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Expansion of the Kinetic Hierarchy for a Massive Particle: The Repeated Ring and Fokker–Planck Equations

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The tagged particle BBGKY hierarchy is systematically expanded in inverse powers of the square root of the particle mass. In the Brownian limit, for fixed Knudsen number, the hierarchy reduces to the Brownian limit of the repeated ring equation which itself reduces to the Fokker–Planck equation. The friction coefficient of the Fokker–Planck equation is found to be a functional of the solution of Dorfman, van Beijeren, and McClure's extended Boltzmann equation for a fixed object in a flowing gas. As a consequence, the tagged particle diffusion coefficient calculated in the Brownian limit of the repeated ring equation is valid for all particle sizes.

KEY WORDS: Kinetic theory; BBGKY hierarchy; Brownian motion; repeated ring equation.

1. INTRODUCTION

Boltzmann or Boltzmann–Enskog theories of tagged particle motion predict that the self-diffusion constant, D, varies as the inverse square of the collision diameter. However, it is well known that large tagged particles follow the Stokes–Einstein (SE) law, with D proportional to R^{-1}, where R is the radius. Surprisingly, the Stokes–Einstein law even appears to be a good approximation to D for a tagged member of a pure simple liquid. Since the R^{-1} Stokes–Einstein behavior is qualitatively incompatible with the results of Boltzmann–Enskog type theories, those theories are of limited

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validity. Thus, construction of a theory which can produce either Boltzmann or Stokes–Einstein D's, as appropriate, is highly desirable.

Two approaches to such a theory naturally suggest themselves. First, a hydrodynamic theory, which easily yields the SE law, might be extended in an attempt to reach low density correctly. Second, simple kinetic theory, which easily yields the correct low-density limit, might be supplemented by collision events which give the SE law at higher density. Here we discuss this latter approach.

Soon after the ring kinetic operator was introduced by Kawasaki and Oppenheim,[1] it became apparent that the rings produced some vestiges of SE behavior. Later on, Ernst and Dorfman[2] obtained a "repeated ring" operator, analysis of which is extremely difficult. Nevertheless, a simplified treatment of the RRO by Mehaffey and Cukier[3] produced the SE law, with a "5π" for a large hard sphere in a dense bath (4π is correct).

Since the drag on a large fixed particle is related in a simple way to D, the problems under discussion must exist for a kinetic theory of the drag. Cercignani, Pagani, and Bassonini,[4] Sone and Aoki,[5] and Dorfman, van Beijeren, and McClure[6] have given theories of the drag which reproduce both the high- and low-density limits. In these theories, the gas is described by the Boltzmann equation—and, thus, can never be truly dense—and the fixed particle provides a source term or boundary conditions. When the particle is large with respect to the mean free path, the SE law is found.

The method of Dorfman, van Beijern, and McClure[6]—the "extended Boltzmann equation"—is of particular interest. In their formulation, calculation of the drag is obviously similar to calculation of D with the repeated rings. Cukier, Kapral, Lebenhaft, and Mehaffey[7] showed that if one assumes that the RR operator is diagonal on the tagged particle velocity, the RRs give the SE law for large particles, with the friction (drag) coefficient given by the hydrodynamic solution of the extended Boltzmann equation. Since the extended Boltzmann equation gives "4π," so, too, does a correct treatment of the RRs.

The background just given should help clarify the goals of this paper. First, despite its desirable features, the RR equation has never been shown to be the true kinetic equation for some limit or other. We will show this (subject to some reasonable assumptions) for a massive particle executing Brownian motion in a dilute gas. In other words, the Brownian limit, the BBGKY hierarchy, our starting point, reduces to a closed kinetic equation, and that kinetic equation is identical to the Brownian limit of the repeated ring equation. Of course, reduction of the hierarchy to the closed Boltzmann equation at low density has been extensively studied; our main result is that the Brownian limit is similarly tractable.

Second, we will show that the Brownian limit of the repeated ring kinetic equation reduces naturally to the simpler Fokker–Planck equation; in fact, the manipulations needed to establish the *RR*s in the limit and those needed to produce the Fokker–Planck equation are the same. Finally, we will show that the friction coefficient in the Fokker–Planck equation may be calculated from the extended Boltzmann equation, so we may carry over all the work of Dorfman[6] *et al.* This means, among other things, that the diffusion coefficient calculated in the Brownian limit is valid for arbitrary particle radius.

Our work is by no means the first study of the high mass limit of formally exact equations for tagged particle motion. Earlier authors[8] have obtained the Fokker–Planck equation, with some expression, generally an integral of a time correlation function, for the friction constant. Our new contribution to this line of research is the relation of the high mass limit of the hierarchy to the repeated ring and extended Boltzmann equations, as well as to the Fokker–Planck equation.

2. THE RAYLEIGH–BOLTZMANN HIERARCHY

We consider a system of hard spheres consisting of a single tagged particle of mass M and radius R and N bath particles of mass m and radius $d/2$. The distribution function for the tagged particle, $F_{1,0} = F$, and the distribution functions for the tagged particle and s bath-particles, $F_{1,s}$ $(s = 1, 2, \ldots)$, are coupled in the infinite hierarchy

$$\begin{gathered}\frac{\partial F_{1,s}}{\partial t} + \mathbf{v}\cdot\nabla F_{1,s} + \sum_{i=1}^{s} v_i\cdot\nabla_{r_i} F_{1,s} - \sum_{i=1}^{s}\bar{T}_-(i)F_{1,s} \\ = n\int d^3r_{s+1}\,d^3v_{s+1}\left\{\bar{T}_-(s+1) + \sum_{i=1}^{s}\bar{T}_-(i,s+1)\right\}F_{1,s+1} \\ |\mathbf{r}_i - \mathbf{r}_j| > d, \qquad i \neq j, \quad i,j = 1,2,\ldots,s, \quad s = 0,1,2,\ldots\end{gathered} \tag{2.1}$$

and the distribution functions for the s bath-particles, F_s $(s = 1, 2, \ldots)$, are coupled in the infinite hierarchy

$$\begin{gathered}\frac{\partial F_s}{\partial t} + \sum_{i=1}^{s}\mathbf{v}_i\cdot\nabla_{r_i}F_s = n\sum_{i=1}^{s}\int d^3r_{s+1}\,d^3v_{s+1}\,\bar{T}_-(i,s+1)F_{s+1} \\ |\mathbf{r}_i - \mathbf{r}_j| > d, \qquad i \neq j, \quad i,j = 1,2,\ldots,s \quad s = 1,2,\ldots\end{gathered} \tag{2.2}$$

Unsubscripted and subscripted variables refer to the tagged and bath particle, respectively, n is the density, $\mathbf{r}$ and $\mathbf{v}$ denote position and velocity; $\bar{T}_-(i)$ and $\bar{T}_-(i,j)$ are binary collision operators, for the tagged particle and the ith bath particle and the jth bath particle, respectively. The binary collision operators[9] are given by the relation

$$\bar{T}_-(i,j) = \sigma^2 \int_{4\pi} d\Omega\, \Theta(\mathbf{g}_{i,j} \cdot \mathbf{n}) |\mathbf{g}_{i,j} \cdot \mathbf{n}| \times \left[\delta(\mathbf{x}_{i,j} - \sigma \mathbf{n}) b_{i,j} - \delta(\mathbf{x}_{i,j} + \sigma n) \right] \tag{2.3}$$

where $d\Omega$ is an element of solid angle, $\mathbf{n}$ is a unit vector in the direction of the point of impact, Θ is the Heaviside function, δ is the Dirac delta function, $\mathbf{x}_{i,j} = \mathbf{r}_i - \mathbf{r}_j$ and $\mathbf{g}_{i,j} = \mathbf{v}_i - \mathbf{v}_j$ are the relative position and velocity, respectively, and σ is the collision diameter of the i,j pair. $\bar{T}_-(i)$ is obtained by identifying the jth particle as the tagged particle and dropping the jth subscript from the relative position and velocity. The operator b_i replaces the precollision (unprimed) velocities with the postcollision (primed) velocities

$$\begin{aligned} \mathbf{v}'_i &= \mathbf{v}_i - \frac{2M}{m+M} (\mathbf{g}_i \cdot \mathbf{n})\mathbf{n} \\ \mathbf{v}' &= \mathbf{v} + \frac{2m}{m+M} (\mathbf{g}_i \cdot \mathbf{n})\mathbf{n} \end{aligned} \tag{2.4}$$

The particular model we wish to discuss is that of a tagged particle of arbitrary size and mass moving in a background gas of point particles whose dynamics is described by the Boltzmann equation. Thus excluded volume effects and dynamic correlations due to the finite size of bath (background) particles must be eliminated. Formally this is achieved by taking the low-density or Boltzmann–Grad limit [$d \to 0$, $n \to \infty$, $m \to 0$, $(nd^2)^{-1}$ fixed, nm fixed).[10] By taking this limit, the bath particle hierarchy can be replaced by the Boltzmann hierarchy[11]

$$\frac{\partial F_s}{\partial t} + \sum_{i=1}^{s} \mathbf{v}_i \cdot \nabla_{r_i} F_s = n \sum_{i=1}^{s} \int d^3 v_{s+1}\, T_0(i, s+1) F_{s+1} \qquad s = 1, 2, \ldots \tag{2.5}$$

Here, T_0 is the binary collision operator for point particles. The Boltzmann hierarchy describes the decay of arbitrary initial correlations on space and time scales on the order of or greater than a mean free path and mean free time. For our purposes, we will assume that at some initial time in the past, the distribution functions for the bath particles were factored into products of one-particle distribution functions (initial molecular chaos). The Boltzmann hierarchy then reduces to the Boltzmann equation

$$\frac{\partial F_1}{\partial t} + v_1 \cdot \nabla_{r_1} F_1 = n \int d^3 v_2\, T_0(1,2) F_1(\mathbf{v}_1) F_1(\mathbf{v}_2) \tag{2.6}$$

For convenience, the space and time dependence of the distribution functions have been suppressed.

The Boltzmann–Grad limit applied at fixed R to the bath-particle subsystem of the hierarchy for $F_{1,s}$ ($s = 0, 1, 2 \ldots$) yields the Rayleigh–Boltzmann hierarchy[2]

$$\begin{aligned} &\frac{\partial F_{1,s}}{\partial t} + \mathbf{v} \cdot \nabla F_{1,s} + \sum_{i=1}^{s} \mathbf{v}_i \cdot \nabla_{r_i} F_{1,s} - \sum_{i=1}^{s} \overline{T}'_-(i) F_{1,s} \\ &\quad = n \int d^3 r_{s+1}\, d^3 v_{s+1}\, \overline{T}'_-(s+1) F_{1,s+1} + n \sum_{i=1}^{s} \int d^3 v_{s+1}\, T_0(i, s+1) F_{1,s+1} \\ &\qquad\qquad s = 0, 1, 2, \ldots \end{aligned} \tag{2.7}$$

The primed binary collision operators indicate the replacement $(R + d/2) \to R$ consistent with the Boltzmann–Grad limit. Unlike nd^2 for the bath-particle hierarchy, nR^2 is not finite in the Boltzmann–Grad limit. However, the collision integral is finite through its implicit dependence on the limit via the distribution functions $F_{1,s}$ ($s = 0, 1, 2, \ldots$). In the Brownian limit, the scaled parameters are again explicit since nR^2 is replaced by nmR^2, which is finite. Notice that in the Rayleigh–Boltzmann hierarchy, in contrast to the Boltzmann hierarchy, the finite size of the tagged particle acts as a source of correlation and is responsible for our interest in the nontrivial nature of this model.

The tagged-particle–bath-particle hierarchy can be recast as a hierarchy for the irreducible correlation functions $G_{1,i}$ ($i = 0, 1, 2 \ldots$). The irreducible correlation functions are defined by the nonequilibrium Ursell cluster-expansions[13]

$$\begin{aligned} F &= G \\ F_{1,1} &= FF_1 + G_{1,1}(1) \\ F_{1,2} &= FF_1(1)F_1(2) + G_{1,1}(1)F_1(2) + G_{1,1}(2)F_1(1) + G_{1,2}(12) \\ &\vdots \end{aligned} \tag{2.8}$$

where the bath-particle labels appear as arguments of the $G_{1,i}$ function. When the cluster expansions are substituted in the Rayleigh–Boltzmann

[2] The expression "Rayleigh–Boltzmann hierarchy" has also been used for systems where the tagged particle is a point particle; of Ref. 12.

hierarchy, the resulting equations reduce to the hierarchy

$$\begin{aligned}
&\frac{\partial G_{1,s}}{\partial t} + \mathbf{v} \cdot \nabla G_{1,s} + \sum_{i=1}^{s} \mathbf{v}_i \cdot \nabla_{r_i} G_{1,s} \\
&\qquad - n \int d^3 r_{s+1}\, d^3 v_{s+1}\, \overline{T}'_-(s+1) G_{1,s} F_1(s+1) \\
&\qquad - \sum_{i=1}^{s} J_{i,s+1}(G_{1,s}\,; F_1) - \sum_{i=1}^{s} \overline{T}'_-(i) G_{1,s} \\
&\quad = \sum_{p} \overline{T}'_-(i) G_{1,s-1} F_1(i) + n \int d^3 r_{s+1}\, d^3 v_{s+1}\, \overline{T}'_-(i) G_{1,s+1} \\
&\qquad + n \sum_{i=1}^{s} \int d^3 r_{s+1}\, T_0(i, s+1) G_{1,s+1} \qquad s = 0, 1, 2, \ldots
\end{aligned} \tag{2.9}$$

where

$$\begin{aligned}
J_{i,s+1}(G_{1,s}\,; F_1) = n d^2 \int d^3 v_{s+1} \int_{4\pi} d\Omega\, \Theta(\mathbf{g}_{i,s+1} \cdot \mathbf{n})\, |\mathbf{g}_{i,s+1} \cdot \mathbf{n}| (1 + P_{i,s+1}) \\
\times \left[G_{1,s}(\mathbf{v}'_i) F_1(\mathbf{v}'_{s+1}) - G_{1,s}(\mathbf{v}_i) F_1(\mathbf{v}_{s+1}) \right]
\end{aligned} \tag{2.10}$$

$P_{i,s+1}$ permutes the velocity variables with subscripts i and $s+1$, and $\sum_p$ indicates a sum over the $s-1$ distinct permutations of the bath-particle labels between $G_{1,s-1}$ and F_1. The function $G_{1,-1}$, which occurs when $s = 0$, is defined to be zero. The reduction is accomplished by using the Boltzmann equation and all the equations for the irreducible correlations functions preceding any given level (a level refers to a particle choice of s) to eliminate from that level any terms which are satisfied identically by all the preceding equations.

The hierarchy for the irreducible correlation functions has the form

$$L_i G_{1,i} = S_{i-1} + S_{i+1}, \qquad S_{-1} = 0, \quad i = 0, 1, 2, \ldots \tag{2.11}$$

where L_i, S_{i-1}, and S_{i+1} can be identified from the equations of (2.9). The form of (2.11) is intended to suggest an inhomogeneous equation where S_{i-1} and S_{i+1} act as sources of $G_{1,i}$. Equation (2.11) is not, however, an inhomogeneous equation of the usual type; i.e., the sources, S_{i-1} and S_{i+1}, depend on the irreducible correlation functions, $G_{1,i-1}$ and $G_{1,i+1}$, respectively. Nonetheless, as we shall see, for space and time scales characteristic of Brownian motion, these equations do become inhomogeneous equations where the sources act as given fields driving the governing equations.

So far, nothing has been said about proximity to equilibrium. From here on, however, we shall assume that the bath is initially in thermal equilibrium and that the complete system is close to equilibrium for all times. The initial distribution functions for the bath particles are Maxwellians

$$F_1(i;\, t=0) = \phi_0(\mathbf{v}_i) = n\left(\frac{\beta m}{2\pi}\right)^{3/2} \exp\left(-\frac{\beta m}{2} v_i^2\right), \qquad i = 1, 2, \ldots \tag{2.12}$$

where $(k\beta)^{-1}$ is the temperature and k is the Boltzmann constant. As is well known, these functions satisfy the Boltzmann equation (2.6) and, as a consequence of the H-theorem, are maintained for all times. When they are substituted in the hierarchy for the irreducible correlation functions together with the alternative forms for the tagged-particle distribution function,

$$F = \phi_0(\mathbf{v})(1 + h) \tag{2.13}$$

and the tagged-particle–bath-particle, irreducible, correlation functions,

$$G_{1,s} = \phi_0(\mathbf{v}) \prod_{i=1}^{s} \phi_0(\mathbf{v}_i)\{h_{1,s}^{\text{eq}} + h_{1,s}\}, \qquad s = 1, 2, \ldots \tag{2.14}$$

a hierarchy, linearized with respect to the bath-particle distribution functions, for the deviations from equilibrium, h and $h_{1,s}$ ($s = 1, 2, \ldots$), results: i.e.,

$$\frac{\partial h}{\partial t} + \mathbf{v} \cdot \nabla h = I_1(h + h_{1,1}) \tag{2.15}$$

$$\begin{aligned} &\frac{\partial h_{1,s}}{\partial t} + \mathbf{v} \cdot \nabla h_{1,s} + \sum_{i=1}^{s} \mathbf{g}_i \cdot \nabla x_i h_{1,s} - I_{s+1} h_{1,s} \\ &\quad - \sum_{i=1}^{s} L_{i,s+1} h_{1,s} - \sum_{i=1}^{s} \overline{T}'_{-}(i) h_{1,s} \\ &= \sum_{i=1}^{s-1} T'_{-}(i) h_{1,s-1} + I_{s+1} h_{1,s+1} + \sum_{i=1}^{s} L'_{i,s+1} h_{1,s+1} \qquad s = 1, 2, \ldots \end{aligned} \tag{2.16}$$

where

$$I_{s+1}\left\{\begin{matrix} h_{1,s} \\ h_{1,s+1} \end{matrix}\right\} = n \int d^3x_s\, d^3g_s\, \phi_0(\mathbf{v}_s) \overline{T}'_{-}(s) \left\{\begin{matrix} h_{1,s} \\ h_{1,s+1} \end{matrix}\right\} \tag{2.17}$$

$$\begin{aligned} L'_{i,s} h_{1,s} &= n \int d^3v_s\, \phi_0(\mathbf{v}_s) \int_{4\pi} d\Omega\, \Theta(\mathbf{g}_{i,s} \cdot \mathbf{n}) |\mathbf{g}_{i,s} \cdot \mathbf{v}| \\ &\quad \times \left[h_{1,s}(\mathbf{v}'_i, \mathbf{v}'_s) - h_{1,s}(\mathbf{v}_i, \mathbf{v}_s) \right] \end{aligned} \tag{2.18}$$

$$\begin{aligned} L_{i,s+1} h_{1,s} &= n \int d^3\mathbf{v}_{s+1}\, \phi_0(\mathbf{v}_{s+1}) \int_{4\pi} d\Omega\, \Theta(\mathbf{g}_{i,s+1} \cdot \mathbf{n}) |\mathbf{g}_{i,s+1} \cdot \mathbf{n}| \\ &\quad \times (1 + P_{i,s+1}) \left[h_{1,s}(\mathbf{v}'_i) - h_{1,s}(\mathbf{v}_i) \right] \end{aligned} \tag{2.19}$$

The bath particle variables, $\mathbf{r}_i$ and $\mathbf{v}_i$, have been replaced by relative variables, $\mathbf{x}_i$ and $\mathbf{g}_i$. Equations (2.13) and (2.14) define the quantities h and $h_{1,s}$ ($s = 1, 2, \ldots$). To ensure that the complete system is close to equilibrium for all times, we also require that h and $h_{1,s}$ ($s = 1, 2, \ldots$) be in some sense small for all times. Typically, one constructs a norm $\|h_{1,s}\|$ ($s = 0, 1, 2, \ldots$) on a suitable function space and requires $\|h_{1,s}\| \ll 1$ for $s = 0, 1, 2, \ldots$.

The linearized hierarchy for the irreducible correlation functions describes the decay of arbitrary initial correlations between the tagged particle and bath particles. If, as we assume, $G_{1,s}$ $(\mathbf{r}, \mathbf{v}, 1, \ldots, s;\ t = 0) = 0$, $s = 1, 2, \ldots$, then the hierarchy describes the buildup of correlations from an uncorrelated initial state. (In this case, $\|h\| \ll 1$ initially should be sufficient for $\|h_{1,s}\| \ll 1$, $s = 0, 1, 2, \ldots$ for all times.) Moreover, if $G_{1,2}$ $(\mathbf{r}, \mathbf{v}, 12;\ t > 0) \cong 0$ for physically interesting times, then the tagged-particle motion is described by the first two equations of the Rayleigh–Boltzmann hierarchy. The first two equations are the tagged-particle equivalent of the repeated ring kinetic equation in the form introduced by Ernst and Dorfman.[(2)] We will show that, in the Brownian limit, the rate of change of the tagged-particle distribution function is sufficiently slow (in the sense that it is higher order in our perturbation expansion) that the condition $G_{1,2}$ $(t > 0) = 0$ is indeed satisfied.

3. FOKKER–PLANCK EQUATION

To derive the Fokker–Planck equation and the Brownian limit of the repeated ring kinetic equation, we must work out the magnitude of the various terms in the linearized hierarchy for a massive tagged particle in a gas of point particle. Since we work with systems near equilibrium, we rescale the velocities of the particles to their equilibrium root mean square values. Then v is small with respect to v_i by a factor of $\epsilon = (m/M)^{1/2}$, and ϵ is the natural small parameter for the problem.

An additional dimensionless parameter, the Knudsen number, $k_n = l/R$, where $l = (nd^2)^{-1}$ is the mean free path of the gas, also appears on taking the tagged particle radius R as a characteristic length for significant variation of the gas-particle distribution function. The Knudsen number enters by estimating the quantities $\nabla_{x_s} h_{1,s}$ ($s = 1, 2, \ldots$) to be of order $1/R$ and then by comparing this estimate with the length l which arises from the gas-particle collision integrals. Later we shall assume the existence of distinct time scales. Since the time scales may depend on both k_n and ϵ, it is possible, even for small ϵ, that k_n may be chosen so that the separation of time scales breaks down. To avoid this difficulty, our approach will be to fix k_n, and then to order the hierarchy in powers of ϵ; that is, for any k_n, we expect that it will be possible to choose ϵ small enough so that the conditions for Brownian motion will be satisfied.

The factors of ϵ enter the hierarchy in five ways:

(1) Through explicit mass dependences which appear in the equations relating the precollision and postcollision velocities [Eq. (2.4)]. This mass dependence is a result of applying the energy and momentum conservation equations to a binary collision.

(2) Through implicit mass dependences which arise from choosing the thermal velocity as the characteristic scale for the tagged-particle velocity and the bath-particle velocities.

(3) Through implicit mass dependences which arise from assuming Taylor series expansions in ϵ for the correlation functions $h_{1,s}$ ($s = 1, 2, \ldots$) consistent with the Brownian limit. It should be emphasized, however, that the choice of a Taylor series expansion for $h_{1,s}$ is suggested by the form the hierarchy equations take after making a mass expansion of the collision integrals. Therefore, it should not be thought of as being a completely separate ad hoc assumption [see the paragraph following Eq. (3.23)].

(4) Through implicit mass dependences which arise from assuming distinct time scales for the Brownian particle processes and the bath particle processes. With (3), the right side of the first hierarchy equation will be proportional to ϵ^2 [see Eq. (3.25) and the discussion following Eq. (3.26)]. The factor ϵ^2 magnifies the time scales and defines the characteristic time $\epsilon^2 t$ for Brownian particle processes as can be seen from

$$\epsilon^2\left[\frac{\partial h}{\partial(\epsilon^2 t)} + \frac{\mathbf{v}}{\epsilon}\,\frac{\partial h}{\partial(\epsilon\mathbf{r})}\right] = \epsilon^2\hat{O}h$$

where $\hat{O}$ is the Fokker–Planck operator.

(5) And finally through implicit mass dependences which arise from taking the length for significant variation of the Brownian particle distribution function to be the natural length in the Brownian limit. Here, the factor ϵ stretches space and introduces the rescaled position vector $\epsilon\mathbf{r}$ as can be seen from the last equation.

We apply the first two ways to obtain to order ϵ the relations between the precollision and postcollision velocities,

$$\mathbf{v}_i' = \mathbf{v}_i^* + \frac{2m}{M}(\mathbf{g}_i \cdot \mathbf{n})\mathbf{n} \tag{3.1}$$

$$\mathbf{v}' = \mathbf{v} + \frac{2m}{M}(\mathbf{g}_i \cdot \mathbf{n})\mathbf{n} \tag{3.2}$$

where

$$\mathbf{v}_i^* = \mathbf{v} - (\mathbf{g}_i \cdot \mathbf{n})\mathbf{n} \tag{3.3}$$

the Maxwell velocity distribution functions,

$$\phi_0(\mathbf{v}_i) = \phi_0(\mathbf{g}_i)(1 - \beta m \mathbf{v} \cdot \mathbf{g}_i), \qquad i = 1, 2, \ldots \tag{3.4}$$

and the correlation functions

$$h_{1,s}(\mathbf{r}, \mathbf{v}, \mathbf{x}_1 + \mathbf{r}, \mathbf{g}_1 + \mathbf{v}, \ldots, \mathbf{x}_s + \mathbf{r}, \mathbf{g}_s + \mathbf{v}; t)$$
$$= h_{1,s}(\mathbf{r}, \mathbf{x}_1, \mathbf{g}_1, \ldots, \mathbf{g}_s; t) + \sum_{i=1}^{s} \left(\mathbf{v} \cdot \nabla_{\mathbf{g}_s} h_{1,s} + \mathbf{r} \cdot \nabla_{x_s} h_{1,s}\right) \quad s = 1, 2 \tag{3.5}$$

The fifth way we apply to estimate the order of magnitude of the terms

$$\mathbf{v} \cdot \frac{\partial h_{1,s}}{\partial \mathbf{r}} = \epsilon^2 \left[\frac{\mathbf{v}}{\epsilon} \cdot \frac{\partial h_{1,s}}{\partial(\epsilon \mathbf{r})} \right]$$

The third and fourth ways we discuss in the remaining portion of Section 3.

The first equation of the tagged-particle hierarchy has a direct part $I_1 h$ and an indirect part $I_1 h_{1,1}$. The direct part gives the rate of change of h due to uncorrelated binary collisions with the bath particles. For a point-tagged particle $I_1 h_{1,1}$ is zero and $I_1 h$ is the familiar Lorentz–Boltzmann collision integral. By assuming h has a Taylor series expansion.

$$h(\mathbf{v}') - h(\mathbf{v}) = \frac{2m}{M} \mathbf{g}_1 \cdot \mathbf{nn} \cdot \nabla_v h + 2\left(\frac{m}{M}\right)^2 (\mathbf{g}_1 \cdot \mathbf{n})^2 \mathbf{nn} : \nabla_v \nabla_v h + \cdots \tag{3.6}$$

the Lorentz–Boltzmann collision integral can be replaced by a series expansion in powers of the gradient of h with respect to the tagged particle velocity. The coefficients of this series are integrals which may be evaluated analytically. The lowest order term (i.e., order ϵ^2) has the Fokker–Planck form[14]

$$\xi_\infty \nabla_v \cdot \left(\mathbf{v} F + (\beta M)^{-1} \nabla_v F\right) \tag{3.7}$$

with a friction coefficient

$$\xi_\infty = \frac{2}{3}^{7/2} n R^2 \pi^{1/2} \frac{m}{M} (\beta m)^{-1/2} \tag{3.8}$$

where the subscript, ∞, indicates that the bath behaves as if it had an infinite mean free path. Instead of evaluating the integrals, the coefficients in the expansion can be replaced by binary collision operators acting on functions of the relative velocity alone. Indeed, if we write

$$\mathbf{g}_i' = \mathbf{g}_i - 2(\mathbf{g}_i \cdot \mathbf{n})\mathbf{n} \tag{3.9}$$

thn it is straightforward to show that the friction coefficient is given by

$$\xi_\infty = -\frac{\beta n m^2}{3M} \int d^3 x_1 \, d^3 g_1 \, \phi_0(\mathbf{g}_1) \mathbf{g}_1 \cdot \overline{T}_-(1) \mathbf{g}_1 \tag{3.10}$$

where the prime on the binary collision operator has been dropped to indicate that it now acts only on relative velocities. This last approach will also be used in the treatment of the full hierarchy, since it will prove to be especially useful for interpreting the results of our perturbation expansion.

The indirect part gives the rate of change of h due to correlated sequences of collisions with the bath particles which are induced by the motion of the tagged particle. The ϵ-expansion of this collision integral and others like it follow from the expansion of the binary collision operator expression $\overline{T}'_-(s)h_{1,s}$. We first consider only factors of ϵ which arise from our scaling assumptions and from explicit factors of m/M. The correlation functions are again assumed to have Taylor series expansions

$$\begin{aligned} &h_{1,s}(\mathbf{v}',\mathbf{v}_s') - h_{1,s}(\mathbf{v},\mathbf{v}_s) \\ &\quad = h_{1,s}(\mathbf{v},\mathbf{v}_s') - h_{1,s}(\mathbf{v},\mathbf{v}_s) + \frac{2m}{M}\mathbf{g}_s\cdot\mathbf{nn}\cdot\nabla_v h_{1,s}(\mathbf{v},\mathbf{v}_s') + \cdots \\ &\quad = h_{1,s}(\mathbf{v},\mathbf{v}_s^*) - h_{1,s}(\mathbf{v},\mathbf{v}_s) + \frac{2m}{M}\mathbf{g}_s\cdot\mathbf{nn}\cdot\nabla_v h_{1,s}(\mathbf{v},\mathbf{v}_s^*) + \cdots \end{aligned} \tag{3.11}$$

where the difference between $\mathbf{v}_s'$ and $\mathbf{v}_s^*$ is higher order in ϵ. By using the identity

$$\begin{aligned} 2\mathbf{g}_s\cdot\mathbf{nn}\cdot\nabla_v h_{1,s}(g_s') \equiv &-\left[\mathbf{g}_s'\cdot\nabla_v h_{1,s}(\mathbf{g}_s') - \mathbf{g}_s\cdot\nabla_v h_{1,s}(\mathbf{g}_s)\right] \\ &+ \mathbf{g}_s\cdot\left[\nabla_v h_{1,s}(\mathbf{g}_s') - \nabla_v h_{1,s}(\mathbf{g}_s)\right] \end{aligned} \tag{3.12}$$

and the expansion (3.5), the binary collision operator expression $\overline{T}'_-(s)h_{1,s}$ to $O(\epsilon)$ is

$$\begin{aligned} \overline{T}'_-(s)h_{1,s} = {}& \overline{T}_-(s)h_{1,s} - \frac{m}{M}T_-(s)\mathbf{g}_s\cdot\nabla_v h_{1,s} + \frac{m}{M}\mathbf{g}_s\cdot\mathbf{T}(s)\nabla_v h_{1,s} \\ &+ \mathbf{v}\cdot\overline{T}_-(s)\nabla_{g_s}h_{1,s} + \sum_{i=1}^{s-1}\mathbf{v}\cdot\nabla_{g_i}\overline{T}_-(s)h_{1,s} \end{aligned} \tag{3.13}$$

where $T_-(s) = \overline{T}_-(s) - \mathbf{g}_s\cdot\hat{\mathbf{x}}_s\delta(x_s - R)$, $\hat{\mathbf{x}}_s = \mathbf{x}_s/|\mathbf{x}_s|$. When the expansion of $\overline{T}'_-(s)h_{1,s}$ is substituted in the collision integral $I_s h_{1,s}$, the integral is given to lowest relevant order in ϵ by

$$(I_s h_{1,s})_1 = -\beta nm\int d^3x_s\,d^3g_s\,\phi_0(\mathbf{g}_s)\cdot\overline{T}_-(s)\left[\mathbf{v}h_{1,s} - (\beta M)^{-1}\nabla_v h_{1,s}\right] \tag{3.14}$$

where the subscript outside the parenthesis indicates the order in ϵ without any additional assumptions about the order of $h_{1,s}$. The indirect part is a special case of $(I_s h_{1,s})$, with $s = 1$.

Under certain circumstances [e.g., the Brownian limit to be discussed following (3.26)], $h_{1,1}$ assumes the simpler form $h_{1,1} = \mathbf{a}\cdot\mathbf{b}$, where $\mathbf{a}$ is a function of the bath-particle independent variables only and $\mathbf{b}$ is a function of the tagged-particle independent variables only. Then the indirect part becomes

$$\begin{aligned} (I_1 h_{1,1})_1 = -\frac{\beta nm}{3}\int d^3x_1\,d^3g_1\,\phi_0(\mathbf{g}_1)\mathbf{g}_1\cdot\overline{T}_-(1)\mathbf{a} \\ \times\left[(\beta M)^{-1}\nabla_v\cdot\mathbf{b} - \mathbf{v}\cdot\mathbf{b}\right] \end{aligned} \tag{3.15}$$

The collision integral $I_{s+1}h_{1,s}$ is analyzed in the same way as the direct part to obtain

$$(I_{s+1}h_{1,s})_2 = -\frac{\beta n m^2}{3}\int d^3x_{s+1}\,d^3g_{s+1}\,\phi(\mathbf{g}_{s+1})\mathbf{g}_{s+1}\cdot \overline{T}_-(s+1)\mathbf{g}_{s+1}$$
$$\times\left[-\mathbf{v}\cdot\nabla_v h_{1,s} + (\beta M)^{-1}\nabla_v^2 h_{1,s}\right] \tag{3.16}$$

The remaining collision operator expressions we need are

$$(T'_-(s)h_{1,s-1})_1 = -\frac{m}{M}T_-(s)\mathbf{g}_s\cdot\nabla_v h_{1,s-1} \tag{3.17}$$

and

$$\left(\overline{T}'_-(s)h_{1,s}\right)_0 = \overline{T}_-(s)h_{1,s} \tag{3.18}$$

The bath-particle collision integrals

$$(L'_{i,s}h_{1,s})_0 = L'_{i,s}h_{1,s} \tag{3.19}$$

$$(L_{i,s+1}h_{1,s})_0 = L_{i,s+1}h_{1,s} \tag{3.20}$$

depend parametrically on the tagged-particle variables and are obtained directly from the expansion of the correlation function, (3.5).

The remaining terms of the hierarchy are, in order of magnitude estimated as $\mathbf{v}_i\cdot\nabla_{r_i}h_{1,s}\sim(v_i/R)h_{1,s}$, $L'_{i,1}h_{1,s}\sim(v_i/l)h_{1,s}$, $L_{i,s+1}h_{1,s}\sim(v_i/l)h_{1,s}$, $\overline{T}_-(i)h_{1,s}\sim(v_i/R)h_{1,s}$, and $T_-(i)h_{1,s-1}\sim(\epsilon v_i/R)h_{1,s-1}$. In general, the friction coefficient which emerges from this treatment will depend on K_n and ϵ.

As remarked earlier, we will regard K_n fixed and independent of ϵ and continue to assume, for ϵ small enough, that the ϵ expansion remains valid. With K_n fixed, the last set of quantities except for $T_-(i)h_{1,s-1}$ are $O(1)$ in ϵ.

We now must find the order of $h_{1,s}$ and its time derivatives. Actually, the order of the time derivatives are *a priori* unknown. Nevertheless, for a sufficiently heavy particle, we expect to find the distinct times 1 and ϵ^{-2} for the bath processes and for the tagged-particle processes, respectively. The separation into two time scales is only approximate for tagged particles of finite mass. Therefore, we adopt the more general multiple time scale expansion

$$\left(\frac{\partial h_{1,s}}{\partial t}\right)_0 + \left(\frac{\partial h_{1,s}}{\partial t}\right)_1 + \left(\frac{\partial h_{1,s}}{\partial t}\right)_2 + \cdots \tag{3.21}$$

where the subscript $0,1,2,\ldots$ indicate the times $1,\epsilon^{-1},\epsilon^{-2},\ldots,$ respectively. Equation (3.21) is the most fundamental assumption of the theory. To obtain the Brownian limit, however, we only require that the lead term in $\partial h_{1,s}/\partial t$ is $O(\epsilon^0)$; the remainder of Eq. (3.21) is not needed unless we desire the first corrections to the limit.

However, we wish to point out that if only the time-independent friction coefficient is desired, we could just as well assume the higher-order distribution functions are functionals of tagged-particle distribution function as far as their phase space coordinates and time are concerned. Then Bogoliubov's method[15] (with the Brownian particle relaxation time replacing the mean free time) could be applied directly to compute the time derivatives of the correlation functions. However, Bogoliubov's procedure yields, to lowest order, a steady-state Boltzmann-like equation for the tagged-particle–bath-particle correlation function. Since the lowest-order equation is time independent, the functional assumption is awkward to apply if one wants to take into account low-frequency motions of the bath such as one might via the Stokes–Boussinesq drag law. The foregoing difficulty is avoided if we directly assume distinct time scales.

Among the terms of the hierarchy, the expression $\overline{T}'_{-}(i)h_{1,s-1}$ plays a special role. It acts to generate higher-order correlations out of lower-order correlations and, for an uncorrelated initial ensemble, it is the sole source of higher-order correlations. The correlations which do appear in time must be developed through this type of term, and it can therefore be used to estimate the asymptotic relation between the various correlation functions. To do this, we need to know the order of magnitude of the action of the collision operator on $h_{1,s-1}$. In fact, we have already shown that $T'_{-}(i)$ $h_{1,s-1}$ is $\sim(\epsilon v_i/R)h_{1,s-1}$. However, $\overline{T}'_{-}(i)h_{1,s-1}$ is $\sim(v_i/R)h_{1,s-1}$ because of the term $\mathbf{g}_i \cdot \hat{\mathbf{x}}_i\delta(x_i - R)h_{1,s-1}$. This last term and others like it are a necessary part of the definition of the binary collision operator which ensures that the correlation functions $h_{1,s}$ $(s = 1, 2, \ldots)$ are zero inside the tagged particle. They do not affect the value of the correlation functions outside the tagged particle; in the latter region, the correlation functions are determined by collisions. Therefore, insofar as we are interested in the relative order of the various correlation functions with respect to each other, we need only consider the order in ϵ of the action of T'_{-}. Nevertheless, the $h_{1,s}$ $(s = 1, 2, \ldots)$ are zero inside the tagged particle and we would like the perturbation expansion to preserve this feature order by order. We are mainly interested in the lower orders of the perturbation expansion, indeed, in the leading order; we transform the first few equations of the hierarchy to illustrate a procedure where this property is maintained. To do this, we define $\tilde{h}_{1,1}$ by the relation $\tilde{h}_{1,1} = h_{1,1} + f_1(x_1)h$, where $f_1(x_1) = -1 + \Theta(x_1)$ is the hard sphere Mayer f-function. The first and second hierarchy equations become

$$\frac{\partial h_{1,1}}{\partial t} + \mathbf{v} \cdot \nabla h = I_1 h + I_1 \tilde{h}_{1,1} \tag{3.22}$$

and

$$\frac{\partial \tilde{h}_{1,1}}{\partial t} + \mathbf{v} \cdot \nabla \tilde{h}_{1,1} + \mathbf{g}_1 \cdot \nabla_{x_1} \tilde{h}_{1,1} - I_2 \tilde{h}_{1,1} - L_{12} \tilde{h}_{1,1} - \bar{T}'_-(1) \tilde{h}_{1,1} + f_1 I_2 \tilde{h}_{1,1}$$
$$= T'_-(1)h + I_2 h_{1,2} + L_{12} h_{1,2} \tag{3.23}$$

Now, on the right side of (3.23), the action of $\mathbf{T}'$ is of order ϵ. On the left side a new term, $f_1 I_2 h_{1,1}$, appears which is $\sim \epsilon^2 f_1 \tilde{h}_{1,1}$.

To complete our perturbation expansion, we now consider the implicit ϵ dependence of $h_{1,s}$. Recall that $h_{1,s}(t=0) = 0$; as time increases these correlation functions become nonzero through the action of terms like $T'_-(i)h_{1,s-1}$ [Eq. (2.16)]. The growth of these correlations, and, thus, the order of the $h_{1,s}$, is determined by our time scale assumptions. Since the characteristic time for the $h_{1,s}$ is $O(1)$, these functions will reach a steady state if driven by a source which varies on the Brownian time scale; the strength of the correlations is just the strength of the source. Now, $h_{1,1}$ is driven by h and $h_{1,s}$. Only the magnitude of the $h_{1,s}$ relative to h is relevant, so we let h be $O(1)$. The h-source has an explicit factor of ϵ and the $h_{1,2}$-source has no explicit ϵ's. Two possibilities then exist. If $h_{1,2}$ is negligible with respect to ϵh, then $h_{1,1}$ is $O(\epsilon)$. The same argument applied to the equation for $h_{1,2}$ gives $h_{1,2} \sim O(\epsilon^2)$, and, in general,

$$h_{1,s} = (h_{1,s})_s + (h_{1,s})_{s+1} + \cdots \tag{3.24}$$

Eq. (3.24) is self-consistent, that is, it is derived from the assumption, $\epsilon h_{1,s-1} \gg h_{1,s+1}$, and it is consistent with that assumption.

The second possibility is $h_{1,2} > \epsilon h$, or, $h_{1,2} \sim O(\epsilon^\alpha)$, $\alpha < 1$; then, we have $h_{1,1} \sim O(\epsilon^\alpha)$. This scenario is inconsistent with Brownian motion, however, as the $h_{1,1}$ term in the equation for h then dominates all the other terms, while the entire equation is of the same order if Eq. (3.24) holds. Thus, our imposition of the Brownian limit and our time scale assumptions yield Eq. (3.24) without extra assumptions. This result makes excellent sense. The higher correlations are driven by the lower, so correlation "cascades" up the hierarchy, with $h_{1,s+1}$ less developed than $h_{1,s}$, by a factor of ϵ.

With the expansion (3.23) and the earlier expansions of the term, of the linearized hierarchy equation, we get, to lowest order,

$$\frac{\partial h}{\partial t} + \mathbf{v} \cdot \nabla h = (I_1 h)_2 + \left(I_1(\tilde{h}_{1,1})_1\right)_1 \tag{3.25}$$

and

$$\left(\frac{\partial (h_{1,1})_1}{\partial t}\right)_0 + \mathbf{g}_1 \cdot \nabla_{x_1} (\tilde{h}_{1,1})_1 - L_{12} (\tilde{h}_{1,1})_1 - \bar{T}_-(1) (\tilde{h}_{1,1})_1$$
$$= -\frac{m}{M} T'_-(1) \mathbf{g}_1 \cdot \nabla_v h \tag{3.26}$$

There are two features worth noting about these equations. First, both of the collision terms on the left side of (3.25) are of order ϵ^2—consistent not only with the picture of two time scales but also with a Brownian time scale (i.e., times like $\epsilon^2 t$). Secondly, equation (3.26) is an integrodifferential equation for the bath particle quantities alone. The expression $\nabla_v h$, which is the only quantity on the right side of Eq. (3.26) that depends on the tagged-particle independent variables is a constant vector as far as this equation is concerned since it varies on the Brownian particle's time and space scales, and what remains of the expression on the right side has a given functional dependence on $\mathbf{x}_1$ and $\mathbf{g}_1$. The equation is, therefore, an inhomogeneous equation of the usual type (where the inhomogeneous term does not depend on any unknown functions of $\mathbf{x}_1$ and $\mathbf{g}_1$) and the right side may be regarded as an external forcing function. Indeed, one might say that the gradient in the tagged particle velocity is driving a flow in the gas.

Equation (3.26) is generally difficult to solve for arbitrary values of K_n. However, it can be put in a more familiar form. Since (3.26) is linear, then the part of $(h_{1,1})_1$, which arises from the inhomogeneous term, must have the form $(h_{1,1})_1 = \mathbf{a}\cdot\mathbf{b}$. The function $\mathbf{a}$ is determined by solving Eq. (3.26) and the function $\mathbf{b}$ is equal to $(m/M)\nabla_v h$. The expression $\mathbf{b}$ can be substituted in $(I_1(h_{1,1})_1)_1$ to yield

$$(I_1(h_{1,1})_1)_1 = -\frac{\beta n m^2}{3M}\int d^3x_1\, d^3g_1\, \phi_0(\mathbf{g}_1)\mathbf{g}_1\cdot \overline{T}_-(1)\mathbf{a}\left[(\beta M)^{-1}\nabla_v^2 h - \mathbf{v}\cdot\nabla_v h\right] \tag{3.27}$$

Equation (3.26), $(I_1 h)_2$ [(3.16), $s=0$], and the definition of h (3.13) can be used to write (3.25) as

$$\frac{\partial F}{\partial t} + \mathbf{v}\cdot\nabla F = \xi\nabla_v\cdot\left[\mathbf{v}F + (\beta M)^{-1}\nabla_v F\right] \tag{3.28}$$

with

$$\xi = -\frac{\beta n m^2}{3M}\int d^3x_1\, d^3g_1\, \phi_0(\mathbf{g}_1)\mathbf{g}_1\cdot \overline{T}_-(1)(\mathbf{g}_1+\mathbf{a}) \tag{3.29}$$

Except for the factor M^{-1}, these equations for the calculation of the friction coefficient in the Brownian motion Fokker–Planck equation are identical to[6] Dorfman, van Beijeren, and McClure's extended Boltzmann equation for the drag on a stationary sphere in a gas flow which is uniform far from the sphere. Now, however, $\nabla_v h$ plays the role of the uniform flow velocity. The extended Boltzmann equation does not make any assumptions about the degree of rarefaction of the gas; therefore, the friction coefficient is generally a function of K_n. The ease with which Eqs. (3.24) and (3.25) were identified with existing work on the extended Boltzmann equation justifies the recasting of the coefficients in the various series expansions in terms of binary collision operators acting on functions of the relative velocity alone.

Finally we wish to point out that our expansions are systematic in ϵ. They can be used to calculate correlations to the Fokker–Planck equation for a tagged particle of finite mass. They are, of course, subject to the restrictions imposed by assuming that the correlation functions have Taylor series expansions. In general, nonanalytic terms in ϵ must be expected to occur and then the expansion may, at best, be asymptotic to actual solutions of the hierarchy equations. Still, the higher-order corrections to the Fokker–Planck equation may be useful for estimating finite mass corrections to the Stokes–Einstein diffusion coefficient.

4. SUMMARY

We have presented a strictly kinetic theory of Brownian motion for a hard sphere Brownian particle of arbitrary size moving in a gas whose dynamics is described by the Boltzmann equation. The theory has a number of important consequences. First, it demonstrates that the repeated ring kinetic equation has, as a natural limit, the Brownian motion Fokker–Planck equation. Second, it shows that under certain circumstances the repeated ring kinetic equation can be derived from the BBGKY (Bogolubov, Born, Green, Kirkwood, Yvon) hierarchy on the basis of a perturbation expansion, rather than on an ad-hoc neglect of the three body irreducible correlation functions. Third, it is a systematic perturbation expansion and may therefore be used to calculate corrections to the Fokker–Planck equation for tagged particles of finite mass.

To carry out the theory, we considered an isothermal system which is near equilibrium at all times. While the theory could be carried out for arbitrary initial correlations, we restricted ourselves to uncorrelated initial ensembles. As such, the theory describes the origin of correlations as an initial value problem, and, in this form, makes the most natural contact with existing work on the repeated ring equation.

The most fundamental assumption made is that there exist distinct time scales for the tagged particle/bath particle system, when the tagged particle is heavy with respect to the bath particles. The existence of distinct time scales does not guarantee a Brownian motion limit. However, if the true motion of the tagged particle is to be preserved on the time scale $\epsilon^2 t$, then, to lowest order, the kinetic operator for the distribution function F is described by the first two equations of the linearized Rayleigh–Boltzmann hierarchy and is of order ϵ^2, consistent with the Brownian limit. The first two equations are the $\epsilon = (m/M)^{1/2} \to 0$ limit of the repeated ring kinetic equation. Further, it can be seen that the three-body correlation function contributes in order ϵ^3 and is thus justifiably neglected in the limit $\epsilon \to 0$.

Finally, we have shown that the friction coefficient appearing in the Fokker–Planck equation may be found by a solution of the extended Boltzmann equation. This reduces calculation of the friction constant to a problem which has already been[4–6] studied, and constitutes a derivation, from kinetic theory, of Einstein's relation between the friction on a Brownian particle and the force on a fixed object in a flowing gas.

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REFERENCES

1. K. Kawasaki and I. Oppenheim, *Phys. Rev.* **139**:A1763 (1965).
2. M. H. Ernst and J. R. Dorfman, *Physica* **61**:157 (1972).
3. J. R. Mehaffey and R. I. Cukier, *Phys. Rev. Lett.* **38**:1039 (1977).
4. C. Cercignani, C. D. Pagani, and P. Bassonini, *Phys. Fluids.* **11**:1399 (1968).
5. Y. Sone and K. Aoki, *Phys. Fluids* **20**:571 (1977).
6. J. R. Dorfman, H. van Beijeren, and C. F. McClure, *Arch. Mech. Stosow.* **28**:333 (1976).
7. R. I. Cukier, R. Kapral, J. R. Lebenhaft, and J. R. Mehaffey, *J. Chem. Phys.* **73**:5244 (1980).
8. J. Liebowitz and R. Rubin, *Phys. Rev.* **31**:2381 (1963); P. Resibois and H. T. Davis, *Physica* **30**:1077 (1964).
9. M. Ernst, J. R. Dorfman, W. Hoegy, and J. van Leeuwen, *Physica* **45**:127 (1969).
10. H. Grad, *Handbuch der Physik*, ed. S. Flugge, Vol. 12 (Springer-Verlag, Berlin, 1958).
11. C. Cercignani, *Transp. Theory Stat. Phys.* **2**:211 (1972).
12. H. Spohn, *Rev. Mod. Phys.* **52**(3):617 (1980).
13. M. S. Green, *J. Chem. Phys.* **25**:836 (1956); *Physica* **24**:393 (1958); E. G. D. Cohen, *Physica* **28**:1025 (1962).
14. Lord Rayleigh, *Phil. Mag.* **32**:424 (1891); M. S. Green, *J. Chem. Phys.* **19**:1036 (1951).
15. N. N. Bogoliubov, *Studies in Statistical Mechanics*, J. DeBoer and G. E. Uhlenbeck, eds. (North-Holland, Amsterdam, 1962).