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A Kinetic Theory of Dense Fluids

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A new kinetic equation is developed which incorporates the desirable features of the Enskog, the Rice–Allnatt, and the Prigogine–Nicolis–Misguich kinetic theories of dense fluids. Advantages of the present theory over the latter three theories are (1) it yields the correct local equilibrium hydrodynamic equations, (2) unlike the Rice–Allnatt theory, it determines the singlet and doublet distribution functions from the same equation, and (3) unlike the Prigogine–Nicolis–Misguich theory, it predicts the kinetic and kinetic–potential transport coefficients. The kinetic equation is solved by the Chapman–Enskog method and the coefficients of shear viscosity, bulk viscosity, thermal conductivity, and self-diffusion are obtained. The predicted bulk viscosity and thermal conductivity coefficients are singular at the critical point, while the shear viscosity and self-diffusion coefficients are not.

KEY WORDS: Kinetic theory; transport properties of dense fluid.

1. THE KINETIC EQUATION

Several years ago Rice and Allnatt[(1)] (RA) developed a promising kinetic theory of liquids based on the following idea: A molecule moving through a dense fluid will undergo a motion in which it experiences a "Brownian" motion through the average potential field of the neighboring molecules with intermittent binary, hard-core-like collisions occurring when the molecule moves within the strongly repulsive force field of a neighboring molecule. More recently Prigogine, Nicolis, and Misguich (PNM)[(2–4)] presented a local equilibrium model which follows the Rice–Allnatt decomposition of the motion into hard-sphere binary collisions plus continuous field interactions.

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The PNM model neglects distortion of the singlet distribution function from local equilibrium and, consequently, cannot be used for prediction of diffusional transport properties. However, for thermal conductivity and viscosity the PNM theory is as good as or better than the RA theory in the low-temperature, high-density region where neglect of the singlet distortions is reasonable.$^{(4)}$

The RA theory has the shortcomings that two different kinetic equations must be solved for the singlet and doublet distribution functions, respectively, and that the RA kinetic equations generate incorrect lowest-order hydrodynamic equations. The PNM theory also does not generate the correct lowest-order hydrodynamic equations and, furthermore, neglects diffusional phenomena and the kinetic contributions to the transport coefficients by neglecting the distortion of the singlet distribution function from local equilibrium.

What we wish to do in this paper is develop a theory which incorporates the desirable features of the RA and PNM theories, eliminates the shortcomings mentioned above, and, not least by any means, takes as a starting point a very simple kinetic equation.

We shall consider a system of N identical structureless particles interacting with pairwise additive, centrally symmetric forces. The pair potential will be decomposed as follows:

$$\begin{aligned} V(r) &= V^{\mathrm{H}}(r) + V^{\mathrm{S}}(r) \\ V^{\mathrm{H}}(r) &= 0, \qquad r \geqslant \sigma \\ V^{\mathrm{S}}(r) &= 0, \qquad r \leqslant \sigma \end{aligned} \tag{1}$$

V^{H} denotes the strongly repulsive, short-range part of the potential energy and V^{S} the softer, longer-range part. The hierarchy equation obeyed by the singlet distribution function $f(\mathbf{x}, \mathbf{v}_1, t)$ for particle 1 of the system is

$$\begin{aligned} \partial_t f + \mathbf{v}_1 \cdot \nabla_1 f &= +(1/m) \int \nabla_1 V(\mathbf{x}_{12}) \cdot \partial_1 f_2(\mathbf{x}_1, \mathbf{x}_2, \mathbf{v}_1, \mathbf{v}_2, t)\, d\mathbf{x}_2\, d\mathbf{v}_2 \\ &= (\partial_c f/\partial t)^{\mathrm{H}} + (1/m) \int \nabla_1 V^{\mathrm{S}}(\mathbf{x}_{12}) \cdot \partial_1 f_2(\mathbf{x}_1, \mathbf{x}_2, \mathbf{v}_1, \mathbf{v}_2 t)\, d\mathbf{x}_2\, d\mathbf{v}_2 \end{aligned} \tag{2}$$

where

$$(\partial_c f/\partial t)^{\mathrm{H}} = (1/m) \int \nabla_1 V^{\mathrm{H}}(\mathbf{x}_{12}) \cdot \partial_1 f_2(\mathbf{x}_1, \mathbf{x}_2, \mathbf{v}_1, \mathbf{v}_2, t)\, d\mathbf{x}_2\, d\mathbf{v}_2 \tag{3}$$

$$\partial_t \equiv \partial/\partial t \tag{4}$$

$$\nabla_i = \partial/\partial \mathbf{x}_i \tag{5}$$

$$\partial_i = \partial/\partial \mathbf{v}_i \tag{6}$$

f_2 is the doublet distribution function, and $\mathbf{x}_{12} = \mathbf{x}_1 - \mathbf{x}_2$.

Equation (2) is a continuity equation for f. The terms on the rhs of (2) represent the rate of change of f due to collisions of particle 1 with the background particles. The first assumption of our model is that the contribution from the strongly repulsive interactions $(\partial_c f/\partial t)^{\mathrm{H}}$ can be approximated by the binary hard-core collision operator. Thus, we have *assumption one*:

$$(\partial_c f/\partial t)^{\mathrm{H}} = \sigma^2 \int_{\mathbf{v}_{21}\cdot\mathbf{k}>0} [f_2(\mathbf{x}_1, \mathbf{x}_1 + \sigma\mathbf{k}, \mathbf{v}_1', \mathbf{v}_2', t) - f_2(\mathbf{x}_1, \mathbf{x}_1 - \sigma\mathbf{k}, \mathbf{v}_1, \mathbf{v}_2, t)]\, \mathbf{v}_{21} \cdot \mathbf{k}\, d\mathbf{k}\, d\mathbf{v}_2 \tag{7}$$

$\mathbf{k}$ is a unit vector directed from the center of molecule 2 to the center of molecule 1, $d\mathbf{k}$ is the incremental solid angle associated with $\mathbf{k}$, and $\mathbf{v}_1'$ and $\mathbf{v}_2'$ are the resulting velocities of a pair of molecules with initial velocities $\mathbf{v}_1$ and $\mathbf{v}_2$ which undergo a hard-sphere collision. Note that we do not make the chaos assumption of Enskog(5) that f_2 can be factorized into the product of the singlet distribution functions and the local equilibrium radial distribution function. Although we shall not do so in any computations presented here, the fact that V^{H} is not the hard-sphere potential for real systems can be compensated for by assuming the cutoff diameter σ to be temperature-dependent. This is done with a good deal of success, for example, in the scaled particle theory of equilibrium properties of liquids.(6)

To obtain a solvable equation for f, we must relate f_2 to f. The so-called "master equations" give a formal solution to this problem by relating f_2 to the initial correlations in the system and to f through a nonlinear, non-Markovian collision operator. In an important paper evolved from the "Brussels school," Severne(7) has shown that in the transport or long-time limit the contribution of the initial correlations decay to zero for fluids with initial correlations of finite range, so that f_2 (and f_n for that matter) is a functional of f.

At this point it is useful to introduce the doublet correlation function g_2 defined by the expression

$$g_2(\mathbf{x}_1, \mathbf{x}_2, \mathbf{v}_1, \mathbf{v}_2, t) = f_2(\mathbf{x}_1, \mathbf{x}_2, \mathbf{v}_1, \mathbf{v}_2, t) - f(\mathbf{x}_1, \mathbf{v}_1, t) f(\mathbf{x}_2, \mathbf{v}_2, t) \tag{8}$$

and its Fourier transform

$$g_2(\mathbf{l}, \mathbf{v}_1, \mathbf{v}_2; \mathbf{x}_1, t) = (1/8\pi^3) \int d\mathbf{x}_{21}\, [\exp(i\mathbf{l}\cdot\mathbf{x}_{21})]\, g_2(\mathbf{x}_1, \mathbf{x}_1 + \mathbf{x}_{21}, \mathbf{v}_1, \mathbf{v}_2, t) \tag{9}$$

To lowest order in the interaction potential (i.e., to the weak coupling approximation), Severne's exact long-time form for g_2 is

$$g_2(\mathbf{l}, \mathbf{v}_1, \mathbf{v}_2; \mathbf{x}_1, t) = \frac{1}{m} \int d\mathbf{x}_2\, \delta(\mathbf{x}_1 - \mathbf{x}_2) \exp\left(-i\nabla_2 \cdot \frac{\partial}{\partial \mathbf{l}}\right) \times \frac{1}{\mathbf{l}\cdot\mathbf{v}_{12} - i(\mathbf{v}_1\cdot\nabla_1 + \mathbf{v}_2\cdot\nabla_2) - i\partial_t - i0} \times V_l \mathbf{l} \cdot \partial_{12} f(\mathbf{x}_1, \mathbf{v}_1, t) f(\mathbf{x}_2, \mathbf{v}_2, t) \tag{10}$$

where $\partial_{12} = \partial_1 - \partial_2$ and V_l is the Fourier transform of $V(\mathbf{x}_{12})$ defined by the relation

$$V_l = (1/8\pi) \int d\mathbf{r}\, [\exp(-i\mathbf{l} \cdot \mathbf{r})]\, V(\mathbf{r}) \tag{11}$$

and where the abbreviation

$$i\pi\, \delta(A) + \mathscr{P}(1/A) \equiv 1/(A - i0) \tag{12}$$

with $A = \mathbf{l} \cdot \mathbf{v}_{12} - i(\mathbf{v}_1 \cdot \nabla_1 + \mathbf{v}_2 \cdot \nabla_2) - i\partial_t$, has been used. Here δ is the Dirac delta function operator and $\mathscr{P}$ is the principal part operator. The operators $\mathbf{v}_i \cdot \nabla_i$ and $i\partial_t$ in A arise, respectively, from the time evolution of spatial delocalization and from the time evolution (memory) of the distribution functions of colliding particles. These "temporal" effects contribute to the nondissipative part of the hydrodynamic equations as well as to the transport fluxes. Dowling and Davis$^{(8,9)}$ have presented a detailed study of the temporal contributions in the weak coupling kinetic equation.

Severne's full result for g_2 involves a complicated operator expansion in powers of the interaction potential V. The integrand of Eq. (10) is the first term of the expansion. According to the diagram theory of Prigogine and co-workers, one tries to pick out a dominant and tractable class of terms from the exact expansion of g_2. The PNM theory, to be discussed in a later section, is based on summing a certain infinite class of terms which, when the f's are approximated by their local equilibrium values, leads to a result of the same basic form as Eq. (10) but with V_l replaced by a combination of the local equilibrium radial distribution functions. Thus, roughly speaking, the effect of the many-body interactions in the fluid is to replace the bare two-body potential in Eq. (10) by an effective many-body potential. On the other hand, one obtains immediately the RA result if, in Eq. (10), (1) the spatial and temporal delocalization operators are neglected, i.e.,

$$\exp(-i\nabla_2 \cdot \partial/\partial\mathbf{l}) \simeq 1 \qquad \text{and} \qquad A \simeq \mathbf{l} \cdot \mathbf{v}_{12} - i0$$

and (2) V_l is replaced by the effective potential $-kTG_l$, where G_l is the Fourier transform of $g(r) - 1$, $g(r)$ being the local equilibrium radial distribution function. The resulting g_2, combined with Eqs. (2) and (7), gives the RA singlet kinetic equation.

What we propose to do now is introduce an ansatz, motivated by the experience of the RA and PNM theories, that incorporates the basic features of these theories and eliminates some of their shortcomings discussed above. Accordingly, our second and last approximation is *assumption two*:

The transport doublet distribution function is of the form

$$
\begin{aligned}
g_2(\mathbf{l}, \mathbf{v}_1, \mathbf{v}_2; \mathbf{x}_1, t) = (1/m) \int d\mathbf{x}_2\, \delta(\mathbf{x}_1 - \mathbf{x}_2) \exp(-i\nabla_2 \cdot \partial/\partial\mathbf{l}) \\
\times \{1/[\mathbf{l} \cdot \mathbf{v}_{12} - i(\mathbf{v}_1 \cdot \nabla_1 + \mathbf{v}_2 \cdot \nabla_2) - i\partial_t - i0]\} \\
\times \bar{V}_l((\mathbf{x}_1 + \mathbf{x}_2)/2, t]\mathbf{l} \cdot \partial_{12} f(\mathbf{x}_1, \mathbf{v}_1, t) f(\mathbf{x}_2, \mathbf{v}_2, t)
\end{aligned}
\tag{13}
$$

where $\bar{V}_l((\mathbf{x}_1 + \mathbf{x}_2)/2, t)$ is an effective potential chosen to satisfy the following conditions:

(1) Equation (13) is exact in the weak coupling limit (i.e., $\bar{V}_l$ reduces to V_l to first order in V).

(2) Equation (13) is exact in the equilibrium limit.

(3) Equation (13), when inserted in the kinetic equation (2), leads to the exact nondissipative hydrodynamic equations which occur in the Chapman–Enskog solution of the kinetic equation.

The choice of $\bar{V}_l$ that satisfies these three conditions is

$$
V_l = -kT((\mathbf{x}_1 + \mathbf{x}_2)/2, t) G_l((\mathbf{x}_1 + \mathbf{x}_2)/2, t) \tag{14}
$$

where

$$
G_l = (1/8\pi^3) \int d\mathbf{r}\, [\exp(-i\mathbf{l} \cdot \mathbf{r})][g(r) - 1] \tag{15}
$$

$T((\mathbf{x}_1 + \mathbf{x}_2)/2, t)$ is the kinetic temperature evaluated at the center of mass of the colliding particles and $g(r)$ is the equilibrium radial distribution function evaluated for the density and kinetic temperature at the center of mass of the colliding particles. This choice of $\bar{V}_l$ also has the advantages that in the limit that the f's have their local equilibrium values, Eq. (13) is very similar to the PNM result for g_2 and in the limit that spatial and time delocalizations in the integrand of Eq. (13) are neglected, the RA kinetic equation results as well as Enskog's original hard-sphere kinetic equation when $V^S = 0$. Because of the neglect of the spatial and time delocalizations in Eq. (13), the RA theory does not satisfy condition 3 and one has to go to a Schmoluchowski equation to calculate part of the transport coefficients.

Thus, in summary, our basic kinetic equation is

$$
\begin{aligned}
\partial_t f + v_1 \cdot \nabla_1 f + m^{-1}\mathbf{F}^S(\mathbf{x}_1, t) \cdot \partial_1 f \\
= \sigma^2 \int_{\mathbf{v}_{2i}\mathbf{k}>0} [f_2(\mathbf{x}_1, \mathbf{x}_1 + \sigma\mathbf{k}, \mathbf{v}_1', \mathbf{v}_2', t) \\
- f_2(\mathbf{x}_1, \mathbf{x}_1 - \sigma\mathbf{k}, \mathbf{v}_1, \mathbf{v}_2, t)]\, \mathbf{v}_{21} \cdot \mathbf{k}\, d\mathbf{k}\, d\mathbf{v}_2 \\
- i(8\pi^3/m) \int V_l{}^S \mathbf{l} \cdot \partial_1 g_2(\mathbf{l}, \mathbf{v}_1, \mathbf{v}_2; \mathbf{x}_1, t)\, d\mathbf{l}\, d\mathbf{v}_2
\end{aligned}
$$

$$\begin{aligned}
&= \sigma^2 \int_{\mathbf{v}_{21}\cdot\mathbf{k}>0} [f(\mathbf{x}_1, \mathbf{v}_1', t) f(\mathbf{x}_1 + \sigma\mathbf{k}, \mathbf{v}_2', t) \\
&\quad - f(\mathbf{x}_1, \mathbf{v}_1, t) f(\mathbf{x}_1 - \sigma\mathbf{k}, \mathbf{v}_2, t)]\, \mathbf{v}_{21}\cdot\mathbf{k}\, d\mathbf{k}\, d\mathbf{v}_2 \\
&\quad + \sigma^2 \int_{\mathbf{v}_{21}\cdot\mathbf{k}>0} \{[\exp(-i\mathbf{l}\cdot\mathbf{k}\sigma)]\, g_2(\mathbf{l}, \mathbf{v}_1', \mathbf{v}_2'; \mathbf{x}_1, t) \\
&\quad - [\exp(+i\mathbf{l}\cdot\mathbf{k}\sigma)]\, g_2(\mathbf{l}, \mathbf{v}_1, \mathbf{v}_2; \mathbf{x}_1, t)\}\, \mathbf{v}_{21}\cdot\mathbf{k}\, d\mathbf{k}\, d\mathbf{v}_2\, d\mathbf{l} \\
&\quad - i(8\pi^3/m) \int V_l^{S}\mathbf{l}\cdot\partial_1 g_2(\mathbf{l}, \mathbf{v}_1, \mathbf{v}_2; \mathbf{x}_1, t)\, d\mathbf{v}_2\, d\mathbf{l} \qquad (16)
\end{aligned}$$

where $\mathbf{F}^{S}(\mathbf{x}_1, t)$ is the Vlasov force

$$\mathbf{F}_1^{S}(\mathbf{x}_1, t) = \nabla_1 \cdot \int V^{S}(\mathbf{x}_{12}) f(\mathbf{x}_2, \mathbf{v}_2, t)\, d\mathbf{x}_2\, d\mathbf{v}_2 \qquad (17)$$

and $g_2(\mathbf{l}, \mathbf{v}_1, \mathbf{v}_2; \mathbf{x}_1, t)$ is given by Eq. (13). The generalization of Eq. (16) to multicomponent systems is immediately obvious and, perhaps more importantly, the generalization to include the rotational degrees of freedom of polyatomic systems. These generalizations are currently being studied.

2. CHAPMAN-ENSKOG SOLUTION TO KINETIC EQUATION

Since we are interested only in linear transport phenomena here, it is useful to expand the spatial and time operators in the integrand of Eq. (13) and keep terms only through first order in ∇_i and ∂_t, i.e.,

$$\exp(-i\nabla_2\cdot\partial/\partial\mathbf{l}) = 1 - i\nabla_2\cdot\partial/\partial\mathbf{l} + \cdots \qquad (18)$$

$$\begin{aligned}
&\frac{1}{\mathbf{l}\cdot\mathbf{v}_{12} - i(\mathbf{v}_1\cdot\nabla_1 + \mathbf{v}_2\cdot\nabla_2 + \partial_t) - i0} \\
&\quad = \frac{1}{\mathbf{l}\cdot\mathbf{v}_{12} - i0} + \frac{i(\mathbf{v}_1\cdot\nabla_1 + \mathbf{v}_2\cdot\nabla_2 + \partial_t)}{(\mathbf{l}\cdot\mathbf{v}_{12} - i0)^2} + \cdots \qquad (19)
\end{aligned}$$

To first order, then, we have

$$g_2(\mathbf{l}, \mathbf{v}_1, \mathbf{v}_2; \mathbf{x}_1, t) = g_2^{(1)} + g_2^{(2)} + g_2^{(3)} + g_2^{(4)} \qquad (20)$$

where

$$g_2^{(1)} = \frac{m^{-1}\tilde{V}_l(\mathbf{x}_1, t)}{\mathbf{l}\cdot\mathbf{v}_{12} - i0}\, \mathbf{l}\cdot\partial_{12} f(\mathbf{x}_1, \mathbf{v}_1, t) f(\mathbf{x}_1, \mathbf{v}_2, t) \qquad (21)$$

$$\begin{aligned}
g_2^{(2)} &= -\frac{i}{m} \int d\mathbf{x}_2\, \delta(\mathbf{x}_1 - \mathbf{x}_2)\, \nabla_2 \cdot \frac{\partial}{\partial\mathbf{l}} \frac{\tilde{V}_l((\mathbf{x}_1 + \mathbf{x}_2)/2, t)}{\mathbf{l}\cdot\mathbf{v}_{12} - i0}\, \mathbf{l} \\
&\quad \cdot \partial_{12} f(\mathbf{x}_1, \mathbf{v}_1, t) f(\mathbf{x}_2, \mathbf{v}_2, t) \qquad (22)
\end{aligned}$$

$$g_2^{(3)} = \frac{i}{m}\,\partial_t \frac{\overline{V}_l(\mathbf{x}_1, t)}{(\mathbf{l}\cdot\mathbf{v}_{12} - i0)^2}\,\mathbf{l}\cdot\partial_{12} f(\mathbf{x}_1, \mathbf{v}_1, t) f(\mathbf{x}_1, \mathbf{v}_2, t) \tag{23}$$

$$g_2^{(4)} = \frac{i}{m} \int d\mathbf{x}_2\, \delta(\mathbf{x}_1 - \mathbf{x}_2) \frac{\mathbf{v}_1\cdot\nabla_1 + \mathbf{v}_2\cdot\nabla_2}{(\mathbf{l}\cdot\mathbf{v}_{12} - i0)^2}\, \overline{V}_l\left(\frac{\mathbf{x}_1 + \mathbf{x}_2}{2}, t\right)\mathbf{l} \\ \cdot\,\partial_{12} f(\mathbf{x}_1, \mathbf{x}_1, t) f(\mathbf{x}_2, \mathbf{v}_2, t) \tag{24}$$

The term $g_2^{(2)}$ arises from the spatial delocalization of colliding particles, $g_3^{(2)}$ from the memory or time dependence of the distribution functions during a collision, and $g_2^{(4)}$ from the evolution of spatial delocalization during a collision.

We shall also introduce in the Boltzmann-like term in Eq. (16) the expansion

$$f(\mathbf{x}_1 \pm \sigma\mathbf{k}, \mathbf{v}_2, t) = f(\mathbf{x}_1, \mathbf{v}_2, t) \pm \sigma\mathbf{k}\cdot\nabla_1 f(\mathbf{x}_1, \mathbf{v}_2, t) + \cdots \tag{25}$$

Introducing the notations

$$J_{B1} = \sigma^2 \int_{\mathbf{v}_{21}\cdot\mathbf{k}>0} [f(\mathbf{x}_1, \mathbf{v}_1', t) f(\mathbf{x}_1, \mathbf{v}_2', t) \\ - f(\mathbf{x}_1, \mathbf{v}_1, t) f(\mathbf{x}_1, \mathbf{v}_2, t)]\, \mathbf{v}_{21}\cdot\mathbf{k}\, d\mathbf{k}\, d\mathbf{v}_2 \tag{26}$$

$$J_{B2} = \sigma^3 \int_{\mathbf{v}_{21}\cdot\mathbf{k}>0} \mathbf{k}\cdot[f(\mathbf{x}_1, \mathbf{v}_1', t)\, \nabla_1 f(\mathbf{x}_1, \mathbf{v}_2', t) \\ - f(\mathbf{x}_1, \mathbf{v}_1, t)\, \nabla_1 f(\mathbf{x}_1, \mathbf{v}_2, t)]\, \mathbf{v}_{21}\cdot\mathbf{k}\, d\mathbf{k}\, d\mathbf{v}_2 \tag{27}$$

$$J(g_2^{(i)}) = \sigma^2 \int_{\mathbf{v}_{21}\cdot\mathbf{k}>0} \{[\exp(-i\mathbf{l}\cdot\mathbf{k}\sigma)]\, g^{(i)}(\mathbf{l}, \mathbf{v}_1', \mathbf{v}_2', \mathbf{x}_1, t) \\ - [\exp(i\mathbf{l}\cdot\mathbf{k}\sigma)]\, g_2^{(i)}(\mathbf{l}, \mathbf{v}_1, \mathbf{v}_2; \mathbf{x}_1, t)\}\, \mathbf{v}_{21}\cdot\mathbf{k}\, d\mathbf{k}\, d\mathbf{v}_2\, d\mathbf{l} \tag{28}$$

$$\mathscr{B}(g_2^{(i)}) = -i(8\pi^3/m) \int V_l{}^{\mathrm{S}}\mathbf{l}\cdot\partial_1 g_2^{(i)}(\mathbf{l}, \mathbf{v}_1, \mathbf{v}_2; \mathbf{x}_1, t)\, d\mathbf{v}_2\, d\mathbf{l} \tag{29}$$

we obtain the following form for the kinetic equation appropriate for the computation of linear transport properties:

$$\partial_t f + \mathbf{v}_1\cdot\nabla_1 f + m^{-1}\mathbf{F}^{\mathrm{S}}(\mathbf{x}_1, t)\cdot\partial_1 f = J_{B1} + J_{B2} + \sum_{i=1}^{4} J(g_2^{(i)}) + \sum_{i=1}^{4} \mathscr{B}(g_2^{(i)}) \tag{30}$$

Equation (30) is still nonlinear in the singlet distribution function f. Linearizing by the Chapman–Enskog method,$^{(5)}$ we obtain

$$h(f^0) = \mathscr{O}_{\mathrm{H}}\phi + \mathscr{O}_{\mathrm{S}}\phi \tag{31}$$

with

$$h(f^0) \equiv \partial_t{}^0 f^0 + \mathbf{v}_1 \cdot \nabla_1 f^0 + m^{-1}\mathbf{F}^{S0}(\mathbf{x}_1, t) \cdot \partial_1 f^0 - J^0_{B2} - \sum_{i=2}^{4} J^0(g_2^{(i)}) - \sum_{i=2}^{4} \mathscr{B}^0(g_2^{(i)}) \tag{32}$$

where

$$\mathscr{A}_{\mathrm{H}}\phi = g(\sigma)\sigma^2 \int_{\mathbf{v}_{21}\cdot\mathbf{k}>0} f^0(1) f^0(2)[\phi'(1) + \phi'(2) - \phi(1) - \phi(2)]\, \mathbf{v}_{21} \cdot \mathbf{k}\, d\mathbf{k}\, d\mathbf{v}_2 - m^{-1}kT\sigma^2 \int_{\mathbf{v}_{21}\cdot\mathbf{k}>0} \left\{ \frac{\exp(-i\mathbf{l}\cdot\mathbf{k}\sigma)}{\mathbf{l}\cdot\mathbf{v}'_{12} - i0}\, \mathbf{l} \cdot [\partial_1{}'\phi(1)' - \partial_2{}'\phi(2)'] - \frac{\exp(i\mathbf{l}\cdot\mathbf{k}\sigma)}{\mathbf{l}\cdot\mathbf{v}'_{12} - i0}\, \mathbf{l} \cdot [\partial_1\phi(1) - \partial_2\phi(2)] \right\} G_l f^0(1) f^0(2)\, \mathbf{v}_{21} \cdot \mathbf{k}\, d\mathbf{k}\, d\mathbf{v}_2\, d\mathbf{l} \tag{33}$$

and

$$\mathscr{A}_{\mathrm{S}}\phi = -(8\pi^4/m^2)\, kT \int G_l V_l{}^{\mathrm{S}} \mathbf{l} \cdot \partial_1 \delta(\mathbf{l}\cdot\mathbf{v}_{12}) f^0(1) f^0(2) \mathbf{l} \cdot \partial_{12}[\phi(1) + \phi(2)] \tag{34}$$

where the superscript 0 on $\mathbf{F}^{S0}$, J^0_{B2}, $J^0(g_2^{(i)})$, and $B^0(g_2^{(i)})$ means that in these expressions we have set $f = f^0$, and $\partial_t{}^0$ denotes the zeroth-order time derivative of hydrodynamic variables. The quantity $f^0(i) = f^0(\mathbf{x}_1, \mathbf{v}_i, t)$ is the local equilibrium distribution function defined as

$$f(i)^0 = n(\mathbf{x}_1, t) \left[\frac{m}{2\pi kT(\mathbf{x}_1, t)} \right]^{3/2} \exp \left\{ - \frac{m}{2kT(\mathbf{x}_1, t)} [\mathbf{v}_i - \mathbf{u}(\mathbf{x}_1, t)]^2 \right\} \tag{35}$$

The quantities n, T, and $\mathbf{u}$ are the local density, temperature, and mass-average velocity, respectively. The quantity $\phi(i)$ represents the deviation of f from local equilibrium and is defined by the relation,

$$f(i) = f(i)^0[1 + \phi(i)] \tag{36}$$

The operator $\mathscr{A}_{\mathrm{S}}\phi$ is identical to the Fokker–Planck part of the Rice–Allnatt collision operator, but $\mathscr{A}_{\mathrm{H}}\phi$ differs from the Enskog operator employed in the Rice–Allnatt theory since we did not use the chaos assumption of Enskog. The added contribution to our hard-sphere collision operator is real since it does not vanish in the weak coupling limit, $-kTG_l \rightarrow V_l$, where our assumption two is exact. The contribution represents dynamic correlations neglected by Enskog's chaos assumption. PNM obtained similar contributions in their local equilibrium theory.

The operators $\mathscr{A}_{\rm H}$ and $\mathscr{A}_{\rm S}$ are symmetric and admit the solutions $\psi_h = m, \mathbf{v}, \mathbf{v}^2$ to the homogeneous equation

$$\mathscr{A}_{\rm H}\psi_h + \mathscr{A}_{\rm S}\psi_h = 0 \tag{37}$$

Thus, the Fredholm solvability condition requires that the left-hand side of Eq. (31) must be orthogonal to m, $\mathbf{v}$, $\mathbf{v}^2$, i.e., the *l*hs of (31) when multiplied by m, $\mathbf{v}_1$, and v_1^2, respectively, and integrated over $d\mathbf{v}_1$ must equal zero. Performing these integrations, we obtain the following solvability conditions:

$$\partial_t^0 n + \nabla_1 \cdot (n\mathbf{u}) = 0 \tag{38}$$

$$\partial_t^0 \mathbf{u} + \mathbf{u} \cdot \nabla_1 \mathbf{u} + (1/mn)\, \nabla_1 P = 0 \tag{39}$$

$$\partial_t^0 T + \mathbf{u} \cdot \nabla_1 T + (T/n\tilde{C}_v)(\partial P/\partial T)_v\, \nabla_1 \cdot \mathbf{u} = 0 \tag{40}$$

These equations (which define the zeroth-order time derivative ∂_t^0) are the exact nondissipative hydrodynamic equations demanded by condition 3 of our model. If, as RA did, we neglect the contributions $g_2^{(2)}$, $g_2^{(3)}$, and $g_2^{(4)}$, the ideal specific heat is $\tilde{C}_v^{\rm ID} = \frac{3}{2}k$ and the hard-sphere pressure $P^{\rm H}$ appear in these equations instead of the correct specific heat and pressure. The correct specific heat is obtained only if the memory and time displacement terms $g_2^{(3)}$ and $g_2^{(4)}$ are retained. The reason for this is that neglect of $g_2^{(3)}$ and $g_2^{(4)}$ is equivalent to assuming the collisions are instantaneous and, therefore, occur too quickly to allow kinetic energy to be stored as potential energy. Therefore, only the ideal heat capacity associated with the kinetic energy will be effective.

Using Eqs. (38)–(41), one can eliminate the time derivatives $\partial_t^0 n$, $\partial_t^0 \mathbf{u}$, and $\partial_t^0 T$ from $h(f^0)$. However, it is not convenient to do this explicitly. In the calculations that follow, we evaluate integrals over $d\mathbf{v}_1$ involving products of $h(f^0)$ with certain functions of $\mathbf{v}_1$. It is generally easier to evaluate the integrals first and then eliminate $\partial_t^0 n$, $\partial_t^0 \mathbf{u}$, and $\partial_t^0 T$ from the results using Eqs. (38)–(41).

On the basis of the kinetic theory of gases, it is expected that a good approximation to ϕ is(5,10)

$$\phi = b_0 \left(\frac{m}{2kT}\right) \mathbf{C}^0\mathbf{C} : \nabla_1 \mathbf{u} + a_1 m \left(\frac{5}{2} - \frac{m\mathbf{C}^2}{2kT}\right) \mathbf{C} \cdot \nabla_1 \ln T + b_2 \left[\frac{15}{8} - \frac{5m\mathbf{C}^2}{4kT} + \frac{m^2\mathbf{C}^4}{8(kT)^2}\right] \nabla_1 \cdot \mathbf{u} \tag{41}$$

where $\mathbf{C}^0\mathbf{C}$ is a traceless dyadic,

$$\mathbf{C}^0\mathbf{C} = \mathbf{C}\mathbf{C} - \tfrac{1}{3}\mathbf{C}^2\mathsf{1} \tag{42}$$

and

$$\mathbf{C} = \mathbf{v} - \mathbf{u} \tag{43}$$

and where the quantities b_0, b_2, and a_1 are determined from the equations

$$\int d\mathbf{v}_1\, \mathbf{C}_1{}^0\mathbf{C}_1 \left\{ h(f^0) - b_0 \left(\frac{m}{2kT}\right) (\mathcal{O}_{\mathrm{H}} + \mathcal{O}_{\mathrm{S}})(\mathbf{C}^0\mathbf{C} : \nabla_1\mathbf{u} \right\} = 0 \tag{44}$$

$$\begin{aligned} &\int d\mathbf{v}_1 \left[\frac{15}{8} - \frac{5m\mathbf{C}_1{}^2}{4kT} + \frac{5m^2\mathbf{C}_1{}^4}{8(kT)^2}\right] \\ &\qquad \times \left\{ h(f^0) - b_2(\mathcal{O}_{\mathrm{H}} + \mathcal{O}_{\mathrm{S}}) \left[\frac{15}{8} - \frac{5m\mathbf{C}^2}{4kT} + \frac{5m^2\mathbf{C}^4}{8(kT)^2}\right] \nabla_1 \cdot \mathbf{u} \right\} = 0 \end{aligned} \tag{45}$$

$$\begin{aligned} &\int d\mathbf{v}_1\, \mathbf{C}_1 \left(\frac{5}{2} - \frac{m\mathbf{C}_1{}^2}{2kT}\right) \\ &\qquad \times \left\{ h(f^0) - a_1 m(\mathcal{O}_{\mathrm{H}} + \mathcal{O}_{\mathrm{S}}) \left(\frac{5}{2} - \frac{m\mathbf{C}^2}{2kT}\right) \cdot \nabla_1 \ln T \right\} = 0 \end{aligned} \tag{46}$$

with $\mathbf{u} = 0$ in Eq. (46). Performing the lengthy integrations indicated in Eqs. (44)–(46) and eliminating $\partial_t{}^0 n$, $\partial_t{}^0\mathbf{u}$, and $\partial_t{}^0 T$ from the results, we obtain

$$b_0 = \frac{-5m}{3(\zeta^{\mathrm{H}}_{(1)} + \zeta^{\mathrm{H}}_{(2)} + \zeta^{\mathrm{S}})} \left[1 + \frac{2(e^{\mathrm{S}} + P^{\mathrm{S}} + P^{\mathrm{H}})}{5nkT} - \frac{\pi n\sigma^3}{5} G(\sigma)(1 - \chi_3)\right] \tag{47}$$

$$\begin{aligned} b_2 = &- \frac{m}{3(\zeta^{\mathrm{H}}_{(1)} + \zeta^{\mathrm{H}}_{(2)} + \zeta^{\mathrm{S}})} \left[1 + \frac{P^{\mathrm{H}}}{nkT} - \frac{4}{n\tilde{C}_v}\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{e^{\mathrm{S}}}{nkT} + \frac{3}{8}\right) \right. \\ &\left. + \frac{12e^{\mathrm{S}}}{nkT} - \frac{\pi}{3} n\sigma^3 G(\sigma) \left(\chi_5 + \frac{7}{8}\chi_3\right)\right] \end{aligned} \tag{48}$$

and

$$\begin{aligned} \mathscr{A}_1 = &\frac{5}{4(\zeta^{\mathrm{H}}_{(1)} + 3\zeta^{\mathrm{H}}_{(2)} + \zeta^{\mathrm{S}})} \left[1 + \frac{3}{5nkT}(e^{\mathrm{S}} + P^{\mathrm{S}} + P^{\mathrm{H}}) \right. \\ &\left. + \frac{1}{3nk}\left(\frac{\partial e^{\mathrm{S}}}{\partial T}\right)_P + \frac{2\pi n\sigma^3}{15} G(\sigma)(8\xi_3 - 12\xi_1 - \chi_3 - 4)\right] \end{aligned} \tag{49}$$

where

$$\zeta^{\mathrm{H}}_{(1)} = \tfrac{8}{3}(\pi mkT)^{1/2}\, n\sigma^2 g(\sigma) \tag{50}$$

$$\zeta^{\mathrm{H}}_{(2)} = -(2\pi/3)\, \sigma^2 G(\sigma)\, n(mkT)^{1/2}[(2/\pi^{1/2}) + 3\chi_2 - 2\chi_4] \tag{51}$$

$$\zeta^{\mathrm{S}} = -(16\pi^4/3)\, n(\pi m/kT)^{1/2} \int_0^\infty dl\, l^3 V_l{}^{\mathrm{S}} G_l \tag{52}$$

$$P^{\mathrm{H}} = (2\pi/3)\, n\sigma^3 g(\sigma)\, nkT \tag{53}$$

$$P^{\mathrm{S}} = -(2\pi/3)\, n^2 \int_0^\infty dr\, r^3[dV^{\mathrm{S}}(r)/dr]\, G(r) \tag{54}$$

$$e^{\mathrm{S}} = 2\pi n^2 \int_0^\infty dr\, r^2 V^{\mathrm{S}}(r)\, G(r) \tag{55}$$

$$\xi_n = -[(-1)^n I_n/8\pi^{3/2}G(\sigma)] \int_1^\infty dx\, xG(\sigma x)\, P_n(x) \tag{56}$$

$$I_n = \int dy[\exp(-y^2)]\, y^{n-1} \tag{57}$$

$$P_n(x) = 16 \int_{-1}^0 d\mu\, [\mu^n/(x^2 - 1 + \mu^2)^{1/2}] \tag{58}$$

$$\chi_n = -\xi_n + (2I_n/\pi^{3/2}n) + [(-1)^n I_n/8\pi^{3/2}G(\sigma)] \int_1^\infty dx\, x^2G(\sigma x)[dP_n(x)/dx] \tag{59}$$

The quantities $P_n(x)$ can be evaluated explicitly. For $x \geqslant 0$ the first five P_n are

$$P_1(x) = -16[x - (x^2 - 1)^{1/2}] \tag{60}$$

$$P_2(x) = 8x - 4(x^2 - 1) \ln|(x + 1)/(x - 1)| \tag{61}$$

$$P_3(x) = -16x + (32/3)[x^3 - (x^2 - 1)^{3/2}] \tag{62}$$

$$P_4(x) = 2x(5 - 3x^2) + 3(x^2 - 1)^2 \ln|(x + 1)/(x - 1)| \tag{63}$$

$$P_5(x) = -16x + (64/3)x^3 - (128/15)[x^5 - (x^2 - 1)^{5/2}] \tag{64}$$

For tracer self-diffusion with $\nabla_1 T = \mathbf{u} = 0$, we can solve the kinetic equation by setting $\phi(2) \equiv 0$ and taking

$$\phi(1) = d\mathbf{v}_1 \cdot \nabla_1 \ln n^* \tag{65}$$

where n^* is the tracer element concentration and where d is obtained from the equation

$$\int dv_1\, \mathbf{v}_1\{h(f^0) - d(\mathcal{C}_{\mathrm{H}}{}^* + \mathcal{C}_{\mathrm{S}}{}^*)\, \mathbf{v}_1 \cdot \nabla_1 \ln n^*\} = 0 \tag{66}$$

The asterisk on $\mathcal{C}_{\mathrm{H}}{}^*$ and $\mathcal{C}_{\mathrm{S}}{}^*$ means that $\phi(2) \equiv 0$ for the self-diffusion case. The result is

$$d = -1/(\zeta^{\mathrm{H}}_{(1)} + \zeta^{\mathrm{H}}_{(3)} + \zeta^{\mathrm{S}}) \tag{67}$$

$$\zeta^{\mathrm{H}}_{(3)} = -(2\pi/3)\, n\sigma^2 G(\sigma)(mkT)^{1/2}\, \chi_2 \tag{68}$$

Finally, the doublet distribution function, to first order in gradients of **u** and T, is of the form

$$g_2(\mathbf{l}, \mathbf{v}_1, \mathbf{v}_2; \mathbf{x}_1, t) = -\frac{m^{-1}kTG_l}{\mathbf{l}\cdot\mathbf{v}_{12} - i0}\,\mathbf{l}\cdot\partial_{12}\{f(1)^0 f(2)^0[\phi(1) + \phi(2)]\} + \sum_{i=1}^{4} g_2^{(i)0} \tag{69}$$

where the superscript 0 on $g_2^{(i)0}$ indicates that we have set $f = f^0$ in the expressions defining these quantities.

3. THE TRANSPORT FLUXES AND TRANSPORT COEFFICIENTS

The kinetic parts of the heat flux $\mathbf{q}$ and momentum flux J are by definition

$$\mathbf{q}_K = \tfrac{1}{2}m \int f(\mathbf{x}_1, \mathbf{v}_1, t)(\mathbf{v}_1 - \mathbf{u})^2(\mathbf{v}_1 - \mathbf{u})\, d\mathbf{v}_1 \tag{70}$$

and

$$\mathsf{J}_K = m \int f(\mathbf{x}_1, \mathbf{v}_1, t)(\mathbf{v}_1 - \mathbf{u})(\mathbf{v}_1 - \mathbf{u})\, d\mathbf{v}_1 \tag{71}$$

The potential energy contributions to $\mathbf{q}$ and J from binary hard-sphere collisions are

$$\begin{aligned}\mathbf{q}_v{}^{\mathrm{H}} = {} & -\tfrac{1}{4}m\sigma^3 \int_{\mathbf{v}_{21}\cdot\mathbf{k}>0} (\mathbf{v}_{21}\cdot\mathbf{k})^2\,\mathbf{k}\mathbf{k}\cdot(\mathbf{v}_1 + \mathbf{v}_2 - 2\mathbf{u}) \\ & \times f_2(\mathbf{x}_1, \mathbf{x}_1 - \sigma\mathbf{k}, \mathbf{v}_1, \mathbf{v}_2, t)\, d\mathbf{k}\, d\mathbf{v}_1\, d\mathbf{v}_2\end{aligned} \tag{72}$$

and

$$\mathsf{J}_v{}^{\mathrm{H}} = \tfrac{1}{2}m\sigma^3 \int_{\mathbf{v}_{21}\cdot\mathbf{k}>0} (\mathbf{v}_{21}\cdot\mathbf{k})^2\,\mathbf{k}\mathbf{k} f_2(\mathbf{x}_1, \mathbf{x}_1 - \sigma\mathbf{k}, \mathbf{v}_1, \mathbf{v}_2, t)\, d\mathbf{k}\, d\mathbf{v}_1\, d\mathbf{v}_2 \tag{73}$$

The potential energy contributions from the soft part of the potential energy are$^{(11)}$

$$\begin{aligned}\mathbf{q}_v{}^{\mathrm{S}} &= \frac{1}{4}\int (\mathbf{v}_1 + \mathbf{v}_2 - 2\mathbf{u})\cdot\left[\mathsf{1}V^{\mathrm{S}}(r) - \mathbf{r}\,\frac{\partial V^{\mathrm{S}}(r)}{\partial\mathbf{r}}\right] \\ &\qquad \times f_2(\mathbf{x}_1, \mathbf{x}_1 + \mathbf{r}, \mathbf{v}_1, \mathbf{v}_2, t)\, d\mathbf{r}\, d\mathbf{v}_1\, d\mathbf{v}_2 \\ &= 2\pi^3 \int (\mathbf{v}_1 + \mathbf{v}_2 - 2\mathbf{u})\cdot\left[\mathsf{1}V_l{}^{\mathrm{S}} + \left(\frac{\partial}{\partial\mathbf{l}}\mathbf{l}V_l{}^{\mathrm{S}}\right)\right] g_2(\mathbf{l}, \mathbf{v}_1, \mathbf{v}_2; \mathbf{x}_1, t)\, d\mathbf{l}\, d\mathbf{v}_1\, d\mathbf{v}_2\end{aligned} \tag{74}$$

$$\begin{aligned}\mathsf{J}_v{}^{\mathrm{S}} &= -\frac{1}{2}\int \mathbf{r}\,\frac{\partial V^{\mathrm{S}}(r)}{\partial\mathbf{r}} f_2(\mathbf{x}_1, \mathbf{x}_1 + \mathbf{r}, \mathbf{v}_1, \mathbf{v}_2, t)\, d\mathbf{r}\, d\mathbf{v}_1\, d\mathbf{v}_2 \\ &= -\frac{n^2}{2}\int \mathbf{r}\,\frac{\partial V^{\mathrm{S}}(r)}{\partial\mathbf{r}}\, d\mathbf{r} + 4\pi^3 \int \left(\frac{\partial}{\partial\mathbf{l}}\mathbf{l}V_l{}^{\mathrm{S}}\right) g_2(\mathbf{l}, \mathbf{v}_1, \mathbf{v}_2; \mathbf{x}_1, t)\, d\mathbf{l}\, d\mathbf{v}_1\, d\mathbf{v}_2\end{aligned} \tag{75}$$

The term involving $f(\mathbf{x}_1, \mathbf{v}_1, t) f(\mathbf{x}_1 + \mathbf{r}, \mathbf{v}_2, t)$, obtained by setting $f_2 = g_2 + f(1) f(2)$, vanishes in Eq. (14) through first order in gradients of n, $\mathbf{u}$, and T and to the same order the corresponding term in Eq. (75) gives the contribution

$$-\frac{n^2}{2}\int \mathbf{r}\,\frac{\partial V^{S}(r)}{\partial \mathbf{r}}\,d\mathbf{r} = -\mathsf{1}\,\frac{n^2}{6}\int r\,\frac{\partial V^{S}(r)}{\partial r}\,d\mathbf{r} \tag{76}$$

Using the values of f, f_2, and g_2 obtained in the preceding sections, we can compute the various contributions to $\mathbf{q}$ and J. Then, comparing the molecular expressions to Fourier's and Newton's laws,

$$\mathbf{q} = -\kappa\,\nabla T \tag{77}$$

and

$$\mathsf{J} = P\mathsf{1} - \Phi\nabla_1\cdot\mathbf{u}\mathsf{1} - \eta[\nabla_1\mathbf{u} + \nabla_1\mathbf{u}^T - \tfrac{2}{3}\nabla_1\cdot\mathbf{u}\mathsf{1}] \tag{78}$$

we obtain the various contributions to the thermal conductivity κ, the shear viscosity η, and the bulk viscosity Φ. The results are as follows.

Thermal Conductivity

$$\kappa_K = \frac{\kappa^*}{(\zeta^{H}_{(1)} + 3\zeta^{H}_{(2)} + \zeta^{S})/\zeta^*}\left[1 + \frac{3}{5nkT}(e^{S} + P^{S} + P^{H}) + \frac{1}{3nk}\left(\frac{\partial e^{S}}{\partial T}\right)_P + \frac{2\pi n\sigma^3}{15}\,G(\sigma)(8\xi_3 - 12\xi_1 - \chi_3 - 4)\right] \tag{79}$$

$$\begin{aligned}\kappa_v{}^{H} = {}& \kappa_K\left[\frac{2}{5}\,\pi n\sigma^3 g(\sigma) + \frac{\pi}{15}\,n\sigma^3 G(\sigma)(1 + 2\chi_3)\right] \\ &+ \kappa^*\left(\frac{128}{225}\,\pi n^2\sigma^6\left[g(\sigma) - \frac{\pi^{1/2}}{4}\,G(\sigma)(\xi_2 - \xi_4)\right]\right. \\ &\left.+ \frac{32\pi}{225}\left(\frac{\pi m}{kT}\right)^{1/2} T\left\{\frac{\partial}{\partial T}\left[n^2\sigma^6 G(\sigma)\left(\frac{kT}{m}\right)^{1/2}\xi_2\right]_P\right\}\right)\end{aligned} \tag{80}$$

$$\begin{aligned}\kappa_v{}^{S} = {}& -\frac{(e^{S} + 9P^{S})}{15nkT}\,\kappa_K + \frac{256\pi^5}{225}\,\kappa^*\left\{\frac{n^2\sigma^2}{kT}\left(5W_1 + \frac{9}{2}\,W_2 + W_3\right)\right. \\ &\left.+ k\left[\frac{\partial}{\partial T}(6n^2\sigma^2 W_1 + n^2\sigma^2 W_2)\right]_P\right\}\end{aligned} \tag{81}$$

where

$$\kappa^* = (75/64\sigma^2)(k^3T/\pi m)^{1/2} \tag{82}$$

and

$$\zeta^* = 8n\sigma^2(\pi mkT)^{1/2}/3 \tag{83}$$

Shear Viscosity

$$\eta_K = \frac{\eta^*}{(\zeta^{\mathrm{H}}_{(1)} + \zeta^{\mathrm{H}}_{(2)} + \zeta^{\mathrm{S}})/\zeta^*}\left[1 + \frac{2(e^{\mathrm{S}} + P^{\mathrm{S}} + P^{\mathrm{H}})}{5nkT} - \frac{\pi n\sigma^3}{5}G(\sigma)(1 - \chi_3)\right] \tag{84}$$

$$\begin{aligned}\eta_v{}^{\mathrm{H}} = {} & \eta_K\left[\frac{4\pi}{15}n\sigma^3 g(\sigma) + \frac{2\pi}{15}n\sigma^3 G(\sigma)(1 - 3\chi_2)\right] \\ & + \frac{64\pi}{75}n^2\sigma^6\eta^*\left[g(\sigma) + \frac{\pi^{1/2}}{4}G(\sigma)\,\chi_2 - \frac{\pi^{1/2}}{2}G(\sigma)(3\xi_4 - 8\xi_2)\right]\end{aligned} \tag{85}$$

$$\eta_v{}^{\mathrm{S}} = \frac{2(e^{\mathrm{S}} - P^{\mathrm{S}})}{5nkT}\eta_K + \frac{128}{75}\frac{\pi^5 n^2\sigma^2}{kT}\eta^*(2W_2 + W_3) \tag{86}$$

where

$$\eta^* = (5/16\sigma^2)(mkT/\pi)^{1/2} \tag{87}$$

Bulk Viscosity

$$\Phi_K = 0 \tag{88}$$

$$\begin{aligned}\Phi_v{}^{\mathrm{H}} = {} & b_2{}^*\pi n\sigma^3 G(\sigma)\,\eta^* + \frac{64\pi}{45}n^2\sigma^6\eta^*\left[g(\sigma) - \frac{6}{5}G(\sigma)\left(\xi_4 - \frac{7}{3}\xi_2\right)\right] \\ & + \frac{16}{15}\left(\frac{\pi}{kT}\right)^{1/2}\eta^*\left\{\left[\left(\frac{\partial}{\partial \ln n}\right)_T + \frac{1}{n\tilde{C}_v}\left(\frac{\partial P}{\partial T}\right)_n\left(\frac{\partial}{\partial \ln T}\right)_n\right]\right. \\ & \left.\times\ [\pi n^2\sigma^6 G(\sigma)(kT)^{1/2}\,\xi_2]\right\}\end{aligned} \tag{89}$$

$$\begin{aligned}\Phi_v{}^{\mathrm{S}} = {} & -\frac{9}{5}b_2{}^*\frac{P^{\mathrm{S}}}{nkT}\eta^* + \frac{128\pi^5}{45}\frac{n^2\sigma^2}{kT}\eta^*\left(8W_2 + \frac{4}{3}W_1 + W_3\right) - \frac{512\eta^*}{15(kT)^{1/2}} \\ & \times\left\{\left[\left(\frac{\partial}{\partial \ln n}\right)_T + \frac{1}{n\tilde{C}_v}\left(\frac{\partial P}{\partial T}\right)_n\left(\frac{\partial}{\partial \ln T}\right)_n\right]\left[\frac{\pi^5 n^2\sigma^2}{(kT)^{1/2}}(W_1 + W_2)\right]\right\}\end{aligned} \tag{90}$$

$$\begin{aligned}b_2{}^* = \frac{3\zeta^*}{m}b_2 = {} & \frac{-\zeta^*}{\zeta^{\mathrm{H}}_{(1)} + \zeta^{\mathrm{H}}_{(2)} + \zeta^{\mathrm{S}}}\left[1 + \frac{P^{\mathrm{H}}}{nkT} - \frac{4}{n\tilde{C}_v}\left(\frac{\partial P}{\partial T}\right)_n\left(\frac{e^{\mathrm{S}}}{nkT} + \frac{3}{8}\right)\right. \\ & \left. + \frac{12e^{\mathrm{S}}}{nkT} - \frac{\pi}{3}n\sigma^3 G(\sigma)\left(\chi_5 + \frac{7}{8}\chi_3\right)\right]\end{aligned} \tag{91}$$

The quantities W_n are by definition

$$W_n = \int_0^\infty dl\, G_l l^n(\partial^{n-1}/\partial l^{n-1})\, V_l{}^{\mathrm{S}} \tag{92}$$

The other quantities in Eqs. (79)–(92) were defined in Eqs. (47)–(59). The total values of κ, η, and Φ are, of course, obtained by summing the three parts given for each.

In the self-diffusion case, the diffusion flux is

$$\mathbf{J}_d = m \int \mathbf{v}_1 f \, d\mathbf{v}_1 = dkT \nabla_1 n^* \tag{93}$$

which, when compared to Fick's law,

$$\mathbf{J}_d = -D \nabla_1 n^* \tag{94}$$

gives for the self-diffusion coefficient the result

$$D = -dkT \tag{95}$$

Taking d from Eq. (67), we obtain

$$D = \frac{kT}{\zeta_{(1)}^{\mathrm{H}} + \zeta_{(3)}^{\mathrm{H}} + \zeta^{\mathrm{S}}} \tag{96}$$

The last terms in Eqs. (81) and (90) arise from the memory and temporal delocalization contributions $g_2^{(3)0}$ and $g_2^{(4)0}$. These terms are singular, and hence of great importance, at the critical point. Also a_1 contains a singular term arising from $g_2^{(3)0}$ and $g_2^{(4)0}$. Thus, the neglect of the memory and time evolution of delocalization would have serious consequences, at least near the critical point. Using van Kampen's$^{(12)}$ approximation to G_l near the critical point, we can conclude from the above results that κ and Φ are singular at the critical point, while η and D are not. This is in qualitative agreement with experiment. However, whether the quantitative nature of the singularities predicted for κ and Φ agree with experiment has not yet been established. Work on this point is underway at present.

The terms in κ, η, Φ, and D involving the χ_n and ξ_n functions arise from the dynamic correlations mentioned earlier. If Enskog's chaos assumption were used in the hard-sphere contributions, these terms would not appear.

Using the values for the radial distribution function computed for the superposition approximation by Kirkwood *et al.*$^{(13)}$ for the truncated Lennard-Jones model, we have computed the self-diffusion coefficient for liquids argon, krypton, and xenon. The quantity $\zeta_{(3)}^{\mathrm{H}}$ is much smaller than $\zeta_{(1)}^{\mathrm{H}} + \zeta^{\mathrm{S}}$ so that Eq. (96) gives essentially the same numerical results as the original Rice–Allnatt approximation, $D = kT/(\zeta_{(1)}^{\mathrm{H}} + \zeta^{\mathrm{S}})$. In Table I, theory and experiment$^{(14)}$ are compared. The theoretical values disagree with experiment by only 20% for temperatures below $0.9T_c$, where T_c is the critical temperature. For higher temperatures the disagreement becomes increasingly greater. Numerical predictions of the viscosity and the thermal conductivity have not been made presently, although in the dense fluid range they should be about 5–15% higher than the predictions of the PNM theory. The PNM theory predicts$^{(4)}$ the viscosity and thermal conductivity

Table I. Self-Diffusivity (in units of cm²/sec) of Liquids Argon, Krypton, and Xenon Along the Vapor Pressure Curve[a]

Substance	T, °K	D(calc) × 10^5	D(obs) × 10^5
Argon	90	3.3	2.4
	110	4.8	4.8
	130	6.9	7.3
	140	8.6	8.6
	148	11.5	9.8
Krypton	120	2.5	1.7
	140	3.2	2.7
	160	4.3	3.7
	180	5.7	4.5
	200	8.2	5.6
Xenon	220	3.8	4.4
	240	4.7	5.2
	260	6.0	6.0
	280	8.0	6.2
	285	9.2	6.2

[a] Theoretical predictions based on Eq. (96) and experimental values taken from Ref. 24.

of the inert gas liquids with generally no more than about 30 % error, usually low, so that we can expect the present theory to predict these transport coefficients with no more than 25 % error.

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REFERENCES

1. S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids*, Wiley, New York (1966).
2. I. Prigogine, G. Nicolis, and J. Misguich, *J. Chem. Phys.* **43**:4516 (1965).
3. J. Misguich, Ph.D. thesis, Université Libre de Bruxelles, 1968; *J. Physique* **30**:221 (1969).
4. J. Palyvos, H. T. Davis, J. Misguich, and G. Nicolis, *J. Chem. Phys.* **49**:4088 (1968).
5. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, Cambridge University Press, Cambridge (1939).
6. H. Reiss, *Adv. Chem. Phys.* **IX**:1 (1965).

7. G. Severne, *Physica* **31**:877 (1965).
8. G. Dowling, Ph.D. Thesis, University of Minnesota, 1971.
9. G. Dowling and H. T. Davis, *J. Chem. Phys.* (to appear).
10. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York (1954).
11. J. H. Irving and J. G. Kirkwood, *J. Chem. Phys.* **18**:17 (1950).
12. N. G. van Kampen, *Phys. Rev.* **135A**:362 (1964).
13. J. G. Kirkwood, V. A. Lewinson, and B. J. Alder, *J. Chem. Phys.* **20**:929 (1952).
14. J. Naghizadeh and S. A. Rice, *J. Chem. Phys.* **36**:2710 (1962).