

## 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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Eu, B.C.

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