Self-diffusion coefficient for the hard-sphere fluid

Jerome J. Erpenbeck and William W. Wood
Los Alamos National Laboratory, Los Alamos, New Mexico 87545
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Previously published Monte Carlo molecular-dynamics data on the velocity autocorrelation function of the hard-sphere fluid are supplemented by data for the time-dependent transport coefficient to yield estimates for the self-diffusion coefficient throughout the fluid regime, from 25 to 1.6 times the close-packed volume. The dependence on system size is explored through results for 108–4000 particles. It is found essential to include long-time contributions to the Green-Kubo integral based on the previously validated mode-coupling theory. It is shown that the calculations of Easteal, Woolf, and Jolly [Physica **121A**, 286 (1983)] fall significantly below the current estimates, which are in qualitative agreement with the Alder, Gass, and Wainwright [J. Chem. Phys. **53**, 3813 (1970)] values.

I. INTRODUCTION

The study of transport coefficients through molecular-dynamics simulation began with the investigation of hard spheres and disks more than 20 years ago.[1] That work led to the discovery[2] of the slow, algebraic decay of the velocity-autocorrelation function (VACF, the time-correlation function for self-diffusion in the Green-Kubo formulation), and the associated enhancement to the self-diffusion coefficient[3] for hard spheres and its divergence for hard disks. Theoretical derivations of the slow decay have been given on the bases of kinetic theory[4–6] and mode-coupling theory.[7,8] Similar slow decays have been derived for the time-correlation functions for the coefficients of viscosity and thermal conductivity,[7–16] and studied for hard spheres by molecular-dynamics simulation.[3,17] In addition, the divergence of the higher-order ("super-Burnett," etc.) self-diffusion coefficients in both two and three dimensions have been predicted theoretically[18–23] and verified for hard disks and spheres by molecular-dynamics simulation.[24] The present authors[25,26] greatly extended the studies of Alder and Wainwright in order to compare the VACF with the theoretical predictions. Nonetheless, we did not, at that time, use the results to improve on the original estimates for the self-diffusion coefficients by Alder, Gass, and Wainwright[3] (AGW), which were based on molecular-dynamics calculations for systems of 108 and 500 particles, extrapolated to the infinite-system limit, including corrections for the long-time tail.

Easteal, Woolf, and Jolly[27,28] (EWJ) have challenged the earlier values for the self-diffusion coefficient based on their molecular-dynamics calculations for systems ranging in size from 128 to 432 particles and even to 4394 particles for one density. It was implied in these studies that the numerical results somehow disprove the appropriateness of the long-time-tail corrections of AGW. Speedy[29] has suggested that all reliable results for the self-diffusion coefficient can be fit within the statistical uncertainty by the empirical expression,

$$D = D_{00}\left[1-\frac{\hat{n}}{1.09}\right][1+\hat{n}^2(0.4-0.83\hat{n}^2)]\ ,$$
$$D_{00} = \frac{3\sigma}{8\hat{n}\sqrt{\pi m\beta}}\ , \tag{1}$$
$$\hat{n} = n\sigma^3\ ,$$

in which D is the diffusion coefficient, D_{00} is the low-density Boltzmann value in the first Enskog approximation, σ is the hard-sphere diameter, n is the number density, m is the particle mass, and $\beta = 1/k_B T$ with k_B the Boltzmann constant, and T the thermodynamic temperature.

In our study of the VACF,[25,26] we used a combination of Monte Carlo and molecular-dynamics (MCMD) methods to extend the Alder-Wainwright calculations to larger systems and more densities in order to compare the VACF with the kinetic-theory and mode-coupling predictions for the long-time tails. These studies strongly supported the theories with respect to the dominant shear-mode contribution to the long-time tail, but with the inclusion of the less dominant acoustic-mode contribution yielding quantitative agreement between the MCMD data for the VACF and a finite-N (N being the number of particles) version of the mode-coupling theory. As a result, we can extend the AGW study both with respect to the system-size dependence of the VACF over the finite range of dynamical time accessible in these calculations but also with respect to the details of the long-time corrections. Moreover, we are able to directly contradict the implication of the EWJ and Speedy studies that the long-time contributions are somehow not needed. In fact, these corrections have been simply ignored in this recent work, without any justification.

The importance of precise estimates for the transport coefficients of hard spheres has increased in recent years with the advent of variational approaches to the transport coefficients, similar in some ways to the so-called "modified" Enskog theory. This theory attempts to provide transport coefficients for both atomic and molecular

fluids by establishing a correspondence between the system of interest and the hard-sphere system.[30–33] It is essential that one begin with precise hard-sphere results if one is to ascribe certain details of the difference between the experimental and the hard-sphere transport coefficients to features of the intermolecular interaction.

In the present paper we report values of D as a function of volume ranging from 25 down to 1.6 times the close-packed volume. This includes, then, essentially the entire fluid regime from dilute gas to near solidification. While the present calculations are based on our earlier results for the VACF, we also use the integral of the VACF as a function of time, the so-called time-dependent self-diffusion coefficient, which was not reported previously. In Sec. II, then, we extend the general discussion of our earlier work to include these additional features. In Sec. III, we present our results and discuss in some detail the methods used for our estimates. The results are compared with the AGW estimates as well as the polynomial fit given by Speedy.

II. SELF-DIFFUSION COEFFICIENT

For a system of N hard spheres of diameter σ in a volume V, the Green-Kubo formalism expresses the self-diffusion coefficient as

$$\begin{aligned} &D=\lim_{t\to\infty} D(t)\ , \\ &D(t)=\mathrm{tlim} D(t;N)\ , \\ &D(t;N)=\int_0^t ds\,\rho_D(s;N)\ , \\ &\rho_D(t;N)=\langle u_{1x}(0)u_{1x}(t)\rangle\ , \end{aligned} \tag{2}$$

where tlim denotes the thermodynamic limit of large system size. The angular brackets denote the average over a statistical mechanical ensemble of initial positions and velocities $\{\mathbf{r}_i(0),\mathbf{v}_i(0)\}$, which, for the present calculations, was chosen to be the microcanonical ensemble. Here $\rho_D(t;N)$ is the velocity-autocorrelation function and $\mathbf{u}_i$, the velocity of particle i in the center-of-mass frame of reference, is given by

$$\begin{aligned} &\mathbf{u}_i=\mathbf{v}_i-\mathbf{P}/Nm\ , \\ &\mathbf{P}=m\sum_i \mathbf{v}_i\ , \end{aligned} \tag{3}$$

with $\mathbf{P}$ the momentum of the center of mass. If the system is subject to periodic boundary conditions, as in this as well as previous studies, then $\mathbf{P}$ is a constant of the motion for a given trajectory.

For the evaluation of D it is valuable to rewrite $D(t;N)$ by taking the time integral through the ensemble average in the last two of Eqs. (2). We have, then,

$$D(t;N)=\langle u_{1x}(0)\Delta R_{1x}(t)\rangle\ , \tag{4}$$

in which $\Delta\mathbf{R}_i(t)$ is the displacement of particle i in the center-of-mass frame of reference,

$$\Delta\mathbf{R}_i(t)=\mathbf{r}_i(t)-\mathbf{r}_i(0)-\mathbf{P}t/Nm\ . \tag{5}$$

Closely related to $D(t;N)$ is the quantity

$$D_f(t;N)=\langle u_{1x}(t)\Delta R_{1x}(t)\rangle\ , \tag{6}$$

which can be shown to be equal to $D(t;N)$ by transforming the average in Eq. (6) from the phase $[\mathbf{r}_i,\mathbf{v}_i]$ at time 0 to that at time t, transforming to the sign-reversed velocities, and using the time-reversal invariance of the trajectory. In passing, we observe that the mean-square displacement $\langle\Delta R_1^2(t)\rangle$, which is the quantity presumably computed by EWJ, is related to our $D_f(t;N)$ [and therefore to $D(t;N)$] through the obvious relationship,

$$D_f(t;N)=\frac{1}{6}\frac{d}{dt}\langle\Delta R_1^2(t)\rangle\ . \tag{7}$$

Our calculations include the evaluation of $D(t;N)$ $D_f(t;N)$, $\langle\Delta R_1^2(t)\rangle$, and $\rho_D(t;N)$ as functions of time. While the first two, evaluated at long times, provide the principal contribution to D, our calculations must also take cognizance of the limits of large system size and long time appearing in Eq. (2). It is in taking account of these limits in our numerical calculations that knowledge of the long-time behavior of $\rho_D(t;N)$ is essential. In fact, we decompose D into short- and long-time contributions,

$$\begin{aligned} &D=D_1(t_c)+D_2(t_c)\ , \\ &D_i(t)=\mathrm{tlim} D_i(t;N)\ , \end{aligned} \tag{8}$$

with the long-time contribution

$$D_2(t;N)=\int_t^\infty ds\,\rho_D(s;N)\ . \tag{9}$$

The short-time contribution $D_1(t;N)$ is evaluated through either of two expressions,

$$\begin{aligned} &D_1^{(a)}(t;N)=\tfrac{1}{2}[D(t;N)+D_f(t;N)]\ , \\ &D_1^{(b)}(t;N)=\frac{1}{6}\frac{d}{dt}\langle\Delta R_1^2(t)\rangle\ . \end{aligned} \tag{10}$$

From the point of view of numerical calculation, it is preferable to avoid numerical differentiation, so that $D_1^{(a)}$ would be the better route to the short-time contribution. In all our calculations, we have evaluated the mean-square displacement from which we obtain $D_1^{(b)}(t;N)$, but in our earliest calculations we did not evaluate $D(t;N)$ and $D_f(t;N)$ so that $D_1^{(a)}(t;N)$ is not always available. It is important to observe that, even though $D(t;N)$ and $D_f(t;N)$ are equal, their numerical estimates will differ by virtue of the incompleteness of the ensemble averaging which can be done numerically. Finally, we observe that our inclusion of the long-time contribution $D_2(t_c)$ is the source of most of the difference between the present results on the one hand and those of EWJ and Speedy on the other.

The choice of the crossover time t_c is dictated largely by the results of our earlier study of the VACF.[25,26] It was found that, for times greater than the acoustic-wave transversal time,

$$t_a=L/c \tag{11}$$

(in which c is the sound speed and L is the period of the cubical system), the periodicity of the system leads to rather strong finite-system effects, with smaller but

significant effects being present at earlier times. The long-time effects can be accounted for by a finite-system version of the mode-coupling theory.[25] As a result, we concluded[26] that the mode-coupling theory was valid at long times and could, therefore, be used to provide the long-time correction, $D_2(t_c)$, of Eq. (9), viz.,

$$D_2(t_c)=\int_{t_c}^{\infty} ds\, \rho_D^{(\mathrm{MC})}(s) \ . \tag{12}$$

The mode-coupling result includes both the well-known dominant contribution from the shear modes, which becomes, in the thermodynamic limit,

$$\begin{aligned} \rho_D^{\perp}(t)&=\frac{\alpha_D}{t^{3/2}} \ , \\ \alpha_D&=\frac{2}{3n\beta m\,[4\pi(D+\nu)]^{3/2}} \ , \\ D_2^{\perp}(t_c)&=\frac{2\alpha_D}{t_c^{1/2}} \ , \end{aligned} \tag{13}$$

as well as the more rapidly damped acoustic-mode contribution,[25] which is given in the thermodynamic limit by

$$\begin{aligned} \rho_D^{\parallel}(t)&=\gamma_D(t)(1-2\beta_D t)\exp(-\beta_D t) \ , \\ \gamma_D(t)&=\frac{1}{3n\beta m\,[4\pi(D+\Gamma_s/2)t]^{3/2}} \ , \\ \beta_D&=\frac{c^2}{4(D+\Gamma_s/2)} \ , \\ D_2^{\parallel}(t_c)&=\gamma_D(t_c)\beta_D^{1/2}\left[\frac{2}{(\beta_D t_c)^{1/2}}\exp(-\beta_D t_c)\right. \\ &\qquad \left.-4\pi^{1/2}\mathrm{erfc}[(\beta_D t_c)^{1/2}]\right] \ , \end{aligned} \tag{14}$$

in which $\gamma_D(t)$ of Eq. (3.40) of our earlier paper[25] has been corrected. [The reader should also observe that Eq. (3.39) of that paper is also in error; a minus sign should precede $\beta_D(t)$ as the third argument of ${}_1F_1$.] Here D and ν are the self-diffusion coefficient and the kinematic viscosity of the fluid, and Γ_s is the acoustic attenuation coefficient,

$$\begin{aligned} \Gamma_s&=D_l+(\gamma-1)D_T \ , \\ D_l&=\frac{\zeta}{nm}+\frac{4\nu}{3} \ , \\ D_T&=\frac{\lambda}{nc_p} \ , \end{aligned} \tag{15}$$

with ζ the bulk viscosity, λ the thermal conductivity, $\gamma=c_p/c_v$, and c_p and c_v the heat capacities per particle at constant pressure and constant volume, respectively. (For the present calculations in the microcanonical or NVE ensemble, we identify $\beta=3N/2E$, where E is the total energy.) Thus, t_c must be chosen sufficiently large that $\rho_D(t_c;N)$ is in agreement with the finite-N version of the $\rho_D^{(\mathrm{MC})}=\rho_D^{\perp}+\rho_D^{\parallel}$ long-time tail at least for the largest N studied, typically $N=4000$.

Turning to the evaluation of D_1, we note that our definition of D, Eq. (2), uses the velocity-autocorrelation function in the center-of-mass frame of reference. This is to be distinguished from that in the laboratory frame,

$$c_D(t;N)=\langle v_{1x}(0)v_{1x}(t)\rangle \ . \tag{16}$$

The relation between the two VACF's is

$$\rho_D(t;N)=c_D(t;N)-\langle v_{1x}^2\rangle/N \ , \tag{17}$$

from which it follows that, while they become identical in the limit of an infinite system, for finite N they cannot both approach zero as $t\to\infty$. It seems reasonable to suppose that it is $\rho_D(\infty;N)$ which vanishes and our numerical results support this. It is for this reason that we have defined D in terms of ρ_D. However, in our earlier study of the hard-disk system,[25] we noted empirically that, except at high density, $c_D(t;N)$ was substantially independent of N for t less than a value $t^*\sim 6t_0$, where t_0 is the actual (density-dependent) mean free time. A similar behavior was found for hard spheres, although we did not previously so note.[26] Thus the infinite-system correction to $D(t^*;N)$ is just $t^*\langle v_{1x}^2\rangle/N$. While we use $t^*\sim 6t_0$ at moderate to low densities, at high densities this N independence of c_D breaks down and we use $t^*=0$.

In either case, we require a second component of D_1 between t^* and t_c, that is, $\Delta D_1=D(t_c;N)-D(t^*;N)$. For those values of the density for which calculations have been performed for a number of system sizes, we simply extrapolate this difference linearly in $1/N$ to the thermodynamic limit. In other cases (where only 4000-particle calculations were done), no such correction has been made, but the quoted uncertainty in the reported D has been inflated as seems appropriate based on the magnitude of the correction observed at other values of the density.

The uncertainty reported for D at a given density consists for the most part in the standard deviation of the mean for $D_1(t_c;N)$ for the largest N studied, plus that associated with the extrapolation of ΔD_1 to the thermodynamic limit. In addition to the adjustment to the uncertainty mentioned above, we have also inflated the uncertainty somewhat at high densities where there is additional uncertainty associated with the choice of transport coefficients to be used in the evaluation of the long-time contribution $D_2(t_c)$.[26]

III. RESULTS

Our calculations for self-diffusion consist of a Monte Carlo average over the microcanonical ensemble of the time-dependent quantities indicated above, the latter being evaluated through molecular-dynamics calculation of the dynamical trajectory. The calculations, which include extensive time averaging on each trajectory as well, were described previously[25,26] in some detail. The results for the self-diffusion coefficient reported here are from the same MCMD simulations in the earlier paper;[26] see Table I therein for the values of the parameters. (We take this occasion to note that the heading for the fourth column of that table should read $h/t_{00}^{(N)}$.) In our present Table I are shown the values of the volume relative to the close-packed volume, $V_0=\sqrt{2}N\sigma^3/2$, the number of par-

TABLE I. Parameters and other quantities for the MCMD calculations of the self-diffusion coefficient: V the volume, V_0 the close-packed volume, N the number of particles. The column labeled "D?" indicates whether $D(t;N)$, Eq. (4), and $D_f(t;N)$, Eq. (6), were computed directly for the given realization; t_a is the acoustic-wave traversal time, Eq. (11). $D_1(t;N)$ is defined in Eq. (10); $t^*=6t_0$ for $V/V_0\geq 4$, $t^*=5.1444t_0$ for $V/V_0=3$ (as shown also in Table II), and $t^*=0$ for $V/V_0\leq 2$. The values of t_c are given in Table III. The numbers in parentheses are the statistical uncertainties (one standard deviation) in the low-order digit.

V/V_0	N	D?	t_a/t_0	$D_1(t^*;N)/D_E$	$D_1(t_c;N)/D_E$
25	4000	yes	12.30		1.0114(11)
18	4000	yes	15.07		1.0181(9)
10	500	yes	10.66	1.0011(6)	1.0357(12)
10	4000	yes	21.32	1.0080(3)	1.0465(6)
5	108	yes	9.26	1.0116(11)	1.0692(22)
5	500	yes	15.44	1.0345(7)	1.1154(18)
5	4000	yes	30.88	1.0396(4)	1.1373(13)
4	108	yes	10.31	1.0186(8)	1.1000(17)
4	1372	yes	24.06	1.0476(8)	1.1777(24)
3	108	yes	11.71	0.9885(11)	1.1306(35)
3	500	yes	19.52	1.0137(10)	1.2037(42)
3	1372	no	27.33	1.0136(9)	1.2251(44)
3	4000	yes	39.04	1.0184(3)	1.2271(12)
2	108	no	13.71	0.0	1.0374(83)
2	500	no	22.85	0.0	1.1202(54)
2	1372	no	32.00	0.0	1.1639(78)
2	4000	yes	45.71	0.0	1.1563(19)
1.8	4000	yes	47.39	0.0	1.0367(16)
1.7	4000	yes	48.28	0.0	0.9327(15)
1.6	4000	yes	49.20	0.0	0.7887(20)

ticles N, and an indication as to whether the time-dependent self-diffusion coefficients were evaluated directly. In order to indicate the onset of substantial finite-system effects for each system, we also list the values of the acoustic-wave traversal time, Eq. (11), obtained from our [3/2] Padé approximation[34,35] to the hard-sphere equation of state.

In computing the long-time-tail corrections, Eq. (12), we have used (except at the four highest densities) the Enskog-theory transport coefficients,

$$
\begin{aligned}
D_E &= \frac{1.018\,96 D_{00}}{\chi}\ , \\
\nu_E &= \frac{\eta_E}{nm}\ , \\
\eta_E &= \frac{\eta_{00}}{\chi}\left[1.016\left[1+\frac{2bn\chi}{5}\right]^2+\frac{48(bn\chi)^2}{25\pi}\right]\ , \\
\eta_{00} &= \frac{5nmD_{00}}{6}\ , \\
\zeta_E &= \frac{16}{5\pi}\frac{\eta_{00}}{\chi}(bn\chi)^2\ , \\
\lambda_E &= \frac{\lambda_{00}}{\chi}\left[1.025\,13\left[1+\frac{3bn\chi}{5}\right]^2+\frac{32(bn\chi)^2}{25\pi}\right]\ , \\
\lambda_{00} &= \frac{25nk_BD_{00}}{8}\ , \\
bn &= \frac{2\pi\sqrt{2}}{3(V/V_0)}\ ,
\end{aligned}
\tag{18}
$$

in which D_{00}, η_{00}, and λ_{00} are the Boltzmann transport coefficients, b is the second virial coefficient, and χ is the pair-correlation function at contact, for which we have used the values from the [3/2] Padé approximant to the equation of state.[34,35] As discussed earlier,[26] the agreement between the molecular-dynamics results and the mode-coupling theory is significantly improved at high densities by using estimates for the actual transport coefficients in the theory. We have, therefore, used the AGW values[3] of D, η, λ, and ζ for the four highest densities.

We express our results for the self-diffusion coefficient relative to the Enskog-theory prediction, D_E, Eq. (18). It should be noted that the latter is the value obtained in the ninth Enskog approximation, as distinguished from the first approximation apparently used by EWJ,[27,28] Speedy,[29] and Alder *et al.*,[3] in reporting their results. We have, therefore, divided these earlier results by 1.018 96 in comparing with ours. Table I shows the values of $D_1(t^*;N)/D_E$ and $D_1(t_c;N)/D_E$ obtained from the simulations, with $t^*=6t_0$ for $V/V_0\geq 4$, $t^*=5.144t_0$ for $V/V_0=3$ (as shown also in Table II), and $t^*=0$ for $V/V_0\leq 2$. The values of t_c are given in Table III.

To illustrate our extrapolation procedure for obtaining our final infinite-system estimates of D, we consider in detail our calculations for the volumes $3V_0$ and $2V_0$. This will also help in providing some understanding of the differences between our results and those of EWJ and Speedy. The various contributions to the self-diffusion coefficient, as previously discussed, are shown in Table II. For $V=3V_0$ we list $D_1(t^*;N)$, obtained from the first of

TABLE II. Details of the calculation of the self-diffusion coefficient for hard-sphere systems at volumes of $3V_0$ and $2V_0$. The time t^*, which is the upper limit of the time for which the VACF in the laboratory frame of reference is independent of the number of particles N, is $5.1440t_0$ for $3V_0$ and zero for $2V_0$. The time t_c, which marks the split between the Monte Carlo molecular-dynamics contribution to the self-diffusion coefficient D and the long-time-tail contribution, is $31.925t_0$ for $3V_0$ and $51.000t_0$ for $2V_0$. The column marked "(3)+(4)" is the sum of the preceding two columns.

V/V_0	N	$D_1(t^*;N)/D_E$	$t^*\langle v_{1x}^2\rangle/ND_E$	(3)+(4)	$\Delta D_1/D_E$	$D_2(t_c)/D_E$
3	108	0.9885(11)	0.0313	1.0198(11)	0.1421(35)	
	500	1.0137(10)	0.0067	1.0204(10)	0.1901(42)	
	1372	1.0136(9)	0.0025	1.0161(9)	0.2115(44)	
	4000	1.0184(3)	0.0008	1.0192(3)	0.2087(12)	
	∞				0.2106(12)	0.0908
2	108				1.0374(83)	
	500				1.1202(54)	
	1372				1.1639(78)	
	4000				1.1563(19)	
	∞				1.1594(19)	0.0898

Eqs. (10) for $N=108$, 500, and 4000 and from the second of Eqs. (10) for 1372 particles, at the time $t^*=5.1440t_0$. Up to this value of the time, the VACF in the laboratory frame of reference appears to be virtually independent of the system size, N. The early-time correction $t^*\langle v_{1x}^2\rangle/N$ for each system is also listed and combined with $D_1(t^*;N)$ in the column labeled "(3)+(4)." The values are seen to be in good agreement, except for the 1372-particle system. The weighted average of the four "(3)+(4)" entries from the table is taken to be

$$\frac{D_1(t^*;\infty)}{D_E}=1.0190\pm0.0003\ . \tag{19}$$

For $V=3V_0$, our results for $\rho_D(t)$ were found[26] to agree rather well with the mode-coupling theory for times greater than about $25t_0$. We have chosen, then, a crossover time $t_c=31.925t_0$ for this density, that being the longest time for which the time-correlation functions were computed for the 1372-particle calculation. The contribution to D_1 for the time interval t^* to t_c was estimated by extrapolating the difference ΔD_1, also listed in Table II, linearly in $1/N$ to the thermodynamic limit. We obtain

$$\frac{\Delta D_1}{D_E}=0.2106\pm0.0012\ , \tag{20}$$

also shown in the table. Finally we compute the long-time-tail contributions from Eqs. (13) and (14), using the Enskog transport coefficients, Eq. (18), to obtain

$$\begin{aligned} &D_2(t_c)=D_2^{\perp}(t_c)+D_2^{\parallel}(t_c)\ ,\\ &\frac{D_2^{\perp}(t_c)}{D_E}=0.0908\ ,\\ &\frac{D_2^{\parallel}(t_c)}{D_E}=-1.3\times10^{-5}\ . \end{aligned} \tag{21}$$

We note that the acoustic-mode contribution is at most 6×10^{-5} for all the cases we have studied. It is small compared to the contribution of the shear mode and to our final estimates of uncertainty, and could have omitted except for an occasional effect on rounding. The final estimate for the $V=3V_0$ self-diffusion coefficient is therefore obtained by summing Eqs. (19)–(21) to obtain

$$\frac{D}{D_E}=1.320\pm0.003\ , \tag{22}$$

in which we have increased the uncertainty slightly in view of the uncertainty in the $N=1372$ contribution to Eq. (19).

For $V=2V_0$ and higher densities, the N independence of $c_D(t;N)$ at early times breaks down. Therefore we choose $t^*=0$ and list in Table II only the values of $D_1(t_c;N)$. Table II shows the extrapolation to the infinite system as well as the long-time-tail contributions. The latter are based on the AGW estimates for the transport coefficients for this and higher densities. The final estimate for D/D_E is then 1.249 ± 0.002. However, we inflate the uncertainty by 0.005, because of the sensitivity of the tail correction to the uncertainties in the AGW

TABLE III. Monte Carlo molecular-dynamics results for the self-diffusion coefficient of the hard-sphere fluid, relative to the Enskog value, in the ninth Enskog approximation, from the present study and from Alder, Gass, and Wainwright (Ref. 3). The time t_c marks the time at which the long-time-tail corrections, Eqs. (9) and (10), are used, and is scaled by the actual mean free time t_0.

V/V_0	t_c/t_0	D/D_E	D_{AGW}/D_E
25	19.955	1.014(2)	
18	22.223	1.021(2)	
10	20.000	1.057(2)	
5	30.000	1.177(3)	1.14
4	30.000	1.242(5)	
3	31.925	1.320(3)	1.32
2	51.000	1.249(7)	1.25
1.8	50.809	1.129(11)	1.13
1.7	50.609	1.010(13)	
1.6	65.505	0.843(10)	0.82

transport coefficients which determine α_D, Eq. (13).

In Table III are listed the estimated values for D. The values adopted for t_c are also listed and can be correlated with the actual comparisons of the VACF and theory.[26] It is important to recognize that the estimates for D for $V/V_0=25$, 18, 1.8, 1.7, and 1.6 contain no finite-system corrections for the interval t^* to t_c because calculations were done only for the single system size, $N=4000$. For this reason, we have somewhat inflated the error estimates. Some feeling for the likely magnitude of this error can be obtained by noting that the difference in Table II between the $\Delta D_1/D_E$ values for $N=\infty$ and $N=4000$ is only about 0.002–0.003. Also listed in Table III are the Alder-Gass-Wainwright estimates,[3] scaled by the same Enskog-theory value as ours. The difference is seen to be statistically significant for $V=5V_0$, but is otherwise small. We should also mention that at $V=5V_0$ the $N=108$ results are somewhat discordant with those for the larger systems as regards both the value of $D_1(t^*;N)+t^*\langle v_{1x}^2\rangle/N$ and a linear dependence of ΔD_1 on $1/N$, and we accordingly omitted those results from our reduction procedure.

IV. DISCUSSION

Our results are plotted against the relative density in Fig. 1. They are well represented [$\chi^2(7)=3.27$; $P(\chi^2>3.27)=0.86$] by the third-degree polynomial fit

$$\frac{D}{D_E}=1+0.054\,034\,49\frac{V_0}{V}+6.365\,616\left[\frac{V_0}{V}\right]^2-10.942\,539\left[\frac{V_0}{V}\right]^3, \tag{23}$$

which is plotted as the dashed curve in the figure. The Speedy expression, Eq. (1), for the density dependence of the self-diffusion coefficient, after conversion to D/D_E, is also shown in Fig. 1. It is clear that it does not include the full enhancement arising near $V=3V_0$. The differences between our results and those of EWJ (and therefore Speedy) can be traced rather clearly to the details of the method employed by EWJ. In particular, EWJ calculate D by differentiating the mean-square displacement with respect to the time for values of t up to the time that the VACF "goes to zero."[27] It is seen from Eq. (7) that this derivative is just our $D_f(t;N)$, Eq. (6), so that both their calculations and ours consider essentially the same quantity. However, since the VACF is not known exactly, presumably the longest times considered by EWJ were those for which the VACF drops to the level of its statistical uncertainty. This cutoff time depends strongly on the precision with which one calculates the VACF and effectively ignores the tail of the VACF beyond the cutoff time.

It appears that EWJ hoped to force the inclusion of an increasing contribution from a long-time tail, if one were present, by extending their calculations to larger system sizes. In actual fact, if the statistical precision of their VACF calculations were essentially independent of N, the cutoff time would then approach (for large N) the time at which $\rho_D(t;\infty)$ decayed to the level of the statistical uncertainty, a value which is relatively insensitive to the length of the molecular-dynamics calculation by virtue of the square-root dependence of the standard deviation of the mean on the trajectory length. It is clear, then, that their values of D for $2V_0$ which include system sizes of from 128 to 4732 particles[28] behave as expected in approaching an asymptotic value, even though the long-time-tail contribution has been severely truncated.

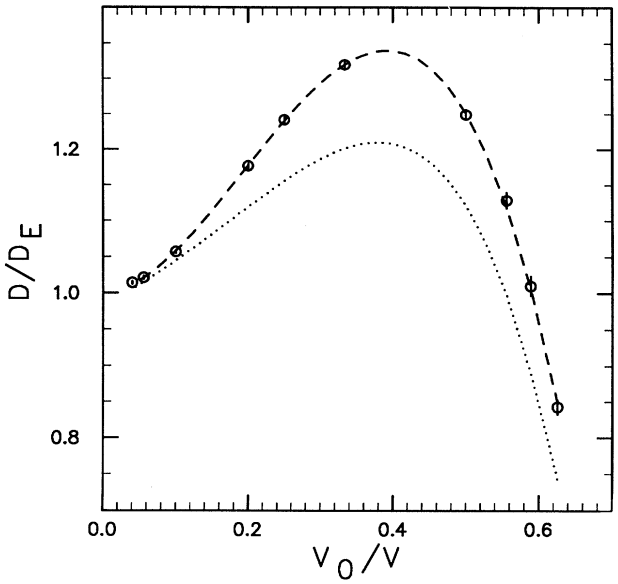

FIG. 1. The hard-sphere self-diffusion coefficient relative to the Enskog prediction, as a function of the density; the volume V is reduced by the close-packed volume V_0. The circles are from the present study, while the dotted line is the empirical expression of Speedy, Eq. (1) (Ref. 29). The dashed line is the third-degree polynomial fit to the present results, Eq. (23). The vertical lines through the points extend one standard deviation above and below the mean.

While the actual values of the time cutoff used by EWJ were not reported, one can see quite reasonable agreement between the EWJ results and our partial results at $V=3V_0$. In Table I we have, for $N=108$, $D_1(t_c;108)/D_E=1.13$ compared to their 1.13 (for $N=128$); for $N=500$, we have 1.20 compared to their value 1.19 for 432 particles. For $V=2V_0$, EWJ obtain a value for D/D_E of 1.10±0.01 for $N\geq 2000$. This is significantly smaller than the value of $D_1(t_c;4000)/D_E=1.1563\pm0.0019$ given in Table I. It would appear that the EWJ cutoff was smaller than our $t_c=51t_0$.

The importance of the long-time-tail contribution to D can be seen by comparing the EWJ result of 1.10 at $V=2V_0$ with our infinite-system extrapolation, 1.251. Beyond the acoustic traversal time of $45.71t_0$ (see Table I) for the 4000-particle system at this density, finite-system effects are expected to become important, and such effects tend to damp the VACF to zero more rapidly than its decrease in an infinite system. The contribution of the infinite-system long-time tail to D/D_E for $t>t_a$ is

about 0.0949 at this density. This alone accounts for about 63% of the difference between our values. The contribution of the finite-system, long-time tail $D_2(t;N)/D_E$ [obtained from Eq. (9) and the finite-N mode-coupling result[25]] is found to be only 0.0363. Thus we see that systems as large as 4000 particles, which naively may seem large, are in fact small as regards the contribution of the long-time tail. We also note that our $V/V_0=2$, $N=4000$ calculation actually extends to $t=196.53t_0$, at which point our *uncorrected* value of D/D_E is 1.184, which considerably exceeds the EWJ value of 1.10. We also note the consistency of the finite-N tail and our MCMD results in that the values of $D(\infty;N)=D_1(t;N)+D_2(t;N)$, whether determined with $t=t_c$ [yielding $(1.1879\pm0.0019)D_E$] or with $t=196.53t_0$ [yielding $(1.186\pm0.004)D_E$], are in good statistical agreement.

One final fact pointing to the necessity for including the long-time-tail contribution is provided by the nonequilibrium molecular-dynamics (NEMD) calculation of Holian and the present authors[24,36,37] for which we reported $D/D_E=1.268\pm0.017$ (based on the ninth Enskog approximation for D_E) for a system of 4000 particles at $V=3V_0$, significantly greater than the value of 1.22 given by Speedy for an infinite system. This computer simulation of an actual self-diffusion process is independent of the Green-Kubo formalism and was undertaken as the result of a question by E. G. D. Cohen as to whether one could in such a way confirm that the long-time tails of the VACF do indeed contribute to the self-diffusion coefficient. Furthermore, in our $N=4000$, $V=3V_0$ calculation at the maximum time $t=123.46t_0$ at which we calculated the time-correlation functions, the value of $D(t;4000)/D_E$ is 1.267 ± 0.029, in excellent agreement with the above NEMD value. Addition of the finite-N tail $D_2(123.46t_0;N)=0.0045D_E$ does not materially affect this agreement.

We close with the following observations.

1. The EWJ calculations of the self-diffusion coefficient are based on evaluating the proportionality constant between the mean-square displacement and the time. Their discussion includes no reference to the length of the dynamical time used in obtaining their results nor any attempt to demonstrate the absence of a long-time tail. Instead, they have concentrated on the N dependence of their results out to some unspecified time, in the apparent belief that all corrections are thereby included.

2. The force of the argument requiring the inclusion of the long-time tail in the self-diffusion coefficient, which is explicitly dismissed by Speedy,[29] seems overwhelming in view of the agreement of the numerical results with mode-coupling theory previously demonstrated both in two[25] and three[26] dimensions as well as the above-discussed agreement of the NEMD and Green-Kubo results. However, some qualifications are necessary. First as we previously emphasized,[25,26] while our VACF results are certainly broadly consistent with the theoretical long-time tails, the statistical power of the comparison tests is quite low with respect, say, to a significant change in the value of α_D at a given density, or even to a hypothetical change in the exponent $-d/2$ of the time decay. Some measure of comfort that we have not gone badly wrong in this regard is provided by the above-mentioned agreement of the NEMD and Green-Kubo results at $V/V_0=3$. Second, there is little theoretical justification for our use of the actual (AGW) transport coefficients in calculating α_D at high density. The kinetic theory[6] sums a certain class of collision events to obtain the expression for α_D containing the Enskog transport coefficients. As we previously noted,[25,26] it may be that in using the actual coefficients at high density, we are simply making a crude allowance for collision events which have not been considered in the theory. See de Schepper and Ernst[38] for a discussion of this question in the two-dimensional case.

3. While the present results are somewhat more accurate than the AGW estimates, it is noteworthy that they agree so well.

4. The uncertainties in the present estimates for D at densities for which data are available for $N=4000$ only could be reduced somewhat if the N dependence of the contribution to the Green-Kubo integral to time t_c were checked through calculations for, say, 500 particles. Unfortunately, we do not foresee being able to do such calculations in the immediate future and choose instead to publish the existing data. There would, however, still remain appreciable uncertainty in the values of α_D at high density, due to the uncertainty as to the appropriate values of the transport coefficients used in its calculation.

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