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Introduction

1.1 What Is Kinetic Theory?

Kinetic theory is a branch of statistical mechanics that aims to derive expressions for the macroscopic properties of fluids in terms of the microscopic properties of the constituent particles. These properties include nonequilibrium quantities, such as diffusion coefficients and viscosities, which do not follow in a straightforward way from the standard techniques based on Boltzmann–Gibbs ensembles. The microscopic properties include single-particle properties, such as particle masses and sizes as well as the interactions between particles, and their interactions through external forces with the outside world, including boundaries. The methods of kinetic theory are based upon the laws of mechanics, either classical or quantum, that describe the motion of the system of particles.[1] However, kinetic theory is not based on solutions of these equations for the full system but rather on estimates of the average behavior of ensembles of mechanically identical systems that differ only in their initial conditions. In this respect, kinetic theory is properly thought of as a branch of statistical mechanics, since it uses statistical methods in order to determine the typical, or most likely, behaviors of systems of many particles. It had its origins almost three centuries ago in the work of D. Bernoulli (1738), who used a simple kinetic theory to derive the perfect gas equation of state. The first application of kinetic theory to transport phenomena may have been accomplished by J. J. Herapath (1847), who used arguments based on collision dynamics to explain experiments by T. Graham on the diffusion of gases through small holes. By the time of J. C. Maxwell's prediction that the viscosity of a gas is independent of density (1860), the use of kinetic theory to explain transport phenomena in gases was accepted by many workers.

   The aim of nonequilibrium statistical mechanics, including kinetic theory, to characterize macroscopic systems that are out of equilibrium requires it to focus

on dynamical processes taking place in the system. First of all, for particles that interact with short-range forces, these are collisions between the constituent particles or between the particles and the boundaries. In the case of particles that interact with long-range forces, such as in the interactions of charged particles, collective effects can dominate the dynamics. The particles of interest can be electrons, nuclei, atoms, molecules, excitations such as phonons, photons, colloidal particles, bits of dust, planets, galaxies, etc. In many cases, the boundaries may also be considered as a type of particle and treated as such in the basic equations. The possibility to treat such a wide variety of systems accounts for many modern applications of kinetic theory, many of which we will explore in this book.[2]

1.2 The Kinetic Theory of Gases

1.2.1 Dilute Gases

The development of kinetic theory began in the eighteenth century with the work of Daniel Bernoulli, who was able to show[3] in 1738 that the pressure of a dilute gas on its container is proportional to the mean square molecular velocity. The theory was further advanced in the first part of the nineteenth century by John Herapath (1820) and by John J. Waterston (1845). The work of these pioneers eventually led to the recognition of the connection between the thermodynamic temperature of a gas and the average kinetic energy of its molecules, which resulted in the well-known kinetic theory derivation of the perfect gas equation of state. It should be noted that this work was carried out at a time when the existence of atoms and molecules as individual particles with empty space between them was not at all obvious, and many prominent scientists at the time did not believe in them. In fact, the atomic picture of matter was not universally accepted until the early part of the twentieth century. The general acceptance of the atomic picture was due, among other things, to A. Einstein's explanation of Brownian motion in terms of fluctuations in a fluid composed of individual particles, followed by J. B. Perrin's quantitative confirmations of Einstein's predictions, and to the successful explanations of thermodynamic and transport properties of solids and fluids based upon statistical thermodynamics and the kinetic theory of gases. The lack of universal acceptance of the atomic picture notwithstanding, the kinetic theory of gases became a central pillar of physics with the work of Maxwell and L. Boltzmann in the later part of the nineteenth century. Today, the methods developed by Herapath and Waterston, based on collisions of particles with each other and with the walls of the container, are often used to provide elementary derivations of the expressions

for thermodynamic and transport properties of rarefied and dilute gases [71, 72].[4] They form the subject matter of elementary books on the kinetic theory of gases.

Maxwell and Boltzmann used statistical methods to compute the properties of gases, recognizing that the random motion of gas molecules could be best described by distribution functions. In addition to giving the equilibrium form of the velocity distribution function for gases, Maxwell derived equations for the transport of mass, energy, and momentum for a dilute gas. For a fictitious gas of molecules that interact with central, two-body repulsive forces proportional to the inverse fifth power of the distance between the centers of a pair of particles, the so-called Maxwell molecules, Maxwell was able to derive explicit expressions for the transport coefficients appearing in the Navier–Stokes equations [465]. In particular, he was able to show that for dilute gases, the coefficients of shear viscosity and thermal conductivity would be independent of the gas density, in agreement with experimental results. The most important advance in the nineteenth century, and one that set the stage for almost all of the later developments in kinetic theory and its many applications, was made by Boltzmann in 1872 [57]. He used mechanical and statistical arguments to obtain an equation – the Boltzmann transport equation – that describes the irreversible time evolution of the single-particle velocity and position distribution function for a dilute gas not in equilibrium. The Boltzmann equation is extremely successful as a tool for calculating the transport properties of dilute gases and gas mixtures, so much so that the results obtained are often used to test different models of pair potentials by comparing theoretical values for given potentials with experimental results.

The first systematic calculations of transport properties of dilute gases and their mixtures based on the Boltzmann equation were carried out independently by S. Chapman [88] and by D. Enskog [175, 176] in 1917.[5] They used this equation as a starting point for a derivation of the Navier–Stokes equations of fluid dynamics and obtained explicit expressions for the transport coefficients appearing in these equations. On the basis of his theoretical work on gas mixtures, Enskog discovered the phenomenon of thermal diffusion, which – years later – provided a method for separation of isotopes of uranium for use in atomic bombs and nuclear reactors [558].

As we will discuss in greater detail in Chapter 2, the Boltzmann equation is not invariant under a time-reversal transformation where all velocities and the direction of time change sign. In fact, Boltzmann constructed a function out of the single-particle distribution function, called the H-function, which decreases monotonically in time unless the gas is at equilibrium. Of course, this means that the Boltzmann equation is not a consequence of only the applications of the basic

equations of mechanics to behavior of dilute gases. Instead, there is embedded in Boltzmann's derivation a stochastic assumption, the Stosszahlansatz, that breaks the time-reversal symmetry of the description of the dynamics of the gas. Although the Stosszahlansatz is not a purely mechanical statement, it reflects the expected and typical behavior of a dilute gas that is not in equilibrium. It can also be thought of as statement about the initial state of the gas that is assumed to be propagated forward in time.

1.2.2 Enskog's Extension of the Boltzmann Equation to Dense, Hard Sphere Gases

The first important extension of the Boltzmann equation to higher densities was made by D. Enskog [175, 176] in 1922. He considered only hard-sphere gases and modified Boltzmann's arguments in a way that includes some but not all of the effects of higher densities. First of all, Enskog took into account excluded volume effects. At finite densities, the presence of other particles reducing the available free volume for a given pair enhances the probability for a collision between this pair. In addition, Enskog realized that the finite size of the particles, coupled with the hard-sphere potential, allows an instantaneous transfer of momentum and energy over a distance of the diameter of a sphere at each binary collision. The inclusion of excluded volume and collisional transfer effects allows the Enskog equation to apply to very dense hard-sphere fluids. The Enskog theory is only an approximation to a kinetic equation for dense gases, but it provides useful estimates for nonequilibrium properties of such gases. As we will see further on, Enskog's methods need to be refined when applied to mixtures of hard spheres; otherwise, one obtains expressions for transport coefficients that are not consistent with the Onsager reciprocal relations [508, 509, 22]. This refinement, now called the *revised Enskog equation*, was obtained by H. van Beijeren and M. H. Ernst in 1973 [644, 645]. It leads to the same transport coefficients as the usual Enskog equation for pure hard-sphere gases and to transport coefficients that satisfy the Onsager relations for mixtures of hard spheres. The Enskog and revised Enskog equations can be applied to other types of monatomic particles besides hard spheres if one replaces the correct interaction potentials by "effective" hard-sphere interactions using effective hard-sphere radii obtained by finding the best fit of some thermodynamic property of the system to a hard-sphere model. In many cases, the results so obtained are in good agreement with experimental results. As we discuss later in this book, the revised Enskog theory is also capable of describing some properties of hard-sphere solids, since the equations of an elastic solid can be obtained from it, with approximate expressions for the elastic coefficients, the heat conduction coefficient, and the sound attenuation constants.

1.2.3 Derivations of the Boltzmann Equation Using the Liouville Equation

In order to derive the Boltzmann equation and to justify the Stosszahlansatz, one must start from some more fundamental equation for the distribution functions characterizing the gas and then obtain the Boltzmann equation by making some plausible [406] and physically motivated assumptions. Such a derivation is also important and even necessary for extending the Boltzmann equation in a systematic way to dense gases. The natural starting point is the Liouville equation [549], which describes the time development of the complete N-particle distribution function for a gas of N particles. This equation is reversible and follows directly from the mechanical equations of motion. While it was long recognized that a derivation of the Boltzmann equation should be based upon the Liouville equation, it was not until the work of N. N. Bogoliubov [55] in 1947, completed later by M. S. Green [270, 271] and by E. G. D. Cohen [98, 99, 100, 101, 102], that satisfactory derivations of the Boltzmann equation were given and progress was made on the rather intricate problem of generalizing it to higher densities [274, 153, 154].[6]

1.2.4 Green–Kubo Formulae

Concurrently with the developments in the work to generalize the Boltzmann equation to higher densities, it was realized that the same methods are extremely useful for the evaluation of the Green–Kubo expressions for transport coefficients, for systems of moderately dense gases. These expressions, derived by M. S. Green [268, 269] and by R. Kubo [405, 408] in the 1950s, express the hydrodynamic transport coefficients as time integrals of equilibrium time correlations of microscopic currents. The Green–Kubo formulae are quite general [709, 608, 705], not restricted to dilute or moderately dense gases, and ideally suited for computer-simulated molecular dynamics [312, 548]. Methods have been developed for the evaluation of the time correlation functions, and results so obtained have been very important for the development and testing of detailed theories of transport phenomena in fluids. The time correlation function method and the Boltzmann equation lead to identical results when the Green–Kubo formulae are applied to dilute gases.[7]

1.2.5 Divergences in the Virial Expansions of Transport Coefficients

The efforts to generalize the Boltzmann equation to higher densities in a systematic way produced a number of discoveries that led to deeper understanding of nonequilibrium processes in gases, and in fluids in general. These results, in essence, opened a new era in the development of kinetic theory.[8] In contrast to

the essentially instantaneous binary collisions that are taken into account in the Boltzmann equation, the higher-density corrections are determined by dynamical events that take place among groups of more than two particles [274, 273, 153, 154]. These can involve much longer time scales, typically on the order of a few mean free times. As a result of these dynamical events taking place in a gas – or, more generally, a fluid – *memory effects* make their appearance in nonequilibrium processes, producing striking results that have no counterparts in equilibrium statistical mechanics. For example, the thermodynamic properties of dense gases over a wide range of gas densities are well represented by virial expansions [549], which are series expansions in powers of the gas density. However, no such virial-type expansions – that is, expansions in powers of the density – exist for transport coefficients. If one assumes that such a density expansion is possible, then one finds that only the first few powers have finite coefficients, while all further coefficients are divergent [677, 580, 581, 154, 256]. The coefficient of each power in the density is determined by the dynamics of a fixed number of particles in an infinite space. The first term in such a virial-like expansion is determined by the dynamics of two particles, the next power is determined by the dynamics of three particles, and the number of particles in the group increases successively for the coefficients of successively higher powers of the density. For two-dimensional systems, only the first term, the Boltzmann contribution from binary collisions, is finite. The coefficients of all higher powers of the density diverge. For three-dimensional systems, the first two terms, namely the two-particle and three-particle terms, are finite. The coefficients of all higher powers diverge.[9] The divergences are due to sequences of correlated collisions that allow for correlations among the particles to extend over large distances and long times.[10] These correlations do not exist when the gas is in equilibrium, but for systems not in equilibrium, they are responsible for the memory effects mentioned earlier. That long-range correlations are present in nonequilibrium fluids has been well confirmed by light scattering experiments [323, 432, 418].

1.2.6 Mode-Coupling Theory and Long-Time Tails

The memory effects lead directly to what are often called *mode-coupling effects* [218, 333, 346, 59, 251]. That is to say, the dominant parts of the memory effects at long times, as will be made more precise later, give rise to a special structure in the kinetic and hydrodynamic equations, in which combinations of what will be called *microscopic hydrodynamic modes* appear.[11] Much of this book will be devoted to the properties of these modes and their effects on nonequilibrium processes. The microscopic hydrodynamical modes are best thought of as the slowest-decaying normal modes of the operator that describes the time dependence of a

spatially nonuniform, nonequilibrium distribution function. Typically these modes describe the time decays of microscopic fluctuations in an equilibrium fluid, or a fluid in a nonequilibrium stationary state, via long-wavelength microscopic collective excitations of the fluid. These collective modes can be classified as shear, sound, thermal, and diffusive modes, and combinations of two or more of them arise naturally in the equations of kinetic theory beyond the Boltzmann, binary collision approximation.

Mode-coupling effects first made their appearance in the context of a theory for the anomalous behavior of transport coefficients near the critical point of gas–liquid phase transitions developed by M. Fixman [218] and by L. P. Kadanoff and J. Swift [333]. In a different direction, people working in kinetic theory – including R. Goldman and E. A. Frieman [256], Y. Pomeau [533, 534, 556, 536], and J. R. Dorfman and E. G. D. Cohen [157, 156, 155] – obtained mode-coupling contributions to the time correlation functions as a consequence of the resummation techniques needed for the renormalization of the divergences in the density expansions of transport coefficients carried out by K. Kawasaki and I. Oppenheim [350]. Kinetic theory is only one approach to obtain expressions of the mode-coupling form. Mode-coupling theories can also be obtained using more general arguments based on the assumption that the large-distance or small-wave-number parts of the microscopic densities of particles, momentum, and energy obey macroscopic hydrodynamic equations. The main observation from this work is that long-range, long-time, dynamically produced correlations exist in a nonequilibrium fluid and are manifested in the existence of algebraic decays in time correlation functions for long times and can be observed in light scattering by a fluid with a stationary temperature gradient, for example.

Dorfman and Cohen [157, 156, 155] showed that these mode-coupling contributions to the time correlation functions, as obtained from kinetic theory, could explain some remarkable results obtained by B. J. Alder and T. E. Wainwright using computer-simulated molecular dynamics. Alder and Wainwright showed that the velocity autocorrelation function that determines the coefficient of self-diffusion via the Green–Kubo relations decays algebraically with time t as $(t/t_0)^{-d/2}$, where d is the number of spatial dimensions of the system and t_0 is some characteristic microscopic time such as the mean free time between collisions for a particle in the gas [9, 10, 673]. These algebraic decays, generally called *long-time tails*, have many important consequences, both experimental and theoretical, which will be discussed in this book.[12] Among other things, the slow inverse time decay of the time correlation functions for two-dimensional systems implies that the transport coefficients appearing in the linearized Navier–Stokes equations for two-dimensional systems are divergent. Although for three-dimensional systems the structure of Navier–Stokes equations is unaffected by the long-time tails, since

the Green–Kubo expressions are convergent, a very similar divergence difficulty appears in the higher-order hydrodynamic equations, such as the Burnett and super-Burnett equations, and leads to a complex description of higher-order hydrodynamics. As a consequence, we learn that for both two- and three-dimensional systems, the equations of fluid dynamics are intrinsically nonanalytic in the gradients of the hydrodynamic fields and may contain effects of the boundaries in the equations themselves. Experimental measurements have confirmed the presence of nonanalytic terms in hydrodynamic equations. For example, the presence of fractional powers of the wave number and related mode-coupling effects have been observed in neutron scattering experiments on fluids [130, 129, 491]. In other cases, such as heat flow in a nonequilibrium stationary state with a temperature gradient, mode-coupling effects closely related to the long-time tails produce long-range spatial correlations that have a very strong influence on the properties of fluctuations of the hydrodynamic fields in nonequilibrium steady states. These effects can be orders of magnitude larger than the effects of static correlations in the fluid. The theory for these fluctuations has been confirmed by very careful light scattering experiments, as discussed in the next subsection [371, 374, 323].

Finally, it should be mentioned that for some complex fluids and for certain magnetic systems, the effects of the long-time tails are even more dramatic. In both smectic and cholesteric liquid crystals [470, 120] and in the hydrodynamic description of helimagnets [369], there are long-range static correlations due to a continuous broken symmetry (Goldstone's theorem) that effectively multiply and amplify the long-time tails. In particular, for these systems, the lower critical dimension of two for ordinary fluids is replaced by four. This, in turn, leads to transport coefficients that diverge in three dimensions for low frequencies as $1/\omega$. That is, for these systems, even in bulk systems, the leading order hydrodynamic description breaks down.

1.2.7 Mode-Coupling Theory and Hydrodynamic Fluctuations

Mode-coupling theories can be applied to many physical situations. We will have occasion in this book to discuss their application to light scattering by fluids in nonequilibrium stationary states, which led to predictions of, among other effects, a striking modification of the strength of the central Rayleigh peak [364, 371, 372, 373, 374, 160, 562, 627], since verified experimentally by J. V. Sengers and co-workers [418, 323].[13] It is also worth mentioning that the application of kinetic theory of moderately dense gases leading to the mode-coupling equations is closely related to the derivation of the Balescu–Lenard–Guernsey (BLG) equation used in the theory of moderately dense plasmas [578].

An important example of the application of mode-coupling theory is to the theory for the behavior of glassy materials and to the theory of the liquid–glass transition [251]. Here the central idea is to construct a self-consistent formulation of mode-coupling theory whereby the hydrodynamic properties of the system under study are determined by integrals that depend upon the same hydrodynamic properties, so that solutions can only be obtained in some self-consistent way. A remarkable feature of such solutions is that, while based upon ad hoc approximations, these theories provide a useful description of the transition of a liquid to an amorphous solid, or glass, and of aspects of the behavior of such a glass [251]. The fluid–glass transition seems to be a dynamical phase transition in the sense that the behavior of the system is sensitive to the time scales associated with external forces applied to the system. In such a case, the system may exhibit some form of hysteresis. Thus, the memory effects incorporated in mode-coupling theory may play an important role in establishing the correlations responsible for the phase transition. It is interesting to note that an exact solution of the dynamics of a system of hard spheres in infinite dimensions has been shown to have a mode-coupling-like glass transition [90, 451]. Further, the complicated features of the many possible metastable states in this system have also been determined. These results are consistent with the RFOT (random first-order transition) theory of the glass transition that was introduced some time ago [389, 519].

It is important to mention that mode-coupling theory can also be obtained in a variety of ways that do not require kinetic theory. The initial work of L. P. Kadanoff and J. Swift [333] was based upon an insightful and clever ansatz for the hydrodynamic modes of an N-particle Liouville operator.[14] These authors took advantage of the fact that the Liouville operator is a linear differential operator. As a result, the product of two or more eigenfunctions is also an eigenfunction. This provides the mechanism for the coupling of two or more hydrodynamic modes.

Perhaps the method most widely used to develop mode-coupling theory is the method of *fluctuating hydrodynamics* [412, 576, 323]. One assumes that the microscopic densities of particles, momentum, and energy in a fluid obey nonlinear Navier–Stokes-type equations in which white noise fluctuations are added to the dissipative fluxes. The main results of mode-coupling theory are obtained as additional terms in the hydrodynamic equations by averaging over the fluctuations. This approach to mode-coupling theory is algebraically simpler than kinetic theory and produces the same leading terms as one obtains by kinetic theory. However, it is not a systematic approach to nonequilibrium processes in fluids, and kinetic theory provides additional terms, however small, that are not obtained by the use of fluctuating hydrodynamics.

1.2.8 Model Systems

As with most, if not all, issues in statistical physics, a great deal can be learned by considering simplified models. Such models are constructed so as to exhibit some central features of more complex and realistic systems and yet are simple enough to allow a more detailed treatment than might be possible for more complicated systems. Kinetic theory utilizes many such model systems. One prominent model already mentioned is the hard-sphere gas. This model can be studied in any number of dimensions and has the advantage that the collisions between particles are all instantaneous, binary collisions [158, 190]. Mixtures of hard spheres are also convenient models for study. The first important extension of the Boltzmann equation to higher densities, the Enskog theory, was specifically formulated for hard-sphere particles for which both excluded volume effects and collisional transport of momentum and energy can be accounted for in a straightforward way [175, 176, 89, 644, 645]. While the Enskog theory does not provide a systematic extension of the Boltzmann equation to higher densities, and it does not account for many dynamical processes taking place in the gas, it nevertheless gives a good representation of experimental data for dense fluids, provided one uses an appropriate value of an effective hard-sphere radius for the particles of the real gas under study.[15] Another version of the Boltzmann equation is the lattice Boltzmann equation [37, 684, 615]. This is a discretized version of the Boltzmann equation appropriate for a system consisting of a collection of particles moving on a lattice. The particles may jump from one site on the lattice to another at discrete times, and particles approaching the same lattice point from different directions collide with each other according to a set of collision rules, which may be either deterministic or probabilistic. All possible particle velocities are directed along the various bonds of the lattice and remain so after each collision. Such a gas is called a cellular automata lattice gas (CALG) [235, 332, 58, 684, 565]. A CALG is easily simulated on a computer since the dynamics can be reduced to the simple integer operations of a Boolean algebra. It was thought at one time that CALGs would provide an efficient way to simulate complicated hydrodynamic flows, and they attracted a great deal of attention for this reason. However, it became clear that some of the early hopes were too optimistic. Nevertheless, CALGs are indeed useful for studying such flows on a computer, and the kinetic theory for them has been studied in some detail.

A mixture of particular interest for the development of kinetic theory is the *Lorentz gas*. This is a binary mixture of two gases, one very heavy and one very light. This model was used by H. A. Lorentz [440, 89] as a way to understand the motion of electrons in metals and to develop a theoretical expression for the resistance of a wire. One limiting case of the model that has been studied in great depth, both theoretically and by means of computer simulations, is the case where the heavy particles are fixed in space (that is, infinitely heavy), and the density

of the light particles is so low that they can be considered as independent and not interacting with each other[16] [69, 70, 299, 48, 617]. One particular version of Lorentz-type models was invented by P. and T. Ehrenfest to clarify and illustrate the assumptions made by Boltzmann in his derivation of the Boltzmann transport equation. In the Ehrenfest model, also known as the *wind-tree model*, the fixed particles (or "trees") are squares in a plane with their diagonals oriented along the *x* and *y* coordinate axes in the plane [173]. The moving particles (or "wind particles") are restricted to have velocities only in the four directions along the coordinate axes ($\pm x$ and $\pm y$). At each collision of a wind particle with a tree, the particle's speed remains constant, but its direction is rotated by $\pm \pi/2$ radians, depending upon the face of the tree with which it collides.

It was discovered by E. H. Hauge and E. G. D. Cohen that, if the trees are allowed to overlap each other in the plane, the model becomes sub-diffusive even at very low densities, and the Boltzmann equation does not apply to it [300, 301]. For all the versions of the Lorentz gas that have been studied, including the wind-tree model, there are interesting long-time tail phenomena taking place that differ in some crucial ways from their counterparts in a pure gas of interacting particles [70, 69]. The quantum Lorentz gas [416, 557, 381, 380, 29] exhibits the phenomenon of *localization*, which means that, under certain circumstances, particles do not diffuse through the system, even when the classical limit of the motion is diffusive. Localization in quantum Lorentz gases is closely related to the long-time tail effects in classical gases [422, 29]. Quantum Lorentz gases have an important application in condensed matter physics, where they are used to understand the behavior of electron transport in disordered systems, for which there is an abundance of experimental data on transport properties.

Another example of a binary mixture is the *Rayleigh model*. Here there is one heavy particle moving in a gas of much lighter particles. The light particles can be taken as either not interacting with each other or with mutual interactions, but, in any case, the light particles do interact with the heavy particle [614]. The Rayleigh model with interactions between the gas particles is a useful model for Brownian motion. In all of these models, a further simplification is possible by making all interactions hard-sphere-like interactions – that is, only instantaneous, binary collisions take place. A version of the Rayleigh model that has attracted considerable attention is the *piston model*, in which the heavy particle is a piston in a tube with gases on either side of it in the tube [617, 433, 93].

1.2.9 Dilute Quantum Gases

A model system of considerable interest is a weakly interacting quantum Bose–Einstein gas. Since such a system undergoes an equilibrium phase transition to

a superfluid phase, the description of the nonequilibrium behavior of the gas near the Bose–Einstein phase transition is an interesting challenge for kinetic theory [385, 382, 384, 529, 530, 431, 524, 278, 537, 626]. The kinetic theory of these weakly interacting quantum gases became particularly important over recent decades because of the experimental realization of such gases and the experimental verification of their Bose–Einstein phase transition. Here we will describe some of the main features and show that below the Bose–Einstein phase transition, the hydrodynamic behavior of such a gas is described by the Landau–Khalatnikov two-fluid equations [438, 545], the two fluids being the normal and superfluid components of the gas.

1.3 Further Applications of Kinetic Theory

By now, it is well known that the methods of kinetic theory, including mode-coupling theory, can be applied to a wide range of topics in fluid, plasma, and colloid physics. Among the topics to which kinetic theory has been applied are the closely related phenomena of Stokes flow around large solid bodies such as spheres and cylinders [637, 638, 574, 80, 575, 478, 586], the motion of Brownian [52, 50] particles in fluids, the motion of ions in solution [340, 341], and the motion of colloidal particles in fluid suspensions [104, 108, 316]. All of these systems have a fundamentally hydrodynamic structure whose source is the interactions of macroscopically large particles with the much smaller particles that make up the surrounding fluid or with each other. The flow of a gas around a large macroscopic object such as a sphere or a cylinder, for example, can be described as a function of a dimensionless parameter – in this case, the Knudsen number, which is the ratio of the mean free path of the surrounding gas molecules to some characteristic size of the object. Kinetic theory has been used with great success to describe the dynamics, for large Knudsen numbers, of rarefied gases [264, 598, 281, 84] and has been extended, as mentioned before, to describe hydrodynamic flow, at small Knudsen numbers, where one recovers the classic results for the flow based upon the applications of the Navier–Stokes equations. Kinetic theory for gases in the small Knudsen number regime has been used to describe the diffusion of a large Brownian particle in a dilute gas. The treatment of Brownian motion often begins with the Langevin equation, where the equation of motion for the particle includes the effects of hydrodynamic friction due to the surrounding fluid. In the Langevin theory, a fluctuating term is added to the equation of motion, which is supposed to account for the fact that the collisions of the Brownian particle with the gas molecules are random, and only the average motion can be described by a frictional force. L. Landau and E. M. Lifshitz had the idea of adding fluctuating terms to

the linearized hydrodynamic equations [412], an idea that was later generalized by R. Zwanzig and M. Bixon [42] as well as by R. Fox and G. E. Uhlenbeck [230, 231], who explored the consequences of adding noise terms to the linearized Boltzmann equation. The addition of such noise terms makes it possible to construct a theory for the macroscopic fluctuations of density in a fluid, the results of which can be used to make predictions about the scattering of light by a fluid under various circumstances [38]. This is of special interest because light scattering experiments are important methods for the study of fluid properties, and provide experimental ways of testing and checking some of the predictions of kinetic theory.

The motions of ions and colloidal particles are often affected by electrodynamic interactions produced by the charges on the particles. Treatment of such interactions leads naturally to a treatment of plasmas where nonequilibrium behavior is almost entirely determined by the Coulomb interactions of the charged particles. The basic kinetic equations of nonequilibrium plasmas are the Vlasov equation and the Balescu–Lenard–Guernsey (BLG) equations [656, 578]. The Vlasov equation, unlike the Boltzmann equation, is time reversible. Nevertheless, it exhibits solutions that decay in time, associated with the phenomenon of *Landau damping*. This apparently paradoxical situation – a time-reversible equation with time-irreversible solutions – is resolved by a careful consideration of the function spaces in which these solutions are embedded. In addition to its importance for plasma physics, the BLG equations are also interesting because they are the analog in plasma physics of the generalized Boltzmann equation with mode-coupling contributions, valid for neutral particles interacting with short-ranged potentials. Due to space limitations, we will not cover colloids and plasmas in this book, but we refer the interested reader to some basic literature [18, 19, 455].

1.3.1 Granular Materials

Some time ago, it was realized that the Boltzmann equation could be applied to obtain a theory for the behavior of granular gases – that is, gases whose particles make inelastic collisions with each other – and the system loses energy to the environment. It is not difficult to obtain the Boltzmann equation for particles that suffer inelastic collisions when one can specify the dynamics of an inelastic binary collision. In general, this is not a simple requirement, since binary collisions – both elastic and inelastic – can have a very complex dynamics, but considerable progress can be made by using tractable and highly simplified models for inelastic collisions [66, 25, 401]. One interesting application of the kinetic theory for granular, inelastic media is to the theory for planetary rings [262, 208].

1.3.2 Chaotic Dynamics

Kinetic theory has recently been applied in a new context – *dynamical systems theory*. Dynamical systems theory attempts to understand the very complicated chaotic motions typical of classical, nonlinear mechanical systems. Such systems, although mechanically reversible and deterministic, have the property that the phase-space trajectories of two systems that start from infinitesimally nearby points in phase space, separate exponentially with time. One consequence of this exponential separation is that a small uncertainty in the specification of the initial state of such a system will lead to an exponential growth of the uncertainty in the location of the phase point with time. The rate of the growth is characterized by a set of exponents called *Lyapunov exponents*. Usually, a system is called *chaotic* if it has at least one positive Lyapunov exponent [569, 513, 243, 152].

A group of mathematicians including Ya. G. Sinai, L. A. Bunimovich, N. Chernov [592, 593], D. Szasz [616], and N. Simanyi [591, 590] have given proofs of the ergodicity of systems of hard-sphere Lorentz gases with d-dimensional spheres as fixed scatterers with $d \geq 2$, and, under certain general conditions, of hard-sphere gases as well [487]. While ergodicity is generally not considered to be essential for the applications of statistical mechanics to such systems, these proofs do suggest that these hard-ball systems have interesting dynamical properties and are, in fact, chaotic. Ya. G. Sinai was the first to establish this line of approach to ergodicity of hard-sphere systems [593, 592]. As we mention later, kinetic theory can be used to calculate Lyapunov exponents and Kolmogorov–Sinai entropies of Lorentz and hard-sphere gases. These studies, while not rigorous, provide evidence that such systems are chaotic and their chaotic properties are accessible to calculations. Computer simulations by P. Gaspard, F. Baras [244, 245], H. Posch, C. Dellago, C. Forster [142], and others have verified, as much as is possible by computer studies, the chaotic nature of these systems and given values for Lyapunov exponents, Kolmogorov–Sinai entropies, topological pressures, and related quantities that characterize their dynamical behavior.

On the other hand, V. Rom-Kedar, D. Turaev [629, 560], and also V. Donnay[148] have shown that if the hard-sphere potential is softened, elliptic islands with positive measure appear in the phase space of these systems. These islands spoil the ergodicity, and their appearance means that not all starting points will exhibit chaotic behavior. For non-integrable systems at high enough energy, it is expected that the fraction of the energy shell in phase space taken up by the elliptic islands is an exponentially decaying function of particle number (at fixed particle and energy density), but to our knowledge, no proofs of this are known. It is not known what conditions a non-hard-sphere potential must satisfy in order that the motion of a system of particles with interactions specified by this potential will be chaotic for

almost all initial points on an energy shell. It is known that not all such potentials lead to elliptic islands in phase space. For instance, A. Knauf [395] has shown that a Lorentz gas where the scatterers are placed on a square lattice and interact with the moving particles via repulsive Yukawa potentials is also a chaotic system, provided the moving particles have sufficiently high energies.

Here we will show how kinetic theory can be used to calculate the dynamical properties of dilute, random hard-sphere Lorentz gases systems. Similar kinetic theory methods, such as the Boltzmann equation and others based on collision dynamics, can be used to extend the work presented here to calculate dynamical properties of dilute hard-sphere gases [135, 132, 134, 133, 663]. We shall be able to obtain expressions for Lyapunov exponents for Lorentz gases with an equilibrium distribution of moving particles as well as for Lorentz gases in a thermostatted electric field [639, 640, 165, 642, 417, 641]. In those cases where comparisons with computer simulations are possible, the agreement between kinetic theory and computer simulation results is excellent. Such results indicate that the systems we study are indeed chaotic but do not constitute mathematical proofs.

1.4 Outline of This Book

Chapters 2, 3, and 4 are devoted to the Boltzmann equation for dilute gases and dilute gas mixtures. We begin in Chapter 2 with Boltzmann's heuristic derivation of this equation. One feature of our presentation is that we incorporate boundary effects directly into the Boltzmann equation by modeling the boundary as a kind of "super-particle" with which the gas particles collide, in addition to their collisions with other particles. Then we prove that the Boltzmann entropy, the negative of the Boltzmann H-function, is monotonically non-decreasing with time, provided there is no heat flowing out of the system. Heat flow will arise naturally in this proof as a result of the way we incorporate the boundaries in the Boltzmann equation. To make this result somewhat less mysterious, especially for those readers encountering the H-theorem for the first time, we will explain the various assumptions that are made in the course of this derivation and discuss the time-symmetry-breaking assumption responsible for the irreversibility of this equation. Simple model systems have been used to clarify and illustrate the ideas, among them the Ehrenfest wind-tree model [173] and the Kac ring model [329]. Here we will discuss the Kac ring model in some detail. In Chapter 3, we present the Chapman–Enskog method for constructing solutions to the Boltzmann equation that describe hydrodynamic flows. We derive the Navier–Stokes equations and obtain expressions for transport coefficients, in particular the coefficients of shear viscosity and thermal conductivity, appropriate for monatomic gases at low densities. At this

point, we summarize the experimental support for the Boltzmann equation and describe various applications of it for hydrodynamic processes. We also discuss the boundary conditions appropriate for various flows and explain how they may be obtained from the Boltzmann equation coupled with models of gas–surface interactions. In Chapter 4, the Chapman–Enskog method is applied to the Boltzmann equation for dilute gas mixtures, and the Onsager reciprocal relations are discussed.

Next, in Chapter 5, we consider a very particular and very useful mixture, the dilute Lorentz gas. As described earlier, this consists of non-interacting particles that move among and collide with a collection of fixed scatterers placed randomly in space, with their average separation distance large compared to their size. This model is often used to study the motion of classical electrons in an amorphous solid. In Chapter 6, we discuss the Liouville equation for both general repulsive potentials and for hard-sphere systems. There we present the BBGKY hierarchy equations, which – in later chapters – will provide the statistical mechanical foundations for the extension of the Boltzmann equation to higher densities. In Chapter 6, we will also give a careful analysis of the dynamics of hard-sphere particles, which will be used as a model system for our later work on dense gases. An earlier and widely used approximate theory for transport in dense hard-sphere fluids, due to Enskog, with the necessary modifications due to H. van Beijeren and Ernst [644, 645], is presented in Chapter 7. Chapter 8 is concerned with the effects of adding noise terms to the linearized Boltzmann equation, a la the Langevin equation, as a way of correcting for the averaging used when deriving the Boltzmann equation. This allows for a treatment of density and other fluctuations in a gas and provides the basis for a description of the scattering of light by the gas.

Two chapters are devoted to the nonequilibrium properties of systems that have been the focus of much activity, namely granular gases and quantum gases including weakly interacting, condensed Bose–Einstein gases. Chapter 9 is devoted to classical dilute gases of particles that suffer inelastic collisions and lose energy to the environment. The latter systems, a part of the general field of granular matter, also exhibit interesting behavior, and the general topic has important applications – among others, to systems of interest for astrophysics, such as planetary rings. Dilute quantum gases, Bose–Einstein gases, below the superfluid phase transition are discussed in Chapter 10.

The next three chapters are devoted to the kinetic theory of moderately dense gases, in particular the microscopic foundations, and applications of mode-coupling theory. In Chapter 11, we describe nonequilibrium cluster expansions that provide the foundations for extending the Boltzmann equation in a systematic way to higher densities. These methods allow for a virial expansion of the generalized Boltzmann equation where the successive powers of the density take into

account dynamical events involving groups of two, three, and so on, particles. As discussed in Chapter 12, virial expansion methods fail for nonequilibrium gases because all but the first few terms in the virial expansion contain secular divergences in time. Resummations designed to cure these divergence problems due to K. Kawasaki and I. Oppenheim [350] are presented in this chapter. When applied to the density dependence of the various transport coefficients, the resummation leads to the appearance of logarithms in the density expansions of transport coefficients. In Chapter 13, we show that the resummations provide a microscopic basis for mode-coupling theory, which, in turn, leads to a kinetic theory description of long-time tails in the Green–Kubo time correlation functions. The presence of the long-time tails shows that there are serious problems in providing a successful foundation for the equations of hydrodynamics, especially, but not exclusively, for two dimensional gases.

The following chapter, Chapter 14, is the final technical chapter. It is devoted to the efforts to reformulate the equations of hydrodynamics for both two- and three-dimensional systems in the light of the difficulties due to the existence of long-range spatial and long-time temporal correlations in the gas produced by sequences of correlated collisions and that are ignored in both the Boltzmann and Enskog equations. This chapter concludes with a discussion of one of the central results in the theory of nonequilibrium processes in fluids, the theory leading to the major enhancement of the central, Rayleigh peak, in the small-angle scattering of light by a fluid maintained in a nonequilibrium stationary state. We conclude the book in Chapter 15 with brief discussions of some of the many applications, some very recent, of kinetic theory that are not covered in the book and with final thoughts on some related developments in cosmology.

The mathematical methods used here are not rigorous. Rigorous results have been obtained for certain areas covered in this book. In particular, there is a large mathematical literature on the existence of solutions of the Boltzmann equation under various conditions, as well as for the ergodic properties of various types of hard-sphere gases. When appropriate, we provide references to the literature so that the interested reader can explore the mathematical discussions at greater depth.

Notes

1 Standard references for the kinetic theory of gases, apart from textbooks, include S. Chapman and T. G. Cowling [89]; H. Grad [265]; E G. D. Cohen [103]; H. Spohn [606]; J. H. Ferziger and H. G. Kaper [215]; C. Cercignani [79, 81, 83, 85]; P. Résibois and M. de Leener [555]; P. Schram [578]; and P. L. Krapivsky, S. Redner, and A. Ben-Naim [401]; among many others.
2 This book is a greatly expanded version of a review article that two of us published in 1976, several years before a number of topics discussed here had been developed [164]. In view of the many advances and applications of kinetic theory, it seemed to us that a more lengthy review of this subject would be warranted.

3 This discussion is based upon historical studies by Steven Brush, as described, for example, in his book *The Kind of Motion We Call Heat* [72].

4 The books by S. Brush [71, 72], to which we refer, contain a bibliography of important papers for the history of kinetic theory as well as a thorough description of this history. We can do no better than to refer to these books rather than to the individual papers.

5 The standard reference for the kinetic theory of dilute gases and gas mixtures is the book by S. Chapman and T. G. Cowling [89]. While their notation is cumbersome, the discussion is complete and clear.

6 There were a number of other efforts to obtain the Boltzmann equation using the Liouville equation as a starting point, in addition to those of N. N. Bogoliubov, M. S. Green, and E. G. D. Cohen. The paper by Cohen [98] provides a comparison of different methods, and the paper by E. G. D. Cohen and T. Berlin [107] exposes an important facet of the Bogoliubov method and gives an essential clue as to the origin of irreversibility in this and other approaches to the derivation of the Boltzmann equation.

7 A proof of the general equivalence of kinetic theory and time correlation function formalisms for evaluating transport coefficients is complicated by the fact that nonanalytic and even divergent terms appear when one looks at either of these methods for gases at moderate or high density. Instead, one can verify the equivalence by explicit calculations as will be discussed in later chapters. For low-density gases, there are several discussions of the equivalence of the two methods. Here we mention only one of them [189].

8 A brief characterization of the various periods in the development of kinetic theory can be found as a footnote in the Introduction to J. Stat. Phys. **109**, Numbers 3/4, by M. H. Ernst, H. van Beijeren, and E. G. D. Cohen [194]. See also the paper by Ernst [180].

9 These remarks apply to gases in which the particles interact with short-range forces, which are repulsive for small inter-particle distances.

10 Several authors almost simultaneously realized that the virial expansions of transport coefficients were plagued by divergence difficulties. The history of this discovery is summarized in volume 3 of Brush's three-volume set of books on kinetic theory [71].

11 If one thinks, loosely speaking, of the hydrodynamic modes as eigenfunctions of the Liouville operator, which is a linear differential operator, it follows that products of these modes are also eigenfunctions.

12 Kinetic theory is one of several approaches for studying the long-time tails. Identical results have been obtained at the same time using mode-coupling or related hydrodynamic arguments by M. H. Ernst, E. H. Hauge, and J. M. J. van Leeuwen [191, 192, 193, 195, 196] and by R. Zwanzig and M. Bixon [706].

13 Closely related work on long-range correlations in fluids maintained in nonequilibrium stationary states was carried out by a number of groups. See, for example, [544, 543, 564, 628, 627].

14 To fully appreciate this method, one has to realize that besides proper eigenfunctions under $\mathcal{L}^2$ norm with purely imaginary eigenvalues, there exist generalized eigenfunctions with real or complex eigenvalues. These are known as Pollicott–Ruelle resonances [567, 532].

15 Values for the effective hard-sphere radius of particles in a real gas are generally obtained by fitting results from equilibrium measurements, such as virial coefficients, to hard-sphere models for those properties.

16 This model is also usually referred to as the Lorentz model. We will indicate whenever necessary which version is under discussion.