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Long-Time Tails in the Velocity Autocorrelation Function of Hard-Rod Binary Mixtures

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The temporal evolution of binary mixtures of hard rods in a ring is simulated in a computer with random initial velocities $\pm v$. The time the system takes to reach a Maxwellian distribution dramatically diverges as the mass ratio $\epsilon \rightarrow 1$ and it also increases, although rather slowly, when $\epsilon \rightarrow \infty$. A negative "long-time tail," i.e., a slow, power-law decay in the velocity autocorrelation function at large values of the time t, is observed whose behavior changes from t^{-3} to $t^{-\delta}$, $\delta \lesssim 1$, as ϵ is increased from $\epsilon = 1$.

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The computation of transport coefficients such as diffusion constants in model systems is sometimes hampered by the appearance of *long-time tail* effects. More specifically, the velocity autocorrelation function (VAF) decays for large values of the time t:

$$\langle v(0)v(t)\rangle \sim t^{-\delta}, \quad t \rightarrow \infty, \tag{1}$$

i.e., very slowly as compared to the Langevin exponential relaxation[1] which usually characterizes the short-time behavior. Given that (1) may last in practice for very long times, the estimation during computer simulations of the diffusion coefficient D by numerical integration of the VAF, as given by the Einstein-Green-Kubo formula[2]

$$D = \int_0^\infty dt\,\langle v(0)v(t)\rangle, \tag{2}$$

may suffer from serious inaccuracies unless the exact form (1) is known. Moreover, the investigation of long-time tails can be fruitful in understanding some details of the kinetic behavior of the system. The present situation concerning these matters, however, is not clear-cut; a brief account follows.

Alder and Wainwright[3] discovered, during a series of numerical experiments in two and three dimensions, that the VAF presents a positive part having a long-time effect (1) with $\delta = d/2$, where d is the dimensionality of the system. This result may affect the same foundations of traditional kinetic theory, namely, the Bogoliubov ideas about sharply separated time scales during the system relaxation from a nonequilibrium initial state to a situation described by hydrodynamics.[1,2] The effect seemed confirmed[4] and several theoretical explanations arose; see Pomeau and Resibois,[5] Dorfman,[6] and van Beijeren[7] for reviews. More recently, however, even though the effect seems now also confirmed by scattering experiments,[8] it has been argued that long-time tails having the usual kinetic significance might have never been observed nor rigorously established by theory so far; see the recent controversy in Fox[9,10] and Adler *et al.*[11] for further details.

At the present time it can in principle be easier to analyze these matters in the context of one-dimensional systems. The exact analytical treatment of the infinite system of identical hard-core particles on a line[12,13] shows that the relaxation of a test particle in the system deviates from the short-time exponential behavior, and the VAF presents then a very small, negative part whose leading term is of the form (1) with $\delta = 3$. That is, the situation differs from the one depicted at $d = 2, 3$, where the tail is positive and the power-law exponent is $d/2$. Previous attempts to observe this effect during the computer simulation of one-dimensional systems[14–16] failed mainly because of bad statistics; recently, however, direct evidence was found for a tail t^{-3} in a one-component Lennard-Jones system in one dimension.[17]

We report in this Letter preliminary results of the temporal evolution in a computer of a binary mixture of 1000 hard rods on a ring. Half the particles, chosen at random, are assigned masses m_1 while the rest are assigned masses m_2. Nevertheless, our main results here probably hold as well when there is only one particle of mass m_2 in a system of light particles, a case where the statistics would be poorer, and it is thus less suitable for a numerical experiment. The system relaxes for different values of the mass ratio $\epsilon = m_2/m_1$ from a homogeneous state where the particles have randomly oriented velocities of equal magnitude, $\pm v$. Our motivation for this particular initial state is twofold: (a) The case with an initial velocity distribution $\pm v$ and $m_1 = m_2$ can be solved exactly[12,13] so that we have a clear guide and one may then concentrate on the particular behavior expected when m_2 becomes different from m_1. (b) The results in this Letter arise from a series of studies concerning the temporal evolution of systems relaxing from nonequilibrium conditions which are mainly focused on the "ergodic" behavior when $m_2 \neq m_1$.[16] Reference 16 states both that our system with $m_1 \neq m_2$ is ergodic in the velocity distribution (unlike the case $m_1 = m_2$) in the sense that, starting with an arbitrary distribution for the velocities, it reaches a Maxwellian distribution, and that other details of the final equilibrium state, such as the radial distribution function, are also practically independent of ϵ. Reference 16 also gives further details of the model and a description of the numerical procedure which introduces slight modifications in the standard algorithm.[3,4] We observe here long-time tails and investigate their dependence on ϵ to conclude about a crossover in δ as one increases the value of ϵ from unity. We also study the relaxation time of the system as a function of ϵ over a broad range of ϵ values.

The relaxation time, τ, is defined as the time the system takes to reach a Maxwellian velocity distribution. This can be estimated by visual examination of the temporal evolution of the velocity distribution (VD) or one may compute the Boltzmann's $H(t)$ function by proper numerical integration of the VD. For all cases, except $\epsilon = 1$, one observes that $H(t)$ monotonically decreases until it reaches the stationary regime where $H(t)$ fluctuates very near a constant value H_{eq}, i.e., $dH(t)/dt = 0$ from that moment which indicates that the VD has approximately a Maxwellian shape. The equilibrium value H_{eq} obtained as a time average over the stationary regime shows a clear dependence on ϵ, namely, it increases with ϵ. The relaxation times τ, estimated visually and estimated by analysis of the onset of condition $dH(t)/dt = 0$, agree very well with each other and show an interesting behavior. This is illustrated in Fig. 1 where τ is plotted versus ϵ. (Note the change of scale of the axes.)

As shown by Fig. 1, τ diverges when $\epsilon \to 1$; for $\epsilon = 1$ the initial velocity distribution $\pm v$ is conserved in time. The latter is consistent with the fact that the system with $\epsilon = 1$ is nonergodic in the VD so that only the distribution of a specified, test particle (otherwise indistinguishable from the others) would exhibit diffusion and approach to equilibrium in this case. By increasing ϵ one observes that τ presents a minimum around $\epsilon = 5$ and that τ increases, though rather slowly in this case, with increasing ϵ. The systems with $\epsilon = 50$ (and less markedly when $\epsilon = 30$) evolve very slowly because the light rods (one on the average) are surrounded by very heavy rods and there is a short-time tendency to reach a local equilibrium condition. Finally, it seems to us (having in mind that any experimental data are limited by necessity) that the systems reach practically the true equilibrium state (e.g., H_{eq}). As, however, one should probably expect that $\tau \to \infty$ when $\epsilon \to \infty$, our experimental points in Fig. 1 for

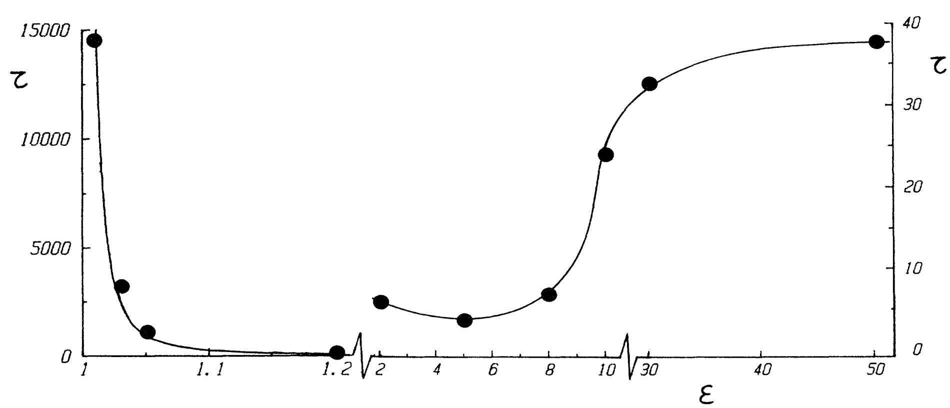

FIG. 1. The relaxation time τ, in units of the overall mean free time t_0, as a function of the mass ratio ϵ. Note the change of scale, both in the vertical and horizontal axes; the scale on the left corresponds to the data for $\epsilon \leq 1.2$, while the scale on the right is for $2 \leq \epsilon \leq 50$. The solid line is a guide to the eye. Note also that one should probably expect that $\tau \to \infty$ when $\epsilon \to \infty$ (see text).

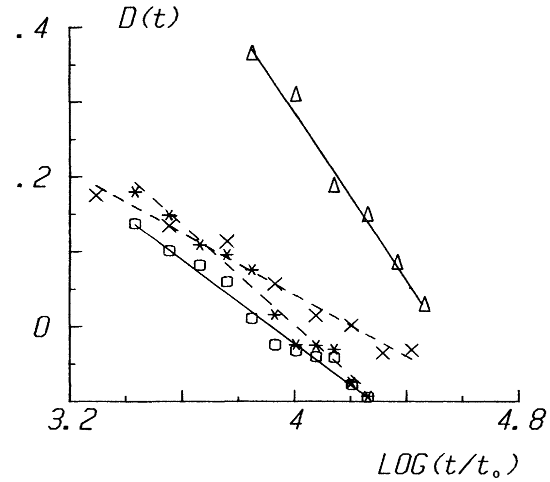

FIG. 2. The function $D_\alpha(t)$, as defined in Eq. (4), in arbitrary units vs $\ln t$. The symbols are as follows: triangles ($\epsilon = 8$, $\alpha = 2$), asterisks ($\epsilon = 2$, $\alpha = 1$), crosses ($\epsilon = 8$, $\alpha = 1$), and circles ($\epsilon = 2$, $\alpha = 2$).

$\epsilon \geqslant 30$ should be viewed as affected by much larger error bars than the others. We cannot be more precise about the large-ϵ limit with our present data; probably one should use a method different from the present numerical analysis in order to study the nature of the expected divergence for $\epsilon \to \infty$. Our data, on the other hand, show that the divergence for small ϵ seems to have a power-law nature, say,

$$\tau \sim (\epsilon - 1)^{-\sigma}, \quad \epsilon \to 1, \tag{3}$$

where $\sigma \lesssim 2$.

The temporal evolution of the VAF, which is computed in practice (for both species of particles) as the average of $v(0)v(t)$ divided by $v(0)^2$, is seen to reach (very small) negative values after the exponential decay for every mass ratio considered here; this is followed by a slow tendency towards zero from below. That is, we observe the long-time tails (1) in one-dimensional mixture systems, to our knowledge for the first time. Moreover, the details of this behavior are intimately related to the result (3). Indeed, we find evidence that $\delta \to 3$ when $\epsilon \to 1$, and that δ quickly decreases towards a value near unity when ϵ increases from $\epsilon = 1$. The former observation is consistent with the result $\delta = 3$ for a test particle starting at $t = 0$ from the origin of an infinite system with a velocity v'. The latter result $\delta \lesssim 1$, however, is probably rather unexpected, although it seems consistent with the situation for one-dimensional lattice systems.[18] We present some evidence of those facts in Fig. 2; this figure requires an explanation.

It is difficult in practice for us to draw conclusions about the details of long-time tails by looking directly to the VAF because the effect is small and the noise is important during the very final relaxation of the system.[14, 15] Thus we have analyzed the function

$$D_\alpha(t) = \left[\sum_{i=1}^{N_\alpha} v_i^2(0)\right]^{-1} \sum_{t'=0}^{t} \left[\sum_{i=1}^{N_\alpha} v_i(0) v_i(t)\right], \tag{4}$$

which behaves rather smoothly. Here $\alpha = 1, 2$ denotes the different species in the system, the computations refer [as well as those reported before for $H(t)$ and τ] to the case $N_1 = N_2 = 500$, and several mass ratios were considered now from $\epsilon = 1$ to $\epsilon = 8$. Note that function (4) is a simple extension to finite times and different masses of the fundamental expression (2). We find in this way that the only reasonable fit to the data for $\epsilon \gg 1$ has the form $D(t) = a + b \ln t$, with $a > 0$ and $b < 0$; as a matter of fact the data clearly deviate from a behavior $D = a + bt^m$, $m < 0$, and one obtains $a < 0$ and $b > 0$ on this assumption. This demonstrates that the negative tail has the behavior (1) with $\delta \simeq 1$; the case $\epsilon = 8$ is illustrated in Fig. 2. When $\epsilon \to 1$, however, the fit $D = a + bt^m$ becomes better, a and b are positive, and m approaches -2, which indicates that $\delta \to 3$ in (1). We expect to pursue these numerical studies and extend the above results to a broader range of ϵ values.

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