Binary collision contribution to the longitudinal current correlation function of dense fluids

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An expression for the binary collision contribution to the first-order space-time memory function of the longitudinal current correlation function has been obtained by using the cluster expansion technique for a fluid whose particles are interacting through a continuous potential. This expression involves the radial distribution function and time dependence of the position, momentum, and acceleration vectors of the particles. The long-wavelength limit of the expression is obtained for use in studying the longitudinal and bulk viscosities of fluid. It is found that for the hard-sphere case, our method provides expressions for the longitudinal and bulk viscosities that agree with Enskog results. [S1063-651X(97)06601-4]

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I. INTRODUCTION

Considerable progress has been made during past four decades in extending our knowledge of atomic dynamics at wavelengths and frequencies of molecular scale in dense gases and liquids [1,2]. The density space-time correlation function provides information about the temporal structure factor and viscous processes in fluids. The longitudinal viscosity associated with the time correlation function of density is $\frac{4}{3}$ times the shear viscosity plus the bulk viscosity. In the past, the shear viscosity of the dense fluids has received much more attention than the bulk viscosity; this may have been due to complications involved in determining the accurate value of the bulk viscosity experimentally. Theoretically, one approach to the space-time correlation function has been through the evaluation of its memory function (MF). Recently, we have calculated expressions for the binary collision contribution to the MF of the self-density correlation function [3] and the transverse current correlation function [4]. When applied to hard-sphere fluids, our expressions provide results for the self-diffusion and the shear viscosity in agreement with the Enskog results [5]. In the present work we derive an expression for the binary collision contribution to the longitudinal current correlation function that is calculable for a continuous potential. The long-wavelength limit of this expression may be used to study the longitudinal viscosity of the fluid. When applied for a system interacting via a hard-sphere potential, our expressions for the longitudinal and bulk viscosities are found to be in agreement with the Enskog value.

The layout of the paper is as follows. In Sec. II the basic formalism and exact relations are given. An expression for the binary collision contribution to the MF of the longitudinal current correlation function is obtained in Sec. III. An expression for the longitudinal viscosity in terms of the long-wavelength limit of the expression obtained in Sec. III is given in Sec. IV. Section IV also contains various exact relation between various viscosities. In Sec. V the expressions for the longitudinal and bulk viscosities are evaluated for particles interacting via a hard-sphere potential. The work is concluded in Sec. VI.

II. BASIC FORMALISM

The longitudinal current correlation function is defined as

$$C(q,t)=\langle j_{xx}^{*}(q,t)j_{xx}(q,0)\rangle, \tag{1}$$

where the dynamical variable is

$$j_{xx}(q,t)=\sum_{i=1}^{N} v_{ix}(t)e^{iqx_i(t)}, \tag{2}$$

with the wave vector $\mathbf{q}$ taken along the x axis. The angular brackets in Eq. (1) represent the ensemble average; $v_{ix}(t)$ and $x_i(t)$ are the x component of the velocity and the position of the ith particle at any time t. The time dependence of any dynamical variable $A(q,t)$ is determined by the equation of motion

$$\frac{\partial A(q,t)}{\partial t}=i\mathcal{L}A(q,t), \tag{3}$$

where $\mathcal{L}$ is the Liouville operator and is defined as

$$\begin{aligned}\mathcal{L}&=\mathcal{L}_0+\sum_{j<k}\mathcal{L}_1(j,k)\\&=-i\sum_j \frac{\mathbf{P}_j}{m}\frac{\partial}{\partial \mathbf{r}_j}-i\sum_{j<k}\mathbf{F}_{jk}\left(\frac{\partial}{\partial \mathbf{P}_j}-\frac{\partial}{\partial \mathbf{P}_k}\right);\end{aligned} \tag{4}$$

$\mathbf{F}_{jk}=-\partial U(r_{jk})/\partial r_j$ is the force and $r_{jk}=|\mathbf{r}_j-\mathbf{r}_k|$. We define the Fourier-Laplace transform of $C(q,t)$ as

$$\begin{aligned}\widetilde{C}(q,z)&=i\int_0^{\infty}dt\ e^{izt}C(q,t),\\&=\left\langle j_{xx}(q,0)\left|\frac{1}{\mathcal{L}-z}\right|j_{xx}(q,0)\right\rangle\end{aligned} \tag{5}$$

for Im$z>0$.

The dynamical structure factor $S(q,\omega)$ is related to $C(q,\omega)$ by

$$S(q,\omega)=\frac{q^2}{\omega^2}\,C(q,\omega). \tag{6}$$

The time evolution of $C(q,t)$ can be determined by using Mori's equation of motion, which in z space is

$$\tilde{C}(q,z)=-\frac{v_0^2}{z+\tilde{K}(q,z)}, \tag{7}$$

where $\tilde{K}(q,z)$ is the first-order memory function of the longitudinal current correlation function and is defined as

$$\tilde{K}(q,z)=\frac{1}{Nv_0^2}\left\langle Q\mathcal{L}j_{xx}(q,0)\left|\frac{1}{Q\mathcal{L}Q-z}\right|Q\mathcal{L}j_{xx}(q,0)\right\rangle. \tag{8}$$

In Eq. (8) $Q=1-P$ is a projection operator orthogonal to $P=v_0^{-2}|j_{xx}(q,0)\rangle\langle j_{xx}(q,0)|$ and $v_0^2=k_BT/m$ is the square of the thermal speed.

The memory function $\tilde{K}(q,z)$ can be expressed in terms of a conventional correlation function whose time evolution is governed by the original Liouville operator rather than the projected one $Q\mathcal{L}Q$ appearing in Eq. (8). By twice applying the identity

$$\frac{z}{\mathcal{L}-z}=-1+\frac{\mathcal{L}}{\mathcal{L}-z} \tag{9}$$

to Eq. (5) we obtain

$$z^2\tilde{C}(q,z)=v_0^2[-z+\tilde{\phi}^L(q,z)], \tag{10}$$

where

$$\tilde{\phi}^L(q,z)=\frac{1}{Nv_0^2}\left\langle \mathcal{L}j_{xx}(q,0)\left|\frac{1}{\mathcal{L}-z}\right|\mathcal{L}j_{xx}(q,0)\right\rangle \tag{11}$$

is the Fourier-Laplace transform of the time correlation function $\phi^L(q,t)$. From Eqs. (7) and (10) we get

$$\tilde{K}(q,z)=\frac{z\tilde{\phi}^L(q,z)}{z-\tilde{\phi}^L(q,z)}. \tag{12}$$

Thus the MF and hence the longitudinal current correlation function can be obtained from the knowledge of $\phi^L(q,t)$ only. In the next section we evaluate $\phi^L(q,t)$ in the binary collision approximation.

III. BINARY COLLISION CONTRIBUTION

The binary collision contribution to $\phi^L(q,t)$ can be obtained microscopically by using the cluster expansion technique [6]. This involves the cluster expansion of the resolvent operator $(\mathcal{L}-z)^{-1}$, which appears in the definition of any time correlation function. The binary collision expansion formula is

$$\frac{1}{\mathcal{L}-z}=\frac{1}{\mathcal{L}_0-z}+\sum_{j<k}\left(\frac{1}{\mathcal{L}_0+\mathcal{L}_1(j,k)-z}-\frac{1}{\mathcal{L}_0-z}\right)+\cdots . \tag{13}$$

In this equation the first term involves free propagation and the second term contains a sum over a pair of particles (j,k) only. The third term involves three particles and so on. This equation has already been used in deriving the low-density formula for the phase-space MF and the first-order space-time MF.

For the dynamical variable $j_{xx}(t)$ we have

$$i\mathcal{L}j_{xx}=\frac{dj_{xx}}{dt}=\sum_i(\dot{v}_{ix}e^{iqx_i}+iqv_{ix}^2e^{iqx_i}), \tag{14}$$

where $\dot{v}_{ix}=(-1/m)\partial U(r)/\partial x_i$ is the x component of the acceleration of particle i. Substituting Eq. (14) into Eq. (11), we obtain

$$\tilde{\phi}^L(q,z)=\frac{1}{v_0^2}\sum_i\sum_j\left\langle\left(-\frac{1}{m}\frac{\partial U(r)}{\partial x_i}+iqv_{ix}^2\right)\times e^{iqx_i}\left|\frac{1}{\mathcal{L}-z}\right|\left(-\frac{1}{m}\frac{\partial U(r)}{\partial x_j}+iqv_{jx}^2\right)e^{iqx_j}\right\rangle. \tag{15}$$

Using the binary collision expansion formula (13), the longitudinal current correlation function $\phi^L(q,t)$ can be written as sum of two terms, i.e.,

$$\phi^L(q,t)=\phi_0^L(q,t)+\phi_1^L(q,t), \tag{16}$$

where $\phi_0^L(q,t)$ and $\phi_1^L(q,t)$ are the contributions corresponding to the first and second terms of Eq. (13) in the time domain. Since Eq. (14) is the sum of the kinetic and potential contributions, Eq. (15) can be written as a sum of four terms. One is a kinetic-kinetic term, two are kinetic-potential (cross) terms, and the fourth is a potential-potential term. Evaluation of the first two contributions is simple; therefore, we illustrate here the evaluation of the potential-potential term only. This term will be the sum of two terms $\phi_0^p(q,t)$ and $\phi_1^p(q,t)$ corresponding to the first two terms in Eq. (13), respectively. Procedures for evaluation of $\phi_0^p(q,t)$ and $\phi_1^p(q,t)$ are quite similar; therefore, we illustrate here only the term $\phi_1^p(q,t)$. Writing the total potential as a sum of pair potentials and using Eq. (13) in Eq. (15), we obtain the potential-potential contribution

$$\tilde{\phi}_1^p(q,z)=\frac{1}{m^2v_0^2}\left\langle\frac{\partial U}{\partial x_1}e^{iqx_1}\sum_{l<k}\left(\frac{1}{\mathcal{L}_0-\mathcal{L}_1(l,k)-z}-\frac{1}{\mathcal{L}_0-z}\right)\times\left(\sum_{j\neq1}\frac{\partial u(r_{1j})}{\partial x_1}e^{iqx_1}+(N-1)\sum_{j\neq2}\frac{\partial u(r_{2j})}{\partial x_2}e^{iqx_2}\right)\right\rangle. \tag{17}$$

The sum over j in the last term can be simplified by noting that all terms except for $j=1$ are equivalent. Noting

$$\sum_{j\neq 2} \frac{\partial u(r_{2j})}{\partial x_2} e^{iqx_2} = \frac{\partial u(r_{21})}{\partial x_2} e^{iqx_2} + (N-2) \frac{\partial u(r_{23})}{\partial x_2} e^{iqx_2}, \tag{18}$$

we write Eq. (17) in the time domain as

$$\phi_1^p(q,t) = \frac{1}{P_0^2} \left\langle \frac{\partial U}{\partial x_1} \left\{ e^{iqx_1}(e^{-i\mathcal{L}_{12}t} - e^{-i\mathcal{L}_0(12)t}) \left((N-1) \times \frac{\partial u(r_{12})}{\partial x_1} e^{-iqx_1} - (N-1) \frac{\partial u(r_{12})}{\partial x_1} e^{-iqx_2} \right) + \left[e^{iqx_1}(e^{-i\mathcal{L}_{23}t} - e^{-i\mathcal{L}_0(23)t})(N-1)(N-2) \times \frac{\partial u(r_{23})}{\partial x_2} e^{-iqx_2} \right] \right\} \right\rangle, \tag{19}$$

where

$$\mathcal{L}_{12} = \mathcal{L}_0(1) + \mathcal{L}_0(2) + \mathcal{L}_1(12) = \mathcal{L}_0(12) + \mathcal{L}_1(12).$$

In the first two terms of Eq. (19) the dynamics of only two particles appears, whereas the last term involves the interaction of three particles and is proportional to the square of the density. It is shown in Appendix B that for a hard-sphere fluid for the recollision process the three-particle terms do contribute to the binary collision dynamics. It can be seen from Eq. (19) that due to the operation of $\mathcal{L}_0$, there will appear some terms containing the force in the form $\mathbf{F}(|\mathbf{r}+pt/m|)$ that are divergent due to the free-particle dynamics. However, such terms exactly cancel with the same divergent terms appearing in $\phi_0^p(q,t)$. Following the procedure of averaging as described in Ref. [3], we finally obtain an expression for $\phi^L(q,t)$ by collecting the terms that involve only binary collisions

$$\begin{aligned}\phi^L(q,t) = {} & \Omega_0^2(3-6a^2+a^4)e^{-a^2/2} + \frac{n\Omega_0^2}{P_0^4} \int\int d\mathbf{r}\, d\mathbf{p}\, G\left\{\frac{p}{\sqrt{2}}\right\} g(r) \{e^{(iq/2)[x-x(t)]}B[p_x(t)] + e^{(iq/2)[x+x(t)]}B[-p_x(t)] \\ & - e^{-iqp_xt/2m}B_0[p_x] - e^{iq[x+(p_xt/2m)]}B_0[-p_x]\} + \frac{in\Omega_0}{P_0^3} \int\int d\mathbf{r}\, d\mathbf{p}\, G\left(\frac{p}{\sqrt{2}}\right) g(r) e^{iqx/2} A_0[p_x](e^{-iqx(t)/2} \\ & - e^{iqx(t)/2}) F_x[r(t)] - \frac{in\Omega_0}{\beta P_0^3} \int\int d\mathbf{r}\, d\mathbf{p}\, G\left(\frac{p}{\sqrt{2}}\right) \frac{\partial g(r)}{\partial x} e^{iqx/2} \{A[p_x(t)]e^{-iqx(t)/2} + A[-p_x(t)]e^{iqx(t)/2} \\ & - A_0[p_x]e^{(-iq/2)[x+(p_xt/m)]} - A_0[-p_x]e^{(iq/2)[x+(p_xt/m)]}\} + \frac{nI_0}{\beta P_0^2} \int\int d\mathbf{r}\, d\mathbf{p}\, G\left(\frac{p}{\sqrt{2}}\right) \frac{\partial g(r)}{\partial x} e^{iqx/2}(e^{-iqx(t)/2} \\ & - e^{iqx(t)/2}) F_x[r(t)].\end{aligned} \tag{20}$$

In this equation we have introduced the notations

$$\Omega_0 = qv_0, \quad a = \Omega_0 t,$$

$$I_n \equiv I_n(q,t) = \int d\mathbf{P}\, G(\sqrt{2}P) P_x^n e^{-(iqP_x/m)t}; \tag{21}$$

$$A[p_x(t)] = \tfrac{1}{4} p_x^2(t) I_0 + p_x(t) I_1 + I_2; \tag{22}$$

and

$$\begin{aligned}B[p_x(t)] = {} & \tfrac{1}{16} p_x^2 p_x^2(t) I_0 + \tfrac{1}{4}[p_x p_x^2(t) + p_x^2 p_x(t)] I_1 \\ & + \tfrac{1}{4}[p_x^2 + p_x^2(t) + 4p_x p_x(t)] I_2 \\ & + [p_x + p_x(t)] I_3 + I_4.\end{aligned} \tag{23}$$

A_0 and B_0 are the values of A and B with $p_x(t) = p_x(0) = p_x$. $g(r)$ is the static correlation function and

$$G(P) = (1/2\pi P_0^2)^{3/2} \exp(-P^2/2P_0^2) \tag{24}$$

is the Maxwellian momentum distribution.

In Eq. (20) the position and momentum vectors $\mathbf{r}(t)$ and $\mathbf{p}(t)$ of the particle moving in a central potential are determined from the equation of motion

$$\frac{1}{2}\frac{dp_x}{dt} = \frac{m}{2}\frac{d^2x}{dt^2} = F_x(r) = -\frac{\partial U(r)}{\partial x}. \tag{25}$$

In the next section we derive an expression for the longitudinal viscosity in terms of the long-wavelength limit of Eq. (20).

IV. LONGITUDINAL VISCOSITY

The expression for the longitudinal viscosity η_1 is [2]

$$\eta_l = \eta_B + \frac{4}{3}\eta_S = \frac{1}{Vk_BT}\int_0^\infty [J_{xx}(t) - \langle J_{xx}(t)\rangle](J_{xx} - \langle J_{xx}\rangle), \tag{26}$$

where

$$J_{\alpha\beta}(t) = \frac{1}{N}\sum_i [mv_{i\alpha}(t)v_{i\beta}(t) + r_{i\alpha}(t)F_{i\beta}(t)] \tag{27}$$

and

$$\langle J_{\alpha\beta}\rangle=\delta_{\alpha\beta}V\left[P+V\left(\frac{dP}{dE}\right)(E-\overline{E})\right], \tag{28}$$

with

$$PV=k_BT-\frac{2\pi n}{3}\int_0^\infty dr\,\frac{\partial U(r)}{\partial r}\,r^3g(r), \tag{29a}$$

$$E=\sum_i \frac{p_i^2}{2m}+\frac{1}{2}\sum_{i,j}{}'\,U(|\mathbf{r}_i-\mathbf{r}_j|), \tag{29b}$$

and

$$\overline{E}=\frac{3}{2}\,k_BT+\frac{n}{2}\int d\mathbf{r}\;U(r)g(r). \tag{29c}$$

In Eq. (27) $r_{i\alpha}(t)$ and $F_{i\alpha}(t)$ are the αth component of position and force on the ith particle at any time t. Expression (28) for $\langle J_{\alpha\beta}\rangle$ is suitable [7] for the canonical ensemble averaging that is used in the present work. Rewriting Eq. (26) and noting that $\langle J_{xx}(t)J_{xx}(0)\rangle$ is given by $\lim_{q\to 0}\phi^L(q,t)/q^2$, we obtain an expression for the longitudinal viscosity

$$\eta_1=\beta n m^2\int_0^\infty\left(\lim_{q\to 0}\frac{\phi^L(q,t)}{q^2}+\langle\langle J_{xx}\rangle\langle J_{xx}(t)\rangle\rangle\right.$$
$$\left.-\langle J_{xx}(t)\langle J_{xx}\rangle\rangle-\langle J_{xx}\langle J_{xx}(t)\rangle\rangle\right)dt \tag{30}$$

$$=\beta n\int_0^\infty S_l(t)dt. \tag{31}$$

In Eq. (31) $S_l(t)$ is m^2 times the integrand of Eq. (30). The expressions for the bulk and shear viscosities are similar to Eq. (26) and are given, respectively, as

$$\eta_B=\beta n\int_0^\infty S_B(t)dt,$$

$$S_B(t)=\sum_{\alpha,\beta}\langle[J_{\alpha\alpha}-\langle J_{\alpha\alpha}(t)\rangle](J_{\beta\beta}-\langle J_{\beta\beta}\rangle)\rangle \tag{32}$$

and

$$\eta_S=\beta n\int_0^\infty \phi^T(t)dt,\quad \phi^T(t)=\langle J_{xy}(t)J_{xy}(0)\rangle. \tag{33}$$

Since $\eta_l=\frac{4}{3}\eta_s+\eta_B$, from Eqs. (31)–(33) we find that

$$S_l(t)=\tfrac{4}{3}\phi^T(t)+S_B(t). \tag{34}$$

Using the above relation, we note that

$$\langle J_{xx}(t)J_{yy}(0)\rangle=\langle J_{xx}(t)J_{xx}(0)\rangle-2\langle J_{xy}(t)J_{xy}(0)\rangle. \tag{35}$$

The expression for $\lim_{q\to 0}\phi^L(q,t)/q^2$ appearing in Eq. (30) can be obtained from Eq. (20) and is

$$\phi^L(t)=\lim_{q\to 0}\frac{\phi^L(q,t)}{q^2}=\frac{3k_BT}{m}+\frac{n}{m^2P_0^2}$$
$$\times\int\int d\mathbf{r}\;d\mathbf{p}\;G\left(\frac{p}{\sqrt{2}}\right)g(r)\left(\frac{I_0}{8}\,[p_x^2p_x^2(t)-p_x^4]\right.$$
$$\left.+\frac{I_2}{2}\,[p_x^2(t)-p_x^2]\right)+\frac{n}{mP_0^2}\int\int d\mathbf{r}\;d\mathbf{p}\;G\left(\frac{p}{\sqrt{2}}\right)$$
$$\times g(r)[(p_x^2I_0/4)+I_2]x(t)F_x[r(t)]$$
$$+\frac{n}{m\beta P_0^2}\int\int d\mathbf{r}\;d\mathbf{p}\;G\left(\frac{p}{\sqrt{2}}\right)\frac{\partial g(r)}{\partial x}$$
$$\times x[p_x^2(t)-p_x^2]\,\frac{I_0}{4}+\frac{nI_0}{2\beta P_0^2}$$
$$\times\int\int d\mathbf{r}\;d\mathbf{p}\;G\left(\frac{p}{\sqrt{2}}\right)$$
$$\times\frac{\partial g(r)}{\partial x}\;x\;x(t)F_x[r(t)]. \tag{36}$$

This expression contains effects of uncorrelated binary collisions only. The derivative of $g(r)$ appears in some terms so the density dependence is more complicated than the explicit linear dependence. In Eq. (36), the first integral represents the purely kinetic term corresponding to the transport of momentum via the displacement of particles, the second and the third integrals are the kinetic-potential (cross) terms, and the last term is due to the potential term arising from the action of interparticle forces. Equation (36) at $t=0$ reduces to

$$\phi^L(0)=\frac{3k_BT}{m}+\frac{n}{m}\int d\mathbf{r}\;g(r)x\;F_x(r)$$
$$+\frac{n}{2m}\int d\mathbf{r}\;\frac{\partial g(r)}{\partial x}\,x^2F_x(r). \tag{37}$$

This expression is the second sum rule of the longitudinal current correlation function in the long-wavelength limit.

The kinetic contribution to $\langle J_{xx}(t)\rangle$ is given by

$$\langle J_{xx}(t)\rangle=\sum_i\frac{p_i^2(t)}{3m}.$$

Using this equation, we can write the second term of Eq. (30) as

$$\langle\langle J_{xx}(t)\rangle\langle J_{xx}(0)\rangle\rangle=\frac{1}{9m^2}\sum_{i,j}\langle p_i^2(t)p_j^2(0)\rangle. \tag{38}$$

The ensemble average involves terms such as $\langle p_{ix}^{\,2}(t)p_{jx}^{\,2}\rangle$ and $\langle p_{ix}^{\,2}(t)p_{jy}^{\,2}\rangle$. The former term can be related to the kinetic part of $\phi^L(t)$ and the latter to the kinetic parts of $\phi^L(t)$ and $\phi^T(t)$ (i.e., the transverse stress correlation function). By using Eq. (35) we finally obtain

$$\langle\langle J_{xx}(t)\rangle\langle J_{xx}(0)\rangle\rangle=[\phi_{kk}^L(t)-\tfrac{4}{3}\phi_{kk}^T(t)]. \tag{39}$$

Similarly, the other two terms in Eq. (30) for the noninteracting part are

$$\langle J_{xx}(t)\langle J_{xx}(0)\rangle\rangle=\langle J_{xx}(0)\langle J_{xx}(t)\rangle\rangle=[\phi_{kk}^{L}(t)-\tfrac{4}{3}\phi_{kk}^{T}(t)]. \quad (40)$$

In the above equation $\phi_{kk}^{L}(t)$ and $\phi_{kk}^{T}(t)$ are the kinetic parts of the long-wavelength limit of the MF of the longitudinal and transverse current correlation functions. Using Eqs. (39) and (40) in Eq. (30) and taking into account only the kinetic-kinetic contribution, we obtain

$$S_{kk}^{l}(t)=\phi_{kk}^{L}(t)+[\phi_{kk}^{L}(t)-\tfrac{4}{3}\phi_{kk}^{T}(t)]-2[\phi_{kk}^{L}(t)-\tfrac{4}{3}\phi_{kk}^{T}(t)]$$
$$=\tfrac{4}{3}\phi_{kk}^{T}(t). \quad (41)$$

This implies that the kinetic part of the longitudinal stress correlation function is $\frac{4}{3}$ times the kinetic part of the transverse stress correlation function. In terms of viscosities we obtain

$$\eta_{l}^{kk}=\tfrac{4}{3}\eta_{S}^{kk} \quad (42)$$

and the relation among three viscosities provides that the kinetic contribution to the bulk viscosity η_B is zero. In the next section we evaluate the longitudinal and bulk viscosities for a system interacting via the hard-sphere potential within the binary collision approximation.

V. HARD-SPHERE LIMIT

In order to calculate the longitudinal viscosity η_l, we have to calculate the various terms in Eq. (30). The expression for the first term given by Eq. (30) can be evaluated by using the well-known hard-sphere dynamics, whereas the last three terms can be simplified for the hard-sphere potential in a manner given below. Using

$$\langle J_{xx}(t)\rangle=\sum_{i}\frac{p_i^2(t)}{3m}(1+\nu), \quad (43)$$

where

$$\nu=\tfrac{2}{3}\pi n\sigma^3 g(\sigma),$$

and considering the second term of Eq. (30), i.e., $\langle\langle J_{xx}\rangle\langle J_{xx}(t)\rangle\rangle$, we write it by using Eq. (43) as

$$\langle\langle J_{xx}\rangle\langle J_{xx}(t)\rangle\rangle=\sum_{i,j}\langle p_i^2(t)p_j^2(0)\rangle\frac{1}{9m^2}(1+\nu)^2. \quad (44)$$

Using Eq. (35) we express Eq. (44) as

$$\langle\langle J_{xx}(t)\rangle\langle J_{xx}(0)\rangle\rangle=(1+\nu)^2(\phi_{kk}^{L}-\tfrac{4}{3}\phi_{kk}^{T}). \quad (45)$$

Similarly, the other two terms of Eq. (30) can be written as

$$\langle J_{xx}(t)\langle J_{xx}\rangle\rangle=(1+\nu)^2[(\phi_{kp}^{L1}-\tfrac{4}{6}\phi_{kp}^{T})+(\phi_{kk}^{L}-\tfrac{4}{3}\phi_{kk}^{T})] \quad (46)$$

and

$$\langle J_{xx}\langle J_{xx}(t)\rangle\rangle=(1+\nu)^2\{[\phi_{kp}^{L2}-\tfrac{4}{6}\phi_{kp}^{T}(t)]+(\phi_{kk}^{L}-\tfrac{4}{3}\phi_{kk}^{T})\}, \quad (47)$$

where ϕ_{kp}^{L1} and ϕ_{kp}^{L2} are the terms corresponding to the two (kinetic-potential) cross terms. Now collecting terms that are independent of density and proportional to the first power of the density, corresponding to the kinetic-kinetic and the kinetic-potential contributions, respectively, we recover Eq. (42) and also obtain

$$\eta_{l}^{kp}=\tfrac{4}{3}\eta_{s}^{kp}. \quad (48)$$

This implies that the kinetic-kinetic and kinetic-potential contributions to bulk viscosities are zero. Similarly, we collect the terms corresponding to the potential-potential contribution to viscosity, i.e., terms proportional to the square of the density and obtain

$$s_1^{pp}(t)=\phi_{pp}^{L}(t)+\nu^2[\phi_{kk}^{L}(t)-\tfrac{4}{3}\phi_{kk}^{T}(t)]-\nu[\phi_{kp}^{L2}(t)+\phi_{kp}^{L1}(t)$$
$$-\tfrac{4}{3}\phi_{kp}^{T}(t)]. \quad (49)$$

This expression does not express the potential-potential contribution to the longitudinal viscosity in terms of the contribution to shear viscosity alone as is done by Eq. (42). This is because the contribution to the bulk viscosity is mainly due to the potential-potential part of stress. In order to determine the potential contribution to longitudinal viscosity we need to evaluate various contributions due to ϕ_{kk}^{L}, ϕ_{kp}^{L1}, and ϕ_{kp}^{L2} for the hard-sphere interaction.

Consider the kinetic-kinetic part of Eq. (36)

$$\phi_{kk}^{L}(t)=\frac{3k_BT}{m}\frac{n}{m^2p_0^2}\int\int d\mathbf{r}\,d\mathbf{p}\,G\left(\frac{p}{\sqrt{2}}\right)g(r)\left(\frac{I_0}{8}[p_x^2p_x^2(t)-p_x^4]+\frac{I_2}{2}p_x^2(t)\right). \quad (50)$$

The time dependence of Eq. (50) is determined by writing

$$\phi_{kk}(t)=\phi_{kk}(0)\left(1+\frac{d\phi_{kk}(t)}{dt}\bigg|_{t=0}t+\cdots\right). \quad (51)$$

The next- and higher-order terms in Eq. (51) involve the correlated binary collisions. Ignoring these, we approximate $\phi_{kk}(t)$ to decay as

$$\phi_{kk}(t)=\phi_{kk}(0)\exp(-t/\tau_R),$$

where

$$\tau_R^{-1}=\frac{d\phi_{kk}(t)}{dt}\bigg|_{t=0}\bigg/\phi_{kk}(0). \quad (52)$$

τ_R^{-1} contains two contributions. The evaluation of the first contribution is discussed in Appendix A at $t=0$, which provides a contribution to the viscosity, given as

$$\eta_{kk}^{L1}=-\frac{nm\phi_{kk}^2(0)}{\left(\frac{d\phi_{kk}(t)}{dt}\right)_{t=0}}=\frac{15(k_BTm)^{1/2}}{16\sqrt{\pi}g(\sigma)\sigma^2}. \quad (53)$$

Similarly, the second contribution of τ_R^{-1} can also be evaluated as explained in Appendix A. Its contribution to the longitudinal viscosity is given as

$$\eta_{kk}^{L2}=\frac{3(k_BTm)^{1/2}}{8\sqrt{\pi}g(\sigma)\sigma^2}. \tag{54}$$

The total kinetic contribution arising due to $\phi^L(t)$ in Eq. (30) is then

$$\eta_{kk}^{L}=\eta_{kk}^{L1}+\eta_{kk}^{L2}=\frac{21(k_BTm)^{1/2}}{16\sqrt{\pi}g(\sigma)\sigma^2}. \tag{55}$$

Here it may be noted that η^L is the contribution to the longitudinal viscosity η_1 due to $\phi^L(t)$ alone. Now we consider the kinetic-potential (cross) contribution to $\phi^L(q,t)$. The binary collision expression for $\phi_{kp}^{L1}(t)$ is given by the second integral of Eq. (36) and is rewritten as

$$\phi_{kp}^{L1}(t)=\frac{n}{mP_0^2}\int\int d\mathbf{r}\, d\mathbf{p}\, G\left(\frac{p}{\sqrt{2}}\right)g(r)[(p_x^2I_0/4)+I_2]\times x(t)F_x[r(t)]. \tag{56}$$

The two terms in this equation can be evaluated in a manner similar to that used for the kinetic-kinetic term in Appendix A. Thus

$$\phi_{kp}^{L1}(t)|_{t=0}=(\tfrac{22}{15}+\tfrac{2}{3})g(\sigma)\sigma^3v_0^2n\pi=\tfrac{16}{5}\nu v_0^2. \tag{57}$$

The time-dependent part of the second cross term appearing in Eq. (36) is simplified to

$$\phi_{kp}^{L2}(t)|_{t=0}=\nu v_0^2. \tag{58}$$

The corresponding contribution to the viscosity due to both cross terms is obtained as

$$\eta_{kp}^{L}=\phi_{kp}^{L}(t)|_{t=0}\tau=\eta_0\,\frac{21\nu}{5g(\sigma)}, \tag{59}$$

where

$$\tau=\frac{5}{16\sigma^2\sqrt{\pi}g(\sigma)nv_0},$$

and

$$\eta_0=\frac{5(k_BTm)^{1/2}}{16\sigma^2\sqrt{\pi}}.$$

The potential-potential part of Eq. (36) is written as

$$\phi_{pp}^{L1}(t)=\frac{nI_0}{2\beta P_0^2}\int\int d\mathbf{r}\, d\mathbf{p}\, G\left(\frac{p}{\sqrt{2}}\right)\times\frac{dg(r)}{dr}\,\frac{x}{r}\,x\,x(t)F_y[r(t)]. \tag{60}$$

Writing $g(r)=-y(r)\exp[-\beta U(r)]$, where $y(r)$ is a continuous function even when both $g(r)$ and $U(r)$ have discontinuities, we obtain

$$g'(r)=y'(r)\exp[-\beta U(r)]+g(r)\delta(r-\sigma^+). \tag{61}$$

The first term in Eq. (61) is nonzero only when $r>\sigma$, so we neglect it; the δ function in the second term yields $\tau=0$ and hence $x(t)=x(0)$. Performing the integration in Eq. (60), we obtain

$$\phi_{pp}^{L1}(t)=\tfrac{4}{5}\sqrt{\pi}n\sigma^4v_0g(\sigma)\delta(t). \tag{62}$$

The last term in Eq. (19) appears to be proportional to n^2; however, it can contribute to the longitudinal viscosity in the binary collision approximation if the collisions that are uncorrelated are separated out. It is noted that the last term of Eq. (19) is the only such term that provides a contribution to longitudinal viscosity of order n^2. The evaluation of this term is given in Appendix B. The result obtained there is

$$\phi_{pp}^{L2}(t)=\frac{n}{5}\,\sigma^4\sqrt{\pi}g(\sigma)v_0\delta(t), \tag{63}$$

The total contribution to the longitudinal viscosity due to $\phi_{pp}^{L1}(t)$ and $\phi_{pp}^{L2}(t)$ is

$$\eta_{pp}^{L}=\frac{36}{5\pi}\,\eta_0\nu^2g(\sigma). \tag{64}$$

Using the Green-Kubo relation for Eq. (49) and substituting the various contributions from Eqs. (55), (59), and (64), we obtain an expression for the potential-potential contribution to longitudinal viscosity

$$\eta_l^{pp}=\frac{36\nu^2}{5\sqrt{\pi}g(\sigma)}\,\eta_0-\frac{4\nu^2}{15g(\sigma)}\,\eta_0. \tag{65}$$

The last term in this equation appears due to the subtraction of the invariant term from $J_{xx}(t)$. Using Eqs. (42) and (48) and our earlier results for the shear viscosity obtained in the binary collision method, we obtain an expression for longitudinal viscosity

$$\eta_1=\frac{\eta_0}{g(\sigma)}\left(\frac{4}{3}+\frac{16}{15}\,\nu+\frac{36}{5\pi}\,\nu^2-\frac{4}{15}\,\nu^2\right). \tag{66}$$

The expression for shear viscosity obtained in our other work [4] is

$$\eta_s=\frac{\eta_0}{g(\sigma)}\left(1+\frac{4}{5}\,\nu+\frac{12}{5\pi}\,\nu^2\right). \tag{67}$$

Using the relation among three viscosities, we obtain

$$\eta_B=a_B\,\frac{\eta_0}{g(\sigma)}\,\nu^2,$$

where $a_B=[4/\pi-\tfrac{4}{15}]=1.0066$. The numerical factor a_B predicted by Enskog is 1.0186. Thus it is gratifying to see that our method provides the value of a bulk viscosity in close agreement with the Enskog result.

VI. CONCLUSION

We have obtained an expression for the binary collision contributions to the first-order memory function of the longitudinal current correlation function using the cluster expansion technique. This expression involves the static pair correlation function and the time dependence of the position, momentum, and acceleration of a particle. The numerical calculations for the continuous interaction potential are feasible due to the appearance of the position and momentum of a particle moving in a central potential. Thus the present formalism provides a methodology to obtain longitudinal and bulk stress autocorrelation functions in the binary collision approximation for a system of particles of the fluid interacting via a continuous potential. In the limit of hard spheres our results for the longitudinal and bulk viscosities are found to be in agreement with the Enskog results.

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APPENDIX A

The first term in the time derivative of Eq. (50)

$$\frac{d\phi_{kk}^{L1}(t)}{dt}=\frac{nI_0}{4m^2P_0^2}\int\int d\mathbf{r}\, d\mathbf{p}\, G\left(\frac{p}{\sqrt{2}}\right)g(r)p_x^2p_x(t)\dot{p}_x(t). \tag{A1}$$

The dynamics of the collision between two hard spheres provides an expression for the time evolution of momentum

$$dp_x(t)/dt=\theta(\sigma^2-b^2)\,\theta(-\hat{\mathbf{r}}\cdot\hat{\mathbf{p}})\,\delta(t-\tau)(-p_x+p_x^*), \tag{A2}$$

where p_x^* is the postcollision momentum

$$p_x^*=p_x-2(\mathbf{p}\cdot\hat{\mathbf{r}})\,\frac{x}{r}, \tag{A3}$$

with collision time

$$\tau=-\frac{m}{p}\,[\mathbf{r}\cdot\hat{\mathbf{p}}+(\sigma^2-b^2)^{1/2}], \tag{A4}$$

$b^2=r^2-(\mathbf{r}\cdot\hat{\mathbf{p}})^2$, and $\theta(x)=1$ if $x>0$ and $\theta(x)=0$ if $x<0$. By substituting the value of $\dot{p}_x(t)$ from Eq. (A2), Eq. (A1) reduces at $t=0$ to

$$\left.\frac{d\phi_{kk}^{L1}(t)}{dt}\right|_{t=0}=-\frac{nI_0}{2m^2P_0^2}\int\int d\mathbf{r}\, d\mathbf{p}\, G\left(\frac{p}{\sqrt{2}}\right)g(r)\times p_x^3(\mathbf{p}\cdot\hat{\mathbf{r}})\,\frac{x}{r}\,\theta(\sigma^2-b^2)\,\theta(-\hat{\mathbf{r}}\cdot\hat{\mathbf{p}})\,\delta(-\tau). \tag{A5}$$

Using the value of τ from Eq. (A4), we note that

$$\delta(-\tau)=\delta\left(\frac{m}{p}\,\{r\mu+[\sigma^2-r^2+(r^2\mu^2)]^{1/2}\}\right), \tag{A6}$$

where μ is the cosine of the angle between $\mathbf{r}$ and $\mathbf{p}$. By noting that the above δ function has poles at $r^2=\sigma^2$, we obtain

$$\delta(-\tau)=\frac{p}{m}\,|\mu|\,\delta(r-\sigma). \tag{A7}$$

Using Eq. (A7) in Eq. (A5) we obtain

$$\left.\frac{d\phi_{kk}^{L1}(t)}{dt}\right|_{t=0}=-\frac{nI_0}{2m^2P_0^2}\int\int d\mathbf{r}\, d\mathbf{p}\times G\left(\frac{p}{\sqrt{2}}\right)g(r)p_x^3\,\frac{x}{r}\,p\mu\,\theta(\sigma^2-b^2)\times\theta(-\hat{\mathbf{r}}\cdot\hat{\mathbf{p}})\,\frac{p}{m}\,|\mu|\,\delta(r-\sigma). \tag{A8}$$

The angular integration in this equation can be done by using the addition theorem, and noting that $r=\sigma$ lies on the boundary we have

$$\left.\frac{d\phi_{kk}^{L1}(t)}{dt}\right|_{t=0}=-\frac{nI_0}{2m^3P_0^2}\,\sigma^2\pi\, g(\sigma)\int p^7dp\times G\left(\frac{p}{\sqrt{2}}\right)\int_0^{\pi}d\theta\,\cos^3\,\theta\,\sin\theta\times\int_0^{2\pi}\sin^2\phi\, d\phi\int_{-1}^{1}\mu^2|\mu|\,\theta(-\mu)d\mu \tag{A9}$$

$$=-\tfrac{48}{5}ng(\sigma)\sigma^2v_0^3\sqrt{\pi}. \tag{A10}$$

APPENDIX B

When combined with $\phi_0^p(q,t)$ the last term in Eq. (19) provides a contribution to $\phi(q,t)$ that is proportional to the square of density and is given as

$$\frac{1}{P_0^2}\left\langle\frac{\partial U}{\partial x_1}\left[e^{iqx_1}e^{-i\mathcal{L}_{23}t}\left((N-1)(N-2)\,\frac{\partial u(r_{23})}{\partial x_2}\,e^{-iqx_2}\right)\right]\right\rangle. \tag{B1}$$

Equation (B1) can also be written as

$$\frac{1}{P_0^2}\left\langle\left(\frac{\partial u_{12}}{\partial x_1}+\frac{\partial u_{13}}{\partial x_1}+(N-3)\,\frac{\partial u_{14}}{\partial x_1}\right)\left[e^{iqx_1}\times e^{-i\mathcal{L}_{23}t}\left((N-1)(N-2)\,\frac{\partial u(r_{23})}{\partial x_2}\,e^{-iqx_2}\right)\right]\right\rangle. \tag{B2}$$

The first two terms in Eq. (B2) give rise to a three-body contribution, whereas the last term gives rise to a four-body contribution that can be eliminated by using the exact relation between the derivative of $g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ and $g_4(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4)$ [8]. After performing the necessary ensemble average we finally obtain

$$\frac{n^2I_0}{\beta P_0^2}\int\int\int d\mathbf{r}\, d\mathbf{r}'d\mathbf{p}'\times G\left(\frac{p'}{\sqrt{2}}\right)\,\frac{\partial g_3(r,r')}{\partial x}\,e^{-iq(x-x'/2)}e^{(-iq/2)x'(t)}F_x[r'(t)]. \tag{B3}$$

This term involves the simultaneous interaction of three arbitrary particles, say, 1, 2, and 3. However, if we consider only the recollision terms in which, say, particle 3 recollides with particle 1, then the number of terms in Eq. (B1) is reduced by $N-1$. Under the weak-coupling approximation the recollision terms can contribute to the binary collision contribution. For example, in the second term of Eq. (B2) there is no direct interaction between particles 1 and 2, whereas particles 2 and 3 are interacting directly. This implies that collisions between particles 1 and 2 and particles 2 and 3 are independent provided that $\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2$ and $\mathbf{r}'=\mathbf{r}_2-\mathbf{r}_3$ satisfy the condition that angles between $\mathbf{r}$ and $\mathbf{r}'$ be greater than $\pi/2$. In view of the above discussion we approximate

$$(N-1)\,\frac{\partial g_3(r,r')}{\partial x}=\frac{\partial g(r)}{\partial x}\,g(r')\,\theta(-\mathbf{r}\cdot\mathbf{r}'), \tag{B4}$$

where $\theta(-\hat{\mathbf{r}},\hat{\mathbf{r}}')$ ensures that particles 1 and 2 remain at a distance where these can be considered as uncorrelated. By substituting Eq. (B4) into Eq. (B3) we obtain

$$\frac{n^2I_0}{\beta P_0^2}\int\int\int d\mathbf{r}\,d\mathbf{r}'d\mathbf{p}'G\left(\frac{p'}{\sqrt{2}}\right)\frac{\partial g(r)}{\partial x}\,g(r')\times\theta(-\hat{\mathbf{r}},\hat{\mathbf{r}}')e^{-iq(x-x'/2)}e^{(-iq/2)x'(t)}F_x[r'(t)]. \tag{B5}$$

In the long-wavelength limit it gives a contribution to the potential-potential part of the stress correlation function

$$\phi_{pp}^{L2}(t)=-\frac{n^2I_0}{2\beta P_0^2(N-1)}\int\int\int d\mathbf{r}\,d\mathbf{r}'d\mathbf{p}'\times G\left(\frac{p'}{\sqrt{2}}\right)\frac{\partial g(r)}{\partial x}\,g(r')\left\{x-\frac{x'}{2}+\frac{x'(t)}{2}\right\}^2\times F_x[r'(t)]\,\theta(-\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}'). \tag{B6}$$

Using the values of $F_x[r'(t)]$ and $g'(r)$ from Eqs. (25), (A2), and (61), respectively, we get

$$\phi_{pp}^{L2}(t)=-\frac{n^2I_0}{2\beta P_0^2(N-1)}\int\int\int d\mathbf{r}\,d\mathbf{r}'d\mathbf{p}'\times G\left(\frac{p'}{\sqrt{2}}\right)g(r)\,\frac{x}{r}\,g(r')\,\delta(r-\sigma)\,\delta(t-\tau)\times\theta(\sigma^2-b^2)\,\theta(-\mu)(-2p\mu)\,\frac{x'}{r'}\times\left(x-\frac{x'}{2}+\frac{x'(t)}{2}\right)^2\theta(-\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}').$$

$r=\sigma$ yields $\tau=0$ and reduces to

$$\phi_{pp}^{L2}(t)=\frac{n^2I_0}{\beta P_0^2(N-1)}\int\int\int d\mathbf{r}\,d\mathbf{r}'d\mathbf{p}'\times G\left(\frac{p'}{\sqrt{2}}\right)\frac{xx'}{rr'}\,x^2g(r)g(r')\,\delta(r-\sigma)\,\delta(t)\times\theta(\sigma^2-b^2)\,\theta(-\mu)p\mu\,\theta(-\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}'). \tag{B7}$$

Integration in Eq. (B7) can be carried out by expanding the θ function in the Legender polynomial. This simplifies the integral to

$$\phi_{pp}^{L2}(t)=\frac{nI_0}{\beta P_0^2}\,\frac{4\pi}{5}\int_{-1}^{0}\cos\lambda\,\sin\lambda\,d\lambda\,2\pi\times\int_{-1}^{0}\mu\,d\mu\int dp'p'^3G\left(\frac{p'}{\sqrt{2}}\right)\delta(t)\int r^4g(r)\times\delta(r-\sigma)dr, \tag{B8}$$

where λ is the angle between $\mathbf{r}$ and $\mathbf{r}'$. Evaluating the integrals in Eq. (B8) we finally obtain Eq. (63).

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