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Long-Time Behavior of the Angular Velocity Autocorrelation Function for a Fluid of Rough Spheres

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According to hydrodynamical and mode-coupling theories, the angular velocity autocorrelation function decays at long times as $\nu_0(t/10^{-14}\ \mathrm{sec})^{-5/2}$. For rough spheres under the conditions reported here, the quantity ν_0 is predicted to be 262. The molecular dynamics studies presented here yield a long-time tail of the form $230(t/10^{-14}\ \mathrm{sec})^{-2.38}$. The disagreement between theory and computer results probably arises from statistical error intrinsic to the computations.

KEY WORDS: Molecular dynamics; computer simulation; rough sphere model fluid; long-time behavior; angular velocity autocorrelation function.

Molecular dynamics studies by Alder and Wainwright[(1)] on systems of identical hard spheres and hard disks and by Levesque and Ashurst[(2)] on a fluid of soft, repulsive particles have shown that the velocity autocorrelation function decays as $\alpha_0 t^{-d/2}$ at long times, where α_0 is a coefficient dependent on the density ρ and d is the dimensionality of the system. The long-time behavior has been explained by kinetic theory[(3)] for small densities and by various hydrodynamic models[(4)] for fluid systems at all densities. Extension of these theoretical attempts to systems with internal degrees of freedom by means of hydrodynamic models[(5)] and microscopic mode-coupling calculations[(6)] have led to predictions of a long-time decay of the angular velocity autocorrelation function (AVCF) in three dimensions as

$$f(t) = \langle \boldsymbol{\omega}(0)\cdot\boldsymbol{\omega}(t)\rangle / \langle \boldsymbol{\omega}(0)^2\rangle \sim \nu_0(t/10^{-14}\ \mathrm{sec})^{-5/2} \quad (1)$$

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We have computed, using the molecular dynamics technique, the AVCF for a test rough sphere in a fluid of rough spheres. The system simulated was one in which a test particle of diameter $\sigma_T = 6$ Å and mass $M = 8m$ was taken in a bath of 94 particles of mass m and diameter $\sigma_b = 2$ Å, contained in a cubic box of side 10.756 Å. Periodic boundary conditions were used. The Percus–Yevick parameter $\xi = (\pi/6)(n_b\sigma_b^3 + n_T\sigma_T^3)$, where n_b and n_T are the number densities of the bath and test particles, respectively, had a value equal to 0.4105.

In an earlier molecular dynamical study[7] on the above system, we considered the behavior of the autocorrelation functions of velocity and angular velocity of the test sphere during the initial time period as well as during the transition between the initial time and asymptotic times. The AVCF is obtained at time $t = kh$, where k is an integer and $h = 1 \times 10^{-14}$ sec, by the time average,

$$f(kh) = \frac{\sum_{l=1}^{p} \boldsymbol{\omega}_T[lh]\cdot\boldsymbol{\omega}_T[(l-k)h]}{\sum_{l=1}^{p} \boldsymbol{\omega}_T(lh)\cdot\boldsymbol{\omega}_T(lh)} \tag{2}$$

where $\boldsymbol{\omega}_T(t)$ is the angular velocity of the test particle at time t. Here ph is the total time for which the system is followed.

Figure 1 (inset) shows a plot of $f(t)$ on a log–log scale. It is seen that after a time corresponding to roughly $23t_c$, where t_c is the mean collision time of the test particle, the decay of the autocorrelation function follows a power law with slope -2.38, i.e., at long times

$$f(t) \sim \nu_0(t/h)^{-2.38}$$

The coefficient of the decay ν_0 is found to be 230. The single error bar marked at $t = 25h$ is an estimate of the standard error (S.E.) assuming that the dynamical process is a Gaussian random process. With this assumption, the square of the standard error is given by[8] the expression

$$\sigma^2[f(\tau)] = \frac{2}{m-l}\sum_{j=0}^{m-l-1}\left(1 - \frac{j}{m-l}\right)[f^2(jh) + f(jh+lh)f(jh-lh)] - \frac{1}{m-l}[f^2(0) + f^2(lh)] \tag{3}$$

where $\tau = lh$. In the general case knowledge of the correlation function alone is not sufficient for error estimation and it is necessary to have available moments of higher order. For long times $\sigma^2[f(\tau)]$ is fairly independent of τ (as found by calculation) and hence the value marked by the error bar is the same over the time range $25h$ to $35h$. This is consistent with that found by Alder *et al.*[9] in molecular dynamical calculations and with that predicted by Zwanzig and Ailawadi,[10] who showed that at long times

$$\text{S.E.} \sim (\tau/T)^{1/2} \tag{4}$$

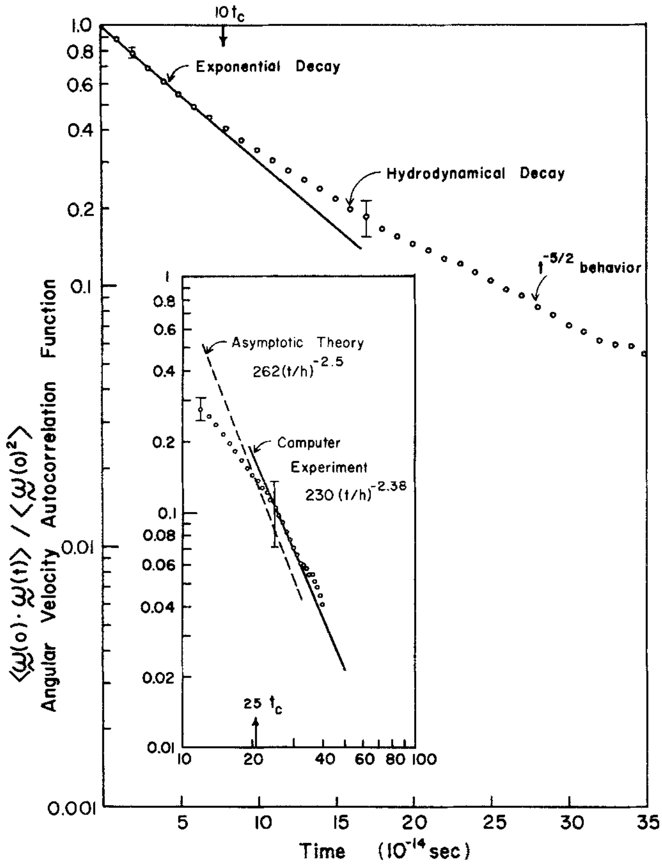

Fig. 1. Normalized autocorrelation function of angular velocity for a test particle. The inset is a log–log plot of the autocorrelation function at long times compared with hydrodynamic theory (dashed line).

A Gaussian random process was assumed and τ is the characteristic decay time if the autocorrelation function is assumed to decay exponentially. The S.E. calculated from (3) agrees with that calculated from (4) if the slope of the initial exponential decay is taken as τ^{-1} (Fig. 1).

The S.E. is 27% of the value of the autocorrelation function at the beginning of the $t^{-5/2}$ decay at $t = 22h$ and is 50% of the value of $t = 32h$, where the scatter in the function appears. For the error to be reduced to 10% it is seen from Eq. (4) that the time period for which the system has to be run would be increased by a factor of nine. Considering that the computation time on a CDC Cyber 74 system to obtain the present data was around 7 h, it was not economically feasible to reduce the error to a more acceptable value. The fact that the data points form a smooth curve arises from the overlapping intervals used in the time average (2). For any scatter to be detected, the individual data points would have to be separated by a time interval of more than a correlation time τ. It must be emphasized that the error estimate is based on a Gaussian process assumption and may be too conservative.

The advantage gained by choosing a large test particle is that the mean collision time t_c is reduced by a factor of 4.4 compared to that of a bath particle. The test particle can be followed for many more collision times than a bath particle for a given system size, before the interference effects due to the periodic boundaries are felt.

We now show that, although the system size is small, the asymptotic behavior of $f(t)$ has been observed for times such that the boundary conditions have no influence on the AVCF. The time t has to be smaller than some characteristic time $t \sim l/c$, where l is the length of the cubic box containing the system and c is the sound velocity,

$$c = \frac{1}{[\rho(c_v/c_p)k_T]^{1/2}} \tag{5}$$

ρ is the density of the system, and c_v and c_p are the specific heats at constant volume and pressure, respectively. Since $n_T \ll n_b$, the isothermal compressibility k_T can be estimated from scaled particle theory,[11] assuming the fluid to be a single-component system with Percus–Yevick parameter ξ:

$$k_T = \frac{\pi a^3}{6} \frac{(1-\xi)^4}{\xi kT(1+2\xi)^2} \tag{6}$$

The ratio of specific heats c_v/c_p for a rough sphere fluid is

$$\frac{c_v}{c_p} = \frac{1}{1 + (pV/3NkT)pk_T} \tag{7}$$

The quantity pV/NkT is obtained from the equation of state of the system. Substitution of (6) and (7) into (5) yields for the sound velocity $c = 2.29 \times 10^5$ cm/sec and the characteristic time $t_0 = l/c = 4.7 \times 10^{-13}$ sec. From Fig. 1 (inset) it is seen that for the data points falling in a straight edge, the time is below t_0. The scatter obtained after $t = 32h$ is therefore due to the interference of the boundary.

The coefficient of the decay ν_0 in Eq. (1) obtained in the computer experiment is compared with that predicted by theory when the coupling between the translational and rotational degrees of freedom is weak (for the rough sphere fluid the cross-correlation functions between angular and linear velocities are exactly zero). This coefficient[5,6] is equal to

$$\nu_0^{\text{theory}} = (\pi I/\rho)[4\pi h(\nu^* + D^*)]^{-5/2} \tag{8}$$

where $I\,(\equiv \frac{1}{10}M\sigma_T^2)$ is the moment of inertia of the test particle, ρ is the mass fluid density, ν^* is the kinematic shear viscosity, and D^* is the diffusivity. The values of ν^* and D^* are estimated for the system as described in the appendix of Ref. 7. If ν^* is calculated using the Stokes–Einstein relation between ν^* and D^*, then $\nu_0^{\text{theory}} = 262$. If ν^* is estimated from the Enskog value for a dense fluid mixture, we obtain $\nu_0^{\text{theory}} = 201$. Considering the uncertainty involved in the slope of the asymptotic decay and the approximation used in estimating the value of the viscosity, there is seen to be fair agreement between theory and computer experiment.

Figure 1 compares the theoretical decay curve $\nu_0^{\text{theory}}(t/h)^{-5/2}$ with the computer results. It is seen that the theoretical result for the asymptotic value of the autocorrelation function lies within a standard deviation of the computer result at $t = 25h$.

Although there is roughly only one layer of bath particles around the test particle in the box, the hydrodynamic effect is not affected by the periodic boundaries. For the time period of $10t_c$ to $20t_c$ in which we observe intermediate-time behavior we have given evidence and reasons why the periodic boundaries do not interfere in an earlier work,[12] where a hard-sphere system was considered in the same sized box, and excellent agreement was obtained with the hydrodynamic model for an infinite system. This justifies taking the viscosity of the bath as that for the infinite system.

The number dependence correction usually used for the velocity correlation function is of the order of $1/N$. This correction arises out of the total linear momentum conservation of a finite system of particles. However, for the rough sphere model, the intrinsic angular momentum is not conserved and the form of the correction for the angular velocity autocorrelation function, if any, is not clear.

We did not include the asymptotic behavior of the velocity autocorrelation function in this report because at times equal to $20t_c$ the autocorrelation function decays to values comparable with the standard error.

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