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Effects of correlated collisions on atomic diffusion in a hard-sphere fluid

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The velocity autocorrelation function in a hard-sphere fluid is calculated by including corrections to the Boltzmann-Enskog theory due to correlated binary (ring) collisions. The memory function describing these processes is reduced to a form suitable for numerical computation by assuming the dominant contributions are due to couplings between hydrodynamic modes. A simple approximation is introduced to account for the effects of nonhydrodynamic modes. Using the interpolation formulas recently suggested by Resibois, we have computed the memory function, the velocity autocorrelation function, and the self-diffusion coefficient D. The diffusion coefficient shows the enhancement effect relative to the Enskog diffusion coefficient that was first observed by computer molecular-dynamics calculations. Our results also show a rapid decrease in D in the high-density region. A comparison of the present work with the analysis of Resibois is made, and further refinements are suggested.

I. INTRODUCTION

In the theory of atomic motions in fluids the study of the velocity autocorrelation function (VCF) is a problem of particular interest.[1] Because the dynamics is relatively simple to visualize, theoretical discussions have focused on this calculation as a measure of our ability to describe the molecular dynamics of classical fluids. Current calculations[2,3] of VCF invariably set out to predict one or both of the following properties which were first uncovered by computer molecular-dynamics experiments.[4-6] At sufficiently high density VCF decays rapidly to a negative value. This is regarded as a manifestation of the cage effects where a particle is trapped temporarily by its neighbors. The behavior has been extensively analyzed; it is now known that it can be obtained through a memory-function description in which the memory function has a finite though microscopic decay time.[7] The second property is that the self-diffusion coefficient D in a hard-sphere fluid shows significant deviations from the values predicted by the Enskog theory. The reason for this is that the VCF does not decay like an exponential either asymptotically or over times of order a few mean collision times.[6]

The purpose of this paper is to present a calculation of the velocity autocorrelation function of hard-sphere fluids using the formalism of renormalized kinetic theory.[2] Our goal is to study the effects of ring collisions on the VCF over the entire time domain and to predict the density dependence of the self-diffusion coefficient. In order to obtain explicit results, a number of approximations have to be introduced. It will be shown that our calculations reproduce many of the essential features of the computer results, but refinements and further work still remain.

The present calculation is essentially an extension of the analysis of Mazenko.[2] In this approach the VCF is governed by a memory-function equation in which the kernel has two contributions, an Enskog term and a contribution from ring, or correlated binary, collisions. Since the latter contains the product of two time-correlation functions one has a nonlinear problem that cannot be solved in any rigorous manner. The approximation adopted by Mazenko was to consider only contributions to the ring collision memory function involving hydrodynamic modes and to use simple expressions for the required time-correlation function. Recently Resibois has carried out an extensive kinetic theory calculation in which he introduced more realistic approximations for the time-correlation functions and obtained results which are in generally good agreement with the computer data.[3] Our calculation is similar, in a number of respects, to the work of Resibois; we will discuss the comparison after presenting our results.

The plan of the paper is as follows. In Sec. II we define the problem and give the explicit expression for the ring-collision memory function. In Sec. III we reduce this expression to an approximate form that is amenable to numerical computations. The VCF and diffusion coefficient results are given in Sec. IV, and we conclude with a number of comments in Sec. V.

II. MEMORY FUNCTIONS WITH RING COLLISIONS

Our calculation of the normalized velocity autocorrelation function

$$V(t) = \langle \vec{v}(t) \cdot \vec{v}(0) \rangle / \langle \vec{v}(0) \cdot \vec{v}(0) \rangle , \tag{2.1}$$

where $\vec{v}(t)$ is the particle velocity at time t, begins with the integro-differential equation

$$\frac{dV(t)}{dt} = - \int_0^t dt' \, K(t-t') V(t') . \tag{2.2}$$

For a fluid of hard spheres the memory function $K(t)$ can be written as the sum of two terms,[2]

$$K(t) = \alpha_E \delta(t) + \delta\phi(t), \tag{2.3}$$

where

$$\alpha_E = \tfrac{8}{3} n \sigma^2 v_0 \sqrt{\pi}\, g(\sigma) = v_0^2 D_E . \tag{2.4}$$

The first term in (2.3) is the Enskog contribution and $\delta\phi(t)$ represents collision effects more complicated than uncorrelated binary collisions. In (2.4), n is the fluid number density, σ the hard-sphere diameter, $v_0 = (m\beta)^{-1/2}$ is the thermal speed, $g(\sigma)$ is the equilibrium pair distribution function at contact, and D_E is the self-diffusion coefficient in the Enskog approximation.

In the present calculation we will take $\delta\phi(t)$ to be the contribution from ring collisions. The explicit form of $\delta\phi(t)$ then becomes[8]

$$\delta\phi(t) = -\frac{1}{n} g^2(\sigma) \int d^3\xi \, d^3\xi' \, d^3\xi'' \, d^3\xi''' \, d^3k \, (2\pi)^{-3} \frac{1}{3} \sum_{\mu=1}^{3} T^{\mu}(k\xi\xi') [S_s(k\xi'\xi''t) S(k\xi\xi'''t) - S_s^0(k\xi'\xi''t) S^0(k\xi\xi'''t)] T^{\mu}(-k\xi''\xi'''), \tag{2.5}$$

where S_s and S are the phase-space single-particle correlation function and the phase-space density correlation function, respectively, the superscript 0 denotes the corresponding function for a free particle, and the function T^{μ} is

$$T^{\mu}(k\xi\xi') = -4iv_0 \int d^3r \, e^{i\vec{k}\cdot\vec{r}} (\vec{p}\cdot\hat{r})^2 \delta(|\vec{r}|-\sigma) \Theta_{-}(\hat{r}\cdot\vec{p}) \hat{r}_{\mu} \tag{2.6}$$

with $\vec{p} = \frac{1}{2}(\vec{\xi} - \vec{\xi}')$. In (2.6), $\Theta_{-}(x)$ is the step function of negative argument.

Since $V(t)$ has a simple exponential solution in the absence of $\delta\phi(t)$, we will look for the difference solution,

$$\rho(t) = V(t) - V_E(t), \tag{2.7}$$

where

$$V_E(t) = e^{-\alpha_E t} \tag{2.8}$$

is the Enskog expression for the velocity autocorrelation function. Inserting (2.7) into (2.2) gives

$$\frac{d\rho(t)}{dt} + \alpha_E \rho(t) = - \int_0^t dt' \, \delta\phi(t-t') [\rho(t') + e^{-\alpha_E t'}] . \tag{2.9}$$

The solution of (2.9) can be carried out using transform methods. We define the Laplace transform of $\rho(t)$,

$$\tilde{\rho}(z) \equiv -i \int_0^{\infty} dt \, e^{izt} \rho(t), \tag{2.10}$$

and similarly for $\delta\phi(t)$. Equation (2.9) then becomes

$$\tilde{\rho}(z) = \frac{\delta\tilde{\phi}(z)}{(z+i\alpha_E)[(z+i\alpha_E) - \delta\tilde{\phi}(z)]} . \tag{2.11}$$

Since $\rho(t)$ is an even function, its Fourier transform is

$$\begin{aligned} \rho(\omega) &= \int_{-\infty}^{\infty} dt \, e^{i\omega t} \rho(t) \\ &= -2 \, \mathrm{Im} \tilde{\rho}(z)|_{z=\omega+i0^+} \\ &= -2 \, \mathrm{Im} \left(\frac{\delta\phi'(\omega) + i\delta\phi''(\omega)}{(\omega+i\alpha_E)[\omega - \delta\phi'(\omega) + i\alpha_E - i\delta\phi''(\omega)]} \right), \end{aligned} \tag{2.12}$$

where

$$\delta\phi'(\omega) = \int_0^{\infty} dt \, \sin\omega t \, \delta\phi(t), \tag{2.13}$$

$$\delta\phi''(\omega) = -\int_0^{\infty} dt \, \cos\omega t \, \delta\phi(t). \tag{2.14}$$

Our approach is to first determine $\delta\phi(t)$, then use (2.12)–(2.14) to find $\rho(\omega)$ and numerically invert to obtain $\rho(t)$.

III. QUASIHYDRODYNAMIC APPROXIMATION

We now develop a method of reducing (2.5) to an approximate but more tractable expression. Consider the expansion

$$S(k\xi\xi't) = \sum_{\alpha,\beta=1}^{\infty} \psi_{\alpha}(\xi) \psi_{\beta}(\xi) S^{\alpha\beta}(k,t) \Phi(\xi) \Phi(\xi'), \tag{3.1}$$

where $\{\psi_{\alpha}\}$ is an orthonormal set of momentum functions which we will choose to be the set of

Hermite functions,[2] and $\Phi(\xi)=(2\pi)^{-3/2}\exp(-\xi^2/2)$. The expansion coefficients $S^{\alpha\beta}(k,t)$ are given by

$$S^{\alpha\beta}(k,t)=\int d^3\xi\, d^3\xi'\, \psi_\alpha(\xi)\psi_\beta(\xi')S(k\xi\xi' t). \tag{3.2}$$

We also expand in a similar way (note difference in weight factor)

$$T^\mu(k\xi\xi')=\sum_{\alpha,\beta=1}^{\infty}\psi_\alpha(\xi)\psi_\beta(\xi)T^\mu_{\alpha\beta}(k), \tag{3.3}$$

where

$$T^\mu_{\alpha\beta}(k)=\int d^3\xi\, d^3\xi'\, \psi_\alpha(\xi)\psi_\beta(\xi')\Phi(\xi)\Phi(\xi')T^\mu(k\xi\xi'). \tag{3.4}$$

Applying these expansions to (2.5), we find

$$\delta\phi(t)=-\frac{1}{3n}g^2(\sigma)\sum_{\mu=1}^{3}\sum_{\alpha,\beta,\gamma,\nu=1}^{\infty}\int\frac{d^3k}{(2\pi)^3}T^\mu_{\alpha\beta}(k)[S_s^{\beta\nu}(k,t)S^{\alpha\gamma}(k,t)-S^{0,\beta\nu}(k,t)S^{0,\alpha\gamma}(k,t)]\,T^\mu_{\nu\gamma}(-k). \tag{3.5}$$

It is clear that an approximation is needed to treat the infinite sums. We next introduce the projection operator[9]

$$P=\sum_{i=1}^{5}|i\rangle\langle i|\equiv 1-Q, \tag{3.6}$$

which projects a function $f(\xi)$ onto the five hydrodynamic states $|i\rangle$, $i=1,\ldots,5$. By definition Q projects the function onto all the other (nonhydrodynamic) states. Consider now the approximations

$$S(k\xi\xi' t)=(P+Q)S(P+Q)\simeq PSP+QSQ \tag{3.7}$$

and

$$QSQ\simeq e^{-\lambda t}QS^0Q\simeq e^{-\lambda t}[S^0-PS^0P]. \tag{3.8}$$

In (3.7) we assume that couplings between hydrodynamic and nonhydrodynamic states through density fluctuations can be neglected while in (3.8) the nonhydrodynamic projections are assumed to have the same wavelength and time dependence as the projections of free-particle density fluctuations modulated by the damping factor $e^{-\lambda t}$, where λ^{-1} is a relaxation-time characteristic of nonhydrodynamic processes. Combining (3.7) and (3.8) we have

$$S(k\xi\xi' t)\simeq S^0(k\xi\xi' t)e^{-\lambda t}+P[S-S^0e^{-\lambda t}]P. \tag{3.9}$$

Using the approximation (3.9) we find, after a few manipulations described in Appendix A, that the integrand of (3.5) becomes

$$T(S_sS-S_s^0S^0)T=TS_sST\simeq T[(P_sS_sP_s)(PSP)-(P_sS_s^0P_s)(PS^0P)e^{-(\lambda+\lambda_s)t}], \tag{3.10}$$

where $P_s=|1\rangle\langle 1|$ is the hydrodynamic projection operator for the single-particle phase-space correlation function. Moreover, by restricting the α and γ sums to only hydrodynamic states we obtain an approximate expression for the ring-collision memory function

$$\delta\phi(t)\simeq-\frac{1}{n}g^2(\sigma)\sum_{\alpha,\gamma=1}^{5}\int\frac{d^3k}{(2\pi)^3}T^\mu_{\alpha 1}(k)[S_s^{11}(k,t)S^{\alpha\gamma}(k,t)-S_s^{0,11}(k,t)S^{0,\alpha\gamma}(k,t)]\,T^\mu_{1\gamma}(-k). \tag{3.11}$$

Comparing (3.11) with (3.5) we see that the effect of our approximation is to retain the hydrodynamic states and take into account approximately the effects of nonhydrodynamic states through the factor $e^{-(\lambda+\lambda_s)t}$.

The functions $T_{1\alpha}$ appearing in (3.11) can be obtained from (2.6). It can be shown that[10]

$$T^\mu_{11}(k)=4\pi v_0\sigma^2 j_1(x)\hat{k}_\mu, \tag{3.12}$$

$$T^\mu_{12}(k)=-i8\sqrt{\pi}\,v_0\sigma^2\left[\frac{d^2j_0(x)}{dx^2}\right]\hat{k}_\mu, \tag{3.13}$$

$$T^\mu_{13}(k)=\frac{4\pi}{\sqrt{6}}v_0\sigma^2 j_1(x)\hat{k}_\mu, \tag{3.14}$$

$$T^\mu_{14}(k)=-i8\sqrt{\pi}\,v_0\sigma^2\frac{1}{x}\frac{dj_0(x)}{dx}\hat{k}_\mu, \tag{3.15}$$

where $j_l(x)$ is the spherical Bessel function of order l, $x=k\sigma$, and $\hat{k}_\mu$ is a Cartesian component of unit vector $\hat{k}$. Since only the couplings between the test-particle density and the longitudinal and transverse currents, T^μ_{12} and T^μ_{14}, survive in the long-wavelength limit, we will assume these are the most important terms in doing the sums over α and γ. Keeping only these terms in (3.11) and doing the angle integrations and the μ sum, we obtain

$$\delta\phi(t)\simeq-\frac{2}{9\pi}\frac{1}{\eta\tau_E^2}\int_0^\infty dx\left\{j_1^2(x)[S_s(k,t)J_t(k,t)-S_s^0(k,t)J_t^0(k,t)e^{-(\lambda+\lambda_s)t}]+\frac{x^2}{2}\left(\frac{d^2j_0(x)}{dx^2}\right)^2[S_s(k,t)J_l(k,t)-S_s^0(k,t)J_l^0(k,t)e^{-(\lambda+\lambda_s)t}]\right\}, \tag{3.16}$$

where $\eta = \frac{1}{6}\pi n\sigma^3$, $\tau_E^{-1} = 4\sqrt{\pi}\, n\sigma^2 v_0 g(\sigma)$. In (3.16), $S_s(k,t)$, $J_t(k,t)$, and $J_l(k,t)$ denote the van Hove self-correlation function, the transverse and longitudinal current correlation functions, respectively. Approximate expressions[3] for these functions which are interpolations between the known short- and long-time behavior are given in Appendix B. The corresponding free-particle correlation functions offer no difficulty since they can be obtained from the phase-space correlation function

$$\begin{aligned} S^0(k\xi\xi' t) &= S_s^0(k\xi\xi' t) \\ &= n\Phi(\xi)\delta(\xi - \xi')e^{-v_0\vec{k}\cdot\vec{\xi}}. \end{aligned} \tag{3.17}$$

One finds

$$S_s^0(x,s) = J_t^0(x,s) = \exp[-\tfrac{1}{2}(xys)^2], \tag{3.18}$$

$$J_l^0(x,s) = [1-(xys)^2]\exp[-\tfrac{1}{2}(xys)^2], \tag{3.19}$$

where

$$y = [4\sqrt{\pi}\, n\sigma^3 g(\sigma)]^{-1},$$

$$s = t/\tau_E.$$

IV. RESULTS AND DISCUSSION

We have evaluated (3.16) numerically using the time-correlation function expressions given in Appendix B. For the parameters λ and λ_s, which should play the role of microscopic relaxation times, we found that a value of $0.8\tau_E^{-1}$ gives reasonably good agreement with the computer experiment. Figure 1 shows the ring-collision memory function at two values of packing fraction η. The principal behavior of $-\delta\phi(t)$ is seen to be a sharp peak at short times followed by a gradual decay. One can show that asymptotically[2]

$$-\delta\phi(t) \simeq \frac{16}{27\sqrt{\pi}} n\sigma^4 v_0 g^2(\sigma)[(D_E + \nu_E)t]^{-3/2}, \tag{4.1}$$

where ν_E is the kinematic viscosity in the Enskog theory. This behavior assures that the velocity autocorrelation function will also decay asymptotically like $t^{-3/2}$.

The short-time structure in $\delta\phi$ is a consequence of the nonhydrodynamic correction factor $e^{-(\lambda+\lambda_s)t}$. When we let $\lambda = \lambda_s = 0$, we obtain the dashed curves in Fig. 1. The reversal in the peak structure comes about because $J_t^0(k,t)$ is greater than $J_t(k,t)$ at short times while $S_s(k,t) > S_s^0(k,t)$.

The numerical values of $\delta\phi(t)$ are next used to generate $\delta\phi'(\omega)$ and $\delta\phi''(\omega)$ which are then inserted into (2.12) to yield $\rho(\omega)$. Finally $\rho(s)$, the difference velocity autocorrelation function, is obtained by a numerical Fourier transform. Figure 2 shows the results at the lowest and highest densities we have considered. Also shown are the computer molecular-dynamics results on a 500-particle system of hard spheres obtained by Alder, Gass, and Wainwright.[6] Our results are quite reasonable at low densities, and although they show a negative region at high densities the details are not in good agreement with the computer data. It appears that the negative region sets in too quickly and too

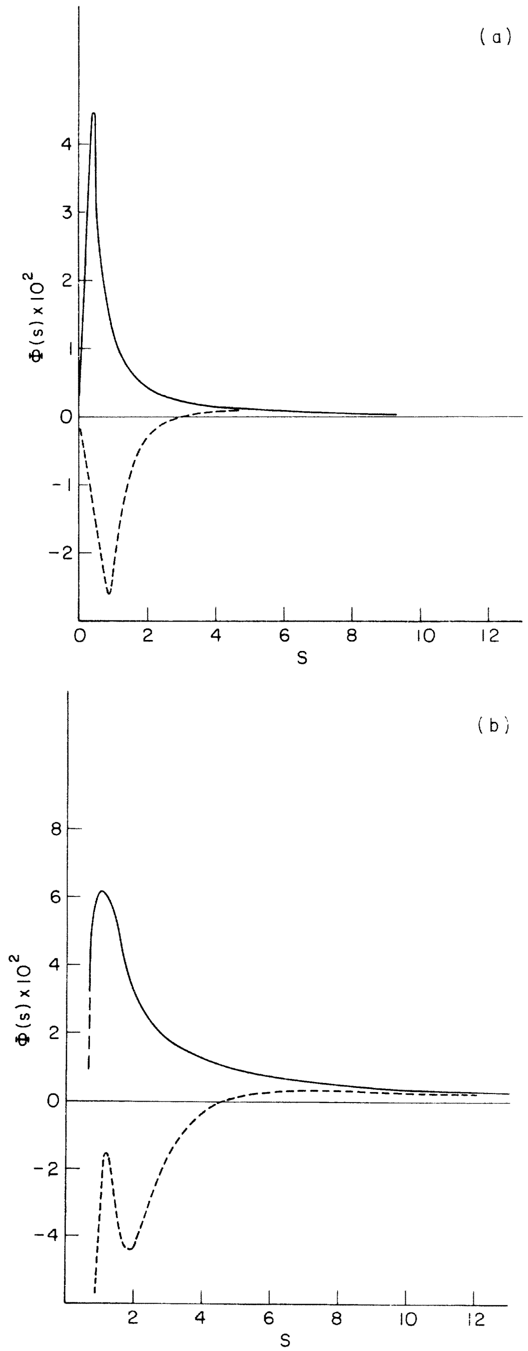

FIG. 1. Ring-collision memory function $\delta\phi(t)$ computed using (3.14) with (solid curves) and without nonhydrodynamic corrections (dashed curves), (a) $\eta = 0.0741$, (b) $\eta = 0.1481$. Dimensionless time s is t/τ_E.

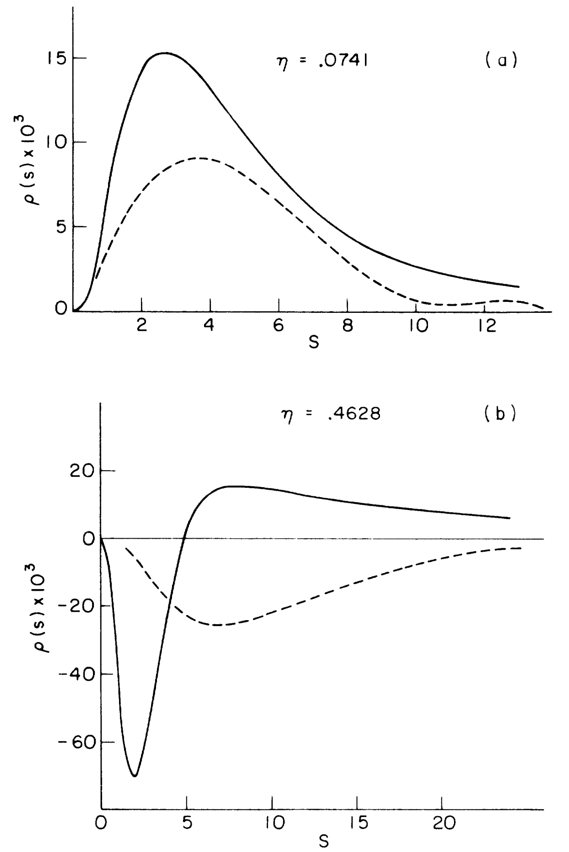

FIG. 2. Comparison of the calculated difference velocity autocorrelation function $\rho(s)$ (solid curves) in a hard-sphere fluid with the results of computer molecular dynamics (dashed curves) (Ref. 6), (a) $\eta = 0.0741$, (b) $\eta = 0.4628$.

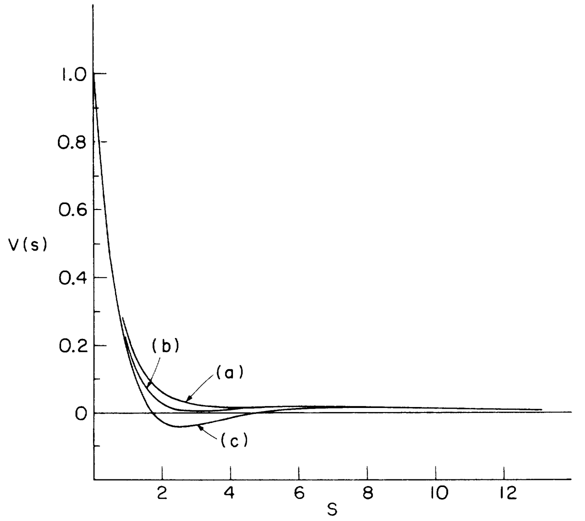

FIG. 3. Theoretical velocity autocorrelation function $V(s)$ in a hard-sphere fluid, (a) $\eta = 0.0741$, (b) $\eta = 0.2468$, and (c) $\eta = 0.4628$.

strongly; also the asymptotic decay which occurs while $\rho(s)$ is positive begins too early. In Fig. 3 we show the calculated velocity autocorrelation function at three densities. On this scale the behavior of $\rho(s)$ in Fig. 2 appears as small though important perturbations. It is interesting to note that at the highest density $V(s)$ has a negative region, a behavior that has been called the backscattering effect.

The self-diffusion coefficient D, defined by

$$D = v_0^2 \int_0^\infty dt\, V(t) \tag{4.2}$$

is an important quantity in any theory of atomic motions in fluids. In discussing the deviations from the Enskog theory it is convenient to consider the ratio D/D_E which can be expressed directly in terms of the ring-collision memory function,

$$\frac{D}{D_E} = \left(1 + \alpha_E \int_0^\infty dt\, \delta\phi(t)\right)^{-1}. \tag{4.3}$$

A comparison of our calculations at five densities with the computer results is given in Table I as well as shown in Fig. 4. There is general agreement in the variation of D/D_E with density over the entire range. Referring to Fig. 2 we know the enhancement in D at low density arises mainly from the positive structure in $\rho(s)$ at short times. At high densities ($V/V_0 < 2$) D/D_E decreases rapidly because of the strong negative region in $\rho(s)$.

V. DISCUSSION

We have presented a calculation of the velocity autocorrelation function in a hard-sphere fluid in which the effects of correlated sequence of two binary collisions between two particles are taken into account. By assuming the dominant contributions to the ring-collision memory function involve only hydrodynamic modes and by using

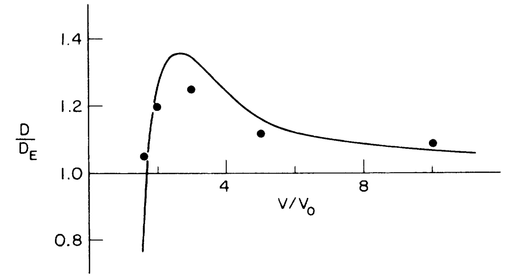

FIG. 4. Variation of self-diffusion coefficient ratio D/D_E with density in a hard-sphere fluid, present calculation (points) and computer molecular dynamics results (curve) (Ref. 6).

TABLE I. Comparison of the calculated self-diffusion coefficients in a hard-sphere fluid at various densities with the results of computer molecular dynamics (Ref. 6).

		D/D_E	
V/V_0	η	Present calc.	Reference 6
10	0.0741	1.09	1.07
5	0.148	1.12	1.16
3	0.247	1.25	1.34
2	0.3702	1.20	1.27
1.6	0.4628	1.05	0.84

interpolation formulas for time-correlation functions, we have computed numerically the memory function $\delta\phi(t)$ and the VCF $V(t)$. Although the approximations used are quite crude, the computed self-diffusion coefficient ratio D/D_E is found to have the same variation with density as the computer molecular-dynamics results. The calculated VCF does not agree as well with the computer data in the high-density region; however, we believe that some of the discrepancies may be removed by refining the present approach.

It is instructive to examine in more detail the behavior of the ratio D/D_E. In the low-density region ($V/V_0 \gtrsim 7$) D is greater than D_E and the enhancement is more or less constant with density. One sees that the effect arises mostly from the deviation in VCF from an exponential at times of order $(1-10)\tau_E$. The well-known long-time tail of the VCF also contributes to the enhancement but the magnitude of this contribution is small. In the intermediate-density region ($2 \lesssim V/V_0 \lesssim 7$) D/D_E varies much more strongly with density, rising to a peak value around $V/V_0 \sim 2.5$. The peak is a consequence of the competition between two processes, the correlated collision which tends to enhance the diffusion and the so-called collision transfer which tends to retard diffusion. In the high-density region ($V/V_0 \lesssim 2$) collision transfer effects dominate and one sees a rapid decrease in D/D_E.

The effects of ring collisions on the VCF in the intermediate-time (prior to the onset of the long-time tail) was first investigated by Mazenko. In this calculation $\delta\phi(t)$ was evaluated using simple hydrodynamic expressions for the time-correlation functions and nonhydrodynamic corrections were not considered ($\lambda = \lambda_s = 0$). The result was that an enhancement in D/D_E was obtained, but the ratio did not decrease at high densities. Also the enhancement was increasingly more overestimated as the density increases. As pointed out by Resibois, the use of the simple hydrodynamic expressions for time-correlation functions leaves out the damping effects of collision transfer which are most important at high densities. An advantage of the interpolation formulas given in Appendix B is that collision transfer effects are taken into account. The dashed curves in Fig. 1 are the results when the calculations were repeated using the interpolation formulas instead of the simple hydrodynamic expressions. The negative structure in Fig. 1 was found to overwhelm the long-time tail and the enhancement effects in D/D_E was lost. For example, at $V/V_0 = 10$ the computed value of D/D_E was 0.804.

From the above observation one may conclude that in the present formulation collision transfer effects do not lead to an enhancement in the diffusion coefficient, but they do appear to be the dominant effects at high densities where D/D_E decreases rapidly with decreasing V/V_0. As shown in Fig. 1 the origin of the enhancement lies in the nonhydrodynamic correction factor $e^{-(\lambda+\lambda_s)t}$. It should be noted, however, that Resibois obtained the enhancement effect without considering the nonhydrodynamic correction.[3] In his calculation he included another contribution to the ring-collision memory function. In addition to our $\delta\phi(t)$ (with $\lambda = \lambda_s = 0$) he considered the effects of correlated sequence of two binary collisions between *three* particles. The latter appears in the calculation as a term involving the three-particle correlation function. Applying the quasihydrodynamic approximation Resibois showed that this term can be expressed as a coupling between the van Hove self-correlation function and the density correlation function. We have evaluated this term numerically and found that it more than compensates for the short-time negative structure in the dashed curves of Fig. 1, and the net result for the ring-collision memory function behavior is qualitatively similar to the solid curves in Fig. 1.

The difference between the present calculation and the analysis of Resibois[3] therefore lies in his inclusion of the binary ring collisions between three particles and our consideration of nonhydrodynamic corrections. In each case the effects are essential to obtaining the enhancement behavior in D/D_E. Although both calculations produce correctly the qualitative variation of D/D_E over the entire density range, neither calculations give completely satisfactory results for the VCF at high densities. In our case we believe that a better approximation for the transverse current correlation function $J_t(k, t)$ and inclusion of additional couplings between hydrodynamic modes could improve the agreement between calculated $\rho(t)$ and the computer results. One should also investigate the validity of the various interpolation formulas for time-correlation functions. As noted by Resibois kinetic model calculations can provide an answer to this question. Work along this direction is underway and we hope to report on the results at a later date.

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APPENDIX A

To derive (3.10) we begin with the approximation (3.9) for S and a similar approximation for S_s. Since one knows that[11]

$$TS_s^0 S^0 T = 0, \tag{A1}$$

we can write the integrand in (3.5) as

$$\begin{aligned} T(S_s S - S_s^0 S)T &= T[P(S - S^\lambda)P + S^\lambda][P_s(S_s - S_s^{\lambda_s})P_s + S_s^{\lambda_s}]T \\ &= TP(S - S^\lambda)PP_s(S_s - S_s^{\lambda_s})P_s T + TP(S - S^\lambda)PS_s^{\lambda_s} T + TS^\lambda P_s(S_s - S_s^{\lambda_s})P_s T, \end{aligned} \tag{A2}$$

where $P_s = |1\rangle\langle 1|$ is the hydrodynamical projection operator for the single-particle phase-space correlation function, $S^\lambda = S^0 e^{-\lambda t}$ and $S_s^{\lambda_s} = S^0 e^{-\lambda_s t}$. Note that we have used (A1) in eliminating a $S^\lambda S_s^{\lambda_s}$ term in (A2). We now argue that the last two terms in (A2) are small for all times and as a first approximation can be ignored. Consider the term $S_s^{\lambda_s} P(S - S^\lambda)P$. This quantity will decay rapidly to zero in time because of the $e^{-\lambda_s t}$ factor. It also vanishes for short times because $S \to S^0$ and $S^\lambda \to S^0$ as $t \to 0$. Since the quantity starts at zero and decays rapidly to zero it is reasonable to ignore it. Similar arguments apply to the $S^\lambda P_s(S_s - S_s^{\lambda_s})P_s$ term. In this approximation (A2) reduces to (3.10).

APPENDIX B

We follow Resibois[3] in constructing interpolation expressions for the correlation functions appearing in (3.16). The basic ingredients used to represent a correlation function $F(k, t)$ are its short-time expansion $F^{st}(k, t)$ and its hydrodynamic limit $F^h(k, t)$. These are then connected together through the relation

$$F(k, s) = F^{st}(k, s)e^{-(\alpha s)^2} + [1 - e^{-(\alpha s)^2}]F^h(k, s), \tag{B1}$$

where $s = t/\tau_E$ is the dimensionless time and α is a parameter. For the three correlation functions under discussion their short-time expressions are

$$\begin{aligned} S_s^{st}(x, s) &= \exp[-\tfrac{1}{2}(xys)^2], \\ J_t^{st}(x, s) &= \exp\left\{-(xy)^2\left[\frac{sf_1}{15y} + \frac{s^2}{2}\left(1 + \frac{\sqrt{\pi}f_2}{15y}\right)^2\right]\right\}, \\ J_l^{st}(x, s) &= [1 - (xys)^2 X(x)]\exp\left\{-(xy)^2\left[\frac{sf_3}{5y^2} + \frac{s^2X(x)}{2}\right]\right\}, \end{aligned} \tag{B2}$$

where $x = k\sigma$, $y = [4\sqrt{\pi}n\sigma^3 g(\sigma)]^{-1}$, and functions f_i and X are defined below. The corresponding hydrodynamic expressions are

$$\begin{aligned} S_s^h(x, s) &= \exp[-(xy)^2 sD(x)], \\ J_t^h(x, s) &= \exp[-(xy)^2 s\nu(x)], \\ J_l^h(x, s) &= \cos[c_0(x)xys]\exp[-(xy)^2 s\Gamma(x)], \end{aligned} \tag{B3}$$

where D, ν, and Γ are the wavelength-dependent coefficients of self-diffusion, shear viscosity, and classical sound attenuation, respectively. They are also given below.

All the quantities in (B2) and (B3) will now be defined. They are

$$\begin{aligned} X(x) &= \frac{4}{3}\left[\frac{c_0(x)}{v_0}\right]^2 + \frac{4}{3}\left(1 + \frac{2\sqrt{\pi}}{15y}f_5\right), \\ D(x) &= \frac{3}{2}, \\ \nu(x) &= \frac{5}{4}\left(1 + \frac{\sqrt{\pi}f_2}{15y}\right)^2 + \frac{f_1}{15y^2}, \\ \Gamma(x) &= \frac{5}{6}\left(1 + \frac{\sqrt{\pi}f_2}{15y}\right)^2 + \frac{f_3}{10y^2} + \frac{5}{36}\left(\frac{\sqrt{\pi}f_2}{15y}\right)^2 \\ &\quad - \frac{x^2 f_3^2}{9800y} + \frac{\lambda(x)}{2}\left[\frac{2}{3} - \frac{1}{C_p(x)}\right], \end{aligned} \tag{B4}$$

where

$$\begin{aligned} c_0^2(x) &= v_0^2[1 - nC(x) + \tfrac{2}{3}(1 + \sqrt{\pi}f_0/6y)^2], \\ C_p(x) &= nk_B\left[\frac{3}{2} + \frac{(1 + \sqrt{\pi}f_0/6y)^2}{1 - nC(x)}\right], \\ \lambda(x) &= \frac{75}{16}\left[1 + \frac{\sqrt{\pi}f_0}{10y}\right]^2 + \frac{f_4}{6y^2}. \end{aligned} \tag{B5}$$

It should be noted that $c_0(x)$ and $C_p(x)$ are the wavelength-dependent adiabatic sound speed and the constant-pressure specific heat, and $\lambda(x)$ is the wavelength-dependent thermal conductivity coefficient. In (B5) $C(x)$ is the direct correlation function. For a hard-sphere fluid we will use the expression[12]

$$nC(x)=\frac{24\eta}{x^2}\left\{\alpha_0(\sin x-x\cos x)+\frac{\alpha_1}{x}[2x\sin x-(x^2-2)\cos x-2]+\frac{\alpha_2}{x^3}[(4x^3-24x)\sin x-(x^4-12x^2+24)\cos x+24]\right\}, \tag{B6}$$

with

$$\alpha_0=\frac{(1+2\eta)^2}{(1-\eta)^4},\quad \alpha_1=-6\eta\,\frac{(1+\eta/2)^2}{(1-\eta)^4},\quad \alpha_2=\eta\alpha_0/2, \tag{B7}$$

and $\eta=\frac{1}{6}\pi n\sigma^3$ is the dimensionless packing parameter. The only quantities yet to be specified are the x-dependent functions f_i, $i=0,\ldots,5$. They are

$$\begin{aligned}
&f_0(x)=(3/x^3)(\sin x-x\cos x),\\
&f_1(x)=(30/x^5)(x\cos x-\sin x)+10/x^2,\\
&f_2(x)=(15/x^5)(3\sin x-3x\cos x-x^2\sin x),\\
&f_3(x)=10/3x^2-(10/x^5)[(x^2-2)\sin x+2x\cos x],\\
&f_4(x)=(6/x^3)(x-\sin x),\\
&f_5(x)=(15/2x^5)[(4x^2-9)\sin x+(9x-x^3)\cos x].
\end{aligned} \tag{B8}$$

The above expressions completely determine the three correlation functions, $S_s(k,t)$, $J_t(k,t)$, and $J_l(k,t)$ in terms of the variables x, y, s, and η.

It should be noted that the short-time correlation functions in (B2) are obtained by considering time expansions of the various correlation functions. On the other hand, the hydrodynamic correlation functions (B3) are obtained by using wavelength-dependent transport coefficients and thermodynamic properties in the well-known expressions one can derive from the equations of linearized hydrodynamics. We have recently shown that a kinetic model representation of the generalized Enskog transport equation, called wave-number-dependent triple-relaxation-time model (QTRT) kinetic equation, provides a reasonable description of the thermal fluctuations in a hard-sphere fluid at arbitrary wavelengths.[13] We have used the sum-rule properties of this kinetic equation to obtain the short-time correlation functions (B2). In addition, the expressions for $\nu(x)$, $\lambda(x)$, $\Gamma(x)$, $C_0(x)$, $C_p(x)$ are all calculated using the QTRT description. [The result for $D(x)$ is obtained using a lower-order kinetic model.[14]] Since our results, aside from a slight difference in $J_l^{st}(x,s)$ and $\Gamma(x)$, are the same as those used by Resibois, we may conclude that these interpolation formulas are at least consistent with the generalized Enskog kinetic theory. By matching (B1) with kinetic equation results one may determine the values of α and α_s. We have not done this; instead in our numerical work we have adopted the values of $\alpha=\alpha_s=\frac{1}{3}$ used by Resibois.

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[1] See, for example, G. F. Mazenko [Phys. Rev. A 7, 209 (1973)] for an extensive list of references. See also Ref. 11.

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[4] B. J. Alder and T. E. Wainwright, in *Transport Properties in Statistical Mechanics*, edited by I. Prigogine (Interscience, New York, 1958).

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[6] B. J. Alder, D. M. Gass, and T. E. Wainwright, J. Chem. Phys. 53, 3813 (1970).

[7] See, for example, B. J. Berne, in *Physical Chemistry* (Academic, New York, 1971), Vol. 8B, p. 539.

[8] Since the publication of Ref. 2 we have made further progress in the formal development of the theory which allows one to treat recollisions in a more symmetric manner (see Ref. 1). The net result of this analysis [which is discussed in a chapter by us in Volume 6 of *Modern Theoretical Chemistry*, edited by B. J. Berne (Plenum, New York, to be published)] is that we pick up a factor of $g(\sigma)$ in Eq. (2.5) that we did not have in the earlier paper. This result is in agreement with Dorfman and Cohen (Ref. 11) where they also find two factors of $g(\sigma)$ in $\delta\phi(t)$.

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