Journal of Statistical Physics, Vol. 27, No. 1, 1982

Evaluation of Time Correlation Functions From a Generalized Enskog Equation

Sidney Yip,[1] W. E. Alley[2] and B. J. Alder[2]

Received August 27, 1980; revised May 5, 1981

Numerical results for the density and current correlation functions in dense hard-sphere fluids are obtained from a kinetic equation which is the extension of the linearized Enskog equation to finite wavelengths in order to demonstrate the convergence of the method of solution. Comparison is made to a previously proposed approximate solution.

KEY WORDS: Space-time correlation functions; convergence of matrix expansion.

1. INTRODUCTION

The Enskog transport equation is an intuitive but successful extension of the Boltzmann equation for hard-sphere particles to moderate gas densities.(1) Although it is widely used for the analysis of transport coefficients,(2) it has been used only in a limited way as a complete description of space-time correlation functions.(3) In the various attempts to derive kinetic equations for dense gases valid at finite wavelengths and frequencies, a result similar to Enskog's has been obtained(4–10) which, however, preserves certain short-time properties that are violated by the Enskog theory. This newer equation gives the same thermodynamic properties and transport coefficients as the Enskog equation; it will be called the generalized Enskog equation in the sense that it more correctly incorporates fluctuation effects at finite wavelengths.

This work was performed in part under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under contract number W-7405-ENG-48 and in part supported by the National Science Foundation.

[1] Department of Nuclear Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

[2] Lawrence Livermore National Laboratory, Livermore, California 94550.

0022-4715/82/0100-0201$03.00/0 © 1982 Plenum Publishing Corporation

In the generalized Enskog equation, as in all kinetic equations characterized by a Boltzmann-type collision integral, collisional dynamics are treated explicitly only as uncorrelated binary collisions. While this approximation becomes inaccurate at high densities, it is always exact at short times. Furthermore, the assumption of molecular chaos makes the kinetic equation amenable to analysis using methods that have been applied to the Boltzmann equation. Thus, the method of kinetic models which has been used to calculate time correlation functions for a low-density gas(11) can be directly applied to the generalized Enskog equation.(6) Because the computational efforts required to calculate time correlation functions using the full kinetic equation are considerable, a low-order kinetic model has been proposed.(12) This model is basically a relaxation-time approximation that treats the collision integral in terms of a few matrix elements for which analytical expressions have been obtained. The model, called QTRT, was intended to be a compromise between accuracy and computational simplicity. It has recently been discovered(13) that this model fails to approach the hydrodynamic limit in the long-wavelength limit due to an improper choice of the sound damping constant.(14) The corrected model, employed here, shall be referred to as QFRT.(15)

The purpose of this paper is to solve the generalized Enskog equation in order to obtain accurate space-time correlation functions. The recent availability of computer molecular dynamics data on density and current correlation functions for hard-sphere fluids at various densities(16) has made it important to have an accurate reference theory for comparison purposes. The main objective of this work is to demonstrate numerical convergence of the method of solution and to determine the accuracy of QFRT. Although the convergence of the expansion of the collision integral is independent of density, results at higher densities will be given in order to illustrate the relative importance of the collision term to the density-dependent streaming term. In the following the generalized Enskog equation is formulated, the method of solution is outlined, the rate of convergence is demonstrated, and finally the results are discussed.

2. THE GENERALIZED ENSKOG EQUATION

The phase-space density correlation function, whose Fourier–Laplace transform in space and time is

$$\tilde{C}(k\bar{p}\bar{p}'s) = \int d^3r \int_0^\infty dt\, e^{i\bar{k}\cdot\bar{r}-st}$$
$$\times \frac{1}{N}\sum_{l,l'}\left\langle \delta\big(\bar{r}-\bar{R}_l(t)\big)\delta\big(\bar{p}-\bar{P}_l(t)\big)\delta\big(\bar{R}_{l'}\big)\delta\big(\bar{p}'-\bar{P}_{l'}\big)\right\rangle \quad (2.1)$$

obeys the kinetic equation

$$\left(s-\frac{i\bar{k}\cdot\bar{p}}{m}\right)\tilde{C}(k\bar{p}\bar{p}'s)-\frac{i\bar{k}\cdot\bar{p}}{m}nf_0(p)\Lambda(k)\int d^3p''\,\tilde{C}(k\bar{p}''\bar{p}'s)$$
$$=g(\sigma)J[\tilde{C}]+C(k\bar{p}\bar{p}'0) \tag{2.2}$$

where

$$\begin{aligned}\Lambda(k)&=C(k)-g(\sigma)C_0(k)\\ C_0(k)&=4\pi\sigma^2 j_1(k\sigma)/k\end{aligned} \tag{2.3}$$

and

$$J[\tilde{C}]=n\sigma^2\int_{\bar{\Omega}\cdot\Delta\bar{p}<0}d\Omega\,d^3p\,\frac{|\bar{\Omega}\cdot\Delta\bar{p}|}{m}$$
$$\times\Big[f_0(\bar{p}^*)\tilde{C}(\bar{p}^*\bar{p}')-f_0(\bar{p})\tilde{C}(\bar{p}\bar{p}')$$
$$+e^{-i\bar{k}\cdot\bar{\Omega}\sigma}f_0(\bar{p}^*)\tilde{C}(\bar{p}^*\bar{p}')-e^{i\bar{k}\cdot\bar{\Omega}\sigma}f_0(\bar{p})\tilde{C}(\bar{p}\bar{p}')\Big] \tag{2.4}$$

Here $f_0(\bar{p})$ is the normalized Maxwellian distribution, $g(\sigma)$ the pair distribution function at contact, $C(k)$ the direct correlation function, j_1 the first-order spherical Bessel function, $\Delta\bar{p}=\bar{p}-\bar{p}'$, and

$$C(kpp'0)=f_0(\bar{p})(\bar{p}-\bar{p}')+f_0(\bar{p})f_0(\bar{p}')[S(k)-1] \tag{2.5}$$

where $S(k)$ is the static structure factor. In Eq. (2.4) the asterisk denotes postcollision momentum, and the dependence of C on k and s has been suppressed.

Equation (2.2) was first derived in a study of kinetic equations valid at short times,(4) and the same result was later obtained in a number of different derivations.(5–10) The term containing $\Lambda(k)$, often called the mean-field term, is seen to be in the form of a contribution arising from a time-dependent self-consistent field, with $-\beta^{-1}\Lambda(k)$ playing the role of an effective potential. The collision integral $J[C]$, aside from the phase factor $\exp(\pm i\bar{k}\cdot\bar{\Omega}\sigma)$, is the one which appears in the linearized Boltzmann equation. Density effects are accounted for through the equilibrium correlations $S(k)$ and $g(\sigma)$.

Comparing Eq. (2.2) with the earlier Enskog equation one finds the two equations differ only in the expression for $\Lambda(k)$.(10) Instead of Eq. (2.3) the earlier Enskog equation gives

$$\Lambda(k)=\frac{C(0)C_0(k/2)}{C_0(0)}-g(\sigma)C_0(k/2) \tag{2.6}$$

The difference appears to be due to two causes: To extend Enskog to finite k one would expect that all quantities such as $C(0)$ should be replaced by their corresponding k-dependent functions. In addition the relevant functions should be evaluated at the positions of the colliding particles rather than at the midpoint between them which leads to replacement of $C_0(k/2)$ by $C_0(k)$. These differences are the reason that the second and third frequency sum rules for the density correlation function are given correctly by Eq. (2.2) but not by the Enskog equation.(3,4) Consequently, Eq. (2.2) is the correct description at short times and should be regarded as the proper extension of the linearized Enskog equation to finite k and ω. The differences in $\Lambda(k)$ are important in the frequency–wave-number region relevant to neutron scattering experiments and computer molecular dynamics simulation. On the other hand, thermodynamic properties and transport coefficients are not affected by $\Lambda(k)$; therefore Eq. (2.2) gives the same results as the conventional Enskog theory.(8)

The kinetic equation corresponding to Eq. (2.2) for the description of the van Hove self-correlation function $\tilde{C}_s(k\bar{p}\bar{p}'s)$ is obtained by setting $\Lambda(k) = 0$, deleting the terms in Eq. (2.4) containing the phase factors $\exp(\pm i\bar{k} \cdot \bar{\Omega}\sigma)$, and setting $S(k) = 1$ in Eq. (2.5).(6,8) The absence of the mean-field term follows mathematically from symmetry arguments, and physically from the fact that the equilibrium distribution of the particles surrounding the tagged particle produces no net force,(4) since it is spherically symmetric. The resulting kinetic equation is thus identical to the Enskog equation for a tagged particle, and except for the factor of $g(\sigma)$ multiplying the collision integral, it is also identical to the Boltzmann equation for a tagged particle.

3. KINETIC MODEL REPRESENTATION

The space-time correlation functions explicitly evaluated are the number density correlation $F(k,t)$, the transverse current correlation $J_t(k,t)$, and the van Hove self-correlation $F_s(k,t)$. They are given by appropriate momentum integrals of $\tilde{C}(k\bar{p}\bar{p}'t)$ or $\tilde{C}_s(k\bar{p}\bar{p}'t)$. In terms of frequency transforms

$$\begin{aligned} S(k,\omega) &= 2\,\mathrm{Re}\int d^3p\, d^3p'\, \tilde{C}(k\bar{p}\bar{p}'s)|_{s=i\omega+\epsilon} \\ J_t(k,\omega) &= 2\,\mathrm{Re}\int d^3p\, d^3p'\, (\hat{a}\cdot\bar{p})(\hat{a}\cdot\bar{p}')\tilde{C}(k\bar{p}\bar{p}'s)|_{s=i\omega+\epsilon} \end{aligned} \tag{3.1}$$

and

$$S_s(k,\omega) = 2\,\mathrm{Re}\int d^3p\, d^3p'\, \tilde{C}_s(k\bar{p}\bar{p}'s)|_{s=i\omega+\epsilon} \tag{3.2}$$

where $\hat{a}$ is a unit vector perpendicular to $\bar{k}$.

For actual computations it is useful to cast Eq. (2.2) in the form of coupled equations involving only the momentum moments of $\tilde{C}(k\bar{p}\bar{p}'s)$. This is accomplished by means of a kinetic model representation of the collision operator.(17) A set of basis functions $\{\psi_\alpha(\bar{p})\}$, $\alpha = 1, \ldots,$ is introduced which is orthonormal with weight function $f_0(\bar{p})$ and complete. In addition, it is required that $\psi_1(\bar{p}) = 1$. Then Eq. (2.2) is rewritten as

$$\left(s - \frac{i\bar{k}\cdot\bar{p}}{m}\right)\tilde{C}(k\bar{p}\bar{p}'s) - \int d^3p''\,\tilde{\Sigma}(k\bar{p}\bar{p}'')\tilde{C}(k\bar{p}''\bar{p}'s) = C(k\bar{p}\bar{p}'0) \quad (3.3)$$

where $\tilde{\Sigma}$ will be called the memory function. The memory function is then expanded and the following approximation is made:

$$\begin{aligned}\tilde{\Sigma}(k\bar{p}\bar{p}') &= \sum_{\alpha,\beta}\psi_\alpha(\bar{p})\psi_\beta(\bar{p}')f_0(p)\Sigma(\alpha\,|\,\beta) \\ &\simeq \sum_{\alpha,\beta}^{N}\psi_\alpha(\bar{p})\psi_\beta(\bar{p}')f_0(p)\Sigma(\alpha\,|\,\beta) - \gamma(k) \\ &\quad\times \sum_{\alpha=N+1}^{\infty}\psi_\alpha(\bar{p})\psi_\alpha(\bar{p}')f_0(p) \end{aligned} \quad (3.4)$$

where

$$\Sigma(\alpha\,|\,\beta) = \int d^3p\,d^3p'\,\psi_\alpha(\bar{p})\psi_\beta(\bar{p}')f_0(p')\tilde{\Sigma}(k\bar{p}\bar{p}') \quad (3.5)$$

and $\gamma(k)$ is a k-dependent quantity to be determined separately. The integral in Eq. (3.3) then becomes

$$\begin{aligned}\int d^3p''\,\tilde{\Sigma}(k\bar{p}\bar{p}'')\tilde{C}(k\bar{p}''\bar{p}s) &= \sum_{\alpha,\beta}^{N}\sum_{\mu}\Gamma_{\alpha\beta}\tilde{C}_{\beta\mu}(ks)\psi_\alpha(\bar{p})\psi_\mu(\bar{p}')f_0(p)f_0(p') \\ &\quad - \gamma(k)\tilde{C}(k\bar{p}\bar{p}'s)\end{aligned} \quad (3.6)$$

where

$$\Gamma_{\alpha\beta} = \Sigma(\alpha\,|\,\beta) + \gamma(k)\delta_{\alpha\beta} \quad (3.7)$$

In arriving at Eq. (3.6) use has been made of the expansion

$$\tilde{C}(k\bar{p}\bar{p}'s) = \sum_{\alpha,\beta}\tilde{C}_{\alpha\beta}(ks)\psi_\alpha(\bar{p})\psi_\beta(\bar{p}')f_0(p)f_0(p') \quad (3.8)$$

with

$$\tilde{C}_{\alpha\beta}(ks) = \int d^3p\,d^3p'\,\psi_\alpha(\bar{p})\psi_\beta(\bar{p}')\tilde{C}(k\bar{p}\bar{p}'s) \quad (3.9)$$

Combining Eq. (3.6) with Eq. (3.3) leads to an explicit kinetic equation for $\tilde{C}(k\bar{p}\bar{p}'s)$ in terms of a finite matrix $\Gamma_{\alpha\beta}$; $\alpha, \beta \leqslant N$, and a set of its momentum integrals $C_{\alpha\beta}(k,s)$. To solve for the correlation functions the equation is multiplied by $\psi_\mu(\bar{p})\psi_\nu(\bar{p}')$ after first dividing through by $s - (i\bar{k}\cdot\bar{p})/m + \gamma(k)$; integrating over $\bar{p}$ and $\bar{p}'$ then gives the set of N algebraic equations

$$\tilde{C}_{\mu\nu}(ks) - \sum_{\alpha,\beta}^{N} \Gamma_{\alpha\beta} D_{\mu\alpha} \tilde{C}_{\beta\nu}(ks) = D_{\mu\nu} + D_{\mu 1}\delta_{\nu 1}\left[S(k) - 1\right] \tag{3.10}$$

where

$$D_{\mu\nu} = \int d^3p \, \frac{\psi_\mu(\bar{p})\psi_\nu(\bar{p}) f_0(p)}{s - (i\bar{k}\cdot\bar{p})/m + \gamma(k)} \tag{3.11}$$

To obtain the correlation functions one has to evaluate $\Gamma_{\alpha\beta}$ and $D_{\mu\nu}$ and then invert an $N \times N$ matrix. The particular set of momentum functions chosen for $\psi_\alpha(\bar{p})$ is based on the presence of the phase factors $\exp(\pm i\bar{k}\cdot\bar{\Omega}\sigma)$ in Eq. (2.4). These render the collision operator no longer spherically symmetric and, hence, the conventional Sonine polynominals are not the convenient basis functions.$^{(6)}$ Instead Hermite functions are chosen so that

$$\psi_{lmn}(\bar{\xi}) = \frac{(l!\,m!\,n)^{-1/2}}{2^{(l+m+n)/2}} H_l\left(\frac{\xi_x}{\sqrt{2}}\right) H_m\left(\frac{\xi_y}{\sqrt{2}}\right) H_n\left(\frac{\xi_z}{\sqrt{2}}\right) \tag{3.12}$$

where $H_l(x)$ is the standard Hermite polynomial, and $\bar{\xi} = \bar{p}/mv_0$. Then

$$\begin{aligned}
\Sigma(\alpha\,|\,\beta) = {} & nv_0 k\Lambda(k)\delta_{0l}\delta_{0m}\delta_{1n}\delta_{0l'}\delta_{0m'}\delta_{0n'} \\
& + \frac{8in\sigma^2 v_0 g(\sigma)}{(2\pi)^3} \int d^3\xi \, d^3\xi' \, d\Omega_r \, e^{-(\bar{\xi}-\bar{\xi}')^2 - \bar{\xi}'^2} (\hat{r}\cdot\bar{\xi}') H(\hat{r}\cdot\bar{\xi}') \\
& \times \psi_\alpha(\bar{\xi})\Big[\psi_\beta(\bar{\xi}) - \psi_\beta\big(\bar{\xi} - 2\hat{r}(\hat{r}\cdot\bar{\xi}')\big) + e^{i\bar{k}\cdot\bar{\Omega}\sigma}\psi_\beta(\bar{\xi} - 2\bar{\xi}') \\
& - e^{-i\bar{k}\cdot\bar{\Omega}\sigma}\psi_\beta\big(\bar{\xi} - 2\bar{\xi}' + 2\hat{r}(\hat{r}\cdot\bar{\xi}')\big)\Big]
\end{aligned} \tag{3.13}$$

with α representing the set of integers (l,m,n) and $\beta = (l',m',n')$. The evaluation of the integral expressions is quite tedious. The general expression has been reduced$^{(18)}$ to a series of nested sums that can be evaluated on a computer. The results are given in the Appendix. Large blocks of $\Sigma(\alpha\,|\,\beta)$ have been generated for $k = 0$ as well as several other k values, which correspond to molecular dynamics data, and used to compute the density and current correlation functions.$^{(16)}$ In addition, blocks of $\Sigma(\alpha\,|\,\beta)$ for $k\sigma = \infty$ were evaluated and used to calculate the van Hove self-correlation function.$^{(6)}$ For certain α and β corresponding to low-order integers (l,m,n) analytic expressions of $\Sigma(\alpha\,|\,\beta)$ have been derived.$^{(12)}$ Using only such matrix elements, the QFRT approximation is derived. These results will be discussed in the next section.

4. CONVERGENCE OF KINETIC MODELS

A kinetic model of order N is defined by Eq. (3.3) and Eq. (3.4), wherein a matrix $\Sigma(\alpha \mid \beta)$, with α, $\beta \leqslant N$, is used. The choice of $\gamma(k)$ also has to be specified. In the present calculations $\gamma(k) = \Sigma(N+1 \mid N+1)$. With Hermite functions as the basis set, the kinetic model order becomes the order of the polynomial $\psi_\alpha(\bar{p})$, i.e., $N = l + m + n$. The number of matrix elements in the square matrix $\Sigma(\alpha \mid \beta)$ of order N for the first few N values are given in Table I. The minimal kinetic model ($N = 2$) is that which preserves the collisional invariants, particle number, momentum, and energy in the long-wavelength limit; it is the wave-number-dependent generalization of a single relaxation time approximation often called in kinetic theory the BGK or Krook model. The next-order model ($N = 3$) considers in addition states which are important for the description of the shear viscosity and thermal conductivity and roughly corresponds to the QFRT model.

It is reasonable to expect that for sufficiently large N the kinetic model approximation will become independent of N so that the calculation can be said to be numerically converged. To demonstrate convergence in the calculation of the density correlation function one can follow the change in $S(k, \omega)$ with the kinetic model order N at various values of the frequency, ω. Such plots are shown in Fig. 1 for a low-density gas. One sees that convergence is slowest at $\omega = 0$, which corresponds to infinite time, where kinetic theory at higher densities is least accurate anyway. Even- and

Table I. Root Mean Square Deviation μ_N in $S(k, \omega)$ and $S_s(k, \omega)$

N	No. of matrix elements	I[a]	II[b]	III[c]	IV[d]	V[e]
2	5	3.20	47.68	21.52	7.74	2.97
3	8	2.54	4.65		5.14	1.58
4	14	2.50	17.29	14.37	13.65	1.05
5	20	3.07	18.21	5.70	7.83	0.69
6	30	1.95	3.22	2.07	2.31	0.47
7	40	2.79	1.90	1.39	1.54	0.39
8	55	0.80	0.55	1.48	0.38	0.28
9	70	2.46	0.55		0.46	0.25
10	91					

[a] $S(k\omega)$ at $V/V_0 = 141$ and $k\sigma = 0.082$.
[b] $S(k\omega)$ at $V/V_0 = 3$, $k\sigma = 0.616$.
[c] $S(k\omega)$ at $V/V_0 = 1.6$, $k\sigma = 0.759$.
[d] $S(k\omega)$ at $V/V_0 = 1.6$, $k\sigma = 2.28$.
[e] $S_s(k\omega)$ at $y = 1$.

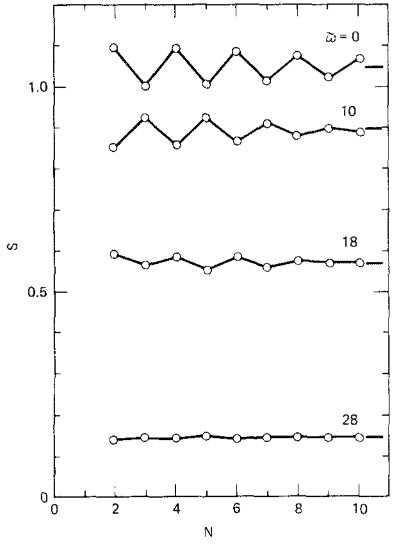

Fig. 1. Convergence for $S(k, \omega)$ for a hard-sphere gas in the low-density Boltzmann limit at $V/V_0 = 141$ and $k\sigma = 0.08$, where $g(\sigma) = 1$ and $S(k) = 1$, as a function of model order, N. Values of $S(k, \omega)$ are shown at several dimensionless frequencies $\tilde{\omega} = \omega\tau_E/k\sigma$, where $\tau^{-1} = 4n\sigma^2 g(\sigma)(\pi k_B T/m)^{1/2}$ is the Enskog collision rate. Horizontal marks indicate values obtained from the linearized Boltzmann equation (Ref. 11). Normalization is such that the integral of S over all positive ω gives $\pi S(k)$.

odd-order results show very pronounced oscillations. The oscillatory behavior is greatly damped as ω increases and in the tail region of the spectrum, which corresponds to short time, there is little or no variation of S with N. Under the particular low-density and long-wavelength conditions chosen, $V/V_0 = 141$, $k\sigma = 0.0802$, the generalized Enskog equation should give the same results as the linearized Boltzmann equation. The Boltzmann equation results using Sonine polynomials as basis functions(11) are also given in Fig. 1. Agreement with model $N = 10$ is seen to be quite close, the maximum deviation being 1.5%. Since the convergence of the expansion is independent of density, because the collision integral is independent of density, the behavior observed in Fig. 2 also holds at other densities and wave numbers as Fig. 3 shows. The N dependence of the spectra themselves is shown in Figs. 4 and 5. The unexpectedly large deviation at $N = 5$ implies that convergence of the intermediate-order kinetic model cannot be taken for granted. However, there is little variation of $S(k, \omega)$ with N for $N \geqslant 8$ and in most cases $N = 7$ gives sufficiently precise results. Also indicated in Figs. 2–3 are the results of QFRT at the appropriate value of N. Figure 6 is included to show that QFRT still does not agree accurately with hydrodynamics at low k and high density because of inaccuracies in

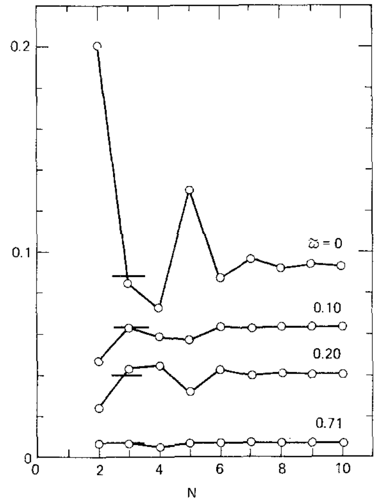

Fig. 2. Same as Fig. 1 except $V/V_0 = 3.0$, $k\sigma = 0.616$ at which $S(k) = 0.149$. Horizontal lines drawn at the appropriate order indicate the QFRT results.

the evaluation of the sound speed. However, the order 5 model is seen to lead to satisfactory results for the Brillouin peak.

Corresponding results for the van Hove self-correlation function are shown in Fig. 7 at a dimensionless wavelength to mean-free path ratio $y = 4\sqrt{2}\, V_0/Vk\sigma = 1$. In the case of $S_s(k, \omega)$ convergence is achieved at lower N relative to $S(k, \omega)$.

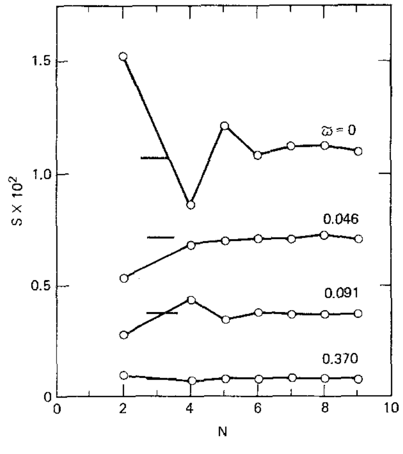

Fig. 3. Same as Fig. 2 except $V/V_0 = 1.6$, $k\sigma = 0.759$ at which $S(k) = 0.0271$.

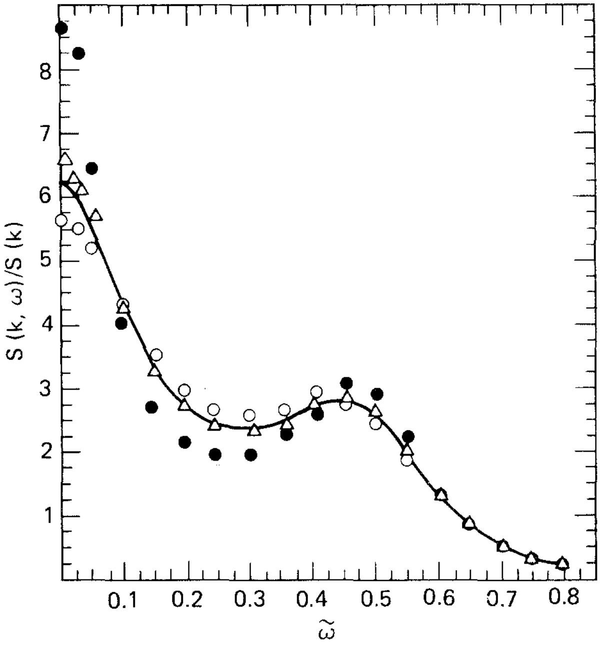

Fig. 4. The initially normalized dynamic structure factor $S(k, \omega)$ of a hard-sphere fluid at $V/V_0 = 3.0$ and $k\sigma = 0.616$. Comparison of $N = 10$ (solid curve), $N = 7$ (triangles), $N = 5$ (solid circles), and $N = 3$ (open circles).

A way to estimate the overall convergence is to evaluate the root-mean-square deviation μ_N,

$$\mu_N = \left[\frac{1}{N_f} \sum_{i=1}^{N_f} (\Delta_i^N)^2 \right]^{1/2} \tag{4.1}$$

where N_f is the number of frequency points at which the deviation, Δ_i^N, is calculated, and

$$\Delta_j^N = \left[\frac{C_{N_{\max}}(k, \omega_j) - C_N(k, \omega_j)}{C_{N_{\max}}(k, \omega_j)} \right] \times 100 \tag{4.2}$$

In Eq. (4.2) subscript $N_{\max}$ denotes the highest-order kinetic model considered and C_N is the value given by the kinetic model of order N. For most cases $N_{\max} = 10$. The frequency points sampled in Eq. (4.1) always include the zero-frequency value ($\omega = 0$) and at least five other equally spaced frequencies covering the region where the correlation function has a significant value. The results for the density and self-correlation functions shown

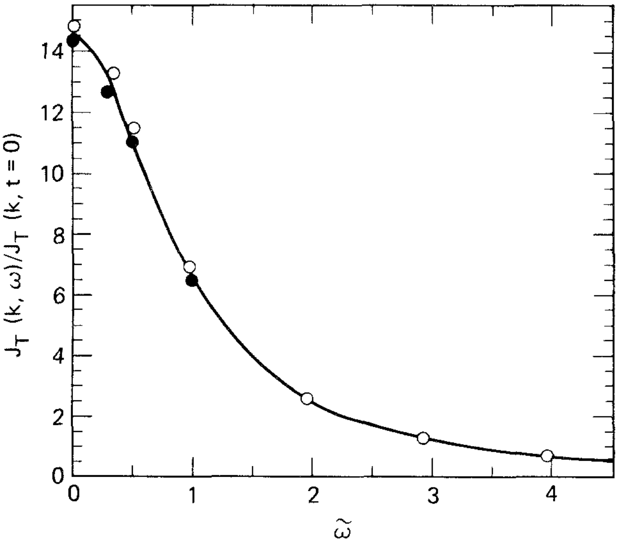

Fig. 5. Same as Fig. 4 except the function is the transverse current correlation. The $N = 7$ results are not indicated because they closely correspond to the results for $N = 10$.

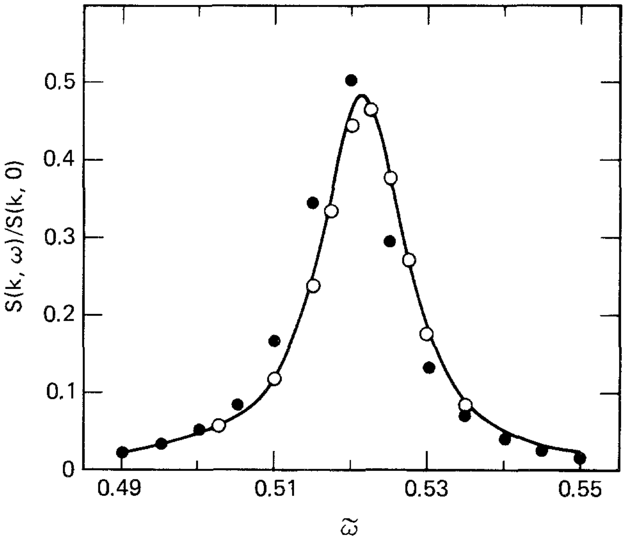

Fig. 6. The Brillouin sound peak of $S(k, \omega)$ in the hydrodynamic limit ($k\sigma = 0.025$) at a density corresponding to $V/V_0 = 3.0$. The solid line is the hydrodynamics result using Enskog transport coefficients. The solid circles correspond to QFRT results and the open circles are the results of order $N = 5$.

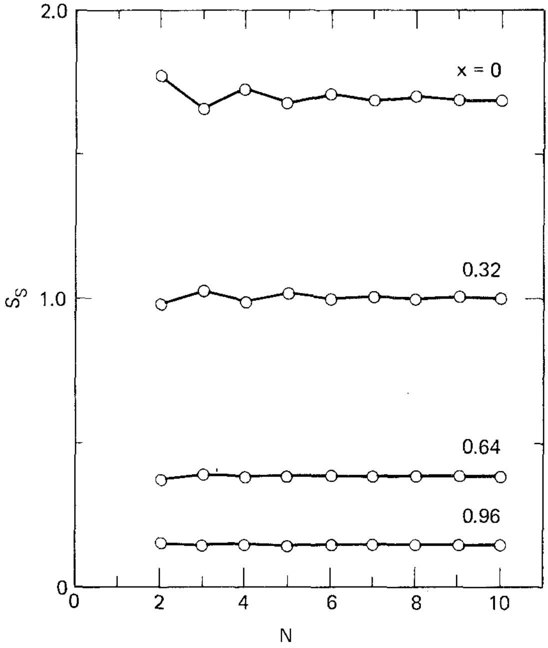

Fig. 7. Convergence for $S_s(k,\omega)$ for a hard-sphere gas at a density such that $\tau_E^{-1} = k\sqrt{\pi k_B T/m}$ for different values of the dimensionless frequency $x = \omega\tau_E$.

in Figs. 1–4 and Fig. 6 are given in Table I. The results of Table I again indicate that convergence of the kinetic model calculations of $S(k,\omega)$ can be rather slow. Generally speaking, the $N = 10$ model results should be accurate to about 1% or better while intermediate-order models, $N = 4$ and 5, can give larger μ_N than the low-order models, $N = 3$.

In the case of self-diffusion the generalized Enskog equation is identical to the linearized Enskog equation$^{(6,8)}$ and the van Hove self-correlation function has a spectral distribution $S_s(k,\omega)$ that is completely governed by a single parameter, $y = 4\sqrt{2}g(\sigma)V_0/Vk\sigma$. It is sufficient to characterize the monotonic behavior of $S_s(k,\omega)$ by its peak height and width at half-maximum as an universal function of y. The results obtained from kinetic model $N = 8$ are shown in Fig. 8. It is evident that at low density or long wavelength, that is for $y \geqslant 2$, the self-correlation function is well described by the diffusion model, $S_s(k,\omega) = Dk^2/[\omega^2 + (Dk^2)^2]$. When the long-wavelength approximation breaks down, the diffusion model overestimates the width and correspondingly underestimates the peak height. Sensitivity of S_s to different kinetic model order is not pronounced; the largest

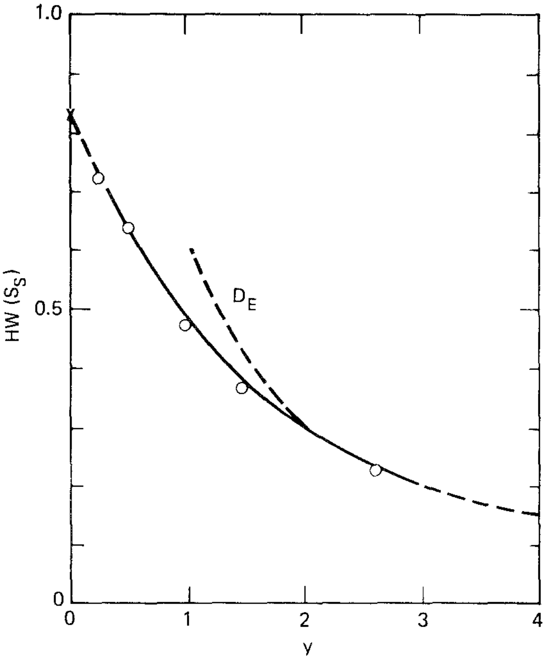

Fig. 8. Half-width ($\Delta\omega_{1/2} = k^2D$) divided by $k(2k_BT/m)^{1/2}$ of the van Hove self-correlation function $S_s(k, \omega)$ for a hard-sphere fluid as a function of $y = 4n\sigma^2 g(\sigma)/k$: $N = 8$ results (solid curve) and previous calculations (Ref. 6) using a model of the same order (open circles). Also shown is the diffusion approximation using $\Delta\omega_{1/2} = k^2D_E$, where D_E is the Enskog diffusion coefficient (dashed curve, marked D_E) and the limiting value of 0.832 for a free-particle system (cross).

difference in the width between a single relaxation time calculation and the $N = 10$ model results is about 5% near $y = 1$.

5. DISCUSSION

The generalized Enskog equation entails two significant improvements over the linearized Boltzmann equation in dense gases at finite wavelength: the first improvement is the self-consistent field interaction and the second is the nonlocal effect in the collision operator. The self-consistent field, $\Lambda(k)$, generally consists of the static contribution [cf. Eq. (2.3)] as expressed by the direct correlation function $C(k)$. Only in the case of hard spheres can the second contribution, which expresses the nonlocal effect through $g(\sigma)$, be separated from the collision integral, $J[\tilde{C}]$. This is because the collisions are instantaneous. For systems with continuous potentials, the collisional part is frequency dependent and the appropriate kinetic equation has not yet been formulated.

While details of the collision dynamics in $J[\tilde{C}]$ may not have large quantitative effects, both the self-consistent field and the nonlocal effects have strong influences on the density correlation function. This is illustrated in Fig. 9 which shows $S(k,\omega)$ as calculated from QFRT for a moderately low-density gas at $V/V_0 = 10$ and $k\sigma = 0.412$, a condition that is close to the hydrodynamic regime. Spectrum A denotes the Boltzmann

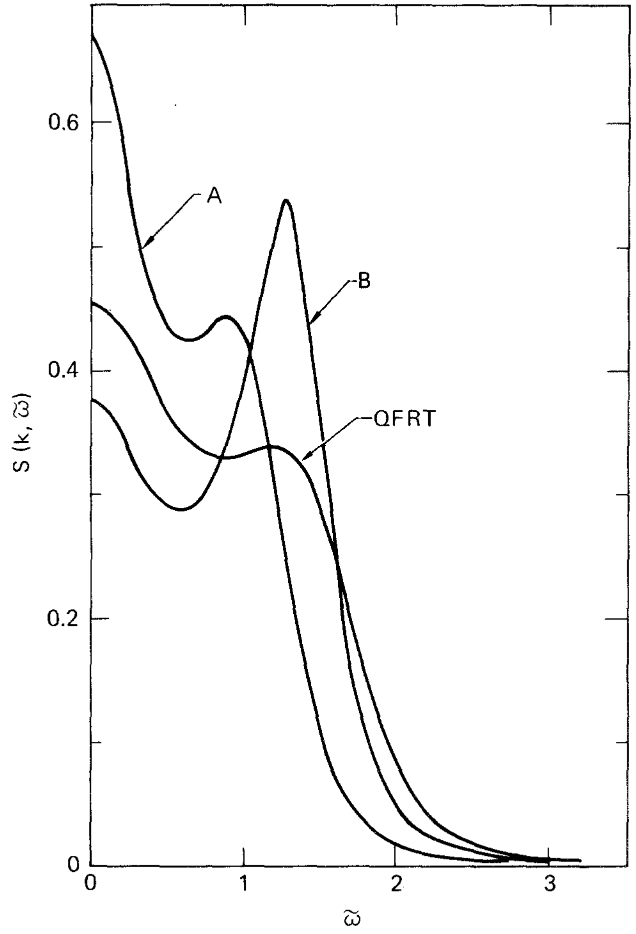

Fig. 9. Dynamic structure factor $S(k,\omega)$ of a hard-sphere fluid at $V/V_0 = 10$ and $k\sigma = 0.412$: QFRT results, compared to a calculation with k set equal to zero in all $\Sigma(\alpha \mid \beta)$ except $\Sigma(2 \mid 1)$ (curve B), and a calculation where in addition $\Sigma(2 \mid 1)$ is set equal to zero (curve A).

equation result which is obtained by ignoring both $\Lambda(k)$ and the phase factors $\exp(\pm i\bar{k}\cdot\bar{\Omega}\sigma)$. In this case one has well-established central (Rayleigh) and propagating (Brillouin) components. Spectrum B, obtained when only the phase factors are ignored, shows the effects of the self-consistent field, namely, strong dispersion in the propagation speed and dramatic changes in the relative intensities of the central and Brillouin peaks. This behavior has been observed previously.(3) When nonlocal effects are included, further changes occur, as shown by the QFRT spectrum.

APPENDIX

This appendix gives an explicit expression for the matrix elements $\Sigma(\alpha\,|\,\beta)$ in terms of nested sums.(18) First rewrite $\Sigma(\alpha\,|\,\beta)$ as

$$\begin{aligned}\Sigma(\alpha\,|\,\beta) &= nv_0k\Lambda(k)\delta_{0l}\delta_{0m}\delta_{1n}\delta_{0l'}\delta_{0m'}\delta_{0n'}\\ &\quad+\frac{8in\sigma^2v_0g(\sigma)}{(2\pi)^3}\langle lmn|\Sigma|l'm'n'\rangle\end{aligned}$$

Then

$$\begin{aligned}\langle lmn|\Sigma|l'm'n'\rangle &= \sum_{l''=0}^{\bar{l}}\sum_{m''=0}^{\overline{m}}\sum_{n''=0}^{\bar{n}}\beta(l,l'',l')\beta(m,m'',m')\beta(n,n'',n')\\ &\quad\times\Big\langle l-l'',m-m'',n-n''|\overline{M}(k\sigma)|l'-l'',\\ &\qquad m'-m'',n'-n''\Big\rangle\end{aligned}$$

where $\bar{l}=\min(l,l')$, etc.,

$$\beta(l,m,n)=\frac{\sqrt{\pi}}{2^{l+n-m}}\,\frac{l!\,n!}{m!\,(l-m)!\,(n-m)!}$$

and

$$\begin{aligned}\Big\langle lmn|\overline{M}(k\sigma)|l'm'n'\Big\rangle &= \langle lmn|M_1(0)|l'm'n'\rangle\\ &\quad+(-1)^{l'+m'+n'}\langle lmn|M_1(k\sigma)|l'm'n'\rangle\end{aligned}$$

The elements M_1 are

$$\begin{aligned}\langle lmn|M_1|l'm'n'\rangle &= \sum_{\bar{l}=0}^{l}\sum_{\overline{m}=0}^{m}\sum_{\bar{n}=0}^{n}\sum_{\bar{l}'=0}^{l'}\sum_{\overline{m}'=0}^{m'}\sum_{\bar{n}'=0}^{n'}\gamma(l,\bar{l})\gamma(m,\overline{m})\gamma(n,\bar{n})\\ &\quad\times\gamma(l',\bar{l}')\gamma(m',\overline{m}')\gamma(n',\bar{n}')\Big\langle\bar{l}\overline{m}\bar{n}|M_2|\bar{l}'\overline{m}'\bar{n}'\Big\rangle\end{aligned}$$

where

$$\gamma(l,m) = \frac{2^{l-1}}{\sqrt{\pi}} \binom{l}{m} (i)^{l-m} \Gamma\left(\frac{l-m+1}{2} \right) \left[1 + (-1)^{l-m} \right]$$

$\Gamma(x)$ is the Euler gamma function, and

$$\binom{l}{m} = \frac{l!}{m!\,(l-m)!}$$

The elements M_2 are

$$\begin{aligned} &\langle lmn | M_2 | l'm'n' \rangle \\ &\quad = \sum_{l''=0}^{l'} \sum_{m''=0}^{m'} \sum_{n''=0}^{n'} \binom{l'}{l''} \binom{m'}{m''} \binom{n'}{n''} (-2)^{l''+m''+n''} \Delta_{l'',m'',n''} \\ &\quad \times \langle l+l'-l'', m+m'-m'', n+n'-n'' | M_3 | l'', m'', n'' \rangle \end{aligned}$$

where $\Delta_{l,m,n} = \delta_{0l}\delta_{0m}\delta_{0n} - 1$.
The elements M_3 are

$$\begin{aligned} \langle lmn | M_3 | l'm'n' \rangle = \pi^{3/2} \left(\frac{-i}{2} \right)^{l+m+n} (i)^{l'+m'+n'} & \sum_{l''=0}^{l} \sum_{m''=0}^{m} \sum_{n''=0}^{n} \\ & \times \gamma(l,l'')\gamma(m,m'')\gamma(n,n'') \\ & \times (1/2)^{l''+m''+n''} \langle l''m''n'' | M_4 | l'm'n' \rangle \end{aligned}$$

Finally the elements M_4 are

$$\langle lmn | M_4 | l'm'n' \rangle = W(l_T' + 1, l_T) F(l+l', m+m', n+n')$$

where $l_T = l + m + n$,

$$W(l,m) = \left\{ \begin{array}{ll} \dfrac{l!}{(l-m)!} \dfrac{i}{2\sqrt{\pi}} \Gamma\left(\dfrac{l-m+1}{2} \right) (-1)^{(l-m)/2}, & l \geqslant m \\ \dfrac{l!}{2\pi} \left[1 - (-1)^{m-l} \right] 2^{m-l-1} \Gamma\left(\dfrac{m-l}{2} \right), & m > l \end{array} \right\}$$

$$\begin{aligned} F(l,m,n) = (-i)^n \left[1 + (-1)^l \right] \left[1 + (-1)^m \right] \Gamma\left(\frac{l+1}{2} \right) \Gamma\left(\frac{m+1}{2} \right) \\ \times 2^{(l+m)/2} G^n_{(l+m)/2}(k\sigma) \end{aligned}$$

$$G^n_m(x) = \frac{d^n}{dx^n} \left[\frac{j_m(x)}{x^m} \right]$$

and $j_m(x)$ is a spherical Bessel function.$^{(19)}$ Even though imaginary numbers occur in the definitions of W and F, the matrix element M_4 is always real.

REFERENCES

1. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, London, 1970); J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
2. See, for example, H. J. M. Hanley, R. D. McCarty, and E. G. D. Cohen, *Physica* **60**:322 (1972).
3. S. Ranganathan and M. Nelkin, *J. Chem. Phys.* **47**:4056 (1967); E. P. Gross and D. Wisnivesky, *Phys. Fluids* **11**:1387 (1968).
4. J. L. Lebowitz, J. K. Percus, and J. Sykes, *Phys. Rev.* **188**:487 (1969).
5. L. Blum and J. L. Lebowitz, *Phys. Rev.* **185**:273 (1969).
6. G. F. Mazenko, T. Y. C. Wei, and S. Yip, *Phys. Rev. A* **6**:1981 (1972).
7. H. Van Beijeren and M. Ernst, *Physica* **68**:437 (1973); **70**:25 (1973).
8. H. H. U. Konijnendijk and J. M. J. van Leeuwen, *Physica* **64**:342 (1973).
9. G. F. Mazenko, *Phys. Rev. A* **7**:209, 222 (1973); **9**:360 (1974).
10. J. Sykes, *J. Stat. Phys.* **8**:279 (1973).
11. A. Sugawara, S. Yip, and L. Sirovich, *Phys. Fluids* **11**:925 (1968).
12. P. M. Furtado, G. F. Mazenko, and S. Yip, *Phys. Rev. A* **13**:1644 (1976).
13. V. Ghaem-Maghami and A. D. May, *Phys. Rev. A* **22**:1686 (1980); L. Letamendia, thesis (University of Bordeaux, 1979); L. Letamendia, J. P. Chabrat, G. Nouchi, J. Rouch, C. Vaucamps, and S. H. Chen, *Phys. Rev. A* **24**:1574 (1981).
14. J. W. Dufty and M. J. Lindenfeld (to be published).
15. E. Leutheusser, thesis (Technical University, Munich, 1979), *J. Phys. C* (to be published).
16. B. J. Alder, W. E. Alley, and S. Yip, (to be published).
17. E. P. Gross and E. A. Jackson, *Phys. Fluids* **2**:432 (1959).
18. G. F. Mazenko, unpublished notes.
19. *Handbook of Mathematical Functions*, M. Abramowitz and I. Stegun, eds. (Dover Publications, New York, 1965).