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Molecular Dynamics Calculations of Shear Viscosity Time-Correlation Functions for Hard Spheres

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The time-correlation function for shear viscosity is evaluated for hard spheres at volumes of 1.6 and 3 times the close-packed volume by a Monte Carlo–molecular dynamics technique. At both densities, the kinetic part of the time-correlation function is consistent, within its rather large statistical uncertainty, with the long-time $t^{-3/2}$ tail predicted by the mode-coupling theory. However, at the higher density, the time-correlation function is dominated by the cross and potential terms out to 25 mean free times, whereas the mode-coupling theory predicts that these are asymptotically negligible compared to the kinetic part. The total time-correlation function decays roughly as $\alpha t^{-3/2}$, with α much larger than the mode-coupling value, similar to the recent observations by Evans in his nonequilibrium simulations of argon and methane. The exact value of the exponent is, however, not very precisely determined. By analogy with the case of the velocity autocorrelation function, for which results are also presented at these densities, it is argued that it is quite possible that at high density the asymptotic behavior is not established until times substantially longer than those attainable in the present work. At the lower density, the cross and potential terms are of the same magnitude as the kinetic part, and all are consistent with the mode-coupling predictions within the relatively large statistical uncertainties.

KEY WORDS: Shear viscosity; Monte Carlo; molecular dynamics; long-time tails; time-correlation functions; velocity autocorrelation function.

1. INTRODUCTION

The mode-coupling theory has recently been used by Ernst *et al.*$^{(1)}$ to evaluate the long-time behavior of the equilibrium time-correlation functions which appear in the Green–Kubo formulas for viscosity, thermal conductivity, and self-diffusion. These results confirm for the most part the

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earlier calculations of Pomeau,(2) Kawasaki,(3) and Wainwright *et al.*(4) and extend the kinetic-theory calculations (for hard spheres and disks) of Dorfman and Cohen(5) and the mode-coupling results of Ernst *et al.*(6) by the inclusion of the so-called "potential" and "cross" terms in addition to the "kinetic" terms.

For the shear viscosity η written as the sum

$$\eta = \eta^{KK} + 2\eta^{K\phi} + \eta^{\phi\phi} \tag{1}$$

the Green–Kubo formula can be written

$$\begin{aligned} \eta^{AB} &= \lim_{t\to\infty} \operatorname{tlim} \eta^{AB}(t) \\ \eta^{AB}(t) &= \beta \int_0^t dt'\, \rho_\eta^{AB}(t') \\ \rho_\eta^{AB}(t) &= \frac{1}{V} \langle J_\eta^A(0) J_\eta^B(t) \rangle \end{aligned} \tag{2}$$

where t is the time, tlim denotes the thermodynamic limit, $\beta = 1/k_B T$, k_B is the Boltzmann constant, T is the temperature, V is the volume, and the angular brackets denote an equilibrium ensemble average. For a system of N particles, each of mass m, having positions and velocities $\mathbf{r}_i$, $\mathbf{v}_i$, and interacting pairwise through a potential $\phi(\mathbf{r}_i - \mathbf{r}_j)$, the microscopic currents are

$$\begin{aligned} J_\eta^K &= T_{xy}^K \\ J_\eta^\phi &= T_{xy}^\phi \\ \mathsf{T}^K &= m \sum_i \mathbf{v}_i \mathbf{v}_i \\ \mathsf{T}^\phi &= -\frac{1}{2} \sum_{i\neq j} \mathbf{r}_{ij} \frac{\partial \phi(\mathbf{r}_{ij})}{\partial \mathbf{r}_{ij}} \end{aligned} \tag{3}$$

where subscripts x and y refer to tensorial components and where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. The mode-coupling analysis yields the long-time correlation functions

$$\rho_\eta^{AB}(t) \sim \alpha_\eta^{AB} t^{-d/2} \tag{4}$$

where d is the dimensionality of the system ($d = 2$ or 3) and where

$$\begin{aligned} \alpha_\eta^{K\phi} &= \alpha_\eta^{\phi\phi} = 0 \\ \alpha_\eta^{KK} &= \frac{1}{d(d+2)\beta^2} \left[\frac{d^2-2}{(2\nu)^{d/2}} + \frac{1}{\Gamma_s^{d/2}} \right] \frac{1}{(4\pi)^{d/2}} \\ \nu &= \eta/nm \\ \Gamma_s &= \frac{(\gamma-1)\lambda}{nC_p} + \frac{2(d-1)\nu}{d} + \frac{\zeta}{nm} \\ \gamma &= C_p/C_v \end{aligned} \tag{5}$$

with λ the thermal conductivity, ν the kinematic viscosity, ζ the bulk viscosity, C_p and C_v the specific heats per particle at constant pressure and volume, respectively, and $n = N/V$.

The Dorfman–Cohen$^{(5)}$ kinetic theory calculation of $\rho_\eta^{KK}(t)$ leads to a similar result, but contains the Enskog dense-gas-theory values for the transport coefficients in α_η^{KK}. Pomeau and Resibois$^{(7)}$ suggest that, for the truly asymptotic time regime, a more complete analysis would lead to the full transport coefficients, at least for the three-dimensional case. Wainwright *et al.*$^{(4)}$ have suggested that the hydrodynamic theory should be made self-consistent by introducing time-dependent transport coefficients in the theory. To display a measure of this uncertainty, we shall exhibit theoretical curves using both the Enskog values and the full values.

An additional question arises in applying the theoretical results, because of the lack of some indication of the time at which the predicted asymptotic $t^{-3/2}$ behavior becomes dominant. Therefore, in studying molecular dynamics results it is important to recognize the possible existence of time intervals, even at quite long times, over which the decay of the time-correlation function is controlled either by dynamical events not incorporated in the mode-coupling formulation or by mode-coupling contributions not yet in the time-asymptotic regime.

Numerical estimates of the self-diffusion correlation function, viz. the velocity autocorrelation function, have been made by Alder and Wainwright$^{(8)}$ and by us$^{(9)}$ for hard disks and hard spheres. The agreement between these results and the kinetic-theory (or mode-coupling) result has been discussed by Wood.$^{(9)}$ For viscosity and thermal conductivity Alder *et al.*$^{(10)}$ report values of the transport coefficients for hard spheres, but the time-correlation functions appear to be too imprecise for comparison with the theory. In a two-dimensional study,$^{(4)}$ however, these same authors compare molecular dynamics results for these time-correlation functions for hard disks (at a volume of twice the close-packed volume) with Eqs. (4) and (5) for shear viscosity and with the corresponding expression for the kinetic part of the thermal conductivity, which they derived from hydrodynamics. While it would appear that the kinetic part of the thermal conductivity agrees well with their theory, the comparison is otherwise not so conclusive.

Evans$^{(11)}$ has studied the shear viscosity in three dimensions for both an atom–atom exp-6 potential modeling methane and for a Lennard-Jones 6–12 potential modeling argon by a nonequilibrium molecular dynamics calculation, with a time-oscillating shear rate. By calculating the frequency dependence of the kinetic and potential parts of the stress tensor, Evans concluded that $\rho_\eta(t)$ behaves as $\alpha t^{-3/2}$, but that α is much larger than given by Eq. (5). The difference was ascribed to the potential and cross contributions.

2. METHOD

We have studied the validity of (4) for hard spheres through a Monte Carlo–molecular dynamics calculation$^{(12)}$ of the shear viscosity time-correlation functions. For hard-core potentials, the force appearing in Eq. (3) for T^{ϕ} is impulsive, so that this expression is not useful for numerical computation. For hard cores of diameter σ under periodic boundary conditions, the momentum flux can be shown$^{(12)}$ to have potential part

$$\mathsf{T}^{\phi} = m \sum_{\gamma=1}^{\infty} \mathbf{r}_{ij}(t_\gamma)\Delta\mathbf{v}_i(t_\gamma)\,\delta(t - t_\gamma) \tag{6}$$

where $t_1, t_2, \ldots$ denote the collision times for the binary collisions, i and j depend on γ and denote the pair of particles which collide at t_γ, and $\Delta\mathbf{v}_i$ is the velocity change for particle i. The $\mathbf{r}_{ij}$ is the line-of-centers vector for the colliding pair. Because of the presence of the δ function, the cross and potential terms of ρ_η cannot be calculated directly by molecular dynamics. Instead we compute the "Einstein" functions

$$S_\eta^{AB}(t) = (1/2t)\langle G_\eta^A(t) G_\eta^B(t)\rangle \tag{7}$$

$$G_\eta^A(t) = \int_0^t dt'\, J_\eta^A(t')$$

From Eqs. (3) and (6), one obtains then

$$G_\eta^{\phi}(t) = m \sum_{\gamma=1}^{\infty} x_{ij}(t_\gamma)\,\Delta v_{yi}(t_\gamma) A(t - t_\gamma) \tag{8}$$

where $A(x)$ is the unit step function and where x_{ij} and Δv_{yi} are, respectively, the x component of $\mathbf{r}_{ij}$ and the y component of $\Delta\mathbf{v}_i$. Evidently G_η^{ϕ} can readily be evaluated along a molecular dynamics trajectory. Functions of the type $S_\eta^{AB}(t)$ were discussed by Helfand.$^{(13)}$ One can show that

$$\rho_\eta^{AB}(t) = V^{-1} \frac{d^2}{dt^2}\, t S_\eta^{AB}(t) \tag{9}$$

by proving the relation

$$\langle G_\eta^A(t) J_\eta^B(t)\rangle = \langle G_\eta^A(t) J_\eta^B(0)\rangle$$

which follows from Liouville's theorem and the dynamical reversibility of the trajectory. Thus, we estimate the correlation function $\rho_\eta^{AB}(t)$ by numerical differentiation of $tS_\eta^{AB}(t)$. It would appear that the Alder *et al.*$^{(4,10)}$ calculations were done in the same way.

For the present calculations, the ensemble average $\langle \cdots \rangle$ is taken in the so-called molecular dynamics ensemble, viz. the subset of the microcanonical ensemble having total momentum $\mathbf{P} = 0$, in addition to fixed energy E, volume V, and number of particles N. The thermodynamic temperature then is given through the relation $\beta = dN/2E$.

We compute the reduced shear viscosity correlation function

$$\bar{\rho}_\eta^{AB}(s) = (\beta t_0/\eta_E)\rho_\eta^{AB}(t_0 s), \qquad s = t/t_0 \tag{10}$$

in which t_0 is the mean free time and η_E is the Enskog dense-gas shear viscosity,(14)

$$\eta_E = \frac{\eta_{00}}{\chi_E}\left[c_\eta^{(d)}\left(1 + \frac{2}{d+2}y\right)^2 + \frac{16dy^2}{(d+2)^2\pi}\right]$$

$$c_\eta^{(3)} = 1.016$$

$$y = 2^{d-2}n\sigma^d\pi\chi_E/d$$

where χ_E is the pair correlation function at contact and η_{00} is the Boltzmann shear viscosity in the first Enskog approximation

$$\eta_{00} = \frac{(d+2)(\beta m)^{1/2}}{8\pi^{1/2}(d-1)\beta\sigma^{d-1}} \tag{11}$$

In the reduction of our data, we have replaced t_0 by the observed value, reported below in units of the low-density, large-system mean free time

$$t_{00} = \frac{1}{2(d-1)n\sigma^{d-1}}\left(\frac{\beta m}{\pi}\right)^{1/2}$$

and computed η_E using χ_E from the Padé (3 × 3) approximant of Ree and Hoover(15) to obtain $\bar{\rho}_\eta^{AB}$.

The Monte Carlo–molecular dynamics program has been described in some detail elsewhere.(12) The current version of the program computes $S_\eta^{AB}(t)$ at observation times which can be closely spaced at short times (where S_η^{AB} changes rapidly) and coarsely spaced at long times, viz. $t = k_1h, 2k_1h, \ldots, n_1k_1h, (n_1k_1 + k_2)h, (n_1k_1 + 2k_2)h, \ldots, (n_1k_1 + n_2k_2)h, \ldots,$ where the n_i and k_i are integers and h is a specified time step. For the current viscosity calculations, $h \approx 0.1t_0$, $\{k_i\} = \{1, 5, 15\}$, and $\{n_i\} = \{30, 14, 40\}$ except for the 4000-particle system, for which $\{n_i\} = \{30, 14, 60\}$. The values of $S_\eta^{AB}(t)$ are obtained as averages over P trajectories, each of which consists of a fixed number θ of time steps, starting from an initial phase sampled by Monte Carlo techniques from the molecular dynamics ensemble. On each trajectory, $S_\eta^{AB}(t)$ is time-averaged(12) by the definition of the phase $\mathbf{r}^N(t)$, $\mathbf{v}^N(t)$ at times $t = 0, \omega h, 2\omega h, \ldots$ as "time origins"; we have used $\omega = 5$ except where noted otherwise in Table I. The spacing of time origins has considerable influence on the smoothness of the $S_\eta^{AB}(t)$ with time as discussed for a time-correlation function for self-diffusion in Ref. 12. This influence is amplified by the differencing of the $S_\eta^{AB}(t)$ to get $\rho_\eta^{AB}(t)$. In order to minimize the jumpiness of $\rho_\eta^{AB}(t)$ with time we have

Table I. Parameters for the Monte Carlo–Molecular-Dynamics Calculations[a]

V/V_0	N	h/t_0	θ	P	$N_c \cdot 10^{-6}$	t_0/t_{00}
1.6	108	0.0996	150,000	88	71	0.20259 ± 0.00003
1.6	500	0.0996	40,000	72	72	0.20114 ± 0.00003
1.6	4000	0.0994	4000	97	77	0.20129 ± 0.00003
1.6[b]	4000	0.9933	320	90	57	0.20140 ± 0.00004
3.0	500	0.1031	40,000	106	109	0.48585 ± 0.00004
3.0[b,c]	4000	1.0286	320	99	65	0.48611 ± 0.0006

[a] h is the time-step length, θ the number of time steps per trajectory, P the number of trajectories, and N_c the total number of collisions.

[b] NVE-ensemble calculation for the velocity autocorrelation function.

[c] Time-origin spacing $\omega = 4$.

chosen a time interval lh for differencing so that the values of t are all time origins, viz. $l = 15$.

3. RESULTS

The kinetic term of the time correlation function is shown in Fig. 1a for systems of 108, 500, and 4000 particles at a volume $V = 1.6V_0$ (V_0 being the close-packed volume), along with the long-time tail given by Eqs. (5) and (10). The parameters of the Monte Carlo–molecular dynamics calculation are given in Table I. To compute the theoretical prediction requires the transport coefficients λ, η, and ζ as well as the heat capacities. To obtain the latter, we use the Ree–Hoover equation of state.(15) For the transport coefficients, we use both the Enskog dense-gas values (solid line) and the Alder *et al.*(10) (molecular dynamics) values[2] (dashed line). In the evaluation of the Enskog transport coefficients, we require χ_E, for which we also use the Ree–Hoover equation of state. The vertical arrows in the figure label the transit time s_a for an acoustic wave across the system (the smaller s_a referring to the 108-particle system; $s_a \approx 49$ for 4000 particles lies beyond the range of the figure). For the velocity autocorrelation function it was found(8,9) that finite system effects become important at times near s_a.

The 108-particle results appear to be in reasonable agreement with the theory (particularly the solid curve), at least for $10 < s < s_a$, but this represents quite a narrow range in the time. Based on the magnitude of the error bars (one standard deviation), it might appear that the solid curve in Fig. 1a is too low to fit the $15 < s < s_a$ data for $N = 500$. Visual compari-

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[2] It is our belief that these authors, in tabulating the transport coefficients relative to their Enskog values, used the first Sonine approximations to the latter. That is, their reported values are for $\eta/\eta_E^{[0]}$, etc., where $\eta_E^{[0]}$ is the first Sonine approximation to η_E.

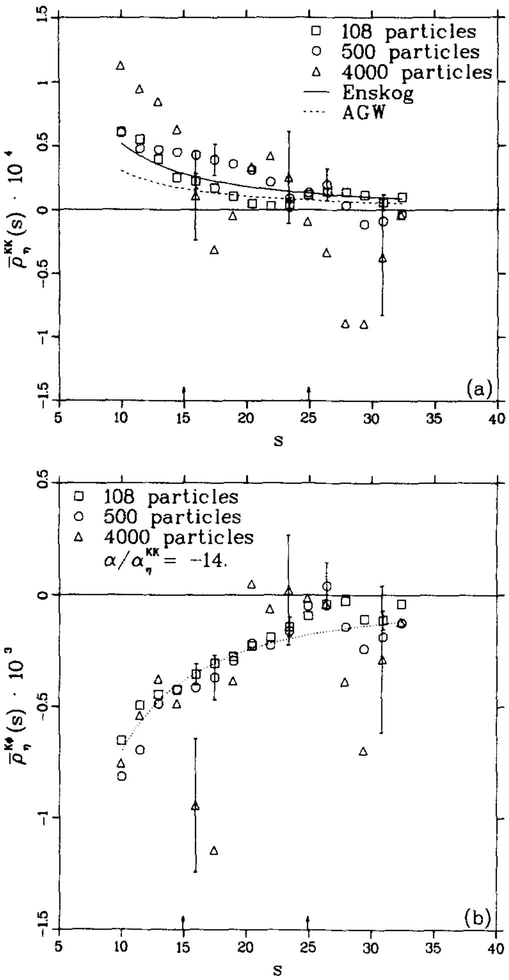

Fig. 1. The reduced shear viscosity time-correlation functions $\bar{\rho}_\eta^{AB}$ as a function of time s, in units of the mean free time, for hard-sphere systems at a volume of 1.6 times close-packed: (a) the kinetic (KK) part, (b) the cross $(K\phi)$ part, (c) the potential $(\phi\phi)$ part. The curves represent $\alpha s^{-3/2}$ decay, with theoretical values of α for the solid (using Enskog transport coefficients) and the dashed (using transport coefficients from Ref. 10) curves; the dotted curves are fitted to the data, with α given relative to the theoretical value based on Enskog transport coefficients.

sons of time-correlation function data with theory can be misleading, however, because of the presence of serial correlations in the data.$^{(12)}$ In this case the usual goodness-of-fit tests for comparing a set of observations with a theoretical curve (such as the χ^2 test) are not appropriate. A quantitative comparison in the presence of such correlation is provided by

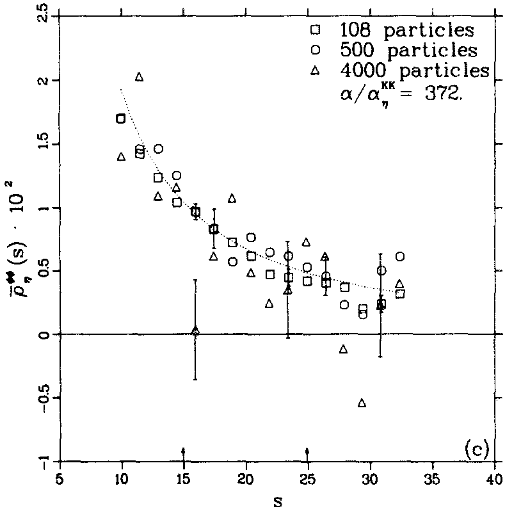

Fig. 1. Continued.

the T^2 statistic of multivariate statistical analysis.(16) If we define $P(T^2)$ to be the probability of observing a value of the statistic between 0 and T^2, then values of $P(T^2)$ which are very close to 0 (say, from 0 to 0.025) indicate a better than expected agreement with the theory, while values very close to 1 (say, from 0.975 to 1) indicate a larger than expected disagreement. We find, for the 72 presumably independent trajectories which enter the mean values shown in Fig. 1a for $N = 500$ and $s = 15.9$–26.4, that T^2 is in fact not exceptional; the calculated probability is $P(T^2) = 0.17$ for comparison with the mode-coupling theory using Enskog transport coefficients and $P(T^2) = 0.19$ using the Alder–Gass–Wainwright transport coefficients. Evidently the data are not sufficiently precise to determine α_η^{KK} accurately; indeed the power-law exponent is not well determined.

The 4000-particle results have such large statistical uncertainties that the rather sizable differences from the theoretical curve prove to be quite unexceptional. For $15 < s < 49$ the T^2 comparison with the long-time tail (using Enskog transport coefficients) yields $P(T^2) = 0.55$.

For these same systems the cross contribution is shown in Fig. 1b and the potential contribution in Fig. 1c. The magnitude of each of these in the $s = 10$–30 time interval is seen to be much greater than the kinetic part. Moreover, the time dependence can be reasonably fitted by the form $\alpha s^{-3/2}$ as shown by the dotted curves, although other power laws could also be equally acceptable. In any case, these high-density results clearly indicate that the asymptotic mode-coupling prediction does not account for the largest portion of the time-correlation function in this time interval.

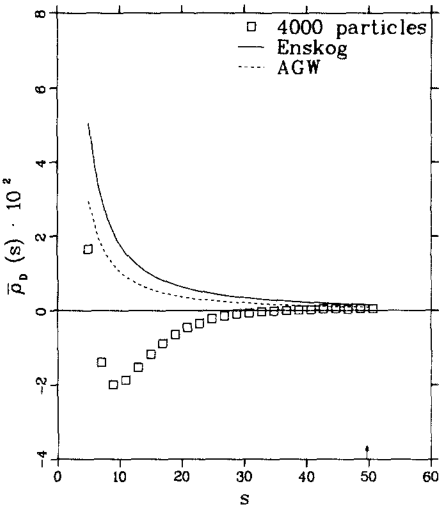

Fig. 2. The reduced velocity autocorrelation function $\bar{\rho}_D$ as a function of time s, in units of the mean free time, for 4000 hard spheres at a volume of 1.6 times close-packed volume. The statistical uncertainty (~0.0001) is smaller than the plotting symbols.

Whether, in fact, at longer times, the kinetic contribution might become dominant, in agreement with theory, cannot be inferred.

It is worthwhile to consider the behavior of the velocity autocorrelation function at this same high density. In Fig. 2 we show the results of a Monte Carlo–molecular dynamics calculation[3] for 4000 hard spheres at a volume of $1.6V_0$ for which we compute estimates of

$$\bar{\rho}_D(s) = \langle u_{1x}(0)u_{1x}(st_0)\rangle / \langle u_{1x}^2(0)\rangle \tag{12}$$

where $\mathbf{u}_i(t)$ is the velocity in the center-of-mass frame of reference,

$$\mathbf{u}_i(t) = \mathbf{v}_i(t) - \mathbf{P}/Nm, \qquad \mathbf{P} = m\sum \mathbf{v}_i(0)$$

The parameters for this calculation are given in Table I.[4] It is seen that the

[3] In this calculation the initial phases $[\mathbf{r}^N(0), \mathbf{v}^N(0)]$ were sampled from the microcanonical (NVE) ensemble rather than the molecular dynamics ensemble. The difference between the velocity autocorrelation functions in the two ensembles is expected to be inconsequential for the 4000-particle system.

[4] It can be shown by a calculation similar to one in Ref. 12 that the collision rate in the molecular dynamics ensemble is a factor $\Gamma[(N-1)d/2]\Gamma(Nd/2+\frac{1}{2})/\{\Gamma(Nd/2)\Gamma[(N-1)d/2+\frac{1}{2}]\}$ [where $\Gamma(x)$ is the gamma function] times that in the NVE ensemble. Applying this correction to the NVE-ensemble value of the mean free time for $N = 4000$, $V = 1.6V_0$ in Table I yields a value $0.20137t_{00}$ in the molecular dynamics ensemble. The latter is in satisfactory agreement with the Table I estimate $0.20129t_{00}$ obtained for the corresponding molecular dynamics ensemble calculation.

velocity autocorrelation function is negative for s between 6 and 38 and has certainly not reached its long-time $s^{-3/2}$ (positive) decay, as shown by the curves in Fig. 2. The dynamical events (viz. "backscattering") responsible for this negative region of $\bar{\rho}_D(s)$ might also increase the time required for $\bar{\rho}_\eta(s)$ to attain its asymptotic time dependence. It should be reemphasized, in this regard, that the $\rho_\eta^{KK}(t)$ data of Fig. 1a are not sufficiently precise to infer that $\rho_\eta^{KK}(t)$ has reached a region of $s^{-3/2}$ decay.

Some additional indication of the presence of high-density effects in the shear viscosity time-correlation functions is afforded by the results of Alder *et al.*(10) at $V = 2V_0$, in which the magnitude of the cross term is comparable to the kinetic term in the $s = 10$–20 interval. More precise results for hard spheres at $V = 3V_0$ for 500 particles are shown in Fig. 3. The parameters for this calculation are given in Table I. It would appear that at this lower density the cross and potential terms vanish within statistical uncertainty between $s = 15.0$ and 21.1 [the T^2 comparison with zero yielding $P(T^2) = 0.85$ and 0.03, respectively]. On the other hand, the kinetic part is in only marginal agreement with a value of zero [$P(T^2) = 0.94$], but does agree well with the theoretical equation (5) [$P(T^2) = 0.64$]. Nonetheless, we note that with such a small time interval and with such relatively large statistical uncertainties, this agreement is principally a check of the magnitude of the kinetic contribution, rather than a confirmation of its $s^{-3/2}$ character. Indeed the values of the time at which these compari-

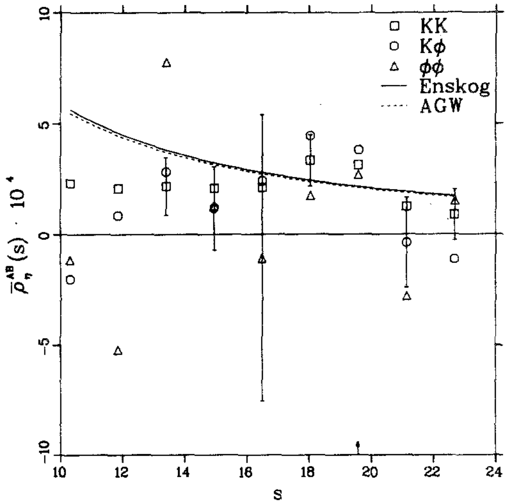

Fig. 3. The reduced shear viscosity time-correlation functions $\bar{\rho}_\eta^{AB}$ as a function of time s, in units of the mean free time, for 500 hard spheres at a volume of three times close-packed volume.

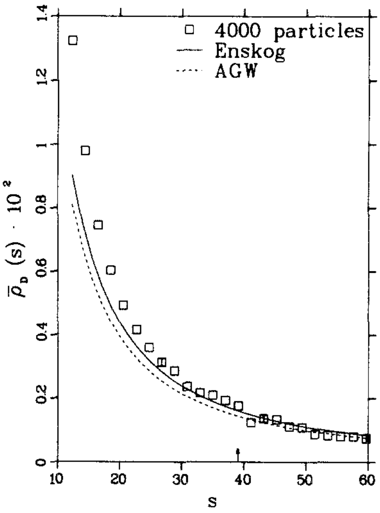

Fig. 4. The reduced velocity autocorrelation function $\bar{\rho}_D$ as a function of time s, in units of the mean free time, for 4000 hard spheres at a volume of three times close-packed volume. The statistical uncertainty (~0.0001) is smaller than the plotting symbols.

sons are made might be too small for the dominance of the mode-coupling result. The velocity autocorrelation function at this density is shown in Fig. 4 for a system of 4000 hard spheres; the parameters are given in Table I. We observe that the molecular dynamics data do not agree with the $s^{-3/2}$ tail before about 30 mean free times.

It is of interest to also compute the coefficient of shear viscosity at high density in order to compare with the Alder *et al.*(10) results and the nonequilibrium molecular dynamics results of Naitoh and Ono.(17,18) The equilibrium molecular dynamics estimate $\eta/\eta_E = 1.44 \pm 0.07$ by Alder *et al.* for 108 particles at $V = 1.6V_0$ does not include, apparently, any correction for the long-time tail or for the extrapolation to an infinite system. From the graphical results of Naitoh and Ono(17) for η/η_E extrapolated to zero rate of shear for 108 particles, one finds values of $\eta/\eta_E = 1.71$ at $V = 1.667V_0$ and $\eta/\eta_E = 2.45$ at $V = 1.575V_0$, which imply, then, a result at $1.6V_0$ well above the equilibrium molecular dynamics value. Similar discrepancies were reported at other high densities, including $V = 1.5V_0$. More recent calculations by Naitoh and Ono(18) at the latter density indicate that their results for systems of 500 or more particles are consistent (within rather large uncertainties arising from the extrapolation to zero shear rate) with the $N = 500$ result of Alder *et al.* at this same density. It would appear that, even though the discrepancies between the results of the two methods are no longer thought to be significant, the actual value of the coefficient of shear viscosity (for the infinite system) at high density is subject to considerable uncertainty.

In order to estimate η in the infinite-system limit, we need to take into account the contribution of the long-time tail, including the portion beyond the longest times computed by molecular dynamics. If we were simply to add the integral of the long-time tail $\alpha s^{-3/2}$, with α corresponding to the sum of the theoretical α_η^{KK} and the α values which fit the data in Fig. 1b and 1c, from the acoustic wave traversal time s_a for $N = 500$ to $s = \infty$, the contribution would be approximately $0.23\eta_E$. The values of $\eta(st_0)/\eta_E$ at $s = s_a(500)$ for the 108-, 500-, and 4000-particle systems are 1.398 ± 0.007, 1.428 ± 0.013, and 1.394 ± 0.041, respectively. If one ignores the relatively imprecise $N = 4000$ value and linearly extrapolates the 108- and 500-particle values to $N = \infty$, one obtains $1.44\eta_E$. The resulting total value of the shear viscosity coefficient is, then, $1.67\eta_E$, well above the Alder *et al.* result. While such a large value is not in conflict with the data, it depends on (1) the existence of large $s^{-3/2}$ tails in the cross and potential terms, which are in conflict with the theory, and (2) to a lesser extent, ignoring the possibility that η in fact is an *increasing* function of $1/N$ for N large enough, as indicated by the 4000-particle result. A reasonable lower bound on the value of η could be obtained by extrapolation to an infinite system of the data at the longest time at which $\eta(st_0)$ is available for each of the three systems, viz. $s \approx 70$, supplemented by the theoretical long-time tail (containing only the kinetic contribution, which proves to be negligible) beyond that time. However, the values of $\eta(st_0)/\eta_E$ are not monotonic in N; viz. 1.465 ± 0.013, 1.510 ± 0.028, and 1.482 ± 0.078 for the 108-, 500-, and 4000-particle systems, respectively. Thus, while linear extrapolation of the 108- and 500-particle data yields $\eta/\eta_E = 1.52 \pm 0.04$ for the infinite system, one must recognize the possibility that η decreases with N for N large and that the N dependence for systems as small as 108 particles is anomalous. In fact, the pressure obtained for these three system sizes displays precisely this behavior. The dependence of the equation of state of hard disks on N was studied in the NpT ensemble earlier.(19) Strong evidence for the nonlinear dependence of the volume on $1/N$ was reported for the higher pressures in that study. To obtain a better estimate of η, then, would appear to require both a theory for the decay of the cross and potential terms and much more extensive molecular dynamics calculations for the 4000-particle system. The latter would appear to be at the limit of practicality with current computer speeds.

In another vein, attention should be called to the assertion(11) that Evans' nonequilibrium method permits the calculation of $\rho_\eta(t)$ with more than two orders of magnitude greater efficiency than by equilibrium molecular dynamics. Improvements of this magnitude are certainly much to be desired, as the present Green–Kubo calculations demand nontrivial computational resources. For example, the calculations reported here for $N = 500$, $V = 1.6V_0$ consumed 34 h of CRAY-1 time. The Evans calculation of $\rho_\eta(t)$, however, involves an adjustment of the particle velocities on each time step of the dynamics which is not dictated entirely by the microscopic forces. It would, therefore, be most desirable to compare both methods for hard spheres, with careful attention to system-size effects.

4. SUMMARY

In agreement with recent nonequilibrium molecular dynamics calculations by Evans(11) for high-density argon and methane fluids, we find the cross and potential contributions to the shear viscosity time-correlation functions for hard spheres at high density (close to the freezing density) and moderately long times (between 15 and 30 mean free times in our case) are much larger than the kinetic contribution. The latter is in approximate agreement as regards its magnitude with the $t^{-3/2}$ prediction of the mode-coupling theory, which predicts a more rapid decay for the cross and potential terms. Again, in agreement with Evans, we find that over this restricted time interval the molecular dynamics results for the cross and potential contributions can also be fitted by a $t^{-3/2}$ power law. However, the data would be consistent with other power-law exponents. Moreover, we question whether we in fact observe the ultimate long-time behavior, inasmuch as the velocity autocorrelation function in this time interval at this density is dominated by backscattering events and attains the expected positive asymptotic values only at later times. Nevertheless, it should be emphasized that the large magnitude of the cross and potential terms at these fairly long times appears to present a strong challenge to the current theories. In addition, we emphasize that the consequent uncertainty entailed in extrapolating the correlation-function contributions to the viscosity coefficient out to infinite time leads to appreciable uncertainty in the Green–Kubo value of the shear viscosity coefficient for hard spheres at high density. We also emphasize our belief that the question of the concordance of the Green–Kubo value of the viscosity with that obtained by the various nonequilibrium molecular dynamics methods in the limit of vanishing shear rate still merits further investigation.

NOTE ADDED IN PROOF

In a recent preprint, Evans has shown how the "thermostating" and the "homogeneous strain" employed in Ref. 11 can be related to the imposition of constraints on the equations of motion.

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