Molecular Chaos, Pair Correlations, and Shear-Induced Ordering of Hard Spheres

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We present results of molecular dynamics simulations that show that the shear-induced ordering of hard spheres is preceded by the apparent decrease to zero (in certain directions) of the anisotropic pair-distribution function (PDF) at contact. This precursor to the ordering is explained on the basis of a careful interpretation of the meaning of "molecular chaos" in hard-sphere systems. An ansatz is proposed to model the nonequilibrium PDF at finite separations and is shown to compare well with simulations. [S0031-9007(96)01073-3]

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Sheared fluids have become the standard testing ground of the methods nonequilibrium statistical mechanics [1,2]. This is because of the ease of characterizing the nonequilibrium state due to the existence of a well-defined control parameter, the shear rate, and the development of reliable simulation methods which do not give rise to complicating features such as boundary layers or significant size effects. It has been known for more than ten years that, at high shear rates, simple fluids undergo an ordering transition whereby the atoms are confined to planes perpendicular to the velocity gradient: In some cases, stringlike arrangements of atoms have been observed [3]. For hard spheres, the only system for which a realistic kinetic theory for moderately dense fluids exists, two closely related Enskog-level microscopic theories of the transition have been formulated, both of which relate it to a small-wavelength hydrodynamic instability [4,5]. These theories, however, offer little insight into the microscopic mechanism driving the ordering. In an effort to better understand the transition, we have performed a series of nonequilibrium molecular dynamics simulations of a sheared hard-sphere fluid in order to characterize the behavior of various quantities, such as the pressure tensor and the structure of the fluid, at a moderate density for which direct comparison with Enskog-based theory is possible. Our purpose here is twofold. First, we report on a structural anomaly which seems to be a direct precursor of the ordering transition: the apparent vanishing of the pair-distribution function (PDF) at contact, in a particular direction, at the transition point. Second, we show that this quantity can be quantitatively modeled by carefully interpreting the assumption of "molecular chaos" that underlies the Enskog description of hard-sphere fluids [6]. A simple extension of these ideas gives a model for the PDF at finite separations that compares well with the simulations.

The simulation method for sheared systems has been described in the literature [7], and its essential elements will only be briefly noted here. We use a cubic simulation cell with the flow along the x direction and the velocity varying linearly in the y direction. The flow is imposed by the use of Lees-Edwards [8] boundary conditions (periodic boundaries in the comoving frame). Because a sheared fluid heats, a thermostat is applied to maintain a nearly constant temperature (defined as the excess kinetic energy relative to the macroscopic flow). In the present simulations, the excess velocities were rescaled whenever the temperature exceeded $1.05T_0$, where T_0 was the desired temperature, to give a new temperature of $0.95T_0$. Since the relevant quantity for characterizing the state is the shear rate times the Boltzmann time, which varies as the inverse square root of the temperature, the effective reduced shear rate varied by approximately $\pm 3\%$. We have performed our simulations on a system of 108 particles at a reduced density of $n^* = 0.5$. The systems were equilibrated for 2×10^6 collisions and statistics were gathered over the next 10^6 collisions. The data were analyzed using Erpenbeck's pooling method [7] to estimate errors. In this Letter, we focus on only two aspects of our simulations: the quantitative determination of the critical shear rate and the behavior of the PDF. In the following, we use units in which the hard-sphere radius and mass and Boltzmann's constant times the temperature are equal to one. The position and momentum of the ith atom will be denoted as $\vec{q}_i$ and $\vec{p}_i$, respectively.

From the work of Erpenbeck [3], we know that the ordering transition occurs gradually as the shear rate increases above a critical value and that the region of coexisting ordered and disordered fluid broadens as the density decreases. Therefore, in order to make a quantitative determination of the critical shear rate we have monitored an "order parameter," intended to be sensitive to a stringlike ordering of the fluid, defined as

$$N_s = \sum_{i \neq j} \langle \Theta(0.25 - q_{ij,y}^2 - q_{ij,z}^2) \rangle . \qquad (1)$$

This is the average over the system of the number of neighbors of each atom which is within a distance of 0.5 when projected on the y-z plane. We have also monitored the anisotropic structure of fluid. First, we consider the PDF at *contact*. Since the PDF cannot be measured at a

point, we have actually monitored the quantity

$$g(\hat{r},\phi) \equiv \frac{1}{2\pi[1-\cos(\phi)]}\frac{2}{N(N-1)} \times \sum_{i<j}\langle\delta(q_{ij}-1)\Theta(\hat{q}_{ij}\cdot\hat{r}-\cos(\phi))\rangle \quad (2)$$

which is the PDF at contact averaged over a solid angle of altitude $\cos(\phi)$ centered on the direction $\hat{r}$. It is normalized so that in the limit $\phi \to 0$ it becomes the PDF at contact in the direction $\hat{r}$. To evaluate this limit, we calculate this quantity for a sequence of 5 values of ϕ, from $\phi = 0.1\pi$ to 0.5π and interpolate these to the value at zero using a polynomial in $x = \cos(\phi)$. In the following, we will only consider the direction $\hat{r} = (\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0)$ in which, by symmetry, the greatest effects are expected.

The behavior of both quantities is summarized in Fig. 1. The order parameter fluctuates near its equilibrium value up to $a^* \approx 0.8$. Above this, it begins to increase monotonically indicating the onset of ordering. The first point that differs from the value at equilibrium by more than the estimated errors of the measurements is at $a^* = 0.91$. A quadratic fit to the values greater than $a^* = 0.81$ crosses the equilibrium value at $a^* = 0.856$. The values between 0.91 and 1.21 vary almost linearly with the shear rate: A straight-line interpolation of these gives a value of 0.84 for the crossing. Finally, the point at 0.81 is marginally consistent, given the estimated errors, with the equilibrium value, but it does lie further above the equilibrium value than does any other point. Since the reduced shear rate fluctuates by about 3%, we expect the order parameter to begin to increase at a reduced shear rate about 3% below the transition point. A very small increase of the order parameter at $a^* = 0.81$ would therefore be consistent with a transition point of $a^* \sim 0.835$.

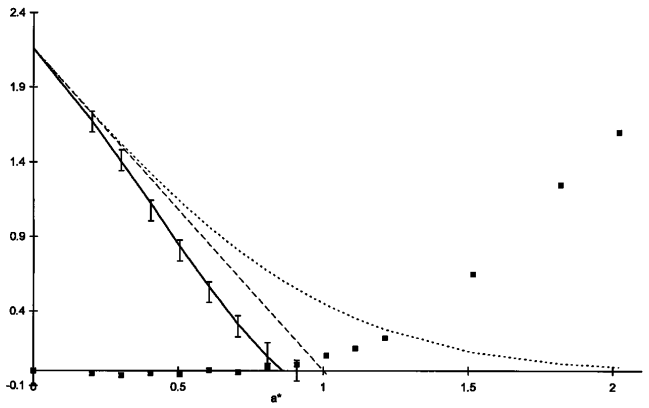

FIG. 1. The quantities N_s (squares) and $g(\hat{r},\phi)$ (bars) as defined in the text and determined by simulation as functions of the reduced shear rate. The bars indicate the estimated error in the latter quantity. The full line is from Eq. (5), the dashed line is from the linearization of Eq. (5), and the dotted line is the local-equilibrium contribution.

In contrast, the PDF at contact in the chosen direction decreases monotonically below the transition and is very small above the transition. Below the critical shear rate, the angular dependence fits well by a quadratic in $\cos(\phi)$, and virtually identical values are obtained for $\phi = 0$ if a cubic is used instead. At low shear rates, the PDF decreases monotonically. Above $a^* \sim 0.9$, the interpolations become highly inaccurate; in fact, for all higher shear rates, the measured value of $g(\hat{r},\phi)$ for the smallest finite angle is no larger than the estimated error, and it no longer appears to be a continuous function of ϕ. To quantify the point at which the PDF appears to vanish, we note that at $a^* \sim 0.9$ we obtain a very small value (approximately 0.001). Again, the 3% fluctuations in the shear rate mean that we would expect the measured value to go to zero at about 3% below the actual transition point. This gives an upper bound of 0.88 for the vanishing point.

To explain the behavior of the PDF at contact, we note that the dynamics of hard spheres consists of two parts: free streaming interrupted by elastic binary collisions. The effect of the latter on, e.g., two body, the distribution function can be summarized as

$$f(1,2)\delta(q_{12}-1) = \left\{\begin{array}{c}\Theta(-\vec{q}_{12}\cdot\vec{p}_{12})f_0(1,2)\\ +\Theta(\vec{q}_{12}\cdot\vec{p}_{12})\hat{b}f_0(1,2)\end{array}\right\} \times \delta(q_{12}-1), \quad (3)$$

where the first term in brackets introduces the *precollisional* distribution, $f_0(1,2)$, whereas the second term expresses the *postcollisional* distribution in terms of the precollisional function. The operator $\hat{b}$ has the effect of replacing the relative momentum by its postcollisional value: $\hat{b}\vec{p}_{12} = \vec{p}_{12} - \vec{q}_{12}\vec{q}_{12}\cdot\vec{p}_{12}$ (where $\vec{q}_{12}$ is evaluated at contact). For hard spheres, the Enskog equation for the one-body distribution may be derived [6] from the first equation of the BBGKY hierarchy [9] by using the assumption of molecular chaos in the form $f(1,2) \approx f(1)f(2)g(\vec{q}_{12})$. However, as has been noted previously [6], this is really an overprescription since only the *precollisional* part of the two-body distribution (at contact) enters into the first BBGKY equation. In our notation, only $f_0(1,2)$ is required. It is therefore sufficient to derive the Enskog equation to make the weaker assumption $f_0(1,2) \approx f(1)f(2)g(\vec{q}_{12})$. This leads us to express the molecular chaos assumption in the form

$$f(1,2)\delta(q_{12}-1) \approx \left\{\begin{array}{c}f(1)f(2)g(\vec{q}_{12})\\ +\Theta(\vec{q}_{12}\cdot\vec{p}_{12})(\hat{b}-1)f(1)f(2)g(\vec{q}_{12})\end{array}\right\} \times \delta(q_{12}-1). \quad (4)$$

This simply expresses the obvious fact that, although one can assume that two atoms are uncorrelated *before* a collision, they are necessarily correlated *after* a collision. Integrating Eq. (4) over momenta gives a consistent

expression for the pair-distribution function at contact including nonequilibrium corrections. In the present case, we make an approximate evaluation using the solution, to first order in the shear rate and in the lowest Sonine approximation, of the Enskog equation, given by $f(p') = \phi(p')[1 - a\nu^* p_x' p_y' + o(a\nu^*)^2]$, where $\phi(p')$ is a Maxwellian and the density-dependent constant, ν^*, is given in the literature [5]. Normalizing to the equilibrium PDF, we obtain

$$\frac{g(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0)}{g_{\rm eq}(1)} \approx 1 - \operatorname{erf}\left(\frac{a}{4}\right) - \frac{a^2\nu^*}{4\sqrt{\pi}} e^{-(1/16)a^2}\left(1 + \frac{a\nu^*}{64}(a^2 - 24)\right). \tag{5}$$

The nonequilibrium corrections in Eq. (5) are calculated to second order in $(a\nu^*)$ even though the distribution as given is only accurate to first order. In fact, we have calculated the full second-order contributions and find them to be negligible: They will henceforth be neglected. The results, as shown in Fig. 1, are in good agreement with the simulations. Also shown separately in Fig. 1 are the local equilibrium contribution (obtained by setting $\nu^* = 0$) and the linearized version of Eq. (5). While the local-equilibrium distribution gives a decrease in the pair-distribution function, it is clear that the dissipative terms and the full nonlinear dependence on the shear rate are needed to fully explain the size of the decrease at large shear rates. Equation (5) indicates that the PDF should vanish, at this density, at $a^* = 0.86$; above this value, it gives negative values which is unphysical and may be traced to the fact that the approximate one-body distribution used is not positive definite. Nevertheless, it appears to accurately model the PDF even quite close to the point at which it becomes unphysical. Interestingly, the onset of unphysical behavior at a density of $n^* = 0.704$ is $a^* \sim 0.7$ which is again close to the critical shear rate of $a^* \sim 0.8$ reported by Erpenbeck [3].

In order to interpret these results, we first note that the PDF at contact for hard spheres is obviously directly related to the collision rate. Suppose that two atoms are separated by a relative position of about $(\frac{\pm 1}{\sqrt{2}}, \frac{\pm 1}{\sqrt{2}}, 0)$ just before a collision. Then, their relative velocity, due to the flow, will be $\sim(\frac{\pm a}{\sqrt{2}}, 0, 0)$, and this tends to *increase* the separation between the atoms. Thus, to have a collision, their relative thermal velocities must be greater than $\frac{a}{\sqrt{2}}$ which immediately implies that, as the shear rate increases, collisions in this direction, and hence the PDF in this direction, must decrease. The same type of argument indicates an increase in the collision rate for relative separations of $(\frac{\pm 1}{\sqrt{2}}, \frac{\mp 1}{\sqrt{2}}, 0)$. For very large shear rates, we can then imagine that the latter collisions dominate and the atoms become confined to planes since, if one moves along the direction of the gradient, a faster atom overtakes it, giving a collision that pushes it in the $(\frac{1}{\sqrt{2}}, \frac{-1}{\sqrt{2}}, 0)$ direction; moving against the gradient, it overtakes a slower atom and is scattered into the $(\frac{-1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0)$ direction.

At finite separations, we expect the postcollisional correlations to decay as a function of distance due to the interaction of the particles with the surrounding fluid. We can model this behavior by assuming that the decay is solely a function of the separation between the particles. This then gives an ansatz for the decay of the correlations of the form

$$f(1,2) \approx f(1)f(2)g(\vec{q}_{12}) + w(\vec{q}_1, \vec{q}_2)\Theta(x - y)(\hat{b}_c - 1)f(1)f(2)g(\vec{q}_{12}), \tag{6}$$

where the prefactor, $w(\vec{q}_1, \vec{q}_2)$, is to be determined subject to the boundary condition that it equals one at contact. The step function tests whether two particles with the given position and momentum would have collided if their trajectories are projected backwards in time neglecting all other particles. Its arguments are $x = \vec{p}_{12} \cdot \vec{q}_{12}/p_{12}q_{12}$ and $y = \sqrt{1 - 1/q_{12}^2}$. The operator $\hat{b}_c$ replaces the relative momentum by its postcollisional value $\hat{b}_c\vec{p}_{12} = \vec{p}_{12} - 2\hat{q}_{12}^{(c)}\hat{q}_{12}^{(c)} \cdot \vec{p}_{12}$, where $\hat{q}_{12}^{(c)}$ is the relative separation at the time of the collision and is given by $\hat{q}_{12}^{(c)} = \vec{q}_{12} - \vec{p}_{12}t_c$ with the time since collision given by $p_{12}t_c = q_{12}(x - \sqrt{x^2 - y^2})$. The only unknown is the amplitude w. To determine it, we substitute Eq. (6) into the second equation of the BBGKY hierarchy and integrate over momenta. The result is a first order partial differential equation for the unknown function. For uniform shear flow, the solution of the equation is difficult to carry out so we have only attempted to determine the amplitude to first order in the shear rate. This necessarily limits the validity of the results to small separations

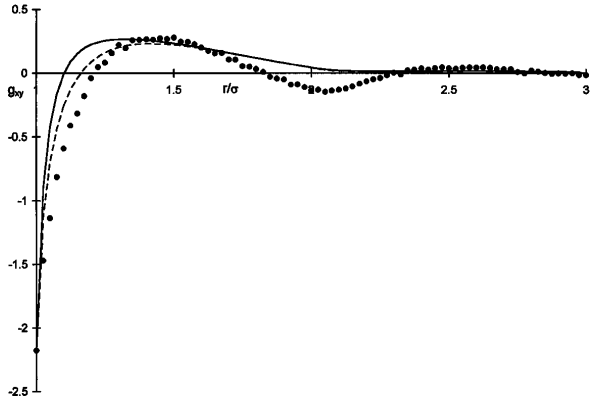

FIG. 2. The quantity $g_{xy}(r)$ for reduced shear rate $a^* = 0.5$. The circles are from simulation, and the lines are from the calculation described in the text and based on Eq. (6). The full line uses the equilibrium value of ν^* while the dashed line uses the value taken from the simulations.

since, at intermediate points in the calculations, functions depending on the combination aq_{12} must be expanded which demands that $aq_{12} \ll 1$. Figure 2 shows the quantity $g_{xy}(r) = \frac{15}{4\pi}\langle \hat{q}_x \hat{q}_y \delta(q - r)\rangle$ as determined by simulation for $a^* = 0.5$ and the result of the ansatz. For small separations, the theory appears to agree reasonably well with the simulation values giving a reasonable estimate for the height and position of the first peak. For larger separations, the ansatz decays too rapidly and does not give as much structure as is observed in the simulations. The shape of the curve is sensitive to the value of ν^* entering in the approximate distribution function. The figure also shows the calculation using the value of this constant determined from the simulations (specifically, from the kinetic part of the shear viscosity), and it is evident that this improves the description of the small distance behavior. Although not reliable at large separations, the ansatz appears to capture the dominant effect which is the rapid decay of the nonequilibrium correlations and the position and height of the first peak. It thus appears that most of the structural difference between the equilibrium and shear fluids arises solely from the effects of momentum correlations generated by two-body collisions.

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