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Binary-collision contributions to atomic motions in fluids

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Binary-collision contributions to the first order space-time memory function in the Mori-Zwanzig representation of a self-current autocorrelation function have been obtained. The expression for the memory function involves the static pair correlation function and the time dependence of the position and the momentum of a particle moving in a central potential. In the limit of long wavelength, the memory function reduces to that for the velocity autocorrelation function (VACF). The self-diffusion coefficient has been found to reduce to the Enskog value in the limit of a hard sphere interaction. Numerical results for the VACF, its memory function, and the self-diffusion coefficient for a Lennard-Jones fluid have been obtained for several thermodynamic states. These results are compared with available molecular dynamics data to identify the extent to which the binary-collision approximation is valid.

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I. INTRODUCTION

There has been considerable progress in our theoretical understanding of atomic dynamics at wavelengths and frequencies of a molecular scale in liquids and dense gases [1,2]. Time autocorrelation functions, such as the ones associated with velocity and density, contain information on the dynamics of atomic motions of a system. Computer simulation techniques and neutron scattering experiments have given a wealth of information on various time correlation functions. Memory functions have played a key role in theoretical calculations of these time correlation functions and the calculation of the memory function in a specific problem can proceed in two ways.

One approach is based on investigations of a generalized phase-space kinetic equation that is an extension of the Boltzmann equation for arbitrary frequency and wavelength. The kinetic equation is conveniently formulated in terms of its associated phase-space memory function and microscopic expressions for binary-collisions contributions, certain sequences of many particle collisions, and mode coupling effects to the memory function have been obtained [3–6]. Due to the mathematical complexity of solving the kinetic equation for continuous potentials, these equations have been applied mostly to hard sphere fluids [7]. The difficulty of extending hard sphere kinetic theory to continuous potential systems lies in the fact that the collisions are no longer instantaneous and many-particle dynamics cannot be decomposed into sequences of two-particle collisions. In cases where kinetic equations have been used for the study of time correlation functions (TCFs) for continuous potentials [8–11], the microscopic expression for the binary-collision contribution to the memory function has been replaced by a phenomenological form. Therefore, it may be said that there is as yet no tractable kinetic equation which can be readily solved to predict time correlation functions and transport coefficients for continuous potentials. In fact, even the binary-collision contributions to the phase-space memory function have not yet been obtained numerically for a continuous potential.

The alternative theoretical approach for the study of time correlation functions is based on space-time memory functions (MFs). The memory functions appearing in the Mori-Zwanzig continued fraction representation of the time correlation function can be so chosen that they preserve a number of properties of TCFs regardless of the explicit form of the MF [12]. The descriptions of TCFs based on assumed phenomenological forms for the MF have provided useful information about relaxation processes in fluids [12,13]. The microscopic derivation of the space-time memory function was first attempted by Götze and Lucke [14] using mode coupling approximations. The MF can be written as a sum of two terms [8,15,16], one reflecting the short time atomic motion while the second is generally thought of as due to correlated multiparticle collisions that are important at longer times. The latter contribution obtained within the mode coupling approximation has been found to be quite successful [17–20], particularly in a strong coupling situation such as the glassy state [16,21]. However, for the study of normal liquid dynamics on time scales accessible by neutron scattering experiments, a microscopic expression for the short time contribution to space-time MFs is very much desirable. Once a tractable, microscopic expression for this so-called binary-collision contribution has been obtained, the mode coupling contribution can be simply added to get the complete memory function and their respective roles in the dynamics of atomic motions in continuous fluids can be studied in detail. The present work is a step in this direction.

In this paper, we derive an expression for the binary-collision contributions to the space-time memory func-

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tion in the Mori-Zwanzig representation of the self-current autocorrelation function. The expression involves the dynamics of a pair of particles moving in a central force field $F(r)$ and the static pair correlation function $g(r)$. The expression for the memory function appears to be the analog of the low density phase-space memory function obtained in the kinetic theory description of the self-density correlation function. In the limit of wave vector tending to zero, the memory function reduces to that for the velocity autocorrelation function (VACF). In addition, in the limit of a hard sphere interaction, the memory function provides exactly the Enskog expression for the self-diffusion coefficient. Therefore, our space-time memory function for the self-current correlation function contains all the essential features of the Boltzmann-Enskog phase-space collision operator.

The dynamics of a particle moving in a Lennard-Jones potential has been obtained by solving Newton's equation of motion. This is then used to calculate the force autocorrelation function using quadrature methods. Numerical results for the VACF, its MF, and the self-diffusion coefficient have been obtained for several densities from low density gas to liquid density and at various temperatures. Our results are compared with available molecular dynamics data to understand the significance and the extent of the binary-collision approximation.

The plan of the paper is as follows. The basic definition and exact relations for the time correlation function are introduced in Sec. II; the binary-collision contributions to the memory function of the self-current—current correlation function for a central potential are also obtained. In Sec. III the corresponding memory function for the VACF, for the continuous potential and the hard sphere potential, are obtained. Numerical results for the Lennard-Jones potential are presented in Sec. IV. Section V contains concluded remarks and our proposals for future work.

II. THEORETICAL FORMULATION

A. Basic definitions

We consider a fluid of N particles, each of mass m, interacting through a continuous potential $u(r)$. The thermodynamic state of the fluid is defined by its density n and temperature T. The longitudinal current correlation function associated with a tagged particle is defined as

$$C_s(q,t)=\langle j_{1x}^{*}(q,t)j_{1x}(q,0)\rangle \ . \tag{1}$$

The tagged particle current is given by $j_{1x}(q,t)=v_{1x}(t)e^{iqx_1(t)}$, where we have chosen the wave vector $\mathbf{q}$ along the x axis. The time dependence of any dynamical variable $A(q,t)$ is determined through the Liouville equation

$$\frac{\partial A(q,t)}{\partial t}=i\mathcal{L}A(q,t) \ ; \tag{2}$$

the Liouville operator is

$$\begin{aligned}\mathcal{L}&=\mathcal{L}_0+\sum_{j<k}\mathcal{L}_1(jk)\\&=-i\sum_j\frac{\mathbf{P}_j}{m}\cdot\frac{\partial}{\partial\mathbf{r}_j}-i\sum_{j<k}\mathbf{F}_{jk}\cdot\left[\frac{\partial}{\partial\mathbf{P}_j}-\frac{\partial}{\partial\mathbf{P}_k}\right] ,\end{aligned} \tag{3}$$

where $\mathbf{F}_{jk}=-\partial u(r_{jk})/\partial\mathbf{r}_j$ is the force and $r_{jk}=|\mathbf{r}_j-\mathbf{r}_k|$. The angular brackets in Eq. (1) and in what follows denote the canonical ensemble average appropriate to the Liouville operator. We define the Fourier-Laplace transform of $C_s(q,t)$ as

$$\begin{aligned}\tilde{C}_s(q,z)&=i\int_0^\infty dt\, e^{izt}C_s(q,t)\\&=\left\langle j_{1x}(q,0)\left|\frac{1}{\mathcal{L}-z}\right|j_{1x}(q,0)\right\rangle\end{aligned} \tag{4}$$

for $\mathrm{Im}z>0$.

The time evolution of the correlation function is obtained, using the Mori-Zwanzig projection operator procedure, in terms of its initial value and a relaxation kernel (or memory function). This is given by

$$\tilde{C}_s(q,z)=-\frac{v_0^2}{z+\tilde{K}_s(q,z)} \ , \tag{5}$$

where the first order memory function is given by

$$\tilde{K}_s(q,z)=\frac{1}{v_0^2}\left\langle Q\mathcal{L}j_{1x}(q,0)\left|\frac{1}{Q\mathcal{L}Q-z}\right|Q\mathcal{L}j_{1x}(q,0)\right\rangle \ ; \tag{6}$$

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

The memory function of the self-current correlation function can be expressed in terms of a conventional correlation function whose time evolution is governed by the original Liouville operator $\mathcal{L}$ rather than the projected one $Q\mathcal{L}Q$ appearing in (6). A simple way of doing this is by applying the identity

$$\frac{z}{\mathcal{L}-z}=-1+\frac{\mathcal{L}}{\mathcal{L}-z} \tag{7}$$

to Eq. (4) twice. This yields

$$z^2\tilde{C}_s(q,z)=v_0^2[-z+\tilde{\phi}_s(q,z)] \ , \tag{8}$$

where

$$\tilde{\phi}_s(q,z)=\frac{1}{v_0^2}\left\langle\mathcal{L}j_{1x}(q,0)\left|\frac{1}{\mathcal{L}-z}\right|\mathcal{L}j_{1x}(q,0)\right\rangle \tag{9}$$

is the stress autocorrelation function. The comparison of Eqs. (5) and (8) gives the desired relation

$$\tilde{K}_s(q,z)=\frac{\tilde{\phi}_s(q,z)}{1-\frac{1}{z}\tilde{\phi}_s(q,z)} \ . \tag{10}$$

Thus if the correlation function $\tilde{\phi}_s(q,z)$ is known, the memory function and the self-current–current correlation function can be obtained from Eqs. (10) and (5), respectively. The self-density correlation function $S_s(q,\omega)$ can then be evaluated.

B. Binary-collision contributions

The exact microscopic evaluation of the memory function is yet an unsolved problem. However, the binary-collision contribution to the memory function can be obtained using the well established cluster expansion technique [22]. This technique involves a cluster expansion of the resolvent operator $(\mathcal{L}-z)^{-1}$ that appears in the definition of any time correlation function. The binary collision expansion (BCE) formula is

$$\frac{1}{\mathcal{L}-z}\approx\frac{1}{\mathcal{L}_0-z}+\sum_{j<k}\left\{\frac{1}{\mathcal{L}_0+\mathcal{L}_1(jk)-z}-\frac{1}{\mathcal{L}_0-z}\right\}+\cdots . \tag{11}$$

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. Equation (11) has been widely used in deriving the low density formula for the kinetic (i.e., phase-space) memory function as well as the first order space-time memory function.

We now evaluate the correlation function (9) using the binary-collision expansion (11). We have

$$i\mathcal{L}j_{1x}=\frac{dj_{1x}}{dt}=\dot{v}_{1x}e^{iqx_1}+iqv_{1x}^2e^{iqx_1} . \tag{12}$$

Using (12), Eq. (9) can be rewritten as

$$\tilde{\phi}_s(q,z)=\frac{1}{v_0^2}\left\langle\left\{-\frac{1}{m}\frac{\partial u}{\partial x}+iqv_{1x}^2\right\}e^{iqx_1}\left|\frac{1}{\mathcal{L}-z}\right|\right.\\ \left.\times\left\{-\frac{1}{m}\frac{\partial u}{\partial x}+iqv_{1x}^2\right\}e^{iqx_1}\right\rangle . \tag{13}$$

In Eq. (13) we use the definition of the acceleration $\dot{v}_{1x}$ in terms of the force (negative derivative of the potential). Equation (13) can be written as a sum of four terms and we illustrate the evaluation of its first term: it can be written in an alternative, exact form as

$$\frac{(N-1)}{P_0^2}\left\langle\frac{\partial u(r_{12})}{\partial x_1}e^{iqx_1}\left|\frac{1}{\mathcal{L}-z}\right|\right.\\ \left.\times\left\{\frac{\partial u(r_{12})}{\partial x_1}+(N-2)\frac{\partial u(r_{13})}{\partial x_1}\right\}e^{iqx_1}\right\rangle , \tag{14}$$

where $P_0=mv_0$ is the momentum. Now the operator $(\mathcal{L}-z)^{-1}$ is expanded using the BCE formula (11). The terms involving $(\mathcal{L}_0-z)^{-1}$ are due to free-particle dynamics and thus are easy to evaluate. In our illustration we will concentrate on its two-particle term. In the time domain the two-particle contribution is

$$\frac{(N-1)}{P_0^2}\left\langle\left\{e^{i\mathcal{L}_{12}t}\frac{\partial u(r_{12})}{\partial x_1}e^{iqx_1}\right\}^*\right.\\ \left.\times\left\{\frac{\partial u(r_{12})}{\partial x_1}+(N-2)\frac{\partial u(r_{13})}{\partial x_1}\right\}e^{iqx_1}\right\rangle. \tag{15}$$

In Eq. (15)

$$\mathcal{L}_{12}=\mathcal{L}_0(1)+\mathcal{L}_0(2)+\mathcal{L}_1(12)\equiv\mathcal{L}_0(12)+\mathcal{L}_1(12) . \tag{16}$$

Now, in the first two terms of (11) the dynamics of two particles only appears and in (15) it has to be averaged over the initial equilibrium configurations of the system. After performing this average, the result can be written as

$$\frac{-n^2}{NP_0^2\beta}\int d\mathbf{r}_1d\mathbf{r}_2d\mathbf{P}_1d\mathbf{P}_2\frac{\partial g(r_{12})}{\partial x_1}G(P_1)G(P_2)\\ \times e^{iqx_1}\left\{e^{i\mathcal{L}_{12}t}\frac{\partial u(r_{12})}{\partial x_1}e^{iqx_1}\right\}^* , \tag{17}$$

where $g(r)$ and $G(P)=(1/2\pi P_0^2)^{3/2}e^{-(P^2/2P_0^2)}$ are the static pair correlation function and Maxwellian momentum distribution. The triplet static correlation function $g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ comes in when the equilibrium ensemble average is carried out in (15); it can be eliminated using the exact relation

$$\frac{\partial g(r_{12})}{\partial x_1}=-\beta g(r_{12})\frac{\partial u(r_{12})}{\partial x_1}\\ -\beta n\int d\mathbf{r}_3g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\frac{\partial u(r_{13})}{\partial x_1} . \tag{18}$$

We now change the variables of integration in (17) to relative and center of mass coordinates defined by

$$\mathbf{p}=\mathbf{P}_1-\mathbf{P}_2,\quad \mathbf{r}=\mathbf{r}_1-\mathbf{r}_2 ,\\ \mathbf{P}=\frac{\mathbf{P}_1+\mathbf{P}_2}{2},\quad \mathbf{R}=\frac{\mathbf{r}_1+\mathbf{r}_2}{2} . \tag{19}$$

The two-particle Liouville operator is then given by

$$\mathcal{L}_{12}=-i\frac{\mathbf{P}}{m}\cdot\frac{\partial}{\partial\mathbf{R}}+i\left\{-\frac{\mathbf{p}}{m}\cdot\frac{\partial}{\partial\mathbf{r}}+2\frac{\partial u(r)}{\partial\mathbf{r}}\cdot\frac{\partial}{\partial\mathbf{p}}\right\} . \tag{20}$$

Using (19) and (20), Eq. (17) simplifies to the expression given by the first term of Eq. (23) (see below).

Using the procedure outlined above it is straightforward, though somewhat lengthy, to evaluate all the terms in (13) in the binary-collision approximation. The final result can be written as

$$\phi_s(q,t)\simeq\phi_0(q,t)+\phi_1(q,t) , \tag{21}$$

where $\phi_0(q,t)$ and $\phi_1(q,t)$ represent, in the time domain, the contributions corresponding to the first and second terms of (11). These are given by

$$\phi_0(q,t)=\Omega_0^2[3-6\Omega_0^2t^2+\Omega_0^4t^4]e^{-\Omega_0^2t^2/2}+\frac{i\Omega_0 n}{P_0^3}\int\int d\mathbf{r}\,d\mathbf{p}\,g(r)G\left[\frac{p}{\sqrt{2}}\right]A_0(p_x)e^{-iqp_xt/2m}F_x\left[\left|\mathbf{r}+\frac{\mathbf{p}t}{m}\right|\right]$$
$$+\frac{nI_0}{\beta P_0^2}\int\int d\mathbf{r}\,d\mathbf{p}\frac{\partial g}{\partial x}G\left[\frac{p}{\sqrt{2}}\right]e^{-iqp_xt/2m}F_x\left[\left|\mathbf{r}+\frac{\mathbf{p}t}{m}\right|\right], \tag{22}$$

$$\phi_1(q,t)=\frac{n\Omega_0^2}{P_0^4}\int\int d\mathbf{r}\,d\mathbf{p}\,G\left[\frac{p}{\sqrt{2}}\right]g(r)[e^{(iq/2)[x-x(t)]}B[p_x(t)]-e^{-iqp_xt/2m}B_0(p_x)]$$
$$+\frac{in\Omega_0}{P_0^3}\int\int d\mathbf{r}\,d\mathbf{p}\,G\left[\frac{p}{\sqrt{2}}\right]g(r)A_0(p_x)\left[e^{(iq/2)[x-x(t)]}F_x[r(t)]-e^{-iqp_xt/2m}F_x\left[\left|\mathbf{r}+\frac{\mathbf{p}t}{m}\right|\right]\right]$$
$$-\frac{in\Omega_0}{\beta P_0^3}\int\int d\mathbf{r}\,d\mathbf{p}\,G\left[\frac{p}{\sqrt{2}}\right]g(r)[e^{(iq/2)[x-x(t)]}A[p_x(t)]-e^{-iqp_xt/2m}A_0(p_x)]$$
$$+\frac{nI_0}{\beta P_0^2}\int\int d\mathbf{r}\,d\mathbf{p}\,G\left[\frac{p}{\sqrt{2}}\right]\frac{\partial g(r)}{\partial x}\left[e^{(iq/2)[x-x(t)]}F_x[r(t)]-e^{-iqp_xt/2m}F_x\left[\left|\mathbf{r}+\frac{\mathbf{p}t}{m}\right|\right]\right]. \tag{23}$$

In (22) and (23), $\Omega_0^2=q^2v_0^2$ and we have introduced the notation

$$I_n=\int d\mathbf{P}\,G(\sqrt{2}P)P_x^n e^{-(iqP_x/m)t}, \tag{24}$$

$$A[p_x(t)]=\tfrac{1}{4}p_x^2(t)I_0+p_x(t)I_1+I_2, \tag{25}$$

$$B[p_x(t)]=\tfrac{1}{16}p_x^2p_x^2(t)I_0+\tfrac{1}{4}\{p_x^2p_x(t)+p_xp_x^2(t)\}I_1$$
$$+\{\tfrac{1}{4}p_x^2+\tfrac{1}{4}p_x^2(t)+p_xp_x(t)\}I_2$$
$$+\{p_x+p_x(t)\}I_3+I_4, \tag{26}$$

and A_0 and B_0 are the values of A and B with $p_x(t)=p_x(0)$. Note that in (23) we have to use the position and momentum vectors $\mathbf{r}(t)$ and $\mathbf{p}(t)$ of the particle moving in the central potential field $u(r)$ as determined by

$$\frac{1}{2}\frac{dp_x}{dt}=\frac{m}{2}\frac{d^2x}{dt^2}=F_x(r)=-\frac{\partial u(r)}{\partial x} \tag{27}$$

while x, p_x, and r are the initial values of these quantities at time $t=0$. It is easy to see that the second and third terms in (22) are divergent due to the appearance of free particle dynamics in the argument of force. These terms arise because initial configurations over which averages are to be performed correspond to the full Liouville operator $\mathcal{L}$ rather than the free particle $\mathcal{L}_0$. However, the two above mentioned divergent terms cancel exactly when combined with the same divergent terms appearing in (23). The final expression for $\phi(q,t)$ does not diverge and provides an exact low density result, correct to first order in density. If only the zero-density term of Eq. (22) is used, which corresponds to the free streaming term, we will get the well-known ideal gas result for $C_s(q,t)$. It can be easily verified that our expression for $\tilde{K}_s(q,z)$ with $\phi(q,t)$ given by (22) and (23) satisfies the zeroth and second frequency moments of the self-current correlation function exactly and, in addition, gives exact two-body contributions to all other higher moments.

There have been calculations of the low density phase-space memory function of the self-density correlation function using the kinetic theory approach. It seems to us that our low density memory function $\tilde{\phi}_s(q,z)$ is the corresponding analog in configuration space. Some terms in our Eqs. (22) and (23) are very indicative of the similarity. However, the complexity of solving the kinetic equation using the phase-space memory function seems to have been overcome, in the low density limit, by our Eqs. (22) and (23). Binary-collision approximations have been used in the study of space-time correlation functions [23,24], but in the present work our emphasis has been on the memory function frequently used in the study of normal and super-cooled liquid dynamics. We also make contact with the phase-space description wherever possible.

III. VELOCITY AUTOCORRELATION FUNCTION

The normalized velocity autocorrelation function

$$\psi(t)=\frac{\langle v_{1x}(t)v_{1x}(0)\rangle}{v_0^2} \tag{28}$$

can easily be obtained as the $q\to 0$ limit of Eq. (1); thus we have

$$\tilde{\psi}(z)=-\frac{1}{z+\tilde{K}(z)}, \tag{29}$$

where we now drop the suffix s and retain the same symbol, but without q, in the arguments. The memory function $\tilde{K}(z)$ is as defined in (6), but with $j_{1x}(q,0)$ replaced by $v_{1x}(0)$. The relation between $\tilde{K}(z)$ and $\tilde{\phi}(z)$ is similar to (10), but we should take the limit of $\tilde{\phi}_s(q,z)$ as $q\to 0$ and we denote this function as $\tilde{\phi}(z)$, whose time transform is just the force autocorrelation function. We obtain the expression for $\phi(t)$ from Eqs. (22) and (23). It is given by

$$\phi(t)=\frac{n}{m2\sqrt{2}}\int\int d\mathbf{r}\,d\mathbf{p}\,G\left[\frac{p}{\sqrt{2}}\right]\frac{\partial g(r)}{\partial x}F_x(r(t)) \ . \tag{30}$$

At $t=0$, Eq. (30) reduces to

$$\phi(0)=\frac{n}{m}\int d\mathbf{r}\frac{\partial g(r)}{\partial x}F_x(r) \ , \tag{31}$$

which is the well-known expression for the mean square force or, equivalently, the Einstein frequency.

There have been attempts in the past to obtain the binary-collision memory function [25,26] of the velocity autocorrelation function. Our expression differs from these results, which can be obtained from Eq. (30) if the low density form of $g(r)$ is used; however, this replacement destroys the exact $t=0$ value of $\phi(t)$ given by (31). Our Eq. (30) contains effects of all *uncorrelated* binary collisions and its density dependence is more complicated than the explicit linear dependence because of the appearance of the derivative of $g(r)$. In the strict low density limit, earlier results will be reproduced. Numerically, the two results should not be too different, especially at low densities. Since the expression for the low density memory function $\phi(t)$ does not possess a density independent term, it can be seen that $K(t)\approx\phi(t)$ in the low density limit.

This approximate expression for $K(t)$ can be simplified further in the case of a hard sphere fluid as follows. Equation (30) can be written as

$$K(t)=\frac{n}{-4\sqrt{2}m}\int\int d\mathbf{r}\,d\mathbf{p}\,G\left[\frac{p}{\sqrt{2}}\right]\frac{\partial g}{\partial x}\frac{dp_x(t)}{dt} \ , \tag{32}$$

using (27). The dynamics of collision between two hard spheres is well known. In this case, the time evolution of momentum in (32) is given by

$$\frac{dp_x(t)}{dt}=\theta(\sigma^2-b^2)\theta(-\hat{\mathbf{r}}\cdot\hat{\mathbf{p}})\delta(t-\tau)(-p_x+p_x^*) \ , \tag{33}$$

where the time of collision is

$$\tau=-\frac{m}{p}[\mathbf{r}\cdot\hat{\mathbf{p}}+(\sigma^2-b^2)^{1/2}] \ , \tag{34}$$

with $b^2=r^2-(\mathbf{r}\cdot\hat{\mathbf{p}})^2$ and $\theta(x)=1$ if $x>0$ and 0 if $x<0$. The post collision momentum is

$$p_x^*=p_x-2(\mathbf{p}\cdot\hat{\mathbf{r}})\frac{x}{r} \ . \tag{35}$$

Using the above results, Eq. (32) reduces to

$$K(t)=\frac{n}{2\sqrt{2}m}\int\int d\mathbf{r}\,d\mathbf{p}\,G\left[\frac{p}{\sqrt{2}}\right]\frac{dg(r)}{dr}\frac{x^2}{r^2}(-\mathbf{p}\cdot\hat{\mathbf{r}})$$
$$\times\theta(\sigma^2-b^2)\theta(-\hat{\mathbf{r}}\cdot\hat{\mathbf{p}})\delta(t-\tau) \ . \tag{36}$$

For $g'(r)$ we use the usual procedure of writing $g(r)=-y(r)e^{-\beta u(r)}$, where $y(r)$ is continuous even when both $g(r)$ and $u(r)$ have discontinuities. We then have

$$g'(r)=y'(r)e^{-\beta u(r)}+g(r)\delta(r-\sigma^+) \ . \tag{37}$$

We neglect the first term in (37), which is nonzero only for $r>\sigma$, and the δ function in the second term yields $\tau=0$. Thus Eq. (36) reduces to

$$K(t)=\frac{2\sqrt{2}n\pi g(\sigma)}{3m}\sigma^2\delta(t)$$
$$\times\int d\mathbf{p}\int_0^{\pi}d\lambda\, pG(p)\sin\lambda\cos\lambda\,\theta(-\hat{\mathbf{r}}\cdot\hat{\mathbf{p}}) \ . \tag{38}$$

The θ function restricts the range of the λ integration from $\pi/2$ to π and we get

$$K(t)=\frac{\sqrt{2}n\pi\sigma^2}{3m}g(\sigma)\delta(t)\int d\mathbf{p}\,p\,G(p) \ , \tag{39}$$

which finally reduces to a Markovian function

$$K(t)=\frac{8\sqrt{\pi}}{3}n\sigma^2v_0g(\sigma)\delta(t) \ . \tag{40}$$

Using the definition of the self-diffusion coefficient

$$D=\frac{v_0^2}{\int_0^{\infty}K(t)dt} \ , \tag{41}$$

we get the well known Enskog result

$$D_E=\frac{3v_0}{8\sqrt{\pi}n\sigma^2g(\sigma)} \tag{42}$$

and the VACF $\psi(t)$ will decay exponentially. It is satisfying to be able to obtain the Enskog result using the *configuration* space memory function and binary-collision expansion method.

IV. RESULTS FOR LENNARD-JONES POTENTIAL

The integral expression (30) for $\phi(t)$ was evaluated for various states using the central force $F(r)$ corresponding to the Lennard-Jones potential. $g(r)$ for each state was obtained from the optimized cluster theory [27]. The six-dimensional integral was reduced to the following three-dimensional integral using a method due to Pope and Johnson [28] based on Hamilton-Jacobi theory:

$$\phi(t)=\frac{4\sqrt{\pi}n}{3m^3v_0^3}\int_0^{\infty}dr\,rg'(r)\int_{u(r)}^{\infty}dE\,e^{-\{[E-u(r)]/mv_0^2\}}$$
$$\times\int_0^{\sqrt{m[E-u(r)]}r}dl\frac{l}{\sqrt{m[E-u(r)]r^2-l^2}}$$
$$\times[\cos[\alpha_+(t)]F(r_+(t))+\cos[\alpha_-(t)]F(r_-(t))] \ . \tag{43}$$

The three variables of integration are r, E (relative energy), and l (magnitude of the relative angular momentum);

$(r_+(t),\alpha_+(t))$ for $\dot{r}(0)>0$ and $(r_-(t),\alpha_-(t))$ for $\dot{r}(0)<0$ are the polar coordinates in the plane of motion of the two-body system. This integral can be replaced by

$$\phi(t)=\frac{4\sqrt{\pi}n}{3m^{5/2}v_0^2}\int_0^\infty dr\, r^2 g'(r)\int_0^\infty dE'\sqrt{E'}e^{-E'/mv_0^2}\int_0^{\pi/2} d\lambda\, \sin\lambda\{\cos[\alpha_+(t)]F(r_+(t))+\cos[\alpha_-(t)]F(r_-(t))\}\ , \tag{44}$$

where $E=E'+u(r)$ and $l=\sqrt{mE'}r\sin\lambda$.

The integration was done using Gauss-Legendre quadrature for finite intervals and Gauss-Laguerre quadrature for the E' integral. For each value of (r,E',λ), Newton's equation was solved approximately to obtain $r_\pm(t),\alpha_\pm(t)$ for $t>0$ as required. A Verlet-type algorithm [29] in polar coordinates with an initial step correct to fourth order in t was used. The dimensionless time variable used is $t^*=t/\tau$, where $\tau=\sqrt{m\sigma^2/48\epsilon}$, and $\phi(t^*)$ was evaluated, as described, for $0\le t^*\le 12.5$.

The results for small t^* were checked by comparison with one-dimensional integral expressions for $\phi(0)$ and $\ddot{\phi}(0)$ which can be readily evaluated; these are

$$\phi(0)=-\frac{4\pi n}{3m}\int_0^\infty dr\, r^2 g'(r)u'(r)\ , \tag{45}$$

$$\begin{aligned}\ddot{\phi}(0)=\frac{8\pi n}{3m^2}\int_0^\infty dr\, g'(r)[&r^2u'(r)u''(r)\\ &-mv_0^2(r^2u'''(r)\\ &+2ru''(r)-2u'(r))]\ .\end{aligned} \tag{46}$$

Results for intermediate values of t^* (say, $0.5<t^*<8$) were checked by studying convergence of the three-dimensional integration with respect to number of points used and the time evolution by convergence with respect to step length used in the algorithm. A total of 327 680 integration points (suitably distributed) and $dt^*=0.025$ were found to be acceptable. For $t^*>8$, $\phi(t^*)$ approaches 0 as expected, but these results are not reliable enough to be useful.

In Fig. 1(a) the results for $\phi(t^*)/\phi(0)$ for a low density state of $n^*=n\sigma^3=0.1$, at three temperatures $T^*=k_BT/\epsilon=1.46$, 2.5, and 6.0, are shown. Similar results for a density of $n^*=0.4$, which is close to the critical density, are shown in Fig. 1(b). It is to be noted that these results are obtained from (21) and thus based on just the first two terms of the BCE and so the exact conditions $\int_0^\infty dt\,\phi(t)=0$ and $\int_0^\infty dt\, t\phi(t)=-1$ are not satisfied. These graphs show the exact contribution to the force autocorrelation function due to a single binary-collision between a pair of particles. It is to be expected that our results will be closer to the molecular dynamics results at lower densities, where effects of multiparticle collisions are not significant. At higher temperatures, where the effect of the attractive part of the potential falls off, it is expected that our results will be close to those obtained using hard sphere interactions.

However, molecular dynamics (MD) results for the force correlation function are scarce. In Fig. 2 our $\phi(t)$ results for (a) a high temperature density state and (b) a state near the triple point are compared to the corresponding MD results of Heyes [30]. As expected, our results portray well the initial decay of the force correlation function at both states and deviate significantly from MD results at longer times especially at triple point density, where the role of multiparticle dynamics is very significant, even at relatively short times.

Our results for the force correlation function are based on the binary-collision expansion and hence are expected to be valid only for short times. To discuss the time dependence, we introduce the Enskog collision time τ_E which, in our dimensionless units, can be written as

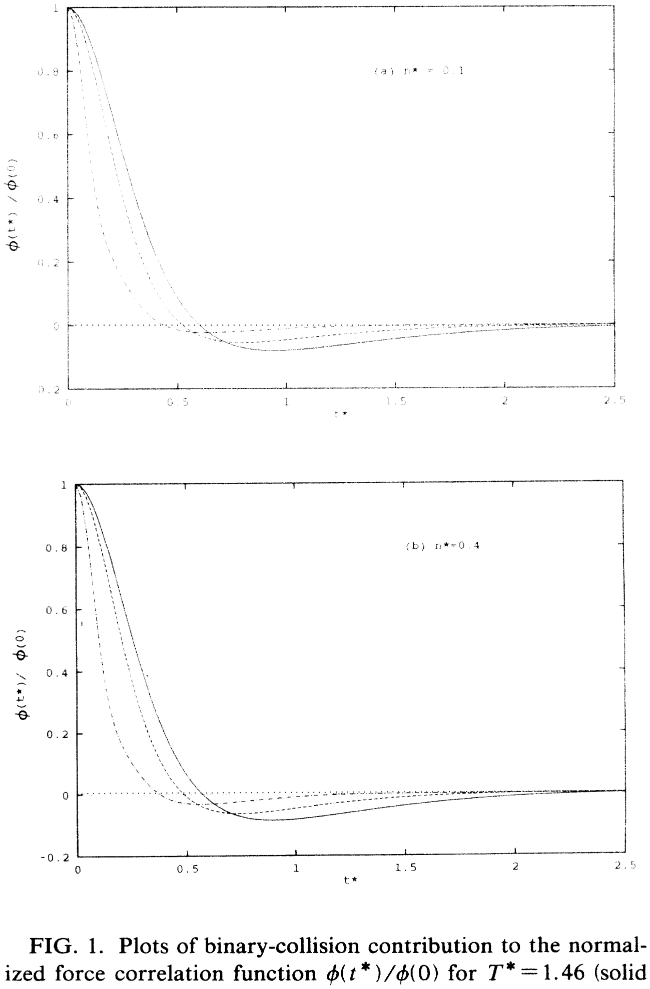

FIG. 1. Plots of binary-collision contribution to the normalized force correlation function $\phi(t^*)/\phi(0)$ for $T^*=1.46$ (solid line), 2.5 (dashed line), and 6.0 (dash-dotted line) with (a) $n^*=0.1$ and (b) $n^*=0.4$.

$$\frac{\tau_E}{\tau}=\frac{2}{3}\sqrt{48}\frac{D^*}{T^*} . \tag{47}$$

This can be viewed as the time for one collision, which for the triple point state is about 0.20. Thus at the triple point we note that our results for the force correlation function are in agreement with the MD results for more than one collision time. We will do a similar comparison for the VACF later.

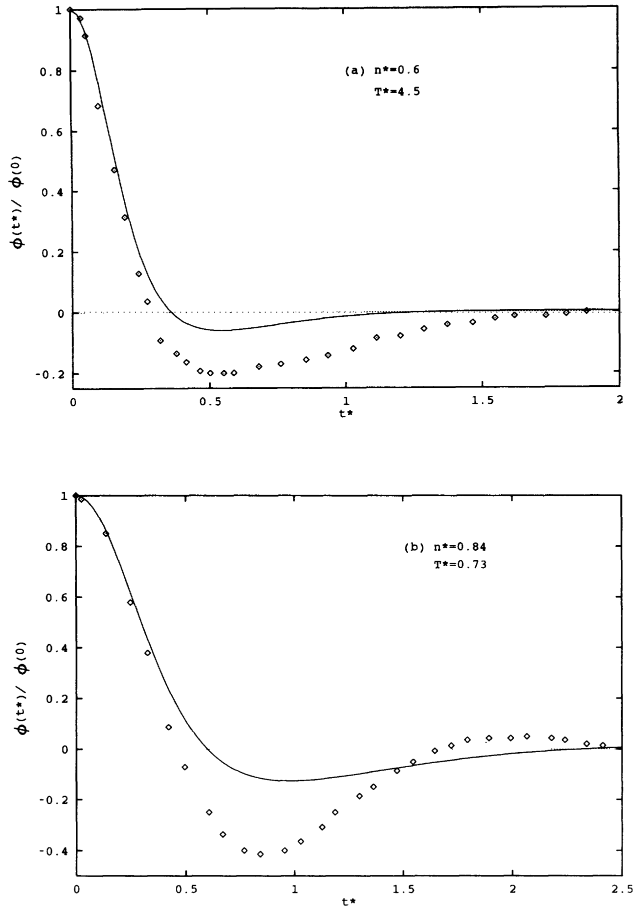

FIG. 2. Comparison of our results for the force correlation function (solid line) with those of molecular dynamics (diamonds) for (a) $n^*=0.6$ and $T^*=4.53$ and (b) $n^*=0.84$ and $T^*=0.73$.

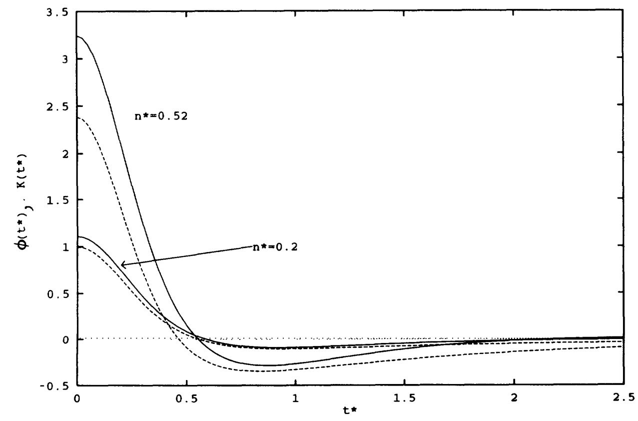

FIG. 3. Plots of the force correlation function $\phi(t^*)$ (solid line) and its memory function $K(t^*)$ (dashed line) for $T^*=1.46$ at two densities $n^*=0.2$ and 0.52.

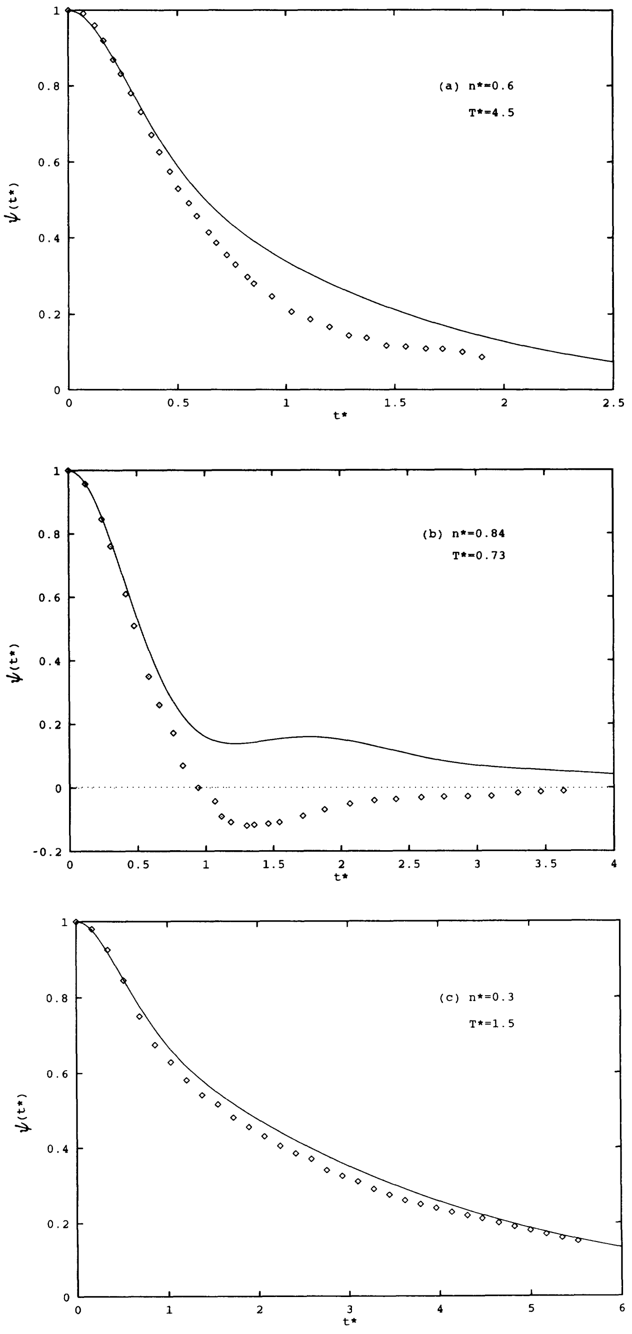

FIG. 4. Comparison of our results for the velocity autocorrelation function (solid line) with those of molecular dynamics (diamonds) for (a) $n^*=0.6$ and $T^*=4.53$, (b) $n^*=0.84$ and $T^*=0.73$, and (c) $n^*=0.3$ and $T^*=1.56$.

The memory function $K(t)$ for the VACF $\psi(t)$ was obtained using Eq. (10) and transforming from frequency space to time domain. $K(t)$ and $\phi(t)$ results for $T^*=1.46$, for a low density and a high density state are shown in Fig. 3. Since our $\phi(t)$ is a BCE approximation, $K(0)=\phi(0)$ is not obtained; however, it can be seen that the disagreement between $K(t)$ and $\phi(t)$ is smallest for the low density states. Similar behavior is seen for other temperature states.

The Fourier transform of the VACF is given by (29). The use of our approximate $K(t)$ to get the VACF produces an unphysical divergence at $t=0$. This divergence arises from the fact that the time integral of our approximate $\phi(t)$ is not zero. This leads to $\tilde{K}(z=0)=0$, from Eq. (10), and to a divergence of the time integral of the resulting VACF, from Eq. (29). In order to get a correct $\phi(t)$, whose time integral is zero, one has to include *correlated* binary collisions (i.e., mode coupling effects) and this will be the objective in our future papers. Because of this divergence, we cannot use our approximate $K(t)$ to obtain the VACF. There are a few approximate ways to remove the zero value of $\tilde{K}(z=0)$. One may, for example, choose to replace $(1/z)\tilde{\phi}(z)$, appearing in the denominator of Eq. (10), by the current-stress correlation function and then apply a BCE to it. We have chosen instead to approximate $\tilde{K}(z)$ by $\tilde{\phi}(z)$ and obtain, for VACF,

$$\psi(t)\simeq\frac{2}{\pi}\int_0^\infty d\omega\cos(\omega t)\frac{\varphi''(\omega)}{[\omega+\varphi'(\omega)]^2+[\varphi''(\omega)]^2}\,, \tag{48}$$

where

$$\begin{aligned}\varphi''(\omega)&=\int_0^\infty dt\,\phi(t)\cos(\omega t)\,,\\ \varphi'(\omega)&=-\int_0^\infty dt\,\phi(t)\sin(\omega t).\end{aligned} \tag{49}$$

This approximation is reasonable since $K(t)$ approaches $\phi(t)$ for low densities anyway. This comes about since the leading term in $\phi(t)$ is linear in density and numerically Fig. 3 reflects this behavior.

In Fig. 4, we show $\psi(t)$ for (a) the high temperature state, (b) the triple point, and (c) a low density state and compare our BCE results with the MD results of Heyes. Since our results are based on a single binary collision between a pair of particles, they will not yield the negative values for the VACF seen near the triple point. We now note that our results at the triple point are in agreement with MD results, up to about $t^*=0.5$, or equivalently for more than two collision times. The agreement for the force correlation function was about half of this time. This is to be expected since we have used Eq. (29) to calculate the VACF wherein the force correlation function is in the denominator and thus has, inherently, a density expansion containing higher orders of density. Of course, the coefficients of density higher than order one are not correct. In the low density state of Fig. 4(c) we have very good agreement between our results and those of MD, throughout. The MD results are at a slightly different temperature. For this state, the Enskog collision time is about 1.8 and thus the VACF decays close to zero in about four collision times.

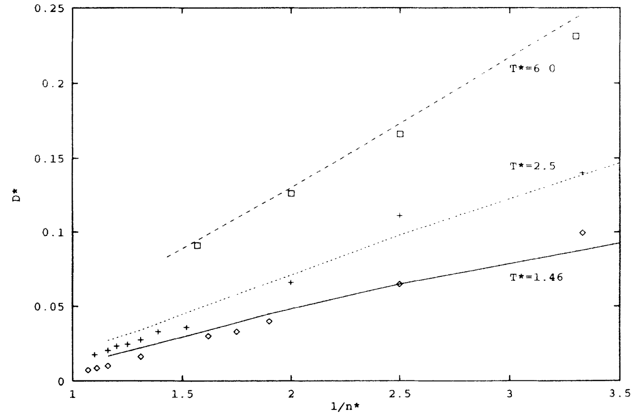

FIG. 5. Plot of D^* as a function of $1/n^*$ for $T^*=1.46$, 2.5, and 6.0. Our results are indicated by lines and those of molecular dynamics by symbols.

The self-diffusion coefficient is given by Eq. (41). Here again we replace $K(t)$ by $\phi(t)$ to obtain D for the various states. In Fig. 5 our results for $D^*=D\tau/\sigma^2$ are plotted against $1/n^*$ and compared with those of molecular dynamics [30]. It is seen that our results are in very good agreement with MD results for lower densities and deviations start to set in as density is increased. The Lennard-Jones self-diffusion coefficients are seen to follow approximately the Enskog linear $\sqrt{T^*}/n^*$ dependence, except at high density, low temperature states. Our results also indicate a similar behavior.

V. CONCLUSIONS

As mentioned in the Introduction, there is, as yet, no tractable microscopic theory involving either a phase-space kinetic equation or a space-time Mori-Zwanzig equation for continuous potentials. A hard sphere kinetic theory has been quite successful in explaining most of the dynamics of atomic motions in hard sphere dense fluids. In this paper, we have taken steps in achieving similar objectives for continuous fluids. Our approach is based on space-time equations as an equivalent phase-space equation is too unwieldy. It seems reasonable to write the space-time memory function as a sum of two parts: one associated with individual binary collisions and thus descriptive of short-time behavior, and the other associated with collective or multiparticle dynamics, which becomes important at longer times. In this paper we have derived exact, microscopic expressions for the memory functions associated with the self-density correlation function and the velocity correlation function, based on binary-collision expansions. Thus a microscopic theory of short time dynamics for continuous potentials has been developed and results for the velocity correlation function and the self-diffusion coefficient for various thermodynamic states have been obtained.

We are in the process of obtaining numerical values for the self-density correlation function $S_s(q,\omega)$ and the memory function associated with it. Future work involves the use of a mode coupling approximation for the collective part of the memory function and when this is combined with the binary part, we will have a microscopic theory for real dense fluids. It will also be interesting to apply these methods to the study of liquid alkaline metals.

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