Journal of Statistical Physics, Vol. 8, No. 3, 1973

Short-Time Kinetic Equations for Hard Spheres: Comparison with Other Theories

J. Sykes[1]

Received February 20, 1973

The short-time kinetic equation for hard spheres derived by Lebowitz, Percus, and Sykes is compared with the Enskog equation. It is shown that, to leading order in the density, the short-time equation and the Enskog equation are identical and equivalent to the memory function equation used by Mazenko, Wei, and Yip. By using simple properties of the collision integrals, the scattering function calculated from the short-time equation can be related to the scattering function obtained from the Enskog equation: This relationship is exact for all values of the density. We examine the relationship in the short-time limit and in the hydrodynamic limit and argue that the short-time kinetic equation gives a better description of the scattering function than does the Enskog equation.

KEY WORDS: Kinetic equations; hard spheres; coherent scattering function.

1. INTRODUCTION

The van Hove(1) time-dependent self-distribution and total distribution functions $G_s(\mathbf{r}, t)$ and $G(\mathbf{r}, t)$ play a central role in the theories of liquids and gases. The Fourier transforms of these functions $S_s(\mathbf{k}, \omega)$ and $S(\mathbf{k}, \omega)$ can be measured for different fluids by neutron scattering experiments and calculated directly for different interaction potentials by molecular dynamics.

---

[1] Physics Department, Duke University, Durham, North Carolina.

Thus, there is an ever-growing body of data which needs to be understood and which at the same time can be used to test existing theories. The theories are usually based on either the solution of a kinetic equation such as the Boltzmann equation, which is the method pioneered by Nelkin and co-workers,(2) or the calculation of memory functions, which were introduced by Zwanzig(3) and Mori.(4) Although these methods and approximations are in many cases very different, they often lead to similar results.(5) Instead of comparing each theory with either the experimental data or machine computations, much effort can be saved by first comparing the theories and then using the best available theory to compare with the data.

In this paper, we compare the short-time kinetic equations derived by Lebowitz, *et al.*(6) with other theories. These equations, which, as their name implies, are exact at short times, are summarized in Section 2. The equations are different for the self-distribution and total distribution functions and for continuous and discontinuous potentials. The equation for the self-distribution function for continuous potentials has already been compared with molecular dynamics calculations by Levesque and Verlet,(7) so here we will concentrate our attention on the equations for hard spheres. The kinetic equation traditionally used to describe hard-sphere systems is the Enskog equation,(8) which is a modification of the Boltzmann equation. The limitations of the Enskog equation have recently been discussed by Gross and Wisnivesky(9) and an approximate form of it has been solved numerically by Ranganathan and Nelkin.(10) In Section 3, we show that the Enskog equation can be written in the same form as the short-time kinetic equation, that is, as a driving term with a Vlasov-type term and a collision integral, the only difference being in the effective potentials in the Vlasov terms. To leading order in the density ρ, the effective potentials are identical and furthermore when the collision integral is also evaluated to leading order in ρ, the resulting equation is equivalent to the memory function equation used by Mazenko *et al.*(11)

The scattering functions $S(\mathbf{k}, \omega)$ are discussed in Section 4. By using simple properties of the collision integral, the scattering function calculated from the short-time kinetic equation can be related to the scattering function obtained from the Enskog equation. This relationship is exact for all ρ and only involves the effective potentials so that if one of the scattering functions is known, the other can be calculated directly from it. We examine this relationship in the short-time limit, which leads to expressions for the sum rules of $S(\mathbf{k}, \omega)$, and in the hydrodynamic limit. A similar relationship is derived relating the scattering function obtained from the short-time equation to the one calculated by Mazenko *et al.* in the low-density limit. From these results, we argue that the short-time kinetic equation gives the best description of the scattering function.

2. SHORT-TIME KINETIC EQUATIONS

We consider a classical system of N particles in a box at density ρ. At $t = 0$, one particle has a normalized distribution function $W(\mathbf{r}, \mathbf{v})$ and the rest of the particles are in equilibrium. The total one-particle distribution function is defined by

$$f(\mathbf{r}_1, \mathbf{v}_1, t) = N \int d\mathbf{r}_2 \int d\mathbf{v}_2 \cdots \int d\mathbf{r}_N \int d\mathbf{v}_N \, \mu(\mathbf{r}_1, \mathbf{v}_1, \ldots, \mathbf{r}_N, \mathbf{v}_N ; t) \quad (1)$$

Here, μ is a symmetrized ensemble density which is the solution of the Liouville equation with the initial condition

$$\mu(\mathbf{r}_1, \mathbf{v}_1, \ldots, \mathbf{r}_N, \mathbf{v}_N ; 0) = \mu_0(\mathbf{r}_1, \mathbf{v}_1, \ldots, \mathbf{r}_N, \mathbf{v}_N) \sum_{i=1}^{N} \frac{W(\mathbf{r}_i, \mathbf{v}_i)}{f_0(\mathbf{r}_i, \mathbf{v}_i)} \quad (2)$$

where μ_0 is the canonical distribution function and $f_0(\mathbf{r}, \mathbf{v}) = \rho h_0(v)$ is the one-particle equilibrium distribution function. We are interested in the departure of $f(\mathbf{r}, \mathbf{v}, t)$ from its equilibrium value, which is given by

$$\begin{aligned} \eta(\mathbf{r}, \mathbf{v}, t) &= f(\mathbf{r}, \mathbf{v}, t) - \rho h_0(v) \int d\mathbf{r}_0 \int d\mathbf{v}_0 \, W(\mathbf{r}_0, \mathbf{v}_0) \\ &= \int d\mathbf{r}_0 \int d\mathbf{v}_0 \, \eta(\mathbf{r}, \mathbf{v}, t/\mathbf{r}_0, \mathbf{v}_0) \, W(\mathbf{r}_0, \mathbf{v}_0) \end{aligned} \quad (3)$$

The last equation can be used to define a conditional distribution function since $\eta(\mathbf{r}, \mathbf{v}, t)$ is a linear functional of $W(\mathbf{r}_0, \mathbf{v}_0)$. At $t = 0$, we have

$$\begin{aligned} \eta(\mathbf{r}, \mathbf{v}, 0) = \int d\mathbf{r}_0 \int d\mathbf{v}_0 \, \{&\delta(\mathbf{r} - \mathbf{r}_0) \, \delta(\mathbf{v} - \mathbf{v}_0) \\ &+ \rho h_0(v)[g(\mathbf{r}, \mathbf{r}_0) - 1]\} \, W(\mathbf{r}_0, \mathbf{v}_0) \end{aligned} \quad (4)$$

where $g(\mathbf{r}, \mathbf{r}_0) \equiv g(|\mathbf{r} - \mathbf{r}_0|)$ is the radial distribution function. For the particular choice

$$W(\mathbf{r}, \mathbf{v}) = \delta(\mathbf{r}) \, h_0(v), \qquad \int d\mathbf{r} \int d\mathbf{v} \, W(\mathbf{r}, \mathbf{v}) = 1 \quad (5)$$

and the van Hove total distribution function is given by

$$G(\mathbf{r}, t) = \int d\mathbf{v} \, \eta(\mathbf{r}, \mathbf{v}, t) \quad (6)$$

Similar definitions can be made for the self-distribution function $f_s(\mathbf{r}, \mathbf{v}, t)$ from which $G_s(\mathbf{r}, t)$ can be calculated. The results will be summarized below and the reader is referred to Ref. 6 for further details.

The method used to derive the short-time kinetic equations in Ref. 6 can be described very simply. We define an operator $O(t)$ such that

$$\eta(t) = O(t)\,\eta(0) \tag{7}$$

Then the time derivative of $\eta(t)$ can be written as

$$\dot{\eta}(t) = \dot{O}(t)\,\eta(0) = \dot{O}(t)\,O^{-1}(t)\,\eta(t) \tag{8}$$

The first-order equations are obtained by evaluating $\dot{O}(t)\,O^{-1}(t)$ at $t = 0$. Second-order equations can also be derived but the details will not be repeated here.

The short-time kinetic equations for the Fourier–Laplace transform $\tilde{f}_s(\mathbf{k}, \mathbf{v}, s)$ of the self-distribution function $f_s(\mathbf{r}, \mathbf{v}, t)$ are of the form(6)

$$(s - i\mathbf{k}\cdot\mathbf{v})\tilde{f}_s(\mathbf{k}, \mathbf{v}, s) = f_s(\mathbf{k}, \mathbf{v}, 0) + \xi_s(\mathbf{k}, s)\, I_s(\tilde{f}_s(\mathbf{k}, \mathbf{v}, s)) \tag{9}$$

where the coefficients $\xi_s(\mathbf{k}, s)$ and the collision integrals I_s are given in Table I. The first-order equation for continuous potentials leads to the ideal gas equation. The second-order equation gives the Fokker–Planck equation with a frequency-dependent friction coefficient which can be related to the velocity autocorrelation function.(6) This equation has been compared with machine calculations by Levesque and Verlet.(7) For hard spheres we obtain a linearized Boltzmann equation with a factor $g(a)$, which is the radial distribution function for a system of hard spheres of diameter a at contact.

The equations for the Fourier–Laplace transform $\tilde{\eta}(\mathbf{k}, \mathbf{v}, s)$ of the total distribution can be written as(6)

$$\begin{aligned}(s - i\mathbf{k}\cdot\mathbf{v})\,\tilde{\eta}(\mathbf{k}, \mathbf{v}, s) &= \eta(\mathbf{k}, \mathbf{v}, 0) + ih_0(v)\,\mathbf{v}\cdot\tilde{\mathbf{Q}}(\mathbf{k}, s)\\ &\quad + \xi(\mathbf{k}, s)\, I(\tilde{\eta}(\mathbf{k}, \mathbf{v}, s))\end{aligned} \tag{10}$$

where $\tilde{\mathbf{Q}}(\mathbf{k}, s)$ is a Vlasov-type term. The functions $\tilde{\mathbf{Q}}(\mathbf{k}, s)$ and $\xi(\mathbf{k}, s)$ and the collision integral I are given in Table II. The equation from the first line of Table II is the Vlasov equation with an effective potential $-\beta C(r)$, where $C(r)$

Table I. Self-Distribution Function

	$\xi_s(\mathbf{k}, s)$	I_s
Continuous potential		
First order	—	0
Second order	$\frac{1}{3}\lambda\tilde{w}_s(s)$	Fokker–Planck
Hard spheres: first order	$\rho g(a)$	Linearized Boltzmann

Table II. Total Distribution Function

	$\tilde{\mathbf{Q}}(\mathbf{k}, s)$	$\xi(\mathbf{k}, s)$	I
Continuous potential			
First order	$-\mathbf{k}\rho C(k)\tilde{n}(\mathbf{k}, s)$	—	0
Second order	$-\mathbf{k}\rho C(k)\tilde{n}(\mathbf{k}, s)$ $+ i\mathbf{\Lambda}(\mathbf{k}, s)\cdot\tilde{\mathbf{j}}(\mathbf{k}, s)$	$\frac{1}{3}\lambda\tilde{w}(s)$	Fokker–Planck
Hard spheres: first order	$-\mathbf{k}\rho[C(k) - g(a)C_0(k)]\tilde{n}(\mathbf{k}, s)$	$\rho g(a)$	Linearized Enskog

is the direct correlation function. This equation has been derived many times by many methods.(12) The next equation has a Vlasov term which depends on the density $\tilde{n}(\mathbf{k}, s) = \int d\mathbf{v}\,\tilde{\eta}(\mathbf{k}, \mathbf{v}, s)$ and the current $\tilde{\mathbf{j}}(\mathbf{k}, s) = \int d\mathbf{v}\,\mathbf{v}\tilde{\eta}(\mathbf{k}, \mathbf{v}, s)$. In Ref. 6, the tensor $\mathbf{\Lambda}$ had the form

$$\mathbf{\Lambda}(\mathbf{k}, s) = \tilde{w}(s)\,\{A(\mathbf{k})(\mathbf{kk}/k^2) + B(\mathbf{k})[\mathbf{I} - (\mathbf{kk}/k^2)]\} \tag{11}$$

where A and B were determined by sum rules and $\tilde{w}(s)$ was unspecified apart from requiring $\tilde{w}(s) = 1/s + \cdots$ as $s \to \infty$. A similar equation was derived by Akcasu and Duderstadt(13) using a memory function approach, the only difference being that $\tilde{w}(s)$ was replaced by $1/[s + \alpha(k)]$. The last equation of Table II is the short-time kinetic equation for hard spheres and this will be discussed in detail in the rest of the paper.

3. COMPARISON OF THEORIES FOR HARD SPHERES

The short-time kinetic equation for the total distribution function for a system of hard spheres is Eq. (10) with the coefficients $\tilde{\mathbf{Q}}(\mathbf{k}, s)$ and $\xi(\mathbf{k}, s)$ given in the last line of Table II. $C_0(k)$ is the direct correlation function at zero density, that is,

$$C_0(k) = -(4\pi a^2/k)\,j_1(ka) \tag{12}$$

where j_1 is a Bessel function. The collision integral I is (6)

$$\begin{aligned} I(\tilde{\eta}(\mathbf{k}, \mathbf{v}, s)) &\equiv \int d\mathbf{v}_0\,\mathscr{B}(\mathbf{k}, s \mid \mathbf{v}, \mathbf{v}_0)\,\tilde{\eta}(\mathbf{k}, \mathbf{v}_0, s) \\ &= a^2 \int d\mathbf{v}_2 \int d\hat{\boldsymbol{\kappa}}\,(\mathbf{v}_2 - \mathbf{v}_1)\cdot\hat{\boldsymbol{\kappa}}\epsilon\{(\mathbf{v}_2 - \mathbf{v}_1)\cdot\hat{\boldsymbol{\kappa}}\} \\ &\quad\times \{h_0(v_2')\,\tilde{\eta}(\mathbf{k}, \mathbf{v}_1', s) - h_0(v_2)\,\tilde{\eta}(\mathbf{k}, \mathbf{v}_1, s) \\ &\quad+ h_0(v_1')[\exp(-ia\mathbf{k}\cdot\hat{\boldsymbol{\kappa}})]\,\tilde{\eta}(\mathbf{k}, \mathbf{v}_2', s) \\ &\quad- h_0(v_1)[\exp(ia\mathbf{k}\cdot\hat{\boldsymbol{\kappa}})]\,\tilde{\eta}(\mathbf{k}, \mathbf{v}_2, s)\} \end{aligned} \tag{13}$$

where

$$\mathbf{v}_1' = \mathbf{v}_1 + \hat{\boldsymbol{\kappa}}[(\mathbf{v}_2 - \mathbf{v}_1)\cdot\hat{\boldsymbol{\kappa}}], \qquad \text{and} \qquad \mathbf{v}_2' = \mathbf{v}_2 - \hat{\boldsymbol{\kappa}}[(\mathbf{v}_2 - \mathbf{v}_1)\cdot\hat{\boldsymbol{\kappa}}] \tag{14}$$

It is convenient for reasons which will become apparent in Section 4 to introduce a new collision operator B which is defined by

$$\begin{aligned}\int d\mathbf{v}_0\, B(\mathbf{k}, s \mid \mathbf{v}, \mathbf{v}_0)\, \tilde{\eta}(\mathbf{k}, \mathbf{v}_0, s) &= ih_0(v)\, \mathbf{v}\cdot\mathbf{k}C_0(k) \int d\mathbf{v}_0\, \tilde{\eta}(\mathbf{k}, \mathbf{v}_0, s)\\ &\quad + \int d\mathbf{v}_0\, \mathscr{B}(\mathbf{k}, s \mid \mathbf{v}, \mathbf{v}_0)\, \tilde{\eta}(\mathbf{k}, \mathbf{v}_0, s)\end{aligned} \tag{15}$$

Then the kinetic equation can be written as

$$\begin{aligned}(s - i\mathbf{k}\cdot\mathbf{v})\, \tilde{\eta}(\mathbf{k}, \mathbf{v}, s) = \eta(\mathbf{k}, \mathbf{v}, 0)&\\ - ih_0(v)\, \mathbf{v}\cdot\mathbf{k}\rho V(k)\, \tilde{n}(\mathbf{k}, s)&\\ + \xi(k) \int d\mathbf{v}_0\, B(\mathbf{k}, s \mid \mathbf{v}, \mathbf{v}_0)\, \tilde{\eta}(\mathbf{k}, \mathbf{v}_0, s)&\end{aligned} \tag{16}$$

where

$$V(k) = C(k); \qquad \xi(k) = \rho g(a) \tag{17}$$

3.1. The Enskog Equation

We now show that the Enskog equation also leads to Eq. (16) but with a different effective potential $V(k)$.

The Enskog equation is⁽⁸⁾

$$\frac{\partial}{\partial t} f(\mathbf{r}, \mathbf{v}_1, t) + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}} f(\mathbf{r}, \mathbf{v}_1, t) = I_E(\mathbf{r}, \mathbf{v}_1, t) \tag{18}$$

where

$$\begin{aligned}I_E(\mathbf{r}, \mathbf{v}_1, t) = a^2 \int d\mathbf{v}_2 \int d\hat{\boldsymbol{\kappa}}\, (\mathbf{v}_2 - \mathbf{v}_1)\cdot\hat{\boldsymbol{\kappa}}\epsilon\{(\mathbf{v}_2 - \mathbf{v}_1)\cdot\hat{\boldsymbol{\kappa}}\}&\\ \times [\chi(\mathbf{r} + \tfrac{1}{2}a\hat{\boldsymbol{\kappa}}) f(\mathbf{r}, \mathbf{v}_1', t) f(\mathbf{r} + a\hat{\boldsymbol{\kappa}}, \mathbf{v}_2', t)&\\ - \chi(\mathbf{r} - \tfrac{1}{2}a\hat{\boldsymbol{\kappa}}) f(\mathbf{r}, \mathbf{v}_1, t) f(\mathbf{r} - a\hat{\boldsymbol{\kappa}}, \mathbf{v}_2, t)]&\end{aligned}$$

Here, $\mathbf{v}_1'$ and $\mathbf{v}_2'$ are given in Eq. (14) and

$$\begin{aligned}\epsilon(x) &= 0 \quad \text{for} \quad x < 0\\ &= 1 \quad \text{for} \quad 0 < x\end{aligned} \tag{19}$$

We now put

$$f(\mathbf{r}, \mathbf{v}, t) = \rho h_0(v) + \eta(\mathbf{r}, \mathbf{v}, t)$$

and keep only those terms which are linear in the displacement from equilibrium $\eta(\mathbf{r}, \mathbf{v}, t)$. For the function $\chi(\mathbf{r})$, we follow the method of Gross and Wisnivesky$^{(9)}$ and take it to be the radial distribution function at contact at the density

$$\rho(\mathbf{r}, t) = \int d\mathbf{v}\, f(\mathbf{r}, \mathbf{v}, t) = \rho + \int d\mathbf{v}\, \eta(\mathbf{r}, \mathbf{v}, t) \tag{20}$$

Then

$$\chi(\mathbf{r}) = g(a)|_{\rho=\rho(\mathbf{r},t)} = g(a) + [dg(a)/d\rho] \int d\mathbf{v}\, \eta(\mathbf{r}, \mathbf{v}, t) + O(\eta^2) \tag{21}$$

where $g(a)$ is at the equilibrium density ρ. The linearized equation is

$$\begin{aligned}
&\frac{\partial}{\partial t}\, \eta(\mathbf{r}, \mathbf{v}_1, t) + \mathbf{v}_1 \cdot \frac{\partial}{\partial \mathbf{r}}\, \eta(\mathbf{r}, \mathbf{v}_1, t) \\
&\quad = \rho^2 a^2 \frac{dg(a)}{d\rho}\, h_0(v_1) \int d\mathbf{v}_2 \int d\hat{\boldsymbol{\kappa}}\, (\mathbf{v}_2 - \mathbf{v}_1) \cdot \hat{\boldsymbol{\kappa}} \epsilon\{(\mathbf{v}_2 - \mathbf{v}_1) \cdot \hat{\boldsymbol{\kappa}}\} \\
&\qquad \times h_0(v_2) \int d\mathbf{v}\, [\eta(\mathbf{r} + \tfrac{1}{2}a\hat{\boldsymbol{\kappa}}, \mathbf{v}, t) - \eta(\mathbf{r} - \tfrac{1}{2}a\hat{\boldsymbol{\kappa}}, \mathbf{v}, t)] \\
&\qquad + \rho a^2 g(a) \int d\mathbf{v}_2 \int d\hat{\boldsymbol{\kappa}}\, (\mathbf{v}_2 - \mathbf{v}_1) \cdot \hat{\boldsymbol{\kappa}} \epsilon\{(\mathbf{v}_2 - \mathbf{v}_1) \cdot \hat{\boldsymbol{\kappa}}\} \\
&\qquad \times [h_0(v_2')\, \eta(\mathbf{r}, \mathbf{v}_1', t) + h_0(v_1')\, \eta(\mathbf{r} + a\hat{\boldsymbol{\kappa}}, \mathbf{v}_2', t) \\
&\qquad - h_0(v_2)\, \eta(\mathbf{r}, \mathbf{v}_1, t) - h_0(v_1)\, \eta(\mathbf{r} - a\hat{\boldsymbol{\kappa}}, \mathbf{v}_2, t)]
\end{aligned} \tag{22}$$

The Fourier–Laplace transform of this equation is the same as Eq. (16) with the effective potential

$$V(k) = \rho[dg(a)/d\rho]\, \tfrac{1}{2}C_0(k/2) + g(a)\, C_0(k) \tag{23}$$

The equation of state for a system of hard spheres is $^{(14)}$

$$\beta p = \rho[1 + \tfrac{2}{3}\pi a^3 \rho g(a)] \tag{24}$$

and $g(a)$ is independent of the temperature $T = 1/k\beta$. Furthermore, the direct correlation function at $k = 0$ is given by

$$1 - \rho C(0) = (\partial/\partial\rho)(\beta p)|_T \tag{25}$$

so that

$$C(0) = -\tfrac{4}{3}\pi a^3 g(a) - \tfrac{2}{3}\pi a^3 \rho\, dg(a)/d\rho \tag{26}$$

The last equation can be used to eliminate $dg(a)/d\rho$ from Eq. (23). The final results for the linearized Enskog equation are

$$V(k) = [C(0) - g(a)\, C_0(0)][C_0(k/2)/C_0(0)] + g(a)\, C_0(k) \tag{27}$$

and

$$\xi(k) = \rho g(a) \tag{28}$$

3.2. The Memory Function Equation of Mazenko, Wei, and Yip

Mazenko(15) has used a thermodynamic Green's function method to calculate in the low-density limit the memory function ϕ associated with the correlation function

$$\begin{aligned} &S(\mathbf{r} - \mathbf{r}', \mathbf{p}, \mathbf{p}', t - t') \\ &\quad = \langle [f(\mathbf{r}, \mathbf{p}, t) - \langle f(\mathbf{r}, \mathbf{p}, t)\rangle][f(\mathbf{r}', \mathbf{p}', t') - \langle f(\mathbf{r}, \mathbf{p}', t')\rangle]\rangle \end{aligned} \tag{29}$$

where

$$f(\mathbf{r}, \mathbf{p}, t) = \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j(t))\, \delta(\mathbf{p} - \mathbf{p}_j(t)) \tag{30}$$

In the notation of this paper, S can be written as

$$S(\mathbf{r} - \mathbf{r}', m\mathbf{v}, m\mathbf{v}', t) = (1/m^6)\, \eta(\mathbf{r}, \mathbf{v}, t/\mathbf{r}', \mathbf{v}')\, \rho h_0(v') \tag{31}$$

where the conditional distribution η is given by Eq. (3). By multiplying Mazenko's equation for S by $m^6 W(\mathbf{r}', \mathbf{v}')/\rho h_0(v')$ and integrating over $\mathbf{r}'$ and $\mathbf{v}'$, it can be written as a kinetic equation for $\eta(\mathbf{r}, \mathbf{v}, t)$.

Recently, Mazenko *et al.*(11) have evaluated the memory function ϕ for a classical system of hard spheres, calculated the scattering function $S(\mathbf{k}, \omega)$, and compared the results with the linearized Boltzmann equation. The scattering function will be discussed in Section 4; here, we will show that the equation of Mazenko *et al.* is also equivalent to Eq. (16).

The Fourier–Laplace transform of the memory function(11) $\phi(\mathbf{k}, \mathbf{p}, \mathbf{p}', is)$ is independent of s and has three parts denoted by $\phi^{(s)}(\mathbf{k}, \mathbf{p})$, $\phi_1^{(c)}(\mathbf{k}, \mathbf{p}, \mathbf{p}')$, and $\phi_2^{(c)}(\mathbf{k}, \mathbf{p}, \mathbf{p}')$, each part giving a contribution to the kinetic equation for $\tilde{\eta}(\mathbf{k}, \mathbf{v}, s)$. From $\phi^{(s)}(\mathbf{k}, \mathbf{p})$, we get the term

$$-ih_0(v)\, \mathbf{v} \cdot \mathbf{k} \rho C(k)\, \tilde{n}(\mathbf{k}, s) \tag{32}$$

Since the memory function is only valid to leading order in the density, Mazenko *et al.* replace $C(k)$ by its zero density limit, that is, $C_0(k)$. The term $\phi_1^{(c)}(\mathbf{k}, \mathbf{p}, \mathbf{p}')$ gives a collision integral which is similar to

$$\int d\mathbf{v}_0\, \mathscr{B}(\mathbf{k}, s \mid \mathbf{v}, \mathbf{v}_0)\, \tilde{\eta}(\mathbf{k}, \mathbf{v}_0, s)$$

Table III. Coefficients for the Kinetic Equation (16)

	$V(k)$	$\xi(k)$
Enskog equation	$[C(0) - g(a)C_0(0)][C_0(k/2)/C_0(0)] + g(a)C_0(k)$	$\rho g(a)$
Short-time Equation	$C(k)$	$\rho g(a)$
Mazenko *et al.*$^{(11)}$	$C_0(k)$	ρ

but differs from it by a change of sign in one of the exponential factors $\exp(ia\mathbf{k}\cdot\hat{\boldsymbol{\kappa}})$. When the contribution from $\phi_1^{(c)}(\mathbf{k}, \mathbf{p}, \mathbf{p}')$ is written as the operator $\mathscr{B}$ with two correction terms, one of the correction terms exactly cancels the contribution from $\phi_2^{(c)}(\mathbf{k}, \mathbf{p}, \mathbf{p}')$ and the combination $\phi_1^{(c)} + \phi_2^{(c)}$ leads to

$$\rho \int d\mathbf{v}_0 \, B(\mathbf{k}, s \mid \mathbf{v}, \mathbf{v}_0) \, \tilde{\eta}(\mathbf{k}, \mathbf{v}_0, s) \tag{33}$$

The resulting kinetic equation is Eq. (16) with

$$V(k) = C_0(k); \qquad \xi(k) = \rho \tag{34}$$

The results of the three different theories are summarized in Table III. In the limit $\rho \to 0$, $C(k) \to C_0(k)$ and $g(a) \to 1$. The Enskog and short-time equations are then identical and furthermore equivalent to the equation of Mazenko *et al.* (The latter authors$^{(11)}$ also derive an equation for the self-distribution function which is the same as the third line of Table I when $g(a)$ is replaced by 1.) In the limit $k \to 0$, $C(k) = C(0) + O(k^2)$ and the Enskog and short-time effective potentials are again identical to order k^2.

4. THE SCATTERING FUNCTION

The Fourier–Laplace transform $\tilde{\chi}(\mathbf{k}, s)$ of the van Hove function $G(\mathbf{r}, t)$ is given by

$$\tilde{\chi}(\mathbf{k}, s) = \int d\mathbf{v} \, \tilde{\eta}(\mathbf{k}, \mathbf{v}, s) \tag{35}$$

where $\tilde{\eta}(\mathbf{k}, \mathbf{v}, s)$ is the solution of a kinetic equation, Eq. (16) in this paper, with the initial condition

$$\eta(\mathbf{k}, \mathbf{v}, 0) = S(k) \, h_0(v) \tag{36}$$

and

$$S(k) = 1/[1 - \rho C(k)] \tag{37}$$

The coherent scattering function $S(\mathbf{k}, \omega)$ is then defined by

$$S(\mathbf{k}, \omega) = (1/\pi) \operatorname{Re} \tilde{\chi}(\mathbf{k}, i\omega)$$

Although the kinetic equations for hard spheres discussed in Section 3 cannot be solved analytically, we can obtain some information about $\tilde{\chi}(\mathbf{k}, s)$ by using the methods of Ref. 6, Section VII. In writing the kinetic equation (16), we have chosen the collision integral B so that

$$\int d\mathbf{v}\, B(\mathbf{k}, s \mid \mathbf{v}, \mathbf{v}') = 0 \tag{38}$$

and

$$B(\mathbf{k}, s \mid \mathbf{v}, \mathbf{v}')\, h_0(v') = B(\mathbf{k}, s \mid \mathbf{v}', \mathbf{v})\, h_0(v) \tag{39}$$

If we now introduce a Green's function G_0 which is the solution of the equation

$$\begin{aligned}(s - i\mathbf{k} \,.\, \mathbf{v})\, G_0(\mathbf{k}, s \mid \mathbf{v}, \mathbf{v}') &= \delta(\mathbf{v} - \mathbf{v}') \\ &\quad + \xi(k) \int d\mathbf{w}\, B(\mathbf{k}, s \mid \mathbf{v}, \mathbf{w})\, G_0(\mathbf{k}, s \mid \mathbf{w}, \mathbf{v}')\end{aligned} \tag{40}$$

then from (38) and (39), G_0 satisfies the conditions

$$i\mathbf{k} \cdot \int d\mathbf{v}\, \mathbf{v} G_0(\mathbf{k}, s \mid \mathbf{v}, \mathbf{v}') = s \int d\mathbf{v}\, G_0(\mathbf{k}, s \mid \mathbf{v}, \mathbf{v}') - 1 \tag{41}$$

and

$$G_0(\mathbf{k}, s \mid \mathbf{v}, \mathbf{v}')\, h_0(v') = G_0(\mathbf{k}, s \mid \mathbf{v}', \mathbf{v})\, h_0(v) \tag{42}$$

These are just the conditions for the method of Ref. 6 to apply, so we quote the final result

$$\begin{aligned}\frac{[1 - \rho V(k)]\, \tilde{\sigma}(\mathbf{k}, s)}{1 - s\rho V(k)\, \tilde{\sigma}(\mathbf{k}, s)} &= \int d\mathbf{v} \int d\mathbf{v}'\, G_0(\mathbf{k}, s \mid \mathbf{v}, \mathbf{v}')\, h_0(v') \\ &\equiv \Phi(\mathbf{k}, s \mid \xi(k))\end{aligned} \tag{43}$$

where

$$\tilde{\sigma}(\mathbf{k}, s) = \tilde{\chi}(\mathbf{k}, s)/S(k) \tag{44}$$

The right side of Eq. (43) is obtained from the solution of Eq. (40) and so only depends on $\xi(k)$ and not on $V(k)$. By making appropriate choices for $V(k)$ and $\xi(k)$, we can use the above equations to relate the scattering function derived from the short-time equation with those from the Enskog and memory function equations.

4.1. Short-Time and Enskog Results

For the short-time equation, we have

$$\frac{[1-\rho C(k)]\,\tilde{\sigma}(\mathbf{k},s)}{1-s\rho C(k)\,\tilde{\sigma}(\mathbf{k},s)}=\Phi(\mathbf{k},s\mid\rho g(a)) \tag{45}$$

and for the Enskog equation

$$\frac{[1-\rho V_E(k)]\,\tilde{\sigma}_E(\mathbf{k},s)}{1-s\rho V_E(k)\,\tilde{\sigma}_E(\mathbf{k},s)}=\Phi(\mathbf{k},s\mid\rho g(a)) \tag{46}$$

Here, functions without subscripts refer to the short-time expressions and functions with subscripts E refer to the Enskog expressions: $V_E(k)$ is given in the first line of Table III. Since the right sides of (45) and (46) are identical, we find

$$\tilde{\sigma}(\mathbf{k},s)=\frac{[1-\rho V_E(k)]\,\tilde{\sigma}_E(\mathbf{k},s)}{1-\rho C(k)+s\rho[C(k)-V_E(k)]\,\tilde{\sigma}_E(\mathbf{k},s)} \tag{47}$$

Thus, if the scattering function is known for the Enskog equation, then it can be calculated for the short-time equation and vice versa. Neither of these functions has in fact been calculated but we can obtain some interesting results by examining the short-time and hydrodynamic limits.

In the short-time limit, that is, for large values of s,

$$\tilde{\chi}(\mathbf{k},s)=\frac{1}{s}\sum_{j=0}^{\infty}\frac{1}{s^j}\,\chi_j(k) \tag{48}$$

where $\chi_j(k)$ denotes the jth sum rule

$$\chi_j(k)=\left.\frac{d^j\chi(k,t)}{dt^j}\right|_{t=0^+} \tag{49}$$

In particular,

$$\chi_0(k)=S(k)$$

and we expect

$$\chi_1(k)=0$$

If we use a similar expression for the Enskog function $\tilde{\chi}_E(\mathbf{k},s)$ with sum rules $\chi_j^E(k)$, then from (47), we find

$$\begin{aligned}\chi_0(k)&=\chi_0^E(k)=S(k)\\ \chi_1(k)&=\chi_1^E(k)=0\\ \chi_2(k)&=\{[1-\rho C(k)]/[1-\rho V_E(k)]\}\,\chi_2^E(k)\\ \chi_3(k)&=\{[1-\rho C(k)]/[1-\rho V_E(k)]\}\,\chi_3^E(k)\end{aligned} \tag{50}$$

etc. We know from previous work that the first four sum rules ($j = 0, 1, 2, 3$) for the short-time equation are exact,(6) whereas only the first two ($j = 0, 1$) are exact when the Enskog equation is used.(9) These results are consistent with (50). Furthermore, we can see that in the limit $\rho \to 0$ and in the limit $k \to 0$, the third and fourth Enskog sum rules become exact.

In the hydrodynamic limit, we expect the intermediate scattering function $\chi(\mathbf{k}, t)$ to be given by(16)

$$\begin{aligned}\sigma(\mathbf{k}, t) &= \frac{\chi(\mathbf{k}, t)}{S(k)} \qquad (51)\\ &= \left(1 - \frac{C_V}{C_P}\right) \exp[-(\kappa/\rho C_P)\, k^2 t] + \frac{C_V}{C_P} \cos(ukt) \exp(-\Gamma k^2 t)\end{aligned}$$

where

$$2\Gamma = \frac{1}{\rho}\left(\frac{4}{3}\eta + \zeta\right) + \frac{\kappa}{\rho C_P}\left(\frac{C_P}{C_V} - 1\right)$$

Here, C_V and C_P are the specific heats; u is the velocity of sound; κ is the thermal conductivity; and η and ζ the coefficients of shear and bulk viscosity. Then

$$\begin{aligned}\tilde{\sigma}(\mathbf{k}, s) = {} & \left[s^2 + k^2u^2\left(1 - \frac{C_V}{C_P}\right) + sk^2A + k^4B\right]\\ & \times \left[s^3 + sk^2u^2 + s^2k^2\left(2\Gamma + \frac{\kappa}{\rho C_P}\right)\right.\\ & \left. + k^4u^2 \frac{\kappa}{\rho C_P} + sk^4C + k^6D\right]^{-1} \qquad (52)\end{aligned}$$

where the coefficients A, B, C, and D are functions of u^2, C_V/C_P, $(\kappa/\rho C_P)$, and Γ. In practice, we start with an approximate kinetic equation and try to calculate $\tilde{\sigma}(\mathbf{k}, s)$ in the limit $s \to 0$, $k \to 0$ with s/k constant. Because the kinetic equation is approximate, the hydrodynamic limit will not necessarily be (52) with the correct coefficients A, B, C, and D (see, for example, Ref. 6, Appendix B). We will take the hydrodynamic limit to be Eq. (52) but will not specify the coefficients A, B, C, and D which are associated with the higher-order terms in the numerator and denominator. From Eq. (47), we find that if the Enskog expression has a hydrodynamic limit of the form of Eq. (52), then so does the short-time result to leading order and

$$\frac{C_P}{C_V} = \left(\frac{C_P}{C_V}\right)_E; \qquad u^2 = u_E{}^2; \qquad \frac{\kappa}{\rho C_P} = \left(\frac{\kappa}{\rho C_P}\right)_E; \qquad \Gamma = \Gamma_E \qquad (53)$$

so that

$$\tfrac{4}{3}\eta + \zeta = (\tfrac{4}{3}\eta + \zeta)_E \qquad (54)$$

4.2. Short-Time and Memory Function Results

For the memory function approach of Mazenko *et al.*,(11) we find from Eq. (43) for a system at density ρ_0

$$\frac{[1-\rho_0 C_0(k)]\,\tilde{\sigma}_0(\mathbf{k},s)}{1-s\rho_0 C_0(k)\,\tilde{\sigma}_0(\mathbf{k},s)} = \Phi(\mathbf{k}, S \mid \rho_0) \tag{55}$$

where

$$\tilde{\sigma}_0(\mathbf{k},s) = \tilde{\chi}_0(\mathbf{k},s)/S_0(k) \tag{56}$$

Here $\tilde{\chi}_0(\mathbf{k},s)$ is the scattering function calculated from the memory function equation for a system at density ρ_0 and $S_0(k)$ is the expansion of $S(k)$ up to linear order in the density ρ_0, that is,

$$S_0(k) = 1 + \rho_0 C_0(k) \tag{57}$$

where $C_0(k)$ is independent of the density and is defined in Eq. (12). The right side of Eq. (55) can be made equal to the right side of Eq. (45) by choosing

$$\rho_0 = \rho g(a) \tag{58}$$

Then

$$\tilde{\sigma}(\mathbf{k},s) = \frac{[1-\rho_0 C_0(k)]\,\tilde{\sigma}_0(\mathbf{k},s)}{\{1-\rho C(k) + s[\rho C(k) - \rho_0 C_0(k)]\,\tilde{\sigma}_0(\mathbf{k},s)\}} \tag{59}$$

where $\tilde{\sigma}(\mathbf{k},s)$ and $C(k)$ are at the density ρ defined by Eq. (58).

As in Section 4.1, we can use Eq. (59) to relate the short-time sum rules and hydrodynamic limit for a system at density ρ to the memory function sum rules and hydrodynamic limit for a system at density ρ_0. Because of the relationship between ρ and ρ_0, Eq. (58), the results are not simple and so will not be written down.

5. CONCLUSION

The scattering function $\tilde{\sigma}(\mathbf{k},s)$ calculated from the short-time kinetic equation satisfies the first four sum rules, whereas $\tilde{\sigma}(\mathbf{k},s)$ derived from the Enskog equation only satisfies the first two sum rules. In the hydrodynamic limit, the scattering functions are the same to leading order. Therefore, we conclude that the short-time equation gives the better description of the scattering function throughout the $(\mathbf{k},s)$ plane. This is confirmed for a one-dimensional system of hard rods, where the exact solution is known.(17) For this system, the short-time equation gives the exact result(18) for $\tilde{\sigma}(\mathbf{k},s)$ but the Enskog equation is exact only in the hydrodynamic limit.(19)

ACKNOWLEDGMENT

It is a pleasure to acknowledge the usefulness of several discussions with Professor J. L. Lebowitz about this work.

NOTE ADDED IN PROOF

Since this paper was written, G. F. Mazenko has developed a Fully Renormalized Kinetic Theory for both the self and total distribution functions [*Phys. Rev.* **A7**:209 and 222 (1973) and preprint.] This theory is very powerful and to leading order gives the same kinetic equations for a system of hard spheres as those obtained from the short time method discussed here. Thus the conclusions of this paper also apply to the recent work of Mazenko. The kinetic equation for the total distribution function has also been derived recently by different methods by H. van Beijeren and M. H. Ernst [*Phys. Letters* **A43**:367 (1973)] and H. H. U. Konijnendijk and J. M. J. van Leeuwen [*Physica* **64**:342 (1973)]. The conclusions of these authors regarding the comparison with the Enskog equation are the same as ours.

REFERENCES

1. L. van Hove, *Phys. Rev.* **95**:249 (1954).
2. M. Nelkin and A. Ghatak, *Phys. Rev.* **135**:A4 (1964); S. Yip and M. Nelkin, *Phys. Rev.* **135**:A1241 (1964).
3. R. Zwanzig, *Lectures in Theoretical Physics*, ed. W. E. Brittin, Wiley, New York, 1961.
4. H. Mori, *Progr. Theoret. Phys.* **33**:423 (1965).
5. M. Nelkin, *Phys. Rev.* **183**:349 (1969).
6. J. L. Lebowitz, J. K. Percus, and J. Sykes, *Phys. Rev.* **188**:487 (1969).
7. D. Levesque and L. Verlet, *Phys. Rev.* **2A**:2514 (1970).
8. D. Enskog, *Kgl. Svenska Vetenskap. Hand.* **4**:63 (1922); S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, Cambridge University Press, London, 1953; J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954.
9. E. P. Gross and D. Wisnivesky, *Phys. Fluids* **11**:1387 (1968).
10. S. Ranganathan and M. Nelkin, *J. Chem. Phys.* **47**:4056 (1967).
11. G. F. Mazenko, T. Y. C. Wei, and S. Yip, *Phys. Rev.* **A6**:1981 (1972).
12. R. Zwanzig, *Phys. Rev.* **144**:170 (1966); M. Nelkin and S. Ranganathan, *Phys. Rev.* **164**:222 (1967); T. Morita, *J. Phys. Soc. Japan, Suppl.* **26**:286 (1969).
13. A. Z. Akcasu and J. J. Duderstadt, *Phys. Rev.* **188**:479 (1969); *Phys. Rev.* **A1**:905 (1970).
14. H. L. Frisch, *Adv. Chem. Phys.* **VI**:229 (1964).
15. G. F. Mazenko, *Phys. Rev.* **A3**:2121 (1971).
16. L. P. Kadanoff and P. C. Martin, *Ann. Phys.* (*N.Y.*) **24**:419 (1963); R. D. Mountain, *Rev. Mod. Phys.* **38**:205 (1966).
17. D. W. Jepsen, *J. Math. Phys.* **6**:405 (1965); J. L. Lebowitz and J. K. Percus, *Phys. Rev.* **155**:122 (1967).
18. J. L. Lebowitz, J. K. Percus, and J. Sykes, *Phys. Rev.* **171**:224 (1968).
19. J. K. Percus, *Phys. Fluids* **12**:1560 (1969).