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Dynamical Correlations in a Hard-Disk Fluid: Generalized Enskog Theory

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The generalized Enskog theory of a hard-disk fluid is solved by a kinetic model method. Time correlation functions of the conserved variables of density, longitudinal and transverse current, and energy density are evaluated. The theoretical results are tested against molecular dynamics data at a density roughly half the solidification density. The good agreement obtained indicates that a kinetic equation which ignores correlated collisions can provide an adequate description of space-time correlations at finite wavelengths and frequencies in dense fluids in two dimensions.

KEY WORDS: Hard-disk fluid; generalized Enskog equation; kinetic model solution; density; longitudinal and transverse current and energy density correlation functions; molecular dynamics results.

1. INTRODUCTION

The study of hard-sphere fluids has contributed to much of the current understanding of dynamical correlations in simple fluid systems.[1] The kinematics of hard-sphere interaction makes it feasible to analyze time correlation functions using a kinetic theory approach which takes into account the effects of uncorrelated binary collisions.[2] Calculations have been carried out using the Enskog equation[3] and the results compared to molecular dynamics simulation data.[4] In this way, one is able to show that in three dimensions the density and current correlation functions in

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simple fluids at densities up to at least half the liquid density can be adequately described (leaving out long time tails) without considering the effects of correlated collisions. Using the simulation data at liquid density one can furthermore pinpoint those features which cannot be calculated from the Enskog equation[4]; it turns out that these features can be obtained by extending the analysis to include correlated collision contributions through a self-consistent mode-coupling approximation.[5]

One may expect the Enskog theory to have a similar range of validity in two-dimensional fluids. However, this has not been demonstrated. Molecular dynamics studies of the velocity autocorrelation function in hard-disk fluids are well known, since these were the results that led to the discovery of the long time tail in time correlation functions.[6,7] More recently, simulation results for the stress correlation function related to the shear viscosity coefficient have appeared.[8] On the theoretical side, Enskog transport coefficients for hard-disk fluid have been derived,[9] and long time asymptotic behavior[10] has been analyzed.

The purpose of this work is to calculate the density and current correlation functions in a two-dimensional hard-sphere fluid using the generalized Enskog equation and to present new molecular dynamics results which demonstrate the validity of the theory. It should be noted at the outset that we are concerned with time correlation function behavior at finite wave numbers and short and intermediate times. In these regions one does not expect any anomalous behavior associated with the asymptotic nonexponential decay.

The paper is organized as follows. In Section 2 we formulate the problem of calculating time correlation functions in terms of a phase-space collision operator (memory function) which contains contributions from binary collisions and correlated events. Keeping only the binary collision contribution reduces the calculation to one based on the generalized Enskog kinetic equation. The solution of the Enskog equation by retaining only the first few matrix elements of the collision operator is discussed in Section 3. In Section 4, numerical results for the density and the transverse and longitudinal current correlation functions are compared with molecular dynamics simulation data at a density of $A/A_0 = 3$, where A_0 is the close-packed area. One finds generally good agreement. In Section 5, we discuss the significance of the present results and the expected deficiency of the Enskog theory at liquid density.

2. KINETIC EQUATION

We consider a system of N disks, each of diameter σ and mass m, in an area A interacting with the hard core potential $u(r) = \infty, 0$ for $r > \sigma$, $r < \sigma$,

respectively. Particle positions and momenta are denoted by $\mathbf{r}_i, \mathbf{p}_i$, $i = 1, \ldots, N$. The fluid density $n = N/A$ can be expressed in terms of the area ratio A/A_0, $n\sigma^2 = (2/\sqrt{3})(A/A_0)^{-1}$, with A_0 being the close-packed area.

The time evolution of the system may be described by a "pseudo"-Liouville operator $\mathscr{L}_\pm$ for forward and backward streaming.[11] For a dynamical variable A, one has $A(t) = e^{i\mathscr{L}_\pm t}A(0)$, for $t \gtrless 0$. The Liouville operator has two parts, $\mathscr{L}_\pm = \mathscr{L}_0 + \mathscr{L}'_\pm$, describing free streaming and two-particle collisions, respectively:

$$\mathscr{L}_0 = -i\sum_n \mathbf{v}_n \nabla_n \tag{1a}$$

$$\mathscr{L}'_\pm = \frac{i}{2}\sum_{n\neq m} \mathbf{v}_{nm}\hat{r}_{nm}\theta(\mp \mathbf{v}_{nm}\hat{r}_{nm})\delta(|\mathbf{r}_{nm}| - \sigma)(b_{nm} - 1) \tag{1b}$$

In Eq. (1b) the operator b_{nm} replaces the momentum $\mathbf{p}_n$ or $\mathbf{p}_m$ by $b_{nm}\mathbf{p}_{n,m} = \mathbf{p}_{n,m} \mp (\mathbf{p}_{nm} \cdot \hat{r}_{nm})\hat{r}_{nm}$, $\mathbf{v}$ denotes the velocity, $\mathbf{r}_{nm} = \mathbf{r}_n - \mathbf{r}_m$, $\hat{r} = \mathbf{r}/|\mathbf{r}|$, and $\theta(x) = 1, 0$ for $x > 0$, $x < 0$, respectively.

The time correlation function of a dynamical variable $A(t)$ is defined by

$$\phi(t) = (A(t) \mid A) \tag{2a}$$

where the brackets denote an equilibrium average $(A \mid A) = \langle \delta A^* \delta A \rangle$ of the fluctuation $\delta A = A - \langle A \rangle$ at temperature T. It is convenient to consider also the Laplace transform of the time correlation function

$$\begin{aligned} \phi(z) &= \pm i\int_{-\infty}^{\infty} dt\, \theta(\pm t) e^{izt}\phi(t), \qquad \operatorname{Im} z \gtrless 0 \\ &= \left(A \middle| (\mathscr{L}_\mp - z)^{-1} \middle| A\right) \end{aligned} \tag{2b}$$

in the form of a resolvent operator matrix element. The spectrum of $\phi(t)$,

$$\phi''(\omega) = \frac{1}{2}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\phi(t) \tag{2c}$$

is the discontinuity of $\phi(z)$ across the real axis, $\phi(\omega \pm i\epsilon) = \phi'(\omega) \pm i\phi''(\omega)$. These formulas may be easily generalized in the case of a set of several dynamical variables.[12]

The basic variable of kinetic theory is the phase space density $f(\mathbf{p}, \mathbf{r}) = (1/\sqrt{N})\sum_i \delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{p} - \mathbf{p}_i)$, simply abbreviated by $f(1)$. After multiplication by suitable momentum functions and integration over momentum it yields the macroscopic variables like the local density, current density, energy density, and so on. The phase-space density correlation function

$$\phi(12, t) = (f(1, t) \mid f(2)) \tag{3}$$

satisfies a formal, exact kinetic equation

$$\left[(z + \mathbf{q}\mathbf{v})\delta_{\mathbf{p}\bar{\mathbf{p}}} + C_{\mathbf{p}\bar{\mathbf{p}}}(\mathbf{q}, z)\right]\phi_{\bar{\mathbf{p}}\mathbf{p}'}(\mathbf{q}, z) = -\chi_{\mathbf{p}\mathbf{p}'}(\mathbf{q}) \tag{4}$$

which may be derived following the same procedure as that used in the analysis of three-dimensional hard-sphere fluids.[5] Here $\chi_{\mathbf{p}\mathbf{p}'}(q) = \varphi(p)\delta_{\mathbf{p}\mathbf{p}'} + \varphi(p)\varphi(p')nh(q)$ is the static phase space correlation function given in terms of the Maxwellian velocity distribution $\varphi(p) = (2\pi mT)^{-1}\exp(-p^2/2mT)$ (we set Boltzmann's constant $k_B = 1$ in the following) and the pair correlation function $ng(r) = (1/N)\langle\sum_{i\neq j}\delta(\mathbf{r} - \mathbf{r}_{ij})\rangle$, with $h(r) = g(r) - 1$. Also Fourier transformations have been introduced as $h(q) = \int d\mathbf{r}\, e^{-i\mathbf{q}\cdot\mathbf{r}}h(r)$, and integration over the momentum variable with an overhead bar is implied.

In Eq. (4) all the interaction effects are described by the operator $C_{\mathbf{p}\mathbf{p}'}(\mathbf{q}, z)$, which consists of three parts,

$$C_{\mathbf{p}\mathbf{p}'}(\mathbf{q}, z) = A_{\mathbf{p}\mathbf{p}'}(\mathbf{q}) + T_{\mathbf{p}\mathbf{p}'}(\mathbf{q}) + M_{\mathbf{p}\mathbf{p}'}(\mathbf{q}, z) \tag{5a}$$

$$A_{\mathbf{p}\mathbf{p}'}(\mathbf{q}) = -\mathbf{q}\mathbf{v}\varphi(p)nc(q) \tag{5b}$$

$$T_{\mathbf{p}\mathbf{p}'}(\mathbf{q}) = t_{\mathbf{p}\mathbf{p}'}(\mathbf{q}) + ng(\sigma)h^{(0)}(q)\varphi(p)\mathbf{q}\mathbf{v}' \tag{5c}$$

$$t_{\mathbf{p}\mathbf{p}'}(\mathbf{q}) = -in\sigma g(\sigma)\int d\hat{r}_{12}\int d\mathbf{p}_1\, d\mathbf{p}_2\,\varphi(p_1)\varphi(p_2)(\mathbf{v}_{12}\hat{\mathbf{r}}_{12})\theta(\mathbf{v}_{12}\hat{r}_{12})$$
$$\times\delta(\mathbf{p} - \mathbf{p}_1)(b_{12} - 1)\left[\delta(\mathbf{p}' - \mathbf{p}_1) + e^{i\mathbf{q}\hat{r}_{12}\sigma}\delta(\mathbf{p}' - \mathbf{p}_2)\right] \tag{5d}$$

The first part $A_{\mathbf{p}\mathbf{p}'}(\mathbf{q})$ is the mean field contribution; it is entirely specified by the direct correlation function $c(q)$ which is related to the static structure factor $S(q) = 1 + nh(q)$ by the Ornstein–Zernike relation $c(q) = h(q)/S(q)$. The second part is the Boltzmann–Enskog collision operator describing instantaneous two-particle collisions; it is the extension of the Boltzmann collision operator for hard disks by taking into account the finite size σ of the particles, hence the wave-number dependence of $T_{\mathbf{p}\mathbf{p}'}(\mathbf{q})$, and the enhanced probability of finding two particles at contact at higher densities. In Eq. (5c) the second part of $T_{\mathbf{p}\mathbf{p}'}(\mathbf{q})$ only ensures particle number conservation, and $h^{(0)}(q)$ is the Fourier transform of $\theta(r - \sigma) - 1$. Notice that $T_{\mathbf{p}\mathbf{p}'}(\mathbf{q})$ is frequency independent due to the instantaneous nature of hard-core collisions.

The last part $M(\mathbf{q}, z)$ in Eq. (5a) describes more complicated collision sequences involving more than two particles, e.g., ring or repeated ring collisions; it is dependent on both wave number and frequency. A formal, exact expression for $M(\mathbf{q}, z)$ may be derived, for example, by using the Zwanzig–Mori projection operator technique. It will not be discussed here since the present calculation is only concerned with the first two terms in

Eq. (5a). In the case of three-dimensional hard-sphere fluids, a self-consistent mode-coupling approximation for $M(\mathbf{q}, z)$ has been developed recently,[5] and it has been shown that this approximation could account for the new qualitative effects which appear only at liquid densities, shear wave propagation at finite wave number and a second relaxation component in the decay of density fluctuations. At lower densities, below roughly half the solid density, viscoelastic behavior does not appear in the density or current correlation functions. If we restrict our attention to this density range, then $M(\mathbf{q}, z)$ may be neglected in a first approximation. The resulting kinetic equation then becomes the generalized Enskog equation, which has been discussed quite extensively in the case of three-dimensional fluids.[2,3] This is the equation we will solve in the next section and compare the results with molecular dynamics simulation data in Section 4.

3. APPROXIMATE SOLUTION

We will solve Eq. (4) using the method of kinetic models. A complete orthonormal set of momentum states $\psi_k(\mathbf{p})$, $k = 1, \ldots$ is first chosen, then the infinite-dimensional matrix of the collision operator $C(\mathbf{q}, z)$ is approximated by retaining matrix elements $C_{ij}(\mathbf{q}, z)$, $i, j < N$, and replacing the remaining part of $C(\mathbf{q}, z)$ by a diagonal matrix with all diagonal elements equal, $C_{ij}(\mathbf{q}, z) = \alpha(q, z)\delta_{ij}$ for i or $j > N$. The kinetic equation is thus converted to a set of coupled algebraic equations and may be solved exactly. The $N \times N$ matrix equation for the N dynamical variables chosen for explicit treatment may be written as[5]

$$\left[z + \Omega^{(0)}(\mathbf{q}) + C(\mathbf{q}, z) + m^{(0)}(\mathbf{q}, z')\right] \cdot \phi(\mathbf{q}, z) = -\chi(\mathbf{q}) \tag{6}$$

Here $\Omega^{(0)}(\mathbf{q})$ is the matrix corresponding to the free-streaming term $\Omega^{(0)}_{ik}(\mathbf{q}) = \langle i|\mathbf{q} \cdot \mathbf{v}|k\rangle$, and $m^{(0)}(\mathbf{q}, z')$ is the matrix of free particle memory functions with a shifted frequency argument $z' = z + \alpha(q, z)$. The appearance of $m^{(0)}$ is the result of eliminating all the other one-particle modes besides the N modes considered explicitly, and it guarantees the correct free-particle limit of the correlation functions $\phi_{ij}(\mathbf{q}, z)$ at large wave numbers.

The set of dynamical variables we are concerned with must contain the four conserved hydrodynamic variables, density, longitudinal and transverse current, and energy densities. In addition, we will include those variables related to the various transport coefficients in order to ensure that the resulting kinetic equation description will have the correct hydrodynamic limit at small wave numbers. Because of rotational invariance, longitudinal and transverse correlations can be treated separately. Thus, the simplest choice is $N = 5$ in the longitudinal case, and $N = 2$ in the transverse case. The two sets of variables, each normalized such that $\chi_{ij}(\mathbf{q}) = \delta_{ij}$,

are

$$A_1(\mathbf{q}) = \frac{1}{[S(q)]^{1/2}} \int d\mathbf{p}\, f_{\mathbf{p}}(\mathbf{q})$$

$$A_2(\mathbf{q}) = \int d\mathbf{p}\, \frac{p_y}{(mT)^{1/2}} f_{\mathbf{p}}(\mathbf{q})$$

$$A_3(\mathbf{q}) = \frac{1}{[C_v(q)]^{1/2}} \int d\mathbf{p} \left(\frac{p^2}{2mT} - 1 \right) f_{\mathbf{p}}(\mathbf{q}) \tag{7a}$$

$$A_4(\mathbf{q}) = \int d\mathbf{p} \left(\frac{p_y^2}{mT} - \frac{p^2}{2mT} \right) f_{\mathbf{p}}(\mathbf{q})$$

$$A_5(\mathbf{q}) = \frac{1}{\sqrt{2}} \int d\mathbf{p} \left(\frac{p^2}{2mT} - 2 \right) \frac{p_y}{(mT)^{1/2}} f_{\mathbf{p}}(\mathbf{q})$$

in the longitudinal case, and

$$A_1(q) = \int d\mathbf{p}\, \frac{p_x}{(mT)^{1/2}} f_{\mathbf{p}}(\mathbf{q})$$

$$A_2(\mathbf{q}) = \int d\mathbf{p}\, \frac{p_x p_y}{mT} f_{\mathbf{p}}(\mathbf{q}) \tag{7b}$$

in the transverse case, where $f_{\mathbf{p}}(\mathbf{q})$ is the Fourier transform of $f(\mathbf{p}, \mathbf{r})$ and $C_v(q) = 1$ is the specific heat at constant volume. Using these states, one can now calculate the matrix elements of the free-streaming term, the mean field term, and the collision operator term as indicated in Eq. (6). The evaluations in the first two cases are straightforward, the details of which will not be reproduced here. The calculation of the matrix elements of the Boltzmann–Enskog collision operator in the basis of two-dimensional Sonine polynomials is of some interest; it is discussed in the Appendix. Denoting the sum of all three contributions by $\Omega_{\mathbf{pp}'}(q) = \mathbf{q} \cdot \mathbf{v}\delta_{\mathbf{pp}'} + A_{\mathbf{pp}'}(\mathbf{q}) + T_{\mathbf{pp}'}(\mathbf{q})$, we find for the calculation of longitudinal correlation functions the results

$$\begin{aligned}
&\Omega_{12}(q) = qv_0/[S(q)]^{1/2}, && \Omega_{34}(q) = i\nu \tfrac{1}{8}(q\sigma)^2 i_2(q\sigma) \\
&\Omega_{22}(q) = i\nu \tfrac{3}{8}(q\sigma)^2 i_4(q\sigma), && \Omega_{35}(q) = qv_0\sqrt{2}\,[1 + \tfrac{3}{4} y i_0(q\sigma)] \\
&\Omega_{23}(q) = qv_0[1 + y i_0(q\sigma)], && \Omega_{44}(q) = i\nu i_7(q\sigma) \\
&\Omega_{24}(q) = qv_0[1 + \tfrac{1}{2} y i_6(q\sigma)], && \Omega_{45}(q) = qv_0 2^{-1/2}[1 + \tfrac{3}{4} y i_6(q\sigma)] \\
&\Omega_{25}(q) = i\nu \frac{3\sqrt{2}}{64} (q\sigma)^2 i_4(q\sigma), && \Omega_{55}(q) = i\nu \tfrac{1}{2} i_8(q\sigma) \\
&\Omega_{33}(q) = i\nu \tfrac{1}{4}(q\sigma)^2 i_3(q\sigma),
\end{aligned} \tag{8a}$$

and for the calculation of transverse correlation functions

$$\begin{aligned}\Omega_{11}(q) &= i\nu\tfrac{1}{8}(q\sigma)^2 i_1(q\sigma)\\ \Omega_{12}(q) &= qv_0\left[1+\tfrac{1}{2}yi_2(q\sigma)\right]\\ \Omega_{22}(q) &= i\nu i_5(q\sigma)\end{aligned} \tag{8b}$$

To complete the kinetic model specification, we choose, more or less arbitrarily, the state $A_6(q) = (1/2)\int d\mathbf{p}[(p^2/2mT)^2 - 4(p^2/2mT) + 2]f_{\mathbf{p}}(\mathbf{q})$, to calculate the diagonal element of C_{ij} for $i, j > N$, thus obtaining $\alpha(q) = i(\nu/2)i_9(q\sigma)$. In Eq. (8) $v_0 = \sqrt{T/m}$ is the thermal velocity, $\nu = 2\sqrt{\pi}\, n\sigma g(\sigma)v_0$ is the Enskog collision frequency, $y = (\pi/2)n\sigma^2 g(\sigma)$ is related to the pressure by $p = nT(1+y)$, and the functions $i_n(x)$, $n = 0, \ldots, 9$, normalized according to $i_n(0) = 1$, are defined in the Appendix in terms of Bessel functions. Notice that $\Omega_{ik} = \Omega_{ki}$, and $\Omega_{k1}(q) = 0$ for $k \neq 2$ in the longitudinal case due to particle number conservation.

The only nonzero matrix elements of the free-particle memory kernels in Eq. (6) are $m_{ik}^{(0)}(q,z)$, $i,k = 4$ and 5, and $m_{22}^{(0)}(q,z)$ in the longitudinal and transverse cases, respectively. The latter follows from the fact that for the noninteracting system the time derivatives of A_1 in the transverse case, for example, is proportional to A_2, and therefore the fluctuating force corresponding to A_1 vanishes. To calculate these matrix elements one can apply Eq. (6) to the noninteracting system and express the memory kernels in terms of the correlation functions $\phi_{ik}^{(0)}(\mathbf{q},z) = [A_i(\mathbf{q})|1/(\mathscr{L}_0 - z)|A_k(\mathbf{q})]$ which are known. The results may be expressed in terms of the complex plasma dispersion function[13] $w(z)$ in a similar way as in the case of three-dimensional fluids,[5] for example, $\phi_{11}^{(0)}(q,z) = i(\pi/2)^{1/2}(qv_0)^{-1} w(z/\sqrt{2}\, qv_0)$. Thus, the correlation functions of the set of variables defined in Eqs. (7) are now completely determined by solving the 5×5 or 2×2 matrix equation,

$$\left[z + \Omega(q) + m^{(0)}(q,z')\right]\phi(q,z) = -1 \tag{9}$$

For the correlation functions of the longitudinal variables Eq. (9) becomes

$$\begin{bmatrix} z & \Omega_{12}(q) & 0 \\ \Omega_{12}(q) & z + q^2 D_l(q,z) & \Omega_{23}(q) + q^3 L(q,z) \\ 0 & \Omega_{23}(q) + q^3 L(q,z) & z + q^2 K(q,z) \end{bmatrix} \phi(q,z) = -1 \tag{10a}$$

For the transverse current correlation function Eq. (9) gives

$$\left[z + q^2 D_t(q,z)\right]\phi_n(q,z) = -1 \tag{10b}$$

Here $\Omega_{12}(q) = qv_0[S(q)]^{-1/2} = \Omega_0(q)$ is a characteristic frequency of the

fluid, and $\Omega_{23}(q) = \{qv_0[C_v(q)]^{-1/2}\}\beta(q)$, where $\beta(q)$ is a wave-number-dependent thermal stress coefficient generalizing $\beta(q=0) = (1/n)(\partial P/\partial T)_n$ in the same way as $S(q)$ is a generalized compressibility $S(q=0) = T(\partial n/\partial p)_T$. Also, wave-number- and frequency-dependent transport coefficients $D_l(q,z), D_t(q,z), K(q,z)$ are introduced which denote the generalized kinematic longitudinal and shear viscosities and heat conductivity, while $L(q,z)$ is a coefficient coupling temperature and longitudinal current fluctuations. These transport coefficients are given (see Ref. 5) in terms of the matrix elements of $\Omega(q)$ and $m^{(0)}(q,z')$.

The zero-wave-number limit of the generalized transport coefficients are time correlation functions of interest. For example,

$$D_t(z) = \lim_{q\to 0} D_t(q,z) = \left(A_2(q=0)\left|\frac{1}{\mathscr{L}_- - z}\right|A_2(q=0)\right) \tag{11}$$

where $A_2(q=0) = (1/\sqrt{N})\sum_n (p_n^x p_n^y/mT)$ is the kinetic transverse stress tensor. The corresponding time correlation function $\langle A_2(t)A_2(0)\rangle$ can be directly determined by molecular dynamics simulation. Provided the zero-frequency limits exist, they yield the transport coefficients of shear viscosity η, bulk viscosity ζ, and thermal conductivity λ according to the standard Green–Kubo[14] formulas

$$\begin{aligned} \lim_{z\to i0} D_t(z) &= i\eta/mn \\ \lim_{z\to i0} D_l(z) &= i(\zeta+\eta)/mn \\ \lim_{z\to i0} K(t) &= i\lambda/nC_v \end{aligned} \tag{12}$$

The results of the approximate solution of the generalized Enskog equation, denoted by superscript E, are

$$\begin{aligned} D_t^E(z) &= i\frac{\nu}{8}\sigma^2 - v_0^2\frac{(1+y/2)^2}{z+i\nu} \\ D_l^E(z) &= i\tfrac{3}{8}\nu\sigma^2 - v_0^2\frac{(1+y/2)^2}{z+i\nu} \\ K^E(z) &= i\frac{\nu}{4}\sigma^2 - v_0^2\frac{(1+\frac{3}{4}y)^2}{z+i\nu/2} \end{aligned} \tag{13}$$

The frequency spectra of the generalized transport coefficients are therefore Lorentzians with widths determined by the collision frequency ν superposed on a constant background. The corresponding time correlation functions have an instantaneous component proportional to $\delta(t)$ and an exponentially decaying component. The presence of a single relaxation time is a direct consequence of our choice of the lowest-order kinetic model description. By including more matrix elements of C_{ij}, i.e., increasing N, one can

systematically improve on this approximation. Based on previous experience,[4] the changes are expected to be small numerically.

The transport coefficients, obtained from Eqs. (11) and (12), are

$$\eta^E/mn = \frac{\nu}{8}\sigma^2 + v_0^2\frac{(1+y/2)^2}{\nu}$$
$$\zeta^E/mn = \frac{\nu}{4}\sigma^2 \tag{14}$$
$$\lambda^E/mn = \frac{\nu}{4}\sigma^2 + 4v_0^2\frac{(1+\frac{3}{4}y)^2}{\nu}$$

These agree with the results[9] derived from the Enskog equation using the first Sonine polynomial approximation.[15]

4. NUMERICAL RESULTS AND COMPARISON WITH MOLECULAR DYNAMICS DATA

In order to obtain numerical results in our analysis of the generalized Enskog kinetic equation, one needs to specify as input data to the theory the static structure factor $S(q)$ and the pair correlation function at contact $g(\sigma)$. Since we will compare our numerical results with computer molecular dynamics simulation data, we will use the value of $S(q)$ obtained by simulation. For $g(\sigma)$ we will use the empirical expression[16]

$$g(0) = \frac{1-7\xi/16}{(1-\xi)^2} - \frac{\xi^3/64}{(1-\xi)^4} \tag{15}$$

where $\xi = \pi n\sigma^2/4$ is the packing fraction, which agrees very well with Monte Carlo results.

For two-dimensional hard-sphere fluids extensive molecular dynamics data on the self-diffusion coefficient and the velocity autocorrelation function are available in the literature.[6–8] By contrast, essentially no information on space-dependent time correlation functions has been reported. We present here molecular dynamics results for the density, longitudinal and transverse current, and energy correlation functions at a fluid density of $n\sigma^2 = 0.385$ or $A/A_0 = 3$, which is roughly half the freezing density.[17] Following the same procedures previously employed,[6] simulation on two different sized systems, $N = 504$ and 2016, has been carried out. For $N = 504$, the system was allowed to run until 29×10^6 collisions have occurred, while for the larger system the total number of collisions was 19×10^6. From these trajectories time correlation functions were computed as averages over 1.138×10^5 and 8,977 time origins, respectively, for the two systems.

The larger simulation system was chosen to have exactly twice the linear dimensions of the smaller system; this makes it convenient to calculate time correlation functions at the same wavelengths and thus obtain an indication of the effects of finite system size. The longest wavelength of fluctuations that could be sustained in the $N = 504$ system, which was a rectangular array of 21×24 particles with periodic boundary conditions, corresponded to a wave number of $q_{\min} = 0.173\sigma^{-1}$ along the longer x direction and $0.1745\sigma^{-1}$ along the shorter y direction. (The simulation cell dimensions were unity and 0.9897 along these two directions.) The corresponding minimum wave numbers for $N = 2016$ would be half these values. Time correlation functions were calculated for particular wave vectors along the x, y or diagonal directions. Comparison of data for wave vectors along different directions offers a measure of the isotropy of the results as well as an indication of the statistical fluctuations in the data.

For comparison with the computer data, the density correlation function $\phi_{11}(q,z)$ is obtained from Eq. (10a),

$$\phi_{11}(q,z) = -\frac{z + q^2\tilde{D}(q,z)}{z^2 - \Omega_0^2(q) + zq^2\tilde{D}(q,z)} \tag{16a}$$

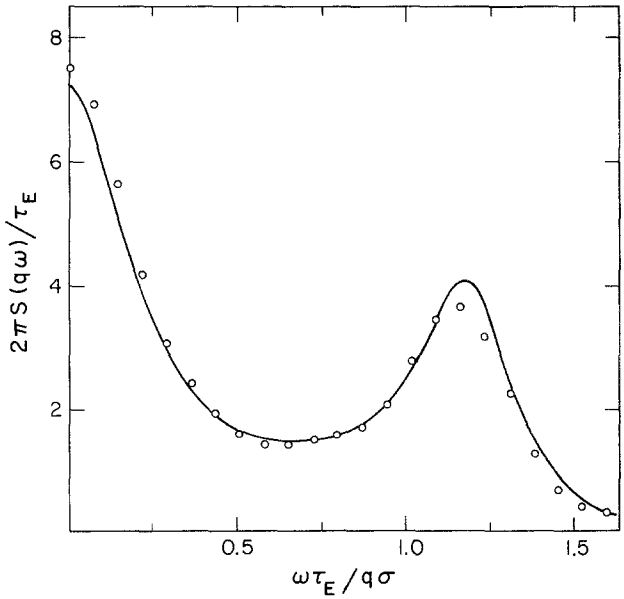

Fig. 1. Dynamical structure factor of hard-disk fluid ($A/A_0 = 3$) at $q\sigma = 0.173$, generalized Enskog theory (full curve) and molecular dynamics data with $N = 504$ (circles). τ_E is the Enskog collision time.

where $\tilde{D}(q,z)$ is essentially the longitudinal viscosity modified by the coupling to temperature fluctuations,

$$\tilde{D}(q,z) = D_l(q,z) - \frac{\left[\Omega_{23}(q) + q^3 L(q,z)\right]^2/q^2}{z + q^2 K(q,z)} \tag{16b}$$

Equation (16a) gives correctly the zeroth and second frequency moments of $\phi_{11}(q,z)$; it is known that the fourth moment of the exact $\phi_{11}(q,z)$ does not exist. The dynamical structure factor $S(q,\omega) = \phi''_{11}(q,\omega)/\pi$ is shown in Fig. 1 at $q\sigma = 0.173$ along with the simulation results. The frequency spectrum is essentially what one would expect of density fluctuations near the hydrodynamic regime of small wave numbers. The Enskog theory, in the present low-order kinetic model approximation, is able to quantitatively account for the diffusive (Rayleigh) and the propagating (Brillouin) modes. The comparison of the intermediate scattering function $F(q,t)$ shows good agreement at several wave numbers between calculation and various simulation data, as can be seen in Fig. 2. One may infer from these computer results that the effects of N-dependence and of statistical uncertainty are

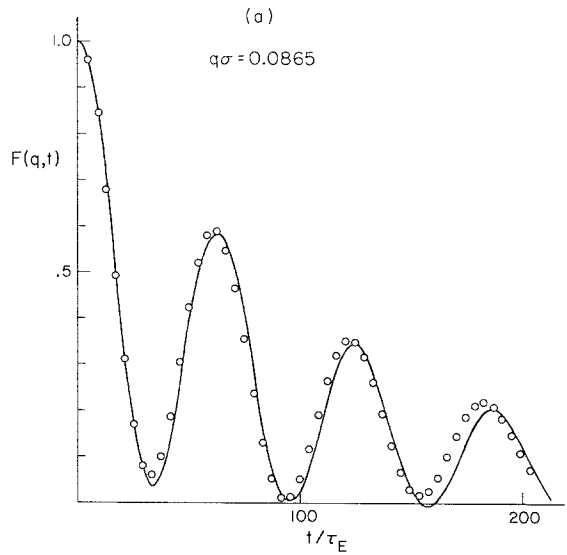

Fig. 2. Intermediate scattering function $F(q,t)$ of hard-disk fluid ($A/A_0 = 3$) at various wave numbers, generalized Enskog kinetic theory (full curve) and molecular dynamics data (open circles). (a) $q\sigma = 0.0865$, simulation data with $N = 2016$. (b) $q\sigma = 0.173$, simulation data with $N = 504$. Additional simulation data with $N = 504$ and $q\sigma = 0.1745$ (crosses) and with $N = 2016$ and $q\sigma = 0.173$ (triangles). (c) $q\sigma = 0.346$, simulation data with $N = 504$.

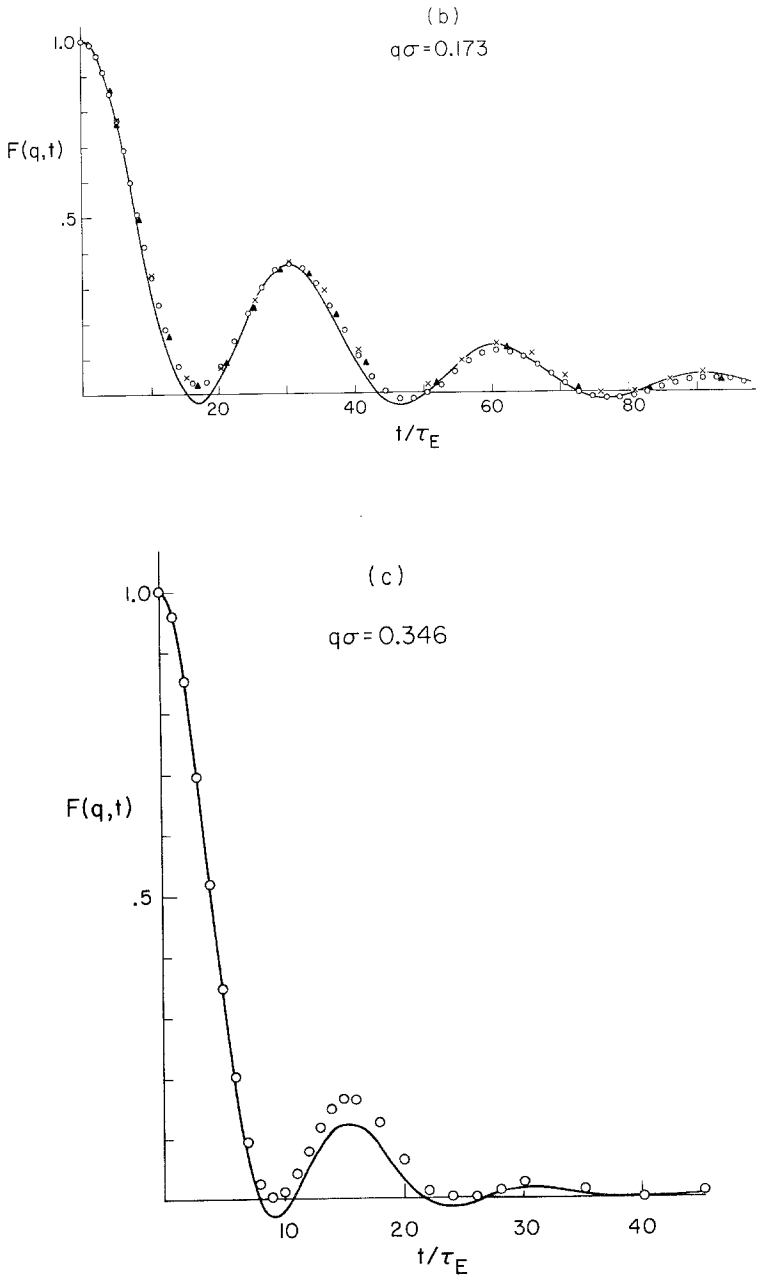

Fig. 2. Continued.

Table I. Static Structure Factor of Hard-Disk Fluid at $A/A_0 = 3$ Obtained by Molecular Dynamics Simulation

$q\sigma$	$S(q)$
0.0865	0.266[a]
0.0874	0.252[a]
0.1223	0.246[a]
0.173	0.254[a]
	0.235[a]
0.1745	0.252[a]
	0.240[b]
0.2447	0.237[b]
0.346	0.240[b]
0.3496	0.242[b]

[a] Data from $N = 2016$ system.
[b] Data from $N = 504$ system.

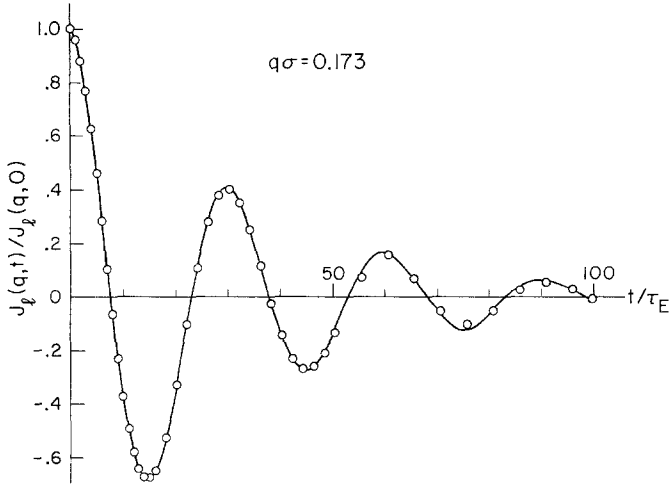

Fig. 3. Longitudinal current correlation function $J_l(q, t)$ of hard-disk fluid ($A/A_0 = 3$) at $q\sigma = 0.173$, generalized Enskog kinetic theory (full curve) and molecular dynamics data with $N = 504$ (circles).

small, a few percent or less, a conclusion that would be consistent with previous experience from the analysis of simulation data on three-dimensional fluids.[4] The most sensitive results appear to be the static structure factor $S(q)$. The present simulation data are summarized in Table I.

The longitudinal current correlation function $\phi_{22}(q,z)$ is directly related to the density correlation function by the continuity equation

$$z\left[z\phi_{11}(q,z)+1\right]=\Omega_0^2(q)\phi_{22}(q,z) \tag{17}$$

which implies for the spectra $\phi''_{22}(q,\omega)=(\omega/\Omega_0)^2\phi''_{11}(q,\omega)$. The Fourier transform $J_l(q,t)$ of the calculated $\phi_{22}(q,z)$ is shown in Fig. 3 along with the molecular dynamics results. Due to the instantaneous hard-core collisions $J_l(q,t)$ is not analytic at small times; its short time expansion

$$J_l(q,t)=1-\tfrac{1}{8}(q\sigma)^2 i_4(q\sigma)\nu|t|+O(t^2) \tag{18}$$

is given correctly by the Enskog theory.[18]

The energy correlation function $\phi_{\epsilon\epsilon}(q,z)$ where $\epsilon(q)=[1+S(q)]^{-1/2}\int(p^2/2mT)f_p(\mathbf{q})$ has not received much attention. Its spectral features resemble those of $S(q,\omega)$ and $\phi''_{22}(q,\omega)$ in that both the diffusive and the propagating modes are prominent. This function can be expressed as

$$\phi_{\epsilon\epsilon}(q,z)=\left\{S(q)\phi_{11}(q,z)+\phi_{33}(q,z)+z\left[S(q)\right]^{1/2}\phi_{13}(q,z)\right\}/\left[1+S(q)\right] \tag{19}$$

A comparison of its Fourier transform with simulation results at $q\sigma=0.173$

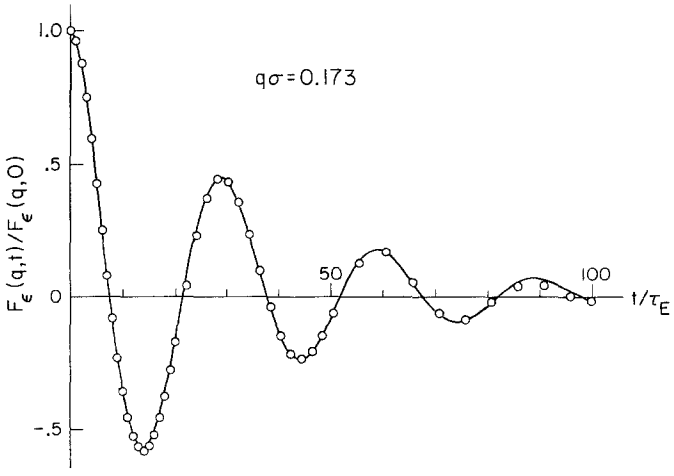

Fig. 4. Energy correlation function $F_\epsilon(q,t)$; same notation as Fig. 3.

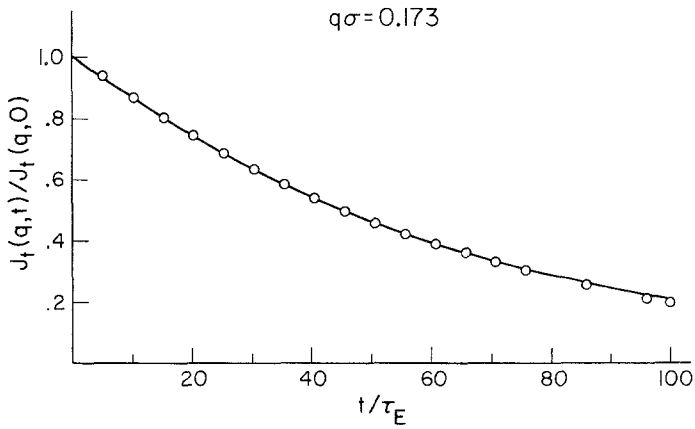

Fig. 5. Transverse current correlation function $J_t(q,t)$; same notation as Fig. 3.

is shown in Fig. 4. The short time expansion of $F_\epsilon(q,t)$ is

$$F_\epsilon(q,t) = 1 - \tfrac{1}{4}(q\sigma)^2 i_3(q\sigma)\nu|t| + O(t^2) \tag{20}$$

The good agreement between generalized Enskog theory and computer simulation data extends also to the transverse current correlation function. Figure 5 shows the results for $q\sigma = 0.173$. Enskog theory again gives correctly the short-time expansion

$$J_t(q,t) = 1 - \tfrac{1}{8}(q\sigma)^2 i_1(q\sigma)\nu|t| + \sigma(t^2) \tag{21}$$

5. DISCUSSION

The generalized Enskog kinetic theory is an attempt to treat transport processes in dense fluids while still considering only uncorrelated binary collisions. Its success in describing the time correlation functions considered here means that the theory is useful over a range of densities up to at least $A/A_0 = 3$. This conclusion is consistent with the results obtained in three dimensions.[4] At liquid densities, $A/A_0 < 1.4$ (freezing[17] occurs at $A/A_0 = 1.31$), one can expect the Enskog results for the dynamic structure factor $S(q,\omega)$ and the transverse current correlation function to show qualitative deficiencies. In $S(q,\omega)$, Enskog theory will be unable to describe properly the low-frequency behavior, whereas in $J_t(q,\omega)$ it will not be able to describe the onset of shear wave propagation,[4] both features being associated with viscoelastic effects in a dense medium. (In addition, it is well known that the Enskog theory is not able to predict the long-time power law decay of time correlation functions.)

It will be useful to perform molecular dynamics simulation at densities $A/A_0 = 1.4$ and higher to confirm the breakdown of the Enskog theory. Availability of such data would provide the motivation to formulate self-consistent mode-coupling calculations for two dimensions. This type of calculation has been carried out for three-dimensional fluids, both hard sphere[5,19] and continuous potential systems,[20] with good results. Our expectation is that the mode-coupling approach will be sufficient to treat the viscoelastic effects in $S(q,\omega)$ and $J_t(q,\omega)$.

The agreement between Enskog theory and simulation data at $A/A_0 = 3$ also implies that collective effects which give rise to nonexponential decay of time correlation functions are not readily observable in the various functions studied here. It is well known that at this density there is a significant enhancement of the self-diffusion coefficient over the Enskog value as a result of the long time tail contribution in the velocity autocorrelation function.[6] In a separate paper[21] we will consider the Enskog equation in two dimensions for the self-correlation function at finite wave number and show that the theory is adequate up to a density of $A/A_0 = 2$. Again, one can go to higher densities by extending the analysis to include correlated collision effects.

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APPENDIX: MATRIX ELEMENTS OF THE COLLISION OPERATOR

We will evaluate the matrix elements of the Enskog collision operator, Eq. (5d), using the Sonine polynomials. Hermite polynomials, on the other hand, also could be chosen as a complete orthonormal set of momentum functions. The Sonine polynomials are defined by

$$\Psi_{NM}(\boldsymbol{\zeta}) = (-1)^N a_{NM} \zeta^{|M|} L_N^{|M|}(\zeta^2) e^{iM\varphi}, \qquad N = 0, 1, \ldots; \quad M = 0, \pm 1, \ldots \tag{A.1}$$

where $\boldsymbol{\zeta} = \mathbf{p}/(2mT)^{1/2}$, $\zeta_x = \zeta \sin\varphi$, $\zeta_y = \zeta \cos\varphi$, and $L_n^m(x)$ are the Laguerre polynomials. $a_{nm} = [n!/(n + |m|)!]^{1/2}$ is a normalization factor such that

$$\langle NM \mid N'M' \rangle = \int d\boldsymbol{\zeta}\, \varphi(\zeta) \Psi_{NM}^*(\boldsymbol{\zeta}) \Psi_{N'M'}(\boldsymbol{\zeta}) = \delta_{NN'}\delta_{MM'} \tag{A.2}$$

where $\varphi(\zeta) = (1/\pi)\exp(-\zeta^2)$ is the Maxwellian velocity distribution.

In deriving the matrix elements using this basis, two formulas will be helpful which can be proved by using the generating function

$$e^{2\gamma\zeta-\zeta^2}=\sum_{N=0}^{\infty}\sum_{M=-\infty}^{\infty}\frac{a_{NM}}{N!}\Psi_{NM}(\gamma)\zeta^{2N+|M|}e^{-iM\varphi} \tag{A.3}$$

The first formula is an addition theorem,

$$\Psi_{NM}(\gamma+\zeta)=\left[N!(N+|M|)!\right]^{1/2}\sum_{\nu,n=0}^{\infty}\sum_{\mu,m=-\infty}^{\infty}\frac{a_{NM}\zeta^{2\nu+|\mu|}e^{i\mu\varphi}}{N!\,\nu!(\nu+|\mu|)!}\Psi_{nm}(\gamma) \tag{A.4}$$

where the summation is restricted by $\mu+m=M$ and $2(\nu+n)+|\mu|+|m|=2N+|M|$. The second formula is the integral

$$\int d\zeta\,\varphi(\zeta)\Psi^*_{nm}(\zeta/\sqrt{2})\Psi_{n'm'}(\zeta/\sqrt{2})$$
$$=\delta_{mm'}(-1)^{n+n'}(1/2)^{n+n'+|m|}a_{nm}a_{n'm'}\frac{(n+n'+|m|)!}{n!\,n'!} \tag{A.5}$$

The collision operator matrix elements are

$$\langle NM|t(\mathbf{q})|N'M'\rangle$$
$$=-i\nu(2\pi)^{1/2}\int\frac{d\hat{r}}{2\pi}\int d\zeta_1\,d\zeta_2\,\varphi(\zeta_1)\varphi(\zeta_2)(\zeta_{12}\cdot\hat{r})\theta(\zeta_{12}\cdot\hat{r})$$
$$\times\Psi^*_{NM}(\zeta_1)\left\{\Psi_{N'M'}(\zeta_1')-\Psi_{N'M'}(\zeta_1)+e^{i\mathbf{q}\hat{r}\sigma}\left[\Psi_{N'M'}(\zeta_2')-\Psi_{N'M'}(\zeta_2)\right]\right\} \tag{A.6}$$

where $\zeta_{1,2}'=\zeta_{1,2}\pm(\zeta_{12}\cdot\hat{r})\hat{r}$ are the momenta after the collision. The evaluations of the various integrals proceeds along the same lines as in the three-dimensional case.[19] After introducing relative and center of mass momenta γ and χ, respectively, by $\gamma=(1/\sqrt{2})(\zeta_1-\zeta_2)$, $\chi=(1/\sqrt{2})(\zeta_1+\zeta_2)$, where $\chi'=\chi$ and $|\gamma'|=|\gamma|$ due to momentum and energy conservation, one may use formula (A.4) to expand $\psi^*_{NM}(\chi+\gamma)/\sqrt{2})$, $\psi_{N'M'}((\chi\pm\gamma')/\sqrt{2})$, and $\psi_{N'M'}((\chi\pm\gamma)/\sqrt{2})$ in terms of $\psi_{nm}(\chi/\sqrt{2})$. Then the integral over the center of mass momentum χ may be performed using formula (A.5). The final integrations over γ and $\hat{r}$ are then straightforward and one obtains

$$\langle NM|t(\mathbf{q})|N'M'\rangle$$
$$=i\nu\left(\frac{1}{\sqrt{2}}\right)^{2(N+N')+|M|+|M'|}\left[N!N'!(N+|M|)!(N'+|M|)!\right]^{1/2}$$
$$\times\left\{\delta_{M,M'}H^{(+)}(NM,N'M')+(-1)^M J_{M-M'}(q\sigma)H^{(-)}(NM,N'M')\right\} \tag{A.7a}$$

where

$$H^{(\pm)}(NM, N'M') = \sum_m \begin{pmatrix} 1 \\ (-1)^m \end{pmatrix} F^{(m)}_{MM'} K_m(NM, N'M') \qquad \text{(A.7b)}$$

$$K_m(NM, N'M') = \sum_{nn'\nu\nu'} (-1)^{n+n'} \times \frac{(n + n' + |m|)!\,\Gamma(\nu + \nu' + (|M - m| + |M' - m| + 3)/2)/\Gamma(3/2)}{\nu!\,\nu'!\,n!\,n'!\,(\nu + |M - m|)!\,(\nu' + |M' - m|)!\,(n + |m|)!\,(n' + |m|)!} \qquad \text{(A.7c)}$$

with the summation restrictions $2(\nu + n) + |M - m| + |m| = 2N + |M|$ and $2(\nu' + n') + |M' - m| + |m| = 2N' + |M'|$ and

$$F^{(m)}_{MM'} = \begin{cases} \left[\dfrac{1}{1 - (M - M')^2} - \dfrac{1}{(M + M' - 2m)^2 - 1} \right], & M + M' \text{ even} \\ (-i)^{M - M'} \dfrac{\pi}{4} \left[\delta_{|M - M'|,1} + (-1)^{M - m} \delta_{|M + M' - 2m|,1} \right], & M + M' \text{ odd} \end{cases} \qquad \text{(A.7d)}$$

and $J_n(x)$ are Bessel functions of order n. Thus, these matrix elements are reduced to a finite threefold sum. We note that the matrix elements of the Lorentz–Enskog collision operator for self-diffusion may be obtained from Eq. (A.7a) by keeping only the first part in the bracket involving $H^{(+)}$.

The results for the set of variables quoted in Eqs. (8a) and (8b) are easily obtained from Eq. (A.7). The functions $i_n(x)$, $n = 0, \ldots, 9$, which reflect the wavenumber dependence are defined as follows:

$$i_0(x) = \frac{2}{x} J_1(x), \qquad i_5(x) = \frac{1}{2}\left[3 - J_0(x) + J_4(x)\right]$$

$$i_1(x) = \frac{8}{x^2}\left[1 - J_0(x) - J_2(x)\right], \qquad i_6(x) = \frac{2}{x}\left[J_1(x) - J_3(x)\right]$$

$$i_2(x) = \frac{8}{x^2} J_2(x), \qquad i_7(x) = \frac{1}{2}\left[3 - J_0(x) - J_4(x)\right]$$

$$i_3(x) = \frac{4}{x^2}\left[1 - J_0(x)\right], \qquad i_8(x) = \frac{1}{16}\left[43 + 27J_2(x) - 27J_2(x)\right]$$

$$i_4(x) = \frac{8}{3x^2}\left[1 - J_0(x) + J_2(x)\right], \qquad i_9(x) = \frac{1}{8}\left[23 - 15J_0(x)\right]$$

These quantities are normalized by $i_n(0) = 1$.

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