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Theory of Transport Coefficients for Moderately Dense Gases

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A general introduction to and bibliography for transport phenomena in gases is provided. Methods for obtaining density expansions of transport coefficients from time-correlation functions in a moderately dense gas with short-range repulsive intermolecular forces are considered. A unified treatment of the two methods appearing in the literature (the t method due to Cohen, Dorfman, and Ernst and the ϵ method due to Zwanzig) is given. Both of these methods lead to integral equations from which the first two terms in the density expansion of transport coefficients can be computed. However, because of many-body effects in the gas, both methods diverge when used to compute terms beyond the first two in these density expansions. Because of this divergence, it is necessary to prove that the t and ϵ methods give the same results for the first two terms in the density expansion of transport coefficients. The required proof is provided, and we conclude that either the t or ϵ method can be used to compute the first two terms in the density expansion of transport coefficients provided one assumes that the remaining (divergent) terms, which are neglected, do not contribute to the first two terms.

CONTENTS

1. INTRODUCTION

Fourier's law of thermal conduction, Fick's law of diffusion, and Ohm's law of electrical conduction are all examples of linear transport equations. Such laws are used to describe the final stage of a system's approach to equilibrium, if the system was not originally in equilibrium, or the behavior of a system in an externally maintained steady state in which there is a small but constant flow of some quantity. In general, these linear, macroscopic laws all relate the flux of some quantity to a gradient in another quantity, i.e.,

$$\begin{aligned} \mathbf{q} &= -\lambda \operatorname{grad} T, && \text{Fourier's law,} \\ \mathbf{J}_e &= -\sigma \operatorname{grad} \phi, && \text{Ohm's law,} \\ \mathbf{J}_p &= -D \operatorname{grad} n, && \text{Fick's law.} \end{aligned} \tag{1.1}$$

That is, the flows in heat, charge, and particles, $\mathbf{q}$, $\mathbf{J}_e$, $\mathbf{J}_p$, are proportional to the gradients in temperature T, electrostatic potential ϕ, and concentration n, respectively. The proportionality constants are called transport coefficients. Here we have illustrated the coefficient of thermal conductivity λ, the coefficient of electrical conductivity σ, and the coefficient of diffusion D.

One of the major problems of nonequilibrium statistical mechanics is to give a *derivation* of these laws and their possible *generalizations*, based upon a knowledge of the *microscopic* properties of the systems involved. In particular one would like to know (1) the range of validity of the macroscopic laws and the correction to them whenever they are no longer adequate to describe the physical situation, and (2) the theoretical predictions for the values of the transport coefficients and their dependence upon the important parameters (such as temperature, density, etc.) that specify the state of the system.

To guide the reader through the sometimes intricate logic of the discussion below, we have outlined the major theoretical developments in Fig. 1.

The most important early discussion of these problems was based upon the Boltzmann equation. [A brief discussion of the Boltzmann equation and its solutions may be found in Uhlenbeck and Ford (1963).] The Boltzmann equation describes the nonequilibrium behavior of the single-particle distribution function of a dilute (only binary collisions are taken into account), monatomic gas. To obtain the transport coefficients for the dilute gas from the Boltzmann equation, one assumes that the system is close to a local equilibrium state, i.e., a state where equilibrium is established in volumes which contain a large number of particles but are small compared to the total volume of the system. Each small volume has its own (local) temperature T, density n, and mean velocity $\mathbf{u}$, but these quantities can

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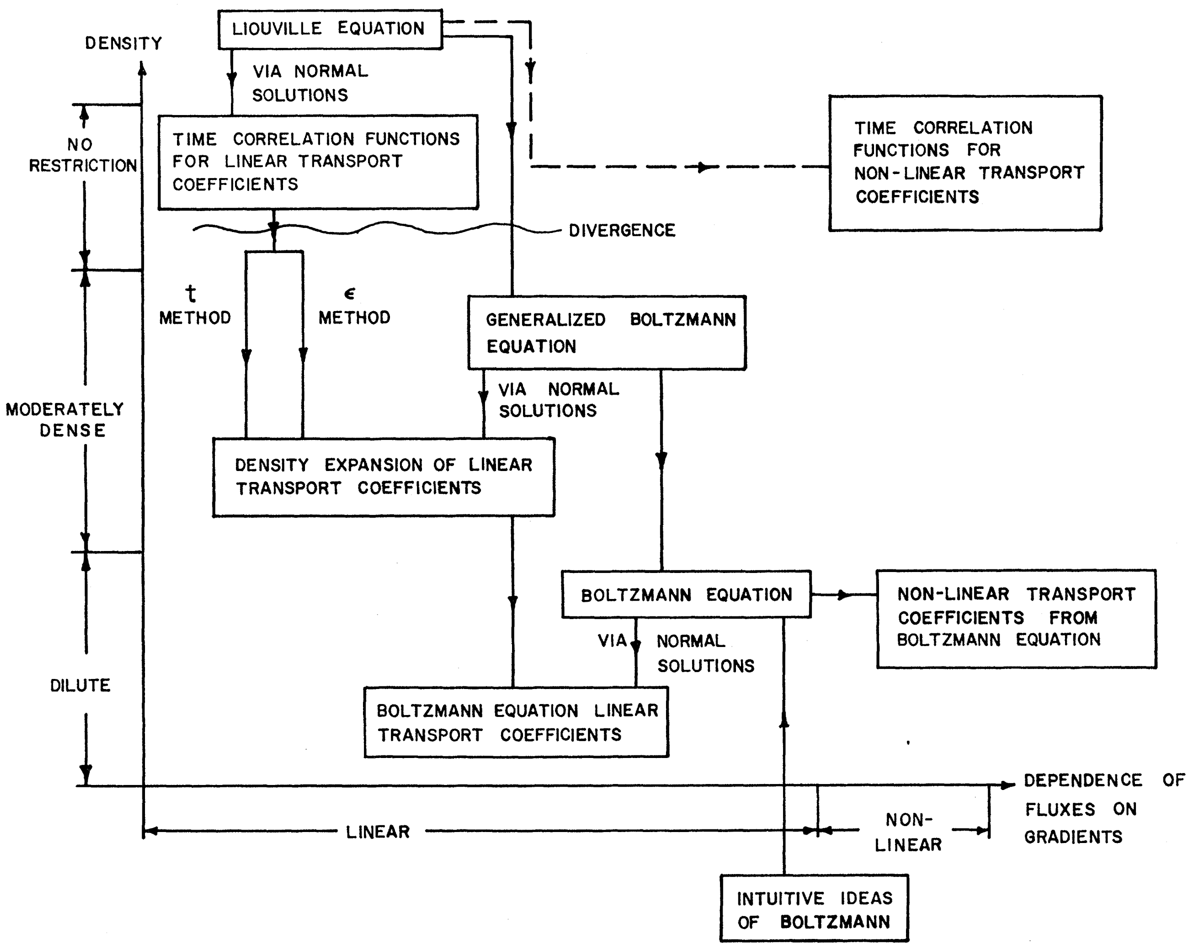

Fig. 1. The logical relationships among the various developments in the theory of transport coefficients.

be different in neighboring volumes. If one then expresses the single-particle distribution function as a local equilibrium distribution plus a correction proportional to the gradients in the local equilibrium quantities, a linearized version of the Boltzmann equation can be obtained and solved. The method of solution, due to Chapman and Enskog (Chapman and Cowling, 1939), depends upon assuming that the single-particle distribution function depends on time only through the time variation of the local equilibrium variables, namely T, n, and $\mathbf{u}$. One obtains, on the basis of this assumption, the so-called "normal solutions" to the Boltzmann equation, that are presumed to be valid for a system either in a steady state, or close to equilibrium. In the Chapman–Enskog method, these solutions are used to establish a theoretical basis for the macroscopic laws and to obtain explicit expressions for the transport coefficients. These expressions are extremely useful and agree quite well with experiment for dilute gas systems.

From the Boltzmann equation it is possible to obtain a *generalization* of the macroscopic laws, Eqs. (1.1), in one direction (leading to so-called Burnett and super-Burnett hydrodynamics) by taking into account, in a systematic way, corrections to the linearized Boltzmann equation and including nonlinear terms (Burnett, 1935; Chapman and Cowling, 1939; Grad, 1949; 1962; Waldmann, 1958). This procedure leads to expressions for the fluxes which contain powers of gradients and higher-order gradients in the macroscopic variables. For example, Fourier's law becomes

$$\begin{aligned}\mathbf{q}=&-\lambda\,\text{grad}\,T\\&+(\theta\,\text{div}\,\mathbf{u}\,\text{grad}\,T+\text{other terms of the same order})\\&+\text{higher-order terms in the gradients.}\qquad(1.2)\end{aligned}$$

These corrected laws are nonlinear and apply only to dilute gases since they are derived from the Boltzmann equation. However, the Boltzmann equation is not adequate for *dense* systems where more than binary collisions are important.

To extend the results of the Boltzmann equation to gases of higher density, one needs a procedure for deriving corrections to the Boltzmann equation which takes into account, in a systematic way, the fact that the gas is no longer dilute and that collisions between three, four, or more molecules are now important. (Such a gas, not dilute but not near to condensing, is said to be moderately dense.)

As originally given by Boltzmann, the derivation of his equation for a dilute gas was intuitive and not based in a truly rigorous way on the laws of mechanics. Lacking Boltzmann's intuition, no one has succeeded[*] in generalizing the derivation of his equation to obtain intuitively an equation which describes the behavior of a moderately dense gas. Rather, all generalizations of the Boltzmann equation have been obtained by solving Liouville's equation. Although this procedure is quite formal, it does have the advantage that Liouville's equation is a consequence of the laws of mechanics, so that a generalized Boltzmann equation derived from Liouville's equation rests on a sound theoretical foundation (provided of course that one can justify all the steps in the derivation!). For a dilute system, a generalized Boltzmann equation derived from Liouville's equation should, of course, reduce to Boltzmann's equation, and thus this procedure can be used to secure the theoretical foundations of the Boltzmann equation.

Starting with the work of Bogoliubov in 1946 (Bogoliubov, 1961), systematic derivations of the Boltzmann equation, from the Liouville equation, including its corrections to higher densities, became possible. Bogoliubov was, in fact, the first to give a prescription for obtaining all the higher order density corrections to the Boltzmann equation. Choh and Uhlenbeck gave an extensive discussion of the first correction (Choh, 1958; Sengers, 1966a; 1967), a correction that takes into account interactions of three particles in the gas. The essence of Bogoliubov's generalization was that each higher density correction to the Boltzmann equation takes into account the interaction of more particles in the gas. The Boltzmann equation itself considers only two-particle interactions (binary collisions); the Choh–Uhlenbeck term, three-particle interactions; and so on. Bogoliubov's methods, however, were based upon an *assumption*, the so-called "functional assumption," that the distribution functions for two or more particles do not depend explicitly upon the time. Instead, these functions depend on time only through the single-particle distribution function. The motivation for this assumption is provided by an extension of the ideas that are used to obtain the macroscopic laws from the Boltzmann equation.

The more recent work of M. S. Green, E. G. D. Cohen, and others (Cohen, 1966; 1967; 1968; Curtiss, 1967; Ford, 1965; Green and Piccirelli, 1963; Hollinger and Curtiss, 1960; Kritz and Sandri, 1966; Ono, 1964; Piccirelli, 1966; Stecki and Taylor, 1965) has provided an alternate derivation of the generalized Boltzmann equation that does not involve a functional assumption and is therefore more rigorous. The work of Green and Cohen is based on methods borrowed from the equilibrium theory of dense gases, in particular on cluster expansion methods (DeBoer, 1949; Uhlenbeck and Ford, 1961).

Once the generalized Boltzmann equation for a moderately dense gas is available, the transport coefficients can be obtained by using methods similar to those used for the Boltzmann equation. The equation is linearized by expanding the distribution function about the local equilibrium value and looking for "normal solutions" of the resulting equations. This procedure was first outlined by Choh and Uhlenbeck (see also Garcia-Colin, Green, and Chaos, 1966) who used it to compute the first density corrections to the Boltzmann equation transport coefficients. Choh and Uhlenbeck obtained an expression for the effect of three-particle interactions on the transport coefficients, which they were not able to explicitly evaluate. In principle, however, one could obtain an expansion for the transport coefficients as a power series in the density. In other words, the development of a generalized Boltzmann equation led rather directly to an expansion for transport coefficients, $\mathfrak{J}$, appropriate to a moderately dense gas, in the form

$$\mathfrak{J}=\mathfrak{J}_0+n\mathfrak{J}_1+n^2\mathfrak{J}_2+\cdots, \tag{1.3}$$

where $\mathfrak{J}_0$ is the result of the Boltzmann equation, $\mathfrak{J}_1$ is the result of Choh and Uhlenbeck, and the higher $\mathfrak{J}$'s are in principle known as integrals that depend on the dynamics of four and more particles.

Before we turn to a consideration of the extent to which the above expression for the transport coefficients represents a completion of the attempts to extend the theory of transport coefficients from dilute to moderately dense gases, we will sketch a parallel development in the theory of transport phenomena which also plays a large role in the theory of transport coefficients in gases. This development is called the method of time-correlation functions.

Time-correlation functions represent the results of an attempt to base a theory of the linear macroscopic transport equations directly on the Liouville equation, avoiding the intermediate step of a generalized Boltzmann equation. In essence the theory goes back to Einstein and Nyquist, but its more recent form is due largely to M. S. Green and later Kubo, Mori, and others.[*] The basic idea of the method of time-correlation functions is to consider the effect of a local equilibrium state on the complete N-particle distribution function for the system. The Liouville equation governs the behavior of the N-particle distribution function of

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[*] An exception is the Enskog equation (Chapman and Cowling, 1939).

[*] In addition to Zwanzig's review article (1965), there are: Andrews (1967), Felderhof and Oppenheim (1965), Green (1961), Komarov (1965), Luttinger (1964), Martin (1965), Mori (1965), Ono (1965), Salistra (1968), Schofield (1968), and Zubarev (1962; 1965; 1966).

the system $F_N(\mathbf{R}_1, \mathbf{p}_1, \cdots, \mathbf{R}_N, \mathbf{p}_N, t)$; this function contains all the available information about the system. In the time-correlation function method, one assumes that F_N is expressible as a local equilibrium N-particle distribution function plus correction terms. The local equilibrium function depends on the local macroscopic variables, temperature, density, and mean velocity, and upon the position and velocities of the N particles in the system. The correction to this distribution function is determined by means of Liouville's equation, and by assuming that at some initial time the system was in a local equilibrium state and is proceeding to relax from local to complete equilibrium. Again one can construct "normal solutions," now to Liouville's equation, and obtain an expression for the corrections to local equilibrium in powers of the gradients of the local variables.* Retaining only the first term in the expansion in the gradients, one derives again the linear macroscopic transport equations but now with *considerably generalized* expressions for the transport coefficients. These expressions depend upon the dynamics of all N particles in the system and apply to any system, irrespective of its density.

In principle one can extend the method to obtain nonlinear transport equations, also from the Liouville equation (Kadanoff and Martin, 1963; McLennan, 1961; 1963b; Mori, 1965; Peterson, 1967; Piccirelli, 1968; Robertson, 1967; Storer and Green, 1962; Zwanzig, 1964). However, this method is still in its early stage, and the nonlinear theory is not yet fully worked out nor understood.

The time-correlation function expressions for the transport coefficients depend for their evaluation upon the solution of the equations of motion for an arbitrarily large system and upon the averaging of such solutions over an equilibrium ensemble. Since this procedure is more difficult than evaluating the partition function for the system, it is necessary to develop approximation methods in order to evaluate the time-correlation function expression. For a dilute or moderately dense gas, the same methods that have been used to derive the generalized Boltzmann equation from the Liouville equation have been used to evaluate the time-correlation function. These methods once again lead to the density expansion, Eq. (1.3) (Curtiss, 1967; Ernst, Dorfman, and Cohen, 1964; 1965; Ernst, 1965; 1966; Fujita, 1962; Green, 1961; Kawasaki and Oppenheim, 1964a; McLennan, 1963; McLennan and Swenson, 1963; Mori, 1961; Ono and Shizume, 1963; Resibois, 1964; Tolmachev, 1957; Zwanzig, 1963).

Thus, the development of a theory of linear, macroscopic transport equations and density expansion expressions for transport coefficients, for gases at least, can proceed in either one of two ways starting from the Liouville equation: (1) via the generalized Boltzmann equation where the local equilibrium solution appears at a late stage in the calculation, *or* (2) via the time-correlation function method where the local equilibrium solution appears early in the calculation and the calculation then proceeds in analogy to the derivation of the generalized Boltzmann equation. If the two methods yield identical results, then the methods can be viewed as completely parallel, the only difference being the order in which various manipulations are carried out.

At this stage in the theory a development took place which has seriously altered the picture presented so far. For some time it had not been possible to explicitly evaluate any of the higher terms in the generalized Boltzmann equation or in the density expansion of the transport coefficients. One only had expressions whose evaluation required a *knowledge of the dynamics* of systems of three, four, or more particles in the gas. It was commonly assumed that with sufficient patience, these expressions could be evaluated and would lead to a mathematically well-behaved (i.e., finite) result. However, until this assumption was verified, one did not really have a *rigorous derivation*, from Liouville's equation, of either the generalized Boltzmann equation or the density expansion of time-correlation functions. In particular, without an adequate discussion of the higher terms in the series, one could not even say that the Boltzmann equation itself was on any more secure foundation than Boltzmann had left it. What one could prove was that the density expansion of transport coefficients obtained from the generalized Boltzmann equation, and the density expansion obtained from the time-correlation function method were identical, provided that all terms appearing in these expressions were well behaved (existed).

As more was learned about the relevant dynamics of three, four, or more particles that contribute to the density expansions, it was discovered that most of the terms in the generalized Boltzmann equation, as well as the corresponding terms in the density expansions of the transport coefficients (by whatever method obtained) *did not exist*; that is, these terms were actually infinite when calculated explicitly (it is customary to say that these terms "diverge" or that there is a "divergence" in the theory). The exact term where the divergence first appears depends upon the dimension of the system. In three dimensions, for ordinary gases, the divergence first appears in the four-body term; in two dimensions it appears in the three-body or Choh–Uhlenbeck term. Moreover, all the higher-order terms in the series are divergent. Needless to say, the appearance of this divergence meant that the theory as then constructed was not correct and that practically all previous results in the theory of transport coefficients

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* The basic idea of local equilibrium states and "normal solutions" is also more or less implicit in those theories where linear response theory is used to derive correlation formulas for thermal transport coefficients [Kadanoff and Martin (1963), Luttinger (1964), Felderhof and Oppenheim (1965)]. Here one employs the hydrodynamic equations for the rate of change of the temperature, density, and mean velocity, and closes this set of equations by assuming that all remaining local thermodynamic functions depend on the aforementioned five quantities through the local equilibrium relations.

for dilute or moderately dense gases were suspect, including the Boltzmann equation.*

The divergence appeared in the four- (or three-) body terms because the region of phase space associated with the relevant dynamics of the particles was of infinite volume. This infinite volume always appears and spoils any attempt at explicit evaluation. For the system of three particles in two dimensions, the divergence is associated with certain sequences of three binary collisions among the three particles. The phase space associated with this sequence grows logarithmically in the time between the first and last of the three binary collisions. The expressions, as given by the theory, require that one take the limit as this time goes to infinity, so that this three-body term, in two dimensions, diverges logarithmically.

As a result of this divergence difficulty, all the methods used before must be re-examined carefully. The derivation of the generalized Boltzmann equation, the evaluation of the time-correlation functions, and the density development of the transport coefficients must all be called into question. Here we shall concentrate our attention on one phase of this problem, the evaluation of the time-correlation function expression for the transport coefficients, since this is the simplest area in which to exhibit all the areas of difficulty.

Two basic methods have been used to obtain the density development of transport coefficients for a moderately dense gas by means of time-correlation functions. Both methods are completely formal developments from the Liouville equation, and each leads to an integral equation for the time-correlation function that determines the transport coefficients. However, the two methods, as presented in the literature, differ considerably in motivation and procedure. One of the methods (t method), due to Cohen, Dorfman, and Ernst (Ernst, Dorfman, and Cohen, 1964; 1965; Ernst, 1965; 1966) makes heavy use of the first hierarchy equation (Uhlenbeck and Ford, 1963, p. 120) and an analogy with equilibrium methods to obtain an integral equation which is formulated in terms of the time t. This integral equation bears a close relation to the generalized Boltzmann equation. The other method (ϵ method) due to Zwanzig (1963) involves an inversion of the Laplace transform of a certain divergent time-dependent operator. The ensuing integral equation is formulated in terms of the Laplace transform variable ϵ which corresponds to the time t. The ϵ integral equation is equivalent to the t equation, but the *form* of the two equations is different. [A similar situation occurs in the theory of the generalized master equation (Balescu, 1961; Fulinski, 1967a; 1967b; Geszti, 1967; Zwanzig, 1960a).] This difference in form is extremely significant when a density development of these equations is contemplated. Due to the divergence in this density expansion the circumstances under which the two methods lead to identical results must be carefully examined.

It is our intention here to pay careful attention to the two methods for evaluating the time-correlation function, since the methods and problems that arise in this discussion are fairly general and are useful in the entire area of nonequilibrium theory of gases. We shall see that the two difficulties, (1) the divergence in density expansions of transport coefficients, and (2) the question of the equivalence of the t and ϵ methods for computing these density expansions, are closely related. We shall provide a critical discussion and comparison of the t and ϵ methods, and in particular their density expansions, for a dilute or moderately dense monatomic gas with short-range repulsive intermolecular forces, from a unified point of view. In a subsequent publication, we shall give a detailed discussion of the attempts to find a convergent theory and their effects on the general area of transport theory.

In either the t or ϵ method, the transport coefficients are expressed in terms of limiting values ($t\rightarrow\infty$, $\epsilon\rightarrow 0$) of special one- and two-particle correlation functions. Cluster expansions are applied to these correlation functions to obtain their expansion in powers of the density. This simple expansion, the "naive density expansion," diverges term by term in the limit needed for the evaluation of transport coefficients, so that the expansion needs further treatment before useful expressions for transport coefficients can be obtained. (This divergence was already noted by Bogoliubov and provided him with one motivation for his "functional assumption" method.) This divergence in the "naive density expansion" is not the crucial divergence and is easily removed. In both methods this is accomplished by showing that a suitable summation of the naive density expansion of the correlation functions is equivalent to the solution of an integral equation. For the sake of a unified treatment, we shall, in this paper, use similar methods to obtain these integral equations. We shall then discuss the relation between the two integral equations and their solutions.

Since the coefficient of self-diffusion is mathematically the simplest transport coefficient to discuss, the body of the paper is devoted to it. In the Appendix we generalize the arguments to include other coefficients, in particular, the viscosity. In Sec. 2 we define the single-particle correlation function appropriate to self-diffusion. In Sec. 3 we give the cluster expansion and obtain the naive density expansion. The integral equation appropriate to the ϵ method is derived in Sec. 4; to the t method, in Sec. 5. Section 6 is devoted to a formal comparison of the two methods. In Secs. 7 and 8 we discuss the comparison of the two methods in some detail, taking particular account of the divergence, and insofar as a power series expansion in the density of the

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* The literature on the divergence is extensive; the following list is essentially complete: Andrews (1966), Dorfman and Cohen (1965; 1967), Dorfman (1967), Frieman and Goldman (1965; 1966; 1967), Fujita (1966a; 1966b; 1967), Goldman (1966; 1967), Haines, Dorfman, and Ernst (1966), Haines (1966), Hauge and Cohen (1967; 1968), Hoegy (1967), Kawasaki and Oppenheim (1965; 1967), Lebowitz and Percus (1967), van Leeuwen and Weyland (1967), Murase (1966), Sengers (1965; 1966b), Weinstock (1963; 1965; 1966), Weyland and van Leeuwen (1968).

transport coefficients exists, we discuss the first few finite terms.

2. THE SELF-DIFFUSION COEFFICIENT IN THE t AND ϵ METHODS

The t method (Ernst, Dorfman, and Cohen, 1964; 1965; Ernst, 1965; 1966) for computing the self-diffusion coefficient begins with the time-correlation expression (Longuet-Higgins and Pople, 1956; Helfand, 1963)

$$D=\tfrac{1}{3}\lim_{t\to\infty}\int_0^t dt_1 \lim_{\infty}\left\langle\frac{\mathbf{p}_1}{m}\cdot\frac{\mathbf{p}_1(-t_1)}{m}\right\rangle, \tag{2.1}$$

where particle 1 has momentum $\mathbf{p}_1$ at time zero and momentum $\mathbf{p}_1(-t)$ at time $(-t)$. The mass of the diffusing molecules is m, and the brackets denote an average over the initial values of the phases x_i of the N molecules using a canonical equilibrium ensemble, i.e.,

$$\langle g(x)\rangle=\int dx_1\cdots dx_N g(x) f_N, \tag{2.2}$$

where

$$f_N=Z_N^{-1}\exp(-\beta H_N). \tag{2.3}$$

Here H_N is the full N-particle Hamiltonian, $\beta=1/kT$ where k is the Boltzmann constant and T the temperature, and Z_N is the canonical partition function

$$Z_N=\int dx_1\cdots dx_N \exp(-\beta H_N). \tag{2.4}$$

We shall use the notation x as an abbreviation for all the phase variables of the system. Similarly, $\mathbf{R}$ and $\mathbf{p}$ will stand for all initial positions and momenta, and we shall sometimes write $f(x)=f(\mathbf{R},\mathbf{p})$. The symbol $\lim_\infty$ stands for the thermodynamic limit $N\to\infty$, $V\to\infty$, $N/V\to n$, where V is the volume of the system and n is the number density. The thermodynamic limit is to be taken before the limit $t\to\infty$.

By introducing the time-displacement or streaming operator S_{-t} which changes the phase variables of a function from their initial values to their values at time $(-t)$ via

$$S_{-t}g(x)=g(x(-t)), \tag{2.5}$$

it is possible to write Eq. (2.1) as

$$D=\tfrac{1}{3}\lim_{t\to\infty}\int_0^t dt_1 \lim_{\infty}\left\langle\frac{\mathbf{p}_1}{m}\cdot S_{-t_1}\frac{\mathbf{p}_1}{m}\right\rangle. \tag{2.6}$$

The explicit expression for the time-displacement operator is

$$S_{-t}=\exp(-t\mathcal{H}), \tag{2.7}$$

where $\mathcal{H}$ is the Liouville operator* which satisfies the Poisson bracket relation

$$\mathcal{H}g(x)=\{g(x),H_N\}. \tag{2.8}$$

If the Hamiltonian for the system is

$$H_N=\sum_{i=1}^{N}\frac{p_i^2}{2m}+\Phi(\mathbf{R}), \tag{2.9}$$

where the total potential energy $\Phi(\mathbf{R})$ is given as the sum of the pair potential energies $\Phi_{ij}(|\mathbf{R}_i-\mathbf{R}_j|)\equiv\Phi_{ij}$ by

$$\Phi(\mathbf{R})=\sum_{1\leq i<j\leq N}\Phi_{ij}, \tag{2.10}$$

then $\mathcal{H}$ is given explicitly by

$$\mathcal{H}=\mathcal{H}_0-\sum_{1\leq i<j\leq N}\theta_{ij}, \tag{2.11}$$

where

$$\mathcal{H}_0=\sum_{i=1}^{N}\frac{\mathbf{p}_i}{m}\cdot\frac{\partial}{\partial\mathbf{R}_i} \tag{2.12}$$

and

$$\theta_{ij}=(\partial\Phi_{ij}/\partial\mathbf{R}_i)\cdot[(\partial/\partial\mathbf{p}_i)-(\partial/\partial\mathbf{p}_j)]. \tag{2.13}$$

We remark in connection with the above formulas that S_{-t} does not change H_N since H_N is a constant of the motion. Nor does it change the equilibrium distribution function f_N. Therefore, the equilibrium distribution function can be written either to the left or right of S_{-t} in the expression (2.6).

Concerning notation, we adopt the convention that quantities which depend on the number of particles such as S_{-t}, $\mathcal{H}$, Φ, etc., are N-particle quantities unless the particles involved are enumerated in parentheses.

We define the first time-correlation function $\mathbf{X}(\mathbf{p}_1,t)$ by

$$\hat{\mathbf{X}}(\mathbf{p}_1,t)=\lim_{\infty}V\int dx_2\cdots dx_N S_{-t}f_N\frac{\mathbf{p}_1}{m}. \tag{2.14}$$

That $\hat{\mathbf{X}}$ is not a function of $\mathbf{R}_1$ follows immediately since H_N and $\mathcal{H}$ depend only on relative positions. In terms of our definition for $\mathbf{X}$, the time-correlation expression for D can be written

$$D=\frac{1}{3}\int d\mathbf{p}_1\frac{\mathbf{p}_1}{m}\cdot\lim_{t\to\infty}\int_0^t dt_1\hat{\mathbf{X}}(\mathbf{p}_1,t_1). \tag{2.15}$$

The circumflex on $\hat{\mathbf{X}}$ is used to distinguish $\hat{\mathbf{X}}(\mathbf{p}_1,t)$ from its Laplace transform $\mathbf{X}(\mathbf{p}_1,\epsilon)$. We always use this notation so that any pair of functions $\hat{f}(t)$ and $f(\epsilon)$ are related by

$$f(\epsilon)=\int_0^\infty dt e^{-\epsilon t}\hat{f}(t). \tag{2.16}$$

Using the definitions of the above paragraphs we now describe the starting point of the ϵ method (Zwanzig, 1963). In this method, D is computed from the time-correlation expression

$$D=\tfrac{1}{3}\lim_{\epsilon\to 0}\int_0^\infty dt e^{-\epsilon t}\lim_{\infty}\left\langle\frac{\mathbf{p}_1}{m}\cdot\frac{\mathbf{p}_1(-t)}{m}\right\rangle \tag{2.17}$$

which can be written

$$D=\frac{1}{3}\int d\mathbf{p}_1\frac{\mathbf{p}_1}{m}\cdot\lim_{\epsilon\to 0}\mathbf{X}(\mathbf{p}_1,\epsilon) \tag{2.18}$$

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* There is a diversity of notation for the Liouville operator. In the literature, the quantity that we call $\mathcal{H}$ has also been written as $\mathcal{L}$, L, $i\mathcal{L}$, and iL, where i is the imaginary unit.

and is to be compared with Eq. (2.15). The ϵ expression for computing D differs from the t expression by the insertion of the convergence factor $e^{-\epsilon t}$. This cannot change anything so long as the limit $t \rightarrow \infty$ in Eq. (2.1) exists, and *we shall always assume that this is so.*

3. NAIVE DENSITY EXPANSION OF THE FIRST TIME-CORRELATION FUNCTION

In order to calculate a density expansion of D from Eqs. (2.15) or (2.18) one needs a density expansion of the first time-correlation function $\hat{\mathbf{X}}$. We shall now obtain such an expansion, called the naive density expansion, by making a cluster expansion of $\hat{\mathbf{X}}$ in analogy to equilibrium statistical mechanics (DeBoer, 1949). However, the terms in this naive density expansion are not well behaved for large t. In fact, the term of order n^r ($r=0, 1, \cdots$), which depends on the dynamics of $r+1$ particles, goes as t^r for large t (Dorfman and Cohen, 1967). Thus none of the individual terms in the naive density expansion of

$$\int_0^t dt_1 \hat{\mathbf{X}}(\mathbf{p}_1, t_1) \quad \text{or of} \quad \mathbf{X}(\mathbf{p}_1, \epsilon)$$

will exist as $t \rightarrow \infty$ or as $\epsilon \rightarrow 0$. Furthermore, the failure of the individual terms in the naive density expansions of

$$\int_0^t dt_1 \hat{\mathbf{X}}(\mathbf{p}_1, t_1) \quad \text{or} \quad \mathbf{X}(\mathbf{p}_1, \epsilon)$$

to exist for large t or small ϵ indicates that some suitable rearrangement or *resummation* of the terms in these expansions must be made before these expansions can be used to compute D in either the t or the ϵ method. We shall discuss these resummations in Secs. 4 and 5.

Preliminary to making the density expansion of $\hat{\mathbf{X}}(\mathbf{p}_1, t)$, we consider the identity

$$S_{-t} = S_{-t}^0 + \int_0^t d\tau S_{-t+\tau}^0 \sum_{1 \leq i < j \leq N} \theta_{ij} S_{-\tau}, \qquad (3.1)$$

where we have defined the free streaming operator S_{-t}^0 as

$$S_{-t}^0 = \exp(-t\mathcal{H}_0). \qquad (3.2)$$

Using Eq. (3.1) we may write Eq. (2.14) as

$$\hat{\mathbf{X}}(\mathbf{p}_1, t) = S_{-t}(1)\phi(1)\mathbf{p}_1/m + \int_0^t d\tau S_{-t+\tau}(1)\hat{O}(\tau)\phi(1)\frac{\mathbf{p}_1}{m}, \qquad (3.3)$$

where we have defined the operator $\hat{O}(t)$ as

$$\hat{O}(t) = \lim_{\infty} V \int dx_2 \cdots dx_N \sum_{1 \leq i < j \leq N} \frac{\theta_{ij} S_{-t} f_N}{\phi(1)}, \qquad (3.4)$$

and where $\phi(1)$ is the normalized Maxwell–Boltzmann momentum distribution function:

$$\phi(1) \equiv \phi(p_1) = A \exp(-\tfrac{1}{2}\beta p_1^2/m);$$
$$\int d\mathbf{p}_1 \phi(p_1) = 1. \qquad (3.5)$$

In deriving Eq. (3.3), Liouville's theorem for free-particle streaming was used in the form

$$\int dx_2 \cdots dx_N S_{-t}^0(12\cdots N) g(x) = S_{-t}(1) \int dx_2 \cdots dx_N g(x) \qquad (3.6)$$

which is a special case of the more general Liouville theorem:

$$\int dx_1 \cdots dx_j S_{-t}(12\cdots j) g(x) = \int dx_1 \cdots dx_j g(x). \qquad (3.7)$$

To obtain the naive density expansion of the operator $\hat{O}(t)$, from which a similar expansion for $\mathbf{X}(\mathbf{p}_1, t)$ is obtained through Eq. (3.3), we introduce cluster operators $\mathcal{U}(12 \mid 3\cdots j, t)$ defined by the recursion relation

$$S_{-t}(12\cdots N) = \mathcal{U}(12, t) S_{-t}(3\cdots N) + \sum_{\text{all one-tuples in } (3\cdots N)} \mathcal{U}(12 \mid 3, t) S_{-t}(4\cdots N) + \cdots. \qquad (3.8)$$

By writing out Eq. (3.8) for $N=2, 3, \cdots$, one obtains a set of equations which can be solved successively for the $\mathcal{U}$'s. In this way one finds

$$\begin{aligned}
\mathcal{U}(12, t) &= S_{-t}(12),\\
\mathcal{U}(12 \mid 3, t) &= S_{-t}(123) - S_{-t}(12) S_{-t}(3),\\
\mathcal{U}(12 \mid 34, t) &= S_{-t}(1234) - S_{-t}(123) S_{-t}(4) - S_{-t}(124) S_{-t}(3) - S_{-t}(12) S_{-t}(34) + 2S_{-t}(12) S_{-t}(3) S_{-t}(4),\\
&\ \ \vdots
\end{aligned} \qquad (3.9)$$

The expansion (3.8) can now be used in Eq. (3.4) to obtain the following expression for $\hat{O}(t)$:

$$\hat{O}(t) = n \int dx_2 \theta_{12} \mathcal{U}(12, t) g(12) \phi(2) + \frac{n^2}{1!} \int dx_2 dx_3 \theta_{12} \mathcal{U}(12 \mid 3, t) g(123) \phi(2) \phi(3) + \frac{n^3}{2!} \int dx_2 dx_3 dx_4 \theta_{12} \mathcal{U}(12 \mid 34, t) g(1234) \phi(2) \phi(3) \phi(4) + \cdots, \qquad (3.10)$$

where Liouville's theorem has been used. We have also taken the thermodynamic limit and defined the equilibrium

j-particle position distribution functions $g(12\cdots j)$ in the conventional manner as

$$g(12\cdots j)\prod_{i=1}^{j}\phi(i)\equiv g(\mathbf{R}_1\mathbf{R}_2\cdots\mathbf{R}_j)\prod_{i=1}^{j}\phi(i)=\lim_{\infty}V^j\int dx_{j+1}\cdots dx_N f_N. \tag{3.11}$$

The distribution functions g can themselves be given as density expansions which we write as

$$\begin{aligned}g(12)&=W(12)+n\int d\mathbf{R}_3 g(12;3)+n^2\int d\mathbf{R}_3 d\mathbf{R}_4 g(12;34)+\cdots,\\ g(123)&=W(123)+n\int d\mathbf{R}_4 g(123;4)+n^2\int d\mathbf{R}_4 d\mathbf{R}_5 g(123;45)+\cdots,\\ &\;\;\vdots\end{aligned} \tag{3.12}$$

In particular, W is given by

$$W(12\cdots j)=\exp[-\beta\Phi(12\cdots j)], \tag{3.13}$$

and explicit formulas for the $g(1\cdots j;j+1\cdots k)$ can be found in the literature (DeBoer, 1949).

Before deriving the complete density expansion of $\hat{O}(t)$, simplified expressions for the operators appearing in Eq. (3.10) are given. These operators have the form

$$\begin{aligned}&[(j-2)!]^{-1}\int dx_2\cdots dx_j\theta_{12}\mathfrak{U}(12\mid 3\cdots j,t)g(12\cdots j)\phi(2)\cdots\phi(j)\\ &\qquad=\int dx_2\cdots dx_j\hat{\tau}(12\cdots j,t)g(12\cdots j)\phi(2)\cdots\phi(j),\end{aligned} \tag{3.14}$$

where

$$\begin{aligned}\hat{\tau}(12,t)&=\theta_{12}S_{-t}(12),\\ \hat{\tau}(123,t)&=\int_0^t dt_1\theta_{12}S_{-t+t_1}(12)[\theta_{13}+\theta_{23}]S_{-t_1}(123),\\ \hat{\tau}(1234,t)&=\int_0^t dt_1\int_0^{t_1}dt_2\theta_{12}S_{-t+t_1}(12)[\theta_{13}+\theta_{23}]S_{-t_1+t_2}(123)[\theta_{14}+\theta_{24}+\theta_{34}]S_{-t_2}(1234),\\ &\;\;\vdots\end{aligned} \tag{3.15}$$

Equation (3.15) can be established by repeatedly using identities similar to Eq. (3.1), for example,

$$S_{-t}(123)=S_{-t}(12)S_{-t}(3)+\int_0^t dt_1S_{-t+t_1}(12)S_{-t+t_1}(3)[\theta_{13}+\theta_{23}]S_{-t_1}(123), \tag{3.16}$$

along with Liouville's theorem and the symmetry of Eq. (3.14) under interchange of the labels $(3\cdots j)$.

The required density expansion of the operator $\hat{O}(t)$ can be found by combining Eqs. (3.10), (3.12), and (3.14). We have

$$\hat{O}(t)=\sum_{r=1}^{\infty}n^r\hat{O}_{r+1}(t), \tag{3.17}$$

where the explicit expressions for the operators $\hat{O}_r$, which depend on the dynamics of r particles, are given by

$$\begin{aligned}\hat{O}_2(t)&=\int dx_2\hat{\tau}(12,t)W(12)\phi(2),\\ \hat{O}_3(t)&=\int dx_2dx_3[\hat{\tau}(123,t)W(123)+\hat{\tau}(12,t)g(12;3)]\phi(2)\phi(3),\\ \hat{O}_4(t)&=\int dx_2dx_3dx_4[\hat{\tau}(1234,t)W(1234)+\hat{\tau}(123,t)g(123;4)+\hat{\tau}(12,t)g(12;34)]\phi(2)\phi(3)\phi(4),\end{aligned} \tag{3.18}$$

We have thus obtained the naive density expansion of $\hat{\mathbf{X}}(\mathbf{p}_1, t)$ in the form

$$\hat{\mathbf{X}}(\mathbf{p}_1, t) = S_{-t}(1)\phi(1)\frac{\mathbf{p}_1}{m} + \sum_{r=1}^{\infty} n^r \int_0^t d\tau S_{-t+\tau}(1)\hat{O}_{r+1}(\tau)\phi(1)\frac{\mathbf{p}_1}{m}. \tag{3.19}$$

We also give the Laplace transformed operators $O_r(\epsilon)$. They can be obtained by replacing $\hat{\tau}(12\cdots j, t)$ by its Laplace transform $\tau(12\cdots j, \epsilon)$ everywhere in Eq. (3.18). The explicit expressions for the $\tau(12\cdots j, \epsilon)$ are

$$\begin{aligned}
\tau(12, \epsilon) &= \theta_{12}G(12, \epsilon), \\
\tau(123, \epsilon) &= \theta_{12}G(12, \epsilon)(\theta_{13}+\theta_{23})G(123, \epsilon), \\
\tau(1234, \epsilon) &= \theta_{12}G(12, \epsilon)(\theta_{13}+\theta_{23})G(123, \epsilon)(\theta_{14}+\theta_{24}+\theta_{34})G(1234, \epsilon), \\
&\ \ \vdots
\end{aligned} \tag{3.20}$$

where $G(12\cdots j, \epsilon)$ is the Laplace transform of $S_{-t}(12\cdots j)$:

$$G(12\cdots j, \epsilon) = \int_0^{\infty} dt e^{-\epsilon t} S_{-t}(12\cdots j) = [\epsilon + \mathcal{H}(12\cdots j)]^{-1}. \tag{3.21}$$

In the following we will also need the Laplace transform of S_{-t}^0 which is

$$G_0(12\cdots j, \epsilon) = \int_0^{\infty} dt e^{-\epsilon t} S_{-t}^0(12\cdots j) = [\epsilon + \mathcal{H}_0(12\cdots j)]^{-1}. \tag{3.22}$$

4. RESUMMATION OF THE ϵ METHOD

In Sec. 3 we derived the naive density expansion of $\hat{\mathbf{X}}(\mathbf{p}_1, t)$. The Laplace transform of Eq. (3.19) gives the density expansion of $\mathbf{X}(\mathbf{p}_1, \epsilon)$ which we write as

$$\mathbf{X}(\mathbf{p}_1, \epsilon) = G(1, \epsilon)[1 + O(\epsilon)]\hat{\mathbf{X}}(\mathbf{p}_1, 0), \tag{4.1}$$

where

$$O(\epsilon) = \sum_{r=1}^{\infty} n^r O_{r+1}(\epsilon) \tag{4.2}$$

and

$$\hat{\mathbf{X}}(\mathbf{p}_1, 0) = \phi(1)\mathbf{p}_1/m. \tag{4.3}$$

Since $\hat{\mathbf{X}}(\mathbf{p}_1, 0)$ and $O(\epsilon)\hat{\mathbf{X}}(\mathbf{p}_1, 0)$ depend only on the momentum $\mathbf{p}_1$, we can replace $G(1, \epsilon)$ by ϵ^{-1} in Eq. (4.1). Hereafter, we suppress the momentum arguments in the $\mathbf{X}$'s.

As mentioned in Sec. 3, none of the terms in this naive density expansion exists as $\epsilon \to 0$. To surmount this difficulty one resums the right-hand side of Eq. (4.1) by the following procedure (which we call inversion): Write Eq. (4.1) as

$$[1 + O(\epsilon)]^{-1}\epsilon\mathbf{X}(\epsilon) = \mathbf{X}(0), \tag{4.4}$$

define $B(\epsilon)$ by

$$1 - B(\epsilon) \equiv [1 + O(\epsilon)]^{-1} \tag{4.5}$$

and the density expansion of B by

$$B(\epsilon) \equiv \sum_{r=1}^{\infty} n^r B_{r+1}(\epsilon). \tag{4.6}$$

Then Eq. (4.4) can be written as*

$$[\epsilon - \epsilon B(\epsilon)]\mathbf{X}(\epsilon) = \hat{\mathbf{X}}(0). \tag{4.7}$$

The operators B_r are found by expanding the geometric series in Eq. (4.5), using the density expansion Eq. (4.2) for $O(\epsilon)$, and equating coefficients of identical powers in the density. In this way one finds

$$\begin{aligned}
B_2 &= O_2, \\
B_3 &= O_3 - O_2^2, \\
B_4 &= O_4 - O_3O_2 - O_2O_3 + O_2^3, \\
&\ \ \vdots
\end{aligned} \tag{4.8}$$

The B_r clearly depend on the dynamics of r particles. Equations (4.6) through (4.8) define the resummed ϵ method.

It is especially interesting to note that the resummed ϵ equations can be obtained by an entirely different procedure involving the use of projection operators (PO method). The idea of the PO method is as follows: All one needs for the computation of the diffusion

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* Equation (4.7) is similar in form to the Dyson equation of quantum electrodynamics [C. Bloch, *Studies in Statistical Mechanics* (North Holland Publishing Co., Amsterdam, 1965), Vol. 3. To see this introduce an "exact" propagator $g(1, \epsilon)$, where

$$\mathbf{X}(\mathbf{p}_1, \epsilon) = g(1, \epsilon)\hat{\mathbf{X}}(\mathbf{p}_1, 0).$$

Then, using Eqs. (4.1) and (4.5) one sees that g satisfies the Dyson equation

$$[\epsilon + \mathcal{H}_0 - M(\epsilon)]g(1, \epsilon) = 1,$$

with self-energy operator $M(\epsilon) = B(\epsilon)G^{-1}(1, \epsilon)$.

coefficient is $\hat{\mathbf{X}}(\mathbf{p}_1, t)$. Since $\hat{\mathbf{X}}$ contains considerably less information than the N-particle operator S_{-t}, one defines a projection operator which projects $\hat{\mathbf{X}}$ out of S_{-t}. The formal realization of these ideas leads to Eqs. (4.6) through (4.8) above. Since the derivation of the resummed ϵ equations using the PO method is rather lengthy, we refer the interested reader to the literature (Zwanzig, 1960a; 1960b; Ernst, 1967).

5. RESUMMATION OF THE *t* METHOD

In Sec. 4, Eq. (4.7), we obtained a resummation for $\mathbf{X}(\epsilon)$ appropriate to the computation of D in the ϵ method via Eq. (2.18). Inspection of the corresponding equation for D in the t method, namely Eq. (2.15), shows that in the t method we shall need to obtain a resummation for $\mathbf{Y}(t)$ where

$$\mathbf{Y}(\mathbf{p}_1, t) = \int_0^t dt_1 \hat{\mathbf{X}}(\mathbf{p}_1, t_1). \tag{5.1}$$

By making use of the identity

$$\mathcal{H}\mathbf{R}_1 = \mathcal{H}(1)\mathbf{R}_1 = \mathbf{p}_1/m \tag{5.2}$$

and the definition of $\hat{\mathbf{X}}$ in Eq. (2.14), we may write $\mathbf{Y}$ as

$$\mathbf{Y}(\mathbf{p}_1, t) = \mathbf{y}(1, t) - \mathbf{y}(1, 0), \tag{5.3}$$

where

$$\mathbf{y}(1, t) = \lim_{\infty} V \int dx_2 \cdots dx_N S_{-t} f_N(-\mathbf{R}_1) \tag{5.4}$$

and where we have written $\mathbf{y}(1, t)$ to emphasize that $\mathbf{y}$ depends on $\mathbf{R}_1$ as well as $\mathbf{p}_1$.

In the literature (Ernst, Dorfman, and Cohen, 1964; 1965; Ernst, 1965; 1966), the resummation of the t method for $\mathbf{Y}$ is accomplished by analogy to equilibrium statistical mechanics. One makes an activity expansion of $\mathbf{y}(1, t)$ and the corresponding two-particle function $\mathbf{y}(12, t)$. The activity is then eliminated between these two expansions to give $\mathbf{y}(12, t)$ in terms of $\mathbf{y}(1, t)$. Finally, the first hierarchy equation, which relates $\mathbf{y}(1, t)$ and $\mathbf{y}(12, t)$, is used to give a closed equation for $\mathbf{y}(1, t)$ alone. Here we follow a shorter procedure which gives precisely the same result.

In exactly the same way as in Eq. (3.3) one can express $\mathbf{y}(1, t)$ in terms of $\hat{O}(t)$:

$$\mathbf{y}(1, t) = S_{-t}(1)\left[1 + \int_0^t d\tau S_\tau(1)\hat{O}(\tau)\right]\mathbf{y}(1, 0), \tag{5.5}$$

where

$$\mathbf{y}(1, 0) = -\mathbf{R}_1\phi(1). \tag{5.6}$$

The term $\hat{O}(t)\mathbf{y}(1, 0)$ does not depend on $\mathbf{R}_1$. This can be seen by considering

$$[\hat{O}(t)\mathbf{y}(1, 0)]_{\mathbf{R}_1 \to \mathbf{R}_1 + \mathbf{a}} - \hat{O}(t)\mathbf{y}(1, 0) = -\mathbf{a}\hat{O}(t)\phi(1) = 0, \tag{5.7}$$

and therefore, the operator $S_\tau(1)$ in Eq. (5.5) may be put equal to unity.

If we now differentiate Eq. (5.5) with respect to t, we obtain the first hierarchy equation for $\mathbf{y}(1, t)$, namely

$$[\partial\mathbf{y}(1, t)/\partial t] + \mathcal{H}(1)\mathbf{y}(1, t) = \hat{O}(t)\mathbf{y}(1, 0). \tag{5.8}$$

Solving Eq. (5.5) for $\mathbf{y}(1, 0)$,

$$\mathbf{y}(1, 0) = \left[1 + \int_0^t d\tau\hat{O}(\tau)\right]^{-1} S_t(1)\mathbf{y}(1, t), \tag{5.9}$$

and inserting this expression into the first hierarchy equation, we find

$$[\partial\mathbf{y}(1, t)/\partial t] + \mathcal{H}(1)\mathbf{y}(1, t) = L(t) S_t(1)\mathbf{y}(1, t), \tag{5.10}$$

where we have defined $L(t)$ by

$$L(t) = \hat{O}(t)\left[1 + \int_0^t d\tau\hat{O}(\tau)\right]^{-1}. \tag{5.11}$$

Finally, by using Eq. (5.3), we obtain the resummed equation for $\mathbf{Y}(\mathbf{p}_1, t)$ which appears in the literature for the t method:

$$\begin{aligned}[\partial\mathbf{Y}(\mathbf{p}_1, t)/\partial t] - L(t)\mathbf{Y}(\mathbf{p}_1, t)& \\ = (\mathbf{p}_1/m)\phi(1) - L(t) S_t(1)\phi(1)\mathbf{R}_1.&\end{aligned} \tag{5.12}$$

The operator $L(t)$ can be given as a density expansion:

$$L(t) = \sum_{r=1}^{\infty} n^r L_{r+1}(t), \tag{5.13}$$

where the operators $L_r(t)$, which involve the dynamics of r particles, are given by

$$\begin{aligned}
L_2(t) &= \hat{O}_2(t), \\
L_3(t) &= \hat{O}_3(t) - \hat{O}_2(t)\int_0^t dt_1\hat{O}_2(t_1), \\
L_4(t) &= \hat{O}_4(t) - \hat{O}_3(t)\int_0^t dt_1\hat{O}_2(t_1) - \hat{O}_2(t)\int_0^t dt_1\hat{O}_3(t_1) \\
&\qquad + \hat{O}_2(t)\int_0^t dt_1\hat{O}_2(t_1)\int_0^t dt_2\hat{O}_2(t_2), \\
&\ \ \vdots
\end{aligned} \tag{5.14}$$

In the next sections the resummed t equation (5.12) and the resummed ϵ equation (4.7) will be compared.

6. FORMAL COMPARISON OF THE *t* AND ϵ METHODS

In Sec. 4 we derived the resummed ϵ Eq. (4.7) for $\mathbf{X}(\epsilon)$:

$$[\epsilon - \epsilon B(\epsilon)]\mathbf{X}(\epsilon) = \phi(1)\mathbf{p}_1/m, \tag{6.1}$$

where the diffusion coefficient in the ϵ method is to be found from Eq. (2.18):

$$D = \frac{1}{3}\int d\mathbf{p}_1 \frac{\mathbf{p}_1}{m} \cdot \lim_{\epsilon \to 0} \mathbf{X}(\mathbf{p}_1, \epsilon). \tag{6.2}$$

Correspondingly, in Sec. 5 we derived the resummed t equation (5.12) for $\mathbf{Y}(t)$:

$$[\partial \mathbf{Y}(t)/\partial t]-L(t)\mathbf{Y}(t)=(\mathbf{p}_1/m)\phi(1)-L(t)S_t(1)\phi(1)\mathbf{R}_1, \qquad (6.3)$$

where the diffusion coefficient in the t method is to be found from Eq. (2.15):

$$D=\frac{1}{3}\int d\mathbf{p}_1\frac{\mathbf{p}_1}{m}\cdot\lim_{t\to\infty}\mathbf{Y}(\mathbf{p}_1,t). \qquad (6.4)$$

Since $\mathbf{Y}$ is defined as

$$\mathbf{Y}(t)=\int_0^t dt_1\hat{\mathbf{X}}(t_1), \qquad (6.5)$$

this equation gives the connection between the t and ϵ methods. Equivalently, Eq. (6.5) can be written as

$$\epsilon\int_0^\infty dte^{-\epsilon t}\mathbf{Y}(t)=\mathbf{X}(\epsilon). \qquad (6.6)$$

In order to make a formal comparison of the t and ϵ methods, we *assume* that the diffusion coefficient exists for the system under consideration, and thus that the limits in Eqs. (6.2) and (6.4) exist:

$$\mathbf{X}(0)=\lim_{\epsilon\to 0}\mathbf{X}(\epsilon); \qquad \mathbf{Y}(\infty)=\lim_{t\to\infty}\mathbf{Y}(t). \qquad (6.7)$$

By computing the Laplace transform of

$$\partial\mathbf{Y}(t)/\partial t=\hat{\mathbf{X}}(t) \qquad (6.8)$$

we see, of course, that

$$\mathbf{Y}(\infty)=\mathbf{X}(0). \qquad (6.9)$$

Furthermore, since it is always true for f and its Laplace transform that

$$\lim_{t\to\infty}\hat{f}(t)=\lim_{\epsilon\to 0}\epsilon f(\epsilon) \qquad (6.10)$$

provided only that the limits exist, we find

$$0=\lim_{\epsilon\to 0}\epsilon\mathbf{X}(\epsilon)=\lim_{t\to\infty}\hat{\mathbf{X}}(t)=\lim_{t\to\infty}[\partial\mathbf{Y}(t)/\partial t]. \qquad (6.11)$$

Using these results we can write the ϵ Eq. (6.1) in the limit as

$$\lim_{\epsilon\to 0}\epsilon B(\epsilon)\mathbf{X}(0)=-\phi(1)\mathbf{p}_1/m \qquad (6.12)$$

or equivalently as

$$\lim_{t\to\infty}\hat{B}(t)\mathbf{X}(0)=-\phi(1)\mathbf{p}_1/m. \qquad (6.13)$$

The t Eq. (6.3) can be written in the limit as

$$\lim_{t\to\infty}L(t)\mathbf{Y}(\infty)=-\phi(1)\mathbf{p}_1/m+\lim_{t\to\infty}L(t)S_t(1)\phi(1)\mathbf{R}_1. \qquad (6.14)$$

7. DENSITY EXPANSION OF THE t AND ϵ EQUATIONS

We recall that the resumed t and ϵ Eqs. (6.3) and (6.1), and especially their limiting forms (6.14) and (6.13) were designed to give a density expansion for the diffusion coefficient. The density expansion of L defined in Eq. (5.13),

$$L(t)=\sum_{r=1}^{\infty}n^rL_{r+1}(t), \qquad (7.1)$$

and the density expansion of $\hat{B}$ defined in Eq. (4.6),

$$\hat{B}(t)=\sum_{r=1}^{\infty}n^r\hat{B}_{r+1}(t), \qquad (7.2)$$

suggest that we assume that $\mathbf{Y}(\infty)$ and $\mathbf{X}(0)$ can be given as density expansions of the following form:

$$\mathbf{Y}(\infty)=n^{-1}\mathbf{Y}_0(\infty)+\mathbf{Y}_1(\infty)+n\mathbf{Y}_2(\infty)+\cdots, \qquad (7.3)$$

$$\mathbf{X}(0)=n^{-1}\mathbf{X}_0(0)+\mathbf{X}_1(0)+n\mathbf{X}_2(0)+\cdots. \qquad (7.4)$$

Assuming the validity of the expansions (7.3) *and* (7.4) leads to the t equations

$$\begin{aligned}
&L_2(\infty)\mathbf{Y}_0(\infty)=-\phi(1)\mathbf{p}_1/m,\\
&L_2(\infty)\mathbf{Y}_1(\infty)=-L_3(\infty)\mathbf{Y}_0(\infty)+\lim_{t\to\infty}L_2(t)\times S_t(1)\phi(1)\mathbf{R}_1,\\
&L_2(\infty)\mathbf{Y}_2(\infty)=-L_4(\infty)\mathbf{Y}_0(\infty)-L_3(\infty)\mathbf{Y}_1(\infty)+\lim_{t\to\infty}L_3(t)S_t(1)\phi(1)\mathbf{R}_1,\\
&\vdots
\end{aligned} \qquad (7.5)$$

which may be solved successively for the $\mathbf{Y}_j(\infty)$, and to the ϵ equations

$$\begin{aligned}
&\hat{B}_2(\infty)\mathbf{X}_0(0)=-\phi(1)\mathbf{p}_1/m,\\
&\hat{B}_2(\infty)\mathbf{X}_1(0)=-\hat{B}_3(\infty)\mathbf{X}_0(0),\\
&\hat{B}_2(\infty)\mathbf{X}_2(0)=-\hat{B}_4(\infty)\mathbf{X}_0(0)-\hat{B}_3(\infty)\mathbf{X}_1(0),\\
&\vdots
\end{aligned} \qquad (7.6)$$

which may be solved successively for the $\mathbf{X}_j$. In writing Eqs. (7.5) and (7.6), we have defined $\hat{B}_r(\infty)$ and $L_r(\infty)$ as

$$\hat{B}_r(\infty)=\lim_{t\to\infty}\hat{B}_r(t); \qquad L_r(\infty)=\lim_{t\to\infty}L_r(t) \qquad (7.7)$$

and assumed that we may interchange the sum over r and the limit as $t\to\infty$ in Eqs. (7.1) and (7.2).

This assumption is, however, not valid since it is well known that a detailed discussion of the dynamical events contributing to the operators L_r and B_r, for a gas of molecules interacting via short-range repulsive forces, shows that these operators diverge (fail to exist) in the limit as $t\to\infty$ if r is greater than 3. In fact, L_4 and $\hat{B}_4$ diverge as $\log t$, while L_r and $\hat{B}_r$ diverge as t^{r-4} $(r>4)$. Only L_2, $\hat{B}_2$, L_3 and $\hat{B}_3$ exist for $t\to\infty$. (In two dimensions the divergence appears one term earlier and only L_2 and B_2 exist.) References to the literature on the divergence may be found in Sec. 1.

The existence of this divergence shows us that only the first two of Eqs. (7.5) and (7.6) are well defined. We might use these equations to find the first two terms in the density expansion of D in both the t and ϵ methods, but we shall certainly not be able to go beyond these two terms without modifying the theory (making further resummations) to take the divergence into account. In a subsequent publication we shall discuss the divergence and its implications for the computation of density expansions of transport coefficients. Here we shall confine ourselves to a discussion of the computation of the first two terms in the density expansion of the diffusion coefficient in both the t and ϵ methods.

The first two of the t equations (7.5) *are* well defined and are customarily assumed to be valid for computing the first two terms in the density expansion of D in the t method:

$$D=\frac{1}{3}\int d\mathbf{p}_1\frac{\mathbf{p}_1}{m}\cdot[n^{-1}\mathbf{Y}_0(\infty)+\mathbf{Y}_1(\infty)+\cdots]. \quad (7.8)$$

Similarly, in the ϵ method, the first two of Eqs. (7.6) are assumed to be valid for computing the first two terms in the density expansion of D in this method:

$$D=\frac{1}{3}\int d\mathbf{p}_1\frac{\mathbf{p}_1}{m}\cdot[n^{-1}\mathbf{X}_0(0)+\mathbf{X}_1(0)+\cdots]. \quad (7.9)$$

Even though we have limited ourselves to the computation of the first two terms in the density expansion of D, we must now answer two questions, both posed by the existence of the divergence. These questions are: (1) Do the t and ϵ methods give the same result for the first two terms of the diffusion coefficient [as calculated from the first two of Eqs. (7.5) and (7.6)]? (2) Are there, beyond the first two terms in D, other terms proportional to n^{-1} or independent of n which would modify the first two terms in D [as calculated from the first two of Eqs. (7.5) and (7.6)]?

With regard to question (1), we see that it is sufficient to prove that

$$\mathbf{Y}_0(\infty)=\mathbf{X}_0(0) \quad (7.10)$$

and

$$\mathbf{Y}_1(\infty)=\mathbf{X}_1(0) \quad (7.11)$$

to show that the first two terms of D are the same in both methods. This will be accomplished if we can establish that the first two equations in (7.5) and (7.6) are identical.

It might be thought that this follows immediately from Sec. 6, where we showed that the solutions of Eqs. (6.13) and (6.14) are identical. The divergence spoils this result, however, as the following mathematical example shows. Think of functions $F^Y(t)$ and $F^X(t)$ [where $F^Y(\infty)$ and $F^X(\infty)$ are analogous to $\mathbf{Y}(\infty)$ and $\mathbf{X}(0)$, respectively] defined as

$$F^Y(t)=n^{-1}+(nt)^{-1}[\exp(-nt)-1], \quad (7.12)$$

$$F^X(t)=n^{-1}+(nt)^{-1}[\exp(-2nt)-1], \quad (7.13)$$

where n and t are dimensionless variables analogous to the number density and the time. Clearly,

$$F^Y(\infty)=F^X(\infty)=n^{-1}, \quad (7.14)$$

but if we write

$$F^Y(t)=\sum_{r=0}^{\infty}n^{r-1}F_r^Y(t);$$

$$F^X(t)=\sum_{r=0}^{\infty}n^{r-1}F_r^X(t), \quad (7.15)$$

we find

$$F_0^Y(\infty)=F_0^X(\infty)=1;$$

$$F_1^Y(\infty)=-1; \qquad F_1^X(\infty)=-2 \quad (7.16)$$

with all other nonzero F_r^Y and F_r^X diverging as $t\to\infty$. This example shows that because of the divergence it must be *proved directly*, by dynamical arguments, that

$$\mathbf{Y}_0(\infty)=\mathbf{X}_0(0); \qquad \mathbf{Y}_1(\infty)=\mathbf{X}_1(0) \quad (7.17)$$

if we are to establish the equality of the first two terms in the density expansion of the diffusion coefficient as computed by the two methods. We will give the required proof in Sec. 8.

With regard to the second question, no definite answer is available. To see why this is so, we consider a slight modification of our mathematical example. Suppose we now define a function $F(t)$ as

$$F(t)=n^{-1}+(nt)^{-1}[\exp(-nt)-1] \quad (7.18)$$

with density expansion

$$F(t)=\sum_{r=0}^{\infty}n^{r-1}F_r(t) \quad (7.19)$$

so that

$$F_0(\infty)=1; \qquad F_1(\infty)=-1 \quad (7.20)$$

with all other nonzero F_r diverging as $t\to\infty$. If we try to write

$$F(\infty)=n^{-1}-1+\cdots, \quad (7.21)$$

we see that the terms beyond the first two in Eq. (7.21) add up in just such a way as to give $+1$ since we know from Eq. (7.18) that

$$F(\infty)=n^{-1}. \quad (7.22)$$

This example clearly shows that it is not impossible for the terms beyond the first two in D to combine in such a way as to modify the first two terms. Whether or not this happens depends of course on the system under consideration. It is generally assumed, for a gas of molecules interacting via short-range repulsive forces, that the first two terms in the density expansion of the diffusion coefficient are not modified by the remaining terms which diverge and are neglected. There is, strictly speaking, no sound basis for this assumption. It is clear from the example that a proof of the assumption would require that we be able to evaluate $L(\infty)$ or $\hat{B}(\infty)$ for this system, either directly or else by means of a fully convergent density expansion (not necessarily a power series expansion). At present, it is not known how to accomplish this, and thus a rigorous answer to question (2) is not available.

For the sake of simplicity, we shall assume that the terms beyond the first two in Eqs. (7.8) and (7.9) do not in fact modify the first two terms. We emphasize, however, that this is an assumption, and that it has not been proved.

8. COMPARISON OF THE t AND ϵ METHODS FOR THE FIRST TWO TERMS IN THE DENSITY EXPANSION OF THE DIFFUSION COEFFICIENT

In Sec. 7 we saw that in the t method, D could be written as

$$D=\frac{1}{3}\int d\mathbf{p}_1\frac{\mathbf{p}_1}{m}\cdot[n^{-1}\mathbf{Y}_0(\infty)+\mathbf{Y}_1(\infty)+\cdots], \tag{8.1}$$

where

$$L_2(\infty)\mathbf{Y}_0(\infty)=-\phi(1)\mathbf{p}_1/m, \tag{8.2}$$

$$L_2(\infty)\mathbf{Y}_1(\infty)=-L_3(\infty)\mathbf{Y}_0(\infty)+\lim_{t\to\infty}L_2(t)S_t(1)\phi(1)\mathbf{R}_1; \tag{8.3}$$

in the ϵ method we had

$$D=\frac{1}{3}\int d\mathbf{p}_1\frac{\mathbf{p}_1}{m}\cdot[n^{-1}\mathbf{X}_0(0)+\mathbf{X}_1(0)+\cdots], \tag{8.4}$$

where

$$\hat{B}_2(\infty)\mathbf{X}_0(0)=-\phi(1)\mathbf{p}_1/m, \tag{8.5}$$

$$\hat{B}_2(\infty)\mathbf{X}_1(0)=-\hat{B}_3(\infty)\mathbf{X}_0(0). \tag{8.6}$$

In this section we shall show that both methods give the same result for the first two terms of the density expansion of the diffusion coefficient.

We first consider Eqs. (8.2) and (8.5). From Eqs. (5.14) and (4.8) we have

$$L_2(t)=\hat{B}_2(t)=\hat{O}_2(t). \tag{8.7}$$

It follows immediately that

$$\hat{B}_2(\infty)=L_2(\infty), \tag{8.8}$$

so that $\mathbf{X}_0(0)$ and $\mathbf{Y}_0(\infty)$ satisfy the same equation and are equal insofar as the solution to this equation is unique (we shall see below that the solution is indeed unique).

To put this result in a more familiar form, we define $\mathbf{\Delta}(\mathbf{p}_1)$ by

$$\phi(p_1)\mathbf{\Delta}(\mathbf{p}_1)\equiv\mathbf{X}_0(0)=\mathbf{Y}_0(\infty). \tag{8.9}$$

Using the first of Eqs. (3.18) and (3.20) we may write Eq. (8.2) as

$$\int dx_2\theta_{12}S_{-\infty}(12)W(12)\phi(2)\phi(1)\mathbf{\Delta}(\mathbf{p}_1)=-\phi(p_1)\mathbf{p}_1/m, \tag{8.10}$$

while (8.5) may be written

$$\lim_{\epsilon\to 0}\epsilon\int dx_2\theta_{12}G(12,\epsilon)W(12)\phi(2)\phi(1)\mathbf{\Delta}(\mathbf{p}_1)=-\phi(p_1)\mathbf{p}_1/m. \tag{8.11}$$

The operators in Eqs. (8.10) and (8.11) are of course equal. Equations (8.10) and (8.11) are a Boltzmann equation for $\mathbf{\Delta}(\mathbf{p}_1)$. Zwanzig has shown this (1963) for the operator in Eq. (8.11), and it has been shown by Bogoliubov (1961) for the operator in Eq. (8.10). Thus the previous proof of the equality of $\mathbf{X}_0(0)$ and $\mathbf{Y}_0(\infty)$ proceeded by demonstrating that Eqs. (8.10) and (8.11) both gave a Boltzmann equation, while we have instead proved the equality of the operators in Eqs. (8.10) and (8.11) directly. For completeness we give the Boltzmann equation (Chapman and Cowling, 1939) resulting from Eqs. (8.10) and (8.11). It is

$$I(\mathbf{\Delta}(\mathbf{p}_1))\equiv\int d\mathbf{p}_2\int bdbd\chi\left(\frac{|\mathbf{p}_1-\mathbf{p}_2|}{m}\right)\times[\mathbf{\Delta}(\mathbf{p}_1')-\mathbf{\Delta}(\mathbf{p}_1)]\phi(p_1)\phi(p_2)=-\phi(p_1)\mathbf{p}_1/m. \tag{8.12}$$

It is well known that the solution for $\mathbf{\Delta}$ is unique up to a vector solution of the homogeneous equation $I(\mathbf{\Delta}(\mathbf{p}_1))=0$. Since no such vector is available, $\mathbf{\Delta}$ is unique and Eq. (8.9) is established.

Having seen how the equivalence of the t and ϵ methods for computing D is established at the Boltzmann level, we turn to the question of the equivalence of the density-independent contributions to D. Here we must show that

$$\mathbf{Y}_1(\infty)=\mathbf{X}_1(0). \tag{8.13}$$

This will be demonstrated by showing that the integral equations (8.3) and (8.6) are identical.

Let us consider the operators $L_3(t)$ and $\hat{B}_3(t)$ where $L_3(t)$ is given by Eq. (5.14) as

$$L_3(t)=\hat{O}_3(t)-\hat{O}_2(t)\int_0^t d\tau\hat{O}_2(\tau), \tag{8.14}$$

and where $\hat{B}_3(t)$ is found by taking the inverse Laplace transform of $B_3(\epsilon)$ in Eq. (4.8):

$$\hat{B}_3(t)=\hat{O}_3(t)-\int_0^t d\tau\hat{O}_2(\tau)\hat{O}_2(t-\tau). \tag{8.15}$$

The elimination of $\hat{O}_3$ between Eqs. (8.14) and (8.15) leads to*

$$L_3(t)=\hat{B}_3(t)-\int_0^t d\tau[L_2(t)-L_2(\tau)]L_2(t-\tau) \tag{8.16}$$

---

* For the case of hard-sphere interactions, where $L_2(t)=L_2(\tau)=L_2(\infty)$, one has

$$L_3(t)=\hat{B}_3(t)$$

(Kawasaki and Oppenheim, 1964b). For the same reason, the right-hand side of Eq. (8.18) vanishes so that the integral equations (8.3) and (8.6) are identical for hard spheres. Similarly, one sees from Eq. (A.40) in the Appendix, that

$$\mathbf{L}_3(t)=\hat{\mathbf{B}}_3(t)$$

for hard spheres.

so that Eq. (8.3) can be written

$$\hat{B}_2(\infty)\mathbf{Y}_1(\infty)=-\hat{B}_3(\infty)\mathbf{X}_0(0)+\lim_{t\to\infty}\left\{\int_0^t d\tau[L_2(t)-L_2(\tau)]L_2(t-\tau)\times\mathbf{Y}_0(\infty)+L_2(t)S_t(1)\phi(1)\mathbf{R}_1\right\}. \quad (8.17)$$

In writing Eq. (8.17) we have made use of Eqs. (8.8) and (8.9).

We must now establish the identity of Eqs. (8.17) and (8.6). This is most conveniently accomplished by using the relation

$$L_2(t)S_t(1)\phi(1)\mathbf{R}_1=\int_0^t d\tau[L_2(t)-L_2(\tau)]\phi(1)\frac{\mathbf{p}_1}{m} \quad (8.18)$$

which can be established by observing that

$$L_2(t)S_t(1)\phi(1)\mathbf{R}_1=L_2(t)\phi(1)[\mathbf{R}_1+(\mathbf{p}_1t/m)] \quad (8.19)$$

and that

$$-\int_0^t d\tau L_2(\tau)\phi(1)\frac{\mathbf{p}_1}{m}=\int_0^t d\tau\frac{\partial L_2(\tau)}{\partial\tau}\phi(1)\mathbf{R}_1=L_2(t)\phi(1)\mathbf{R}_1. \quad (8.20)$$

In writing Eq. (8.20) we made use of the relation

$$\mathbf{p}_1/m=\mathcal{H}(1)\mathbf{R}_1=\mathcal{H}(12)\mathbf{R}_1 \quad (8.21)$$

and the explicit form of L_2 given in Eq. (3.18) as

$$L_2(t)=\int dx_2\theta_{12}S_{-t}(12)W(12)\phi(2). \quad (8.22)$$

Using Eq. (8.18), the term in braces in (8.17) can now be written as

$$\lim_{t\to\infty}\left\{\int_0^t d\tau[L_2(t)-L_2(\tau)]\left[L_2(t-\tau)\mathbf{Y}_0(\infty)+\phi(1)\frac{\mathbf{p}_1}{m}\right]\right\}. \quad (8.23)$$

In order to discuss the limit in (8.23) we need to know the behavior of $L_2(t)$ as $t\to\infty$. If we examine $L_2(t)$ as given by Eq. (8.22), we see that $S_{-t}(12)$ moves particles 1 and 2 from their initial phase points to their phase points at time $(-t)$. However, the operator θ_{12}, defined in Eq. (2.13), will be zero unless the particles are initially within the range of the force, r_0. Therefore, the operator $S_{-t}(12)$ moves particles 1 and 2 from their initial phase points where $|\mathbf{R}_1-\mathbf{R}_2|\lesssim r_0$ to their phase points at time $(-t)$. Since the force is repulsive and short range, the particles are separated after a finite time on the order of the duration of a collision, τ_0, where

$$\tau_0\approx mr_0|\mathbf{p}_1-\mathbf{p}_2|^{-1}. \quad (8.24)$$

Thus for all times $t\gtrsim\tau_0$, the particles are separated and $\Phi(|\mathbf{R}_1-\mathbf{R}_2|)=0$, so that $W(12)=1$. Also the momenta $\mathbf{p}_1$ and $\mathbf{p}_2$ will have attained their asymptotic values $\mathbf{p}_1'$ and $\mathbf{p}_2'$, i.e.,

$$L_2(t)=L_2(\infty) \quad \text{if} \quad t\gtrsim\tau_0. \quad (8.25)$$

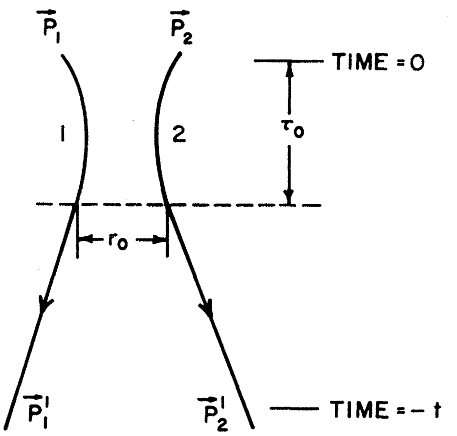

Fig. 2. The effect of $L_2(t)$. Molecules 1 and 2 must be initially within the range of the force, r_0, to make any contribution to $L_2(t)$. For times t greater than the time of a collision, τ_0, the molecules are separated, have attained their asymptotic momenta $\mathbf{p}_1'$ and $\mathbf{p}_2'$, and $L_2(t)$ takes its asymptotic value, $L_2(\infty)$.

A diagram is given in Fig. 2.

We now use the result of Eq. (8.25) to discuss the limit in Eq. (8.23) for large t ($t\gg\tau_0$). Since $L_2(\tau)$ in Eq. (8.23) approaches its asymptotic value in a time τ_0, the integrand of the τ integral vanishes for $\tau\gtrsim\tau_0$. Thus, as $t\to\infty$, we may replace $L_2(t-\tau)$ by $L_2(\infty)$. By using Eq. (8.2), we see immediately that the limit in Eq. (8.23) is zero. Equation (8.17) is therefore

$$\hat{B}_2(\infty)\mathbf{Y}_1(\infty)=-\hat{B}_3(\infty)\mathbf{X}_0(0), \quad (8.26)$$

which establishes the equality of the inhomogeneous terms in the integral equations (8.3) and (8.6).

We have thus proved that both integral equations (and their solutions) are identical, or that the first density correction to the coefficient of self-diffusion is the same in both t and ϵ methods.

9. CONCLUSION

We have given a unified discussion of the ϵ method (due to Zwanzig) and the t method (due to Cohen, Dorfman, and Ernst) for computing the density expansion of transport coefficients from time-correlation functions. We had in mind a system which was a moderately dense gas with repulsive short-range forces. Taking the self-diffusion coefficient as an example, we saw that it could be computed in a density expansion from

$$D=\frac{1}{3}\int d\mathbf{p}_1\frac{\mathbf{p}_1}{m}\cdot\begin{cases}\lim\limits_{t\to\infty}\mathbf{Y}(\mathbf{p}_1,t) & (t \text{ method})\\ \lim\limits_{\epsilon\to0}\mathbf{X}(\mathbf{p}_1,\epsilon) & (\epsilon \text{ method})\end{cases} \quad (9.1)$$

provided a density expansion of the first time-correlation functions $\mathbf{Y}$ or $\mathbf{X}$ was available. A straightforward cluster expansion of the first time-correlation functions was obtained in Sec. 3 which led to a density expansion of $\mathbf{Y}$ and $\mathbf{X}$. This expansion, which we called the naive density expansion, was clearly unsuitable for computing a density expansion of D since *none* of the terms in the expansion existed in the appropriate limit.

This difficulty was surmounted, at least for the first two terms in the density expansion of D, by making a rearrangement of the naive density expansion. The two procedures commonly used to do this, the ϵ method and the t method, were outlined in Secs. 4 and 5, and in Sec. 6 it was shown that they led to the following two integral equations for $\mathbf{Y}(\infty)=\mathbf{X}(0)$:

$$\lim_{t\to\infty}\hat{B}(t)\mathbf{X}(0)=-\phi(1)\mathbf{p}_1/m, \tag{9.2a}$$

$$\lim_{t\to\infty}L(t)\mathbf{Y}(\infty)=-\phi(1)\mathbf{p}_1/m+\lim_{t\to\infty}L(t)S_t(1)\phi(1)\mathbf{R}_1. \tag{9.2b}$$

The utility of these integral equations lay in the possibility of obtaining from them density expansions of $\mathbf{Y}(\infty)$ and $\mathbf{X}(0)$ in the form

$$\mathbf{Y}(\infty)=n^{-1}\mathbf{Y}_0(\infty)+\mathbf{Y}_1(\infty)+\cdots, \tag{9.3a}$$

$$\mathbf{X}(0)=n^{-1}\mathbf{X}_0(0)+\mathbf{X}_1(0)+\cdots. \tag{9.3b}$$

In Sec. 7 the density expansions of the integral operators $\hat{B}(t)$ and $L(t)$

$$\hat{B}(t)=\sum_{r=1}^{\infty}n^r\hat{B}_{r+1}(t);$$

$$L(t)=\sum_{r=1}^{\infty}n^rL_{r+1}(t), \tag{9.4}$$

were introduced into Eqs. (9.2). Provided that the limit $t\rightarrow\infty$ in (9.2) and the sum over powers of the density in (9.4) were interchanged, well-defined integral equations for $\mathbf{Y}_0$ and $\mathbf{Y}_1$ were obtained in the t method, as were well-defined equations for $\mathbf{X}_0$ and $\mathbf{X}_1$ in the ϵ method. The equations for $\mathbf{Y}_0$ and $\mathbf{X}_0$ depended, through L_2 and $\hat{B}_2$, upon the dynamics of two interacting molecules in the gas, while the equations for $\mathbf{Y}_1$ and $\mathbf{X}_1$ depended, through L_3 and $\hat{B}_3$, upon the dynamics of three interacting gas molecules. We mentioned that the equations for the terms in the expansions (9.3) beyond $\mathbf{Y}_1$ and $\mathbf{X}_1$ failed to exist because of the well-known divergence of the operators $\hat{B}_r(t)$ and $L_r(t)$ for $r>3$ as $t\rightarrow\infty$. Therefore, without further resummations the t and ϵ methods could only give the first two terms in the density expansions of transport coefficients.

We studied a mathematical example which showed that because of the divergence it was necessary to prove explicitly (by dynamical arguments) that

$$\mathbf{Y}_0(\infty)=\mathbf{X}_0(0);\qquad \mathbf{Y}_1(\infty)=\mathbf{X}_1(0). \tag{9.5}$$

Equation (9.5) did *not* follow directly from the equality of $\mathbf{Y}(\infty)$ and $\mathbf{X}(0)$. We gave the proof which established Eq. (9.5) in Sec. 8 and showed thereby that the t and ϵ methods as formulated in the literature and in this paper gave the same results for the first two terms in the density expansion of the diffusion coefficient:

$$D=n^{-1}D_0+D_1+\cdots. \tag{9.6}$$

A similar result is established for the shear viscosity

$$\eta=\eta_0+n\eta_1+\cdots \tag{9.7}$$

in the Appendix [a different approach to this proof for the viscosity has been given by Kawasaki and Oppenheim (1964a)].

The mathematical example also showed that it would not be impossible for the divergent terms, beyond the first two in Eq. (9.3), when properly resummed, to modify either or both of the first two terms in Eq. (9.3). This *could*, in principle, affect the values of either of the first or second terms in the density expansions of transport coefficients as computed from the t and ϵ methods. Whether or not this happens is in fact not known, and *we wish to stress that one cannot have a truly rigorous derivation of the Boltzmann Eq.* (8.12) *until this question is settled.* In order to assert with complete confidence that the first two terms are not modified, it would be necessary either to evaluate $B(\infty)$ or $L(\infty)$ in (9.4) in closed form (a task more difficult than evaluating the partition function in closed form) or to have available a systematic procedure which would give either $\hat{B}(\infty)$ or $L(\infty)$ as a density expansion (not necessarily a power series) with finite coefficients. Since it is not known at present how to accomplish either of these procedures, it is usually assumed, for gases with short-range repulsive intermolecular forces, that the first two terms in the density expansions of transport coefficients can be correctly computed from the t or ϵ method, and that they are unmodified by the divergent terms in (9.6) and (9.7) which are neglected. With this assumption, either the t or the ϵ method provides the machinery to compute the first two terms in the density expansion of transport coefficients, and we have seen that the results are independent of the method used.

Because of the divergence of the operators $\hat{B}_r$ and L_r for $r>3$, the analogy between density expansions of equilibrium properties (virial expansion) of a gas and the density expansions of its transport properties breaks down at low densities. Thus, in the nonequilibrium case (in contrast to the equilibrium situation) it is not possible to obtain a power series expansion of transport coefficients in the density with coefficients depending only on the interactions of r particles by using the t and ϵ methods, at least if r is greater than 3. It would appear that collective effects become important at rather low densities when density expansions of transport coefficients are attempted.

In order to obtain terms beyond the first two in a density expansion of transport coefficients, it is necessary to make a resummation of the divergent operators in Eq. (9.4). Kawasaki and Oppenheim (1965) have suggested a procedure for resumming certain terms in Eq. (9.4) in the ϵ method. In essence this resummation has the effect that the free motion, between binary collisions, of the four molecules which contribute to B_4

is modified (damped) by binary collisions with all other molecules in the gas. These considerations lead to a modified $\hat{B}_4$ operator which is not divergent and which can be used to obtain the third term in the density expansion of transport coefficients. This method of resummation indicates that the third term in the density expansion of the self-diffusion coefficient should have a density dependence of $n \log n$, while the third term in the shear viscosity should behave as $n^2 \log n$ (Dorfman, 1967). For various model systems, the effects of further resummations have been discussed by Weyland and van Leeuwen (1968), Hoegy (1967), Lebowitz and Percus (1967), and Hauge and Cohen (1967, 1968).

APPENDIX

In this Appendix we outline briefly how the results of the text for the diffusion coefficient can be generalized to the shear viscosity η. The notation is in general the same as in the body of the paper, and we shall use boldface letters to denote certain operators (e.g., **B**, **L**, **O**; *not vectors*), generalized to the viscosity.

The viscosity is given by the following time-correlation expression (Mori, 1961):

$$\eta = \lim_{\epsilon\to 0} \lim_{\infty} \frac{\beta}{10V} \int_0^\infty dt e^{-\epsilon t} \langle J : S_{-t} J \rangle \qquad (A.1)$$

appropriate to the ϵ method; for the t method one has an expression analogous to Eq. (2.6). The dyadic current J is given by

$$J = \sum_{i=1}^{N} \left\{ \frac{\mathbf{p}_i \mathbf{p}_i}{m} \right\} - \sum_{1\le i<j\le N} \left\{ \mathbf{r}_{ij} \frac{\partial \Phi_{ij}}{\partial \mathbf{r}_{ij}} \right\}, \qquad (A.2)$$

where $\mathbf{r}_{ij} = \mathbf{R}_i - \mathbf{R}_j$, and where $\{A_{\alpha\beta}\}$ stands for the traceless symmetric part of the tensor $A_{\alpha\beta}$ (Greek subscripts stand for x, y, or z):

$$\{A_{\alpha\beta}\} \equiv \tfrac{1}{2}(A_{\alpha\beta} + A_{\beta\alpha}) - \tfrac{1}{3}\delta_{\alpha\beta} \sum_{\gamma} A_{\gamma\gamma}. \qquad (A.3)$$

In analogy to Sec. 2, we introduce the time-correlation functions

$$\hat{X}(12\cdots s, t) = \lim_{\infty} V^s \int dx_{s+1} \cdots dx_N S_{-t} f_N J \qquad (A.4)$$

in terms of which the viscosity can be expressed as

$$\eta = \eta_k + \eta_\phi. \qquad (A.5)$$

The kinetic part η_k is given by

$$\eta_k = \tfrac{1}{10}(n\beta) \int d\mathbf{p}_1 \frac{\mathbf{p}_1 \mathbf{p}_1}{m} : \lim_{\epsilon\to 0} X(\mathbf{p}_1, \epsilon), \qquad (A.6)$$

where the notation shows explicitly that $\hat{X}(1, t)$ depends only on $\mathbf{p}_1$ and not on $\mathbf{R}_1$. The potential part η_ϕ is given by

$$\eta_\phi = -\tfrac{1}{20}(n^2\beta) \int d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{r}_{12} \mathbf{r}_{12} \frac{\partial \Phi_{12}}{\partial \mathbf{r}_{12}} : \lim_{\epsilon\to 0} X(12, \epsilon) \qquad (A.7a)$$

$$= \tfrac{1}{40}(n^2\beta) \int d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{r}_{12} \mathbf{p}_{12} \mathbf{r}_{12} \theta_{12} : \lim_{\epsilon\to 0} X(12, \epsilon) \qquad (A.7b)$$

with $\mathbf{p}_{12} = \mathbf{p}_1 - \mathbf{p}_2$. Equation (A.7b), which is convenient for later use, can be reduced to (A.7a) by partial integration with respect to $\mathbf{p}_1$ and $\mathbf{p}_2$. The expressions for the t method corresponding to Eqs. (A.6) and (A.7) are obtained by replacing $\lim_{\epsilon\to 0} X(12\cdots s, \epsilon)$ by $\lim_{t\to\infty} \hat{Y}(12\cdots s, t)$, where $\hat{Y}(12\cdots s, t)$ is defined by

$$\hat{Y}(12\cdots s, t) = \int_0^t d\tau \hat{X}(12\cdots s, \tau). \qquad (A.8)$$

Using the identity

$$J = \sum_{i=1}^{N} \mathcal{H} \{\mathbf{p}_i \mathbf{R}_i\} \qquad (A.9)$$

in the definition of $\hat{X}$, we may write

$$\hat{Y}(12\cdots s, t) = \hat{y}(12\cdots s, t) - \hat{y}(12\cdots s, 0), \qquad (A.10)$$

where

$$\hat{y}(12\cdots s, t) = \lim_{\infty} V^s \int dx_{s+1} \cdots dx_N S_{-t} f_N \sum_{i=1}^{N} \{-\mathbf{p}_i \mathbf{R}_i\}. \qquad (A.11)$$

Following the procedure of Sec. 3 we now derive the naive density expansion of $\hat{y}(1, t)$. Analogous to Eq. (3.3) we find

$$\hat{y}(1, t) = S_{-t}(1) \left[1 + \int_0^t d\tau S_\tau(1) \hat{\mathbf{O}}(\tau) \right] \hat{y}(1, 0), \qquad (A.12)$$

where

$$\hat{y}(1, 0) = -\{\mathbf{p}_1 \mathbf{R}_1\} \phi(1) \qquad (A.13)$$

and

$$\hat{\mathbf{O}}(t) = \lim_{\infty} V \int dx_2 \cdots dx_N \times \sum_{1\le i<j\le N} \theta_{ij} S_{-t} f_N \sum_{k=1}^{N} P_{1k} [\phi(1)]^{-1} \qquad (A.14a)$$

$$= n \int dx_2 \hat{T}(12, t) g(12) \phi(1) \phi(2) \sum_{i=1}^{2} P_{1i} [\phi(1)]^{-1} + n^2 \int dx_2 dx_3 \hat{T}(123, t) g(123) \phi(1) \phi(2) \phi(3) \times \sum_{i=1}^{3} P_{1i} [\phi(1)]^{-1} + \cdots. \qquad (A.14b)$$

The permutation operator P_{1i} interchanges the labels 1 and i. In deriving Eq. (A.14) we have used the relation $\int d\mathbf{p}_1 \hat{y}(1, 0) = 0$. The operator $\hat{\mathbf{O}}(t)$ can be expanded in powers of the density

$$\hat{\mathbf{O}}(t) = \sum_{r=1}^{\infty} n^r \hat{\mathbf{O}}_{r+1}(t), \qquad (A.15)$$

and it follows immediately from Sec. 3 that the $\hat{\mathbf{O}}_r$ operators can be obtained from the $\hat{O}_r$ operators in

Eq. (3.18) provided the following replacements are made everywhere in Eq. (3.18):

$$\hat{\tau}(12\cdots j,t)\phi(2)\cdots\phi(j)\rightarrow\hat{\tau}(12\cdots j,t)$$
$$\times\phi(1)\phi(2)\cdots\phi(j)\sum_{i=1}^{j}P_{1i}[\phi(1)]^{-1}. \quad (\text{A.16})$$

We have thus obtained the naive density expansion of $\hat{y}(1,t)$ in the form

$$\hat{y}(1,t)=S_{-t}(1)\hat{y}(1,0)$$
$$+\sum_{r=1}^{\infty}n^{r}\int_{0}^{t}d\tau S_{-t+\tau}(1)\hat{\mathbf{O}}_{r+1}(\tau)\hat{y}(1,0). \quad (\text{A.17})$$

In contrast to Sec. 4 we now apply the ϵ method to $y(1,\epsilon)$ instead of $X(1,\epsilon)$. Taking the Laplace transform of Eq. (A.12) and inverting this equation, we obtain

$$[1+\mathbf{O}(\epsilon)]^{-1}G^{-1}(1,\epsilon)y(1,\epsilon)=\hat{y}(1,0). \quad (\text{A.18})$$

Next we introduce the operator $\mathbf{B}(\epsilon)$ defined by

$$1-\mathbf{B}(\epsilon)=[1+\mathbf{O}(\epsilon)]^{-1} \quad (\text{A.19})$$

and write its density expansion as

$$\mathbf{B}(\epsilon)=\sum_{r=1}^{\infty}n^{r}\mathbf{B}_{r+1}(\epsilon). \quad (\text{A.20})$$

It is clear that the operators $\mathbf{B}_r(\epsilon)$ have the same relation to $\mathbf{O}_r(\epsilon)$ as do the $B_r(\epsilon)$ to the $O_r(\epsilon)$ in (4.8). Since it follows from (A.8) and (A.10) that

$$\epsilon y(1,\epsilon)=X(\mathbf{p}_1,\epsilon)+\hat{y}(1,0), \quad (\text{A.21})$$

we obtain, from (A.18), the resummed equation[*] for $X(\mathbf{p}_1,\epsilon)$:

$$[\epsilon-\epsilon\mathbf{B}(\epsilon)]X(\mathbf{p}_1,\epsilon)=\{\mathbf{p}_1\mathbf{p}_1/m\}\phi(1)$$
$$-\mathbf{B}(\epsilon)G^{-1}(1,\epsilon)\phi(1)\{\mathbf{p}_1\mathbf{R}_1\}. \quad (\text{A.22})$$

In deriving this equation we have observed that

$$G^{-1}(1,\epsilon)X(\mathbf{p}_1,\epsilon)=\epsilon X(\mathbf{p}_1,\epsilon) \quad (\text{A.23})$$

and that

$$[\epsilon-G^{-1}(1,\epsilon)]\hat{y}(1,0)=\mathcal{H}(1)\{\mathbf{p}_1\mathbf{R}_1\}\phi(1)$$
$$=\{\mathbf{p}_1\mathbf{p}_1/m\}\phi(1). \quad (\text{A.24})$$

The resummation of the first time-correlation function in the t method parallels the treatment in Sec. 5. We derive an equation for $\hat{y}(1,t)$ by differentiating (A.12) with respect to time:

$$\partial\hat{y}(1,t)/\partial t=-\mathcal{H}(1)\hat{y}(1,t)+\hat{\mathbf{O}}(t)\hat{y}(1,0). \quad (\text{A.25})$$

In Eq. (A.12) $\hat{\mathbf{O}}(\tau)\hat{y}(1,0)$ is independent of $\mathbf{R}_1$. This can be verified by replacing $\mathbf{R}_1$ by $\mathbf{R}_1+\mathbf{a}$ and using Eqs. (A.13) and (A.14) and the conservation of total momentum. We may, therefore, replace $S_\tau(1)$ by unity in Eq. (A.12) and solve for $\hat{y}(1,0)$ to find

$$\hat{y}(1,0)=\left[1+\int_{0}^{t}d\tau\hat{\mathbf{O}}(\tau)\right]^{-1}S_t(1)\hat{y}(1,t). \quad (\text{A.26})$$

Eliminating $\hat{y}(1,0)$ between (A.25) and (A.26) and using (A.10) gives the resummed equation for $\hat{Y}(\mathbf{p}_1,t)$:

$$\partial\hat{Y}(\mathbf{p}_1,t)/\partial t-\mathbf{L}(t)\hat{Y}(\mathbf{p}_1,t)$$
$$=\{\mathbf{p}_1\mathbf{p}_1/m\}\phi(1)-\mathbf{L}(t)S_t(1)\phi(1)\{\mathbf{p}_1\mathbf{R}_1\}. \quad (\text{A.27})$$

We have defined $\mathbf{L}(t)$ as

$$\mathbf{L}(t)=\hat{\mathbf{O}}(t)\left[1+\int_{0}^{t}d\tau\hat{\mathbf{O}}(\tau)\right]^{-1} \quad (\text{A.28})$$

and its density expansion as

$$\mathbf{L}(t)=\sum_{r=1}^{\infty}n^{r}\mathbf{L}_{r+1}(t). \quad (\text{A.29})$$

The coefficients $\mathbf{L}_r$ are expressed in terms of $\hat{\mathbf{O}}_r$ in the same way as L_r is given in terms of $\hat{O}_r$ in Eq. (5.14).

As in Sec. 6, one may make a formal comparison of the resummed equations (A.22) and (A.27) in the limits $\epsilon\rightarrow0$ and $t\rightarrow\infty$, respectively. However, if a density expansion of the resummed equations is considered, one finds that the operators $\hat{\mathbf{B}}_r(t)$ and $\mathbf{L}_r(t)$ have the same divergent behavior ($t\rightarrow\infty$) for $r>3$ as do the operators $\hat{B}_r(t)$ and $L_r(t)$ in the case of the diffusion coefficient. Therefore, all of the remarks of Sec. 7 apply to the viscosity as well, and one has to establish explicitly the equivalence of the results of the two methods for the shear viscosity, to lowest and first order in the density.

If one *assumes* expansions of the form

$$X(0)=n^{-1}X_0(0)+X_1(0)+\cdots \quad (\text{A.30})$$

and

$$\hat{Y}(\infty)=n^{-1}\hat{Y}_0(\infty)+\hat{Y}_1(\infty)+\cdots \quad (\text{A.31})$$

in which for convenience of notation the argument $\mathbf{p}_1$ is dropped, the following well-defined equations are obtained:

$$\hat{\mathbf{B}}_2(\infty)X_0(0)=-\{\mathbf{p}_1\mathbf{p}_1/m\}\phi(1), \quad (\text{A.32})$$

$$\hat{\mathbf{B}}_2(\infty)X_1(0)=-\hat{\mathbf{B}}_3(\infty)X_0(0)$$
$$+\lim_{t\rightarrow\infty}\left[\hat{\mathbf{B}}_2(t)+\int_{0}^{t}d\tau\hat{\mathbf{B}}_2(\tau)\mathcal{H}(1)\right]\phi(1)\{\mathbf{p}_1\mathbf{R}_1\}, \quad (\text{A.33})$$

and

$$\mathbf{L}_2(\infty)\hat{Y}_0(\infty)=-\{\mathbf{p}_1\mathbf{p}_1/m\}\phi(1), \quad (\text{A.34})$$

$$\mathbf{L}_2(\infty)\hat{Y}_1(\infty)=-\mathbf{L}_3(\infty)\hat{Y}_0(\infty)$$
$$+\lim_{t\rightarrow\infty}\mathbf{L}_2(t)S_t(1)\phi(1)\{\mathbf{p}_1\mathbf{R}_1\}. \quad (\text{A.35})$$

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[*] In Sec. 4 of the text, we could just as well have applied the ϵ method to $\mathbf{y}(1,\epsilon)$ for the diffusion coefficient. We would then have obtained the following equation:

$$[\epsilon-\epsilon B(\epsilon)]\mathbf{X}(\mathbf{p}_1,\epsilon)=[\phi(1)\mathbf{p}_1/m]-B(\epsilon)G^{-1}(1,\epsilon)\phi(1)\mathbf{R}_1.$$

One can show directly from the definition of $\hat{O}$ that

$$O(\epsilon)G^{-1}(1,\epsilon)\phi(1)\mathbf{R}_1=0,$$

which implies in turn that

$$B(\epsilon)G^{-1}(1,\epsilon)\phi(1)\mathbf{R}_1=0,$$

so that Eq. (4.7) is recovered.

One has immediately that

$$\hat{\mathbf{B}}_2(t)=\hat{\mathbf{O}}_2(t)=\mathbf{L}_2(t) \tag{A.36}$$

which implies

$$X_0(0)=\hat{Y}_0(\infty). \tag{A.37}$$

To study the equivalence of Eqs. (A.33) and (A.35) we note that (A.33) can be written

$$\hat{\mathbf{B}}_2(\infty)X_1(0)=-\mathbf{B}_3(\infty)X_0(0) + \lim_{t\to\infty}\left[\mathbf{L}_2(t)\phi(1)\{\mathbf{p}_1\mathbf{R}_1\}+\int_0^t d\tau\mathbf{L}_2(\tau)\phi(1)\left\{\frac{\mathbf{p}_1\mathbf{p}_1}{m}\right\}\right] \tag{A.38}$$

where we have used Eqs. (A.36) and (A.24). Further, since

$$\mathbf{L}_2(t)S_t(1)\phi(1)\{\mathbf{p}_1\mathbf{R}_1\}=\mathbf{L}_2(t)\phi(1)\{\mathbf{p}_1\mathbf{R}_1\} + \int_0^t d\tau\mathbf{L}_2(t)\phi(1)\left\{\frac{\mathbf{p}_1\mathbf{p}_1}{m}\right\} \tag{A.39}$$

and

$$\mathbf{L}_3(t)=\hat{\mathbf{B}}_3(t)-\int_0^t d\tau[\mathbf{L}_2(t)-\mathbf{L}_2(\tau)]\mathbf{L}_2(t-\tau), \tag{A.40}$$

we may write Eq. (A.35) as

$$\begin{aligned}\hat{\mathbf{B}}_2(\infty)\hat{Y}_1(\infty)&=-\hat{\mathbf{B}}_3(\infty)X_0(0) + \lim_{t\to\infty}\left[\mathbf{L}_2(t)\phi(1)\{\mathbf{p}_1\mathbf{R}_1\}+\int_0^t d\tau\mathbf{L}_2(\tau)\phi(1)\left\{\frac{\mathbf{p}_1\mathbf{p}_1}{m}\right\}\right]\\&\quad+\lim_{t\to\infty}\int_0^t d\tau[\mathbf{L}_2(t)-\mathbf{L}_2(\tau)]\\&\quad\times[\mathbf{L}_2(t-\tau)\hat{Y}_0(\infty)+\phi(1)\{\mathbf{p}_1\mathbf{p}_1/m\}],\end{aligned} \tag{A.41}$$

where we have used Eqs. (A.36) and (A.37). The arguments of Sec. 8, along with (A.34), show that the second limit in Eq. (A.41) is zero. This establishes the equivalence of Eqs. (A.33) and (A.35), so that their solutions $\hat{Y}_1(\infty)$ and $X_1(0)$ are also identical.

Thus the ϵ and t methods give the same results for the first two terms in the density expansion of the kinetic part of the viscosity, η_k.

So far, our treatment of the viscosity has been limited to a discussion of η_k. We have seen that the methods for computing and comparing the first two terms in the density expansion of η_k are almost identical to the methods used in the text to discuss the diffusion coefficient. However, in order to give a complete discussion of the first two terms in the density expansion of η, it is necessary to investigate the contribution of η_ϕ. Fortunately, the resummation of the two-particle time-correlation function is already contained in the foregoing.

Let us now briefly discuss the ϵ method for the function $y(12,\epsilon)$, which according to Eqs. (A.8) and (A.10) is related to $X(12,\epsilon)$ by

$$X(12,\epsilon)=\epsilon y(12,\epsilon)-\hat{y}(12,0). \tag{A.42}$$

When Eq. (A.42) is used in Eq. (A.7) to compute η_ϕ, $\hat{y}(12,0)$ does not give any contribution, so we need only find a resummed expression for $\epsilon y(12,\epsilon)$. We do this by writing Eq. (A.11) as

$$y(12,\epsilon)=\lim_{\infty} V^2\int dx_3\cdots dx_N \times G(\epsilon)f_N\sum_{i=1}^N P_{1i}[\phi(1)]^{-1}\hat{y}(1,0) \tag{A.43}$$

so that

$$\begin{aligned}\epsilon\theta_{12}y(12,\epsilon)&=\lim_{\infty} V^2\int dx_3\cdots dx_N\theta_{12}\\&\quad\times G(\epsilon)f_N\sum_{i=1}^N P_{1i}[\phi(1)]^{-1}[1+\mathbf{O}(\epsilon)]^{-1}\\&\quad\times[\epsilon X(\mathbf{p}_1,\epsilon)+G^{-1}(1,\epsilon)\hat{y}(1,0)],\end{aligned} \tag{A.44}$$

where we have used Eqs. (A.18) and (A.21). In order to find the first density correction to η_ϕ via Eq. (A.7b) one only needs Eq. (A.44) to lowest order in the density:

$$\begin{aligned}\lim_{\epsilon\to 0}\epsilon\theta_{12}y(12,\epsilon)&=n^{-1}\lim_{\epsilon\to 0}\epsilon\tau(12,\epsilon)W(12)\\&\quad\times[\phi(2)X_0(\mathbf{p}_1,0)+\phi(1)X_0(\mathbf{p}_2,0)]+\cdots \end{aligned}\tag{A.45a}$$

$$\begin{aligned}&=n^{-1}\lim_{t\to\infty}\hat{\tau}(12,t)W(12)\\&\quad\times[\phi(2)\hat{Y}_0(\mathbf{p}_1,\infty)+\phi(1)\hat{Y}_0(\mathbf{p}_2,\infty)]+\cdots.\end{aligned} \tag{A.45b}$$

All of the above remarks apply directly to the t method for the resummation of $\hat{Y}(12,t)$ or $\hat{y}(12,t)$ as well, and we find

$$\begin{aligned}\theta_{12}\hat{y}(12,t)&=\lim_{\infty} V^2\int dx_3\cdots dx_N\theta_{12}S_{-t}f_N\sum_{i=1}^N P_{1i}[\phi(1)]^{-1}\\&\quad\times\left[1+\int_0^t d\tau\hat{\mathbf{O}}(\tau)\right]^{-1}[\hat{Y}(\mathbf{p}_1,t)+S_t(1)\hat{y}(1,0)].\end{aligned} \tag{A.46}$$

In the limit as $t\to\infty$ the lowest-order contribution in the density is obviously identical to Eq. (A.45b).

We have shown, therefore, that the ϵ and t methods both give the same results for the first two terms in the density expansion of the viscosity

$$\eta=\eta_0+n\eta_1+\cdots. \tag{A.47}$$

GLOSSARY

The notation $\hat{B}(B)$ means that both $\hat{B}$ and its Laplace transform B are used.

$\hat{B}(B)$	Single-particle correlation operator for the ϵ method [Eq. (4.5)]
$\hat{B}_r(B_r)$	Coefficient operators in the density expansion of B [Eq. (4.6)]
$\hat{\mathbf{B}}(\mathbf{B})$	$\hat{B}$ for the viscosity [Eq. (A.19)]
$\hat{\mathbf{B}}_r(\mathbf{B}_r)$	$\hat{B}_r$ for the viscosity [Eq. (A.20)]

D	Self-diffusion coefficient [Eq. (2.1)]
D_0, D_1	First two terms in the density expansion of D [Eq. (9.6)]
f_N	Canonical equilibrium distribution [Eq. (2.3)]
F_N	N-particle distribution function (Sec. 1)
$F^Y, F^X, F, F_r^Y, F_r^X, F_r$	Equations (7.12), (7.13), (7.15), (7.18), and (7.19)
$g(12\cdots j)$	Equilibrium j-particle position distribution function [Eq. (3.11)]
$g(1\cdots j; j+1\cdots k)$	Integrands of higher-order terms in the density expansion of $g(12\cdots j)$ [Eq. (3.12)]
G	Laplace transform of S_{-t} [Eq. (3.21)]
G_0	Laplace transform of S_{-t}^0 [Eq. (3.22)]
H_N	Hamiltonian for the gas [Eq. (2.9)]
$\mathcal{H}$	Liouville operator [Eq. (2.7)]
$\mathcal{H}_0$	Free-particle Liouville operator [Eq. (2.12)]
I	Boltzmann collision operator [Eq. (8.12)]
J	Current (dyadic) for the viscosity [Eq. (A.2)]
$\mathbf{J}_e, \mathbf{J}_p$	Charge, particle currents [Eq. (1.1)]
k	Boltzmann's constant
L	Single-particle correlation operator for the t method [Eq. (5.11)]
L_r	Coefficient operators in the density expansion of L [Eq. (5.13)]
$\mathbf{L}$	L for the viscosity [Eq. (A.28)]
$\mathbf{L}_r$	L_r for the viscosity [Eq. (A.29)]
m	Molecular mass
n	N/V=number density
N	Number of molecules in the gas
$O\ (O)$	Single-particle correlation operator [Eq. (3.4)]
$\hat{O}_r\ (O_r)$	Coefficient operators in the (naive) density expansion of $\hat{O}$ [Eq. (3.17)]
$\hat{\mathbf{O}}\ (\mathbf{O})$	$\hat{O}$ for the viscosity [Eq. (A.14)]
$\hat{\mathbf{O}}_r\ (\mathbf{O}_r)$	$\hat{O}_r$ for the viscosity [Eq. (A.15)]
$\mathbf{p}$	Momentum of all molecules in the gas
$\mathbf{p}_i$	Momentum of molecule i
$\mathbf{p}_i'$	Momentum of molecule i after a collision
$\mathbf{p}_{ij}$	$\mathbf{p}_i-\mathbf{p}_j$
P_{ij}	Permutation operator [Eq. (A.14)]
$\mathbf{q}$	Heat current [Eq. (1.1)]
r_0	Range of intermolecular force [Eq. (8.24)]
$\mathbf{r}_{ij}$	$\mathbf{R}_i-\mathbf{R}_j$
$\mathbf{R}$	Position of all molecules in the gas
$\mathbf{R}_i$	Position of molecule i
S_{-t}	Time-displacement (streaming) operator [Eq. (2.5)]
S_{-t}^0	Free-particle streaming operator [Eq. (3.2)]
t	Time
T	Absolute temperature
$\mathfrak{J}$	General transport coefficient [Eq. (1.3)]
$\mathfrak{J}_0, \mathfrak{J}_1, \mathfrak{J}_2$	Coefficients in density expansion of a general transport coefficient [Eq. (1.3)]
$\mathbf{u}$	Local average molecular velocity (Sec. 1)
$\mathfrak{U}(12 \mid 3\cdots j, t)$	j-Particle cluster operator [Eq. (3.8)]
V	Volume of the gas
$W(12\cdots j)$	First term in the density expansion of $g(12\cdots j)$ [Eq. (3.13)]
x	Phase variable of all molecules in the gas
x_i	Phase variable of molecule i
$\hat{\mathbf{X}}\ (\mathbf{X})$	Single-particle correlation function for the self-diffusion [Eq. (2.14)]
$\mathbf{X}_i$	Coefficients in the density expansion of $\mathbf{X}(0)$ [Eq. (7.4)]
$\hat{X}\ (X)$	Correlation functions (dyadic), analogous to $\hat{\mathbf{X}}\ (\mathbf{X})$, for the viscosity [Eq. (A.4)]
X_i	Coefficients in the density expansion of $X(0)$ [Eq. (A.30)]
$\mathbf{y}$	Single-particle correlation function used in the t method [Eq. (5.4)]
$\hat{y}\ (y)$	Correlation functions (dyadic), analogous to $\mathbf{y}$, for the viscosity [Eq. (A.11)]
$\mathbf{Y}$	Time integral of $\hat{\mathbf{X}}$; the single-particle correlation function used in the t method [Eq. (5.1)]
$\mathbf{Y}_i$	Coefficients in the density expansion of $\mathbf{Y}(\infty)$ [Eq. (7.3)]
$\hat{Y}\ (Y)$	Correlation functions (dyadic), analogous to $\mathbf{Y}$, for the viscosity [Eq. (A.8)]
$\hat{Y}_i$	Coefficients in the density expansion of $Y(\infty)$ [Eq. (A.31)]
Z_N	Canonical partition function [Eq. (2.4)]
β	$1/kT$
$\mathbf{\Delta}$	Equation (8.9)
ϵ	Laplace transform variable

η	Shear viscosity [Eq. (A.1)]
η_0, η_1	First two terms in the density expansion of η [Eq. (9.7)]
η_k, η_ϕ	Kinetic, potential contributions to the viscosity [Eqs. (A.6), (A.7)]
θ	Nonlinear transport coefficient [Eq. (1.2)]
θ_{ij}	Interaction part of Liouville operator for molecules i and j [Eq. (2.13)]
λ	Coefficient of thermal conductivity [Eq. (1.1)]
σ	Coefficient of electrical conductivity [Eqs. (1.1)]
τ_0	Time *of* an intermolecular encounter [Eq. (8.24)]
$\hat{\tau}(1\cdots j, t)(\tau)$	j-Particle dynamical operators appearing in the naive density expansion of $\hat{O}$ [Eq. (3.15)]
ϕ	Electrostatic potential [Eq. (1.1)]
$\phi(i)$	Normalized Maxwell–Boltzmann momentum distribution function for molecule i [Eq. (3.5)]
Φ	Total potential energy of the gas [Eq. (2.9)]
Φ_{ij}	Potential energy of molecules i and j [Eq. (2.10)]

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Review of Some Experimental and Analytical Equations of State

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Four different polynomial equations and seven nonlinear equations, all applicable to both solids and liquids, are compared theoretically and statistically. Detailed curve-fitting results are presented for recent water and Hg isothermal data. Uncommonly used methods of statistical analysis and comparison, including generalized least squares, are described, justified compared to usual methods, and applied. In general, certain polynomial equations are found to yield significantly better fits of many different water and Hg data sets than any nonlinear equation considered. The Tait and Murnaghan equations, in particular, lead to strong systematic behavior of all residuals calculated herein with them, showing that they are inadequate models for all the data considered. Even a nonlinear equation derived from a second-order expansion of the bulk modulus K in powers of the pressure, which is shown to include several frequently used equations as special cases, is inferior to selected polynomial equations but is still the best equation examined when appreciable extrapolation is necessary. The method of volume normalization almost always used heretofore in statistical fitting of equations of state to P–V data is shown to be inadequate and two alternative approaches are proposed and employed herein. Critical comparison of previous analyses of water and Hg data is made with the results of the present, more refined approach. The likelihood of important systematic errors in P–V data, particularly data derived from ultrasonic measurements on liquids under pressure, is pointed out and high probability of their occurrence in some of the data analyzed is demonstrated. Even the combination of the best data apparently available and the use of better statistical-analysis methods than have been employed before does not yet allow one to obtain highly accurate values of the K_0' parameter of water or Hg, and only an order-of-magnitude estimate of the K_0'' parameter seems currently possible. Nevertheless, it appears that near room temperature K_0'' is positive for water and probably negative for Hg and that its appreciable magnitude for both materials renders a second-order expansion of K inadequate.

CONTENTS

> *It is the mark of an educated man to look for precision in each class of things just so far as the nature of the subject admits.*
>
> Aristotle

I. INTRODUCTION

Hayward (1967) has recently stated, "The subject of compressibility equations for liquids is really a very simple one. Unfortunately, it has been so badly treated in the literature that it has been made to appear unnecessarily complex . . ." In the present work I hope to demonstrate by example the truth of Hayward's first statement and to show, using the work of Hayward and others, the applicability of his second statement.

Isothermal compressibility equations are differential, or difference, forms of equations of state which are more commonly written in directly useful pressure–volume form. Thus, statements about compressibility equations apply, *mutatis mutandis,* to their corresponding equations of state. Although I shall here illustrate the usefulness of the equations considered using data for liquids, several of these equations have wide applicability as well to homogeneous, isotropic solids under hydrostatic compression.