Short-Time Correlations in Liquids: Molecular-Dynamics Simulation of Hard Spheroids

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The velocity and angular velocity autocorrelation functions obtained by molecular-dynamics simulations of liquids composed of hard spheroids indicate the existence of damped oscillations with periods as long as 40 times the mean time between molecular collisions. In addition, little correlation is found between successive collisions. This suggests that the damped oscillations are not due to semicoherent molecular librations in cells.

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In high-density molecular liquids the crowded molecules carry out rapid, *rattling* motions, both translational and rotational, within a *cage*. One would like to understand the structure and behavior of the cage as well as that of the rattling molecule within the cage. If the cages had rigid walls, the dynamical properties of trapped molecules would be described entirely by local modes, i.e., modes with wavelengths no longer than the dimensions of the cages, or equivalently of the molecules; these motions might truly be called "rattling motions." But in reality the walls of the cages are mobile, with characteristic correlation times similar to those of the trapped molecules,[1] and because of this, the dynamical behavior of individual molecules may be coupled to longer-wavelength modes. It is, in fact, well known that both the velocity and angular velocity autocorrelation functions (VACF and AVACF, respectively) have long-time tails which arise because of coupling of the molecular motions to collective modes.[2-4] Our concern here is not with such long-time tails but with dynamical behavior at *intermediate* times. In particular, it is known from molecular-dynamic (MD) simulations[5] and from far-infrared absorption[6] (the so-called Poley absorption) that in dense fluids both the VACF and the AVACF reverse sign within a few picoseconds; this sign reversal is often taken as evidence of *coherent* or *correlated rattling within a cage,* and in the rotational case is associated with torsional librations.[7] Reference 7 contains a summary of many such models. The present study suggests that for molecular liquids the sign reversal in these molecular correlation functions may, in fact, be dominantly determined by the dynamical behavior of the surrounding solvent, i.e., by modes with wavelengths considerably longer than molecular dimensions.

We have carried out molecular-dynamics simulations on 125 hard prolate spheroids with a 2:1 axial ratio and uniform mass distribution at a density 0.8 times the close-packed density ρ_c. (This density is close to the freezing density, while for hard spheres the freezing density is only $0.65\rho_c$.) Whereas hard spheres serve as a model for atomic liquids, hard ellipsoids can serve as a model for molecular liquids. The ellipsoids are treated as linear rotors, and the dynamics are solved collision by collision; further details are given elsewhere.[8,9] Although such a system lacks some of the interactions found in real liquids, it has many dynamical properties which are similar to those of real liquids. A useful feature, which we exploit, of liquids composed of hard particles is the unambiguous specification of an intermolecular collision and, consequently, the clear specification of times between collisions and of a *mean free intercollision time* τ_c. By examining reduced times, t/τ_c, we can get insight into the rattling motions within a cage; in Fig. 1 we see that if the time dependence of the VACF and AVACF are interpreted as evidence of heavily damped oscillatory (or rather, elastic bouncing) behavior, the period is about $40\tau_c$ rather than the approximately $2\tau_c$ one would expect if it arose as the result of semicoherent oscillations within a cage, τ_c being the time to "cross" the cage. Of course, the relevant time may actually be the mean time for velocity sign reversal. From Fig. 2 we see that it takes two to three collisions on average to reverse the sign of the velocity, but that the mean time for velocity sign reversal is still only about $\frac{1}{7}$ the time needed for the VACF and the AVACF to reach their minima. This is one of our primary results, and it

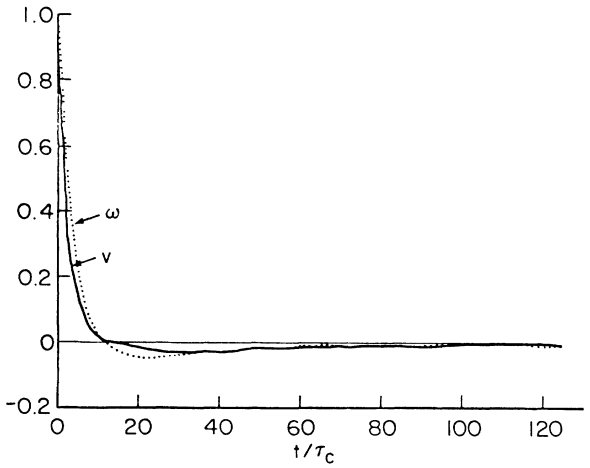

FIG. 1. $\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle/\langle \mathbf{v}(0)\cdot\mathbf{v}(0)\rangle$ and $\langle \boldsymbol{\omega}(0)\cdot\boldsymbol{\omega}(t)\rangle/\langle \boldsymbol{\omega}(0)\cdot\boldsymbol{\omega}(0)\rangle$, where ω is the angular velocity.

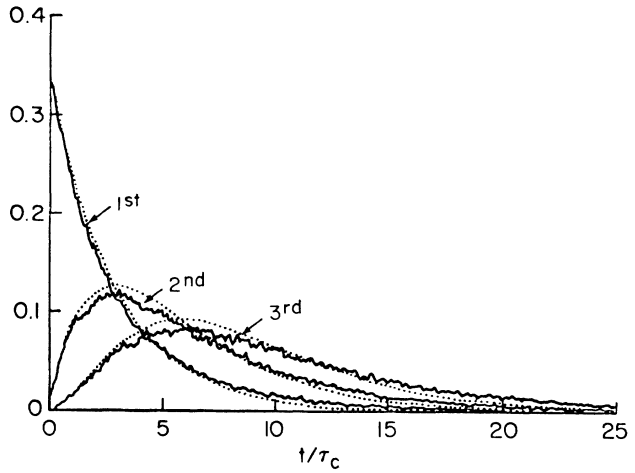

FIG. 2. Distribution of collision-initiated-velocity-reversal times [times which elapse between changes in sign in $v_x(t)$]. Times to first, second, and third collisions after a collision. The dotted line represents calculations for completely randomizing collisions.

leads us towards the suggestion that the apparent damped-oscillator behavior observed in the VACF and AVACF has *little to do with the rapid rattling motion within a cage; the period of oscillation corresponds to too many collisions for it to be connected with the bouncing off cage walls.* For hard spheres the results[10-12] are less dramatic, but from the work of Alder and co-workers[10,11] one finds that the time for the VACF to reach its minimum is still of order $9\tau_c$. Preliminary results suggest that for hard spheres in a frozen-high-density liquid environment, a situation in which only rattling within cages is relevant, the minimum in the VACF occurs at only $3\tau_c$ to $4\tau_c$. (Keep in mind that at low densities there is no negative dip in the VACF although there certainly is a mean velocity-sign-reversal time.)

We must still check whether the rattling motion could be appreciably correlated over the many collision times required for the VACF and AVACF to reach their minima. To do so we first examined the distribution of collision-initiated-free-flight times, i.e., the times between collisions, and from these we determined the mean time τ_c. This distribution is very nearly random (Poisson). Of course, even if the rattling motion for a given molecule in its cage were quite coherent and oscillatory, the distribution of collision-initiated-free-flight times could appear to be quite random because the distribution of local environments, and hence of different cages with different oscillatory frequencies, could be quite broad. To check this we examined the distribution of *scaled collision-initiated-free-flight times* t_{scale}; such times are obtained by recording the time for a collision-initiated-free-flight event for a given particle and dividing the time for each successive collision-initiated-free-flight event for that particle by the time of the first one. This is done repeatedly for each particle, and because an intercollision time for each particle (in its particular cage) is divided by its own preceding intercollision time, the effect of a broad distribution of different cages (*inhomogeneity*) should be minimized. The distribution of such scaled collision-initiated-free-passage times depicted in Fig. 3 indicates very little correlation between the times elapsed between successive collisions. From Fig. 2 we see that the distribution of collision-initiated-velocity-reversal times is also nearly random (Poisson). Our second main result is that the apparent Markovian character of the distribution of intercollision and velocity-reversal times supports the hypothesis that *the short-time rattling motion within a given cage is highly incoherent and not likely to exhibit oscillatory behavior.* This con-

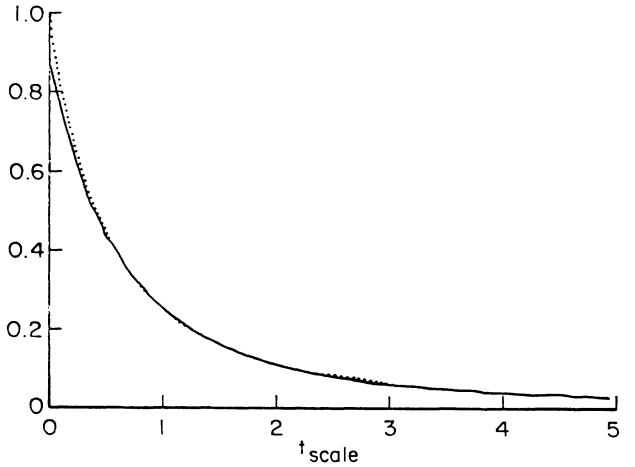

FIG. 3. Distribution of scaled collision-initiated-free-flight times for first free-flight time following the free-flight time used for scaling. The solid line is the simulation result; the dotted line is the calculation for completely randomizing collisions. Perfect oscillatory behavior would lead to a δ function at time $t_{\text{scale}} = 1$.

clusion is compatible with that of Vesely and Evans[13] who found little correlation between recollisions of a pair of tagged particles in a hard-sphere system.

The VACF, $\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle$, where $\mathbf{v}$ is the velocity and $\langle\ \rangle$ indicates an ensemble average, is an average which weights high velocities more than low ones; this suggests that the dynamical behavior of $\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle$ could be less revealing than expected. To check the effect of such weighting, we examined two other velocity correlation functions which involve rather different averages: $\langle \hat{\mathbf{v}}(0)\cdot\hat{\mathbf{v}}(t)\rangle$ and $\langle \mathrm{sgn}[v_x(0)]\mathrm{sgn}[v_x(t)]\rangle$, where $\hat{\mathbf{v}}(t)=\mathbf{v}(t)/|\mathbf{v}(t)|$ and $\mathrm{sgn}[v_x(t)]$ is the sign of $v_x(t)$ with v_x being the x component of $\mathbf{v}$. In Fig. 4 we see that the different averaging accounts for only slight differences in the functional form of the correlation functions. Although it may be a consequence of our choice of moment of inertia, the VACF and the AVACF seem to have very similar time dependences. It is also interesting to note that the time required for one of our ellipsoids to *diffuse* a distance comparable with its effective hydrodynamic radius is about $180\tau_c$, a time long compared to that required for the correlation functions to reach their minima. We estimate the sound traversal time in our simulation box to be about $60\tau_c$.

If it is not associated with coherent molecular oscillations in a cage, to what, then, do we attribute the apparently heavily damped oscillatory behavior of the VACF and AVACF? Because of their long periods we associate the oscillations with phenomena whose wavelengths appreciably exceed the dimensions of the local cage. A number of theories have been proposed to describe the negative lobe of the VACF: that of Zwanzig and Bixon,[14] which is a generalized hydrodynamic theory, and those of Cukier and Mahaffey,[15] of Kirkpatrick and Nieuwoudt,[16] and of Kumar and Evans[17] which are kinetic theories which encompass coupling to density and momentum modes. Evans[18] has also utilized such a kinetic theory to describe the negative lobe in the AVACF.

We now offer tentative interpretations for the relatively long time elapsed before the VACF and the AVACF reverse sign. In a mode-coupling picture, the relevant modes are composed of bilinear products of conserved variables. These product modes may have oscillations and dispersion relations similar to those of sound modes, and the high-frequency waves may give rise to the sign reversal in the VACF. In the absence of viscoelastic effects, the oscillation frequencies and decay rates are of order c/λ and $\pi\eta/\rho\lambda^2$, respectively[19] (where η is the coefficient of longitudinal viscosity, ρ is the mass density, λ is the wavelength, and c is the sound speed); this indicates that phonons are overdamped for wavelengths less than $\pi\eta/c\rho$. Thus if the single-particle motions are coupled to a continuum of such modes of all wavelengths, modes with wavelengths less than $\pi\eta/c\rho$ correspond to dissipative behavior, while those of longer wavelength

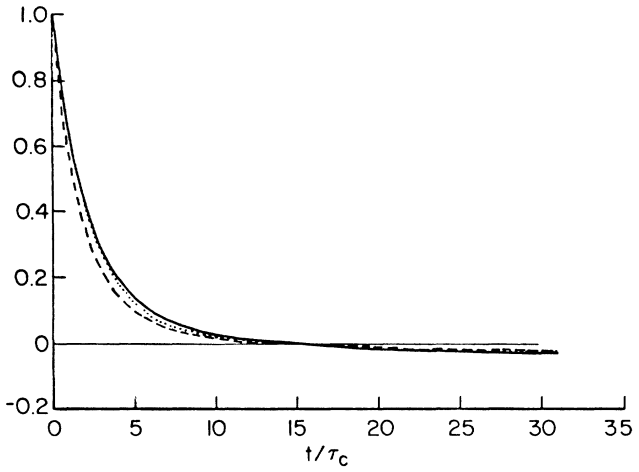

FIG. 4. Three different velocity autocorrelation functions: ——, $\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle/\langle \mathbf{v}(0)\cdot\mathbf{v}(0)\rangle$; ---, $\langle \hat{\mathbf{v}}(0)\cdot\hat{\mathbf{v}}(t)\rangle$; and ····, $\langle \mathrm{sgn}[v_x(0)]\mathrm{sgn}[v_x(t)]\rangle$.

may be oscillatory. For $c=10^5$ cm s^{-1}, $\rho=1$ g cm^{-3}, and $\eta=10^{-2}$ P, the minimum wavelength at which oscillatory behavior is observed is about 3 nm, a length far greater than the diameter of a cage around a small molecule. This qualitative picture could account for the observed damped oscillatory behavior in the VACF: The short-wavelength modes (which correspond to rattling within a cage) could be purely dissipative with no sign of oscillatory behavior, and, though the long-wavelength modes oscillate, interference between oscillations at different wavelengths could dampen the oscillatory effect on the autocorrelation functions. What one then observes in the autocorrelation functions at intermediate times is the expected damped oscillation with wavelength about $\pi\eta/c\rho$. If this estimate is meaningful, the critical wavelength is larger than the simulation box used, in which case our quantitative results are in doubt; however, the argument that the MD simulation indicates the presence of correlated lengths larger than the cage size should still hold.

A possible physical model which can rationalize the phenomena discussed above is the following. We note that the velocity of a molecule rattling in a cage rapidly *averages out, not to zero but to the drift velocity of the cage* as a whole. In turn, the cage composed of nearest neighbors rattles rather more slowly within a larger cage composed of its nearest neighbors, and its velocity averages out somewhat more slowly to the drift velocity of the larger, encompassing cage. There is a continuous hierarchy of such cages (which might be associated with density and velocity fluctuations), and for cages above some size, oscillations might be discernible, and these oscillations could establish the drift velocity of the entrapped molecules. To date no quantitative test of this suggested model has been given.

It could be that though the quantitative character of

our results hold for hard ellipsoids, they might not hold for liquids composed of molecules interacting through realistic intermolecular potentials. In some cases it has been found that for more realistic intermolecular potentials the oscillations in the correlation functions are less damped than for our spheroids, and an additional oscillation can sometimes be observed.[5] For these more realistic potentials one does not have an unambiguous way of specifying intermolecular collisions and so one cannot scale times to the mean intercollision time; however, for these more realistic potentials it would be of interest to scale the times to the mean collision-initiated-velocity-reversal time.

Calculations for different asphericities, densities, and moments of inertia will be reported elsewhere; however, preliminary results indicate that the start of the negative lobe in the VACF for hard ellipsoids moves out to longer scaled times as the density is lowered, disappearing completely at densities of about 0.4, and that the start of the negative lobe moves out with increasing asphericity. Additional insight into the relative importance of intracage and extracage effects can perhaps be obtained by studying systems in which all but one particle are frozen.

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