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The Enskog Repeated Ring Equations for Tagged Molecule Motion and Variational Solutions

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The Enskog repeated ring equations (ERRE) for tagged molecule motion are derived from the BBGKY hierarchy. The hierarchical deviation demonstrates the problem associated with using naive truncations for complex fluid systems. A moment-variational solution is suggested for the ERRE. The moment-variational method is applied to the ERRE for the two- and three-dimensional overlapping Lorentz gas (LG). Both self-consistent and non-self-consistent equations for the diffusion constant are solved. The results compare favorably with previous calculations and molecular dynamics (MD).

KEY WORDS: Kinetic theory; Enskog repeated ring equation; polyatomic liquids; variational principles; Lorentz model; kinetic boundary layers.

1. INTRODUCTION

A major focus of kinetic theory is to achieve a microscopic understanding of transport processes in condensed phases (see, e.g., Ref. 1). While progress has been made during the last 20 years in this direction, it is still not possible to predict most transport coefficients via kinetic theory. Neither Boltzmann theory, which ignores all correlations, nor Enskog (or modified Enskog) theory, which retains static (equilibrium) correlations, yet neglects dynamic correlations, provides a comprehensive description of physical processes in dense fluids.(2) These theories are strictly applicable to dilute or moderately dense gases or to the initial time behavior in condensed phases. It is reasonable to ignore many-body correlaltions in dilute fluids and at short times in dense fluids, before the correlations have

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built up. Success for any other regime in dense fluids cannot generally be expected.

The simplest theory that incorporates many-body dynamic correlations(3) is the repeated ring (RR) theory.(4) It includes pair dynamic correlations and ignores static correlations, in contrast to Enskog theory. The RR theory predicts an R^{-1} (R is the radius of the tagged particle) dependence of the single-particle diffusion constant characteristic of Stokes'-law hydrodynamics,(5–7) whereas Enskog theory predicts an R^{-2} dependence. This is but one example of the necessity of incorporating many-body correlations to obtain the correct physics in dense fluids. Other phenomena that can be treated only with the inclusion of dynamic correlations are the long-time tails(8,9) in the Green–Kubo expressions and the vanishing of the diffusion constant at the percolation density for the overlapping Lorentz gas.(10–12)

The RR theory treats only part of the problem, for static correlations must also be considered. Sung and Dahler(13) and Masters and Keyes(14) considered the problem of calculating the behavior of a tagged spherical particle in an atomic fluid. The equations they derived account for tagged-particle–bath-particle dynamical correlations, while retaining the static structure of the fluid. Their equations represent the specific form of the Enskog repeated ring equations (ERRE) (the general form to be derived below) restricted to the calculation of the velocity correlation function (VCF) of a spherical particle in an atomic bath. The ERRE were shown to predict Stokes'-law behavior and long time tails(12) in the VCF.

Masters and Keyes(15,16) (MK), using Cercignani's integral variational principle(17,18) (IVP) generalized to the RR equations for the LG, were able to calculate the self-diffusion constant D over the full range of densities. Furthermore, utilizing a self-consistent form of the RR equations(10) (denoted SCRRE), they obtained quantitatively accurate values for the diffusion constant, including the vanishing of D at a critical density of scatterers. The IVP has *not* been demonstrated for more complex fluid systems, in particular, those with nonoverlapping scatterers and nontrivial static structure.

The purpose of this work is twofold. First, we present a derivation of the *general* ERRE for tagged molecule motion. The derivation proceeds from the BBGKY hierarchy appropriate to (nonspherical) rigid ovaloids. To the best of our knowledge, this is the first *hierarchical* derivation of more complex RR equations. The derivation is enlightening, in that it clearly demonstrates the problem associated with naively using truncations from dilute gas kinetic theory. Consistency conditions on the reduced distribution functions serve as a guide in choosing the correct truncation. Once the appropriate truncation is made, the derivation is straightforward.

We believe that this discussion may serve as a guide in deriving more complex RR equations to study collective particle properties of condensed phases.

Second, we suggest an approach toward obtaining numerical solutions based upon a new differential variational principle (DVP) applicable to the *full ERRE*, retaining their complex static structure. This has *not* proved possible with the IVP. This DVP was established by Cercignani(18) for the Boltzmann equation. A calculation of the self-diffusion constant D for the overlapping LG is presented utilizing the DVP. The results for D, for two- and three-dimensional systems, are compared with both molecular dynamics (MD)(19,20) and accurate numerical results.(14–16) This example is meant to serve as a guide in implementing the variational procedure and to estimate its value in reproducing known results.

We have completed calculations of the full VCF for the LG using the DVP. The VCF calculations represent new results unobtainable by other methods. These results will be reported in a subsequent paper, further demonstrating the utility of this new DVP.

2. ENSKOG REPEATED RING EQUATIONS

We now derive the Enskog repeated ring equations. The starting point is the pseudo-Liouville equation for the N-molecule distortion

$$\frac{\partial}{\partial t}\,\delta\tilde{F}^{(N)} = iL_{+}^{(N)\dagger}\,\delta\tilde{F}^{(N)} \tag{1}$$

Here $\delta\tilde{F}^{(N)}$ is the distortion from equilibrium of the full N-molecule distribution function

$$\tilde{F}^{(N)}(\mathbf{x}^N, t) = \tilde{F}_{\mathrm{eq}}^{(N)}(\mathbf{x}^N) + \delta\tilde{F}^{(N)}(\mathbf{x}^N, t) \tag{2}$$

where $\tilde{F}_{\mathrm{eq}}^{(N)}(\mathbf{x}^N)$ is the absolute equilibrium distribution function and $x^s = (\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_s)$, $\mathbf{x}_j$ denoting the phase point of molecule j. Also in Eq. (1) are the N-molecule pseudo-Liouville operator(21,22) and its adjoint, defined by

$$iL_{\pm}^{(N)} = \sum_j iL_j^{(1)} + \sum_{j,k} T_{jk}^{(\pm)} \tag{3a}$$

$$iL_{\pm}^{(N)\dagger} = -\sum_j iL_j^{(1)} - \sum_{j,k} T_{jk}^{(\pm)\dagger} \tag{3b}$$

Here $iL_j^{(1)}$ is the single-molecule Liouville operator for particle j, written in terms of the single-molecule kinetic energy K_j,

$$iL_j^{(1)}a = i\{K_j, a\} \tag{4}$$

with $\{A, B\}$ denoting the Poisson bracked of A with B, and $T_{jk}^{(\pm)}$ represents the binary collision operator for molecules j and k. In Eq. (3b) we have used the result that $L_j^{(1)}$ is self-adjoint. Explicitly, $T_{jk}^{(\pm)}$ and $T_{jk}^{(\pm)\dagger}$ are

$$T_{jk}^{(\pm)} = \theta(\pm \dot{l}_{jk})\, \delta(l_{jk})\, |\dot{l}_{jk}|\, (\hat{b}_{jk} - 1) \tag{5a}$$

$$T_{jk}^{(\pm)\dagger} = \delta(l_{jk})\, \dot{l}_{jk} \{\theta(\pm \dot{l}_{jk}) \hat{b}_{jk} + \theta(\mp \dot{l}_{jk})\} \tag{5b}$$

where l_{jk} represents the smallest distance between the surfaces of the convex ovaloids j and k.[3] Here $\dot{l}_{jk}$ is the time rate of change of l_{jk}, and $\theta(x)$ and $\delta(x)$ denote the Heaviside and delta functions, respectively. The operator $\hat{b}_{jk}$ acts on the momenta, changing the pre- (post-) hit momenta to the post- (pre-) hit momenta. See Fig. 1 for a pictorial representation of the collision geometry. Equation (1) holds for molecules that interact via rigid impulsive forces.

To proceed, we define the reduced distribution functions

$$\delta \tilde{f}^{(s)} = \frac{N!}{(N-s)!} \int d\mathbf{x}_{s+1} \cdots d\mathbf{x}_N\, \delta \tilde{F}^{(N)} \tag{6a}$$

and note that these functions are interrelated,

$$\delta \tilde{f}^{(s)} = \frac{1}{N-s} \int d\mathbf{x}_{s+1}\, \delta \tilde{f}^{(s+1)} \tag{6b}$$

These relations will serve as consistency conditions on the truncation schemes to be discussed. With the reduced distribution functions defined,

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[3] When j and k overlap, l_{jk} is defined as the maximum distance between the molecular surfaces defining the overlapping region.

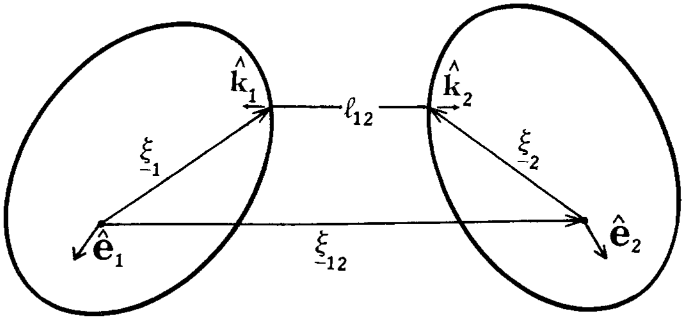

Fig. 1. Representation of a collisional configuration between two rigid ovaloids. The unit vectors $\hat{e}_1$ and $\hat{e}_2$ orient the molecules, l_{12} is the minimum distance between the molecular surfaces, and $\hat{k}$ denotes the unit surface normal at the surface point nearest the collision partner.

the BBGKY hierarchy for $\delta\bar{f}(s)$ is obtained from Eq. (1). The first few equations are

$$\left(\frac{\partial}{\partial t}+iL_1^{(1)}\right)\delta\bar{f}^{(1)}(\mathbf{x}_1,t)=\int d\mathbf{x}_2\,T_{12}^{(+)\dagger}\,\delta\bar{f}^{(2)}(\mathbf{x}_1,\mathbf{x}_2,t) \tag{7a}$$

$$\begin{aligned}\left(\frac{\partial}{\partial t}+iL_1^{(1)}+iL_2^{(1)}-T_{12}^{(+)\dagger}\right)&\delta\bar{f}^{(2)}(\mathbf{x}_1,\mathbf{x}_2,t)\\ &=\int d\mathbf{x}_3\,(T_{13}^{(+)\dagger}+T_{23}^{(+)\dagger})\,\delta\bar{f}^{(3)}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,t)\end{aligned} \tag{7b}$$

Because we consider molecules that interact impulsively, the distribution functions for this system vanish identically whenever $l_{jk}<0$ (overlap condition) for any j and k. For later convenience, we choose to factor out of $\delta\bar{f}(s)$ its discontinuous part and define $\delta f^{(s)}$ through the relation

$$\delta\bar{f}^{(s)}=W^{(s)}\,\delta f^{(s)} \tag{8}$$

where $W^{(s)}$ is zero if any $l_{jk}<0$ $(j,k=1,\ldots,s)$ and is unity otherwise. The function $\delta f^{(s)}$ is a smooth function of the s-molecule phases. Inserting this relation into Eqs. (7a) and (7b), we obtain

$$\left(\frac{\partial}{\partial t}+iL_1^{(1)}\right)\delta f^{(1)}(\mathbf{x}_1,t)=\int d\mathbf{x}_2\,T_{12}^{(+)\dagger}\,\delta f^{(2)}(\mathbf{x}_1,\mathbf{x}_2,t) \tag{9a}$$

$$\begin{aligned}&\delta f^{(2)}(\mathbf{x}_1,\mathbf{x}_2,t)(iL_1^{(1)}+iL_2^{(1)})\,W_{12}^{(2)}\\ &\quad+W_{12}^{(2)}\left(\frac{\partial}{\partial t}+iL_1^{(1)}+iL_2^{(1)}-T_{12}^{(+)\dagger}\right)\delta f^{(2)}(\mathbf{x}_1,\mathbf{x}_2,t)\\ &\qquad=\int d\mathbf{x}_3\,W_{123}^{(3)}(T_{13}^{(+)\dagger}+T_{23}^{(+)\dagger})\,\delta f^{(3)}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,t)\end{aligned} \tag{9b}$$

Now, we utilize the following identities:

$$(iL_1^{(1)}+iL_2^{(1)})\,W_{12}^{(2)}=\dot{l}_{12}\,\delta(l_{12})\,W_{12}^{(2)} \tag{10}$$

$$T_{12}^{(+)\dagger}-\dot{l}_{12}\,\delta(l_{12})=T_{12}^{(-)} \tag{11}$$

in order to rewrite the hierarchy,

$$\left(\frac{\partial}{\partial t}+iL_1^{(1)}\right)\delta f_1^{(1)}=\int d\mathbf{x}_2\,T_{12}^{(+)\dagger}\,\delta f_{12}^{(2)} \tag{12a}$$

$$\begin{aligned}W_{12}^{(2)}\left(\frac{\partial}{\partial t}+iL_1^{(1)}+iL_2^{(1)}-T_{12}^{((-)}\right)&\delta f_{12}^{(2)}\\ &=W_{12}^{(2)}\int d\mathbf{x}_3\,W_{13}^{(2)}\,W_{23}^{(2)}(T_{13}^{(+)\dagger}+T_{23}^{(+)\dagger})\,\delta f_{123}^{(3)}\end{aligned} \tag{12b}$$

It is now necessary to truncate the hierarchy in order to obtain a manageable closed set of equations.

Many truncations have been proposed. They all share a common feature, that of ignoring high-order *dynamical* correlations. For example, the Boltzmann *ansatz* is

$$f^{(2)}(\mathbf{x}_1^*, \mathbf{x}_2^*, t) = f^{(1)}(\mathbf{x}_1^*, t)\, f^{(1)}(\mathbf{x}_2^*, t) \tag{13}$$

where the star denotes the precollisional state. The truncation assumes that precollisionally, the two colliding molecules are uncorrelated. However, no assumptions concerning the postcollisional form of $f^{(2)}$ are made. This distinction between the past (precollision) and future (postcollision) in the truncation introduces an irreversible evolution. We are not required to make an explicit distinction between the future and past in our truncation; it is implicit in Eq. (12), where the coupling of the $\delta f^{(n)}$ term is to the *precollisional* part of $\delta f^{(n+1)}$.

If we were to proceed naively, we might propose a truncation of the form

$$\begin{aligned} \tilde{f}^{(1)}(\mathbf{x}_1, t) &= \tilde{f}^{(1)}_{\mathrm{eq}}\{1 + \phi(\mathbf{x}_1, t)\} \\ \tilde{f}^{(2)}(\mathbf{x}_1, \mathbf{x}_2, t) &= \tilde{f}^{(2)}_{\mathrm{eq}}\{1 + \phi^{(1)}(\mathbf{x}_1, t) + \phi^{(2)}(\mathbf{x}_1, \mathbf{x}_2, t)\} \\ \tilde{f}^{(3)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, t) &= \tilde{f}^{(3)}_{\mathrm{eq}}\{1 + \phi^{(1)}(\mathbf{x}_1, t) + \phi^{(2)}(\mathbf{x}_1, \mathbf{x}_2, t) + \phi^{(2)}(\mathbf{x}_1, \mathbf{x}_3, t)\} \end{aligned} \tag{14}$$

However, this truncation does not satisfy the consistency conditions on the reduced distribution functions, Eq.(6b). For example, $\tilde{f}^{(3)}$ integrates to

$$\tilde{f}^{(2)}(\mathbf{x}_1, \mathbf{x}_2, t) + [1/(N-2)] \int d\mathbf{x}_3\, \tilde{f}^{(3)}_{\mathrm{eq}}\, \phi^{(2)}(\mathbf{x}_1, \mathbf{x}_3, t)$$

and not to $\tilde{f}^{(2)}$ as required. The consistency conditions are guaranteed if we write a general truncation in terms of the full N-body distribution

$$\begin{aligned} \tilde{F}^{(N)} \simeq \tilde{F}^{(N)}_{\mathrm{eq}} \Bigg\{ & 1 + \chi^{(1)'}(\mathbf{x}_1, t) + \sum_{j_2 \neq 1}^{N} \chi^{(2)'}(\mathbf{x}_1, \mathbf{x}_{j_2}, t) \\ & + \cdots + \sum_{j_2, j_3, \ldots, j_s \neq 1}^{N} \chi^{(s)'}(\mathbf{x}_1, \mathbf{x}_{j_2}, \ldots, x_{j_s}, t) \Bigg\} \end{aligned} \tag{15}$$

where the reduced distribution functions are obtained from $\tilde{F}^{(N)}$ using Eq. (6a). Truncations of this form have been utilized by many workers and have been given a systematic justification in terms of a maximum entropy formalism.(23)

The ERRE are derived by setting $s=2$ in Eq. (15). This choice leads to the following reduced distribution functions:

$$\bar{f}^{(1)}(\mathbf{x}_1, t)=\bar{f}^{(1)}_{\text{eq}}\{1+\chi^{(1)'}(\mathbf{x}_1, t)\}+\int d\mathbf{x}_2\, \bar{f}^{(2)}_{\text{eq}}\chi^{(2)'}(\mathbf{x}_1, \mathbf{x}_2, t) \tag{16a}$$

$$\bar{f}^{(2)}(\mathbf{x}_1, \mathbf{x}_2, t)=\bar{f}^{(2)}_{\text{eq}}\{1+\chi^{(1)'}(\mathbf{x}_1, t)+\chi^{(2)'}(\mathbf{x}_1, \mathbf{x}_2, t)\}$$
$$+\int d\mathbf{x}_3\, \bar{f}^{(3)}_{\text{eq}}\chi^{(2)'}(\mathbf{x}_1, \mathbf{x}_3, t) \tag{16b}$$

At first, these forms appear odd. It is more convenient to work with a singlet distortion $\chi^{(1)}$ rather than a singlet distortion $\chi^{(1)'}+[\bar{f}^{(1)}_{\text{eq}}]^{-1}\int d\mathbf{x}_2\, \bar{f}^{(2)}_{\text{eq}}\chi^{(2)'}$, since the singlet distortion determines the physical quantities we want to calculate. Thus, we define unprimed distortions

$$\chi^{(1)}(\mathbf{x}_1, t)=\chi^{(1)'}(\mathbf{x}_1, t)+\int d\mathbf{x}_2\, f^{(1)}_{\text{eq}}\tilde{G}^{(2)}_{12}\chi^{(2)'}(\mathbf{x}_1, \mathbf{x}_2, t) \tag{17a}$$

$$\chi^{(2)}(\mathbf{x}_1, \mathbf{x}_1, t)=\chi^{(2)'}(\mathbf{x}_1, \mathbf{x}_2, t) \tag{17b}$$

where $\tilde{G}^{(s)}_{1,2,\ldots,s}$ is a static equilibrium s-body distribution function for molecules 1, 2,..., s.

Our choice of singlet distortion implies a truncation of the form

$$\tilde{F}^{(N)}=\tilde{F}^{(N)}_{\text{eq}}\left\{1+\mathbf{x}^{(1)}(\mathbf{x}_1, t)-\int d\mathbf{x}_j\, f^{(1)}_{\text{eq}}(\mathbf{x}_j)\, \tilde{G}^{(2)}_{1j}\chi^{(2)}(\mathbf{x}_1, \mathbf{x}_j, t)\right.$$
$$\left.+\sum_{j=2}^{N}\chi^{(2)}(\mathbf{x}_1, \mathbf{x}_j, t)\right\} \tag{18}$$

and, further, leads to the reduced distribution functions

$$\delta f^{(1)}(\mathbf{x}_1, t)=f^{(1)}_{\text{eq}}(\mathbf{1})\, \chi^{(1)}(\mathbf{x}_1, t) \tag{19a}$$

$$\delta f^{(2)}(\mathbf{x}_1, \mathbf{x}_2, t)$$
$$=f^{(1)}_{\text{eq}}(\mathbf{1})\, f^{(1)}_{\text{eq}}(\mathbf{2})\, G^{(2)}_{12}\left\{\chi^{(1)}(\mathbf{x}_1, t)+\chi^{(2)}(\mathbf{x}_1, \mathbf{x}_2, t)\right.$$
$$\left.-\int d\mathbf{x}_3\, f^{(1)}_{\text{eq}}(\mathbf{3})\, W^{(2)}_{13}G^{(2)}_{13}\chi^{(2)}(\mathbf{x}_1, \mathbf{x}_3, t)\right\}$$
$$+f^{(1)}_{\text{eq}}(\mathbf{1})\, f^{(1)}_{\text{eq}}(\mathbf{2})\int d\mathbf{x}_3\, f^{(1)}_{\text{eq}}(\mathbf{3})\, W^{(2)}_{13}W^{(2)}_{23}G^{(3)}_{123}\chi^{(2)}(\mathbf{x}_1, \mathbf{x}_3, t) \tag{19b}$$

$$\begin{aligned}
&\delta f^{(3)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, t)\\
&\quad = f_{\mathrm{eq}}^{(1)}(\mathbf{1})\, f_{\mathrm{eq}}^{(1)}(\mathbf{2})\, f_{\mathrm{eq}}^{(1)}(\mathbf{3})\, G_{123}^{(3)} \Big\{\chi^{(1)}(\mathbf{x}_1, t) + \chi^{(2)}(\mathbf{x}_1, \mathbf{x}_2, t)\\
&\qquad + \chi^{(2)}(\mathbf{x}_1, \mathbf{x}_3, t) - \int d\mathbf{x}_4\, f_{\mathrm{eq}}^{(1)}(\mathbf{4})\, W_{14}^{(2)} G_{14}^{(2)} \chi^{(2)}(\mathbf{x}_1, \mathbf{x}_4, t)\Big\}\\
&\qquad + f_{\mathrm{eq}}^{(1)}(\mathbf{1})\, f_{\mathrm{eq}}^{(1)}(\mathbf{2})\, f_{\mathrm{eq}}^{(1)}(\mathbf{3}) \int d\mathbf{x}_4\, f_{\mathrm{eq}}^{(1)}(\mathbf{4})\, W_{14}^{(2)} W_{24}^{(2)} W_{34}^{(2)} G_{1234}^{(4)} \chi^{(2)}(\mathbf{x}_1, \mathbf{x}_4, t)
\end{aligned} \tag{19c}$$

Again, the functions $\delta f^{(2)}$ and $\delta f^{(3)}$ appear strange, while $\delta f^{(1)}$ seems appropriate. We have introduced a new definition here, not new physics. One could work with either set of χ's, but, with the primed set, the interesting quantity $\delta f^{(1)}$ is not given by $\chi^{(1)'}$ alone. This point is essential in the construction of consistent truncations from Eq. (15).

Inserting the reduced distribution functions of Eq. (19) into the BBGKY hierarchy of Eq. (12), utilizing the equilibrium form of the BBGKY hierarchy to eliminate the ∇G terms, and integrating by parts, we obtain the Enskog repeated ring equations. They are

$$\begin{aligned}
&\left(\frac{\partial}{\partial t} + iL_1^{(1)} - \int d\mathbf{x}_2\, f_{\mathrm{eq}}^{(1)}(\mathbf{2})\, G_{12}^{(2)} T_{12}^{(+)^\dagger}\right) \chi^{(1)}(\mathbf{x}_1, t)\\
&\quad = \int d\mathbf{x}_2\, f_{\mathrm{eq}}^{(1)}(\mathbf{2})\, W_{12}^{(2)} \Big\{G_{12}^{(2)} T_{12}^{(+)^\dagger}\\
&\qquad + \int d\mathbf{x}_3\, f_{\mathrm{eq}}^{(1)}(\mathbf{3}) [W_{23}^{(2)} G_{123}^{(3)} - G_{12}^{(2)} G_{13}^{(2)}]\, T_{13}^{(+)^\dagger}\Big\}\, \chi^{(2)}(\mathbf{x}_1, \mathbf{x}_2, t)
\end{aligned} \tag{20a}$$

$$\begin{aligned}
&W_{12}^{(2)} \hat{A} \chi^{(2)}(\mathbf{x}_1, \mathbf{x}_2, t)\\
&\quad = W_{12}^{(2)} \Big\{T_{12}^{(-)} G_{12}^{(2)} + \int d\mathbf{x}_3\, f_{\mathrm{eq}}^{(1)}(\mathbf{3}) [W_{23}^{(2)} G_{123}^{(3)} - G_{13}^{(2)} G_{12}^{(2)}]\, T_{13}^{(-)}\Big\}\, \chi^{(1)}(\mathbf{x}_1, t)
\end{aligned} \tag{20b}$$

where

$$\begin{aligned}
\hat{A} = \Big\{ & G_{12}^{(2)} \left(\frac{\partial}{\partial t} + iL_1^{(1)} + iL_2^{(1)}\right)\\
& + \int d\mathbf{x}_3\, f_{\mathrm{eq}}^{(1)}(\mathbf{3})\, W_{13}^{(2)} [W_{23}^{(2)} G_{123}^{(3)} - G_{12}^{(2)} G_{13}^{(2)}] \left(\frac{\partial}{\partial t} + iL_1^{(1)} + iL_3^{(1)}\right) \hat{P}_{23}\\
& - \int d\mathbf{x}_3\, f_{\mathrm{eq}}^{(1)}(\mathbf{3})\, W_{13}^{(2)} W_{23}^{(2)} G_{123}^{(3)} [T_{13}^{(-)} + T_{23}^{(-)} (1 + \hat{P}_{23})]
\end{aligned}$$

$$
\begin{aligned}
&-\int d\mathbf{x}_3\, f_{\mathrm{eq}}^{(1)}(\mathbf{3})\, W_{13}^{(2)}\{W_{23}^{(2)}G_{123}^{(3)} - G_{12}^{(2)}G_{13}^{(2)}\}\, T_{13}^{(-)}\hat{P}_{23} \\
&-\int d\mathbf{x}_3\, d\mathbf{x}_4\, f_{\mathrm{eq}}^{(1)}(\mathbf{3})\, f_{\mathrm{eq}}^{(1)}(\mathbf{4})\, W_{13}^{(2)}W_{14}^{(2)}[W_{34}^{(2)}\, W_{23}^{(2)}\, W_{24}^{(2)}\, G_{1234}^{(4)} - W_{34}^{(2)}G_{12}^{(2)}G_{134}^{(3)} \\
&- W_{24}^{(2)}G_{13}^{(2)}G_{124}^{(3)} + G_{12}^{(2)}G_{13}^{(2)}G_{14}^{(2)}]\, T_{14}^{(-)}\hat{P}_{23} \\
&+\int d\mathbf{x}_3\, d\mathbf{x}_4\, f_{\mathrm{eq}}^{(1)}(\mathbf{3})\, f_{\mathrm{eq}}^{(1)}(\mathbf{4})\, W_{13}^{(2)}W_{14}^{(2)}W_{34}^{(2)}[W_{23}^{(2)}W_{24}^{(2)}G_{1234}^{(4)} \\
&- G_{12}^{(2)}G_{134}^{(3)}]\, \dot{l}_{34}\, \delta(l_{34})\, \hat{P}_{23} \\
&- T_{12}^{(-)}\left[G_{12}^{(2)} + \int d\mathbf{x}_3\, f_{\mathrm{eq}}^{(1)}(\mathbf{3})\, W_{13}^{(2)}(W_{23}^{(2)}G_{123}^{(3)} - G_{12}^{(2)}G_{13}^{(2)})\, \hat{P}_{23}\right]\Bigg\} \qquad (21)
\end{aligned}
$$

Here the $\hat{P}_{jk}$ are operators which permute the indices j and k. Equations (20) and (21) represent the most general RR equations for tagged molecule motion. They are not restricted to the analysis of a particular problem or initial condition.

The form of the ERRE appropriate to the self-diffusion of a spherical particle in an atomic bath has been derived independently by Sung and Dahler(13) and Masters and Keyes.(14) Both derivations employ a Mori formalism, choosing as relevant variables the set

$$\left\{\delta(\mathbf{v}-\mathbf{v}_1)\,\delta(\mathbf{r}-\mathbf{r}_1),\ \delta(\mathbf{v}-\mathbf{v}_1)\,\delta(\mathbf{r}-\mathbf{r}_1)\sum_{j=2}^{N}\,\delta(\mathbf{v}_j-\mathbf{v}_2)\,\delta(\mathbf{r}_j-\mathbf{r}_2)\right\}$$

The equations derived by Masters and Keyes are obtained from Eqs. (20) and (21) by substituting $\chi^{(1)}(\mathbf{x}_1,\, t=0)=\mathbf{v}_1$ as the initial condition on the singlet distortion, and utilizing the following explicit forms:

$$\mathbf{x}_j \rightarrow (\mathbf{r}_j, \mathbf{v}_j), \qquad iL_j^{(1)} \rightarrow \mathbf{v}_j \cdot \nabla_{r_j}$$

$$\dot{l}_{ij}\delta(l_{ij}) \rightarrow (\mathbf{v}_j - \mathbf{v}_i)\cdot \hat{r}_{ij}\, \delta(r_{ij} - \sigma_{ij})$$

where $\mathbf{r}_{ij}=\mathbf{r}_j-\mathbf{r}_j$ and σ_{ij} is the collision radius of particles i and j. The equivalence of Eqs. (20) and (21) with the equations of Masters and Keyes for self-diffusion of a spherical particle serves as a check on the truncation of the BBGKY hierarchy proposed in this section.

3. A VARIATIONAL SOLUTION

A standard method for obtaining numerical results in kinetic theory is an expansion of the unknown quantities in a complete set of functions. In practice, the utility of these moment expansions is lost if a large number of terms is required. It is known that moment solutions to kinetic equations involving only $\chi^{(1)}$ (e.g., Boltzmann or Enskog equations) converge rapidly. It is also known that a moment expansion of $\chi^{(2)}$ required in RR theories suffers from prohibitively slow convergence.(24) Master and Keyes(15,16) have recently demonstrated an integral form of Cercignani's variational principle (IVP) applicable to the RR equations for the LG. This IVP yields what are believed to be highly accurate results. However, the Masters and Keyes method suffers from its inability to be generalized to more complex equations (for example, the ERRE).

We suggest that a reasonable approach is one that expands $\chi^{(1)}$ in a truncated set of moments and treats $\chi^{(2)}$ within the framework of a variational principle. For the ERRE we will demonstrate a differential form of a kinetic variational principle (DVP) due to Cercignani.(18)

The method is as follows: First expand $\chi^{(1)}$ in a finite, orthonormal set of functions of momenta, denoted ϕ_j, $j=1, 2,\dots, m$:

$$\chi^{(1)} = \sum_{j=1}^{m} a_j \phi_j \tag{22}$$

where the a_j are expansion coefficients to be determined. The moments are assumed orthonormal under the Maxwellian weight function. Inserting this expansion into the first of the ERRE, Eq. (20), premultiplying with $\psi_0(\mathbf{1})\,\phi_k(\mathbf{1})$, where ψ_0 is a Maxwellian normalized to unity, and integrating over the momenta, we obtain a set of moment equations for the unknown expansion coefficients:

$$\begin{aligned}
&\left\{z + \int d\mathbf{x}_1\,\psi_0(\mathbf{1})\,\phi_k(\mathbf{1})\,iL_1^{(1)}\,\phi_k(\mathbf{1}) - \int d\mathbf{x}_1\,\psi_0(\mathbf{1})\,\phi_k(\mathbf{1})\,\hat{K}_{\mathrm{LE}}(\mathbf{1})\,\phi_k(\mathbf{1})\right\} a_k \\
&\quad = \int d\mathbf{x}_1\,\psi_0(\mathbf{1})\,\phi_k(\mathbf{1})\,\chi^{(1)}(\mathbf{x}_1, t=0) \\
&\qquad - \sum_{j\neq k} \left\{\int d\mathbf{x}_1\,\psi_0(\mathbf{1})\,\phi_k(\mathbf{1})\,iL_1^{(1)}\phi_j(\mathbf{1}) - \int d\mathbf{x}_1\,\psi_0(\mathbf{1})\,\phi_k(\mathbf{1})\,\hat{K}_{\mathrm{LE}}(\mathbf{1})\,\phi_j(\mathbf{1})\right\} a_j \\
&\qquad + \int d\mathbf{x}_1\,d\mathbf{x}_2\,\psi_0(\mathbf{1})\,f_{\mathrm{eq}}^{(1)}(\mathbf{2})\,W_{12}^{(2)}\chi^{(2)}(\mathbf{x}_1, \mathbf{x}_2, z)\,\hat{\mathbf{T}}_{12}^{(+)}\phi_k(\mathbf{1})
\end{aligned} \tag{23}$$

Here z is the Laplace transform variable, $\chi^{(1)}(\mathbf{x}_1, t=0)$ is the initial condition, $\hat{K}_{\mathrm{LE}}$ represents the Lorentz–Enskog operator

$$\hat{K}_{\mathrm{LE}}(\mathbf{i})\,f(\mathbf{i}) = \int d\mathbf{x}_j\,f_{\mathrm{eq}}^{(1)}(j)\,G_{ij}^{(2)}T_{ij}^{(+)\dagger}\,f(\mathbf{i}) \tag{24}$$

where $\mathbf{i}$ refers to the momenta of molecule i, and the operator $\hat{\mathbf{T}}_{12}^{(\pm)}$ is defined by

$$\hat{\mathbf{T}}_{12}^{(\pm)} = G_{12}^{(2)} T_{12}^{(\pm)} + \int d\mathbf{x}_3 \, f_{\mathrm{eq}}^{(1)}(\mathbf{3}) \, [W_{23}^{(2)} G_{123}^{(3)} - G_{12}^{(2)} G_{13}^{(2)}] \, T_{13}^{(\pm)} \tag{25}$$

In deriving the expansion of Eq. (23), use of the adjoint relations satisfied by $T_{ij}^{(\pm)}$ has been made.

The problem now lies in the determination of $\chi^{(2)}$. Actually, we require not $\chi^{(2)}$ itself, but the last term of the rhs of Eq. (23). The equation satisfied by $\chi^{(2)}$ is

$$W_{12}^{(2)} \hat{A} \chi^{(2)}(\mathbf{x}_1, \mathbf{x}_2, z) = W_{12}^{(2)} \hat{\mathbf{T}}_{12}^{(-)} \chi^{(1)}(\mathbf{x}_1, z) \tag{26}$$

Here both $\hat{A}$ and $\hat{\mathbf{T}}$ are linear operators. Inserting the moment expansion of $\chi^{(1)}$ into Eq. (26), utilizing the definition of linear operators, we obtain

$$W_{12}^{(2)} \hat{A} \chi^{(2)} = W_{12}^{(2)} \sum_{j=1}^{m} a_j \hat{\mathbf{T}}_{12}^{(-)} \phi_j(\mathbf{1}) \tag{27}$$

The function $\chi^{(2)}$ can be similarly expanded

$$\chi^{(2)}(\mathbf{x}_1, \mathbf{x}_2, z) = \sum_{j=1}^{m} a_j(z) \, \Phi_j^{(2)}(\mathbf{x}_1, \mathbf{x}_2, z) \tag{28}$$

where the coefficients are identical to the expansion coefficients of $\chi^{(1)}$, and the functions $\Phi_j^{(2)}$ satisfy the equations

$$W_{12}^{(2)} \hat{A} \Phi_j^{(2)} = W_{12}^{(2)} \hat{\mathbf{T}}_{12}^{(-)} \phi_j(\mathbf{1}) \tag{29}$$

Variational principles suggest themselves when symmetric operators are involved. However, the operator $\hat{A}$ is not symmetric, i.e.,

$$\langle \Psi | \hat{A} | \Phi \rangle \neq \langle \Phi | \hat{A} | \Psi \rangle \tag{30}$$

where

$$\langle \Psi | \Phi \rangle = \frac{1}{V} \int d\mathbf{x}_1 \, d\mathbf{x}_2 \, W_{12}^{(2)} \psi_0(\mathbf{1}) \, \psi_0(\mathbf{2}) \, \Psi \Phi \tag{31}$$

and the quantity V is the system volume. Following Cercignani, we introduce the parity operator in velocity space $\hat{R}$. Operating on the equations for $\Phi_j^{(2)}$ with $\hat{R}$, we get

$$W_{12}^{(2)} \hat{R} \hat{A} \Phi_j^{(2)}(\mathbf{x}_1, \mathbf{x}_2, z) = W_{12}^{(2)} \hat{\mathbf{T}}_{12}^{(+)} \hat{R} \phi_j^{(1)}(\mathbf{1}) \tag{32}$$

where the identity $\hat{R}\hat{\mathbf{T}}^{(-)} = \hat{\mathbf{T}}^{(+)}\hat{R}$ was used. Now utilizing the properties $\hat{R}\mathbf{T}^{(\pm)} = \mathbf{T}^{(\mp)}\hat{R}$ and freely changing the integration variables from $\{\mathbf{x}_1, \mathbf{x}_1\}$ to $\{\hat{R}\mathbf{x}_1, \hat{R}\mathbf{x}_2\}$, whose Jacobian is unity, it is a straightforward, albeit tedious, exercise to demonstrate that the operator product $\hat{R}\hat{A}$ [where $\hat{A}$ is defined in Eq. (21)] is symmetric, i.e.,

$$\langle \Phi | \hat{R}\hat{A} | \Psi \rangle = \langle \Psi | \hat{R}\hat{A} | \Phi \rangle \tag{33}$$

The variational principle is presented by defining the functionals

$$J_{jk}(\tilde{\Phi}^{(2)}) = \langle \tilde{\Phi}_j^{(2)} | \hat{R}\hat{A} | \tilde{\Phi}_k^{(2)} \rangle - \langle \tilde{\Phi}_j^{(2)} | \hat{\mathbf{T}}_{12}^{(+)}\hat{R} | \phi_k^{(1)} \rangle - \langle \Phi_k^{(2)} | \hat{\mathbf{T}}_{12}^{(+)}\hat{R} | \phi_j^{(1)} \rangle \tag{34}$$

where $\tilde{\Phi}_j^{(2)}$ represents an arbitrary trial function. Assuming that the singlet moments $\phi_j^{(1)}$ have well-defined time-reversal eigenvalues (this can always be arranged), which we denote t_j, the functional can be written

$$J_{jk}(\tilde{\Phi}^{(2)}) = \langle \tilde{\Phi}_j^{(2)} | \hat{R}\hat{A} | \tilde{\Phi}_k^{(2)} \rangle - t_k \langle \tilde{\Phi}_j^{(2)} | \hat{\mathbf{T}}^{(+)} | \phi_k^{(1)} \rangle - t_j \langle \tilde{\Phi}_k^{(2)} | \hat{\mathbf{T}}^{(+)} | \phi_j^{(1)} \rangle \tag{35}$$

Allowing $\delta\Phi_j^{(2)}$ to denote the deviation of the trial function from the true solution to Eq. (29), it is easily demonstrated: (1) that the first variation of $J_{jk}(\tilde{\Phi}^{(2)})$ vanishes, and (2) that the stationary value is

$$t_j \langle \Phi_k^{(2)} | \hat{\mathbf{T}}^{(+)} | \phi_j^{(1)} \rangle = -t_k \langle \Phi_j^{(2)} | \hat{\mathbf{T}}^{(+)} | \phi_k^{(1)} \rangle$$

Inserting $\tilde{\Phi}_j^{(2)} = \Phi_j^{(2)} + \delta\Phi_j^{(2)}$, where $\Phi_j^{(2)}$ is the solution of Eq. (29), into $J_{jk}(\tilde{\Phi}^{(2)})$, we get

$$J_{jk}(\tilde{\Phi}^{(2)}) = \text{Stat } J_{jk} + \delta J_{jk}^{(1)} + \delta^2 J_{jk}^{(2)} \tag{36}$$

where

$$\begin{aligned}\text{Stat } J_{jk} = {} & \langle \Phi_j^{(2)} | \hat{R}\hat{A} | \Phi_k^{(2)} \rangle - \langle \Phi_j^{(2)} | \hat{R}\hat{\mathbf{T}}^{(-)} | \phi_k^{(1)} \rangle \\ & - \langle \Phi_k^{(2)} | \hat{R}\hat{\mathbf{T}}^{(-)} | \phi_j^{(1)} \rangle \end{aligned} \tag{37a}$$

$$\begin{aligned}\delta J_{jk}^{(1)} = {} & \langle \delta\Phi_j^{(2)} | \hat{R}\hat{A} | \Phi_k^{(2)} \rangle + \langle \Phi_j^{(2)} | \hat{R}\hat{A} | \delta\Phi_k^{(2)} \rangle \\ & - \langle \delta\Phi_j^{(2)} | \hat{R}\hat{\mathbf{T}}^{(-)} | \phi_k^{(1)} \rangle - \langle \delta\Phi_k^{(2)} | \hat{R}\hat{\mathbf{T}}^{(-)} | \phi_j^{(1)} \rangle \end{aligned} \tag{37b}$$

$$\delta^2 J_{jk}^{(2)} = \langle \delta\Phi_j^{(2)} | \hat{R}\hat{A} | \delta\Phi_k^{(2)} \rangle \tag{37c}$$

The first and second terms on the rhs of Eq. (37a) cancel because of Eq. (29), yielding $-\langle \Phi_k^{(2)} | R\mathbf{T}^{(-)} | \phi_j^{(1)} \rangle$, which equals $-t_j \langle \Phi_k^{(2)} | \mathbf{T}^{(+)} | \phi_j^{(1)} \rangle$. Also, using the symmetric property of the operator product $\hat{R}\hat{A}$, the first and third terms on the rhs of Eq. (37a) cancel, yielding $-t_k\langle\Phi_j^{(2)}|\hat{\mathbf{T}}^{(+)}|\phi_k^{(1)}\rangle$. Thus, statement 2 is verified. Using identical arguments, it is easy to see that the first and third terms and the second and fourth terms on the rhs of Eq. (37b) cancel, yielding $\delta J_{jk}^{(1)}=0$. Thus, statement 1 is substantiated.

Finally, the unknown quantity in the moment equations [Eq. (23)], $\langle\chi^{(2)}|\hat{\mathbf{T}}^{(+)}|\phi_k^{(1)}\rangle$, is simply related to the stationary values of the functionals $J_{jk}(\tilde{\Phi}^{(2)})$. Expanding $\chi^{(2)}$, we get

$$\begin{aligned}\langle\chi^{(2)}|\hat{\mathbf{T}}^{(+)}|\phi_k\rangle &= a_k\langle\Phi_k^{(2)}|\hat{\mathbf{T}}^{(+)}|\phi_k\rangle + \sum_{j\neq k} a_j\langle\Phi_j^{(2)}|\hat{\mathbf{T}}^{(+)}|\phi_k\rangle \\ &= -a_k t_k \operatorname{Stat} J_{kk}(\Phi^{(2)}) - t_k \sum_{j\neq k} a_j \operatorname{Stat} J_{jk}(\Phi^{(2)}) \qquad (38)\end{aligned}$$

Therefore, inserting Eq. (38) into Eq. (23), we obtain a set of moment equations for the a_j in terms of the stationary values of the functional $J_{jk}(\Phi^{(2)})$:

$$\begin{aligned}&\left\{z+\int d\mathbf{x}_1\,\psi_0(\mathbf{1})\,\phi_k(\mathbf{1})\,iL_1^{(1)}\,\phi_k(\mathbf{1})-\int d\mathbf{x}_1\,\psi_0(\mathbf{1})\,\phi_k(\mathbf{1})\,\hat{K}_{\mathrm{LE}}\phi_k(\mathbf{1})\right.\\ &\qquad\left.+\,t_k\operatorname{Stat} J_{kk}(\Phi^{(2)})\right\}a_k\\ &=\int d\mathbf{x}_1\,\psi_0(\mathbf{1})\,\phi_k(\mathbf{1})\,\chi^{(1)}(\mathbf{x}_1,t=0)-\sum_{j\neq k}\left\{\int d\mathbf{x}_1\,\psi_0(\mathbf{1})\,\phi_k(\mathbf{1})\,iL_1^{(1)}\,\phi_j(\mathbf{1})\right.\\ &\qquad\left.-\int d\mathbf{x}_1\,\psi_0(\mathbf{1})\,\phi_k(\mathbf{1})\,\hat{K}_{\mathrm{LE}}\phi_j(\mathbf{1})-t_k\operatorname{Stat} J_{jk}(\Phi^{(2)})\right\}a_j \qquad (39)\end{aligned}$$

Equations (29), (34), (36), and (39) represent the desired moment-variational solution of the ERRE for $\chi^{(1)}$.

We must decide on the appropriate functions in which to expand to singlet distortion $\chi^{(1)}$. Much work has been carried out on this choice of basis functions when working with equations for the singlet distortions (such as the Boltzmann or Enskog equations). We suggest that this work also applies to the ERRE. Second, we are faced with the more difficult choice of trial functions $\tilde{\Phi}_j^{(2)}$. Variational principles are, by their very nature, dependent on the development of a physical intuition relating to the problem at hand. Some of the insight that we desire is found in the kinetic theory treatment of the transition regime.(17,18) We hope to build on this intuition by demonstrating a variation solution of the ERRE for the overlapping Lorentz gas.

4. AN APPLICATION: THE OVERLAPPING LORENTZ GAS

In this section we apply the formalism developed in Section 3 to the calculation of the diffusion constant in the overlapping Lorentz gas. In a subsequent paper, the above formalism is applied to the calculation of the full VCF for the Lorentz gas. Below, we present the equations specific to the 3D LG. However, we will report the numerical results for both the two- and three-dimensional systems.

The overlapping LG represents perhaps the simplest nontrivial "fluid" system. It consists of a point particle moving with constant speed v_0 through a fluid of randomly placed, fixed, overlapping spherical scatters of radius R. Important simplifications of the equations of Sections 2 and 3 result from the simplicity of the overlapping Lorentz model. They are:

1. All static correlation functions (including all $W_{jk}^{(2)}$ except for $W_{1k}^{(2)}$, $k \geqslant 2$) are unity due to the overlapping fluid structure.
2. The expansion of $\chi^{(1)}$ reduces to the single moment

$$\chi^{(1)} = \rho(z)\, \mathbf{v}_1 \tag{40}$$

   where $\rho(z)$ is the Laplace transform of the VCF and $\mathbf{v}_1$ is the velocity of the tagged particle. This is due to the impulsive nature of the scattering dynamics and the fact that the initial condition on $\chi^{(1)}$ for the calculation of D is $\chi^{(1)}(t=0) = \mathbf{v}_1$.
3. All operators related to the motion of particles other than the tagged particle disappear, due to the fact that all particles but the tagged particle are held fixed.

With the above simplifying features, the moment equations (39) reduce to

$$\begin{aligned}(z + \nu_{\mathrm{B}})\, \rho(z) &= 1 + \langle \mathbf{v}_1 \cdot | T_{12}^{(+)\dagger} | \chi^{(2)} \rangle \\ &= 1 + \mathrm{Stat}\, J(\chi^{(2)})\end{aligned} \tag{41}$$

where ν_{B} is the Boltzmann friction. The variational functional is

$$J(\chi^{(2)}) = \langle \chi^{(2)} \cdot | \hat{R} \hat{A}_{\mathrm{LG}} | \chi^{(2)} \rangle - 2 \langle \chi^{(2)} \cdot | \hat{R} \hat{T}_{12}^{(-)} | \chi^{(1)} \rangle \tag{42a}$$

and

$$\hat{A}_{\mathrm{LG}} = z + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}} - \rho \lambda(\mathbf{1}) - T_{12}^{(-)} \tag{42b}$$

where $\mathbf{r}$ is the position of the tagged particle relative to the fixed scatterer 2. The operator $\rho\hat{\lambda}(\mathbf{1})$ is the Lorentz–Boltzmann operator

$$\rho\hat{\lambda}(\mathbf{1})\, f(\mathbf{v}_1) = -\nu\left[f(\mathbf{v}_1) - \frac{1}{4\pi}\int d\hat{v}'_1\, f(\mathbf{v}'_1)\right] \tag{43}$$

ν is the friction, ρ is the singlet density, and $\mathbf{v}'_1$, the precollisional velocity, is related to the postcollisional velocity $\mathbf{v}_1$ by

$$\mathbf{v}'_1 = \mathbf{v}_1 - 2(\mathbf{v}_1 \cdot \hat{\sigma})\hat{\sigma} \tag{44}$$

where $\hat{\sigma}$ is the unit surface normal at the point of contact.

Equation (43) requires some clarification. In fact, Eq. (43) is not precisely the form of the Lorentz–Boltzmann operator because ν and not ν_{B} (the Boltzmann friction) appears. By defining ν as the true fluid friction (yet to be determined), we obtain a self-consistent equation [Eq. (60)] for the friction. Masters and Keyes$^{(10)}$ argued that the replacement of ν_{B} with ν in Eq. (43) is reasonable because $\hat{A}_{\mathrm{LG}}$ describes the motion of the tagged particle in the presence of particle 2, and that motion should be the result of the true friction, which is different from ν_{B} at high densities. This replacement of ν_{B} with ν results in the self-consistent repeated ring equation for the diffusion constant. Writing ν_{B} instead results in the repeated ring expression for the diffusion constant.

The task at hand is to choose an appropriate trial function. The pair function $\chi^{(2)}$ is the solution of the equation $\hat{A}_{\mathrm{LG}}\chi^{(2)} = T_{12}^{(-)}\chi^{(1)}$; explicitly,

$$\left[z + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}} - \rho\lambda(\mathbf{1})\right]\chi^{(2)} = T_{12}^{(-)}[\chi^{(2)} + \chi^{(1)}] \tag{45}$$

The lhs of this equation is the Lorentz–Boltzmann kinetic equation and the rhs represents boundary conditions (BC) on $\chi^{(2)}$. The BC are those of a spherical surface source feeding the surrounding fluid. We are confronted with a kinetic boundary layer problem (originally suggesting a variational treatment).

We know that far from the boundary, the distribution function $\chi^{(2)}$ reduces to a normal form $\chi_{\mathrm{N}}^{(2)}$,$^{(25)}$

$$\chi_{\mathrm{N}}^{(2)} = \left[1 - \nu^{-1}\mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}}\right]\mathbf{M}(\mathbf{r}, z) \tag{46}$$

where $\mathbf{M}(r, z)$ is an as yet undetermined function of position. Yet, within a few mean free paths (mfp) of the boundary there exist complicated boundary layer solutions, which we denote $\chi_{\mathrm{K}}^{(2)}$.

In order to specify the form of the kinetic boundary layer function, we propose the following intuitive picture of the kinetic molecular processes occurring near the surface source. The spherical boundary acts as a source feeding the surrounding fluid (of correlations). The source is the result of the change in $\chi^{(1)}$ due to the collision between the tagged particle and the fixed scatterer, denoted 2. A "particle" *just emitted into the fluid contributes to the* $\chi_{\mathrm{K}}^{(2)}$ part of the distribution function. After undergoing many collisions in the fluid, this recently emitted particle will behave (in a statistical sense) in a normal, hydrodynamic fashion, thus contributing to the normal $\chi_{\mathrm{N}}^{(2)}$ portion of the distribution function. To specify $\chi_{\mathrm{K}}^{(2)}$, we adopt the view that after a single collision the kinetic "particle" is transformed from kinetic in nature to normal. This is an extreme description of the dynamical processes. However, due to the isotropic scattering cross section present in the 3D LG, we believe (and the results demonstrate) that the above picture is reasonable. Further, we assume that $\chi_{\mathrm{N}}^{(2)}$ does not contribute to the source of $\chi_{\mathrm{K}}^{(2)}$.

With this model in mind, $\chi_{\mathrm{K}}^{(2)}$ must be the solution of the equation

$$\left[z+\mathbf{v}\cdot\frac{\partial}{\partial\mathbf{r}}+\nu\right]\chi_{\mathrm{K}}^{(2)}=0, \qquad |\mathbf{r}|>R \tag{47}$$

with BC, obtained from the rhs of Eq. (45) (omitting $\chi_{\mathrm{N}}^{(2)}$, in agreement with the discussion of the last paragraph), at $|\mathbf{r}|=R$

$$\chi_{\mathrm{K}}^{(2)}(\mathbf{r},\hat{v},z)=\begin{cases}\chi^{(1)\mathrm{precollision}}-\chi^{(1)\mathrm{postcollision}} & \hat{r}\cdot\hat{v}>0\\ 0 & \hat{r}\cdot\hat{v}<0\end{cases} \tag{48}$$

Given Eqs. (40) and (44), the BC can be written

$$\chi_{\mathrm{K}}^{(2)}(R\hat{r},\hat{v},z)=\begin{cases}-2(\mathbf{v}\cdot\hat{r})\,\hat{r}\rho(z) & \hat{r}\cdot\hat{v}>0\\ 0 & \hat{r}\cdot\hat{v}<0\end{cases} \tag{49}$$

The solution to the set of equations (47) and (49) is obtained by the method of integration along characteristic paths.$^{(17)}$ The solution is

$$\chi_{\mathrm{K}}^{(2)}=-(2\rho(z)/v_0^2)\exp[-(\nu+z)|\mathbf{r}-\mathbf{r}_0|/v_0]\,\hat{r}_0\cdot\mathbf{v}_1\hat{r}_0\Omega(\hat{v}_1) \tag{50}$$

where $\Omega(\hat{v}_1)$ equals unity if the particle travels directly away from the fixed scatterer, and is zero otherwise. Also, $\hat{r}_0$ is the outward surface normal at the emission point on the surface and $|\mathbf{r}-\mathbf{r}_0|$ is the rectilinear distance traveled by the tagged particle since colliding with the fixed scatterer.

Given the explicit form of $\chi_{\mathrm{K}}^{(2)}$, we need only to determine $\mathbf{M}(\mathbf{r},z)$ in the normal part of $\chi^{(2)}$. We appeal to the variational principle to determine the optimum form of $\mathbf{M}(\mathbf{r}, z)$. Inserting $\chi^{(2)} = \chi_{\mathrm{N}}^{(2)} + \chi_{\mathrm{K}}^{(2)}$ into the variational functional $J(\chi^{(2)})$ and performing a functional derivative with respect to $\mathbf{M}$, we get

$$\int d\mathbf{r}\, W_{12}^{(2)}\, \delta\mathbf{M} \cdot \left[(-z + D\nabla_r^2)\mathbf{M} - \nu \mathbf{S}' + \frac{D}{\rho} (\hat{r} \cdot \nabla_r \mathbf{M})\, \delta(|\mathbf{r}| - R) \right] = 0 \tag{51}$$

where $\delta\mathbf{M}$ represents the variation of $\mathbf{M}$, and the function $\mathbf{S}'$ is defined by

$$\mathbf{S}'(\mathbf{r}, z) = -\frac{1}{4\pi} \int d\hat{v}\, \chi_{\mathrm{K}}^{(2)}(\hat{v}, \mathbf{r}, z) \tag{52}$$

Because Eq. (51) is zero for arbitrary variations $\delta\mathbf{M}$, the integrand must vanish. Thus, the optimum equation for $\mathbf{M}(\mathbf{r}, z)$ is

$$(-z + D\nabla_r^2)\mathbf{M} = \nu \mathbf{S}', \qquad |\mathbf{r}| > R \tag{53a}$$

$$\hat{r} \cdot \nabla_r \mathbf{M} = 0, \qquad |\mathbf{r}| = R \tag{53b}$$

where $D = v_0^2/3\nu$. Equations (53a) and (53b) represent the hydrodynamic diffusion equation with diffuse source term $\nu\mathbf{S}'$ and specular reflecting BC. Given the form for $\chi_{\mathrm{K}}^{(2)}$ and $\mathbf{M}$, as the solution of Eqs. (53a) and (53b), the stationary value of $J(\tilde{\chi})$ becomes

$$\operatorname{Stat} J(\tilde{\mathbf{X}}) = \nu\rho(z)\{[\mathbf{M}; \mathbf{S}'] - [\mathbf{S}'; \mathbf{S}']\} \tag{54}$$

where the square bracket $[\mathbf{A}; \mathbf{B}]$ signifies

$$[\mathbf{A}; \mathbf{B}] = \int d\mathbf{r}\, W_{12}^{(2)} \mathbf{A}(\mathbf{r}) \cdot \mathbf{B}(\mathbf{r}) \tag{55}$$

This form of the stationary value of J is similar in form to that obtained by Masters and Keyes.(15,16)

We present here only the stationary $z = 0$ calculations. We are faced with the problem of solving the stationary diffusion equation

$$\nabla_r^2 \mathbf{M}(\mathbf{r}) = (\nu/D)\, \mathbf{S}'(\mathbf{r}), \qquad |\mathbf{r}| > R \tag{56a}$$

$$\hat{r} \cdot \nabla_r \mathbf{M}(\mathbf{r}) = 0, \qquad |\mathbf{r}| = R \tag{56b}$$

where we drop the $z = 0$ term in the argument of $\mathbf{M}$ and $\mathbf{S}'$. The solution of Eqs. (56) can be formulated in terms of the Green's function $G(\mathbf{r}, \mathbf{r}')$. The function $G(\mathbf{r}, \mathbf{r}')$ is defined to be the solution of the equation

$$\nabla^2 G(\mathbf{r}, \mathbf{r}') = -4\pi\delta(\mathbf{r} - \mathbf{r}') \tag{57}$$

with appropriate boundary conditions. Following standard techniques, we can explicitly evaluate G; the result is

$$G(\mathbf{r},\mathbf{r}') = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} g_l(r,r')\, Y_{lm}^*(\hat{r}')\, Y_{lm}(\hat{r}) \tag{58a}$$

with

$$g_l(r,r') = \frac{4\pi}{2l+1} \left\{ r_<^l + \frac{lR^{2l+1}}{l+1} r_<^{-(l+1)} \right\} r_>^{-(l+1)} \tag{58b}$$

Here $Y_{lm}(\hat{x})$ represents the lth-rank spherical harmonic of the angles $\hat{x}$, $r_<$ denotes the lesser of r and r', and $r_>$ denotes the greater. With G in hand, $\mathbf{M}$ is expressed as

$$\mathbf{M}(\mathbf{r}) = -\frac{v}{4\pi D} \int d\mathbf{r}'\, G(\mathbf{r},\mathbf{r}')\, \mathbf{S}'(\mathbf{r}') \tag{59}$$

Inserting this expression for $\mathbf{M}$ into the Stat J in Eq. (54), and defining reduced (starred) quantities, we find for the expression for the friction, Eq. (41),

$$\frac{v^*}{v_{\mathrm{B}}^*} = 1 + \frac{\rho^* v^*}{\pi v_{\mathrm{B}}^*} \left([\tilde{s},\tilde{s}] + v^{*2} [\tilde{n},\tilde{s}] \right) \tag{60}$$

where

$$\begin{aligned} [\tilde{n},\tilde{s}] = {} & \int_0^1 dy\, y^{-2} s(y^{-1}) \int_y^1 dy'\, s(y'^{-1})(y'^{-5} + y'^{-2}/2) \\ & + \int_0^1 dy\, s(y^{-1})(y^{-5} + y^{-2}/2) \int_0^y dy'\, s(y'^{-1})\, y'^{-2} \end{aligned} \tag{61a}$$

$$[\tilde{s},\tilde{s}] = \int_0^1 dy\, y^{-4} [s(y^{-1})]^2 \tag{61b}$$

The reduced quantities are $v^* = Rv/v_0$ and $\rho^* = \rho R^3$, and the $s(x)$ function is defined by

$$s(x) = 2\pi \int_{\mu_m}^1 d\mu\, \exp(-v^* d^*)\, a(x,\mu)\, b(x,\mu) \tag{62}$$

where

$$\mu_m = (1 - x^{-2})^{1/2} \tag{63a}$$

$$a(x,\mu) = [1 - x^{-2}(1-\mu^2)]^{1/2} = \hat{r}_0 \cdot \hat{v}_1' \tag{63b}$$

$$b(x,\mu) = a(x,\mu)\mu + \{(1-\mu^2)[1 - a^2(x,\mu)]\}^{1/2} = \hat{r}_0 \cdot \hat{r} \tag{63c}$$

$$d^* = \{[1 - b^2(x,\mu)]/(1-\mu^2)\}^{1/2} = |\mathbf{r} - \mathbf{r}_0|/R \tag{63d}$$

The RR friction is obtained by replacing all ν^* on the rhs of Eq. (60) with ν_{B}^* (the reduced Boltzmann friction). We have presented the equation for ν^* which is the consequence of a self-consistent RR theory.$^{(10)}$ We are able to express the friction from a renormalized kinetic theory in terms of rather simple integrals (from a computational point of view).

There are several interesting points concerning the expression for ν^* in Eq. (57). First, in the low-density limit ρ^*, $\nu^* \to 0$, ν^*/ν_{B}^* becomes

$$\nu^*/\nu_{\mathrm{B}}^* \simeq 1 + (\rho^* \nu^*/\pi \nu_{\mathrm{B}}^*)[\tilde{s}, \tilde{s}] \tag{64}$$

which, replacing ν^* with ν_{B}^* on the rhs, represents the low-density form of ν^* obtained from an analysis of the RR equations.$^{(10)}$ At high densities, the term $\nu^{*2}[\tilde{n}, \tilde{s}]$ dominates $[\tilde{s}, \tilde{s}]$. The term $\nu^{*2}[\tilde{n}, \tilde{s}]$ is the SCRR correction to the Boltzmann expression obtained by projecting $\chi^{(2)}$ onto the hydrodynamic mode. Hydrodynamic theories of this type are believed to be accurate when $\nu^* \gg 1$, and the predictions of Eq. (57) for large ν^* are excellent.

The required integrals can be evaluated by numerical quadrature. We have carried out the calculations for both the two- and three-dimensional LG; the explicit derivations above are for the three-dimensional system. Before presenting the results, we comment on the difference between the two- and three-dimensional Lorentz models. Theoretically, the three-dimensional LG is much simpler to handle. The reason for this simplicity is that the Lorentz collision operator (43) is of a Bhatnagar–Gross–Krook (BGK)$^{(26)}$ form; the scattering cross section is isotropic. This is partly responsible for the simplicity of our final results. In two dimensions, however, the collision operator contains an anisotropic scattering cross section and hence is not of a BGK form. We nevertheless wish to present results for the two-dimensional case, where the molecular dynamics calculations reach the percolation density; they do not in the three-dimensional molecular dynamics. For this reason, and so that we may compare our results directly with those of Masters and Keyes, who also assumed a BGK form for the 2D collision operator, we make a BGK approximation to the two-dimensional system. We write

$$\rho\hat{\lambda}(1) f(\mathbf{v}_1) = -\nu_{\mathrm{B}}^{(2)} \left[f(\mathbf{v}_1) - \frac{1}{2\pi} \int d\hat{v}_1' \, f(\mathbf{v}_1') \right] \tag{65}$$

where $\nu_{\mathrm{B}}^{(2)}$, the two-dimensional Boltzmann friction, is $(8/3) v_0 R\rho$. Once this approximation is made, the two- and three-dimensional results appear quite similar.

We first discuss the three-dimensional calculations. In Fig. 2 we plot our results for D/D_{B} within the RR theory and compare with the accurate

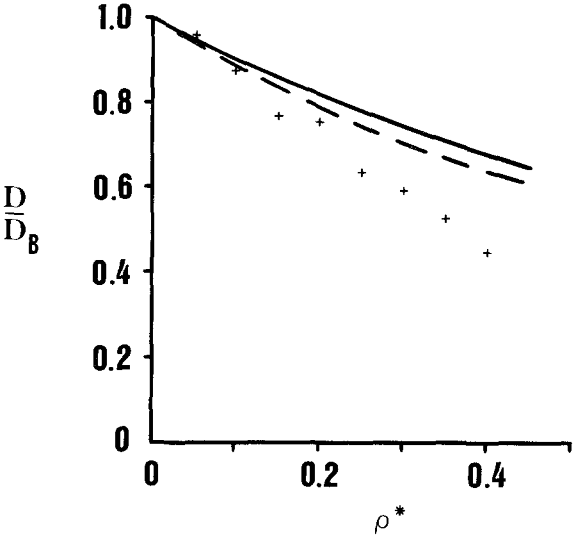

Fig. 2. The density dependence of the diffusion constant in three dimensions. (+) The molecular dynamics of Bruin, (--) the RRA of Masters and Keyes, (—) the RRA of Eq. (60).

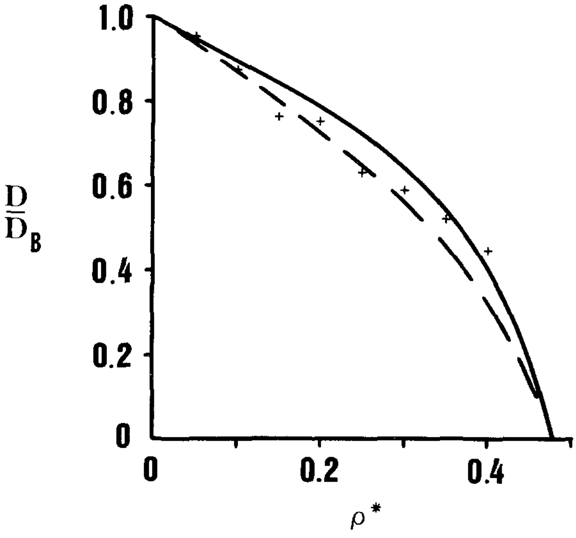

Fig. 3. The density dependence of the self-consistent diffusion constant in three dimensions. (+) The MD of Bruin, (--) the SCRRA of Masters and Keyes, (—) the SCRRA of Eq. (60).

calculations of Masters and Keyes. We see that there is good agreement between the two calculations. Also plotted are the MD results of Bruin.(19) The agreement between the MD and RR results is poor. In order for the theory to agree with the MD, a self-consistent RR (SCRR) theory is required. The SCRR results are presented in Fig. 3, along with the self-consistent results of Masters and Keyes and Bruin's MD. Again, our predictions are in accord with other results. From Figs. 2 and 3, we see that there is good agreement between our results and the more accurate MK results at low and high densities, as we would expect from the above discussion. The maximum disagreement is in the neighborhood $\rho^* \sim 0.3$.

In Fig. 4 we plot our 2D results for D/D_B in the RR theory, along with Masters and Keyes' RR results and the 2D MD calculations of Bruin(19) and Alder and Alley.(20) Again, the RR diffusion constants are in dramatic disagreement with MD. Our calculations are in accord with the MK variational RR diffusion constant, though our results are somewhat high. Carrying our the self-consistent calculation and plotting all results in Fig. 5, we observe that the two-dimensional results are not as accurate as the 3D SCRR results of Fig. 3. The 2D SCRR predictions retain the qualitative aspect, but have lost the quantitative nature of the 3D results. Again, the 2D results are somewhat larger than the MK results and we observe a maximum disagreement with the MD at intermediate densities. We can only speculate that the inaccuracy of our 2D theory as compared

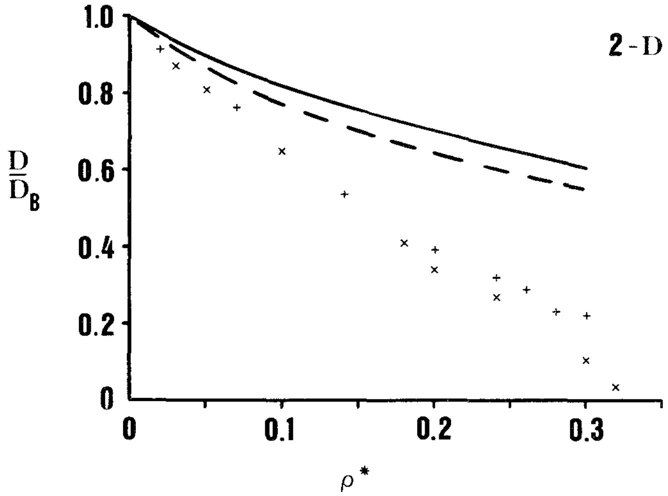

Fig. 4. The density dependence of the diffusion constant in two dimensions. (×) The MD of Alder and Alley, (+) the MD of Bruin, (– –) the RRA of Masters and Keyes, (——) RRA of this work.

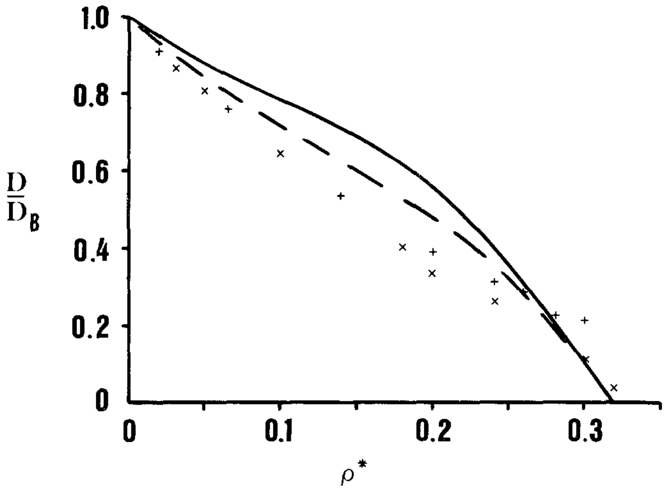

Fig. 5. The density dependence of the self-consistent diffusion constant in two dimensions. (×) The MD of Alder and Alley, (+) the MD of Bruin, (– –) the SCRRA of MK, (——) the SCRRA of this work.

to the 3D work may reside in the BGK approximation we utilized. This is the only difference between the two- and three-dimensional work.

In all calculations, our final results for D were high compared to the Masters and Keyes' variational calculations. It is tempting to speculate on the nature of the stationary value of the functional $J(\tilde{\chi})$. While we are able to demonstrate that the first variation of J vanishes, we do not know whether the stationary value represents a minimum or maximum. Clearly, knowledge of the nature of the stationary value of J would prove useful in applications of this variational principle.

Finally, we comment on the value of the critical densities predicted for both the two- and three-dimensional systems. The Masters and Keyes' predictions for ρ_c^* are π^{-1} for 2D and $3/2\pi$ for 3D. These results are obtained by projecting $\chi^{(2)}$ onto the hydrodynamic mode in order to formulate a self-consistent equation for the friction. Because our SC equation for ν in the $\nu \to \infty$ limit becomes identical with the SC equation obtained by projecting onto the hydrodynamic mode, we predict the same critical densities for the vanishing of D.

5. DISCUSSION AND CONCLUSIONS

We have given a hierarchical derivation of the most general kinetic equations for tagged molecule motion that incorporate pair dynamic correlations, the Enskog repeated ring equations. We believe this to be the first derivation of more complicated RR equations from the BBGKY hierarchy. This derivation demonstrates the difficulties encountered when naive hierarchy truncations are attempted. We believe that this derivation will prove useful in finding other RR equations, for example, modeling collective particle behavior in liquids. We anticipate that the inclusion of static correlations into a RR theory will prove valuable in predictions of nonequilibrium phenomena in condensed phases.

The utility of these equations can only be fully realized when methods for obtaining accurate solutions are available. In this vein, we have demonstrated the existence of a variational principle. Utilizing this variational principle, we proposed a method yielding solutions to these equations, which can be summarized as a combination moment expansion for $\chi^{(1)}$ and a variational solution for $\chi^{(2)}$. The differential VP proposed here for the ERRE differs in one important aspect from the integral VP utilized by Masters and Keyes in their calculation of the diffusion constant for the LG. The differential VP *can* be demonstrated for the ERRE, the VP of Masters and Keyes *cannot.*

The variation solution for $\chi^{(2)}$, as with all variational principles, requires the development of an intuition (concerning the nature of pair correlations in liquids). Some intuition already exists that a hydrodynamic form for $\chi^{(2)}$ is appropriate at large separations, yet when the molecular separation is on the order of a few mean free paths this hydrodynamic form is no longer realized. We speculated that the kinetic boundary layer exists solely due to the presence of molecules that are freely streaming away from the boundary. Once these particles undergo a single collision on the surrounding bath, they are immediately transformed into a normal (hydrodynamic) form. This simple intuitive picture of the fluid leads to reasonable results for the LG. We suggested that part of this success rests in the fact that the collision operators in the 3D LG contain isotropic scattering cross sections which truly randomize velocities in a single collision. For other anisotropic scattering cross sections, this intuitive picture of the fluid may not be as appropriate, although we suspect that it remains qualitative. Perhaps a more complete study of the 2D LG, with anisotropic scattering cross section will be instructive in this respect, extending our intuition to more realistic and chemically interesting systems.

Equations (53a) and (53b), derived from the variational principle assuming the above picture of the kinetic boundary layer, represent a generalized hydrodynamic diffusion equation. This hydrodynamic equation, with diffuse kinetic source term, is applicable to the transition regime between large and small Knudsen numbers. Schemes exist that attempt to incorporate the existence of a finite kinetic boundary layer into a hydrodynamic theory, simply modifying the usual BC.(27,28) Equations

(53a) and (53b) represent an alternative approach, where the finite boundary layer is incorporated into a diffuse source term extending into the fluid.

The ERRE, Eqs. (20) and (21), are extremely complicated yet their solution may hold the key to quantitative predictions of tagged molecular motion in liquids. We do not wish to imply that, by demonstrating a variational principle for these complex equations, we have eliminated the problems in predicting tagged particle motion in liquids. We only sugest that approaching the problem with this DVP may prove useful.

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REFERENCES

1. Special issue, "Fluids out of equilibrium," *Physics Today* **37**(1):25 (1984).
2. P. Resibois and M. DeLeener, *Classical Kinetic Theory of Fluids* (Wiley, New York, 1977).
3. J. R. Dorfman, in *Fundamental Problems in Statistical Mechanics*, Vol. 3, E. G. Cohen, ed. (North-Holland, Amsterdam, 1975).
4. M. H. Ernst and J. R. Dorfman, *Physics* **61**:157 (1972).
5. J. R. Dorfman, H. van Beijeren, and C. F. McClure, *Arch. Mech.* **28**:333 (1976); H. van Beijeren and J. R. Dorfman, *J. Stat. Phys.* **23**:335 (1980); H. van Beijeren and J. R. Dorfman, *J. Stat. Phys.* **23**:443 (1980).
6. R. I. Cukier, R. Kapral, J. R. Lebenhaft, and J. R. Mehaffey, *J. Chem. Phys.* **73**:5244 (1980).
7. J. Mercer, Ph.D. thesis, Yale Yniversity (1981), unpublished.
8. B. Alder and T. Wainwright, *Phys. Rev. A* **1**:18 (1970).
9. J. Dorfman and E. Cohen, *Phys. Rev. A* **6**:776 (1972).
10. A. Masters and T. Keyes, *Phys. Rev.* **26**:2129 (1982).
11. A. J. Masters, Ph.D. thesis, University of Cambridge (1980), unpublished.
12. W. Gotze, E. Leutheusser, and S. Yip, *Phys. Rev. A* **23**:2634 (1981); **25**:533 (1982).
13. W. Sung and J. S. Dahler, *J. Chem. Phys.* **78**:6267 (1983).
14. A. Masters and T. Keyes, *J. Stat. Phys.* **33**:149 (1983).
15. A. J. Masters and T. Keyes, *Phys. Rev. A* **25**:1010 (1982).
16. A. J. Masters and T. Keyes, *Phys. Rev. A* **27**:2603 (1983).
17. C. Cercignani, *Theory and Application of the Boltzmann Equation* (Elsevier, New York, 1975).
18. C. Cercignani, *J. Stat. Phys.* **1**:297 (1969).
19. C. Bruin, *Physica* **72**:261 (1974).
20. B. J. Alder and W. E. Alley, *J. Stat. Phys.* **19**:341 (1978).

21. M. J. Ernst, J. R. Dorfman, W. R. Hoegy, and J. M. J. van Leeuwen, *Physica* **45**:127 (1968).
22. R. G. Cole, D. R. Evans, and D. K. Hoffman, *J. Chem. Phys.* **82**:2061 (1985).
23. J. Karkheck and G. Stell, *Phys. Rev. A* **25**:3302 (1982).
24. T. Keyes and J. Mercer, *Physica* **95A**:473 (1979).
25. J. A. McLennen, *Phys. Fluids* **8**:1580 (1965).
26. P. F. Bhatnagar, E. P. Gross, and M. Krook, *Phys. Rev.* **94**:511 (1954).
27. C. Cercignani and G. Tironi, *J. Plasma Phys.* **2**:293 (1968).
28. J. T. Hynes, R. Kapral, and M. Weinberg, *J. Chem. Phys.* **70**:1456 (1979).