

Decay of Angular Correlations in Hard-Sphere Fluids

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The decay of the collisional contribution to the shear-stress autocorrelation function is shown to be inconsistent with a $t^{-3/2}$ inverse-power law. The decay of the self part (a combination of pair and triplet correlations) indicates a stretched-exponential decay with a density-independent exponent. The pair contribution by itself also shows stretched-exponential behavior in both two and three dimensions, with different, but still density-independent, exponents. At very long times this stretched-exponential decay of the pair correlations switches over to an algebraic decay, consistent with the diffusional separation of pairs of particles.

KEY WORDS: Angular correlations; hard spheres; long-time tails; stretched exponential; viscosity.

1. INTRODUCTION

This is a report of further progress in understanding why the viscosity of simple fluids just prior to freezing is much larger than the predictions of the Enskog kinetic theory. This is an appropriate topic on the occasion of Prof. E. G. D. Cohen's celebration, because a fundamental understanding of the kinetic theory of gases has been a long-standing interest of his, and moreover is an area in which he has made major contributions. It is well known that the high-density deviations from kinetic theory are caused by a collective dynamical effect that leads to a slow decay of the collisional contributions to the shear-stress autocorrelation function. It is strongly suspected that this mechanism is fundamentally different from the hydrodynamic vortex flow that gives rise to the inverse-power-law tail in the velocity autocorrelation function and in the kinetic fluxes related to shear viscosity and thermal conductivity.⁽¹⁾ As yet there is no detailed

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molecular mechanism for the slow decay of the collisional fluxes, nor even a convincing numerical or theoretical characterization of the functional form of the decay. Our current understanding of this “molasses” effect is based on extended-mode-coupling theories,^(2,3) which are of hydrodynamic origin, but which also include shorter wavelength fluctuations, primarily those close to the first peak in the structure factor. These theories are consistent with the not very accurate molecular dynamics data available for the shear-stress correlation function.⁽²⁾ However, statistical errors and finite-size effects, associated with the interference between sound waves, make it very expensive computationally to obtain sufficiently accurate data for a stringent test of these theories. Instead we have focused on related correlation functions that examine the decay (in time) of the orientational correlations between colliding pairs of particles. These correlation functions can be calculated with a high degree of precision by molecular dynamics simulations and then used to test the predictions of theoretical models. Our new calculations confirm our earlier conclusion⁽⁴⁾ that the angular correlations between recolliding pairs of particles decay as a stretched exponential in time with a density-independent exponent.

A quantitative relationship between the decay of the collisional contributions to the shear stress and orientational (xy) correlations of “bonds” linking colliding pair of particles has been established at long times and high densities^(4,5) as follows. The transverse momentum current J_{xy} (equal to minus the product of the shear stress and the volume) in a hard-sphere fluid of particles of mass m contained in a volume V can be written as a sum of kinetic and potential contributions,

$$J_{xy}^K = \sum_i m \dot{x}_i \dot{y}_i \quad (1)$$

$$J_{xy}^P = \sum_c (-m \mathbf{r}_{ij} \cdot \mathbf{v}_{ij}) \frac{x_{ij} y_{ij}}{r_{ij}^2} \delta(t - t_c) \quad (2)$$

The potential contribution occurs only at the collision times t_c , because of the impulsive hard-sphere interaction. The vector \mathbf{r}_{ij} connects the centers of the colliding pair, and $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ is the relative velocity before collision. It has been shown numerically^(4,5) that beyond about 10 mean collision times, $(-m \mathbf{r}_{ij} \cdot \mathbf{v}_{ij})$ can be replaced by its average value per collision $(\pi m k T \sigma^2)^{1/2}$, where k is Boltzmann’s constant, T is the temperature, and σ is the collision diameter. This leads to a quantitative factorization of Eq. (2), valid at long times and high densities,

$$\langle J_{xy}^P(t) J_{xy}^P(0) \rangle = \pi m k T \sigma^2 \langle K_{xy}(t) K_{xy}(0) \rangle \quad (3)$$

where the orientational factor K_{xy} is given by

$$K_{xy} = \sum_c \frac{x_{ij} y_{ij}}{r_{ij}^2} \delta(t - t_c) \quad (4)$$

2. RESULTS

As before,⁽⁴⁾ we define an orientational pair correlation function, with the factorization of Eq. (3) and the usual Enskog scaling, as

$$\rho_2(t) = \frac{\pi m \sigma^2 \tau}{V \eta_E} \left\langle \sum_{i>j} K_{xy}^{ij}(t) K_{xy}^{ij}(0) \right\rangle \quad (5)$$

where η_E is the Enskog shear viscosity and τ is the mean collision time. The pair correlation function is singled out for special study since it can be measured much more accurately and for much longer times than correlations of collective fluctuations. Previous results⁽⁴⁾ indicated a stretched-exponential decay for $\rho_2(t)$, that is,

$$\rho_2(t) = A \exp[-(t/t_2)^\alpha] \quad (6)$$

with a density-independent stretched exponent α . To demonstrate the universal stretched-exponential decay of the pair correlations, we plot (Fig. 1) the logarithm of the pair correlation function against the time raised to the power $\alpha = 0.7$, which was found to be the optimum value of the stretched exponent. It can be seen from the excellent fit of the numerical data over two decades of decay that a stretched-exponential relaxation with a density-independent exponent is well verified, at least at high density. Our new result for the exponent, $\alpha = 0.70 \pm 0.005$, is within the error bars ($\alpha = 0.73 \pm 0.03$) of the earlier simulations.⁽⁴⁾ The data in Fig. 1 are also scaled by the relaxation time t_2 [Eq. (6)], which varies by an order of magnitude over the density range $V/V_0 = 1.5 - 2$. To our surprise, we found that the data for times corresponding to $(t/t_2)^{0.7} < 6$ reduced to a single straight line independent of density, although in Fig. 1 the plots are shifted for clarity of presentation. A more careful examination showed a slight variation in amplitude at the lowest density $V/V_0 = 2$, but nevertheless there is essentially only one density-dependent parameter, t_2 , needed to describe the relaxation in the stretched-exponential regime.

The new simulation data (Fig. 1) clearly show two separate regimes of decay, a stretched-exponential region at intermediate times followed by a slower algebraic decay, characteristic of pair diffusion, at long times. Previously we were unable to identify unambiguously the asymptotic power-law decay even at low densities.⁽⁴⁾ By contrast, the much more extensive

runs reported here show the changeover from stretched-exponential to algebraic decay at all densities (Fig. 1). The shift to an algebraic decay occurs at times corresponding roughly to a characteristic diffusion time $\sigma^2/4D$, or for $(t/t_2)^{0.7} \approx 5$. The long-time decay is only shown for the $N=500$ -particle systems because for the smaller $N=108$ -particle systems the periodic images interfere with the diffusional spreading at relatively short times, approximately $(L/2)^2/12D$, where L is the box length and D is the diffusion constant, or at $(t/t_2)^{0.7} \approx 5.5$.

An extended-mode-coupling theory of the pair correlation function has been derived recently by Kirkpatrick.⁽⁶⁾ The theory predicts a relaxation by mutual diffusion of pairs of particles, as in the case of the depolarized-light-scattering pair correlation function,⁽⁷⁾

$$\rho_2(t) = \frac{2\pi kTt_E}{15\eta_E\sigma^3} [n\sigma^3 g(\sigma)]^2 \left(\frac{\sigma^2}{4Dt}\right) \exp\left(-\frac{\sigma^2}{4Dt}\right) I_{5/2}\left(\frac{\sigma^2}{4Dt}\right) \quad (7)$$

where $n = N/V$, $g(\sigma)$ is the pair distribution function at contact, and $I_{5/2}$ is

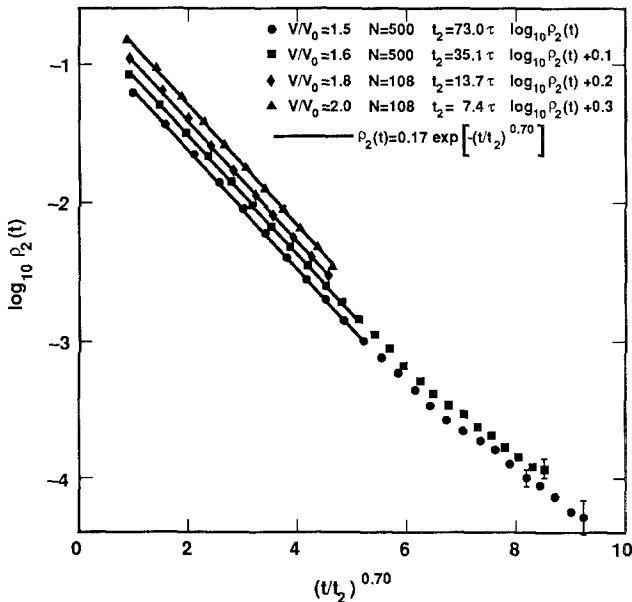


Fig. 1. Decay of the pair orientation autocorrelation function at four densities. The logarithm of the pair correlation function $\rho_2(t)$ is plotted against time, scaled by the relaxation time t_2 , raised to the density-independent power $\alpha = 0.70$. For clarity, the correlation functions at different densities are shifted successively by 0.1 (on a \log_{10} scale). However, the actual amplitude of the stretched exponential has a constant value of 0.170 at $V/V_0 = 1.5, 1.6,$ and 1.8 and it shifts only slightly to 0.178 at $V/V_0 = 2.0$. The statistical errors, indicated by the vertical bars, are only significant at long times.

a modified Bessel function. It should be pointed out that, although we are in the diffusional regime by a time corresponding to $(t/t_2)^{0.7} = 6$, according to Eq. (7) the asymptotic $t^{-7/2}$ regime will not dominate the decay until times that are about an order of magnitude longer. Equation (7) follows the decay of the molecular dynamics data quite closely at long times $(t/t_2)^{0.7} > 6$, but the amplitude is too small by about a factor of 2. In the intermediate-time regime $(t/t_2)^{0.7} < 5$ this simple diffusion model does not predict the correct functional form for the relaxation either. However, incorporating a potential of mean force into the diffusion model⁽⁸⁾ leads to a correlation function $\rho_2(t)$ which is in excellent agreement with the molecular dynamics data throughout the intermediate-time and long-time regimes ($t > 10\tau$), although this requires an effective diffusion constant about 10% less than for a single particle.

The pair correlation function $\rho_2(t)$ measures the memory of the xy orientation of the initial collision when the same pair of particles recollides. Relaxation can occur either by rotation of the pair or by mutual diffusion; one would expect that at high densities rotation is favored, while at low densities diffusion is more important. However, at long enough times pair correlations should eventually decay by diffusion, as long as the system is in a liquid state, and thus be characterized by an algebraic decay, varying as $t^{-7/2}$ asymptotically. Thus, the freezing out of the diffusive modes, reflected by the absence of a diffusional power-law tail in the pair correlation function, could be a useful criterion for the onset of glass formation. Experimentally, a closely related correlation function can be measured by NMR relaxation.⁽⁹⁾

The two-dimensional results shown in Fig. 2 are very similar to the three-dimensional ones. A stretched-exponential decay with a density-independent exponent is observed over a wide time regime, followed by a changeover to an algebraic decay at very long times. The stretched exponent is larger in two dimensions than in three dimensions, while the relaxation time is again strongly density dependent and the amplitude roughly density independent. Earlier, less extensive data failed to identify the stretched-exponential region in two dimensions, and, as in the three-dimensional case, missed the diffusive region entirely.⁽⁴⁾ At present the two-dimensional version of the diffusion model⁽⁶⁾ has not been worked out, so we cannot yet numerically verify that the observed long-time decay is diffusive, but it seems almost certain that it is.

The angular self-correlation function, a combination of pair and triplet contributions,⁽⁴⁾

$$\rho_s(t) = \frac{\pi m \sigma^2 \tau}{V \eta_E} \left\langle \sum_{\substack{i \\ j, k \neq i}} K_{xy}^{ij}(t) K_{xy}^{ik}(0) \right\rangle \quad (8)$$

is more closely related to the total collisional correlation function than the pair correlation function discussed above. It is a collective fluctuation and its relaxation time is similar to, though somewhat longer than, the relaxation time associated with the total collisional correlation function. It has the important advantage that it can be measured with \sqrt{N} better statistical accuracy than the total correlation function and this has been exploited to characterize the decay of these correlations fairly precisely. The results are shown in Fig. 3 for systems up to $N=4000$ particles at three high-density fluid states. The diffusional power-law tail found for the pair correlations (Figs. 1 and 2) is absent in the self-correlations because of the cancellation of two-particle and three-particle static correlations at long wavelengths, as in the analogous case of the depolarized-light-scattering correlation functions.⁽⁷⁾ As a result, we see clear evidence of a stretched-exponential decay over the whole measurable time regime, particularly for the highest density, $V/V_0 = 1.5$, $N = 4000$ -particle system. At the lowest densities there is weak evidence of a changeover to exponential behavior, indicating a

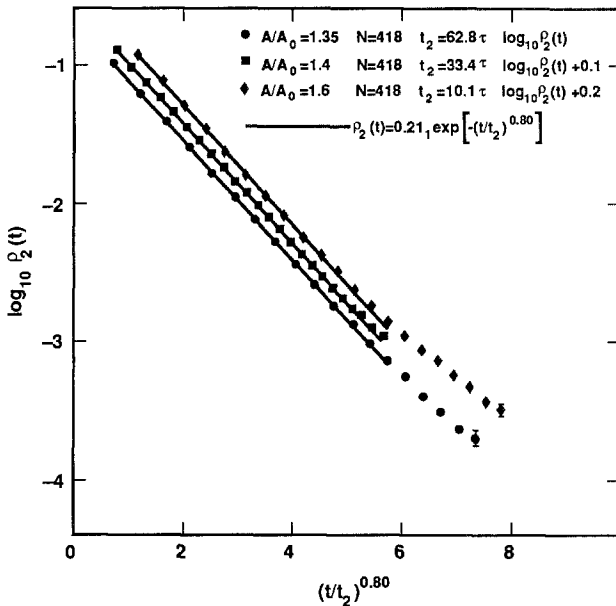


Fig. 2. Decay of the two-dimensional pair orientation autocorrelation at three densities. The logarithm of the pair correlation function $\rho_2(t)$ is plotted against time, scaled by the relaxation time t_2 , raised to the density-independent power $\alpha = 0.80$. For clarity, the correlation functions at different densities are shifted successively by 0.1 (on a \log_{10} scale). However, the actual amplitudes of the stretched exponential vary only slightly with density, from 0.20 at $A/A_0 = 1.35$, to 0.22 at $A/A_0 = 1.6$. The statistical errors, indicated by the vertical bars, are only significant at long times.

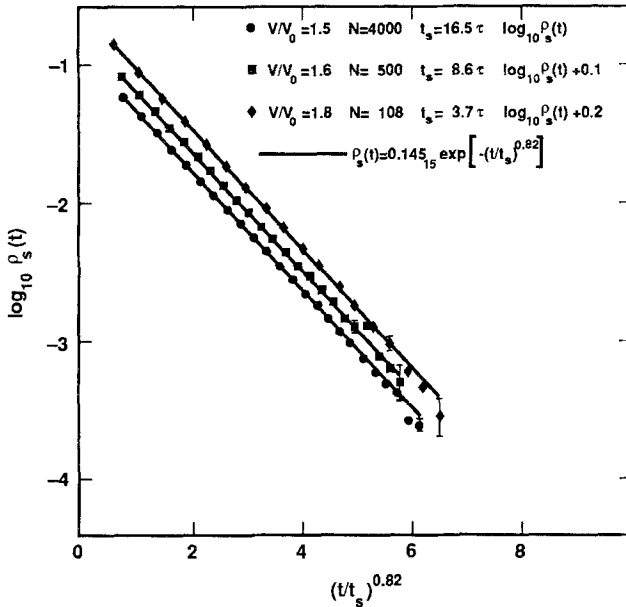


Fig. 3. Decay of the self-orientation autocorrelation function at three densities. The logarithm of the self-correlation function $\rho_s(t)$ is plotted against time, scaled by the relaxation time t_s , raised to the density-independent power $\alpha = 0.82$. For clarity, the correlation functions at different densities are shifted successively by 0.1 (on a \log_{10} scale). However, the actual amplitudes of the stretched exponential vary only slightly with density, from 0.13 at $V/V_0 = 1.5$ to 0.16 at $V/V_0 = 1.8$. The statistical errors, indicated by the vertical bars, are only significant at long times.

finite sum of exponentially damped modes, but this may simply be an effect of the finite system size. As in the case of the pair correlations, the stretched exponent appears to be independent of density, but, in contrast to our previous suggestions,⁽⁴⁾ the new data allow a clear differentiation between the stretched exponents for the pair and self-correlations. Again the amplitude is also only weakly density dependent.

The “molasses tail” itself can be characterized most accurately at the highest fluid density $V/V_0 = 1.5$ and we have carried out extensive calculations of the collisional shear-stress autocorrelation function $\langle J_{xy}^P(t) J_{xy}^P(0) \rangle$ at this density. In Fig. 4 we show a log-log plot of the collisional correlation function $\rho_\eta(t)$ normalized by the usual Enskog scaling

$$\rho_\eta(t) = \frac{\tau}{VkT\eta_E} \langle J_{xy}^P(t) J_{xy}^P(0) \rangle \tag{9}$$

for $N = 500$ and $N = 4000$ particles. The 500-particle system was run for 10^8 collisions and the 4000-particle system was run five times longer, so that

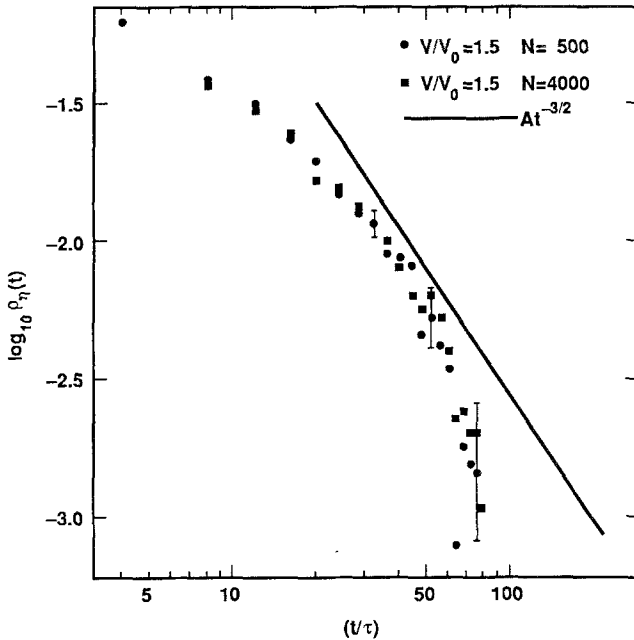


Fig. 4. Relaxation of the total collisional contribution to the shear-stress autocorrelation function at $V/V_0 = 1.5$. The logarithm of the normalized collisional shear-stress correlation function $\rho_\eta(t)$ is plotted against the logarithm of the time, measured in units of the mean collision time τ . The power-law $t^{-3/2}$ decay is plotted, with an arbitrary amplitude, for comparison. The statistical errors, indicated by the vertical bars, are comparable for $N = 500$ and $N = 4000$.

the statistical errors for both systems were similar. Our results establish that, contrary to earlier speculation,⁽¹⁰⁾ the collisional shear-stress correlation function does *not* decay algebraically as $t^{-3/2}$ at long times, but considerably faster. However, even with these very long runs, the data do not allow us to distinguish between the exponential behavior predicted by extended-mode-coupling theories⁽³⁾ and the stretched-exponential behavior that has been shown to characterize the decay of the closely related, angular self-correlation function. It seems plausible that the tail of the collisional shear-stress correlation function will ultimately be shown to exhibit a stretched-exponential decay also.

Finally, we have examined the related correlation function associated with depolarized light scattering.^(7,11) This is because it has been noticed experimentally that dielectric and viscous relaxation processes show a similar stretched-exponential decay.⁽¹²⁾ Our numerical studies indicate that the decay of the depolarized-light-scattering correlation function is similar, but *not* identical, to the stress relaxation. The studies also show that earlier

depolarized-light-scattering data⁽¹¹⁾ were unreliable, because a spherical cutoff of the long-range dipole-induced-dipole polarizability was replaced by a cubic, nearest-image truncation, which introduces spurious angular correlations and leads to a 20% error in the relaxation time at high densities.

3. CONCLUSIONS

The results presented here have shown that the decay of the pair and self angular correlations can be accurately represented over at least two decades by a stretched exponential with a density-independent exponent. Moreover, with the usual Enskog scaling [Eq. (5)], the amplitude of the stretched exponential is essentially independent of density also. Thus, the only density-dependent parameter in Eq. (6) is the relaxation time t_2 . Unfortunately, with present computational limitations, the relaxation of the total (four-particle) collective fluctuations cannot be determined with sufficient accuracy to differentiate between exponential and stretched-exponential decay. However, we can now, with reasonable certainty, exclude a long-time $t^{-3/2}$ decay for the collisional shear-stress correlation function. Attempts to apply the concepts of extended mode-coupling theory to the pair correlations⁽⁶⁾ have not been successful. While the theory predicts a diffusional relaxation at long time which agrees in functional form and relaxation time with the simulation data, the amplitude of the correlation function is too small. Moreover, the theory has the wrong functional form in the intermediate-time, stretched-exponential regime. A theory based on pair diffusion in a potential of mean force⁽⁸⁾ has been more successful in fitting the simulation data, but only by using a diffusion coefficient about 10% less than that for a single particle.

Although this work provides accurate numerical data for theoretical comparison, it does not *per se* yield insight into the mechanism for the relaxation. For that purpose studies are underway to observe the decay and spreading of an initially localized stress field. In particular, we want to distinguish among three possible mechanisms for relaxation of the initial stress: namely a hydrodynamic mechanism,^(2,3) in which we expect the relaxation time to grow roughly as the square of the distance from the origin of the stress, a gridlock mechanism,⁽¹³⁾ where by contrast the outer regions decay first, and a stress-induced ordering, where the ordering process, perhaps into temporary crystalline-like structures, sets the relaxation time.

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