Long-time behavior of the velocity autocorrelation function for moderately dense, soft-repulsive, and Lennard-Jones fluids

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The long-time behavior of the velocity autocorrelation function (VAF), for hard disk and sphere systems, has been extensively explored. Its behavior for systems interacting via a soft repulsive or attractive potential is less well known. We explore the conditions under which the nonexponential, long-time tail in the velocity autocorrelation function of a tagged atom, in soft-repulsive sphere (Weeks–Chandler–Andersen) and Lennard-Jones atomic fluids, may be readily observed by the molecular dynamics method. The effect of changing the system size, the fluid density, the form of the interatomic force and the mass of the tagged atoms are investigated. We were able to observe this long-time tail only for systems of moderate density. At low density the effect, if it exists, is at longer times than we can currently simulate owing to limitations of system size and at higher densities these tails were not observed possibly due to other effects dominating the behavior of the VAF and masking this behavior. Under the physical conditions that are simulated here attractive forces have very little effect on the behavior of the VAF. However, as the mass of the tagged particles is increased the time at which the long-time tail commences is lengthened and its magnitude is significantly increased. This later effect suggests that by increasing the mass of the tagged particles one may be able to study more readily the behavior, nature and physical origin of long-time behavior of the VAF both by computational and by experimental techniques.

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INTRODUCTION

One of the most significant discoveries made by means of numerical statistical mechanics is the existence of long-time, nonexponential tails in the velocity autocorrelation function (VAF), $C(t)=\langle \underline{v}(0)\cdot\underline{v}(t)\rangle$ of a tagged particle in a dense hard-sphere fluid [1]. Since the pioneering work of Alder and Wainwright [1], much theoretical [2–8], experimental [9–15] and computational [16–20] work has been undertaken in order to understand aspects of the long-time behavior of the VAF in a homogenous fluid and in a binary mixture. The molecular dynamics simulation by Alder and Wainwright of 500 hard disk and hard sphere particles at the moderate reduced density of 0.47 indicated that a particle's velocity was correlated with its initial velocity even after a time period corresponding to approximately 20 collisions [1]. The velocity autocorrelation function measured by Alder from molecular dynamics (MD) simulations decayed as $t^{-d/2}$ (d being the dimensionality of the system being simulated) at times which are long on the molecular time-scale ($\sim 10^{-13}$ seconds for Ar). Alder [21] rationalized the long-time $t^{-d/2}$ decay of the VAF in the following way. Particle momentum is dissipated by sound waves (longitudinal hydrodynamic modes) or as a vortex (governed by transverse modes). At long times, the transverse hydrodynamic (vortex) mode dominates leading to a long-time tail in the decay of the VAF.

At the time, this long-time (i.e., nonexponential) decay in the velocity autocorrelation function was in contradiction to the results obtained from the accepted Boltzmann–Enskog kinetic theory [22] and the macroscopically based Langevin equation [22]. These theories predicted that on time scales, which are long on the molecular scale, particles executed a random walk leading to an exponential type decay for the velocity autocorrelation function.

Dorfman and Cohen [4] were able to show theoretically that kinetic theory was able to account for long-time tails in the VAF in hard disk and hard sphere systems by a resummation in the binary-collision expansion used to calculate the VAF. They were able to show that the kinetic theory basis for the slowly decaying hydrodynamic modes (leading to vortex formation) was, amongst other reasons, recollisions between particles. They also noted that their results were not truly asymptotic but could be compared with MD results over the time intervals ranging from 10 to 50 mean free collision times and estimated that the long-time tail should remain for at least 40 collision mean free times.

The vortex flow patterns have been observed computationally in two dimensions, in MD simulations of hard disks by Alder and Wainwright [1] and MD simulations of soft-repulsive particles interacting with a larger circular obstruction (or a large particle) by Rapaport and Clementi [23]. Similar results have been observed using lattice gas methods for fluid flow around colloidal particles in two dimensions [24]. Therefore, the hypothesis of the formation of the vortex field being the dominant effect giving rise to a long-time tail is well supported, at least in two dimensions.

Finally, Erpenbeck and Wood [17–19] using mode-coupling theory for a finite system (based on the mode-coupling theory of Ernst, Hauge, and van Leeuween [3]) extended the hard disk and hard sphere MD studies initiated by Alder out to much larger correlation times and showed that their results are in agreement with Alder [1] and Dorfman [4] and others. Thus, the basis for long-time tails in a hard disk/sphere system is now considered to be well understood.

In contrast the long-time behavior of the VAF for systems of particles interacting via a continuous potential is largely uncharacterized. This point takes on added importance when it is realized that nearly all experimental evidence for long-time behavior in the VAF of moderately dense fluids is based on experimental work done on systems of particles interacting via potentials which may be more closely modelled by a continuous potential of the Lennard-Jones or screened Coulomb type than by a discontinuous hard sphere potential. For example, experiments such as dynamic light scattering [10,12] or diffusive wave spectroscopy [14,15] from colloid particles and neutron scattering experiments on liquid argon [11], rubidium [11], and sodium [13] all indicate the presence of a long-time tail in the VAF. The overall objective of this paper is to begin a systematic MD study for these types of systems. The specific aims of this study are as follows.

(i) Investigate the effect of interparticle attraction on the decay of the velocity autocorrelation function for a single component system.

(ii) Investigate how the long-time tail is affected as the particle/fluid mass ratio increases in order to relate to measurements of the long-time tails in the VAF for very large colloidal particles suspended in a background molecular fluid [10,12].

(iii) Investigate the density regime under which a long-time tail can readily be observed for a system of particles interacting via a continuous potential.

(iv) Determine whether the long-time tail still exists out to long correlation times or alternatively whether it is only observably finite in duration.

MOLECULAR DYNAMICS METHOD

Determination of the long-time behavior of the velocity correlation function by molecular dynamics is limited by the number of particles N in the simulation because the VAF can only be determined for correlation times such that the boundary conditions have no influence. This maximum correlation time, $t_{\max}$, is estimated to be the time it takes a density disturbance in the form of a sound (pressure) wave of speed c_s to cross the periodic box of length $(N/\rho_N)^{1/3}$, i.e., $t_{\max} \approx (N/\rho_N c_s^3)^{1/3}$, where ρ_N is the number density [6].

Erpenbeck and Wood were able to overcome this limitation for hard disk/sphere systems by applying a mode coupling theory developed for a finite periodic NVT ensemble and used this to correct for finite-system effects [17,18] and thus calculated the VAF out to correlation times larger than 20 picoseconds which corresponds to over 100 mean free collision times. However this approach is not strictly valid for particles interacting via a continuous potential and in addition gives rise to large error bars at the long correlation times. Thus we have computed the VAF for systems as large as 32 000 particles in order to directly observe the behavior of the VAF out to long times.

NVT molecular dynamics (MD) calculations were performed on a Quintek Fast9 Transputer Network and a DEC Alpha workstation using up to 32 000 particles for up to 101 000 time steps. The MD algorithms on the Transputer are based on a parallel implementation of the Link-Cell method by Hockney and Eastwood [26], a full treatment of this computational method used is given elsewhere [27]. The MD calculations on the DEC Alpha workstation used a simple neighbor list algorithm [28]. Both methods used a Verlet algorithm [28] in periodic boundary conditions using double precision (64 bit) arithmetic.

The forces used were based on the truncated and shifted two-body potential functions ϕ_{TS} given by Eq. (1):

$$\begin{aligned}\phi_{\mathrm{TS}}(r) &= \phi(r) + \phi(r_{\mathrm{CUT}}), \quad r \leqslant r_{\mathrm{CUT}} \\ &= 0, \quad\quad r \geqslant r_{\mathrm{CUT}},\end{aligned} \tag{1}$$

where

$$\phi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6].$$

Two such potentials were used, i.e., the Chandler–Weeks–Anderson (CWA) soft repulsive potential [25] with $r_{\mathrm{CUT}} = (2)^{1/6}\sigma$ and the often used, truncated and shifted Lennard-Jones potential [28] with $r_{\mathrm{CUT}} = 2.5\sigma$.

Simulations were performed at a reduced number of densities ($\rho_N^* = \rho_N \sigma^3$), ranging from 0.05 to 0.75, at a reduced temperature $T^* = kT/\varepsilon = 2.17$. Most of this work was undertaken at $\rho_N^* = 0.45$ using the CWA potential and it is assumed that these were the conditions used in the discussion section unless it is specifically stated otherwise. At this density and temperature we calculated the thermodynamic properties, by CWA hard sphere perturbation theory or MD simulations, to be (the values in brackets are from Ref. [16]): $pV/Nk_BT = 2.70 \pm 0.01$ (2.72), $U_i/Nk_BT = 0.2192 \pm 0.002$ (0.347), $Cv/Nk_B = (dU/dT)_V = 1.69 \pm 0.01$ (1.89), $(k_BT)^{-1}(\partial p/\partial \rho_N)_T = 5.61 \pm 0.02$ (5.70), and $(k_B\rho_N)^{-1}(\partial p/\partial T)_\rho = 2.32 \pm 0.01$ (2.34), where p is the pressure, U_i is the configurational part of the internal energy, k_B is Boltzmann's constant. The error estimates were made using block averages. The sound velocity c_s was found to be $0.631\sigma/\tau_0$ (0.621) where $\tau_0 = (m\sigma^2/48\varepsilon)^{1/2}$ is the unit of time used by Levesque and Ashurst [16]. The integration time step used in this study is given by $\Delta t = 0.032\,416\tau_0$.

The normalized VAF $c(t) = C(t)/C(0) = \langle \underline{v}(0)\cdot\underline{v}(t)\rangle / \langle \underline{v}(0)\cdot\underline{v}(0)\rangle$ was calculated using Eq. (2):

$$\begin{aligned}\frac{\langle \underline{v}(0)\cdot\underline{v}(n\Delta t)\rangle}{\langle \underline{v}(0)\cdot\underline{v}(0)\rangle} &= (c\Delta t) \\ &= \frac{\sum_{i=1}^{N_i}\sum_{j=1}^{N_0} (\underline{v}_i[(n+j)\Delta t]\cdot\underline{v}_i[j\Delta t])}{\sum_{i=1}^{N_i}\sum_{j=1}^{N_0} \underline{v}_i[(n+j)\Delta t]\cdot\underline{v}_i[(n+j)\Delta t]},\end{aligned} \tag{2}$$

where n runs from 1 to the maximum number of correlation channels N_C, $n\Delta t$ is the correlation time, the summation over i runs over all N_t tagged particles and the summation over j runs over all N_0 time origins.

For each particular run, the system was equilibrated for a minimum of 5000 time steps before the velocity autocorrelation data was collected. The VAF was calculated using 64 bit (double) precision and was averaged over the N_t tagged particles in the system ($N_t \leqslant N$) and was also averaged over

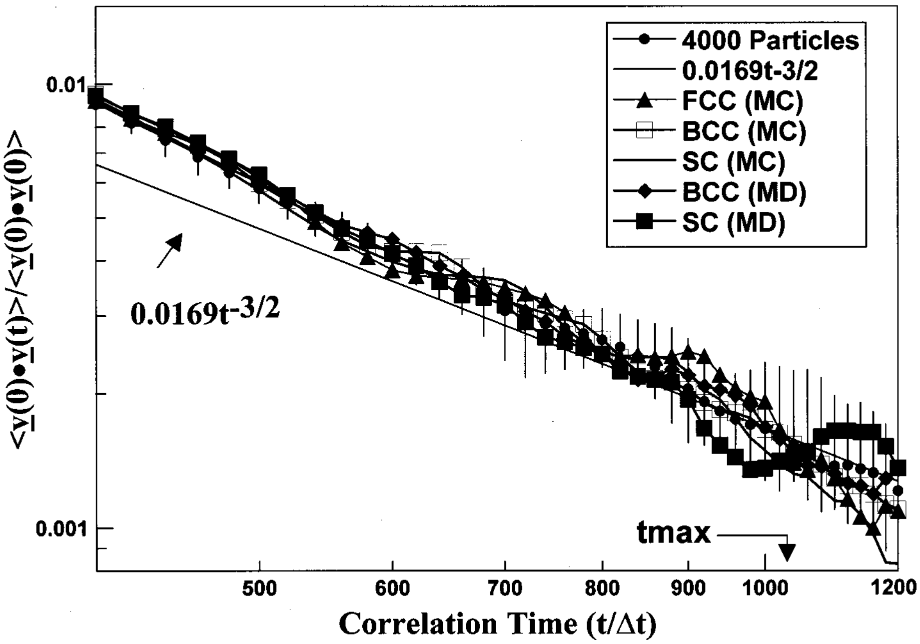

FIG. 1. A log–log plot of the normalized velocity autocorrelation function $c(t)$ versus correlation time t for the CWA system of $N = 4000$ atoms at $T^* = 2.17$ and $\rho^* = 0.45$ compared with the line $At^{-3/2}$. The data gives a comparison of the data for the 12 runs used to estimate uncertainties and the independent runs not used in this averaging process.

a number of time origins N_0 ranging from 4960 to 9900. MD simulations were performed for up to 101 000 time steps in order that reasonable averaging could be performed over time origins in order to obtain data of sufficient statistical accuracy at the longest correlation times.

In order to carry out the aims stated in the Introduction we needed an estimate of the uncertainties in the computed VAF's. Unfortunately the normal method used to estimate uncertainties in VAF's [29] is not applicable here because this method assumes that the correlated variable is a Gaussian random variable which is clearly not the case in the region of the long-time tail.

Thus, an estimate of statistical errors due to the finite time averaging of the velocity autocorrelation function was determined by calculating the maximum and minimum deviation from the mean value obtained over twelve 4000 particle data runs with different starting configurations. The different starting configurations were obtained by equilibrating the system between 5000 and 60 000 timesteps in 5000 time step increments. This was done because the usual method of estimating errors, i.e., using block averages of sufficient size that the correlations between successive block averages is small would be very time consuming here owing to the large number of particles used and the lengths of the runs required to calculate $c(t)$ out to very long times. Figure 1 shows (as error bars) the estimation of errors in the decay of the velocity autocorrelation function in a system of 4000 particles under the same thermodynamic conditions as the MD simulations of Levesque and Ashurst [16].

It was thought that the above error estimates might not be realistic due to the possibility of averaging over highly correlated data. Thus we tested the reasonableness of our error estimates by performing a second series of five statistically independent 4000 particle runs. These were carried out as above but were started from entirely independent initial configurations in order to make them statistically independent. The starting configurations were (1) a static simple cubic lattice (SC); (2) a static body centered cubic (BCC) lattice; (3) configurations obtained by Monte Carlo (MC) simulations of 450 000 steps which commenced from SC, FCC, and BCC starting configurations, respectively.

Figure 1 compares the results from this second series of statistically independent runs with the averaged data and error bars from the first set of runs. This comparison shows that this new data lies within our initial error estimates indicating that this method gives reasonable estimates of uncertainties. Furthermore our results also agree with those of Levesque and Ashurst [16] to within the combined uncertainties of each set of results.

BACKGROUND HYDRODYNAMIC THEORY

Using the conservation equations of classical hydrodynamics under the local equilibrium hypothesis, it can be shown that [2–6,22,30].

$$c(t) \underset{t\to\infty}{\to} \frac{2}{3\rho_N}(4\pi(D_s+v)t)^{-3/2}, \tag{3}$$

where D_s the self-diffusion coefficient and v is the kinematic viscosity.

The hydrodynamic explanation for this nonexponential decay of $c(t)$ is that the velocity field propagates via two pathways [6].

Longitudinal sound waves, which are fast processes associated with fluctuations in density and temperature. They are predicted to propagate at the speed of sound c_s in the medium which is supported by neutron scattering experiments on simple liquids [11,31,32]. These modes decay exponentially and limit the maximum correlation time obtainable by the MD method using periodic boundary conditions and

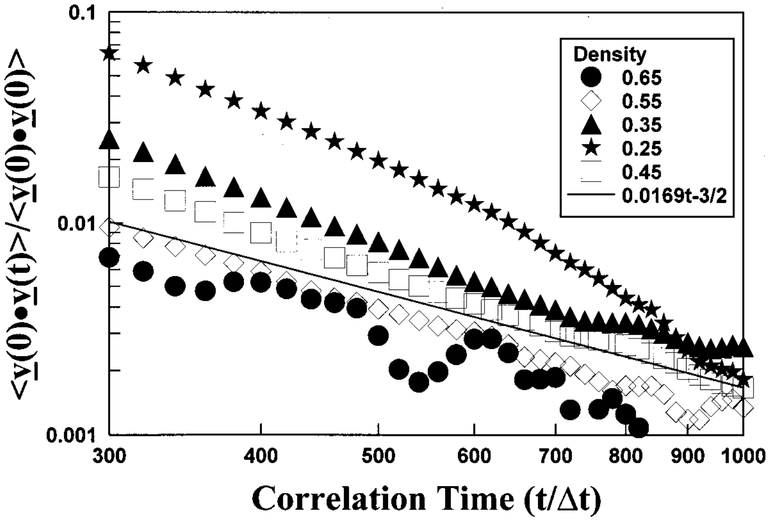

FIG. 2. A log–log plot $c(t)$ versus t for the CWA system of 4000 atoms at $T^*=2.17$ as a function of density.

these modes are expected to influence the velocity field after a time t_{max}, where $t_{max} \sim (N/\rho_N c_s^3)^{1/3}$.

Transverse shear modes, which propagate via a slow diffusive process with a velocity proportional to $[(\eta/\rho_N)]^{1/2}$ and dominate at long times, where η is the coefficient of shear viscosity. They are largely responsible for the vortex formation in the velocity field which gives rise to the $t^{-3/2}$ decay in $c(t)$.

VELOCITY AUTOCORRELATION RESULTS

Effect of density on the decay of $c(t)$ for CWA and Lennard-Jones (LJ) particles

In order to investigate the effect of density on the formation of long-time tails we studied systems of 4000 particles of the same mass interacting via a CWA potential with reduced density varying from 0.05 to 0.75 and a reduced temperature of 2.17. Figure 2 shows a log–log plot of the decay of the resultant $c(t)$ for some of these systems. The data indicates that the $t^{-3/2}$ tail exists in the reduced density range 0.35 to 0.55 at this temperature. The maximum correlation time t_{max} before periodic boundary effects influence $c(t)$ was calculated from the following formula by means of CWA hard sphere perturbation theory [25]:

$$t_{max}=(N/\rho_N c_s^3)^{1/3}=\frac{(N/\rho_N)^{1/3}}{\left[\left(\frac{\partial P}{\partial \rho_N}\right)_T+\frac{VT}{\rho_N}\left(\frac{\partial P}{\partial T}\right)_V^2\left(\frac{\partial T}{\partial U}\right)_V^2\right]^{1/2}}. \tag{4}$$

Table I gives the calculated sound speed, c_s and t_{max} at $T^*=2.17$ and from these values it would appear that the noticeable oscillation in the $\rho_N^*=0.55$ data in Fig. 2 after 800 correlation time steps is likely due to corruption caused by the influence of boundary conditions.

Alder measured the formation time of the long-time tail in terms of the Enskog theory [23] collision mean free time (τ_E) for a system of hard spheres of diameter d at a reduced density $\rho_N d^3$ which is given by

$$\tau_E=\frac{(1-\frac{1}{6}\pi\rho_N d^3)^3}{4\rho_N d^2[\pi\langle \underline{v}(0)\cdot\underline{v}(0)\rangle]^{1/2}(1-\frac{1}{12}\pi\rho_N d^3)}. \tag{5}$$

Following the ideas of hard sphere perturbation theory and assuming $\rho_N\sigma^3=\rho_N d^3$ we can calculate τ_E to give an estimate of the number of collisions occurring before the transverse hydrodynamic (or vortex) mode dominates in our systems. The Enskog time t_E is 0.16 ps at $\rho_N^*=0.55$ and 0.35 ps

TABLE I. Speed of sound, c_s, and maximum correlation time, t_{max} for a system of CWA particles calculated by means of CWA hard sphere perturbation theory. The value in brackets is from Ref. [16].

Reduced density (ρ^*)	Sound speed c_s (in units of $\sigma/\Delta t$)	Maximum correlation time t_{max} for 4000 particles (in units of Δt)
0.05	0.301	4414
0.15	0.363	2228
0.25	0.439	1772
0.35	0.529	1315
0.45	0.631(0.621)	1012
0.55	0.759	787
0.65	0.906	623
0.75	1.089	494

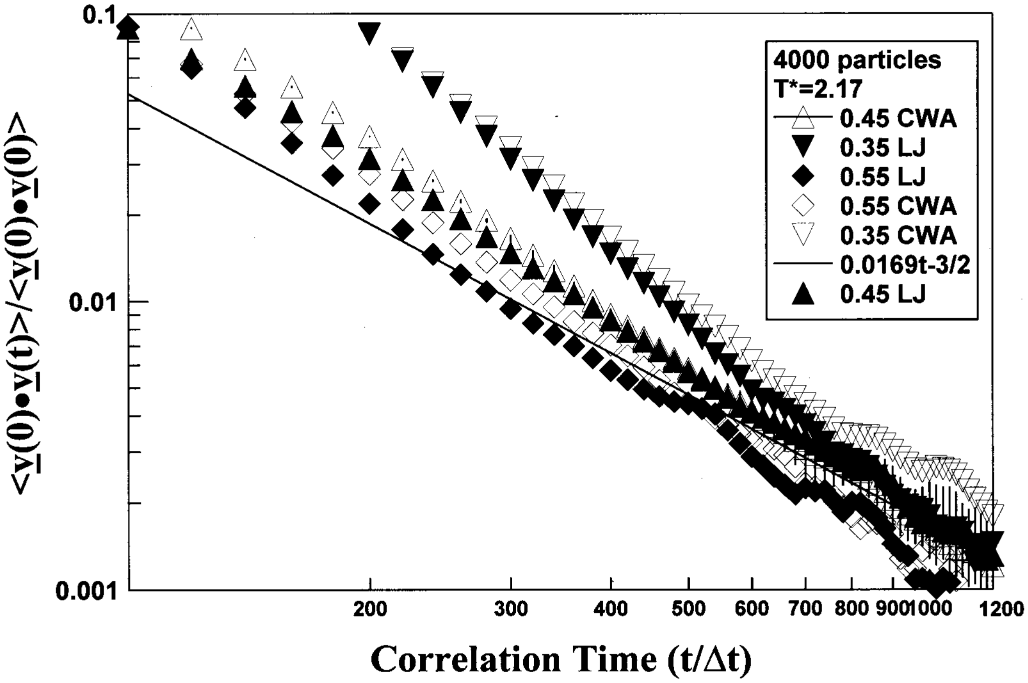

FIG. 3. A comparison of $c(t)$ for the CWA and LJ 12-6 systems at various densities for $N=4000$ and $T^{*}=2.17$.

at $\rho_N^{*}=0.35$ for argon and from Fig. 2 we estimate that the long-time tail is apparent after approximately 450 (4.4 ps or $15.5\tau_E$) and 550 (5.4 ps or $27.5\tau_E$) time steps, respectively, for the 0.55 and 0.35 density data. For comparison Alder obtained a time of about $20\tau_E$ for the appearance of the long-time tail for hard spheres at $\rho_N\sigma^3=0.47$.

Further data for $\rho_N\leqslant 0.15$ (not shown here) indicated that $c(t)$ may be well approximated by an exponential decay over the entire time regime considered here indicating that for these densities particle-fluid momentum transfer occurs largely through longitudinal hydrodynamic modes and vortex formation is not sustained. Hence if such formation occurs at these low densities then our data suggests that they must exist at considerably greater times than we are able to make accurate estimates of $c(t)$.

For $\rho_N^{*}>0.55$ within the accuracy of our calculations we could not observe a long-time, nonexponential decay of $c(t)$. This may be because it does not exist at these densities or that other effects are tending to mask the long-time analytic behavior, e.g., insufficient precision, $t_{\max}$ being too small or masking by dynamical effects such as backscattering. It would thus appear that the observation of nonexponential long-time tails in $c(t)$ for simple fluids by the MD method may, at present, only be readily made for moderate reduced densities of around 0.45.

To illustrate the effect of interparticle attraction we compare, in Fig. 3, the decay of $c(t)$ for CWA and LJ particles, in the reduced density range 0.35 to 0.55. The results show that the decay of $c(t)$ is remarkably similar in either case indicating the effect of interparticle attraction on the formation of transverse hydrodynamic modes is minimal under the conditions studied here. This is perhaps not surprising at this temperature since the properties of the CWA and LJ systems are almost identical at high temperatures and quite similar in general. However, significant lowering of the temperature at densities where long-time tails are observable for CWA particles would put the system in the unstable two phase region of the LJ phase diagram and, therefore, be of no physical relevance. On the other hand, significant increase of density and simultaneous decrease in temperature would lead to strengthening of the effects such as backscattering, which, judging from our results on the CWA potential, would mask the effect of long-time tails in $c(t)$. Thus, there would seem to be little point in exploring these conditions.

Effect of varying particle/fluid mass ratio

Experimental observation of the long-time tail in the VAF for molecular fluids has only been made indirectly [10–15]. Direct measurements of the effect seems to be only possible, at least at present, for the self-motion of large colloidal or ''Brownian'' particles suspended in a fluid of molecular sized particles [10,12], where the ratio α of the mass of tagged particles, m_t to that of the background fluid particles, m_f is extremely large, i.e., effectively α is infinite. By contrast in MD simulations to date $\alpha=1$. Thus, it is important to investigate the effect that changing α has on the form of $c(t)$. In particular it is important to see if the long-time tail still exists and, if so, whether it has the same time dependence as when $\alpha=1$.

Pomeau [34] has studied the general case of the long-time decay of $c(t)$ for N_t tagged particles of mass m_t in a binary mixture of N_f other particles of mass m_f (i.e., $N=N_t+N_f$) using the Landau–Placzeck theory. The expression for $c(t)$ as $t\rightarrow\infty$ is rather complex but simplifies greatly in the limit where the concentration of tagged particles to the surround-

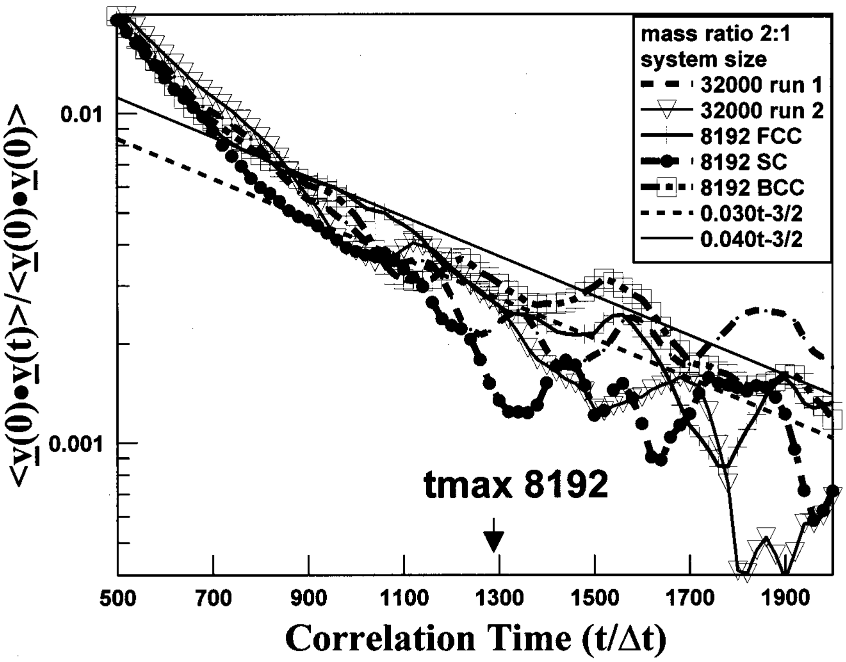

FIG. 4. A log–log plot of $c(t)$ for a CWA system with $T^*=2.17$ and $\rho^*=0.45$ for mass ratio of tagged to fluid atoms α of 2 for various systems compared with the equation $At^{-3/2}$.

ing fluid is low. In this low concentration limit (in which the parameter γ defined below tends to zero) $c(t)$ in the binary mixture of tagged/fluid particles [34] is given by

$$c(t)=\lim_{\substack{t\to\infty\\ \gamma\to 0}}\frac{2}{3\left(\rho_N^t+\dfrac{\rho_N^f}{\alpha}\right)(4\pi(D_s(\alpha)+v))^{3/2}}t^{-3/2}. \quad (6)$$

Here ρ_N^t is the number density of the tagged particles, ρ_N^f is the number density of the fluid particles, $\alpha=m_t/m_f$ the ratio of the mass m_t of the tagged particles to the mass m_f of the fluid particles, $D_s(\alpha)$ is the self-diffusion of the tagged particles in the system and $\gamma=\rho_N^t(\rho_N^t+\rho_N^f)\to 0$ constitutes the low concentration limit.

Now for a tracer particle identical to the other particles in the system, i.e., $\alpha=1$ we have from Eq. (6),

$$c(t)\to 2/[3\rho_N\{4\pi(D_s+v)\}^{3/2}]t^{-3/2} \quad (7)$$

which is identical to the result given by (3).

For the case $\alpha\to\infty$ if one assumes that $m_t\gg m_f$ and $N_t\ll N_f\approx N$, i.e., $\rho_m^t\ll\rho_m^f$ and $v=v_f\gg D_s(\alpha)$ and then (6) reduces to

$$c(t)\to 2m_t/[\{3\rho_m^f(4\pi v_f)^{3/2}\}]t^{-3/2} \quad (8)$$

which is the result for a massive particle suspended in a fluid of light particles obtained from the macroscopically based Boussinesq equation [12,33] that describes the nonsteady motion of a sphere of radius R in a fluid of mass density ρ_m^f and kinematic viscosity v_f.

Furthermore, Eq. (6) predicts that the ratio of the magnitude of the long-time tail for a mixture to that for a single component system A is given by

$$A=[N/\{N_t+N_f/\alpha\}][\{D_s+v\}/\{D_s(\alpha)+v\}]^{3/2}. \quad (9)$$

So if we assume that $D_s=D_s(\alpha)$ and $N_t\ll N_f=N$ then the expression for A reduces to

$$A=m_t/m_f \quad (10)$$

and thus the magnitude of the long-time tail is predicted to increase as the ratio of the mass of the tracer particles to the mass of the background fluid particles increases.

In order to test this theory for intermediate values of the mass of the tagged particles to that of the background particles we have simulated a system of N particles, all having the same diameter σ and interaction potential, but N_t of which are tagged particles of mass greater than that of the other $N-N_t$ fluid particles. To supplement our data for $\alpha=1$ we made a series of runs using either an 8192 or 32 000 particle system of which 1000 were tagged particles with particle/fluid mass ratio of 1:1, 2:1, and 4:1 and a reduced density and temperature of 0.45 and 2.17, respectively (i.e., we simulated 1000 heavy tracer particles in a bath of either 7192 or 31 000 fluid particles). Note that $t_{\max}=1285$ for $N=8192$ and 2024 for $N=32\,000$.

Log–log plots of $c(t)$ verses time, Figs. 4 and 5, clearly displays long-time behavior consistent with a tail of the form $At^{-3/2}$ and a prefactor A which increases as the mass ratio increases in accord with the above theory. The data also shows that the time for the appearance of this effect increases as α increases.

In order to further test the predictions of Pomeau's theory we adopted the procedure used by Levesque and Ashurst to estimate A. For $\alpha=1$, they assumed that for $t>t_{\rm long}c(t)=At^{-3/2}$ and found the value of $A(A_{\rm fit})$ by fitting to their computer results. They then computed $A(A_{\rm calc})$ theoretically from Eq. (7), assuming that v was equal to the value for the bulk fluid obtained from an independent nonequilibrium MD simulation and that D_s could be obtained from

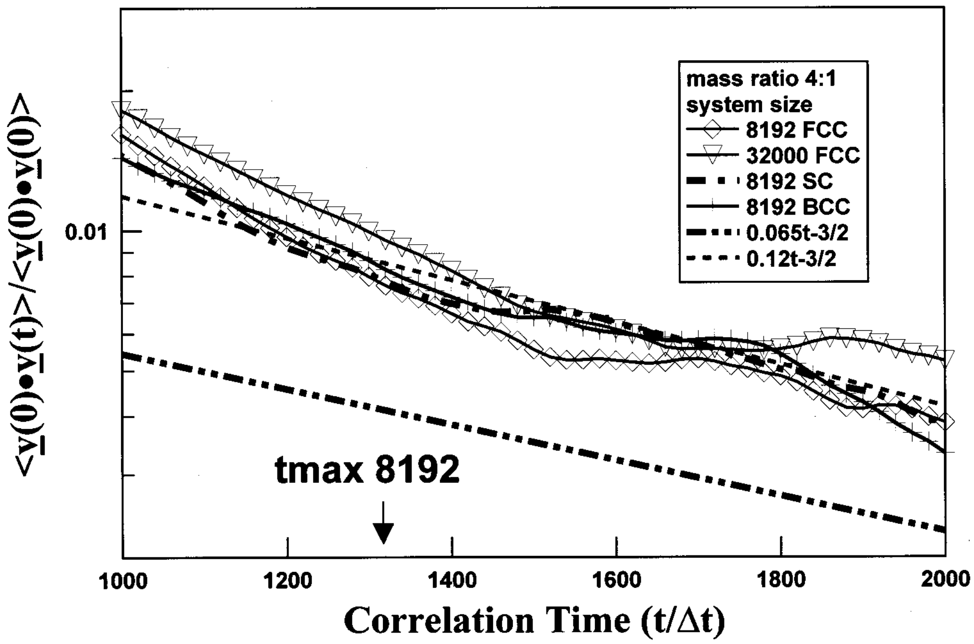

FIG. 5. A log–log plot of $c(t)$ for a CWA system with $T^*=2.17$ and $\rho^*=0.45$ for mass ratio of tagged to fluid atoms α of 4 for various systems compared with the equation $At^{-3/2}$.

$$D=D_{\rm short}+D_{\rm long}=1/3\int_0^{t_{\rm long}}\langle \underline{v}(0)\cdot\underline{v}(t)\rangle dt + 1/3\int_{t_{\rm long}}^{\infty}\langle \underline{v}(0)\cdot\underline{v}(t)\rangle dt, \qquad (11)$$

where the first term was found by integrating their computed values of $c(t)$ and the second term was evaluated analytically from their fitted values of $At^{-3/2}$. They found agreement between the $A_{\rm fit}$ and $A_{\rm calc}$ to within the combined uncertainties of both procedures (20%) and that $A_{\rm fit}>A_{\rm calc}$.

We have applied the same procedure to analyze our data for $c(t)$ and find the following results shown in Table II from which we may conclude in agreement with Levesque and Ashurst that for $\alpha=1$ $A_{\rm fit}>A_{\rm calc}$ but that the agreement between $A_{\rm calc}$ and $A_{\rm fit}$ is very reasonable. However for $\alpha>1$ the agreement is not very good although A does increase as α increases in agreement with theory. The disagreement between the fitted and calculated values of A may be due to a variety of causes, e.g., uncertainties in the MD values of $c(t)$, the need to use modified values of the transport coefficients $D(\alpha)$ and v appearing in (6) (i.e., whether to use ''dressed'' or ''bare'' values) or factors neglected in deriving (6). We have also calculated A using only the short-range contribution to $D(\alpha)$ in Eq. (11) which makes little difference to the value of A and finally we used Eq. (8) appropriate as $\alpha\to\infty$ which gives better agreement with the MD data for $\alpha=4$ only, see Table II.

Thus, we may conclude that long-time tails do exist for tracer systems with $\alpha>1$, their form is consistent with the form $At^{-3/2}$ and the prefactor A increases as α increases as predicted by Pomeau [34]. However, more work is clearly needed in order to make independent theoretical estimates of the prefactor A for $\alpha>1$ [35].

Lifetime of the long-time tails

As discussed earlier an estimate of the maximum correlation time, which can be used in this study, is given by $t_{\rm max}\sim(N/\rho_N c_s^3)^{1/3}$. Thus the system size ($N$) must be large enough to allow large correlation times to be observed. The devia-

TABLE II. The values of A obtained by fitting $At^{-3/2}$ to $c(t)$ for $t>t_{\rm long}$ and those obtained from Eq. (6). Data in the third row using the data from Ref. [16].

α [a]	N_t	N	$N_{\rm run}$ [b]	$t_{\rm long}$ [c]	$A_{\rm fit}$ [d]	$A_{\rm calc}$ [e]	$A_{\rm calc}$ [f]	$A_{\rm calc}$ [g]
1	4000	4000	12	460	0.0190	0.0169	0.0178	0.0337
1	1000	32 000	1	460	0.0190	0.0169	0.0177	0.0337
1 [h]	4000	4000	2	460	0.0200	0.0168	0.0177	0.0337
1	1000	8192	1	460	0.0190	0.0168	0.0178	0.0337
2	1000	32 000	2	900	0.043	0.034	0.0354	0.0654
2	1000	8192	3	900	0.040	0.032	0.0330	0.0601
4	1000	32 000	1	1200	0.13	0.065	0.0683	0.123
4	1000	8192	3	1200	0.12	0.056	0.0566	0.0987

[a] m_t/m_f.
[b] Number of runs used.
[c] Units of Δt.
[d] Value of the prefactor A in $At^{-3/2}$ obtained by fitting to the MD $c(t)$ data.
[e] Value of A obtained from Eq. (6) using $D_s(\alpha)=D_{\rm short}+D_{\rm long}$.
[f] Value of A obtained from Eq. (6) using $D_s(\alpha)=D_{\rm short}$.
[g] Value of A obtained from Eq. (6) using $D_s(\alpha)=0$.
[h] Using the data from Ref. [16].

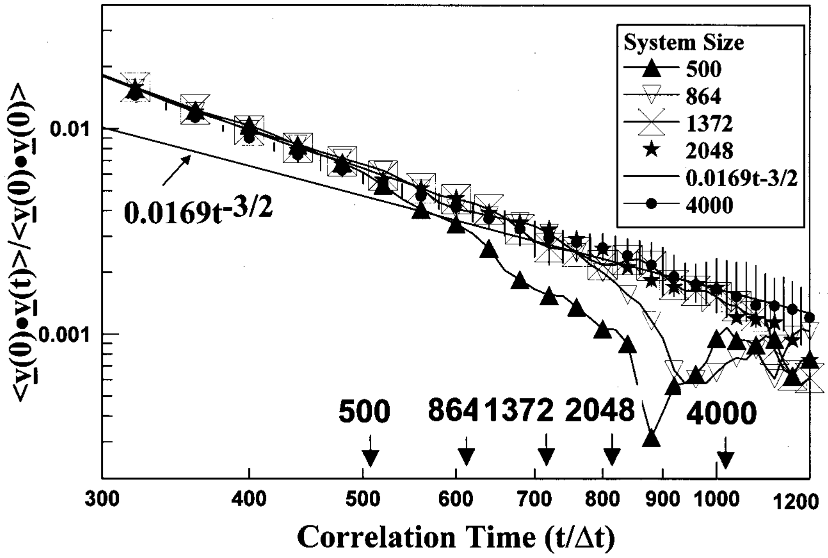

FIG. 6. As for Fig. 1 but with varying numbers of atoms N. The arrows on the correlation time axis indicate the approximate value of the time $t_{\max}$ beyond which the effects of the periodic boundaries may influence the value of $c(t)$.

tion from $t^{-3/2}$ behavior in the decay of the velocity autocorrelation function, either due to destruction of the vortex or due to other processes dominating, must occur before the correlation time $t_{\max}$, otherwise the deviation may well be due to a corruption of the velocity autocorrelation function caused by the periodic boundary conditions.

Figures 6 and 7 give the normalized velocity autocorrelation $c(t)$ as a function of correlation time t (in units of the MD time step, Δt) for $N=500$, 864, 1372, 2048, 4000, and 32 000, respectively, with $\alpha=1$ for which $t_{\max}=506$, 607, 708, 810, 1012, and 2024, respectively. The error bars (using the previously discussed method) shown in these figures were used as an indicator to determine when the decay of $c(t)$ has statistically deviated from $t^{-3/2}$.

Figure 6 shows that for the 500 particle system, a long-time tail is not observed, this was also found in simulations with $N<500$ particles. Alder's results for hard spheres [1] showed that a $t^{-3/2}$ decay in $c(t)$ was observed for 500 hard spheres, in contrast to the behavior of these soft spheres. Also for $N\leqslant 500$ the correlation time at which $c(t)$ initially deviates from that for systems of larger numbers of particles is very close to $t_{\max}$ and the deviation is not an abrupt process. However, for $500<N\leqslant 4000$ significant deviation of $c(t)$ from the $t^{-3/2}$ behavior, if it occurs, is for correlation times t greater than $t_{\max}$ and also does not happen abruptly as can clearly be seen from Fig. 6. This suggests that the effect of periodic boundary conditions (probably primarily due to longitudinal modes) is not a sudden, drastic process but occurs slowly in time for $t>t_{\max}=(N/\rho_N c_s^3)^{1/3}$.

Finally, in order to further investigate the question of the finite lifetime in Fig. 7 we compare $c(t)$ for a 4000 and 32 000 particle system under the same conditions as Fig. 6. However, this shows that there is no disappearance of the long-time tail for times twice as long as for our other simulations.

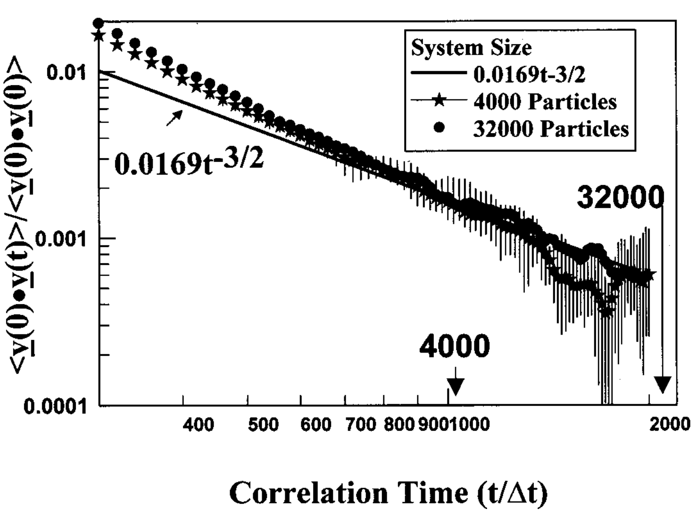

FIG. 7. As for Fig. 6 but for $N=4000$ and $N=32\,000$.

CONCLUSION

In order to complement previous work on hard disk and hard sphere systems we have studied the formation of long-time, nonexponential tails in the velocity autocorrelation function for systems of particles interacting via a continuous potential function.

For system sizes simulated here the observation of non-exponential long-time tails in $c(t)$ for simple fluids is only routinely directly observable for moderate reduced densities of around 0.45. If they do occur at considerably lower reduced densities (around 0.15) then they must occur at considerably greater times than we can currently simulate and if they occur at high reduced density then they must be masked by other effects viz. insufficient precision, $t_{\max}$ being too small and/or the masking effect of other physical processes on $c(t)$ such as backscattering.

Comparing the decay of $c(t)$ for CWA and LJ particles, in the density range 0.35 to 0.55 at $T^*=2.17$ shows that this decay is similar in either case which indicates the effect of interparticle attraction having a minimal influence under the conditions studied here. However, it is also argued that it will be very difficult to study the long-time tail under other physically realistic conditions for a LJ potential.

We investigated systems where the ratio of the mass of tagged particles to background particles α is greater than one and our results indicate the following:

(i) The long-time decay of the VAF in these cases clearly indicates a long-time, nonexponential tail which is consistent with the form $At^{-3/2}$.

(ii) The time for the appearance of this effect increases as α increases.

(iii) The magnitude of the effect increases as α increases.

(iv) More work needs to be done on finding an independent theoretical estimate of the prefactor A.

Points (ii) and (iii) suggest that the effect of the mass ratio of tagged particles to fluid particles is a fruitful area for future research as the effect is at longer times and is much larger than for a one component fluid even for a mass ratio of only 2. This means that scattering experiments on heavy atoms or small colloidal particles suspended in a simple fluid may well be able to directly observe the long-time tails in $c(t)$.

Finally for a system of soft repulsive spheres at moderate density we have shown that if the number of particles $N < 864$, a long-time $t^{-3/2}$ tail in the VAF is not observed, but that it does occur if $N \geqslant 864$. Furthermore, significant deviation in $c(t)$ from $t^{-3/2}$ behavior for these systems occurs only at correlation times greater than the time, $t_{\max}$ and occurs slowly over time. We are unable to determine if the long-time tail has a finite duration and were, thus, unable to see if the vortex field which is primarily responsible for the long-time tail has a finite lifetime.

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