Molecular-dynamics calculations of the velocity autocorrelation function: Hard-sphere results

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The velocity autocorrelation function for the hard-sphere fluid is computed for ten values of the volume ranging from 25 to 1.6 times the close-packed volume V_0 for systems of from 108 to 4000 hard spheres, using a Monte Carlo, molecular-dynamics technique. The results are compared with the theoretical predictions of the mode-coupling theory, modified to take into account the finite size of the system and the periodic boundary conditions. The data are found to be in good agreement with the theory, evaluated using Enskog values for the transport coefficients, for values of the time greater than roughly 15 to 30 mean free times (depending on density), for volumes as small as $2V_0$. The higher-density results do not agree with the theory, unless the actual transport coefficients (evaluated using molecular dynamics) are used in the theory. The latter version of the theory, however, fails to fit the data at lower densities, except at very long times. To answer the recent critique by Fox, the data are further compared with the theory over time intervals for which the molecular-dynamics trajectories retain some measure of accuracy. The agreement between the data and the theory is largely unaffected, except at a volume $1.8V_0$ for which there is a marginally significant difference at very long times only.

I. INTRODUCTION

The slow decay of the time correlation functions which appear in the Green-Kubo theory of transport was first reported 15 years ago in a landmark study of the velocity autocorrelation function of hard spheres and disks at fluid densities.[1] In the interim, a wealth of theoretical[2] and numerical[3] evidence has accumulated tending to support the existence of the so-called long-time tails, viz., that the time correlation function $\rho_\mu(t)$ for transport coefficient μ decays at long times as

$$\rho_\mu(t)\approx\alpha_\mu(t/t_0)^{-d/2}\,, \tag{1}$$

where t_0 is the mean free time, for systems of dimension $d=2$ or 3 and for μ including self-diffusion D, shear viscosity η, and thermal conductivity λ. Indeed, many regard the evidence for the validity of Eq. (1), particularly for the case of the self-diffusion coefficient (for which ρ_D is the velocity autocorrelation function), as overwhelming.

On the other hand, under critical examination, the evidence is seen to be less than complete. Fox[4] has recently summarized some of the weaknesses of the case for Eq. (1). Inasmuch as the theoretical arguments, whether from kinetic theory or from mode-coupling theory, have never claimed rigor, the ultimate case for long-time tails (and hence for the assumptions underlying the theory) rests on the numerical results and the concurrence of these results with the predictions of the theory. Fox has stressed the inability of the molecular-dynamics method to generate an accurate N-particle trajectory beyond of the order of ten mean free times. Since the long-time behavior in question is certainly not manifested before a time of perhaps $15t_0$, there is clearly reason to be concerned.

In addition, the numerical evidence, even if accepted as accurate within its apparent statistical uncertainty, is not at all compelling except for the case of self-diffusion in two dimensions.[3(f)] The calculations for other transport coefficients contain relatively larger statistical uncertainties by virtue of the fact that only the velocity autocorrelation function $\rho_D(t)$ (abbreviated VACF hereafter) is a single-particle function and hence can be "observed" simultaneously for each of the N particles in the system (although all N such observations may not necessarily be independent).

For the case of two dimensions, the present authors[3(f)] have made extensive comparisons between molecular-dynamics results and a finite-system version of the mode-coupling theory.[2(b)] These comparisons showed satisfactory agreement over a broad range of density. The effect of trajectory accuracy was also investigated by using two separate calculations of the VACF, one based on "single-precision" arithmetic for the trajectory calculation (14 floating-decimal digits) and one based on "double-precision." At the level of statistical precision achieved, no significant difference was found between the two sets of results over the time interval $10t_0$ to $20t_0$ for which the double-precision trajectory remains accurate while the single-precision calculation has lost its accuracy. While this result is in the right direction to answer Fox's criticism, it nonetheless does not extend long enough in time and is for a lower density than those cases for which evidence for the long-time tail is strongest.

For the case of three dimensions, the numerical evidence is not particularly strong, even for hard spheres. The comparison made by Alder and Wainwright[1] between the observed coefficient α_D and the mode-coupling theory appeared on reexamination[3(a)] to show evidence for disagreement. The calculation by Levesque and

Ashurst[3(c)] of $\rho_D(t)$ for a truncated Lennard-Jones potential supported the functional form Eq. (1), but no comparison was possible between the observed coefficient and the theory because the transport coefficients D and η which determine α_D theoretically are not known for that interaction potential.

It is our purpose here to present some extensive numerical results for the VACF of systems of hard spheres at a series of fluid densities and to compare our results with the theory by using the finite-N version of mode-coupling theory which was detailed in I [Ref. 3(f)]. In Sec. II we summarize the numerical methods and the scaling of the results. In order to answer Fox's criticism, we investigate in Sec. III the accuracy of the trajectory calculation, finding that the present results for the VACF are accurate for times as large as 100 mean free times, depending on density. In Sec. IV we present our VACF results at a series of densities and describe the comparison with theory. In addition to making these comparisons using our VACF data from some initial time to the final time for which we have data (viz., to final times of 60 to 240 mean free times, depending on density), we also make comparisons over more limited time intervals, viz., for values of the time which are sufficiently long that the long-time tail has become dominant and yet sufficiently short that our trajectory calculation remains accurate.

II. METHOD

The method used to obtain estimates for the VACF has been described in considerable detail previously.[5] To summarize, we consider a system of N hard spheres of mass m and diameter σ which, at time t, have positions $r^N(t)=(r_1(t),r_2(t),\ldots,r_N(t))$ and velocities $v^N(t)=(v_1(t),v_2(t),\ldots,v_N(t))$, subject to periodic boundary conditions (PBC's). It will be convenient here to describe our system in terms of the "infinite-checkerboard" version of PBC's, whereby the $r_i(t)$ designate the positions of the N particles, irrespective of crossings of cell "boundaries;" with this stipulation, the $r_i(t)$ are the integrals of the $v_i(t)$.

To obtain estimates for the VACF, define

$$\begin{aligned} &\rho_D(t)=\langle u_{1x}(0)u_{1x}(t)\rangle \ , \\ &u_i(t)=v_i(t)-P(t)/Nm \ , \\ &P(t)=m\sum v_i(t) \ , \end{aligned} \tag{2}$$

in which u_i is the velocity in the center-of-mass reference frame and the angular brackets denote an average over an equilibrium statistical mechanical ensemble of initial states $x^N(0)$, where $x^N(t)=[r^N(t),v^N(t)]$ is the phase. By virtue of the PBC's, the linear momentum $P(t)$ is conserved; $P(t)=P$ for all t. Our calculations consist of the application of the Monte Carlo method to obtain a sequence of Q initial states $x_p^N(t)$ $(p=1,2,\ldots,Q)$ sampled from the microcanonical ensemble. For each such phase, we then generate a molecular-dynamics (MD) trajectory $x_p^N(t)$ of fixed time length, from which we obtain an estimate $\rho_{Dp}(t)$ as an average over "time origins" $t=0,\omega h,2\omega h,\ldots,\Omega h$ in which h is the fundamental observation time along the trajectory (see I for details). The overall mean values of the VACF as well as estimates of its statistical precision are obtained from the Q values $\{\rho_{Dp}(t);\ p=1,2,\ldots,Q\}$. We refer to this combined calculation as the Monte Carlo, molecular-dynamics (MCMD) method.

In analyzing our hard-disk data, we found in I that, in some instances, it was statistically favorable to obtain $\rho_D(t)$ from the mean-square displacement,

$$\begin{aligned} &S(t)=\sum_i \langle \Delta r_i(t)^2\rangle/(2dNt) \ , \\ &\Delta r_i(t)=r_i(t)-r_i(0)-Pt/Nm \ , \end{aligned} \tag{3}$$

using the relation

$$\rho_D(t)=d^2tS(t)/dt^2 \ . \tag{4}$$

In particular, at long times, we estimate $\rho_D(t)$ through the second difference of $tS(t)$, denoted by ${}_k[tS(t)]''$ in which kh denotes the central differencing interval; provided k is chosen equal to the time-origin spacing ω, the differenced quantity typically (for small enough ωh) has a smaller standard deviation than the directly computed VACF. At times less than roughly $20t_0$, the systematic error in approximating the second derivative, Eq. (4), by second differences dictated against the use of $[tS(t)]''$. In the present calculations the spacing of time origins is such that the systematic errors appear to affect the results in a number of cases. In many instances, then, we report the directly computed $\rho_D(t)$.

As in I, we define reduced quantities relative to the predictions of the Enskog theory,

$$\begin{aligned} &\bar{D}=D/D_E=\lim_{s\to\infty}\bar{D}(s) \ , \\ &\bar{D}(s)=\int_0^s \bar{\rho}_D(s')ds' \ , \end{aligned} \tag{5}$$

with, then, the reduced VACF and the reduced time defined by

$$\begin{aligned} &\bar{\rho}_D(s)=t_0\rho_D(st_0)/D_E \ , \\ &s=t/t_0 \end{aligned} \tag{6}$$

in which the Enskog value is

$$\begin{aligned} &D_E=1.018\,96D_{00}/\chi \ , \\ &D_{00}=3t_{00}/2\beta m \ , \\ &t_{00}=\frac{V(m\beta)^{1/2}}{N(2\sigma)^2\pi^{1/2}} \ , \end{aligned} \tag{7}$$

with χ denoting the pair correlation function at contact.

III. ACCURACY

The assessment of the accuracy of the MCMD results for the VACF is discussed in this section, not from the point of view of the statistical uncertainties inherent in simulation methods, but rather with respect to the numerical errors which arise in the generation of the MD trajectory.

To make the discussion quantitative, we follow Ref. 5 in defining the phase $x_p^N(t;m)$ to be the numerical representation of the true trajectory $x_p^N(t)$, based on the use of

m-digit arithmetic in the trajectory calculation. Further, we define the reduced root-mean-square errors $\Delta_r(t,m)$ and $\Delta_v(t,m)$ in position and velocity, respectively, as

$$\Delta_r^2(t,m)=\frac{1}{N\sigma^2}\sum_i \langle [r_i(t;m)-r_i(t)]^2\rangle \ ,$$
$$\Delta_v^2(t,m)=\frac{\beta m}{3N}\sum_i \langle [v_i(t;m)-v_i(t)]^2\rangle \ . \tag{8}$$

While it is clear that the accuracy of $x_p^N(t;m)$ depends on the number of particles N as well as on the arithmetic hardware in a particular computer and the computer code used to generate numerically the trajectory, we expect the errors to depend largely on "register length" m; only the latter dependence is notated.

To estimate Δ_r and Δ_v, we generate a series of trajectories from the same initial configurations in both "single" and "double" precision, i.e., using $m=14$ digit accuracy and 28-digit accuracy, computing Δ_r and Δ_v as in Eq. (8), except that the $x_p^N(t;2m)$ replace the exact $x_p^N(t)$. For times t such that the double-precision trajectory retains some degree of accuracy, the MCMD quantities

$$\tilde{\Delta}_r^2(t;m)=\frac{1}{NQ\sigma^2}\sum_p\sum_i [r_{ip}(t;m)-r_{ip}(t;2m)]^2 \ ,$$
$$\tilde{\Delta}_v^2(t;m)=\frac{\beta m}{3NQ}\sum_p\sum_i [v_{ip}(t;m)-v_{ip}(t;2m)]^2 \tag{9}$$

will be estimates of Δ_r^2 and Δ_v^2.

In Fig. 1 are shown semilog plots of Δ_r and Δ_v as functions of the time for four different values of the reduced volume τ,

$$\tau=V/V_0 \ ,$$
$$V_0=N\sigma^3/2^{1/2} \ , \tag{10}$$

where V_0 is the close-packed volume, viz., $\tau=10$, 3, 2, and 1.7. While each of the calculations is for a system of 108 particles, the results are nearly independent of system size over the range of N reported in this work. We note that for each density the error $\tilde{\Delta}_v$ appears to reach a plateau which is independent of density and very close in value to that expected if $v_{ip}(t;m)$ and $v_{ip}(t;2m)$ were independent Maxwellian velocities. On the other hand, $\tilde{\Delta}_r$ appears to grow slowly at long times, consistent with the expectation that the single- and double-precision values of $r_i(t)$ "diffuse" away from each other in the infinite checkerboard. The slopes of these curves at late times are, in fact, of the order of magnitude one would predict from the diffusion constant in the Enskog-theory approximation.

It is interesting to note that the growth in error seen in Fig. 1 is accelerated at late times at least in the case of the two higher densities. The time at which this effect takes place is found to agree with the time at which the single-precision trajectories typically omit collisions which occur for the double-precision trajectories. Evidently, the growth of error is controlled by a rather different mechanism beyond this point than the exponential divergence of trajectories which holds while the trajectory is more accurate.

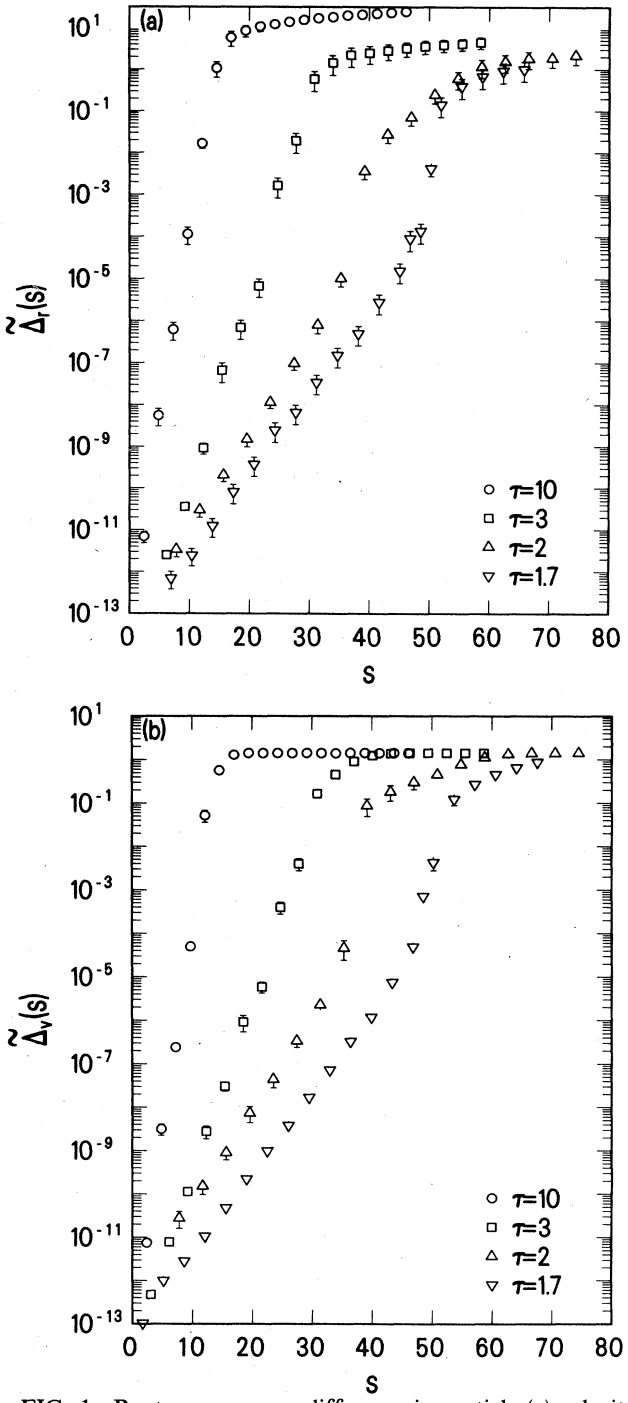

FIG. 1. Root-mean-square difference in particle (a) velocity $\tilde{\Delta}_r$ and (b) position $\tilde{\Delta}_v$, Eq. (9), between single- and double-precision trajectory calculations, as a function of reduced time s for four different values of the reduced volume τ.

We associate, then, the time of attainment of the plateau with the complete loss of accuracy on the part of the single-precision trajectory, viz., $t/t_0=13$, 33, 38, and 48 for $\tau=10$, 3, 2, and 1.7, respectively. Except for a very few calculations, our VACF calculations reported below were done in double precision. Thus the loss of accuracy

for such calculations can be expected to occur at double these times.

In assuming that these times represent the limits for the generation of accurate MD trajectories, it is important to recognize the additional assumption that time averaging, as introduced in Sec. II, introduces no bias in the statistical averaging. For the present purposes we regard the validity of MD time averaging as an empirical result, based on the well-known agreement[6] of Monte Carlo and molecular-dynamics calculations of the equation of state.[7] Attempts to justify MD time averaging[8] on the basis of the Anosov-Bowen theorem of ergodic theory cannot be completely justified for hard spheres and disks, as discussed by Fox.[4]

Finally, we remark that the MD results for the VACF might be accurate at times beyond those at which the trajectories lose their accuracy. In I we reported a comparison of the VACF from a single-precision and a double-precision calculation. Such a study could have shown a significant difference in the VACF between the two in the time interval for which only the double-precision trajectories were accurate. Instead, the comparison showed no statistically significant difference, with at most a 10% difference in the mean VACF's at the 95% confidence level.

IV. VACF AT LONG TIMES

The velocity autocorrelation function has been calculated using the MCMD method described in Sec. II for the systems tabulated in Table I. The various parameters discussed in Sec. II are included in the table, along with the observed values of the mean free time. In Figs. 2–10 the observed VACF is plotted as a function of time, in units of the mean free time, along with the predictions of the theories. The latter include (a) the infinite-system long-time tail, Eq. (1) (the dotted curves in the figures), with α_D given by

$$\alpha_D=(2/3n\beta m)[4\pi(D+\nu)t_0]^{-3/2}\ , \tag{11}$$

where n is the number density and ν is the kinematic viscosity, η/nm, and (b) the finite-system version of the mode-coupling theory, called the Ernst–Hauge–van Leeuwen (EHvL) finite-N theory (the curves labeled by the number of particles).

The evaluation of the theoretical curves, as detailed in I, requires values for the coefficients of self-diffusion and shear viscosity and also the thermal conductivity in the case of the EHvL finite-N curves. The question of what values should be used has been discussed repeatedly.[2(b),3(d),3(f)] In our present considerations we shall primarily use Enskog values for these transport coefficients, as was done in I. In addition, we shall use values for the finite-system transport coefficients, defined as the infinite time integral of the appropriate finite-system time correlation function. We refer to the latter procedure as "self-consistent," even though more elaborate self-consistent methods have been proposed.[9]

Expressions for the Enskog transport coefficients are given explicitly in I for both two and three dimensions. For hard spheres they depend on the pair correlation function at contact [i.e., $g(r_{12})$ for $r_{12}=\sigma$], which can be obtained from the equation of state. For the latter, we use

TABLE I. Parameters of the Monte Carlo, molecular-dynamics calculations of the velocity autocorrelation function of hard spheres. Q is the number of trajectories; the notation "/n" indicates that observations for n trajectories were coarse-grain averaged. h is the time-step length. ω is the time-origin spacing in units of h. M is the maximum number of time steps for which the VACF was evaluated. θ is the total number of time steps in each trajectory. N_c is the total number of collisions (in millions) for all trajectories. p denotes the arithmetic precision of the trajectory calculation, 1 for single precision, 2 for double precision. The quoted uncertainty in the mean free time is one standard deviation.

V/V_0	N	Q	h/t_{00}	ω	M	θ	N_c	p	t_0/t_{00}
25	4000	50	0.5	4	120	320	17	2	0.927 32±0.000 22
18	4000	73	0.5	4	120	320	26	2	0.900 21±0.000 21
10	500	150/3	0.5	4	120	480	11	2	0.823 52±0.000 24
10	4000	100	0.5	4	120	320	39	2	0.824 18±0.000 13
5	108	100/2	0.1	20	600	14 400	6	1	0.670 11±0.000 37
5	500	100	0.1	10	620	5000	12	2	0.667 66±0.000 18
5	4000	50	0.5	4	120	320	24	2	0.666 84±0.000 13
4	108	100	0.2	10	300	7200	13	2	0.597 52±0.000 24
4	1372	50	0.2	10	300	7200	12	1	0.595 36±0.000 14
3	108	200	0.2	10	120	1000	5	2	0.487 56±0.000 26
3	500	50	0.2	10	120	1000	5	2	0.486 63±0.000 19
3	1372	30	1.0	2	16	100	4	2	0.485 83±0.000 21
3	4000	99	0.5	4	120	320	66	1	0.486 11±0.000 06
2	108	72	0.1	10	200	1000	1	2	0.306 57±0.000 26
2	500	32	0.1	10	200	1000	3	2	0.305 14±0.000 09
2	1372	15	1.0	2	20	100	3	2	0.305 62±0.000 20
2	4000	50	0.5	4	120	320	52	2	0.305 38±0.000 05
1.8	4000	50	0.5	4	120	320	63	2	0.255 92±0.000 04
1.7	4000	88	0.2	4	100	320	49	2	0.229 27±0.000 04
1.6	4000	100	0.2	4	100	320	64	2	0.201 40±0.000 04

the Padé 3×3 approximant to the virial series of Ree and Hoover;[10] at the level of accuracy of the present VACF calculations, the difference in the theoretical VACF based on a more exact equation of state[11] would not be consequential.

The quantitative comparison between the EHvL finite-N theory and the molecular-dynamics results is summarized in Table II, which gives the results of application of the Hotelling T^2 test[12] of multivariate statistical analysis for the various systems. While the application of the test is detailed in I, for the present purposes it is sufficient to note that $P(T^2)$ is the cumulative distribution function for the T^2 statistic, evaluated at the value of T^2 observed in a particular comparison. For a particular density and system size, the value of T^2 depends on the magnitude of the deviations between theory and "experiment" and on the observed correlations between the values of the VACF at successive values of the time. Values of $P(T^2)$ greater than, say, 0.95 would indicate, under the hypothesis that the theoretical VACF is correct, an unexpectedly large disagreement between numerical results and the theory, while values near zero would indicate an unexpectedly close agreement. The parameter $\Delta g_{0.95}$ is an approximate measure of the sensitivity (power function) of the T^2 test

TABLE II. Hotelling T^2 test results for the comparison of MCMD results with the finite-N EHvL theory. Column labeled f specifies the manner of evaluation of the VACF: d denotes direct evaluation, as in Eq. (2), and s denotes evaluation from $S(t)$, via Eq. (4).

V/V_0	N	k	s_i	s_f	$P(T^2)$	$\Delta g_{0.95}$	f
10	500	21	21.9	70.4	0.85	299.5	s
10	4000	23	17.0	70.4	0.98	1.5	s
		22	19.4	70.4	0.33	1.8	s
5	108	23	20.9	86.6	0.53		s
		22	23.9	86.6	0.37	188.4	s
5	500	31	22.5	89.9	0.99		d
		30	24.7	89.9	0.78	2.9	d
		13	22.5	49.4	0.94		d
		12	24.7	49.4	0.37	2.7	d
5	4000	22	24.0	87.0	0.94		s
		21	27.0	87.0	0.80	0.6	s
		10	24.0	50.9	0.96		s
		9	27.0	50.9	0.72	0.5	s
4	108	24	20.1	97.1	0.98		s
		23	23.4	97.1	0.46	12.2	s
4	1372	23	23.5	97.4	0.97		s
		22	26.9	97.4	0.46	0.5	s
		3	23.5	30.2	1.00		s
		2	26.9	30.2	0.93	0.5	s
3	108	9	16.4	49.2	0.95		d
		8	20.5	49.2	0.06	3.2	d
3	500	9	16.4	49.3	1.00		d
		8	20.5	49.3	0.84	0.4	d
3	1372	5	16.5	32.9	1.00		d
		4	20.6	32.9	0.85	0.6	d
3	4000	24	28.8	123.4	0.93		d
		23	32.9	123.4	0.71	0.2	d
		9	28.8	61.7	0.98		d
		8	32.9	61.7	0.88	0.2	d
2	108	18	9.8	65.2	0.92		d
		17	13.0	65.2	0.63	0.5	d
2	500	18	9.8	65.5	0.97		d
		17	13.1	65.5	0.39	0.2	d
2	1372	10	9.8	65.4	0.96		d
		9	13.1	65.4	0.15	0.3	d
2	4000	29	13.1	196.5	0.93		d
		28	16.4	193.2	0.58	0.1	d
		11	13.1	78.6	1.00		d
		10	16.4	75.3	0.72	0.1	d
1.8	4000	33	171.9	234.4	0.96		d
		39	27.4	101.6	0.94		d
		37	31.3	101.6	0.85	0.2	d
1.7	4000	6	65.4	87.2	0.97		d
1.6	4000	5	79.4	99.3	1.0		d

to an actual disagreement. Large values of $\Delta g_{0.95}$ indicate that the true VACF could be far from the EHvL finite-N theory, in the sense of a multiplicative factor $1\pm\Delta g_{0.95}$ applied to the theoretical $\rho_D(t)$. If the true VACF were given by $(1\pm\Delta g_{0.95})\rho_D(t)$, then the T^2 test would reject the hypothesized $\rho_D(t)$ with high probability. The calculation of $\Delta g_{0.95}$ is, however, approximate and only acts as a guide to the significance of the T^2 test.

Our procedure in making the test is to select a time interval $[t_i,t_f]$, or in reduced units $[s_i,s_f]$, over which to make the comparison, with a spacing of time values Δt such that the number k of values of the time in the interval is less than the number of trajectories Q; the T^2 statistic is singular at $k=Q-1$. Typically, t_f was chosen to be the final time for which the VACF was calculated, although we present results for more limited comparisons as well. T^2 was then calculated for a number of values of t_i (and thus k), so as to find values for which the test yields a large $P(T^2)$ (say roughly 0.95 or greater) for one value of t_i and a more nominal value of $P(T^2)$ for the next larger value of t_i. In Table II, then, we have entered the test results for this pair of t_i values. It should be noted that this procedure will probably tend to give values of $P(T^2)>0.5$ for the "next larger value of t_i."

In the following we discuss the data for each density in turn, beginning with the lowest-density system.

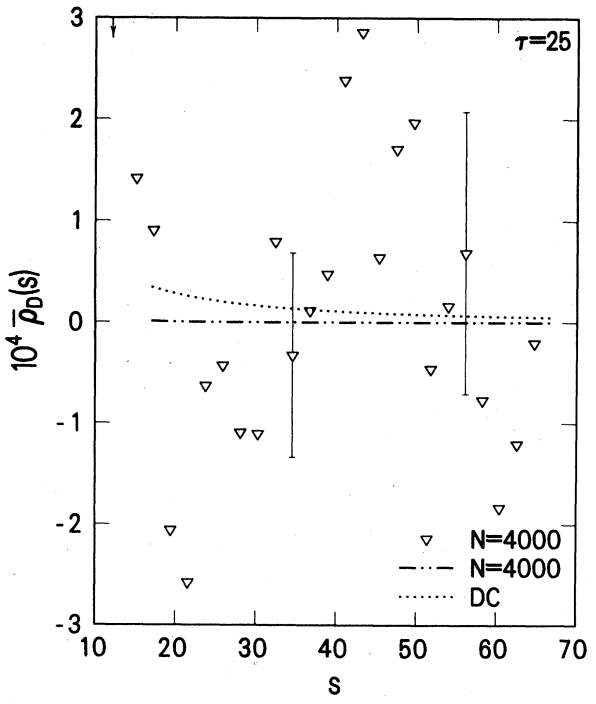

FIG. 2. Reduced velocity autocorrelation function for 4000 hard spheres at a volume of $25V_0$ as a function of reduced time s. Curves show the theoretical results, with the asymptotic large-system result [from Dorfman and Cohen, DC, Ref. 2(a)] given by the dotted curve. The dash-dot curve (and, in subsequent figures, the dashed curves as well) is the prediction of the finite-system mode-coupling theory. The latter is coincident with the $\rho_D=0$ axis beyond $s=20$. Arrows mark the acoustic wave traversal time.

A. Low densities: $\tau\geq 10$

For the lowest-density case, viz., $\tau=25$, a single realization, for $N=4000$, is shown in Table I. In Fig. 2 we plot the observed VACF as well as the usual theoretical predictions. The finite-N EHvL theory is, however, indistinguishable from the $\rho_D=0$ line. At this density the long-time tail is so small (i.e., ρ_D is so small) that the VACF is reduced to the level of the statistical fluctuations in the long-time region. The T^2 test (not given in Table II for this realization) indicates satisfactory agreement with the finite-N theory even to very early values of the time, but the values of $\Delta g_{0.95}$ are so large that it is clear that the agreement is not very meaningful—the test would also indicate agreement for a theoretical value of α_D 100 times as large. The situation shown in Fig. 3 for $\tau=18$, again for $N=4000$, represents only a slight improvement in this regard.

For a volume of $10V_0$, realizations for 500 and 4000 particles are listed in Table I, with data for both realizations plotted in Fig. 4. Because the 500-particle realization is relatively short (11×10^6 collisions) and because finite-systems effects reduce the VACF to the level of the statistical fluctuations at relatively early times, a comparison with theory is not very productive; Table II shows a typical value of $P(T^2)$ which does not change greatly for quite a range of time intervals $[t_i,t_f]$ for the comparison. The $N=4000$ realization is more interesting because finite-system effects are delayed to later times. As seen from Table II, the T^2 test indicates satisfactory agreement between the MCMD data and the theory for $t_i=19.4t_0$. Moreover, the value of $\Delta g_{0.95}=1.8$, while yet large, is not astronomical as is the case for the 500-particle realization (as well as for the $\tau=18$ and 25 comparisons).

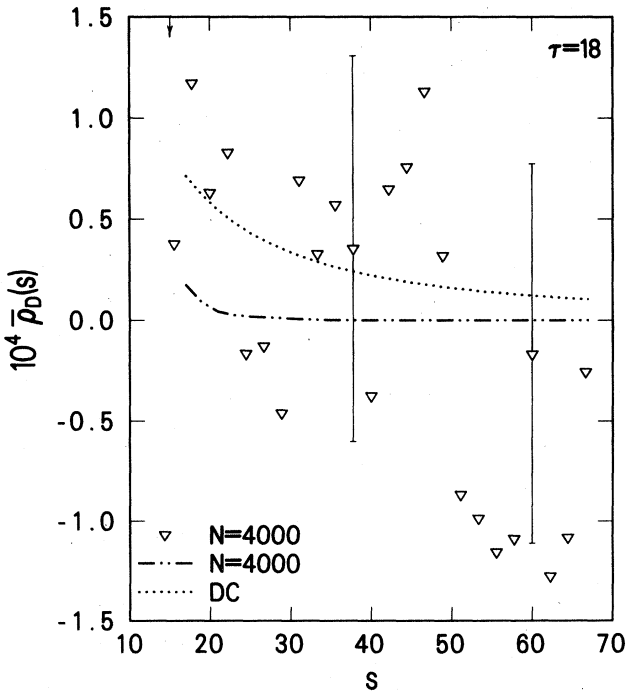

FIG. 3. Same as Fig. 2, but for a volume of $18V_0$.

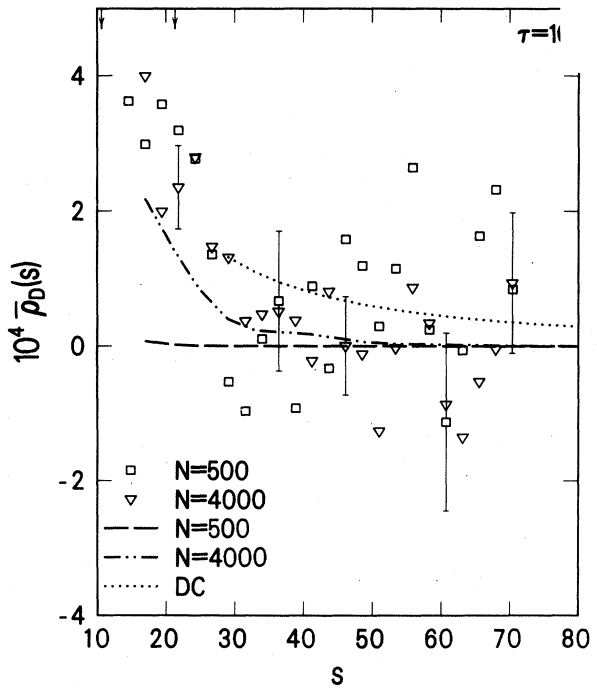

FIG. 4. Same as Fig. 2, but for a volume of $10V_0$ and two different system sizes.

B. Intermediate densities: $5 \geq \tau \geq 2$

At a volume of $5V_0$, results have been obtained for systems of 108, 500, and 4000 particles, as shown in Fig. 5. While the 108-particle run is short, the others are quite extensive. The T^2 tests in Table II show the 108-particle realization to agree with theory, subject to very large uncertainties. On the other hand, the 500- and 4000-particle results, for $s_i = 24.7$ and 27.0, respectively, show rather sharper agreement as reflected in the smaller values of $\Delta g_{0.95}$.

It is worthwhile to observe that the efficacy of the finite-N version of the EHvL theory is evident from Fig. 5. The infinite-system theory (dotted curve) lies well above most of the data except at early times; the finite-N theory demonstrates a remarkable improvement. In terms of the T^2 test we find a significant difference $[P(T^2) > 0.95]$ (not displayed in the table) between the data and the infinite-system theory even for s_i as large as 33.

Both of the above 500- and 4000-particle comparisons were made over the entire length of times $s > s_i$ for which the VACF was evaluated. If, instead, we limit the comparison to those times for which the trajectories are expected to retain some accuracy, viz., $s < 50$ by rough interpolation of the results of Sec. III, then we obtain the second set of test results listed in Table II. Again, the values of $P(T^2)$ continue to support the validity of the theory, with values of $\Delta g_{0.95}$ not very different from the comparison to longer times. Evidently, the data support the theory in the range $25 < s < 50$ for which the trajectories are accurate and at longer times as well.

At $\tau = 4$, realizations of 108 and 1372 particles are given in Table I, with the VACF plotted in Fig. 6. While both realizations are rather extensive in terms of the total number of collisions, the $N = 108$ VACF is reduced to the magnitude of the error bars for times beyond $20t_0$ because of finite-system effects. The T^2 test has a significant $P(T^2)$ when all the points in the figure are included in the comparison. When the leftmost point is excluded, the test

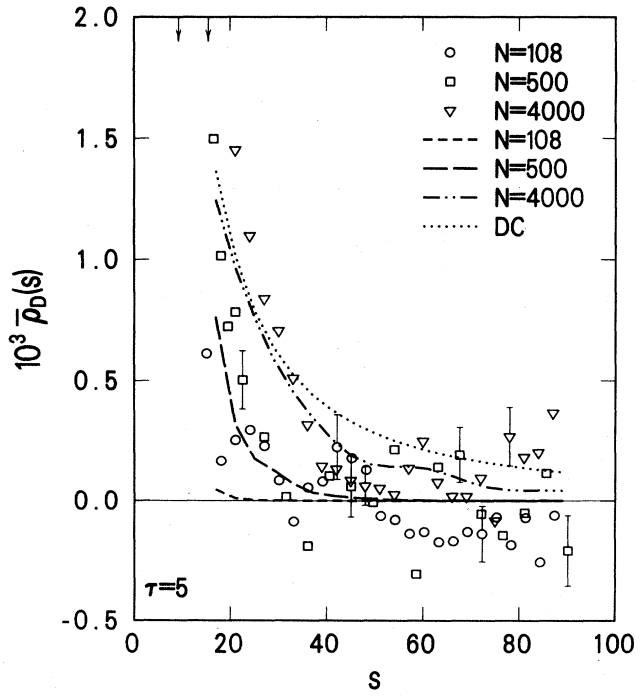

FIG. 5. Same as Fig. 2, but for a volume of $5V_0$ and for systems of 108, 500, and 4000 hard-sphere particles.

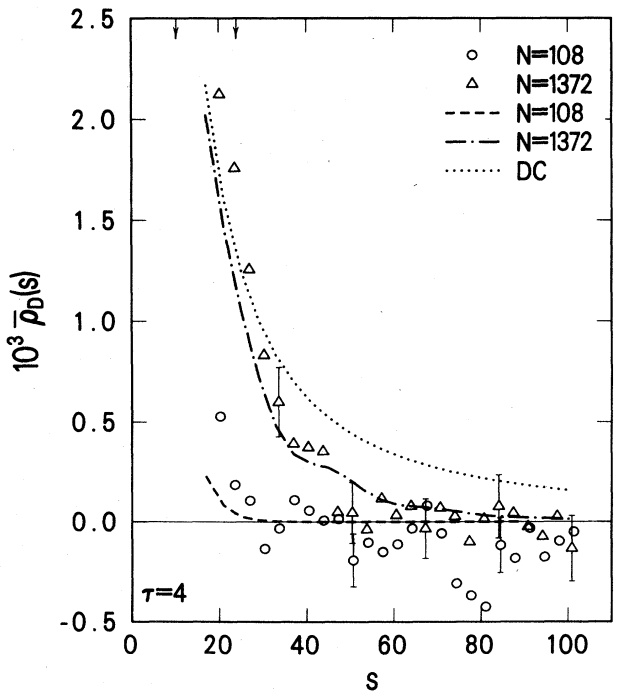

FIG. 6. Same as Fig. 2, but for a volume of $4V_0$ and for systems of 108 and 1372 particles.

shows no significant disagreement. Nonetheless, $\Delta g_{0.95}$ is large. For the 1372-particle realization, the test results in Table II indicate agreement with the theory for $s \geq 23$. Because this realization uses single precision in the trajectory generation, it is seen from Fig. 1 that the trajectories lose accuracy at roughly $s = 30$. The comparison for time intervals only up to $s = 30$ is also given in Table II, with results consistent with the full-interval comparison, although the $P(T^2)$ are slightly larger, to the point that one would tend not to claim agreement at quite so early a time.

For $\tau = 3$, realizations of 108, 500, 1372, and 4000 particles are shown in Table I, with the data plotted in Fig. 7. The 4000-particle calculation is much more extensive than the others. In addition, only for the 4000-particle run are data beyond $s = 50$ available. For the three smaller system sizes, the values obtained from the T^2 test, Table II, show agreement with the finite-N EHvL theory beyond roughly $20t_0$. The more precise data for $N = 4000$ show disagreement unless $t > 32t_0$.

If we limit our comparison to those times for which the MD trajectories retain some accuracy, then for $\tau = 3$ we consider times less than $s = 65$ only (for double-precision calculations). Only the 4000-particle results are then affected. The second pair of entries in Table II for this realization shows the effect of this limitation; while the values of T^2 for a given s_i are less probable, the value remains unexceptional for $t_i = 32.9t_0$.

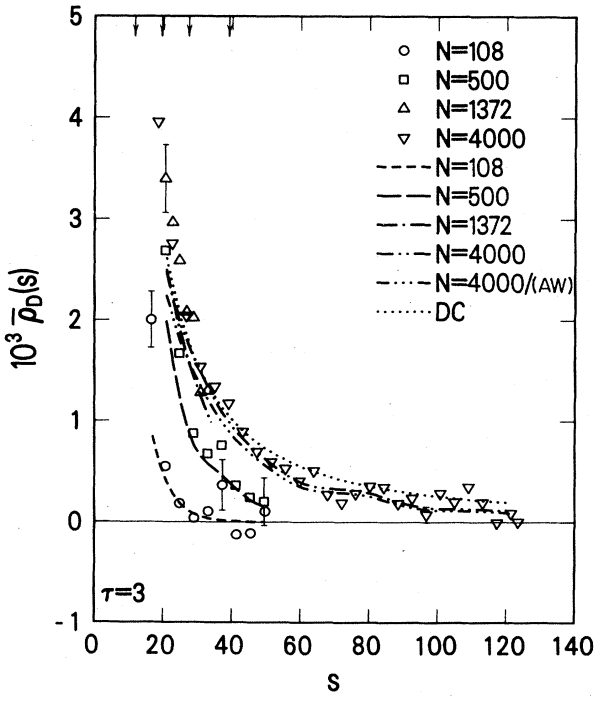

FIG. 7. Same as Fig. 2, but for a volume of $3V_0$ and for systems of 108, 500, 1372, and 4000 particles. The dash—triple-dot curve with "AW" appended to its identifier in the legend is the finite-N version of the theory, but using MD estimates for the transport coefficients from Alder and Wainwright (Ref. 1) listed in Table III. The error bars for the 4000-particle results are roughly the size of the plotting symbols.

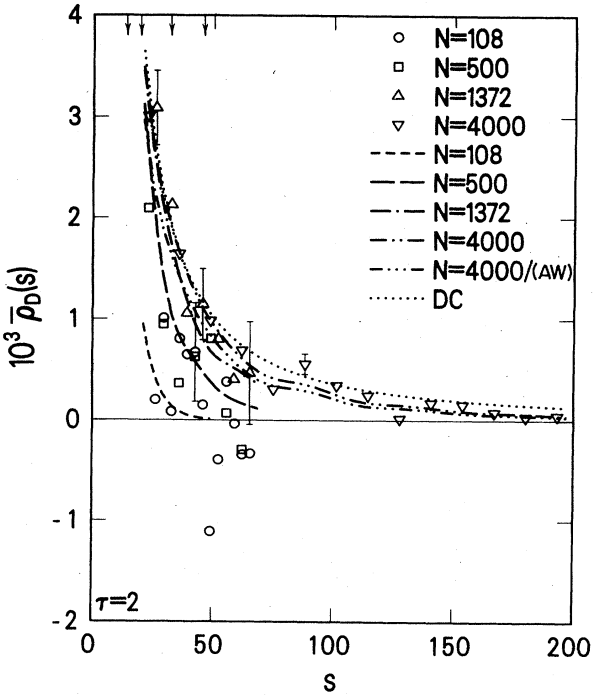

FIG. 8. Same as Fig. 7, but for a volume of $2V_0$ and for systems of 108, 500, 1372, and 4000 particles.

At a reduced volume $\tau = 2$, realizations for $N = 108$, 500, 1372, and 4000 are tabulated in Table I. The VACF is shown in Fig. 8. We note that the 4000-particle data have much smaller error bars than the smaller-system results and extend to much longer times, viz., $s = 190$. In Table II we tabulate the results of the T^2 tests, comparing the observed VACF with the finite-N EHvL theory. The values of the time for which the tests indicate unexceptional values of T^2 are seen to be somewhat smaller than for lower densities. Moreover, the uncertainty in the indicated agreement with theory as reflected in $\Delta g_{0.95}$ is much less than at lower densities, especially for the largest system. Finally, if the time interval of the comparison is limited to times less than roughly $76t_0$, so that the MD trajectory retains some accuracy, then the T^2 test yields the second set of entries in Table II for $N = 4000$, again indicating agreement with the theory. For the smaller systems, this limitation on the time holds for the entire interval for which data are reported.

C. High densities: $1.8 \geq \tau \geq 1.6$

For the higher densities, only realizations of 4000 particles were generated. Figure 9 shows the data for $\tau = 1.8$ which includes results to $234t_0$; every second data point is plotted. T^2 comparisons between these data and the finite-N EHvL theory are characterized by the presence of a marginally significant difference at long times; in Table II the comparison for $s_i = 172$ is typical. Comparisons over longer ranges of the time are similar. Detailed statistical analysis shows that the long-time data lie below the theory on the average. If we compare only up to the time ($s = 100$) for which the trajectories retain some accu-

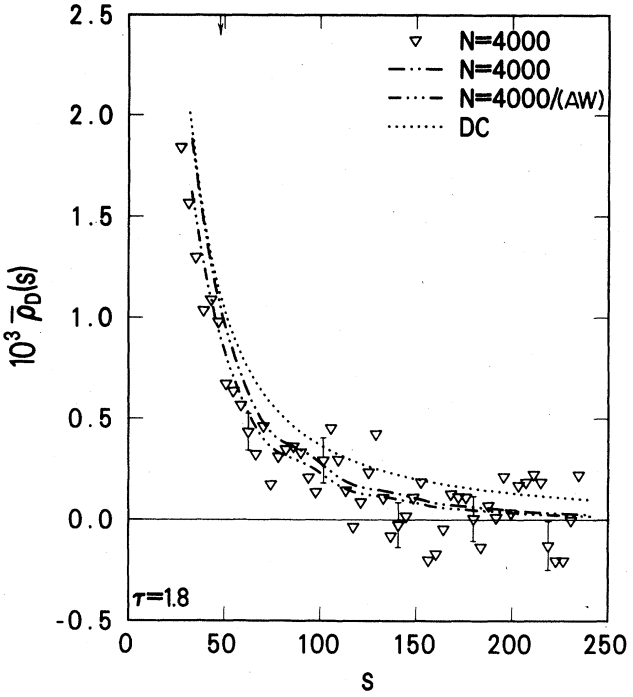

FIG. 9. Same as Fig. 7, but for a volume of $1.8\,V_0$.

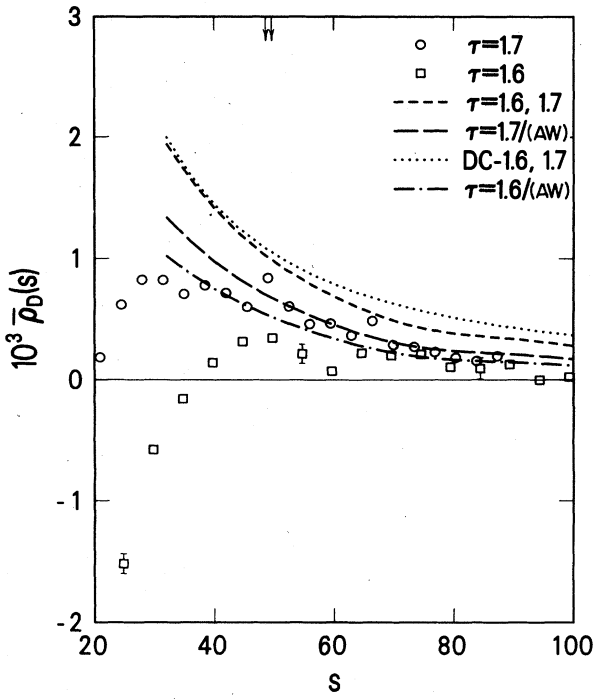

FIG. 10. Same as Fig. 7, but for volumes of $1.7\,V_0$ and $1.6\,V_0$. The arrows mark the acoustic wave traversal time, with the lower-density value on the left. The theoretical curves for $\tau=1.6$ are indistinguishable from the $\tau=1.7$ curves, except those using actual (AW) transport coefficients.

racy, then we seem to obtain more favorable test results, as seen from Table II. There is perhaps the suggestion, then, that the observed VACF decays slightly more rapidly than predicted by the theory at times beyond roughly $100t_0$; whether the effect is an artifact of the loss of accuracy of the MD trajectory or a real effect is open to speculation.

The two highest-density realizations studied here are for $\tau=1.7$ and 1.6. The VACF for each of these is shown in Fig. 10, along with the theoretical curves for both densities which are indistinguishable on this scale. For these realizations, the VACF was calculated only to times up to roughly $100t_0$; every second point is plotted in the figure. Evidently, these differ significantly from the theory, irrespective of the time interval for comparison; typical results are given in Table II.

A similar discrepancy was observed at high density in our study of the VACF of hard disks.[3(f)] There we hypothesized that a self-consistent interpretation of the theory might be useful, based on the use of the actual transport coefficients in the theory, rather than the Enskog values. For the case of hard disks, values for the actual transport coefficients (self-diffusion, shear viscosity, and thermal conductivity) are largely unknown; indeed, in the thermodynamic limit the mode-coupling and kinetic theories predict them to be infinite. For hard spheres, values are known for a number of densities and system sizes from the MD calculations of Alder, Gass, and Wainwright,[3(b)] the present authors,[3(d)] and the current calculations. We have therefore repeated our comparisons between theory and the MD "experiments," using molecular-dynamics estimates for the transport coefficients for several densities at which the transport coefficients are appreciably different from the Enskog values, viz., $\tau<3$. The values used for D/D_E, η/η_E, and λ/λ_E are tabulated in Table III, and the associated T^2 test results are given in Table IV, including those for the same values of $[s_i,s_f]$ as in Table II as well as those for some additional intervals. In the cases in which large-system values are not known, the 108- or 500-particle values were

TABLE III. Transport coefficients relative to the Enskog values, used in evaluating the EHvL theory of the VACF for T^2 tests in Table IV.

V/V_0	N	D/D_E	η/η_E	λ/λ_E	Notes
3	108	1.13	1.02	1.00	a
	500	1.22	1.02	1.00	a,b
	1372	1.26	1.02	1.00	a,b
	4000	1.27	1.02	1.00	a,b
2	108	1.06	1.11	1.02	a
	500	1.14	1.10	1.07	a
	1372	1.16	1.10	1.07	a,b
	4000	1.19	1.10	1.07	a,b
1.8	4000	1.06	1.10	1.03	a,b
1.7	4000	0.94	1.27	1.04	a,b
1.6	4000	0.78	1.48	1.05	a,b,c

[a]Values from Ref. 3(b) or interpolated (or extrapolated) from values given in Ref. 3(b).
[b]Value of D/D_E obtained from present calculations, from $D(s)$, Eq. (5), evaluated at the time $t=Mh$.
[c]Value of η/η_E from Ref. 3(d).

TABLE IV. Hotelling T^2 test for the comparison of the MCMD VACF results with the finite-N EHvL theory, using Table III values for the transport coefficients.

V/V_0	N	k	s_i	s_f	$P(T^2)$	$\Delta g_{0.95}$
3	108	9	16.4	49.2	0.98	
		8	20.5	49.2	0.07	3.8
3	500	9	16.4	49.3	1.00	
		8	20.5	49.3	1.00	
		7	24.7	49.3	0.71	0.8
3	1372	5	16.5	32.9	1.00	
		4	20.6	32.9	0.91	0.6
3	4000	24	28.8	123.4	1.00	
		23	32.9	123.4	0.98	
		22	37.0	123.4	0.98	
		21	41.1	123.4	0.82	0.3
		9	28.8	61.7	1.00	
		8	32.9	61.7	1.00	
		5	45.3	61.7	0.95	
		4	49.4	61.7	0.88	0.5
2	108	18	9.8	65.2	0.77	0.4
		17	13.0	65.2	0.82	0.7
2	500	18	9.8	65.5	0.58	0.2
		17	13.1	65.5	0.23	0.3
2	1372	10	9.8	65.4	0.56	0.3
		9	13.1	65.4	0.72	0.4
2	4000	29	13.1	196.5	1.00	
		28	16.4	193.2	0.89	
		28	19.6	196.5	0.99	
		27	22.9	193.2	0.82	0.1
		11	13.1	78.6	1.00	
		10	16.4	75.3	1.00	
		9	26.2	78.6	1.00	
		8	29.5	75.3	0.63	0.2
1.8	4000	33	27.4	230.5	1.00	
		41	23.4	101.6	0.99	
		39	27.4	101.6	0.66	0.2
1.7	4000	12	39.3	87.2	0.97	
		11	43.6	87.2	0.65	0.4
1.6	4000	9	59.6	99.3	1.00	
		8	56.7	99.3	0.37	0.7

used, e.g., for η and λ for 4000 particles. The modified theoretical VACF is also shown in Figs. 7–10. In Table IV we note that the non-Enskog values of the transport coefficients lead to improved agreement with the data for $\tau=1.6$ and 1.7. Provided we limit our comparison to those times for which the MD trajectory remains accurate, the $\tau=1.8$ agreement is also improved. At lower density, however, the modified theory does not agree as well as the theory using Enskog coefficients. This disagreement is particularly increased at early times, as can be seen in Figs. 7 and 8 for the 4000-particle systems, and is borne out by the values of $P(T^2)$ reported in Table IV. Indeed, the time at which satisfactory agreement is achieved is moved to later times. For the smaller systems, the values of the self-diffusion constant lie nearer the Enskog values and the MCMD data are not so extensive; hence the modified theory has little effect on the comparison.

Overall, then, it does not seem that the self-consistent approach leads to a better representation of the data, except at high density. The theory based on Enskog coefficients appears to fit all the data except the highest two densities.

V. DISCUSSION

Our aim has been to compare the molecular-dynamics data for the VACF with the predictions of the mode-coupling theory, taking into account the recent critique of Fox[4] which indicates we should limit our comparison to times for which the MD trajectories are accurate. It is clear that the use of the finite-N modification of the theory permits us to extend the comparison to a much broader range of system sizes and times than would be possible using only the asymptotic Eq. (1). We have demonstrated satisfactory agreement with the theory except at high density, thereby providing strong support for the theory.

Moreover, at high density, by using molecular-dynamics estimates for the transport coefficients based on

the given values of N and density in place of the Enskog value in order to evaluate the theoretical VACF, we find agreement for the high-density results. However, using the same approach leads to less satisfactory agreement at lower densities. We conclude, therefore, that the mode-coupling result is well supported by the available data, except perhaps at high density, viz., $\tau < 1.8$ (and perhaps at $\tau = 1.8$ for times beyond those for which the trajectories remain accurate). In this regard, it should be emphasized that finite-system effects exist in addition to those accounted for by the finite-N EHvL theory. The remaining discrepancies between theory and the MD results might reasonably be expected to arise from such effects.

In addition, we recognize that the mode-coupling theory most certainly does not give a complete description of the VACF at long times. Thus, at high density the VACF contains a negative piece (see Fig. 10) which persists to quite large values of the time. Inasmuch as such behavior is not predicted by the mode-coupling approach, the apparent negative discrepancy between the MD data and the theory might well reflect a long-lived contribution associated with this "backscattering" effect.

We would also like to draw the reader's attention to the way we have estimated the power function in our comparisons with theory. In addition to the approximate nature of this calculation, it should be noted that the test was contrived only with respect to a multiplicative factor applied to the theoretical VACF. The test does not, for example, speak to the suitability of the functional form of the theory or the value of the exponent of the time dependence of the long-time tail. Such questions can presumably be treated by means similar to those used here, but we have not attempted to consider them for the present.

With regard to the concerns raised by Fox,[4] the data show no evidence for a different behavior beginning at the time of loss of trajectory precision. The one exception occurs at a volume of $1.8V_0$ for which the VACF was obtained for times as large as $240t_0$, a time well beyond the $100t_0$ for which the individual trajectories are accurate. Limiting the comparison to shorter times shows satisfactory agreement. Beyond $100t_0$ the data seem to contain an oscillatory component not accounted for by the finite-N mode-coupling theory. While one might attribute this to the loss of trajectory precision, one can equally well ascribe it to the beginning of the high-density region for which the mode-coupling theory, at least based on Enskog transport coefficients, is not valid. This also suggests the possibility that we are seeing another manifestation of some unknown process which dominates the high-density behavior of the time-correlation function for shear viscosity[3(d)] at similar values of the time and which also is not accounted for by mode-coupling theory.

ACKNOWLEDGMENTS

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