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J. R. Dorfman, Henk van Beijeren, T. R. Kirkpatrick
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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

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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

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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

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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.

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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

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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