

## Binary collision contribution to the longitudinal current correlation function of dense fluids: Numerical results

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Numerical results are obtained for the binary collision contribution to the longitudinal stress correlation function of Lennard-Jones fluids for a few selected densities and temperatures. It is found that the time evolution of the correlation function cannot be approximated by a simple, fast decaying function, like a Gaussian, at any thermodynamic state. [S1063-651X(98)12005-6]

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In an earlier paper [1], hereafter referred to as I, we derived an expression for the binary collision contribution to the first order space-time memory function of the longitudinal current correlation function for a fluid interacting through a continuous potential.

The Fourier-Laplace transform of the longitudinal current correlation function  $C(q,t)$  is given in the Mori-Zwanzig representation by

$$\tilde{C}(q,z) = v_0^2 [z + \tilde{K}(q,z)]^{-1}, \quad (1)$$

where  $v_0 = \sqrt{k_B T/m}$  is the thermal speed of the particle and  $\tilde{K}(q,z)$  is the first-order memory function. An exact expression for  $K$  is given by Eq. (12) of I in terms of  $\tilde{\phi}^L(q,z)$ , the longitudinal stress correlation function. But to be consistent with the spirit of the binary collision approximation, we keep only those terms that have an explicit density dependence of up to first order in density and this requires that we take  $\tilde{K}(q,z) \approx \tilde{\phi}^L(q,z)$ . In addition, only  $\lim_{q \rightarrow 0} \phi^L(q,t)/q^2 \equiv \phi^L(t)$  is required to compute the correlation function of interest in this paper. The Kubo time integral of this function yields the longitudinal viscosity. In fact, it is shown analytically in I that  $\phi^L(t)$  and hence viscosity reduces to the well-known Enskog result for a hard-sphere fluid. We first obtain three-dimensional integral expressions for  $\phi^L(t)$ , reduced from the original six-dimensional integrals, and then evaluate them numerically for the Lennard-Jones potential for a few density-temperature states.

Introducing the kinetic-kinetic ( $kk$ ), kinetic-potential ( $kp$ ), and potential-potential ( $pp$ ) parts, we write

$$\phi^L(t) = \phi_{kk}(t) + \phi_{kp}(t) + \phi_{pp}(t). \quad (2)$$

Equation (36) of I yields the terms

$$\begin{aligned} \phi_{kk}(t) = & 3v_0^2 + \frac{n}{16\sqrt{2}m^2p_0^2} \int d\mathbf{r} d\mathbf{p} g(r)G(p/\sqrt{2})[p_x^2 + p_0^2] \\ & \times [p_x(t)^2 - p_x^2], \end{aligned} \quad (3a)$$

$$\begin{aligned} \phi_{kp}(t) = & \frac{n}{8\sqrt{2}mp_0^2} \int d\mathbf{r} d\mathbf{p} g(r)G(p/\sqrt{2}) \frac{x(t)^2}{r} F(r(t)) \\ & \times [p_x^2 + 2p_0^2] + \frac{n}{8\sqrt{2}m^2} \int d\mathbf{r} d\mathbf{p} g'(r)G(p/\sqrt{2}) \\ & \times \frac{x^2}{r} [p_x(t)^2 - p_x^2], \end{aligned} \quad (3b)$$

$$\phi_{pp}(t) = \frac{n}{4\sqrt{2}m} \int d\mathbf{r} d\mathbf{p} g'(r)G(p/\sqrt{2}) \frac{x^2}{r} x(t)F_x(r(t)), \quad (3c)$$

where  $G(p) = (2\pi p_0^2)^{-3/2} e^{-p^2/2p_0^2}$  and  $p_0 = mv_0$ . The time evolution of  $\mathbf{r}(t)$  and  $\mathbf{p}(t)$  is governed by Newton's law in the form

$$\ddot{x} = \dot{p}_x = \frac{2}{m} F_x(r) = -\frac{2}{m} \frac{\partial u(r)}{\partial x},$$

where  $u(r)$  is the two-body central potential.

The integrals appearing in Eq. (3) are six dimensional since they involve momentum and position of a particle. Johnson and Pope [2] have developed a procedure that reduces the dimensionality of the integrals to three; these variables are the radial distance  $r$ , the total relative energy  $E$ , and the relative angular momentum  $l$ . It is also necessary to sum over both positive and negative initial radial velocities; this is indicated by the symbol  $\Sigma_\nu$  with  $\nu = +1$  for  $\dot{r}(0) > 0$  and  $\nu = -1$  for  $\dot{r}(0) < 0$ . Now defining the new variables  $s$  and  $\lambda$  by  $E = u(r) + mv_0^2 s$  and  $l = mv_0 \sqrt{s} r \sin \lambda$  and writing  $\Delta u_\nu(t) = u(r) - u(r_\nu(t))$ , Eqs. (3) can be reduced to the following form, suitable for numerical evaluation using Gaussian quadrature:

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$$\begin{aligned} \phi_{kk}(t) = & 3v_0^2 + \frac{4\sqrt{\pi n}v_0^2}{15} \int_0^\infty dr r^2 g(r) \int_0^\infty ds e^{-s} s^{1/2} \int_0^{\pi/2} d\lambda \sin \lambda \sum_\nu \left\{ (5+4s) \frac{\Delta u_\nu(t)}{mv_0^2} - 2s^2 \right. \\ & \left. + \nu \frac{2s\sqrt{s}\dot{r}_\nu(t)r \sin \lambda}{v_0 r_\nu(t)} \sin 2[\lambda - \nu\alpha_\nu(t)] + 2s \left[ s \left( 1 - \frac{2r^2 \sin^2 \lambda}{r_\nu(t)^2} \right) + \frac{\Delta u_\nu(t)}{mv_0^2} \right] \cos 2[\lambda - \nu\alpha_\nu(t)] \right\}, \end{aligned} \quad (4a)$$

$$\begin{aligned} \phi_{kp}(t) = & \frac{4\sqrt{\pi n}}{15m} \int_0^\infty dr r^2 g(r) \int_0^\infty ds e^{-s} s^{1/2} \int_0^{\pi/2} d\lambda \sin \lambda \sum_\nu r_\nu(t) F(r_\nu(t)) \{5+4s+2s \cos 2[\lambda - \nu\alpha_\nu(t)]\} \\ & + \frac{4\sqrt{\pi n}v_0^2}{15} \int_0^\infty dr r^3 g'(r) \int_0^\infty ds e^{-s} s^{1/2} \int_0^{\pi/2} d\lambda \sin \lambda \sum_\nu \left\{ \frac{\Delta u_\nu(t)}{mv_0^2} [2 + \cos 2\alpha_\nu(t)] \right. \\ & \left. + s \left( 1 - \frac{2r^2 \sin^2 \lambda}{r_\nu(t)^2} \right) \cos 2\alpha_\nu(t) - s \cos 2\lambda - \frac{\sqrt{s}\dot{r}_\nu(t)r \sin \lambda}{v_0 r_\nu(t)} \sin 2\alpha_\nu(t) \right\}, \end{aligned} \quad (4b)$$

$$\phi_{pp}(t) = \frac{2\sqrt{\pi n}}{15m} \int_0^\infty dr r^3 g'(r) \int_0^\infty ds e^{-s} s^{1/2} \int_0^{\pi/2} d\lambda \sin \lambda \sum_\nu r_\nu(t) F(r_\nu(t)) [2 + \cos 2\alpha_\nu(t)]. \quad (4c)$$

The integrals in Eq. (4) have been evaluated for the Lennard-Jones potential  $u(r) = 4\epsilon[(r/\sigma)^{-12} - (r/\sigma)^{-6}]$  for selected density and temperature states;  $g(r)$  was obtained from optimized cluster theory [3]. A Verlet-type algorithm was used to obtain  $r_\nu(t)$  and  $\alpha_\nu(t)$  for each  $r$ ,  $s$ ,  $\lambda$ , and  $\nu$  required by the quadrature. Dimensionless units are  $t^* = t/\tau$ , where  $\tau = (m\sigma^2/48\epsilon)^{1/2}$  ( $\approx 0.31$  ps for argon),  $n^* = n\sigma^3$ , and  $T^* = k_B T/\epsilon$ . Some details of similar calculations have been described in our earlier papers [4,5], and a more complete description of the method is given by Johnson and Pope [2]. Therefore, in this paper we simply present the numerical results for a few selected thermodynamic states, the object being to study the time evolution of the binary component of the stress autocorrelation function for the Lennard-Jones potential.

Figure 1(a) shows the results for  $\phi^L(t)$  in dimensionless units [to convert to physical units multiply by  $\sigma^2/\tau^2 \approx 1.2 \times 10^6$  m<sup>2</sup>/s<sup>2</sup> for argon], as a function of  $t^*$  for  $(n^*, T^*)$  equal to (0.2, 1.46), and Fig. 1(b) for (0.2, 2.5). From these figures it is seen that only the  $kk$  and  $pp$  contributions are appreciable for  $t^* < 1$ , and that the  $kp$  contribution remains small for all time. The  $kk$  contribution persists for  $t^* > 1$ , but the  $pp$  is negligible for  $t^* > 2$ . (This result is especially true for the higher temperature state.) Figures 2(a) and 2(b) show  $\phi^L(t)$  for medium density states of (0.4, 1.46) and (0.4, 2.5). For this higher density the  $pp$  contribution is dominant for  $t^* < 0.5$  and is comparable to the  $kk$  contribution for  $0.5 < t^* < 2$ . The  $kk$  term decays slowly compared to the other two contributions, but is not considered significant. Figure 3 shows the result for the argon triple-point state (0.84, 0.72). It indicates that the  $pp$  is the dominant contribution.

There are no computer simulation data available to compare with our numerical results. However, two significant points are to be noted from our results. The first is that the binary collision contribution is appreciable at all thermodynamic states, and not just for short times. It does contribute at intermediate times,  $0.5 < t^* < 2$ . Secondly, the binary col-

lision contribution for a realistic fluid does have negative regions, particularly at high density and low temperature states. Thus it cannot be described by a simple fast decaying function, as is often assumed. This notion is possibly valid

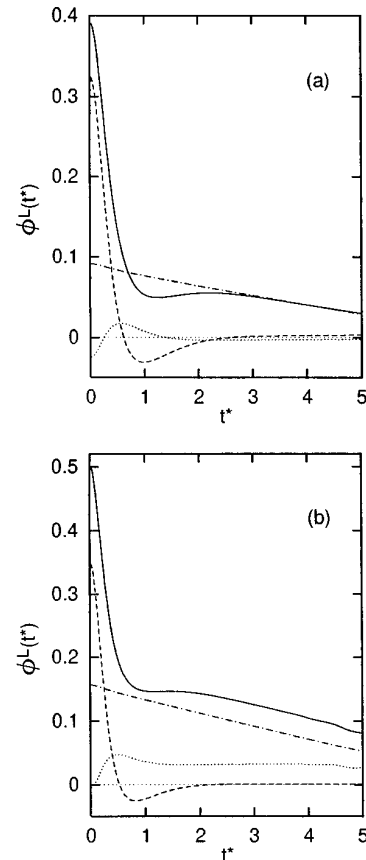


FIG. 1. Plot of the longitudinal stress correlation function  $\phi^L(t^*)$  as a function of time (in dimensionless units defined in the text). The solid curve is the total; the dashed is its  $pp$  component; the dotted its  $kp$  component; and the dash-dotted line its  $kk$  component. (a)  $n^* = 0.2$ ,  $T^* = 1.46$ ; (b)  $n^* = 0.2$ ,  $T^* = 2.5$ .

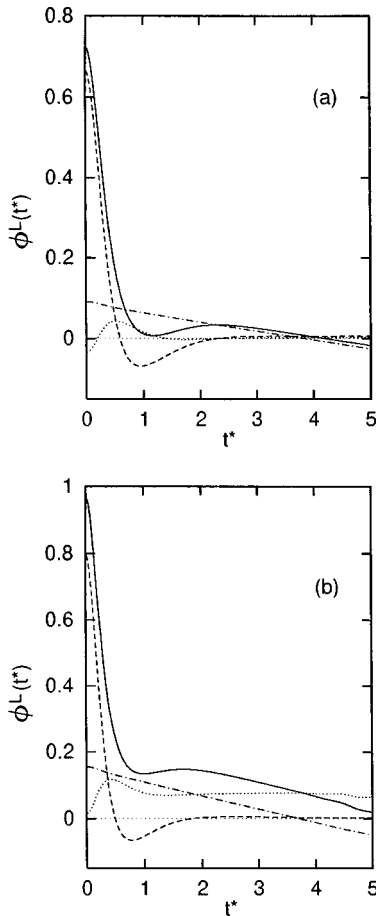


FIG. 2. Same as Fig. 1, but for (a)  $n^* = 0.4$ ,  $T^* = 1.46$ ; (b)  $n^* = 0.4$ ,  $T^* = 2.5$ .

for a hard sphere model in which the two-particle collisions are instantaneous. In the case of the Lennard-Jones potential the particles experience the effect of the force for a much longer length (or equivalently time) scale. In fact, one must include the effects of both bound and scattering states of the particle in a continuous potential.

It would be of interest to relate the time scales of our binary collision contribution results to ‘‘collision times.’’ Since one cannot define a collision time unambiguously for a continuous potential, we introduce an Enskog collision time  $\tau_E$ , modified for a continuous potential [6] through the relation

$$\tau_E^* \equiv \frac{\tau_E}{\tau} = 32 \frac{D^*}{T^*}, \quad (5)$$

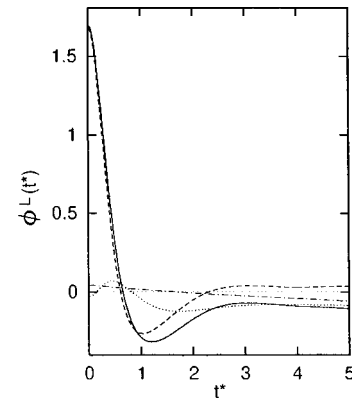


FIG. 3. Same as Fig. 1, but for the triple point of argon;  $n^* = 0.84$ ,  $T^* = 0.72$ .

where  $D^*$  is the diffusion coefficient in reduced units. Using the appropriate numbers, we find that the collision time varies between 0.2 at the triple point to 2.0 at the lowest density considered. Thus we note from the figures that at the triple point, the binary collision contribution goes negative at about two collision times and then slowly decays to zero at about ten collision times. At the lowest density considered, there is a fast decay until about half a collision time followed by a considerably slower decay to zero at about two collision times.

A perusal of our earlier calculations [4,5] clearly indicates similar time evolutions for the memory functions associated with the velocity correlation function and transverse current correlation function. Since computer simulation data were available for these correlation functions, we were able to identify the time scales for which binary collisions are significant for a continuous potential and when multiparticle collisions start to play a significant role.

It is believed that a truly microscopic theory of time correlation functions of realistic fluids would involve an appropriate combination of binary and multiparticle collision contributions. The latter contribution has been traditionally handled by mode coupling theories, while the former has been modeled by a Gaussian or similar fast decaying function with no negative features. However, our results indicate that the time evolution of the binary component is not simple and that there is an overlap with time scales involved in mode coupling. Hence a simple addition of these two components, as is common practice, is not justified. It is not as yet clear how to include both effects in a microscopic theory for a continuous potential. It is hoped that our results would be useful in the development of a tractable microscopic theory of fluids.

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