{Re}k \rightarrow \pm\infty. \tag{6.103}$$

Furthermore, because  $\widehat{c}(k)$  is an even function of  $k$  according to (6.93), it also follows that

$$K_+(k) K_-(k) = K_+(-k) K_-(-k) \quad (6.104)$$

and

$$K_-(k) = K_+(-k) \equiv \widehat{K}(-k). \quad (6.105)$$

Thus we find that under the assumption of a pair of complex zeros of  $M(k)$ , the Fourier transform of the direct correlation function factors to the form

$$1 - n\widehat{c}(k) = \frac{(k^2 + k_c^2)}{(k - i\varepsilon)(k + i\varepsilon)} \widehat{K}(k) \widehat{K}(-k) \quad (6.106)$$

if there is only a pair of imaginary zeros. For hard sphere fluids, according to Baxter [9], factorization takes the form

$$1 - n\widehat{c}(k) = \widehat{K}(k) \widehat{K}(-k). \quad (6.107)$$

This factorization is permissible in the liquid density regime because hard sphere fluids do not have liquid-vapor (first-order) phase transitions. Hence  $M(k)$  does not vanish as  $k \rightarrow 0$ , and the temperature is lowered at a liquid density. However, if a hard sphere solidifies to a crystal or an amorphous solid and the transition is first order, then the factorization must be modified appropriately. The factorization (6.106) is different from (6.107) used by Baxter for hard sphere fluids by the factor

$$\frac{(k^2 + k_c^2)}{(k - i\varepsilon)(k + i\varepsilon)},$$

and the factor  $(k^2 + k_c^2)$  is responsible for the possibility that  $M(k)$  vanishes under suitable circumstances and gives rise to a description of a first-order phase transition.<sup>5</sup> Therefore the present factorization of  $M(k)$  in (6.106) is more general than Baxter's and should still remain valid even for hard sphere fluids.

With the factorization, (6.94) can be rearranged to the form

$$\left[1 + n\widehat{h}(k)\right] (k^2 + k_c^2) \widehat{K}(k) = \left[\widehat{K}(-k)\right]^{-1} (k - i\varepsilon)(k + i\varepsilon), \quad (6.108)$$

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<sup>5</sup> There should be some connection between the Wiener-Hopf factorization theorem leading to (6.58) and the Yang-Lee theorem [50]. Consideration on the basis of the grand canonical partition function and in the light of the Yang-Lee theorem on the zeros of the grand canonical partition function in the complex activity plane suggests that, even for hard sphere fluids,  $M(k)$  should have zeros in the complex  $k$  plane. This author believes that one may seek the theoretical foundations of the analyticity postulates made here in the Yang-Lee theorem on the distribution of zeros of the grand canonical partition function.

whereas (6.106) may be cast into the form

$$(k^2 + \varepsilon^2) [1 - n\hat{c}(k)] = (k^2 + k_c^2) \hat{K}(k) \hat{K}(-k). \quad (6.109)$$

These two equations give rise to a pair of integral equations for the total and the direct correlation function, respectively.

Before proceeding further, it is useful to define the Fourier transform of the factorization function. Because according to (6.103),  $K(k)$  is bounded and

$$|\hat{K}(k)| \rightarrow 1 \quad \text{as } |k| \rightarrow \infty,$$

it is possible to define  $K(r)$  for  $r > 0$  such that

$$2\pi n K(r) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \left[ 1 - \hat{K}(k) \right] \exp(-ikr). \quad (6.110)$$

The inverse of this relation is

$$\hat{K}(k) = 1 - 2\pi n \int_{-\infty}^{\infty} dr K(r) \exp(ikr). \quad (6.111)$$

Because  $K(k)$  is regular in the strip  $-\varepsilon < \text{Im}k < \varepsilon$ ,  $|\hat{K}(k)| \rightarrow 1$  as  $|k| \rightarrow \infty$ , and has no zeros within the strip—this latter condition is not necessary for the property of  $K(r)$  below—by closing the contour in the upper half in the  $k$  plane for  $r < 0$ , we find

$$K(r) = 0 \quad (r < 0). \quad (6.112)$$

This is one of the important properties of the factorization function  $K(r)$ . Because of this property,  $\hat{K}(k)$  may be written as

$$\hat{K}(k) = 1 - 2\pi n \int_0^{\infty} dr K(r) \exp(ikr). \quad (6.113)$$

This will be found useful.

### Integral Equation for the Direct Correlation Function

To derive the integral equation for the direct correlation function, it is useful to rearrange (6.109) to the form

$$(k^2 + k_c^2) \left[ n\hat{c}(k) + \hat{K}(k)\hat{K}(-k) - 1 \right] = (\varepsilon^2 - k_c^2) [1 - n\hat{c}(k)]. \quad (6.114)$$

Upon inserting (6.110) in (6.114) and taking the inverse Fourier transform, we obtain for  $r > 0$

$$\left( -\frac{\partial^2}{\partial r^2} + k_c^2 \right) \phi(r) = \frac{(\varepsilon^2 - k_c^2)}{2\pi n} [\delta(r) - 2\pi n C(r)], \quad (6.115)$$

where the function  $\phi(r)$  is defined by

$$\phi(r) = C(r) - K(r) + 2\pi n \int_r^\infty dt K(t) K(t-r). \quad (6.116)$$

Equation (6.115) is an inhomogeneous wave equation for an evanescent wave of correlation. Physically, it is a kind of potential of mean force in the fluid. Because

$$C(r), K(r) \rightarrow 0 \quad \text{as } r \rightarrow \infty$$

it follows that

$$\phi(r) \rightarrow 0 \quad \text{as } r \rightarrow \infty. \quad (6.117)$$

Differentiating (6.115) with respect to  $r$  yields the differential equation

$$\left( \frac{\partial^2}{\partial r^2} - k_c^2 \right) \frac{\partial \phi(r)}{\partial r} = -\frac{(\varepsilon^2 - k_c^2)}{2\pi n} \left[ \frac{\partial}{\partial r} \delta(r) + 2\pi n r c(r) \right], \quad (6.118)$$

for which we impose the boundary condition at  $r = 0$

$$\left[ \frac{d\phi(r)}{dr} \right]_{r=0} = \text{finite}. \quad (6.119)$$

Equation (6.118) will be used to determine  $\phi(r)$  in the present theory.

Differentiation of (6.116) with respect to  $r$  yields the integral equation for the direct correlation function  $c(r)$ :

$$rc(r) = -K'(r) + 2\pi n \int_r^\infty dt K'(t) K(t-r) - \frac{\partial \phi}{\partial r}, \quad (6.120)$$

where the prime on  $K(r)$  denotes differentiation with respect to  $r$ , the variable of the factorization function  $K(r)$ . Equation (6.120) is one of the integral equations sought in the Wiener-Hopf method. The third term on the right of (6.120) arises from the presence of zeros in  $M(k)$ , and it is the point of departure from the integral equation for  $rc(r)$  obtained by Baxter [9] for hard sphere fluids. This equation indicates that for a disordered system the direct correlation function decays exponentially as  $r \rightarrow \infty$ , as will be shown, and the correlation range of this function has to do with the zero of the inverse isothermal compressibility.

### Integral Equation for the Total Correlation Function

Equation (6.108) can be rearranged similarly to the direct correlation function:

$$(k^2 + k_c^2) \left\{ \left[ \hat{K}(k) - 1 \right] + n\hat{h}(k) + n\hat{h}(k) \left[ \hat{K}(k) - 1 \right] - \left[ \frac{1}{\hat{K}(-k)} - 1 \right] \right\} \\ = \frac{(\varepsilon^2 - k_c^2)}{\hat{K}(-k)}. \quad (6.121)$$

Upon taking the inverse Fourier transform of this equation, there follows the equation for  $H(r)$ , which may be written as

$$\left( \frac{\partial^2}{\partial r^2} - k_c^2 \right) \psi(r) = \frac{(k_c^2 - \varepsilon^2)}{2\pi n} \delta(r), \quad (6.122)$$

where  $\psi(r)$  is defined by

$$\psi(r) = H(r) - K(r) - 2\pi n \int_0^\infty dt K(t) H(|r-t|). \quad (6.123)$$

The boundary conditions on  $\psi(r)$  at  $r = \infty$  and at  $r = 0$  are

$$\psi(\infty) = 0 \quad \psi'(0) = 0. \quad (6.124)$$

To obtain this result, we have used the following:

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} dk \exp(-ikr) \left[ 1/\hat{K}(-k) - 1 \right] = 0, \quad (6.125)$$

where the integral vanishes because  $\hat{K}(-k)$  is regular and bounded in the strip  $-\varepsilon < \text{Im}k < \varepsilon$ , tending to unity as  $|k| \rightarrow \infty$ .

Equation (6.122) is solved with the help of Green's function defined by the differential equation

$$\left( \frac{\partial^2}{\partial r^2} - k_c^2 \right) G(r, r') = -4\pi\delta(r - r'). \quad (6.126)$$

Green's function is easily obtained by the method of Fourier transform and contour integration:

$$G(r, r') = \frac{\pi}{k_c} \exp[-k_c|r - r'|]. \quad (6.127)$$

According to the Green's function method [47], the solution for (6.122) can be readily obtained:

$$\psi(r) = \left[ \psi_0 - \frac{(k_c^2 - \varepsilon^2)}{8\pi n k_c} \right] \exp(-k_c r). \quad (6.128)$$

The boundary condition at  $r = 0$  implies that

$$\psi_0 - \frac{(k_c^2 - \varepsilon^2)}{8\pi n k_c} = 0. \quad (6.129)$$

Therefore, the integral equation involving  $H(r)$  and  $K(r)$  turns out to be simply the same equation as that when the zeros of the isothermal compressibility are absent:

$$H(r) = K(r) + 2\pi n \int_0^\infty dt K(t) H(|r - t|). \quad (6.130)$$

This is the other of the integral equations in the Wiener–Hopf method, which this time involves  $H(r)$  and  $K(r)$ . It is coupled to (6.116) for  $C(r)$ .

Differentiating (6.130) with respect to  $r$  yields the equation for the total correlation function [10]

$$rh(r) = -K'(r) - 2\pi n \int_0^\infty dt (t - r) K(t) h(|r - t|). \quad (6.131)$$

This equation is coupled to (6.120).

Equations (6.118), (6.120), and (6.131) are equivalent to the OZ equation, but there are three equations for four functions,  $h(r)$ ,  $c(r)$ ,  $K(r)$ , and  $\phi(r)$ , to be determined. For this reason, a closure relation must be imposed before the solution procedure is implemented.

### Thermodynamically Consistent Closure

It was shown earlier that thermodynamic consistency is satisfied by the closure relation given in (6.76). Because the gauge function  $q(r)$  vanishes at the boundaries at  $r = 0$  and  $r = \infty$ , it follows that

$$\int_0^\infty dr \frac{\partial q}{\partial r} = 0.$$

This gauge function cannot be determined within the framework of the present integral equation theory unless the partition function is calculated exactly. Therefore, it must be suitably guessed or approximated, if the integral equation theory is to be implemented successfully.

When the function  $r^{d-1}\phi(r)$ , in which  $d$  is the dimensionality of the system, is carefully examined, we observe that it satisfies the requirement for the gauge function exactly because  $\phi$  vanishes exponentially as  $r \rightarrow \infty$  because of the property of  $\phi$  at  $r = \infty$ . The function  $\phi$ , moreover, contains the information on the internal dynamics of the fluid, being a kind of potential of mean force, as will be shown. Therefore just as for the gauge function, there holds the condition

$$\int_0^\infty \frac{\partial r^{d-1}\phi}{\partial r} = 0. \quad (6.132)$$

Consequently, inasmuch as the gauge function is arbitrary although it should contain dynamic information about the fluid, it seems reasonable to identify the gauge function as follows [10]:

$$q = nr^2\sigma^{-1}\phi(r), \quad (6.133)$$

for  $d = 3$ . This identification is still an assumption of closure. Then the thermodynamically consistent closure (6.76) becomes

$$c(r) = \frac{1}{6nr^2}f(r)\frac{\partial^2}{\partial r \partial n}n^2r^3y(r,\rho) + \frac{\sigma}{r^2}\frac{\partial(r/\sigma)^2\phi}{\partial r}. \quad (6.134)$$

This is the proposition for thermodynamically consistent closure in this work. Just as for any other closure in the theory of liquids, it is only a proposition, and its correctness must be checked with its consequences for the thermodynamics of liquids. Elimination of  $c(r)$  from (6.118) and (6.120) by using (6.134) gives rise to a closed set of integro-differential equations for  $h(r)$ ,  $K(r)$ , and  $\phi(r)$ ; see (6.135)–(6.139) below.

To implement a solution procedure for this set of integral equations, it is convenient to cast them in dimensionless reduced variables, so that we can work with nondimensionalized equations. Thus, if we define the nondimensionalized quantities

$$\begin{aligned} x &= r/\sigma, & \eta &= \frac{\pi}{6}\sigma^3\rho, & \xi &= k_c\sigma, & \alpha &= \varepsilon\sigma, \\ p^* &= pv_0/\epsilon, & T^* &= k_B T/\epsilon, & K^* &= K\sigma^{-2}, & \varphi &= \phi\sigma^{-2}, \end{aligned}$$

where  $\beta^* = 1/T^*$ ,  $v_0 = \pi\sigma^3/6$  is the volume of the hard core, and  $\epsilon$  is the well depth (or interaction strength) of the potential (e.g., the Lennard-Jones potential), then the reduced integral equations are

$$xh(x) = -K^{*\prime}(x) - 12\eta \int_0^\infty dt (t-x)K^*(t)h(|x-t|), \quad (6.135)$$

$$\begin{aligned} \frac{f(x)}{6\eta x} \frac{\partial^2}{\partial x \partial \eta} \eta^2 x^3 y(x, \eta) &= -K^{*\prime}(x) + 12\eta \int_x^\infty dt K^{*\prime}(t)K(t-x) \\ &\quad - 2\varphi(x) - (1+x) \frac{\partial \varphi}{\partial x}, \end{aligned} \quad (6.136)$$

$$\left( \frac{\partial^2}{\partial x^2} - \alpha^2 \right) \Psi(x) = -\frac{(\alpha^2 - \xi^2)}{12\eta} R(x), \quad (6.137)$$

where

$$\Psi(x) = \frac{\partial \varphi(x)}{\partial x}, \quad (6.138)$$

$$R(x) = \frac{\partial}{\partial x} \delta(x) - 12\eta K^{*\prime}(x) + 144\eta^2 \int_x^\infty dt K^{*\prime}(t)K(t-x). \quad (6.139)$$

We have used the closure relation (6.134) to recast (6.120) and (6.118) into (6.136) and (6.137), respectively. The set (6.135)–(6.137) is the main formal result of the present theory. It should be emphasized that these integro-differential equations are valid for any finite-range potential model.

The parameter  $k_c$ , namely, the zeros of  $M(0)$ , must be determined as a function of density and temperature so that the solution of the integro-differential equations exists. In other words,  $k_c$  or  $\xi$  must be determined from the solvability condition of the integro-differential equations. To deduce what we mean by this condition, we will examine the equation of the gauge function, (6.137).

#### 6.6.4 Gauge Function

Inspection of (6.137) indicates that because  $\varphi(x)$  is indirectly coupled to  $h(x)$  through  $K^*(x)$ , the three coupled equations (6.135)–(6.137) can be reduced to two coupled equations for  $h(x)$  or  $y(x)$  and  $K^*(x)$ , if (6.137) is formally solved. The formal solution of (6.137) is given by

$$\Psi(x) = c_1 e^{-\alpha x} + \frac{(\alpha^2 - \xi^2)}{24\eta\alpha} \left[ e^{-\alpha x} \int_0^x dt R(t) e^{\alpha t} + e^{\alpha x} \int_x^\infty dt R(t) e^{-\alpha t} \right], \quad (6.140)$$

where  $c_1$  is an integration constant. This solution suggests that  $\Psi(x)$  is well behaved with respect to  $(\alpha^2 - \xi^2)$  and regular in  $(\alpha^2 - \xi^2)$ .

In the Wiener-Hopf method,  $\pm\alpha$  determine the width of the strip in the complex  $k$  plane, but the width is arbitrary except that  $-\alpha < \xi < \alpha$ , because  $\alpha$  can be as close to  $\xi$  as can be. Therefore, having obtained the general solution which is regular with respect to  $(\alpha^2 - \xi^2)$  and well behaved, it now is appropriate to take the limit  $\alpha \rightarrow \xi + 0$ . Then the solution in the limit is

$$\Psi(x) = c_1 e^{-\xi x}. \quad (6.141)$$

This solution now suggests that  $\varphi(x)$  is a correlation function decaying exponentially and  $\xi$  has to do with the inverse correlation range. Because we are at present interested in hard sphere fluids we will determine  $\Psi(x)$  and  $\varphi(x)$  for hard sphere fluids in the following. For nonhard sphere fluids, they can be similarly determined.

Because the potential energy for hard sphere fluids is given by the form

$$\begin{aligned} u(x) &= \infty \quad \text{for } x < 1 \\ &= 0 \quad \text{for } x > 1 \end{aligned}$$

the total correlation function  $h(x)$  must be such that

$$\begin{aligned} h(x) &= -1 \quad \text{for } x < 1 \\ &= h_2(x) \neq 0 \quad \text{for } x > 1, \end{aligned}$$

where  $h_2(x)$  is to be determined in the range  $x > 1$  by the integro-differential equations (6.135)–(6.137). This property of  $h(x)$  suggests that  $\varphi(x)$  should be taken equal to zero for  $x < 1$  so as to make it consistent with the total correlation function for hard sphere fluids. Because the behavior of  $\varphi(x)$  must be consistent with  $h(x)$  and its properties are also closely associated with those of  $K(x)$  for  $x > 1$ , as will be seen later, it is appropriate to look for  $\varphi(x)$  such that

$$\begin{aligned}\varphi(x) &= 0 \quad \text{for } x < 1, \\ &\neq 0 \quad \text{for } x > 1.\end{aligned}\tag{6.142}$$

This means that it is necessary to examine (6.137) only in the range  $1 < x < \infty$ . It is emphasized that (6.142) is only for hard sphere fluids or fluids with a hard core.

Because  $\Psi(1)$  must be finite at  $x = 1$  and  $\Psi(\infty) = 0$  by the boundary conditions, it follows from the solution (6.141) that

$$\varphi(x) - \varphi(1) = \int_1^x dx \Psi(x) = \xi^{-1} e^{-\xi} \left[ 1 - e^{-\xi(x-1)} \right] c_1$$

and we find

$$\varphi(x) = \varphi(1) + \xi^{-1} e^{-\xi} \left[ 1 - e^{-(x-1)\xi} \right] c_1.$$

But

$$\varphi(\infty) = 0,$$

it follows that

$$c_1 = -\xi e^\xi \varphi(1)$$

and

$$\varphi(x) = \varphi(1) e^{-\xi(x-1)} \quad (x > 1).\tag{6.143}$$

This is the solution of the gauge function for hard sphere fluids. Normalizing it, we obtain  $\varphi(1) = \xi$  and thus

$$\varphi(x) = \xi e^{-\xi(x-1)},\tag{6.144}$$

$$\Psi(x) = -\xi^2 e^{-\xi(x-1)}.\tag{6.145}$$

These show that the gauge function is closely associated with correlations of particles and also with the zeros of  $[1 - \rho\hat{c}(k)]$ . The parameter  $\xi$  should be determined within the framework of the present theory. This can be done, as will be shown.

The result presented for  $\varphi(x)$  turns out to be independent of the potential energy models for fluids, except that it is given only in the range  $1 < x < \infty$  for hard sphere fluids. For nonhard sphere potentials, the range is  $0 \leq x < \infty$ , and  $\varphi(x)$  is determined from (6.141) in the whole  $x$  range, irrespective of the potential models. Consideration for  $\varphi(x)$  and  $\Psi(x)$  up to this point implies that  $\varphi(x)$  is a potential of mean force describing correlations of particles in the

fluid. It is therefore a mean field in the fluid, but not an additional potential tail for hard spheres. Clearly, even hard spheres should create such a mean field if a multitude of them are confined close to each other in a volume, and this is one of obvious advantages of the Wiener–Hopf factorization (6.106) in the present theory.

## 6.7 Equation for Inverse Correlation Length

The inverse correlation length  $\xi$  appearing in the gauge function should be determined within the framework of the theory based on the integral equations presented. Equation (6.97) in the limit of  $\alpha \rightarrow \xi + 0$  becomes

$$\left( \frac{\partial \beta^* p^*}{\partial \eta} \right)_T = \hat{K}^2(0). \quad (6.146)$$

Because  $\hat{K}(0)$  is related to the zeroth moment of  $K^*(x)$ ,

$$\hat{K}(0) = 1 - 12\eta \int_0^\infty dx K^*(x) \equiv m_0, \quad (6.147)$$

we may write (6.146) as

$$m_0^2 = \left( \frac{\partial \beta^* p^*}{\partial \eta} \right)_T. \quad (6.148)$$

Furthermore, because the Fourier transform of the OZ equation at  $k = 0$  may also be written as

$$\left( \frac{\partial \beta^* p^*}{\partial \eta} \right)_T \left[ 1 + 24\eta \int_0^\infty dx x^2 h(x) \right] = 1, \quad (6.149)$$

with the help of (6.148) this equation may be written as

$$m_0^2 \left[ 1 + 24\eta \int_0^\infty dx x^2 h(x) \right] = 1. \quad (6.150)$$

Either this equation (6.150) or (6.148) may be used to determine  $\xi$  because they must be satisfied by the solutions of the integral equations presented, and the solutions are functions of the yet undetermined parameter  $\xi$ . Either one of these equations will be called the constraint equation, which is an algebraic equation relating  $\xi$  to  $\eta$  and  $\beta^*$  for the fluid of interest.

Either (6.148) or (6.150) must be combined with the integral equations (6.135) and (6.136) in developing the solution algorithm. Solving (6.135) and (6.136) subject to the condition (6.148) or (6.150) is a kind of eigenvalue problem, for which there is only one value of  $\xi$  at a given value of  $\eta$  that satisfies the equations. It must be emphasized that (6.148) and (6.150), as they stand, are exact and valid independently of interaction potential energy models for fluids. They become approximate when approximations are made

of the moment  $m_0$  and the total correlation function  $h(x)$  or  $p^*$ , but such approximations must be made so that the exact relation implied by the OZ equation is satisfied. In this sense, the approximate solutions for the integral equations are renormalized to satisfy the relation demanded by the OZ equation.

The formal theory of integral equations for pair correlation functions is now complete. It can be shown with hard sphere fluids as an example how this theory works for liquids.

## 6.8 Application to Hard Sphere Fluids

Equations (6.135)–(6.137) become somewhat simpler for hard sphere fluids than for fluids obeying other potential models. Because the theory has not yet been applied to nonhard sphere potential models, it will be discussed for hard sphere fluids. For hard sphere fluids, the aforementioned solvability condition (i.e., the constraint equation) and also the determination of  $k_c$  can be more readily seen than the nonhard sphere potential models. Here the solution procedure is sketched briefly, and the results for the equation of state and pair correlation function are presented. The details are referred to the original work [10].

### 6.8.1 Integro-Differential Equations for Hard Sphere Fluids

For hard sphere fluids, the total correlation function is discontinuous in the following manner:

$$h(x) = [\theta(x - 1) - 1] + \theta(x - 1) h_2(x), \quad (6.151)$$

where  $h_2(x) = h(x > 1)$  and  $\theta(t)$  is the Heaviside step function defined earlier; see (6.19). Because of this property of the correlation functions and the intimate relation of  $\phi$  to them, we have argued that it is appropriate to seek  $\phi$  such that  $\phi(x) = 0$  for  $x < 1$  and the range of  $x$  for  $\phi(x)$  can be taken as  $1 < x < \infty$  instead of  $0 < x < \infty$ , which should be taken for continuous intermolecular potentials. Because of these properties of  $h(x)$  and  $\phi(x)$ , there arise two sets of integro-differential equations [10] from (6.135) and (6.136):

In the range of  $x < 1$

$$K^{*\prime}(x) = x - 12\eta \int_0^\infty dt (t - x) K^*(t) h(|x - t|), \quad (6.152)$$

$$\frac{-1}{6\eta x} \frac{\partial^2}{\partial x \partial n} n^2 x^3 y(x, n) = -K^{*\prime}(x) + 12\eta \int_0^\infty dt K^{*\prime}(t) K^*(t - x), \quad (6.153)$$

$$\varphi(x) = 0 \quad (6.154)$$

and in the range of  $x > 1$

$$x[y(x, n) - 1] = -K^{*\prime}(x) - 12\eta \int_0^\infty dt(t-x) K^*(t) h(|x-t|), \quad (6.155)$$

$$K^{*\prime}(x) = 12\eta \int_0^\infty dt K^{*\prime}(t) K^*(t-x) - 2\varphi(x) - (1+x) \frac{\partial \varphi}{\partial x}, \quad (6.156)$$

where  $\varphi(x)$  is given by (6.144).

The factorization function  $K^*(x)$  also should have two different forms in the ranges of  $x < 1$  and  $1 < x < \infty$ . Therefore, it is appropriate to define two functions

$$\begin{aligned} K_1(x) &= K^*(x) & \text{for } x < 1 \\ K_2(x) &= K^*(x) & \text{for } 1 < x < \infty. \end{aligned} \quad (6.157)$$

Because  $K^*(x)$  must be continuous, it is required that

$$K_1(1) = K_2(1). \quad (6.158)$$

Therefore  $K^*(x)$  may be expressed as

$$K^*(x) = [1 - \theta(x-1)] K_1(x) + \theta(x-1) K_2(x). \quad (6.159)$$

The integro-differential equations (6.152)–(6.156) immediately provide some formal results for thermodynamic functions that can be useful for developing solution procedures. We discuss them first.

### 6.8.2 Differential Equation for Pressure

The integro-differential equation (6.153) gives rise to a differential equation for pressure, which can be determined if  $K^*(x)$  is determined from Eqs. (6.152), (6.155), and (6.156), which also yield the total correlation function in the range of  $x > 1$ . Because the virial equation of state for hard sphere fluids is given by [2]

$$p^* \beta^* = \eta + 4\eta^2 y(1, \eta), \quad (6.160)$$

upon integration of (6.153) over  $x \in [0, 1]$ , there follows the differential equation for pressure:

$$\frac{\partial}{\partial \eta} (p^* \beta^* - \eta) = 24\eta \int_0^1 dx x R^{(i)}(x) + 288\eta^2 \int_0^1 dx x R^{(o)}(x), \quad (6.161)$$

where

$$R^{(i)}(x) = K'_1(x) - 12\eta \int_x^1 dt K'_1(t) K_1(t-x), \quad (6.162)$$

$$R^{(o)}(x) = - \int_1^{x+1} dt K_1(t-x) K'_2(t) - \int_{x+1}^\infty dt K_2(t-x) K'_2(t). \quad (6.163)$$

Superficially,  $R^{(i)}(x)$  is the contribution from the inner region ( $x < 1$ ), which is made up of  $K_1(x)$  in the inner region corresponding to the hard core, whereas  $R^{(o)}(x)$  represents in the main the contribution from the outer region ( $x > 1$ ). There now remains the task of calculating  $K_1(x)$  and  $K_2(x)$  to obtain the equation of state by integrating (6.161) with respect to  $\eta$ . The integral of  $R^{(i)}(x)$  in (6.161) constitutes the principal contribution to the equation of state for hard sphere fluids. Note that the equation of state determined by (6.161) is thermodynamically consistent regardless of whether it is calculated exactly or approximately because there is only one equation of state possible in the present theory. Note also that the cavity function  $y(1, \eta)$  can be calculated only through  $p^* \beta^*$  or the right-hand side of (6.161) in the present theory.

### 6.8.3 Pair Correlation Function

The total correlation function, and hence the pair correlation function, can be calculated from the integral equations (6.152), (6.155), and (6.156), but this approach is rather cumbersome. Instead, because it is permissible to take the limit  $\alpha \rightarrow \xi + 0$ , it may be calculated directly with the Fourier transform of the OZ equation

$$\rho \hat{h}(k) = \frac{\rho \hat{c}(k)}{1 - \rho \hat{c}(k)}, \quad (6.164)$$

with  $\hat{c}(k)$  given by the Fourier transform of the thermodynamically consistent closure (6.134), which for hard sphere fluids takes the form

$$\begin{aligned} c(x) &= -y(x, \eta) - \left( \frac{1}{3} \frac{\partial y}{\partial \ln x} + \frac{1}{2} \frac{\partial y}{\partial \ln y} + \frac{1}{6} \frac{\partial^2 y}{\partial \ln x \partial \ln \eta} \right) \quad \text{for } x < 1 \\ &= \frac{1}{x} \left[ 2\varphi(x) + x \frac{\partial \varphi}{\partial x} \right] \quad \text{for } x > 1 \end{aligned} \quad (6.165)$$

with  $\varphi(x)$  given in (6.144). This approach is found more readily amenable to an approximation with good accuracy, which is also independent of the approximation for  $K_1(x)$  and  $K_2(x)$ . In regard to the closure (6.165), it is useful to note that inasmuch as the closure is an assumption, it is permissible to simply take, instead of the closure (6.165), the closure

$$\begin{aligned} c(x) &= -y(x, \eta) \quad \text{for } x < 1 \\ &= \frac{1}{x} \left[ 2\varphi(x) + x \frac{\partial \varphi}{\partial x} \right] \quad \text{for } x > 1, \end{aligned} \quad (6.166)$$

which is a modification of the PY closure.<sup>6</sup> This form of closure, which is an approximation of (6.165), will give rather accurate pair correlation functions.

#### 6.8.4 A Perturbation Solution Method

To solve the integro-differential equations approximately for hard sphere fluids, (6.152), (6.155), and (6.156) are cast into the forms

$$\begin{aligned} K'_1(x) &= m_0x + m_1 \\ &\quad - 12\eta \int_{x+1}^{\infty} dt K_2(t)(t-x)y_2(t-x), \end{aligned} \quad (6.167)$$

$$x[y_2(x) - 1] = -K'_2(x) + 12\eta L(x) + 12\eta \Lambda(x), \quad (6.168)$$

$$K'_2(x) = 12\eta \Pi_2(x) - 2\varphi(x) - (x+1)\frac{\partial \varphi}{\partial x}, \quad (6.169)$$

where  $y_2(t)$  is the cavity function in the outer range. Equation (6.167) is defined in the range  $x < 1$ , whereas (6.168) and (6.169) are defined in  $x > 1$ . The moment  $m_0$  of  $K^*(x)$  has been already defined [see (6.147)] and the first moment  $m_1$  of  $K^*(x)$  is defined by

$$m_1 = 12\eta \int_0^{\infty} dx x K^*(x). \quad (6.170)$$

The symbols  $\Pi_2(x)$  and  $\Lambda(x)$  are the abbreviations for the convolution integrals defined below

$$\Pi_2(x) = \int_x^{x+1} dt K'_2(t) K_1(t-x) + \int_{x+1}^{\infty} dt K'_2(t) K_2(t-x) \quad (x > 1), \quad (6.171)$$

and

$$L(x) = [1 - \theta(x-2)] L_1(x) + \theta(x-2) L_2(x), \quad (6.172)$$

$$\Lambda(x) = [1 - \theta(x-2)] \Lambda_1(x) + \theta(x-2) \Lambda_2(x) \quad (6.173)$$

---

<sup>6</sup> This is a kind of GSMA closure [7] with  $c(x)$  given for  $x > 1$  by the gauge function and its derivative. Not only is the form of  $c(x)$  for  $x > 1$  different from Waisman's form, but also its mathematical origin is rooted in the Wiener-Hopf method, unlike the original GSMA closure.

with the definitions

$$L_1(x) = \int_{x-1}^1 dt K_1(t)(t-x) + \int_1^{x+1} dt K_2(t)(t-x) \quad (1 < x < 2), \quad (6.174)$$

$$L_2(x) = \int_{x-1}^{x+1} dt K_2(t)(t-x) \quad (x > 2), \quad (6.175)$$

$$\begin{aligned} A_1(x) &= \int_0^{x-1} dt K_1(t)(x-t) h_2(x-t) \\ &\quad - \int_{x+1}^{\infty} dt K_2(t)(t-x) h_2(t-x) \quad (1 < x < 2), \end{aligned} \quad (6.176)$$

$$\begin{aligned} A_2(x) &= \int_0^1 dt K_1(t)(x-t) h_2(x-t) + \int_1^{x-1} dt K_2(t)(x-t) h_2(x-t) \\ &\quad - \int_{x+1}^{\infty} dt K_2(t)(t-x) h_2(t-x) \quad (x > 2). \end{aligned} \quad (6.177)$$

One feature that is immediately obvious in this set of equations is that because temperature does not appear in the equation,  $\xi$  must be independent of it, but depends only on  $\eta$ . Therefore,  $\xi$  does not change as the temperature of the system changes. This is expected as mentioned earlier, because hard sphere fluids are athermal and have no first-order liquid-vapor phase transition although there can be a liquid-crystal, or a liquid-amorphous solid, transition. However, because the closure is no longer given by (6.165) for potentials other than the hard sphere potential,  $\xi$  is expected to depend generally on both temperature and density. A first-order liquid-vapor phase transition is therefore expected as the zeros close onto the origin of the complex  $k$  plane.

The inhomogeneous terms of (6.167) consist of simple algebraic forms in the inner region, whereas the contribution from the outer region on the right-hand side—the integral term—is a correction for the contribution from the inner region (hard core) made up of only  $K_1(x)$  and its integral. The role of (6.168) and (6.169) in the outer region is then to provide a correction for (6.167) and for the differential equation for pressure. These features of the integral equations suggest that the equation of state may be calculated by a perturbation technique that treats the contribution from the outer region as a perturbation, and the packing fraction may be treated as a perturbation parameter for the purpose. Because the integral equations are of the Volterra type [51], it is sufficient to generate iterative series to obtain a perturbation series.

Thus the lowest order iterative solution for  $K_1(x)$  is

$$K_1(x) \simeq \kappa + \frac{1}{2}m_0x^2 + m_1x, \quad (6.178)$$

where

$$\kappa = K_2(1) - \frac{1}{2}m_0 - m_1. \quad (6.179)$$

Similarly, we obtain from (6.169)  $K_2(x)$  to the same order:

$$K_2(x) = [1 - \xi(x + 1)] e^{-\xi(x-1)} + O(\eta) \quad (6.180)$$

and from (6.169)

$$xy_2(x) = x + \xi[2 - \xi(1 + x)] e^{-(x-1)\xi} + O(\eta). \quad (6.181)$$

In this order of approximation

$$\kappa_2 \equiv K_2(1) = 1 - 2\xi. \quad (6.182)$$

This will provide us with  $\xi$  as will be seen later, when  $\kappa_2$  is determined as a function of  $\eta$ .

To obtain the equation of state beyond that of the ideal gas, it is necessary to calculate the differential equation to the order of  $\eta$ . This means that at least the integral of  $R^{(i)}(x)$  must be calculated with the lowest order solution for  $K_1(x)$ , and the term involving  $R^{(o)}(x)$  may be neglected. Thus on using the result for  $K_1(x)$ , the differential equation for pressure (6.161) becomes

$$\begin{aligned} \frac{\partial}{\partial \eta} (p^* \beta^* - \eta) &= 4\eta(2m_0 + 3m_1)(2\eta m_0 + 3\eta m_1 + 1) \\ &\quad - 12\eta^2(3m_0 + 4m_1)\kappa_2. \end{aligned} \quad (6.183)$$

The density dependence of the moments  $m_0$  and  $m_1$  must be determined from their definitions, (6.147) and (6.170). With the lowest order solutions given earlier for  $K_1(x)$ ,  $K_2(x)$ , and  $y_2(x)$ , we obtain the moments as

$$\begin{pmatrix} m_0 \\ m_1 \end{pmatrix} = \frac{1}{(\eta - 1)^2} \begin{pmatrix} 2\eta + 1 \\ -\frac{3}{2}\eta \end{pmatrix} + \frac{6\eta\kappa_2}{(\eta - 1)} \begin{pmatrix} 2 \\ -1 \end{pmatrix}. \quad (6.184)$$

Equation (6.183) is then given by

$$\frac{\partial}{\partial \eta} \left[ p^* \beta^* - \frac{\eta(1 + \eta + \eta^2)}{(1 - \eta)^3} \right] = \frac{12(\eta + 5)\eta^2}{(\eta - 1)^3} \kappa_2 + \frac{144\eta^3}{(\eta - 1)^2} \kappa_2^2. \quad (6.185)$$

To determine  $\kappa_2$  or  $\xi$ , we now use the constraint equation (6.148). Using (6.184) and (6.185), the physically acceptable solution for  $\xi$  is

$$\xi = \frac{1}{2},$$

that is,  $\kappa_2 = 0$ , and the corresponding equation of state is

$$p^* \beta^* = \frac{\eta(1 + \eta + \eta^2)}{(1 - \eta)^3}. \quad (6.186)$$

This is the well-known equation of state for hard sphere fluids obtained via the isothermal compressibility route in the PY closure. In the present theory,

it is thermodynamically consistent, that is, it is the same as that obtained via the virial route. When this result is substituted in (6.160), the cavity function is obtained. It is the only way to obtain  $y(1, \eta)$  for hard sphere fluids because the cavity function for  $x < 1$  is defined by (6.153), which gives rise to the differential equation for pressure.

The equation of state (6.186) can be improved even if the higher order solutions are not employed for  $K_1(x)$  and so forth. We notice that only a very small correction for  $\kappa_2$  is necessary. Therefore, we may take  $\kappa_2$  on the right-hand side of (6.185) as a small number, say,

$$\kappa_2 = \frac{(4 - \eta) \eta}{c(1 - \eta)} \quad (6.187)$$

where  $c$  is a sufficiently large number that assures the smallness of  $\kappa_2$ : it may be taken as  $c = 60$  or  $120$ , for example. Then (6.148) is used together with (6.184) and (6.185). For  $c = 60$ , this yields the inverse correlation length  $\xi$  in the form

$$\xi = \frac{1}{2} - \frac{2\eta + 1}{24\eta(1 - \eta)} + \frac{1}{24\eta(1 - \eta)} \sqrt{1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4 + \omega}, \quad (6.188)$$

$$\omega = \frac{(5 - 4\eta^2 + \eta^3)(\eta - 4)\eta^3}{25}. \quad (6.189)$$

Suppose that the equation of state is known as a function of density, as it is for the Carnahan–Starling (CS) equation of state [52]. By using the CS equation of state for  $(\partial p^* \beta^* / \partial \eta)_T$  in (6.148),

$$\xi = \frac{1}{2} - \frac{2\eta + 1}{24\eta(1 - \eta)} + \frac{\sqrt{4\eta + 4\eta^2 - 4\eta^3 + \eta^4 + 1}}{24\eta(1 - \eta)}. \quad (6.190)$$

The difference between these  $\xi$  values is rather minor, and  $\xi$  is about 0.5 in the liquid density range.

Substituting  $\kappa_2$  given in (6.187) in (6.185) and integrating the equation, we obtain the equation of state in closed form

$$(p^* \beta^*)_{\text{th1}} = \frac{\eta(1 + \eta + \eta^2)}{(1 - \eta)^3} + \frac{7}{5} \ln(1 - \eta) + \frac{\eta(1050\eta - 770\eta^2 + 165\eta^3 + 21\eta^4 - 25\eta^5 + 3\eta^6 - 420)}{300(\eta - 1)^3}. \quad (6.191)$$

If  $c = 120$ , then the equation of state is given by

$$(p^* \beta^*)_{\text{th2}} = \frac{\eta(1 + \eta + \eta^2)}{(1 - \eta)^3} - \frac{1}{4} \ln(1 - \eta) + \frac{(550\eta^2 - 750\eta + 525\eta^3 + 81\eta^4 - 25\eta^5 + 3\eta^6 + 300)\eta}{1200(\eta - 1)^3}. \quad (6.192)$$

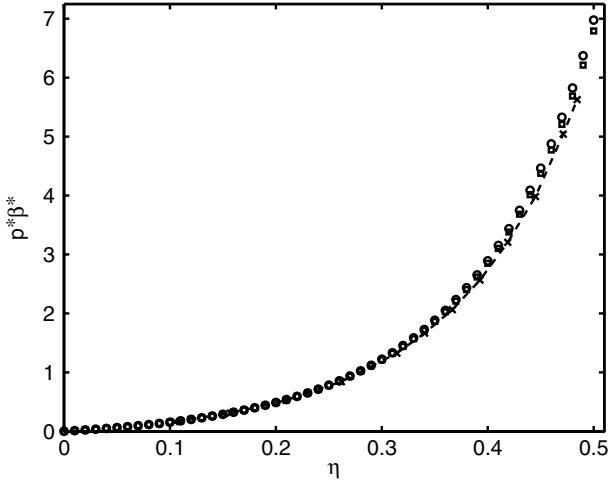


Fig. 6.6.  $p^*\beta^*$  vs.  $\eta$  for a hard sphere fluid

The PY equation of state is corrected in these equations of state, although the corrections are minor. In Fig. 6.6, the equation of state  $(p^*\beta^*)_{th1}(O)$  and  $(p^*\beta^*)_{th2}(\square)$  are compared with the MC simulation results [53] and CS equation of state (broken curve). Note that the CS equation of state is comparable with the MC simulation results.

#### 6.8.5 Numerical Results for the Pair Correlation Function

The perturbation solution for the total correlation function for  $x > 1$ , (6.181), is not sufficiently accurate to use for calculating quantities other than  $K_1(x)$ . To calculate a sufficiently accurate total correlation function, (6.164) may be used together with an approximation of the closure (6.165), for example, an approximate form corresponding to the iterative solution used for the equation of state presented earlier.

It was found that the approximate closure (6.166) was simple from the computational standpoint yet sufficiently accurate for the total correlation function. We will first examine to what order of approximation of the thermodynamically consistent closure (6.165) the aforementioned closure (6.166) corresponds. It can be shown that for hard sphere fluids

$$\int_0^1 dx x \left( \frac{1}{3} \frac{\partial y}{\partial \ln x} + \frac{1}{2} \frac{\partial y}{\partial \ln y} + \frac{1}{6} \frac{\partial^2 y}{\partial \ln x \partial \ln \eta} \right) = 0 \quad (6.193)$$

and, moreover,

$$x \left( \frac{1}{3} \frac{\partial y}{\partial \ln x} + \frac{1}{2} \frac{\partial y}{\partial \ln y} + \frac{1}{6} \frac{\partial^2 y}{\partial \ln x \partial \ln \eta} \right) \simeq O(\eta). \quad (6.194)$$

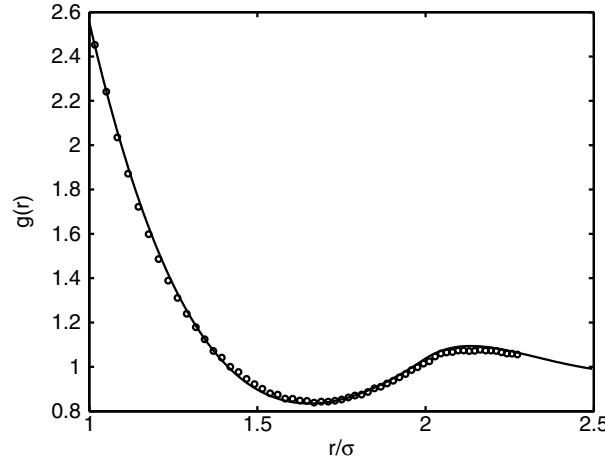
Because the terms of  $O(\eta)$  are neglected in approximations (6.178) and (6.180) for  $K_1(x)$  and  $K_2(x)$  and the cavity function  $y(x, \eta)$  is at least  $O(1)$ , the second term in the first line of closure (6.165) may be neglected to obtain closure (6.166).

On the basis of this analysis, the OZ equation (6.164) with closure (6.166) for the direct correlation function was solved in [10]. Equation (6.164) can be solved iteratively together with (6.166) for an arbitrarily chosen value of  $\xi$  until the solution is convergent, and then the consistency of the solution with the constraint equation is checked

$$\left[ \frac{2\eta + 1}{(\eta - 1)^2} + \frac{12\eta}{(\eta - 1)} (1 - 2\xi) \right]^2 \left[ 1 + 24\eta \int_0^\infty dx x^2 h(x) \right] = 1. \quad (6.195)$$

If this constraint equation is not satisfied within the given tolerance for a chosen value of  $\xi$ , then the value of  $\xi$  is suitably altered and the OZ equation is solved repeatedly until the constraint equation is satisfied within the given tolerance. It was found that for hard sphere fluids in the liquid density range  $\xi \simeq 0.5$ , the pair correlation function thus calculated compares with the MC simulation results [53] in Fig. 6.7. As is evident, the pair correlation function by the method described is quite accurate.

In view of the results obtained for the equation of state and the pair correlation function, it is quite evident that the integro-differential equations (6.167)–(6.169), which correspond to the OZ equation with a thermodynamically consistent closure, are expected to yield reliable and accurate results for the equation of state and the pair correlation function for liquids, if they are solved exactly.



**Fig. 6.7.** Comparison of  $g(r)$ , computed by solving the OZ equation with (6.166) for the closure, with the MC simulation results of Barker and Henderson [53]. The open circles ( $\circ$ ) are the MC simulation results, whereas the solid curve is theoretical

### 6.8.6 The Laguerre Transform Method

Having ascertained that the integro-differential equations (6.167)–(6.169) are capable of yielding a correctly behaved equation of state and total pair correlation function, it is appropriate to seek a more accurate method of solving them. Because the gauge function obtained earlier is given as an exponential function, which may be regarded as the weight function for Laguerre polynomials, it seems reasonable to develop a transform method by employing Laguerre polynomials. Laguerre polynomials are orthogonal functions, so the method [54] we have in mind is a Galerkin method based on orthogonal polynomials. This particular transform method will be henceforth called the Laguerre transform method. The range of variable  $x$  is from  $x = 1$  to infinity for the problem involving hard sphere, so it is appropriate to expand  $h_2(x)$  and  $K_2(x)$  as follows:

$$xh_2(x) = \sqrt{2\xi} \sum_{k \geq 0} H_k \exp[-\xi(x-1)] L_k[2\xi(x-1)], \quad (6.196)$$

$$K_2(x) = \sqrt{2\xi} \sum_{k \geq 0} K_k \exp[-\xi(x-1)] L_k[2\xi(x-1)], \quad (6.197)$$

where  $L_k(s)$  is the Laguerre polynomial of order  $k$  and argument  $s$  and the amplitudes  $H_k$  and  $K_k$  are the Laguerre transforms of  $xh_2(x)$  and  $K_2(x)$ , respectively. The Laguerre transforms  $H_k$  and  $K_k$  should be determined from the Laguerre transforms of (6.168) and (6.169), which must be subject to constraint (6.150) determining the value of  $\xi$ . The Laguerre polynomials are orthogonal and normalized according to Bateman's definition of Laguerre polynomials [55]:

$$\int_0^\infty ds e^{-s} L_k(s) L_j(s) = \delta_{jk}. \quad (6.198)$$

The Laguerre transforms  $H_j$  and  $K_j$  are obtained upon multiplying

$$\sqrt{2\xi} \exp[-\xi(x-1)] L_j[2\xi(x-1)]$$

by (6.196) and (6.197) and integrating over  $x \in [1, \infty]$ :

$$H_j = \sqrt{2\xi} \int_1^\infty dx x h_2(x) e^{-\xi(x-1)} L_j[2\xi(x-1)], \quad (6.199)$$

$$K_j = \sqrt{2\xi} \int_1^\infty dx K_2(x) e^{-\xi(x-1)} L_j[2\xi(x-1)]. \quad (6.200)$$

In this connection, note that

$$\begin{aligned} h(x) &= h_2(x) = y_2(x) - 1 && \text{for } x > 1 \\ &= -1 && \text{for } x < 1. \end{aligned}$$

Therefore, the cavity function can be similarly expanded in Laguerre polynomials.

### Equations for Moments

We begin the solution algorithm based on Laguerre transforms with the equations for the moments  $m_0$  and  $m_1$ . If the definitions of the moments are used, they are expressible in terms of the Laguerre transforms of  $xh_2$  and  $K_2(x)$ . In matrix form, the equations for  $m_0$  and  $m_1$  are given by

$$\begin{pmatrix} m_0 \\ m_1 \end{pmatrix} = \begin{pmatrix} \mu_0 \\ \mu_1 \end{pmatrix} + 12\sqrt{2\xi}\eta \sum_{k \geq 0} K_k \begin{pmatrix} \mu_{0k} \\ \mu_{1k} \end{pmatrix}, \quad (6.201)$$

where

$$\begin{pmatrix} \mu_0 \\ \mu_1 \end{pmatrix} = \frac{1}{(\eta - 1)^2} \begin{pmatrix} 2\eta + 1 \\ -\frac{3}{2}\eta \end{pmatrix}, \quad (6.202)$$

$$\begin{pmatrix} \mu_{0k} \\ \mu_{1k} \end{pmatrix} = \frac{-1}{(\eta - 1)^2} \begin{pmatrix} \Delta M_k^{(0)} \\ \frac{1}{2}\Delta M_k^{(1)} \end{pmatrix}. \quad (6.203)$$

In (6.203),  $\Delta M_k^{(0)}$  and  $\Delta M_k^{(1)}$  are defined by quantities consisting of Laguerre transforms of  $xh_2$  and  $K_2(x)$  and quadratures of Laguerre polynomials. They are given by [54]

$$\begin{aligned} \Delta M_k^{(0)} &= 1 - \eta + \frac{(-1)^k}{\xi^2} [\xi(2\eta + 1) - 12\eta(1 + k)] \\ &\quad + \frac{12\eta}{\xi^5} [\xi(2\eta + 1) J_k^{(0)} - 6\eta J_k^{(1)}] \\ &\quad + \frac{12\sqrt{2}\eta}{\xi^{\frac{7}{2}}} \sum_{j \geq 0} [\xi(2\eta + 1) J_{jk}^{(0)} - 6\eta J_{jk}^{(1)}] H_j, \end{aligned} \quad (6.204)$$

$$\begin{aligned} \Delta M_k^{(1)} &= -1 + 7\eta + \frac{(-1)^k}{\xi^2} [3\eta\xi - 4(1 - 4\eta)(1 + k)] \\ &\quad + \frac{12\eta}{\xi^5} [3\eta\xi J_k^{(0)} - 2(1 - 4\eta) J_k^{(1)}] \\ &\quad + \frac{12\sqrt{2}\eta}{\xi^{\frac{7}{2}}} \sum_{j \geq 0} [3\eta\xi J_{jk}^{(0)} - 2(1 - 4\eta) J_{jk}^{(1)}] H_j, \end{aligned} \quad (6.205)$$

where  $J_k^{(l)}$  and  $J_{jk}^{(l)}$  ( $l = 0, 1$ ) are quadratures of Laguerre polynomials defined by

$$J_k^{(l)}(\xi) = \int_0^\xi dx x^l \int_x^\xi ds \int_s^\infty du (u + \xi - s) e^{-u} L_k(2u), \quad (6.206)$$

$$J_{jk}^{(l)}(\xi) = \int_0^\xi dx x^l \int_x^\xi ds e^{-s} \int_0^\infty du e^{-2u} L_j(2u) L_k(2s + 2u). \quad (6.207)$$

These quadratures can be evaluated exactly as functions of  $\xi$  by using the properties of Laguerre polynomials, but the results are rather complicated polynomials of  $\xi$  weighted by  $\exp(-\xi)$ ; they are expressible as linear combinations of Laguerre polynomials of  $\xi$ .

With the help of the formulas for  $m_0$  and  $m_1$  it is now possible to express  $K_1(x)$  as follows:

$$\begin{aligned} K_1(x) &= \frac{1}{2}\mu_0(x^2 - 1) + \mu_1(x - 1) + 12\sqrt{2\xi}\eta \sum_{k \geq 0} K_k \mathfrak{K}_k^{(0)}(\xi x) \\ &\quad + \frac{24\eta}{\xi} \sum_{j,k \geq 0} H_j K_k \mathfrak{K}_{jk}^{(1)}(\xi x), \end{aligned} \quad (6.208)$$

where

$$\mathfrak{K}_k^{(0)}(\xi x) = 1 + \frac{\mu_{0k}}{2\xi^2} [(\xi x)^2 - \xi^2] + \frac{\mu_{1k}}{\xi} (\xi x - \xi) + \frac{1}{\xi^3} A_k^{(1)}(\xi x), \quad (6.209)$$

$$\mathfrak{K}_{jk}^{(1)}(\xi x) = \frac{\sqrt{2}}{\xi^{3/2}} \sum_{j \geq 0} H_j A_{jk}^{(2)}(\xi x). \quad (6.210)$$

In these expressions,  $A_k^{(1)}(s)$  and  $A_{jk}^{(2)}(s)$  are the abbreviations for the linear combinations of Laguerre polynomials as follows:

$$\begin{aligned} A_k^{(1)}(s) &= (\xi + 1) [e^{-s} L_k(2s) - e^{-\xi} L_k(2\xi)] \\ &\quad - 2^k (2\xi + 3) \sum_{j=0}^k \binom{k}{j} \left(\frac{-1}{2}\right)^j [e^{-s} L_{k-j-1}(s) - e^{-\xi} L_{k-j-1}(\xi)] \\ &\quad + 2^k (\xi + 2) \sum_{j=0}^k \binom{k}{j} \left(\frac{-1}{2}\right)^j [e^{-s} L_{k-j-2}(s) - e^{-\xi} L_{k-j-2}(\xi)] \\ &\quad - 2^k \sum_{j=0}^k \binom{k}{j} \left(\frac{-1}{2}\right)^j [e^{-s} L_{k-j-3}(s) - e^{-\xi} L_{k-j-3}(\xi)], \end{aligned} \quad (6.211)$$

$$\begin{aligned} A_{jk}^{(2)}(s) &= \frac{1}{2} \delta_{j0} \{e^{-s} [L_k(s) - L_{k-1}(s)] - e^{-\xi} [L_k(\xi) - L_{k-1}(\xi)]\} \\ &\quad + \frac{e^{-s}}{2} \sum_{m=0}^{k-1} (\delta_{m,k-j} - \delta_{m,k-j-1}) [L_m(s) - L_{m-1}(s)] \\ &\quad - \frac{e^{-\xi}}{2} \sum_{m=0}^{k-1} (\delta_{m,k-j} - \delta_{m,k-j-1}) [L_m(\xi) - L_{m-1}(\xi)]. \end{aligned} \quad (6.212)$$

In connection with the quadratures presented earlier, it is useful to note that

$$\begin{aligned} J_k^{(l)} &= \int_0^\xi ds s^l A_k^{(1)}(s), \\ J_{jk}^{(l)} &= \int_0^\xi ds s^l A_{jk}^{(2)}(s), \end{aligned} \quad (6.213)$$

which on evaluation yield linear combinations of Laguerre polynomials if the expressions in (6.211) and (6.212) are used. Thus we see that  $K_1(x)$  is at most quadratic with respect to the Laguerre transforms of  $xh_2(x)$  and  $K_2(x)$ .

### Amplitude Equations

The Laguerre transforms, namely, the amplitude equations, of (6.168) and (6.169) can be obtained similarly to the equations for moments  $m_0$  and  $m_1$ . The amplitude equations will be a pair of algebraic equations for Laguerre transforms  $H_j$  and  $K_j$  but involve numerous quadratures. They may be expressed in the forms [54]

$$\begin{aligned} \sum_{k \geq 0} (S_{nk} H_k + \Theta_{nk} K_k) &= \frac{\eta}{\sqrt{2}\xi^{9/2}} I_n^{(H)} + \frac{24\sqrt{2}\eta}{\xi^{1/2}} \sum_{j,k \geq 0} N_{jkn}^{(H)} H_j K_k \\ &\quad + \frac{24\sqrt{2}\eta}{\xi^{1/2}} \sum_{j,k,l \geq 0} N_{jknl}^{(H)} H_j K_k H_l, \end{aligned} \quad (6.214)$$

$$\begin{aligned} \sum_{k \geq 0} M_{nk} K_k &= \frac{\sqrt{2\xi}}{4} [(4\xi - 3) \delta_{n0} - \delta_{n1}] + 24\sqrt{2\xi}\eta \sum_{j,k \geq 0} N_{jkn}^{(K)} K_j K_k \\ &\quad + 288\sqrt{2\xi}\eta^2 \sum_{j,k,l \geq 0} N_{jknl}^{(K)} K_j K_k H_l, \end{aligned} \quad (6.215)$$

where

$$D_{nk} = \delta_{nk} + 2 \sum_{j=0}^{k-1} \delta_{nj}, \quad (6.216)$$

the inhomogeneous term  $I_n^{(H)}$  is defined by

$$I_n^{(H)} = \mu_0 \Lambda_n^{(1/1)} + 4\xi \mu_1 \Lambda_n^{(1/2)}, \quad (6.217)$$

linear coefficients by the formulas

$$\begin{aligned} \Theta_{nk} &= -\xi D_{nk} - \frac{24\eta}{\xi^2} \left( \Lambda_{nk}^{(1/3)} + 12\eta\xi \Lambda_{nk}^{(1/7/0)} + \Lambda_{nk}^{(2/1)} \right), \\ S_{nk} &= \delta_{nk} - \frac{12\eta}{\xi^3} \left[ \mu_0 \left( \Lambda_{nk}^{(1/4)} + \Lambda_{nk}^{(2/2)} \right) + 2\mu_1 \xi \left( \Lambda_{nk}^{(1/5)} + \Lambda_{nk}^{(2/3)} \right) \right], \\ M_{nk} &= -\xi D_{nk} - \frac{12\eta}{\xi^2} \left( \mu_0 Q_{nk}^{(1)} + 2\mu_1 \xi Q_{nk}^{(2)} \right), \end{aligned} \quad (6.218)$$

and nonlinear coefficients by the formulas

$$\begin{aligned} N_{jkn}^{(H)} &= 12\eta A_{jkn}^{(1/8/0)} + 12\eta A_{jkn}^{(2/6/0)} - A_{jkn}^{(1/6)} - A_{jkn}^{(2/4)} - A_{jkn}^{(2/5)} + \frac{A_{jkn}^{(1/7/1)}}{\sqrt{2}\xi^{3/2}}, \\ N_{njk}^{(H)} &= 12\eta A_{njk}^{(1/8/1)} + 12\eta A_{njk}^{(2/6/1)}, \\ N_{jkn}^{(K)} &= Q_{jkn}^{(3)} + 12\eta Q_{jkn}^{(4/0)}, \\ N_{njk}^{(K)} &= Q_{njk}^{(4/1)}. \end{aligned} \quad (6.219)$$

All linear and nonlinear coefficients consist of various quadratures of Laguerre polynomials,  $A_n^{(1/1)}$ , etc. and  $Q_{nk}^{(1)}$ , etc. All can be exactly evaluated by using the properties of Laguerre polynomials but give rise to fairly complicated algebraic series of  $\xi$ . The quadratures may be classified into the following three classes:

$$A^{(1/p)}, A^{(1/p/q)} = \int_0^\xi ds e^{-s} L_n(2s) F(s), \quad (6.220)$$

$$A^{(2/p)}, A^{(2/p/q)} = \int_\xi^\infty ds e^{-s} L_n(2s) G(s), \quad (6.221)$$

$$Q^{(p)}, Q^{(p/q)} = \int_0^\infty ds e^{-s} L_n(2s) P(s), \quad (6.222)$$

which are summarized in Tables 6.1–6.3. Inspecting these tables for quadratures, we notice that some of the quadratures in Class  $(Q^{(p)}, Q^{(p/q)})$  can be expressed in terms of quadratures in Classes  $(A^{(\omega/p)}, A^{(\omega/p/q)})$  ( $\omega = 1, 2$ ).

**Table 6.1.** Quadratures of Laguerre polynomials Class  $A$

$A^{(1/p)}, A^{(1/p/q)}$	$F(s)$
$A_n^{(1/1)}$	$(s + \xi)(s + 5\xi)(s - \xi)^2$
$A_n^{(1/2)}$	$(s + 2\xi)(s - \xi)^2$
$A_{nk}^{(1/3)}$	$\int_\xi^{s+\xi} du(u - s)e^{-u} L_k(2u)$
$A_{nk}^{(1/4)}$	$\int_0^s du e^{-u} L_k(2u) [(s - u)^2 - \xi^2]$
$A_{nk}^{(1/5)}$	$\int_0^s du e^{-u} L_k(2u)(s - u - \xi)$
$A_{jkn}^{(1/6)}$	$e^{-\xi} \int_0^\infty du e^{-2u} L_k[2(u + s + \xi)] L_j(2u)$
$A_{nk}^{(1/7/0)}$	$\int_s^\xi du(u - s - \xi)\mathfrak{K}_k^{(0)}(u)$
$A_{jkn}^{(1/7/1)}$	$\int_s^\xi du(u - s - \xi)\mathfrak{K}_{kj}^{(1)}(u)$
$A_{jkn}^{(1/8/0)}$	$\int_0^s du e^{-u} L_j(2u) \mathfrak{K}_k^{(0)}(s - u)$
$A_{jknl}^{(1/8/1)}$	$\int_0^s du e^{-u} L_j(2u) \mathfrak{K}_{kl}^{(1)}(s - u)$

**Table 6.2.** Quadratures of Laguerre polynomials Class A

$A^{(2/p)}, A^{(2/p/q)}$	$G(s)$
$A_{nk}^{(2/1)}$	$\int_{s-\xi}^{s+\xi} du(u-s)e^{-u}L_k(2u)$
$A_{nk}^{(2/2)}$	$\int_{s-\xi}^s du [(u-s)^2 - \xi^2] e^{-u} L_k(2u)$
$A_{nk}^{(2/3)}$	$\int_{s-\xi}^s du (u-s-\xi) e^{-u} L_k(2u)$
$A_{jkn}^{(2/4)}$	$e^\xi \int_0^{s-\xi} du L_k [2(s-u-\xi)] L_j(2u)$
$A_{jkn}^{(2/5)}$	$e^{-\xi} \int_0^\infty du e^{-2u} L_k [2(s+u+\xi)] L_j(2u)$
$A_{jkn}^{(2/6/0)}$	$\int_{s-\xi}^\xi du \mathfrak{K}_k^{(0)}(s-u) e^{-u} L_j(2u)$
$A_{jknl}^{(2/6/1)}$	$\int_{s-\xi}^\xi du \mathfrak{K}_{kl}^{(1)}(s-u) e^{-u} L_j(2u)$

**Table 6.3.** Quadratures of Laguerre polynomials Class Q

$Q^{(p)}, Q^{(p/q)}$	$P(s)$
$Q_{nk}^{(1)}$	$\int_s^{s+\xi} du [(u-s)^2 - \xi^2] \frac{d}{du} e^{-u} L_k(2u)$
$Q_{nk}^{(2)}$	$\int_s^{s+\xi} du (s-u-\xi) \frac{d}{du} e^{-u} L_k(2u)$
$Q_{jkn}^{(3)}$	$e^\xi \int_{s+\xi}^\infty du e^{-u} L_j [2(u-s-\xi)] \frac{d}{du} e^{-u} L_k(2u)$
$Q_{jkn}^{(4/0)}$	$\int_s^{s+\xi} du \mathfrak{K}_{1k}^{(0)}(u-s) \frac{d}{du} e^{-u} L_j(2u)$
$Q_{njkl}^{(4/1)}$	$\int_s^{s+\xi} du \mathfrak{K}_{kl}^{(1)}(u-s) \frac{d}{du} e^{-u} L_j(2u)$

The amplitude equations are subject to the constraint equation

$$\begin{aligned} & \frac{1}{(\eta-1)^4} \left[ 1 + 2\eta - 12\sqrt{2\xi}\eta \sum_{k \geq 0} \Delta M_k^{(0)}(\xi) K_k \right]^2 \\ & \times \left\{ 1 - 8\eta + \frac{24\sqrt{2}\eta}{\sqrt{\xi}} \sum_{k \geq 0} (-1)^k \left[ 1 + \frac{1}{\xi} (2k+1) \right] H_k \right\} = 1, \end{aligned} \quad (6.223)$$

where the Laguerre transforms  $H_k$  and  $K_k$  are the solutions of the amplitude equations presented and  $\Delta M_k^{(0)}(\xi)$  is defined by (6.204). This constraint equation makes it possible to determine  $\xi$ . The point made here is that the amplitude equations (6.214) and (6.215) are nonlinear algebraic equations with coefficients that can be evaluated exactly as functions of  $\xi$ . The algorithm for solving the integro-differential equations (6.167)–(6.169) is now complete. The amplitude equations may be solved iteratively in the region of  $\xi$  away from the singular points of  $\xi$  where  $\xi$  vanishes.

With the solutions for (6.214), (6.215), and (6.223),  $K_1(x)$ ,  $K_2(x)$ , and  $h_2(x)$  can be calculated and therewith the thermodynamically consistent equation of state can be computed from (6.161), (6.162), and (6.163). The

Laguerre transform  $H_k$  of  $xh_2(x)$ , namely, the solutions of the amplitude equations, also provides the structure factor of the liquid, which is defined by

$$S(\mathbf{q}) = 1 + 8\pi^3\sigma^{-3}\rho^*\delta(\mathbf{q}) + \rho^*\Delta S(\mathbf{q}) \quad (6.224)$$

where  $\rho^* = \rho\sigma^3$  and

$$\Delta S(\mathbf{q}) = \int d\mathbf{x} \exp(i\mathbf{q} \cdot \mathbf{x}) h(x). \quad (6.225)$$

This integral can be readily evaluated in terms of the Laguerre transforms  $H_j$ , and the wave number  $q$  as follows:

$$\begin{aligned} \Delta S(\mathbf{q}) &= -\frac{4\pi}{q} j_1(q) \\ &\quad + \frac{4\pi\sqrt{2\xi}}{q(q^2 + \xi^2)^{1/2}} \sum_{j \geq 0} (-1)^j \sin \left[ q + (2j + 1) \arctan \left( \frac{q}{\xi} \right) \right] H_j, \end{aligned} \quad (6.226)$$

where  $j_1(q)$  is the spherical Bessel function of order one:

$$j_1(q) = q^{-2} (\sin q - q \cos q).$$

This shows that knowledge of the Laguerre transforms  $H_j$  and  $K_j$  and the parameter  $\xi$ , which is the magnitude of the zeros of  $[1 - \rho\hat{c}(k)]$ , will enable us to compute all the thermodynamic properties of the hard sphere fluid as functions of density.

## 6.9 Concluding Remarks

As will be shown in the subsequent chapters, because transport coefficients of liquids, although dynamic in origin, can be expressed in terms of equilibrium quantities such as the pair correlation function and the equation of state, it is important to be able to calculate them by statistical mechanics methods. In this chapter, as an important preparation for that aim, we have developed the generic van der Waals equation of state, namely, the canonical equation of state, which, together with the MC simulation methods for the pair correlation functions of liquids, provides a crucial ingredient for computing transport properties of liquids. As will be seen later, the canonical equation of state occupies the keystone position in the edifice of the statistical mechanics theory of transport coefficients of liquids we will present, and we have now equipped ourselves with that crucial theoretical tool in this chapter.

It is also shown that the pair correlation functions of liquids can be studied by integral equations derived from the OZ equation with a thermodynamically consistent closure for the direct correlation function. This theory is different from the conventional integral equation theories in the literature [4]. The

present integral equations derived from the OZ equation for pair correlation functions take into account the possibility of isothermal compressibility of real fluids to become infinity as the system approaches the critical point for a first-order phase transition. The theory can be easily made to include more zeros in the complex plane off the imaginary axis instead of a single pair on the imaginary axis. The result of this generalization would describe how the system approaches the real axis at a finite nonzero wave number, as temperature and density vary. It might thus provide a way to examine freezing phenomena of disordered liquids. The example taken with hard sphere fluids and for simplicity of the formalism, although limited because of the type of zeros (i.e., zeros on the imaginary axis) and their number, shows that even if there is no first-order liquid-vapor phase transition, the Wiener-Hopf factorization taken for the theory presented is appropriate and physically acceptable because it still foretells the possibility of transition to a disordered solid. Furthermore, it also describes the long-range correlation of particles in hard sphere fluids and yields the potential of mean force. In any case, the idea that the analyticity of correlation functions in the complex  $k$  plane—Fourier space—should be taken into consideration has far reaching theoretical consequences in developing the statistical mechanical theory of matter in general, which is worthwhile studying in depth. Aside from these points, the theory presented for correlation functions and the thermodynamically consistent equation of state may be used as theoretical tools to study the transport properties of dense gases and liquids and the structures of liquids in general.

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## Generalized Boltzmann Equation

The Boltzmann equation has been shown to provide the kinetic theory foundations [1, 2] of irreversible processes in dilute monatomic gases, but also, as described in Chap. 3, yields statistical mechanical formulas for transport coefficients of dilute gases, which are known capable of accounting for experimental data on them. Since nonlinear transport processes in gases can be built on the linear transport coefficients as shown in Chaps. 3 and 5 and in the literature [1,2], the Boltzmann equation is a good mathematical model for description of nonequilibrium monatomic gases far removed from equilibrium. As shown in Chap 5, the Boltzmann kinetic theory of monatomic gases can be satisfactorily extended to molecular gases. Therefore, the Boltzmann kinetic theory suggests the direction in which the kinetic theory of dense gases and liquids may proceed to describe transport phenomena in them. Such a theory [1, 2] has been already proposed and used by the author in formulating the thermodynamics of irreversible processes and generalized hydrodynamics. The kinetic equation used for the purpose is called the generalized Boltzmann equation. This kinetic equation has features basic to the Boltzmann equation, the most important of which is the irreversibility and, because of it, enables the kinetic equation to serve as the kinetic theory foundations of irreversible thermodynamics of liquids. In this chapter, we introduce and describe the generalized Boltzmann equation for nonreacting monatomic dense fluids.

The generalized Boltzmann equation was initially formulated in a canonical ensemble, but it was possible to formulate it in the grand ensemble [2, 3]. The grand ensemble kinetic theory appears to be more appropriate and interesting. In [3], the generalized Boltzmann equation in the grand ensemble was employed to formulate only a theory of irreversible processes and generalized hydrodynamics, but the theory of transport processes was left unformulated because the main aim of the monograph [2] was in formulating the thermodynamics of irreversible processes. In this work, we will consider transport processes to make the theory serve as the foundation of the study of transport coefficients of nonreacting liquids.

## 7.1 Grand Ensemble and Kinetic Equation

We consider a nonreacting fluid mixture composed of  $N_1, N_2, \dots, N_r$  monatomic molecules of species  $1, \dots, r$  contained in volume  $V$ . The system is open, exchanging matter as well as energy with its surroundings. Therefore, the numbers of particles are not fixed. The species will be distinguished by lower case italic subscripts  $a, b$ , and so on, and the particles of species will be denoted by lower case italic subscripts  $i, j$ , and so on. For example, the composite subscript  $ja$  denotes particle  $j \in a$ . The position and conjugate momentum vectors of particles will be denoted, respectively, by  $\mathbf{r}_{ja}$  and  $\mathbf{p}_{ja}$  and so on. The phases will be denoted by  $x_{ja} = (\mathbf{p}_{ja}, \mathbf{r}_{ja})$  for particle  $j \in a$ , and the total phase by  $x^{(N)} = (x_1^{(N_1)}, \dots, x_r^{(N_r)})$ , where  $\mathbf{N} = (N_1, N_2, \dots, N_r)$  and  $x_a^{(N_a)} = (x_{1a}, \dots, x_{N_a a})$ .

The Liouville operator for the system consisting of  $\mathbf{N}$  particles is then defined by

$$\begin{aligned} L^{(\mathbf{N})} = & \sum_{a=1}^r \sum_{ja=1}^{N_a} \left[ \mathbf{v}_{ja} \cdot \nabla_{ja} + \frac{1}{2} \sum_{b=1}^r \sum_{kb=1}^{N_b} \mathbf{F}_{jakb}(\mathbf{r}_{jakb}) \cdot (\nabla_{\mathbf{p}_{ja}} - \nabla_{\mathbf{p}_{kb}}) \right] \\ & + \sum_{a=1}^r \sum_{ja=1}^{N_a} m_a \mathbf{F}_a(\mathbf{r}_{ja}) \cdot \nabla_{\mathbf{p}_{ja}}, \end{aligned} \quad (7.1)$$

where  $\mathbf{r}_{jakb} = \mathbf{r}_{ja} - \mathbf{r}_{kb}$ ,  $\mathbf{v}_{ja} = \mathbf{p}_{ja}/m_a$  with  $m_a$  denoting the mass of species  $a$ , and  $\mathbf{F}_{jakb}(\mathbf{r}_{jakb})$  denoting the intermolecular force

$$\begin{aligned} \mathbf{F}_{jakb}(\mathbf{r}_{jakb}) &= -\frac{\partial}{\partial \mathbf{r}_{jakb}} V_{jakb}(\mathbf{r}_{jakb}), \\ \nabla_{ja} &= \frac{\partial}{\partial \mathbf{r}_{ja}}, \quad \nabla_{\mathbf{p}_{ja}} = \frac{\partial}{\partial \mathbf{p}_{ja}}. \end{aligned} \quad (7.2)$$

Here,  $V_{jakb}(\mathbf{r}_{jakb})$  denotes 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 vary slowly over the range of intermolecular interactions. Therefore, molecular collisions from intermolecular forces will not be affected by the slowly changing external forces—the body forces. The Hamiltonian of molecule  $ja$  will be abbreviated by  $H'_{ja}$ :

$$H'_{ja} = \frac{1}{2} m_a C_{ja}^2 + \frac{1}{2} \sum_{b=1}^r \sum_{kb=1}^{N_b} V_{jakb}(r_{jakb}) + V_a^{(ex)}(r_{ja}), \quad (7.3)$$

with  $\mathbf{C}_{ja}$  denoting the peculiar velocity of particle  $ja$ :  $\mathbf{C}_{ja} = \mathbf{v}_{ja} - \mathbf{u}$ , and  $V_a^{(\text{ex})}(r_{ja})$  denoting the external potential on particle  $ja$ . The kinetic energy is therefore defined relative to the frame of reference moving at fluid velocity  $\mathbf{u}$ , which is the average particle velocity.

Because the number of particles in the system changes as the system interacts with the surroundings and hence the dimension of the phase space keeps on changing, it is not possible to describe the dynamic evolution of the system in a phase space of fixed dimensions. This difficulty can be overcome if the idea of Gibbs [4] is followed. Gibbs constructs a petit ensemble consisting of representative systems of  $\mathbf{N}$  particles in volume  $V$ . Because  $\mathbf{N}$  is fixed for the petit ensemble, the phase space of the petit ensemble has well-defined dimensions. He then constructs a grand ensemble made up of petit ensembles of all possible values of  $\mathbf{N}$ , that is, the value of  $\mathbf{N}$  changes from petit ensemble to petit ensemble. The petit ensembles are subsystems of the grand ensemble. If there are  $n^{(\mathbf{N})}$  subsystems (petit ensembles) of  $\mathbf{N}$  particles in  $V$ , then in the grand ensemble there are petit ensembles numbering

$$\omega = \sum_{\mathbf{N} \geq 0} n^{(\mathbf{N})}$$

and the total number of particles in the grand ensemble is

$$\mathcal{N} = \sum_{\mathbf{N} \geq 0} \mathbf{N} n^{(\mathbf{N})}.$$

This grand ensemble is isolated. Therefore, the grand ensemble has a phase space of fixed dimensions corresponding to  $\mathcal{N}$ . As the petit ensembles weakly interact and exchange energy and particles with each other within the grand ensemble, the latter reaches equilibrium. Letting the petit ensembles exchange particles changes only the distribution of  $n^{(\mathbf{N})}$  but does not affect the dimensions of the phase space of the grand ensemble because it is closed. Neither does the exchange of particles alter the phase space dimensions of the petit ensembles.

The distribution function of finding the  $\mathcal{N}$  particles of the grand ensemble at  $x^{(\mathcal{N})}$  and  $t$  will be denoted by  $F^{(\mathcal{N})}(x^{(\mathcal{N})}, t)$ . This distribution function is normalized as

$$\int dx^{(\mathcal{N})} F^{(\mathcal{N})}(x^{(\mathcal{N})}, t) = 1. \quad (7.4)$$

It is appropriate to consider the distribution function for a representative system (subsystem) to acquire a value of  $\mathbf{N}$  and phase  $x^{(\mathbf{N})}$  corresponding to  $\mathbf{N}$  regardless of the distribution of the rest of the subsystems in the grand ensemble. The distribution function of the subsystem of  $\mathbf{N}$  particles at time  $t$  will be denoted by  $F^{(\mathbf{N})}(x^{(\mathbf{N})}; t)$ . It is the probability of finding  $\mathbf{N}$  particles in the phase volume  $dx^{(\mathbf{N})}$  around phase  $x^{(\mathbf{N})}$  at time  $t$ . This distribution function  $F^{(\mathbf{N})}(x^{(\mathbf{N})}; t)$  clearly is a reduced distribution function of  $F^{(\mathcal{N})}(x^{(\mathcal{N})}, t)$ .

It may be obtained from  $F^{(\mathcal{N})}(x^{(\mathcal{N})}, t)$  according to the definition

$$F^{(\mathbf{N})}(x^{(\mathbf{N})}; t) = \frac{\mathcal{N}!}{(\mathcal{N} - N)!} \int dx^{(\mathcal{N}-N)} F^{(\mathcal{N})}(x^{(\mathcal{N})}; t), \quad (7.5)$$

where

$$N = \sum_{a=1}^r N_a.$$

Therefore, it follows that

$$\int dx^{(N)} F^{(\mathbf{N})}(x^{(\mathbf{N})}; t) = \frac{\mathcal{N}!}{(\mathcal{N} - N)!}. \quad (7.6)$$

It was shown in [3] that analogous to the Boltzmann equation, the kinetic equation for  $F^{(\mathbf{N})}(x^{(\mathbf{N})}; t)$  may be assumed to be

$$\left( \partial_t + L^{(\mathbf{N})} \right) F^{(\mathbf{N})}(x^{(\mathbf{N})}; t) = \Re[F^{(\mathbf{N})}], \quad (7.7)$$

where the collision term on the right stands for the phase integral over  $(\mathcal{N} - N)$  phases

$$\Re[F^{(\mathbf{N})}] = \frac{\mathcal{N}!}{(\mathcal{N} - N)!} \int dx^{(\mathcal{N}-N)} (-i) T^{(\mathcal{N})} F^{(\mathcal{N})}(x^{(\mathcal{N})}; t), \quad (7.8)$$

$$F^{(\mathcal{N})}(x^{(\mathcal{N})}; t) = \prod_{\omega=\{\mathbf{N}, \mathbf{N}' \dots\}} F^{(\omega)}(x^{(\omega)}; t). \quad (7.9)$$

The product in (7.9) is formed with the distribution functions  $F^{(\mathbf{N})}, F^{(\mathbf{N}')}, \dots$  for all petit ensembles in the grand ensemble. A derivation of this kinetic equation is described in Appendix A. In this expression for the collision integral  $\Re[F^{(\mathbf{N})}]$ , the operator  $T^{(\mathcal{N})}$  is the classical collision operator describing the collision process of particles in  $\omega$  subsystems making up the isolated grand ensemble. The operator  $T^{(\mathcal{N})}$  obeys the classical Lippmann–Schwinger integral equation for the scattering operator in the phase space. The reader is referred to [1] in which a considerable space is devoted to classical scattering theory in connection with  $T^{(\mathcal{N})}$ . Here it is sufficient to note that a useful model for it is

$$\begin{aligned} \Re[F^{(\mathbf{N})}] = & \frac{\mathcal{N}!}{(\mathcal{N} - N)!} \int dx^{(\mathcal{N}-N)} \left[ W(x^{(\mathcal{N})*}|x^{(\mathcal{N})}) F^{(\mathcal{N})*}(x^{(\mathcal{N})*}; t) \right. \\ & \left. - W(x^{(\mathcal{N})}|x^{(\mathcal{N})*}) F^{(\mathcal{N})}(x^{(\mathcal{N})}; t) \right], \end{aligned} \quad (7.10)$$

where  $W(x^{(\mathcal{N})*}|x^{(\mathcal{N})})$  is the transition probability that describes the dynamic transition of the systems in the ensemble from the precollision state  $x^{(\mathcal{N})}$  to the postcollision state  $x^{(\mathcal{N})*}$  in the time interval  $dt$ . In semiclassical theory,

in which only the particles collisions are treated quantum mechanically, it is possible to show that  $W(x^{(\mathcal{N})}|x^{(\mathcal{N})*})$  is the classical limit of the quantum mechanical quantity

$$W\left(x^{(\mathcal{N})*}|x^{(\mathcal{N})}\right) = \left[2\pi T_{if}^\dagger \delta(\mathcal{H}_i^0 - \mathcal{H}_f^0) T_{if}\right]_{\hbar \rightarrow 0}, \quad (7.11)$$

where  $\mathcal{H}_i^0$  and  $\mathcal{H}_f^0$  are the free particle super-Hamiltonian operators for the initial ( $i$ ) and the final ( $f$ ) state in the superspace, respectively, and  $T_{if}$  is the quantum mechanical Lippmann–Schwinger transition operator describing the collision process  $i \rightarrow f$  in the Hilbert space. See Appendix A for a discussion of this relationship.

The transition probability  $W(x^{(\mathcal{N})}|x^{(\mathcal{N})*})$  satisfies the symmetry property

$$\int dx^{(\mathcal{N})*} W\left(x^{(\mathcal{N})}|x^{(\mathcal{N})*}\right) = \int dx^{(\mathcal{N})*} W\left(x^{(\mathcal{N})*}|x^{(\mathcal{N})}\right). \quad (7.12)$$

This is a generalization of the symmetry property described in (4.8) in Chap. 4. Henceforth, we will assume that the collision operator  $T^{(\mathcal{N})}$  represents (7.10). The transition probability  $W(x^{(\mathcal{N})}|x^{(\mathcal{N})*})$  is such that when the subsystems consist of a single particle in the dilute gas limit, the collision integral (7.10) reduces to that of the Boltzmann equation. In other words, if  $W(x^{(\mathcal{N})}|x^{(\mathcal{N})*})$  is expanded in cluster contributions, its leading term consists of binary collision operators, from which the Boltzmann collision integral is recovered. With this understanding, it is possible to develop a theory of transport processes in dense gases and liquids. The transition probability may then be more specifically modeled when the transport coefficients are computed for specific systems. We note that it is possible to formulate the theory with the quantum mechanical Liouville–von Neumann operator and then take the classical limit ( $\hbar \rightarrow 0$ ,  $\hbar = \text{Planck constant}/2\pi$ ) of the results to recover the classical formulation.

Property (7.12) gives rise to the inequality<sup>1</sup>

$$-\sum_{\{\mathbf{N}\} \geq 0} \frac{1}{\mathbf{N}!} \int dx^{(N)} \ln F^{(\mathbf{N})}(x^{(\mathbf{N})}, t) \Re[F^{(\mathbf{N})}] \geq 0, \quad (7.C1)$$

where

$$\mathbf{N}! = \prod_{a=1}^r N_a!.$$

This inequality is basically the  $H$  theorem satisfied by the kinetic equation. The equality holds only at equilibrium, which is reached in a long time:

$$\Re[F_{\text{eq}}^{(\mathbf{N})}] = 0. \quad (7.C2)$$

With the help of mechanical conservation laws of mass, momentum, and energy, this equation uniquely defines the equilibrium distribution function. We

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<sup>1</sup> In [2],  $N!$  does not appear in the condition below.

have used such an equilibrium distribution function to calculate the equation of state of the fluid in Chapter 6. If the densities of conserved quantities, such as mass, total momentum, and energy, are collectively denoted by

$$I(x^{(N)}; \mathbf{r}) = \sum_{a=1}^r \sum_{ja=1}^{N_a} I_{ja}(x^{(N)}) \delta(\mathbf{r}_{ja} - \mathbf{r}), \quad (7.13)$$

where  $I_{ja}$  can be equal to unity,  $I_{ja}(x^{(N)}) = m_a$  for mass,  $I_{ja}(x^{(N)}) = \mathbf{p}_a$  for momentum, and  $I_{ja}(x^{(N)}) = H'_{ja}$  for energy, then the collision term  $\mathfrak{R}[F^{(N)}]$  is such that

$$\sum_{\{\mathbf{N}\} \geq 0} \frac{1}{\mathbf{N}!} \int_V d\mathbf{r} \int dx^{(N)} \sum_{a=1}^r \sum_{ja=1}^{N_a} I_{ja}(x^{(N)}) \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathfrak{R}[F^{(N)}] = 0 \quad (7.C3)$$

identically. This condition also follows from the symmetry properties of  $W(x^{(\mathcal{N})}|x^{(\mathcal{N})*})$  under interchanges of particle phases and (7.12).

In [2], the kinetic equation (7.7) equipped with Conditions (7.C1)–(7.C3) was employed to develop a thermodynamic theory of irreversible processes in liquids. Condition (7.C1) assures the existence of Boltzmann entropy satisfying the H theorem and consequently the asymptotic stability of equilibrium characterized by  $F_{eq}^{(N)}$ , which is uniquely determined by Condition (7.C2). Condition (7.C3) guarantees the conservation laws of mass, momentum, and energy—namely, the equation of continuity, the momentum balance equation, and the internal energy balance equation. Recall that these conditions are also met by the Boltzmann kinetic equation and many variants of it known in the literature.

In the literature [5] on the foundations of kinetic theory and, in particular, the Boltzmann equation, one gets the impression that the Boltzmann equation is derivable from mechanical equations of motion for the system of interest. It must be emphasized that the Boltzmann equation is *a postulate for the fundamental evolution equation for the probability distribution function of a fluid system* consisting of statistically uncorrelated subunits, each of which is made up of a single particle. It is not derivable from the time-reversal invariant Newtonian dynamic 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 (7.7) is a fundamental postulate in the same spirit as originally taken for the Boltzmann equation by its inventor Boltzmann [6]. The kinetic equation (7.7) is inclusive of the equilibrium Gibbs ensemble theory in which only equilibrium is of interest since at equilibrium (7.C1) holds and

$$\frac{\partial F_{eq}^{(N)}}{\partial t} = 0. \quad (7.14)$$

In this connection, it must be noted that because Condition (7.C2) ensures that  $F_{eq}^{(N)}$  must be a function of the Hamiltonian of the system, (7.14) naturally follows from the kinetic equation (7.7).

## 7.2 Conservation Laws

The kinetic equation presented gives rise to the conservation laws of mass, momentum, and internal energy owing to the conditions on the kinetic equation listed earlier, if the macroscopic variables appropriately defined are employed.

Phase space averages of dynamic quantities for the grand ensemble are in general defined by the formula

$$\left\langle F^{(N)} M \left( x^{(N)}; t \right) \right\rangle = \sum_{\{N\} \geq 0} \frac{1}{N!} \int_V dx^{(N)} F^{(N)} \left( x^{(N)}; t \right) M \left( x^{(N)}; t \right). \quad (7.15)$$

The grand ensemble phase space averages of dynamic quantities will henceforth be denoted by angular brackets. We define various conserved and non-conserved variables:

Mass density

$$\begin{aligned} \rho(\mathbf{r}, t) &= \sum_{a=1}^r \rho_a(\mathbf{r}, t) \\ &= \sum_{a=1}^r \left\langle \sum_{ja=1}^{N_a} m_a \delta(\mathbf{r}_{ja} - \mathbf{r}) F^{(N)} \right\rangle; \end{aligned} \quad (7.16)$$

Momentum density

$$\begin{aligned} \rho \mathbf{u}(\mathbf{r}, t) &= \sum_{a=1}^r \rho_a \mathbf{u}_a(\mathbf{r}, t) \\ &= \sum_{a=1}^r \left\langle \sum_{ja=1}^{N_a} m_a \mathbf{v}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) F^{(N)} \right\rangle; \end{aligned} \quad (7.17)$$

Energy density

$$\rho \mathcal{E}(\mathbf{r}, t) = \sum_{a=1}^r \left\langle \sum_{ja=1}^{N_a} H'_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) F^{(N)} \right\rangle. \quad (7.18)$$

It is also convenient to define a generalized virial tensor operator  $\mathbf{W}_{jakb}$  by the formula

$$\mathbf{W}_{jakb} = \int_0^1 d\zeta \mathbf{r}_{jakb} \mathbf{F}_{jakb} \exp(-\zeta \mathbf{r}_{jakb} \cdot \nabla). \quad (7.19)$$

This tensor operator acts on delta function  $\delta(\mathbf{r}_{kb} - \mathbf{r})$  in statistical mechanics expressions for macroscopic variables. With the definition of peculiar velocity

$$\mathbf{C}_{ja} = \mathbf{v}_{ja} - \mathbf{u}, \quad (7.20)$$

we then define the diffusion fluxes, stress (pressure) tensor, and heat flux as follows:

Diffusion fluxes

$$\mathbf{J}_a = \left\langle \sum_{ja=1}^{N_a} m_a \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) F^{(\mathbf{N})} \right\rangle, \quad (7.21)$$

Stress tensor

$$\begin{aligned} \mathbf{P} &= \mathbf{P}_k + \mathbf{P}_v \\ &= \sum_{a=1}^r \left( \mathbf{P}_a^{(k)} + \mathbf{P}_a^{(v)} \right), \end{aligned} \quad (7.22)$$

$$\begin{aligned} \mathbf{P}_k &= \sum_{a=1}^r \mathbf{P}_a^{(k)} \\ &= \sum_{a=1}^r \left\langle \sum_{ja=1}^{N_a} m_a \mathbf{C}_{ja} \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) F^{(\mathbf{N})} \right\rangle, \end{aligned} \quad (7.23)$$

$$\begin{aligned} \mathbf{P}_v &= \sum_{a=1}^r \mathbf{P}_a^{(v)} \\ &= \frac{1}{2} \sum_{a,b=1}^r \left\langle \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) F^{(\mathbf{N})} \right\rangle, \end{aligned} \quad (7.24)$$

Heat flux

$$\begin{aligned} \mathbf{Q} &= \mathbf{Q}_h + \mathbf{Q}_w \\ &= \sum_{a=1}^r \left( \mathbf{Q}_a^{(h)} + \mathbf{Q}_a^{(w)} \right), \end{aligned} \quad (7.25)$$

$$\begin{aligned} \mathbf{Q}_h &= \sum_{a=1}^r \mathbf{Q}_a^{(h)} \\ &= \sum_{a=1}^r \left\langle \sum_{ja=1}^{N_a} H'_{ja} \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) F^{(\mathbf{N})} \right\rangle, \end{aligned} \quad (7.26)$$

$$\begin{aligned} \mathbf{Q}_w &= \sum_{a=1}^r \mathbf{Q}_a^{(w)} \\ &= \frac{1}{2} \sum_{a,b=1}^r \left\langle \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \mathbf{W}_{jakb} \cdot \mathbf{C}_{ja} \delta(\mathbf{r}_{kb} - \mathbf{r}) F^{(\mathbf{N})} \right\rangle. \end{aligned} \quad (7.27)$$

To this list of macroscopic nonconserved variables, we add the mean intermolecular force  $\mathcal{F}_a$  on species  $a$ :

$$\rho_a \mathcal{F}_a = \sum_{b=1}^r \left\langle \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \mathbf{F}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) F^{(\mathbf{N})} \right\rangle. \quad (7.28)$$

The intermolecular interaction energy part  $\mathbf{P}_v$  of stress tensor  $\mathbf{P}$  did not appear for dilute gases. The virial tensor contribution  $\mathbf{Q}_w$  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 intermolecular forces. This component appears only in statistical mechanics, but its appearance is not obvious in the phenomenological theory. It is possible to derive the balance equations for the conserved variables from the kinetic equation (7.7) by using the statistical mechanical definitions (7.16)–(7.27) and the method of Irving and Kirkwood [7]. Their derivation is well documented in the literature [1, 2], so we will simply list them here:

$$\partial_t \rho = -\nabla \cdot \rho \mathbf{u} \quad \text{or} \quad \rho d_t v = \nabla \cdot \mathbf{u}, \quad (7.29)$$

$$\rho d_t c_a = -\nabla \cdot \mathbf{J}_a, \quad (7.30)$$

$$\rho d_t \mathbf{u} = -\nabla \cdot \mathbf{P} + \rho \mathbf{F}, \quad (7.31)$$

$$\rho d_t \mathcal{E} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a. \quad (7.32)$$

$\mathbf{F}_a$  is the external force on a unit mass of species  $a$  defined by

$$\mathbf{F}_a = -m_a^{-1} \nabla V^{(ex)}(r),$$

and  $\mathbf{F}$  is the mean external force

$$\rho \mathbf{F} = \sum_{a=1}^r \rho_a \mathbf{F}_a.$$

These conservation laws of mass, momentum, and energy are superficially identical to those for dilute gases considered in Chaps. 2 and 4. However, the statistical mechanical definitions of the macroscopic quantities involved are different in the sense that for dilute gases the singlet distribution function is used and the potential energy contributions are absent, whereas for dense gases and liquids a many-particle distribution function is employed and the potential energy contributions are present. The potential energy contributions in the stress tensor and the heat flux contain the virial tensor contributions,

which are often neglected in dense fluid kinetic theories in the literature (e.g., linear response theory [8] and the BBGKY approach [5]), but they contribute a major portion to the stress tensor and the heat flux and are important in elucidating the mechanism of momentum and energy transfers between molecules, as will be shown later when the density fluctuation theory is discussed for transport processes in Chaps. 10–12.

### 7.3 Constitutive Equations

To discuss transport processes in dense fluids it is necessary to have nonconserved variables appropriately defined and their evolution equations derived from the kinetic equation. These evolution equations are the constitutive equations for the nonconserved variables of the system, which describe the constitutive properties of the substance of interest. We collectively denote the molecular formulas of nonconserved variables, such as the stress tensors, heat fluxes, diffusion fluxes, and so on, of various species by

$$\bar{h}_a^{(q)} = \sum_{ja=1}^{N_a} h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \quad (q \geq 1). \quad (7.33)$$

Its mean value is then computed by the formula

$$\Phi_{qa} = \rho \hat{\Phi}_{qa} = \left\langle \sum_{ja=1}^{N_a} h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) F^{(N)} \right\rangle. \quad (7.34)$$

Here, the symbols  $\Phi_{qa}$  have the same meanings and are ordered in the same manner as those in Chaps. 3 and 5. The explicit forms for  $h_{ja}^{(q)}$  can be systematically obtained by deriving the hierarchy of macroscopic evolution equations starting with the equation of continuity, which leads us to the definition of velocity, the evolution of which gives rise to the definition of the stress tensor, and so on. In this manner, the entire set of molecular expressions  $\{h_{ja}^{(q)}\}$  can be generated for macroscopic variable densities. We assume that there is a complete set of functions  $h_{ja}^{(q)}$ ,  $q \geq 1$ . If the sequence of mechanical expressions so derived for the macroscopic variables is arranged according to the order of nonconserved variables in this work (see Chap. 2 for the order), we obtain the leading members of the set relevant to the present work as follows:

The traceless, symmetric part of the stress tensor  $\Phi_{1a} = \boldsymbol{\Pi}_a$ :

$$\begin{aligned} h_{ja}^{(1)} \delta(\mathbf{r}_{ja} - \mathbf{r}) &= [m_a \mathbf{C}_{ja} \mathbf{C}_{ja}]^{(2)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \\ &+ \frac{1}{2} \sum_{b=1}^r \sum_{\substack{kb=1 \\ (ja \neq kb)}}^{N_b} [\mathbf{W}_{jakb}]^{(2)} \delta(\mathbf{r}_{kb} - \mathbf{r}); \end{aligned} \quad (7.35)$$

The excess normal stress  $\Phi_{2a} = \Delta_a$ :

$$\begin{aligned} h_{ja}^{(2)} \delta(\mathbf{r}_{ja} - \mathbf{r}) &= \left( \frac{1}{3} m_a C_{ja}^2 - m_a p_a / \rho_a \right) \delta(\mathbf{r}_{ja} - \mathbf{r}) \\ &+ \frac{1}{6} \sum_{b=1}^r \sum_{\substack{k b=1 \\ (ja \neq kb)}}^{N_b} \text{Tr} \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}); \end{aligned} \quad (7.36)$$

The heat flux  $\Phi_{3a} = \mathbf{Q}'_a = \mathbf{Q}_a - \hat{h}_a \mathbf{J}_a$ :

$$\begin{aligned} h_{ja}^{(3)} \delta(\mathbf{r}_{ja} - \mathbf{r}) &= (H'_{ja} - m_a \hat{h}_a) \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \\ &+ \frac{1}{2} \sum_{b=1}^r \sum_{\substack{j a=1 \\ (ja \neq kb)}}^{N_a} \sum_{k b=1}^{N_b} \mathbf{W}_{jakb} \cdot \mathbf{C}_{ja} \delta(\mathbf{r}_{kb} - \mathbf{r}); \end{aligned} \quad (7.37)$$

The diffusion flux  $\Phi_{4a} = \mathbf{J}_a$ :

$$h_{ja}^{(4)} \delta(\mathbf{r}_{ja} - \mathbf{r}) = m_a \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}). \quad (7.38)$$

The molecular expressions for higher order moments can be obtained similarly. The hydrostatic pressure of species  $a$  is denoted by  $p_a$ , and  $\hat{h}_a$  is the enthalpy per unit mass of species  $a$ .

The evolution equations for  $\Phi_{qa}$  can be derived from the kinetic equation and the statistical mechanics formula (7.34):

$$\rho d_t \hat{\Phi}_{qa} = -\nabla \cdot \boldsymbol{\psi}_{qa} + \mathcal{Z}_{qa} + \Lambda_{qa}, \quad (7.39)$$

where the dissipation term  $\Lambda_{qa}$  is defined by

$$\Lambda_{qa} = \sum_{ja=1}^{N_a} \left\langle h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) \Re[F^{(\mathbf{N})}] \right\rangle \quad (7.40)$$

the kinematic term  $\mathcal{Z}_{qa}$  by

$$\mathcal{Z}_{qa} = \sum_{ja=1}^{N_a} \left\langle F^{(\mathbf{N})} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathcal{D}_t^{(\mathbf{N})} h_{ja}^{(q)} \right\rangle \quad (7.41)$$

with operator  $\mathcal{D}_t^{(\mathbf{N})}$  denoting the operator sum

$$\mathcal{D}_t^{(\mathbf{N})} = d_t + L^{(\mathbf{N})} + \mathbf{C}_{ja} \cdot \nabla, \quad (7.42)$$

and  $\psi_{qa}$  is defined by the statistical mechanical formula

$$\psi_{qa} = \sum_{ja=1}^{N_a} \left\langle \mathbf{C}_{ja} h_{ja}^{(q)} \delta(\mathbf{r}_{ja} - \mathbf{r}) F^{(\mathbf{N})} \right\rangle. \quad (7.43)$$

Physically, this quantity is the flux of  $\Phi_{ka}$ , but, mathematically, it is a moment one order higher than  $\Phi_{ka}$ . The physical meaning of the term  $\Lambda_{qa}$  is also the same as for the dilute gas counterpart; it is the term responsible for energy dissipation in the system and is closely related to the calortropy production of the system; see [2] for this aspect.

We would like to add the following remark regarding the dissipation term. The dissipation term  $\Lambda_{qa}$  is the dense fluid generalization of the dissipation term arising from the Boltzmann equation, which we have seen in Chap. 2. If the Irving–Kirkwood procedure [7] is used to derive the evolution equations for  $\Phi_{qa}$  with the Liouville equation, as Irving and Kirkwood have done in their work, instead of the kinetic equation (7.7), then the dissipation term  $\Lambda_{qa}$  will be missing from (7.39), and there will be no energy dissipation mechanism in the theory formulated therewith. Of course, this has to do with the absence of irreversibility in the Liouville equation. The term  $\mathcal{Z}_{qa}$  in (7.39) is the kinematic term, which is also the dense fluid generalization of the kinematic term that appears in the dilute gas theory discussed in Chap. 2. It can be explicitly evaluated, given its molecular definition.

Because the interaction energy contributions involve rather complicated expressions, it is useful and convenient to define the following quantities related to potential energy contributions to the kinematic terms. First with the abbreviations of tensor operators akin to and closely associated with the virial tensor operator  $\mathbf{W}_{jakb}$  already introduced:

$$\mathfrak{R}_{jakb} = \int_0^1 d\zeta \mathbf{C}_{jakb} \mathbf{F}_{jakb} \exp(-\zeta \mathbf{r}_{jakb} \cdot \nabla), \quad (7.44)$$

$$\mathfrak{S}_{jakb} = \int_0^1 d\zeta \mathbf{r}_{jakb} [\mathbf{C}_{jakb} \cdot \nabla_{\mathbf{r}_{jakb}} \mathbf{F}_{jakb}] \exp(-\zeta \mathbf{r}_{jakb} \cdot \nabla), \quad (7.45)$$

$$\mathfrak{N}_{jakb} = \int_0^1 d\zeta \zeta [\mathbf{r}_{jakb} \mathbf{F}_{jakb}]^{(2)} \exp(-\zeta \mathbf{r}_{jakb} \cdot \nabla), \quad (7.46)$$

$$\mathbf{W}_{jakblc} = \int_0^1 d\zeta \mathbf{F}_{jalc} \mathbf{r}_{jakb} \exp(-\zeta \mathbf{r}_{jakb} \cdot \nabla), \quad (7.47)$$

we define the macroscopic quantities

$$\psi_{qa}^{(\mathbf{w})} = \psi_{qa}^{(\mathbf{w}1)} + \psi_{qa}^{(\mathbf{w}2)} \quad (q = 1, 3), \quad (7.48)$$

where

$$\psi_{1a}^{(w1)} = \frac{1}{2} \sum_{b=1}^r \sum_{\substack{j=1 \\ (ja \neq kb)}}^{N_a} \sum_{k=1}^{N_b} \left\langle F^{(N)} \mathbf{C}_{jakb} \mathfrak{N}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle, \quad (7.49)$$

$$\psi_{1a}^{(w2)} = \sum_{b=1}^r \sum_{\substack{j=1 \\ (ja \neq kb)}}^{N_a} \sum_{k=1}^{N_b} \left\langle F^{(N)} \mathbf{r}_{jakb} [\mathfrak{R}_{jakb}]^{(2)} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle, \quad (7.50)$$

$$\begin{aligned} \psi_{3a}^{(w1)} &= \frac{1}{2} \sum_{b=1}^r \sum_{\substack{j=1 \\ (ja \neq kb)}}^{N_a} \sum_{k=1}^{N_b} \left[ \left\langle F^{(N)} \mathbf{W}_{jakb} \cdot \mathbf{C}_{ja} \mathbf{C}_{ja} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle \right. \\ &\quad \left. + \left\langle F^{(N)} \left( \frac{H'_{ja}}{m_a} - \hat{h}_a \right) \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle \right], \end{aligned} \quad (7.51)$$

$$\psi_{3a}^{(w2)} = \frac{1}{2} \sum_{b,c=1}^r \sum_{\substack{j=1 \\ (ja \neq kb \neq lc)}}^{N_a} \sum_{k=1}^{N_b} \sum_{l=1}^{N_c} \left\langle F^{(N)} \frac{1}{m_a} \mathbf{W}_{jakb} \cdot \mathbf{W}_{jakblc} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle, \quad (7.52)$$

and

$$\mathbf{V}_a^{(1)} = \mathbf{V}_{Ca}^{(1)} + \frac{1}{2} \mathbf{V}_{Fa}^{(1)}, \quad (7.53)$$

$$\mathbf{V}_a^{(3)} = \mathbf{V}_{a1}^{(3)} + \mathbf{V}_{a2}^{(3)} + \mathbf{V}_{a3}^{(3)} + \mathbf{V}_{a4}^{(3)} + \mathbf{V}_{a5}^{(3)}, \quad (7.54)$$

$$\varphi_a^{(3)} = \varphi_a^{(3k)} + \varphi_{a1}^{(3w)} + \varphi_{a2}^{(3w)} + \varphi_{a3}^{(3w)}. \quad (7.55)$$

In these sums of tensors, various terms are defined by expressions involving intermolecular forces

$$\mathbf{V}_{Fa}^{(1)} = \frac{1}{2} \sum_{b=1}^r \sum_{\substack{j=1 \\ (ja \neq kb)}}^{N_a} \sum_{k=1}^{N_b} \left\langle F^{(N)} [\mathfrak{R}_{jakb} + \mathfrak{S}_{jakb}] \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle, \quad (7.56)$$

$$\mathbf{V}_{Ca}^{(1)} = \frac{1}{2} \sum_{b=1}^r \sum_{\substack{j=1 \\ (ja \neq kb)}}^{N_a} \sum_{k=1}^{N_b} \left\langle F^{(N)} \mathbf{F}_{jakb} \mathbf{C}_{jakb} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle, \quad (7.57)$$

$$\begin{aligned} \mathbf{V}_{a1}^{(3)} &= \frac{1}{2} \sum_{b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left\langle F^{(\mathbf{N})} \mathbf{F}_{jakb} \cdot \mathbf{C}_{ja} \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle \\ &\quad + \frac{1}{2} \sum_{b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left\langle F^{(\mathbf{N})} \mathbf{F}_{jakb} \cdot \mathbf{C}_{ja} \mathbf{C}_{ja} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle, \end{aligned} \quad (7.58)$$

$$\begin{aligned} \mathbf{V}_{a2}^{(3)} &= \frac{1}{2} \sum_{b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left[ \left\langle F^{(\mathbf{N})} \left( \frac{H'_{ja}}{m_a} - \hat{h}_a \right) \mathbf{F}_{jakb} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle \right. \\ &\quad \left. + \left\langle F^{(N)} \left( \frac{H'_{ja}}{m_a} - \hat{h}_a \right) \mathbf{F}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle \right], \end{aligned} \quad (7.59)$$

$$\begin{aligned} \mathbf{V}_{a3}^{(3)} &= \frac{1}{2} \sum_{b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left\langle F^{(\mathbf{N})} \delta(\mathbf{r}_{ja} - \mathbf{r}) \mathbf{C}_{jakb} \cdot (\nabla_{\mathbf{r}_{jakb}} \mathbf{W}_{jakb}) \cdot \mathbf{C}_{ja} \right\rangle, \end{aligned} \quad (7.60)$$

$$\mathbf{V}_{a4}^{(3)} = \frac{1}{2} \sum_{b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left\langle F^{(\mathbf{N})} \frac{1}{m_a} \mathbf{W}_{jakb} \cdot \mathbf{F}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle, \quad (7.61)$$

$$\begin{aligned} \mathbf{V}_{a5}^{(3)} &= \frac{1}{2} \sum_{b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \sum_{lc=1}^{N_c} \left[ \left\langle F^{(\mathbf{N})} \frac{1}{m_a} \mathbf{W}_{jakb} \cdot \mathbf{F}_{jalc} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle \right. \\ &\quad \left. + \left\langle F^{(\mathbf{N})} \frac{1}{m_a} \mathbf{W}_{jakb} \cdot \mathbf{F}_{jalc} \delta(\mathbf{r}_{lc} - \mathbf{r}) \right\rangle \right]. \end{aligned} \quad (7.62)$$

And lastly

$$\varphi_a^{(3k)} = \sum_{ja=1}^{N_a} \left\langle F^{(\mathbf{N})} \mathbf{C}_{ja} \mathbf{C}_{ja} \mathbf{C}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\rangle, \quad (7.63)$$

$$\varphi_{a1}^{(3w)} = \frac{1}{2} \sum_{b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left\langle F^{(\mathbf{N})} \mathbf{W}_{jakb} \mathbf{C}_{ja} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle, \quad (7.64)$$

$$\varphi_{a2}^{(3w)} = \frac{1}{2} \sum_{b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \begin{cases} \left\langle F^{(N)} \mathbf{C}_{ja} \mathbf{W}_{jakb} \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle, \\ (ja \neq kb) \end{cases} \quad (7.65)$$

$$\varphi_{a3}^{(3w)\alpha\beta\gamma} = \frac{1}{2} \sum_{b=1}^r \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \begin{cases} \left\langle F^{(N)} \mathbf{W}_{jakb}^{\alpha\gamma} \mathbf{C}_{ja}^\beta \delta(\mathbf{r}_{kb} - \mathbf{r}) \right\rangle, \\ (ja \neq kb) \end{cases} \quad (7.66)$$

The lower case Greek superscripts  $\alpha, \beta, \gamma$  affixed to the tensors in (7.66) denote their Cartesian tensor components. The leading examples of kinematic terms are given in Table 7.1, which should be compared with their dilute gas counterparts in Table 3.1.

**Table 7.1.** Leading kinematic terms for liquids

$\mathcal{Z}_{1a}$	$-2p_a [\nabla \mathbf{u}]^{(2)}$ $-2 [d_t \mathbf{u} \mathbf{J}_a]^{(2)} + 2 [\mathbf{F}_a \mathbf{J}_a]^{(2)} - 2 [\Pi_a \cdot \nabla \mathbf{u}]^{(2)}$ $-2\Delta_a [\nabla \mathbf{u}]^{(2)} + 2 [\mathbf{V}_a^{(1)}]^{(2)}$ $-\nabla \cdot \psi_{1a}^{(w)}$
$\mathcal{Z}_{2a}$	$-\frac{2}{3}p_a \nabla \cdot \mathbf{u} - p_a d_t (p_a v)$ $-\frac{2}{3}\Pi_a : \nabla \mathbf{u} - \frac{2}{3}\Delta_a \nabla \cdot \mathbf{u} - \frac{2}{3}(d_t \mathbf{u} - \mathbf{F}_a) \cdot \mathbf{J}_a$ $-\mathbf{J}_a \cdot \nabla (p_a / \rho_a) + \frac{2}{3}\text{Tr} \mathbf{V}_a^{(1)}$ $-\nabla \cdot \frac{1}{3}\text{Tr} \psi_{1a}^{(w)}$
$\mathcal{Z}_{3a}$	$-p_a \hat{C}_{pa} T \nabla \ln T$ $-d_t \mathbf{u} \cdot (\mathbf{P}_a - p_a \delta) - \mathbf{J}_a d_t \hat{h}_a - \mathbf{Q}'_a \cdot \nabla \mathbf{u}$ $- (\mathbf{P}_a - p_a \delta) \cdot \nabla \hat{h}_a - \varphi_a^{(3)} : \nabla \mathbf{u}$ $+ (\mathbf{P}_a - p_a \delta) \cdot \mathbf{F}_a + \mathbf{V}_a^{(3)}$ $-\nabla \cdot \psi_{3a}^{(w)}$
$\mathcal{Z}_{4a}$	$-p \mathbf{d}_a + \rho_a \mathcal{F}_a$ $- (x_a - c_a) \nabla \cdot (\Delta \delta + \Pi) - \Pi \cdot \nabla x_a$ $- \Delta \nabla x_a - \mathbf{J}_a \cdot \nabla \mathbf{u}$ $+ \nabla \cdot \mathbf{P}_a^{(k)}$

We note that they are formally the same except for the intermolecular force contributions in the last line for each  $\mathcal{Z}_{qa}$  in Table 7.1. The term in the first line for each kinematic term represents the thermodynamic driving force for the nonconserved variable, such as the velocity gradient, pressure gradient, temperature gradient, and density gradient or mean force on the particle of the species. The divergence terms

$$-\nabla \cdot \psi_{qa}^{(w)}, \quad +\nabla \cdot \mathbf{P}_a^{(k)}$$

in Table 7.1 add up to the divergence term  $-\nabla \cdot \psi_{qa}$  ( $q = 1, \dots, 4$ ) in (7.39), respectively. Therefore, the intermolecular force contributions to the kinematic terms in the constitutive equations are made up only of  $\mathbf{V}_a^{(1)}$ ,  $\text{Tr}\mathbf{V}_a^{(1)}$ , and  $\mathbf{V}_a^{(3)}$ . As shown in Chap. 8 for polyatomic molecules, these molecular force contributions include intramolecular interaction energy contributions that describe conformational changes in the molecules arising from the interactions. The effects of these terms may have significance in the rheological behavior of polyatomic molecules, including polymers.

The evolution equation for  $\hat{\Phi}_{qa}$  is a constitutive equation. If transport properties of the fluid are desired, then explicit forms for the constitutive equations are required. For this reason, we will examine them in more detail later in this chapter.

## 7.4 Generalized Hydrodynamics

When the evolution equations for the set of macroscopic variables that includes the conserved and nonconserved variables presented earlier are subjected to the laws of thermodynamics, then they ensure a macroscopic description of irreversible processes that is thermodynamically consistent. The set of macroscopic evolution equations is called the generalized hydrodynamic equations, and the hydrodynamic theory based on them is called generalized hydrodynamics. The linear transport coefficients in which we are interested in this work can be extracted from the constitutive equations presented for nonconserved variables by linearizing them with regard to nonconserved variables. To implement this line of approach to transport of matter and energy, it is necessary to express the dissipation terms in the constitutive equations for the nonconserved variables in terms of the macroscopic variables chosen.

The physical mechanism of energy dissipation in the system is vested in the dissipation terms or the collision term in the kinetic equation. It, however, is not practically feasible to calculate the dissipation terms in an exact form because to realize them in such forms it will be necessary to solve in analytic form the many-body dynamic problem involved. It is therefore imperative to bring out, at least formally, the essential and major contribution in an appropriate form. It has been found that the first-order cumulant approximation achieves the desired aim for the dissipation terms because it provides sufficiently adequate formal descriptions of nonlinear and linear transport processes in liquids, as the applications of the present line of kinetic theory have demonstrated in the literature [9–14].

To develop the first-order cumulant approximation [1, 2, 15] for the dissipation terms, we begin by expressing the grand ensemble distribution function  $F_c^{(\mathbf{N})}(x^{(\mathbf{N})}, t)$  in the form

$$k_B \ln F_c^{(\mathbf{N})} (x^{(\mathbf{N})}, t) = - \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} \mathcal{H}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) - k_B \ln(c\Xi), \quad (7.67)$$

where

$$\mathcal{H}_{ja} = T^{-1} \left( H'_{ja} + \sum_{q \geq 1} X_{qa} h_{ja}^{(q)} - m_a \hat{\mu}_a \right), \quad (7.68)$$

$$c = h^{3N} \prod_{a=1}^r N_a!, \quad (7.69)$$

$X_{qa}$  is the generalized potential conjugate to  $h_{ja}^{(q)}$ , and

$$\Xi = \left\langle \exp \left[ -k_B^{-1} \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} \mathcal{H}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right] \right\rangle. \quad (7.70)$$

Then it can be shown that in the first-order cumulant approximation [2] the dissipation term is given by the expression

$$\Lambda_{qa} = (\beta g)^{-1} q(X) \sum_{b=1}^r \sum_{s \geq 1} R_{ab}^{(qs)} X_{sb}, \quad (7.71)$$

where

$$g = \frac{1}{n^2 d^2} \sqrt{\frac{m}{2k_B T}}, \quad (7.72)$$

$$q(X) = \kappa^{-1} \sinh \kappa, \quad (7.73)$$

$$\kappa = \left[ \sum_{a,b=1}^r \sum_{q,s \geq 1} X_{qa} R_{ab}^{(qs)} X_{sb} \right]^{1/2}, \quad (7.74)$$

$R_{ab}^{(qs)}$  are collision bracket integrals associated with the collision operator  $\Re[F_c^{(N)}]$ , and  $\kappa^2$  again denotes the Rayleigh dissipation function. The meaning of  $g$  is the same as in the dilute gas theory, in particular, with  $d$  denoting the characteristic size of the molecule. The formulas for  $R_{ab}^{(qs)}$ , which are associated with shear viscosity, bulk viscosity, thermal conductivity, thermal diffusion, and diffusion are presented in Table 7.2, where the subscripted angular brackets stand for the collision bracket integral,

$$\langle AB \rangle_c = \frac{1}{n^2 d^2} \sum_{\{N\} \geq 0} \frac{1}{N!} \int d\mathbf{x}^{(N)} F_{eq}^{(N)} A \widehat{\Re}[B], \quad (7.75)$$

with  $\widehat{\mathfrak{R}}$  denoting the reduced collision operator

$$\widehat{\mathfrak{R}}[B] = d \sqrt{\frac{m_r}{2k_B T}} \mathfrak{R}[B], \quad (7.76)$$

and

$$\widehat{h}_{ja}^{(\alpha)} = \delta(\mathbf{r}_{ja} - \mathbf{r}) h_{ja}^{(\alpha)} \quad (\alpha = 1, \dots, 4). \quad (7.77)$$

The collision bracket integral in (7.75) is a dense fluid generalization of the collision bracket integral in the dilute gas kinetic theory based on the Boltzmann equation, which was discussed in Chaps. 2 and 3.

Since  $X_{qa}$  can be shown to be proportional to the fluxes  $\Phi_{qa}$ , it is appropriate to express them in the forms

$$X_{qa} = -g_a^{(q)}(\Phi) \Phi_{qa} \quad (q \geq 1), \quad (7.78)$$

where  $g_a^{(q)}(\Phi)$  then are functions of  $\Phi_{qa}$ . These functions can be explicitly calculated if the nonequilibrium grand canonical ensemble partition  $\Xi$  is calculated. For the nonequilibrium statistical thermodynamics relations between  $X_{qa}$  and the nonequilibrium grand canonical partition function, see [2, 16]. In this work, we are interested mostly in linear transport processes and associated transport coefficients. In such cases, it is sufficient to approximate the nonlinear dissipation term in (7.71) to the linear order in  $\Phi_{qa}$ , and  $g_a^{(q)}(\Phi)$  are given approximately by the formulas

$$g_a^{(1)} \simeq \frac{1}{2p_a}, \quad g_a^{(2)} \simeq \frac{3}{2p_a}, \quad g_a^{(3)} \simeq \frac{1}{\widehat{C}_p T p_a}, \quad g_a^{(4)} \simeq \frac{1}{\rho_a}, \quad (7.79)$$

so that

$$\begin{aligned} X_{1a} &\simeq -\frac{1}{2p_a} \mathbf{\Pi}_a, & X_{2a} &\simeq -\frac{3}{2p_a} \Delta_a, \\ X_{3a} &\simeq -\frac{1}{\widehat{C}_p T p_a} \mathbf{Q}'_a, & X_{4a} &\simeq -\frac{1}{\rho_a} \mathbf{J}_a. \end{aligned} \quad (7.80)$$

**Table 7.2.** Collision bracket integrals for constitutive equations

C.B.I.	kinetic theory formula	type
$R_{ab}^{(11)}$	$\frac{\beta^2}{5} \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left\langle -\widehat{h}_{ja}^{(1)} : h_{kb}^{(1)} \right\rangle_c$	shear viscosity
$R_{ab}^{(22)}$	$\beta^2 \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left\langle -\widehat{h}_{ja}^{(2)} h_{kb}^{(2)} \right\rangle_c$	bulk viscosity
$R_{ab}^{(33)}$	$\frac{\beta^2}{3} \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left\langle -\widehat{h}_{ja}^{(3)} \cdot h_{kb}^{(3)} \right\rangle_c$	heat conductivity
$R_{ab}^{(34)}$	$\frac{\beta^2}{3} \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left\langle -\widehat{h}_{ja}^{(3)} \cdot h_{kb}^{(4)} \right\rangle_c$	thermal diffusion
$R_{ab}^{(43)}$	$\frac{\beta^2}{3} \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left\langle -\widehat{h}_{ja}^{(4)} \cdot h_{kb}^{(3)} \right\rangle_c$	thermal diffusion
$R_{ab}^{(44)}$	$\frac{\beta^2}{3} \sum_{ja=1}^{N_a} \sum_{kb=1}^{N_b} \left\langle -\widehat{h}_{ja}^{(4)} \cdot h_{kb}^{(4)} \right\rangle_c$	diffusion

Note that these are first-order approximations obtained from the nonequilibrium partition function  $\Xi$ , which hold near equilibrium. Since linear transport processes hold near equilibrium, the approximation for  $X_{qa}$  here is appropriate.

Since we will have an opportunity to discuss nonlinear transport processes built on linear transport processes, first we present the constitutive equations in the first-order cumulant approximation. Then they will be specialized to linear transport processes and used to obtain linear transport coefficients. In the first-order cumulant approximation the constitutive equations for nonlinear transport processes are as follows:

$$\rho d_t \hat{\Phi}_{qa} = -\nabla \cdot \psi_{qa} + \mathcal{Z}_{qa} - \left( \beta g g_a^{(q)} \right)^{-1} q(\Phi) \sum_{b=1}^r \sum_{s \geq 1} \mathbb{R}_{ab}^{(qs)} \Phi_{sb}, \quad (7.81)$$

where  $1 \leq a \leq r$ ,  $q \geq 1$  and

$$\mathbb{R}_{ab}^{(qs)} = g_a^{(q)} R_{ab}^{(qs)} g_b^{(s)}. \quad (7.82)$$

The set of evolution equations for macroscopic variables (7.29)–(7.32) and (7.81) is the first-order cumulant approximation version of generalized hydrodynamic equations, consistent with thermodynamic laws.

## 7.5 Linear Transport Coefficients

The constitutive equations (7.81) contain the linear thermodynamic force–flux relations because the former are constitutive equations for macroscopic fluxes. The thermodynamic force–flux relations can arise from the aforementioned constitutive equations if the steady-state constitutive equations are linearized with respect to the fluxes and the thermodynamic gradients. Therefore, in the linear limit there follow the linear constitutive relations

$$\mathcal{Z}_{qa}^{(l)} - \left( \beta g g_a^{(q)} \right)^{-1} \sum_{b=1}^r \sum_{s \geq 1} \mathbb{R}_{ab}^{(qs)} \Phi_{sb} = 0 \quad (q \geq 1; r \geq a \geq 1), \quad (7.83)$$

where  $\mathcal{Z}_{qa}^{(l)}$  are the thermodynamic gradients that drive linear irreversible processes, that is, the linear transport processes [17]:

$$\begin{aligned} \mathcal{Z}_{1a}^{(l)} &= -2p_a [\nabla \mathbf{u}]^{(2)}, \\ \mathcal{Z}_{2a}^{(l)} &= -\frac{2}{3} p_a \nabla \cdot \mathbf{u}, \\ \mathcal{Z}_{3a}^{(l)} &= -p_a \hat{C}_{pa} T \nabla \ln T, \\ \mathcal{Z}_{4a}^{(l)} &= -p \mathbf{d}_a + \rho_a \mathcal{F}_a, \quad \text{etc.} \end{aligned} \quad (7.84)$$

Note that  $-\nabla \cdot \psi_{4a} + \nabla \cdot \mathbf{P}_a = 0$ . Linear transport coefficients are readily identified from the linear constitutive relations (7.83). To simplify the discussion, we consider a single-component fluid to obtain expressions for the transport coefficients. The procedure can be easily generalized to mixtures in the same manner as that for dilute gas mixtures discussed in Chap. 3 if the constitutive equations (7.83) are used. Therefore derivation of transport coefficients for mixtures will be left to the reader as an exercise.

Since fluxes of different tensorial ranks do not couple with each other for reasons of symmetry in the linear approximation and, moreover, there are no diffusion fluxes present for a single-component fluid, we have three independent constitutive equations if the fluids are pure. Therefore, the constitutive equations (7.83) for a single-component fluid read

$$\mathcal{Z}_q^{(l)} - (\beta g g^{(q)})^{-1} \mathbb{R}^{(qq)} \Phi_q = 0 \quad (q = 1, 2, 3), \quad (7.85)$$

where the subscripts pertaining to the species have been omitted.

### 7.5.1 Shear Viscosity

The shear viscosity of a single-component fluid can be readily obtained by comparing the constitutive equation (7.85) for  $q = 1$  with the phenomenological thermodynamic force–flux relation for shear flow—namely, the Newtonian law of viscosity

$$\Pi = -2\eta [\nabla \mathbf{u}]^{(2)}. \quad (7.86)$$

We thereby identify the viscosity coefficient with the kinetic theory formula

$$\eta = \frac{\beta g}{2\mathbb{R}^{(11)}}. \quad (7.87)$$

To calculate the shear viscosity of liquids, it is required to compute the collision bracket integral  $\mathbb{R}^{(11)}$  as a function of density and temperature. Computation of collision bracket integrals such as  $\mathbb{R}^{(11)}$  remains one of the outstanding problems in dense fluid kinetic theory because of the well-known difficulty of solving many-body collision dynamics.

### 7.5.2 Bulk Viscosity

The phenomenological constitutive equation for the excess normal stress  $\Delta$  of a single-component fluid is

$$\Delta = -\eta_b \nabla \cdot \mathbf{u}, \quad (7.88)$$

which should be compared with the kinetic theory constitutive equation (7.85) for  $q = 2$ . The comparison yields the bulk viscosity formula

$$\eta_b = \frac{\beta g}{\mathbb{R}^{(22)}}. \quad (7.89)$$

As for shear viscosity, the collision bracket integral  $\mathbb{R}^{(22)}$  is required for bulk viscosity.

### 7.5.3 Thermal Conductivity

As for viscosities, the kinetic theory formula for the thermal conductivity of a single-component dense fluid can be identified if the phenomenological constitutive equation for the heat flux

$$\mathbf{Q} = -\lambda \nabla \ln T \quad (7.90)$$

is compared with the kinetic theory counterpart given in (7.85) for  $q = 3$ . This comparison yields the kinetic theory formula for the thermal conductivity of a dense single-component fluid:

$$\lambda = \frac{\beta g}{\mathbb{R}^{(33)}}. \quad (7.91)$$

Therefore, as for viscosities, it is sufficient to compute the collision bracket integral  $\mathbb{R}^{(33)}$  as a function of density and temperature to obtain a molecular theory expression for the thermal conductivity.

It is now clear how the procedure employed to derive the kinetic theory expressions for the transport coefficients for a single-component fluid can be generalized to those of a mixture: it is only required to solve formally the constitutive equations (7.85), a linear set of equations, to obtain the fluxes in terms of thermodynamic gradients and identify the transport coefficients in comparison with the phenomenological constitutive equations. This procedure was, in fact, carried through in detail in Chap. 3 for dilute gases. Therefore, we will not repeat it here.

## 7.6 Formal Consideration of the Collision Bracket Integrals

In this section, some formal aspects of the collision bracket integrals, which will help to evaluate them by numerical methods, will be examined. For the purpose, we will recast the collision bracket integrals into forms more suitable for numerical methods, for example, computer simulation methods such as Monte Carlo or molecular dynamics simulation methods. Because, as we have seen earlier, thermal conductivity may be related to shear viscosity—note that bulk viscosity can also be related to shear viscosity—it is sufficient to consider the collision bracket integral for shear viscosity for the example.

If the collision bracket integral  $\mathbb{R}^{(11)}$  for shear viscosity is explicitly written out for a single-component monatomic fluid in the collision operator ( $T^{(\mathcal{N})}$ ) representation, it is given by the formula involving the many-particle collision operator [1]

$$\begin{aligned} \mathbb{R}^{(11)} &= \frac{4p^2}{5n^2\sigma^3(k_B T)^2} \sqrt{\frac{2k_B T}{m_r}} \\ &\times \sum_{N \geq 0} \binom{\mathcal{N}}{N} \int dx^{(\mathcal{N})} F_{\text{eq}}^{(\mathcal{N})} \sum_{j=1}^N \delta(\mathbf{r}_j - \mathbf{r}) h_j^{(1)} : i\hat{T}^{(\mathcal{N})} \sum_{k=1}^{\mathcal{N}} h_k^{(1)}. \end{aligned} \quad (7.92)$$

The operator  $\widehat{T}^{(\mathcal{N})}$  is the reduced collision operator

$$\widehat{T}^{(\mathcal{N})} = T^{(\mathcal{N})} \sigma \sqrt{\frac{m_r}{2k_B T}}, \quad (7.93)$$

where  $T^{(\mathcal{N})}$  denotes the collision operator of  $\mathcal{N}$  particles obeying the classical Lippmann–Schwinger equation [1]. Because particles are identical, this formula for  $\mathbb{R}^{(11)}$  may be written as

$$\mathbb{R}^{(11)} = \frac{4p^2}{5n^2\sigma^3 (k_B T)^2} \sqrt{\frac{2k_B T}{m_r}} \int dx^{(\mathcal{N})} F_{\text{eq}}^{(\mathcal{N})} \sum_{j,k=1}^{\mathcal{N}} \delta(\mathbf{r}_j - \mathbf{r}) h_j^{(1)} : i\widehat{T}^{(\mathcal{N})} h_k^{(1)} \quad (7.94)$$

for which we have used

$$\sum_{N \geq 0} \binom{\mathcal{N}}{N} \sum_{j=1}^N \delta(\mathbf{r}_j - \mathbf{r}) h_j^{(1)} = \sum_{j=1}^{\mathcal{N}} \delta(\mathbf{r}_j - \mathbf{r}) h_j^{(1)}. \quad (7.95)$$

With this identification, the formula for  $\mathbb{R}^{(11)}$  in Eq. (7.94) is a microcanonical average of

$$\sum_{j,k=1}^{\mathcal{N}} \delta(\mathbf{r}_j - \mathbf{r}) h_j^{(1)} : i\widehat{T}^{(\mathcal{N})} h_k^{(1)}.$$

We may take for  $T^{(\mathcal{N})}$  the model given in (7.10). In (7.92) and (7.94) for the collision bracket integral it should be understood that  $i = \sqrt{-1}$  and  $h_j^{(1)}$  is the single-component version of the traceless, symmetric part of the pressure tensor:

$$h_j^{(1)} = [m\mathbf{C}_j \mathbf{C}_j]^{(2)} - \frac{1}{2} \sum_{l \neq j}^N \frac{[\mathbf{r}_{jl} \mathbf{r}_{jl}]^{(2)}}{r_{jl}} \mathcal{V}'_{jl}(r_{jl}), \quad (7.96)$$

$$\mathcal{V}'_{jl}(r_{jl}) = \frac{\partial \mathcal{V}_{jl}(r_{jl})}{\partial r_{jl}}.$$

Note that in the Chapman–Enskog method for transport coefficients, the pressure tensor does not include the displacement operator because the displacement operator [see (7.19)] should be neglected in the first-order Chapman–Enskog solution. The collision operator  $T^{(\mathcal{N})}$  requires solving the classical  $\mathcal{N}$ -particle Lippmann–Schwinger equation, so it is not trivial to calculate the collision bracket integrals. For this reason, the problem of calculating  $\eta$  by using formula (7.87) remains largely unresolved at present except for hard sphere fluids [1], for which an approximate solution is available [1, 18].

It is found convenient to decompose the shear viscosity of fluids into two parts; the kinetic and potential contributions,

$$\eta = \eta_k + \eta_v. \quad (7.97)$$

Both contributions depend on density  $n$  as well as temperature  $T$ . However, there exists a density-independent limit at low (normal) density:

$$\lim_{n \rightarrow 0} \eta(n) = \eta_k^0, \quad (7.98)$$

which is the Chapman–Enskog viscosity for a dilute gas. Therefore, we may identify  $\eta_k^0$  with the Chapman–Enskog shear viscosity  $\eta_0$  for a dilute gas [19].

To put the collision bracket integral in a form parallel to the decomposition of  $\eta$  given in Eq. (7.97), we define the collision bracket integral  $\mathbb{R}_0^{(11)}$  for the kinetic part by the formula

$$\begin{aligned} \mathbb{R}_0^{(11)} &= \frac{4p^2}{5n^2\sigma^3(k_B T)^2} \sqrt{\frac{2k_B T}{m_r}} \sum_{j,k=1}^N \int dx^{(\mathcal{N})} F_{eq}^{(\mathcal{N})} \delta(\mathbf{r}_j - \mathbf{r}) \\ &\times [m\mathbf{C}_j \mathbf{C}_j]^{(2)} : i\hat{T}^{(\mathcal{N})} [m\mathbf{C}_k \mathbf{C}_k]^{(2)}. \end{aligned} \quad (7.99)$$

Then, it is possible to identify  $\eta_k$  in the form,

$$\eta_k = \frac{g}{k_B T \mathbb{R}_0^{(11)}} \quad (7.100)$$

and  $\eta_v$  with the statistical mechanical formula

$$\eta_v = \left( \frac{g}{k_B T} \right) \frac{1}{\mathbb{R}_0^{(11)}} \left( \mathbb{R}_0^{(11)} - \mathbb{R}^{(11)} \right) \frac{1}{\mathbb{R}^{(11)}}, \quad (7.101)$$

where

$$\Delta \mathbb{R} = \mathbb{R}_0^{(11)} - \mathbb{R}^{(11)}. \quad (7.102)$$

If the density expansion<sup>2</sup> of the collision bracket integral  $\mathbb{R}^{(11)}$  is calculated by using a cluster expansion of the collision operator  $T^{(N)}$ , the leading term in the density expansion [1] of the collision bracket integral  $\mathbb{R}_0^{(11)}$  is the Chapman–Enskog collision bracket integral of the Boltzmann kinetic theory [19]. Since the density-dependent part of  $\eta_k$  is much smaller than the strongly density-dependent potential part  $\eta_v$  in the liquid density regime,

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<sup>2</sup> If  $\mathcal{N} > 2$  and a simple binary collision expansion is carried out for  $T^{(\mathcal{N})}$ , then the series contains divergence-causing terms and thus gives rise to a divergence difficulty. This is discussed in [20]. See also Chap. 9 of [1] for discussions of this aspect.

the Chapman–Enskog shear viscosity  $\eta_0$  may be used for  $\eta_k^0$  in the lowest order approximation, especially, for the kinetic part without significantly affecting  $\eta_v$  in the liquid density regime:

$$\eta_k \approx \eta_0(T). \quad (7.103)$$

The potential contribution  $\eta_v$  has to do with the intermolecular interactions.

The expression for  $\eta_v$  in (7.101) may be rewritten as

$$\eta_v = \frac{k_B T \eta_0^2}{g} \frac{\Delta \mathbb{R}}{\left(1 - \frac{k_B T \eta_0}{g} \Delta \mathbb{R}\right)}. \quad (7.104)$$

To obtain this form, the collision bracket integrals are eliminated from (7.101) with the help of (7.87) and (7.100).

We examine  $\Delta \mathbb{R}$  a little more closely. If the cross terms between the momentum and potential parts of the pressure tensor are neglected to the lowest approximation of the effects of collisions, then we obtain  $\Delta \mathbb{R}$  in the form

$$\begin{aligned} \Delta \mathbb{R} &\simeq \frac{\beta^2 p^2}{5n^2 \sigma^3} \sqrt{\frac{2k_B T}{m_r}} \\ &\times \left\langle F_{\text{eq}}^{(\mathcal{N})} \sum_{l \neq j=1}^N \frac{[\mathbf{r}_{jl} \mathbf{r}_{jl}]^{(2)}}{r_{jl}} \mathcal{V}'_{jl} \delta(\mathbf{r}_j - \mathbf{r}) : i\hat{T}^{(\mathcal{N})} \sum_{m \neq k=1}^N \frac{[\mathbf{r}_{km} \mathbf{r}_{km}]^{(2)}}{r_{km}} \mathcal{V}'_{km} \right\rangle, \end{aligned} \quad (7.105)$$

which is a collision bracket integral of virial tensors. Thus, we see that  $\Delta \mathbb{R}$  is determined by the collisional evolution of intermolecular forces and related virial tensors. The operator  $\hat{T}^{(\mathcal{N})}$  may be replaced by the transition probability  $W(x^{(\mathcal{N})*}|x^{(\mathcal{N})})$  introduced earlier. This collision bracket integral  $\Delta \mathbb{R}$  may be amenable to Monte Carlo simulation. Investigation of this possibility is left for work in the future.

## 7.7 A Monte Carlo Method for the Stress Tensor

Instead of calculating the collision bracket integral by a numerical method, we may compute the stress tensor and, in particular, the shear stress tensor by employing Monte Carlo simulation. Application of Monte Carlo simulation to calculate the shear viscosity is made feasible by the nonequilibrium grand canonical ensemble distribution function or the nonequilibrium canonical ensemble distribution function provided by the generalized Boltzmann equation, particularly because the nonequilibrium distribution functions in the absence of thermal conduction resemble those used in equilibrium problems. One drawback is that this method cannot yield the zero shear rate viscosity, the Newtonian viscosity, which should be calculated or supplied from another source.

The method is implemented in the paper by Farhat and Eu [21]. We briefly describe the method and present the numerical results for the non-Newtonian shear viscosities of simple liquids.

A single-component simple liquid is subjected to shearing at constant temperature in the same flow configuration as that considered in Section 3.2.4 in Chap. 3, where a non-Poiseuille velocity profile is obtained for channel flow. Because temperature is uniform for the flow, it is sufficient to use the non-equilibrium canonical distribution function for  $N$  particles given by

$$F_c^{(N)} = \exp \left[ -\beta \sum_{i=1}^N \left( \frac{1}{2} m C_i^2 + \sum_{i \neq j=1}^N \mathcal{V}_{ij} + \mathbf{X}_1 : \mathbf{h}_i^{(1)} - m \hat{A} \right) \right], \quad (7.106)$$

where  $\mathcal{V}_{ij}$  is the potential of particle pair  $(ij)$ , the molecular moment  $\mathbf{h}_i^{(1)}$  is defined by

$$\mathbf{h}_i^{(1)} = m [\mathbf{C}_i \mathbf{C}_i]^{(2)} + \sum_{k>i}^N F_{ik} \mathbf{r}_{ik} \mathbf{r}_{ik}, \quad (7.107)$$

$$F_{ik} = -\frac{1}{r_{ik}} \frac{\partial \mathcal{V}_{ik}}{\partial r_{ik}}, \quad (7.108)$$

and  $\hat{A}$  is the work function per unit mass. We have approximated the virial tensor  $\mathbf{W}_{ik}$  with its lowest order form in (7.107)

$$\mathbf{W}_{ik} \simeq F_{ik} \mathbf{r}_{ik} \mathbf{r}_{ik}.$$

This approximation is necessary to implement the MC simulation method. We will assume a soft repulsive potential

$$\mathcal{V}_{ik}(r_{ik}) = \epsilon \left( \frac{\sigma}{r_{ik}} \right)^{12}. \quad (7.109)$$

This potential model can be readily generalized to include an attractive potential.

To implement the MC simulation method, only the potential energy part of the distribution function is necessary, which in the flow configuration under consideration may be written as

$$F_p^{(N)} = \frac{1}{Z} \exp \left[ -\beta \epsilon \sum_{i>k=1}^N \left( \frac{\sigma}{r_{ik}} \right)^{12} \left( 1 + 24w \frac{x_{ik} y_{ik}}{r_{ik}^2} \right) \right], \quad (7.110)$$

where

$$Z = \int d\mathbf{r}^{(N)} \exp \left[ -\beta \epsilon \sum_{i>k=1}^N \left( \frac{\sigma}{r_{ik}} \right)^{12} \left( 1 + 24w \frac{x_{ik} y_{ik}}{r_{ik}^2} \right) \right]. \quad (7.111)$$

In the flow configuration considered, the generalized potential  $\mathbf{X}_1$  has only an  $xy$  component, which is denoted by

$$w = X_{1xy}. \quad (7.112)$$

The distribution function  $F_p^{(N)}$  therefore looks formally the same as the equilibrium distribution function except that the potential energy is dressed up by the generalized potential times the virial;

$$24w \left( \frac{\sigma}{r_{ik}} \right)^{12} \frac{x_{ik}y_{ik}}{r_{ik}^2}.$$

This formal similarity is what makes the MC simulation method applicable, even if the system is not at equilibrium.

The relation useful to recall in this connection is the formal result,

$$X_1 = -k_B T \left( \frac{\partial \ln \Xi}{\partial \hat{\boldsymbol{\Pi}}} \right)_{T,V}, \quad (7.113)$$

where  $\hat{\boldsymbol{\Pi}} = \boldsymbol{\Pi}/\rho$  and

$$\Xi = \frac{1}{h^{3N} N!} \int dx^{(N)} \exp \left[ -\beta \sum_{i=1}^N \left( \frac{1}{2} m C_i^2 + \sum_{i \neq j=1}^N \mathcal{V}_{ij} + \mathbf{X}_1 : \mathbf{h}_i^{(1)} \right) \right]. \quad (7.114)$$

Therefore, shear stress  $\hat{\boldsymbol{\Pi}}$  may be regarded as a function of the generalized potential  $\mathbf{X}_1$  and vice versa.

Now, if the shear stress is decomposed into kinetic and potential energy parts

$$\boldsymbol{\Pi}_{xy} = \boldsymbol{\Pi}_{xy}^{\text{kin}} + \boldsymbol{\Pi}_{xy}^{\text{pot}}, \quad (7.115)$$

then the kinetic part can be calculated exactly by using the kinetic part of the nonequilibrium partition function

$$\boldsymbol{\Pi}_{xy}^{\text{kin}} = -2n k_B T \frac{w}{1-w^2}. \quad (7.116)$$

This result suggests that it is possible to look for  $\boldsymbol{\Pi}_{xy}$  in the form,

$$\boldsymbol{\Pi}_{xy} = -\frac{a_0 w}{1-a_1 w^2}, \quad (7.117)$$

where  $a_0$  and  $a_1$  are constants.  $a_0$  may be calculated by calculating the limit:

$$\begin{aligned} \lim_{w \rightarrow 0} \frac{\boldsymbol{\Pi}_{xy}}{w} &= -a_0 \\ &= -2 \left[ n k_B T + \frac{1}{V k_B T} \left\langle \left( \sum_{i < k}^N r_{ik}^x F_{ik}^y \right)^2 \right\rangle_{\text{eq}} \right]. \end{aligned} \quad (7.118)$$

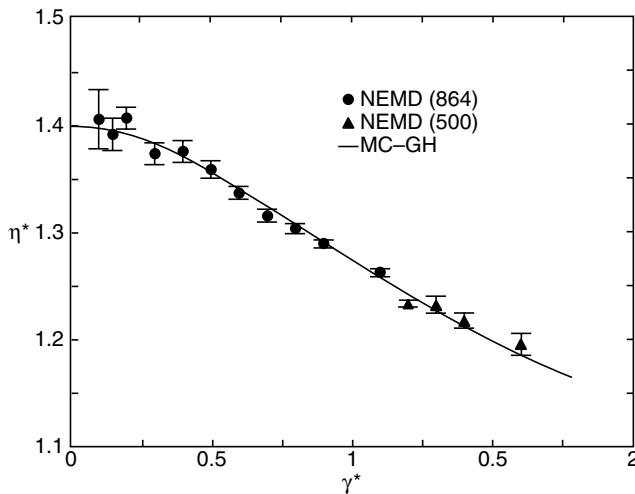
In this expression,  $\langle \dots \rangle_{\text{eq}}$  denotes the equilibrium average, and the superscripts  $x$  and  $y$  denote the Cartesian components. By using the constitutive equation for  $\Pi$  presented earlier—the steady state form of (7.81)—it can be shown that the non-Newtonian viscosity is given by the formula,

$$\eta(\gamma) = -\frac{\Pi_{xy}}{\gamma} = \frac{\eta_0 q_e(\tau\gamma)}{1 - a_1 (\eta_0 \gamma / a_0)^2 q_e^2(\tau\gamma)}, \quad (7.119)$$

where  $\gamma$  is the shear rate defined by  $\gamma = (\partial u_x / \partial y)$  and

$$\begin{aligned} q_e(\tau\gamma) &= \frac{\sinh^{-1}(\tau\gamma)}{\tau\gamma}, \\ \tau &= \sqrt{\frac{2\beta g p \eta_0}{a_0}}, \\ g &= \sqrt{\frac{m}{2k_B T}} (n\sigma)^{-2}. \end{aligned} \quad (7.120)$$

We recall that a similar formula for the non-Newtonian viscosity was obtained and discussed for a dilute gas. The reason for the similarity is in the constitutive equation for the shear stress, which remains more or less the same in form for both gases and liquids except for the difference in the meaning of the Newtonian viscosity and the term related to intermolecular forces, which



**Fig. 7.1.** Reduced non-Newtonian viscosity vs. reduced shear rate. The symbols are MD simulation results and the curve is the MC simulation result. [Reproduced from Hikmat Farhat and Byung Chan Eu, J. Chem. Phys. **110**, 97 (1999). Copyright 1999 American Institute of Physics.]

do not play a significant role in lower order theories. The parameters  $a_0$  and  $a_1$  are determined by fitting  $\Pi_{xy}$  computed by MC simulation to the relation given in (7.117). Their values are

$$a_0 = 30.2, \quad a_1 = 48.$$

To calculate the non-Newtonian viscosity with regard to density and temperature it is necessary to know the density and temperature dependence of the Newtonian viscosity  $\eta_0$ . The MC simulation method does not supply them. They should be obtained from another source. In [21], they are obtained from molecular dynamics simulations. However, we now know that the Newtonian viscosity may be computed by the modified free volume theory discussed in Chap. 12. The non-Newtonian viscosity of a soft-repulsive liquid calculated by MC simulation for  $\Pi_{xy}$  and MD simulation for  $\eta_0$  is compared with MD simulation data in Fig. 7.1, where  $\eta^* = \eta\sigma^2(m\epsilon)^{-1/2}$  and  $\gamma^* = \gamma\sigma(m/\epsilon)^{1/2}$ . The symbols with error bars are the nonequilibrium molecular dynamics simulation results—*filled circles* for 864 particle simulations and *filled triangles* for 500 particle simulations—and the curve is the MC simulation results described earlier. The agreement is excellent, indicating the validity of the MC simulation method coupled with the generalized hydrodynamics described in this section. In particular, it validates the non-Newtonian viscosity formula (7.119) derived from the constitutive equation for shear stress [1, 2, 21, 22],

$$-2p[\nabla \mathbf{u}]^{(2)} - 2[\Pi \cdot \nabla \mathbf{u}]^{(2)} - (\beta gg^{(1)})^{-1} \mathbb{R}^{(11)} \Pi q(\Pi) = 0, \quad (7.121)$$

which is the adiabatic approximation of (7.81) or the steady-state form in the coordinate system moving at  $\mathbf{u}$ .

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## Generalized Boltzmann Equation for Polyatomic Liquids

In this chapter, the kinetic theory developed for simple liquids in the previous chapter is extended to polyatomic liquids consisting of molecules with internal structures. Since both translational and internal degrees of freedom are involved, they must be properly taken into account for the molecular theoretical description of the thermophysical evolution of complex liquids. Nevertheless, the formal development of the theory, albeit more complicated, is parallel to the kinetic theory of simple liquids. For this reason and for lack of space, we will be as brief as possible in describing the theory. We will present the generalized hydrodynamic equations and map out the general methodology for studying transport and flow processes in complex fluids.

As in the previous chapter, we will begin the discussion with the assumption of no chemical reaction in the fluids. This assumption will then be removed in the last part of this chapter where we will formulate a generalized theory in which chemical reactions are allowed. This generalization is an important motivation for including this chapter in this work. The generalized Boltzmann equation for reacting fluids will enable us to study chemical kinetics and attendant transport phenomena in solutions, although we will not discuss its application to the subjects for lack of time and space and also for the reason that we have not had an opportunity to apply the theory to chemical kinetics in liquid solutions. We hope that this theory of reacting fluids will ultimately enable us to study in detail chemical kinetics and attendant transport processes in solutions in the future and thereby bring us closer to the eventual study of transport processes in biological systems where chemical reactions occur concurrently with the transport of matter and energy.

### 8.1 Notational Preliminary

To prepare for the development of the theory we define various symbols beyond those necessary for the simple liquid theory. We consider an  $r$ -component liquid mixture of  $\mathbf{N} = (N_1, N_2, \dots, N_r)$  polyatomic molecules contained in

volume  $V$ . There are  $l_a$  atoms (sites) in the molecule of species  $a$ . We reserve lower case Roman subscripts  $a, b, c, \dots$  for species, and lower case Greek subscripts  $\nu, \sigma, \tau, \dots$  for sites (e.g., atoms or groups) on molecules. Thus the subscripts ( $a\nu$ ) stand for site  $\nu$  of molecule  $i$  of species  $a$  ( $\nu \in i \in a$ ). The position of the  $\nu$ th site (atom) in molecule  $i$  of species  $a$  therefore will be denoted by  $\mathbf{r}_{a\nu}$ , and its momentum by  $\mathbf{p}_{a\nu}$ . It is convenient to abbreviate the set of positions and momentum vectors, respectively, by

$$\begin{aligned}\mathbf{r}^{(N)} &= (\mathbf{r}_{a11}, \mathbf{r}_{a12}, \dots, \mathbf{r}_{a1l_a}; \dots; \mathbf{r}_{aN_a1}, \mathbf{r}_{aN_a2}, \dots, \mathbf{r}_{aN_al_a}), \\ \mathbf{p}^{(N)} &= (\mathbf{p}_{a11}, \mathbf{p}_{a12}, \dots, \mathbf{p}_{a1l_a}; \dots; \mathbf{p}_{aN_a1}, \mathbf{p}_{aN_a2}, \dots, \mathbf{p}_{aN_al_a}),\end{aligned}\quad (8.1)$$

where  $1 \leq a \leq r$ . In addition to the abbreviations defined, it is useful to collect the definitions of other symbols used for discussing the kinetic theory of polyatomic fluids.

Since the mass  $m_{a\nu}$  of site  $\nu$  is the same for all molecules of species  $a$ , we will find it useful to express the mass of  $(aj\nu)$  as  $m_{a\nu} \equiv m_{aj\nu}$  to simplify the equations involved, which may require multiple summations. Thus,

$$m_a = \sum_{\nu=1}^{l_a} m_{a\nu} = \text{molecular mass of a polyatomic molecule};$$

for the position variables

$$\begin{aligned}\mathbf{R}_{aj} &= \text{center-of-mass position vector of molecule } j \text{ of species } a, \\ \boldsymbol{\xi}_{aj\nu} &= \text{distance of the } \nu \text{th site of molecule } j \in a \text{ from the center of mass} \\ &\quad \text{located at } \mathbf{R}_{aj} \text{ relative to the coordinate origin,} \\ \mathbf{r}_{aj\nu bk\gamma} &= \text{relative distance vector between sites } \nu \in j \in a \text{ and } \gamma \in k \in b;\end{aligned}$$

for velocity variables

$$\begin{aligned}\mathbf{v}_{aj\nu} &= \dot{\mathbf{r}}_{aj\nu}, \\ &= \text{velocity vector of particle (site) } \nu \in j \in a, \\ \mathbf{V}_{aj} &= \dot{\mathbf{R}}_{aj} \\ &= \text{center of mass velocity vector of molecule } j \in a \\ &\quad \text{relative to the coordinate origin;}\end{aligned}$$

and for momentum and related variables

$$\begin{aligned}\mathbf{u} &= \text{mean fluid velocity of the fluid,} \\ \mathbf{P}_{aj} &= m_a \mathbf{V}_{aj} = \text{momentum conjugate to } \mathbf{R}_{aj}, \\ \mathcal{P}_{aj\nu} &= m_{a\nu} \dot{\boldsymbol{\xi}}_{aj\nu} = \text{momentum conjugate to } \dot{\boldsymbol{\xi}}_{aj\nu}, \\ \mathcal{C}_{aj\nu} &= \dot{\mathbf{r}}_{aj\nu} - \mathbf{u} = \text{peculiar velocity of particle (site) } a \in j \in a, \\ \mathbf{C}_{aj} &= \mathbf{V}_{aj} - \mathbf{u} = \text{peculiar velocity of molecule } j \in a.\end{aligned}$$

The gradient operators will be abbreviated as follows:

$$\nabla_{\mathbf{r}_{aj\nu}} = \partial/\partial \mathbf{r}_{aj\nu}, \quad \nabla_{\mathbf{p}_{aj\nu}} = \partial/\partial \mathbf{p}_{aj\nu}.$$

In a space-fixed coordinate system adopted for the polyatomic fluid considered here, there then holds the relation

$$\mathbf{r}_{aj\nu} = \mathbf{R}_{aj} + \boldsymbol{\xi}_{aj\nu}. \quad (8.2)$$

Consequently, it follows: that

$$\sum_{\nu=1}^{l_a} m_{a\nu} \xi_{aj\nu} = 0 \quad (8.3)$$

and

$$\sum_{\nu=1}^{l_a} m_{a\nu} \dot{\xi}_{aj\nu} = 0. \quad (8.4)$$

The Hamiltonian function  $\mathcal{H}$  can then be written for the system of interest as follows:

$$\mathcal{H} = \sum_{a=1}^r \sum_{j=1}^{N_a} \sum_{\nu=1}^{l_a} \frac{1}{2m_{a\nu}} \mathbf{p}_{aj\nu} \cdot \mathbf{p}_{aj\nu} + U_N(\mathbf{r}^{(N)}), \quad (8.5)$$

where  $U_N(\mathbf{r}^{(N)})$  is the potential energy of the mixture. We assume that the potential energy  $U_N(\mathbf{r}^{(N)})$  is pairwise additive:

$$\begin{aligned} U_N(\mathbf{r}^{(N)}) = & \frac{1}{2} \sum_{a=1}^r \sum_{j=1}^{N_a} \sum_{\nu=1}^{l_a} \sum_{\gamma=1}^{l_a} w_{aj\nu aj\gamma}(r_{aj\nu b j\gamma}) \\ & \quad (\nu \neq \gamma) \\ & + \frac{1}{2} \sum_{a,b=1}^r \sum_{j=1}^{N_a} \sum_{k=1}^{N_b} \sum_{\nu=1}^{l_a} \sum_{\gamma=1}^{l_b} \mathcal{V}_{aj\nu bk\gamma}(r_{aj\nu b k\gamma}) \\ & \quad (j \neq k, \nu \neq \gamma) \\ & + \sum_{a=1}^r \sum_{j=1}^{N_a} \sum_{\nu=1}^{l_a} \mathcal{V}_a^{(ex)}(\mathbf{r}_{aj\nu}), \end{aligned} \quad (8.6)$$

where  $r_{aj\nu bk\gamma}$  is the distance between the pair of sites  $(aj\nu, bk\gamma)$ ,  $r_{aj\nu bk\gamma} = |\mathbf{r}_{aj\nu} - \mathbf{r}_{bk\gamma}| = |\mathbf{r}_{bk\gamma} - \mathbf{r}_{aj\nu}|$ ;  $w_{aj\nu aj\gamma}(r_{aj\nu aj\gamma})$  is the intramolecular potential for the two sites (atoms)  $\nu$  and  $\gamma$  of molecule  $j$ ;  $\mathcal{V}_{aj\nu bk\gamma}(r_{aj\nu bk\gamma})$  is the intermolecular (site-site) interaction potential of the pair of sites  $\nu \in j \in a$  and  $\gamma \in k \in b$  on different molecules  $j \in a$  and  $k \in b$ , respectively; and  $\mathcal{V}_a^{(ex)}(\mathbf{r}_{aj\nu})$  is the external potential on  $j\nu \in a$ . The intramolecular potential energies  $w_{aj\nu aj\gamma}(r_{aj\nu aj\gamma})$  are of two qualitatively different kinds, one responsible for the bonding of adjacent sites and the other for van der Waals type interactions between nonbonded sites on the molecule. These two types of potentials

are not distinguished by different symbols for brevity of notation; they can be recognized by the subscripts once a suitable numbering convention is adopted for the molecule. The latter type of interaction potential may be modeled by the Lennard-Jones potential which may be assumed for site-site interactions, whereas the former type may be assumed to be harmonic or anharmonic potentials. According to the site-site interaction model, the interaction between two atomic sites on different molecules or nonbonded sites on a molecule is assumed to consist of the same type; for example, the Lennard-Jones potential

$$\mathcal{V}_{aj\nu bk\gamma}(\mathbf{r}_{aj\nu bk\gamma}) = 4\epsilon_{a\nu b\gamma} \left[ \left( \frac{\sigma_{a\nu b\gamma}}{r_{aj\nu bk\gamma}} \right)^{12} - \left( \frac{\sigma_{a\nu b\gamma}}{r_{aj\nu bk\gamma}} \right)^6 \right], \quad (8.7)$$

where  $-\epsilon_{a\nu b\gamma}$  is the well depth and  $\sigma_{a\nu b\gamma}$  is the size parameter for the site pair  $\nu \in a$  and  $\gamma \in b$ .

The Liouville operator for the system is then given by

$$\begin{aligned} L^{(\mathbf{N})} = & \sum_{a=1}^r \sum_{j=1}^{N_a} \sum_{\nu=1}^{l_a} L_{aj\nu} + \frac{1}{2} \sum_{a,b=1}^r \sum_{j=1}^{N_a} \sum_{k=1}^{N_b} \sum_{\nu=1}^{l_a} \sum_{\gamma=1}^{l_b} L_{aj\nu bk\gamma}^{(v)} \\ & + \sum_{a=1}^r \sum_{j=1}^{N_a} \sum_{\nu=1}^{l_a} L_{aj\nu}^{(\text{ex})}, \end{aligned} \quad (8.8)$$

where

$$L_{aj\nu} = \mathbf{v}_{aj\nu} \cdot \nabla_{aj\nu} + \frac{1}{2} \sum_{\gamma=1 (\alpha \neq \gamma)}^{l_a} L_{aj\nu aj\gamma}^{(s)}, \quad (8.9)$$

$$L_{aj\nu aj\gamma}^{(s)} = \mathbf{F}_{aj\nu aj\gamma}^{(s)} \cdot (\nabla_{\mathbf{p}aj\nu} - \nabla_{\mathbf{p}aj\gamma}), \quad (8.10)$$

$$L_{aj\nu bk\gamma}^{(v)} = \mathbf{F}_{aj\nu bk\gamma}(\mathbf{r}_{aj\nu bk\gamma}) \cdot (\nabla_{\mathbf{p}aj\nu} - \nabla_{\mathbf{p}bk\gamma}), \quad (8.11)$$

$$L_{aj\nu}^{(\text{ex})} = m_{a\nu} \mathbf{F}_a(\mathbf{r}_{aj\nu}) \cdot \nabla_{\mathbf{p}aj\nu}. \quad (8.12)$$

In these formulas,  $\mathbf{v}_{aj\nu} = \mathbf{p}_{aj\nu}/m_{a\nu}$  and the forces are defined by

$$\begin{aligned} \mathbf{F}_{aj\nu bk\gamma}(\mathbf{r}_{aj\nu bk\gamma}) &= -\frac{\partial}{\partial \mathbf{r}_{aj\nu bk\gamma}} \mathcal{V}_{aj\nu bk\gamma}(r_{aj\nu bk\gamma}), \\ \mathbf{F}_{aj\nu aj\gamma}^{(s)}(\mathbf{r}_{aj\nu aj\gamma}) &= -\frac{\partial}{\partial \mathbf{r}_{aj\nu aj\gamma}} w_{aj\nu aj\gamma}(r_{aj\nu aj\gamma}), \\ m_{a\nu} \mathbf{F}_a(\mathbf{r}_{aj\nu}) &= -\frac{\partial}{\partial \mathbf{r}_{aj\nu}} \mathcal{V}_a^{(\text{ex})}(r_{aj\nu}). \end{aligned} \quad (8.13)$$

The isolated molecule and intermolecular Liouville operators are separated out in the Liouville operator  $L^{(N)}$ . The intramolecular Liouville operator  $L_{aj\nu}$  may be further separated into the bonded part and the nonbonded interaction part accounting for the interaction of nonbonded sites within the molecule. The presence of the interaction Liouville operator, the second term on the right in (8.9) for  $L_{aj\nu}$ , is the major point of difference between the simple and complex fluid Liouville operators, apart from the differences in the meanings of the subscripts in the intermolecular interaction Liouville operator  $L_{aj\nu bk\gamma}^{(v)}$ . Except for the extra subscripts having to do with the sites in the molecules, the interaction Liouville operator  $L_{aj\nu bk\gamma}^{(v)}$  has the same form as that for simple fluids.

We notice that, apart from the Hamiltonian and the corresponding Liouville operator for bonded particles, the Hamiltonian and Liouville operator for the nonbonded particles—for relative motions and interparticle interactions—are formally similar to those for mixtures of simple fluids. If the indexes for the sites on the polyatomic molecule are regarded as the indexes for species in a mixture, the Hamiltonian and the Liouville operator in question may be regarded as those for the mixture of simple fluids of interest. For this reason, except for the contributions made by bonded particles, the kinetic theory relevant to relative intermolecular motions can be readily translated into those of polyatomic fluids. To exploit this feature we compress the composite subscripts into single subscripts  $\mathbf{j} = (aj\nu)$ ,  $\mathbf{k} = (bk\gamma)$ , and so forth. Then the Liouville operator  $L^{(N)}$  may be expressed in the form

$$L^{(N)} = \sum_{j=1}^N L_j + \frac{1}{2} \sum_{j \neq k=1}^N L_{jk}^{(v)} + \sum_{j=1}^N L_j^{(ex)}, \quad (8.14)$$

where  $L_j$ ,  $L_{jk}^{(v)}$ , and  $L_j^{(ex)}$  stand for the Liouville operators defined, respectively, in (8.9)–(8.12). It will be convenient to split  $L_j$  into free and interactions parts as in

$$L_j = L_j^{(0)} + \frac{1}{2} \sum_{j' \neq j} L_{jj'}^{(s)}, \quad (8.15)$$

where the sum over the primed subscript  $j'$  is understood to be over the sites in molecule  $j$ . One may, of course, combine the intramolecular Liouville operator  $L_{jj'}^{(s)}$  with the Liouville operator  $L_{jk}^{(v)}$ , the intermolecular interaction Liouville operator. In this compact form, the Liouville operator  $L^{(N)}$  formally acquires the same form as that for the Liouville operator of simple fluids, and with the subscripts and the summations appropriately understood we may simply transcribe the kinetic theory results for simple fluids into those for polyatomic liquid mixtures.

We now consider a grand ensemble consisting of petit ensembles of fixed  $N$ , which varies from zero to an arbitrarily large value. If there are  $n^{(N)}$  petit ensembles of  $N$ , there are

$$\omega = \sum_{N \geq 0} n^{(N)}$$

representative systems in the grand ensemble. The total number of molecules is then given by

$$\mathcal{N} = \sum_{\mathbf{N} \geq 0} \mathbf{N}_n^{(\mathbf{N})}.$$

We shall denote by  $F^{(\mathcal{N})}(x^{(\mathcal{N})}, t)$  the probability distribution function of finding  $\mathcal{N}$  molecules in  $dx^{(\mathcal{N})}$  around  $x^{(\mathcal{N})}$ . This distribution function is normalized to unity:

$$\sum_{\mathcal{N} \geq 0} \int dx^{(\mathcal{N})} F^{(\mathcal{N})}(x^{(\mathcal{N})}; t) = 1. \quad (8.16)$$

The reduced distribution functions are obtained from  $F^{(\mathcal{N})}(x^{(\mathcal{N})}, t)$  by integrating over a portion of the phase space. For example, the reduced distribution function  $F^{(\mathbf{N})}(x^{(\mathbf{N})}, t)$  is defined by

$$F^{(\mathbf{N})}(x^{(\mathbf{N})}, t) = \frac{\mathcal{N}!}{(\mathcal{N} - N)!} \int dx^{(\mathcal{N}-N)} F^{(\mathcal{N})}(x^{(\mathcal{N})}; t). \quad (8.17)$$

This is the probability of finding  $\mathbf{N}$  particles at  $x^{(\mathbf{N})}$  regardless of  $(\mathcal{N} - N)$  particles distributed in the phase space of  $x^{(\mathcal{N})}$ . As it is for simple liquids, this distribution function obeys the generalized Boltzmann equation

$$\left( \partial_t + L^{(\mathbf{N})} \right) F^{(\mathbf{N})}(x^{(\mathbf{N})}; t) = \mathfrak{R} [F^{(\mathbf{N})}], \quad (8.18)$$

where the collision operator  $\mathfrak{R}$  is, as for simple liquids, given by

$$\mathfrak{R} [F^{(\mathbf{N})}] = \frac{\mathcal{N}!}{(\mathcal{N} - N)!} \int dx^{(\mathcal{N}-N)} (-i) T^{(\mathcal{N})} F^{(\mathcal{N})}(x^{(\mathcal{N})}; t) \quad (8.19)$$

with  $T^{(\mathcal{N})}$  denoting the collision operator for  $\mathcal{N}$  particles making up the grand ensemble and

$$F^{(\mathcal{N})}(x^{(\mathcal{N})}; t) = \prod_{\{\mathbf{N}\}} F^{(\mathbf{N})}(x^{(\mathbf{N})}; t).$$

The product is over  $\{\mathbf{N}\}$ , the set of petit ensembles of  $\mathbf{N}$  particles in the grand ensemble of  $\mathcal{N}$  particles. This collision operator has the meaning extended to include the internal degrees of freedom beyond the meaning of the collision operator we have used for simple liquids in Chap. 7. Nevertheless, it can be still assumed that it fulfills the conditions (7.C1)–(7.C3). As a matter of fact, the collision operator  $(-i) T^{(\mathcal{N})}$  may be taken as  $W(x^{(\mathcal{N})}|x^{(\mathcal{N})*})$ , so that

$$\begin{aligned} \mathfrak{R} [F^{(\mathbf{N})}] &= \frac{\mathcal{N}!}{(\mathcal{N} - N)!} \int dx^{(\mathcal{N}-N)} \left[ W(x^{(\mathcal{N})*}|x^{(\mathcal{N})}) F^{(\mathcal{N})*}(x^{(\mathcal{N})*}; t) \right. \\ &\quad \left. - W(x^{(\mathcal{N})}|x^{(\mathcal{N})*}) F^{(\mathcal{N})}(x^{(\mathcal{N})}; t) \right], \end{aligned} \quad (8.20)$$

where  $W(x^{(\mathcal{N})}|x^{(\mathcal{N})*})$  has the properties discussed in Chap. 7. The kinetic equation can be obtained, as described in Appendix A. See also Section A.2 of Appendix A for the scattering theory meaning of  $W(x^{(\mathcal{N})}|x^{(\mathcal{N})*})$ .

The structural similarity of the kinetic equation to that of the kinetic equation for simple liquids indicates that the kinetic theory of polyatomic liquids will be parallel to that of simple liquids developed in Chap. 7, although there are features related to the internal degrees of freedom for polyatomic molecules. They will be pointed out at appropriate places. For this reason, we will present the evolution equations and indicate where the differences lie, even if they appear formally the same as their simple fluid counterparts.

## 8.2 Evolution Equations for Macroscopic Variables

The method of deriving evolution equations from the kinetic equation (8.18) is the same as that used for simple fluids in Chap. 7. Therefore, we will simply present only the result in this chapter. For the purpose, it is convenient to summarize the definitions of the molecular expressions for various macroscopic variables, which are obtained when the molecular expressions are averaged with the nonequilibrium grand ensemble distribution function obeying the kinetic equation postulated. The leading members of the set for the molecular expressions are listed in Table 8.1, where we use the notation of composite subscripts used in connection with the Liouville operators in Eq. (8.14) under the understanding that  $m_i \equiv m_{a\nu}$ ,  $p_i \equiv p_a$ , and  $\hat{h}_i = \hat{h}_{a\nu}$ , and the primed index means that only one of the composite elements is varied unlike for the unprimed in which all three indexes are varied; for example,  $i' = (ai\gamma)$ , where only  $\gamma$  is variable, whereas all three indexes are variable in  $i = (aiv)$ . In the table, the potential energy

$$V^{(N)} = \frac{1}{2} \sum_i \sum_{\substack{k \\ (i \neq k)}} \mathcal{V}_{ik} (\mathbf{r}_i, \mathbf{r}_k) \quad (8.21)$$

represents the sum of intramolecular and intermolecular potential energy. If the intramolecular and intermolecular parts are explicitly distinguished,  $V^{(N)}$  may be written as

$$V^{(N)} = \frac{1}{2} \sum_i \sum_{i'} w_{ii'} (\mathbf{r}_i, \mathbf{r}_{i'}) + \frac{1}{2} \sum_i \sum_{\substack{k \\ (i \neq k)}} \mathcal{V}_{ik} (\mathbf{r}_i, \mathbf{r}_k). \quad (8.22)$$

In the same manner as for  $V^{(N)}$ , whenever the intramolecular and intermolecular virial tensors appear together and there is no possibility of confusion, they will be written with the single symbol  $\mathbf{W}_{ik}$  under the subscript

convention introduced earlier for the simplicity of the equations involved. The intramolecular and intermolecular virial tensors  $\mathbf{W}_{ii'}^{(s)}$  and  $\mathbf{W}_{ik}$  are defined by

$$\mathbf{W}_{ii'}^{(s)} = \int_0^1 d\lambda \mathbf{F}_{ii'}^{(s)} \mathbf{r}_{ii'} \exp(-\mathbf{r}_{ii'} \cdot \nabla_{\mathbf{r}}), \quad (8.23)$$

$$\mathbf{W}_{ik} = \int_0^1 d\lambda \mathbf{F}_{ik} \mathbf{r}_{ik} \exp(-\mathbf{r}_{ik} \cdot \nabla_{\mathbf{r}}) \quad (8.24)$$

with the definition of

$$\mathbf{F}_{ii'}^{(s)} = -\frac{\partial w^{(\mathbf{N})}}{\partial \mathbf{r}_{ii'}}, \quad (8.25)$$

$$\mathbf{F}_{ik} = -\frac{\partial \mathcal{V}^{(\mathbf{N})}}{\partial \mathbf{r}_{ik}}, \quad (8.26)$$

$$w^{(\mathbf{N})} = \frac{1}{2} \sum_i \sum_{i' \neq i} w_{ii'}, \quad (8.27)$$

$$\mathcal{V}^{(\mathbf{N})} = \frac{1}{2} \sum_i \sum_{k \neq i} \mathcal{V}_{ik}. \quad (8.28)$$

They are in the same form as the virial tensor defined for simple fluids in Chap. 7. These tensors play an important role in the description of transport processes in liquids, as we have already seen in the kinetic theory of simple fluids.

### 8.2.1 Macroscopic Variables

Macroscopic variables are defined as averages of the molecular expressions of dynamic observables, the leading examples of which are given in Table 8.1.

**Table 8.1.** Molecular expressions for the leading members in the moment set

name	$h_i^{(q)}$	mathematical expression
mass density		$m_i$
momentum		$m_i \mathbf{v}_i$
energy		$\frac{1}{2} m_i \mathcal{C}_i^2 + \frac{1}{2} \sum_{k \neq i} \mathcal{V}_{ik}$
shear stress	$h_i^{(1)}$	$m_i [\mathcal{C}_i \mathcal{C}_i]^{(2)} + \frac{1}{2} \sum_{k \neq i} [\mathbf{W}_{ik}]^{(2)}$
bulk stress	$h_i^{(2)}$	$\frac{1}{3} m_i \mathcal{C}_i^2 + \frac{1}{6} \sum_{k \neq i} \text{Tr} \mathbf{W}_{ik} - m_i p_i / \rho_i$
heat flux	$h_i^{(3)}$	$\left[ \frac{1}{2} m_i \mathcal{C}_i^2 + \frac{1}{2} \sum_{k \neq i} \mathcal{V}_{ik} \right] \mathcal{C}_i$ $+ \frac{1}{2} \sum_{k \neq i} \mathbf{W}_{ik} \cdot \mathcal{C}_k - \hat{h}_i m_i \mathcal{C}_i$
diffusion flux	$h_i^{(4)}$	$m_i \mathcal{C}_i$
angular momentum	$h_i^{(5)}$	$m_i \mathbf{r}_i \times \dot{\mathbf{r}}_i$

The grand ensemble average in the phase space is again denoted by angular brackets

$$\left\langle A \left( x^{(\mathbf{N})} \right) F^{(\mathbf{N})} \right\rangle = \sum_{\mathbf{N} \geq 0} \frac{1}{\mathbf{N}!} \int dx^{(N)} A \left( x^{(\mathbf{N})} \right) F^{(\mathbf{N})} \left( x^{(\mathbf{N})}, t \right), \quad (8.29)$$

$$A \left( x^{(\mathbf{N})} \right) = \sum_{a=1}^r \sum_{\mathbf{i}_a} A_{\mathbf{i}} \left( x^{(\mathbf{N})} \right) \delta \left( \mathbf{r}_{\mathbf{i}} - \mathbf{r} \right), \quad (8.30)$$

where  $\mathbf{i}_a$  (or, alternatively,  $\mathbf{i}^{(a)}$ ) stands for the set of indexes  $(i\nu)$  ranging from  $1 \leq i \leq N_a$  and  $1 \leq \nu \leq l_a$ , and

$$\mathbf{N}! = \prod_{a=1}^r N_a!.$$

The conserved variables thus are defined by the grand ensemble averages:

$$\rho(\mathbf{r}, t) = \sum_{a=1}^r \rho_a(\mathbf{r}, t) = \sum_{a=1}^r \left\langle \sum_{\mathbf{i}_a} m_{\mathbf{i}} \delta(\mathbf{r}_{\mathbf{i}} - \mathbf{r}) F^{(\mathbf{N})} \right\rangle, \quad (8.31)$$

$$\rho \mathbf{u}(\mathbf{r}, t) = \sum_{a=1}^r \rho_a \mathbf{u}_a(\mathbf{r}, t) = \sum_{a=1}^r \left\langle \sum_{\mathbf{i}_a} m_{\mathbf{i}} \mathbf{v}_{\mathbf{i}} \delta(\mathbf{r}_{\mathbf{i}} - \mathbf{r}) F^{(\mathbf{N})} \right\rangle, \quad (8.32)$$

$$\rho \mathcal{E}(\mathbf{r}, t) = \left\langle \sum_{\mathbf{i}} \left( \frac{1}{2} m_{\mathbf{i}} \mathcal{C}_{\mathbf{i}}^2 + \frac{1}{2} \sum_{\mathbf{k} \neq \mathbf{i}} \mathcal{V}_{\mathbf{ik}} \right) \delta(\mathbf{r}_{\mathbf{i}} - \mathbf{r}) F^{(\mathbf{N})} \right\rangle. \quad (8.33)$$

We have defined the mass density  $\rho(\mathbf{r}, t)$  and the momentum density  $\rho \mathbf{u}(\mathbf{r}, t)$  in terms of species mass density  $\rho_a(\mathbf{r}, t)$  and species momentum density  $\rho_a \mathbf{u}_a(\mathbf{r}, t)$ , respectively. The former will be necessary for defining mass fractions, and the latter for diffusion fluxes appearing in the theory of mixtures. Of course, the internal energy density  $\rho \mathcal{E}(\mathbf{r}, t)$  may be decomposed into species components, but such a decomposition is unnecessary in the theory presented. These conserved variables obey the conservation laws or the balance equations of mass, momentum, and internal energy, which follow from the kinetic equation (8.18) because of Conditions (7.C1)–(7.C3). They will be presented shortly.

The nonconserved macroscopic variables are derived by averaging the molecular expression presented in Table 8.1 or expressions generated systematically by applying the method of Irving and Kirkwood [1]. The stress tensor, heat flux, and diffusion fluxes are defined with the expressions for  $h_{\mathbf{i}}^{(q)}(x^{(\mathbf{N})})$  ( $q \geq 1$ ) given in Table 8.1

$$\mathbf{P}(\mathbf{r}, t) = \sum_{a=1}^r \mathbf{P}_a(\mathbf{r}, t) = \sum_{a=1}^r [\boldsymbol{\Pi}_a(\mathbf{r}, t) + \Delta_a(\mathbf{r}, t) \boldsymbol{\delta} + p_a \boldsymbol{\delta}], \quad (8.34)$$

$$\boldsymbol{\Pi}(\mathbf{r}, t) = \sum_{a=1}^r \boldsymbol{\Pi}_a(\mathbf{r}, t) = \sum_{a=1}^r \left\langle \sum_{\mathbf{i}_a} h_{\mathbf{i}}^{(1)} \delta(\mathbf{r}_i - \mathbf{r}) F^{(\mathbf{N})} \right\rangle, \quad (8.35)$$

$$\Delta(\mathbf{r}, t) = \sum_{a=1}^r \Delta_a(\mathbf{r}, t) = \sum_{a=1}^r \left\langle \sum_{\mathbf{i}_a} h_{\mathbf{i}}^{(2)} \delta(\mathbf{r}_i - \mathbf{r}) F^{(\mathbf{N})} \right\rangle, \quad (8.36)$$

$$\mathbf{Q}'(\mathbf{r}, t) = \sum_{a=1}^r \mathbf{Q}'_a = \sum_{a=1}^r \left\langle \sum_{\mathbf{i}_a} h_{\mathbf{i}}^{(3)} \delta(\mathbf{r}_i - \mathbf{r}) F^{(\mathbf{N})} \right\rangle, \quad (8.37)$$

$$\mathbf{J}_a(\mathbf{r}, t) = \left\langle \sum_{\mathbf{i}_a} h_{\mathbf{i}}^{(4)} \delta(\mathbf{r}_i - \mathbf{r}) F^{(\mathbf{N})} \right\rangle, \quad (8.38)$$

$$\mathfrak{S}(\mathbf{r}, t) = \sum_{a=1}^r \mathfrak{S}_a(\mathbf{r}, t) = \left\langle \sum_{\mathbf{i}} h_{\mathbf{i}}^{(5)} \delta(\mathbf{r}_i - \mathbf{r}) F^{(\mathbf{N})} \right\rangle. \quad (8.39)$$

To this list of macroscopic variables must be added the mean force  $\mathcal{F}_a$  defined by

$$\rho_a \mathcal{F}_a(\mathbf{r}, t) = \left\langle \sum_{\mathbf{i}_a} \sum_{\mathbf{j} < \mathbf{i}} \mathbf{F}_{ij}(\mathbf{r}_{ij}) \delta(\mathbf{r}_j - \mathbf{r}) F^{(\mathbf{N})} \right\rangle. \quad (8.40)$$

This is the mean force exerted by other particles on a molecule of species  $a$  located at  $\mathbf{r}$ . We will find it convenient to define the nonconserved variables with a unified symbol

$$\begin{aligned} \Phi_q(\mathbf{r}, t) &= \rho \hat{\Phi}_q(\mathbf{r}, t) = \sum_{a=1}^r \rho \hat{\Phi}_{qa}(\mathbf{r}, t) \\ &= \sum_{a=1}^r \left\langle \sum_{\mathbf{i}_a} h_{\mathbf{i}}^{(q)} \delta(\mathbf{r}_i - \mathbf{r}) F^{(\mathbf{N})} \right\rangle \end{aligned} \quad (8.41)$$

and also its flux

$$\psi_q(\mathbf{r}, t) = \sum_{a=1}^r \psi_{qa}(\mathbf{r}, t) = \sum_{a=1}^r \left\langle \sum_{\mathbf{i}_a} C_i h_{\mathbf{i}}^{(q)} \delta(\mathbf{r}_i - \mathbf{r}) F^{(\mathbf{N})} \right\rangle \quad (8.42)$$

for all  $q \geq 1$ . Because of the appearance of  $\psi_{qa}$ , the evolution equations form an open set of hierarchical equations, which must be suitably closed before hydrodynamic processes are examined within the framework of the laws of thermodynamics. Because we are not concerned with a thermodynamic theory of irreversible processes, closure will not be considered in this work. We simply remark that on setting  $\psi_{qa} = 0$  for all  $q$  except for  $q = 2$  (excess normal stress) and  $4$  (diffusion flux), we may close the open hierarchy of evolution equations for nonconserved variables.

### 8.2.2 Conservation Laws

The conservation laws of mass, momentum, and energy are easily obtained by using the definitions (8.31)–(8.33) and the kinetic equation (8.18):

$$\rho \frac{dv}{dt} = \nabla \cdot \mathbf{u}, \quad (8.43)$$

$$\rho \frac{d}{dt} c_a = -\nabla \cdot \mathbf{J}_a, \quad (8.44)$$

$$\rho \frac{d}{dt} \mathbf{u} = -\nabla \cdot \mathbf{P} + \rho \mathbf{F}, \quad (8.45)$$

$$\rho \frac{d}{dt} \mathcal{E} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \mathbf{F}_a, \quad (8.46)$$

where  $c_a = \rho_a / \rho$ ;  $\mathbf{F}$  is the mean external force per unit mass

$$\rho \mathbf{F} = \sum_{a=1}^r \rho_a \mathbf{F}_a;$$

$\mathbf{F}_a$  is the mean external force on unit mass of species  $a$  at  $\mathbf{r}$ , which is defined by the average

$$\rho_a \mathbf{F}_a = \left\langle \frac{1}{2} \sum_{\mathbf{i}_a} \sum_{\mathbf{k} \neq \mathbf{i}} \mathbf{F}_a(\mathbf{r}_i) \delta(\mathbf{r}_i - \mathbf{r}) F^{(N)} \right\rangle \quad (8.47)$$

and  $\mathbf{Q}$  is the heat flux defined by the energy flux

$$\mathbf{Q}(\mathbf{r}, t) = \sum_{a=1}^r \mathbf{Q}_a = \sum_{a=1}^r \left\langle \sum_{\mathbf{i}_a} (h_i^{(3)} + \hat{h}_i m_i c_i) \delta(\mathbf{r}_i - \mathbf{r}) F^{(N)} \right\rangle. \quad (8.48)$$

Since its relation to  $\mathbf{Q}'$  is

$$\mathbf{Q} = \mathbf{Q}' + \sum_{a=1}^r \hat{h}_a \mathbf{J}_a, \quad (8.49)$$

it does not include the energy transported by matter itself. Note that  $\mathbf{V}_a^{(2)}$  and  $\mathbf{V}_a^{(3)}$  consist of contributions from the intra- and intermolecular forces under the convention of notation for indexes. We reiterate that the virial tensor  $\mathbf{W}_{ik}$  in Table 8.1 also consists of the intra- and intermolecular virial tensors  $\mathbf{W}_{ii'}$  and  $\mathbf{W}_{ik}$  according to the subscript convention mentioned. Furthermore, because of these virial tensors in the molecular expression for the definition of  $h_i^{(3)}$ , the heat flux  $\mathbf{Q}$  contains intramolecular and intermolecular fluxes of stress work. These intricate effects from the virial tensors should not be ignored. It is quite important to give careful treatment to the stress work if the heat conductivity is to be correctly accounted for in the liquid density regime, as will be seen in later chapters.

### 8.2.3 Evolution Equations for Nonconserved Variables

The evolution equations for nonconserved variables are derived from the kinetic equation and their statistical mechanics definitions (8.41). On differentiating (8.41) with respect to time and using the kinetic equation (8.18), we obtain the evolution equation for  $\Phi_{qa}$ :

$$\rho \frac{d}{dt} \hat{\Phi}_{qa} = -\nabla \cdot \psi_{qa} + \mathcal{Z}_{qa} + \Lambda_{qa} \quad (q \geq 1; 1 \leq a \leq r), \quad (8.50)$$

where  $\mathcal{Z}_{qa}$  and  $\Lambda_{qa}$  are the kinematic and dissipation terms defined, respectively, by the statistical mechanics expressions

$$\mathcal{Z}_{qa} = \left\langle \sum_{\mathbf{i}_a} \left( \mathcal{D}_t^{(\mathbf{N})} h_{\mathbf{i}}^{(q)} \right) \delta(\mathbf{r}_i - \mathbf{r}) F^{(\mathbf{N})} \right\rangle, \quad (8.51)$$

$$\Lambda_{qa} = \left\langle \sum_{\mathbf{i}_a} h_{\mathbf{i}}^{(q)} \delta(\mathbf{r}_i - \mathbf{r}) \Re[F^{(\mathbf{N})}] \right\rangle, \quad (8.52)$$

where

$$\mathcal{D}_t^{(\mathbf{N})} = d_t + L^{(\mathbf{N})} + \mathcal{C}_i \cdot \nabla,$$

as for simple fluids, but with the appropriate meanings given to  $L^{(\mathbf{N})}$  and  $\mathcal{C}_i$  in accordance with the subscript convention. When these definitions are explicitly worked out, we obtain the constitutive equations for nonconserved variables, which explicitly contain the intramolecular and intermolecular contributions. Since the method for evaluating them is similar to that for simple fluid mixtures, which has been already explained in Chap. 7, we will not dwell on it here. Only the results will be presented in Table 8.2. The potential energy contributions, such as  $\mathbf{V}_a^{(2)}$ ,  $\mathbf{V}_a^{(3)}$ , and  $\mathbf{V}_a^{(4)}$  in the kinematic terms given

**Table 8.2.** Kinematic terms for the constitutive equations of polyatomic fluids

	$\hat{\Phi}_{qa}$	$\mathcal{Z}_{qa}$
shear stress	$-2[\mathbf{J}_a(d_t \mathbf{u} - \mathbf{F}_a)]^{(2)} - 2[\mathbf{P}_a \cdot \nabla \mathbf{u}]^{(2)} + 2 \left[ \mathbf{V}_a^{(1)} \right]^{(2)}$ $-\nabla \cdot \psi_{1a}^{(w)}$	
excess normal stress	$-\frac{2}{3}p_a \nabla \cdot \mathbf{u} - p_a d_t \ln(p_a v) - \frac{2}{3}\mathbf{J}_a \cdot (d_t \mathbf{u} - \mathbf{F}_a)$ $-\frac{2}{3}\mathbf{P}_a \cdot \nabla \mathbf{u} - \frac{2}{3}\Delta_a \nabla \cdot \mathbf{u} - \mathbf{J}_a \cdot \nabla(p_a v_a) + \frac{2}{3}\text{Tr} \mathbf{V}_a^{(1)}$ $-\nabla \cdot \frac{1}{3}\text{Tr} \psi_{1a}^{(w)}$	
heat flux	$-\mathbf{J}_a \cdot d_t \hat{h}_a - (d_t \mathbf{u} - \mathbf{F}_a) \cdot (\mathbf{P}_a - p_a \boldsymbol{\delta})$ $-\mathbf{Q}'_a \cdot \nabla \mathbf{u} - \varphi_a^{(3)} : \nabla \mathbf{u} - \mathbf{P}_a \cdot \nabla \hat{h}_a + \mathbf{V}_a^{(3)}$ $-\nabla \cdot \psi_{3a}^{(w)}$	
diffusion flux	$-p \mathbf{d}_a + \rho_a \mathcal{F}_a - (x_a - c_a) \nabla \cdot (\mathbf{P} - p \boldsymbol{\delta})$ $-\mathbf{J}_a \cdot \nabla \mathbf{u} - (\mathbf{P} - p \boldsymbol{\delta}) \cdot \nabla x_a + \nabla \cdot \mathbf{P}_k$	
angular momentum	$\mathbf{P} - \mathbf{P}^t$	

in Table 8.2 contain, in addition to the usual intermolecular force contributions, intramolecular contributions absent in their simple fluid counterparts; see Table 7.1 for the details of the kinematic terms  $\mathcal{Z}_{qa}$  for simple fluids.

When the nonequilibrium grand ensemble form is taken for  $F^{(\mathbf{N})}$  as was done for simple fluid mixtures in Chap. 7, the dissipation terms  $\Lambda_{qa}$  can be calculated by applying the cumulant expansion method previously discussed [2, 3]. If the cumulant approximation so obtained and the kinematic terms are substituted in the evolution equation (8.50), there follow the constitutive equations for nonconserved variables. The transport coefficients of polyatomic fluid mixtures then can be extracted from the constitutive equations when the latter are linearized with respect to thermodynamic gradients and nonconserved variables such as stress tensors, heat fluxes, diffusion fluxes, and so forth. This part of the theory is formally parallel to the simple fluid counterpart.

By following the same procedure as for simple fluid mixtures, we obtain the dissipation terms in the first-order cumulant approximation in the form

$$\Lambda_{qa} = (\beta g)^{-1} q(\mathbf{X}) \sum_{b=1}^r \sum_{s \geq 1} R_{ab}^{(qs)} \mathbf{X}_{sb}, \quad (8.53)$$

where

$$g = \sqrt{\frac{m_r}{2k_B T}} (nd)^{-2}$$

with  $m_r$  denoting the mean reduced mass of the molecules,  $n$  the mean number density,  $d$  the mean size parameter of the molecules, and  $\mathbf{X}_{sb}$  is the generalized potential conjugate of the nonconserved variable  $\Phi_{sb}$ . The coefficients  $R_{ab}^{(qs)}$  are tensors made up of the collision bracket integrals

$$R_{ab}^{(qs)} = \beta^2 g \left\langle \sum_{\mathbf{j}_a} h_{\mathbf{j}}^{(q)} \delta(\mathbf{r}_j - \mathbf{r}) \Re \left[ \sum_{\mathbf{k}_b} h_{\mathbf{k}}^{(s)} F_e^{(\mathbf{N})} \right] \right\rangle, \quad (8.54)$$

where  $F_e^{(\mathbf{N})}$  denotes the equilibrium grand canonical ensemble distribution function. The nonlinear factor  $q(\mathbf{X})$  is defined by

$$q(\mathbf{X}) = \frac{\sinh \kappa(\mathbf{X})}{\kappa(\mathbf{X})} \quad (8.55)$$

with  $\kappa^2(\mathbf{X})$  denoting the dissipation function

$$\kappa(\mathbf{X}) = \left[ \sum_{a=1}^r \sum_{b=1}^r \sum_{q,s \geq 1} \mathbf{X}_{qa} R_{ab}^{(qs)} \mathbf{X}_{sb} \right]^{1/2}. \quad (8.56)$$

The collision bracket integrals  $R_{ab}^{(qs)}$  are expressible in terms of irreducible isotropic tensors and contract with the tensors  $\mathbf{X}_{qa}$  and  $\mathbf{X}_{sb}$ . It is helpful

to note that, as for simple fluids,  $\kappa^2(\mathbf{X})$  is the kinetic theory version of the Rayleigh dissipation function.

The generalized potentials are possible to calculate in terms of the non-equilibrium grand partition function<sup>1</sup> and are proportional to  $\Phi_{qa}$ :

$$\mathbf{X}_{qa} = -g_a^{(q)}\Phi_{qa}, \quad (8.57)$$

where  $g_a^{(q)}$  are scalar functions of invariants of tensors  $\{\mathbf{X}_{qa}\}$ . These scalar functions are possible to calculate from the nonequilibrium grand canonical partition function of the fluid in question [4]. Near equilibrium,  $g_a^{(q)}$  for the leading  $q$  may be approximated by the formulas

$$g_a^{(1)} \simeq \frac{1}{2p_a}, \quad g_a^{(2)} \simeq \frac{3}{2p_a}, \quad g_a^{(3)} \simeq \frac{1}{Tp_a \hat{C}_{pa}}, \quad g_a^{(4)} \simeq \frac{1}{\rho_a}. \quad (8.58)$$

For linear transport coefficients these approximations (8.58) are sufficient for the generalized potentials.

In the following, we present the leading examples of evolution equations—constitutive equations—for the nonconserved variables in the first-order cumulant approximation and in the linear approximation of  $g_a^{(q)}$

$$\rho d_t \hat{\mathfrak{S}} = -\nabla \cdot \psi^{(5)} + \mathbf{P} - \mathbf{P}^t, \quad (8.59)$$

$$\begin{aligned} \rho d_t \hat{\mathbf{\Pi}}_a &= -\nabla \cdot \psi_a^{(p)} - 2[\mathbf{J}_a d_t \mathbf{u}]^{(2)} - 2[\mathbf{P}_a \cdot \nabla \mathbf{u}]^{(2)} \\ &\quad + [\mathbf{V}_a^{(1)}]^{(2)} + A_{1a}, \end{aligned} \quad (8.60)$$

$$\begin{aligned} \rho d_t \hat{\Delta}_a &= -\nabla \cdot \psi_a^{(b)} - \frac{2}{3} \mathbf{J}_a \cdot d_t \mathbf{u} - \frac{2}{3} (\mathbf{P}_a - p_a \boldsymbol{\delta}) \cdot \nabla \mathbf{u} \\ &\quad - \mathbf{J}_a \cdot \nabla (p_a v_a) - p_a d_t \ln(p_a v^{5/3}) + \frac{2}{3} \text{Tr} \mathbf{V}_a^{(1)} + A_{2a}, \end{aligned} \quad (8.61)$$

$$\begin{aligned} \rho d_t \hat{\mathbf{Q}}'_a &= -\nabla \cdot \psi_a^{(h)} - \mathbf{J}_a \cdot d_t \hat{h}_a - (d_t \mathbf{u} - \mathbf{F}_a) \cdot (\mathbf{P}_a - p_a \boldsymbol{\delta}) \\ &\quad - \mathbf{Q}'_a \cdot \nabla \mathbf{u} - \varphi_a^{(3)} : \nabla \mathbf{u} - \mathbf{P}_a \cdot \nabla \hat{h}_a + \mathbf{V}_a^{(3)} + A_{3a}, \end{aligned} \quad (8.62)$$

$$\begin{aligned} \rho d_t \hat{\mathbf{J}}_a &= \rho_a \mathcal{F}_a + p \mathbf{d}_a - \mathbf{J}_a \cdot \nabla \mathbf{u} - (x_a - c_a) \nabla \cdot (\mathbf{P} - p \boldsymbol{\delta}) \\ &\quad - (\mathbf{P} - p \boldsymbol{\delta}) \cdot \nabla x_a + A_{4a}, \end{aligned} \quad (8.63)$$

etc.

Although these constitutive equations look formally the same as those for simple fluids, it should be remembered that the tensor  $\mathbf{V}_a^{(1)}$  and the vector

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<sup>1</sup> For a method of calculating the nonequilibrium partition function of dilute monatomic gases, see [4].

$\mathbf{V}_a^{(3)}$  consist of intramolecular and intermolecular components. These components can be explicitly worked out by using the subscript convention adopted earlier in this chapter. In the constitutive equations (8.59)–(8.63), the dissipation terms may be taken with the first-order cumulant approximation given in (8.53)–(8.54).

Equations (8.59)–(8.63) together with the conservation laws—balance equations for mass, momentum, and internal energy (8.43)–(8.46)—constitute generalized hydrodynamics for polyatomic fluids. With the dissipation terms  $\Lambda_{qa}$  given by the aforementioned first-order cumulant approximation, the generalized hydrodynamic equations are consistent with the laws of thermodynamics. These dissipation terms also consist of intramolecular and intermolecular components because  $h_i^{(q)}$  is decomposable into the aforementioned components.

They can also form the basis of the theory of transport processes in polyatomic fluids, from which the linear transport coefficients can be extracted in terms of statistical mechanics formulas together with molecular theory expressions for all thermophysical properties involved. The procedure is also parallel to that used for simple fluid mixtures in Chapter 7. These topics therefore are left to the reader as exercises to work out.

For the drift velocity of species the appropriate evolution equation can be obtained if the mass fraction balance equation (8.44), the momentum balance equation (8.45), and the constitutive equation (8.63) for  $\mathbf{J}_a$  are combined. Thus we obtain from them the constitutive equation for the drift velocity  $\mathbf{u}_a$  of species  $a$ :

$$\begin{aligned} \rho_a d_t \mathbf{u}_a = & -\nabla \cdot [x_a \mathbf{P} - \rho_a (\mathbf{u}_a - \mathbf{u}) (\mathbf{u}_a - \mathbf{u})] \\ & -\rho_a (\mathbf{u}_a - \mathbf{u}) \cdot \nabla \mathbf{u}_a + \rho_a \mathbf{F}_a + \rho_a \mathcal{F}_a + \Lambda_{4a}. \end{aligned} \quad (8.64)$$

The effects on the mobility of the internal structure of a polyatomic molecule are contained in the term  $\rho_a \mathcal{F}_a$  among others; see (8.40) for the definition of  $\mathcal{F}_a$ . The first term on the right gives the effect primarily from the stress on the flow of molecules, the second the effect of diffusion, and the third the effect of the external force. The last term, of course, describes the dissipation of energy from diffusion of molecules. This constitutive equation may be applied to study the mobility of polyatomic molecules in solution.

### 8.3 Kinetic Theory of Reacting Fluids

Restricting the kinetic theory of polyatomic mixtures to nonreacting fluids has considerably simplified the theory, and we have been able to construct the basis for the theory of transport processes in polyatomic fluids, unencumbered by chemical reactions intruding into the energy and momentum transfer processes examined. Chemical reactions in liquid solutions are important in chemistry and also in many aspects of biology. Therefore it is necessary to face up to the subject of chemical reactions in liquids, which have been generally

avoided in the kinetic theory of liquids. There is only a relatively scant body of literature on the kinetic theory of chemical reactions in gases [5–9] and liquids [10], and even in the existing literature, only some special aspects [11,12] have been studied. In this work, we will try to be general, but its application will not be considered because the theory presented is rather recent and has not had a chance to see its application to chemical kinetics problems.

It is well recognized that chemical reactions cannot be discussed in terms of classical mechanics alone. Their important aspects require quantum mechanics, although some other aspects can be adequately treated by classical mechanics. Especially, collision dynamics problems associated with chemical reactions must be treated quantum mechanically. For this reason, we should begin with the density matrix formalism and formulate the theory, but the theory in the end may be taken to the classical limit, wherever permissible. When this line of approach is taken, in the end, quantum mechanics is seen only in the description of reactive collision dynamics associated with chemical reactions appearing in the collision integral operator of the kinetic equation. The rest of the kinetic theory description of usual transport processes can be made in the classical formalism if the temperature is sufficiently high to warrant using classical statistical mechanics. For this reason, we may couch the kinetic theory of interest in the language of classical mechanics except for the description of reactive collision dynamics. This will be the approach taken in this work.

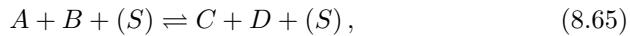
Quantum mechanics of chemical reactions is generally understood with the help of the Born–Oppenheimer approximation [13] for nuclear motions, in which nuclei or molecules move on the potential energy surface—the electronic energy eigenvalue of the Hamiltonian of the system. This approximation is reasonable because the much lighter electrons move faster than the heavy and sluggish nuclei of the atoms involved in the molecules. In a chemical reaction, the electronic energy eigenvalues are distinctive before and after chemical reactions in the diabatic representation because rearrangements of chemical bonds of constituent molecules, reactants and products, occur in chemical reactions. In other words, there are two distinctive potential energy sheets (i.e., electronic energy eigenvalues) required for the initial and final states of a chemical reaction. These distinctive potential energy surfaces cross each other if they are spatially continued as the molecules in the chemical reaction approach each other within a critical distance at which the chemical bonds either rearrange to those of the products or remain unaltered as those of the reactants. Therefore, a kinetic theory of chemical reactions must take into account the motions of molecules in the two distinctive potential energy surfaces on the timescale beyond the chemical reaction time, whereas in the duration of the chemical reaction timescale, the effects of the potential energy surface crossing must be considered somehow.

In this manner of describing reacting systems, it is necessary to distinguish petit ensembles of a grand ensemble, in each of which particles are entirely confined to a single potential sheet, so that there is no possibility of a chemical

rearrangement. The absence of chemical rearrangements implies that the associated collision processes are either elastic or inelastic. On the other hand, if there is a chemical rearrangement then a finite region of the configuration space exists in which the chemical rearrangement in a reactive collision time span occurs. This region of space is around the locus along which the potential energy sheets characterizing the reactants and products cross each other. We imagine that collision complexes or transition states of the reacting systems are formed in the localized region around the locus along which the potential energy sheets cross. In this manner, the often used notion of transition states or collision complexes in chemistry will be incorporated into the kinetic theory of reacting fluids formulated in this chapter.

## 8.4 Kinetic Equation for Reacting Fluids

We consider the same polyatomic fluid mixtures as those described in the previous section, but they are now assumed capable of chemical transformations. The chemical reaction involved is also assumed to be bimolecular for simplicity of discussion; it may be schematically expressed as



where  $A, B, C$ , and  $D$  represent species. In this reaction scheme, the solvent species may be explicitly included as a spectator species  $S$  to indicate that it can play a role in the chemical reaction, energetically and otherwise, except that it does not transform itself in reaction with the solute species undergoing the chemical reaction. The reactant mixture, including the solvent species, which may not be chemically involved in the reaction, consists of  $\mathbf{N}^{(r)} \equiv (N_a, N_b, \dots)$ , whereas the product mixture, also including the solvent species, consists of  $\mathbf{N}^{(p)} \equiv (N_c, N_d, \dots)$ .

We will use the same convention for the subscripts for sites, molecules, and species as that used for nonreacting polyatomic fluids in which intra- and intermolecular degrees of freedom are not distinguished but designated by a unified subscript subject to the subscript convention on the intramolecular and intermolecular degrees of freedom. The total interaction potential for the reactant mixture will be denoted by  $U_{\mathbf{N}^{(r)}}(\mathbf{r}^{(\mathbf{N}^{(r)})})$ , which is written as

$$U_{\mathbf{N}^{(c)}}(\mathbf{r}^{(\mathbf{N}^{(c)})}) = \frac{1}{2} \sum_{\mathbf{i}^{(c)} \neq \mathbf{j}^{(c)}} \mathcal{V}_{\mathbf{i}^{(c)}\mathbf{j}^{(c)}}(\mathbf{r}_{\mathbf{i}^{(c)}\mathbf{j}^{(c)}}) + \sum_{\mathbf{i}^{(c)}} \mathcal{V}_{\mathbf{i}^{(c)}}^{(\text{ex})}(\mathbf{r}_{\mathbf{i}^{(c)}}), \quad (8.66)$$

where we have affixed the superscript  $c = r$  or  $p$  on  $\mathbf{i}^{(c)}$  and  $\mathbf{j}^{(c)}$  to distinguish reactants and products. It should be recalled that  $\mathbf{i}^{(c)}$  is an alternative notation for  $\mathbf{i}_c$  introduced in the subscript convention we use in this chapter; see Sect. 8.2.1. The first term on the right is a shorthand notation for terms consisting of intramolecular and intermolecular interaction energies, that is,

the potential energy  $\mathcal{V}_{\mathbf{i}^{(c)}\mathbf{j}^{(c)}}$  is made up of intermolecular potential energies in addition to intramolecular potential energies  $w_{\mathbf{i}^{(c)}\mathbf{j}^{(c)'}}$ . These intramolecular potential energies represent the electronic energy eigenvalues of the system corresponding to  $c$  in the Born–Oppenheimer approximation for the motion of nuclei of atoms that are chemically bonded to form molecules. Therefore, the total potential energy written as in (8.66) closely reflects the notion that the reactant and product molecules, which are well separated beyond the reaction range after the reaction, move in different potential energy surfaces (sheets). These surfaces must cross each other as the reactant and product species come within a small volume in space, in which short-range electronic coupling interactions come into action and chemical bonds are rearranged to give a chemical reaction. For this reason, the forces responsible for chemical bond rearrangements—chemical reactions—are much shorter ranged than van der Waals dispersion forces. Therefore, as the species of reactants or products become separated from each other beyond the chemical force ranges, the fluid acts as if it is a nonreactive mixture, and the interaction potential for such a configuration of the fluid is simply the sum of the interaction potential energies of the reactants and products as given in (8.66):

$$U_{\mathbf{N}^{(r+p)}}(\mathbf{r}^{(\mathbf{N}^{(r+p)})}) = \frac{1}{2} \sum_{c \in r, p} \sum_{\mathbf{i}^{(c)} \neq \mathbf{j}^{(c)}} \mathcal{V}_{\mathbf{i}^{(c)}\mathbf{j}^{(c)}}(\mathbf{r}_{\mathbf{i}^{(c)}\mathbf{j}^{(c)}}) + \sum_{c \in r, p} \sum_{\mathbf{i}^{(c)}} \mathcal{V}_{\mathbf{i}^{(c)}}^{(\text{ex})}(\mathbf{r}_{\mathbf{i}^{(c)}}). \quad (8.67)$$

The first term on the right is again the short-hand notation for interaction energy consisting of intramolecular interaction potential energies and longer range intermolecular interaction energies that are not responsible for chemical bonding. We assume that the nonreactive collision processes in the fluid are described by the potential energy model given in Eq. (8.67). This potential energy does not include the potentials of bond-switching chemical forces.

The representation of the potential energy of the system, as in Eq. (8.66), implies that the Liouville operators must also be defined with different potential energy surfaces. We generalize the definition given for the Liouville operator in (8.14) and (8.15) with accompanying definitions of component Liouville operators. Thus we write the Liouville operators in the form,

$$L^{(\mathbf{N}^{(c)})} = \sum_{\mathbf{j}^{(c)}=\mathbf{1}}^{\mathbf{N}^{(c)}} L_{\mathbf{j}^{(c)}}^{(0)} + \frac{1}{2} \sum_{\mathbf{j}^{(c)} \neq \mathbf{k}^{(c)}=\mathbf{1}}^{\mathbf{N}^{(c)}} L_{\mathbf{j}^{(c)}\mathbf{k}^{(c)}}^{(v)} + \sum_{\mathbf{j}^{(c)}=\mathbf{1}}^{\mathbf{N}^{(c)}} L_{\mathbf{j}^{(c)}}^{(\text{ex})} \quad (8.68)$$

in which the superscript  $c$  has the same meaning as in (8.66),  $c = r$  or  $p$ . The subscript convention used for the potential energies also applies to this Liouville operator. Therefore the second term consists of intramolecular and intermolecular interaction Liouville operators. The first term on the right is made up of free Liouville operators of noninteracting particles.

The grand ensemble is constructed for each of the reactant and product mixtures, and the reduced distribution function  $F^{(\mathbf{N}^{(c)})}(x^{(\mathbf{N}^{(c)})}, t)$  of the

grand ensemble is assumed to obey the kinetic equation,

$$\left( \frac{\partial}{\partial t} + L^{(\mathbf{N}^{(r)})} \right) F^{(\mathbf{N}^{(r)})}(x^{(\mathbf{N}^{(r)})}, t) = \mathfrak{R}_{r+p} \left[ F^{(\mathbf{N}^{(r+p)})} \right] + \mathfrak{R}_{rp} \left[ F^{(\mathbf{N}^{(r)})} \right], \quad (8.69)$$

$$\left( \frac{\partial}{\partial t} + L^{(\mathbf{N}^{(p)})} \right) F^{(\mathbf{N}^{(p)})}(x^{(\mathbf{N}^{(p)})}, t) = \mathfrak{R}_{r+p} \left[ F^{(\mathbf{N}^{(r+p)})} \right] + \mathfrak{R}_{pr} \left[ F^{(\mathbf{N}^{(p)})} \right]. \quad (8.70)$$

The nonreactive ( $\mathfrak{R}_{r+p}$ ) and reactive ( $\mathfrak{R}_{rp}$ ,  $\mathfrak{R}_{pr}$ ) collision operators in these equations are defined by the collision integrals,

$$\mathfrak{R}_{r+p} \left[ F^{(\mathbf{N})} \right] = \frac{\mathcal{N}!}{(\mathcal{N}-N)!} \int dx^{(\mathcal{N}-N)} (-i) T_{r+p}^{(\mathcal{N})} F^{(\mathcal{N})}(x^{(\mathcal{N})}; t), \quad (8.71)$$

$$\begin{aligned} \mathfrak{R}_{rp} \left[ F^{(\mathbf{N}^{(r)})} \right] &= \frac{\mathcal{N}^{(r)}!}{(\mathcal{N}^{(r)}-N^{(r)})!} \\ &\times \int dx^{(\mathcal{N}^{(r)}-\mathbf{N}^{(r)})} (-i) T_{rp}^{(\mathcal{N}^{(r)})} F^{(\mathcal{N}^{(r)})}(x^{(\mathcal{N}^{(r)})}; t), \end{aligned} \quad (8.72)$$

$$\begin{aligned} \mathfrak{R}_{pr} \left[ F^{(\mathbf{N}^{(p)})} \right] &= \frac{\mathcal{N}^{(p)}!}{(\mathcal{N}^{(p)}-N^{(p)})!} \\ &\times \int dx^{(\mathcal{N}^{(p)}-\mathbf{N}^{(p)})} (-i) T_{pr}^{(\mathcal{N}^{(p)})} F^{(\mathcal{N}^{(p)})}(x^{(\mathcal{N}^{(p)})}; t), \end{aligned} \quad (8.73)$$

where

$$F^{(\mathcal{N})} = \prod_{\{\mathbf{N}\}} F^{(\mathbf{N})}, \quad F^{(\mathcal{N}^{(c)})} = \prod_{\{\mathbf{N}^{(c)}\}} F^{(\mathbf{N}^{(c)})} \quad (c = r, p), \quad (8.74)$$

and  $\mathcal{N} = \mathcal{N}^{(r)} + \mathcal{N}^{(p)}$ ,  $N = N^{(r)} + N^{(p)}$  with  $N^{(c)} = \sum_{a \in c} N_a$ . The product sign runs over all petit ensembles of the grand ensemble of interest.

The collision operator  $T_{r+p}^{(\mathcal{N})}$  is defined in the potential energy surface  $U_{\mathbf{N}^{(r+p)}}(\mathbf{r}^{(\mathbf{N})})$ , which characterizes the reactants and the products through nonreactive interaction forces, whereas the collision operators  $T_{rp}^{(\mathcal{N}^{(r)})}$  and  $T_{pr}^{(\mathcal{N}^{(p)})}$  represent the reaction part of the many-particle collision operator, which transfer the reactant species from the reactant potential energy surface to the product potential energy surface, and vice versa. Because chemical transformations are caused by short-range chemical forces from electronic interactions (overlaps) at short distances of the order of a few atomic radii at most,  $T_{r+p}^{(\mathcal{N})}$  describes elastic and inelastic collision processes, whereas  $T_{rp}^{(\mathcal{N}^{(r)})}$  and  $T_{pr}^{(\mathcal{N}^{(p)})}$  describe reactive collision processes, which we will assume are achieved through the formation of collision complexes—transition

states. We impose the conditions on these collision operators: that they are such that Conditions (7.C1)–(7.C3) are satisfied so as to ensure consistency with the laws of thermodynamics. It is worth reiterating the following point regarding the kinetic equations: The essential chemical and physical reason underlying the kinetic equations (8.69) and (8.70) is that there is a separation of spatial scales in the course of chemical reactions; that of the longer scale is nonreactive and that of the shorter scale is reactive. Such a separation of spatial scales gives two separate collisional contributions on the right-hand sides of the kinetic equations.

Chemical reactions occur locally as reactant or product molecules come within a characteristic distance of the order of chemical bond lengths and on a timescale faster than hydrodynamic relaxation times. Therefore hydrodynamic processes in reacting mixtures may be studied as if they occur in an inert nonreacting mixture. This suggests that we may employ the kinetic equation (8.18) with (8.19) for the collision operator, provided that  $\mathbf{N}$  and the Liouville operator  $L^{(\mathbf{N})}$  are for the mixture consisting of the reactants and products. The role of the kinetic equations (8.69) and (8.70) is then in describing the density evolution of species that arise from the chemical reaction in an adiabatic condition in which hydrodynamic variables remain fixed on the timescale of the chemical reaction of interest. For this reason, by using the kinetic equations (8.69) and (8.70), we will examine only chemical reaction kinetics.

## 8.5 Collision Operators

### 8.5.1 Nonreactive Collision Operator

The nonreactive collision operator  $\mathfrak{R}_{r+p}$  is similar to the collision operator for nonreactive polyatomic mixtures considered earlier; see (8.20) with collision processes described by the potential energy of interaction given by (8.67). Since the collision operator  $\mathfrak{R}_{r+p}$ , therefore, has the same properties as that given in terms of  $W(x^{(\mathcal{N})}|x^{(\mathcal{N})*})$  in (8.20), there is no need to repeat the list here.

### 8.5.2 Reactive Collision Operators

The reactive collision operators  $\mathfrak{R}_{rp}$  and  $\mathfrak{R}_{pr}$  may be modeled in forms similar to nonreactive collision operators, except that the pre- and postreaction configurations should be distinguished. Thus, we take  $\mathfrak{R}_{rp}$  in the form

$$\begin{aligned}\mathfrak{R}_{rp} \left[ F^{(\mathbf{N}^{(r)})} \right] &= \frac{\mathcal{N}^{(r)}!}{(\mathcal{N}^{(r)} - N^{(r)})!} \int dx^{(\mathcal{N}^{(r)} - N^{(r)})} \\ &\times \left[ W_{rp} \left( x^{(\mathcal{N}^{(r)})*} | x^{(\mathcal{N}^{(p)})} \right) F^{(\mathcal{N}^{(p)})*}(x^{(\mathcal{N}^{(p)})*}; t) \right. \\ &\quad \left. - W_{rp} \left( x^{(\mathcal{N}^{(r)})} | x^{(\mathcal{N}^{(p)})*} \right) F^{(\mathcal{N}^{(r)})}(x^{(\mathcal{N}^{(r)})}; t) \right],\end{aligned}\quad (8.75)$$

where the transition probability  $W_{rp} \left( x^{(\mathcal{N}^{(r)})} | x^{(\mathcal{N}^{(p)})*} \right)$  has the symmetry property

$$\int dx^{(\mathcal{N}^{(p)})*} W_{rp} \left( x^{(\mathcal{N}^{(r)})} | x^{(\mathcal{N}^{(p)})*} \right) = \int dx^{(\mathcal{N}^{(p)})*} W_{pr} \left( x^{(\mathcal{N}^{(p)})*} | x^{(\mathcal{N}^{(r)})} \right). \quad (8.76)$$

A more concrete model for the transition probability  $W_{rp} \left( x^{(\mathcal{N}^{(r)})} | x^{(\mathcal{N}^{(p)})*} \right)$  will be given later. For the moment, this property is sufficient for developing a formal theory by using (8.75). Similarly,

$$\begin{aligned} \mathfrak{R}_{pr} \left[ F^{(\mathcal{N}^{(p)})} \right] &= \frac{\mathcal{N}^{(p)}!}{(\mathcal{N}^{(p)} - N^{(p)})!} \int dx^{(\mathcal{N}^{(p)} - N^{(p)})} \\ &\times \left[ W_{pr} \left( x^{(\mathcal{N}^{(p)})*} | x^{(\mathcal{N}^{(r)})} \right) F^{(\mathcal{N}^{(r)})*} (x^{(\mathcal{N}^{(r)})*}; t) \right. \\ &\left. - W_{pr} \left( x^{(\mathcal{N}^{(p)})} | x^{(\mathcal{N}^{(r)})*} \right) F^{(\mathcal{N}^{(p)})} (x^{(\mathcal{N}^{(p)})}; t) \right]. \end{aligned} \quad (8.77)$$

The transition probability  $W_{pr} \left( x^{(\mathcal{N}^{(p)})} | x^{(\mathcal{N}^{(r)})*} \right)$  has the same symmetry property as  $W_{rp} \left( x^{(\mathcal{N}^{(r)})} | x^{(\mathcal{N}^{(p)})*} \right)$ ;

$$\int dx^{(\mathcal{N}^{(r)})*} W_{pr} \left( x^{(\mathcal{N}^{(p)})} | x^{(\mathcal{N}^{(r)})*} \right) = \int dx^{(\mathcal{N}^{(r)})*} W_{pr} \left( x^{(\mathcal{N}^{(r)})*} | x^{(\mathcal{N}^{(p)})} \right).$$

Because

$$dx^{(\mathcal{N}^{(p)})} = dx^{(\mathcal{N}^{(p)})*} = dx^{(\mathcal{N}^{(r)})*} = dx^{(\mathcal{N}^{(r)})},$$

we find

$$\int dx^{(\mathcal{N}^{(r)})} W_{rp} \left( x^{(\mathcal{N}^{(r)})} | x^{(\mathcal{N}^{(p)})*} \right) = \int dx^{(\mathcal{N}^{(p)})} W_{pr} \left( x^{(\mathcal{N}^{(p)})} | x^{(\mathcal{N}^{(r)})*} \right). \quad (8.78)$$

These properties are useful for establishing the symmetry properties of the reaction rate equations in the following and also for proving the H theorem with the kinetic equation.

## 8.6 Density Evolution Equations and Chemical Kinetics

The kinetic equations (8.69) and (8.70) may be used to derive evolution equations for macroscopic variables describing transport processes in reacting fluids. Because we will pay attention only to chemical kinetics, but not transport processes in general in the reacting fluid, we will consider only reaction rate equations and associated mass flux evolution equations in the following. This is possible if it is assumed that there is no flow of matter and the temperature is uniform in space, so that stress tensors and heat flux are absent. Consequently, the diffusion fluxes are the only nonconserved variables relevant to the discussion.

### 8.6.1 Reaction Rate Equations

On multiplying

$$\sum_{\mathbf{i}^{(a)}} m_{a\mathbf{i}^{(a)}} \delta(\mathbf{r}_{a\mathbf{i}^{(a)}} - \mathbf{r}) \quad (8.79)$$

from the left to the kinetic equation (8.69) and integrating over the phase  $x^{(\mathbf{N}^{(r)})}$ , there follows the evolution equation for the mass density  $\rho_a$  for  $a \in r$ , where  $r$  denotes the totality of reactant species:

$$\rho \frac{dc_a}{dt} = -\nabla \cdot \mathbf{J}_a + A_a^{(\text{ch})}. \quad (8.80)$$

The symbol  $\mathbf{i}^{(a)}$  abbreviates the composite indexes  $(i, \nu)$  ( $1 \leq i \leq N_a, 1 \leq \nu \leq l_a$ ) for species  $a$ , and  $A_a^{(\text{ch})}$  denotes the change in mass fraction  $c_a$  from the chemical reaction; it is defined by

$$A_a^{(\text{ch})} = \left\langle \sum_{\mathbf{i}^{(a)}} m_{a\mathbf{i}^{(a)}} \delta(\mathbf{r}_{a\mathbf{i}^{(a)}} - \mathbf{r}) \mathfrak{R}_{rp} [F^{(\mathbf{N}^{(r)})}] \right\rangle \quad (8.81)$$

for reactant species  $a$  and similarly for reactant species  $b$ . For the product species  $d \in p$ , where  $p$  denotes the totality of product species, equations for  $c_d$  similar to (8.80) can be derived from the kinetic equation (8.70):

$$\rho \frac{dc_d}{dt} = -\nabla \cdot \mathbf{J}_d + A_d^{(\text{ch})}, \quad (8.82)$$

where

$$A_d^{(\text{ch})} = \left\langle \sum_{\mathbf{i}^{(d)}} m_{d\mathbf{i}^{(d)}} \delta(\mathbf{r}_{d\mathbf{i}^{(d)}} - \mathbf{r}) \mathfrak{R}_{pr} [F^{(\mathbf{N}^{(p)})}] \right\rangle. \quad (8.83)$$

The meaning of the symbol  $\mathbf{i}^{(d)}$  is similar to that of  $\mathbf{i}^{(a)}$ , and  $p$  denotes product species  $C$  and  $D$ . The nonreactive collision operator  $\mathfrak{R}_{r+p} [F^{(\mathbf{N}^{(r+p)})}]$  does not give a dissipation term in the mass fraction balance equations because mass is conserved in nonreactive collisions. However, reactive collision processes give nonvanishing dissipation terms  $A_a^{(\text{ch})}$  and  $A_d^{(\text{ch})}$ , which are intimately related to the rate coefficients, as will be shown. Equations (8.80) and (8.82) indicate that the change in mass fraction consists of two distinctive parts; one from mass transport and the other from the chemical reaction. Therefore, chemical kinetics is described by rate equations, which may be written as

$$\rho \frac{d_c c_a}{dt} = A_a^{(\text{ch})}, \quad (8.84)$$

$$\rho \frac{d_c c_d}{dt} = A_d^{(\text{ch})}, \quad (8.85)$$

where the time derivative  $d_c/dt$  stands for the reactive part of the mass change involved. Under the condition that diffusion is divergenceless, that is,

$$\nabla \cdot \mathbf{J}_a = 0, \quad \nabla \cdot \mathbf{J}_d = 0 \quad (8.86)$$

for  $a \in r$  and  $d \in p$ , the time derivatives in the rate equations become the ordinary time derivative in the coordinate system moving at the fluid velocity  $\mathbf{u}$ . In this connection, it should be recalled that flow is absent in the fluid if the mean velocity of the fluid is equal to zero. From the standpoint of the kinetic theory, the conventional rate equations in chemical kinetics then should be understood in the sense of condition (8.86), and the following discussion will be given without further reference to condition (8.86), although the ordinary time derivative  $d/dt$  is employed in the rate equations.

### 8.6.2 Evolution Equations for Diffusion Fluxes

Because diffusion fluxes occur in the mass fraction balance equations, it is necessary to examine the evolution equations for the diffusion fluxes, the constitutive equations for  $\mathbf{J}_a$  and so on. It is straightforward to derive them from the kinetic equations:

$$\rho \frac{d\hat{\mathbf{J}}_a}{dt} = -\nabla \cdot \mathbf{P}_a + c_a \nabla \cdot \mathbf{P} - \mathbf{J}_a \cdot \nabla \mathbf{u} + \rho_a \mathcal{F}_a + \Lambda_{4a} + \Lambda_{4a}^{(ch)}, \quad (8.87)$$

$$\rho \frac{d\hat{\mathbf{J}}_d}{dt} = -\nabla \cdot \mathbf{P}_d + c_d \nabla \cdot \mathbf{P} - \mathbf{J}_d \cdot \nabla \mathbf{u} + \rho_d \mathcal{F}_d + \Lambda_{4d} + \Lambda_{4d}^{(ch)}, \quad (8.88)$$

where  $\Lambda_{4a}$  and  $\Lambda_{4d}$  are dissipation terms arising from nonreactive collision operator  $\mathfrak{R}_{r+p} [F^{(\mathbf{N}^{(r+p)})}]$  and the additional dissipation terms  $\Lambda_{4a}^{(ch)}$  and  $\Lambda_{4d}^{(ch)}$  are the contributions from the reactive collision operators. They are defined by

$$\Lambda_{4a}^{(ch)} = \left\langle \sum_{\mathbf{i}^{(a)}} m_{a\mathbf{i}^{(a)}} \mathcal{C}_{a\mathbf{i}^{(a)}} \delta(\mathbf{r}_{a\mathbf{i}^{(a)}} - \mathbf{r}) \mathfrak{R}_{rp} [F^{(\mathbf{N}^{(r)})}] \right\rangle, \quad (8.89)$$

$$\Lambda_{4d}^{(ch)} = \left\langle \sum_{\mathbf{i}^{(d)}} m_{d\mathbf{i}^{(d)}} \mathcal{C}_{d\mathbf{i}^{(d)}} \delta(\mathbf{r}_{d\mathbf{i}^{(d)}} - \mathbf{r}) \mathfrak{R}_{pr} [F^{(\mathbf{N}^{(p)})}] \right\rangle, \quad (8.90)$$

for  $a \in r$  and  $d \in p$ . The nonreactive dissipation terms  $\Lambda_{4a}$  and  $\Lambda_{4d}$  are defined by the same form as for the dissipation term for nonreactive fluids considered earlier. To discuss the effects on chemical kinetics of mass transport, it is sufficient to consider either one of (8.87) and (8.88). Especially, for near-equilibrium effects it is sufficient to consider the forms linearized with regard to transport processes, so that we may take the equations

$$\rho \frac{d\hat{\mathbf{J}}_a}{dt} = -\frac{p}{\rho_a} \mathbf{d}_a + \Lambda_{4a} + \Lambda_{4a}^{(ch)}, \quad (8.91)$$

$$\rho \frac{d\hat{\mathbf{J}}_d}{dt} = -\frac{p}{\rho_d} \mathbf{d}_d + \Lambda_{4d} + \Lambda_{4d}^{(ch)}, \quad (8.92)$$

where  $\mathbf{d}_j$  ( $j = a$  or  $d$ ) is the thermodynamic force for diffusion

$$\mathbf{d}_j = \nabla \left( \frac{n_j}{n} \right) + \left( \frac{n_j}{n} - \frac{\rho_j}{\rho} \right) \nabla \ln p + \frac{\rho_j}{p} (\mathbf{F} - \mathbf{F}_j). \quad (8.93)$$

In the absence of external forces and a pressure gradient this thermodynamic force  $\mathbf{d}_j$  simply reduces to a concentration gradient or, more precisely, a mole fraction gradient. A particular case of constitutive equations for diffusion fluxes will be considered later.

### 8.6.3 Pair Density Evolution Equations

To discuss chemical kinetics in solution it is particularly necessary to consider pair density evolution equations because pair densities would give measures of lifetimes of transient binary species formed during reactions. Note that these binary species are not necessarily stable chemical species, but chemically nonbonded clusters. The pair density is defined by the statistical formula

$$\rho_{ab}(\mathbf{r}, t) = \left\langle \sum_{\mathbf{i}^{(a)}} \sum_{\mathbf{j}^{(b)}} \frac{m_{a\mathbf{i}^{(a)}} m_{b\mathbf{j}^{(b)}}}{M} \delta(\mathbf{r}_{a\mathbf{i}^{(a)}} - \mathbf{r}) \delta(\mathbf{r}_{b\mathbf{j}^{(b)}} - \mathbf{r}) F^{(\mathbf{N}^{(a+b)})} \right\rangle, \quad (8.94)$$

where  $M = m_a + m_b \equiv m_{a\mathbf{i}^{(a)}} + m_{b\mathbf{j}^{(b)}}$ . According to this definition, the ratio  $[\rho_{ab}(\mathbf{r}, t) / \rho] d\mathbf{r}$  is the probability of finding a pair  $ab$  at  $\mathbf{r}$  in the interval  $\mathbf{r} \sim \mathbf{r} + d\mathbf{r}$  at  $t$ .

The evolution equation for  $\rho_{ab}(\mathbf{r}, t)$  then can be derived by multiplying the kinetic equation (8.69) by the molecular expression for the pair density

$$\sum_{\mathbf{i}^{(a)}} \sum_{\mathbf{j}^{(b)}} \frac{m_{a\mathbf{i}^{(a)}} m_{b\mathbf{j}^{(b)}}}{M} \delta(\mathbf{r}_{a\mathbf{i}^{(a)}} - \mathbf{r}) \delta(\mathbf{r}_{b\mathbf{j}^{(b)}} - \mathbf{r})$$

and following the same procedure as for the evolution equation for diffusion flux  $\mathbf{J}_a$ . Thus, we obtain the equation

$$\frac{dc_{ab}}{dt} = -\nabla \cdot \mathbf{J}_{ab} + \dots + A_{ab}^{(\text{pair})} + A_{ab}^{(\text{tran})}, \quad (8.95)$$

where

$$\mathbf{J}_{ab} = \left\langle \sum_{\mathbf{i}^{(a)}} \sum_{\mathbf{j}^{(b)}} \mu_{ab} \mathcal{C}_{ab} \delta(\mathbf{r}_{a\mathbf{i}^{(a)}} - \mathbf{r}) \delta(\mathbf{r}_{b\mathbf{j}^{(b)}} - \mathbf{r}) F^{(\mathbf{N}^{(a+b)})} \right\rangle, \quad (8.96)$$

$$A_{ab}^{(\text{pair})} = \left\langle \sum_{\mathbf{i}^{(a)}, \mathbf{j}^{(b)}} \mu_{ab} \delta(\mathbf{r}_{a\mathbf{i}^{(a)}} - \mathbf{r}) \delta(\mathbf{r}_{b\mathbf{j}^{(b)}} - \mathbf{r}) \mathfrak{R}_{r+p} [F^{(\mathbf{N}^{(r+p)})}] \right\rangle, \quad (8.97)$$

$$A_{ab}^{(\text{tran})} = \left\langle \sum_{\mathbf{i}^{(a)}, \mathbf{j}^{(b)}} \mu_{ab} \delta(\mathbf{r}_{a\mathbf{i}^{(a)}} - \mathbf{r}) \delta(\mathbf{r}_{b\mathbf{j}^{(b)}} - \mathbf{r}) \mathfrak{R}_{rp} [F^{(\mathbf{N}^{(r)})}] \right\rangle \quad (8.98)$$

with  $\mu_{i^{(a)}j^{(b)}}$  denoting the reduced mass of pair  $ab$

$$\mu_{ab} = \frac{m_{ai^{(a)}} m_{bj^{(b)}}}{M}$$

and  $\mathcal{C}_{ab}$  the peculiar velocity of the pair  $(a, b)$

$$\mathcal{C}_{ab} = \mathbf{v}_{ai^{(a)}} + \mathbf{v}_{bj^{(b)}} - \mathbf{u}.$$

These evolution equations become useful at the order of description of chemical reactions in which the effects of pair correlation should be taken into account. The dots  $\dots$  in (8.95) represent the terms involving nonconserved variables, gradients of velocity, and so on, which appear in the full equation but may be neglected if the transport of momentum and energy is ignored when the evolution equations are linearized with respect to fluxes and thermodynamic forces.

Now if we use the forms for the collision operators presented in (8.75) and (8.77), the statistical mechanical formulas for the reaction rate coefficients can be readily identified in comparison with the phenomenological rate equations,

$$-\frac{d_c c_a}{dt} = k_{\text{for}} c_a c_b - k_{\text{rev}} c_c c_d. \quad (8.99)$$

Upon comparison of the statistical mechanical rate equations with the phenomenological rate equations, the statistical mechanical expressions for the rate coefficients can be identified as follows:

$$k_{\text{for}} = \frac{1}{\rho c_a c_b} \left\langle \sum_{i^{(a)}} m_{ai^{(a)}} \delta(\mathbf{r}_{ai^{(a)}} - \mathbf{r}) W_{rp} \left( x^{(\mathcal{N}^{(r)})} | x^{(\mathcal{N}^{(p)})*} \right) F^{(\mathcal{N}^{(r)})} \right\rangle, \quad (8.100)$$

$$k_{\text{rev}} = \frac{1}{\rho c_c c_d} \left\langle \sum_{i^{(d)}} m_{di^{(d)}} \delta(\mathbf{r}_{di^{(d)}} - \mathbf{r}) W_{pr} \left( x^{(\mathcal{N}^{(p)})} | x^{(\mathcal{N}^{(r)})*} \right) F^{(\mathcal{N}^{(p)})} \right\rangle. \quad (8.101)$$

In these expressions the angular brackets stand for integration in the phase of  $\mathcal{N}^{(r)}$  particles for  $k_{\text{for}}$  or  $\mathcal{N}^{(p)}$  particles for  $k_{\text{rev}}$ . To obtain the second term in the rate equation (8.99) we have used the symmetry property of the transition probability of the reaction. A similar rate equation can be derived for the product species from the kinetic equation, but it contains the same information as (8.99). Therefore there is no need for the equation here.

#### 8.6.4 Rate Coefficients for Diffusion-Limited Reactions

Based on the idea of Smoluchowski [14], who developed the theory of colloid coagulation kinetics as a diffusion-limited process, the effects of diffusion on chemical reaction rates have been studied by a number of

authors [15–21] in the field of chemical kinetics in solution. In this class of theories, reactants are assumed to have reacted as they come within a critical distance from each other. Therefore, Fick's law of diffusion plays an important role in the calculation of observed reaction rates for chemical reactions in solution. We would like to examine to what extent and under what conditions the present kinetic theory of reacting mixtures can recover the theory of diffusion-limited chemical reaction rates in the literature. For the discussion, we will use the bimolecular chemical reaction (8.65) as an example.

Consider a chemical reaction proceeding predominantly in the forward direction. Then, by adopting the same assumption as that made on the relative magnitude of the forward and reverse rate coefficients in the theory of chemical kinetics in the literature [19, 21], we neglect the contribution of the reverse reaction. The rate equation is then given by

$$-\frac{dc_a}{dt} = k_{\text{for}} c_a c_b. \quad (8.102)$$

Now we examine the effect of diffusion on the forward reaction rate constant. To this end, we return to the constitutive equation for diffusion fluxes and investigate the conditions under which the conventionally used rate coefficient can arise.

We assume that the fluid is not too displaced from equilibrium with regard to diffusion and also assume that the pressure and temperature are uniform in the fluid and external forces are absent. If the diffusion is steady in the coordinate system moving at the fluid velocity or if the fluid is stagnant, then the substantial time derivative term in (8.102) may be replaced with the total time derivative. Furthermore, if the chemical reaction is faster than diffusion and other transport processes, then on the timescale of diffusion and other hydrodynamic processes the chemical reaction should have been completed. This implies that, upon taking into account the fact that there is only one independent diffusion flux and also only one independent thermodynamic force for a binary mixture, the steady-state constitutive equation, Fick's law of diffusion, can be derived from (8.91). It is given by the equation

$$\mathbf{J}_b = -\rho_b D_{ba} \mathbf{d}_a = \rho_b D_{ba} \mathbf{d}_b. \quad (8.103)$$

Note that  $\mathbf{d}_a + \mathbf{d}_b = 0$ .

Because the reaction is faster than diffusion, the particle arriving at the critical sphere of radius  $r_m$  may have already reacted with  $A$  or certainly will have reacted while diffusing toward  $A$  within the critical sphere. If the reaction cross section is denoted by  $\sigma_{AB}$ , then the critical distance  $r_m$  is estimated by  $r_m = \sqrt{\sigma_{AB}/\pi}$ . The flux of species  $b$  crossing the surface of the critical sphere may be equated to the reaction rate. Thus, we obtain

$$-4\pi r_m^2 \mathbf{J}_b / \rho_b = k_{\text{for}} \frac{n_b}{n}. \quad (8.104)$$

Eliminating  $\mathbf{J}_b$  from (8.104) with the help of (8.103) and integrating the resulting equation from  $r = 0$  to  $r = r_m$ , we obtain

$$\frac{n_b}{n} = \left( \frac{n_b}{n} \right)_{r=r_m} - \frac{k_{\text{for}}}{4\pi r_m D_{ba}} \left( \frac{n_b}{n} \right). \quad (8.105)$$

Because the relation  $n_b/n = c_b \rho / m_b n$  holds, upon rearranging (8.105) we obtain

$$c_b = \frac{c_b(r_m)}{1 + k_{\text{for}}/4\pi r_m D_{ba}}. \quad (8.106)$$

Substituting this result in (8.102), we find the phenomenologically observed rate constant

$$k_{\text{obs}} = \frac{4\sqrt{\pi\sigma_{AB}}D_{ba}}{k_{\text{for}} + 4\sqrt{\pi\sigma_{AB}}D_{ba}} k_{\text{for}}. \quad (8.107)$$

Except for the meaning of  $r_m$  given in terms of the reaction cross section, this formula is identical to the result of the theory of diffusion-limited rate coefficients in the literature, which is in the class of the Smoluchowski theory of colloid coagulation. Apart from various assumptions made in connection with the constitutive equations for diffusion, the assumption (8.104) is the key to the rate coefficient formula.

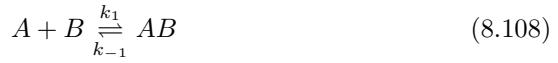
Therefore, it is clear that the present kinetic theory includes of the conventional theory of reaction rates of Noyes [19], if the assumption (8.104) is added. Note that all quantities in the present theory are calculable by the kinetic equations presented earlier and statistical mechanics attendant thereon. Therefore, we now have a kinetic theory of rate coefficient  $k_{\text{obs}}$  for diffusion-limited chemical reactions. It requires calculating the formula (8.100) for  $k_{\text{for}}$  in addition to  $D_{ba}$ , which can be computed by the modified free volume theory of diffusion described in Chap. 11.

### 8.6.5 Transition State Theory

In the Smoluchowski model [14] for chemical reactions, namely the theory of diffusion-limited rate coefficients, there is no notion of transition states or collision complexes. However, in chemical kinetics the notion of transition states [22] has a long history. Moreover, it has been widely taken advantage of in solution chemical kinetics [23] although what is meant exactly by transition states has not always been clear. It seems that the nebulous nature of the notion itself allows one the liberty of an ill-defined proposition for a transition state. We now examine how the notion of transition states (e.g., collision complexes) may be exploited in the present kinetic theory of reacting fluids and attempt to quantify the notion from the viewpoint of quantum mechanics. More specifically, we will investigate a way to characterize the transition states quantum mechanically in terms of collision complexes that form in a chemical reaction.

If the chemical reaction proceeds through a collision complex, then the rate equations should include those related to the formation and decomposition of

the collision complex into products and reactants. The reactions involving such collision complexes may then be written as



Here  $AB$  and  $AB^*$  are transition states or collision complexes in different states that are interconverted over a time span owing to the internal dynamics among the particles involved, perhaps, including the solvent molecules. In these reaction schemes the solvent may be included to make its role more explicit, because in solution kinetics and, in particular, in the formation and decomposition of collision complexes in solution the role of solvent molecules should be important and, at least, relevant to kinematic conditions such as energy conservation. According to this model, the corresponding macroscopic rate equations are

$$-\frac{dc_a}{dt} = k_1 c_a c_b - k_{-1} c_{ab}, \quad (8.111)$$

$$\frac{dc_{ab}}{dt} = k_1 c_a c_b - (k_{-1} + k_2) c_{ab} + k_{-2} c_{ab^*}, \quad (8.112)$$

$$\frac{dc_{ab^*}}{dt} = k_2 c_{ab} - (k_{-2} + k_3) c_{ab^*} - k_{-3} c_c c_d. \quad (8.113)$$

As is often done in chemical kinetics, we assume that  $k_{-3} = 0$ ; in other words, the collision complexes break up into the products in an overwhelmingly high probability. Then at the steady state of the collision complex population there hold the equations

$$k_1 c_a c_b - (k_{-1} + k_2) c_{ab} + k_{-2} c_{ab^*} = 0,$$

$$k_2 c_{ab} - (k_{-2} + k_3) c_{ab^*} = 0.$$

Eliminating  $c_{ab^*}$  from these equations, we obtain

$$k_1 c_a c_b = \left[ (k_{-1} + k_2) - \frac{k_2 k_{-2}}{(k_{-2} + k_3)} \right] c_{ab},$$

which may be rearranged to

$$c_{ab} = \frac{k_1 (k_{-2} + k_3)}{(k_{-1} + k_2) (k_{-2} + k_3) - k_2 k_{-2}} c_a c_b. \quad (8.114)$$

Substituting in (8.111), we obtain

$$-\frac{dc_a}{dt} = \frac{k_1}{1 + (k_{-1}/k_2)(1 + k_{-2}/k_3)} c_a c_b. \quad (8.115)$$

This may be equated to the overall reaction rate of formation of the product

$$\frac{dc_p}{dt} = k_{\text{obs}} c_a c_b \quad (p = c, d). \quad (8.116)$$

Thus we obtain the phenomenologically observed rate coefficient

$$k_{\text{obs}} = \frac{k_1}{1 + (k_{-1}/k_2)(1 + k_{-2}/k_3)}. \quad (8.117)$$

The rate coefficients  $k_{-1}$ ,  $k_2$ ,  $k_{-2}$ , and  $k_3$  are closely associated with the correlated pair ( $ab$ ) and its concentration  $c_{ab}$ , which obeys (8.95). The present kinetic theory makes it possible to study the evolution of  $c_{ab}$  and calculate the attendant rate constants. In chemical kinetics, such a study is often made unnecessary by phenomenologically motivated assumptions or approximations. We will use such approximations. Since if the overall reaction is predominantly in the forward direction then it implies that

$$k_{-1}/k_2 \ll 1, \quad k_{-2}/k_3 \ll 1,$$

$k_{\text{obs}}$  in (8.117) can be approximated by

$$k_{\text{obs}} \simeq k_1. \quad (8.118)$$

This means that the observed bimolecular reaction rate is approximately equal to  $k_1$ , which is given by the kinetic theory formula

$$k_1 = \frac{1}{\rho c_a c_b} \left\langle \sum_{\mathbf{i}^{(a)}} m_{a\mathbf{i}^{(a)}} \delta(\mathbf{r}_{a\mathbf{i}^{(a)}} - \mathbf{r}) W_{rp} \left( x^{(\mathcal{N}^{(r)})} | x^{(\mathcal{N}^{(p)})*} \right) F^{(\mathcal{N}^{(r)})} \right\rangle. \quad (8.119)$$

It is interesting that, regardless of whether or not the existence of collision complexes is assumed, the approximate statistical mechanical expression for the observed rate coefficient remains formally the same as the forward reaction rate  $k_{\text{for}}$  defined earlier without a model, if the aforementioned approximations are made for the rate coefficients related to the collision complexes. However, note that the quantum mechanical method of evaluating the reactive collision cross-sections should be different from the case in which collision complexes play no role at all, because in the model based on the formation of collision complexes the dynamic mechanism for collision is quite different from the model in which collision complexes are not formed. We will investigate a method of evaluating the rate coefficient (8.119) in the following.

## 8.7 Scattering Theory and Rate Coefficients

Now the question remains of how the reaction rate coefficient  $k_1$  might be calculated by incorporating the notion of collision complexes formed in a chemical reaction in solution. The first step to answer the question is to make the transition probability more explicit.

Because the solvent is ubiquitously present during a reaction in solution and affects the outcome, it is necessary to take the solvent into consideration. The transition probability  $W_{rp} \left( x^{(\mathcal{N}^{(r)})} | x^{(\mathcal{N}^{(p)})*} \right)$  converts the prereaction phase  $x^{(\mathcal{N}^{(r)})}$  to the postreaction phase  $x^{(\mathcal{N}^{(p)})*}$  for the whole system. Therefore it is related to the collision cross-section for the many-particle system in hand. The many-particle collision cross-section may be expressed in terms of binary, ternary,  $\dots$ , encounters of reacting molecules dispersed in the solvent. Therefore, in practice, it is useful to employ such a representation under the assumption that the mixture is dilute with regard to the solute. Thus, we assume a dilute solution and take the transition probability in terms of collision operators for pairs of reactant molecules embedded in the solvent, whose role is merely that of an energy reservoir, that is,<sup>2</sup>

$$W_{rp} \left( x^{(\mathcal{N}^{(r)})} | x^{(\mathcal{N}^{(p)})*} \right) = 2\pi T_{ab,cd}^\dagger \delta(E_{ab} - E_{cd}) T_{ab,cd}, \quad (8.120)$$

where  $T_{ab,cd}$  is the quantum mechanical transition operator for pair  $(ab)$  that obeys the Lippmann–Schwinger integral equation [25], in the field of the inert solvent (consisting of spectators) providing a medium and the energy reservoir.  $E_{ab}$  and  $E_{cd}$  are the energies of the reactants and the products, respectively.

A comment is required for the representation of the classical quantity  $W_{rp}$  with a quantum mechanical transition operator in (8.120). First of all, note that the kinetic theory of chemical reactions may be formulated by using the quantum mechanical Liouville equation, as shown in [8], where quantum Boltzmann equations have been derived for a reacting gaseous mixture under some assumptions. The procedure may be easily extended to reacting liquid mixtures, and the kinetic equations (8.69) and (8.70) then may be regarded as the classical limits of the quantum kinetic equations for density matrices. Therefore, the representation of  $W_{rp}$  given in (8.120) can be interpreted as keeping the quantum mechanical transition probability [24] without taking its classical limit, which should be the classical cross-section defined in terms of impact parameter and scattering angles. Also note that energies  $E_{ab}$  and  $E_{cd}$  may include the energy of the solvent. Therefore, the conservation of energy takes into account the energy of the solvent molecules, although they play the role of spectators for interactions between molecules. This idea can be easily implemented by using the resolvent operator for the pair  $(a,b)$  or  $(c,d)$  plus inert spectator solvent molecules representative of the system in hand.

Upon using the representation (8.120) of  $W_{rp}$  in the rate coefficient (8.119), it is possible to show that

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<sup>2</sup> For the relation of a transition operator in the superspace (classically, the phase space) and the transition operator in the Hilbert space, see [24] in which a relation is derived between the transition probability  $W$  and the (quantum mechanical) operator  $T$ . See also Sect. A.2 of Appendix A.

$$k_1 = \sum_{s,s'} k_1(s|s'; T), \quad (8.121)$$

$$k_1(s|s'; T) = \frac{1}{n_a n_b} \int d\mathbf{p}_a \int d\mathbf{p}_b \int d\Omega_{ab} g_{ab} \sigma_{AB}(s, \mathbf{p}_a | s' \mathbf{p}_b) f_a^{\text{eq}} f_b^{\text{eq}}, \quad (8.122)$$

where  $g_{ab}$  is the relative speed,  $\Omega_{ab}$  is the scattering angle,  $\sigma_{AB}(s, \mathbf{p}_a | s' \mathbf{p}_b)$  is the reaction cross section, and  $f_r^{\text{eq}}(\mathbf{p}_r)$  is the equilibrium distribution function,<sup>3</sup>

$$f_r^{\text{eq}}(\mathbf{p}_r) = \frac{n_a}{q_r} (2\pi m_r k_B T)^{-3/2} \exp[-\beta(E_{rs} + \varepsilon_{rs})] \quad (r = a, b) \quad (8.123)$$

with  $q_r$  denoting the internal partition function treated quantum mechanically:

$$q_r = \sum_s \exp[-\beta\varepsilon_{as}] \quad (r = a \text{ or } b), \quad (8.124)$$

and  $\varepsilon_{rs}$  and  $E_s$ , respectively, denoting the internal energy of species  $r$  in state  $s$  and the translational energy of the state characterized by  $s$ . The internal degrees of freedom are treated quantum mechanically, because the collision processes are treated quantum mechanically to be consistent with the collision complex model. For such a description of collision processes it is appropriate to revert to a quantum mechanical description of the internal degrees of freedom. Because of the assumption on the diluteness of the reacting species, the pair correlation function has been set equal to unity. This assumption may be removed, for example, if the pair correlation function  $g(r_m)$  of the reacting pair  $(a, b)$  at distance  $r_m = \sqrt{\sigma_{AB}/\pi}$  is inserted in (8.122) to account for the probability of finding the pair in the collision volume. The reaction cross section  $\sigma_{AB}$  must be evaluated by taking the formation and decomposition of collision complexes into consideration.

## 8.8 The R Matrix Theory of Collision

To evaluate the reaction cross section on the basis of a collision complex formation model we rely on the **R** matrix theory of collision, which was originally formulated for nuclear reactions by Wigner and Eisenbud [26, 27] and later applied to chemical reactions by Eu and Ross [28]. The application of the theory to chemical reactions has remained dormant in the last 40 years, but with suitable characterization of collision complexes, which was not done in the original application, the **R** matrix theory can be given fresh life. First we review the **R** matrix theory of scattering and then apply it to evaluate the rate coefficient  $k_1$  presented.

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<sup>3</sup> This distribution function is normalized in the momentum space.

To describe a bimolecular reaction undergoing formation and decomposition of collision complexes it is necessary to specify the initial and final states of reactants and products. The internal quantum states of the reactants are characterized by a set of quantum states to which we assign the symbol  $s$  and the corresponding coordinates are denoted by boldface  $\mathbf{s}$ . The total rotational angular momentum of the reactants is given by the quantum number  $l_s$ , and the initial orbital angular momentum of the relative motion by the quantum number  $l$ . The total angular momentum  $\mathbf{J}$  of the system is the vector sum of  $\mathbf{l}$  and  $\mathbf{l}_s$  with values ranging from  $|\mathbf{l} - \mathbf{l}_s|$  to  $|\mathbf{l} + \mathbf{l}_s|$ . The  $z$  components of  $\mathbf{J}$ ,  $\mathbf{l}$ , and  $\mathbf{l}_s$  in the space-fixed coordinate system are, respectively, denoted by  $\mu$ ,  $m$ , and  $\nu$  for which the angular momentum conservation requires  $\mu = m + \nu$ . The primes on the quantum numbers refer to the products of the reaction. The wave function of the internal degrees of freedom will be denoted by  $\psi_{sv}$  where the angular momentum  $l_s$  is absorbed into the quantum number set  $s$  for brevity. The transition states are formed in a well-defined region of the configuration space. The region, in fact, can be characterized by a certain type of potential for the system. This region is called the internal region—a hypersphere—as opposed to the external region where the constituent molecules of the reactants or products are well separated from each other.

### 8.8.1 Internal Wave Functions

The wave function in the internal region is a solution of the Schrödinger equation with the Hamiltonian for the entire system

$$\mathbf{H}\Psi = E\Psi, \quad (8.125)$$

where

$$\mathbf{H} = -\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + V(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (8.126)$$

for  $N$  particles interacting through the potential energy  $V(\mathbf{r}_1, \dots, \mathbf{r}_N)$ . The unimportant center-of-mass Hamiltonian has been set equal to zero.

Let us denote the eigenfunction of the transition state (collision complex) in the quantum state  $(j, J, \mu)$  by  $X_{j\mu}^{(J)}$  and the corresponding eigenvalue by  $E_j$ . The eigenvalue problem for the collision complex is

$$\mathbf{H}X_{j\mu}^{(J)} = E_j X_{j\mu}^{(J)}. \quad (8.127)$$

The dependence on  $J$  of  $E_j$  is suppressed for brevity of notation. The boundary condition on  $X_{j\mu}^{(J)}$  is that

$$\left( \frac{\partial X_{j\mu}^{(J)}}{\partial \mathbf{n}} \right)_{r_s=a_s} = -\frac{(l+1)}{a_s} X_{j\mu}^{(J)}, \quad (8.128)$$

where  $\mathbf{n}$  is the unit normal vector at the surface separating the internal and external regions at  $r_s = a_s$ . Therefore,  $X_{j\mu}^{(J)}$  is a solution of the eigenvalue problem subject to this boundary condition. An arbitrary wave function in the energy state characterized by  $k$  in the internal region can be expanded in the complete set of wave functions for the collision complex

$$\Psi_{sl\mu k}^{(J)} = \sum_j A_{slkj} X_{j\mu}^{(J)}, \quad (8.129)$$

where  $A_{slkj}$  are the expansion coefficients. We have omitted indexes  $J$  and  $\mu$  from the expansion coefficients for notational brevity. These expansion coefficients must be determined by matching the internal and external wave functions at the surface  $\mathcal{S}$  separating the internal and external regions.

The wave function for translational motion in the external region is the free particle wave function with appropriate boundary conditions. In spherical coordinates, we have for the independent solutions

$$r_s^{-1} \mathfrak{C}_{sl}(k_s r_s) Y_m^l(\Omega_s), \quad r_s^{-1} \mathfrak{S}_{sl}(k_s r_s) Y_m^l(\Omega_s),$$

where  $Y_m^l(\Omega_s)$  is a spherical harmonic. The boundary conditions on the radial functions are

$$\begin{aligned} \mathfrak{C}_{sl}(k_s a_s) &= \sqrt{\frac{m_s}{\hbar}}, \quad \left( \frac{d\mathfrak{C}_{sl}}{dr_s} \right)_{r_s=a_s} = -\frac{l}{a_s} \sqrt{\frac{m_s}{\hbar}}, \\ \mathfrak{S}_{sl}(k_s a_s) &= 0, \quad \left( \frac{d\mathfrak{S}_{sl}}{dr_s} \right)_{r_s=a_s} = \sqrt{\frac{m_s}{\hbar}}. \end{aligned} \quad (8.130)$$

The functions  $\mathfrak{C}_{sl}(k_s r_s)$  and  $\mathfrak{S}_{sl}(k_s r_s)$  may be taken with linear combinations of spherical Bessel and Neumann functions [29] of order  $(l + \frac{1}{2})$ :

$$\mathfrak{C}_{sl}(k_s r_s) = N_{sl1} \sqrt{\frac{\pi r_s}{2k_s}} J_{l+\frac{1}{2}}(k_s r_s) - J_{sl1} \sqrt{\frac{\pi r_s}{2k_s}} N_{l+\frac{1}{2}}(k_s r_s), \quad (8.131)$$

$$\mathfrak{S}_{sl}(k_s r_s) = J_{sl2} \sqrt{\frac{\pi r_s}{2k_s}} N_{l+\frac{1}{2}}(k_s r_s) - N_{sl2} \sqrt{\frac{\pi r_s}{2k_s}} J_{l+\frac{1}{2}}(k_s r_s). \quad (8.132)$$

The expansion coefficients in these linear combinations can be determined with the help of the boundary conditions:

$$\begin{aligned} J_{sl1} &= \sqrt{\frac{m_s}{\hbar}} k_s a_s [(l+1) j_l(k_s a_s) + k_s a_s j'_l(k_s a_s)], \\ N_{sl1} &= \sqrt{\frac{m_s}{\hbar}} k_s a_s [(l+1) n_l(k_s a_s) + k_s a_s n'_l(k_s a_s)], \\ J_{sl2} &= \sqrt{\frac{m_s}{\hbar}} k_s a_s j_l(k_s a_s), \\ N_{sl2} &= \sqrt{\frac{m_s}{\hbar}} k_s a_s n_l(k_s a_s), \end{aligned} \quad (8.133)$$

where  $j_l(z)$  and  $n_l(z)$  are spherical Bessel and Neumann functions of argument  $z$  and order  $l$ :

$$\begin{aligned} j_l(z) &= \sqrt{\frac{\pi}{2z}} J_{l+\frac{1}{2}}(z), \quad j'_l(z) = \frac{d j_l(z)}{dz}, \\ n_l(z) &= \sqrt{\frac{\pi}{2z}} N_{l+\frac{1}{2}}(z), \quad n'_l(z) = \frac{d n_l(z)}{dz}. \end{aligned} \quad (8.134)$$

Two independent solutions for the Schrödinger equation in the external region for a given total angular momentum  $J$  and its  $z$  component  $\mu$  are then given by

$$\mathcal{D}_{sl\mu}^{(J)}(r_s, \mathbf{s}) = \sum_m \mathcal{S}_{\mu-m, m}^{(J)}(l_s, l) r_s^{-1} \mathfrak{S}_{sl}(k_s r_s) Y_m^l(\Omega_s) \psi_{s, \mu-m}(\mathbf{s}), \quad (8.135)$$

$$\mathcal{V}_{sl\mu}^{(J)}(r_s, \mathbf{s}) = \sum_m \mathcal{S}_{\mu-m, m}^{(J)}(l_s, l) r_s^{-1} \mathfrak{C}_{sl}(k_s r_s) Y_m^l(\Omega_s) \psi_{s, \mu-m}(\mathbf{s}), \quad (8.136)$$

where  $\mathcal{S}_{\mu, \mu'}^{(J)}(l_s, l)$  denotes the Wigner vector coupling coefficient. The wave function  $\Psi_{sl\mu e}^{(J)}$  in the external region is then given by a linear combination of  $\mathcal{D}_{sl\mu}^{(J)}(r_s, \mathbf{s})$  and  $\mathcal{V}_{sl\mu}^{(J)}(r_s, \mathbf{s})$ :

$$\Psi_{sl\mu e}^{(J)} = \mathcal{D}_{sl\mu}^{(J)}(r_s, \mathbf{s}) + \sum_{s', l'} R_{sl; s' l'}^{(J)} \mathcal{V}_{s' l' \mu}^{(J)}(r_s, \mathbf{s}). \quad (8.137)$$

The coefficient matrix,  $\mathbf{R}$  matrix, is independent of  $\mu$  because of the isotropy of space in the absence of an external force. The  $\mathbf{R}$  matrix is determined by matching the internal and external wave functions and their normal derivatives at the channel surface, the hypersurface of the internal region. For this purpose, we use the orthogonality of  $\mathcal{V}_{sl\mu}^{(J)}(r_s, \mathbf{s})$  at the channel surface:

$$\int_S dS \mathcal{V}_{sl\mu}^{(J)*}(a_s, \mathbf{s}) \mathcal{V}_{s' l' \mu}^{(J)}(a_s, \mathbf{s}) = \left( \frac{m_s}{\hbar} \right) \delta_{ss'} \delta_{ll'}, \quad (8.138)$$

where the integration is performed over the hypersurface  $S$ . Therefore, it is useful to define

$$\widehat{\mathcal{V}}_{sl\mu}^{(J)}(a_s, \mathbf{s}) = \sqrt{\frac{\hbar}{m_s}} \mathcal{V}_{sl\mu}^{(J)}(a_s, \mathbf{s}), \quad (8.139)$$

which is normalized at the channel entrance at  $a_s$ .

### 8.8.2 The $\mathbf{R}$ and $\mathbf{S}$ Matrices

The  $\mathbf{R}$  matrix is given by

$$R_{sl; s' l'}^{(J)} = \sum_j \frac{\gamma_{slj} \gamma_{s' l' j}}{E_j - E}, \quad (8.140)$$

where  $\gamma_{slj}$  is the reduced width defined by

$$\gamma_{slj} = \frac{\hbar}{\sqrt{2m_s}} \int_S dS X_{j\mu}^{(J)*} \hat{V}_{sl\mu}^{(J)}(a_s, \mathbf{s}). \quad (8.141)$$

In matrix form,

$$\mathbf{R}^{(J)} = \sum_j \frac{\gamma_j \gamma_j}{E_j - E}. \quad (8.142)$$

This  $\mathbf{R}$  matrix is related to the  $\mathbf{S}$  matrix [25] as follows:

$$\mathbf{S}^{(J)} = \omega \frac{1 + i\mathbf{C} + i\mathbf{B}\mathbf{R}\mathbf{B}}{1 - i\mathbf{C} - i\mathbf{B}\mathbf{R}\mathbf{B}} \omega, \quad (8.143)$$

where  $\mathbf{B}$ ,  $\omega$ , and  $\mathbf{C}$  are diagonal matrices defined by

$$B_{sl} = k_s^{3/2} a_s [j_{l-1}^2(k_s a_s) + n_{l-1}^2(k_s a_s)]^{1/2}; \\ B_{s0} = \sqrt{k_s} \quad (l > 1), \quad (8.144)$$

$$C_{sl} = -(k_s a_s)^2 [j_l(k_s a_s) j_{l-1}(k_s a_s) + n_l(k_s a_s) n_{l-1}(k_s a_s)]; \\ C_{s0} = 0 \quad (l > 1), \quad (8.145)$$

$$\omega_{sl} = i^{-l} [j_{l-1}(k_s a_s) - i n_{l-1}(k_s a_s)] [j_{l-1}^2(k_s a_s) + n_{l-1}^2(k_s a_s)]^{1/2}; \\ \omega_{s0} = e^{-ik_s a_s} \quad (l > 1). \quad (8.146)$$

It is useful to note that the reduced widths  $\gamma_{slj}$  are Franck–Condon factors seen in spectroscopy. Therefore, chemical reactions may be regarded<sup>4</sup> as Franck–Condon transitions at the channel entrance from the reactant to a state of collision complex which makes a Franck–Condon transition to the final product state, and vice versa. Such Franck–Condon transitions are possible energetically even if the relative kinetic energy is below “the activation energy” because of the energy uncertainty during the short collision time, during which the energy fluctuates owing to the energy conversion processes between the translational and internal degrees of freedom in the course of collision and the involvement of the spectator solvent acting as the energy reservoir. The fundamental question still remains as to the dynamic characterization of transition states. It will be discussed later.

The  $\mathbf{S}$  matrix may be put into more useful forms, albeit approximate, which enable us to connect formally with the existing model theories in chemical kinetics; the absolute reaction rate theory [22] and the Marcus theory [31–34].

### 8.8.3 Multilevel Formula

The  $\mathbf{S}$  matrix given in (8.143) may be written as a multilevel formula in which each level contributes a Lorentzian form for the energy dependence of

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<sup>4</sup> For the Franck–Condon model for chemical reactions, see also [30], in which the Franck–Condon model is argued for chemical reactions from another viewpoint.

the reaction cross section. If we assume that one can replace all the terms of  $\mathbf{R}$ , except for one, with an energy independent term denoted by  $\mathbf{R}_\infty$

$$\mathbf{R} = \frac{\gamma_j \gamma_j}{E_j - E} + \mathbf{R}_\infty, \quad (8.147)$$

the following multilevel formula for  $\mathbf{S}^{(J)}$  is obtained:

$$\mathbf{S}^{(J)} = \omega \frac{1 + i\mathbf{C}}{1 - i\mathbf{C}} \omega + \sum_j \frac{2i\omega (\alpha_j \times \alpha_j) \omega}{E_j + \Delta_j^{(J)} - E - \frac{1}{2}i\Gamma_j^{(J)}}. \quad (8.148)$$

Here, various quantities are defined by the expressions

$$\mathbf{C}' = \mathbf{C} + \mathbf{B}\mathbf{R}_\infty\mathbf{B}, \quad (8.149)$$

$$\alpha_j = \frac{\mathbf{B}\gamma_j}{1 - i\mathbf{C}'}, \quad (8.150)$$

$$\Gamma_j^{(J)} = \sum_{s,l} \Gamma_{slj}^{(J)} = 2 \sum_{s,l} |\alpha_{slj}|^2, \quad (8.151)$$

$$\Delta_j^{(J)} = \sum_{s,l} \Delta_{slj}^{(J)} = \frac{1}{2} \sum_{s,l} C'_{sl} \Gamma_{slj}^{(J)}. \quad (8.152)$$

The  $\mathbf{R}$  matrix may be written as in (8.147) if the levels are well separated compared with the level widths. Because  $\mathbf{B}$ ,  $\mathbf{C}$ , and  $\omega$  depend on energy  $E$ , the level width  $\Gamma_j^{(J)}$  and the level shift  $\Delta_j^{(J)}$  also depend on  $E$ . This multilevel formula will be used to evaluate the rate coefficient  $k_1$  presented earlier in the limit of vanishing level widths.

## 8.9 Collision Complexes and Rate Coefficient

Because the collision cross-section for the collision process  $(s, l) \rightarrow (s', l')$  is given by <sup>5</sup>

$$\sigma_{AB}(s, k_s | s', k_{s'}) = \frac{\pi}{k_s^2} \sum_{ll'} (2J+1) \left| S_{sl;s'l'}^{(J)} \right|^2, \quad (8.153)$$

upon using the multilevel formula for  $S_{sl;s'l'}^{(J)}$  in the specific rate coefficient formula we obtain

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<sup>5</sup> This is the reaction cross section for a state-to-state chemical transformation, which is not averaged over angular momentum polarizations.

$$k_1(s|s';T) = \frac{h^{-4} (2\pi M k_B T)^{3/2}}{(Q_a/V)(Q_b/V)} e^{-\beta(\varepsilon_{as} + \varepsilon_{sb})} \sum_{ll'J} (2J+1) \\ \times \int_0^\infty dE_s \exp(-\beta E_s) \left| \sum_j \frac{2i\omega_{sl} (\alpha_j \times \alpha_j)_{sl;sl'} \omega_{s'l'}}{E_j + \Delta_j^{(J)} - E - \frac{1}{2}i\Gamma_j^{(J)}} \right|^2, \quad (8.154)$$

where  $M = m_a + m_b$ , the relative kinetic energy of the pair  $(a, b)$  is denoted by  $E_s$ , and

$$Q_r/V = \frac{(2\pi m_r k_B T)^{3/2}}{\hbar^3} q_r \quad (r = a, b).$$

To reduce this reaction rate expression to a simpler and more transparent form we will assume that the level widths are much smaller than the level spacing between the energy levels of the collision complex. This assumption is equivalent to the assumption that the collision complexes are long-lived compared with the mean frequency of transition between different energy levels of the collision complex. With this assumption, the following approximation is possible for the Lorentian forms:

$$\frac{\Gamma_j^{(J)}}{(E_j + \Delta_j^{(J)} - E)^2 + \frac{1}{4}\Gamma_j^{(J)2}} \simeq 2\pi\delta(E_j + \Delta_j^{(J)} - E). \quad (8.155)$$

Here it must be observed that  $E = E_s + \varepsilon_{as} + \varepsilon_{bs}$ . In this approximation for the Lorentian form, the specific rate coefficient is given by the formula

$$k_1(s|s';T) = \frac{1}{\hbar} \frac{h^3}{(2\pi m k_B T)^{3/2}} \sum_{jJl'l'} (2J+1) \frac{\Gamma_{slj} \Gamma_{s'l'j}}{\Gamma_j} e^{-\beta E_j} \quad (8.156)$$

with  $m = m_a m_b / M$ . Finally, the observed rate coefficient  $k_1$  may be written as

$$k_1 = \kappa \frac{q_{ab}^\ddagger}{q_a q_b}, \quad (8.157)$$

where

$$\kappa = \frac{\langle \Gamma \rangle \Lambda^3}{\hbar}, \quad (8.158)$$

$$\langle \Gamma \rangle = \sum_{j,J} (2J+1) \Gamma_j^{(J)} \frac{e^{-\beta(E_j + \Delta_j^{(J)})}}{q_{ab}^\ddagger}, \quad (8.159)$$

$$q_{ab}^\ddagger = \sum_{j,J} (2J+1) e^{-\beta(E_j + \Delta_j^{(J)})}, \quad (8.160)$$

$$\Lambda = \frac{\hbar}{\sqrt{2\pi m k_B T}}. \quad (8.161)$$

Since it is possible to write

$$\frac{q_{ab}^{\ddagger}}{q_a q_b} = \exp(-\beta \Delta g_{ab}^{\ddagger}), \quad (8.162)$$

the rate coefficient may be written as

$$k_1 = \kappa \exp(-\beta \Delta g_{ab}^{\ddagger}), \quad (8.163)$$

where  $\Delta g_{ab}^{\ddagger}$  is the internal free energy change of formation for the collision complex and  $\kappa$  is the transmission factor. This formula for  $k_1$  is formally reminiscent of the rate constant formula in the Marcus theory or the absolute reaction rate theory, both of which assume formation of a collision complex—a transition state—in a chemical reaction.

It is significant that  $\langle \Gamma \rangle$  may be regarded as an ensemble average of the Franck–Condon factors for formation or decomposition of the collision complex at the channel entrances of the hypersurface of the internal region in which the collision complex is confined; see (8.150) and (8.151). To appreciate this point better, we examine an approximation for  $\langle \Gamma \rangle$  preserving the desired feature. To the lowest order neglecting  $\mathbf{C}'$ , we obtain from (8.150) and (8.151)

$$\Gamma_j^{(J)} \approx 2 \sum_{s,l} |B_{sl} \gamma_{slj}|^2. \quad (8.164)$$

If asymptotic formulas for the spherical Bessel functions are used, the factor  $B_{sl}$  may be approximated by

$$B_{sl} \approx \hbar^{-1} \left[ 2m_s \left( E_j + \Delta_j^{(J)} - \varepsilon_{as} - \varepsilon_{bs} \right) \right]^{1/2} \quad (m \equiv m_s). \quad (8.165)$$

Therefore, by using (8.141) for the reduced width  $\gamma_{slj}$  we find

$$\Gamma_j^{(J)} \approx \sum_{s,l} \left( E_j + \Delta_j^{(J)} - \varepsilon_{as} - \varepsilon_{bs} \right) \left| \int_S dS X_{j\mu}^{(J)*} \widehat{\mathcal{V}}_{sl\mu}^{(J)} (a_s, \mathbf{s}) \right|^2, \quad (8.166)$$

which obviously is proportional to the Franck–Condon factor at the channel entrance and the energy difference between the collision complex and the internal energy in channel  $s$ . This energy is comparable to the translational energy of the collision pair. This derivation shows that the transmission factor is given by the absolute square of the mean Franck–Condon factor multiplied by the flux at the channel entrance. The formula derived provides statistical means of calculating the rate coefficient by studying the quantum mechanics of complex formation in a reaction.

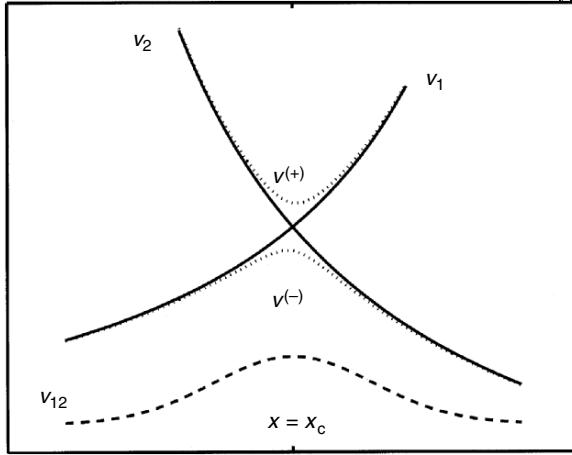
## 8.10 Characterization of Collision Complexes

To formulate the theory presented for the rate coefficient  $k_1$ , it was sufficient to assume the existence of long-lived collision complexes in a chemical reaction,

properly equipping them with wave functions and eigenvalues. The rate coefficient  $k_1$  presented enables us to give the following physical interpretation.

Such collision complexes are confined to a finite volume around the locus of crossing of two potential energy surfaces corresponding to the reactants and the products, respectively. In the diabatic representation, the two potential energy surfaces are the electronic energy eigenvalues for nuclear configurations of reactants or products, whose wave functions are coupled to each other by electronic coupling interactions localized in the neighborhood of the locus of crossing. In the adiabatic representation the potential energy surfaces, however, become two separated sheets owing to the non-crossing rule of potential energy surfaces. Either way, it is evident that the collision complexes involve the two sheets of potential energy in either the adiabatic representation or the diabatic representation. To calculate the reaction rate constant as a function of temperature and molecular characteristics, it is necessary to solve the eigenvalue problem for the collision complex and compute with the solution the reduced widths  $\gamma_{slj}$  and the partition function for the collision complex. The aforementioned eigenvalue problem, however, takes us beyond the scope of this work, because it is a collision theory problem, which forms its own field of discipline and discussing it in detail would take us too far afield. Therefore, we will only briefly sketch the essential feature required for characterizing the collision complexes or transition states in the present line of theory.

Because the lifetime of collision complexes is probably of the order of a few vibrational periods, the energy uncertainty that is inversely proportional to the lifetime is comparably large. This large energy uncertainty conspires with the energy fluctuations caused by the solvent and internal dynamics of the collision pair. To elaborate on this viewpoint, we observe that because of the solvent present throughout the collision process and also the internal degrees of freedom of the reactant or product molecules, there are considerable chances for energy fluctuations to occur, which facilitate the reactant or product pairs to make Franck–Condon type transitions between the states in the lower and upper potential energy surfaces around the potential energy crossing. In this picture, the states in the lower potential energy surface in the adiabatic representation represent either the states of the reactants or the products, whereas the states in the upper potential energy surface represent the states of the collision complex formed in the course of collision. If this situation is schematically depicted in one dimension along the suitably chosen reaction coordinate without making the internal molecular degrees of freedom, it is as shown in Fig. 8.1. The figure simply depicts the relative radial coordinates of the reactant pair and also of the product pairs without being encumbered by the internal degrees of freedom of the molecules involved. The diabatic potentials cross at the origin of the coordinate system chosen, but in the adiabatic representation the potentials separate as two curves whose distance of separation is determined by the coupling potential  $V_{12}$ . The minimum or the maximum is located at the crossing point. The collision complex is characterized by the upper potential curve.



**Fig. 8.1.** Diabatic and adiabatic potentials plotted along the “reaction coordinate” in the neighborhood of the curve crossing point.  $V_1$  and  $V_2$  are diabatic potentials and the dashed curve is the coupling potential,  $V_{12}$ .  $V^{(+)}$  and  $V^{(-)}$  are the adiabatic potentials (dotted curves). The diagram is schematic and one-dimensional. Other degrees of freedom are suppressed.

If this picture is translated into full multi-dimensional surfaces that include the internal degrees of freedom for the molecules, then the *upper curve* will become an upper hypersurface, and the *lower curve* a lower hypersurface. Collision complexes are determined in the upper surface by their eigenvalue problem subject to the boundary condition (8.128).

In the schematic example representing Fig. 8.1, which contains the essential feature of the collision complex, the Schrödinger equations are

$$\left[ -\frac{\hbar^2}{2m_s} \frac{d^2}{dx^2} + V^{(+)}(x) \right] u_j^{(+)}(x) = E_j u_j^{(+)}(x), \quad (8.167)$$

$$\left[ -\frac{\hbar^2}{2m_s} \frac{d^2}{dx^2} + V^{(-)}(x) \right] u_k^{(-)}(x) = E_k u_k^{(-)}(x), \quad (8.168)$$

where  $m_s$  is the reduced mass and the two potential curves are given by

$$V^{(\pm)}(x) = \frac{1}{2}(V_1 + V_2) \pm \frac{1}{2}\sqrt{(V_1 - V_2)^2 + V_{12}^2}.$$

Note that the radial part of the wave function  $X_j$  is related to  $u_j^{(+)}$  as follows:

$$X_j = \frac{u_j^{(+)}(x)}{x},$$

and similarly for the wave function for the lower curve. Therefore, the boundary condition on the normal derivative of  $u_j^{(+)}(x)$  reads:

$$\left[ \frac{d}{dn} u_j^{(+)}(x) \right]_{r_s=a_s} = -u_j^{(+)}(a_s)$$

because we are considering the  $l = 0$  wave in the one-dimensional model. Unlike in the diabatic representation, the wave functions  $u_j^{(\pm)}(x)$  in the adiabatic representation are not coupled, but the coupling between the initial and final state of the collision process is achieved through  $u_j^{(+)}$  and the  $\mathbf{R}$  matrix. The Schrödinger equations (8.167) and (8.168) can be solved by a variety of methods. In particular, if  $E_j > \max(V^{(+)})$ , there can be bound states, which can break up either into the reactant or the product, and the probability of breakup is proportional to the line width squared—the Franck–Condon factor squared. This schematic description can be made more elaborate and dynamically complete by including the internal degrees of freedom. The essential point is that the upper curve of the adiabatic potential is associated with the collision complex we have in mind.

In this manner, the collision complex can be dynamically characterized by the quantum mechanical eigenvalue problem in the upper sheet of the potential energy surfaces, subject to the boundary condition (8.128) on wave functions  $X_{j\mu}^{(J)}$  for the collision complex. The position of channel entrance  $r_s = a_s$  may be defined as the distance of closest approach for the colliding pair (i.e., either the reactant pair or the product pair) at the relative translational kinetic energy of channel  $s$  and determined by the potential energy surface around the crossing point of the diabatic potential energy surfaces. Therefore, the energy eigenvalue problem for the wave functions  $X_{j\mu}^{(J)}$  of the collision complex can be generally solved subject to the boundary condition mentioned, once the potential energy surfaces and the coupling potentials are specified. With the wave functions and energy eigenvalues of the collision complex so determined, it is now possible to calculate the mean Franck–Condon factor  $\langle \Gamma \rangle$  and the free energy change  $\Delta g_{AB}^\ddagger$  and thus the temperature dependence of the rate coefficient  $k_1$ . A number of models, such as the WKB methods [13, 35], can be developed together with approximate methods for the wave functions and energy eigenvalues. However, the subject is beyond the scope of this monograph.

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## Dynamic Ornstein–Zernike Equation

The constitutive equations derived for various macroscopic fluxes from the generalized Boltzmann equations in the previous two chapters allow us to develop the Chapman–Enskog line of kinetic theory or the moment theory for dense gases and liquids. The transport coefficients in such an approach are given in terms of collision bracket integrals. However, such an approach is not the only conceivable one. There can be an alternative to it, as will be shown in the subsequent chapters. The development of such an alternative method requires various lower order reduced nonequilibrium distribution functions and, particularly, nonequilibrium pair distribution functions. To prepare ourselves for such an alternative development, we discuss a dynamic extension of the Ornstein–Zernike equation to nonequilibrium phenomena in this chapter before we discuss the density fluctuation theory of transport coefficients in subsequent chapters. More specifically, we present the dynamic Ornstein–Zernike equation for dynamic pair distribution functions. This formal theory will equip us with a mathematical technique for treating nonequilibrium phenomena without directly solving the generalized Boltzmann equation for dense fluids. Nevertheless, note that the generalized Boltzmann equation is still at the foundation of the dynamic Ornstein–Zernike equation because the nonequilibrium grand ensemble distribution function employed in the development of the theory is provided by the generalized Boltzmann equation. Moreover, the aforementioned constitutive equations derived from the generalized Boltzmann equation for nonconserved variables will be required if solutions of nonlinear order are sought for the dynamic Ornstein–Zernike equation.

### 9.1 Nonequilibrium Ensemble Distribution Function

The grand ensemble kinetic equation (7.7) for an  $r$ -component mixture of simple fluids has a unique equilibrium solution, which is a solution of the equilibrium condition (7.C2) owing to the H theorem satisfied by the kinetic equation

$$\Re \left[ F_{\text{eq}}^{(\mathbf{N})} \right] = 0. \quad (9.1)$$

This equation is satisfied by the equilibrium grand canonical ensemble distribution function

$$F_{\text{eq}}^{(\mathbf{N})} \left( x^{(\mathbf{N})} \right) = (c\Xi_{\text{eq}})^{-1} \exp \left[ - \int_V d\mathbf{r} \beta(\mathbf{r}) \sum_{a=1}^r \sum_{ja=1}^{N_a} \mathcal{H}_{ja}^{\text{eq}} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right], \quad (9.2)$$

where

$$\mathcal{H}_{ja}^{\text{eq}} = H'_{ja} - m_a \hat{\mu}_a \quad (9.3)$$

with  $H'_{ja}$  denoting the Hamiltonian of particle  $j \in a$  defined in Chap. 7 [see (7.3)];  $\hat{\mu}_a$  is the chemical potential per unit mass of species  $a$ ;  $\Xi_{\text{eq}}$  is the equilibrium grand canonical ensemble partition function

$$\Xi_{\text{eq}} = \left\langle \exp \left\{ - \int_V d\mathbf{r} \beta(\mathbf{r}) \sum_{a=1}^r \sum_{ja=1}^{N_a} \mathcal{H}_{ja}^{\text{eq}} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right\} \right\rangle; \quad (9.4)$$

and  $c$  stands for the factor

$$c = h^{3\mathbf{N}} \prod_{a=1}^r N_a! \quad (9.5)$$

with  $h$  denoting the Planck constant and  $\beta = 1/k_B T$ , where  $T$  is the local absolute temperature. The angular brackets have the same meaning for averages as those in Chap. 7—the grand ensemble averages. Note that the equilibrium state is achieved in the dynamic grand ensemble when the petit ensembles of  $\mathbf{N}$  particles therein are equilibrated with regard to energy and the number of particles because the energy and particle number of the grand ensemble are invariants of collision operator  $\mathfrak{R}[F^{(\mathbf{N})}]$ .

The nonequilibrium grand canonical ensemble distribution function is then introduced in the same spirit as for the dilute gas counterpart, which was constructed on the basis of the Boltzmann equation [1,2]. Although presented in Chap. 7, we introduce it here again to help ease reading the topics discussed in this chapter:

$$F_c^{(\mathbf{N})}(x^{(\mathbf{N})}, t) = c^{-1} \exp \left\{ - \int_V d\mathbf{r} \beta(\mathbf{r}, t) \left[ \sum_{j=1}^N \mathcal{H}_j \delta(\mathbf{r}_j - \mathbf{r}) - \rho \Upsilon(\mathbf{r}, t) \right] \right\}, \quad (9.6)$$

where

$$\mathcal{H}_{ja} = T^{-1} \left( H'_{ja} + \sum_{q \geq 1} X_{qa} h_{ja}^{(q)} - m_a \hat{\mu}_a \right), \quad (9.7)$$

$$\Xi = \left\langle \exp \left[ -k_B^{-1} \int_V d\mathbf{r} \sum_{a=1}^r \sum_{ja=1}^{N_a} \mathcal{H}_{ja} \delta(\mathbf{r}_{ja} - \mathbf{r}) \right] \right\rangle, \quad (9.8)$$

and

$$-k_B \ln \Xi = \int_V d\mathbf{r} \rho \Upsilon(\mathbf{r}, t) / T(\mathbf{r}, t). \quad (9.9)$$

The notation is the same as in Chap. 7.

As the generalized potentials  $X_{qa}$  ( $q \geq 1$ ;  $1 \leq a \leq r$ ) vanish, the nonequilibrium distribution function  $F_c^{(N)}$  tends to the equilibrium distribution function  $F_{eq}^{(N)}(x^{(N)})$ . If  $F_c^{(N)}(x^{(N)}, t)$  is substituted in the kinetic equation (7.7) and the evolution equations for the intensive variables such as  $T$ ,  $\hat{\mu}_a$ , and  $X_{qa}$  in the expression for  $F_c^{(N)}$  are derived and solved, then  $F_c^{(N)}$  fully becomes a solution of the kinetic equation. This procedure, however, is not pursued in the thermodynamic theory of irreversible processes in the framework of generalized thermodynamics [3] because the aforementioned parameters are treated as thermodynamic—phenomenological—intensive variables uniform in an elementary volume located around position  $\mathbf{r}$  and at time  $t$  in generalized thermodynamics. In this connection, it must be noted that although the nonequilibrium grand canonical distribution function (9.6) assures a thermodynamic structure parallel to equilibrium thermodynamics, as shown in [2], it is merely the thermodynamic branch of the nonequilibrium distribution function. It becomes the solution of the kinetic equation only in the limit of vanishing fluctuations [2] of the variables  $X_{qa}$  from their thermodynamic values. These generalized potentials  $X_{qa}$  are conjugate to the molecular moments  $h_{ja}^{(q)}$  in the exponential form of the distribution function. We do not discuss this aspect of the theory because it is beyond the scope of this work. For the details of this point, see Sections 7.4, 7.5, and 10.5 of [2].

## 9.2 Dynamic Ornstein–Zernike Equation

Before we discuss the density fluctuation theory itself, it is necessary to develop a theoretical tool to treat nonequilibrium reduced distribution functions that we will encounter in the theory. The desired tool is provided by the dynamic version of the Ornstein–Zernike equation. Its derivation is discussed below.

Beginning in 1946, the statistical mechanics of dense gases and liquids was initiated by papers by Bogoliubov [4], Born and Green [5], and Kirkwood [6], who were preceded by Yvon [7]. In this approach, both equilibrium and nonequilibrium theories were studied, couched in the same idea. In the equilibrium theories, a hierarchy of reduced distribution functions was developed from the equilibrium distribution function, for example, the canonical ensemble distribution function, whereas in nonequilibrium theories a hierarchy of evolution equations for reduced nonequilibrium distribution functions was developed from the Liouville equation. Such hierarchies are, respectively, known in the literature as the equilibrium and the nonequilibrium Bogoliubov–Born–Green–Kirkwood–Yvon (BBGKY) hierarchy, or simply the BBGKY hierarchies. They are open sets of integral or integro-differential equations for

reduced distribution functions, which must be closed by assuming a closure relation by some arbitrary means and then solved either numerically or by an approximation method. There are numerous articles on the subject in the literature since its inception, too many to quote them here. The results of various approximate methods of solution for the BBGKY hierarchy for both equilibrium and nonequilibrium, however, have been disappointing because of the necessity of a closure, which has been usually made in the form of the Kirkwood superposition approximation for the triplet distribution function. The ensuing approximation methods required for their solutions have been found inadequate. The situation is even worse in nonequilibrium. The computer simulation methods developed in recent years have relegated the BBGKY hierarchy approach to a state of disuse, and little has been done in the approach to both equilibrium and nonequilibrium phenomena.

In equilibrium statistical mechanics of liquids, the Ornstein–Zernike (OZ) equation has turned out to be a much more productive approach. The OZ integral equation [8], relating the total and direct correlation function, also requires a closure relation, as does the BBGKY hierarchy. If the Percus–Yevick (PY) form [9] of closure is employed, the OZ integral equation even gives an analytic solution of the equation of state for hard sphere fluids [10, 11], as discussed in Chap. 6. This aspect of the OZ integral equation approach is very attractive because the hard sphere PY closure solution can serve as the base solution for a perturbation theory of liquids. Motivated by such hopes, numerous authors have investigated the OZ integral equations (see references cited in Chap. 6). The OZ integral equation results in a suitable resummation of cluster diagrams, as demonstrated in the literature [12]. However, it was derived by Percus [13] by using functional derivative techniques applied to the equilibrium grand canonical ensemble distribution function. Since the BBGKY hierarchy is also derived from the same distribution function, it is quite clear that the OZ integral equation is a resummed form of the BBGKY hierarchy of integral equations for reduced distribution functions. The former turns out to be much simpler to treat and generally more accurate than the latter. It also presents considerable potential for improving the currently available theories, as discussed in Chap. 6.

Because nonequilibrium reduced distribution functions appear in the density fluctuation theory of transport processes and it is necessary to provide methodological tools for determining them for completeness of the theory, we will present a derivation of the dynamic Ornstein–Zernike (DOZ) integral equation for dynamic total and direct correlation functions of nonequilibrium dense fluids. The derivation uses functional derivative techniques [14].

We consider a single-component nonequilibrium simple liquid contained in volume  $V$  for the sake of simplicity of derivation. To connect with the canonical ensemble theory it is useful to express  $F_c^{(N)}(x^{(N)}, t)$  in the following manner:

$$F_c^{(N)}(x^{(N)}, t) = \frac{\mathfrak{z}^N Q_N}{c \Xi} \mathcal{P}^{(N)}(x^{(N)}, t), \quad (9.10)$$

where  $\mathcal{P}^{(N)}$  is the nonequilibrium canonical distribution function of  $N$  particles

$$\mathcal{P}^{(N)}(x^{(N)}, t) = Q_N^{-1} \exp \left[ - \int_V d\mathbf{r} \beta(\mathbf{r}, t) \sum_{j=1}^N (H_j + H_j^1) \delta(\mathbf{r}_j - \mathbf{r}) \right] \quad (9.11)$$

with  $H_j^1$  denoting the nonequilibrium contribution

$$H_j^1 = \sum_{q \geq 1} X_q(\mathbf{r}, t) h_j^{(q)}(x^{(N)}). \quad (9.12)$$

The nonequilibrium canonical partition function  $Q_N$  in the expression is defined by the phase space integral,

$$Q_N = \int dx^{(N)} \exp \left[ - \int_V d\mathbf{r} \beta(\mathbf{r}, t) \sum_{j=1}^N (H_j + H_j^1) \delta(\mathbf{r}_j - \mathbf{r}) \right], \quad (9.13)$$

and  $\mathfrak{z}$  is the nonequilibrium activity defined by the formula,

$$\mathfrak{z}^N = \exp \left[ \int_V d\mathbf{r} \sum_{j=1}^N m\hat{\mu}(\mathbf{r}, t) \beta(\mathbf{r}, t) \delta(\mathbf{r}_j - \mathbf{r}) \right]. \quad (9.14)$$

The integral in the exponent may be regarded as the volume average of the integrand. In this sense, the activity  $\mathfrak{z}$  defined by (9.14) is a volume averaged quantity.

Define reduced distribution functions,

$$f_N^{(n)}(x^{(n)}, t) = \frac{N!}{(N-n)!} \int dx^{(N-n)} \mathcal{P}^{(N)}(x^{(N)}, t), \quad (9.15)$$

where  $x^{(N-n)}$  is the phase of  $(N-n)$  particles, excluding those in the set of  $n$  particles of interest

$$x^{(n)} = (x_i : i = 1, \dots, n) \equiv (\mathbf{p}_i, \mathbf{r}_i : i = 1, \dots, n).$$

This conforms to the notation used in Chap. 7. This reduced distribution function is the probability of finding particles  $1, \dots, n$  at phases  $x_1, \dots, x_n$ , respectively, given the rest of the particles randomly distributed in the phase  $x^{(N-n)}$ . With  $f_N^{(n)}(x^{(n)}, t)$  so defined for the nonequilibrium canonical ensemble, the reduced distribution function in the grand ensemble theory is defined by the average

$$f^{(n)}(x^{(n)}, t) = \sum_{N \geq 0} f_N^{(n)}(x^{(n)}, t) P_N, \quad (9.16)$$

where the probability  $P_N$  is defined by

$$P_N = \frac{\mathfrak{z}^N Q_N}{c \Xi}. \quad (9.17)$$

Because  $\mathcal{P}^{(N)}(x^{(N)}, t)$  is normalized to unity, there follows the normalization for  $f_N^{(n)}$

$$\int dx^{(n)} f_N^{(n)}(x^{(n)}, t) = \frac{N!}{(N-n)!}, \quad (9.18)$$

and hence the normalization condition for  $f^{(n)}$  is

$$\int dx^{(n)} f^{(n)}(x^{(n)}, t) = \sum_{N \geq 0} \frac{N!}{(N-n)!} P_N \equiv \left\langle \frac{N!}{(N-n)!} \right\rangle. \quad (9.19)$$

This formalism is parallel to that of the equilibrium grand canonical ensemble theory [15] owing to the mathematical similarity of the distribution functions in both equilibrium and nonequilibrium.

We use the functional derivative method [14] to derive the DOZ equation. For the purpose of the present derivation, it is necessary to isolate the one-particle Hamiltonian from  $\mathcal{H}_j$ , which is written in the form

$$\mathcal{H}_j = H_j^{(1)}(x_j) + \sum_{k>j} V_{jk} + \sum_{k>j} H'_{jk}. \quad (9.20)$$

Here,  $H_j^{(1)}$  is the one-particle Hamiltonian which may consist of the kinetic energy and the external potential energy as well as a complete set of products of one-particle currents and their conjugate molecular variables that arise from nonequilibrium effects:

$$H_j^{(1)}(x_j) = \frac{1}{2} m C_j^2 + u_j(\mathbf{r}_j) + H_j^{(k)\prime},$$

where  $u_j(\mathbf{r}_j)$  is the external potential energy on particle  $j$  and  $H_j^{(k)\prime}$  is the single particle part of nonequilibrium flux terms for particle  $j$  consisting of the kinetic part of  $h_j^{(q)}$  given in (9.7). We will denote the one-particle contributions to the distribution function by the symbol

$$E_j(x_j) = \int_V d\mathbf{r} \beta(\mathbf{r}, t) H_j^{(1)}(x_j) \delta(\mathbf{r}_j - \mathbf{r}) \quad (9.21)$$

and similarly for the many-particle contributions

$$E^{(N)}(x^{(N)}) = \sum_{j=1}^N \sum_{k>j}^N \int_V d\mathbf{r} \beta(\mathbf{r}, t) (V_{jk} + H'_{jk}) \delta(\mathbf{r}_j - \mathbf{r}). \quad (9.22)$$

In this expression,  $H'_{jk}$  are the many-particle contributions to  $H_j^1$ , which generally vanish if the particles do not interact. In this notation the distribution

function can be expressed as

$$F^{(N)}(x^{(N)}; t) = (c\Xi)^{-1} \mathfrak{z}^N \exp \left[ -E^{(N)}(x^{(N)}) \right] \prod_{j=1}^N e_\varepsilon(x_j), \quad (9.23)$$

where

$$e_\varepsilon(x_j) = \exp[-E_j(x_j)]. \quad (9.24)$$

The nonequilibrium grand canonical ensemble partition function now may be accordingly written as

$$\Xi = \sum_{N \geq 0} \frac{\mathfrak{z}^N}{c} \int dx^{(N)} \exp \left[ -E^{(N)}(x^{(N)}) \right] \prod_{j=1}^N e_\varepsilon(x_j). \quad (9.25)$$

With this preparation, we are ready to investigate the functional derivatives of  $\Xi$  and their relations. We regard this nonequilibrium partition function as a function of  $E_j$  or  $e_\varepsilon(x_j)$ . In this functional derivative method, we examine the effects of a perturbation of particles by an external field or of a nonequilibrium perturbation, resulting in changes in one-particle energies. Because particles are correlated through their mutual interactions, such variations in single particle energies result in a variation of the collective states for the system as a whole and, consequently, of the nonequilibrium partition function. This variation in  $\Xi$  is exploited to obtain an evolution equation for a pair of two-particle distribution functions in the functional derivative method.

The first variation of  $\Xi$  from variations in single particle energies is

$$\delta\Xi[\varepsilon] = \sum_{N \geq 0} \frac{\mathfrak{z}^N}{c} \sum_{j=1}^N \int dx^{(N)} \delta e_j(x_j) e^{-E^{(N)}(x^{(N)})} \prod_{k \neq j}^N e_\varepsilon(x_k). \quad (9.26)$$

This means that the first functional derivative is given by

$$e_\varepsilon(x_1) \frac{\delta\Xi[\varepsilon]}{\delta e_\varepsilon(x_1)} = \sum_{N \geq 0} \frac{N\mathfrak{z}^N}{c} \int dx^{(N-1)} e^{-E^{(N)}(x^{(N)})} \prod_{k=1}^N e_\varepsilon(x_k), \quad (9.27)$$

where

$$dx^{(N-1)} = \prod_{k \neq 1}^N dx_k.$$

According to the definitions of reduced distribution function  $f^{(1)}$  and the probability distribution function  $P_N$  introduced earlier, this functional derivative is related to the singlet distribution function:

$$\frac{\delta \ln \Xi[\varepsilon]}{\delta \ln e_\varepsilon(x_1)} = f^{(1)}(x_1). \quad (9.28)$$

Note that  $f^{(1)}(x_1)$  itself is a functional of  $e_\varepsilon(x_1)$ , namely,  $f^{(1)}(x_1|e_\varepsilon)$ , but this fact is not made explicit for brevity of notation.

Because

$$\delta e_\varepsilon(x_1) = \int dx_2 \frac{\delta e_\varepsilon(x_1)}{\delta e_\varepsilon(x_2)} \delta e_\varepsilon(x_2), \quad (9.29)$$

but  $e_\varepsilon(x_i)$  are independent, we conclude that the functional derivative involved in this integral must be a delta function:

$$\frac{\delta e_\varepsilon(x_1)}{\delta e_\varepsilon(x_2)} = \delta(x_1 - x_2). \quad (9.30)$$

Here the Dirac delta function  $\delta(x_1 - x_2)$  is an abbreviation for the six-dimensional delta function in the phase space:

$$\delta(x_1 - x_2) = \delta(\mathbf{p}_1 - \mathbf{p}_2) \delta(\mathbf{r}_1 - \mathbf{r}_2). \quad (9.31)$$

By using the identity (9.30), we obtain the functional derivative of  $f^{(1)}(x_1)$  in the form

$$\begin{aligned} \frac{\delta f^{(1)}(x_1)}{\delta \ln e_\varepsilon(x_2)} &= \delta(x_1 - x_2) \frac{\delta \ln \Xi[\varepsilon]}{\delta \ln e_\varepsilon(x_1)} - \frac{\delta \ln \Xi[\varepsilon]}{\delta \ln e_\varepsilon(x_1)} \frac{\delta \ln \Xi[\varepsilon]}{\delta \ln e_\varepsilon(x_2)} \\ &+ \frac{e_\varepsilon(x_1) e_\varepsilon(x_2)}{\Xi[\varepsilon]} \frac{\delta^2 \Xi[\varepsilon]}{\delta e_\varepsilon(x_1) \delta e_\varepsilon(x_2)}. \end{aligned} \quad (9.32)$$

Taking the variation of  $\delta \Xi[\varepsilon]$  once again, that is, taking the second variation of  $\Xi[\varepsilon]$ , and using the definition of reduced distribution functions, we obtain

$$\frac{e_\varepsilon(x_1) e_\varepsilon(x_2)}{\Xi[\varepsilon]} \frac{\delta^2 \Xi[\varepsilon]}{\delta e_\varepsilon(x_1) \delta e_\varepsilon(x_2)} = f^{(2)}(x_1, x_2) \quad (9.33)$$

and finally the functional derivative on the left-hand side of (9.32) in the form,

$$\frac{\delta f^{(1)}(x_1)}{\delta \ln e_\varepsilon(x_2)} = \delta(x_1 - x_2) f^{(1)}(x_1) - f^{(1)}(x_1) f^{(1)}(x_2) + f^{(2)}(x_1, x_2). \quad (9.34)$$

The structure of the right-hand side of this equation motivates the definitions of dynamic Ursell functions

$$U^{(1)}(x_1) = f^{(1)}(x_1),$$

$$U^{(2)}(x_1, x_2) = f^{(2)}(x_1, x_2) - f^{(1)}(x_1) f^{(1)}(x_2),$$

$$U^{(3)}(x_1, x_2, x_3) = f^{(3)}(x_1, x_2, x_3) - f^{(2)}(x_1, x_2) f^{(1)}(x_3)$$

$$\begin{aligned} &- f^{(2)}(x_1, x_3) f^{(1)}(x_2) - f^{(2)}(x_2, x_3) f^{(1)}(x_1) \\ &+ 2 f^{(1)}(x_1) f^{(1)}(x_2) f^{(1)}(x_3), \end{aligned} \quad (9.35)$$

$\dots$

which is the nonequilibrium version of the equilibrium Ursell functions [16] used in equilibrium statistical mechanics. Then it is possible to show that  $U^{(2)}(x_1, x_2)$  is related to the second functional derivative in the following manner:

$$e_\varepsilon(x_1) e_\varepsilon(x_2) \frac{\delta^2 \ln \Xi[\varepsilon]}{\delta e_\varepsilon(x_1) \delta e_\varepsilon(x_2)} = U^{(2)}(x_1, x_2). \quad (9.36)$$

In general,

$$e_\varepsilon(x_1) \cdots e_\varepsilon(x_n) \frac{\delta^n \ln \Xi[\varepsilon]}{\delta e_\varepsilon(x_1) \cdots \delta e_\varepsilon(x_n)} = U^{(n)}(x_1, \dots, x_n). \quad (9.37)$$

In analogy to the equilibrium theory [9], the nonequilibrium direct pair distribution function  $c^{(2)}(x_1, x_3)$  may be defined by the formula,

$$\frac{\delta \ln e_\varepsilon(x_1)}{\delta f^{(1)}(x_3)} = \frac{\delta(x_1 - x_3)}{f^{(1)}(x_3)} - c^{(2)}(x_1, x_3). \quad (9.38)$$

The functional derivative on the left-hand side is the inverse of the functional derivative giving the relation in (9.34) and thus of the nonequilibrium Ursell function  $U^{(2)}(x_1, x_2)$ . For this reason, the nonequilibrium direct correlation function  $c^{(2)}(x_1, x_3)$  may be regarded as related to the inverse of  $U^{(2)}(x_1, x_2)$ . Because

$$\begin{aligned} \delta(x_1 - x_2) &= \int dx_3 \frac{\delta e_\varepsilon(x_1)}{\delta f^{(1)}(x_3)} \frac{\delta f^{(1)}(x_3)}{\delta e_\varepsilon(x_2)} \\ &= \frac{e_\varepsilon(x_1)}{e_\varepsilon(x_2)} \int dx_3 \frac{\delta \ln e_\varepsilon(x_1)}{\delta f^{(1)}(x_3)} \frac{\delta f^{(1)}(x_3)}{\delta \ln e_\varepsilon(x_2)}, \end{aligned} \quad (9.39)$$

insertion of the functional derivatives, calculated earlier, in the right-hand side of this equation yields the following relation:

$$\begin{aligned} \delta(x_1 - x_2) &= \frac{e_\varepsilon(x_1)}{e_\varepsilon(x_2)} \int dx_3 \left[ \frac{\delta(x_1 - x_3)}{f^{(1)}(x_3)} - c^{(2)}(x_1, x_3) \right] \\ &\quad \times \left[ \delta(x_3 - x_2) f^{(1)}(x_3) + U^{(2)}(x_3, x_2) \right]. \end{aligned} \quad (9.40)$$

This is the inverse relation between two operators represented by the quantities in the square brackets, which will be more precisely formalized later. On expanding the integrand on the right-hand side, there follows the equation

$$f^{(1)}(x_2) c^{(2)}(x_1, x_2) - \frac{U^{(2)}(x_1, x_2)}{f^{(1)}(x_1)} + \int dx_3 c^{(2)}(x_1, x_3) U^{(2)}(x_3, x_2) = 0. \quad (9.41)$$

If the total nonequilibrium correlation function  $h^{(2)}(x_1, x_2)$  is defined by

$$U^{(2)}(x_3, x_2) = f^{(1)}(x_1) f^{(1)}(x_2) h^{(2)}(x_1, x_2), \quad (9.42)$$

then (9.41), when divided by  $f^{(1)}(x_2)$ , yields the equation

$$\begin{aligned} h^{(2)}(x_1, x_2, t) &= c^{(2)}(x_1, x_2, t) \\ &+ \int dx_3 c^{(2)}(x_1, x_3, t) f^{(1)}(x_3, t) h^{(2)}(x_3, x_2, t). \end{aligned} \quad (9.43)$$

This is the dynamic Ornstein–Zernike equation for nonequilibrium pair distribution functions which we set out to derive. Note that  $x_i$  ( $i = 1, 2, 3$ ) are the phases of the particles involved. We have restored the time dependence to make it explicit in this equation.

In connection with this equation and the definition of  $h^{(2)}(x_1, x_2, t)$  in (9.42), the following must be noted: Because

$$f^{(1)}(x_1, t) f^{(1)}(x_2, t) h^{(2)}(x_1, x_2, t) = f^{(2)}(x_1, x_2, t) - f^{(1)}(x_1, t) f^{(1)}(x_2, t),$$

if the pair correlation function  $g^{(2)}(x_1, x_2, t)$  is defined by the relation

$$f^{(2)}(x_1, x_2, t) = f^{(1)}(x_1, t) f^{(1)}(x_2, t) g^{(2)}(x_1, x_2, t), \quad (9.44)$$

it then follows that there holds the relation

$$h^{(2)}(x_1, x_2, t) = g^{(2)}(x_1, x_2, t) - 1. \quad (9.45)$$

The DOZ equation (9.43) is isomorphic to the equilibrium OZ equation for pair correlation functions in the configuration space. However, it must be emphasized that the former lives in the phase space  $(x_1, x_2, x_3)$ , not in the configuration space  $(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ , as does the latter. The DOZ integral equation presented is new to nonequilibrium statistical mechanics and replaces the nonequilibrium BBGKY hierarchy. The pair distribution functions defined by the DOZ integral equation can be used to express macroscopic properties in nonequilibrium statistical mechanics if a suitable closure is made for it. This will be discussed later in this chapter.

### 9.3 Connection with Existing Theory

The DOZ integral equation (9.43) is given in the phase space, which is larger in dimension than the configuration space of two particles in which the equilibrium OZ equation lives. It is useful to examine under what condition (9.43) gives the equilibrium OZ equation and also the integral equation for the non-equilibrium pair correlation function used for studying the effect of shearing on the nonequilibrium liquid structure in the literature [17, 18].

For this specific purpose, it is useful to define the reduced distribution function by

$$n(\mathbf{r}_1, t) = \int d\mathbf{p}_1 f^{(1)}(x_1, t), \quad (9.46)$$

which, on integration over volume and division by volume, gives the mean bulk density

$$n = \frac{\bar{N}}{V} = V^{-1} \int d\mathbf{r} n(\mathbf{r}, t) = V^{-1} \int dx f^{(1)}(x, t). \quad (9.47)$$

Recall that according to (9.19)

$$\int dx f^{(1)}(x, t) = \langle N \rangle. \quad (9.48)$$

Hence,

$$\bar{N} = \langle N \rangle. \quad (9.49)$$

Therefore,  $n(\mathbf{r}, t)$  is the probability of finding a particle in the volume element  $d\mathbf{r}$  around position  $\mathbf{r}$  in the fluid. In a uniform fluid with translational symmetry  $n(\mathbf{r}, t)$  is independent of  $\mathbf{r}$ , and it is identical with the bulk density  $n$ , which may still depend on time. In the light of this meaning for  $n(\mathbf{r}, t)$ , it will be convenient to factor  $f^{(1)}(x_1, t)$  as

$$f^{(1)}(x_1, t) = n(\mathbf{r}_1, t) \phi(x_1, t), \quad (9.50)$$

where  $\phi(x_1, t)$  is such that

$$\int d\mathbf{p}_1 \phi(x_1, t) = 1. \quad (9.51)$$

In the limit of equilibrium, the function  $\phi(x_1, t)$  becomes the local equilibrium Boltzmann factor of a single particle energy. By following the manner in which the density distribution is defined, the pair correlation function  $f^{(2)}(x_1, x_2, t)$  may be integrated over the momentum space, and the nonequilibrium pair density distribution  $n^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t)$  may be defined by the integral

$$n(\mathbf{r}_1, t) n(\mathbf{r}_2, t) n^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t) = \int d\mathbf{p}_1 \int d\mathbf{p}_2 f^{(2)}(x_1, x_2, t). \quad (9.52)$$

Therefore,  $n^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t)$  is a reduced distribution function of  $f^{(2)}(x_1, x_2, t)$ . Substituting (9.44) into (9.52) and using the factorized singlet distribution function in (9.50), a more precise meaning of  $n^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t)$  is gained:

$$n^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t) = \int d\mathbf{p}_1 \int d\mathbf{p}_2 \phi(x_1, t) \phi(x_2, t) g^{(2)}(x_1, x_2, t). \quad (9.53)$$

If the nonequilibrium pair correlation function  $g^{(2)}(x_1, x_2, t)$  is independent of momenta to an approximation, that is, if

$$g^{(2)}(x_1, x_2, t) \simeq g^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t), \quad (9.54)$$

then  $n^{(2)}$  is simply equal to  $g^{(2)}$ :

$$n^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t) \simeq g^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t). \quad (9.55)$$

According to the various quantities defined earlier, we find

$$\begin{aligned}\varrho^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t) &\equiv n^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t) - 1 \\ &= \int d\mathbf{p}_1 \int d\mathbf{p}_2 \phi(x_1, t) \phi(x_2, t) h^{(2)}(x_1, x_2, t),\end{aligned}\quad (9.56)$$

which, in the approximation for  $g^{(2)}$  in (9.54), takes the form

$$\varrho^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t) \simeq h^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t). \quad (9.57)$$

A reduced form of the nonequilibrium direct correlation function can be similarly defined. Let

$$\gamma(\mathbf{r}_1, \mathbf{r}_2, t) = \int d\mathbf{p}_1 \int d\mathbf{p}_2 \phi(x_1, t) \phi(x_2, t) c^{(2)}(x_1, x_2, t). \quad (9.58)$$

It then reduces to

$$\gamma(\mathbf{r}_1, \mathbf{r}_2, t) \simeq c^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t), \quad (9.59)$$

if the nonequilibrium direct correlation function is independent of the momenta,

$$c^{(2)}(x_1, x_2, t) \simeq c^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t). \quad (9.60)$$

If the approximations (9.54) and (9.60) are used in the DOZ integral equation, it readily reduces to the form in the configuration space

$$h^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t) = c^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t) + \int d\mathbf{r}_3 c^{(2)}(\mathbf{r}_1, \mathbf{r}_3, t) n(\mathbf{r}_3, t) h^{(2)}(\mathbf{r}_3, \mathbf{r}_2, t). \quad (9.61)$$

This is the nonequilibrium OZ equation that was obtained from the non-equilibrium Kirkwood hierarchy under a set of approximations and used for studying shearing effects in [1, 17, 18]. In time-independent processes where  $h^{(2)}$  and  $c^{(2)}$  become independent of time, (9.61) clearly becomes the equilibrium OZ equation. The present DOZ integral equation therefore contains the equilibrium OZ equation as well as the nonequilibrium OZ equation in the configuration space that has been used in the study of shear-induced effects on simple liquids in [1, 17, 18] mentioned earlier.

## 9.4 Local Equilibrium Equation of State

To calculate nonequilibrium observables by using the nonequilibrium ensemble distribution function, it is necessary to define and calculate local equilibrium variables because they will serve as the variables of the reference state with respect to which nonequilibrium effects on the macroscopic observables may be calculated. The local equilibrium variables are defined by the local equilibrium

distribution function (9.2) in which the intensive variables such as temperature  $T$ , chemical potential  $\hat{\mu}_a$ , and pressure  $p$  depend on the position of the small local volume of interest. Within the small local volume the intensive variables are uniform, but, being field variables obeying hydrodynamic field equations, they vary from elementary volume to elementary volume, as mentioned earlier.

#### 9.4.1 Virial Equation of State

In a nonequilibrium situation the pressure in a fluid is not necessarily isotropic because the pressure applied in, say, the  $z$  direction of the coordinate system may be different from those in the transversal directions because of some conditions in a nonequilibrium state. An example of such a situation may be sound wave propagation or heat flow in a fluid. In such a nonequilibrium situation the aforementioned reference variables cannot be arbitrarily chosen, but their choice must be consistent with the generalized thermodynamics [3] of the fluid. Because the selection has an important bearing on the definition of non-equilibrium observables themselves employed in generalized thermodynamics of fluids, it is necessary to examine the statistical mechanical definitions of reference variables. In this subsection, we pay special attention to pressure.

We define the local equilibrium ‘pressure’  $\mathfrak{p}$  as the quantity equal to the mean of normal stresses

$$\mathfrak{p} = \frac{1}{3} \text{Tr} \left\langle \sum_{j=1}^N \left[ m \mathbf{C}_j \mathbf{C}_j \delta(\mathbf{r}_j - \mathbf{r}) + \frac{1}{2} \sum_{j \neq k=1}^N \mathbf{W}_{jk} \delta(\mathbf{r}_k - \mathbf{r}) \right] \right\rangle_{\text{eq}} , \quad (9.62)$$

where the subscript eq means that the averaging is performed with  $F_{\text{eq}}^{(N)}$  and  $\mathbf{W}_{jk}$  is a virial tensor operator defined previously; we present it once again for the sake of uninterrupted reading:

$$\mathbf{W}_{jk} = \int_0^1 d\lambda \mathbf{r}_{jk} \mathbf{F}_{jk}(\mathbf{r}_{jk}) \exp(-\lambda \mathbf{r}_{jk} \cdot \partial/\partial \mathbf{r}) . \quad (9.63)$$

In this expression,  $\mathbf{F}_{jk}$  is the intermolecular force between particles  $j$  and  $k$  and  $\mathbf{r}_{jk} = \mathbf{r}_j - \mathbf{r}_k$ .

As will be seen presently, the expression for  $\mathfrak{p}$  in (9.62) is not for hydrostatic pressure because of the spatial nonuniformity of density. It is reducible to a form given in terms of lower order reduced distribution functions. By using the reduced distribution functions defined earlier, we obtain from (9.62) the expression

$$\begin{aligned} \mathfrak{p} = & \frac{1}{3} \int d\mathbf{p}_1 m C^2 f_{\text{eq}}^{(1)}(\mathbf{r}, \mathbf{p}_1) \\ & + \frac{1}{6} \int dx_1 \int dx_2 \text{Tr} \mathbf{W}_{12}(\mathbf{r}_{12}) \delta(\mathbf{r}_2 - \mathbf{r}) f_{\text{eq}}^{(2)}(x_1, x_2) , \end{aligned} \quad (9.64)$$

where  $f_{\text{eq}}^{(1)}(\mathbf{r}, \mathbf{p}_1)$  and  $f_{\text{eq}}^{(2)}(x_1, x_2)$  are the local equilibrium forms of nonequilibrium reduced distribution functions  $f^{(1)}(\mathbf{r}, \mathbf{p}_1; t)$  and  $f^{(2)}(x_1, x_2, t)$ , respectively. This form of pressure equation can be recast into a form more comparable with the equilibrium counterpart.

In view of the reduced distribution function in (9.46) and (9.50), the first term—the kinetic term—on the right of (9.64) may be written as

$$\frac{1}{3} \int d\mathbf{p}_1 mC^2 f_{\text{eq}}^{(1)}(\mathbf{r}, \mathbf{p}_1) = \frac{1}{3} n(\mathbf{r}) \int d\mathbf{p}_1 mC^2 \phi_{\text{eq}}(\mathbf{r}, \mathbf{p}_1), \quad (9.65)$$

where  $\phi_{\text{eq}}(\mathbf{r}, \mathbf{p}_1)$  is the local equilibrium form of  $\phi(\mathbf{r}, \mathbf{p}_1, t)$ ;  $n(\mathbf{r}) \phi_{\text{eq}}(\mathbf{r}, \mathbf{p}_1)$  is simply the local equilibrium Maxwell distribution function. It is consistent with the generalized thermodynamic theory [2] of nonequilibrium fluids to put the average of the peculiar velocity squared on the right of (9.65) in a more familiar looking form of the local temperature of the fluid<sup>1</sup>

$$\frac{1}{3} \int d\mathbf{p}_1 mC^2 \phi_{\text{eq}}(\mathbf{r}, \mathbf{p}_1) = \beta^{-1}(\mathbf{r}) = k_B T(\mathbf{r}). \quad (9.66)$$

This can be easily verified with the local equilibrium Maxwell distribution function for  $n(\mathbf{r}) \phi_{\text{eq}}(\mathbf{r}, \mathbf{p}_1)$ .

Because  $\mathbf{W}_{12}(\mathbf{r}_{12})$  is an operator in the configuration space, it is possible to reduce the distribution function  $f_{\text{eq}}^{(2)}(x_1, x_2)$  to the local equilibrium version of the form given in (9.52) and cast the equation of state in the form

$$\begin{aligned} p = & n(\mathbf{r}) k_B T(\mathbf{r}) + \frac{1}{6} \int_0^1 d\lambda \int d\mathbf{r}_1 \int d\mathbf{r}_2 \mathbf{r}_{12} \cdot \mathbf{F}_{12} \delta(\mathbf{r}_2 + \lambda \mathbf{r}_{12} - \mathbf{r}) \\ & \times n(\mathbf{r}_1) n(\mathbf{r}_2) g_{\text{eq}}^{(2)}(\mathbf{r}_1, \mathbf{r}_2), \end{aligned} \quad (9.67)$$

for which we have used the definition of  $\mathbf{W}_{jk}$ . The density  $n(\mathbf{r})$  and the temperature  $T(\mathbf{r})$  in this expression still can vary from elementary volume to elementary volume. This is the local equilibrium virial form for pressure when the virial tensor is used for the definition of pressure, but it differs from the equilibrium virial equation of state [15]

$$p = n k_B T + \frac{1}{6} n^2 \int d\mathbf{r}_{12} r_{12} F_{12} g_{\text{eq}}(r_{12}), \quad (9.68)$$

which gives the hydrostatic pressure that is spatially uniform and isotropic.

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<sup>1</sup> The definition of temperature for a fluid in a nonequilibrium state is subtle and requires careful thought. Here, the symbol  $T(\mathbf{r})$  may be regarded as a representation of the average on the left, which is the kinetic energy part of the pressure exerted by the fluid in a nonequilibrium state. Within the framework of the generalized thermodynamics implied by the nonequilibrium grand canonical ensemble distribution function  $F_c^{(N)}$ , this representation for  $T(\mathbf{r})$  is consistent with  $\beta = 1/k_B T(\mathbf{r}, t)$  in  $F_c^{(N)}$ . See [2].

On changing variables to the center of mass coordinate  $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$  and the relative coordinate  $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$  and performing the integration over  $\mathbf{R}$ , there follows from (9.67) the equation:

$$\mathfrak{p} = n(\mathbf{r}) k_B T(\mathbf{r}) \quad (9.69)$$

$$+ \frac{1}{6} \int_0^1 d\lambda \int d\mathbf{r}_{12} \mathbf{r}_{12} \cdot \mathbf{F}_{12} n[\mathbf{r} + (1 - \lambda)\mathbf{r}_{12}] n(\mathbf{r} - \lambda\mathbf{r}_{12}) g_{\text{eq}}^{(2)}(\mathbf{r}_{12}).$$

This expression indicates that the density can vary over the intermolecular force range and such a variation can contribute to the equation of state if the density is not uniform. To see this effect, we expand the bulk densities in series of  $\mathbf{r}_{12}$ :

$$\begin{aligned} n[\mathbf{r} + (1 - \lambda)\mathbf{r}_{12}] &= n(\mathbf{r}) + (1 - \lambda)\mathbf{r}_{12} \cdot \nabla n(\mathbf{r}) + \dots \\ n(\mathbf{r} - \lambda\mathbf{r}_{12}) &= n(\mathbf{r}) - \lambda\mathbf{r}_{12} \cdot \nabla n(\mathbf{r}) + \dots \end{aligned} \quad (9.70)$$

and insert the expansions in (9.69) to obtain the equation of state in the form,

$$\begin{aligned} \mathfrak{p} = n(\mathbf{r}) k_B T(\mathbf{r}) &+ \frac{1}{6} n^2(\mathbf{r}) \int d\mathbf{r}_{12} r_{12} F_{12} g_{\text{eq}}^{(2)}(\mathbf{r}_{12}) \\ &- \frac{1}{18} [\nabla n(\mathbf{r})] \cdot [\nabla n(\mathbf{r})] \int d\mathbf{r}_{12} r_{12}^3 F_{12} g_{\text{eq}}^{(2)}(\mathbf{r}_{12}) \\ &+ O([n(\mathbf{r}, t)]^4) + \dots \end{aligned} \quad (9.71)$$

Thus we see that density variations over the distance of the intermolecular force range contribute to the local equilibrium equation of state, which to the leading order is proportional to the square of the density gradient. When these correction terms are neglected or as the density becomes uniform over space, the equation of state for hydrostatic pressure (9.68) given earlier arises.

As will be seen presently and was done in the formulation of generalized thermodynamics [3] and also generalized hydrodynamics [2], the excess normal stress is defined with reference to the hydrostatic pressure, and the consideration for  $\mathfrak{p}$  given in (9.71) suggests that  $\mathfrak{p}$  cannot be in general the reference pressure for studying nonequilibrium effects on the stress in a fluid unless a physical consideration warrants it otherwise. The “pressure”  $\mathfrak{p}$  is, a normal stress, which is a kind of nonequilibrium pressure. We will return to this aspect of nonequilibrium effects later when linear transport processes are discussed. Nevertheless, before proceeding to discuss linear transport processes, we note that the density fluctuations mentioned arise from the virial tensor given in terms of the displacement operator, which has been commonly ignored in the statistical mechanics of liquids in the literature. It is important that it is not ignored if transport processes are to be understood properly from the viewpoint of molecular theory.

### 9.4.2 Compressibility of Nonequilibrium Fluids

In equilibrium statistical mechanics the equation of state can also be obtained from the isothermal compressibility of a fluid [12]. This results in the pressure expressed in terms of the direct correlation function obeying the OZ integral equation. Here, we would like to examine the isothermal compressibility of nonequilibrium fluids and its relation to the nonequilibrium correlation functions introduced earlier.

For this purpose, let us now return to the normalization integral (9.19) for  $f^{(n)}$ . By subtracting the square of the normalization integral of  $f^{(1)}$  from the normalization integral of  $f^{(2)}$ , there follows the relation:

$$\frac{1}{\langle N \rangle} \int dx_1 \int dx_2 f^{(1)}(x_1; t) f^{(1)}(x_2; t) h^{(2)}(x_1, x_2; t) = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} - 1. \quad (9.72)$$

The density fluctuation term on the right-hand side of this equation can be related to thermodynamic quantities as in equilibrium theory. This is possible because the extended Gibbs relation exists [2, 3] for the calortropy density  $\hat{\Psi}$

$$Td\hat{\Psi} = d\mathcal{E} + pdv + \sum_{q \geq 1} X_q d\hat{\Phi}_q. \quad (9.73)$$

This differential form is for a single-component system. In this expression,  $\mathcal{E}$  is the internal energy density and  $\hat{\Phi}_q$  ( $q \geq 1$ ) are nonconserved variables whose constitutive equations have been derived in earlier chapters for systems removed from equilibrium. The calortropy density  $\hat{\Psi}$  reduces to the equilibrium (Clausius) entropy as the system reaches equilibrium, that is, as  $X_q \rightarrow 0$  for all  $q$ . This extended Gibbs equation is accompanied by the nonequilibrium Gibbs–Duhem equation [2, 3],

$$d\mu = -\hat{\Psi}dT + vdp + \sum_{q \geq 1} \hat{\Phi}_q dX_q, \quad (9.74)$$

which may be regarded as the integrability condition [19] for the extended Gibbs relation, because addition of (9.73) and (9.74) gives an integral of the extended Gibbs relation. From the nonequilibrium Gibbs–Duhem equation follows the thermodynamic relation

$$\left( \frac{\partial \mu}{\partial v} \right)_{T,X} = v \left( \frac{\partial p}{\partial v} \right)_{T,X}. \quad (9.75)$$

Note that this relation is for nonequilibrium because of the presence of the condition on  $X$  in the subscript. Because  $n = 1/v$ , it follows that  $dn = -v^{-2}dv$  and, if  $V$  is kept constant,

$$\langle N \rangle \left( \frac{\partial \mu}{\partial \langle N \rangle} \right)_{V,T,X} = \left( \frac{\partial p}{\partial n} \right)_{T,X}. \quad (9.76)$$

Since in the grand ensemble theory

$$\left(\frac{\partial n}{\partial \mu}\right)_{V,T,X} = \beta V^{-1} \left[ \langle N^2 \rangle - \langle N \rangle^2 \right], \quad (9.77)$$

we find

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \beta^{-1} \left(\frac{\partial n}{\partial p}\right)_{T,X} \equiv n\beta^{-1}\kappa. \quad (9.78)$$

Therefore, the density fluctuation is related to the isothermal compressibility of the system subjected to the nonequilibrium disturbance characterized by  $\{X_q\}$ —generalized potentials [2, 3]. On inserting this result in (9.72), there follows the equation;

$$\frac{1}{\langle N \rangle} \int dx_1 \int dx_2 f^{(1)}(x_1; t) f^{(1)}(x_2; t) h^{(2)}(x_1, x_2; t) = n\beta^{-1}\kappa - 1. \quad (9.79)$$

This form is isomorphic to the equilibrium counterpart [12, 15], which relates the total correlation function  $h^{(2)}(r_{12})$  to the isothermal compressibility of the fluid:

$$n \int d\mathbf{r}_{12} h_{\text{eq}}^{(2)}(r_{12}) = n\beta^{-1}\kappa_{\text{eq}} - 1, \quad (9.80)$$

where  $h_{\text{eq}}^{(2)}(r_{12})$  is the equilibrium counterpart of  $h^{(2)}(x_1, x_2; t)$  and  $\kappa_{\text{eq}}$  is the isothermal compressibility of the equilibrium fluid. It is understandable that similar relations should hold because the density fluctuations can occur as the pressure is varied in the fluid regardless of whether the system is in an equilibrium or nonequilibrium state. Furthermore, the mathematical structure [19] of nonequilibrium thermodynamics is parallel to that of equilibrium thermodynamics owing to the extended Gibbs relation (9.73) and the nonequilibrium Gibbs–Duhem equation (9.74).

#### 9.4.3 Abstract Form of the Dynamic Ornstein–Zernike Equation

To learn about the relation of this compressibility equation to the DOZ equation we return to its precursor to the DOZ integral equation (9.40) and examine it in more detail. Because

$$\frac{e_\varepsilon(x_2)}{e_\varepsilon(x_1)} \delta(x_1 - x_2) = \delta(x_1 - x_2),$$

Equation (9.40) may be written as

$$\begin{aligned} \delta(x_1 - x_2) &= \int dx_3 \left[ \frac{\delta(x_1 - x_3)}{f^{(1)}(x_3, t)} - c^{(2)}(x_1, x_3, t) \right] \\ &\times \left[ \delta(x_3 - x_2) f^{(1)}(x_3, t) + f^{(1)}(x_3, t) h^{(2)}(x_3, x_2, t) f^{(1)}(x_2, t) \right]. \end{aligned} \quad (9.81)$$

Let us define abstract operators  $\mathbf{C}$ ,  $\mathbf{H}$ , and  $\mathbf{f}$  in the phase space spanned by vectors of phase  $x$ . Considerable insight into this equation is gained if we introduce in the phase space Dirac's bra and ket vectors [20, 21],  $\langle x |$  and  $|x \rangle$ , which are normalized to unity  $\langle x | x \rangle = 1$ . The phase space representations of the aforementioned abstract operators then are postulated to be given by

$$\langle x_1 | \mathbf{f} | x_2 \rangle = f^{(1)}(x_2; t) \delta(x_1 - x_2), \quad (9.82)$$

$$\langle x_1 | \mathbf{f}^{-1} | x_2 \rangle = \frac{\delta(x_1 - x_2)}{f^{(1)}(x_2; t)}, \quad (9.83)$$

$$\begin{aligned} \langle x_3 | \mathbf{H} | x_2 \rangle &= f^{(1)}(x_3, t) \delta(x_3 - x_2) \\ &\quad + f^{(1)}(x_3, t) h^{(2)}(x_3, x_2, t) f^{(1)}(x_2, t), \end{aligned} \quad (9.84)$$

$$\langle x_1 | \mathbf{C} | x_3 \rangle = \frac{\delta(x_1 - x_3)}{f^{(1)}(x_3, t)} - c^{(2)}(x_1, x_3, t). \quad (9.85)$$

These definitions give ways to compute the abstract operators on the left according to the right-hand side. Thus, with the representations of the total and direct correlation functions

$$\langle x_3 | \mathbf{h} | x_2 \rangle = h^{(2)}(x_3, x_2, t), \quad (9.86)$$

$$\langle x_1 | \mathbf{c} | x_3 \rangle = c^{(2)}(x_1, x_3, t), \quad (9.87)$$

we may write  $\mathbf{H}$  and  $\mathbf{C}$  in the following operator forms:

$$\begin{aligned} \mathbf{H} &= \mathbf{f} + \mathbf{f} \mathbf{h} \mathbf{f}, \\ \mathbf{C} &= \mathbf{f}^{-1} - \mathbf{c}. \end{aligned} \quad (9.88)$$

With the representations of the abstract operators, as in (9.82)–(9.87), (9.81) can be written as

$$\int dx_3 \langle x_1 | \mathbf{C} | x_3 \rangle \langle x_3 | \mathbf{H} | x_2 \rangle = \delta(x_1 - x_2). \quad (9.89)$$

This implies that the abstract operators  $\mathbf{H}$  and  $\mathbf{C}$  are inversely related to each other. Written in a more explicit form, the inverse relation is

$$(\mathbf{f}^{-1} - \mathbf{c})(\mathbf{f} + \mathbf{f} \mathbf{h} \mathbf{f}) = \mathbf{I}. \quad (9.90)$$

It is clear from this expression that the two factors on the left are inverse to each other. By expanding the factors on the left of this equation, this relation may be equivalently expressed as

$$\mathbf{h} = \mathbf{c} + \mathbf{c} \mathbf{f} \mathbf{h}, \quad (9.91)$$

which is the abstract operator version of the DOZ integral equation (9.61). From (9.90) we find

$$\mathbf{f}\mathbf{h}\mathbf{f} = (\mathbf{f}^{-1} - \mathbf{c})^{-1} - \mathbf{f} = (\mathbf{f}^{-1} - \mathbf{c})^{-1} \mathbf{c}\mathbf{f} = \mathbf{f}\mathbf{c} (\mathbf{f}^{-1} - \mathbf{c})^{-1}. \quad (9.92)$$

Alternatively,

$$\mathbf{c} = (\mathbf{f} + \mathbf{f}\mathbf{h}\mathbf{f})^{-1} \mathbf{f}\mathbf{h} = \mathbf{h}\mathbf{f} (\mathbf{f} + \mathbf{f}\mathbf{h}\mathbf{f})^{-1}. \quad (9.93)$$

By using these formal abstract operator relations, it is possible to examine the dynamic isothermal compressibility formula.

Because the phase space representation of (9.92) is

$$\langle x_1 | \mathbf{f}\mathbf{h}\mathbf{f} | x_2 \rangle = \left\langle x_1 \left| (\mathbf{f}^{-1} - \mathbf{c})^{-1} \right| x_2 \right\rangle - f^{(1)}(x_2; t) \delta(x_1 - x_2), \quad (9.94)$$

it follows from (9.79) that the dynamic isothermal compressibility can be obtained from the formula,

$$n\beta^{-1}\kappa = \frac{\int dx_1 \int dx_2 \left\langle x_1 \left| \mathbf{f} (\mathbf{I} - \mathbf{c}\mathbf{f})^{-1} \right| x_2 \right\rangle}{\int dx_1 \int dx_2 \langle x_1 | \mathbf{f} | x_2 \rangle}. \quad (9.95)$$

For this expression, note that with the bra-ket notation  $\langle N \rangle$  may be written as

$$\begin{aligned} \langle N \rangle &= \int dx f^{(1)}(x, t) = \int dx_1 \int dx_2 f^{(1)}(x_2, t) \delta(x_1 - x_2) \\ &= \int dx_1 \int dx_2 \langle x_1 | \mathbf{f} | x_2 \rangle. \end{aligned} \quad (9.96)$$

Compare it with (9.47), which follows if (9.82) is used. We have thus seen that the bra-ket notation puts nonequilibrium thermodynamic quantities in insightful forms, which are parallel to their equilibrium counterparts, and also provides computational algorithms for them. The isomorphism of equilibrium and nonequilibrium OZ equations suggests that the dynamic OZ equation may be solvable by Fourier transform in the phase space, if a suitable closure is introduced for the dynamic direct correlation function. This subject, however, will not be discussed here.

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## Density Fluctuation Theory: Simple Fluids

We have presented in Chaps. 7 and 8 constitutive equations for various macroscopic fluxes, such as the stress tensor, heat flux, and diffusion fluxes, in dense gases and liquids. They have been derived from the generalized Boltzmann equations for dense fluids and are generally nonlinear with regard to the fluxes, namely, nonconserved variables. On linearizing the steady-state constitutive equations with respect to the fluxes and the thermodynamic gradients driving the former and comparing them with the phenomenological thermodynamic force–flux relations, such as Newtonian law of viscosity, Fourier’s law of heat conduction, and Fick’s law of diffusion, the kinetic theory formulas have been derived for the linear transport coefficients of such fluids. The linear transport coefficients thus obtained are given in terms of collision bracket integrals involving  $N$  particle dynamics, and they can be shown to reduce to the Chapman–Enskog theory formulas for transport coefficients of dilute gases, as the density diminishes. Although formally parallel to the well-established Boltzmann kinetic theory approach to transport processes in dilute gases and the theory has been applied [1, 2] to dense hard sphere fluids to calculate the viscosity and thermal conductivity that show correctly behaved density dependences, the theory has not been applied to dense fluids obeying a more realistic potential model, such as the Lennard-Jones potential, because of the difficulty and labor involved in solving the associated many-particle collision dynamics and calculating cross sections for collision processes. Therefore, the Chapman–Enskog approach [3] to the generalized Boltzmann equation still awaits achieving its goal, which is to obtain practical forms for computing the density and temperature dependence of transport coefficients.

In this and subsequent chapters in this work, we take an alternative approach within the general framework of the generalized Boltzmann equation and develop a more readily practicable method of calculating the desired transport coefficients. The generalized Boltzmann equation is still at the foundation of the present approach. Not only is the nonequilibrium canonical or grand ensemble distribution function employed in the development of the theory provided by the generalized Boltzmann equation, but also the underlying

dynamic Ornstein–Zernike (DOZ) equation and the nonlinear constitutive equations, both of which stem from the generalized Boltzmann equation, are required to extend the theory into the nonlinear regime beyond the treatment given in the present density fluctuation theory of transport processes in the linear regime.

The principal strategy of the development is in deriving the constitutive properties (e.g., viscosity, thermal conductivity, etc.) of the stress tensor, heat flux, and diffusion fluxes, namely, the nonconserved variables  $\Phi_{qa}$ , in forms that are readily amenable to computer simulations, because analytic or semianalytic methods are not available for them in realistic fluid models. The desired reduction of the complicated  $N$  particle problems will be shown achievable if density fluctuations over the range of intermolecular forces are taken advantage of and expressed in terms of diffusion of particles.

In the basic viewpoint taken in this approach, density fluctuations within the intermolecular force range are responsible for the mechanism of momentum and energy transfers between molecules in dense fluids and, in particular, in liquids. According to this viewpoint, transport coefficients of liquids can be derived that are given in terms of intermolecular forces and the equilibrium pair correlation function, which can be computed by either Monte Carlo or molecular dynamics simulation methods or, alternatively, an integral equation method. It should be emphasized that the only quantity needing simulations is the equilibrium pair correlation function of the fluid in the approach taken here. Therefore, the  $N$  particle collision operator appearing in the Chapman–Enskog approach is not encountered at all; instead, the equilibrium structure of the fluid of interest provides the transport properties through the pair correlation function. This is a tremendous advantage from the computational standpoint.

## 10.1 Excess Normal Stress

The expression for  $\mathfrak{p}$  in (9.71) of Chap. 9 can be put into a form that gives a little more physical insight if the notion of excess normal stress is used. It will presently become apparent that  $\mathfrak{p}$  has an intimate relation to excess normal stress.

For simple fluids, the excess normal stress  $\Delta$  is defined relative to hydrostatic pressure  $p$  by the formula [4]

$$\Delta = \frac{1}{3} \text{Tr} \left\langle \sum_{j=1}^N \left[ m \mathbf{C}_j \mathbf{C}_j \delta(\mathbf{r}_j - \mathbf{r}) + \frac{1}{2} \sum_{j \neq k=1}^N \mathbf{W}_{jk} \delta(\mathbf{r}_k - \mathbf{r}) \right] \right\rangle - p. \quad (10.1)$$

In the literature, we occasionally come across the definition of pressure in the context of kinetic theory of nonequilibrium processes, given as the average of the trace of the molecular stress tensor divided by three. If such a definition

is to be sensible with regard to its operational meaning within the framework of nonequilibrium statistical thermodynamics, the pressure so defined must be interpreted as a nonequilibrium pressure, distinguished from hydrostatic pressure. Therefore if we so wish, the first term on the right of (10.1) may be called the kinetic or nonequilibrium pressure. Then, the excess normal stress  $\Delta$  may be interpreted as a fluctuation of pressure from the hydrostatic pressure in a nonequilibrium fluid.

Because, as shown in earlier chapters,  $\Delta$  is related to the bulk viscosity of the fluid through the relation

$$\Delta = -\eta_b \nabla \cdot \mathbf{u}, \quad (10.2)$$

where  $\eta_b$  is the bulk viscosity coefficient and  $\mathbf{u}$  is the mean fluid velocity, the bulk viscosity should be computable from the statistical expression for  $\Delta$ . A method of computing the bulk and shear viscosities is developed for a simple liquid in [5,6] and for molecular liquids in [7,8]. The methods will be described in what follows.

For the purpose in hand, we consider a flow configuration in which the fluid is periodically compressed or decompressed in a direction. This situation is realizable if a sound wave propagates, say, in the  $z$  direction of the space-fixed coordinate system in the fluid. Then the density will vary in the  $z$  direction, whereas it will remain invariant in the transversal directions. The  $z$  component of the force on the plane perpendicular to the  $z$  axis is the normal stress component  $P_{zz}$  which will equilibrate with the hydrostatic pressure. In this condition, the relaxation times for  $P_{zz}$  and the transversal components  $P_{xx}$  and  $P_{yy}$  are not generally the same. Hence, the normal stress is no longer isotropic, that is,  $P_{xx} - P_{zz}$  is not equal to zero. This difference is intimately related to the bulk viscosity of the fluid. If it is assumed that  $P_{zz}$  relaxes to the hydrostatic pressure before the other two components of the stress tensor do, then the excess normal stress for the flow configuration can be written as

$$\Delta = \frac{1}{3}(P_{xx} + P_{yy}) - \frac{2}{3}P_{zz}.$$

Because the normal stress is isotropic in the  $x$  and  $y$  directions, namely,  $P_{xx} = P_{yy}$ , it follows that

$$\Delta = \frac{2}{3}(P_{xx} - P_{zz}), \quad (10.3)$$

which shows that the excess normal stress for the flow configuration is simply proportional to the primary normal stress difference  $\mathfrak{N}_1 = P_{xx} - P_{zz}$ .

On application of the procedure to obtain (9.67) starting from (9.62), the excess normal stress can be given in the form

$$\begin{aligned} \Delta &= -\frac{1}{6} \int_0^1 d\lambda \int d\mathbf{r}_{12} \left( r_{12} - \frac{3z_{12}^2}{r_{12}} \right) \mathcal{V}'_{12}(r_{12}) \\ &\quad \times n[\mathbf{r} + (1 - \lambda)z_{12}] n(\mathbf{r} - \lambda z_{12}) n^{(2)}(\mathbf{r}_{12}, t), \end{aligned} \quad (10.4)$$

where  $\mathcal{V}'_{12}(r_{12}) = d\mathcal{V}_{12}/dr_{12}$ . Upon expanding the densities as in (9.70), there follows from (10.4) the formula,

$$\begin{aligned}\Delta = & -\frac{1}{36} \int d\mathbf{r}_{12} \mathcal{V}'_{12}(r_{12}) \left( r_{12} - \frac{3z_{12}^2}{r_{12}} \right) z_{12}^2 n^{(2)}(r_{12}, t) \left( \frac{\partial n}{\partial z} \right)^2 \\ & + O \left[ \left( \frac{\partial n}{\partial z} \right)^4 \right].\end{aligned}\quad (10.5)$$

Use of spherical coordinates and integration over the angular variables yields it in the form,

$$\Delta = -\frac{4\pi}{135} \int_0^\infty dr r^5 \mathcal{V}'(r) n^{(2)}(r, t) \left( \frac{\partial n}{\partial z} \right)^2 + O \left[ \left( \frac{\partial n}{\partial z} \right)^4 \right]. \quad (10.6)$$

The nonequilibrium pair correlation function  $n^{(2)}(r, t)$  may be obtained as a solution for the DOZ integral equation by imposing a suitable closure. Studies [9,10] of the DOZ equation in the past subject to a Percus–Yevick type closure indicate that the nonequilibrium effect on  $n^{(2)}(r, t)$  is not large. Therefore, it may be approximated by the equilibrium pair correlation function  $g_{\text{eq}}^{(2)}(r)$  in the following manner:

$$n^{(2)}(r, t) \simeq g_{\text{eq}}^{(2)}(r) \theta(r - \xi), \quad (10.7)$$

where  $\xi$  is the parameter specifying the maximum range of density fluctuation. In general, this cutoff parameter is equal to or less than the range  $r_{\max}$  of the intermolecular force. Using this approximation, there follows from (10.6) the excess normal stress in the form,

$$\Delta = -\frac{2\omega_b(\xi)}{9D} \left( \frac{\partial n}{\partial z} \right)^2, \quad (10.8)$$

where

$$\omega_b(\xi) = \frac{2\pi}{15} \int_0^\infty dr r^5 \mathcal{V}'(r) g_{\text{eq}}^{(2)}(r) \theta(r - \xi). \quad (10.9)$$

### 10.1.1 Bulk Viscosity of Simple Fluids

To make progress from the expression for  $\Delta$  in (10.8) we now use the constitutive relation for fluid velocity. The velocity  $\mathbf{u}$  of a fluid is the drift velocity of a fluid particle and as such it may be related to the friction coefficient or the self-diffusion coefficient  $D$  of the fluid through the equation

$$u_z = -\frac{D}{n} \frac{\partial n}{\partial z}. \quad (10.10)$$

For a kinetic theory derivation of this constitutive equation, see Appendix B. Here, the self-diffusion coefficient generally depends on density and temperature. Observing that  $D = D'(n)/n$  with  $D'(n)$  is a weak function of  $n$  and differentiating (10.10) with respect to  $z$ , we obtain

$$\frac{\partial u_z}{\partial z} = \frac{2D}{n^2} \left( \frac{\partial n}{\partial z} \right)^2 - \frac{D}{n} \frac{\partial^2 n}{\partial z^2}.$$

If the density changes slowly in space, then the second-order derivative should be much smaller than the first, and the second term on the right may be neglected. Thus, we obtain

$$\frac{\partial u_z}{\partial z} \simeq \frac{2D}{n^2} \left( \frac{\partial n}{\partial z} \right)^2. \quad (10.11)$$

Eliminating the density derivative between (10.8) and (10.11), we finally obtain the constitutive equation for  $\Delta$  in the form

$$\Delta = -\frac{n^2}{9D} \omega_b(\xi) \frac{\partial u_z}{\partial z}. \quad (10.12)$$

Comparing this constitutive equation with the phenomenological counterpart,

$$\Delta = -\eta_b \frac{\partial u_z}{\partial z}, \quad (10.13)$$

the statistical mechanical formula for the bulk viscosity coefficient is obtained:

$$\eta_b = \frac{n^2 \omega_b(\xi)}{9D}. \quad (10.14)$$

The density in the expression for  $\eta_b$  depends on position. Therefore, it will vary over the distance of density fluctuation range  $\xi$ , which is of the order of the intermolecular force range. The present density fluctuation theory, however, cannot provide information on the density variation within that distance. Therefore, it is appropriate to take the mean bulk density for  $n(r)$ . The equilibrium pair correlation function within the correlation range will be evaluated at that mean bulk density. The value of the density fluctuation range  $\xi$  is not given precisely within the present density fluctuation theory. If we are to maintain rigor in treating the theory, the bulk viscosity formula in (10.14) must also be averaged over the distribution of  $\xi$ , say,  $P(\xi)$ . This distribution function is extraneous to the present density fluctuation theory, in which density variations are considered over the scale of  $\xi$ . An idea of its form may be gained if the distribution of voids in a fluid is investigated with regard to their sizes. In the absence of knowledge of  $P(\xi)$ , the bulk viscosity formula in (10.14) implies the assumption that  $P(\xi)$  is a delta function

$\delta(\xi' - \xi)$ , because, on averaging over  $\xi'$ , we therewith obtain (10.14):

$$\begin{aligned}\eta_b &= \int_0^\infty d\xi' \eta_b(\xi') P(\xi') \\ &= \int_0^\infty d\xi' \frac{n^2 \omega_b(\xi')}{9D} \delta(\xi' - \xi) \\ &= \frac{n^2 \omega_b(\xi)}{9D}.\end{aligned}\tag{10.15}$$

The bulk viscosity formula used in this chapter should be understood in this sense unless stated otherwise.

It is interesting to note that (10.14) is reminiscent of the Stokes–Einstein (SE) relation [11] between the viscosity  $\eta_{se}$  and diffusion coefficient  $D$ ,

$$\eta_{se} = \frac{k_B T}{6\pi\sigma_{se} D},\tag{10.16}$$

where  $\sigma_{se}$  is the SE radius of the particle. Note that this is the SE relation under the stick boundary condition. If the slip boundary condition were applied instead, then the factor  $6\pi$  in the denominator should be replaced by  $4\pi$ . In deference to the tradition in the literature, we have used the symbol  $D$  for the diffusion coefficient.

The SE relation was originally derived by combining the hydrodynamically calculated result for the force exerted by the solvent on a macroscopic particle immersed in a continuum liquid of viscosity  $\eta_{se}$  and the Brownian motion theory result for the mean motion of a macroscopic particle moving under the frictional influence of the randomly moving molecules constituting the solvent—the former result was by Stokes [12,13] and the latter was by Einstein [11]. Therefore, it is clear that  $D$  in the SE relation is the diffusion coefficient of the tracer particle diffusing in the solvent but not the self-diffusion coefficient we have used in this work.

Except for the feature that the bulk viscosity  $\eta_b$  is inversely proportional to  $D$  in the same manner as  $\eta_{se}$  is inversely proportional to  $D$ , the two equations (10.14) and (10.16) are not the same because the coefficient factors are quite different. Also note that despite numerous attempts [14–18] at derivation of the SE relation by statistical mechanics, its derivation has not been fully satisfactory. Later, we will have an occasion to assess the SE relation from the standpoint of formula (10.14).

It is worthwhile to summarize the gist of the theory developed for  $\eta_b$ : by taking density variation within the intermolecular force range into account, the statistical mechanical formula for  $\Delta$  is calculated to  $O[(\partial n/\partial z)^2]$  and the constitutive equation for  $u_z$ , (10.10), is used to replace  $(\partial n/\partial z)^2$  in (10.8) and, as a result, to obtain the formula for  $\eta_b$ .

Equation (10.14) is also reminiscent of the potential energy part of the expression for the bulk viscosity of simple fluids, which was obtained by Kirkwood et al. [19], in that the self-diffusion coefficient appears in the denominator. However, it is not the same as their formula, and the method for deriving it is entirely different from theirs, which is based on the Fokker–Planck equation for the Brownian motion model originally developed by Kirkwood [20] for liquids. In this connection, note that there is no dilute gas limit term in (10.14), that is, the first term in their expression, which indicates that the bulk viscosity does not vanish as the density vanishes in contrast to the experimental evidence on simple fluids. The present formula (10.14) shows that the bulk viscosity vanishes with vanishing density in accordance with experiment, and hence it predicts the correct limiting law.

### 10.1.2 Comparison of Theory with Experiment

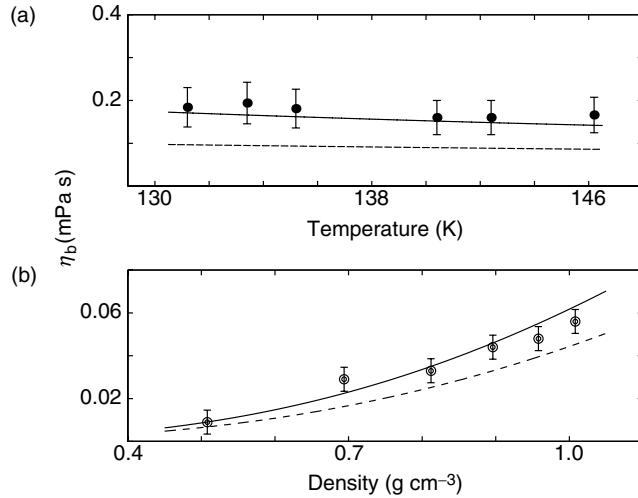
There are two basic building blocks for (10.14): the equilibrium pair correlation function that gives the structure of the fluid and the macroscopic constitutive equation (10.10) for  $u_z$ , through which the self-diffusion coefficient of the fluid enters the theory. The density fluctuation theory itself does not provide us with the self-diffusion coefficient, which gives time- and spatial scales of diffusive motions of molecules within a fluid that occur within the range of  $\xi$ . These quantities therefore must be supplied from other sources. It is possible to treat  $D$  as an empirical input if there are experimental data available for it. Then, if the pair correlation function can be suitably calculated by some means, it is possible to calculate a bulk viscosity of a fluid as a function of temperature and density.

At the early stage of the development of the density fluctuation theory, such a procedure was taken, in which the pair correlation function was calculated by employing the Percus–Yevick (PY) integral equation for the pair correlation function, whereas either experimental or computer simulation data were used for the self-diffusion coefficient.

In Fig. 10.1, the theoretical predictions by (10.14) are compared with the experimental data on argon for the temperature and density dependence of the bulk viscosity. The potential model employed was the Lennard-Jones potential,

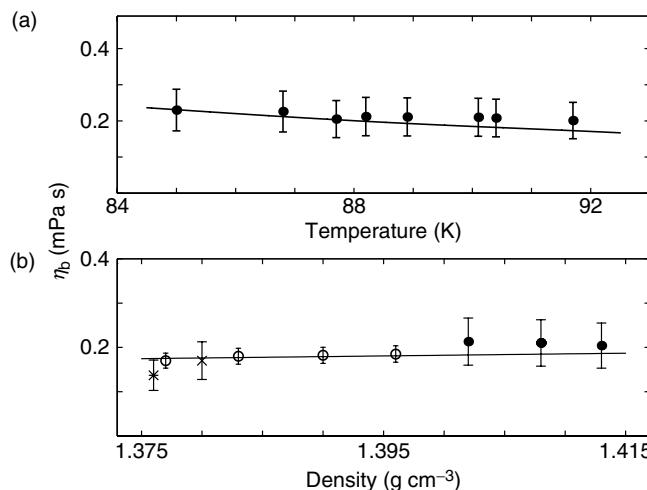
$$\mathcal{V}(r) = 4\varepsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right], \quad (10.17)$$

where the well depth was taken as  $\varepsilon/k_B = 119.8\text{ K}$  and  $\sigma = 0.3405\text{ nm}$  for argon and the PY integral equation was employed to calculate the pair correlation function. The critical temperature  $T_c$  of argon is  $130\text{ K}$ , and in the region of  $T \gtrsim 130\text{ K}$  the range of density fluctuation  $\xi$  is empirically found larger than or equal to the intermolecular force range  $r_{\max}$ . In this case,  $\omega_b$



**Fig. 10.1.** (a) Bulk viscosity vs. temperature at  $\rho = 1062 \text{ kg m}^{-3}$  for argon near the critical temperature  $T = 130 \text{ K}$ . The symbols are experimental data. See the text for the description of the figure. (b) Bulk viscosity vs. density at  $T = 234 \text{ K}$  for argon. The symbol  $\odot$  is for the experimental data reported in [22]. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, Phys. Rev. Lett. **83**, 4566 (1999). Copyright 1999 American Physical Society.]

has no adjustable parameter, and hence the theory is free of parameters. On the other hand, if  $T$  is well below  $T_c$  and, especially, in the neighborhood of the triple point, the value of  $\xi$  is in the neighborhood of  $2\sigma$ , presumably because the molecules are closely packed and the density can fluctuate in a cavity of size  $2\sigma$ . In panel a, the *solid curve* is the theoretical  $\eta_b$  calculated with the Naghizadeh–Rice data [21] and the Madigosky data [22] for  $D$ . The bulk viscosity calculated with  $D$  provided by Heyes [23], who computed  $D$  by a molecular dynamics simulation method based on the linear response theory formula [24] and fitted the results to a mathematical form, is indicated by the *broken curve*. The meanings of the symbol and the curves in panel b are the same as those in panel a. The results for  $\eta_b$  obtained with the Heyes data are only qualitatively correct compared with experiment, and it seems to indicate the quality of the simulation results based on the linear response theory formula. It is not clear whether the deviations from the experimental data arise from the numerical accuracy of the simulation method or the Kubo formula itself. On the other hand, the present density fluctuation theory predicts bulk viscosity within the experimental error indicated by the error bars. The comparison here is quite significant for the present density fluctuation theory because it is free of the adjustable parameter  $\xi$  in the temperature range for this figure owing to the fact that  $\xi > r_{\max}$ .



**Fig. 10.2.** (a)  $\eta_b$  vs.  $T$  at  $\rho = 1,408 \text{ kg m}^{-3}$  for argon near the triple point. The symbols ( $\bullet$ ) are experimental [29]; the *solid curve* is the present theory computed with  $D_{\text{NR}}$  for  $D$ . (b)  $\eta_b$  vs.  $\rho$  at  $T = 90 \text{ K}$  for argon computed with  $D_{\text{NR}}$ . The symbols are experimental data: \* [28];  $\times$  [27];  $\circ$  [30];  $\bullet$  [29].  $\vartheta = 0.21$  for the theoretical  $\eta_b$ . [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **83**, 4566 (1999). Copyright 1999 American Physical Society.]

In the neighborhood of the triple point, the range of density fluctuations found was much less than  $r_{\max}$ . It was in the neighborhood of  $2\sigma$ . For computational convenience, a parameter  $\vartheta$  was introduced in lieu of  $\xi$  such that<sup>1</sup>

$$\int_0^\xi dr r^5 \mathcal{V}'(r) g_{\text{eq}}^{(2)}(r) = \vartheta \int_0^\infty dr r^5 \mathcal{V}'(r) g_{\text{eq}}^{(2)}(r). \quad (10.18)$$

With the choice of  $\vartheta = 0.21$ , the bulk viscosity of argon was calculated in the neighborhood of the triple point and compared with experimental data reported by various authors [27–30] in Fig. 10.2. The theoretical values for the bulk viscosity versus temperature, represented by the *solid curve* in Fig. 10.2a, were calculated with  $D$  (denoted by  $D_{\text{NR}}$ ) provided by Naghizadeh and Rice [21] and the *filled circles* are experimental data by Naugle et al. [27]. In Fig. 10.2b, the theoretical density dependence is compared with experiment. The *solid curve* is the theory and the symbols are experimental data: \* [28] and  $\circ$  [30]. The bulk viscosity thus calculated behaves correctly with regard to temperature and density and is within the limits of experimental errors throughout the temperature and density ranges in which experiments

<sup>1</sup> In the development subsequent to this initial version of the density fluctuation theory, the parameter  $\vartheta$  has been examined from the standpoint of the distribution of the cutoff parameter  $\xi$  [25, 26].

were performed. The comparisons in the two figures indicate the utility of the bulk viscosity formula, which is simple mathematically, and validate the underlying density fluctuation theory for transport coefficients.

Finally, note that the bulk viscosity of simple fluids vanishes as the density tends to zero, unlike other transport coefficients of gases, such as the viscosity and thermal conductivity, and the formula for  $\eta_b$  clearly exhibits this limiting behavior as  $n \rightarrow 0$ : *simple (monatomic) dilute gases do not have a bulk viscosity in the density fluctuation theory.*

## 10.2 Shear Stress

As we have done for the excess normal stress, we will begin with the theory of shear viscosity of simple fluids in the present chapter and extend the theory to complex fluids in the following chapter. The important point of the theory is, as for the bulk viscosity, that density fluctuations within the range of the order of intermolecular forces are responsible for momentum transfers between elementary volumes in liquids and the shear viscosity formula can be derived with the help of the macroscopic constitutive equation for velocity  $\mathbf{u}$ .

To derive such a constitutive equation for the shear stress, consider a simple fluid, which consists of molecules of mass  $m$  contained in volume  $V$  at temperature  $T$ . The temperature is assumed to be uniform in  $V$ . The fluid is confined between two parallel plates separated by distance  $L$ , which move in opposite directions at speed  $u/2$ . Therefore, the flow configuration is that of plane Couette flow [31]. The plates are assumed to be aligned parallel to the  $x$  axis, perpendicular to the  $z$  axis, and positioned at  $z = \pm L/2$ , respectively. Therefore, there is a velocity gradient in the  $z$  direction while the fluid flows in the  $x$  direction. It is assumed that the flow is laminar. The channel is also assumed to be infinite in length. This makes the flow translationally invariant in the  $x$  direction. The fluid velocity, therefore, has only the  $x$  component, which is a function of  $z$  only but independent of  $x$  and  $y$ . The constitutive equation can now be derived for the traceless symmetric part of the stress tensor in the flow configuration described.

As shown in the previous chapters, the traceless symmetric part  $\mathbf{\Pi}$  of the stress tensor  $\mathbf{P}$  is given by the statistical mechanical expression [4],

$$\mathbf{\Pi} = \left\langle \sum_{j=1}^N \left[ [m\mathbf{C}_j\mathbf{C}_j]^{(2)} \delta(\mathbf{r}_j - \mathbf{r}) + \frac{1}{2} \sum_{j \neq k=1}^N [\mathbf{W}_{jk}]^{(2)} \delta(\mathbf{r}_k - \mathbf{r}) \right] \right\rangle. \quad (10.19)$$

Recall that the symbol  $[\mathbf{A}]^{(2)}$  denotes the traceless symmetric part of the second-rank tensor  $\mathbf{A}$ . The statistical mechanical averaging is weighted by the nonequilibrium grand canonical ensemble distribution function introduced earlier; the angular brackets stand for such an averaging operation in the

appropriate phase space. This expression, similarly to the excess normal stress, can also be given in terms of the local density and the density correlation function.

Because the virial tensor is made up of pairwise additive interaction forces, the integral in the  $N$  particle phase space can be reduced to integrals in one- or two-particle phase space, each involving either a one-particle or a two-particle reduced distribution function. The procedure is the same as that for the excess normal stress. The shear stress in the flow configuration mentioned earlier can thus be expressed as

$$\begin{aligned} \boldsymbol{\Pi}_{xz} = & \int d\mathbf{p} [m\mathbf{C}_x\mathbf{C}_z]^{(2)} f^{(1)}(\mathbf{r}, \mathbf{p}, t) \\ & + \frac{1}{2} \int_0^1 d\lambda \int d\mathbf{r}_1 \int d\mathbf{r}_2 [\mathbf{r}_{12}\mathbf{F}_{12}]_{xz}^{(2)} \\ & \times \delta(\mathbf{r}_2 + \lambda\mathbf{r}_{12} - \mathbf{r}) n(\mathbf{r}_1, t) n(\mathbf{r}_2, t) n^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t). \end{aligned} \quad (10.20)$$

The first term on the right of (10.20) is the kinetic part, and the second the potential part.

If the system is near equilibrium and subject to a small velocity gradient caused by the applied shearing perturbation then shear stress  $\boldsymbol{\Pi}$  obeys the following Newtonian law of viscosity [1]:

$$\boldsymbol{\Pi}_{xz} = -2\eta [\nabla \mathbf{u}]_{xz}^{(2)}, \quad (10.21)$$

where  $\eta$  is the Newtonian shear viscosity and  $[\nabla \mathbf{u}]^{(2)}$  is the traceless symmetric part of the velocity gradient  $\nabla \mathbf{u}$ ,

$$[\nabla \mathbf{u}]^{(2)} = \frac{1}{2} \left[ \nabla \mathbf{u} + (\nabla \mathbf{u})^t \right] - \frac{1}{3} \delta \nabla \cdot \mathbf{u}. \quad (10.22)$$

The assumption here is that the norm (i.e., magnitude)  $\|[\nabla \mathbf{u}]^{(2)}\|$  is so small that the linear relationship holds between the shear stress and the velocity gradient, as in (10.21). The superscript ‘ $t$ ’ denotes the transpose of the tensor. Shear stress  $\boldsymbol{\Pi}$  is also the traceless symmetric part of the stress (pressure) tensor  $\mathbf{P}$ :

$$\boldsymbol{\Pi} = \frac{1}{2} (\mathbf{P} + \mathbf{P}^t) - \frac{1}{3} \delta \text{Tr} \mathbf{P}. \quad (10.23)$$

It should be recalled that the Newtonian viscosity is defined within the validity of the linear constitutive law. Therefore, the aforementioned assumption is necessary for the analysis below.

### 10.2.1 Shear Viscosity

We aim to relate (10.20) to the phenomenological constitutive equation for shear stress (10.21) to derive a statistical mechanical expression for the shear viscosity  $\eta$ . The two terms on the right of (10.20) are qualitatively different in

their physical origins and suggest that the shear viscosity  $\eta$  should consist of two distinctive components: one is the kinetic energy part and the other is the potential energy part. The former will be denoted by  $\eta_k$ , and the latter by  $\eta_v$ . Before proceeding further, we note that the result of the Chapman–Enskog theory for  $\eta$  derived from the generalized Boltzmann equation in the earlier chapter supports this mode of splitting  $\eta$  into the two components mentioned.

### The Kinetic Part of Shear Viscosity

It is clear that the kinetic part of the shear viscosity is related to the kinetic part of the stress tensor, and their relationship can be examined from the standpoint of the stress tensor of a dilute simple fluid.

Because we are interested in the linear process near equilibrium, it is sufficient to expand the singlet distribution function in the leading moments. The temperature is assumed uniform over the system and the fluid is of a single component. Therefore there is only the stress tensor to consider. The singlet distribution function then can be expanded in moments,

$$f = f_0(\mathbf{w}) \left( 1 + k_B T \mathbf{w} \cdot \mathbf{w} A + k_B T [\mathbf{w} \mathbf{w}]^{(2)} : \mathbf{B} \right), \quad (10.24)$$

where  $f_0$  is the local equilibrium Maxwell distribution function

$$f_0 = n (m/2\pi k_B T)^{3/2} \exp(-\frac{1}{2} w^2) \quad (10.25)$$

and  $\mathbf{w}$  is the reduced peculiar velocity defined by

$$\mathbf{w} = \sqrt{m\beta} \mathbf{C} \quad (\beta = 1/k_B T). \quad (10.26)$$

The coefficients  $A$  and  $\mathbf{B}$  are the scalar and tensor moments to be determined. Since the normalization is preserved, there follows

$$n = \int d\mathbf{p} f(\mathbf{p}, \mathbf{r}, t) = \int d\mathbf{p} f_0(\mathbf{p}). \quad (10.27)$$

Multiply  $m\mathbf{C} \cdot \mathbf{C}$  by (10.24) and integrate over  $\mathbf{p}$  to obtain

$$\begin{aligned} \text{Tr}\mathbf{P}_k &= \int d\mathbf{p} m\mathbf{C} \cdot \mathbf{C} f(\mathbf{p}, \mathbf{r}, t) \\ &= 3nk_B T + 15n(k_B T)^2 A. \end{aligned}$$

Therefore,  $A$  is given by

$$A = \frac{1}{5k_B T} \left( \frac{1}{3nk_B T} \text{Tr}\mathbf{P}_k - 1 \right) \equiv \frac{\Delta_k}{5n(k_B T)^2}. \quad (10.28)$$

Multiplying  $[m\mathbf{CC}]^{(2)}$  by (10.24) and integrating over  $\mathbf{p}$ , we obtain

$$\begin{aligned}\boldsymbol{\Pi}_k &= \int d\mathbf{p} [m\mathbf{CC}]^{(2)} f(\mathbf{p}, \mathbf{r}, t) \\ &= 2n(k_B T)^2 [\mathbf{B}]^{(2)},\end{aligned}$$

that is,

$$[\mathbf{B}]^{(2)} = \frac{\boldsymbol{\Pi}_k}{2n(k_B T)^2}. \quad (10.29)$$

Collecting these results, we finally obtain for the moment expansion of  $f$ :

$$f = f_0(\mathbf{w}) \left[ 1 + \mathbf{w} \cdot \mathbf{w} \frac{\Delta_k}{5nk_B T} + [\mathbf{w}\mathbf{w}]^{(2)} : \frac{\boldsymbol{\Pi}_k}{2nk_B T} \right]. \quad (10.30)$$

There remains the problem of determining  $\boldsymbol{\Pi}_k$  in terms of the shear rate or, more generally, the velocity gradient. The kinetic theory of dilute gases discussed in Chaps. 2 and 3 provides well-developed procedures for the purpose. Availing ourselves of them, we obtain the result for  $\eta_k$  as follows:

$$\boldsymbol{\Pi}_k = -2\eta_k [\nabla \mathbf{u}]^{(2)}, \quad (10.31)$$

for which  $\eta_k$  can be calculated with the Chapman–Enskog formula

$$\eta_k \equiv \eta_0 = \frac{3\Omega_1^{(2)}(2)}{5\Omega_{12}^{(1)}(1)} n D_0 \equiv c n D_0. \quad (10.32)$$

Here,  $\Omega_1^{(2)}(2)$  and  $\Omega_{12}^{(1)}(1)$  are collision bracket integrals in the Chapman–Enskog first approximation [32] and  $D_0$  is the Chapman–Enskog self-diffusion coefficient [32]. Tables for the collision bracket integrals for the Lennard-Jones potential are available in the literature [33]. From the tabulated values of the collision bracket integrals, we find that the ratio  $\Omega_1^{(2)}(2)/\Omega_{12}^{(1)}(1)$  is approximately 1.1 for the Lennard-Jones potential and thus  $c \approx 0.7$ . It must be noted that the formula in (10.32) is an approximation of  $\eta_k$  because the singlet distribution function  $f$ , rigorously speaking, is not a dilute gas singlet distribution function but the singlet reduced distribution function contracted from  $F_c^{(N)}$ . The viscosity coefficient  $\eta_k$  therefore should be density-dependent in general, but such a correction is not warranted because  $\eta_k$  is negligibly small compared with the potential energy part  $\eta_v$  of the shear viscosity in the liquid density regime. We will use the expression given in (10.32) for the kinetic part of the shear viscosity in this work.

### The Potential Part of Shear Viscosity

To calculate the potential energy part of the shear viscosity in a method alternative to the Chapman–Enskog method that requires the collision bracket

integrals, the dynamic pair correlation function must be examined with regard to the  $\mathbf{r}_{12}$  dependence on density factors  $n(\mathbf{r} - \lambda\mathbf{r}_{12})$  and  $n[\mathbf{r} + (1 - \lambda)\mathbf{r}_{12}]$ . This  $\mathbf{r}_{12}$  dependence of bulk density indicates that the potential energy part of the stress tensor varies over the length scale of the intermolecular force. It can have a significant effect because shearing perturbation is accompanied by density variations. In this respect, the basic procedure employed here is the same as that for the bulk viscosity considered earlier. It also is important to recognize that the density variation is possible because the fluid is compressible.

Expansion of the bulk densities in the series of  $\lambda\mathbf{r}_{12}$  and approximation of the dynamic pair correlation function  $n^{(2)}(\mathbf{r}_1, \mathbf{r}_2, n, t)$  with the equilibrium pair correlation function  $g_{\text{eq}}^{(2)}$  because the system is near equilibrium yields the potential part of shear stress  $\boldsymbol{\Pi}_v$  in the form,

$$\Pi_{vzz} = \frac{2\pi}{45} \int_0^\infty dr r^5 \mathcal{V}'(r) g_{\text{eq}}^{(2)}(r, n) \theta(\xi - r) \frac{\partial n}{\partial x} \frac{\partial n}{\partial z}, \quad (10.33)$$

where  $\mathcal{V}'(r) = d\mathcal{V}(r)/dr$ . For this expression, we have taken into account the fact that the density varies in the  $xz$  plane, whereas it remains invariant in the  $y$  direction. The mean bulk density is to be used for the density dependence of  $g_{\text{eq}}^{(2)}(r, n)$ . The cutoff in the integration range is introduced in this expression by replacing the nonequilibrium pair distribution function  $n^{(2)}(r, n, t)$  with  $g_{\text{eq}}^{(2)}(r, n) \theta(\xi - r)$  on the same physical ground as argued for the excess normal stress; see (10.7) and the related discussion. The cutoff distance  $\xi$  can be as small as about  $2\sigma$  in the low-temperature regime (e.g., near the triple temperature), but as large as, or larger than, the intermolecular force range  $r_{\max}$  at higher temperatures, in particular, in the supercritical regime.

For the single-component fluid under consideration, the mean velocity  $\mathbf{u}^*$  of the tracer particle (i.e., the particle of attention) is related to the density gradient by the following constitutive equation:

$$n\mathbf{u}^*(\mathbf{r}) = -D \frac{\partial n}{\partial \mathbf{r}}, \quad (10.34)$$

where  $D$  is the self-diffusion coefficient. The tracer particle velocity balances the fluid particle<sup>2</sup> velocity  $\mathbf{u}$ , that is,  $\mathbf{u} = -\mathbf{u}^*$ . Therefore, the constitutive equation in terms of fluid particle velocity reads

$$n\mathbf{u}(\mathbf{r}) = D \frac{\partial n}{\partial \mathbf{r}}. \quad (10.35)$$

For a statistical mechanical derivation of this constitutive relation, see Appendix B. If the density variation with  $\mathbf{r}$  is so small that the second derivative is

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<sup>2</sup> By fluid particle, we mean a packet of molecules contained in an elementary volume of the fluid, not a molecule, in conformation with the usual notion adopted in fluid mechanics [34]. Therefore,  $\mathbf{u}$  is the mean velocity of a group of molecules contained in the elementary volume which are sufficiently numerous to justify statistical mechanical averaging.

negligible, then the velocity gradient for the Couette flow configuration under consideration is given by

$$\begin{aligned}\frac{\partial u_x}{\partial z} &= \frac{\partial}{\partial z} D \frac{\partial n}{\partial x} \\ &\simeq -\frac{2D}{n^2} \frac{\partial n}{\partial x} \frac{\partial n}{\partial z}\end{aligned}\quad (10.36)$$

for which we have used the property of  $D \approx D'/n$  where  $D'$  is a slowly changing function of  $n$ —the same assumption as used for the bulk viscosity in the previous subsection. Note that the removal of this assumption does not basically alter the result presented below.

Because the phenomenological constitutive equation (Newtonian law of viscosity) for the plane Couette flow configuration for  $\Pi_{vzx}$  is

$$\Pi_{vzx} = -\eta_v \frac{\partial u_x}{\partial z}, \quad (10.37)$$

on eliminating the product of density gradients by using (10.36), there follows from (10.33) the equation for  $\Pi_{vzx}$  in the form

$$\Pi_{vzx} = -\frac{n^2 \omega(n)}{6D} \frac{\partial u_x}{\partial z}, \quad (10.38)$$

where

$$\omega(n, \xi) = \frac{2\pi}{15} \int_0^\infty dr r^5 \mathcal{V}'(r) g_{\text{eq}}^{(2)}(r, n) \theta(\xi - r). \quad (10.39)$$

Comparing (10.37) and (10.38), the potential part of the shear viscosity is identified in the form

$$\eta_v = \frac{n^2 \omega(n, \xi)}{6D}. \quad (10.40)$$

Because the density fluctuation range, which is related to the correlation range, generally has a distribution, this viscosity formula should be averaged over the distribution. Thus, more precisely, the potential energy part of the shear viscosity should be given by

$$\langle \eta_v \rangle = \int_0^\infty d\xi' \frac{n^2 \omega(n, \xi')}{6D} P(\xi'), \quad (10.41)$$

where  $P(\xi)$  is the distribution function of  $\xi$ . We may take, for example,

$$P(\xi') = \delta(\xi' - \xi). \quad (10.42)$$

The formula given for  $\omega(n, \xi)$  in (10.39) is understood in this sense. This form of  $P(\xi')$  will be relaxed in Chap. 12.

Equation (10.40) is similar to the SE relation between the viscosity and the diffusion coefficient. Despite the apparent similarity, it is not the same as the SE relation because the factor  $n^2 \omega(n)$  depends on density, temperature,

and intermolecular potential parameters—the molecularity of the fluid—and  $D$  is the self-diffusion coefficient of the liquid, not a tracer diffusion coefficient used for a macroscopic particle (e.g., a colloidal particle) in the SE relation. In this connection, recall that in Einstein's derivation  $D$  in the SE relation is the diffusion coefficient of macroscopic Brownian particles suspended in a solvent of viscosity  $\eta$ ; see (10.16).

### 10.2.2 Shear Viscosity and the Diffusion Coefficient

By combining the kinetic and potential parts, Equations (10.32) and (10.40), we finally obtain the shear viscosity of the fluid in the form,

$$\eta = cnD_0 + \frac{n^2\omega(n)}{6D}. \quad (10.43)$$

In the limit of vanishing density this formula gives rises to the Chapman–Enskog viscosity [32] of the gas, which is independent of density (it is independent of density because  $nD_0 = \text{constant}$ , independent of  $n$ ), whereas in the limit of high densities in the liquid regime it takes the SE relation-like form because the second term on the right is dominant over the first term, the Chapman–Enskog theory contribution. Therefore, formula (10.43) explains how the Chapman–Enskog theory prediction of the  $\eta - D$  relation crosses over to the SE relation-like form of the  $\eta - D$  relation as the density increases from the dilute gas regime to the liquid regime. This crossover behavior had been defying our understanding until the present density fluctuation theory was formulated. We see that in the dilute gas regime the momentum relaxation dominates because the intermolecular part of the stress relaxes faster than the momentum transfer rate (momentum flux), whereas in the liquid density regime the stress from the intermolecular interactions dominates because it relaxes more slowly than the momentum transfer rate in the gas phase owing to the more constrained configuration of particles at liquid density. As the density varies, one trend overtakes the other. The diffusion process sets the time- and spatial scales for momentum transfers giving viscous phenomena. This is the fundamental reason underlying the expression for viscosity in (10.43), which gives  $\eta$  in terms of the self-diffusion coefficient. The potential energy part offers the interpretation: *that momentum transfers giving rise to viscous phenomena in the liquid density regime is a result of the combination of density variation creating voids and subsequent diffusion of particles into the voids created in the liquid.*

The formula derived suggests that if there are experimental or simulation data available for  $D$ , then the shear viscosity can be calculated from (10.43). Since the self-diffusion coefficient is much easier to simulate on the computer than the shear viscosity, formula (10.43) can be quite useful in practice, provided it is sufficiently reliable. The utility of the formula has been tested against experimental data in the literature [7, 8], and the results of the test

are summarized in the following. We will show in Chap. 12 that this empirical approach can be removed, and the theory can thus be made fully molecular.

Equation (10.43) is also reminiscent of the formula derived by Kirkwood et al. [19] who obtained it by using a different method, which requires solutions for a hierarchy of kinetic equations for Brownian particles. These kinetic equations are Fokker–Planck equations that Kirkwood derived in his earlier paper [20] for reduced distribution functions for particles immersed in its own kind of particles, which are treated as a continuous medium exerting a force on the particles of interest. Their equation can be given the same form as (10.43) if an approximate form is taken for the  $\psi_2$  factor appearing in their equation, which gives rise to a different numerical coefficient in the viscosity formula. For example, if the lowest order approximation is taken for  $\psi_2$ , namely,  $\psi_2 \approx r^2/2$  [see (31) of [19]], then the following viscosity formula follows from (10) of [19]:

$$\eta = \frac{1}{2}nD + \frac{n^2\omega_{\text{KBG}}(n)}{6D}, \quad (10.44)$$

where

$$\omega_{\text{KBG}}(n) = \frac{\pi}{5} \int_0^\infty dr r^5 \mathcal{V}'(r) g_{\text{eq}}^{(2)}(r, n). \quad (10.45)$$

This result must be compared with (10.43). Thus we find that, apart from the cutoff factor, a relation holds between the potential energy part of the present theory result and that of the Kirkwood–Buff–Green theory:

$$\omega(n) = \frac{2}{3}\omega_{\text{KBM}}(n). \quad (10.46)$$

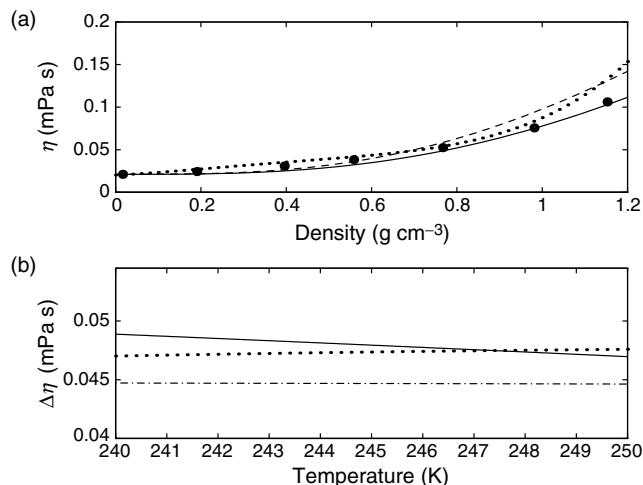
It is remarkable that this relation arises despite the fact that the method of Kirkwood et al. is quite different from the present method. In this connection, note that the Rice–Allnatt theory [35] also gives formulas for viscosities in terms of a hard sphere friction constant in forms reminiscent of the viscosity formula presented here, but they are much more complicated than either (10.43) or (10.44).

### 10.2.3 Comparison of the Theory with Experiment

The formula (10.43) for the shear viscosity of simple fluids has been validated in comparison with experimental data available in the literature. Specifically, the shear viscosity of argon was calculated for its density and temperature dependence in comparison with experimental data. The density dependences of viscosity for krypton and xenon were also examined. The values of the self-diffusion coefficient  $D$ , which is necessary for calculating  $\eta$ , were computed with either the formula obtained by fitting the Naghizadeh–Rice data [21] to a mathematical form or the formula proposed by Heyes [23] for fitting his molecular dynamics simulation results. The self-diffusion coefficients now can be calculated with good accuracy by the free volume theory of diffusion, which will be discussed in Chap. 12. In this chapter, the empirical approach

mentioned is taken for  $D$  following the original course of development of the theory. The pair correlation function in the expression for  $\omega(n)$  was obtained from the numerical solution of the PY integral equation [36] for the pair correlation function. With the pair correlation function so obtained, the integral was numerically evaluated at different temperatures and densities.

In Fig. 10.3a, the density and temperature dependence of the shear viscosity of argon at  $T = 273.0\text{ K}$  are compared with those predicted by the Haynes formula [37], which he obtained by fitting his own experimental data. The potential parameters for argon are  $\sigma = 0.340\text{ nm}$  and  $\epsilon/k_B T = 119.8\text{ K}$  [33]. The *dotted curve* is the prediction by the Haynes formula. The *solid* and *broken curves* are the theoretical values of the density fluctuation theory, which have been, respectively, computed with the values of  $D$  by using the Heyes formula ( $D_{\text{Heyes}}$ ) and the Naghizadeh–Rice formula ( $D_{\text{NR}}$ ). The latter is an empirical fitting formula. In all of the calculations for these figures, the experimental value of the dilute gas viscosity has been used for  $\eta_k = cnD_0$  because the Chapman–Enskog theory  $\eta_k$  is about 10% lower than the experimental value at  $T = 273.0\text{ K}$ , and 4–5% in the range of  $T = 240$ – $250\text{ K}$ , although it agrees well with the experimental values around the triple point. Since the principal aim here is to show the results of a test of the formula for the excess shear viscosity  $\eta_v$ —the potential part of  $\eta$  and the part obeying the SE relation-like form—it is appropriate to remove the uncertainty in the kinetic part  $\eta_k$  of  $\eta$  by simply using the empirical value for  $\eta_k$ . The *filled circles* ( $\bullet$ ) are the experimental



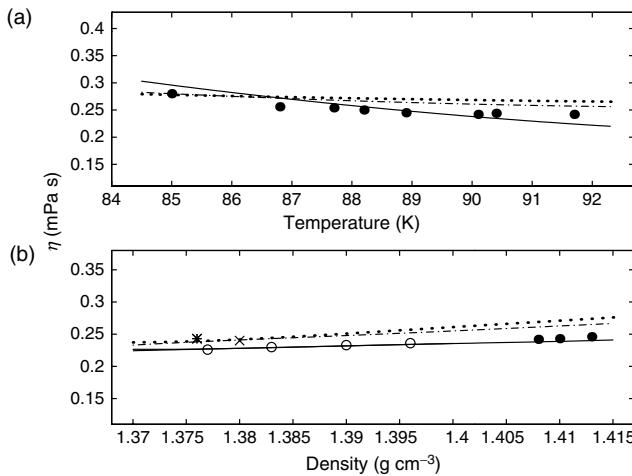
**Fig. 10.3.** (a)  $\eta$  vs.  $\rho$  for argon at  $T = 273.0\text{ K}$ . The *solid* and *dashed* curves are theoretical. The *filled circles* ( $\bullet$ ) are experimental [38]. (b)  $\Delta\eta = \eta - \eta_k$  vs.  $T$  at  $\rho = 900\text{ kg m}^{-3}$ . The *solid* curve is theoretical. The *dotted* and *broken* curves are the experimental  $T$  dependence. Because  $\xi \geq r_{\text{max}}$ , there is no adjustable parameter in this case. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **60**, 4105 (1999). Copyright 1999 American Institute of Physics.]

values by Michels et al. [38]. In this case, the range  $\xi$  of density variation is equal to or larger than the intermolecular force range  $r_{\max} \equiv |\mathbf{r}_{12}|_{\max}$ . Therefore the viscosity values computed are free from parameters other than potential parameters. The agreement with experiment is good, validating the formula for  $\eta$ .

In Fig. 10.3b, the temperature dependence of the shear viscosity at  $\rho_m = mn = 900 \text{ kg m}^{-3}$  is compared with the experimental values. The *solid curve* is for the excess shear viscosity  $\Delta\eta = \eta - \eta_k$  calculated with  $D_{\text{Heyes}}$ , the *dotted curve* was computed by the empirical formula reported by Haynes [37], and the *dash-dot curve* was obtained with the formula reported by Younglove and Hanley [40]. The latter two curves are therefore experimental. In this case,  $\xi \geq r_{\max}$  and hence the formula for  $\eta_v$  is free from the parameter  $\xi$ . The temperature dependence by the density fluctuation theory shows a negative temperature derivative of  $\Delta\eta$ , as do the Younglove–Hanley formula and molecular dynamic simulation data [39], whereas the Haynes formula [37] shows a positive temperature derivative. On physical grounds, the temperature gradient of  $\Delta\eta$  is expected to be negative, and the behavior of  $\eta$  is consistent with experiment except for the Haynes data.

As the temperature approaches the triple point of argon, the value of  $\xi$  is less than  $r_{\max}$ . For the analysis of data in this regime of temperature, a parameter  $\vartheta$  was introduced in the integral for  $\omega(n)$  in the same manner as for the normal stress for computational convenience; see (10.18). For Fig. 10.4a and b,  $\vartheta = 0.175$  was chosen, which corresponds approximately to the cutoff parameter value  $\xi \approx 2\sigma$ , and the temperature dependence of the shear viscosity of argon at  $\rho = 1,408 \text{ kg m}^{-3}$  was calculated as shown.

In Fig. 10.4a, the *solid curve* is the theoretical shear viscosity computed with  $D_{\text{NR}}$ , and the Chapman–Enskog theory shear viscosity ( $\eta_{\text{CE}}$ ) is used for the kinetic part of  $\eta$ ,  $\eta_k = \eta_{\text{CE}}$ . As mentioned in connection with Fig. 10.3, the Chapman–Enskog theory shear viscosities at the temperatures of interest here agree well with experiment. Because  $D_{\text{Heyes}}$  was judged inapplicable in the temperature range considered here, no comparison was made for the viscosity calculated with it and thus a comparison is not available. The *dotted* (· · ·) and *dash-dot* (— · —) curves were, respectively, computed with the Haynes [37] and Younglove–Hanley formulas [40], which are empirical. Therefore, they are experimental. The *filled circles* (●) are the experimental data quoted by Naugle et al. [27] who, to obtain them, interpolated or extrapolated the data reported in the papers by Lowry et al. [41], Davis and Luks [42], and Saji and Kobayashi [43]. The temperature derivative of  $\eta$  is negative, as expected. The qualitative behavior of the theoretical prediction shows a correct tendency. Figure 10.4b shows the density dependence of the shear viscosity at  $T = 90.0 \text{ K}$ . The meanings of the curves are the same as in Fig. 10.4a. The symbols represent experimental data: ○ from [30]; \* from [28]; × from [29]; and ● from [27]. The theoretical prediction, with one adjustable parameter, agrees well with experiment in the density range where experimental values



**Fig. 10.4.** (a)  $\eta$  vs.  $T$  for argon at  $\rho = 1,408 \text{ kg m}^{-3}$ . The solid curve is theoretical. The dotted and dash-dot curves are the experimental  $T$  dependence calculated with the empirical formulas [37, 40]. The filled circles ( $\bullet$ ) are experimental values reported by Naugle et al. [27]. (b)  $\eta$  vs.  $\rho$  at  $T = 90.0 \text{ K}$ . The meanings of the curves are the same as in panel a. The symbols represent the experimental data indicated in the text. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **60**, 4105 (1999). Copyright 999 American Institute of Physics.]

are available. In Table 10.1, the viscosity and bulk viscosity values calculated with  $D_{\text{NR}}$  and by Heyes are listed together with the experimental values at various densities. The columns  $D_{\text{NR}}$  and  $D_{\text{Heyes}}$  in Table 10.1 represent the theoretical values of viscosities computed with  $D_{\text{NR}}$  and  $D_{\text{Heyes}}$  for the self-diffusion coefficient. The column Exp1 is for experimental viscosities reported in [22], whereas the column Exp2 is for the viscosities computed with the Younglove–Hanley and Haynes formulas (in parentheses). Column Exp3 is for the experimental bulk viscosities reported in [22].

By using the bulk viscosity formula obtained earlier, we find the relation between  $\eta_b$  and  $\eta_v$

$$\eta_b = \frac{2}{3} \eta_v. \quad (10.47)$$

Therefore, the ratio  $\eta_b/\eta$  in the liquid density regime is approximately independent of density and temperature:

$$\eta_b = \frac{2\eta}{3(1 + \eta_k/\eta_v)} \simeq \frac{2}{3}\eta, \quad (10.48)$$

because  $\eta_k \ll \eta_v$ . The experimental values for the ratio  $\eta_b/\eta$  are, on the average, 0.85 from [27], 0.78 from [30], 0.56 from [28], and 0.69 [29]. Therefore, the theoretical prediction is comparable to the mean value 0.72 of the

**Table 10.1.** Shear and bulk viscosities at  $T = 273.0\text{ K}$ 

$\rho^\dagger$	$\eta^\ddagger$				$\eta_b^\ddagger$		
	$D_{\text{NR}}$	Heyes	Exp1	Exp2	$D_{\text{NR}}$	$D_{\text{Heyes}}$	Exp3
508	0.032	0.028	0.0365	0.033 (0.033)	0.009	0.0066	0.009
694	0.052	0.043	0.051	0.044 (0.044)	0.022	0.016	0.029
812	0.071	0.056	0.060	0.054 (0.055)	0.035	0.025	0.033
896	0.087	0.068	0.067	0.063 (0.065)	0.046	0.033	0.044
958	0.10	0.078	0.073	0.071 (0.074)	0.055	0.040	0.048
1008	0.11	0.086	0.08	0.079 (0.083)	0.063	0.045	0.056

$\dagger$  in units of  $\text{kg m}^{-3}$ .

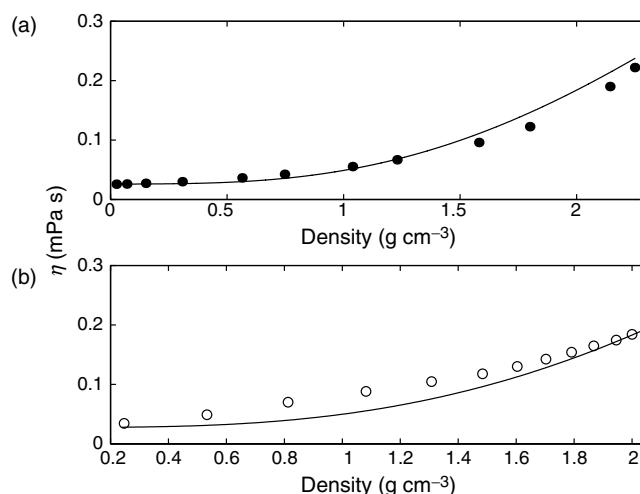
$\ddagger$  in units of  $\text{mPas}$ .

**Table 10.2.** Ratio of  $\eta_b$  to  $\eta$  at  $T = 273.0\text{ K}$ 

$\rho (\text{kg m}^{-3})$	$\eta_b/\eta$		
	$D_{\text{NR}}$	$D_{\text{Heyes}}$	Exp.
508	0.28	0.24	0.25
694	0.42	0.31	0.57
812	0.49	0.45	0.55
896	0.53	0.49	0.66
958	0.55	0.51	0.66
1008	0.57	0.52	0.70

experimental values. On the other hand, at  $T = 273.0\text{ K}$  its value varies from 0 to  $\sim 0.6$  as the density increases from 0 to  $1,000\text{ kg m}^{-3}$ , as indicated by some of the higher density values shown in Table 10.2, where the experimental data are calculated on the basis of the data reported in [22]. The ratio clearly vanishes as the density vanishes because  $\eta_b, \eta_v \sim n^3$  as  $n \rightarrow 0$ . These comparisons of the ratio  $\eta_b/\eta$  indicate that the formulas obtained for viscosities in the density fluctuation theory have qualitatively correct and mutually consistent properties and therefore are judged reliable.

The shear viscosity formula has been applied to other simple fluids to calculate the density dependence of krypton at  $T = 298.1\text{ K}$  and of xenon at  $T = 373.1\text{ K}$ . The results are presented in Fig. 10.5a and b. The potential parameters for krypton are  $\sigma = 0.360\text{ nm}$  and  $\epsilon/k_B = 171\text{ K}$ , whereas  $\sigma = 0.410\text{ nm}$  and  $\epsilon/k_B = 221\text{ K}$  for xenon. The values of the potential parameters were taken from [28, 33]. These parameters give the reduced temperature at  $T^* = 1.74$  for krypton and  $T^* = 1.69$  for xenon. Therefore, the two fluids are at comparable reduced temperatures. For the calculation of the shear



**Fig. 10.5.** (a)  $\eta$  vs.  $\rho$  for krypton at  $T = 298.1\text{ K}$  ( $T^* = 1.74$ ). The solid curve is theoretical and the filled circles are the experimental values. (b)  $\eta$  vs.  $\rho$  for xenon at  $T = 373.1\text{ K}$  ( $T^* = 1.69$ ). The solid curve is theoretical and the open circles are the experimental values. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **60**, 4105 (1999). Copyright 1999 American Institute of Physics.]

viscosities of these fluids,  $\xi \geq r_{\max}$ . Therefore, the viscosity formula involves only the potential parameters and hence is free from the adjustable parameter. In Fig. 10.5a for the density dependence of the shear viscosity of krypton, the *solid curve* is theoretical whereas the *filled circles* are the experimental values reported by Trappeniers et al. [44]. The Chapman–Enskog shear viscosity is used for the kinetic part of  $\eta$ , which was found to agree well with experiment. In Fig. 10.5b for the density dependence of the shear viscosity of xenon, the *solid curve* shows theoretical values calculated with the Chapman–Enskog shear viscosity for the kinetic part of  $\eta$ , whereas the *open circles* are the experimental values reported by Reynes and Thodos [45]. In this case, the Chapman–Enskog shear viscosity slightly underestimates the experimental viscosities at low densities. Agreement with experiment and theory is not as good as for krypton at intermediate densities, but the density dependence found is qualitatively correct. Because the law of corresponding states was reportedly [46, 47] obeyed by simple fluids such as argon, krypton, and xenon examined here, agreement between experiment and theory for krypton and xenon could have been expected. Nevertheless, the comparison presented for krypton and xenon ensures the reliability of the viscosity formula obtained by the density fluctuation theory and also verifies the law of corresponding states for the fluids considered.

#### 10.2.4 Assessment of the Stokes–Einstein Relation

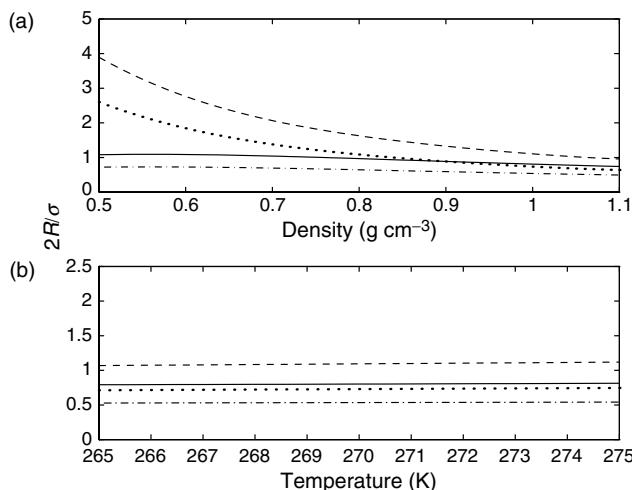
The SE relation is widely applied in the fields of transport processes and related topics in the literature. Its application is often uncritical and beyond the limits of its applicability. There have been some serious efforts [48, 49] to assess its range of applicability but with inconclusive outcomes. Since the viscosity formula (10.43) is not the SE relation although it resembles it and, moreover, it correctly predicts the density and temperature dependence of viscosities, it may be used to assess the SE relation by investigating under what conditions the SE relation and formula (10.43) yield the same or comparable density and temperature dependence. Comparing the SE relation (10.16) with the formula for  $\eta_v$  in (10.40) under the assumption that  $\eta_{se} = \eta_v$ , we obtain

$$\begin{aligned}\frac{\sigma}{2R} &= \frac{\pi\sigma}{2k_B T} n^2 \omega(n) \quad (\text{stick boundary condition}) \\ &= \frac{\pi\sigma}{3k_B T} n^2 \omega(n) \quad (\text{slip boundary condition}),\end{aligned}\tag{10.49}$$

where  $R = \sigma_{se}$ , the SE radius. If we assume  $\eta_{se} = \eta$  instead of  $\eta = \eta_v$ , we obtain

$$\begin{aligned}\frac{\sigma}{2R} &= \frac{3\pi\sigma}{k_B T} cnD_0 D + \frac{\pi\sigma}{2k_B T} n^2 \omega(n) \quad (\text{stick boundary condition}) \\ &= \frac{2\pi\sigma}{k_B T} cnD_0 D + \frac{\pi\sigma}{3k_B T} n^2 \omega(n) \quad (\text{slip boundary condition}).\end{aligned}\tag{10.50}$$

If the ratio  $\sigma/2R$  remains independent of  $T$  and  $n$ , the SE relation and the shear viscosity formula (10.43) will be equivalent within a constant factor despite the appearance of (10.43) to the contrary. The SE relation was assessed for argon. In Fig. 10.6, the values of  $2R/\sigma$  are plotted against density and temperature, respectively, in panels a and b. The *broken* (---) and *dotted* (···) curves are the results computed for slip and stick boundary conditions with the formulas in (10.49), respectively. The *solid* (—) and *dash-dot* (- · -) lines are the results computed for slip and stick boundary conditions with the formulas in (10.50), respectively. The density dependence of the ratio is computed for argon at  $T = 273.0$  K, and the temperature dependence is computed at  $\rho = 1,000$  kg m<sup>-3</sup>. The value of parameter  $\xi$  is taken larger than  $r_{max}$ . Therefore, the viscosity formula is practically free from the parameter  $\xi$ . The density dependence is almost absent if the full viscosity  $\eta$  is used, although the values of  $2R/\sigma$  for different boundary conditions used differ by an almost constant factor. On the other hand, the  $2R/\sigma$  values computed with (10.49) show density dependence but no temperature dependence. Therefore, we conclude that it is the full viscosity that gives a constant  $2R/\sigma$ , but not  $\eta_v$ . In Fig. 10.7, the density and temperature dependence of  $2R/\sigma$  are examined

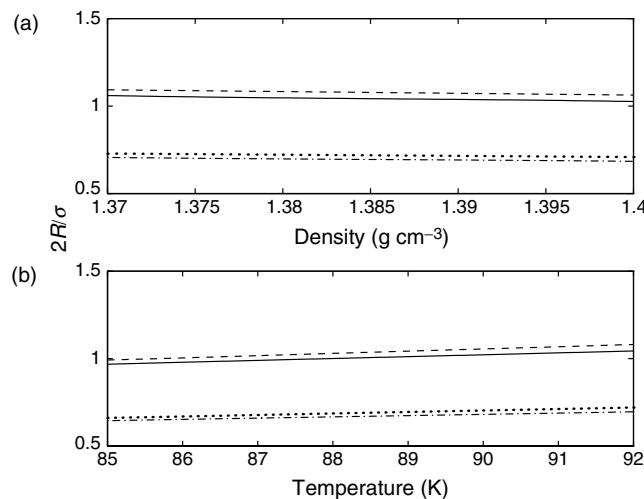


**Fig. 10.6.** (a) Density dependence of  $2R/\sigma$  for argon at  $T = 273.0\text{ K}$ . (b) Temperature dependence for argon at  $\rho = 1,000\text{ kg m}^{-3}$ . The broken (- -) and dotted (· · ·) lines are computed with (10.49). The solid (—) and dash-dot (--) lines are computed with (10.50). [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **60**, 4105 (1999). Copyright 1999 American Institute of Physics.]

for argon near the triple point at  $T = 90\text{ K}$  for the density dependence, and at  $\rho = 1,408\text{ kg m}^{-3}$  for the temperature dependence. For these figures, the parameter  $\vartheta$  in lieu of  $\xi$  was taken as  $\vartheta = 0.175$ . The meanings of the lines are the same as in Fig. 10.6. The values of  $2R/\sigma$  remain virtually constant for all cases, indicating that the SE relation is obeyed. These figures suggest that in the density and temperature range examined here, the SE relation remains valid for  $\eta$  for simple liquids, even if the particle is of molecular size, and that the question of slip or stick boundary condition is irrelevant from the viewpoint of statistical mechanics. If one is prepared to take  $R$  as an adjustable parameter, it should be taken with a value in the neighborhood of  $\sigma/2$ . The assessment here of the relation provides useful insight into the question of the range of applicability of the SE relation. In any case, from the perspective of (10.43) the question of the validity of the SE relation for molecular particles is irrelevant because it is a relation holding for fluids consisting of molecular particles, not for a continuum fluid for which the SE holds.

### 10.2.5 Density Fluctuation Theory Viewed from the Chapman–Enskog Theory

The generalized Boltzmann equation lies in the foundation of the density fluctuation theory because the latter approach requires the local grand canonical ensemble distribution function  $F_c^{(N)}$  that the former provides. In this regard, it should be recalled that the reduced pair distribution functions are generated



**Fig. 10.7.** (a) Density dependence of  $2R/\sigma$  for argon at  $T = 90$  K. (b) Temperature dependence of argon at  $\rho = 1,408 \text{ kg m}^{-3}$ . For these figures,  $\vartheta = 0.175$ . The meanings of the curves are the same as Fig. 10.6. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **60**, 4105 (1999). Copyright 1999 American Institute of Physics.]

from the local grand canonical ensemble distribution function, and they will have to be eventually calculated by a suitable equation if a more complete theory is to be developed beyond that presented up to this point. The DOZ integral equation, for example, can be the theoretical vehicle for the full theoretical implementation of the density fluctuation theory. The same parentage of the density fluctuation theory and the Chapman–Enskog theory for transport coefficients of liquids based on the generalized Boltzmann equation, consequently, begs the question of how the two theories are related. At least, it will be interesting to explore what might be done to see their connection and gain insight into possible ways to develop the Chapman–Enskog theory in more practical forms for liquids. This latter aspect has been already considered in Chap. 7, although briefly, because there is no concrete method for implementing the theory that we can discuss in detail. We recall that in the discussion the viscosity is expressed as the sum of kinetic and potential parts

$$\eta = \eta_k + \eta_v,$$

and whereas the kinetic part is identified with the Chapman–Enskog formula for a dense fluid [see (7.100)], the potential part is expressible in the form

$$\eta_v = \frac{k_B T \eta_k^2}{g} \frac{\Delta \mathbb{R}}{\left(1 - \frac{k_B T \eta_k}{g} \Delta \mathbb{R}\right)}. \quad (10.51)$$

Here  $\Delta\mathbb{R}$  is defined by (7.102) consisting of collision bracket integrals. We have argued that in the approximation neglecting the cross terms of the kinetic and potential parts of the pressure tensor  $\Delta\mathbb{R}$  may be given by (7.105), which presents a rather cogent formula suggesting a computational method. The formal result of the density fluctuation theory indicates that this potential part of  $\eta$  should be identified with

$$\eta_v = \frac{n^2 \omega(n, T)}{6D}.$$

The question remains whether it is possible to show that

$$\frac{k_B T \eta_k^2}{g} \frac{\Delta\mathbb{R}}{\left(1 - \frac{k_B T \eta_k}{g} \Delta\mathbb{R}\right)} = \frac{n^2 \omega(n, T)}{6D} \quad (10.52)$$

and under what conditions. In any case, it will be interesting to evaluate  $\Delta\mathbb{R}$  by some numerical means and compute the shear viscosity in the liquid density regime. This question is left for study in the future.

### 10.3 Heat Flux

In the previous sections of this chapter, we have shown that the density fluctuation theory can give formulas for the bulk viscosity and shear viscosity of simple liquids quite accurately and adequately over the entire density and temperature ranges experimentally studied, if an empirical  $D$  is used. In this section, we show that the same approach to the thermal conductivity of simple liquids can also produce a sufficiently accurate and reliable theory in the experimentally studied ranges of temperature and density. Compared to bulk and shear viscosities, the thermal conductivity is considerably more difficult to analyze from the viewpoint of molecular theory because its statistical mechanical expression is much more involved than the former. As has been for bulk and shear viscosities, thermal conductivity will be studied separately for simple and complex fluids because simple fluids are easier to study from the technical standpoint, and the point of the density fluctuation theory can be made more effectively in a more concise manner.

We again consider a system of  $N$  monatomic molecules contained in volume  $V$ . The statistical mechanical expression for heat flux in such a fluid is given by

$$\begin{aligned} \mathbf{Q} = & \left\langle \sum_{j=1}^N \left( \frac{1}{2} m C_j^2 + \sum_{k>j}^N \mathcal{V}_{jk} \right) \mathbf{C}_j \delta(\mathbf{r}_j - \mathbf{r}) F_c^{(N)} \right\rangle \\ & + \left\langle \frac{1}{2} \sum_{j \neq k=1}^N \mathbf{W}_{jk} \cdot \mathbf{C}_k \delta(\mathbf{r}_k - \mathbf{r}) F_c^{(N)} \right\rangle, \end{aligned} \quad (10.53)$$

where the notation is the same as before and the ensemble average is performed with the nonequilibrium grand canonical distribution function  $F_c^{(N)}(x^{(N)}; t)$ .

The term containing the virial tensor operator  $\mathbf{W}_{jk}$  in (10.53) arises from the coupling of molecular flow with the stress created by intermolecular interactions within the fluid. This stress is accounted for by the tensor  $\mathbf{r}_{12}\mathbf{F}_{12}$ , which is the work done to displace a pair of molecules interacting with force  $\mathbf{F}_{12}$  by distance  $\mathbf{r}_{12}$ . This work is carried by the molecules in flow and contributes to the heat flux within the fluid. From the viewpoint of the internal energy conservation law that must be satisfied by the fluid, the heat flux formula given in (10.53) is an inevitable conclusion that can be drawn from the kinetic equation. Therefore the appearance of the virial tensor in the expression for the heat flux  $\mathbf{Q}$  is not arbitrary, as it does inevitably appear in the expression for the stress tensors considered earlier. It must be noted that in the conventional treatment of thermal conductivity, such as the linear response theory and the Chapman–Enskog theory, the virial tensor operator  $\mathbf{W}_{jk}$  is usually approximated by the tensor  $\mathbf{r}_{12}\mathbf{F}_{12}$ . But it is important to avoid such an approximation, particularly, in the density fluctuation theory because, as shown for stress tensors, the displacement operator  $\exp(-\zeta \mathbf{r}_{12} \cdot \nabla)$  in  $\mathbf{W}_{jk}$  is important in accounting for the effects of density variation on heat flux and also is necessary if improved accuracy is desired for the thermal conductivity because of its major contribution, especially, in the high density regime. We emphasize again that the displacement operator  $\exp(-\zeta \mathbf{r}_{12} \cdot \nabla)$  in the virial tensor acts on the Dirac delta function  $\delta(\mathbf{r}_k - \mathbf{r})$  in the statistical mechanical expression for heat flux.

Heat flux consists of three physically distinctive parts. Therefore, it is convenient to split it into three parts as follows:

$$\mathbf{Q} = \mathbf{Q}_k + \mathbf{Q}_v + \mathbf{Q}_w, \quad (10.54)$$

where

$$\mathbf{Q}_k = \left\langle \frac{1}{2} \sum_{j=1}^N m C_j^2 \mathbf{C}_j \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle, \quad (10.55)$$

$$\mathbf{Q}_v = \left\langle \frac{1}{2} \sum_{j \neq k=1}^N \mathcal{V}_{jk} \mathbf{C}_j \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle, \quad (10.56)$$

$$\mathbf{Q}_w = \left\langle \frac{1}{2} \sum_{j \neq k=1}^N \mathbf{W}_{jk} \cdot \mathbf{C}_j \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle. \quad (10.57)$$

Heat flux  $\mathbf{Q}_k$  represents the kinetic energy flux,  $\mathbf{Q}_v$  is the potential energy transported by mass flow, and  $\mathbf{Q}_w$  arises from the coupling of the stress with mass flow; it is a flow of stress-related work. If the density is high,  $\mathbf{Q}_v$  and  $\mathbf{Q}_w$  are comparable in magnitude and constitute the major portion of heat conductivity, whereas the kinetic part plays a minor role in the liquid density

regime. Because the dynamic mechanism of energy transport at high density is basically different from that at low density, the dilute gas kinetic theory does not give good guidance for developing a theory of energy transport at high density, as we have already seen for bulk and shear viscosities. The aforementioned three components of  $\mathbf{Q}$  will be considered separately in the following.

### 10.3.1 Kinetic Part of Heat Flux

Because particles are identical and the kinetic part consists only of single particle variables,  $\mathbf{Q}_k$  can be reduced to a form involving the singlet distribution function; it is given by

$$\mathbf{Q}_k = \int d\mathbf{p} \frac{1}{2} m C^2 \mathbf{C} f^{(1)}(\mathbf{p}, \mathbf{r}; t), \quad (10.58)$$

where  $f^{(1)}(\mathbf{p}, \mathbf{r}; t)$  is the nonequilibrium singlet distribution function. To a good approximation,  $f^{(1)}(\mathbf{p}, \mathbf{r}; t)$  in the low-density regime obeys the Boltzmann equation, which will follow from the generalized Boltzmann equation when the superposition approximation is made for the doublet distribution function and the approximation is also made that the singlet distribution functions are spatially uniform within the collision volume. The solution of the Boltzmann equation has been discussed in Chaps. 2 and 3, and the kinetic part of the heat flux can be accordingly calculated to first order in temperature gradient. We obtain the kinetic part of thermal conductivity by comparing the result with the phenomenological constitutive equation for  $\mathbf{Q}_k$ , namely, Fourier's law of heat conduction:

$$\mathbf{Q}_k = -\lambda_k \nabla T(\mathbf{r}), \quad (10.59)$$

where  $T(\mathbf{r})$  is the local absolute temperature. In this manner,  $\lambda_k$  may be identified with the Chapman–Enskog thermal conductivity [32]. In the following treatment of thermal conductivity of simple fluids  $\lambda_k$  will be taken for the Chapman–Enskog thermal conductivity, whose kinetic theory formula is already known. Therefore we will not dwell on it here.

### 10.3.2 Potential Energy Transport

Because the potential energy is assumed to be pairwise additive, the potential energy contribution  $\mathbf{Q}_v$  to the heat flux may be reduced to a form that involves the nonequilibrium pair distribution function  $f^{(2)}(x_1, x_2; t)$ :

$$\mathbf{Q}_v = \frac{1}{2} \int dx_1 \int dx_2 \mathcal{V}(r_{12}) \mathbf{C}_i \delta(\mathbf{r}_i - \mathbf{r}) f^{(2)}(x_1, x_2; t) \quad (i = 1 \text{ or } 2), \quad (10.60)$$

where  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ . Because of the symmetry of potential energy  $\mathcal{V}(r_{12})$  and the pair distribution function  $f^{(2)}(x_1, x_2; t)$  with respect to the interchange of particle positions  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , either particle index  $i = 1$  or  $2$  can be chosen. To

recast this integral further into a little more useful form the following reduced distribution functions are defined.

Various nonequilibrium reduced distribution functions were defined in Sect. 9.2 of Chap. 9. In particular, density distribution functions  $n(\mathbf{r}, t)$  and  $n^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t)$  were defined by integrating the singlet distribution function  $f^{(1)}(\mathbf{p}, \mathbf{r}, t)$  and the doublet distribution function, respectively, over momentum; see (9.50) and (9.53). When they are employed, the doublet reduced distribution function can be factored as

$$f^{(2)}(x_1, x_2; t) = f^{(1)}(x_1, t)f^{(1)}(x_2, t)g^{(2)}(x_1, x_2; t), \quad (10.61)$$

where  $g^{(2)}(x_1, x_2; t)$  is the doublet correlation function, which may be expressed as

$$g^{(2)}(x_1, x_2; t) = \phi^{(2)}(x_1, x_2; t)n^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t). \quad (10.62)$$

Because the singlet distribution functions can be factored, it is useful to express  $f^{(2)}(x_1, x_2; t)$  in the form,

$$f^{(2)}(x_1, x_2; t) = \psi^{(2)}(x_1, x_2; t)n(\mathbf{r}_1, t)n(\mathbf{r}_2, t)n^{(2)}(\mathbf{r}_1, \mathbf{r}_2, t), \quad (10.63)$$

where  $\psi^{(2)}(x_1, x_2; t)$  is defined by the product

$$\psi^{(2)}(x_1, x_2; t) \equiv \phi(x_1, t)\phi(x_2, t)\phi^{(2)}(x_1, x_2; t). \quad (10.64)$$

With this reduced pair distribution function  $\psi^{(2)}(x_1, x_2; t)$ , it is possible to define the mean conditional velocity

$$\mathbf{V}(\mathbf{r}, \mathbf{r} + \mathbf{r}_{12}, t) = \int d\mathbf{p}_1 \int d\mathbf{p}_2 \mathbf{v}_2 \psi^{(2)}(\mathbf{r} + \mathbf{r}_{12}, \mathbf{r}, \mathbf{p}_1, \mathbf{p}_2, t), \quad (10.65)$$

which is the mean velocity of particle 2, given that the pair of particles (12) is separated by distance  $\mathbf{r}_{12}$  whereas their center of mass is located at  $\mathbf{r}$ , regardless of the distribution of other particles in the system. Then  $\mathbf{Q}_v$  may be written in the form

$$\begin{aligned} \mathbf{Q}_v &= \frac{1}{2} \int d\mathbf{r}_{12} \mathcal{V}(r_{12}) n(\mathbf{r}, t)n(\mathbf{r} + \mathbf{r}_{12}, t)n^{(2)}(\mathbf{r}_{12}, t) \\ &\times [\mathbf{V}(\mathbf{r}, \mathbf{r} + \mathbf{r}_{12}; t) - \mathbf{u}(\mathbf{r}, t)]. \end{aligned} \quad (10.66)$$

This expression for  $\mathbf{Q}_v$  implies that density and mean velocity variations over the intermolecular force range are the physical mechanism for potential energy transport in liquids.

By expanding the density and the mean velocity in the integrand in (10.66) in a series of  $\mathbf{r}_{12}$ , we obtain

$$\begin{aligned} n(\mathbf{r} + \mathbf{r}_{12}, t) &= n(\mathbf{r}, t) + \mathbf{r}_{12} \cdot \nabla n(\mathbf{r}, t) + \frac{1}{2} \mathbf{r}_{12} \mathbf{r}_{12} : [\nabla n(\mathbf{r}, t)]^2 + \dots, \\ \mathbf{V}(\mathbf{r}, \mathbf{r} + \mathbf{r}_{12}; t) &= \mathbf{u}(\mathbf{r}, t) + \mathbf{r}_{12} \cdot \nabla \mathbf{u}(\mathbf{r}, t) + \frac{1}{2} \mathbf{r}_{12} \mathbf{r}_{12} : [\nabla \mathbf{u}(\mathbf{r}, t)]^2 + \dots, \end{aligned} \quad (10.67)$$

where the double dot symbol  $(:)$  stands for double contraction of the tensors and we have used the fact that

$$\mathbf{V}(\mathbf{r}, t) = \mathbf{u}(\mathbf{r}, t).$$

Substituting these expansions in (10.66), we obtain the potential part of heat flux  $\mathbf{Q}_v$  to first order in the density derivative

$$\begin{aligned} \mathbf{Q}_v &= \frac{1}{2}n(\mathbf{r}, t) \int d\mathbf{r}_{12} \mathcal{V}(r_{12}) n^{(2)}(\mathbf{r}_{12}, t) \mathbf{r}_{12} \mathbf{r}_{12} : \nabla n(\mathbf{r}, t) \nabla \mathbf{u}(\mathbf{r}, t) \\ &\quad + O[(\nabla n)^2]. \end{aligned} \quad (10.68)$$

The product of density and velocity gradients on the right of (10.68) is a tensor of rank three. It must be related to the temperature gradient. Before examining such a relation we proceed to consider the virial tensor part  $\mathbf{Q}_w$  of the heat flux.

### 10.3.3 Virial Transport

We now consider the intermolecular force contribution making up heat flux  $\mathbf{Q}_w$  defined by (10.57). This contribution, when explicitly worked out, is given by the formula

$$\mathbf{Q}_w = \frac{1}{2} \int_0^1 d\zeta \int dx^{(2)} \mathbf{r}_{12} \mathbf{F}_{12} \cdot \mathbf{C}_1 e^{-\zeta \mathbf{r}_{12} \cdot \nabla} \delta(\mathbf{r}_1 - \mathbf{r}) f^{(2)}(x_1, x_2, t). \quad (10.69)$$

Because the particles are identical, this expression can be given in terms of a reduced distribution function in the same manner as for  $\mathbf{Q}_v$ :

$$\begin{aligned} \mathbf{Q}_w &= \frac{1}{2} \int_0^1 d\zeta \int d\mathbf{r}_{12} \mathbf{r}_{12} \mathbf{F}_{12} n(\mathbf{r} - \zeta \mathbf{r}_{12}, t) n[\mathbf{r} + (1 - \zeta) \mathbf{r}_{12}, t] n^{(2)}(\mathbf{r}_{12}, t) \\ &\quad \times \{\mathbf{V}[\mathbf{r} - \zeta \mathbf{r}_{12}, \mathbf{r} + (1 - \zeta) \mathbf{r}_{12}; t] - \mathbf{u}(\mathbf{r}, t)\}. \end{aligned} \quad (10.70)$$

By expanding the density and the mean velocity in a Taylor series, retaining the terms of linear order in  $\nabla n(\mathbf{r}, t)$  and  $\nabla \mathbf{u}(\mathbf{r}, t)$ , and integrating with respect to the charging parameter  $\zeta$ , we obtain the formula for  $\mathbf{Q}_w$  to linear order with respect to  $\nabla n(\mathbf{r}, t)$  and  $\nabla \mathbf{u}(\mathbf{r}, t)$ , respectively,

$$\begin{aligned} \mathbf{Q}_w &= \frac{1}{6}n(\mathbf{r}, t) \int d\mathbf{r}_{12} n^{(2)}(\mathbf{r}_{12}; t) \mathbf{r}_{12} \mathbf{F}_{12} \mathbf{r}_{12} \mathbf{r}_{12} : \nabla n(\mathbf{r}, t) \nabla \mathbf{u}(\mathbf{r}, t) \\ &\quad + O[(\nabla n \nabla \mathbf{u})^2]. \end{aligned} \quad (10.71)$$

This has the same mathematical structure as  $\mathbf{Q}_v$  in (10.68) except that the virial term  $\mathbf{r}_{12} \mathbf{F}_{12}/3$  replaces the potential energy  $\mathcal{V}(r_{12})$  in  $\mathbf{Q}_v$ .

Now, the derivation of the constitutive equation for the potential part of heat flux  $\mathbf{Q}_p$

$$\mathbf{Q}_p \equiv \mathbf{Q}_v + \mathbf{Q}_w \quad (10.72)$$

is reduced to the question of relating the third-rank tensor  $\nabla n(\mathbf{r}, t) \nabla \mathbf{u}(\mathbf{r}, t)$  to a term composed of the temperature gradient and, possibly, the molecular parameters as well as other quantities or functions characterizing molecular interactions and correlations, such as pair correlation functions. In this step, the hydrodynamic description of heat flow enters the theory as will be shown presently.

#### 10.3.4 Thermal Conductivity

To implement the intended hydrodynamic description and to derive the constitutive equation for heat flux in a simple fluid, it is necessary to consider a flow configuration explicitly. We assume the following flow configuration. The fluid is confined between two parallel plates separated by a distance, say,  $L$ , and is subject to a static temperature difference, so that the global temperature gradient is  $\Delta T/L$ , where  $\Delta T$  is the temperature difference between the plates. This temperature difference generates a local temperature gradient  $\nabla T(\mathbf{r})$  at point  $\mathbf{r}$  within the fluid. The direction of the temperature gradient is assumed to be along the  $z$  axis of the coordinate system. The temperature gradient produces a local density variation over the range of intermolecular forces. We have already seen that, as in the theory of viscosity in the previous subsections, the local density variation gives the potential part of the heat flux that is proportional to the tensor product  $\nabla n(\mathbf{r}, t) \nabla \mathbf{u}(\mathbf{r}, t)$ , which must be related to the temperature gradient in the flow configuration considered.

#### The Third-Rank Tensor of Density and Velocity Gradients

The fluid velocity and density variations,  $\nabla \mathbf{u}(\mathbf{r}, t)$  and  $\nabla n(\mathbf{r}, t)$ , are attributed to the effects of an externally applied temperature gradient producing  $\nabla T(\mathbf{r}, t)$  in the system. Because the temperature gradient may be assumed static, as it often is when measuring thermal conductivity in a steady-state, all macroscopic variables are regarded as independent of time. Thus we assume that spatial derivatives of density and velocity are independent of time and examine their relations to the temperature gradient  $\nabla T(\mathbf{r})$ . To obtain such relations it is convenient to examine a typical experimental situation that is evidently macroscopic and thus requires hydrodynamic consideration.

For the flow configuration assumed earlier, the continuity equation in the steady state can be integrated to the form

$$\rho u_z = C, \quad (10.73)$$

where  $\rho$  is the mass density and  $C$  is a constant with respect to the position in the fluid but generally dependent on density and temperature. The

one-dimensional momentum balance equation for the flow configuration in hand is

$$\frac{\partial}{\partial z} \rho u_z u_z + \frac{\partial p}{\partial z} - \frac{\partial}{\partial z} \eta_l \frac{\partial u_z}{\partial z} = 0, \quad (10.74)$$

where  $\eta_l$  is the longitudinal viscosity defined by

$$\eta_l = \frac{4}{3} \eta + \eta_b \quad (10.75)$$

with  $\eta$  and  $\eta_b$  denoting the shear viscosity and the bulk viscosity, respectively; and  $\eta$  is the sum of the kinetic part  $\eta_k$  and the potential part  $\eta_v$ , which have been already treated in Sect. 10.2. The longitudinal viscosity  $\eta_l$  therefore can be calculated with the formulas developed in Sects. 10.1 and 10.2.

In the present consideration, we assume that an isobaric condition is imposed on the system. Then, because

$$\frac{\partial p}{\partial z} = \left( \frac{\partial p}{\partial \rho} \right)_T \frac{\partial \rho}{\partial z} + \left( \frac{\partial p}{\partial T} \right)_\rho \frac{\partial T}{\partial z} = 0,$$

it follows that

$$\frac{\partial \rho}{\partial z} = -\rho \alpha \frac{\partial T}{\partial z}, \quad (10.76)$$

where  $\alpha$  is the isobaric thermal expansion coefficient

$$\alpha = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_p. \quad (10.77)$$

This relates the density derivative to the temperature derivative.

On integrating the one-dimensional momentum balance equation, there follows the integral surface in space  $(\rho, T)$

$$\frac{C^2}{\rho} + p - \eta_l \frac{\partial u_z}{\partial z} = C_0, \quad (10.78)$$

where  $C_0$  is an integration constant generally dependent on density and temperature. We have used (10.73) for (10.78). It is helpful to note that the isobaric condition means that  $\nabla p$  is absent in (10.74). Consequently,  $p$  does not appear in (10.78), but it is restored in the equation because both  $C_0$  and  $p$  are constants.

At this point, we assume the phenomenological thermodynamic force–flux relation for momentum  $\rho u_z$  (mass flux, i.e., the momentum):

$$\rho u_z = -D \frac{\partial \rho}{\partial z} - D_T \frac{\partial T}{\partial z}, \quad (10.79)$$

where  $D$  is the self-diffusion coefficient and  $D_T$  is the thermal diffusion coefficient. For a statistical mechanics derivation of this equation, see Appendix B.

When viscosities were discussed in Sect. 10.2, the temperature gradient term in the phenomenological relation (10.79) did not appear because the temperature was kept uniform over the system. It also follows from (10.79) that

$$\rho u_z = -D_e \frac{\partial \rho}{\partial z} = C, \quad (10.80)$$

where  $D_e$  is the effective self-diffusion coefficient defined by

$$D_e = D - \frac{D_T}{\rho \alpha}. \quad (10.81)$$

Upon differentiating  $u_z = C/\rho$  with  $z$  and using the second equality in (10.80), the velocity gradient can be written as

$$\frac{\partial u_z}{\partial z} = \frac{C^2}{\rho^2 D_e}. \quad (10.82)$$

Substituting (10.82) in (10.78), we obtain  $C^2$ :

$$C^2 = \frac{\rho^2 D_e (C_0 - p)}{(\rho D_e - \eta_l)} \quad (10.83)$$

and consequently

$$\frac{\partial u_z}{\partial z} = \frac{(C_0 - p)}{(\rho D_e - \eta_l)}. \quad (10.84)$$

Combining this result with (10.76), we obtain the desired relation for the product of density and velocity gradients:

$$\frac{\partial n}{\partial z} \frac{\partial u_z}{\partial z} = - \frac{n \alpha (C_0 - p)}{(\rho D_e - \eta_l)} \frac{\partial T}{\partial z}. \quad (10.85)$$

In the present approach, the momentum and energy are thought to be transported by the tagged (tracer) particles in a manner similar to the mean free path theory for gases. Therefore, the hydrodynamic considerations made earlier leading to (10.85) are for tracer particles whose mean velocity is  $u_z^*$ , which is opposite in direction to the mean fluid velocity  $u_z$ . This means that in (10.85)

$$\frac{\partial u_z}{\partial z} \Rightarrow - \frac{\partial u_z}{\partial z}.$$

Thus, with this taken into account, (10.85) may be written as

$$\frac{\partial n}{\partial z} \frac{\partial u_z}{\partial z} = \frac{n k_B \kappa^*}{m D} \frac{\partial T}{\partial z}, \quad (10.86)$$

where<sup>3</sup>

$$\kappa^* = \frac{mD\alpha(C_0 - p)}{k_B(\rho D_e - \eta_l)}. \quad (10.87)$$

The factor  $\kappa^*$  is not determined until  $D_e$  and  $C_0$  are determined definitively.  $C_0$  can be determined from the boundary conditions on the momentum balance equation. For the flow configuration under consideration, the boundary conditions, however, are experimental inputs that are not determined from molecular theory. In any case, it is clear that  $C_0$  must be of order of  $p$ ; it may be related, for example, to the speed of sound in the fluid. We will return to the equation for  $\kappa^*$  after the question of  $D_e$  is dealt with.

### Thermal Diffusion Coefficient

By combining (10.79) and (10.76), there follows the equation:

$$\rho u_z = \rho \alpha D_e \frac{\partial T}{\partial z}. \quad (10.88)$$

On multiplying (10.82) and (10.88) side by side, we obtain the relation

$$\rho u_z \frac{\partial u_z}{\partial z} = \frac{\alpha C^2}{\rho} \frac{\partial T}{\partial z}. \quad (10.89)$$

After inserting (10.82), the momentum balance equation (10.74) is recast in the form

$$\rho u_z \frac{\partial u_z}{\partial z} = \left( \frac{\partial \eta_l}{\partial T} \right)_p \frac{C^2}{\rho^2 D_e} \frac{\partial T}{\partial z} + \frac{\alpha \eta_l C^2}{\rho^2 D_e} \left[ 2 + \frac{\rho}{D_e} \frac{\partial D_e}{\partial \rho} \right] \frac{\partial T}{\partial z} \quad (10.90)$$

for which we have used the relation

$$\frac{\partial \eta_l}{\partial z} = \left( \frac{\partial \eta_l}{\partial \rho} \right)_T \frac{\partial \rho}{\partial z} + \left( \frac{\partial \eta_l}{\partial T} \right)_\rho \frac{\partial T}{\partial z}. \quad (10.91)$$

Note that this relation, using (10.76), can be written as

$$\frac{\partial \eta_l}{\partial z} = \left[ \left( \frac{\partial \eta_l}{\partial \rho} \right)_T - \alpha \rho \left( \frac{\partial \eta_l}{\partial T} \right)_\rho \right] \frac{\partial T}{\partial z} = \left( \frac{\partial \eta_l}{\partial T} \right)_p \frac{\partial T}{\partial z}, \quad (10.92)$$

---

<sup>3</sup> In the expression for  $\kappa^*$  in (50) in the paper by Rah and Eu [50] on the thermal conductivity of simple liquids, the mass factor  $m$  is unfortunately missing. The formula should read

$$\kappa^* = m D \alpha (C_0 - p) / k_B (\rho D_e - \eta_l).$$

Because

$$\left(\frac{\partial \eta_l}{\partial T}\right)_p = \left(\frac{\partial \eta_l}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial T}\right)_p + \left(\frac{\partial \eta_l}{\partial T}\right)_\rho. \quad (10.93)$$

By combining (10.88) and (10.90) and canceling out the common factor, we obtain the differential equation for  $D_e$ ,

$$\frac{\partial \ln \rho D_e}{\partial \ln \rho} = \frac{\rho D_e}{\eta_l} - \left[ 1 + \frac{1}{\alpha} \left( \frac{\partial \ln \eta_l}{\partial T} \right)_p \right]. \quad (10.94)$$

Change the variable

$$\varrho = \ln \left( \frac{\rho}{\rho_0} \right),$$

where  $\rho_0$  is the reference mass density suitably chosen, and define the abbreviation

$$\Theta(\rho, T) = 1 + \frac{1}{\alpha(\rho, T)} \left( \frac{\partial \ln \eta_l}{\partial T} \right)_p. \quad (10.95)$$

The solution for (10.94) then is given by

$$\begin{aligned} \rho D_e(\rho, T) &= (\rho D_e)_0 \exp \left[ - \int_0^\varrho dt \Theta(t, T) \right] \\ &\times \left\{ 1 - (\rho D_e)_0 \int_0^\varrho dt \frac{1}{\eta_l(t, T)} \exp \left[ - \int_\varrho^t dt' \Theta(t', T) \right] \right\}^{-1}, \end{aligned} \quad (10.96)$$

where the reference density  $\rho_0$  for  $\varrho$  may be taken with the density of the fluid at which the Chapman–Enskog transport coefficients hold for the gas, for example, the normal density of the gas. Hence,  $(\rho D_e)_0$  is the  $\rho D_e$  at  $\rho = \rho_0$ , that is, the Chapman–Enskog  $D_e$ . We note that for hard spheres

$$(\rho D)_0 = 1.204 \eta_k, \quad (10.97)$$

where  $\eta_k$  is the Chapman–Enskog shear viscosity of the gas. Because the right-hand side of (10.96) is known as a function of density and temperature,  $D_e$  is known. Provided that  $D$  is known, (10.96) for  $D_e$  gives a method of calculating the thermal diffusion coefficient  $D_T$  from information on the viscosity and self-diffusion coefficient of the liquid. The method of calculating  $D_T$  for liquids is not much studied in the literature. This formal result also appears to be new for  $D_T$  for the liquid of interest.

### 10.3.5 Potential Part of Thermal Conductivity

We now return to the question of  $C_0$ . If the momentum  $\rho u_z$  and the velocity gradient at the boundaries are known for various temperatures, this integration constant can be determined. However, such information is not available. Some other means must be sought to figure out the constant.

Because the thermal conductivity is given by the Chapman–Enskog formula at the normal density limit, it is useful to examine the low-density limit of  $\kappa^*$ . For this purpose, it is convenient to note the following limiting behavior of various quantities involved:

$$\begin{aligned}\lim_{n \rightarrow 0} (p - nk_B T) &= 0, \\ \lim_{n \rightarrow 0} \rho D &= 1.204\eta_k, \\ \lim_{n \rightarrow 0} \eta_l &= \frac{4}{3}\eta_k, \\ \lim_{n \rightarrow 0} \alpha T &= 1.\end{aligned}$$

Then these limits imply

$$\lim_{n \rightarrow 0} \kappa^* = 1.2 \times \frac{3}{4} \lim_{n \rightarrow 0} \frac{(C_0/p - 1)}{(\rho D_e/\eta_l - 1)}. \quad (10.98)$$

Because the limiting value of  $\kappa^*$  on empirical grounds should be a constant as follows:

$$\lim_{n \rightarrow 0} \kappa^* \simeq 0.40,$$

we infer the limiting behavior of the limit on the right of (10.98) as

$$\lim_{n \rightarrow 0} \frac{(C_0/p - 1)}{(\rho D_e/\eta_l - 1)} \simeq \frac{1}{2}. \quad (10.99)$$

Furthermore, in the same low-density limit we find

$$\rho D_e = \frac{4}{3}\eta_k \left( 1 + \frac{1}{2\alpha T} \right). \quad (10.100)$$

On the basis of the limits (10.98)–(10.100), we find empirically that  $\kappa^*$  may be put in the form

$$\kappa^* = \frac{a_0 \alpha T}{1 + 2\alpha T}, \quad (10.101)$$

where  $a_0 \simeq 1.2$  may be taken for argon considered in the analysis of the theory. With  $\kappa^*$  in (10.101) its low-density limit is reproduced, and the thermal conductivity calculated with  $\kappa^*$  in (10.101), as will be shown, has excellent behavior with regard to density and temperature. However, the theory in this form has become semiempirical because the limiting behavior of  $\kappa^*$  at low density must be fixed by choosing  $a_0$  suitably with the help of the empirical thermal conductivity at low density.

It is worthwhile to examine the chain of arguments leading to the formula for  $\kappa^*$  obtained in (10.101). The identification of  $\kappa^*$  in (10.101) implies that  $C_0$  may be written as

$$C_0 - p = a_0 \frac{k_B T (\rho D_e - \eta_l)}{m D (1 + 2\alpha T)}. \quad (10.102)$$

Having written  $C_0$  in this form, we see that because  $C_0$  is related to the boundary values of the flow variables, the parameter  $a_0$  may be regarded as related to the boundary conditions. The present procedure giving rise to  $C_0$  in (10.102) may be regarded as a kinetic theory method of determining the boundary condition for the mass balance equation because all quantities other than  $a_0$  on the right-hand side of (10.102) can be calculated by statistical mechanics. To pursue this line of examination a little further we substitute the expression for  $C_0$  given in (10.102) in (10.83) to obtain

$$C = \sqrt{a_0} \rho \sqrt{\frac{k_B T D_e}{m(1 + 2\alpha T) D}}. \quad (10.103)$$

This then may be interpreted as the boundary condition on the momentum of the fluid at the boundaries, and  $\sqrt{a_0}$  is the proportionality constant relating the molecular quantity to the boundary value of the momentum. Except for the proportionality constant  $\sqrt{a_0}$  all quantities on the right-hand side of (10.103) can be calculated by statistical mechanics. Therefore, in retrospect, if the boundary condition on the momentum  $\rho u_z$  were taken with the expression in (10.103), then (10.87) would have resulted directly. Equation (10.103) may be taken as a conjecture for the boundary condition on the momentum. The kinetic theory foundation for this boundary condition is absent at present. It may be worthy of further examination in the future. In this work, we have not taken this conjecture approach to be faithful to the original development of the theory.

By using the formula for  $\kappa^*$  in (10.101),  $\mathbf{Q}_p$ , which is the intermolecular force contribution to thermal conductivity, can be obtained in the form

$$\mathbf{Q}_p = -\lambda_p(n, T) \left( \frac{\partial T}{\partial z} \right), \quad (10.104)$$

where  $\lambda_p(n, T)$  is given by the formula,

$$\lambda_p(n, T) = \frac{n^2}{6D} \chi(n, T) \quad (10.105)$$

with the definition of the molecular factor  $\chi(n, T)$

$$\chi(n, T) = \frac{4\pi k_B \kappa^*}{m} \int_0^\infty dr r^4 \left[ \frac{r \mathcal{V}'(r)}{5} - \mathcal{V}(r) \right] g_{\text{eq}}^{(2)}(r, n) \theta(r - \xi). \quad (10.106)$$

In the same spirit as for the bulk and shear viscosity formulas, the dynamic pair correlation function (PCF)  $n^{(2)}(\mathbf{r}_{12}, t)$  in (10.68) and (10.71) has been replaced with the equilibrium pair correlation function  $g_{\text{eq}}^{(2)}(r_{12}, n)$  weighted by  $\theta(r_{12} - \xi)$  to the lowest order approximation. Here  $\theta(r - \xi)$  is again a step function defined by  $\theta(r - \xi) = 1$  for  $r < \xi$  and  $\theta(r - \xi) = 0$  for  $r > \xi$ . On the same physical grounds as for the stress tensors considered in the density fluctuation theory of bulk and shear viscosities, the cutoff parameter  $\xi$  is introduced

to account for the finiteness of the spatial range  $\xi$  of density variation caused by an applied temperature gradient. As was found in the theories of shear and bulk viscosities, the magnitude of  $\xi$  is less than the range of the intermolecular force  $r_{\max}$  and of the order of a few molecular diameters at temperatures below the critical point, in particular, near the triple point, whereas  $\theta(r - \xi)$  becomes unity at temperatures above and in the neighborhood of the critical point. Because at present no molecular theories are available for the range of density variations caused by an external perturbation, it plays the role of an adjustable parameter for temperature below the critical point, especially, near the triple point. However, the value of  $\xi$  cannot be arbitrary for thermal conductivity, because the thermal conductivity must be consistent with the shear and bulk viscosities. To maintain this desired mutual consistency, it is necessary to take the same value of  $\xi$  for all three transport coefficients, the shear and bulk viscosities and the thermal conductivity. Therefore, if the value of  $\xi$  is fixed for bulk and shear viscosities, then it is no longer an adjustable parameter for thermal conductivity, and vice versa.

Collecting the kinetic and potential energy parts of thermal conductivity, we obtain the final expression for the thermal conductivity of simple liquids as follows:

$$\lambda(n, T) = \lambda_k(T) + \frac{\rho^2}{6D}\chi(n, T). \quad (10.107)$$

This will be used to calculate the thermal conductivity of simple liquids and will be validated in comparison with the experimental data available in the literature.

### 10.3.6 Eucken Relation

For dilute monatomic gases the Eucken relation holds [32] between thermal conductivity and the shear viscosity

$$\lambda_k = \varepsilon C_v \eta_k, \quad (10.108)$$

where  $\varepsilon$  is the Eucken factor (a numerical factor),  $C_v$  the heat capacity of the gas at constant volume, and  $\eta_k$  is the shear viscosity of the gas. According to the Eucken relation,  $\lambda_k$  and  $\eta_k$  can be calculated from each other. The Chapman–Enskog theory based on the Boltzmann equation supports this relation [32]. However, because the potential part becomes very important and dominant over the kinetic part in accounting for the thermal conductivity of liquids, there is no assurance that a similar relation holds between the shear viscosity and the thermal conductivity. From theoretical and practical viewpoints, it should be interesting to examine a relationship between the thermal conductivity and the shear viscosity of liquids.

Because the potential energy part  $\lambda_v$  of the thermal conductivity consists of contributions arising from the potential energy transport and the work related to the virial tensor, it may be useful to consider each contribution separately for the relation in mind. We write

$$\chi(n, T) = \chi_v(n, T) + \chi_w(n, T), \quad (10.109)$$

where

$$\chi_v(n, T) = -\frac{4\pi k_B \kappa^*}{m} \int_0^\infty dr r^4 \mathcal{V}(r) g_{eq}^{(2)}(r, n) \theta(r - \xi), \quad (10.110)$$

$$\chi_w(n, T) = \frac{4\pi k_B \kappa^*}{5m} \int_0^\infty dr r^5 \mathcal{V}'(r) g_{eq}^{(2)}(r, n) \theta(r - \xi) \quad (10.111)$$

and then examine the possibility of an Eucken relation for the potential energy part. Because the potential energy part  $\eta_v$  of the shear viscosity of a simple liquid was shown to be expressible by the formula

$$\eta_v = \frac{\rho^2}{6D} \omega(n, T), \quad (10.112)$$

where

$$\omega(n, T) = \frac{2\pi}{15} \int_0^\infty dr r^5 \mathcal{V}'(r) g_{eq}^{(2)}(r, n) \theta(r - \xi), \quad (10.113)$$

we obtain the following relation for the heat conductivity of a simple liquid:

$$\lambda = \lambda_k(T) + C_1 \eta_v, \quad (10.114)$$

where

$$\begin{aligned} C_1 &= \frac{\chi(n, T)}{\omega(n, T)} \\ &\approx \frac{6k_B \kappa^*}{m} \left[ 1 + \frac{\chi_v(n, T)}{\chi_w(n, T)} \right]. \end{aligned} \quad (10.115)$$

In the second line of this equation, as mentioned earlier, the value of  $\xi$  has been assumed to be identical for both the shear viscosity and thermal conductivity, although the nature of the external perturbation to cause such density variations is different. This factor  $C_1$  is made up of the intermolecular force and the pair correlation function only, apart from the parameter  $\kappa^*$ . The relation (10.114) may be regarded as a generalized Eucken relation for liquids. It will be discussed further when the thermal conductivity is calculated in the subsequent section.

Because the derivation of the thermal conductivity formula is somewhat lengthier than those for viscosity and bulk viscosity, it is useful to summarize the important steps and the major approximations necessary for the derivation:

1. The statistical mechanical expression for heat flux is calculated in a series of density and velocity gradients. For linear transport processes it is sufficient to limit the series to the first order in density and velocity gradients.

2. For the first-order contribution to the heat flux, the dynamic pair correlation function may be approximated by the equilibrium pair correlation function weighted by a step function  $\theta(r - \xi)$ , where  $\xi \leq r_{\max}$ .
3. The velocity gradient  $\nabla \mathbf{u}$  in the gradient expansion is calculated by using the mass and momentum balance equation given in terms of either the self-diffusion coefficient, the thermal diffusion coefficient, or an empirical parameter determinable from the boundary conditions on fluid velocity. Because of the empirical parameter, the factor  $\kappa^*$  becomes semiempirical. We have noticed that the parameter  $a_0$  appearing in  $\kappa^*$  may be related to the boundary condition on the momentum.
4. By eliminating the velocity gradient thus obtained from the density gradient expansion for  $\mathbf{Q}$ , we obtain the potential energy part  $\mathbf{Q}_p$  of the thermal conductivity in terms of a self-diffusion coefficient, integrals involving the intermolecular potential energy, an equilibrium pair correlation function, and the Chapman–Enskog thermal conductivity for a dilute gas. The result is in a form parallel to the expressions for the shear and bulk viscosity of liquids discussed in the previous sections. This parallelism in features gives rise to a generalized Eucken relation between the thermal conductivity and the shear viscosity of the liquid.
5. The equilibrium pair correlation function may be calculated by an approximate theory such as the PY integral equation, a Monte Carlo simulation method, or a molecular dynamics method. The self-diffusion coefficient should be either treated empirically or computed by a separate theory of diffusion. The density fluctuation theory does not provide it.

### 10.3.7 Comparison with Experiment

Formula (10.107) derived for the thermal conductivity has been validated in comparison with experiment in the literature, and it is reviewed in this subsection. As for shear and bulk viscosity, (10.107) requires a self-diffusion coefficient, either experimental or theoretical, at the desired density and temperature. Because a fairly reliable theory of diffusion is available at present, which was developed after the development of the theory discussed here, the theory can be validated with the theoretical self-diffusion coefficient provided by the theory of diffusion. However, formula (10.107) was originally validated with either experimental self-diffusion coefficients or viscosity data because of the absence of the theoretical  $D$  or  $\eta$ . For this reason, the empirical method of validation originally used in the literature will be discussed. Because the experimental data for  $D$  of liquid argon available in the literature at the time were limited to those along the coexisting curve, whereas a large body of experimental data was available for the shear viscosity of argon (see, for instance, [51] and references therein), experimental shear viscosity data were predominantly employed for the validation by using the generalized Eucken relation that can provide the thermal conductivity from viscosity data. For the purpose, the generalized Eucken relation (10.114) can be rewritten as

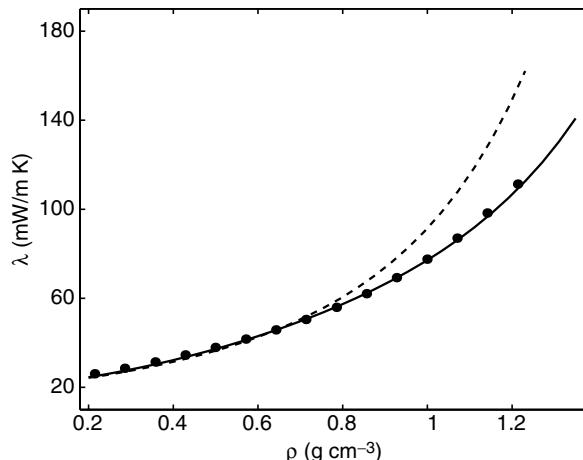
$$\lambda = \lambda_k(T) + \frac{\chi(n, T)}{\omega(n, T)} \eta_v. \quad (10.116)$$

The experimental data on the viscosity of argon were used. The Lennard-Jones potential is exclusively used for intermolecular interactions with potential parameters  $\epsilon/k_B = 119.8$  and  $\sigma = 0.3405$  nm. The temperature and density are reduced in the usual manner.

For the equilibrium pair correlation function  $g_{\text{eq}}^{(2)}(r)$  required, either the Monte Carlo (MC) simulation method or the Percus–Yevick (PY) integral equation was used, depending on the thermodynamic states of interest. In the approach using the PY integral equation, the solution was achieved numerically by combining iteration and fast Fourier transform methods.

The critical point of argon is at  $\rho_c = 535.7 \text{ kg m}^{-3}$  and  $T_c = 150.86 \text{ K}$ . When the temperature was approximately above twice the critical temperature and mass density  $\rho$  was higher than  $450 \text{ kg m}^{-3}$  ( $\rho^* = 0.27$ ), the pair correlation functions obtained from the MC simulations were used, whereas  $g_{\text{eq}}^{(2)}(r)$  computed with the PY integral equation theory was employed for other thermodynamic states at  $\rho \lesssim 450 \text{ kg m}^{-3}$  or  $T < 2T_c$ , unless stated otherwise. For the description of the Monte Carlo simulations for the pair correlation functions, see [50].

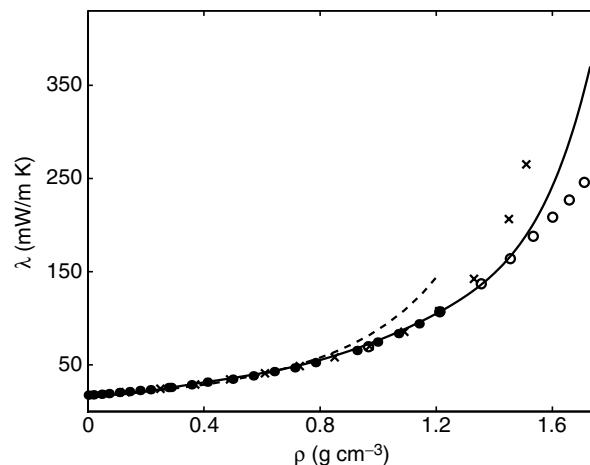
In Fig. 10.8, the density dependence of the thermal conductivity at  $T = 348.15 \text{ K}$  is shown. The *dashed* and *solid curves* are calculated, respectively, with  $\kappa^* = 0.4$  and with  $\kappa^*$  given by (10.101). As the temperature is elevated, the theory with  $\kappa^* = 0.4$  overestimates the thermal conductivity of argon,



**Fig. 10.8.**  $\lambda$  vs.  $\rho$  for argon at  $T = 348.15 \text{ K}$ . The *solid curve* was calculated from the formula (10.116) with  $\kappa^*$  given in (10.101), and the *dashed curve* was calculated with  $\kappa^* = 0.4$ . The *filled circles* ( $\bullet$ ) are experimental data. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **115**, 9370 (2001). Copyright 2001 American Institute of Physics.]

compared with experiment, particularly when the density is higher than approximately  $800 \text{ kg m}^{-3}$ , whereas the results with  $\kappa^*$  given by (10.101) are excellent in the range of density examined. The isobaric expansion coefficient  $\alpha$  in (10.101) was computed with the empirical formula proposed by Tegeler et. al. [52] in their work on the equation of state for argon. Because the thermal conductivity in the liquid density regime is of primary interest here, the experimental value was used for  $\lambda_k(T)$  in (10.116) instead of the Chapman–Enskog thermal conductivity for the gas. However, note that the latter is in fairly good agreement with the former. The pair correlation functions employed to calculate the thermal conductivity of argon presented in Fig. 10.8 were obtained from MC simulations. The integrals for  $\chi(n, T)$  and  $\omega(n, T)$  were, respectively, evaluated with  $g_{\text{eq}}^{(2)}(r)$  thus obtained in the simulated thermodynamic states over the density range of  $200$ – $1220 \text{ kg m}^{-3}$ . An interpolation scheme, if necessary, was used to estimate  $\chi(n, T)$  and  $\omega(n, T)$  at densities in the range other than the simulated density states. Monte Carlo simulation methods were employed at  $T = 348.15 \text{ K}$  because the PY integral equation theory was found unreliable at that temperature.

The reliability of (10.116) and (10.101) was also tested at different temperatures. In Fig. 10.9, the density dependence of  $\lambda$  calculated with (10.116) for argon at  $T = 298.15 \text{ K}$  is shown and compared with experimental values [38, 53]. The *dashed* and *solid curves* are the results calculated from (10.116), respectively, with  $\kappa^* = 0.4$  and the formula (10.101). For  $T \sim 2T_c$ , the pair correlation function  $g_{\text{eq}}^{(2)}(r)$  was obtained from MC simulations. The agreement between the theory and experiment (symbols) is excellent up to



**Fig. 10.9.**  $\lambda$  vs.  $\rho$  for argon at  $T = 298.15 \text{ K}$ . The *solid curve* was calculated with formulas (10.116) and (10.101), and the *dashed curve* was obtained with  $\kappa^* = 0.4$ . The symbols are experimental data. There was no adjustable cutoff parameter used. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **115**, 9370 (2001). Copyright 2001 American Institute of Physics.]

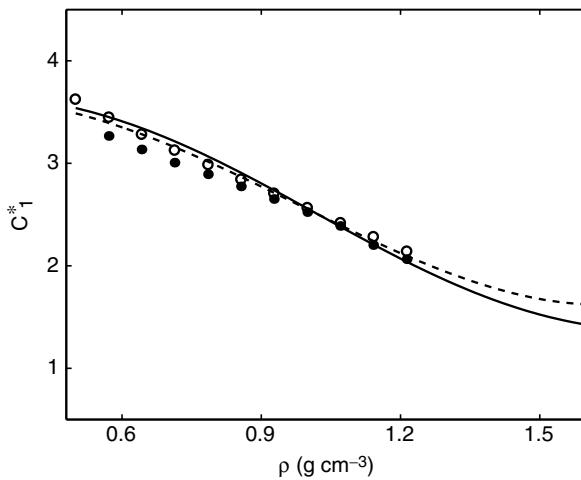
a density of about  $1600 \text{ kg m}^{-3}$  ( $\rho^* = 0.95$ ), after which the deviation from the experimental data increases. However, note that the shear viscosity values used for  $\eta_v$  in (10.116) are subject to larger errors for density higher than approximately  $1300 \text{ kg m}^{-3}$ , which is the upper limit for the empirical fitting formula for the experimental viscosity for  $T \gtrsim 200 \text{ K}$ . For the sake of comparison, the thermal conductivity ( $\times$ ), which was evaluated by interpolation or extrapolation from the Younglove–Hanley empirical fitting formula [51] for argon, is shown. The *open circles* ( $\circ$ ) in Fig. 10.9 are the only experimental data readily available in the literature for the thermal conductivity of argon at a density higher than approximately  $1300 \text{ kg m}^{-3}$ . Some independent experiments at such high density would be useful to make the comparison of the theory with experiment more definitive.

There was no cutoff parameter used so far for calculating the thermal conductivity coefficients of argon at  $T > T_c$ . It indicates that the range of density fluctuations  $\xi$  caused by a temperature gradient at  $T \gtrsim T_c$  is comparable with or larger than the intermolecular force range. However, when temperature is below  $T_c$ , especially near the triple point, the cutoff parameter  $\xi$  is no longer equal to or larger than the range of the interaction potential.

It is well established in the kinetic theory of gases that the ratio of  $\lambda/C_v\eta$  for a dilute gas is independent of density. However, as the density increases, the ratio deviates from the constant Eucken ratio, and for argon the ratio  $\lambda/C_v\eta$  was empirically demonstrated [38] to deviate from a constant value independent of density, as the density increases. The factor of interest regarding this question is  $C_1$  in (10.115). It is convenient to rearrange (10.115) to the following form

$$\frac{\lambda}{C_v\eta} = \frac{\lambda_k}{C_v\eta} \left( 1 + C_1 \frac{\eta_v}{\lambda_k} \right). \quad (10.117)$$

The reduced form of  $C_1^* \equiv C_1/C_v$  is shown as a function of density in Fig. 10.10, for which the heat capacity  $C_v$  is evaluated from the empirical equation of state for argon [52]. The curves are the density fluctuation theory results: *solid curve* at 298 K and *broken curve* at 348 K for  $\kappa^*$  given by (10.101), whereas the symbols are from the experiments by Michels et al. [38]: *filled circles* ( $\bullet$ ) at 298 K and *open circles* ( $\circ$ ) at 348 K. The pair correlation functions used for the calculations were obtained from MC simulations. As shown in Fig. 10.10, the ratio  $C_1^*$  decreases noticeably as density increases. The coefficient  $C_1$  is a decreasing function of density in the range of liquid density, and the heat capacity  $C_v$  monotonically increases as density increases. Note that the ratio of  $\chi_v/\chi_w$  in (10.115) is of the order of unity at liquid density but increases with density at constant temperature. It clearly implies that the contribution of the virial part  $\chi_w$  to the thermal conductivity is comparable with that from the potential energy transport  $\chi_v$ . This is another indication that the displacement operator in the virial part is as important as the potential energy part for heat flux in the liquid density range and hence should not be ignored.



**Fig. 10.10.** Density dependence of  $C_1^* \equiv C_1/C_v$  at two isotherms. The curves are theoretical: *solid curve* at 298 K and *broken curve* at 348 K, whereas the symbols are experimental: *filled circles* ( $\bullet$ ) at 298 K and *open circles* ( $\circ$ ) at 348 K. Equation (10.101) was used for  $\kappa^*$ . [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **115**, 9370 (2001). Copyright American Institute of Physics.]

#### 10.4 Concluding Remarks

Historically, the density and temperature dependence of transport coefficients of liquids and dense gases has been one of the important motivations for developing the kinetic theory of matter beyond the level of the Boltzmann equation, which was found good only for dilute gases. The theory of Enskog [54] only pointed the direction to take to solve the problem. The intensive attention paid to the BBGKY hierarchy theory since 1946 attests to the importance of the problem and the influence of the Enskog theory. Yet the problem has remained intractable to a practical solution by the BBGKY approach and other approaches, including the linear response theory. Although the generalized Boltzmann equations described in earlier chapters provide formal expressions for transport coefficients of liquids and dense gases as does the linear response theory, the difficulty of obtaining solutions for many-particle collision dynamics in accurate and practical forms has rendered the approach to remain only formal. The density fluctuation theory discussed for simple fluids in this chapter provides a breakthrough of the barrier posed by the problem simply because the transport coefficients, such as bulk and shear viscosity and thermal conductivity, are expressed in terms of quantities readily computable by computer simulation for equilibrium liquids. In this density fluctuation theory approach, nonconserved variables evolve as functionals of conserved variables such as density, momentum, and internal energy, which are described by the conservation laws or suitable constitutive equations for

the conserved variables. The many-particle collision effects are borne by the pair correlation functions, which intimately reflect the structures of liquids and dense gases, and the self-diffusion coefficient, which determines the time- and spatial scale of transport processes in fluids. These latter components of the theory are computable by computer simulation or other theoretical means. When the aforementioned factors are combined for transport coefficients, there result formulas whose potential energy contributions are reminiscent of the celebrated Stokes–Einstein relation, although the molecular theory contents of the formulas derived are quite different from the Stokes–Einstein relation. It should be emphasized that the Stokes–Einstein-like formulas for transport coefficients are statistical mechanical and for fluids consisting of molecules, whereas the original Stokes–Einstein relation is hydrodynamic and for macroscopic particles suspended in a continuous medium. As will be shown in Chap. 12, diffusion coefficients can be calculated on the basis of intermolecular forces if the simulation data for the pair correlation functions are available, and thus the density fluctuation theory can be made fully molecular.

The density fluctuation theory presented in this work is only a leading order theory, which should be refined to include higher orders, so that nonlinear transport processes can also be described. This subject remains to be studied in the future.

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# 11

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## Density Fluctuation Theory: Complex Fluids

In this chapter, the density fluctuation theory developed for simple liquids in Chap. 10 is generalized to study transport processes and associated transport coefficients of complex fluids. The theory will be developed with particular examples of diatomic fluids, but it can be easily adapted to deal with more complicated polyatomic fluids. The basic ideas of the density fluctuation theory remain the same as those for simple fluids. The presence of internal degrees of freedom necessitates suitably generalizing symbols. For example, the pressure and virial tensors get more complicated because there are contributions from the internal degrees of freedom. In the dilute fluid regime, the singlet distribution function also involves the internal distribution function. Therefore, it must be described by a suitably generalized kinetic equation for the singlet distribution functions involving also internal degrees of freedom. The remarkable feature of the resulting theory is that despite all the changes made necessary by the presence of internal degrees of freedom the transport coefficients can still be described in terms of a self-diffusion coefficient, which sets time- and spatial scales for the transport processes, and equilibrium site-site pair distribution functions. Thus, once these basic quantities are known with regard to their density and temperature dependence it is possible to understand the density and temperature dependence of transport coefficients such as bulk and shear viscosity and thermal conductivity of complex fluids. We will be using the system of notation already developed in Chap. 8 for the polyatomic kinetic equation.

Because the shear viscosities and thermal conductivities of molecular liquids have been little studied in statistical mechanics and there is no reliable molecular theory method for them except for some computer simulation methods, the present density fluctuation theory, although the self-diffusion coefficient is treated semiempirically to validate the theory, provides a long sought, practicable, and reliable method of computing them by a statistical mechanical method based on an interaction potential model. It, furthermore, gives a way to assess, from the standpoint of experiments on transport coefficients, the qualities of simulation and experimental data on self-diffusion coefficients.

reported in the literature, if the formula, for example, for shear viscosity obtained is used in reverse to estimate the self-diffusion diffusion coefficient and compare the result with those by simulations or experiment.

### 11.1 Nonequilibrium Ensemble Distribution Function

We consider a single-component polyatomic fluid consisting of molecules of  $l$  atoms or sites. The grand ensemble kinetic equation for polyatomic fluids has an equilibrium solution, which is a solution of the equilibrium condition

$$\Re \left[ F_{\text{eq}}^{(N)} \right] = 0. \quad (11.1)$$

This equation is a consequence of the H theorem satisfied by the polyatomic kinetic equation. Its solution subject to momentum and energy conservation is satisfied by the equilibrium grand canonical ensemble distribution function for polyatomic fluids

$$F_{\text{eq}}^{(N)} \left( x^{(N)} \right) = (c \Xi_{\text{eq}})^{-1} \exp \left[ - \int_V d\mathbf{r} \beta(\mathbf{r}) \sum_{j=1}^N \sum_{\alpha=1}^l \mathcal{H}_{j\alpha}^{\text{eq}} \delta(\mathbf{r}_{j\alpha} - \mathbf{r}) \right], \quad (11.2)$$

where the subscript  $a$  refers to the sites, the subscript  $j$  refers to particles in a molecule of species  $a$ , and other symbols are

$$\mathcal{H}_{j\alpha}^{\text{eq}} = H'_{j\alpha} - m_\alpha \hat{\mu}_\alpha \quad (11.3)$$

with  $H'_{j\alpha}$  denoting the Hamiltonian of particle  $\alpha \in j$  defined below [see (11.10) and also (7.3) in Chap. 7.],  $\Xi_{\text{eq}}$  is the equilibrium grand canonical ensemble partition function

$$\Xi_{\text{eq}} = \left\langle \exp \left[ - \int_V d\mathbf{r} \beta(\mathbf{r}) \sum_{j=1}^N \sum_{\alpha=1}^l \mathcal{H}_{j\alpha}^{\text{eq}} \delta(\mathbf{r}_{j\alpha} - \mathbf{r}) \right] \right\rangle \quad (11.4)$$

and  $c$  stands for the factor

$$c = h^{3lN} N! \quad (11.5)$$

with  $h$  denoting the Planck constant and  $\beta(\mathbf{r}) = 1/k_B T(\mathbf{r})$ . The angular brackets for averages in this chapter also have the same meaning as those in Chap. 8—the grand canonical ensemble averages. We reiterate that the equilibrium state is achieved in the dynamic grand ensemble when the petit ensembles therein are equilibrated with regard to energy and particle numbers.

The nonequilibrium grand canonical ensemble distribution function is then introduced in the same spirit as for the dilute gas counterpart, which was constructed on the basis of the Boltzmann equation [1, 2]. Although presented

in Chap. 8, we introduce it again here to help in reading this topic:

$$F_c^{(N)}(x^{(N)}, t) = c^{-1} \exp \left\{ - \int_V d\mathbf{r} \beta(\mathbf{r}, t) \left[ \sum_{j=1}^N \sum_{\alpha=1}^l \mathcal{H}_{j\alpha} \delta(\mathbf{r}_{j\alpha} - \mathbf{r}) - \rho \Upsilon(\mathbf{r}, t) \right] \right\}, \quad (11.6)$$

where

$$\mathcal{H}_{j\alpha} = T^{-1} \left( H'_{j\alpha} + \sum_{q \geq 1} X_q h_{j\alpha}^{(q)} - m_a \hat{\mu}_a \right), \quad (11.7)$$

$$\Xi = \left\langle \exp \left[ -k_B^{-1} \int_V d\mathbf{r} \sum_{j=1}^N \sum_{\alpha=1}^l \mathcal{H}_{j\alpha} \delta(\mathbf{r}_{j\alpha} - \mathbf{r}) \right] \right\rangle, \quad (11.8)$$

and

$$k_B \ln \Xi = - \int_V d\mathbf{r} \rho \Upsilon(\mathbf{r}, t) / T(\mathbf{r}, t). \quad (11.9)$$

The notation is the same as that used in the previous chapters. As all  $X_q$  vanish,  $F_c^{(N)}$  tends to the equilibrium distribution function  $F_{\text{eq}}^{(N)}(x^{(N)})$ . If  $F_c^{(N)}(x^{(N)}, t)$  is substituted in the kinetic equation (8.18) and the evolution equations for the intensive variables such as  $T$ ,  $\hat{\mu}_a$ , and  $X_q$  in the expression for  $F_c^{(N)}$  are derived and solved, then  $F_c^{(N)}$  fully becomes a solution of the kinetic equation. This procedure, however, is not pursued in the thermodynamic theory of irreversible processes in the framework of generalized thermodynamics [3] because the intensive variables in thermodynamics are treated as phenomenological inputs, as for simple fluids. We have discussed the status of  $F_c^{(N)}$  in connection with generalized thermodynamics in Chap. 8, and the same remarks apply to the nonequilibrium grand canonical ensemble distribution function presented here. For details of this point, see also Sects. 7.4, 7.5, and 10.5 of [2].

## 11.2 Excess Normal Stress

We consider  $N$  polyatomic molecules of a single component contained in volume  $V$  at temperature  $T$ . Our interest in this section lies in the excess normal stress in a complex fluid. We have seen in the previous chapter that density fluctuations can have significant effects on the nonequilibrium behavior of the stress in simple fluids when the fluids are removed from equilibrium. They will have similar effects on complex fluids but in a more complicated manner. In the classification scheme used for fluids in this work diatomic liquids are included in complex fluids. In this chapter, our attention on complex fluids will be eventually focused on diatomic fluids because experimental data are available for validating the theory developed for diatomic fluids and they are

the simplest of complex fluids that illustrate the essential features of the theory as concisely as possible. Nevertheless, in this section some definitions will be made for generic polyatomic fluids consisting of  $l$  sites.

For such a polyatomic fluid, the Hamiltonian for atom (site)  $j$  is assumed to be given by

$$H'_{j\alpha} = \frac{1}{2}m_\alpha C_{j\alpha}^2 + \frac{1}{2} \sum_{\alpha \neq \gamma=1}^l w_{j\alpha j\gamma} + \frac{1}{2} \sum_{k=1}^N \sum_{\substack{\gamma=1 \\ (k \neq j)}}^l V_{j\alpha k\gamma} + V_{j\alpha}^{(\text{ex})}, \quad (11.10)$$

where  $w_{j\alpha j\gamma}$  is the potential energy responsible for binding neighboring sites  $\alpha$  and  $\gamma$  in molecule  $j$  or the intramolecular site–site interaction energy if  $\alpha$  and  $\gamma$  are nonadjacent sites and thus not directly bonded,  $V_{j\alpha k\gamma}$  is the intermolecular site–site interaction potential ( $j \neq k$ ), and  $V_{j\alpha}^{(\text{ex})}$  is the external potential energy on site  $\alpha \in j$ .

Once we have the distribution function  $F_c^{(N)}(x^{(N)}, t)$  in accordance with the definition given in Chap. 8, we may compute the ensemble average of any dynamic variable  $\mathcal{A}$ , for which the microscopic density may be written as

$$\mathcal{A} = \sum_{j=1}^N \sum_{\alpha=1}^l \mathcal{A}_{j\alpha}(x^{(N)}) \delta(\mathbf{r}_{j\alpha} - \mathbf{r}). \quad (11.11)$$

We thereby obtain, for example, the mass density

$$\rho(\mathbf{r}, t) = \left\langle \sum_{j=1}^N \sum_{\alpha=1}^l m_\alpha \delta(\mathbf{r}_{j\alpha} - \mathbf{r}) F_c^{(N)} \right\rangle \quad (11.12)$$

and the momentum density  $\rho\mathbf{u}$

$$\rho\mathbf{u}(\mathbf{r}, t) = \left\langle \sum_{j=1}^N \sum_{\alpha=1}^l \mathbf{p}_{j\alpha} \delta(\mathbf{r}_{j\alpha} - \mathbf{r}) F_c^{(N)} \right\rangle, \quad (11.13)$$

where  $\mathbf{u}(\mathbf{r}, t)$  is the fluid velocity.

The stress (pressure) tensor  $\mathbf{P}$  for the complex fluid can be decomposed into three parts

$$\mathbf{P} = \mathbf{P}_k + \mathbf{P}_v^{(\text{s})} + \mathbf{P}_v^{(\text{m})}, \quad (11.14)$$

where  $\mathbf{P}_k$  is the kinetic part,  $\mathbf{P}_v^{(\text{s})}$  is the intramolecular site–site potential energy part, and  $\mathbf{P}_v^{(\text{m})}$  is the intermolecular site–site potential energy part. Their statistical mechanical expressions are

$$\mathbf{P}_k = \sum_{j=1}^N \sum_{\alpha=1}^l \left\langle m_{j\alpha} C_{j\alpha} C_{j\alpha} \delta(\mathbf{r}_{j\alpha} - \mathbf{r}) F_c^{(N)} \right\rangle, \quad (11.15)$$

$$\mathbf{P}_v^{(s)} = \frac{1}{2} \sum_{j=1}^N \sum_{\alpha=1}^l \left\langle \mathbf{W}_{j\alpha j\gamma}^{(s)} \delta(\mathbf{r}_{k\gamma} - \mathbf{r}) F_c^{(N)} \right\rangle, \quad (11.16)$$

$$\mathbf{P}_v^{(m)} = \frac{1}{2} \sum_{j \neq k=1}^N \sum_{\alpha, \gamma=1}^l \left\langle \mathbf{W}_{j\alpha k\gamma} \delta(\mathbf{r}_{k\gamma} - \mathbf{r}) F_c^{(N)} \right\rangle, \quad (11.17)$$

where  $\mathbf{W}_{j\alpha j\gamma}^{(s)}$  and  $\mathbf{W}_{j\alpha k\gamma}$  are, respectively, intramolecular and intermolecular virial tensors for the polyatomic fluid. They are defined by

$$\mathbf{W}_{j\alpha j\gamma}^{(s)} = \int_0^1 d\zeta \mathbf{r}_{j\alpha j\gamma} \mathbf{F}_{j\alpha j\gamma}^{(s)}(\mathbf{r}_{j\alpha j\gamma}) \exp(-\zeta \mathbf{r}_{j\alpha j\gamma} \cdot \nabla), \quad (11.18)$$

$$\mathbf{W}_{j\alpha k\gamma} = \int_0^1 d\zeta \mathbf{r}_{j\alpha k\gamma} \mathbf{F}_{j\alpha k\gamma}(\mathbf{r}_{j\alpha k\gamma}) \exp(-\lambda \mathbf{r}_{j\alpha k\gamma} \cdot \nabla), \quad (11.19)$$

where  $\mathbf{F}_{j\alpha j\gamma}^{(s)}$  is the intramolecular interaction force between sites  $\alpha \in j$  and  $\gamma \in j$ , whereas  $\mathbf{F}_{j\alpha k\gamma}$  is the intersite interaction force between sites  $\alpha \in j$  and  $\gamma \in k$  ( $j \neq k$ ). The intramolecular virial tensor  $\mathbf{W}_{j\alpha j\gamma}^{(s)}$  is the additional contribution, which is not present in simple liquids. Note that there are also indirect contributions to the intermolecular virial tensor from the internal degrees of freedom. In both cases, the exponential displacement operator in the generalized virial tensor operators is an important factor that gives rise to spatial variation of one-particle densities within the site-site interaction range and over the volume comparable to the molecular size in the density fluctuation theory. We will consider these quantities in diatomic liquids for the sake of simplicity in formalism.

### 11.2.1 Kinetic Part of the Stress Tensor

For the simplicity of formalism, the discussion will be limited to a two-interaction site model—for example, a diatomic molecule. The fluid is also assumed to be a single component. The general expression for the kinetic part  $\mathbf{P}_k$  of the stress tensor given by (11.15) for a site-site interaction model is expressible in terms of the relative and center-of-mass coordinates and momenta of the diatomic, or two-site, molecules. The two sites of a molecule are denoted by 1 and 2. To achieve the desired aim we introduce the relative coordinate  $\mathbf{r}_{12j}$  and the center-of-mass coordinate  $\mathbf{R}_{cj}$  as well as their conjugate momenta or velocities denoted by  $\mathbf{v}_{12j}$  and  $\mathbf{V}_{cj}$ :

$$\mathbf{r}_{12j} = \mathbf{r}_{j2} - \mathbf{r}_{j1}, \quad M\mathbf{R}_{cj} = m_1\mathbf{r}_{j1} + m_2\mathbf{r}_{j2}, \quad (11.20)$$

where  $M = m_1 + m_2$ ,  $\mathbf{r}_{j1}$  and  $\mathbf{r}_{j2}$  are the position vectors of the two-interaction sites in a fixed coordinate system. The conjugate momenta transform as follows:

$$\begin{aligned}\mathbf{P}_{cj} &= M\dot{\mathbf{R}}_{cj} = M\mathbf{V}_{cj} = \mathbf{p}_{j1} + \mathbf{p}_{j2}, \\ \mathbf{p}_{12j} &= m\dot{\mathbf{r}}_{12j} = m\mathbf{v}_{12j} = \frac{m_1}{M}\mathbf{p}_{j2} - \frac{m_2}{M}\mathbf{p}_{j1},\end{aligned}\quad (11.21)$$

where

$$\mathbf{p}_{j1} = m_1\dot{\mathbf{r}}_{j1}, \quad \mathbf{p}_{j2} = m_2\dot{\mathbf{r}}_{j2} \quad (11.22)$$

with  $m$  denoting the reduced mass of the diatomic molecule  $m = m_1 m_2 / M$ .

By using these transformations in the expression for  $\mathbf{P}_k$ , we obtain for homonuclear diatomic fluids

$$\begin{aligned}\mathbf{P}_k(\mathbf{r}, t) &= \left\langle \sum_{j=1}^N M \mathbf{C}_j \mathbf{C}_j \mathfrak{D}_C \delta(\mathbf{R}_{cj} - \mathbf{r}) F_c^{(N)} \right\rangle \\ &\quad - \left\langle \sum_{j=1}^N m [\mathbf{C}_j, \mathbf{v}_{j12}] \mathfrak{D}_{CI} \delta(\mathbf{R}_{cj} - \mathbf{r}) F_c^{(N)} \right\rangle \\ &\quad + \left\langle \sum_{j=1}^N m \mathbf{v}_{12j} \mathbf{v}_{12j} \mathfrak{D}_I \delta(\mathbf{R}_{cj} - \mathbf{r}) F_c^{(N)} \right\rangle,\end{aligned}\quad (11.23)$$

where  $\mathbf{C}_j = \mathbf{V}_{jc} - \mathbf{u}$  is the peculiar velocity of the center of mass of the molecule  $j$ ,  $[\mathbf{C}_j, \mathbf{v}_{j12}]$  is a symmetric tensor defined by

$$[\mathbf{C}_j, \mathbf{v}_{j12}] = \mathbf{C}_j \mathbf{v}_{j12} + \mathbf{v}_{j12} \mathbf{C}_j$$

and various displacement operators are abbreviated as follows:

$$\begin{aligned}\mathfrak{D}_C &= \frac{m_1}{M} \exp\left(-\frac{m}{m_1} \mathbf{r}_{j12} \cdot \nabla_r\right) + \frac{m_2}{M} \exp\left(\frac{m}{m_2} \mathbf{r}_{j12} \cdot \nabla_r\right), \\ \mathfrak{D}_{CI} &= \exp\left(-\frac{m}{m_1} \mathbf{r}_{j12} \cdot \nabla_r\right) - \exp\left(\frac{m}{m_2} \mathbf{r}_{j12} \cdot \nabla_r\right), \\ \mathfrak{D}_I &= \frac{m}{m_1} \exp\left(-\frac{m}{m_1} \mathbf{r}_{j12} \cdot \nabla_r\right) + \frac{m}{m_2} \exp\left(\frac{m}{m_2} \mathbf{r}_{j12} \cdot \nabla_r\right).\end{aligned}$$

To derive  $\mathbf{P}_k$  in this form the delta functions have been written in the form

$$\delta\left(\mathbf{R}_{cj} \pm \frac{m}{m_\alpha} \mathbf{r}_{12j} - \mathbf{r}\right) = \exp\left(\mp \frac{m}{m_\alpha} \mathbf{r}_{12j} \cdot \nabla_r\right) \delta(\mathbf{R}_{cj} - \mathbf{r}). \quad (11.24)$$

If the delta functions are cast in the forms given in (11.24), the mean velocity  $\mathbf{u}$  defined earlier may be expressed in a form more amenable to physically more insightful interpretation: with the definition of displacement operators

$$\mathbf{W}_{j12}^{(\mp)} = \frac{m}{m_\alpha} \int_0^1 d\lambda \mathbf{r}_{j12} \cdot \nabla_{\mathbf{r}} \exp \left( \mp \frac{\lambda m}{m_\alpha} \mathbf{r}_{j12} \cdot \nabla_{\mathbf{r}} \right), \quad (11.25)$$

$\rho \mathbf{u}(\mathbf{r}, t)$  can be cast in the alternative form

$$\begin{aligned} \rho \mathbf{u}(\mathbf{r}, t) &= \sum_{j=1}^N \left\langle \mathbf{P}_{cj} \delta(\mathbf{R}_{cj} - \mathbf{r}) F_c^{(N)} \right\rangle \\ &\quad + \sum_{j=1}^N \left\langle \left( \frac{m_2}{M} \mathbf{P}_{cj} - \mathbf{p}_{j12} \right) \cdot \nabla_{\mathbf{r}} \mathbf{W}_{j12}^{(+)} \delta(\mathbf{R}_{cj} - \mathbf{r}) F_c^{(N)} \right\rangle \\ &\quad - \sum_{j=1}^N \left\langle \left( \frac{m_1}{M} \mathbf{P}_{cj} + \mathbf{p}_{j12} \right) \cdot \nabla_{\mathbf{r}} \mathbf{W}_{j12}^{(-)} \delta(\mathbf{R}_{cj} - \mathbf{r}) F_c^{(N)} \right\rangle. \end{aligned} \quad (11.26)$$

This form for the mean velocity of diatomic fluids suggests that it consists of the center-of-mass velocity of the molecule as well as the motions of the sites relative to the center of mass. From the expression, we see that if the molecule is not rigid the mean velocity of the molecule can be significantly affected by the motions of the interaction sites relative to the center of mass. If the variation with respect to  $\nabla_{\mathbf{r}}$  is ignored, then the mean velocity is given by the center-of-mass part only:

$$\rho \mathbf{u}(\mathbf{r}, t) = \sum_{j=1}^N \left\langle \mathbf{P}_{cj} \delta(\mathbf{R}_{cj} - \mathbf{r}) f^{(N)}(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}; t) \right\rangle. \quad (11.27)$$

If molecules are homonuclear diatomic molecules or of identical two sites the formulas are simplified, and we obtain  $\mathbf{P}_k$  in the form

$$\begin{aligned} \mathbf{P}_k(\mathbf{r}, t) &= \left\langle \sum_{j=1}^N M \mathbf{C}_j \mathbf{C}_j \cosh \left( \frac{1}{2} \mathbf{r}_{j12} \cdot \nabla_{\mathbf{r}} \right) \delta(\mathbf{R}_{cj} - \mathbf{r}) F_c^{(N)} \right\rangle \\ &\quad + \left\langle \sum_{j=1}^N m \mathbf{v}_{j12} \mathbf{v}_{j12} \cosh \left( \frac{1}{2} \mathbf{r}_{j12} \cdot \nabla_{\mathbf{r}} \right) \delta(\mathbf{R}_{cj} - \mathbf{r}) F_c^{(N)} \right\rangle \\ &\quad - \left\langle \sum_{j=1}^N 2m [\mathbf{C}_j, \mathbf{v}_{j12}] \sinh \left( \frac{1}{2} \mathbf{r}_{j12} \cdot \nabla_{\mathbf{r}} \right) \delta(\mathbf{R}_{cj} - \mathbf{r}) F_c^{(N)} \right\rangle. \end{aligned} \quad (11.28)$$

Because the Jacobian is unity for the coordinate transformation

$$d\mathbf{p}_{j1} d\mathbf{p}_{j2} d\mathbf{r}_{j1} d\mathbf{r}_{j2} = d\mathbf{P}_{cj} d\mathbf{R}_{cj} d\mathbf{p}_{12j} d\mathbf{r}_{12j},$$

we may retain the meaning of the angular bracket symbol unchanged for the integration in the phase space of the new variables.

It is now useful to introduce the singlet distribution function  $f$  for molecule  $j$  defined by

$$f(X_c, x_{12}, t) = N \iint d\mathbf{r}^{(N-1)} d\mathbf{p}^{(N-1)} F_c^{(N)}(x^{(N)}, t), \quad (11.29)$$

where  $X_c = (\mathbf{P}_{cj}, \mathbf{R}_{cj})$  and  $x_{12} = (\mathbf{p}_{12j}, \mathbf{r}_{j12})$  are the phases of the pair of particles (12). This distribution function is the reduced probability of finding molecule  $j$  at  $(X_c, x_{12})$  in the phase space of the pair regardless of the distribution of the  $N - 1$  molecules in the phase space of  $N$  molecules. In contrast to a monatomic fluid, this singlet distribution function contains the distribution function for the internal degrees of freedom.

Because molecules are identical and the integrands involve only single-molecule variables, the integral in (11.29) reduces to the one that involves the singlet distribution function, and the kinetic part of the stress tensor (11.28) for  $\mathbf{P}_k$  then reduces to the formula

$$\begin{aligned} \mathbf{P}_k = & \int d\mathbf{P}_c \int d\mathbf{R}_c \int d\mathbf{p}_{12} \int d\mathbf{r}_{12} f(X_c, x_{12}, t) \\ & \times \left[ (M\mathbf{C}\mathbf{C} + m\mathbf{v}_{12}\mathbf{v}_{12}) \cosh \left( \frac{1}{2}\mathbf{r}_{12} \cdot \nabla_{\mathbf{r}} \right) \right. \\ & \left. - 2m(\mathbf{C}\mathbf{v}_{12} + \mathbf{v}_{12}\mathbf{C}) \sinh \left( \frac{1}{2}\mathbf{r}_{12} \cdot \nabla_{\mathbf{r}} \right) \right] \delta(\mathbf{R}_c - \mathbf{r}). \end{aligned} \quad (11.30)$$

Here the subscript  $j$  is omitted from the variables involved. The singlet distribution function  $f$  must be determined from the solution of the kinetic equation. If the variation of the singlet distribution function  $f$  over  $\mathbf{r}_{12}$  is neglected, the second integral in (11.30) may be ignored in the lowest order approximation, and the approximate  $\mathbf{P}_k$  follows:

$$\mathbf{P}_k(\mathbf{r}, t) = \int d\mathbf{P}_c \int d\mathbf{p}_{12} \int d\mathbf{r}_{12} (M\mathbf{C}\mathbf{C} + m\mathbf{v}_{12}\mathbf{v}_{12}) f(X_c, x_{12}; t). \quad (11.31)$$

Thus it is seen that the kinetic contribution to the stress tensor for a diatomic fluid consists of both the translational motion of the center of mass and the internal motion of the molecule, as intuitively expected. It is reiterated that the expression (11.31) for  $\mathbf{P}_k$  is an approximation obtained from (11.30) by neglecting the variation of the singlet distribution function  $f$  over the intramolecular distance  $\mathbf{r}_{12}$  between the atoms (sites) in the molecule. If the diatomic molecule is long then the density variation accompanying the variation of  $f$  can be sizable, and it is expected that there should be a significant effect from it.

If the molecule is a rigid diatomic molecule with bond length  $b$ , then because  $\mathbf{v}_{j12}$  can be expressed simply in terms of the bond length and angular velocity  $\omega_{12j}$ ,  $b\omega_{12j}$ , which is related to the angular momentum  $\mathbf{j}$  of the molecule, the tensor  $m\mathbf{v}_{12}\mathbf{v}_{12}$  may be written as

$$m\mathbf{v}_{12}\mathbf{v}_{12} = \frac{\mathbf{j}\mathbf{j}}{I}, \quad (11.32)$$

where  $I$  is the moment of inertia  $I = mb^2$  of the molecule. Thus in this case we finally obtain  $\mathbf{P}_k$  in the form,

$$\mathbf{P}_k(\mathbf{r}, t) = \int d\mathbf{P}_c \int d\mathbf{p}_{12} \int d\mathbf{r}_{12} \left( M\mathbf{CC} + \frac{\mathbf{j}\mathbf{j}}{I} \right) f(X_c, x_{12}; t), \quad (11.33)$$

for a rigid diatomic molecular fluid. We will discuss an approximate method of evaluating this expression for  $\mathbf{P}_k$  later.

### 11.2.2 Potential Part of the Stress Tensor

We now reduce the potential energy parts of the stress tensor under the assumption of a rigid homonuclear diatomic fluid or a rigid linear polyatomic molecular fluid of two identical sites. For rigid diatomic or rigid linear polyatomic molecules, intramolecular bonding forces are equal to zero,  $\nabla_{\mathbf{r}_{j\alpha}} w_{12}(\mathbf{r}_{j1}, \mathbf{r}_{j2}) = 0$ . Therefore, the intramolecular virial tensor  $\mathbf{W}_{j\alpha k\gamma}^{(s)}$  in (11.18) vanishes. The potential energy contribution to the stress tensor then consists only of the intermolecular contribution  $\mathbf{P}_v^{(m)}$ , which is made up of the terms involving interactions and pair correlation involving sites on different molecules. Furthermore, because the particles are identical, the dynamic pair distribution function  $n^{(2)}(\mathbf{r}, \mathbf{r}'; t)$  may be written in the form,

$$n^{(2)}(\mathbf{r}, \mathbf{r}', t) = n(\mathbf{r}, t) n(\mathbf{r}', t) g^{(2)}(\mathbf{r}, \mathbf{r}', t), \quad (11.34)$$

where  $g^{(2)}(\mathbf{r}, \mathbf{r}', t)$  denotes the dynamic pair correlation function between sites on two different molecules and  $n(\mathbf{r}, t)$  is the density of molecules at position  $\mathbf{r}$  at time  $t$ . The potential energy part of the stress tensor then can be expressed in the form,

$$\mathbf{P}_v^{(m)}(\mathbf{r}, t) = -\frac{1}{2} \int_0^1 d\lambda \int d\mathbf{R} \frac{\mathbf{R}\mathbf{R}}{R} \mathcal{V}'(R) n^{(2)}[\mathbf{r} - \lambda\mathbf{R}, \mathbf{r} + (1 - \lambda)\mathbf{R}; t], \quad (11.35)$$

where  $\mathbf{R}$  denotes the distance between the sites on two different molecules and  $\mathcal{V}'(R) = d\mathcal{V}(R)/dR$ . We notice that because the intramolecular degrees of freedom have been integrated out, there is no quantity in the integrand that directly manifests the molecularity of the fluids, although the pair correlation function  $n^{(2)}(\mathbf{r}, \mathbf{r}', t)$  implicitly contains that piece of information because it must be a solution of the evolution equations for site-site pair correlation functions of the fluids, for example, dynamic Ornstein-Zernike equations (see Chap. 9) for site-site pair correlation functions. For the model of diatomic fluids under consideration the potential energy part  $\mathbf{P}_v$  of the stress tensor is then simply

$$\mathbf{P}^{(v)} = \mathbf{P}_v^{(m)}(\mathbf{r}, t). \quad (11.36)$$

This expression for  $\mathbf{P}^{(v)}$  implies that all contributions to  $\mathbf{P}^{(v)}$  are superficially from the intermolecular site-site interactions if rigid diatomic or two-site molecules are considered. However, it should be emphasized that the molecular structure does have influence indirectly through the intermolecular site-site correlation functions.

### 11.2.3 Bulk Viscosity of Rigid Homonuclear Diatomic Fluids

To derive the bulk viscosity formula for a rigid homonuclear diatomic liquid we consider a flow configuration identical with that previously considered for simple liquids.

Therefore we suppose, for example, that a sound wave passes through a fluid periodically compressing the fluid in the direction of the wave, and then take into account the density variation from the average equilibrium density value owing to the compressional/dilatational effects of the sound wave.

We assume that the sound wave propagates in the  $z$  direction in a suitably fixed Cartesian coordinate system. We have shown in Chap. 10 that the excess normal stress in such a flow configuration is given by

$$\Delta = \frac{2}{3} (P_{xx} - P_{zz}) \quad (11.37)$$

in terms of the primary normal stress difference.

Because the stress tensor  $\mathbf{P}$  is decomposable into kinetic and potential energy as shown earlier from statistical mechanics considerations,  $\Delta$  is also decomposable into kinetic and potential energy:

$$\Delta = \Delta_k + \Delta_v, \quad (11.38)$$

where  $\Delta_k$  and  $\Delta_v$  are, respectively, the kinetic and the potential energy of the excess stress tensor. They are defined by

$$\Delta_k = \frac{1}{3} \text{Tr} \mathbf{P}_k - p, \quad (11.39)$$

$$\Delta_v = \frac{2}{3} (P_{xx}^{(v)} - P_{zz}^{(v)}), \quad (11.40)$$

where  $p$  is the hydrostatic pressure. It is therefore possible to identify the kinetic and the potential energy parts of the bulk viscosity if they can be put into forms that can be compared with the phenomenological constitutive equations for them:

$$\Delta_k = -\eta_b^k \frac{\partial u_z}{\partial z}, \quad (11.41)$$

$$\Delta_v = -\eta_b^v \frac{\partial u_z}{\partial z}. \quad (11.42)$$

For monatomic liquids it has been shown in Chap. 10 that  $\Delta_k = 0$ , but for nonsimple or molecular liquids with internal degrees of freedom it does not necessarily vanish. This means that there is a kinetic energy contribution to the bulk viscosity, even at low densities, if the fluid consists of molecules with an internal structure. This is well known in the dilute polyatomic gas kinetic theory [4]. Thus the bulk viscosity of a molecular fluid consists of two components, kinetic and potential,

$$\eta_b = \eta_b^k + \eta_b^v. \quad (11.43)$$

The two components have different physical origins. The potential energy contribution  $\eta_b^v$ , which has to do with the intermolecular site-site interactions, makes a major contribution in the high-density regime, whereas the kinetic energy contribution, which is dominant in the low-density regime and arises from the coupling of translational and rotational motions of the molecule, makes a minor contribution in the liquid density regime. The calculation of the potential energy contribution  $\eta_b^v$  will be the principal objective of this section. The theory of the kinetic energy contribution is available in the literature on polyatomic gases [4].

### Kinetic Energy Part of Bulk Viscosity

To calculate  $\eta_b^k$  we consider the singlet distribution function  $f(X_c, x_{12}; t)$  for a fluid consisting of rigid linear molecules, which are assumed to obey the Boltzmann–Curtiss kinetic equation [5] introduced in Chap. 4. As shown in the chapter, the singlet distribution function may be expanded in moments in the form

$$\begin{aligned} f(\mathbf{P}_c, \mathbf{r}, \mathbf{x}_{12}; t) = f_{\text{eq}}(\mathbf{P}_c, \mathbf{x}_{12}) & \left[ 1 + A_0 \left( \frac{2}{3}w^2 - 1 \right) + \mathbf{A}_1 \cdot \mathbf{w} \left( w^2 - \frac{5}{2} \right) \right. \\ & + \mathbf{A}_2 : [\mathbf{w}\mathbf{w}]^{(2)} + B_0 (\phi^2 - 1) + \mathbf{B}_1 \cdot \mathbf{w} \left( w^2 - \frac{5}{2} \right) \\ & \left. + \mathbf{B}_2 : [\phi\phi]^{(2)} + \dots \right], \end{aligned} \quad (11.44)$$

where  $\mathbf{x}_{12} = (\mathbf{p}_{12}, \mathbf{r}_{12})$  and other symbols are defined by

$$\begin{aligned} \mathbf{w} &= \sqrt{\frac{M\beta}{2}} \mathbf{C}, \\ \phi &= \sqrt{\frac{\beta}{2I}} (\mathbf{j} - \langle \mathbf{j} \rangle) \equiv \sqrt{\frac{\beta}{2I}} \mathbf{J}. \end{aligned} \quad (11.45)$$

Here  $f_{\text{eq}}(\mathbf{P}_c, \mathbf{x}_{12})$  is the local equilibrium distribution function given by

$$f_{\text{eq}}(\mathbf{P}_c, \mathbf{x}_{12}) = n(\mathbf{r}) \left( \frac{M\beta}{2\pi} \right)^{3/2} \left( \frac{\beta}{8\pi^2 I} \right) \exp \left( -\frac{\beta MC^2}{2} - \frac{\beta J^2}{2I} \right). \quad (11.46)$$

According to the moment method [1, 2] the coefficients  $A_0$ ,  $B_0$ , and so on are given in terms of the conjugate nonconserved variables as follows:

$$\begin{aligned} A_0 &= 3\Delta_k/2p, & \mathbf{A}_1 &= \mathbf{Q}_k/p\hat{C}_p T, & \mathbf{A}_2 &= \boldsymbol{\Pi}_k/p, \\ B_0 &= (E_{\text{rot}} - k_B T)/p, & \mathbf{B}_1 &= \mathbf{Q}_{\text{rot}}/p\hat{C}_{\text{rot}} T, & \mathbf{B}_2 &= 15\Theta/4p, \end{aligned} \quad (11.47)$$

where  $E_{\text{rot}} = \langle H_{\text{rot}} \rangle$  with  $H_{\text{rot}}$  denoting the rotational Hamiltonian;  $\hat{C}_p = 5k_B/2m$ ,  $\hat{C}_{\text{rot}} = k_B$ , the rotational heat capacity per unit mass;  $\mathbf{Q}_k$  and  $\mathbf{Q}_{\text{rot}}$  are the translational and rotational parts of heat flux, respectively; and

$$\Theta = \int d\mathbf{P}_c \int d\mathbf{p}_{12} \int d\mathbf{r}_{12} [\phi\phi]^{(2)} f(X_c, x_{12}; t). \quad (11.48)$$

Because the  $\mathbf{jj}/I$  term is not related to the velocity gradient  $\nabla\mathbf{u}$  in the linear order with respect to nonconserved variables such as momentum and heat fluxes, it does not have anything to do with the viscosity; it only contributes to  $\mathbf{P}_k$  a term from the polarization of the angular momentum, which is a physical effect different from that for viscosity. Therefore, for the bulk viscosity it is sufficient to consider, by using the distribution function in (11.44), the kinetic energy part  $\Delta_k$  of the excess normal stress  $\Delta$  in the form

$$\Delta_k = \frac{1}{\beta} \int d\mathbf{P}_c \int d\mathbf{p}_{12} \int d\mathbf{r}_{12} \left( \frac{2}{3} w^2 - 1 \right) f(X_c, x_{12}; t). \quad (11.49)$$

The right-hand side does not vanish if the gas molecule has internal degrees of freedom. It gives rise to a bulk viscosity according to the kinetic theory that can be developed on the basis of the Boltzmann–Curtiss kinetic equation of polyatomic gases. Thus, by implementing the moment method for the Boltzmann–Curtiss kinetic equation for bulk viscosity, it is possible to obtain the kinetic part of the bulk viscosity  $\eta_b^k$  which is easily shown to be given by the Chapman–Enskog collision bracket integral [4] for a rigid linear molecule in the lowest order of approximation. For a detailed formula for dilute gas bulk viscosity the reader is referred to the literature on polyatomic gases [4], where the kinetic theory is developed with the Waldmann–Snider equation, but the Boltzmann–Curtiss kinetic theory results can be easily recovered therefrom. Replacing the kinetic contribution to the bulk viscosity with that of a dilute gas at the same temperature may be considered a reasonable approximation. In the actual analysis of experimental data on diatomic liquids later in this chapter, the kinetic contribution  $\eta_b^k$  to the bulk viscosity is taken as an empirical reference value at normal gas density because the bulk viscosity in the dense gas and liquid density regimes is examined relative to the kinetic energy contribution. Therefore  $\eta_b^k$  is not of interest and hence will not be further considered in this work on transport coefficients in the liquid density regime.

### The Potential Energy Part of Bulk Viscosity

Because the internal stress tensor  $\mathbf{P}_v^{(s)}$  is equal to zero for rigid linear molecular fluids the potential energy part of the excess normal stress  $\Delta_v$  is given entirely by the following formula in terms of the reduced dynamic pair distribution function:

$$\Delta_v = \frac{1}{6} \int_0^1 d\zeta \int d\mathbf{r}_{12} \left( r_{12} - \frac{3z_{12}^2}{r_{12}} \right) \frac{dV(r_{12})}{dr_{12}} \times n^{(2)} [r_{12}; z - \zeta z_{12}, z + (1 - \zeta)z_{12}, t]. \quad (11.50)$$

Owing to the site-site representation of correlations, the virial in the integral for  $\Delta_v$  does not explicitly involve the internal degrees of freedom of the molecule. As a consequence, it has been possible to reduce the distribution function  $F_c^{(N)}$  to the site-site pair distribution function  $n^{(2)}$  as in (11.50), and  $\Delta_v$  for rigid linear molecular fluids takes exactly the same form as that for the excess normal stress for simple liquids given in (10.4). Therefore the integral in (11.50) can be treated in the same manner as the integral in (10.4). Thus we obtain the expression for  $\Delta_v$  for rigid molecular liquids:

$$\Delta_v = -\frac{2}{9}\omega_b(\xi) \left( \frac{\partial n}{\partial z} \right)^2, \quad (11.51)$$

where

$$\omega_b(\xi) = \frac{2\pi}{15} \int_0^\infty dr r^5 \frac{dV(r)}{dr} g_{eq}^{(2)}(r) \theta(\xi - r). \quad (11.52)$$

Note that the pair correlation function in (11.50) can be determined by solving the DOZ equation under a suitable closure. The density derivatives of  $g_{eq}^{(2)}(r_{12}; n)$  can be estimated to be of relatively smaller magnitude than the leading term and hence have been neglected. As it was for simple liquids, this argument admittedly requires a more rigorous analysis, but the approximation yields practical and sufficiently accurate results for bulk viscosity. A theory of dynamic pair correlation function is not yet in a sufficiently mature state and awaits further development.

The density variation within the correlation range  $\xi$  will be approximated by the mean bulk density as it was for simple liquids. It is also expected, similarly to simple liquids, that the value of  $\xi$  depends on temperature. Thus, if the fluid is near the critical point the density fluctuations are extended over a long distance (long range), and their range  $\xi$  may be equal to or larger than  $r_{max}$ , the range of intermolecular force. But if  $T$  is sufficiently below the critical temperature  $T_c$  and, particularly, near the triple point, the value of  $\xi$  may be of the order of a few molecular diameters. This finiteness of the range of density fluctuation is taken into account in the integral by approximating  $n^{(2)}(r, t)$  by  $n^{(2)}(r, t) \simeq g_{eq}^{(2)}(r) \theta(\xi - r)$ . In this manner of approximation, there is no contribution to the integral for  $\omega_b(\xi)$  from the region of  $r > \xi$ .

By proceeding similarly to simple liquids by using the constitutive relation for the drift velocity of fluid particle,

$$n\mathbf{u} = -D\nabla n, \quad (11.53)$$

where  $D$  denotes the self-diffusion coefficient of the liquid, which depends on density as well as temperature, and by eliminating the density derivative from (11.51) with the help of (11.53), the molecular theory formula for the potential energy part of the bulk viscosity of rigid linear molecular liquids is obtained:

$$\eta_b^v(n, T) = \frac{n^2 \omega_b(n, T)}{9D(n, T)}. \quad (11.54)$$

Here  $n$  stands for the mean bulk density. Finally, the bulk viscosity of the liquid of interest is given by the formula

$$\eta_b(n, T) = \eta_b^k + \frac{n^2 \omega_b(n, T)}{9D(n, T)}. \quad (11.55)$$

Unlike the bulk viscosity of simple fluids, the kinetic part  $\eta_b^k$  does not vanish because of the internal degrees of freedom, which present modes for energy transfer between molecules in the fluid. Similarly to simple liquids, the potential energy part  $\eta_b^v(n, T)$  has a form resembling the SE relation, but it differs from the SE relation because of the strong temperature and density dependence of the coefficient factor.

#### 11.2.4 Intermolecular Site–Site Pair Correlation Functions

It is necessary to find a way to calculate the site–site pair correlation function for the liquid of interest for  $\omega_b(n, T)$  and the bulk viscosity. As will be seen later, shear viscosity and thermal conductivity also require them. Therefore, we consider the question of computing the site–site pair correlation functions. They may be calculated, of course, by computer simulations. However, integral equation methods have been found practicable. Therefore, we discuss an integral equation theory method in the following. In particular, the Farhat–Eu (FE) integral equation theory [6] of molecular liquids is employed for validation. Because this theory is not the same as the integral equation theory for the radial distribution function of simple liquids, the basic idea of the theory will be briefly discussed below to introduce the reader to it. For the sake of simplicity, a single-component, rigid homonuclear diatomic fluid is assumed uniform in space.

Let us first introduce some useful notations and functions necessary for the discussion. The total correlation function  $h(\alpha, \alpha'; \zeta, \zeta')$  for the site pair  $(\alpha, \alpha')$  on two different molecules, which interact at the strengths of potentials  $\zeta$  and  $\zeta'$  (charging parameters), is denoted by

$$h(\alpha, \alpha'; \zeta, \zeta') = g(\alpha, \alpha'; \zeta, \zeta') - 1. \quad (11.56)$$

The prime is used to designate the site on a different molecule. The total correlation function  $h(\alpha, \alpha'; \zeta, \zeta')$  is defined through the OZ equation. The Fourier transform of the OZ equation for a homogeneous fluid of spherical potential energy has the form

$$\hat{h}(\mathbf{k}) = \hat{c}(\mathbf{k}) + \rho \hat{c}(\mathbf{k}) \hat{h}(\mathbf{k}), \quad (11.57)$$

where  $\hat{h}(\mathbf{k})$  and  $\hat{c}(\mathbf{k})$  are, respectively, the Fourier transforms of  $h(\mathbf{r})$  and  $c(\mathbf{r})$ ,

$$\hat{h}(\mathbf{k}; \zeta, \zeta') = \int d\mathbf{r} \exp(-i\mathbf{k} \cdot \mathbf{r}) h(\mathbf{r}; \zeta, \zeta'), \quad (11.58)$$

$$\hat{c}(\mathbf{k}; \zeta, \zeta') = \int d\mathbf{r} \exp(-i\mathbf{k} \cdot \mathbf{r}) c(\mathbf{r}; \zeta, \zeta'), \quad (11.59)$$

where  $\mathbf{r} \equiv \mathbf{r}_{\alpha\alpha'}$  and  $\alpha, \alpha' = 1, 2$ . The charging parameters  $\zeta$  and  $\zeta'$ , ranged in value from zero to unity, are used to indicate the degree of interaction between the two intermolecular sites  $\alpha$  and  $\alpha'$ ; however, note that to obtain the correlation functions for fully interacting particles integrations over the charging parameters will be performed in the end. Henceforth,  $\hat{c}(\mathbf{k}; \zeta, \zeta')$  will be abbreviated by

$$\hat{c}(\mathbf{k}) = \hat{c}(\mathbf{k}; \zeta = 1, \zeta' = 1), \quad \hat{c}_0(\mathbf{k}) = \hat{c}(\mathbf{k}; \zeta = 0). \quad (11.60)$$

The Fourier transform of the intramolecular correlation function  $\tau(\mathbf{r}_{12})$  will be specifically denoted by  $\hat{\tau}(\mathbf{k})$ ;

$$\hat{\tau}(\mathbf{k}) = \int d\mathbf{r}_{12} \exp(-i\mathbf{k} \cdot \mathbf{r}_{12}) \tau(\mathbf{r}_{12}). \quad (11.61)$$

If a rigid diatomic molecule has bond length  $b$ , this Fourier transform takes the form

$$\hat{\tau}(k) = \frac{\sin kb}{kb}, \quad (11.62)$$

because  $\tau(\mathbf{r}_{12})$  becomes a delta function:

$$\tau(\mathbf{r}_{12}) = \delta(\mathbf{r}_{12} - b) / 4\pi b^2. \quad (11.63)$$

It can be shown that the OZ equation for a rigid diatomic fluid has the form

$$\hat{h}(\mathbf{k}) = \tilde{c}'(\mathbf{k}) [\hat{\tau}(\mathbf{k}) + 1] + 2\rho \tilde{c}'(\mathbf{k}) \hat{h}(\mathbf{k}), \quad (11.64)$$

where

$$\tilde{c}'(\mathbf{k}) = \hat{c}_0(\mathbf{k}) \hat{\tau}(\mathbf{k}) + \hat{c}(\mathbf{k}). \quad (11.65)$$

This is the FE integral equation, derived from the Kirkwood hierarchy by using the Kirkwood superposition approximation [7] and an approximation for the cavity function [6]. There is an integral equation in the literature, which is

slightly different from the FE integral equation. It is called the RISM–PY integral equation [8] and has the form,

$$\hat{h}(\mathbf{k}) = [\hat{\tau}(\mathbf{k}) + 1] \hat{c}(\mathbf{k}) [\hat{\tau}(\mathbf{k}) + 1] + 2\rho\hat{c}'(\mathbf{k})\hat{h}(\mathbf{k}). \quad (11.66)$$

This RISM–PY equation follows from the FE integral equation if  $\hat{c}_0(\mathbf{k}) \approx \hat{c}(\mathbf{k})$  in (11.64).

In [9–11] on molecular fluids the site–site intermolecular correlation function is calculated by using (11.64) or (11.66), which are solved numerically by a combination of iteration and fast Fourier transform methods for a Lennard–Jones potential. Both theories yield comparable pair correlation functions. See Fig. 1 of [10] for such a comparison. Equation (11.64) gives rise to a more stable numerical solution for the Lennard–Jones fluids, especially at low density, than (11.66) of the RISM–PY theory, but at the cost of a little longer computation time. In the RISM–PY theory it was found difficult or impossible to get a physically meaningful solution when the density was lower than the critical density. On the other hand, the FE theory was found free from such a difficulty when a numerical solution was employed.

For a rigid diatomic molecule with site–site interactions, only the intermolecular site–site correlation function is needed, but not the intramolecular site–site correlation function, because there are no intramolecular virial tensors contributing to the potential energy part of the shear viscosity owing to the fact that the bond distance is fixed. However, note that the molecular structure does have influence on the fluid properties such as shear viscosity through the intermolecular site–site correlation function as in (11.64) or (11.66). This is one of the characteristic features absent in the theory for monatomic fluids.

The selection of the liquids for validation is limited by the availability of experimental data. The kinetic energy part of bulk viscosity has been treated as known because the theory is well developed for it by the Chapman–Enskog theory of polyatomic gases and therefore it is not the principal interest of this monograph.

### 11.2.5 Comparison with Experiment

Formula (11.55) with the expression for  $\omega_b(n, T)$  in (11.52) needs validation because it is not an exact statistical mechanical result. In any case, even an exact result needs a demonstration of its utility for understanding laboratory phenomena. Such validations have been reported in the literature [9], and the results are summarized in the following. To implement the validation procedure self-diffusion coefficients measured experimentally may be used to compute  $\eta_b(n, T)$ . This approach has been employed in the validation discussed in the following because of the absence of a reliable theory for self-diffusion coefficients at the time when the density fluctuation theory was developed.

### Bulk Viscosity of Nitrogen

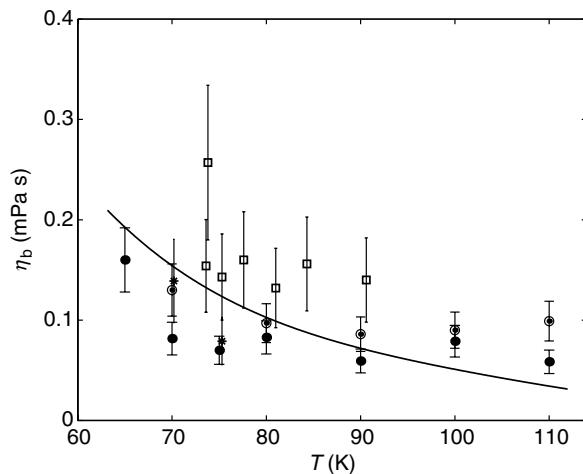
The potential and molecular parameters for nitrogen have the same values as those used in [12]:  $\epsilon = 0.515 \times 10^{-21}$  J,  $\sigma = 0.3310$  nm, and  $b = 0.3292\sigma$ . Because sufficient experimental data are absent for the self-diffusion coefficient of nitrogen, especially, for its temperature and density dependence, the simulation results by Barojas et al. [13] have been fitted to the formula,

$$D^*n^* = 0.1225\sqrt{T^*} - 0.1283, \quad (11.67)$$

where the asterisk denotes the reduced quantity,

$$D^* = \frac{D}{\sigma} \left( \frac{M}{\epsilon} \right)^{1/2}, \quad T^* = k_B T / \epsilon, \quad n^* = n \sigma^3.$$

In Fig. 11.1, the bulk viscosities of liquid nitrogen are examined. They were calculated along the liquid–vapor coexistence curve above the triple point ( $T_t = 63.15$  K,  $\rho_t = 867.9$  kg m<sup>-3</sup>). The critical point of nitrogen is at  $T_c = 126.2$  K and  $\rho_c = 314$  kg m<sup>-3</sup>. The symbols in the figure are for the experimental data reported in the literature, which were determined by sound attenuation:  $\square$  from [40];  $*$  from [14];  $\odot$  from [15]; and  $\bullet$  from [16]. The *solid curve* is for the bulk viscosity of saturated liquid nitrogen calculated by the density fluctuation theory, (11.55), with the aforementioned FE integral equation theory used for the intermolecular site–site equilibrium correlation functions. The kinetic energy component  $\eta_b^k$  of the total bulk viscosity was



**Fig. 11.1.** Bulk viscosity of coexisting liquid nitrogen. The solid curve is the prediction by (11.55) with  $\xi = 4.0\sigma$ . Various symbols are experimental data. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **114**, 10436 (2001). Copyright 2001 American Institute of Physics]

calculated from the experimental data for  $N_2$  gas by Prangsma et al. [17] and were fitted to the formula,

$$\eta_b^k(\text{mPa s}) = 1.0 \times 10^{-3} (0.0001 T^2 + 0.0232 T - 0.3719). \quad (11.68)$$

This fitting formula is almost linear with respect to temperature. Use of the experimental data for the self-diffusion coefficient of nitrogen  $D_{N_2}$  measured by Krynicki et al. [18] yields the bulk viscosities calculated therewith with about  $\pm 10\%$  deviations from the *solid curve* in the range covered by their  $D_{N_2}$  data. The bulk viscosities of nitrogen predicted from the density fluctuation theory lie well within the range of experimental results which have rather wide margins of error. The vertical bars in the figure indicate the experimental error ranges reported by the authors of the experiment. Contrary to other transport coefficients such as shear viscosity and thermal conductivity, large experimental errors are inherent to the sound attenuation methods used for determining bulk viscosity, which count on precise information for other transport coefficients such as shear viscosity, thermal conductivity, and other thermal data. Moreover, sound attenuation from the bulk viscosity is a minor part of the whole and thus one is measuring the bulk viscosity near the limits of experimental error. Nevertheless, by observing the bulk viscosity behavior shown in the figure, the conclusion can be reached that the bulk viscosity of liquid nitrogen decreases as the temperature increases along the coexistence curve, at least, far away from the critical point.

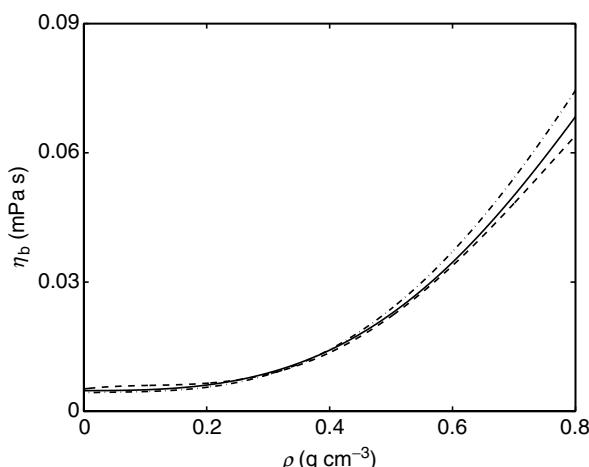
In Table 11.1, the bulk viscosities of nitrogen, which were calculated at the same conditions of density and temperature, are compared with the experiments. In the table, column Expt is for the experimental data [40], column theo.1 is for the theoretical values predicted without adjustable parameters—that is,  $\xi = r_{\max}$ , and column theo.2 is for the theoretical values calculated with  $\xi = 4.0\sigma$ , which give an idea of the size of the effects of the cutoff parameter  $\xi$ , the spatial range of density fluctuations from the average equilibrium

**Table 11.1.** Bulk viscosity of liquid nitrogen

$\rho (\text{kg m}^{-3})$	$T (\text{K})$	$\eta_b (\text{mPa s})$		
		expt.	theo.1	theo.2
841	75.0	0.211	0.195	0.142
822	77.6	0.187	0.172	0.126
822	80.9	0.166	0.159	0.116
820	77.5	0.160	0.172	0.126
806	77.6	0.156	0.133	0.120
787	84.3	0.144	0.130	0.098
786	85.5	0.163	0.124	0.094
746	90.6	0.140	0.102	0.075
690	109.5	0.088	0.064	0.048
682	105.0	0.140	0.066	0.050
671	109.2	0.078	0.060	0.045
671	113.4	0.114	0.057	0.043

density. The densities quoted, however, are higher than those of saturated liquid nitrogen at the given temperatures. Therefore, the set of  $(n, T)$  described in Table 10.1 is for high-pressure states at the given temperature. The self-diffusion coefficient was computed by using the same formula as that used for Fig. 10.2, and the FE integral equation theory was exclusively used for calculating the correlation functions involved. The kinetic part  $\eta_b^k$  was also calculated from formula (11.68). All values listed in Table 10.1 seem to agree qualitatively in the sense that the bulk viscosity is decreasing with decreasing density, although there appear to be some fluctuations in the experimental data. The experimental results in Table 10.1 compare generally better with those calculated with  $\xi = r_{\max}$  than those calculated with  $\xi = 4.0\sigma$ .

Figure 11.2 shows the density dependence of the excess bulk viscosity of nitrogen predicted from formula (11.55) for  $T > T_c$ , where no cutoff parameter is required. The self-diffusion coefficient and the kinetic energy part  $\eta_b^k$  were, respectively, computed from the same formulas as those used for Fig. 10.1. As shown in Fig. 10.2, the calculated bulk viscosity clearly demonstrates that the potential energy part  $\eta_b^v$  of the bulk viscosity becomes dominant as the density increases and its temperature dependence appears to be relatively weak. It is interesting to observe the crossover behavior between two isotherms as the density varies from the gas density to the liquid density: the higher the temperature, the less strong the density dependence of the potential energy part  $\eta_b^v$ , which dominates over the low-density limit of the bulk viscosity (i.e.,  $\eta_b^k$ ), as the density increases. No comparison with experiments is made



**Fig. 11.2.**  $\eta_b$  vs.  $\rho$  for nitrogen at different temperatures. The *dash-dotted* ( $- \cdots -$ ) curve is for  $T = 130$  K, the *solid* curve for  $T = 140$  K, and the *dashed* ( $-$ ) curve for  $T = 150$  K, respectively; the self-diffusion coefficient was calculated from the empirical fit of the simulation results. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **114**, 10436 (2001). Copyright 2001 American Institute of Physics]

owing to the absence of experimental data for  $\eta_b$  in the literature, especially, for  $T > T_c$ .

### Bulk Viscosity of Carbon Dioxide

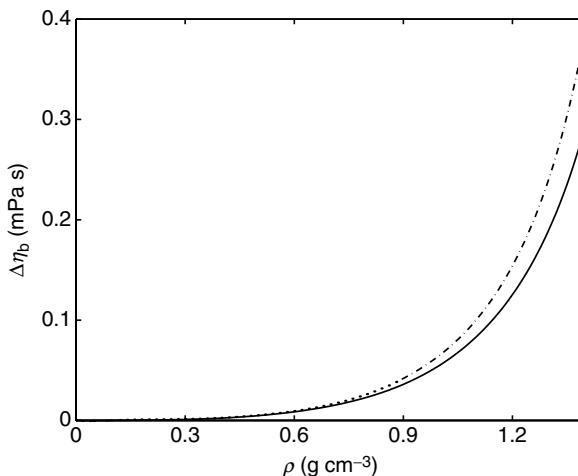
Carbon dioxide is an important substance because it is of considerable interest scientifically and from the industrial and environmental standpoints. Furthermore, because measured or simulated self-diffusion coefficients ( $D_{CO_2}$ ) are available for carbon dioxide in the literature, it's a good example of the application of the theory to validate the theory developed here.

Although carbon dioxide is not a diatomic molecule, it is virtually rigid and, with the carbon atom overshadowed by two larger oxygen atoms, acts almost like a rigid diatomic molecule. This approximation is, of course, unrealistic for spectroscopy, but it is a reasonable approximation to model it as a rigid diatomic molecule for calculating transport properties.

The parameters for the two-center Lennard-Jones potential and the bond length between the two oxygen atoms of the  $CO_2$  molecule have the same values as those employed in the molecular dynamics simulation by Fincham et al. [19]:,  $\epsilon/k_B = 163.3$  K,  $\sigma = 0.3035$  nm, and  $b = 0.7809\sigma$ . The quadrupole interaction potential, which is significant for  $CO_2$ , is not explicit in the site-site intermolecular interaction potentials taken in the present model but may be regarded as implicit in the potential model taken. Although the site-site interaction model does not require the quadrupole potential, the site-site interaction potential parameters are determined [19, 20] that they give a good agreement with the experiment.

For the self-diffusion coefficient  $D_{CO_2}$  necessary for calculating the bulk viscosity with (11.55), the experimental data obtained by Etesse et al. [21] and Gross et al. [22], who used an NMR technique, and the computer simulation data by Singer et al. [20] have been employed. There are tracer isotope experimental values [23, 24] for  $D_{CO_2}$  available in the literature, but they were excluded from the validation study discussed here because when they were used for calculating shear viscosity they gave values which were irreconcilable with the most reliable experimental results for shear viscosity available at the present time.

Figure 11.3 shows the density dependence of the excess bulk viscosity, namely, the potential part  $\Delta\eta_b \equiv \eta_b - \eta_b^k$  of the bulk viscosity  $\eta_b$ , of carbon dioxide at temperatures above the critical point ( $T_c = 304.1$  K,  $\rho_c = 467.7$  kg m<sup>-3</sup>). In the figure, the curves are the predictions by the density fluctuation theory. The *solid curve* is for the density dependence of  $\Delta\eta_b$  at  $T = 328.15$  K, which was calculated with the self-diffusion coefficient computed with the empirical (EZK) formula of Etesse et al. for  $D_{CO_2}$ . The *dash-dot curve* (— · —) is at  $T = 280.15$  K below the critical point. No cutoff parameter was used for the calculations for this figure. The *dotted portion* of the  $\Delta\eta_b$  curve for  $T = 280.15$  K is an interpolation of the theoretical  $\Delta\eta_b$  curves of



**Fig. 11.3.** The excess bulk viscosity  $\Delta\eta_b$  vs. density for CO<sub>2</sub>. The *solid curve* for  $T = 328.15$  K and the *dash-dotted* (— · —) for  $T = 280.15$  K are theoretical predictions. No adjustable parameters were used for the calculations. The dotted (···) portion of the curve for  $T = 280.15$  K represents an interpolation of the excess bulk viscosities of the liquid and vapor branches. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **114**, 10436 (2001). Copyright 2001 American Institute of Physics]

the vapor ( $\rho_v = 120$  kg m<sup>-3</sup>) and liquid ( $\rho_l = 880$  kg m<sup>-3</sup>) branches; in this part of the density regime, which includes the range of density corresponding to the thermodynamically metastable or unstable regime of the fluid at the given temperature, the bulk viscosity may not be measurable. The values calculated by the present theory indicate that the density dependence of the bulk viscosity increases dramatically as the density increases, especially, in the range of density higher than approximately twice the critical density. In Table 11.2, to make comparisons more definitive the density, temperature, and self-diffusion coefficient used for the calculations for Fig. 11.3 are summarized together with the predicted  $\Delta\eta_b$  value of carbon dioxide at the given conditions.

The temperature dependence of bulk viscosity is of interest also for carbon dioxide. In Fig. 11.4, the bulk viscosities at various values of the  $(\rho, T)$  set of the coexisting liquid carbon dioxide are presented for the cutoff parameter  $\xi = 6.5\sigma$ , which is the same value as that used for the shear viscosity calculations for saturated liquid carbon dioxide that will be discussed in the section on shear viscosity in this chapter. For this purpose, the self-diffusion coefficients were computed from the formula,

$$\rho^* D_{\text{CO}_2}^* = 0.1291\sqrt{T^*} - 0.1097.$$

**Table 11.2.** Density dependence of the excess bulk viscosity of carbon dioxide

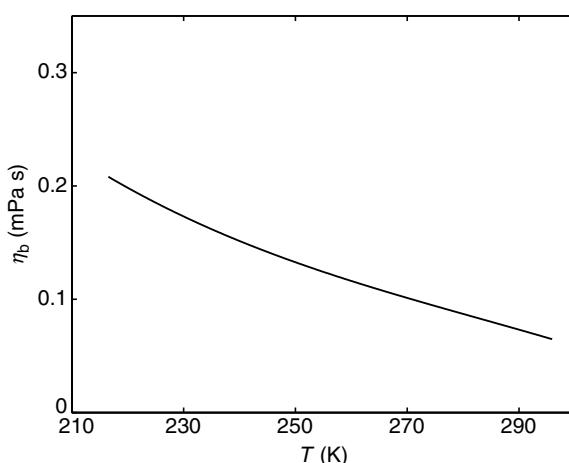
$\rho$ (kg m <sup>-3</sup> )	$T = 280.15\text{K}$		$T = 328.15\text{ K}$	
	$D \times 10^9$ (m <sup>2</sup> s <sup>-1</sup> )	$\Delta\eta_b$ (mPa s)	$D \times 10^9$ (m <sup>2</sup> s <sup>-1</sup> )	$\Delta\eta_b$ (mPa s)
883	15.7	0.0389	17.9	0.0334
920	14.3	0.0459	16.4	0.0392
1,000	11.7	0.0651	13.5	0.0551
1,080	9.37	0.0918	11.0	0.0767
1,160	7.41	0.130	8.80	0.106
1,240	5.72	0.184	6.92	0.148
1,320	4.29	0.264	5.30	0.207
1,400	3.08	0.387	3.91	0.293

This formula fits the simulation data reported by Singer et al. [20]. The density-independent part  $\eta_b^k$  was estimated from formula (11.68). The FE integral equation theory was used to calculate the intermolecular site–site correlation function. The *solid curve* represents the theoretical bulk viscosity values calculated with the FE integral equation theory [6] for the intermolecular site–site correlation function. The coexisting temperature and density were taken in the range from the triple point ( $T_t = 216.6\text{ K}$ ,  $\rho_t = 1178\text{ kg m}^{-3}$ ) up to near the critical point from the paper by Span and Wagner [25]. Note that if  $\eta_b$  were plotted against  $\rho_l^{-1}$ , the saturated liquid density, then the figure would give the density dependence of  $\eta_b$ , showing the bulk viscosity increasing with increasing density.

It is useful for practical purposes to note that the kinetic energy contribution to the bulk viscosity of carbon dioxide can be estimated by using the approximate, although rough, procedure suggested by Assael et al. [26] for the ratio of shear viscosity  $\eta_0$  to the bulk viscosity  $\eta_b^0$  of a dilute gas,

$$\frac{\eta_0}{\eta_b^0} \approx \frac{60\tau}{13\tau + 6}, \quad (11.69)$$

with the parameter  $\tau$  given by  $\tau = 4I_R/(m\sigma_R^2)$ , where  $\sigma_R$  is the diameter of the rough sphere and  $I_R$  its moment of inertia resulting from the internal distribution of mass within the sphere. This relation was obtained in the first-order Chapman–Enskog theory. For carbon dioxide gases a constant value of  $\tau$  estimated was 0.048. For Fig. 11.4, this formula was used without further modification or improvement in the calculations of  $\eta_b^k$ . The shear viscosity  $\eta_0$  of CO<sub>2</sub> can be obtained from the experiments [27] or theoretical calculations [10] by means of the spherical approximation for the Chapman–Enskog shear viscosity for a dilute diatomic gas with effective spherical scaling parameters for  $\sigma$  and  $\epsilon/k_B$ . Note that if  $2\xi \approx r_{\max}$  is taken instead of  $\xi = 6.5\sigma$  for



**Fig. 11.4.**  $\eta_b$  vs.  $T$  for the coexisting liquid  $\text{CO}_2$  calculated for  $\xi = 6.5\sigma$ . The self-diffusion coefficients were taken from the fitting formula to the simulation data by Singer et al. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **114**, 10436 (2001). Copyright 2001 American Institute of Physics]

Fig. 11.4, the bulk viscosity gives an approximately 10 % increase throughout the  $(n, T)$  set examined.

### 11.2.6 Summary for Bulk Viscosity

In summary of the theory of bulk viscosities of simple and complex liquids, the density fluctuation theory of bulk viscosity applied to diatomic fluids gives a simple formula for the bulk viscosity, whose potential energy part is reminiscent of the Stokes–Einstein relation. For the diatomic fluids considered, the theory quite adequately compares with experiment, as has been for simple liquids. Given the quality of the experimental data available in the literature, the theoretical predictions for the temperature dependence of the bulk viscosity of nitrogen compares qualitatively well with experiment. Its density dependence also appears to be reasonable qualitatively. The results presented for the bulk viscosities of nitrogen and carbon dioxide therefore indicate the utility of the density fluctuation theory for bulk viscosity, not only because of the reasonable numerical results but also because the method employed for the calculation results in formulas so simple from the standpoint of current computational techniques and resources, that it readily provides a theoretical means to analyze bulk viscosities of simple and molecular liquids, which are rather difficult to compute otherwise. All that is required for the purpose outside the framework of the density fluctuation theory is the self-diffusion coefficient for the system of interest, and self-diffusion coefficients are much easier to simulate than any other transport coefficients liquids. To make the

theory fully statistical mechanical for there now remains the theory of self-diffusion that can make us predict the temperature and density dependence of  $D$  in the formulas for the bulk viscosities presented. A theory to this end will be discussed in Chap. 12, where free volume theory is presented for diffusion.

### 11.3 Shear Stress

As it is the theory of shear viscosity of simple fluids, the important point of the theory of shear viscosity of complex fluids is that density fluctuations within the range of distance of the order of intersite (intermolecular) forces are responsible for momentum transfers between elementary volumes in liquids subjected to shearing perturbation.

The density fluctuation theory applied to the excess normal stress and related bulk viscosity of complex fluids in Sect. 11.2 can be employed for the shear viscosity of complex fluids in a manner exactly parallel to the procedure used for the former. The formalism developed for the excess normal stress can be taken over for most steps related to the stress tensor. Specifically, the shear viscosities of nitrogen and carbon dioxide will be calculated by using the self-diffusion coefficient data obtained by experiments, computer simulations, or NMR techniques and the site-site pair correlation functions provided by the FE integral equation theory [6] for polyatomic liquids, in which an Ornstein-Zernike equation is solved for polyatomics under the PY closure or a computer simulation method.

We consider the same system as for the excess normal stress of polyatomic fluids discussed in Sect. 11.2. The discussion will be limited to single-component diatomic fluids contained in volume  $V$  at temperature  $T$  after a general formalism is established for complex fluids. We also consider the same flow configuration as that taken for the shear stress of simple liquids in the previous chapter.

#### 11.3.1 Kinetic Part of Shear Stress

The kinetic energy part  $\Pi_k$  of the shear stress tensor  $\Pi$  is readily obtained from (11.28) for homonuclear diatomic fluids. It may be put in the form

$$\begin{aligned} \Pi_k(\mathbf{r}, t) = & \left\langle \sum_{j=1}^N \left( M [\mathbf{C}_j \mathbf{C}_j]^{(2)} + m [\mathbf{v}_{j12} \mathbf{v}_{j12}]^{(2)} \right) \delta(\mathbf{R}_{cj} - \mathbf{r}) F_c^{(N)} \right\rangle \\ & - \frac{1}{2} \Delta \Pi_k^{(1)}(\mathbf{r}, t) + \frac{1}{2} \Delta \Pi_k^{(2)}(\mathbf{r}, t), \end{aligned} \quad (11.70)$$

where

$$\begin{aligned} \Delta \Pi_k^{(1)}(\mathbf{r}, t) = & \int_0^1 d\lambda \sum_{j=1}^N \left\langle \left( M [\mathbf{C}_j \mathbf{C}_j]^{(2)} + m [\mathbf{v}_{j12} \mathbf{v}_{j12}]^{(2)} \right) \right. \\ & \times \mathbf{r}_{j12} \cdot \nabla_{\mathbf{r}} \sinh \left( \frac{\lambda}{2} \mathbf{r}_{j12} \cdot \nabla_{\mathbf{r}} \right) \delta(\mathbf{R}_{cj} - \mathbf{r}) F_c^{(N)} \Big\rangle, \end{aligned} \quad (11.71)$$

$$\begin{aligned} \Delta\boldsymbol{\Pi}_k^{(2)}(\mathbf{r}, t) = & \int_0^1 d\lambda \sum_{j=1}^N \left\langle 2m [\mathbf{C}_j \mathbf{v}_{j12} + \mathbf{v}_{j12} \mathbf{C}_j]^{(2)} \right. \\ & \times \mathbf{r}_{j12} \cdot \nabla_{\mathbf{r}} \cosh \left( \frac{\lambda}{2} \mathbf{r}_{j12} \cdot \nabla_{\mathbf{r}} \right) \delta(\mathbf{R}_{cj} - \mathbf{r}) F_c^{(N)} \left. \right\rangle. \end{aligned} \quad (11.72)$$

The quantities  $\Delta\boldsymbol{\Pi}_k^{(1)}(\mathbf{r}, t)$  and  $\Delta\boldsymbol{\Pi}_k^{(2)}(\mathbf{r}, t)$  contribute terms of order higher than the first term on the right of (11.70), and because we are interested in the states of fluids near equilibrium  $\Delta\boldsymbol{\Pi}_k^{(1)}(\mathbf{r}, t)$  and  $\Delta\boldsymbol{\Pi}_k^{(2)}(\mathbf{r}, t)$  may be ignored calculating the linear viscosity. Thus, we consider only  $\boldsymbol{\Pi}_k(\mathbf{r}, t)$  in the form

$$\boldsymbol{\Pi}_k(\mathbf{r}, t) = \left\langle \sum_{j=1}^N [M \mathbf{C}_j \mathbf{C}_j + m \mathbf{v}_{j12} \mathbf{v}_{j12}]^{(2)} \delta(\mathbf{R}_{cj} - \mathbf{r}) F_c^{(N)} \right\rangle. \quad (11.73)$$

In the same manner as for (11.31) this can be reduced to the form

$$\boldsymbol{\Pi}_k(\mathbf{r}, t) = \int d\mathbf{P}_c \int d\mathbf{p}_{12} \int d\mathbf{r}_{12} [M \mathbf{C}_j \mathbf{C}_j + \mathbf{j}\mathbf{j}/I]^{(2)} f(X_c, x_{12}; t). \quad (11.74)$$

The term related to the angular momentum, the second term in the integrand, can be ignored in determining the kinetic part of the shear viscosity for a rigid diatomic molecular fluid because it is not related linearly to the shear viscosity.

The kinetic energy part  $\eta_k$  of the shear viscosity is then determined if the same flow configuration and procedure are taken as that for the shear viscosity of simple fluids and if  $\boldsymbol{\Pi}_k(\mathbf{r}, t)$  in (11.74) is calculated to the first order in the shear rate  $\partial u_x / \partial z$ , so that it can be compared with the phenomenological form, Newton's law of viscosity,

$$\boldsymbol{\Pi}_{kxz} = -\eta_k \frac{\partial u_x}{\partial z}. \quad (11.75)$$

In this manner,  $\eta_k$  is identified with the Chapman–Enskog shear viscosity of a dilute diatomic gas. Because the dilute gas transport coefficients are not the main objects of interest in this work and the theory is well developed for them [4], we pay no further attention to the kinetic part  $\eta_k$  of the shear viscosity of diatomic fluids here.

### 11.3.2 Potential Part of Shear Stress

Because the intramolecular force part  $\mathbf{P}_v^{(s)}$  of the stress tensor vanishes for rigid diatomic molecules, there is only the intermolecular force part  $\mathbf{P}_v^{(m)}$  remaining. Therefore, a the potential energy part of the shear stress is simply equal to the traceless symmetric part of  $\mathbf{P}_v^{(m)}$  given in (11.35)

$$\begin{aligned} \boldsymbol{\Pi}_v(\mathbf{r}, t) = & -\frac{1}{2} \int_0^1 d\zeta \int d\mathbf{r}_{12} \frac{[\mathbf{r}_{12} \mathbf{r}_{12}]^{(2)}}{r_{12}} \mathcal{V}'(r_{12}) \\ & \times n^{(2)} [\mathbf{r} - \zeta \mathbf{r}_{12}, \mathbf{r} + (1 - \zeta) \mathbf{r}_{12}; t]. \end{aligned} \quad (11.76)$$

We follow the same procedure as that employed for the shear stress of simple fluids in Sect. 10.2, Chap. 10 to obtain the equation for the potential energy part  $\Pi_{vxx}$  of the shear stress:

$$\Pi_{vxx} = \frac{1}{3} \omega(n) \frac{\partial n}{\partial x} \frac{\partial n}{\partial z}. \quad (11.77)$$

In this expression

$$\omega(n) = \frac{2\pi}{15} \int_0^\infty dr r^5 \mathcal{V}'(r) g_{\text{eq}}^{(2)}(r, n) \theta(\xi - r). \quad (11.78)$$

Equation (11.77) is in the same form as (10.33) of Chap. 10 for simple liquids owing to the fact that site-site pair distribution functions are used and their symmetry is with respect to the interchange of sites because of the identicalness of the sites. Here  $g_{\text{eq}}^{(2)}(r, n)$  is the site-site intermolecular pair distribution function. Equation (11.77) should be compared with the phenomenological constitutive equation, Newton's law of viscosity,

$$\Pi_{vxx} = -\eta_v \frac{\partial u_x}{\partial z}. \quad (11.79)$$

For this purpose, the density derivatives in (11.77) are replaced with  $\partial u_x / \partial z$  by using the constitutive equation for fluid velocity as for simple liquids; see (10.34)–(10.37), Chap. 10. Thus the intermolecular part of the shear viscosity of a rigid diatomic liquid also has the same form as that for simple liquids except for the different meaning of the pair distribution function in  $\omega(n)$ :

$$\eta_v = \frac{n^2 \omega(n, T)}{6D(n, T)}. \quad (11.80)$$

Therefore, we finally obtain the shear viscosity of a rigid homonuclear diatomic fluid in the following form:

$$\eta = \eta_0 + \frac{n^2 \omega(n, T)}{6D(n, T)}, \quad (11.81)$$

where  $\eta_k$  is replaced by  $\eta_0$ , which is the Chapman–Enskog theory shear viscosity of a rigid diatomic gas [4]. If the anisotropic part of the potential makes a sufficiently small contribution to the viscosity, then it may be approximated with good accuracy by the shear viscosity of a spherical molecule and thus by

$$\eta_0 \approx cnD_0.$$

The formula derived also suggests that if the self-diffusion coefficient data, experimental, by computer simulation, or by another theory, are available the shear viscosity can be calculated from (11.81). The pair correlation function in the factor  $\omega(n, T)$  in the potential energy part may be obtained from the integral equation theory [6] for the pair correlation function for polyatomic liquids or computer simulations [28–30]. In Chap. 12, the free volume theory will be used to calculate  $D$  based on intersite forces.

### 11.3.3 Comparison with Experiment

The site-site pair correlation function necessary to compute shear viscosity with formula (11.81) can be obtained by solving the FE integral equation or by computer simulations. For the validation of the formula discussed in this subsection, the FE integral equation was employed. The data on self-diffusion coefficients were taken from the literature.

Using the correlation functions calculated numerically with the FE integral equation theory [6] and the self-diffusion coefficients available in the literature, the viscosities of nitrogen and carbon dioxide were calculated with formula (11.81) under the assumption that they are rigid linear molecules with two sites. The Lennard-Jones potential was assumed for intermolecular site-site interactions. The theoretical results are compared with the experimental values available for  $N_2$  and  $CO_2$  from the literature in the following figures. However, no comparison is made with the molecular dynamic simulation results [31] for the shear viscosity of  $N_2$  because the available simulation data tend to suffer from the presence of a longtime tail in the autocorrelation function, especially, at low temperature. This makes the simulated shear viscosity data unreliable for quantitative comparison.

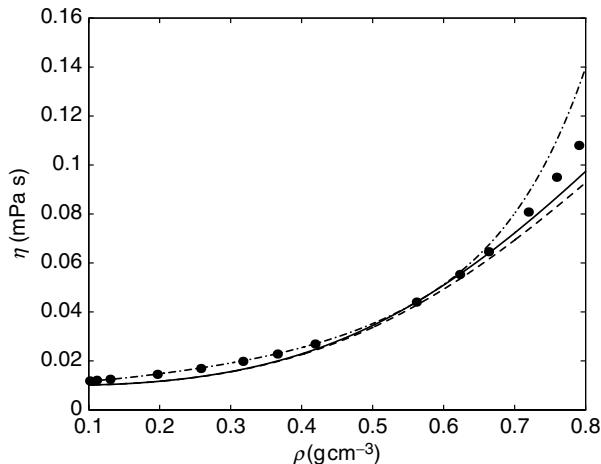
For the self-diffusion coefficients required for calculating the shear viscosity of nitrogen the empirical fitting formula of Barojas et al. [13] given in (11.67) was used. It was a reasonable fit to the available experimental data that are somewhat scattered. The potential and molecular parameters used for nitrogen were the same as those for the excess normal stress.

In Fig. 11.5, the density dependence of the shear viscosity of nitrogen at  $T = 150.0$  K, which is above the critical point ( $T_c = 126.2$  K,  $\rho_c = 314$  kg/m<sup>3</sup>), is shown. In this case, because the cutoff parameter  $\xi$  is larger than  $r_{\max}$ , there is no adjustable parameter in  $\omega(n)$ .

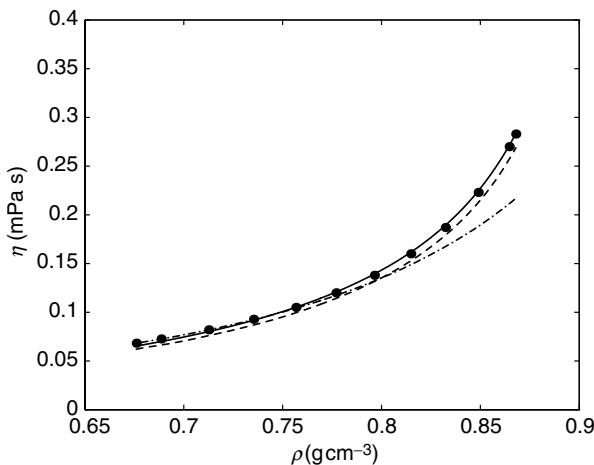
The values represented by the *solid circles* (●) were generated from the tabulated values of experimental data by Younglove [32]. The *solid curve* is the shear viscosity of nitrogen calculated by the density fluctuation theory with the FE integral equation theory used for the intermolecular site-site correlation function, and the *dashed curve* (— —) with the RISM-PY theory [8]. The *dash-dot curve* (— · —) is also from the experimental data fitted to an analytical formula proposed by Stephan et al. [33]. In the high-density region, the deviation of the theoretical values from the experimental values is comparable with the discrepancy between the predictions by the fitting formula of Stephan et al. and the data by Younglove, whereas the calculated viscosities, when compared with the experimental values, tend to be underestimated in the low-density region from 100 to 400 kg m<sup>-3</sup>. But the agreement should be judged acceptable, given the quality of the self-diffusion coefficients and the site-site correlation functions used for the calculations. This variance may be attributed to the precision of the intermolecular site-site correlation function predicted by the FE integral equation theory or the RISM-PY theory [8], especially at the contact value when the density is low; it will be found that the

Monte Carlo simulation method produces better results, as shown in Chap. 12. The kinetic energy part of the shear viscosity may be calculated by the spherical approximation with effective spherical scaling parameters for  $\sigma$  and  $\epsilon/k_B$ , if they are taken, respectively, 0.3652 nm and 98.4 K given in the literature [34]. The Chapman–Enskog shear viscosity thus calculated agrees well with the experimental value within less than 1% at high temperature, but the discrepancy grew to  $\sim 8\%$  as the triple point ( $T_t = 63.15$  K,  $\rho_t = 867.9$  kg m $^{-3}$ ) was approached. For this reason, for Fig. 11.5 the experimental limiting value was taken for the kinetic contribution  $\eta_0$  instead of the Chapman–Enskog shear viscosity calculated as described earlier. It is reported [10] that the use of the Chapman–Enskog value for  $\eta_0$  did not alter the conclusion. In any case, the agreement on the shear viscosity by the theory and experiment appears to be good enough to demonstrate the utility of the density fluctuation theory for the system studied.

The shear viscosity of liquid nitrogen below the critical temperature along the coexistence line from the triple point was also calculated. At high density and low temperature, especially near the triple point, the cutoff parameter  $\xi$  was, as expected, smaller than the intermolecular interaction range. For the calculation of the shear viscosity of liquid nitrogen along the liquid–vapor coexistence line a single value of  $\xi = 4.0\sigma$  was used. The shear viscosities so calculated are presented in Fig. 11.6, where the *solid curve* represents the



**Fig. 11.5.**  $\eta$  vs.  $\rho$  for nitrogen at  $T = 150.0$  K. The *solid* and *dashed* (— —) lines are the results of the density fluctuation theory obtained, respectively, with the FE integral equation theory [6] and the RISM-PY theory [8] for the site–site intermolecular correlations. The symbols (●) are the experimental data and the *dash-dot* line (— · —) is by the empirical formula of Stephan et al. [33]. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **112**, 7118 (2000). Copyright 2000 American Institute of Physics]



**Fig. 11.6.**  $\eta$  vs.  $\rho$  for coexisting liquid nitrogen. The *solid curve* is by the density fluctuation theory using the FE integral equation theory, and the *dashed curve* (— — —) by the RISM-PY theory. The *filled circles* and the *dash-dot curve* are experimental. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **112**, 7118 (2000). Copyright 2000 American Institute of Physics]

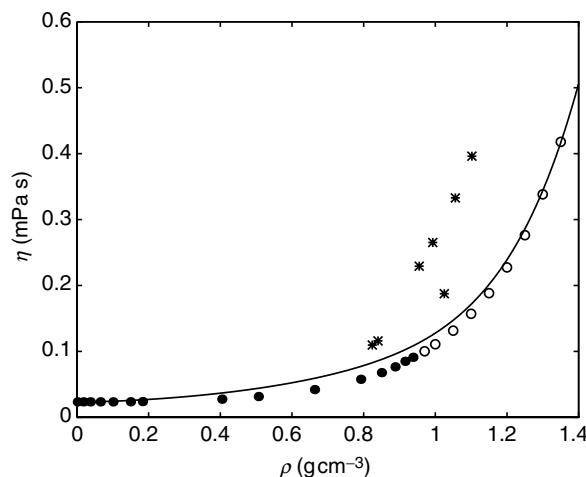
theoretical viscosity computed with  $g_{\text{eq}}^{(2)}(r)$  calculated with the FE integral equation theory, and the *dashed curve* (— — —) represents the theoretical viscosity computed with  $g_{\text{eq}}^{(2)}(r)$  by the RISM-PY theory. The *filled circles* (•) are experimental values reported by Younglove [32] and the *dash-dot curve* (— · —) is the experimental viscosity reproduced by the empirical formula given by Stephan et al. [33]. Even with the single parameter, they are in good agreement quantitatively as well as qualitatively with the experimental values reported by Younglove. For the self-diffusion coefficients, the formula fitted with the experimental data of Barojas et al. [13] was employed.

Because the anisotropy of the nitrogen potential is relatively small, it was found useful to test the theory with a more nonspherical molecule. To this end, the same procedure as that for nitrogen was applied to carbon dioxide to calculate the shear viscosity. Carbon dioxide was chosen for the test because there are abundant experimental data for the shear viscosity available for comparison, and also some simulated or measured self-diffusion coefficients  $D_{\text{CO}_2}$  are available in the literature. Furthermore, carbon dioxide, to a good approximation is a rigid linear molecule and is of considerable interest scientifically and from the industrial and environmental standpoints. Because there is no reliable method known for computing the shear viscosity of such an important substance, the present validation study also seems to fill the need for such a method at the same time.

For the Lennard-Jones potential parameters and the bond length between the two oxygen atoms of the  $\text{CO}_2$  molecule, the same values were used as those

employed for the excess normal stress in the previous section. As for the  $D_{\text{CO}_2}$  values necessary for calculating the shear viscosity, the experimental data obtained by the NMR data of Etesse et al. [21] were used and also the data by Timmerhaus and Drickamer [23], who used an isotope tracer method, as well as the computer simulation data by Singer et al. [20]. More recently, Gross et al. [22] have also measured  $D_{\text{CO}_2}$  with an NMR technique in the temperature range from 223 to 450 K and pressures up to 200 MPa. The data of Etesse et al. [21] and Gross et al. [22] were converted from  $D_{\text{CO}_2}(p, T)$  to  $D_{\text{CO}_2}(n, T)$  by using the equation of state provided by Angus et al. [35] and Span and Wagner [25]. In the high-density regime, where there are no experimental data, an extrapolation was made of the empirical formula proposed by Etesse et al. with the hard sphere diameter equal to 0.358 nm.

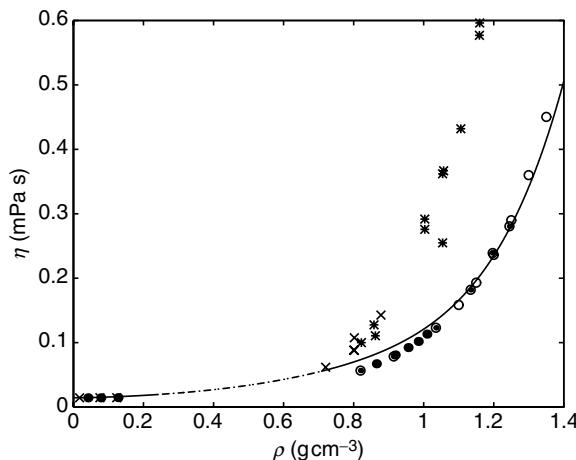
Figure 11.7 shows the density dependence of the shear viscosity of carbon dioxide at  $T = 323.15$  K, which is above the critical point ( $T_c = 304.107$  K,  $\rho_c = 0.46769 \text{ kg m}^{-3}$  according to [36]). In the figure, the *solid curve* is the experimental data reproduced by the empirical (FWV) formula proposed by Fenghour et al. [27] for  $\eta$ . The symbols are the density fluctuation theory results: the asterisks (\*) were calculated with the Timmerhaus–Drickamer  $D_{\text{CO}_2}$  data, the *solid circles* (●) were calculated with the  $D_{\text{CO}_2}$  values reported by Etesse et al. [21], and the *open circles* (○) were calculated with the  $D_{\text{CO}_2}$  values predicted by the extrapolated empirical (EZK) formula obtained by Etesse et al. for  $D_{\text{CO}_2}$ . The theoretical values for the shear viscosities have an excellent qualitative density dependence in the NMR  $D_{\text{CO}_2}$ .



**Fig. 11.7.**  $\eta$  vs.  $\rho$  for carbon dioxide  $\text{CO}_2$  at  $T = 323.15$  K. The solid curve is the experimental data calculated by using empirical formula [27]. The symbols represent the theoretical values computed with  $D$  from different sources. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **112**, 7118 (2000). Copyright 2000 American Institute of Physics]

data, whereas the tracer isotope data for  $D_{CO_2}$  give viscosity values of considerable variance from the experimental values. The hard sphere diameter for this empirical formula was taken as  $\sigma_{HS} = 0.358$  nm. The FE integral equation theory was used for the intermolecular site-site correlation functions. Note that the maximum deviation from the experimental value is about 20% for the shear viscosities calculated with the  $D_{CO_2}$  data by the NMR method. It is estimated [21] that the NMR  $D_{CO_2}$  data and the  $D_{CO_2}$  data obtained by other authors are scattered around the fitting formula and agree within about 20% from each other. Therefore, the theoretical prediction by the density fluctuation theory could fall on either side of the experimental curve, depending on which values were taken for the self-diffusion coefficient. The uncertainty from  $D_{CO_2}$  can be removed when the free volume theory is used to compute the self-diffusion coefficient, as will be seen in Chap. 12. From the perspective of the density fluctuation theory, the tracer isotope experimental values for  $D_{CO_2}$  by Timmerhaus et al. [23] yield shear viscosity values irreconcilable with the most reliable experimental results [27, 36] for the shear viscosity available at the present time.

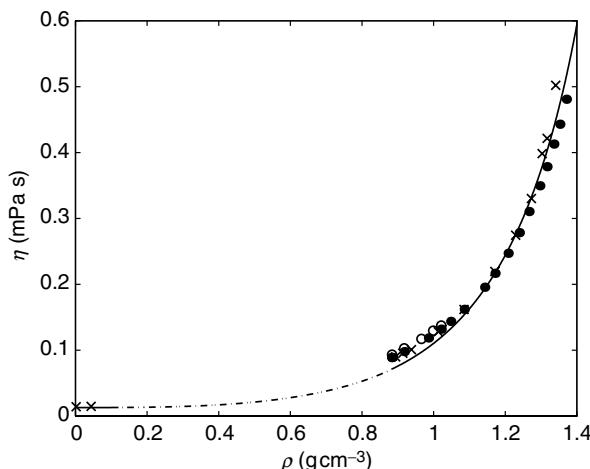
In Fig. 11.8, the theoretical shear viscosities are compared with the experimental data reproduced by the FWV empirical formula at  $T = 298$  K. The meanings of the symbols are the same as those in Fig. 11.7, except for  $\times$ , which represents the shear viscosity calculated with the  $D_{CO_2}$  value obtained



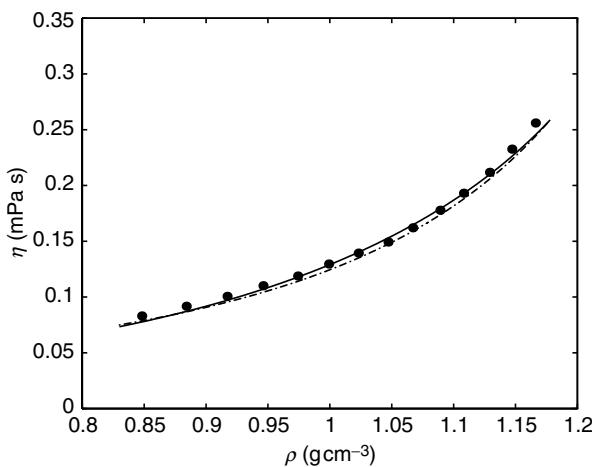
**Fig. 11.8.** Density dependence of the shear viscosity  $\eta$  of  $CO_2$  at  $T = 298$  K. The symbols have the same meanings as in Fig. 10.7 except that  $\times$  represents the theoretical shear viscosity calculated with  $D_{CO_2}$  by Robb and Drickamer [24] and the *dash-dotted portion* of the theoretical curve represents an interpolation of the liquid and vapor viscosity branches. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **112**, 7118 (2000). Copyright 2000 American Institute of Physics.]

by Robb and Drickamer [24], who also used a tracer isotope method, and the *dash-dot curve* ( $-\cdot-$ ) connecting the *solid curves* at  $\rho_l = 717.7 \text{ kg m}^{-3}$  and  $\rho_v = 240.9 \text{ kg m}^{-3}$ , as given by Span et al. [25]. This dash-dot portion of the viscosity curve is an interpolation of the theoretical viscosity curves of the vapor and liquid branches because in that part of the density regime the viscosity is not measured. It should be observed that the  $D_{\text{CO}_2}$  values measured by Robb and Drickamer at low densities appear to give correct shear viscosities at low densities. This does not necessarily mean that the  $D_{\text{CO}_2}$  values yield a correct order of magnitude for the potential energy part of the shear viscosity because the potential energy part  $\eta_v$  makes a negligible contribution to the total shear viscosity at low density. The same comment applies to  $D_{\text{CO}_2}$  obtained by the NMR method. In other words, the shear viscosity values in the very low density regime cannot tell the accuracy of the self-diffusion coefficients measured at the liquid density values mentioned.

Figure 11.9 shows the density dependence of the shear viscosity of carbon dioxide at  $T = 280 \text{ K}$ , which is below the critical point. It was found that there was no need for a cutoff parameter for this temperature. In the figure, the *solid curve* is the theoretical shear viscosity, which is calculated from (11.81), and the self-diffusion coefficient was computed with the EZK formula. The symbols are experimental shear viscosity values:  $\bullet$  by van der Gulik [37];  $\circ$  by Diller and Ball [38]; and  $\times$  by Ulybin and Makarushkin [39]. The meaning of the *dash-dot* portion of the curve is the same as that in Fig. 11.8.



**Fig. 11.9.**  $\eta$  vs.  $\rho$  for  $\text{CO}_2$  at  $T = 280 \text{ K}$ . The *solid curve* is the theoretical prediction by the density fluctuation theory with the empirical EZK formula [21] for  $D_{\text{CO}_2}$ .  $\sigma = 0.358 \text{ nm}$ . The symbols ( $\bullet$ ,  $\circ$ ,  $\times$ ) are experimental [37–39]. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **112**, 7118 (2000). Copyright 2000 American Institute of Physics]



**Fig. 11.10.**  $\eta$  vs.  $\rho$  for coexisting liquid carbon dioxide. The *solid curve* is theoretical. The *filled circles* are experimental [38], and the *dash-dot curve* was obtained with the FWV empirical formula [27] for  $\eta$ . [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **112**, 7118 (2000). Copyright 2000 Americal Institute of Physics.]

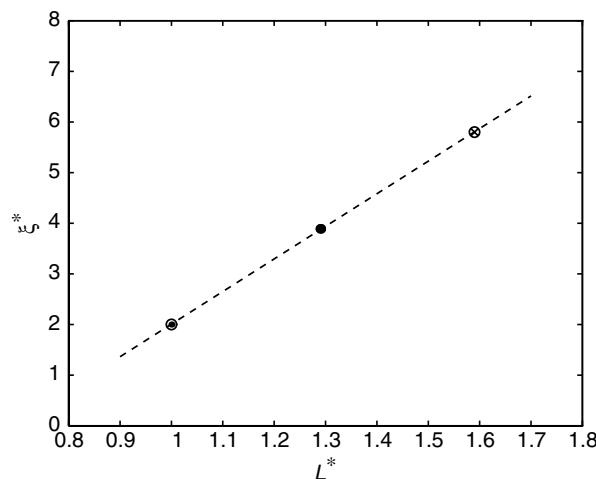
In Fig. 11.10, the shear viscosities at various values of the  $(\rho, T)$  set of the coexisting liquid  $\text{CO}_2$  are presented for the cutoff parameter  $\xi = 6.5\sigma$ . The self-diffusion coefficient values were taken from the simulation data reported by Singer and Lunsford [40]. The *solid curve* is the theoretical viscosity calculated with  $g_{\text{eq}}^{(2)}(r)$  obtained from the FE integral equation theory. The  $D_{\text{CO}_2}$  values for the theoretical calculation were computed with the fitting formula for the simulation data [20]. The *filled circles* ( $\bullet$ ) are the experimental viscosity values reported by Diller and Ball [38] and the *dash-dot curve* ( $-\cdot-$ ) is a reproduction of the experimental data by using the FWV empirical formula [27] for  $\eta$ . The coexisting temperature and density were taken in the range from the triple point up to near the critical point compiled by Span and Wagner [25]. The comparison indicates that the density fluctuation theory gives a qualitatively correct density dependence for the shear viscosity of molecular liquids. Incidentally, note that if the abscissa in Fig. 11.10 is replaced by  $T^{-1}$ , then the figure gives the temperature dependence of  $\eta$ , showing the viscosity decreasing with increasing temperature.

The theoretical predictions for the shear viscosities of molecular liquids presented and compared with experiment indicate that the density fluctuation theory can be quite useful for understanding and analyzing shear viscosity data of molecular liquids because of the simplicity of the formula and the quantities required for the calculation of the shear viscosity. All that should be required outside the framework of the density fluctuation theory is the

self-diffusion coefficient for the system of interest. This latter quantity can be readily calculated with the modified free volume theory as described in Chap. 12.

At  $T$  well below  $T_c$  the density fluctuation theory requires a cutoff parameter  $\xi$  in the integral for  $\omega(n, T)$ . The value of  $\xi$  increases with the length of the molecule. This aspect is worth examining a little more closely because it may provide some useful insights and, especially, with regard to its possible connection with the structure of molecules. For this purpose, in Fig. 11.11 the values of  $\xi^* = \xi/\sigma_A$  are plotted against the reduced length of the molecule defined by  $L^* = (b + \sigma)/\sigma_A$ , where  $\sigma_A$  is the diameter of argon and  $\sigma$  the diameter of the end atom (e.g., N or O). Therefore,  $L^*$  is the total length of the molecule. For argon,  $\xi = 2\sigma_A$  was taken along the coexisting line of the equation of state for liquid argon. Along the coexisting lines of the equations of state for liquid  $N_2$  and  $CO_2$  the values of  $\xi$  are  $4.0\sigma_N$  and  $6.5\sigma_O$ , respectively, for  $N_2$  and  $CO_2$ .

In Fig. 11.11, the symbols denote the following:  $\odot$  is for argon,  $\bullet$  is for  $N_2$ , and  $\otimes$  is for  $CO_2$ . The correlation between  $\xi^*$  and  $L^*$  is perfectly linear with high accuracy and is independent of temperature and density between the triple point and the critical point. This correlation line suggests that one may choose the value for  $\xi$  by using this linear relation for a given rigid linear molecule in the subcritical region in the equation of state and calculate the shear viscosity of fluids in the same class. If this empirical linear relation is accepted for the class of liquids, the cutoff parameter is no longer an adjustable



**Fig. 11.11.** Reduced cutoff distance vs. the reduced length of a molecule in the liquid. The symbols are:  $\odot$  for argon,  $\bullet$  for nitrogen, and  $\otimes$  for carbon dioxide along the coexisting liquid line in the equation of state. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **112**, 7118 (2000). Copyright 2000 American Institute of Physics]

parameter but is predicted by the size of the molecule. This examination of the cutoff parameter indicates that the range of density fluctuations is directly related to the size of the molecule and, perhaps, to the average size of the cage around a molecule in the liquid—that is, the void.

#### 11.3.4 Assessment of the Stokes–Einstein Relation

Because the applicability of the SE relation to the shear viscosity of diatomic liquids is also of interest, the question has been examined. If the SE relation is written as

$$\eta_{se} D = \frac{k_B T}{a\pi R}, \quad (11.82)$$

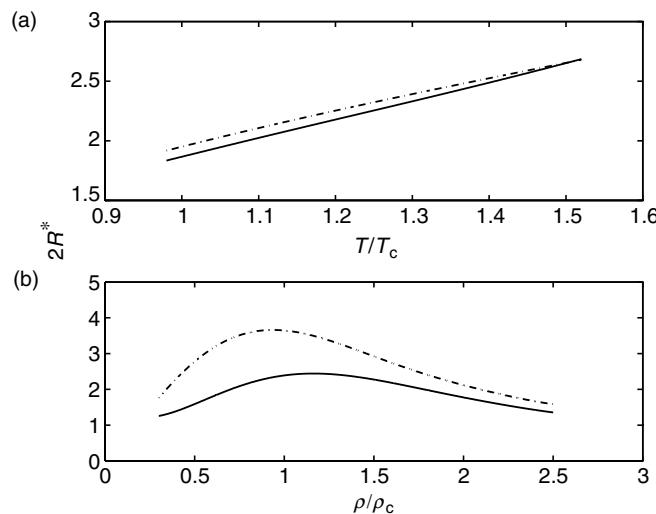
where  $a = 6$  for the stick boundary condition and  $a = 4$  for the slip boundary condition, then on setting  $\eta_{se} = \eta$  and eliminating of  $\eta$  from (11.81) and (11.82), there follows the equation,

$$\frac{1}{a\pi R} = \frac{cnD_0 D}{k_B T} + \frac{n^2 \omega(n, T)}{6k_B T}. \quad (11.83)$$

For the SE relation applicable to molecular liquids,  $R^* = R/\sigma$  should remain constant—in fact, unity—with respect to  $T$  and  $n$ . In Fig. 11.12, the temperature and density dependence of  $2R^*$  are tested for liquid carbon dioxide and liquid nitrogen for  $a = 4$ . The experimental values were used for the kinetic energy part  $\eta_0$  of  $\eta$  for both fluids considered. Unlike that in simple fluids,  $2R^*$  has significant temperature and density dependences as shown in the figure. In fact, there is no range of temperature or density in which it remains constant. The temperature and density dependence of the ratio  $2R^*$  are not unexpected because the SE relation was derived for a spherical particle. Therefore it should be concluded that from the standpoint of the density fluctuation theory the SE relation does not hold for the molecular liquids considered. This is in contrast to simple fluids for which the SE relation holds with a fair degree of accuracy even if the particles are of molecular size, but are not macroscopic particles assumed in the original SE theory, provided that the total viscosity is used instead of the potential energy part  $\eta_V$ . We note that the SE relation also breaks down for glass-forming liquids [41–43], which are generally made up of complex molecules.

## 11.4 Heat Flux

In this section, we show that the density fluctuation theory can also be applied to the thermal conductivity of complex liquids, and it also produces sufficiently accurate and reliable theories in the experimentally studied ranges of temperature and density. As it is for simple fluids, compared with the bulk and shear viscosities, the thermal conductivity of complex fluids is considerably



**Fig. 11.12.** Test of the Stokes–Einstein relation for  $\text{N}_2$  and  $\text{CO}_2$ . (a) The temperature dependence of  $R^*$ : *solid line* is for  $\text{CO}_2$  at  $\rho = 1000 \text{ kg/m}^3$  and the *dash-dot line* is for  $\text{N}_2$  at  $\rho = 600 \text{ kg/m}^3$ . (b) Density dependence of  $R^*$ : *solid line* is for  $\text{CO}_2$  at  $T = 308.15 \text{ K}$  and the *dash-dot line* is for  $\text{N}_2$   $T = 150.0 \text{ K}$ . [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **112**, 7118 (2000). Copyright 2000 American Institute of Physics.]

more difficult to analyze from the viewpoint of molecular theory because its statistical mechanical expression is much more involved.

Nevertheless, the theory of thermal conductivity of complex fluids can be developed parallel to the theory for simple fluids. The theory of viscosities of complex fluids, in fact, can serve as a guide because the basic idea employed will be the same as that for it: in the density fluctuation theory we uphold the viewpoint that the density variation over the intermolecular force range plays a crucially important role as the physical mechanism for relating energy and momentum transfers to the transport coefficients. In this approach, the complexity of the many-particle problem of transport phenomena in liquids is again borne by the pair correlation function and the self-diffusion or diffusion coefficient, in sharp contrast to the conventional Chapman–Enskog kinetic theory [1, 2, 4, 44, 45], in which dynamic collisions events over the intermolecular force range are the focus of attention. The latter theory is designed mainly for gas kinetic transport coefficients, and the density variation over the intermolecular force range is not of primary concern in gas kinetic theory.

As it is for simple fluids, in the formal statistical mechanical expression for thermal conductivity the potential energy contribution to the molecular expression for heat flux consists of products of momentum and potential energies or intermolecular forces. And the appearance of such cross products of momentum- and position-dependent quantities makes statistical mechani-

cal calculation of the thermal conductivity rather vexing, mainly because the nonequilibrium grand canonical distribution function is generally not separable into momentum and position-dependent parts if there is heat flow in the system. In the simple fluid theory it has been shown possible to overcome the difficulty in describing the thermal conductivity if the equation of continuity and the momentum balance equation are used for obtaining relations between the density and temperature gradients when the density variation is described at the hydrodynamic level. We put the same idea to work for complex fluids.

#### 11.4.1 Heat Flux of Complex Liquids

In the same system of notation as that for the stress tensor of complex fluids and as has been done for the heat flux of simple fluids, the heat flux of complex fluids can be decomposed into kinetic energy, potential energy, and virial parts:

$$\mathbf{Q} = \mathbf{Q}_k + \mathbf{Q}_v + \mathbf{Q}_w^{(s)} + \mathbf{Q}_w^{(m)}, \quad (11.84)$$

where the statistical mechanical expression for each part is given by

$$\mathbf{Q}_k = \left\langle \sum_{j=1}^N \sum_{\alpha=1}^l \frac{1}{2} m_{j\alpha} C_{j\alpha}^2 \mathbf{C}_{j\alpha} \delta(\mathbf{r}_{j\alpha} - \mathbf{r}) F_c^{(N)} \right\rangle, \quad (11.85)$$

$$\begin{aligned} \mathbf{Q}_v = & \left\langle \frac{1}{2} \sum_{j=1}^N \sum_{\gamma \neq \alpha}^l w_{j\alpha j\gamma} (\mathbf{r}_{j\alpha}, \mathbf{r}_{j\gamma}) \mathbf{C}_{j\alpha} \delta(\mathbf{r}_{j\alpha} - \mathbf{r}) F_c^{(N)} \right\rangle \\ & + \left\langle \frac{1}{2} \sum_{j \neq k=1}^N \sum_{\gamma \neq \alpha}^l \mathcal{V}_{j\alpha k\gamma} \mathbf{C}_{j\alpha} \delta(\mathbf{r}_{j\alpha} - \mathbf{r}) F_c^{(N)} \right\rangle, \end{aligned} \quad (11.86)$$

$$\mathbf{Q}_w^{(s)} = \left\langle \frac{1}{2} \sum_{j=1}^N \sum_{\alpha, \gamma=1}^l \mathbf{W}_{j\alpha j\gamma}^{(s)} \cdot \mathbf{C}_{j\alpha} \delta(\mathbf{r}_{j\alpha} - \mathbf{r}) F_c^{(N)} \right\rangle, \quad (11.87)$$

$$\mathbf{Q}_w^{(m)} = \frac{1}{2} \left\langle \sum_{j \neq k=1}^N \sum_{\alpha, \gamma=1}^l \mathbf{W}_{j\alpha k\gamma} \delta(\mathbf{r}_{k\gamma} - \mathbf{r}) F_c^{(N)} \right\rangle. \quad (11.88)$$

The virial tensors  $\mathbf{W}_{j\alpha j\gamma}^{(s)}$  and  $\mathbf{W}_{j\alpha k\gamma}$  are defined in (11.18) and (11.19); the former is intramolecular and the latter intermolecular. It will be found convenient to group together the contributions from the interaction potential energy. Such a potential energy contribution will be collectively referred to as  $\mathbf{Q}_p$ :

$$\mathbf{Q}_p = \mathbf{Q}_v + \mathbf{Q}_w^{(s)} + \mathbf{Q}_w^{(m)}. \quad (11.89)$$

$\mathbf{Q}_k$  represents the kinetic energy flux,  $\mathbf{Q}_v$  is the potential energy transported by mass flow, and  $\mathbf{Q}_w^{(s)}$  and  $\mathbf{Q}_w^{(m)}$  arise from the coupling of the intramolecular and intermolecular stresses with mass flow. When the density is high, the kinetic energy part contributes a relatively insignificant amount to heat

conductivity, compared with that of the potential energy part. Repulsive forces dominate the dynamics of particles at high density, and incessant hard collisions of particles in close proximity contribute significantly to the dynamics of energy transport. Consequently, as for the thermal conductivity of simple fluids the dynamic mechanism of energy transport at high density is fundamentally different from that at low density, where the dynamics is dominated by long-range attractive forces; in the latter regime the dilute gas kinetic theory that takes long-range collisions of particles into account is applicable.

Therefore, the experimental thermal conductivity observed is an interpolation of the two contributions from qualitatively and diametrically different mechanisms of energy transport: soft long-range collisions from the attractive potential and harsh short-range collisions from hard repulsive interactions. The four components of  $\mathbf{Q}$  will be considered separately in the following.

As we have for the stress tensor of complex fluids, we will confine the discussion to rigid homonuclear diatomic (or two-site) fluids for simplicity of the formalism. Because intramolecular forces are absent from such fluids, there is no intramolecular virial term  $\mathbf{Q}_w^{(s)}$  contributing, and hence

$$\mathbf{Q}_p = \mathbf{Q}_v + \mathbf{Q}_w^{(m)} \quad (11.90)$$

for the potential part of the heat flux. By using the coordinate transformation to translational and internal coordinates as described in (11.20)–(11.22), the heat fluxes  $\mathbf{Q}_k$ ,  $\mathbf{Q}_v$ , and  $\mathbf{Q}_w^{(m)}$  can be put into more suitable forms.

#### 11.4.2 Kinetic Energy Transport

We consider first the kinetic energy part  $\mathbf{Q}_k$  of heat flux. The general expression for  $\mathbf{Q}_k$  given by (11.85) is expressible in terms of the relative and center-of-mass coordinates and momenta of diatomic (two-site) molecules.

By using the coordinate transformation (11.20)–(11.22), we obtain  $\mathbf{Q}_k$  in the form

$$\begin{aligned} \mathbf{Q}_k = & \frac{1}{2} m N \left\langle C_{j1}^2 \left( \mathbf{C}_{jc} + \frac{1}{2} \mathbf{v}_{j12} \right) \exp \left( -\frac{1}{2} \mathbf{r}_{j12} \cdot \nabla_{\mathbf{r}} \right) \delta(\mathbf{R}_{jc} - \mathbf{r}) \right\rangle \\ & + \frac{1}{2} m N \left\langle C_{j2}^2 \left( \mathbf{C}_{jc} - \frac{1}{2} \mathbf{v}_{j2} \right) \exp \left( \frac{1}{2} \mathbf{r}_{j12} \cdot \nabla_{\mathbf{r}} \right) \delta(\mathbf{R}_{jc} - \mathbf{r}) \right\rangle, \end{aligned} \quad (11.91)$$

where the index  $j$  is for an arbitrary molecule in the set of  $N$  molecules. We will eventually choose one particular molecule, say,  $j = 1$ . For the derivation of this formula the delta functions

$$\delta \left( \mathbf{R}_{jc} \pm \frac{m}{m_\alpha} \mathbf{r}_{j12} - \mathbf{r} \right)$$

are expressed in terms of a displacement operator as in (11.24). If the average over the singlet distribution is denoted by

$$\langle Af \rangle_1 = \int d\mathbf{R}_c \int d\mathbf{P}_c \int d\mathbf{r}_{12} \int d\mathbf{p}_{12} A(\mathbf{R}_c, \mathbf{P}_c, \mathbf{r}_{12}, \mathbf{p}_{12}) f(X_c, x_{12}, t), \quad (11.92)$$

where the subscript 1 to the angular brackets refers to molecule 1, the kinetic part of heat flux  $\mathbf{Q}_k$  can be recast in the form

$$\begin{aligned} \mathbf{Q}_k = & \frac{1}{2} m \left\langle C_1^2 \left( \mathbf{C}_c + \frac{1}{2} v_{12}^2 \right) f \left( \mathbf{r} - \frac{1}{2} \mathbf{r}_{12} \right) \right\rangle_1 \\ & + \frac{1}{2} m \left\langle C_2^2 \left( \mathbf{C}_c - \frac{1}{2} v_{12}^2 \right) f \left( \mathbf{r} + \frac{1}{2} \mathbf{r}_{12} \right) \right\rangle_1, \end{aligned} \quad (11.93)$$

where  $\mathbf{C}_c = \mathbf{P}_c/M - \mathbf{u}$  is the specific velocity of the center of mass of the molecule; and  $\mathbf{P}_c$ ,  $x_{12}$ , and  $t$  in  $f(X_c, x_{12}, t)$  are suppressed for brevity of notation. Upon expanding the distribution functions in power series in  $\mathbf{r}_{12}$ , we obtain to first order

$$\begin{aligned} \mathbf{Q}_k = & \left\langle \left( \frac{M}{2} C_c^2 + \frac{m}{2} v_{12}^2 + m \mathbf{v}_{12} \mathbf{v}_{12} \cdot \right) \mathbf{C}_c f(\mathbf{r}) \right\rangle_1 \\ & - \frac{1}{4} \left\langle \left( \frac{M}{2} C_c^2 + \frac{m}{2} v_{12}^2 + 4m \mathbf{C}_c \mathbf{C}_c \cdot \right) \mathbf{v}_{12} \mathbf{r}_{12} \cdot \nabla_{\mathbf{r}} f(\mathbf{r}) \right\rangle_1 + O(\mathbf{r}_{12}^2). \end{aligned} \quad (11.94)$$

The second line in this expression for  $\mathbf{Q}_k$  gives higher order derivatives of thermodynamic forces (gradients) when the Chapman–Enskog expansion [44] or the moment expansion [2] is used for the singlet distribution function  $f(\mathbf{r})$ . Such terms will be of negligible magnitude if the system is near equilibrium. As we are considering near-equilibrium phenomena for which a linear thermodynamic force–flux relation holds, the kinetic part of the heat flux is represented approximately by the first term in (11.94). In this connection, note that the singlet distribution function  $f^{(1)}(X_c, x_{12}, t)$  for a diatomic fluid contains the distribution function for the internal degrees of freedom. Because the molecules are regarded as rigid, the term  $m v_{12}^2 / 2$  is simply the internal rotational kinetic energy of a rigid diatomic molecule.

Furthermore, because  $\mathbf{v}_{12} = b\boldsymbol{\omega}$  for a rigid rotator of bond length  $b$  and angular velocity  $\boldsymbol{\omega}$  and the rotational angular momentum vector  $\mathbf{j}$  for a rigid diatomic molecule is given by  $\mathbf{j} = I\boldsymbol{\omega}$ , where  $I$  is the moment of inertia defined by  $I = mb^2$ , the heat flux  $\mathbf{Q}_k$  may be written in the form

$$\mathbf{Q}_k = \left\langle \left( \frac{M}{2} C_c^2 + \frac{1}{2I} j^2 + \frac{1}{I} \mathbf{j} \mathbf{j} \cdot \right) \mathbf{C}_c f(\mathbf{r}) \right\rangle_1. \quad (11.95)$$

As it is for simple fluids, it is possible to extract from this formula the kinetic part of the thermal conductivity, if the Chapman–Enskog theory is applied by

employing the Boltzmann equation for diatomic gases. We have described it in Chap. 4. Because the procedure is also well documented in the literature [4] and it is not the principal interest of this work, there is no need to delve into the subject here.

### 11.4.3 Kinetic Part of Thermal Conductivity

By calculating  $\mathbf{Q}_k$  with the first-order Chapman–Enskog solution of the Boltzmann equation for diatomic gases and comparing the result with the phenomenological Fourier law of heat conduction,

$$\mathbf{Q}_k = -\lambda_k \nabla T, \quad (11.96)$$

the kinetic energy part of the thermal conductivity  $\lambda_k$  can be identified with the Chapman–Enskog thermal conductivity of a rigid diatomic gas. The reader is referred to the literature [4] for details of the dilute gas thermal conductivity  $\lambda_k$ .

In practice, the Chapman–Enskog thermal conductivity of a spherical molecule with effective isotropic molecular parameters could be used as an approximation in many cases, particularly if high accuracy is not sought. For the thermal conductivity of liquids the kinetic part plays a minor role in comparison with that of the potential energy part. For this reason, an isotropic approximation for  $\lambda_k$  is often adequate for the kinetic energy part of the thermal conductivity of liquids. Especially, if the density and temperature dependence of the interaction part of heat conductivity is of interest as it is in this work, the empirical data may be employed for  $\lambda_k$  in the actual analysis of experimental results for thermal conductivity to avoid use of gas kinetic theory formulas, which require rather time-consuming labor to compute the elastic and inelastic collision cross sections involved in the collision bracket integrals. Although known to be quite accurate for the thermal conductivities of gases, the cost to compute  $\lambda_k$  from its kinetic theory formula is disproportionately high for the minor contribution it makes in the high density regime.

### 11.4.4 Potential Part of Heat Flux

The interaction potential energy part of heat flux will be considered for rigid homonuclear diatomic (two site) fluids in the following. For rigid diatomic or linear polyatomic molecules, the intramolecular bonding forces are equal to zero;  $\nabla_{\mathbf{r}_{j\alpha}} w_{j\alpha j\gamma} = 0$ . The intramolecular virial tensor  $\mathbf{W}_{j\alpha j\gamma}^{(s)}$  therefore vanishes. Furthermore, there is no intramolecular potential energy contribution to the potential energy flux. Consequently, the potential energy part of heat flux is made up of only the terms involving interactions of the sites on different molecules. This was also the case for the shear stress of rigid diatomic fluids.

### Potential Energy Transport

The potential energy contribution  $\mathbf{Q}_v$  to heat flux consists of intermolecular (site–site) potential energy contributions, and (11.86) can be written in terms of the doublet distribution function  $f^{(2)}(X_c, x_{12}; t)$ :

$$\begin{aligned}\mathbf{Q}_v = & \frac{1}{2} \int dX_c \int dx_{12} \mathcal{V}(r_{12}) \left( \frac{1}{2} \mathbf{C}_c + \mathbf{v}_{12} \right) \\ & \times \delta(\mathbf{R}_c + \frac{1}{2} \mathbf{r}_{12} - \mathbf{r}) f^{(2)}(X_c, x_{12}; t),\end{aligned}\quad (11.97)$$

where  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$  denotes the intermolecular site–site distance, which should not be confused with the intramolecular site–site distance used in the kinetic energy part of the heat flux discussed earlier. By using the factored distribution function introduced earlier, it is possible to express  $\mathbf{Q}_v$  in the form

$$\mathbf{Q}_v = \frac{1}{2} \int d\mathbf{r}_{12} \mathcal{V}(r_{12}) [\mathbf{V}(\mathbf{r}, \mathbf{r} + \mathbf{r}_{12}; t) - \mathbf{u}(\mathbf{r}, t)] n^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{r}_{12}; t), \quad (11.98)$$

where the velocity vector  $\mathbf{V}(\mathbf{r}, \mathbf{r} + \mathbf{r}_{12}; t)$  is defined as the momentum space average of velocity  $\mathbf{v}_2$

$$\mathbf{V}(\mathbf{r}, \mathbf{r} + \mathbf{r}_{12}; t) \equiv \int d\mathbf{P}_c \int d\mathbf{p}_{12} \mathbf{v}_2 \psi^{(2)}(\mathbf{P}_c, \mathbf{p}_{12}, \mathbf{r}, \mathbf{r} + \mathbf{r}_{12}, t) \quad (11.99)$$

with velocity  $\mathbf{v}_2$  expressed by

$$\mathbf{v}_2 = \mathbf{V}_c + \frac{1}{2} \mathbf{v}_{12}. \quad (11.100)$$

Therefore  $\mathbf{V}(\mathbf{r}, \mathbf{r} + \mathbf{r}_{12}, t)$  is the velocity of a pair of particles in the field of the rest of the particles in the system regardless of the distribution of the latter. Therefore  $\mathbf{V}(\mathbf{r}, \mathbf{r} + \mathbf{r}_{12}; t)$  is the mean velocity of a site at  $\mathbf{r}$  with the other site (on a difference molecule) positioned at  $\mathbf{r} + \mathbf{r}_{12}$ , irrespective of the distribution of the remaining sites in the system. Note that because the site–site potential energy is made up of isotropic pair potentials, the pair density correlation function, as it does for simple fluids, depends only on the relative vector  $\mathbf{r}_{12}$ :

$$n^{(2)}(\mathbf{r}, \mathbf{r} + \mathbf{r}_{12}; t) = n(\mathbf{r}, t) n(\mathbf{r} + \mathbf{r}_{12}, t) g^{(2)}(\mathbf{r}_{12}, t). \quad (11.101)$$

According to the formula for  $\mathbf{Q}_v$  in (11.98), the fluid density varies over distances  $\mathbf{r}_{12}$  of the two sites in the molecule that are comparable with the intermolecular force range, so that the interactions of sites over distances of  $O(\mathbf{r}_{12})$  would be important in the liquid density regime. This density variation over such distances must be carefully accounted for to calculate  $\mathbf{Q}_v$  for a liquid.

By expanding the quantities in the integrand in (11.98) in power series of  $\mathbf{r}_{12}$ , we obtain

$$\begin{aligned} n(\mathbf{r} + \mathbf{r}_{12}, t) &= n(\mathbf{r}, t) + \mathbf{r}_{12} \cdot \nabla n(\mathbf{r}, t) + \frac{1}{2} \mathbf{r}_{12} \mathbf{r}_{12} : [\nabla n(\mathbf{r}, t)]^2 + \dots, \\ \mathbf{V}(\mathbf{r}, \mathbf{r} + \mathbf{r}_{12}; t) &= \mathbf{u}(\mathbf{r}, t) + \mathbf{r}_{12} \cdot \nabla \mathbf{u}(\mathbf{r}, t) + \frac{1}{2} \mathbf{r}_{12} \mathbf{r}_{12} : [\nabla \mathbf{u}(\mathbf{r}, t)]^2 + \dots, \end{aligned} \quad (11.102)$$

where we have used of the fact that

$$\mathbf{V}(\mathbf{r}, t) = \mathbf{u}(\mathbf{r}, t). \quad (11.103)$$

Thus we find that the heat flux arising from the potential energy transport  $\mathbf{Q}_v$  is, to first order in the density derivative, expressible as

$$\mathbf{Q}_v = \frac{1}{2} n(\mathbf{r}, t) \int d\mathbf{r}_{12} g^{(2)}(\mathbf{r}_{12}, t) \mathcal{V}(r_{12}) \mathbf{r}_{12} \mathbf{r}_{12} : \nabla n(\mathbf{r}, t) \nabla \mathbf{u}(\mathbf{r}, t). \quad (11.104)$$

This expression for  $\mathbf{Q}_v$  is in the same form as that we obtained for simple fluids in Chap. 10. Hence the molecular structure does not appear explicitly in the expression because of the site-site interaction model for the interaction potential. However, note that the molecular structure does have influence, though indirectly, on the intermolecular interactions through the intermolecular site-site pair correlation functions. This point was further elucidated when the site-site pair correlation functions and their determination were discussed in the previous section on the shear viscosity of molecular liquids.

### Virial Transport

The remainder of the potential energy part of heat flux is the contribution  $\mathbf{Q}_w^{(m)}$  from the intermolecular virial tensor. By using reduced distribution functions introduced earlier, this contribution can be expressed as

$$\begin{aligned} \mathbf{Q}_w^{(m)} &= \frac{1}{2} \int_0^1 d\zeta \int d\mathbf{r}_{12} \mathbf{r}_{12} \mathbf{F}_{12} g^{(2)}(\mathbf{r}_{12}, t) n(\mathbf{r} - \zeta \mathbf{r}_{12}, t) \\ &\quad \times n[\mathbf{r} + (1 - \zeta \mathbf{r})_{12}, t] \{ \mathbf{V}[\mathbf{r} - \zeta \mathbf{r}_{12}, \mathbf{r} + (1 - \zeta \mathbf{r})_{12}; t] - \mathbf{u}(\mathbf{r}, t) \}, \end{aligned} \quad (11.105)$$

where we have used the property of the displacement operator and

$$g^{(2)}[\mathbf{r} - \zeta \mathbf{r}_{12}, \mathbf{r} + (1 - \zeta \mathbf{r})_{12}; t] = g^{(2)}(\mathbf{r}_{12}; t).$$

Note that  $\mathbf{r}_{12}$  is the intersite distance between intermolecular sites, not the relative distance between intramolecular sites. To linear order in  $\nabla n(\mathbf{r})$

$$\begin{aligned} &\int_0^1 d\zeta \{ \mathbf{V}[\mathbf{r} - \zeta \mathbf{r}_{12}, \mathbf{r} + (1 - \zeta \mathbf{r})_{12}; t] - \mathbf{u}(\mathbf{r}, t) \} n(\mathbf{r} - \zeta \mathbf{r}_{12}, t) \\ &\quad \times n[\mathbf{r} + (1 - \zeta \mathbf{r})_{12}, t] \\ &\simeq \frac{1}{3} n(\mathbf{r}, t) \mathbf{r}_{12} \mathbf{r}_{12} : \nabla n(\mathbf{r}, t) \nabla \mathbf{u}(\mathbf{r}, t). \end{aligned} \quad (11.106)$$

Therefore the formula for  $\mathbf{Q}_w^{(m)}$  to linear order in  $\nabla n(\mathbf{r}, t)$  can be given in the form

$$\mathbf{Q}_w^{(m)} = \frac{1}{6} n(\mathbf{r}, t) \int d\mathbf{r}_{12} g^{(2)}(\mathbf{r}_{12}, t) \mathbf{F}_{12} \mathbf{r}_{12} \mathbf{r}_{12} \mathbf{r}_{12} : \nabla n(\mathbf{r}, t) \nabla \mathbf{u}(\mathbf{r}, t). \quad (11.107)$$

The mathematical structure of this formula is the same as that for  $\mathbf{Q}_v$  in (11.104) except for the intermolecular virial tensor—more specifically,  $\mathbf{r}_{12}\mathbf{F}_{12}/3$ —replacing the potential  $\mathcal{V}(r_{12})$  in (11.104); it is also the same as the one for simple fluids in Chap. 10.

#### 11.4.5 Potential Part of Thermal Conductivity

Computation of the sum of (11.104) and (11.107) giving the potential energy part  $\mathbf{Q}_p$  is now reduced, as it was for simple fluids, to the problem of relating  $\nabla n(\mathbf{r}, t) \nabla \mathbf{u}(\mathbf{r}, t)$  to the temperature gradient and, possibly, some thermo-physical parameters such as material functions and the thermal expansion coefficient of the liquid. The relation in question would require hydrodynamic consideration. Inasmuch as the hydrodynamic equations are valid for both simple and molecular liquids, the method used previously for simple liquids is equally applicable to the molecular liquids considered here. Therefore we will simply use the result already derived for simple fluids.

By assuming the same flow configuration as for simple fluids, we obtain

$$\frac{\partial n}{\partial z} \frac{\partial u_z}{\partial z} = - \frac{\alpha n (C_0 - p)}{(n D_e - \eta)} \frac{\partial T}{\partial z}. \quad (11.108)$$

The symbols bear meanings similar to those for simple fluids. It also has been empirically found that the coefficient of the temperature gradient in this equation can be expressed in terms of the isobaric expansion coefficient  $\alpha$  [46]:

$$\frac{\alpha (C_0 - p) m D}{k_B (n D_e - \eta)} = \frac{a_0 \alpha T}{1 + 2\alpha T} \equiv \kappa^* \quad (11.109)$$

as it was for simple fluids. Here,  $a_0$  is an empirical parameter, which is, with excellent accuracy,  $a_0 \simeq 1.68$  for  $T > T_c$  for nitrogen and carbon dioxide treated as rigid diatomic molecules. Note that this empirical form is tantamount to the boundary condition on  $C_0$ :

$$C_0 = p + a_0 \frac{k_B T (n D_e - \eta)}{m D (1 + 2\alpha T)}. \quad (11.110)$$

Also note that  $\kappa^*(n, T)$  becomes a constant value, which assumes  $\kappa^* \simeq 0.56$  as  $\alpha T \rightarrow 1$  in the gas density regime. When  $\kappa^*$  is treated in this manner, the theory becomes semiempirical. The appearance of the isobaric thermal expansion coefficient  $\alpha$  in the numerator of  $\kappa^*$  in (11.109) is not arbitrary as for simple fluids. It has significance for the behavior of thermal conductivity.

Because the momentum and energy are also transported by tagged (tracer) particles in complex fluids as in simple fluids, the hydrodynamic consideration

leading to (11.108) is for tracer particles, whose mean velocity is opposite to the mean fluid velocity  $u_z$ . This can be taken into account in (11.108) by

$$\frac{\partial u_z}{\partial z} \implies -\frac{\partial u_z}{\partial z}, \quad (11.111)$$

and finally we have the following relation between gradients:

$$\frac{\partial n}{\partial z} \frac{\partial u_z}{\partial z} = \frac{nk_B\kappa^*}{D} \frac{\partial T}{\partial z}, \quad (11.112)$$

in the same manner as for simple fluids.

By using this result in the expression for the potential energy part of heat flux  $\mathbf{Q}_p$ , the potential energy contribution to thermal conductivity can be obtained. We find  $\mathbf{Q}_p$  from (11.104), (11.107), and (11.112) in the following form:

$$\mathbf{Q}_p = -\lambda_v(n, T) \left( \frac{\partial T}{\partial z} \right), \quad (11.113)$$

where  $\lambda_v(\rho, T)$  is given by the formula

$$\lambda_v(n, T) = \frac{n^2}{6D} \chi(n, T), \quad (11.114)$$

with  $\chi(n, T)$  defined as

$$\chi(n, T) = \frac{4\pi k_B\kappa^*}{m} \int_0^\infty dr r^4 \left[ \frac{r\mathcal{V}'(r)}{5} - \mathcal{V}(r) \right] g_{eq}^{(2)}(r, n) \theta(\xi - r). \quad (11.115)$$

In (11.115), the dynamic pair correlation function  $g^{(2)}(\mathbf{r}_{12}; t)$  has been replaced with the equilibrium intermolecular site-site pair correlation function at  $n$ , weighted by a cutoff function  $\theta(\xi - r)$ :

$$g^{(2)}(\mathbf{r}, t) \approx g_{eq}^{(2)}(r, n) \theta(\xi - r).$$

The Heaviside step function  $\theta(\xi - r)$  is introduced in the integral, as before, to account for the finiteness of the spatial range  $\xi$  of the density variation caused by the applied temperature gradient, in the same spirit as that for the heat flux of simple fluids and for the stress tensors. The magnitude of  $\xi$  is of the order of a few molecular diameters at temperatures well below the critical point and, in particular, near the triple point, whereas  $\xi$  becomes comparable with or larger than the intermolecular force range  $r_{max}$  if  $T > T_c$ .

#### 11.4.6 Thermal Conductivity of Diatomic Fluids

Collecting the kinetic and potential parts of thermal conductivity, the final expression for the thermal conductivity of rigid homonuclear diatomic liquids in the site-site interaction model can be written as

$$\lambda(n, T) = \lambda_k(T) + \frac{n^2}{6D} \chi(n, T). \quad (11.116)$$

This expression will be validated by comparing with the experimental thermal conductivities of molecular liquids available in the literature.

For dilute diatomic gases the Eucken relation holds approximately between the thermal conductivity and the shear viscosity [44]

$$\lambda_k = \varepsilon C_v \eta_k, \quad (11.117)$$

where  $\varepsilon$  is the Eucken factor,  $C_v$  is the heat capacity of the gas at constant volume, and  $\eta_k$  is the shear viscosity. This relation can be generalized to diatomic liquids. Because the potential energy part  $\eta_v$  of the shear viscosity of homonuclear rigid diatomic liquids is expressible in the site-site interaction model by the formula [10]

$$\eta_v = \frac{n^2}{6D} \omega(n, T), \quad (11.118)$$

where

$$\omega(n, T) = \frac{2\pi}{15} \int_0^\infty dr r^5 \mathcal{V}'(r) g_{\text{eq}}^{(2)}(r, n) \theta(\xi - r), \quad (11.119)$$

we obtain the relation

$$\lambda = \varepsilon C_v \eta_k + C_1 \eta_v \quad (11.120)$$

between the thermal conductivity and the shear viscosity of a homonuclear diatomic liquid. In this relation, the coefficient  $C_1$  is defined by the ratio

$$C_1 = \frac{\chi(n, T)}{\omega(n, T)}. \quad (11.121)$$

This generalized Eucken relation is also useful for computing thermal conductivity from the shear viscosity of a fluid if self-diffusion coefficient data are not available. The coefficient  $C_1$  will be referred to as the generalized Eucken factor for diatomic liquids.

#### 11.4.7 Comparison of Theory and Experiment

The thermal conductivity formula, (11.116), derived in the previous subsection has been validated with regard to the density and temperature dependence in comparison with the thermal conductivity coefficients of liquid nitrogen and liquid carbon dioxide under the assumption that both are linear rigid molecules with two interaction sites. For the thermal conductivity of complex fluids (11.116) also requires precise information on the self-diffusion coefficient at the desired density and temperature. However, experimental or simulation data for  $D$  for liquid nitrogen and carbon dioxide are available only over limited ranges of density and temperature in the literature [12, 13, 18, 21–24, 40],

whereas a large body of experimental data has been compiled for the shear viscosity of carbon dioxide (see, for instance, [27, 36] and references therein). Therefore it was found convenient to use the shear viscosity data in place of the self-diffusion coefficient data by employing the generalized Eucken relation to calculate the thermal conductivity. For this purpose, the thermal conductivity coefficient can be rewritten in the form

$$\lambda = \lambda_k(T) + \frac{\chi(\rho, T)}{\omega(\rho, T)} \eta_v, \quad (11.122)$$

where the Heaviside step function  $\theta(\xi - r)$  is set equal to unity for  $T > T_c$ , unless stated otherwise.

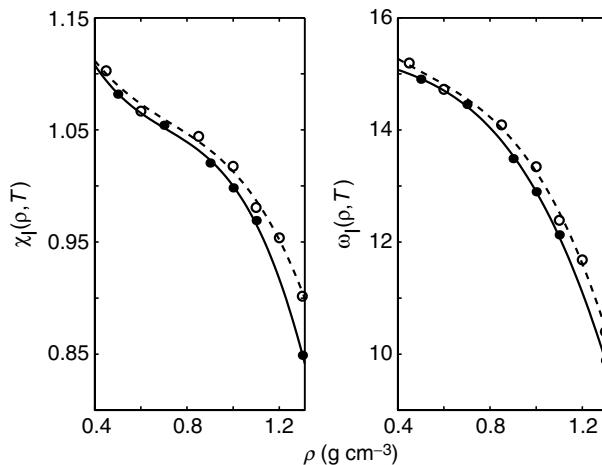
For the intersite potential the Lennard-Jones potential is used exclusively. The parameter values for the site-site Lennard-Jones potential and the bond length  $b$  between the two atoms (sites) are the same as those employed previously in the literature;  $\epsilon = 0.515 \times 10^{-21}$  J,  $\sigma = 0.3310$  nm, and  $b = 0.3292\sigma$  for nitrogen [12]; and  $\epsilon/k_B = 163.3$  K,  $\sigma = 0.3035$  nm, and  $b = 0.7809\sigma$  for carbon dioxide [19]. The reduced temperature and density are defined in the usual manner.

The equilibrium intermolecular site-site pair correlation function  $g_{\text{eq}}^{(2)}(r)$  was calculated either by the Monte Carlo (MC) simulations described in [11] or via the FE integral equation theory [6] for site-site intermolecular correlation functions. Unless stated otherwise, the pair correlation function  $g_{\text{eq}}^{(2)}(r, n)$  used for the calculations was obtained from MC simulations when the mass density  $\rho$  was higher than  $400 \text{ kg m}^{-3}$  (e.g.,  $\rho^* = 0.27$  for CO<sub>2</sub>), whereas for  $\rho \lesssim 400 \text{ kg m}^{-3}$  they were computed with the FE integral equation solved numerically by a combination of iteration and fast Fourier transform methods. Because the generalized Eucken relation was employed to calculate the thermal conductivity, its reliability is assessed in Fig. 11.13 with regard to the density dependence of the integral parts

$$\chi_I(n, T) \equiv \int_0^\infty dr r^4 \left[ \frac{r \mathcal{V}'(r)}{5} - \mathcal{V}(r) \right] g_{\text{eq}}^{(2)}(r; n), \quad (11.123)$$

$$\omega_I(n, T) \equiv \int_0^\infty dr r^5 \mathcal{V}'(r) g_{\text{eq}}^{(2)}(r; n), \quad (11.124)$$

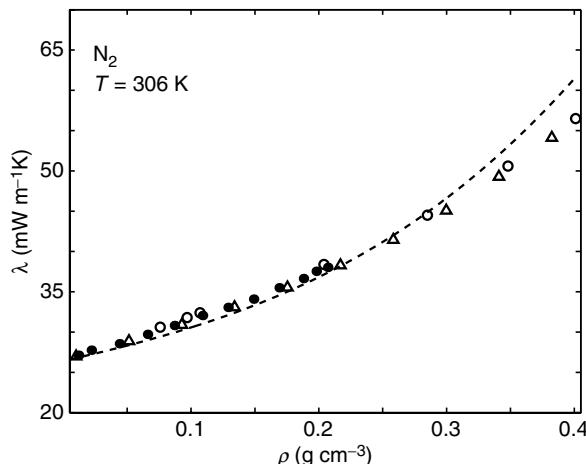
of (11.115) and (11.119) for carbon dioxide. They were evaluated numerically with the pair correlation function  $g_{\text{eq}}^{(2)}(r)$  obtained from MC simulations, where  $g_{\text{eq}}^{(2)}(r > r_c) \simeq 1$  was assumed after the potential cutoff point at  $r_c = 4.5\sigma$ . The symbols were computed with the MC results for  $g_{\text{eq}}^{(2)}(r; n)$  and the curves were drawn to guide the eyes; the *open circles* ( $\circ$ ) are at  $T = 470$  K and the *filled circles* ( $\bullet$ ) at  $T = 503$  K. Both  $\chi_I(n, T)$  and  $\omega_I(n, T)$  decrease with increasing density. The integrals  $\chi_I(n, T)$  and  $\omega_I(n, T)$  for nitrogen reportedly [11] behave similarly to those of carbon dioxide.



**Fig. 11.13.** Density dependence for carbon dioxide of  $\chi_1(n, T)$  and  $\omega_1(n, T)$  defined by (11.123) and (11.124), respectively. The symbols were computed numerically by using  $g_{\text{eq}}^{(2)}(r)$  obtained from the MC simulations described in [11], with  $g_{\text{eq}}^{(2)}(r > r_c) \simeq 1$  assumed after the potential cutoff  $r_c = 4.5\sigma$ . The open circles ( $\circ$ ) are for  $T = 470$  K, and the filled circles ( $\bullet$ ) for  $T = 503$  K. Curves have been drawn only to guide the eyes. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **117**, 4386 (2002). Copyright 2002 American Institute of Physics.]

With the pair correlation function obtained, the thermal conductivity of both nitrogen and carbon dioxide for  $T > T_c$  have been calculated by employing (11.122). The necessary information on  $\eta_v$  was obtained from the papers by Younglove [32] for nitrogen and by Fenghour et al. [27] for carbon dioxide; both are subject to uncertainties of about  $\pm 5\%$  or larger at the highest pressures. The isobaric thermal expansion coefficient  $\alpha$  in (11.109) was computed numerically from the empirical equations of state for nitrogen [47] and carbon dioxide [25, 35].

In Fig. 11.14, the density dependence is shown of the thermal conductivity  $\lambda$  of nitrogen  $N_2$  at  $T = 308$  K, which is approximately  $2.4T_c$  (critical temperature,  $T_c = 126.2$  K). The critical density is  $\rho_c = 313.3 \text{ kg m}^{-3}$ . The dashed curve was calculated from (11.122) using the low-density limit of  $\kappa^*$  empirically determined as  $\lim_{\rho \rightarrow 0} \kappa^* = 0.56$ ; this value gives  $a_0 = 1.68$  in (11.109). The experimental data [37] were used for  $\lambda_k(T)$  in (11.122) to reduce the labor of computing a quantity that makes only a minor contribution in the liquid density regime. We note that a full kinetic theory computation of  $\lambda_k$  for a diatomic molecule system can be done by using the Chapman–Enskog formula, but it could require a major investment in time and labor to calculate the necessary collision cross sections. The filled circles ( $\bullet$ ) are for the experiment by Mostert et al. [37] and the empirical data ( $\circ, \triangle$ ) were estimated from the interpolation formulas for  $\lambda$  of nitrogen proposed by Younglove [32]

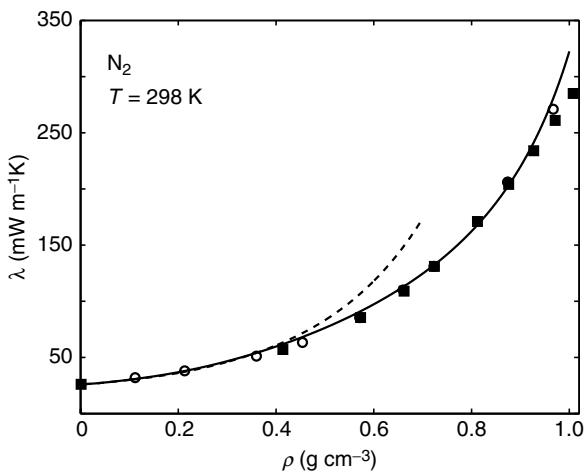


**Fig. 11.14.**  $\lambda$  vs.  $\rho$  for nitrogen at  $T = 306\text{ K}$ . The *dashed curve* was calculated with  $\kappa^* = 0.56$ . The *filled circles* ( $\bullet$ ) are experimental [37], whereas the *open symbols* ( $\circ, \triangle$ ) are empirical data estimated from interpolation formulas by Younglove [32] and by Stephan et al. [33], respectively. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **117**, 4386 (2002). Copyright 2002 American Institute of Physics.]

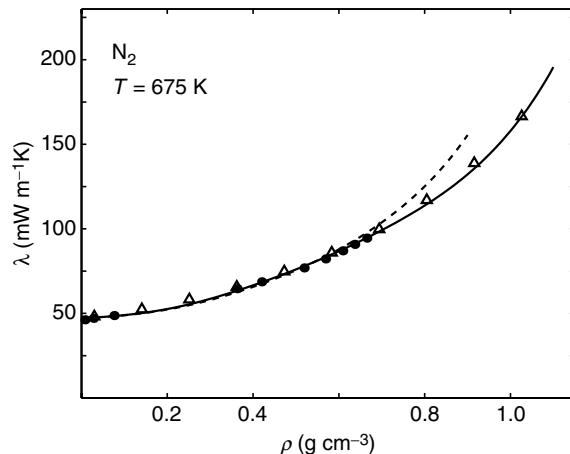
and by Stephan et al. [33], respectively. For  $\rho \gtrsim 300\text{ kg m}^{-3}$ , the constant empirical value of  $\kappa^* = 0.56$  no longer appears appropriate to account for the experimental data for  $\lambda$  with good accuracy.

In Fig. 11.15, the density dependence of the thermal conductivity of nitrogen is shown for  $T = 298\text{ K}$ . In the figure, the *solid curve* was calculated according to the density fluctuation theory from (11.122), and  $\kappa^*(n, T)$  from (11.109) with  $a_0 = 1.68$  determined from Fig. 11.14 in the low-density regime. The *dashed curve* was computed with  $\kappa^* = 0.56$ . The *filled squares* ( $\blacksquare$ ) are the experimental data by Le Neindre et al. [48], and the *open circles* are from Younglove [32]. For density in the range of  $300\text{--}1,000\text{ kg m}^{-3}$  the integrals for  $\chi(n, T)$  and  $\omega(n, T)$  in (11.122) were evaluated by using the intermolecular site-site pair correlation function  $g_{\text{eq}}^{(2)}(r)$  obtained from Monte Carlo simulations described in [11]. An interpolation scheme for  $\chi(n, T)$  and  $\omega(n, T)$  was employed for densities other than those at which simulations were actually performed. For  $\rho < 300\text{ kg m}^{-3}$  the pair correlation functions computed from the FE integral equation theory were employed. No cutoff parameter was used for the calculations. The theory therefore is free of the adjustable parameter. There is very good agreement between the theory (*solid curve*) and experiment.

Figure 11.16 shows the density dependence of the thermal conductivity of carbon dioxide at  $T = 675\text{ K}$ , which is approximately  $2.2T_c$  ( $T_c = 304.1\text{ K}$ ). The critical density is  $\rho_c = 467.7\text{ kg m}^{-3}$ . The two curves show the density



**Fig. 11.15.**  $\lambda$  vs.  $\rho$  for  $N_2$  at  $T = 298$  K. The *solid curve* is the theoretical prediction made with  $\kappa^*(n, T)$  given by (11.109) and  $a_0 = 1.68$ , and the *dashed curve* with  $\kappa^* = 0.56$ . The symbols are experimental: *filled squares* (■) from [48] and *open circles* (○) from [32].  $g_{\text{eq}}^{(2)}(r)$  was obtained from MC simulations for  $\rho = 300 - 1,000 \text{ kg m}^{-3}$  and from the FE integral equation for  $\rho < 300 \text{ kg m}^{-3}$ . No cutoff parameter was used for these calculations. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **117**, 4386 (2002). Copyright 2002 American Institute of Physics.]

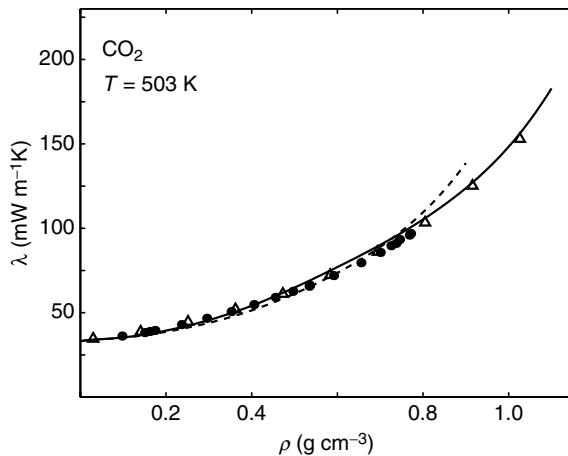


**Fig. 11.16.**  $\lambda$  vs.  $\rho$  for carbon dioxide at  $T = 675$  K. The *curves* are the theoretical predictions by using (11.109) with  $a_0 = 1.68$  for the *solid curve* and  $\kappa^* = 0.56$  for the *dashed curve*. The symbols are experimental data: (●) from [49] and ( $\Delta$ ) from [36]. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **117**, 4386 (2002). Copyright 2002 American Institute of Physics.]

dependence of  $\lambda$  calculated from (11.122), where the *solid curve* was obtained by using (11.109) for  $\kappa^*(n, T)$  with  $a_0 = 1.68$ , whereas the *dashed curve* was calculated with  $\kappa^* = 0.56$ . As the density increases approximately above  $800 \text{ kg m}^{-3}$ , the *dashed curve* starts to deviate from the experimental data for  $\lambda$ , whereas the *solid curve* remains in excellent agreement with the experimental data ( $\bullet$ ) of Tufeu and Le Neindre [49]. The results ( $\Delta$ ) estimated from the empirical fitting formula by Fenghour et al. [27] are also shown for the thermal conductivity of carbon dioxide. The experimental value [49] was used for  $\lambda_k(T)$ . For the density range of  $400\text{--}1300 \text{ kg m}^{-3}$ ,  $\chi(n, T)$  and  $\omega(n, T)$  necessary for (11.122) were calculated with the intermolecular site-site pair correlation function  $g_{\text{eq}}^{(2)}(r)$  obtained from MC simulations, whereas for  $\rho \lesssim 400 \text{ kg m}^{-3}$  the pair correlation functions were computed from the FE integral equation [6].

In Fig. 11.17, the experimental density dependence of the thermal conductivity for carbon dioxide is compared with the theoretical prediction calculated at two isotherms by using the density fluctuation theory. In Fig. 11.17, where  $T = 503 \text{ K}$ , the *solid curve* was predicted from (11.122) in conjunction with (11.109) for  $\kappa^*$  and the *dashed curve* was computed with  $\kappa^* = 0.56$ . The experimental data are from Tufeu and Le Neindre ( $\bullet$ ) [49] and Vesovic et al. ( $\Delta$ ) [36].

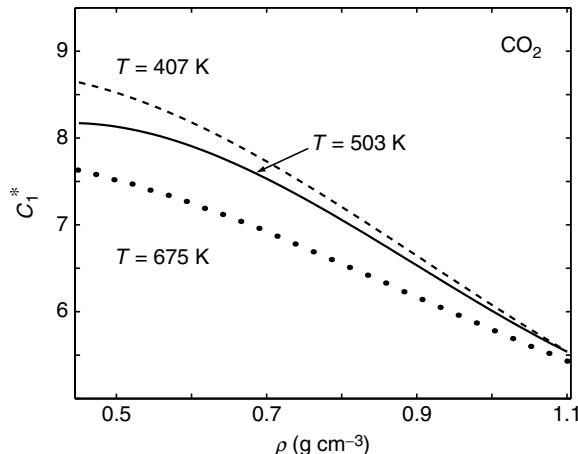
From both theoretical and practical viewpoints the relationship between the thermal conductivity and shear viscosity of molecular liquids is very useful and important. For liquids the potential energy part dominates the kinetic energy part in accounting for the thermal conductivity. The generalized Eucken factor (11.121) between the thermal conductivity and shear viscosity has been also examined for liquid carbon dioxide. Based on the methodology developed



**Fig. 11.17.** The same as Fig. 10.16 except that the results are for  $T = 503 \text{ K}$ . [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **117**, 4386 (2002). Copyright 2002 American Institute of Physics.]

in the density fluctuation theory, the factor  $C_1$  in (11.121) was calculated as a function of density at three isotherms all above  $T_c$ . The results are shown in Fig. 11.18, where the reduced form of  $C_1^* \equiv C_1/R$  ( $R$  is the gas constant), is plotted against density: the *dashed*, *solid*, and *dotted curves* correspond to temperatures at  $T = 407$ ,  $503$ , and  $675\text{ K}$ , respectively. The coefficient  $C_1$  is a rapidly decreasing function of density, indicating that the generalized Eucken factor  $C_1$  becomes strongly density-dependent in the high density regime. This decreasing behavior of  $C_1$  with respect to density reportedly [11] cancels out to some extent the rather dramatic increasing trend of shear viscosity with increasing density, especially in the high density regime. This seems to explain, at least qualitatively, why density dependence of the thermal conductivity is weaker than the density dependence of the shear viscosity that can be observed when their theoretical and experimental density dependences are compared. It would be useful to construct an appropriate empirical form for  $C_1$  that can be employed for calculating the thermal conductivity on an empirical basis in terms of shear viscosity. This task is of interest to experimenters and will be left to them to work out.

No cutoff parameter has been used for the calculations of thermal conductivity at the temperatures considered for molecular liquids. However, the range of  $\xi$  in the step function  $\theta(\xi - r)$  in (11.115) may no longer be comparable with the intermolecular force range when the temperature is well below  $T_c$  because the range of density variation is narrower than the intermolecular force range at low temperature and, in particular, near the triple point unlike



**Fig. 11.18.** The density dependence of  $C_1^* \equiv C_1/R$  for three isotherms of carbon dioxide, where  $C_1$  is given by (11.121). The curves are theoretical: the *dashed curve* for  $407\text{ K}$ , the *solid curve* for  $503\text{ K}$ , and the *dotted curve* ( $\cdots$ ) for  $675\text{ K}$ . (11.109) was used for all three curves, and  $g_{\text{eq}}^{(2)}(r)$  was obtained from MC simulations. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **117**, 4386 (2002). Copyright 2002 American Institute of Physics.]

at  $T \gtrsim T_c$ , where  $\xi$  becomes comparable with or larger than the intermolecular force range. Nevertheless, it is useful to remember that the same value of  $\xi$  should be taken as that used for shear viscosity, especially, in view of the generalized Eucken relation. Because of this relation,  $\xi$  is no longer an adjustable parameter for thermal conductivity; it is already fixed for the calculation of the shear viscosity of the same substance, if the shear viscosity is first calculated and compared with experiment.

## 11.5 Concluding Remarks on the Density Fluctuation Theory

Historically, the reductionist philosophy of macroscopic phenomena in matter has driven science to develop a kinetic theory of matter based on particulate concept of matter. This culminated in the mean free path theory of Clausius [50] and the more successful kinetic theory of gases of Maxwell [51]. Maxwell's kinetic theory of gases was continued and improved in a very important way by Boltzmann [52], who discovered the kinetic equation that now bears his name and provides us with the foundations of molecular theory for irreversible thermodynamics [1, 2, 53] through the H theorem of Boltzmann. Maxwell's elucidation of the molecular theory of transport coefficients such as viscosity, thermal conductivity, and diffusion coefficients became a great impetus for further experimental examination of the density and temperature dependence of transport coefficients. Maxwell's theory predicted that the transport coefficients of normal state gases are independent of density, but it was discovered by Kundt and Warburg [54] in their study of rarefied gases that Maxwell's prediction was contradicted: the transport coefficients depend on density as density diminishes. Thus the desire to understand the density dependence of transport coefficients in the rarefied gas limit has motivated the kinetic theory of gases to develop rarefied gas dynamics [55], in which we study the density and temperature dependence of transport coefficients of gases and their fluid dynamic consequences. We have discussed an example of such a density dependence in Chap. 3.

The kinetic theory of Maxwell and Boltzmann was synthesized by J. W. Gibbs [56], who included matter in the condensed phase in his statistical mechanics, although the theory was limited to equilibrium phenomena. Gibbs' ensemble theory of statistical mechanics inevitably points to the possibility of the density dependence of transport coefficients of matter as density increases.

Experimental investigation of transport coefficients in the early part of the twentieth century showed that the transport coefficients of dense gases and liquids depend strongly on density and temperature, unlike the transport coefficients of gases in normal states. Enskog's theory of dense gases [57] was an early pioneering work attempting to extend the Boltzmann kinetic theory. The kinetic theory of dense gases and liquids after the advent of the BBGKY hierarchy theory [58–61] in 1946 may be said to have been devoted to improving the Enskog approach and answering the questions arising in his theory.

The linear response theory [62–64] is another theory in this category of theories. The generalized Boltzmann equation described in this work is still another approach to try to answer the questions. The BBGKY line of theories, the generalized Boltzmann equation approach via the Chapman–Enskog method of solution, and the linear response theory all require solutions of many-particle collision dynamics, which are impossible to achieve in practical and reliable forms. Consequently, they have not proven practical for understanding the desired density and temperature dependence of transport coefficients of dense gases and liquids. In recent years, computer simulation methods, such as molecular dynamics simulation and Monte Carlo simulation, have been providing tools to obtain desired information on thermophysical properties of matter in the condensed phase, although they have their own limitations.

The density fluctuation theory presented in the previous and present chapters is aimed at answering the aforementioned question regarding the density and temperature dependence of transport coefficients of matter in the condensed phase by an approach rather different from the aforementioned theories. In the density fluctuation theory, the transport of matter, momentum, and energy is achieved through local density fluctuations within intermolecular force ranges and resulting alterations in the fluid structure. Matter, momentum, and energy transport are intimately controlled by diffusion of particles, and diffusion of particles in fluids provides temporal and spatial scales of the transport of the aforementioned quantities. Thus, at the mathematical level of such transport processes the transport coefficients are scaled by the self-diffusion coefficient or the diffusion coefficients of the fluid of interest and are also determined by the structure of the fluid. Consequently, the temperature and density dependence of transport coefficients of a fluid are computable in terms of the self-diffusion or diffusion coefficients and the equilibrium pair correlation function, given appropriate intermolecular and intramolecular interaction potentials. Self-diffusion or diffusion coefficients may be taken from empirical or computer simulation data, and the equilibrium pair correlation function can be computed either by an integral equation theory or a computer simulation method (e.g., Monte Carlo simulation). If the self-diffusion coefficient is supplied empirically or from computer simulations, then the density fluctuation theory becomes a semiempirical theory of transport coefficients. Irrespective of whether it is semiempirical or molecular, using the density fluctuation theory we are now able to calculate the density and temperature dependence comparable with that from experimental data with good accuracy.

As will be discussed in the following chapter, self-diffusion coefficients may be calculated by free volume theory and thereby the semiempiricism of the density fluctuation theory can be effectively removed. In removal of semiempiricism, the crucial role is played by the generic van der Waals equation of state—the canonical equation of state—owing to which the density fluctuation theory of transport coefficients provides a practical method for computing the density and temperature dependence of dynamic thermophysical observables by Monte Carlo simulations of fluid structures and related equilibrium thermophysical properties.

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## 12

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### Free Volume Theory and Transport Coefficients

The density fluctuation theory described in the previous two chapters has provided formulas for the potential energy parts of the transport coefficients of liquids in forms reminiscent of the Stokes–Einstein relation between viscosity and the diffusion coefficient. The formulas derived can successfully account for the density and temperature dependence of transport coefficients of simple as well as complex liquids, provided that the self-diffusion coefficient and equilibrium pair correlations are available for the liquid of interest. They can be obtained by computer simulation methods. Therefore, if we are satisfied with such an approach, the theory may be regarded as sufficient for computing and analyzing data on transport coefficients of liquids. However, simulating self-diffusion coefficients for liquids is a still time-consuming effort and also costly. Furthermore, we would like to push the subject matter to the edge of molecular theory, so that our understanding of the subject can be as refined as possible. In this respect, the free volume theory of diffusion seems to meet the desired aim to a large extent at present, given the complexity of the problem in hand. With the free volume theory described and validated in this chapter, the density fluctuation theory can be made a practicable molecular theory of transport coefficients that requires only equilibrium pair correlation functions that can be obtained either from the solutions of integral equations or more accurately by computer simulation methods—typically Monte Carlo simulation [1]. It is interesting and significant that dynamic quantities, such as transport coefficients, can be calculated only with equilibrium pair correlation functions, and it frees the theory of transport coefficients of liquids from some delicate questions related to the meanings of temperature, the modes of applying external perturbations, and associated algorithms (such as the Hamiltonian of Nosé and Hoover) in molecular dynamics simulation methods [2, 3].

It would not take long reflection to see that the essence of comprehending the physical mechanisms of transport processes in liquids must lie in the behavior of the voids in liquids. Notwithstanding the clarity of the picture that voids play the key role in transport processes in liquids, their mode

for entering into the molecular theory of transport processes is not obvious. There appear to be two levels on which they enter into the whole structure of the theory: at the dynamics level and at the equilibrium structure level. By dynamics here, we mean dynamics in the nonequilibrium processes of the transport of matter, momentum, and energy. In this author's opinion, the free volume theory of Cohen and Turnbull [4] provides a significant measure of understanding at the dynamic and kinematic levels. It, however, would require a method of computing the mean free volume in addition to knowledge of other parameters in their theory. The practical utility of their theory hinges upon what is meant by the mean free volume from the viewpoint of molecular theory. We show that the desired molecular theory meaning of the mean free volume is provided by the generic van der Waals equation of state discussed in Chap. 6, because the latter gives a molecular theory representation for the mean free volume in terms of the equilibrium pair correlation function. The desired molecular structure of the liquid and the equilibrium structure of voids in the liquid are adequately provided by the equilibrium pair correlation function. How the roles of voids in liquids are played out in the free volume theory—called the modified free volume (MFV) theory [5] in the following—is described in this chapter, and then the theory will be validated in comparison with experiment.

There are other free volume theories in the literature [6–12], but they are either empirical or have been found inadequate for our purpose. Therefore we will not discuss them here except for mentioning their existence.

## 12.1 Modified Free Volume Theory of Diffusion

### 12.1.1 Free Volume Theory

We briefly discuss the essential feature of the Cohen–Turnbull free volume theory [4] and then a suitably modify it, so that it can be made molecular to the maximum extent within the framework of the free volume concept. We consider a simple liquid consisting of hard spheres for the sake of simplicity. This restriction, however, is not mandatory and may be relaxed.

In closely packed liquids the attractive force felt by a particle is much screened out by its nearest neighbors. Consequently, particles move in an almost constant force field in a cage provided by the nearest-neighbor particles surrounding them. Therefore, a hard sphere model mimics the behavior of closely packed liquids rather well. Denote the volume per molecule in the liquid by  $v$  and the excluded volume per molecule (i.e., the molecular volume) by  $v_0$ . The latter is the volume that cannot be occupied by other molecules. The difference  $v - v_0$  is then the volume per molecule that is available to other molecules excluding the molecule of attention. We will regard this as the free volume. Diffusion is then simply treated as translation of molecules across the void within its cage and beyond. If the idea of mean free path theory [13, 14]

is employed, then translational diffusion coefficient  $D(v)$  within the estimated free volume is given by the formula

$$D(v) = \mathbf{g} u a(v), \quad (12.1)$$

where  $\mathbf{g}$  is a geometric factor,  $u$  is the thermal speed (e.g., the mean gas kinetic speed), and  $a(v)$  is roughly the diameter of the cage representative of free volume  $v$ . This diffusion coefficient will be equal to zero if the free volume is less than a characteristic value large enough to allow the molecule to move into the void created by the displacement of a molecule. The translational diffusion coefficient  $D$  of the liquid is then a weighted superposition (i.e., average) of all possible diffusional contributions from molecules that have different available free volumes:

$$\begin{aligned} D &= \int_{v^*}^{\infty} dv D(v)p(v) \\ &= \mathbf{g} u \int_{v^*}^{\infty} dva(v)p(v), \end{aligned} \quad (12.2)$$

where  $p(v)$  is the probability of finding free volume  $v$  between  $v$  and  $v + dv$  and  $v^*$  is the critical free volume activating diffusion. The difficulty of the Cohen–Turnbull theory is in the poorly defined parameters  $\mathbf{g}, u, a(v)$ , and  $v^*$  in addition to the mean free volume per molecule  $v_f$  appearing below, all of which are not precisely related to molecular interaction parameters and the structure of the liquid in hand. This weakness should be removed as much as possible to make the theory function better.

In any case, because free volume is randomly distributed, the Cohen–Turnbull theory calculates  $p(v)$  by employing a statistical mechanics method. Imagine that the total range of free volume is divided into small regions  $i$  having average value  $v_i$ . Let there be  $N_i$  molecules having free volume in the  $i$ th region of size  $v_i$ . If there are  $N$  molecules in the liquid, then there are

$$W = \frac{N!}{\prod_i N_i!} \quad (12.3)$$

ways of distributing  $N$  molecules into free volumes  $v_1, v_2, \dots, v_i, \dots$ . This distribution is subject to the conditions,

$$N = \sum_i N_i, \quad (12.4)$$

$$Nv_f = \alpha \sum_i N_i v_i, \quad (12.5)$$

where  $v_f$  is the mean free volume per molecule and  $\alpha$  is a geometric factor correcting for the free volume overlap. Cohen and Turnbull [4] estimated that it is between 1 and 1/2.

Applying the Lagrange method of undetermined multipliers, the probability distribution function  $p(v)$  is obtained from (12.3)–(12.5):

$$p(v) = \frac{\alpha}{v_f} \exp\left(-\frac{\alpha v}{v_f}\right), \quad (12.6)$$

which is normalized to unity

$$\int_0^\infty dv p(v) = 1. \quad (12.7)$$

By using this distribution function in (12.2) and assuming that  $a(v)$  is a slowly changing function, we obtain the self-diffusion coefficient

$$D \simeq g u a(v^*) \exp\left(-\frac{\alpha v^*}{v_f}\right). \quad (12.8)$$

This is the main result of the Cohen–Turnbull free volume theory [4], which is reminiscent of the empirical formula used by Doolittle [9]. Although the present version of free volume theory is rather compelling conceptually, it contains six parameters, which are not precisely defined. They will have to be given more precise meanings if the theory is to be useful for understanding transport processes and the behavior of related transport coefficients of liquids. In the modified free volume (MFV) theory [5], the self-diffusion coefficient in (12.8) is given a more useful and explicit molecular theory form.

In closely packed liquids molecules behave like hard spheres, and translational diffusion of such particles in a cage should closely resemble hard sphere diffusion across mean free path  $a(v^*)$ . Therefore it is appropriate to replace the factor  $g u a(v^*)$  with the Chapman–Enskog hard sphere self-diffusion coefficient [14]

$$g u a(v^*) \Rightarrow D_0 = 1.019 \frac{3}{8n\sigma^2} \sqrt{\frac{k_B T}{\pi m}}, \quad (12.9)$$

where  $n$  is the density,  $\sigma$  is the diameter of the hard sphere, and  $m$  is the reduced mass of the molecule. The numerical factor 1.019 in the expression for  $D_0$  may be safely replaced with unity. With the replacement suggested in (12.9), the three poorly known parameters are now disposed of and there remains the question of parameter  $\alpha$ ,  $v^*$ , and the mean free volume  $v_f$ .

Unless the Cohen–Turnbull free volume theory is totally reformulated and its basic premises are abandoned, it is not possible to fix the parameter  $\alpha$  within the framework of their theory. Therefore it will be left as an adjustable parameter. Because it is about unity, we will find it reasonable to set it equal to unity if we are willing to accept slight numerical inaccuracy, or it may be simply absorbed into the minimum (or critical) free volume  $v^*$ . This will leave the minimum free volume  $v^*$  and the mean free volume per molecule to consider. It is relatively straightforward to make a physically sensible interpretation and estimate of the minimum free volume  $v^*$ —it may be taken as

the molecular volume that can be squeezed through the minimum size void created in the liquid to accomplish diffusion. This leaves  $v_f$  undetermined. In the original Cohen–Turnbull theory [4],  $v_f$  is expanded in a series of  $T$  with phenomenological parameters, and with a suitable expansion it was possible to show that the well-known Williams–Landel–Ferry (WLF) formula [15] could be recovered, which is known to fit experimental data on transport properties of glass-forming liquids to a useful extent. Nevertheless, such an expansion is not satisfactory nor is there a molecular theory basis in their treatment to do otherwise. We believe, however, that the Cohen–Turnbull free volume theory contains a more worthy aspect than the recovery of the WLF formula. The crux of the matter lies in what is meant by the mean free volume per molecule  $v_f$  from the standpoint of statistical mechanics. It seems to require a different approach.

### 12.1.2 Mean Free Volume

Mean free volume is a concept that is rather compelling from a physical standpoint but also has been rather elusive to catch in a definitive mathematical form for quantitative and sufficiently accurate calculation by statistical mechanics. The concept of free volume originates from the van der Waals equation of state. Science historians [16, 17] relate that the quantification of the concept<sup>1</sup> had troubled van der Waals throughout his life because he had not been satisfied with his definition. The other existing free volume theories quoted earlier are also hampered by the lack of sufficiently precise quantification of free volume.

The solution to this difficulty in quantifying mean free volume  $v_f$  is provided by the generic van der Waals equation of state introduced in Chap. 6. We have shown that the generic van der Waals equation of state—a canonical equation of state—makes it possible to identify most naturally the mean free volume with the form

$$v_f = v [1 - B(n, T) n], \quad (12.10)$$

where, for a potential that has repulsive and attractive branches and therefore has a zero at  $r = \sigma$ , the generic van der Waals parameter  $B(n, T)$  is given by

$$B(n, T) = \frac{(2\pi/3) \int_0^\sigma dr r^3 y(r) \frac{df(r)}{dr}}{1 + (2\pi/3)n \int_0^\sigma dr r^3 y(r) \frac{df(r)}{dr}}. \quad (12.11)$$

---

<sup>1</sup> According to Brush [18], Maxwell, who was the external examiner of the Ph.D dissertation of van der Waals, expressed his opinion that van der Waals' estimate of the excluded volume was inadequate. That prophecy of Maxwell turned out to be on the mark. The van der Waals parameters and, in particular, the excluded volume parameter  $b$  should not be independent of temperature and density, if the van der Waals equation of state is to account properly for the subcritical behavior of fluids.

In this expression  $y(r)$  is the cavity function. This is a statistical mechanical representation of mean excluded volume per molecule of the fluid. For a potential model in which the soft repulsive potential is replaced by a hard core of diameter  $\sigma$ , this formula becomes

$$B(n, T) = \frac{(2\pi/3) \sigma^3 y(\sigma)}{1 + (2\pi/3) \sigma^3 n y(\sigma)}. \quad (12.12)$$

If the generic van der Waals equation of state,

$$[p + A(n, T) n^2] [1 - B(n, T) n] = n k_B T, \quad (12.13)$$

where

$$A(n, T) = -\frac{2\pi}{3\beta} \int_{\sigma}^{\infty} dr r^3 y(r) \frac{df(r)}{dr}, \quad (12.14)$$

is employed, the mean free volume  $v_f$  may be alternatively written in the form

$$v_f = \frac{k_B T}{p + A(n, T) n^2}. \quad (12.15)$$

Compare this with the mean free volume in the van der Waals theory

$$v_f = \frac{k_B T}{p + an^2},$$

where  $a$  is the van der Waals parameter representative of the attractive force and a constant, as is  $b$ . Recall that  $a$  is the lowest order approximation of the zero density limit of  $A(n, T)$ : see (6.24) of Chap. 6. Before proceeding further, note that the choice of the position  $\sigma$  at which the virial integral is divided into the generic van der Waals parameters  $A$  and  $B$  is not unique. There is room for variation in this position. For example, it is possible to choose the minimum  $r_{\min}$  of the potential or a point between  $\sigma$  and  $r_{\min}$ . However,  $\sigma$  at which the potential energy  $\mathcal{V}(\sigma)$  is equal to zero seems to be unambiguous and physically clear-cut for the meaning of  $B(n, T)$ . Note that  $A(n, T)$  and  $B(n, T)$  are generally nonanalytic functions of  $n$  and  $T$ ; see Chap. 6.

### 12.1.3 Self-Diffusion Coefficient in the Modified Free Volume Theory

Now, using  $v_f$  identified as in (12.10) in the expression for the self-diffusion coefficient yields the formula

$$D = 1.019 \frac{3}{8n\sigma^2} \sqrt{\frac{k_B T}{\pi m}} \exp \left\{ -\frac{\alpha v_0}{v [1 - B(n, T) n]} \right\}, \quad (12.16)$$

where  $v^*$  has been identified with the molecular volume  $v_0 = \pi\sigma^3/6$ , that is,  $v^* = v_0$ . Because  $\alpha$  is usually rather close to unity, it is acceptable to

set  $\alpha = 1$  if we are willing to have a little reduced accuracy. We note that instead of the aforementioned identification of  $v^*$  with  $v_0$ , it is possible to take  $\alpha v^* = \pi\sigma^3/6$  with the value of  $\sigma$  suitably adjusted as the diameter of the minimum cavity allowing passage of a molecule. With the identifications of mean free volume  $v_f$  and  $\alpha v^*$  as indicated, the self-diffusion coefficient of the CT free volume theory is now free from unknown parameters. Then the formula for  $D$  thus obtained is completely free from adjustable parameters, and now we have a molecular theory of self-diffusion coefficients of simple fluids.

Alternatively,  $D$  may be expressed as

$$D = 1.019 \cdot \frac{3}{8n\sigma^2} \sqrt{\frac{k_B T}{\pi m}} \exp \left\{ -\frac{\alpha v_0 [p + A(n, T) n^2]}{k_B T} \right\}, \quad (12.17)$$

where the numerator in the exponent may be interpreted as the work  $W_c$  to create a cavity of size  $\alpha v_0$  against the effective pressure  $p_{\text{eff}} = p + A(n, T) n^2$ , so that diffusion is activated in the liquid:

$$W_c = \alpha v_0 [p + A(n, T) n^2] = \alpha v_0 p_{\text{eff}}. \quad (12.18)$$

In this interpretation, the self-diffusion coefficient so expressed

$$D = 1.019 \cdot \frac{3}{8n\sigma^2} \sqrt{\frac{k_B T}{\pi m}} \exp \left( -\frac{W_c}{k_B T} \right) \quad (12.19)$$

is formally in an Arrhenius form, but note that the activation energy  $W_c$  and the preexponential factor depend on temperature and density. Equation (12.16), (12.17), or (12.19) is a principal result of the modified free volume theory of self-diffusion in simple fluids. The accuracy of the theory may be somewhat improved if the hard sphere gas self-diffusion given in (12.9) is improved with a higher order Chapman–Enskog self-diffusion coefficient. However, it will be empirically verified that (12.16), (12.17), or (12.19) is generally sufficient for simple fluids in the liquid density regime.

Finally, note that because  $v_f \rightarrow \infty$  as the fluid density approaches the gas density, the self-diffusion coefficient formula (12.16) tends to the hard sphere gas formula:

$$\lim_{n \rightarrow 0} nD = 1.019 \cdot \frac{3}{8\sigma^2} \sqrt{\frac{k_B T}{\pi m}}. \quad (12.20)$$

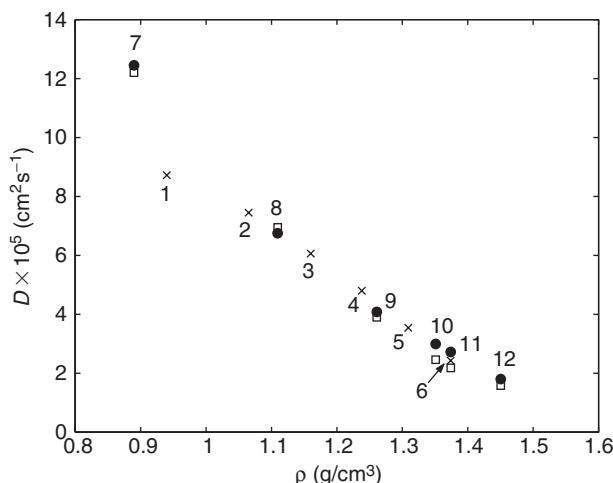
Therefore,  $D$  has an appropriate limiting form in the dilute gas regime of density.

## 12.2 Comparison with Experiments

The self-diffusion coefficient of the MFV theory, (12.16), has been tested against experimental data with the cavity function calculated either with the

Percus–Yevick (PY) integral equation [19] or by Monte Carlo (MC) simulations [1]. A comparison shows that once the parameter  $\alpha$  is chosen at a state, the self-diffusion coefficient formula predicts the density and temperature dependence of  $D$  correctly and, quite accurately, over the entire ranges of density and temperature within experimental error. At the initial stage in the development of the MFV theory a square-well model was used to calculate  $D$  by an MC simulation method. The temperature dependence of  $D$  for liquid argon along the liquid–vapor coexistence curve [20] was very good in comparison with experimental data reported by [21]. The same self-diffusion coefficient has been more extensively investigated for density and temperature dependence in [22] by using the Lennard-Jones potential model. The Lennard-Jones potential parameters for argon [23] were  $\epsilon/k_B = 120.0$  K and  $\sigma = 3.405$  Å. The critical parameters are reported [24] to be  $p_c = 4.863$  MPa,  $T_c = 150.68$  K, and  $\rho_c = 535.6$  kg m<sup>-3</sup>.

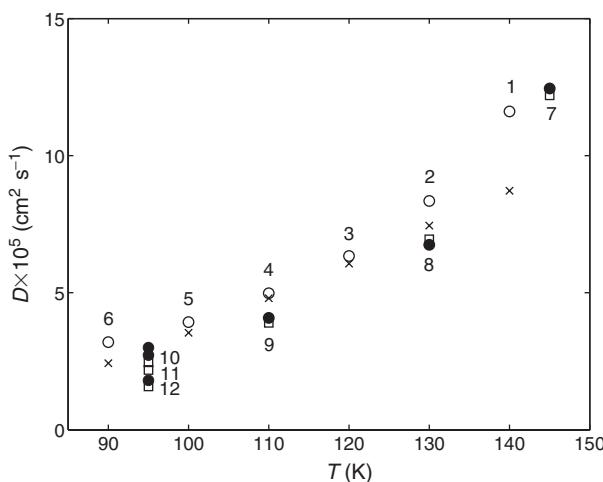
In Fig. 12.1, the density dependence of  $D$  is compared with the experimental data and molecular dynamics simulation results [25] at various temperatures. The *filled circles* (●) are the MFV theory, the *open circles* (□) are the molecular dynamics data, and the *crosses* (×) are experimental data by Naghizadeh and Rice [21]. The Arabic numerals indicate the absolute temperatures at which the self-diffusion coefficients are measured or computed: 1 = 140; 2 = 130; 3 = 120; 4 = 110; 5 = 100; 6 = 90; 7 = 145; 8 = 130; 9 = 110; 10 = 95; 11 = 95; and 12 = 95 K, respectively. For the calcula-



**Fig. 12.1.** Comparison of self-diffusion coefficient  $D$  at various temperatures as a function of density. The *filled circles* (●) are the MFV theory; the *open circles* (□) are the molecular dynamics data; and the *crosses* (×) are experimental data by Naghizadeh and Rice [21]. The meanings of the numerals are given in the text. [Reproduced with permission from R. Laghaei, A. Eskandari Nasrabad, and B. C. Eu, J. Phys. Chem. B **109**, 5873 (2005). Copyright 2005 American Chemical Society.]

tion of  $D$ , the minimum free volume activating diffusion was chosen such that  $\alpha v^* = 1.1v_c$  ( $v_c = \pi\sigma^3/6$ ). The comparison indicates that the MFV theory data with  $1.1v_c$  for  $\alpha v^*$  agree excellently with the molecular dynamics simulation results throughout the entire density range for which simulation and experimental data are available. Whereas the simulation data are in accord with the theory throughout the density range, there are considerable differences from experimental data at the low-density end. We may attribute the deviation to some experimental errors. It is not clear whether it is the theory or the experimental error is large at the high temperature end. On the basis of the comparison, the MFV theory formula for  $D$  in (12.16) is judged reliable and thus validated.

In Fig. 12.2, the temperature dependence of the self-diffusion coefficients of argon predicted by the MFV theory are compared with both experimental and simulation results. Each of the pairs 1–6 in the experimental ( $\times$ ) and theoretical ( $\circ$ ) data sets belongs to an isochore. Pairs of the *filled circle* ( $\bullet$ ) and *open square* ( $\square$ ) in pairs 7–12 belong to different isochores, which are also different from the former sets containing 1–6. The pair correlation functions used for  $D$  in this figure have also been obtained by the NVT MC simulation method described in [22]. The same value of  $\alpha v^*$ , as for it is Fig. 12.1, was chosen for this figure. The thermodynamic states of data points marked by

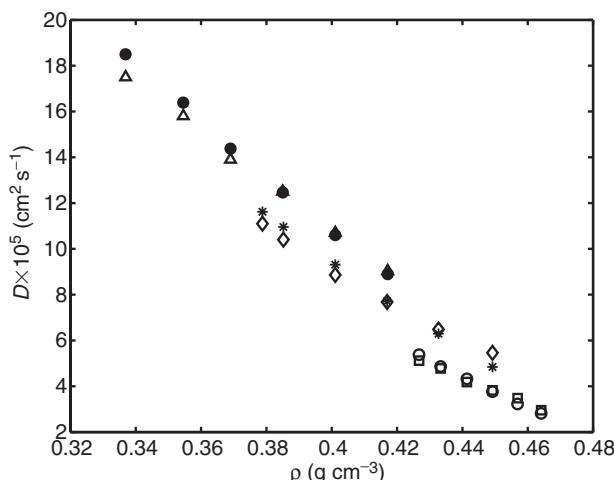


**Fig. 12.2.**  $D$  vs.  $T$  for argon. The *filled circles* ( $\bullet$ ) and the *open circles* ( $\circ$ ) are theoretical, the *open squares* ( $\square$ ) are the simulation data, and the *crosses* ( $\times$ ) are experimental data. The meanings of the numerals are the same as those for Fig. 12.1. The pairs 1–6 of experimental ( $\times$ ) and theoretical ( $\circ$ ) values belong to an isochore. The pairs 8–12 are simulation ( $\square$ ) and theoretical ( $\bullet$ ) values belonging to an isochore. [Reproduced with permission from R. Laghaei, A. Eskandari Nasrabad, and B. C. Eu, J. Phys. Chem. B **109**, 5873 (2005). Copyright 2005 The American Chemical Society.]

the numerals correspond to those in Fig. 12.1. The experimental data were obtained by Naghizadeh and Rice [21]. There is good agreement between the theory and simulation results, but the experimental data deviate from both simulation and theoretical results in the low and high temperature ends.

Liquid methane is not a simple liquid as are inert monatomic fluids, but it is known in the literature [26–32] that it behaves almost as if it is a simple liquid—a rigid spherical structureless molecule—when its thermodynamic properties are examined. Therefore, on the basis of such empirical evidence accumulated so far in the literature, Laghaei et al. [22] calculated the self-diffusion coefficient of liquid methane, treating it as if it were a simple liquid. The Lennard-Jones potential parameters for methane were taken from [33]:  $\epsilon/k_B = 147.9\text{ K}$  and  $\sigma = 3.7\text{ \AA}$ , and its critical parameters [34] are  $p_c = 4.599\text{ MPa}$ ,  $T_c = 190.56\text{ K}$ , and  $\rho_c = 162.66\text{ kg m}^{-3}$ .

In Fig. 12.3, the self-diffusion coefficients of methane computed by the MFV theory are compared with experimental data at various temperatures. The meanings of the symbols are as follows: • (theory),  $\triangle$  (experiment) at  $T = 160\text{ K}$ ; \* (theory),  $\diamond$  (experiment) at  $T = 140\text{ K}$ ;  $\circ$  (theory),  $\square$  (experiment) at  $T = 110\text{ K}$ . For methane, we have taken  $\alpha v^* = 1.13v_c$  for  $T = 110\text{ K}$ ,  $0.9v_c$  for  $T = 140\text{ K}$ , and  $0.8v_c$  for  $T = 160\text{ K}$ . For methane, it was found that the critical free volume giving rise to diffusion is slightly density dependent, probably because the critical free volume for diffusion is sensitive to the internal structure of the molecule. Because methane is not spherical

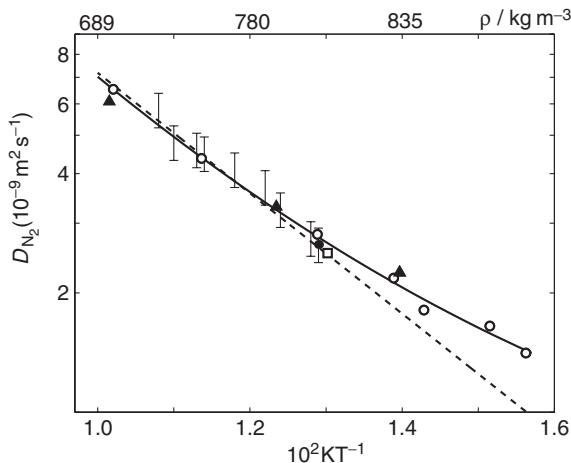


**Fig. 12.3.**  $D$  vs.  $\rho$  for methane at various temperatures. The meanings of the symbols are as follows: • (MFV theory),  $\triangle$  (experiment) at  $T = 160\text{ K}$ ; \* (theory),  $\diamond$  (experiment) at  $T = 140\text{ K}$ ; and  $\circ$  (theory),  $\square$  (experiment) at  $T = 110\text{ K}$ . [Reproduced with permission from R. Laghaei, A. Eskandari Nasrabad, and B. C. Eu, J. Phys. Chem. B **109**, 5873 (2005). Copyright 2005 The American Chemical Society.]

and has vertices, diffusion of the vertices should depend on the environment of the molecule and thus the density. For example, to achieve diffusion the molecule does not have to move into a void as a whole, but its vertices may sequentially move into voids. Therefore such a sequential movement should depend on the density of the medium. Here,  $v_c$  is the mean volume of the molecule, which was estimated on the basis of the literature value for the van der Waals radius by using the empirical rule suggested by Edward [35]. Agreement with experimental data for all three cases is quite satisfactory.

Judging on the basis of the self-diffusion coefficients presented for simple liquids in Figs. 12.1–12.3, there is little doubt that the MFV theory of diffusion yields self-diffusion coefficients for simple liquids, which are sufficiently reliable and accurate for other purposes, such as calculating transport coefficients examined in the density fluctuation theory. We will show in the following that it also gives equally accurate and robust self-diffusion coefficients for complex liquids, more specifically, rigid two-interaction site liquids.

The MFV theory of diffusion can be applied to diatomic or two-interaction site liquids such as nitrogen or carbon dioxide, which may be regarded as rigid rotors, provided that the site–site pair correlation functions are suitably calculated. By using a square-well model for the site–site interaction, the temperature dependence of  $D$  for nitrogen liquid [36] was computed from the MFV theory formula. The result is replotted and presented in Fig. 12.4. The potential parameters were as follows:  $\sigma = 0.3290 \text{ nm}$ ,  $\epsilon/k_B = 53.7 \text{ K}$ , and the well width was  $1.87\sigma$ . The value of  $\alpha$  was  $\alpha = 1.1$ . The symbols in Fig. 12.4 are as follows: The *open circles* ( $\circ$ ) are the theoretical predictions made with Monte Carlo simulations for the pair correlation functions and the

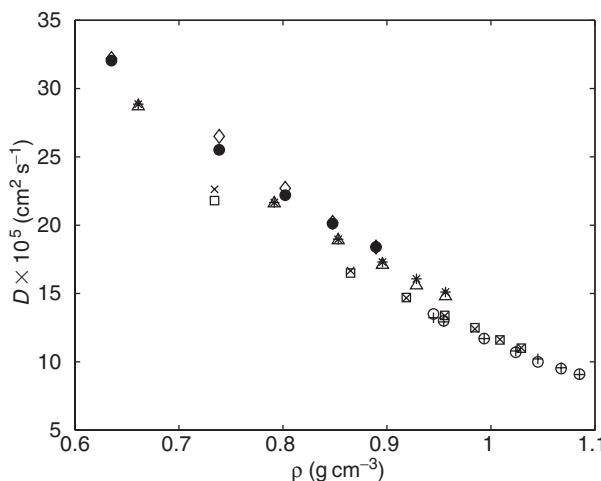


**Fig. 12.4.**  $D$  vs.  $T^{-1}$  ( $\rho$ ) for liquid nitrogen in the temperature range of 64 to 98 K and the density range of  $865$  to  $701 \text{ kg m}^{-3}$  along the liquid–vapor coexistence line.  $\alpha = 1.1$ . See [36].

*solid curve* is for guiding the eyes. The *filled circles* ( $\bullet$ ) are experimental data obtained by the NMR spin echo method by Krynicki et al. [37]. The vertical bars represent experimental errors. The *filled triangles* ( $\blacktriangle$ ) are the molecular dynamics simulation results by Cheung and Powles [38], and the *open squares* ( $\square$ ) are the computer simulation results by Barojas et al. [39]. The *broken line* is the Arrhenius activation energy representation of  $D$  used by Krynicki et al.:  $D = 238 \times 10^{-9} \exp(-350/T) \text{ m}^2 \text{ s}^{-1}$ . The temperature dependence predicted by the MFV theory of diffusion is deemed fairly good.

Recently, the MFV theory of diffusion has also been validated for carbon dioxide. The density dependence of  $D$  for carbon dioxide is shown in Fig. 12.5. In this figure, the symbols have the following meanings:  $\diamond$  (experiment),  $\bullet$  (theory) at  $T = 348.15 \text{ K}$ ;  $\triangle$  (experiment),  $*$  (theory) at  $T = 323.15 \text{ K}$ ;  $\square$  (experiment),  $\times$  (theory) at  $T = 298.15 \text{ K}$ ; and  $\circ$  (experiment),  $+$  (theory) at  $T = 273.15 \text{ K}$ . The critical parameters of carbon dioxide are  $p_c = 7.38 \text{ MPa}$ ,  $T_c = 304.2 \text{ K}$ , and  $\rho_c = 466 \text{ kg m}^{-3}$ . Therefore, the isotherms ( $\diamond, \bullet$ ) and ( $\triangle, *$ ) are supercritical, whereas the isotherms ( $\square, \times$ ) and ( $\circ, +$ ) are subcritical. The parameter  $\alpha$  was set at  $\alpha = 1$  for all temperatures, and then the critical free volume  $v_0$  was estimated with the diameter of the sphere given by

$$r_0 = \frac{2^{1/6}\sigma}{\left(1 + \sqrt{1 + \frac{3T^*}{2}}\right)^{1/6}},$$



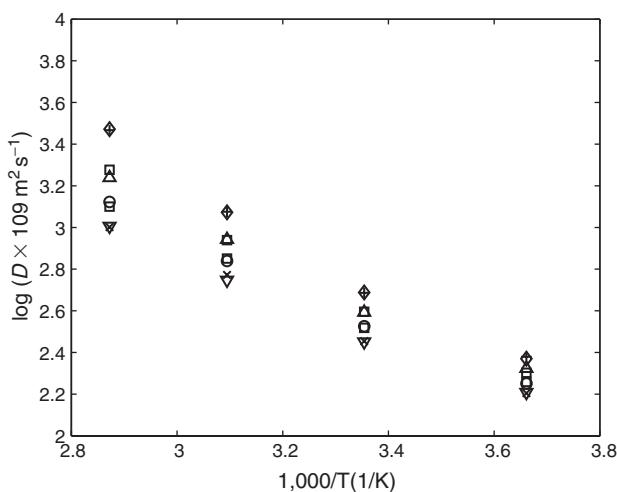
**Fig. 12.5.** Theoretical  $D$  vs.  $\rho$  for carbon dioxide at various temperatures. The meanings of the symbols are  $\diamond$  (experiment),  $\bullet$  (theory) at  $T = 348.15 \text{ K}$ ;  $\triangle$  (experiment),  $*$  (theory) at  $T = 323.15 \text{ K}$ ;  $\square$  (experiment),  $\times$  (theory) at  $T = 298.15 \text{ K}$ ; and  $\circ$  (experiment),  $+$  (theory) at  $T = 273.15 \text{ K}$ . [Reproduced with permission from A. Eskandari Nasrabad, R. Laghaei, and B. C. Eu, J. Phys. Chem. B **109**, 8171 (2005). Copyright 2005 American Chemical Society.]

where  $\sigma$  is the diameter of the van der Waals sphere estimated for carbon dioxide. The  $r_0$  is the value for the classical turning point of a head-on collision for the Lennard-Jones potential at temperature  $T$ , which arises under the assumption that  $\sigma$  of the van der Waals sphere is the Lennard-Jones potential size parameter for carbon dioxide at  $T = 0$ . With  $r_0$  thus estimated, we obtain  $v_0$  for carbon dioxide in the form,

$$v_0 = \frac{\sqrt{2}}{\left(1 + \sqrt{1 + \frac{3T^*}{2}}\right)^{1/2}} v_E,$$

where  $v_E = \pi\sigma^3/6$  is the van der Waals volume of carbon dioxide estimated according to the Edward rule [35]. The temperature dependence of  $D$  for carbon dioxide is shown in Fig. 12.6. The meanings of the symbols in Fig. 12.6 are  $\diamond$  (experiment),  $+$  (theory) at  $p = 20.89$  MPa;  $\square$  (experiment),  $\triangle$  (theory) at  $p = 27.03$  MPa;  $\circ$  (experiment),  $\times$  (theory) at  $p = 34.61$  MPa; and  $\nabla$  (experiment),  $+$  (theory) at  $p = 41.51$  MPa. It is again found that agreement with experiment is excellent for all isobars considered. The temperature dependence of  $D$  is not of the Arrhenius type because since  $\ln D$  vs.  $T^{-1}$  is not linear.

The assessment of the MFV theory formula for self-diffusion coefficients, which we have made for both simple and complex liquids in this section,



**Fig. 12.6.** Theoretical  $D$  vs.  $T$  for carbon dioxide compared with experimental data along various isobars. The meanings of the symbols are  $\diamond$  (experiment),  $+$  (theory) at  $p = 20.89$  MPa;  $\square$  (experiment),  $\triangle$  (theory) at  $p = 27.03$  MPa;  $\circ$  (experiment),  $\times$  (theory) at  $p = 34.61$  MPa; and  $\nabla$  (experiment),  $+$  (theory) at  $p = 41.51$  MPa. [Reproduced with permission from A. Eskandari Nasrabad, R. Laghaei, and B. C. Eu, J. Phys. Chem. B **109**, 8171 (2005). Copyright 2005 American Chemical Society.]

clearly indicates that it is sufficiently reliable in accuracy and behavior with regard to temperature and density. Therefore it is possible to apply it to study other transport coefficients such as viscosity and thermal conductivity.

### 12.3 Modified Free Volume Theory of Mixtures

The MFV theory of diffusion for pure simple fluids can be generalized [40, 41] to mixtures of simple fluids. Here, we consider a binary mixture of simple fluids of densities  $n_1$  and  $n_2$  contained in volume  $V$  at temperature  $T$  and pressure  $p$ . The distribution of constituents is assumed nonuniform in the  $z$  direction of a space-fixed Cartesian coordinate system. The  $z$  component of the mean (barycentric) velocity of the fluid will be denoted by  $u$ . Therefore the particles may be imagined moving in the coordinate frame at a uniform mean velocity  $u$ .

#### 12.3.1 Free Volume and Diffusion Fluxes

Given the flow configuration, it is necessary to count the number of molecules passing through a unit area per unit time to calculate diffusion fluxes of species. To achieve this aim we imagine a plane passing through the origin of the coordinate system perpendicularly to the  $z$ -axis and count the number of molecules crossing the plane at  $z = 0$  per unit area per unit time from the negative to the positive side. Let  $l_1$  denote the mean free path of molecules of species 1. This mean free path generally depends on voids around the particle of attention, which will be denoted by  $v$  for a molecule. Thus  $l_1 = l_1(v)$ .

Particles of mean (peculiar) velocity  $\bar{C}_1$  at positions in the interval  $-l_1 \leq z < 0$  will cross the plane toward the positive direction in unit time, whereas particles of mean (peculiar) velocity  $-\bar{C}_1$  at positions in the interval  $0 < z \leq l_1$  will cross the plane toward the negative direction in unit time. The nonequilibrium effects on the mean velocity of the particles are ignored. On applying the kinetic theory method, we find that the mean number of particles crossing the unit area of the plane at  $z = 0$  in the positive direction in unit time is

$$N_+ = \frac{1}{4} \bar{C}_1 n_1(-l_1),$$

where  $n_1(-l_1)$  is the density of Constituent 1 at position  $z = -l_1$ , whereas the mean number crossing the plane in the opposite direction in unit time is

$$N_- = \frac{1}{4} \bar{C}_1 n_1(l_1),$$

where  $n_1(l_1)$  is the density of Constituent 1 at position  $z = l_1$ . Therefore, the net mean number of particles crossing the plane per unit area per unit time is

$$\Delta N = \frac{1}{4} \bar{C}_1 \{ n_1 [-l_1(v)] - n_1 [l_1(v)] \}. \quad (12.21)$$

The size of a void is arbitrary and distributed within the fluid, and  $l_1$  depends on the size of the void in the fluid as noted earlier.

Let  $P(v)$  denote the distribution function of voids. Because there should be a minimum void  $v^c$  for a particle to move into as it is left by a particle that has just moved elsewhere, the quantity of interest must be expressed in terms of the mean value of the formula in (12.21) over the distribution of voids. The net flux  $J_1$  for Constituent 1 toward the positive direction in the coordinate system moving at  $u$  is therefore given by a weighted sum of the formula in (12.21) of the “particle flow” contribution,

$$J_1 = n_1 u + \int_{v^c}^{\infty} dv \frac{1}{4} \bar{C}_1 \{ n_1 [-l_1(v)] - n_1 [l_1(v)] \} P(v). \quad (12.22)$$

On expanding the densities and neglecting the density derivatives of orders higher than the first, the expression for  $J_1$  follows in the form

$$J_1 = n_1 u - \int_{v^c}^{\infty} dv \frac{1}{2} \bar{C}_1 l_1(v) P(v) \frac{\partial n_1}{\partial z}. \quad (12.23)$$

Henceforth the higher order density derivatives will be neglected so as to be consistent with this formula. A similar argument can be made for Constituent 2 to obtain the expression for the net flux  $J_2$  for Constituent 2:

$$J_2 = n_2 u - \int_{v^c}^{\infty} dv \frac{1}{2} \bar{C}_2 l_2(v) P(v) \frac{\partial n_2}{\partial z}, \quad (12.24)$$

where  $l_2(v)$  is the mean free path of Constituent 2, which also depends on voids, and  $\bar{C}_2$  is the mean peculiar velocity of Constituent 2. It is assumed that there is a common minimum void  $v^c$  for the two constituents of the fluid mixture.

Furthermore, because the pressure and temperature are kept constant in the system, it follows that under a steady-state condition

$$\frac{\partial n_1}{\partial z} + \frac{\partial n_2}{\partial z} = 0. \quad (12.25)$$

This condition implies that there is only one independent density gradient.

To make further progress from the expressions for diffusion fluxes  $J_1$  and  $J_2$  it is necessary to have an explicit form for the void distribution function  $P(v)$ . This distribution function can be obtained by following the free volume theory [4] of Cohen and Turnbull for self-diffusion in the same manner as for single-component fluids considered in the previous section. According to their theory  $P(v)$  is easily obtained by discretizing the voids into sizes  $v_i$ , counting the number of ways of distributing  $N$  particles into voids (cells) of different sizes ( $N_i$  is the number of particles occupying voids of size  $v_i$ )

$$W = \frac{N!}{\prod_i N_i!},$$

and extremizing  $W$  by the Lagrange method of undetermined multipliers subject to the fixed total free volume and the number of particles. It is given by the formula,

$$P(v) = \frac{\alpha}{v_f} \exp\left(-\alpha \frac{v}{v_f}\right), \quad (12.26)$$

with the same meanings for the parameters as before. This distribution function is normalized in the interval  $0 \leq v < \infty$ .

Because  $l_1(v)$  and  $l_2(v)$  should be functions of  $v$  varying slowly compared to  $P(v)$ , which varies rapidly with regard to  $v$ , the integrals in (12.23) and (12.24) can be calculated from the form

$$\int_{v^c}^{\infty} dv \frac{1}{2} \bar{C}_i l_i(v) P(v) \frac{\partial n_i}{\partial z} = \frac{1}{2} \bar{C}_i l_i(v^c) P_c(v^c) \frac{\partial n_i}{\partial z} \quad (i = 1, 2), \quad (12.27)$$

where

$$P_c(v^c) = \int_{v^c}^{\infty} dv \left( \frac{\alpha}{v_f} \right) \exp\left(-\alpha \frac{v}{v_f}\right) = \exp\left(-\alpha \frac{v^c}{v_f}\right). \quad (12.28)$$

Thus we obtain the diffusion fluxes in the form

$$J_i = n_i u - \frac{1}{2} \bar{C}_i l_i(v^c) \exp\left(-\alpha \frac{v^c}{v_f}\right) \frac{\partial n_i}{\partial z} \quad (i = 1, 2). \quad (12.29)$$

These diffusion fluxes can be used to identify the diffusion coefficients.

### 12.3.2 Diffusion Coefficient of a Mixture

Eliminating the first term on the right-hand side in the expressions for  $J_1$  and  $J_2$  yields the equation,

$$n_2 J_1 - n_1 J_2 = -\frac{1}{2} (n_2 \bar{C}_1 l_1 + n_1 \bar{C}_2 l_2) \exp\left(-\alpha \frac{v^c}{v_f}\right) \frac{\partial n_1}{\partial z}. \quad (12.30)$$

Because the fluxes are steady, it follows that

$$J_1 + J_2 = 0 \quad (12.31)$$

and thus from (12.30) and (12.31) follows the expression for diffusion flux

$$J_1 = -J_2 = - \left[ \frac{n_2 \bar{C}_1 l_1(v^c)}{2(n_1 + n_2)} + \frac{n_1 \bar{C}_2 l_2(v^c)}{2(n_1 + n_2)} \right] \exp\left(-\alpha \frac{v^c}{v_f}\right) \frac{\partial n_1}{\partial z}. \quad (12.32)$$

Because the pressure and temperature are uniform in space and external forces are absent, the diffusion coefficient of the binary mixture is phenomenologically defined by the linear force-flux relation (i.e., Fick's law of diffusion),

$$J_1 = -D_{12} \frac{\partial n_1}{\partial z} \quad (12.33)$$

with the symmetry  $D_{12} = D_{21}$  in accordance with Onsager reciprocal relations [42]. Thus the diffusion coefficient is given by the formula,

$$D_{12} = \left[ \frac{n_2 \bar{C}_1 l_1 (v^c)}{2(n_1 + n_2)} + \frac{n_1 \bar{C}_2 l_2 (v^c)}{2(n_1 + n_2)} \right] \exp \left( -\alpha \frac{v^c}{v_f} \right) \quad (12.34)$$

for binary liquid mixtures.

At this point, we assume that for binary mixtures the common characteristic volume  $v^c$  for the two species of the mixture is given by a mean value of molecular volumes as follows:

$$\alpha v^c \equiv v_{12}^c = \alpha_1 v_1^0 X_1 + \alpha_2 v_2^0 X_2, \quad (12.35)$$

where  $v_i^0 = \pi \sigma_i^3 / 6$  ( $i = 1, 2$ ) with  $\sigma_i$  denoting the diameter of molecule  $i$  is the molecular volume of species  $i$  in its pure liquid state;  $\alpha_i$  is the parameter corresponding to  $\alpha$  when the free volume theory is developed for a pure liquid component  $i$  and thus accounts for the deviation of  $v_i^0$  from the characteristic free volume of the pure liquid  $i$ ; and  $X_i$  is the mole fraction of species  $i$  defined by

$$X_i = \frac{n_i}{n_1 + n_2}.$$

If there is a significant disparity in the sizes of the constituent molecules, it is advisable to take volume fractions for  $X_i$  instead of mole fractions

$$X_i^{(v)} = \frac{n_i v_i^0}{n_1 v_1^0 + n_2 v_2^0} \quad (i = 1, 2). \quad (12.36)$$

The expression for  $\alpha v^c \equiv v_{12}^c$  in (12.35) is a proposition for the characteristic free volume for a mixture of molecules of comparable sizes. It is quite reasonable physically because  $\alpha v^c$  is the mean molar characteristic free volume weighted by  $\alpha$ . The test of the resulting theory, which will be carried out later, in a way validates this proposition for the characteristic free volume  $v^c$ . Under this assumption, the expression for  $D_{12}$  in (12.34) is written in the form

$$D_{12} = \left[ \frac{n_2 \bar{C}_1 l_1 (v^c)}{2(n_1 + n_2)} + \frac{n_1 \bar{C}_2 l_2 (v^c)}{2(n_1 + n_2)} \right] \exp \left( -\frac{v_{12}^c}{v_f} \right). \quad (12.37)$$

The preexponential factor in the square brackets in (12.37) is the mean free path expression for the diffusion coefficient of a binary mixture of fluids, which is modulated by the exponential factor describing the probability of finding a critical void of size  $v_{12}^c$  in the binary liquid.

This preexponential factor is in exactly the same form as the mean free path formula for the diffusion coefficient of a binary gaseous mixture. Because

the mean free path formula for a gas mixture well approximates the corresponding Chapman–Enskog formula for the diffusion coefficient [14] if the mean free path is suitably estimated, as has been done for single-component fluids in Sect. 12.1, we propose to replace it with the Chapman–Enskog expression for the diffusion coefficient, denoted by  $D_{12}^0$ , which can be calculated in a well-defined manner once the interaction potential is specified. We will find it sufficient to employ  $D_{12}^0$  for hard spheres, especially, in a high density regime where hard cores of the molecules play a dominant role in determining the transport properties of liquids. Thus we finally obtain the diffusion coefficient  $D_{12}$  for a binary liquid mixture in the form [40, 41],

$$D_{12} = D_{12}^0 \exp\left(-\frac{v_{12}^c}{v_f}\right). \quad (12.38)$$

This is the diffusion coefficient for a binary liquid mixture in the MFV theory of diffusion [40, 41].

In summary, this formula for the diffusion coefficient is derived in the spirit of the mean free path method combined with the Cohen–Turnbull free volume approach, in which molecules are imagined to diffuse through space by continuous jigglings of molecules into voids (free volumes) left by neighboring molecules that have moved into other positions under density fluctuations. If the density and temperature dependence are known for  $v_f$ , then the density and temperature dependence of  $D_{12}$  can be calculated.

Note that the preexponential factor in (12.37) is the binary mixture theory counterpart of the factor  $g_{CT} \equiv g_{ua}(v)$  in the Cohen–Turnbull free volume theory of self-diffusion in a single-component liquid. This factor  $g_{CT}$  is equivalent to the mean free path expression for the self-diffusion coefficient of the gas; see (12.9). Because the quantity in the square brackets in (12.37) clearly is in the same form as the mean free path formula for the diffusion coefficient of the gas mixture, we have replaced it with the kinetic theory expression—the Chapman–Enskog theory formula—for the diffusion coefficient, which does not involve an elusive quantity such as mean free path—a nice concept physically but a quantity not easy to compute with sufficient generality and accuracy, especially, in the liquid density regime.

Because the exponent in the exponential factor in (12.38) vanishes as  $n$  vanishes, the formula obtained for  $D_{12}$  clearly tends to the Chapman–Enskog formula for the diffusion coefficient  $D_{12}^0$  of a dilute gas mixture.  $D_{12}^0$  can be calculated in terms of the intermolecular potential energy in a well-defined manner by following the result of the kinetic theory of gases [14] and the free volume or the equation of state can be also calculated, as will be shown in the following, in terms of intermolecular potential as accurately as desired. Therefore we now have a well-defined molecular theory expression for the diffusion coefficients of simple liquid mixtures, which have been defying a well-defined practical theoretical formula.

For the sake of simplicity of the formula we will assume that  $D_{12}^0$  is the Chapman–Enskog diffusion coefficient [14] for a binary mixture of hard spheres, which is given by the formula

$$D_{12}^0 = \frac{3}{8\rho\sigma_{12}^2(1-\Delta_d)} \left( \frac{k_B T}{2m} \right)^{1/2}, \quad (12.39)$$

where  $k_B$  is the Boltzmann constant,  $m = m_1 m_2 / (m_1 + m_2)$  is the reduced mass with  $m_i$  denoting the molecular mass for component  $i$ , and  $\Delta_d$  stands for the correction arising from a higher order Sonine polynomial expansion. The correction  $\Delta_d$  generally depends on the composition and mass ratio; details for  $\Delta_d$ , are referred to [14]. In the single-component limit, where molecular parameters such as the size and mass of two species are set equal, the expression (12.38) properly reduces, as it should, to the self-diffusion coefficient [40] of constituent 1, say,

$$D_1 = \frac{3}{8\rho\sigma_1^2} \left( \frac{k_B T}{m_1} \right)^{1/2} \exp \left[ -\alpha_1 v_1^0 / v_f \right], \quad (12.40)$$

where  $v_f$  is the mean free volume per molecule of pure liquid 1, namely, at  $X_1 = 1$ ; see the discussion on the generic van der Waals equation of state for the details of  $v_f$  in the subsequent subsection. It was found in previous study of self-diffusion coefficients in [41] that  $\alpha_1$  is of the order of unity and weakly depends only on temperature. Therefore it may be set equal to unity in this work, unless stated otherwise, when theoretical results are compared with experiment.

As  $X_2 \rightarrow 0$ , we obtain from (12.35) and (12.38) the expression for the tracer diffusion coefficient  $D_t$  as follows:

$$D_t = D_{12}^0 \exp \left( \frac{-\alpha_1 v_1^0}{v_f} \right). \quad (12.41)$$

This formula suggests that the cross effect between solute and solvent molecules plays its role only through  $D_{12}^0$  given in (12.39) and the free volume effect is determined solely by the properties of solvent molecules. It also implies that the tracer diffusion coefficient is generally different from the self-diffusion coefficient of the solvent. The former is a joint property of the tracer and the solvent molecules through which the tracers are diffusing, whereas the latter is determined by the properties of the pure species. The formula in (12.41) is tested later in this chapter by calculating  $D_t$  therewith and comparing the result with the experiment reported in the literature.

### 12.3.3 Mean Free Volume for Binary Mixtures

Now it will be shown how the free volume required for  $D_{12}$  can be calculated in terms of the equilibrium pair correlation function of a liquid, which contains information on the liquid structure and its relation to the generic van der Waals equation of state [43]. To this end, we use the results obtained in Chap. 6, which are reproduced to making reading about the theory easy.

If the potential energy of a  $c$ -component mixture of simple liquids at temperature  $T$  and density  $n$  is pairwise additive, the generic van der Waals equation of state—the canonical equation of state

$$(p + An^2)(1 - Bn) = nk_B T, \quad (12.42)$$

has generic van der Waals parameters in the forms

$$A = \sum_{i,j=1}^c A_{ij}(n, T) X_i X_j, \quad (12.43)$$

$$B = \sum_{i,j=1}^c B_{ij}(n, T) X_i X_j \left[ 1 + n \sum_{i,j=1}^c B_{ij}(n, T) X_i X_j \right]^{-1}, \quad (12.44)$$

where

$$A_{ij} = -\frac{2\pi}{3\beta} \int_{\sigma_{ij}}^{\infty} dr r^3 y_{ij}(r) \frac{d}{dr} f_{ij}(r), \quad (12.45)$$

$$B_{ij} = \frac{2\pi}{3} \int_0^{\sigma_{ij}} dr r^3 y_{ij}(r) \frac{d}{dr} f_{ij}(r). \quad (12.46)$$

The symbols in the expressions are as follows:  $\beta = 1/k_B T$ ,  $n_i$  is the number density of constituent  $i$ , and  $\{n_k\}$  denotes the set of  $n_k$  ( $k = 1, \dots, c$ ). Here,  $f_{ij}$  is the Mayer function of pair potential  $u_{ij}(r)$ , and  $y_{ij}(r)$  is the cavity function of the pair  $ij$  defined as usual by the relation

$$y_{ij}(r; \{n_k\}, T) = \exp[\beta u_{ij}(r)] g_{ij}(r; \{n_k\}, T), \quad (12.47)$$

where  $g_{ij}(r)$  is the equilibrium pair correlation function of pair  $(ij)$ . The total number density  $n$  is given by

$$n = \sum_{k=1}^c n_k, \quad (12.48)$$

and the mole fraction is defined by  $X_i = n_i/n$ .

The expressions in (12.45) and (12.46), together with (12.43) and (12.44), give rigorous statistical mechanical representations of the generic van der Waals parameters  $A$  and  $B$ . Because  $B$  is closely related to the repulsive parts of the intermolecular potential energies and thus  $Bn$  is a measure of the excluded volume in the mixture, as it is for single-component fluids, it is natural to define the mean free volume per molecule  $v_f$  by the formula

$$v_f = v(1 - Bn), \quad (12.49)$$

where  $v = 1/n$  is the specific volume. With the free volume identified with  $v_f$  for the mixture as in this formula and with the help of the generic van

der Waals equation of state, the diffusion coefficient (12.38) now becomes computable by statistical mechanics alone, apart from the parameter  $\alpha$ . The parameters  $\alpha_i$  also turn out to be approximately equal to unity. Therefore, if they are set equal to unity then there are no parameters other than the potential parameters in the theory.

If a square-well (SW) potential with  $\varepsilon_{ij}$  and  $\lambda_{ij}$  for the potential well depth and the range of the well, respectively, is taken as a model to represent the intermolecular interactions

$$u_{ij}(r) = \begin{cases} \infty & \text{for } r < \sigma_{ij}, \\ -\varepsilon_{ij} & \text{for } \sigma_{ij} < r < \lambda_{ij}, \\ 0 & \text{for } r > \lambda_{ij}, \end{cases} \quad (12.50)$$

there then follows from (12.44), (12.46), and (12.49) the statistical mechanical representation of mean free volume for the mixture in the form,

$$v_f = v \left[ 1 + \frac{2\pi}{3} n \sum_{i=1}^c \sum_{j=1}^c \sigma_{ij}^3 y_{ij}(\sigma_{ij}) X_i X_j \right]. \quad (12.51)$$

Therefore, the mean free volume so defined can be evaluated exactly, provided that  $y_{ij}(\sigma_{ij})$  are obtained, for example, from Monte Carlo (MC) or molecular dynamics (MD) simulations.

The diffusion coefficient derived can also be related to that of the Arrhenius activation theory of diffusion, if the generic van der Waals equation of state is used. Because, as shown earlier, the virial equation of state can be transformed into a form analogous to the van der Waals equation of state given in (12.42), the exponent  $v_{12}^c/v_f$  in  $P_c$  may be written as

$$\frac{v_{12}^c}{v_f} = \frac{p_{\text{eff}} v_{12}^c}{k_B T}, \quad (12.52)$$

where the effective pressure  $p_{\text{eff}}$  is given by the formula

$$p_{\text{eff}} = p + An^2. \quad (12.53)$$

Therefore, the numerator in (12.52) is the work to create a void of size  $v_{12}^c$  against the effective pressure  $p_{\text{eff}}$  in the liquid mixture

$$W_c = v_{12}^c (p + An^2). \quad (12.54)$$

Thus we find that  $P_c(v_{12}^c)$  is expressible in the form

$$P_c(v_{12}^c) = \exp \left[ -\frac{W_c(n, T)}{k_B T} \right]. \quad (12.55)$$

Therefore the work may be interpreted as the Arrhenius activation energy  $E_a$  of diffusion, which, however, is not a constant but depends on temperature and

density. In this interpretation of the exponent of  $P_c(v_{12}^c)$  the present theory of diffusion appears as in the Arrhenius activation theory:

$$D_{12} = D_{12}^0(T, n) \exp \left[ -\frac{W_c(n, T)}{k_B T} \right], \quad (12.56)$$

which is quite similar in form to the simple fluid result.

This formula also suggests that diffusion coefficients can be computed with empirical data on the equation of state of liquids. This aspect is extremely interesting from the practical viewpoint, because to compute diffusion coefficients all we need for the transport coefficients is the equilibrium thermodynamic data, provided we use the Chapman–Enskog theory formula for  $D_{12}^0$ . Once the diffusion coefficients have been computed, other transport coefficients such as viscosity, bulk viscosity, and thermal conductivity can also be computed with the help of some equilibrium thermophysical data according to the theories discussed in Chaps. 10 and 11 on density fluctuation. In this manner, the density fluctuation theory fully achieves the status of a molecular theory of transport processes in liquids, as will be shown later.

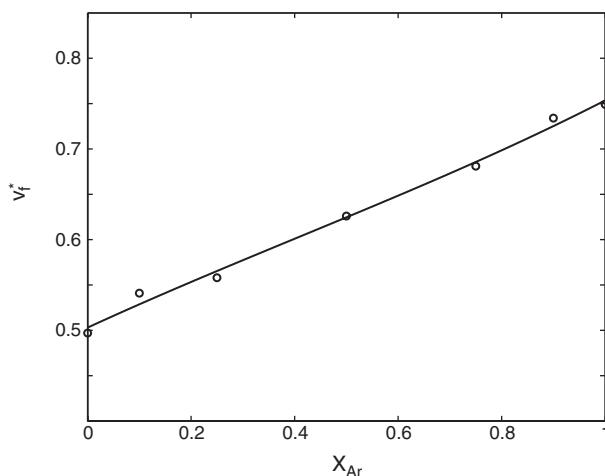
## 12.4 Validation of the Mixture Theory

### 12.4.1 Simple Liquid Mixtures

Having given the statistical mechanical representation of free volume in a mixture, we now discuss validation of the diffusion coefficient of a binary mixture for its accuracy in comparison with experiment or computer simulation data. The validation has been made with a square-well potential model for its simplicity. The cross potential parameters are prescribed by the combining rules  $\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)$ ,  $\varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2}$ , and  $\lambda_{12} = \frac{1}{2}(\lambda_1 + \lambda_2)$ , where  $\sigma_i$  ( $i = 1, 2$ ),  $\varepsilon_i$ , and  $\lambda_i$  are for component  $i$ , respectively. However, the combining rules are not mandatory, although expedient.

Because it is helpful for insight to learn about the composition dependence of free volume, the free volume is plotted against the composition variable in Fig. 12.7. In the figure, the free volume reduced by the mean molecular volume of the mixture,  $v_f^* \equiv v_f / (\pi \sigma_{12}^3 / 6)$ , is calculated from the formula (12.51) for liquid Ar–Kr mixtures at  $T = 121$  K and a fixed number density of  $n^*$  ( $\equiv n \sigma_{12}^3$ ) = 0.62 and is plotted against the mole fraction for the argon–krypton mixture. The *open circles* indicate the theoretical values computed with formula (12.51) for which the cavity functions  $y_{ij}(\sigma_{ij})$  are computed by the MC simulations with the potential parameters [44] listed in Table 12.1. The *solid curve* guides the eyes. The free volume increases as the mole fraction of the smaller (argon) molecules gets larger, and this is as expected intuitively.

By using (12.35), (12.38), (12.39), (12.44), and (12.51), Rah and Eu calculated the diffusion coefficient of binary mixtures. In Fig. 12.8, the composition dependence of  $D_{12}$  is shown for liquid Ar–Kr mixtures at  $T = 121$  K and

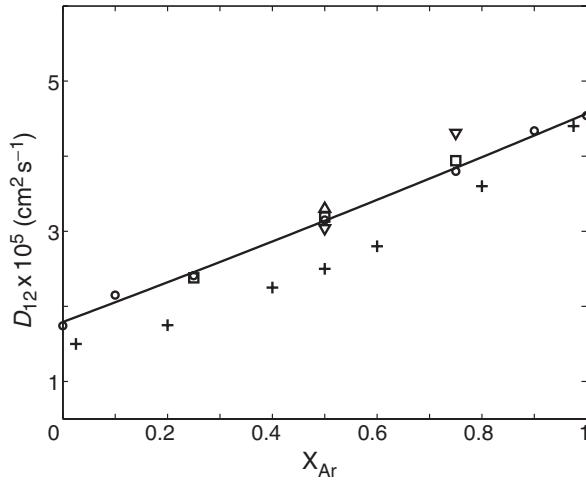


**Fig. 12.7.** The composition dependence of free volume. The *open circles* indicate the free volume values computed with the cavity function  $y_{ij}(\sigma_{ij})$  obtained by MC simulations, and the *solid curve* is drawn to guide the eyes. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **116**, 7967 (2002). Copyright 2002 American Institute of Physics.]

**Table 12.1.** Square-well potential parameters

molecule	$\sigma$ (nm)	well width/ $\sigma$	$\epsilon/k_B$ (K)
argon	0.3162	1.85	69.4
krypton	0.336	1.85	98.3
nitrogen	0.3290	1.87	53.7
methane	0.3400	1.85	88.8

at a fixed number density of  $n^* = 0.62$ . The *open circles* are the theoretical values evaluated with the formula for  $D_{12}$ , for which the cavity functions  $y_{ij}(\sigma_{ij})$  were computed by MC simulations. The *solid curve* is a least-squares fit to the theoretical values, drawn to guide the eyes. Because no experimental data were available in the literature for comparison, the theoretical predictions were compared only with some computer simulation results [45, 46]. The crosses (+) are the MD simulation results by Hayes [45] for which the simulation time limit  $t_{\max}$  is  $\sim 2.5$  ps, whereas the other symbols are for simulation results by Zhou and Miller [46], who obtained the diffusion coefficients from the mean-square displacements ( $\triangle, \square, \nabla$ ) and the velocity correlation functions ( $*, \bullet, \blacksquare$ ) with  $t_{\max} = 20$  ps (for  $\triangle, \square, \bullet, \blacksquare$ ) or 80 ps (for  $\nabla, *$ ) and the number of particles  $N = 512$  (for  $\square, \nabla, *, \bullet, \blacksquare$ ) or  $N = 1728$  (for  $\triangle, \blacksquare$ ) for the simulations. The modified free volume theory yields diffusion coefficients in good agreement with the simulation results of Zhou and Miller and, at least qualitatively, with those of Heyes. These results suggest that the more abundant, the smaller and lighter molecules (argon) at a fixed number density,

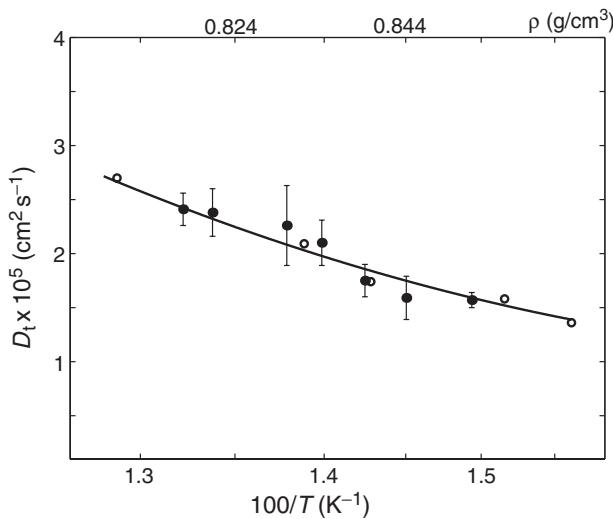


**Fig. 12.8.** The composition dependence of  $D_{\text{Ar-Kr}}$  of liquid Ar–Kr mixtures at  $T = 121\text{ K}$  and  $\rho^* = 0.62$ . The open circles indicate the theoretical values, and the solid curve is drawn to guide the eyes. Various symbols (+,  $\triangle$ ,  $\square$ ,  $\nabla$ , \*,  $\bullet$ , ■) are the MD simulation results from [45] and [46]. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, Phys. Rev. Lett. **88**, 065901 (2002). Copyright 2002 American Physical Society.]

the faster the mutual diffusion. This is intuitively comprehensible because the mutual diffusion is more of an outcome of diffusion accomplished by smaller molecules diffusing through interstitial space formed by larger molecules that move around more sluggishly than smaller molecules.

Note that the diffusion coefficients at  $X_i \rightarrow 0$  and 1, respectively, are for trace limits, not self-diffusion coefficients. The former estimated from (12.41) are  $D_t(\text{Kr}) = 4.49 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , as  $X_{\text{Kr}} \rightarrow 0$  and  $D_t(\text{Ar}) = 1.67 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  as  $X_{\text{Kr}} \rightarrow 1$ , respectively. The latter evaluated from (12.40) are  $D_{\text{Ar}} = 5.56 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  and  $D_{\text{Kr}} = 1.27 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ , respectively. Experimental studies on this aspect in the future should be useful for more definite comparisons with the theory.

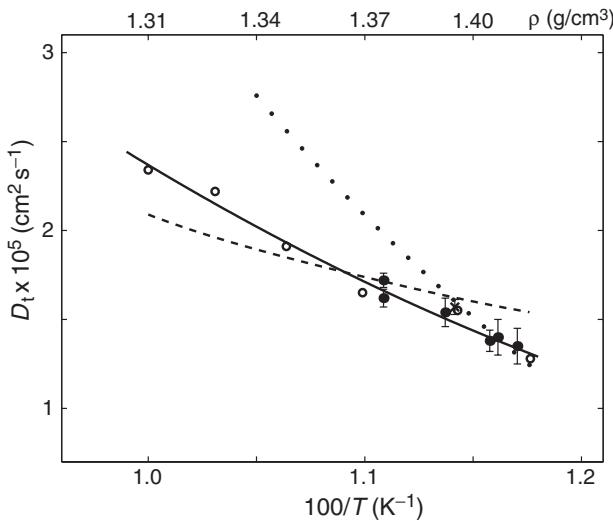
In Fig. 12.9, the temperature (density) dependence of the tracer diffusion coefficient of argon in liquid nitrogen is presented in the temperature (density) range  $64\text{ K} \leq T \leq 78\text{ K}$  ( $865 \text{ kg m}^{-3} \geq n_{\text{N}_2} \geq 806 \text{ kg m}^{-3}$ ) at about 0.92 atm pressure where the actual experiments [47] were carried out by using a capillary cell technique. The density value, for instance,  $857 \text{ kg/m}^3$ , corresponds to the state of  $T = 66\text{ K}$  and  $p = 0.92$  atm. The open circles indicate the theoretical predictions computed with  $y_{ij}(\sigma_{ij})$  obtained from MC simulations, and the solid curve is just their least-squares fit drawn to guide the eyes. The vertical bar on the experimental data points ( $\bullet$ ) represents the uncertainty of the experimental value. Within the experimental error ranges, there appears to be excellent agreement between the MFV theory and the experimental



**Fig. 12.9.**  $D_t$  vs.  $T(\rho)$  for Ar in liquid N<sub>2</sub> in the temperature (density) range of  $64 \text{ K} \leq T \leq 78 \text{ K}$  ( $865 \text{ kg m}^{-3} \geq \rho_{\text{N}_2} \geq 806 \text{ kg m}^{-3}$ ) and  $p = 0.9 \text{ atm}$ . The open circles ( $\circ$ ) are theoretical values and the solid curve is drawn to guide the eyes. The filled circles ( $\bullet$ ) are the experimental data [47]. The density dependence is indicated in the upper scale of the figure. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **116**, 7967 (2002). Copyright 2002 American Institute of Physics.]

data, quantitatively as well as qualitatively. Note that the parameter value  $\alpha_{\text{N}_2} = 1.1$  was determined from the experimental [37] self-diffusion coefficient data  $D_{\text{N}_2}$  and thus was used for the calculations to maintain consistency.

In Fig. 12.10, theoretical predictions are compared with experimental data [48,49] for the tracer diffusion of Kr in liquid Ar in the temperature (density) range  $84 \text{ K} \leq T \leq 100 \text{ K}$  ( $1131 \text{ kg m}^{-3} \geq \rho_{\text{Ar}} \geq 1141 \text{ kg m}^{-3}$ ) along the co-existing line of liquid argon. The open circles are the results by the MFV theory and the solid curve is drawn through the open circles to guide the eyes. The filled circles ( $\bullet$ ) are for the experimental data by Cini-Castagnoli and Ricci [48] at 2 atm pressure, whereas the cross ( $\times$ ) is by Dunlop and Bignell [49] at 1.2 atm pressure. The pressure difference between the two experiments appears to have little effect on the density value of liquid argon [50] employed for the calculations, at least, in the temperature range considered. Agreement is good between the theory and experiment. Because the Enskog theory [51] and the modified Enskog theory [52] also provide diffusion coefficients in forms comparable in simplicity to the MFV theory formula, the predictions of the diffusion coefficient by them are also made in Fig. 12.10. The dotted curve is by the modified Enskog theory and the broken curve is by the Enskog theory. Both of them compare poorly with experiment.



**Fig. 12.10.**  $D_t$  of Kr in liquid Ar in the temperature (density) range  $84\text{ K} \leq T \leq 100\text{ K}$  ( $1.131\text{ kg m}^{-3} \geq \rho_{\text{Ar}} \geq 1.141\text{ kg m}^{-3}$ ) along the coexisting line of liquid Ar. The *open circles* ( $\circ$ ) are theoretical and the *solid line* is their least-squares fit. The *filled circles* ( $\bullet$ ) and the *crosses* ( $\times$ ) are experimental. The *dotted curve* is the prediction by the modified Enskog theory and the *broken curve* by the Enskog theory. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **116**, 7967 (2002). Copyright 2002 American Institute of Physics.]

The Enskog theory for a binary diffusion coefficient may be expressed by

$$D_{12} = \chi D_{12}^0, \quad (12.57)$$

where  $D_{12}^0$  is the Chapman–Enskog diffusion coefficient for a binary hard sphere mixture of gases and  $\chi$  is the correction factor, especially, for the density dependence. The *dashed curve* in Fig. 12.10 was calculated with  $\chi = 1/g_{12}(\sigma_{12})$ , where  $g_{12}(\sigma_{12})$  was computed by using the formula from [53] with the hard sphere diameter values,  $\sigma_{\text{Ar}} = 0.347\text{ nm}$  and  $\sigma_{\text{Kr}} = 0.401\text{ nm}$ , respectively. They were calculated [54] such that they give self-diffusion coefficients of the gases computed therewith in agreement with experimental values. The *dotted curve* is calculated by the modified Enskog theory, in which  $\chi$  is expressed in the form [44]

$$\chi = \frac{n (B_2 + T \frac{dB_2}{dT})}{\left[ \frac{1}{nk_B} \left( \frac{\partial p}{\partial T} \right)_\rho - 1 \right]}.$$

Here,  $B_2(T)$  is the second virial coefficient, which is numerically estimated by using the Lennard-Jones (LJ) potential model with parameters [44],  $\sigma_{\text{Ar}} = 0.3405\text{ nm}$  and  $\varepsilon_{\text{Ar}}/k_B = 119.8$  for argon and  $\sigma_{\text{Kr}} = 0.360\text{ nm}$  and  $\varepsilon_{\text{Kr}}/k_B =$

171.0 for krypton, respectively. The LJ potential parameters were determined from the experimental  $B_2$  data for each of the corresponding gases. As to the estimation of  $(\partial p/\partial T)_\rho$ , an empirical formula [55] of the equation of state for argon was used and the pressure contribution of the tracer (krypton) molecules was neglected.

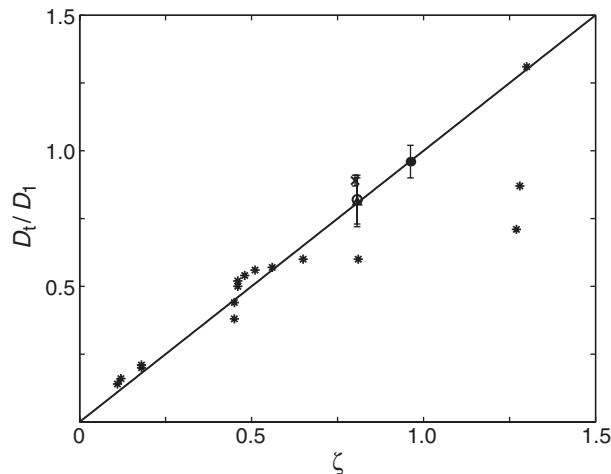
The ratio of  $D_{t2}$  to  $D_1$  can be easily calculated from (12.40) and (12.41):

$$\frac{D_t}{D_1} = \sqrt{\frac{m_1}{2\mu}} \left( \frac{\sigma_1}{\sigma_{12}} \right)^2 = \sqrt{\frac{1+m_1/m_2}{2}} \left( \frac{2}{1+\sigma_2/\sigma_1} \right)^2, \quad (12.58)$$

where the contribution from  $\Delta_d$  has been neglected for simplicity. The ratio  $D_t/D_1$  is independent of temperature and density. This is another relation between transport coefficients, many of which we have seen in Chaps. 10 and 11. This particular relation implies that given the information about  $\sigma_2/\sigma_1$  and  $m_2/m_1$ , the self-diffusion coefficient of solvent  $D_1$  can be readily calculated if  $D_t$  is known or measured, and vice versa. A numerical correction, if necessary [56], may be made for  $D_t/D_1$  by using the value for  $\Delta_d$  in (12.39), particularly when  $m_1/m_2 < 1$ .

In Fig. 12.11, the relation (12.58) is tested for the dependence of  $D_t/D_1$  on the size and mass ratios of the tracer for the solvent molecule

$$\zeta = 2^{3/2} (1 + \sigma_2/\sigma_1)^{-2} \sqrt{1 + m_1/m_2}.$$



**Fig. 12.11.**  $D_t/D_1$  vs.  $\zeta$  (size ratio). The solid line is predicted from formula (12.58), and the symbols with error bars are experimental data: ● from [47] for Ar in liquid N<sub>2</sub>, △ from [48] and ○ from [49] for Kr in liquid Ar, and × from [49] for Kr in liquid N<sub>2</sub>, respectively. The asterisks (\*) are the results of computer simulation [58] for a modified Lennard-Jones potential model. [Reproduced with permission from Kyunil Rah and Byung Chan Eu, J. Chem. Phys. **116**, 7967 (2002). Copyright 2002 American Institute of Physics.]

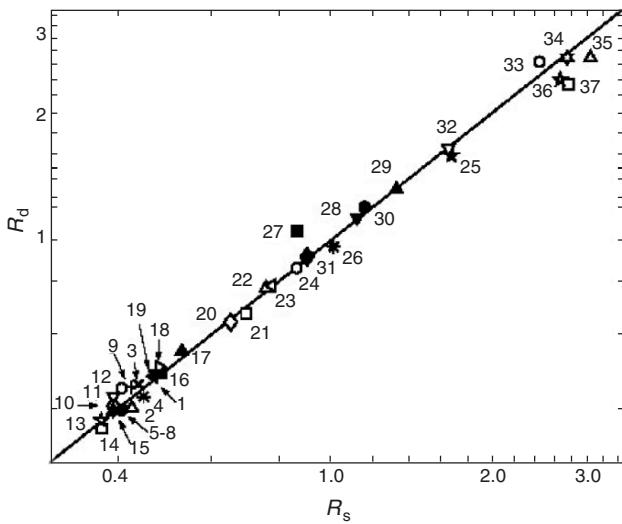
The *solid line* is predicted by the present theory from the formula in (12.58). The various symbols with the vertical bars to indicate the approximate uncertainty of the data, which depend on the values of  $D_1$  [48, 57] and the thermodynamic states used for the estimations, are experimental: • is from [47] for Ar in liquid N<sub>2</sub>; △ from [48]; ○ from [49] for Kr in liquid Ar; and × from [49] for Kr in liquid N<sub>2</sub>, respectively. Computer simulation results denoted by stars (\*) are taken from the literature [58] and presented in the figure, although they are for a modified Lennard-Jones potential model. There is reasonably good correlation between the theory and experiment.

#### 12.4.2 Empirical van der Waals Volume for Polyatomic Molecules

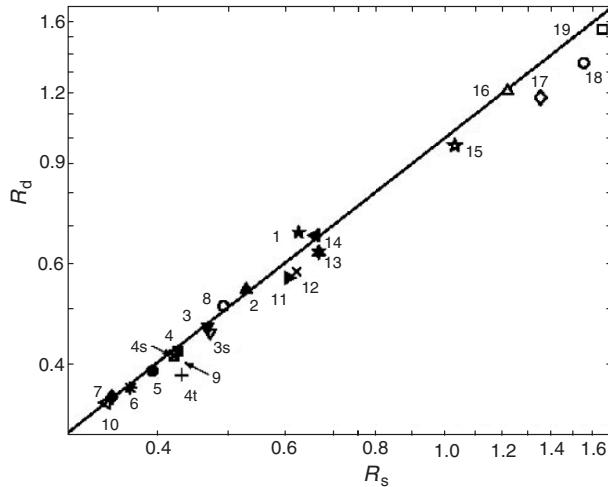
Because the MFV theory is formulated for simple liquids, it cannot be directly applied to polyatomic and polymeric liquids unless rather drastic simplifying assumptions are made. For small polyatomic liquids, it is possible to apply the MFV theory by assuming that the molecules are roughly spherical and if the van der Waals radii of such molecules are estimated properly [59]. Bondi [60] and Edward [35] formulated an empirical rule to calculate the van der Waals radii of relatively small polyatomic molecules for the purpose of evaluating the diffusion coefficients on the basis of the SE relation. In their empirical procedure the van der Waals radius  $r_w$  of a polyatomic (organic) molecule is defined by  $r_w = (3v_w/4\pi)^{1/3}$ , where  $v_w$  is the van der Waals volume. This  $r_w$  is then calculated according to the Edward rule by which increments contributed by chemical groups in the molecule are added up for the van der Waals volume  $v_w$ . By adopting the Edward rule and setting  $\sigma = r_w$  for the MFV theory diffusion coefficients, Rah et al. [59] calculated the diffusion coefficients and  $D_t/D_1$  for polyatomic liquids. According to the relation the ratio  $D_t/D_1 = R_d$  should be a constant, which should be given by the van der Waals radii of the solute and solvent as follows:

$$R_d = \left( \frac{2}{1 + r_{w2}/r_{w1}} \right)^2 \left[ \frac{1}{2} \left( 1 + \frac{m_1}{m_2} \right) \right]^{1/2} \equiv R_s.$$

In Figs. 12.12 and 12.13,  $R_d$  vs  $R_s$  is plotted on a logarithmic scale, and the figures verify the theoretical prediction nearly perfectly, indicating the robustness of the relation (12.58) and the values of the van der Waals radii estimated according to the Edward rule. In Fig. 12.12, where  $R_d$  vs.  $R_s$  is plotted where the solvation effects are assumed negligible, the *solid line* is the prediction by the present theory and the symbols are experimental data for  $R_d$ . The solvent for the tracer diffusion of 1–19 is water and the solute is benzene for 1; toluene for 2; aniline for 3; phenol for 4; *o*-creosol for 5; *m*-creosol for 6; *p*-creosol for 7; 2-chlorophenol for 8; chlorobenzene for 9; 1,2-dichlorobenzene for 10; 1,4-dichlorobenzene for 11; bromobenzene for 12; 1,2-dibromobenzene for 13; 1,4-dibromobenzene for 14; 3-nitrophenol for 15; pyridine for 16, acetone for 17; DMSO for 18; and 2-butanone for 19, respectively. The solvent for



**Fig. 12.12.**  $R_d = D_t/D_1$  vs.  $R_s$  when the solvation effects are assumed negligible. See the text for the meanings of symbols and numerals. [Reproduced with permission from K. Rah, S. Kwak, B. C. Eu, and M. Lafleur, *J. Phys. Chem. A* **106**, 11841 (2002). Copyright 2002 American Chemical Society.]



**Fig. 12.13.** Size and mass ratio dependence of  $R_d = D_t/D_1$  vs.  $R_s$  when the solvation effects are present. See the text for the meanings of symbols and numerals. [Reproduced with permission from K. Rah, S. Kwak, B. C. Eu, and M. Lafleur, *J. Phys. Chem. A* **106**, 11841 (2002). Copyright 2002 American Chemical Society.]

20–24 is acetone, whereas the solute is propiophenone for 20; acetophenone for 21; chlorobenzene for 22; toluene for 23; and benzene for 24; respectively. For 25–31 the solvent is benzene, whereas the solute is MeOH for 25; EtOH for 26; *n*-hexane for 27; 1-PrOH for 28; DMSO for 29; acetone for 30; and cyclohexane for 31, respectively. For 32–37 the solute is water, whereas the solvent is acetonitrile for 32; benzene for 33; toluene for 34; *p*-xylene for 35; cyclohexane for 36; and *n*-hexane for 37, respectively.

In Fig. 12.13, where  $R_d$  vs.  $R_s$  is plotted when the hydration effects are taken into account, the *solid line* is the prediction by the present theory and the symbols are the experimental data. Water is the solvent for 1–10 whereas the tracers are MeOH for 1; EtOH for 2; 1-PrOH for 3; 2-PrOH for 3s; 1-BuOH for 4; 2-BuOH and *i*-BuOH for 4s; *t*-BuOH for 4t; 1-pentanol for 5; 1-hexanol for 6; 1-heptanol for 7; ethylene glycol for 8; glycerol for 9; and pentaerythritol for 10, respectively. Acetone is the solvent for 11–14, whereas the solute is 2-chlorophenol for 11; *p*-creosol for 12; phenol for 13; and aniline for 14, respectively. For 15–19 water is the tracer in the solvent of MeOH for 15; EtOH for 16; acetone for 17; DMSO for 18; and ethyl acetate for 19, respectively.

The good correlation obtained between  $R_d$  and  $R_s$  indicates the accuracy of the relation (12.58) and the theory underlying it. The conclusion that can be drawn from this exercise is that the MFV theory diffusion coefficients can be applied even to organic polyatomic liquids, which may be treated as roughly spherical molecules, provided that their van der Waals radii are appropriately estimated by using the Edward rule [35]. Such a relation can be useful, especially when  $D_1$  is difficult to measure in practice, whereas  $D_t$  is available, for example, for very high density liquids. Tracer diffusion coefficients can be also useful for understanding transport data on glass-forming supercooled liquids [61].

## 12.5 Transport Coefficients of Ordinary Liquids

Because an adequate theory for diffusion was lacking, transport coefficients such as viscosities and thermal conductivity of simple and complex liquids in the density fluctuation theory were calculated semiempirically by using the experimental or molecular dynamics simulation data for self-diffusion coefficients. Now equipped with the self-diffusion and diffusion coefficients that can be easily and accurately calculated by statistical mechanics, as shown in the previous sections, it is possible to remove the semiempiricism of the density fluctuation theory formulas for transport coefficients and make the theory of transport coefficients of liquids statistical mechanical. In this section, we show that the density fluctuation theory is capable of providing a long sought molecular theoretical tool for computing the temperature and density dependence of transport coefficients of liquids. The demonstration achieved so far is for shear viscosities of simple liquids and diatomic liquids of two-interaction

sites. However, for the remaining transport coefficients, it is quite clear that the method described for shear viscosities is applicable equally successfully because the semiempirical method has already shown the capability of the density fluctuation theory formulas. Moreover, because the bulk and thermal conductivity can be related to the shear viscosity, the validation of the viscosity formula is sufficient for making the aforementioned statement regarding the capability of the density fluctuation theory formulas for the bulk viscosity and thermal conductivity of liquids.

Before we begin the desired validation of the combination of the density fluctuation theory for shear viscosity and the modified free volume theory, we elaborate on the averaging of the potential energy part of viscosity, which was introduced in (10.41). Averaging is with regard to the distribution of  $\xi$ .

As mentioned in Chaps. 10 and 11, the density fluctuation theory presumes that the fluid density fluctuates locally around position  $\mathbf{r}$  in the fluid (liquid) and the fluctuations give momentum and energy transfers within local volumes of the liquid. To account for the local variation of  $\xi$  we assume that the range  $\xi$  of density fluctuations has a stretched exponential distribution [62, 63] as follows:

$$P(\xi, n, T) = P_0 \left( \frac{\xi}{r} \right)^{\gamma-1} \exp \left[ -\hat{\zeta}(n, T) \left( \frac{\xi}{r} \right)^\gamma \right]. \quad (12.59)$$

This form presumes that the distribution of  $\xi$  is inhomogeneous in the sense that it depends on position  $r$ . By taking this form for the distribution of  $\xi$ , we are asserting that the effect of density fluctuations is localized around the radial position  $r$ . In this formula  $\gamma$  and  $\hat{\zeta}(n, T)$  are parameters. Using the normalization condition

$$\int_0^\infty d\xi P(\xi, r, T) = 1, \quad (12.60)$$

we find

$$P_0 = \frac{\gamma \hat{\zeta}(n, T)}{r} \quad (12.61)$$

and hence

$$P(\xi, n, T) = \frac{\gamma \hat{\zeta}(n, T) \xi^{\gamma-1}}{r^\gamma} \exp \left[ -\hat{\zeta}(n, T) \left( \frac{\xi}{r} \right)^\gamma \right]. \quad (12.62)$$

With this form for the distribution function, the average  $\langle \omega(n) \rangle$  is calculated as follows:

$$\langle \omega(n) \rangle = \frac{2\pi}{15} \int_0^\infty dr r^5 u'(r) g_{\text{eq}}^{(2)}(r, n) \Theta(n, T|r), \quad (12.63)$$

where

$$\Theta(n, T|r) = \int_0^\infty d\xi \theta(\xi - r) P(\xi, n, T). \quad (12.64)$$

On explicit evaluation of this integral,  $\Theta(n, T|r)$  is found independent of  $r$  and given by the formula depending only on  $n$  and  $T$ :

$$\Theta(n, T|r) = \exp\left[-\hat{\zeta}(\rho, T)\right]. \quad (12.65)$$

Therefore, the average  $\langle \omega(n) \rangle$  is given by

$$\langle \omega(n) \rangle = \frac{2\pi}{15} \exp\left[-\hat{\zeta}(n, T)\right] \int_0^\infty dr r^5 u'(r) g_{\text{eq}}^{(2)}(r, n) \quad (12.66)$$

and the potential energy part of the shear viscosity is given by

$$\eta_v = \frac{n^2 \omega(n, T)}{6D} \exp\left[-\hat{\zeta}(n, T)\right], \quad (12.67)$$

where

$$\omega(n, T) = \frac{2\pi}{15} \int_0^\infty dr r^5 u'(r) g_{\text{eq}}^{(2)}(r, n). \quad (12.68)$$

The formula (12.67) will be used for calculating the potential energy part of the shear viscosity. Note that the same averaging procedure applied to the thermal conductivity formula in the density fluctuation theory yields the expression

$$\lambda_p(n, T) = \frac{n^2 \chi(n, T)}{6D} \exp\left[-\hat{\zeta}(n, T)\right], \quad (12.69)$$

where

$$\chi(n, T) = \frac{4\pi k_B \kappa^*}{m} \int_0^\infty dr r^4 \left[ \frac{r \mathcal{V}'(r)}{5} - \mathcal{V}(r) \right] g_{\text{eq}}^{(2)}(r, n). \quad (12.70)$$

See (10.105) and (10.106) for the meanings of the symbols.

The parameter  $\hat{\zeta}(n, T)$  should be determined empirically. Because the correlation range parameter  $\xi$  should be larger than the interaction potential range  $r_{\max}$ , as the correlation range increases together with the density fluctuation range the parameter  $\hat{\zeta}(n, T)$  should be such that

$$\hat{\zeta}(n, T) \rightarrow 0,$$

as  $T \rightarrow T_c$  or higher. Therefore we look for it in the form<sup>2</sup>

$$\hat{\zeta}(n, T) = \theta(T_c - T) \zeta(n), \quad (12.71)$$

where  $\theta(T_c - T) = 0$  for  $T_c < T$ ,  $\theta(T_c - T) = 1$  for  $T_c > T$  and  $\zeta(n)$  depends only on  $n$ . The form for  $\zeta(n)$  can be determined at a value of  $T$ .

In recent papers by Laghaei et al. [22] and Eskandari Nasrabad et al. [66], using the MFV theory self-diffusion coefficients validated in the previous

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<sup>2</sup> The step function  $\theta(T_c - T)$  may be replaced by a smoothed switching function  $\{1 + \exp[\beta_0(T - T_c)]\}^{-1}$  ( $\beta_0 > 0$ ).

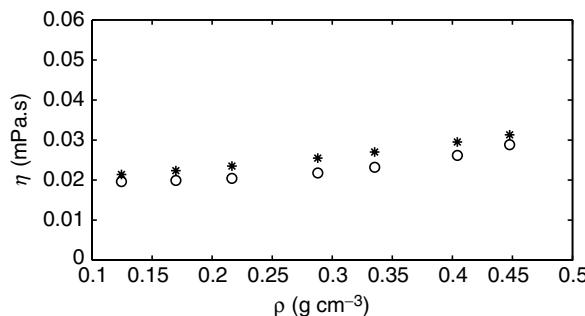
section, the shear viscosities have been calculated for argon, methane, and carbon dioxide in both the supercritical and subcritical regimes. They found that the shear viscosity formula becomes free of the parameter  $\zeta(n)$ , that is,  $\zeta(n) = 0$ , in the supercritical regime. They also found that in the subcritical regime, not only the parameter  $\zeta(n)$  for  $T < T_c$  can be expressible in the series form

$$\zeta(n) = \zeta_0 + \zeta_1\rho + \zeta_2\rho^2, \quad (12.72)$$

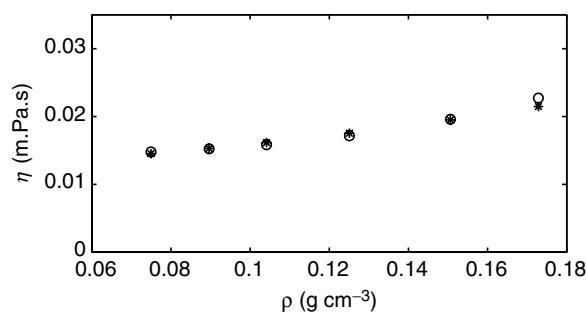
where  $\rho$  is the mass density ( $\text{g cm}^{-3}$ ), but also a single form for  $\zeta(n)$  is uniformly valid for all subcritical temperatures. With  $\zeta(n)$  thus fixed at a subcritical temperature, the shear viscosity at other subcritical temperatures was predicted and compared with experimental data for a number of different temperatures. The same method was applied to liquid krypton, and the shear viscosity calculated was in good agreement with experiment.

In Fig. 12.14, the theoretical shear viscosity of argon [64] at  $T = 250\text{ K}$  (supercritical) is compared with experiment. The *open circles* ( $\circ$ ) are theoretical values, whereas the asterisks (\*) are experimental [65]. Although there is a uniform deviation from the experimental data, the agreement is quite good. The comparison of the theory with experiment in the supercritical temperature regime is significant because the theory is free from the empirical parameter  $\zeta(n)$  and thus predicts the shear viscosity, based on only an intermolecular potential energy. The potential parameters are the same as for Fig. 12.1 for the self-diffusion coefficient, for which  $\alpha = 1$  and  $v_0 = \pi\sigma'^3/6$  with  $\sigma' = 1.1^{1/3}\sigma$ . The critical volume activating diffusion is slightly larger than the molecular volume defined by the potential parameter  $\sigma$ .

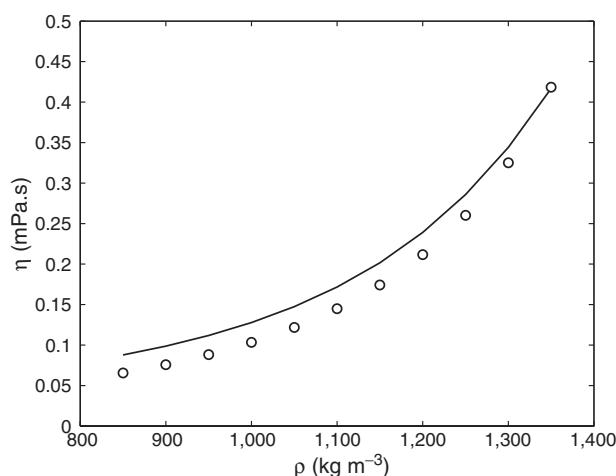
Similarly, the shear viscosity of methane at  $T = 320\text{ K}$  in the supercritical regime is compared in Fig. 12.15. The *open circles* ( $\circ$ ) are theoretical values whereas the *asterisks* (\*) are experimental [65]. In this case, the agreement with experiment is better than that for argon.



**Fig. 12.14.** Shear viscosity vs. density ( $\rho$ ) at  $T = 250\text{ K}$  in the supercritical regime of argon. The *open circles* ( $\circ$ ) are theoretical, whereas the asterisks (\*) are experimental [65]. [Reproduced with permission from R. Laghaei, A. Eskandari Nasrabad, and B. C. Eu, *J. Phys. Chem. B* **109**, 5873 (2005). Copyright 2005 American Chemical Society.]



**Fig. 12.15.** Shear viscosity vs. density ( $\rho$ ) at  $T = 320\text{ K}$  in the supercritical regime of methane. The *open circles* ( $\circ$ ) are theoretical, whereas the *asterisks* (\*) are experimental [65]. [Reproduced with permission from R. Laghaei, A. Eskandari Nasrabad, and B. C. Eu, *J. Phys. Chem. B* **109**, 5873 (2005). Copyright 2005 American Chemical Society.]



**Fig. 12.16.** Shear viscosity vs. density ( $\rho$ ) for carbon dioxide at  $T = 323\text{ K}$ . The *solid curve* is the experimental data represented by the fitting formula proposed by Fenghour et al. [67], and the *open circles* ( $\circ$ ) are the theoretical predictions. [Reproduced with permission from A. Eskandari Nasrabad, R. Laghaei, and B. C. Eu, *J. Phys. Chem. B* **109**, 8171 (2005). Copyright 2005 American Chemical Society.]

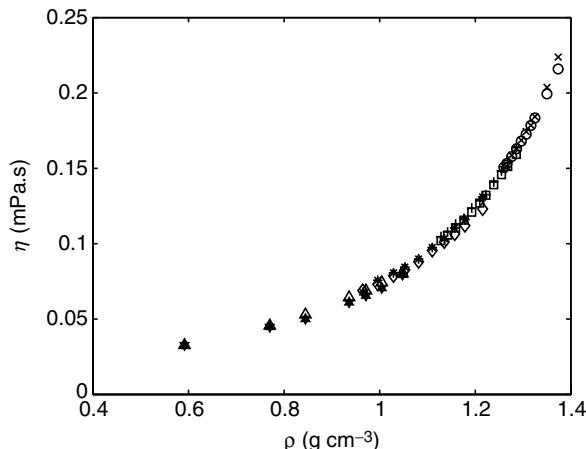
The density dependence of the shear viscosity of carbon dioxide in the supercritical regime was also examined. In Fig. 12.16, the theoretical shear viscosity of carbon dioxide versus density at  $T = 323\text{ K}$  in the supercritical regime is compared with experiment. The *open circles* ( $\circ$ ) are the theoretical predictions [66], whereas the *solid curve* represents the experimental data according to the fitting formula proposed by Fenghour et al. [67]. In this case, the theoretical values are a little lower than the experimental values, but the qualitative behavior looks the same as in the experiment. If the critical free

volume  $v_0$  were increased just a little so that the self-diffusion coefficients were lowered correspondingly throughout the density range, agreement between the theory and experiment could have been improved. The point is that the density fluctuation theory yields a qualitatively correct, and almost quantitatively correct, shear viscosity with knowledge of the intermolecular potential energy alone.

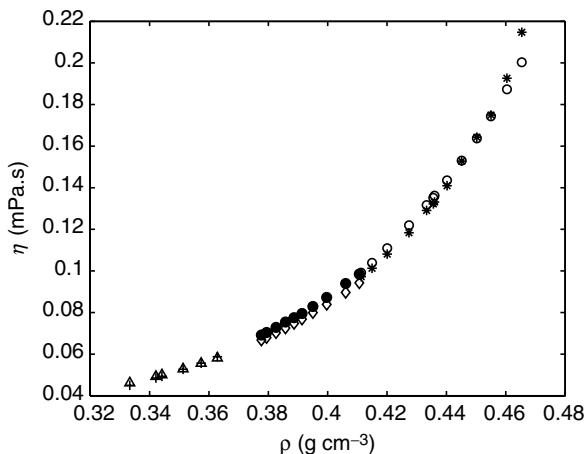
The theoretical shear viscosities of simple and complex liquids in the subcritical regime were also examined in comparison with experimental data. In the subcritical regime, the density fluctuation range depends on density. Therefore for argon it was necessary to choose

$$\zeta_0 = 0.3890, \quad \zeta_1 = 0.5180 \text{ cm}^3 \text{ g}^{-1}, \quad \zeta_2 = 0.2578 \text{ cm}^6 \text{ g}^{-2},$$

which were determined at  $T = 139 \text{ K}$  below the critical temperature. This gives 0.234 for the value of  $\exp(-\zeta)$ , for example, at  $\rho = 1.26 \text{ g cm}^{-3}$ . This value roughly corresponds to  $\xi = 2\sigma$  for the density fluctuation range. Once  $\zeta(\rho)$  is determined at a value of  $T$ , the shear viscosities for the remaining temperature values in the subcritical regime can be correctly computed for all densities. Such results are shown in Fig. 12.17 for argon at various subcritical temperatures. The meanings of the symbols in Fig. 12.18 are  $\times$  (theory),  $\circ$  (exp.) at  $T = 107 \text{ K}$ ;  $+$  (theory),  $\square$  (exp.) at  $T = 125 \text{ K}$ ;  $*$  (theory),  $\diamond$  (exp.) at  $T = 139 \text{ K}$ ; and  $\star$  (theory),  $\triangle$  (exp.) at  $T = 143 \text{ K}$ . Laghaei et al. [22] also showed that with the formula



**Fig. 12.17.** Shear viscosity vs. density for argon at various subcritical temperatures. The meanings of the symbols are as follows:  $\times$  (theory),  $\circ$  (exp.) at  $T = 107 \text{ K}$ ;  $+$  (theory),  $\square$  (exp.) at  $T = 125 \text{ K}$ ;  $*$  (theory),  $\diamond$  (exp.) at  $T = 139 \text{ K}$ ; and  $\star$  (theory),  $\triangle$  (exp.) at  $T = 143 \text{ K}$ . [Reproduced with permission from R. Laghaei, A. Eskandari Nasrabad, and B. C. Eu, J. Phys. Chem. B **109**, 5873 (2005). Copyright 2005 The American Chemical Society.]



**Fig. 12.18.** Shear viscosity vs. density for liquid methane at various subcritical temperatures. The symbols mean \* (theory), ○ (exp.) at  $T = 120\text{ K}$ ; ● (theory), ◇ (exp.) at  $T = 140\text{ K}$  (theory); and + (theory), △ (exp.) at  $T = 180\text{ K}$ . [Reproduced with permission from R. Laghaei, A. Eskandari Nasrabad, and B. C. Eu, *J. Phys. Chem. B* **109**, 5873 (2005). Copyright 2005 American Chemical Society.]

$$\zeta(\rho) = 1.105 + 0.0885\rho + 0.0465\rho^2,$$

the shear viscosities of liquid krypton at various subcritical temperatures can be correctly predicted; see Fig. 12.6 of [22].

For liquid methane they showed that with the parameter  $\zeta$  given by

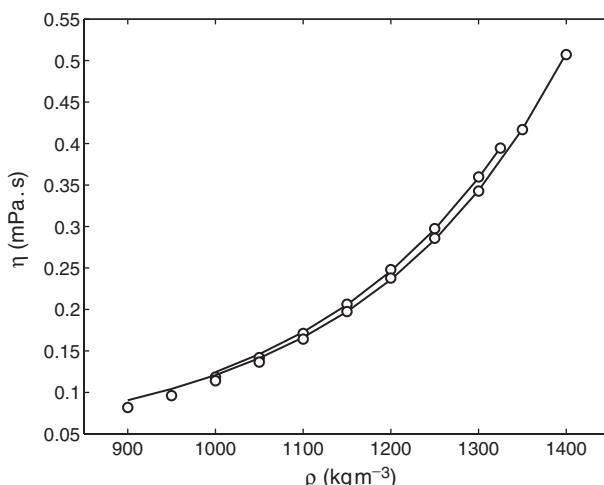
$$\zeta(\rho) = 0.4992 + 2.665\rho + 0.3327\rho^2$$

the shear viscosities can be correctly predicted for all subcritical temperatures examined. The results are presented in Fig. 12.18. The meanings of the symbols in Fig. 12.18 are \* (theory), ○ (exp.) at  $T = 120\text{ K}$ ; ● (theory), ◇ (exp.) at  $T = 140\text{ K}$  (theory); and + (theory), △ (exp.) at  $T = 180\text{ K}$ . Therefore it is reasonable to conclude that the viscosity formula presented can be employed to predict the subcritical viscosities of simple liquids if  $\zeta(\rho)$  is fixed at an arbitrary subcritical temperature, and in the supercritical temperature it is not even necessary to have  $\zeta(\rho)$  to predict correct viscosities qualitatively.

The shear viscosity formula for rigid diatomic liquids in the density fluctuation theory was also applied to compute the shear viscosity of carbon dioxide in the subcritical regime, and the results were compared with experiment by Eskandari Nasrabad et al. [66]. For carbon dioxide liquid they found

$$\zeta(\rho) = 4.70 - 8.51\rho + 3.86\rho^2,$$

which was obtained with the experimental data at  $T = 240\text{ K}$ . With this form of  $\zeta(\rho)$ , the shear viscosities of carbon dioxide were predicted with the same

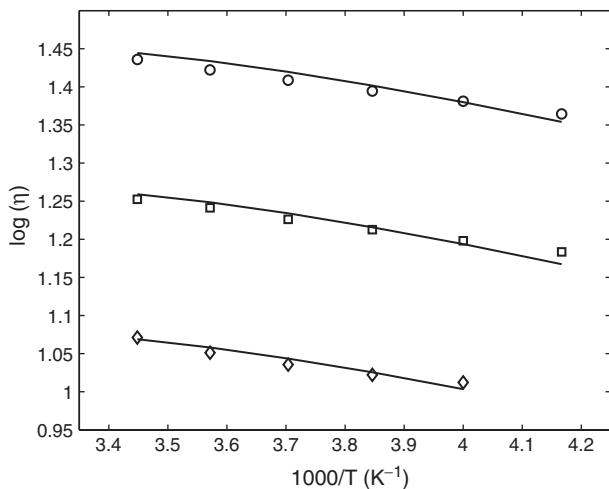


**Fig. 12.19.** Shear viscosity vs. density for carbon dioxide at  $T = 250$  and  $280\text{ K}$ . The *solid curves* are experimental [67], and the *open circles* ( $\circ$ ) are theoretical. The *upper curve* is for  $T = 250\text{ K}$  and the *lower curve* is for  $T = 280\text{ K}$ . [Reproduced with permission from A. Eskandari Nasrabad, R. Laghaei, and B. C. Eu, *J. Phys. Chem. B* **109**, 8171 (2005). Copyright 2005 American Chemical Society.]

Lennard-Jones site–site potential as for the supercritical viscosity discussed earlier. An example of the results is shown in Fig. 12.19. In the figure, the *solid curves* are experimental [67] and the *open circles* ( $\circ$ ) are theoretical. The *upper curve* is for  $T = 250\text{ K}$  and the *lower curve* is for  $T = 280\text{ K}$ . The experimental curves were produced from the empirical fitting formula proposed by Fenghour et al. [67]. Agreement between experiment and theory is excellent. Similar computation was also performed for  $T = 260$  and  $290\text{ K}$  with similarly excellent agreement between theory and experiment; see Fig. 12.6 in [66].

The temperature dependence of the shear viscosity of carbon dioxide was also examined in [66] and found in good agreement with experiment. Figure 12.20 shows such a comparison. In Fig. 12.20, the *upper curve* is at  $\rho = 1.20\text{ g cm}^{-3}$ , the *middle curve* is at  $\rho = 1.25\text{ g cm}^{-3}$ , and the *lower curve* is at  $\rho = 1.30\text{ g cm}^{-3}$ . The *solid curves* are experimental data reproduced by the fitting formula of Fenghour et al. [67] and the symbols are theoretical. The theoretical predictions agree well with experiment. The comparisons in the figures for carbon dioxide indicate that the shear viscosity formula for rigid diatomic liquids obtained by the density fluctuation theory is also accurate and robust in predicting the density and temperature dependence of the shear viscosity.

The molecular theory approach discussed in this chapter is still in progress. The theory is generally simple yet robust. Nevertheless, there are still many more aspects to be studied in the future, which hopefully will shed light on transport processes in liquids.



**Fig. 12.20.** Temperature dependence of the shear viscosity of carbon dioxide at various isobars. The *upper curve* is at  $\rho = 1.20\text{ g cm}^{-3}$ , the *middle curve* is at  $\rho = 1.25\text{ g cm}^{-3}$ , and the *lower curve* is at  $\rho = 1.30\text{ g cm}^{-3}$ . The *solid curves* are experimental and the symbols are theoretical. [Reproduced with permission from A. Eskandari Nasrabad, R. Laghaei, and B. C. Eu, J. Phys. Chem. B **109**, 8171 (2005). Copyright 2005 American Chemical Society.]

Thermal conductivities have not as yet been calculated by using the density fluctuation theory combined with the modified free volume theory, but the outcome of such calculations can be easily expected to be successful because the semiempirical treatment of the density fluctuation theory discussed in Chaps. 10 and 11 has been successful for thermal conductivities when the self-diffusion coefficients are treated as empirical inputs. The generalized Eucken relation further supports this expectation because of the successful validation of the theory for shear viscosities presented in this chapter.

## 12.6 Conclusion

—Form is void, void is form.  
Heart Sutra

The preceding enunciation in the *Heart Sutra* is one of the principal tenets of Buddhism. It is metaphysical and has, of course, no relevance to physics. It is just amusing to notice that the human vocabulary is so limited that we tend to use the same word to mean different things in totally different contexts. The term void is as elusive a philosophical and religious notion as the notion of physical voids in liquids and condensed matter in general has been difficult to capture and put in a firm and practical mathematical framework so as to make it work for science. One is believed to have attained

*the other shore* when the aforementioned religious tenet is mastered and one is thus enlightened. Likewise, however will-o'-the-wispish the notion of void in physics may be, it<sup>3</sup> seems to lie at the heart of understanding the thermal behavior of condensed matter in general from the viewpoints of the particulate universe consisting of a denumerably infinite number of molecules with finite particle sizes, and statistical mechanics that aims to describe their collective behavior by mechanical and mathematical laws.

In this work, we have seen a confluence of the kinetic theory, the density fluctuation theory, the generic van der Waals equation of state for matter in equilibrium, and the free volume theory of flow in matter. They make it possible to obtain a molecular theory in which, at worst, only a few parameters appear that can be fixed at an isotherm. Thus experimental data for the rest of the temperature range can be predicted only by intermolecular forces. It has produced a practical theory. In the theory presented, the underlying notion is that the time- and spatial scales of transport processes in liquids are set by diffusion or self-diffusion of the molecules therein. The density fluctuation theory, born of the generalized Boltzmann equations, thus relates the self-diffusion or the diffusion coefficient to transport coefficients such as viscosity and thermal conductivity by using hydrodynamic descriptions of flow. And the notion has resulted in the forms for the transport coefficients which in part resemble the well known Stokes–Einstein relation. The generic van der Waals equation of state makes it possible to represent the mean free volume in terms of the equilibrium pair correlation function, and the modified free volume theory finally provides a molecular theory for calculating the self-diffusion or diffusion coefficient on the basis of molecular interaction potentials. Thus we now have a molecular theory that provides practical means to compute the temperature and density dependence of transport coefficients, which has been one of the principal goals in nonequilibrium statistical mechanics for so long. The formulas presented for transport coefficients can be regarded as, at least in the subcritical regime, semiempirical fitting formulas for transport coefficients that can be calculated with models for intermolecular forces if a few parameters are fixed at an isotherm.

Specifically, in Chap. 12, we have shown how the Cohen–Turnbull free volume theory can be used to predict the temperature and density dependence of self-diffusion coefficients of simple liquids when it is combined with the generic van der Waals equation of state and an integral equation theory for the equilibrium pair correlation function or the Monte Carlo simulation method for it. Except for an undetermined parameter (i.e.,  $\alpha$ ) the theory is thereby completely molecular. We have called this theory the modified free volume theory. Because the parameter  $\alpha$  is rather close to unity in many cases, the theory becomes fully molecular and free from an adjustable parameter if we are willing to sacrifice accuracy a little. We have also formulated a free volume theory

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<sup>3</sup> One way of quantifying voids in liquids is to use the concepts of Voronoi polyhedra and Delaunay spheres [68]. Then it becomes natural to examine their distributions in liquids.

of diffusion coefficients for binary mixtures of simple liquids. It combines the ideas of the mean free path theory, the free volume theory, and the generic van der Waals equation of state, which provides the statistical mechanical representation of free volume that permits calculation of free volume in terms of the pair correlation functions of the liquid mixture. The generic van der Waals equation of state provides a rather simple free volume expression for a mixture, which is easy to compute accurately. The formulas developed for diffusion coefficients account for the composition and temperature dependence of the binary diffusion coefficients of simple liquid mixtures as well as the tracer diffusion coefficients in liquid solvents, both in good agreement with the experimental or computer simulation results reported in the literature. It is possible to generalize the diffusion coefficient formula to more complex liquids because the basic ideas of the theory are simple and quite generic. As an example of such a theory, polymer melts have been treated by the present line of the free volume theory, and the self-diffusion coefficient derived has been tested in comparison with experimental and found satisfactory [69].

As has been shown in Chaps. 10 and 11, because transport coefficients of liquids can be expressed in terms of diffusion or self-diffusion coefficients and the equilibrium pair correlation function, with the diffusion coefficients presented and satisfactorily tested in this chapter, the transport coefficients of liquids can now be calculated [70–74] within the limits of current computation techniques and without relying on empirical data or molecular dynamics simulation results for diffusion or self-diffusion coefficients. The significance of the theoretical results presented in this chapter for self-diffusion or diffusion coefficients therefore lies in the fact that the density fluctuation theories presented in Chaps. 10 and 11 can now be fully statistical mechanical with the help of the modified free volume theory, which in turn relies on the generic van der Waals equation of state. This form of equation of state therefore is the keystone of the present theory of transport coefficients of liquids.

Another practical and important result of the density fluctuation theory is the set of relations between transport coefficients, such as the SE-like relation, the generalized Eucken relation, and the relation between the shear and bulk viscosities, which make it possible to compute one transport coefficient from knowledge of another. These relations are robust over wide ranges of density and temperature.

Thus the important conclusion of this and the preceding two chapters is that transport properties can be calculated on the basis of the information on liquid structures provided by equilibrium statistical mechanics. The equilibrium liquid structures can be acquired by a variety of techniques developed for equilibrium statistical mechanics. The diffusion and self-diffusion coefficients presented in this work also have considerable significance for the study of the structures of supercooled liquids and nonequilibrium phenomena therein [75, 76]. There is a study reported [61] on the subject, but we will have to leave further study of the subject matter for the future work, being content that the surface is now broken and the trail is shown for a practical molecular theory of transport processes in simple and complex liquids.

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# A

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## Grand Ensemble Kinetic Equation

In this Appendix, the generalized Boltzmann equation for dense fluids used in Chap. 7 is derived by using a method of coarse-graining in time and space. This method follows the spirit of Kirkwood [1], who employed a similar method to derive the Boltzmann equation from the Liouville equation. We follow<sup>1</sup> his idea with a grand ensemble consisting of petit ensembles representative of the fluid contained in volume  $V$  at constant temperature and chemical potentials. A grand ensemble is more suitable for deriving the generalized Boltzmann equation than a canonical ensemble. This method can be readily extended to derive the generalized Boltzmann equation for fluids with internal degrees of freedom, which forms the subject discussed in Chap. 8. The Boltzmann equation emerges as a special case of the generalized Boltzmann equation derived. In Section A.2, we give the relation of the collision operator in superspace to the transition operators in Hilbert space. This relation gives a practical model for the collision term in the generalized Boltzmann equation.

### A.1 Derivation of the Kinetic Equation

The grand ensemble consists of petit ensembles of  $N, N', N'', \dots$  particles, and the total number of such petit ensembles is assumed to be  $\omega$ , which can be denumerably infinite. Then the total number of particles in the grand ensemble is  $\mathcal{N} = N + N' + N'' + \dots$ . In this manner of counting, the values of some of  $N, N', \dots$  can be the same, say,  $n^{(N)}$  times. Then  $\omega$  can be written as  $\omega = n^{(N)} + n^{(N')} + n^{(N'')} + \dots$ , and thus  $\mathcal{N}$  now may be written as  $\mathcal{N} = n^{(N)}N + n^{(N')}N' + \dots$  where  $N \neq N' \neq \dots$ . The former manner requires a simpler notation than the latter. Therefore, we will use the former.

Petit ensembles therefore may be regarded as subsystems of the grand assembly, which is isolated. Petit ensembles weakly interact with each other

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<sup>1</sup> For the generalized Boltzmann equation obtained for a grand ensemble in a different line of approach, see [2]. Also see [3, 4] in which kinetic equations for reacting fluids are derived for density matrices.

exchanging energy and matter and eventually reach equilibrium. Note that, as the petit ensembles exchange matter, the number of petit ensembles, that is, their distribution  $(n^{(N)}, n^{(N')}, n^{(N'')}, \dots)$ , changes, but the petit ensembles are still characterized by  $N$ ,  $N'$ , and so on.

If the distribution functions for the subsystems (petit ensembles) are denoted by  $F^{(m)}(x^{(m)}, t)$  ( $m = N, N', N'', \dots$ ), then the distribution function for the entire grand assembly is given by

$$F^{(\mathcal{N})}(x^{(\mathcal{N})}, t) = \prod_{m \in GA} F^{(m)}(x^{(m)}, t), \quad (\text{A.1})$$

where the product runs over all members of the grand assembly ( $GA$ ). This distribution function is normalized to unity:

$$\int dx^{(\mathcal{N})} F^{(\mathcal{N})}(x^{(\mathcal{N})}, t) = 1. \quad (\text{A.2})$$

The reduced distribution function of  $F^{(\mathcal{N})}(x^{(\mathcal{N})}, t)$  is defined by

$$F^{(m)}(x^{(m)}, t) = \frac{\mathcal{N}!}{(\mathcal{N}-m)!} \int dx^{(\mathcal{N}-m)} F^{(\mathcal{N})}(x^{(\mathcal{N})}, t). \quad (\text{A.3})$$

Thus  $F^{(m)}(x^{(m)}, t)$  is such that

$$\int dx^{(m)} F^{(m)}(x^{(m)}, t) = \frac{\mathcal{N}!}{(\mathcal{N}-m)!}. \quad (\text{A.4})$$

Because the grand ensemble is isolated, the distribution function obeys the Liouville equation,

$$\left( \frac{\partial}{\partial t} + L^{(\mathcal{N})} \right) F^{(\mathcal{N})}(x^{(\mathcal{N})}, t) = 0, \quad (\text{A.5})$$

where  $L^{(\mathcal{N})}$  is the Liouville operator for  $\mathcal{N}$  particles contained in volume  $V_g = \omega V$ . A typical value of  $m$  is  $N$ .

We are interested in the probability  $F^{(N)}(x^{(N)}, t)$  of finding a system containing  $N$  particles among  $\mathcal{N}$  particles in the phase space. Integrating the Liouville equation (A.5) over the  $(\mathcal{N}-N)$  phases and multiplying by  $\frac{\mathcal{N}!}{(\mathcal{N}-N)!}$ , we obtain the evolution equation for  $F^{(N)}(x^{(N)}, t)$ :

$$\left( \frac{\partial}{\partial t} + L^{(N)} \right) F^{(N)}(x^{(N)}, t) = -\frac{\mathcal{N}!}{(\mathcal{N}-N)!} \int dx^{(\mathcal{N}-N)} L_{\text{int}}^{(\mathcal{N})} F^{(\mathcal{N})}(x^{(\mathcal{N})}, t), \quad (\text{A.6})$$

where

$$L_{\text{int}}^{(\mathcal{N})} = L^{(\mathcal{N})} - L^{(N)}$$

is the interaction Liouville operator between the subsystem (petit ensemble) of  $N$  particles and the rest of the petit ensembles in the grand assembly. The

magnitude of this interaction energy corresponding to  $L_{\text{int}}^{(\mathcal{N})}$  is proportional to the surface area of the petit ensembles, whereas the magnitudes of the total “internal” interaction energies of the petit ensembles are proportional to their volumes. Therefore, the former is relatively weak compared with the latter. This justifies the product form for the distribution function  $F^{(\mathcal{N})}$ .

To avail ourselves of scattering theory techniques [5, 6], it is convenient to use a self-adjoint Liouville operator, which is obtained by multiplying the Liouville operator by  $-i = -\sqrt{-1}$ :

$$\mathcal{L}^{(\mathcal{N})} = -iL^{(\mathcal{N})}. \quad (\text{A.7})$$

In this notation, (A.5) now reads

$$\left(i\frac{\partial}{\partial t} - \mathcal{L}^{(N)}\right) F^{(N)}(x^{(N)}, t) = \frac{\mathcal{N}!}{(\mathcal{N}-N)!} \int dx^{(\mathcal{N}-N)} \mathcal{L}_{\text{int}}^{(\mathcal{N})} F^{(\mathcal{N})}(x^{(\mathcal{N})}, t). \quad (\text{A.8})$$

The distribution functions are coarse-grained in time by averaging them over a time interval  $\tau$ , which is sufficiently long compared with the collision time between particles but much shorter than the hydrodynamic relaxation time. The averaged distribution function is therefore given by

$$\bar{F}^{(N)}(x^{(N)}, t) = \frac{1}{\tau} \int_0^\tau ds F^{(N)}(x^{(N)}, t+s). \quad (\text{A.9})$$

This time coarse-graining presumes the existence of different timescales in the kinetic evolution of the grand assembly. The coarse-grained kinetic equation for  $\bar{F}^{(N)}(x^{(N)}, t)$  therefore is obtained by averaging (A.8) over the time interval  $0 < s < \tau$ . We find that

$$\begin{aligned} \left(i\frac{\partial}{\partial t} - \mathcal{L}^{(N)}\right) \bar{F}^{(N)}(x^{(N)}, t) &= \frac{\mathcal{N}!}{(\mathcal{N}-N)!} \\ &\times \frac{1}{\tau} \int_0^\tau ds \int dx^{(\mathcal{N}-N)} \mathcal{L}_{\text{int}}^{(\mathcal{N})} F^{(\mathcal{N})}(x^{(\mathcal{N})}, t+s). \end{aligned} \quad (\text{A.10})$$

According to the evolution equation (A.5)

$$F^{(\mathcal{N})}(x^{(\mathcal{N})}, t+s) = e^{-is\mathcal{L}^{(\mathcal{N})}} F^{(\mathcal{N})}(x^{(\mathcal{N})}, t). \quad (\text{A.11})$$

Therefore the integral on the right of (A.10) may be written as

$$\Omega^{(\mathcal{N})} = \frac{1}{\tau} \int_0^\tau ds \int dx^{(\mathcal{N}-N)} \mathcal{L}_{\text{int}}^{(\mathcal{N})} e^{-is\mathcal{L}^{(\mathcal{N})} s} F^{(\mathcal{N})}(x^{(\mathcal{N})}, t). \quad (\text{A.12})$$

This integral describes the collisional evolution of the grand assembly and since  $\tau$  is much longer than the particle collision time, it is reasonable to take  $\tau$  as infinite in the timescale of the collision. Thus we may equate the limit to Abel’s limit

$$\Omega^{(\mathcal{N})}(\infty) = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau ds \int dx^{(\mathcal{N}-N)} \mathcal{L}_{\text{int}}^{(\mathcal{N})} e^{-s/\tau} e^{-is\mathcal{L}^{(\mathcal{N})}} F^{(\mathcal{N})}(x^{(\mathcal{N})}, t), \quad (\text{A.13})$$

where the convergence factor  $e^{-s/\tau}$  is inserted. This procedure is generally used in the formal theory of scattering [6]. Evaluating the integral over  $s$ , we find that

$$\Omega^{(\mathcal{N})}(\infty) = \lim_{\epsilon \rightarrow 0} i\epsilon \int dx^{(\mathcal{N}-N)} \mathcal{L}_{\text{int}}^{(\mathcal{N})} \mathcal{R}^{(\mathcal{N})}(\epsilon) F^{(\mathcal{N})}(x^{(\mathcal{N})}, t), \quad (\text{A.14})$$

where  $\epsilon = 1/\tau$  and  $\mathcal{R}^{(\mathcal{N})}(\epsilon)$  is the resolvent operator defined by

$$\mathcal{R}^{(\mathcal{N})}(\epsilon) = (i\epsilon - \mathcal{L}^{(\mathcal{N})})^{-1}. \quad (\text{A.15})$$

In the language of formal scattering theory in phase space [5], there holds the relation between the resolvent operator  $\mathcal{R}^{(\mathcal{N})}$  and the collision operator  $T^{(\mathcal{N})}(\epsilon)$

$$\mathcal{L}_{\text{int}}^{(\mathcal{N})} \mathcal{R}^{(\mathcal{N})}(\epsilon) = T^{(\mathcal{N})}(\epsilon) \mathcal{R}_0^{(\mathcal{N})}(\epsilon), \quad (\text{A.16})$$

where  $\mathcal{R}_0^{(\mathcal{N})}(\epsilon)$  is the free resolvent operator defined by

$$\mathcal{R}_0^{(\mathcal{N})}(\epsilon) = (i\epsilon - \mathcal{L}_0^{(\mathcal{N})})^{-1} \quad (\text{A.17})$$

with  $\mathcal{L}_0^{(\mathcal{N})}$  denoting the Liouville operator describing the free evolution of the petit ensembles making up the grand ensemble:

$$\mathcal{L}^{(\mathcal{N})} = \mathcal{L}_0^{(\mathcal{N})} + \sum_{m,m' \in GA} \mathcal{L}_{mm'}^{(\mathcal{N})} \quad (\text{A.18})$$

with  $\mathcal{L}_{mm'}^{(\mathcal{N})}$  denoting the interaction Liouville operator describing interaction between the members  $m$  and  $m'$  of the grand assembly. Therefore we finally obtain  $\Omega^{(\mathcal{N})}(\infty)$  in the form,

$$\Omega^{(\mathcal{N})}(\infty) = \lim_{\epsilon \rightarrow 0} i\epsilon \int dx^{(\mathcal{N}-N)} T^{(\mathcal{N})}(\epsilon) \mathcal{R}_0^{(\mathcal{N})}(\epsilon) F^{(\mathcal{N})}(x^{(\mathcal{N})}, t). \quad (\text{A.19})$$

In the following, we will suppress the limit sign for brevity, but it must be understood and taken when the scattering problem is completely solved.

At this point, we observe that the Liouville operator for a petit ensemble may be written in terms of the center-of-mass Liouville operator and the “relative” Liouville operator describing the “relative” motion of the particles within the petit ensemble:

$$L^{(N)} = \mathbf{V}_c \cdot \frac{\partial}{\partial \mathbf{R}_c} + L_{\text{rel}}^{(N)}. \quad (\text{A.20})$$

Here  $\mathbf{R}_c$  and  $\mathbf{V}_c$  are, respectively, the position and velocity of the center of mass of the petit ensemble, and  $L_{\text{rel}}^{(N)}$  is the relative motion part of  $L^{(N)}$ .

The Liouville operators for all petit ensembles in the grand ensemble can be written as in (A.20). If the system is also coarse-grained in space, as in time, such that each factor making up  $F^{(N)}(x^{(N)}, t)$ —recall that it is a product of petit ensemble distribution functions—remains uniform with respect to its center-of-mass motion, and furthermore, the eigenvalues  $\lambda_{\text{rel}}$  of  $L_{\text{rel}}^{(N)}$  for all petit ensembles are random so that they sum up to zero:<sup>2</sup>

$$\sum L_{\text{rel}}^{(N)} F^{(N)}(x^{(N)}, t) = \sum \lambda_{\text{rel}} F^{(N)}(x^{(N)}, t) = 0, \quad (\text{A.21})$$

then it follows that

$$\mathcal{R}_0^{(N)}(\epsilon) F^{(N)}(x^{(N)}, t) = \frac{1}{i\epsilon} F^{(N)}(x^{(N)}, t). \quad (\text{A.22})$$

On coarse-graining the  $\Omega^{(N)}(\infty)$  so obtained over time again and assuming that

$$\lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau ds F^{(N)}(x^{(N)}, t+s) = \bar{F}^{(N)}(x^{(N)}, t) = \prod_m \bar{F}^{(m)}(x^{(N)}, t), \quad (\text{A.23})$$

we obtain the kinetic equation coarse-grained in time and space:

$$\begin{aligned} \left( \frac{\partial}{\partial t} + L^{(N)} \right) \bar{F}^{(N)}(x^{(N)}, t) &= \frac{N!}{(N-N)!} \\ &\times \int dx^{(N-N)} (-i) T^{(N)}(\epsilon) \bar{F}^{(N)}(x^{(N)}, t), \end{aligned} \quad (\text{A.24})$$

where

$$\bar{F}^{(N)}(x^{(N)}, t) = \prod_{m \in GA} \bar{F}^{(m)}(x^{(m)}, t).$$

This product property of coarse-grained distribution functions is an assumption or, at least, an approximation. This equation is the generalized Boltzmann equation used in the text, where the coarse-grained distribution functions are used without the overbar. The generalized Boltzmann equation must be understood in the sense of the derivation given here with coarse grainings in time and space. The derivation given here should be regarded as a rationalization rather than a derivation. We would like to take the generalized Boltzmann equation as a postulate rather than an equation derived.

The Boltzmann equation is recovered from (A.24) if  $N = 1$  for all petit ensembles, and  $T^{(N)}(\epsilon)$  is approximated by its binary collision terms in its cluster expansion. If  $T^{(N)}(\epsilon)$  is expanded in the cluster expansion

$$T^{(N)}(\epsilon) = \sum_{j < k} T_{jk}(\epsilon) + \sum_{j < k < l} T_{jkl}(\epsilon) + \dots, \quad (\text{A.25})$$

---

<sup>2</sup> This assumption that eigenvalues  $\lambda_{\text{rel}}$  are random is equivalent to the random phase assumption for distribution functions.

where  $T_{jk}(\epsilon)$  are binary collision operators,  $T_{jkl}(\epsilon)$  are three-particle collision operators, and so on, and if only the binary collision terms are retained, the Boltzmann equation follows. For this subject, see the literature [15] cited earlier.

## A.2 Relation Between Collision and Transition Operators

To obtain the desired relation [3,4] between collision and transition operators—the former obeying the Lippmann–Schwinger equation in superspace and the latter obeying the Lippmann–Schwinger equation in Hilbert space—it is necessary to use a quantum mechanical formalism starting from the quantum mechanical Liouville–von Neumann equation for the density operator instead of the classical formalism. Because it is possible to derive the coarse-grained kinetic equation for the phase space distribution function of the grand ensemble in exactly the same form and manner as that presented earlier, it is sufficient to regard the collision operator  $T^{(\mathcal{N})}(\epsilon)$  as a quantum mechanical operator. The resolvent operators also should be regarded as quantum mechanical operators. Their classical limits then may be taken after desired formulas have been appropriately obtained, if the classical limits are desired. To implement this method it is useful to briefly review the notation for operators and to distinguish the operators in Hilbert space (i.e., dyadic space) and superspace (i.e., tetradic space). The essential aspects of the relation can be shown without encumbering the discussion with many-particle operators because the system of notation developed for two-particle operators can be easily generalized to many-particle versions.

The quantum mechanical Liouville operator  $\mathcal{L}$  is, of course, the commutator defined by

$$\mathcal{L}\rho = [\mathbf{H}, \rho], \quad (\text{A.26})$$

where  $\mathbf{H}$  is the Hamiltonian operator and  $\rho$  is the density matrix. Associated with this Liouville operator are the resolvent operators

$$\mathcal{R}(z) = (z - \mathcal{L})^{-1}, \quad (\text{A.27})$$

$$\mathcal{R}_0(z) = (z - \mathcal{L}_0)^{-1}, \quad (\text{A.28})$$

where  $z$  is a complex number, which in the context of the kinetic theory under discussion will turn out to be  $z = i\epsilon$ , and  $\mathcal{L}_0$  is the free Liouville operator corresponding to the kinetic energy Hamiltonian  $\mathbf{H}_0$ . It is therefore defined by

$$\mathcal{L}_0\rho = [\mathbf{H}_0, \rho]. \quad (\text{A.29})$$

The tetradic collision operator  $T(z)$  satisfies the Lippmann–Schwinger equation in superspace

$$T(z) = \mathcal{L}' + \mathcal{L}'\mathcal{R}_0(z)T(z). \quad (\text{A.30})$$

The Liouville operator  $\mathcal{L}$  may be written as

$$\mathcal{L} = \mathcal{L}_0 + \mathcal{L}' . \quad (\text{A.31})$$

In the tetradic notation, the Hamiltonian operator is written as [4]

$$\begin{aligned} \mathcal{H} &= \mathbf{H} \otimes \mathbf{I}, \\ \mathcal{H}^* &= \mathbf{I} \otimes \mathbf{H}^*, \\ \mathcal{H}_0 &= \mathbf{H}_0 \otimes \mathbf{I}, \\ \mathcal{H}_0^* &= \mathbf{I} \otimes \mathbf{H}_0^*, \\ \mathcal{V} &= \mathbf{V} \otimes \mathbf{I}, \\ \mathcal{V} &= \mathbf{I} \otimes \mathbf{V}, \end{aligned} \quad (\text{A.32})$$

where  $\mathbf{I}$  is the identity operator and  $\mathbf{V}$  is the potential energy operator. In this notation, the Liouville operators are given by

$$\begin{aligned} \mathcal{L} &= \mathcal{H} - \mathcal{H}^*, \\ \mathcal{L}_0 &= \mathcal{H}_0 - \mathcal{H}_0^*. \end{aligned} \quad (\text{A.33})$$

In the tetradic notation, the tetradic operators are calculated as follows: for example,

$$\begin{aligned} \mathcal{H}_{ij;kl} &= (\mathbf{H} \otimes \mathbf{I})_{ij;kl} = H_{ik}\delta_{jl}, \\ \mathcal{L}_{ik;jl} &= \mathcal{H}_{ik;jl} - \mathcal{H}_{ik;jl}^* = H_{ik}\delta_{jl} - \delta_{ik}H_{jl}. \end{aligned} \quad (\text{A.34})$$

The Green's functions—resolvent operators in Hilbert space—are related to the resolvent  $\mathcal{R}(z)$  in the following manner. In the representation in which the Hamiltonian is diagonal with respect to energy

$$\mathcal{R}_{ij;kl}(z) = (z - \mathcal{L})_{ij;kl}^{-1} = (z + E_j - E_i)^{-1} \delta_{ik}\delta_{jl} = [G(z + E_j)]_{ik} \delta_{jl}, \quad (\text{A.35})$$

where

$$G(z + E_j) = (z + E_j - E_i)^{-1} = \left[ (z + E_j - \mathbf{H})^{-1} \right]_i \quad (\text{A.36})$$

and similarly for  $\mathcal{R}_0$ . With these computational rules established for tetradic operators, the tetradic collision operator  $T(z)$  can be related to the transition operator  $\mathcal{T}(z)$  obeying the Lippmann–Schwinger equation in Hilbert space

$$\mathcal{T}(E^+) = \mathbf{V} + \mathbf{V}G_0(E^+) \mathcal{T}(E^+), \quad (\text{A.37})$$

where

$$E^+ = E + i\epsilon.$$

It is useful to note the relation between the tetradic element of  $\mathcal{T}(\mathcal{H}_0^* + z)$  in superspace and the dyadic element of  $\mathcal{T}(E^+)$  in Hilbert space:

$$\begin{aligned} [\mathcal{T}(\mathcal{H}_0^* + z)]_{ij;kl} &= \mathcal{T}_{ik}(E_j^+) \delta_{jl}, \\ [\mathcal{T}^*(\mathcal{H}_0 + z^*)]_{ij;kl} &= \mathcal{T}_{ij}^\dagger \delta_{ik}, \end{aligned} \quad (\text{A.38})$$

where  $\mathcal{T}^\dagger$  is the Hermitean adjoint of  $\mathcal{T}$ .

We now observe that the Lippmann–Schwinger equation for  $T(z)$  may be written as

$$T(z) = \mathcal{V} - \mathcal{V}^* + (\mathcal{V} - \mathcal{V}^*) \mathcal{R}_0(z) T(z). \quad (\text{A.39})$$

With the help of the Lippmann–Schwinger equations for  $\mathcal{T}$

$$\mathcal{T}(\mathcal{H}_0^* + z) = \mathcal{V} + \mathcal{V}\mathcal{R}_0(z) \mathcal{T}(\mathcal{H}_0^* + z), \quad (\text{A.40})$$

$$\mathcal{T}^*(\mathcal{H}_0 + z^*) = \mathcal{V}^* - \mathcal{V}^*\mathcal{R}_0(z) \mathcal{T}^*(\mathcal{H}_0 + z^*), \quad (\text{A.41})$$

Equation (A.39) can be formally solved, and we obtain

$$T(z) = \mathcal{T} - \mathcal{T}^* - \mathcal{T}\mathcal{R}_0\mathcal{T}^* - \mathcal{T}^*\mathcal{R}_0\mathcal{T} + \Delta T, \quad (\text{A.42})$$

where

$$\begin{aligned} \Delta T &= \mathcal{T}^*\mathcal{R}_0\mathcal{T}\mathcal{R}_0(1 + \mathcal{T}^*\mathcal{R}_0\mathcal{T}\mathcal{R}_0)^{-1}\mathcal{T}^*(1 + \mathcal{R}_0\mathcal{T}) \\ &\quad - \mathcal{T}\mathcal{R}_0\mathcal{T}^*\mathcal{R}_0(1 + \mathcal{T}\mathcal{R}_0\mathcal{T}^*\mathcal{R}_0)^{-1}\mathcal{T}(1 - \mathcal{R}_0\mathcal{T}^*). \end{aligned} \quad (\text{A.43})$$

Because the correction term  $\Delta T$  turns out to be small, we obtain the approximate relation

$$T(z) \simeq \mathcal{T} - \mathcal{T}^* - \mathcal{T}\mathcal{R}_0\mathcal{T}^* - \mathcal{T}^*\mathcal{R}_0\mathcal{T}. \quad (\text{A.44})$$

This is the relation we use in the generalized Boltzmann equation with appropriate generalizations of the operators to a many-particle situation. Noting that

$$\mathcal{R}_0^*(z) = -\mathcal{R}_0(z) \quad (\text{A.45})$$

and using the optical theorem in scattering theory [6]

$$\mathcal{T}^*(\mathcal{H}_0) - \mathcal{T}(\mathcal{H}_0^*) = 2\pi i \mathcal{T}^*(\mathcal{H}_0^*) \delta(\mathcal{H}_0 - \mathcal{H}_0^*) \mathcal{T}(\mathcal{H}_0), \quad (\text{A.46})$$

Equation (A.44) can be written as [8, 24]

$$T(z) = 2\pi i \mathcal{T}^*(\mathcal{H}_0) \delta(\mathcal{H}_0 - \mathcal{H}_0^*) \mathcal{T}(\mathcal{H}_0^*) - 2\pi i \mathcal{T}^*(\mathcal{H}_0^*) \delta(\mathcal{H}_0 - \mathcal{H}_0^*) \mathcal{T}(\mathcal{H}_0). \quad (\text{A.47})$$

This implies that the transition probability  $W(x^*|x)$  in the collision term of the generalized Boltzmann equation (7.10) in Chap. 7 can be identified with

$$W(x^*|x) = 2\pi T^*(\mathcal{H}_0) \delta(\mathcal{H}_0 - \mathcal{H}_0^*) T(\mathcal{H}_0^*) \quad (\text{A.48})$$

if the quantum mechanical analog of  $W(x^*|x)$  is used. A similar identification can be made for the collision term of the generalized Boltzmann equation in Chap. 8, (8.20), if the formalism is suitably generalized to polyatomic fluids.

## B

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### The Constitutive Equation for Velocity

In this Appendix, the constitutive equation for the mean velocity is derived from a statistical mechanical viewpoint. Note that we have so far assumed the velocity constitutive equation on phenomenological grounds, but a statistical mechanical derivation of the constitutive equation is possible. This derivation clarifies the limits of validity of the phenomenological constitutive equation for the mean velocity.

The mean velocity is given by the formula

$$\rho \mathbf{u}(\mathbf{r}, t) = \left\langle \sum_{j=1}^N \mathbf{p}_j \delta(\mathbf{r}_j - \mathbf{r}) F_c^{(N)} \right\rangle, \quad (\text{B.1})$$

where

$$\rho(\mathbf{r}, t) = \left\langle \sum_{j=1}^N m \delta(\mathbf{r}_j - \mathbf{r}) F_c^{(N)} \right\rangle. \quad (\text{B.2})$$

The angular brackets, as before, denote the grand ensemble average.

To calculate the desired constitutive equation, we imagine a cluster of two molecules, say, particles 1 and 2. We then change variables for the pair:

$$\begin{aligned} \mathbf{r}_{12} &= \mathbf{r}_1 - \mathbf{r}_2, \\ \mathbf{R} &= \frac{1}{2}\mathbf{r}_1 + \frac{1}{2}\mathbf{r}_2 \end{aligned} \quad (\text{B.3})$$

Inverting the transformation, we find

$$\begin{aligned} \mathbf{r}_1 &= \mathbf{R} + \frac{1}{2}\mathbf{r}_{12}, \\ \mathbf{r}_2 &= \mathbf{R} - \frac{1}{2}\mathbf{r}_{12}. \end{aligned} \quad (\text{B.4})$$

Therefore momenta of particles are expressible as

$$\begin{aligned}\mathbf{p}_1 &= \frac{m}{M} \mathbf{P} + \mathbf{p}_{12}, \quad \mathbf{p}_2 = \frac{m}{M} \mathbf{P} - \mathbf{p}_{12}, \\ \mathbf{P} &= M \mathbf{R}, \quad \mathbf{p}_{12} = \mu \mathbf{r}_{12} (\mu = \frac{1}{2} m).\end{aligned}\tag{B.5}$$

Then the statistical mechanical formula for the mean velocity may be written as

$$\begin{aligned}\rho \mathbf{u}(\mathbf{r}, t) &= \int dx_1 \int dx_2 m \mathbf{v}_2 \delta(\mathbf{r}_2 - \mathbf{r}) f^{(2)}(x_1, x_2, t) \\ &= m \int d\mathbf{R} \int d\mathbf{r}_{12} \int d\mathbf{p}_1 \int d\mathbf{p}_2 \mathbf{v}_2 \delta\left(\mathbf{R} - \frac{1}{2} \mathbf{r}_{12} - \mathbf{r}\right) \\ &\quad \times \psi^{(2)}\left(\mathbf{p}_1, \mathbf{p}_2, \mathbf{R} + \frac{1}{2} \mathbf{r}_{12}, \mathbf{R} - \frac{1}{2} \mathbf{r}_{12}, t\right) \\ &\quad \times n\left(\mathbf{R} - \frac{1}{2} \mathbf{r}_{12}, t\right) n\left(\mathbf{R} + \frac{1}{2} \mathbf{r}_{12}, t\right) n^{(2)}(\mathbf{r}_{12}, t),\end{aligned}\tag{B.6}$$

where

$$\psi^{(2)}(x_1, x_2; t) = \phi(x_1, t) \phi(x_2, t) \phi^{(2)}(x_1, x_2; t).$$

See the main text for this mode of writing a pair distribution function.

We now define

$$\begin{aligned}\mathbf{V}\left(\mathbf{R} + \frac{1}{2} \mathbf{r}_{12}, \mathbf{R} - \frac{1}{2} \mathbf{r}_{12}, t\right) &= \int d\mathbf{p}_1 \int d\mathbf{p}_2 \mathbf{v}_2 \\ &\quad \times \psi^{(2)}\left(\mathbf{p}_1, \mathbf{p}_2, \mathbf{R} + \frac{1}{2} \mathbf{r}_{12}, \mathbf{R} - \frac{1}{2} \mathbf{r}_{12}, t\right).\end{aligned}\tag{B.7}$$

Physically, this is interpreted as the mean velocity of particle 2 located at  $\mathbf{r}_{12}$  from particle 1 at  $\mathbf{r}_1$  or, alternatively, from their center-of-mass position  $\mathbf{R}$ . The integral (B.7) may be estimated as follows: First cast it in the form,

$$\begin{aligned}\mathbf{V}\left(\mathbf{R} + \frac{1}{2} \mathbf{r}_{12}, \mathbf{R} - \frac{1}{2} \mathbf{r}_{12}, t\right) &= \frac{1}{m} \int d\mathbf{P} \int d\mathbf{p}_{12} \left(\frac{1}{2} \mathbf{P} - \mathbf{p}_{12}\right) \\ &\quad \times \psi^{(2)}\left(\mathbf{p}_1, \mathbf{p}_2, \mathbf{R} + \frac{1}{2} \mathbf{r}_{12}, \mathbf{R} - \frac{1}{2} \mathbf{r}_{12}, t\right) \\ &= \bar{\mathbf{V}} - \frac{1}{2} \int d\mathbf{P} \int d\mathbf{p}_{12} \dot{\mathbf{r}}_{12} \\ &\quad \times \psi^{(2)}\left(\mathbf{p}_1, \mathbf{p}_2, \mathbf{R} + \frac{1}{2} \mathbf{r}_{12}, \mathbf{R} - \frac{1}{2} \mathbf{r}_{12}, t\right).\end{aligned}$$

The second term on the right in the second equality is a mean relative velocity. This may be estimated approximately by  $\mathbf{r}_{12}/\tau$ , where  $\tau$  is the mean time during which the particle pair (1, 2) moves in the direction parallel to  $\mathbf{r}_{12}$ ,

that is, the mean flight time of particle 2. Thus, we obtain

$$\mathbf{V} \left( \mathbf{R} + \frac{1}{2} \mathbf{r}_{12}, \mathbf{R} - \frac{1}{2} \mathbf{r}_{12}, t \right) = \bar{\mathbf{V}} - \frac{1}{2\tau} \mathbf{r}_{12} = -\frac{1}{2\tau} \mathbf{r}_{12}, \quad (\text{B.8})$$

because  $\bar{\mathbf{V}} = 0$ . Because

$$\rho \mathbf{u}(\mathbf{r}, t) = m \int d\mathbf{r}_{12} \mathbf{V}(\mathbf{r} + \mathbf{r}_{12}, \mathbf{r}, t) n(\mathbf{r}, t) n(\mathbf{r} + \mathbf{r}_{12}) n^{(2)}(\mathbf{r}_{12}, t), \quad (\text{B.9})$$

it follows that

$$\begin{aligned} \rho \mathbf{u}(\mathbf{r}, t) &= -\frac{m}{2\tau} n(\mathbf{r}, t) \int d\mathbf{r}_{12} \mathbf{r}_{12} n(\mathbf{r} + \mathbf{r}_{12}) n^{(2)}(\mathbf{r}_{12}, t) \\ &= -\frac{m}{6\tau} n^2(\mathbf{r}, t) \int d\mathbf{r}_{12} \mathbf{r}_{12} \cdot \mathbf{r}_{12} n^{(2)}(\mathbf{r}_{12}, t) \nabla_{\mathbf{r}} n + \dots, \end{aligned}$$

and finally

$$\rho \mathbf{u} = -\frac{\rho}{6\tau} n(\mathbf{r}, t) \int d\mathbf{r}_{12} \mathbf{r}_{12} \cdot \mathbf{r}_{12} n^{(2)}(\mathbf{r}_{12}, t) \nabla_{\mathbf{r}} n + \dots. \quad (\text{B.10})$$

From this expression, the self-diffusion coefficient may be identified with the statistical mechanics formula

$$D = \frac{1}{6\tau} n^2(\mathbf{r}, t) \int d\mathbf{r}_{12} \mathbf{r}_{12} \cdot \mathbf{r}_{12} n^{(2)}(\mathbf{r}_{12}, t), \quad (\text{B.11})$$

and the mean velocity may be written as

$$\rho \mathbf{u}(\mathbf{r}, t) = -D \nabla_{\mathbf{r}} \rho + O[(\nabla_{\mathbf{r}} n)^2], \quad (\text{B.12})$$

which is the constitutive equation we set out to derive. Note that (B.11) is reminiscent of the form originally defined for  $D$  by Einstein.

If there is a temperature gradient in the fluid, then the number density depends on temperature, which varies from point to point in space. Therefore

$$\rho \mathbf{u}(\mathbf{r}, t) = -\frac{m}{2\tau} n(\mathbf{r}, t) \int d\mathbf{r}_{12} \mathbf{r}_{12} n[\mathbf{r} + \mathbf{r}_{12}, T(\mathbf{r} + \mathbf{r}_{12})] n^{(2)}(\mathbf{r}_{12}, t). \quad (\text{B.13})$$

Here the temperature dependence of  $n^{(2)}(\mathbf{r}_{12}, t)$  is suppressed because it is not an important factor. The density  $n[\mathbf{r} + \mathbf{r}_{12}, T(\mathbf{r} + \mathbf{r}_{12})]$  may be expanded in a series of  $\mathbf{r}$ . To the first order, we obtain

$$\rho \mathbf{u} = -D \nabla_{\mathbf{r}} \rho - D_T \nabla_{\mathbf{r}} T + O[(\nabla_{\mathbf{r}} n)^2], \quad (\text{B.14})$$

where

$$D_T = \frac{m}{6\tau} n(\mathbf{r}, t) \frac{\partial n}{\partial T} \int d\mathbf{r}_{12} \mathbf{r}_{12} \cdot \mathbf{r}_{12} n^{(2)}(\mathbf{r}_{12}, t). \quad (\text{B.15})$$

This is the thermal diffusion coefficient. If the flow occurs at constant pressure, then the expansion of the fluid is isobaric, and we have the relation

$$D_T = -m\alpha D, \quad (\text{B.16})$$

where  $\alpha$  is the local isobaric expansion coefficient

$$\alpha = -\frac{1}{n} \left( \frac{\partial n}{\partial T} \right)_p. \quad (\text{B.17})$$

It is interesting that the thermal diffusion coefficient is negative. It is known in the Chapman–Enskog theory that the thermal diffusion coefficient of gas is generally negative. (See [7], pp. 187–188.) The present formal result is consistent with the Chapman–Enskog theory for gases.

These constitutive equations derived from nonequilibrium statistical mechanics are used throughout the density fluctuation theory in the text.

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