Long-time behavior of the velocity autocorrelation function at low densities and near the critical point of simple fluids

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Numerous theoretical and numerical works have been devoted to the study of the algebraic decrease at large times of the velocity autocorrelation function of particles in a fluid. The derivation of this behavior, the so-called long-time tail, generally based on linearized hydrodynamics, makes no reference to any specific characteristic of the particle interactions. However, in the literature doubts have been expressed about the possibility that by numerical simulations the long-time tail can be observed in the whole fluid phase domain of systems in which the particles interact by soft-core and attractive pair potentials. In this work, extensive and accurate molecular-dynamics simulations establish that the predicted long-time tail of the velocity autocorrelation function exists in a low-density fluid of particles interacting by a soft-repulsive potential and near the liquid-gas critical point of a Lennard-Jones system. These results contribute to the confirmation that the algebraic decay of the velocity autocorrelation function is universal in these fluid systems.

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I. INTRODUCTION

The long-time tail of the velocity autocorrelation function (VAF), first discovered by the pioneering work of Alder and Wainwright [1] using molecular-dynamics (MD) simulations of elastically colliding hard disks and spheres, came as a complete surprise. This result was in contradiction with the prediction of an exponential decay of the VAF supported by the explicit solutions of almost all known solvable models, such as the linearized Boltzmann equation [2] and the Fokker-Planck equation [3].

Alder and Wainwright found that the VAF long-time tail was well fitted by the analytic form $\alpha t^{-3/2}$. They explained this unexpected behavior by a simple hydrodynamic model, describing the motion of a hard disk or sphere by that of a circular or spherical particle in a continuum fluid formed by the surrounding disks or spheres. The forward motion of the particle gives rise in the fluid to a vortex, whose size is approximately 3 particle diameters. This vortex mode predominates at long times, leading to the long-time tail $\alpha t^{-3/2}$ of the VAF.

For fluid systems and without reference to the details of the particle interactions, Ernst *et al.* [4,5] were able to derive the asymptotic time behavior of the VAF by using the linearized Navier-Stokes equation and assuming a local statistical equilibrium in every point of the system. This latter condition means that, at a mesoscopic scale ($\sim$1000 particles), the system properties can be described in terms of density, temperature, or transport coefficients [6]. For systems of hard disks and hard spheres, Dorfman and Cohen [7] derived the long-time tail of the VAF from kinetic theory. They showed that a sequence of correlated binary collisions, *ring collisions*, is the main molecular process responsible for the vortex formation leading to the slow decay of the VAF.

Light-scattering experiments [8,9] or diffusive wave spectroscopy [10,11] indicate the presence of the long-time tail of the VAF of colloidal particles immersed in a fluid. These experimental results agree with the theoretical description of the Brownian particle motion [12,13]. Neutron scattering experiments [14,15] also indicate that, in atomic liquids, the VAF decreases algebraically at large times. However, present experimental evidence of the VAF long-time tail is restricted to a few types of liquids (colloids, alkaline liquids, and liquid argon) and a few thermodynamic states.

Furthermore, in MD simulations, doubts remain about the possibility of observing the long-time tail in a low-density fluid of soft-repulsive particles [16] and in a Lennard-Jones (LJ) fluid in thermodynamic states close to the liquid-vapor critical point [17]. According to the simulation results [16] it seems that the nonexponential decrease of the VAF with time is easily observed only for systems at moderate densities, since, in this work, the $\alpha t^{-3/2}$ tail is not found at low densities. The simulations of Ref. [17] indicate that, for a LJ system, the VAF decays at long times in agreement with the theoretical exponent $-3/2$ only at high densities, and that, along an isochore close to the critical density, the VAF decreases with an exponent equal to -3.

Motivated by these apparent disagreements between these simulation results and the theoretical prediction of the VAF asymptotic time behavior, it is shown in this paper, by means of accurate and extensive MD simulations, that the VAF exhibits the predicted $\alpha t^{-3/2}$ power-law decay for a fluid of soft-repulsive particles at low densities and for a LJ fluid close to the critical point, confirming the theoretical claim of a universal power-law tail of the VAF in all the thermodynamic states of simple fluids [5], independent of the particle interactions.

In Sec. II we give a theoretical overview, and in Sec. III the MD simulation details. Section IV presents and discusses

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the simulation results for the VAF. Conclusions are presented in Sec. V.

II. THEORETICAL OVERVIEW

The expression of the velocity autocorrelation function for a three-dimensional (3D) fluid at large times is given by [4]

$$\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle = \frac{2k_BT}{\rho m}\frac{1}{[(4\pi(D+\nu)t\ ]^{3/2}} = \alpha t^{-3/2}, \tag{1}$$

where $\mathbf{v}$ is the particle velocity vector at time t, k_B is the Boltzmann's constant, T is the temperature, m is the mass of the particles, ρ is the particle density, and D is the self-diffusion coefficient. Here, ν, the kinematic viscosity of the fluid, is equal to $\eta/(m\rho)$, η being the shear viscosity. The angular brackets indicate an equilibrium ensemble average.

The derivation of Eq. (1) is made under the general assumption that the approach of nonequilibrium distributions to local equilibrium distributions evolves at long times according to the laws of hydrodynamics [4]. The following arguments, which summarize this derivation, are taken from [18,19]. We consider a d-dimensional system of N particles in equilibrium, containing a tagged particle with an initial velocity $\mathbf{v}(0)=\mathbf{v}_0$. From this initial nonequilibrium state, the evolution of the system towards equilibrium is supposed to be described by means of linearized hydrodynamic equations

$$\frac{\partial P(\mathbf{r},t)}{\partial t} = D\nabla^2 P(\mathbf{r},t), \tag{2}$$

$$\frac{\partial \mathbf{u}_\perp(\mathbf{r},t)}{\partial t} = -\nu\nabla\times[\nabla\times\mathbf{u}_\perp(\mathbf{r},t)], \tag{3}$$

where $P(\mathbf{r},t)$ is the probability density for the tagged particle to be at position $\mathbf{r}$ at time t, and $\mathbf{u}_\perp(\mathbf{r},t)$ is the transverse part of the velocity density field. The longitudinal part of the velocity density field does not appear in the equations because its contribution to the velocity autocorrelation decays exponentially [19].

From the Fourier transforms of Eqs. (2) and (3), it is shown that

$$\tilde{P}(k,t) = e^{-Dk^2t}, \tag{4}$$

$$\tilde{\mathbf{u}}_\perp(\mathbf{k},t) = \left(\mathbf{v}_0 - \frac{(\mathbf{v}_0\cdot\mathbf{k})\mathbf{k}}{k^2}\right)e^{-\nu k^2 t}. \tag{5}$$

With the assumption that, at long times, the tagged particle has the same average velocity as its neighboring particles, we have

$$\mathbf{v}(t) = \int d^dr P(\mathbf{r},t)\frac{1}{\rho}\mathbf{u}_\perp(\mathbf{r},t) = \frac{1}{\rho}\frac{1}{(2\pi)^d}\int d^dk\tilde{P}(k,t)\tilde{\mathbf{u}}_\perp(-\mathbf{k},t). \tag{6}$$

The insertion of Eqs. (4) and (5) into Eq. (6) gives

$$\mathbf{v}(t) = \frac{1}{\rho}\frac{1}{(2\pi)^d}\int d^dk\left(\mathbf{v}_0 - \frac{(\mathbf{v}_0\cdot\mathbf{k})\mathbf{k}}{k^2}\right)e^{-(\nu+D)k^2t} = \frac{1}{\rho}\frac{d-1}{d}\frac{1}{[(4\pi(D+\nu)t\ ]^{d/2}}\mathbf{v}_0, \tag{7}$$

where the $(d-1)/d$ coefficient comes from the fact that only the transverse part of the velocity field contributes at large times.

Averaging over $\mathbf{v}_0$ with respect to the Maxwell-Boltzmann velocity distribution

$$\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle = \frac{1}{\rho}\frac{d-1}{d}\frac{1}{[(4\pi(D+\nu)t\ ]^{d/2}} \times \int d^dv_0\left(\frac{m}{2\pi k_BT}\right)^{d/2} v_0^2 e^{-mv_0^2/2k_BT}, \tag{8}$$

leads to the expression of the VAF given by Eq. (1)

$$\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle = \frac{(d-1)k_BT}{m\rho}\frac{1}{[(4\pi(D+\nu)t\ ]^{d/2}}. \tag{9}$$

The derivation of Eq. (1) from kinetic theory, valid for particle systems with short-range repulsive potentials such as the hard disk or sphere systems, is more sophisticated [7,20,21]. As mentioned above, the vortex mode responsible for the long-time tail of the VAF finds its origin in so-called ring collisions, a sequence of correlated binary collisions where the initial momentum of the tagged particle is transferred to the surrounding particles in a ringlike motion. It can even be found from more complex derivations [20] that the $t^{-3/2}$ long-time behavior of the VAF is the first term in an infinite series of general order t^{-l}, where $l=1/2^n-2$ with n integer $\geqslant 1$ and $-2\leqslant l\leqslant -3/2$.

In the expression of the VAF derived by kinetic theory, the so-called "bare" transport coefficients D_0 and ν_0 appear [7], corresponding to a bare value α_0 of the long-time tail amplitude α. D and ν are computed by integrating the time autocorrelation functions of particle velocities and stress tensor components; the bare transport coefficients are estimates of D and ν in which, in these integrals, the contribution of the long-time tails is missing. The values of D_0 and ν_0 are close but not identical to those of D and ν of the hydrodynamical approach. The numerical simulations compute a long-time tail with a bare amplitude for times between 10 and 50 mean collision times; it is only for longer times that the hydrodynamic amplitude α is obtained [19].

In summary, the asymptotic behavior of the VAF has been determined either by means of hydrodynamical assumptions, independent of the details of the particle interactions, or by kinetic theory for hard-core particles. Both approaches predict the $\alpha t^{-3/2}$ long-time tail of the VAF.

III. MOLECULAR DYNAMICS SIMULATIONS

To determine the long-time behavior of the VAF by MD simulation, we have to be sure that there is no influence of the periodic boundary conditions of the simulation cell on the VAF computation [21,22]. To achieve this goal, we

choose a maximum correlation time t_{max} smaller than the time needed by a sound wave to cross the entire periodic cell, i.e.,

$$t_{max} \leqslant (N/\rho c_s^3)^{1/3}, \tag{10}$$

where c_s is the speed of sound in the fluid. It is expected that, at times larger than t_{max}, the VAF becomes strongly influenced by the sound modes [22]. Thus, before computing the VAF for any system of an arbitrary, but reasonably large number of particles ($N>500$), it is first necessary to estimate the velocity of sound c_s at the state point we want to study from the formula [23],

$$c_s = \sqrt{\frac{1}{m}\left(\frac{\partial P}{\partial \rho}\right)_T + \frac{T}{m\rho^2\left(\frac{\partial E}{\partial T}\right)_V}\left(\frac{\partial P}{\partial T}\right)_V^2}, \tag{11}$$

where P is the pressure, E is the total energy per particle, and V is the volume. Once the value of c_s is obtained, the maximum correlation time t_{max} is estimated by Eq. (10).

To test the theoretical prediction $\alpha t^{-3/2}$ of the behavior of the VAF at long times against the simulation results, we have to make an estimate of α, which depends on the diffusion coefficient and kinematic viscosity. We use the Green-Kubo integral formula [24] to calculate the self-diffusion coefficient,

$$D = \frac{1}{3N}\sum_{i=1}^{N}\int_0^\infty \langle \mathbf{v}_i(0)\cdot\mathbf{v}_i(t)\rangle dt = \frac{k_B T}{m}\int_0^\infty dt F_{VAF}(t), \tag{12}$$

where the average over all the particles is used to reduce the statistical uncertainty on the normalized velocity autocorrelation function $F_{VAF}(t)=[\Sigma_i\langle \mathbf{v}_i(0)\cdot\mathbf{v}_i(t)\rangle]/[\Sigma_i\langle \mathbf{v}_i(0)\cdot\mathbf{v}_i(0)\rangle]$. The kinematic viscosity ν is obtained through the shear viscosity η given by [24],

$$\eta = \lim_{t_u\to\infty}\eta(t_u) = \frac{1}{k_B T V}\int_0^{t_u}\langle \sigma^{xz}(t)\sigma^{xz}(0)\rangle dt, \tag{13}$$

where σ^{xz} is an off-diagonal element of the stress tensor

$$\sigma^{xz} = \sum_{i=1}^{N}\left(mv_{ix}v_{iz} + \frac{1}{2}\sum_{j\neq i}^{N} x_{ij}F_{ij}^z\right), \tag{14}$$

with F_{ij}^z being the z component of the force between particles i and j, and x_{ij} the x component of the distance vector joining particles i and j.

In this paper, we use the reduced quantities $T^*=k_BT/\epsilon$, $\rho^*=\rho\sigma^3$, $t^*=t\sqrt{\epsilon/m\sigma^2}$, and $r^*=r/\sigma$, where ϵ and σ are the energy and length parameters of the LJ potentials $v_{LJ}(r)$. The unit of time is thus $\tau_0=\sqrt{m\sigma^2/\epsilon}$.

We have considered mainly two systems: a low-density system, at $\rho^*=0.2$ and $T^*=2.07$, of 32 000 particles interacting via a soft-repulsive potential,

$$v(r) = v_{LJ}(r) + \epsilon = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \epsilon \quad \text{for } r \leqslant 2^{1/6}\sigma$$
$$= 0 \quad \text{for } r > 2^{1/6}\sigma, \tag{15, 16}$$

and a LJ system near the liquid-vapor critical point at $\rho^*=0.3$ and $T^*=1.35$ of 10 976 particles interacting by a LJ potential truncated at a cutoff distance equal to $r^*=6.5$. This value of the cutoff is the same as that used in the work of Meier *et al.* [17], in which a t^{-3} behavior of the VAF was reported near the critical point. In addition, the VAF of a LJ system at $\rho^*=0.3$ and $T^*=1.98$ has been calculated. This computation was done to establish that the time dependence of the VAF asymptotic decay for states of a LJ system near and far from the critical point was identical within the statistical error. Such a comparison allows us to show that the long-time decay of the VAF near the critical point is not misinterpreted.

The simulations were realized at constant energy using the standard Verlet algorithm with a time step $\Delta t^*=0.003$ for the soft-sphere fluid and $\Delta t^*=0.001$ for the LJ fluid near the critical point to insure the stability of the total energy value to within 0.01%. The simulations were carried out for 100 000 equilibration time steps followed by 10×10^6 time steps, during which the VAF or the stress-correlation function were computed over blocks of $2000\Delta t^*$ to allow an evaluation of the statistical errors.

For the soft-repulsive particle system at $\rho^*=0.2$ and $T^*=2.07$, the computed thermodynamic properties are $P^*=0.632$, $E^*=3.242$, and $c_s=2.682\sigma/\tau_0$ and, near the LJ critical point at $\rho^*=0.3$ and $T^*=1.35$: $P^*=0.153$, $E^*=-0.15$, and $c_s=1.45\sigma/\tau_0$. The thermodynamic state of the LJ system at $\rho^*=0.3$ and $T^*=1.97$ corresponds to $P^*=0.478$, $E^*=1.05$, and $c_s=2.48\sigma/\tau_0$. From Eq. (10), we find the maximum correlation time t_{max}^* equal to 20.2 in the first case, 22.8 near the LJ critical point, and 13.3 for the LJ system at $\rho^*=0.3$ and $T^*=1.97$. The derivatives on P and E in Eq. (11) were computed from canonical ensemble MD simulations performed at densities and temperatures close to those of the considered thermodynamic states.

IV. VELOCITY AUTOCORRELATION RESULTS

We give in Fig. 1 the normalized VAF multiplied by $t^{3/2}$ for two considered systems. In such a plot the time domain where the VAF decays as $t^{-3/2}$ appears as a constant plateau within the statistical error. The maximum correlation times are those determined by c_s. The statistical error on the normalized VAF is estimated to be $\pm2\times10^{-5}$, which gives a relative error of 10% on the asymptotic part of the VAF. The data clearly indicate the existence of $t^{-3/2}$ behavior in both cases.

For the soft-particle system, the asymptotic tail appears above $t^*=10$. This explains why, in the work of McDonough *et al.* [16], it was not possible to observe the long-time tail at a density $\rho^*=0.25$ because it occurs at larger times than the maximum correlation time considered in this work, which is equal to ~5. Noticing that the system size is equal to 4000 particles, it was not possible to consider correlation times larger than 7 due to the coupling between diffusion and sound modes [22].

Figure 2 shows a log-log plot of the VAF versus reduced time for the soft-repulsive fluid. A linear fit of the data in the

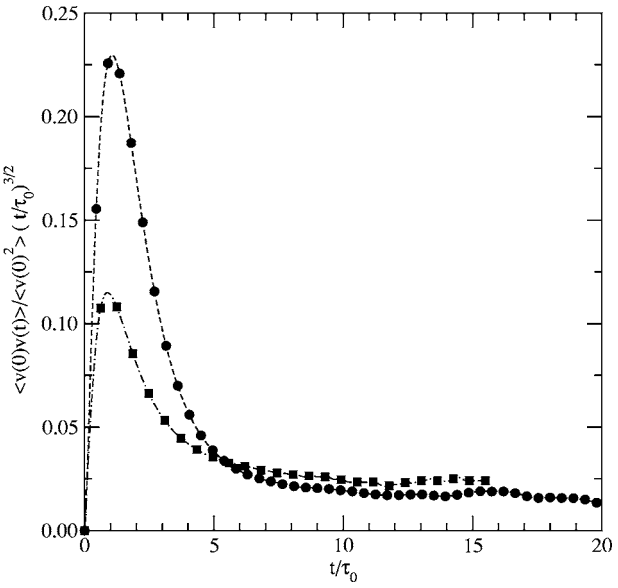

FIG. 1. The normalized VAF multiplied by $(t/\tau_0)^{3/2}$ vs time in reduced unit t/τ_0. The dashed-dotted line and black squares: the system of soft-repulsive particles at $\rho^*=0.2$ and $T^*=2.07$; the dashed line and black circles: LJ system at $\rho^*=0.3$ and $T^*=1.35$.

range $11<t^*<18$ gives: $\ln F_{VAF}(t)=(-4.05\pm0.08)-(1.50\pm0.03)\ln t^*$, leading to a value of $\alpha_{fit}=0.0174\pm0.0015$. In order to validate the theoretical value of α, we have computed the diffusion coefficient from the integral of the VAF [cf. Eq. (12)] up to $t^*=11$, in agreement with the remark quoted above [19]. The value found was $D^*=0.294\pm0.002$. Since the long-time tail begins at $t^*=11$, a contribution equal to ~0.015 should add to this value of D^*. A similar computation was done for the kinematic viscosity. Figure 3 shows the stress-correlation function Eq. (14) computed up to a correlation time t_u equal to $5\tau_0$. Beyond this time, the stress-correlation function is zero within the statistical error, larger than that of the $F_{VAF}(t)$ by a factor of $\sim\sqrt{N}$, i.e., almost two orders of magnitude. By using $t_u=5\tau_0$ in Eq. (13), a contribution to η can be missing, due to the long-time part of the stress-correlation function. This contribution can account for about 15–20% of the η value as was shown [25]. In Fig. 3, the plot of the integral $\eta(t_u)$ over the stress-tensor correlation is also included. The plateau gives the value of η and that of the kinematic viscosity equal to $\nu^*=1.71\pm0.08$, to which we should add a systematic error of ~0.3. The corresponding calculated value for the amplitude $\alpha_{cal}=0.026\pm0.006$ including the systematic error on ν^*. Then, the agreement between the fitted and theoretical values of α is correct. The difference of 20–30% between the α estimates, reported in the literature [16,26], is probably due to the uncertainty of ν^*.

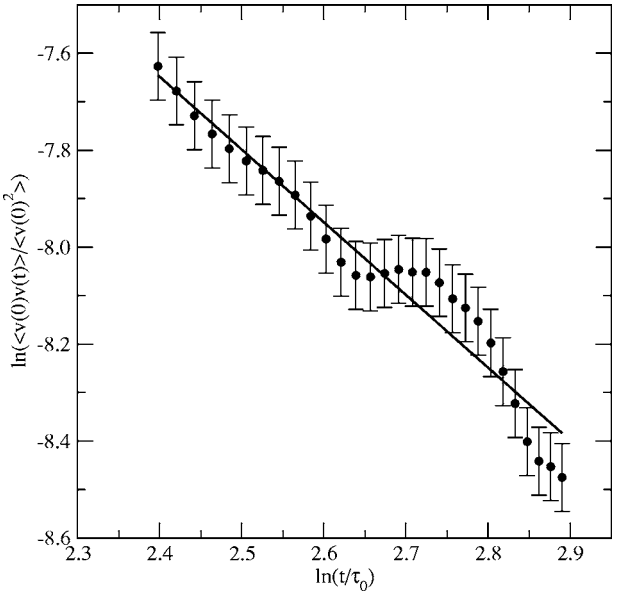

FIG. 2. A log-log plot of the normalized VAF of the soft-repulsive particle system at $\rho^*=0.2$ and $T^*=2.07$. Circles and error bars: the simulation results; thick line: a linear fit to the simulation results.

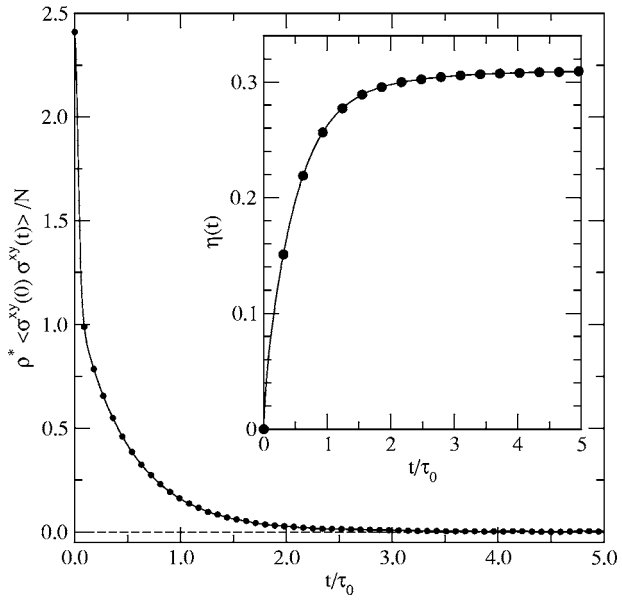

FIG. 3. For a soft-repulsive particle system at $\rho^*=0.2$ and $T^*=2.07$, the stress tensor correlation function [cf. Eq. (14)] vs time in a reduced unit t/τ_0; inset: the integral $\eta(t)$ [cf. Eq. (13)] vs time in a reduced unit t/τ_0; the circle size corresponds to the statistical error.

Figure 4 gives a log-log plot of the VAF versus reduced time for the LJ fluid near the critical point. A linear fit of the data in the range $9<t^*<15$ gives. $\ln F_{vaf}(t)=(-3.66\pm0.05)-(1.53\pm0.02)\ln t^*$, leading to a value of $\alpha_{fit}=0.0258\pm0.0015$. As for the soft-sphere system, the computation of the diffusion coefficient and kinematic viscosity gives the values $D^*=0.620\pm0.007$ and $\nu*=1.20\pm0.06$. The contribution of the long-time tail to D^* should amount to ~0.018. The stress-tensor correlation function versus reduced time is given in Fig. 5 together with its integral. Inserting these values of D^* and $\nu*$ into Eq. (1) gives the result $\alpha_{cal}=0.02$. The difference between the fitted and calculated values in this case amounts to 13%, which stays within the statistical and systematic errors of ν^* as for the soft-sphere system. In the inset of Fig. 4, the log-log plot of the VAF for the LJ system at $\rho^*=0.30$ and $T^*=1.97$ is displayed. The

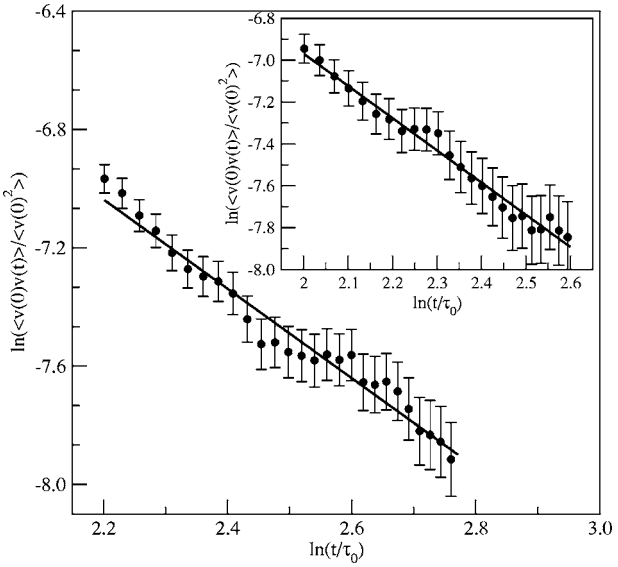

FIG. 4. Log-log plot of the normalized VAF of the LJ system at $\rho^*=0.3$ and $T^*=1.35$. Circles and error bars: the simulation results; thick line: a linear fit to the simulation results. Inset: log-log plot of the normalized VAF of the LJ system at $\rho^*=0.3$ and $T^*=1.98$. Circles and error bars: the simulation results; thick line: a linear fit to the simulation results.

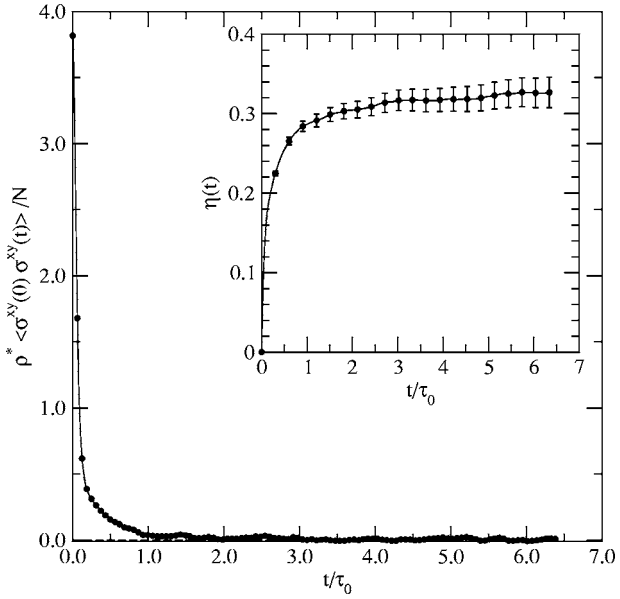

FIG. 5. For the LJ system at $\rho^*=0.3$ and $T^*=1.35$, stress tensor correlation function [cf. Eq. (14)] vs time in a reduced unit t/τ_0; inset: integral $\eta(t)$ [cf. Eq. (13)] vs time in a reduced unit t/τ_0 with error bars.

linear fit, performed in the time domain $7.4<t^*<13.4$, i.e., $2.0<\ln t^*<2.6$, is

$$\ln F_{vaf}(t) = (-3.89 \pm 0.06) - (1.53 \pm 0.02)\ln t^*$$

and is quite similar to that found near the LJ critical point. This satisfactory agreement shows that the general slowing down of the correlation decay near the critical point does not preclude the observation of the long-time decay of the VAF. The present results confirm the universality of the $t^{-3/2}$ behavior of the VAF at long times, also in the temperature and density domain close to the liquid-vapor critical point.

V. CONCLUSION

The velocity autocorrelation function has been computed by constant energy MD simulations for a fluid of soft-repulsive particles at low density and for a LJ system near the critical point. By using larger systems, and by correlating over longer times than those used in the literature [16,17], we show that the velocity autocorrelation function presents the universal asymptotic behavior $\alpha t^{-3/2}$ as predicted by the theory. The difference between the computed and fitted values of the amplitude α of the asymptotic part of the VAF is mainly due to the uncertainty of the kinematic viscosity.

These results remove all ambiguities related to the existence of the long-time tail in almost all domains of the fluid phase. However, close to triple point, the onset of long-lived damped oscillations in the VAF due to the backscattering of particles by their next neighbors [24] precludes the computation of the long-time tail. Therefore, the observation of the VAF asymptotic behavior in these thermodynamic states remains a challenge.

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