

## Shear-Induced Alignment of Colloidal Particles in the Presence of a Shear Flow

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We observed a shear-induced alignment of colloidal particles in a Brownian-dynamics simulation carried out in the presence of an oscillating shear flow. As the shear rate  $\gamma$  is increased for temperatures near the melting point, we first observe shear thinning followed by a transition to a state with two-dimensional order in the plane perpendicular to the flow. In contrast to earlier nonequilibrium molecular-dynamics studies which also found a similar result, no thermostat is needed to keep the system stable.

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Charge-stabilized colloidal suspensions are very valuable model systems for probing the effect of shear flow on the properties of dense fluids and solids.<sup>1</sup> Because of the large particle size and spacing, the energy density and elastic constants for charge-stabilized suspensions are orders of magnitude smaller than those in conventional atomic systems. Thus, at shear rates which are readily accessible in the laboratory, it is possible to perform experiments in which the applied stresses are comparable to the energy density. As a result, many new phenomena have been observed. One such phenomenon is shear-induced melting,<sup>2</sup> in which a dilute or semidilute suspension which has long-range crystalline order (either bcc<sup>2</sup> or fcc<sup>3</sup>) at zero shear is observed to undergo a series of structural changes as the shear rate is increased. These structures include a flowing crystal, sliding layers, and string and amorphous ordering of particles. Other effects including laser-induced freezing<sup>4</sup> and shear-induced ordering<sup>5</sup> have also been observed.

There have also been a number of theoretical<sup>6</sup> and computational<sup>7</sup> investigations of the effect of high shear rate  $\gamma$ , though mostly for atomic fluids. The conventional simulation technique for studying the relation of rheological properties to microscopic particle order in pure fluids is nonequilibrium molecular dynamics (NEMD). However, to observe any effect for atomic systems,  $\gamma$  has to be very large ( $10^{10}$ – $10^{12}$  sec<sup>-1</sup>). This introduces considerable energy into the system which must be continuously removed by rescaling<sup>7</sup> the pseudovelocity of each particle,  $\mathbf{v}_i(t) - \hat{\mathbf{e}}_x v_T(z_i(t))$ . Here  $\mathbf{r}_i(t)$  and  $\mathbf{v}_i(t)$  denote the position and velocity of particle  $i$ ,  $z_i(t)$  is the  $z$  component of  $\mathbf{r}_i(t)$ , and  $\hat{\mathbf{e}}_x v_T$  is the expected profile of the velocity in the  $z$  direction,  $v_T(z) = z\gamma$ . Using this technique, several groups<sup>7</sup> have observed the formation of particle layers with the shear direction normal to the layers and the formation of strings of particles parallel to the velocity direction. However, because  $\gamma$ 's used in the NEMD are so high, one must be concerned about whether the observed phenomena are real or an artifact of the technique. One indication of the latter was recently dis-

cussed by Evans and Morriss<sup>8</sup> who found that the shear-induced alignment of particles into strings in these earlier NEMD studies<sup>7</sup> was in fact not real but simply due to the form of the temperature thermostat. While their results do not rule out a string-ordered phase entirely, they do<sup>8</sup> suggest that one should not expect to find it for dense atomic fluids.

It is also not clear whether any simulation on atomic fluids can be applied to colloidal suspensions. In particular, they do not take into account the liquid in which the particles are suspended, either in the form of its contribution to the suspension viscosity or in terms of the hydrodynamic interactions induced by the back flow of the surrounding fluid. For these reasons, we have decided to carry out a Brownian-dynamics simulation of suspensions of charge-stabilized polystyrene spheres (polyballs) in the presence of an oscillating shear flow. Because the polyballs are large ( $> 300$  Å) compared to the surrounding fluid, we treat the fluid as a viscous medium in which the motion of the polyballs is overdamped. In Ref. 9, we studied the self-diffusion in the fluid under shear flow. We found, in agreement with the experimental results of Qiu *et al.*,<sup>10</sup> that aside from the usual enhancement of the diffusion due to Taylor dispersion<sup>11</sup> in the shear-flow direction, there is an additional contribution to the self-diffusion coefficient  $D$  in all three directions which increases as  $\gamma$  increases. Here we study a similar system in the vicinity of the melting point where we observe string ordering of the particles at relatively low shear rates. Our results differ from earlier observations of this phenomena in that no thermostat is needed in our Brownian-dynamics simulations. The strong damping of the particles due to the viscous medium is sufficient to keep the system stable. In this paper, we present evidence for the string-ordered phase and determine the phase diagram as a function of reduced temperature and shear rate.

The system we considered consists of  $N$  identical spheres of radius  $R$  dispersed in a fluid of dielectric constant  $\epsilon$  at temperature  $T$ . Alexander *et al.*<sup>12</sup> have shown

that in the dilute limit, the interaction between polyballs can be treated by a repulsive Yukawa potential with a renormalized charge  $Z^*$  which differs from the bare charge  $Z$ ,

$$U(r) = U_0 a \exp(2\kappa R) (1 + \kappa R)^{-2} \exp(-\kappa r) / \epsilon r. \quad (1)$$

Here  $\epsilon$  is the background dielectric constant,  $\kappa$  is the inverse screening length, and  $U_0 = Z^{*2} e^2 / \epsilon a$ . Experimentally,  $\kappa$  can be changed by adding counterions to the fluid. We used the Brownian-dynamics method of Ermak<sup>13,14</sup> which is based on the Smoluchowski equation, except that we added a shear flow in the  $x$  direction and velocity gradient in the  $z$  direction. We neglected hydrodynamic interactions in the present study. Thus in the presence of an oscillating shear of frequency  $\omega$  and amplitude  $A$ , the particle trajectories at time  $t + \Delta t$  are determined by

$$\begin{aligned} \mathbf{r}_i(t + \Delta t) = & \mathbf{r}_i(t) + (D_0/kT) \mathbf{F}_i(t) \Delta t \\ & + \delta \mathbf{r}_i^G + \hat{\mathbf{e}}_x A z_i \sin(2\pi\omega t) \Delta t, \end{aligned} \quad (2)$$

where  $F_i(t)$  is the force on particle  $i$  from the other particles. We set the mass  $m$  of each particle equal to 1. The random displacement  $\delta r_{ia}^G$  is chosen independently from a Gaussian distribution with zero mean and variance  $\langle [\delta r_{ia}^G(t)]^2 \rangle = 2D_0 \Delta t$ . Here  $D_0$  is the free diffusion constant and  $A$  is the maximum displacement along the shear velocity direction ( $x$ ) (see inset of Fig. 1) by which two particles can be separated due to shear flow if the distance between them is one unit along the  $z$  direction. We used periodic boundary conditions in all three directions and kept the volume constant. If a particle exited

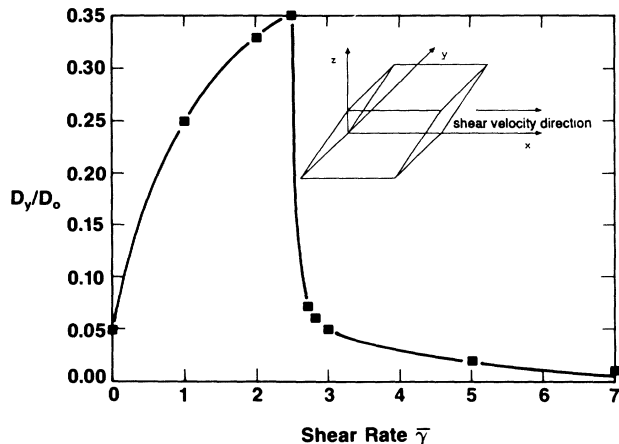


FIG. 1. Diffusion coefficients  $D_y/D_0$  as a function of shear rate  $\bar{\gamma}$  at reduced temperature  $\tilde{T} = 2.82 \times 10^{-3}$ .  $D_y/D_0$  increases monotonically for  $\bar{\gamma} < \bar{\gamma}_c$ . At  $\bar{\gamma}_c \approx 2.7$ ,  $D_y/D_0$  drops rapidly to a small value. Similar behavior occurs for  $D_z$ . Inset: The coordinate system in which the shear flow is along the  $x$  axis and the shear gradient is along  $z$ . The shear rate is linear along the  $z$  direction and does not change in the  $y$  direction.

from the top, it was introduced at the bottom with a shift  $AL_z \sin(2\pi\omega t)$ , where  $L_z$  is the length of the box in the  $z$  direction. The average shear rate can be defined as

$$\bar{\gamma} = \langle dx/dt \rangle / z = 2\pi\omega A \langle \cos(2\pi\omega t) \rangle = 4A\omega, \quad (3)$$

where the average  $\langle \rangle$  is over  $\frac{1}{4}$  of a cycle. We chose the time step  $\Delta t$  in the simulation to be  $0.001 \tau_0$ , where  $\tau_0$  is the time for a noninteracting polyball to diffuse an interparticle spacing  $a = (N/V)^{-1/3}$ . In our simulation, the amplitude  $A$  ranged from 1 to 10 and the Peclet number  $P_c = a^2 \bar{\gamma} / D > 1$ , indicating that the particles are convected much further than they diffuse.

For definiteness, we chose parameters to be comparable with the recent experiments by Qiu *et al.*,<sup>10</sup> who measured  $D$  in two directions under shear. The particle size is  $R = 0.091 \mu\text{m}$  and effective charge is  $Z^* = 400$ . The screening length  $\lambda = a\kappa$  is chosen to be 5. For Yukawa systems,<sup>15</sup> it is convenient to scale  $T$  by the Einstein frequency for the fcc lattice at  $T=0$ ,  $\tilde{T} = kT / m\omega_E^2 a^2$ . For  $\lambda = 5$ ,  $m\omega_E^2 a^2 / U_0 \approx 0.3438$  and the melting point is at  $\tilde{T}_m \approx 3.8 \times 10^{-3}$ . Most of the simulations were for  $N = 500$  particles in a cubic box. Some runs were made with  $N = 504$  in a rectangular box with the ratio of lengths of the three sides of the box equal to  $7b : 8(\sqrt{3}/2)b : 9(\frac{2}{3})^{1/2}b$  ( $b = 2^{1/6}a$ ) to check that the string-ordered phase was not an artifact of the cubic box. In this system the  $x$  direction lays parallel to lines of atoms in the  $x$ - $y$  plane and a shear flow in the  $x$  direction would be along the most stable shear plane, the (111) face.<sup>3</sup>

We started most of our simulations from a liquid state far above  $\tilde{T}_m$  and reduced the density slowly to reach the desired phase point. Since all of the runs were either slightly above or below  $\tilde{T}_m$ , the  $\gamma = 0$  diffusion coefficients were significantly less than  $D_0$ . We then applied a shear flow to the system by increasing  $\bar{\gamma}$  slowly from zero, letting the system come to a stable state before increasing  $\bar{\gamma}$  further. Typically we ran  $(3-8) \times 10^4 \Delta t$  at each point. The diffusion coefficients in the two directions perpendicular to the flow,  $D_y$  and  $D_z$ , increase monotonically<sup>9,10</sup> with  $\bar{\gamma}$ , as shown in Fig. 1. Above a shear rate  $\bar{\gamma}_c$ , which depends on  $\tilde{T}$ , the diffusion coefficients drop very rapidly with increasing  $\bar{\gamma}$ , indicating that some type of ordering may be occurring. To try to understand what is happening above  $\bar{\gamma}_c$  we examined the projections of the position of each particle onto the  $x$ - $y$ ,  $x$ - $z$ , and  $y$ - $z$  planes. From these projections, like those shown in Fig. 2 for the temporal evolution of the system after the shear was switched on, we can see that when the shear rate is high enough, there is string ordering along the  $x$  direction, in each  $x$ - $y$  plane, close packed along the  $z$  direction. Within each string the particles are not ordered. Below  $\bar{\gamma}_c$ , we saw no evidence for string ordering. Note that this string ordering is similar to that observed earlier by NEMD simulations,<sup>7</sup> though there it may be due to artifacts of the thermostat.<sup>8</sup>

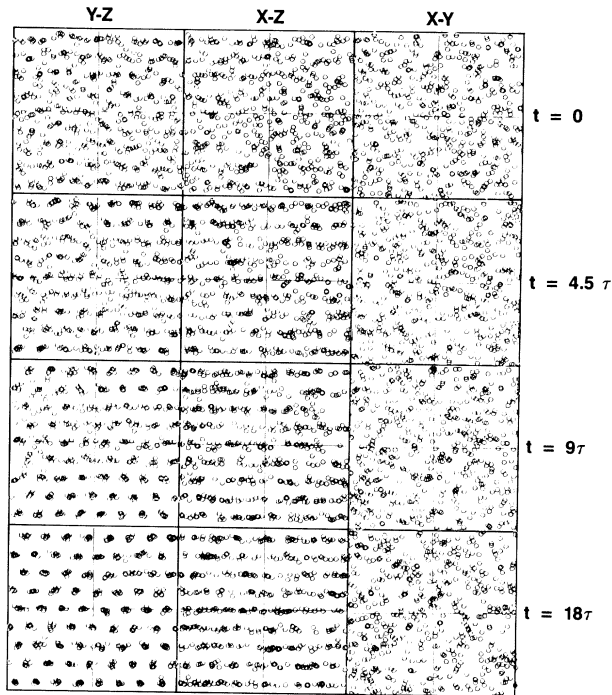


FIG. 2. Time evolutions starting from  $t=0$  when shear was applied. Three projection planes for a system in the string-ordered phase,  $\bar{T}=3.41 \times 10^{-3}$  and  $\bar{\gamma}=20$ .

We also calculated the structure factor  $S(\mathbf{k})$ . Since the system is anisotropic under shear flow, we calculated the anisotropic structure factor, e.g.,  $S(k_z)$  by choosing  $\mathbf{k}$  parallel to  $\mathbf{z}$ . As shown in Fig. 3, the peak in  $S(k_z)$  increases dramatically as  $\bar{\gamma}$  increases, confirming that in the presence of a shear flow layering has occurred. For  $\bar{\gamma}$  far above  $\bar{\gamma}_c$ , the peak height reaches a value of order  $N$ , indicative of a near-perfect layering into planes with a well-defined layer spacing. Along  $k_y$ , the structure factor does not depend on the shear rate below  $\bar{\gamma}_c$ , in agreement with our earlier results.<sup>9</sup> However, when  $\gamma$  exceeds  $\bar{\gamma}_c$ , the second peak in  $S(k_y)$  becomes larger than the first peak. This increase in the height of the second peak is due to the ordering of the strings into a triangular lattice in the  $y$ - $z$  plane as seen in Fig. 2.

The transition to the string-ordered phase appears to be continuous. We made several runs in which we increased the shear rate to values above  $\bar{\gamma}_c$  and then back down again. No hysteresis was observed. Over the range of amplitudes  $1 < A < 6$  and frequency  $\omega$  that we could study, the shear ordering and  $S(\mathbf{k})$  did not depend on  $A$  and  $\omega$  separately, only on the product  $\bar{\gamma}$ . However, at lower frequencies where the diffusive motion dominates over the convective motion, it is possible that the shear ordering may depend on amplitude and frequency separately. This is an interesting regime for further study.

To check that this string ordering was not an artifact

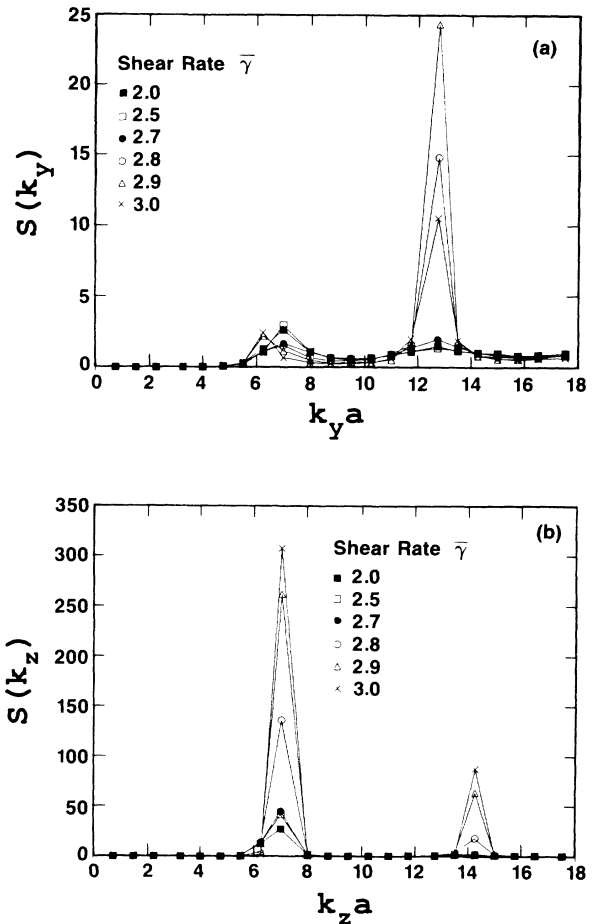


FIG. 3.  $S(k_y)$  and  $S(k_z)$  at different shear rates for  $\bar{T}=2.82 \times 10^{-3}$ . For low shear, below  $\bar{\gamma}_c=2.7$ , the second peak in  $S(k_y)$  is lower than the first peak, while in the string-ordering phase, the second peak is much larger than the first one.

of the cubic box, we also made some runs with a rectangular box containing 504 particles. We observed a very similar string ordering in this system as well. The critical shear rate  $\bar{\gamma}_c$  was essentially the same as for  $N=500$ . From the projection on the  $y$ - $z$  plane as well as  $S(\mathbf{k})$ , we can easily distinguish the string-ordered phase from a sliding fcc phase. Even though the  $N=504$  system is more favorable than the cubic  $N=500$  system for simply sliding the fcc layers over each other, the system prefers to reorganize into the string-ordered phase. Since we find similar results for the two systems, we believe that our results are probably not due to any artificial constraint imposed on the system by the shape of the box. As a final check, we also started our simulations from the fcc phase and a layered state with only eight layers. In both cases the final string-ordered state was identical to that discussed above.

In Fig. 4 we present the phase diagram where we ob-

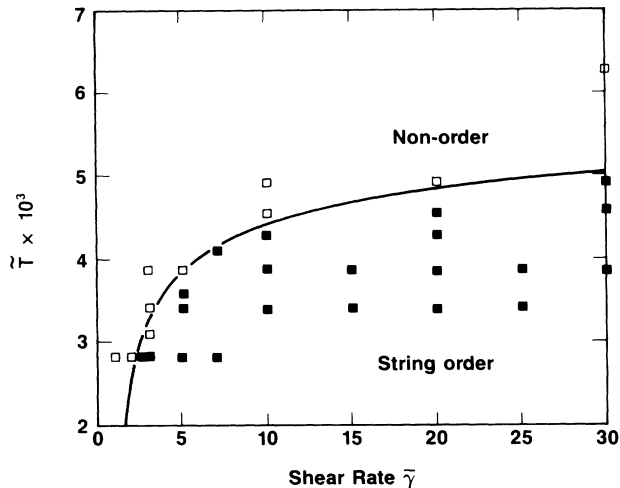


FIG. 4. The phase diagram of the string ordering, for  $\lambda = \kappa a = 5$ . The melting temperature is  $\tilde{T}_m \approx 3.8 \times 10^{-3}$ .

serve string ordering in terms of  $\tilde{T}$  and  $\bar{\gamma}$  for  $\lambda = 5$ . We used the height of the peaks in  $S(k_y)$  as a simple criteria to determine this phase diagram. When the height of the second peak exceeded the first, we labeled this as the string-ordered phase. The phase boundary agreed with the point where the diffusion coefficients (Fig. 1) decreased rapidly with increasing  $\bar{\gamma}$ . From the phase diagram we can see that most string order occurs in the supercooled liquid region below  $\tilde{T}_m$ . Only for higher shear rates is the phase boundary close to  $\tilde{T}_m$ . For  $T$  far above  $\tilde{T}_m$ , there is no string ordering, consistent with the experiments of Qiu *et al.*<sup>10</sup> and our earlier simulations.<sup>9</sup> Thus for charged colloids it appears that one must be close to the melting line to observe the string-ordered phase. This is in agreement with simulations we have carried out for  $\lambda = 3$  and 9.

We also tested whether the shear string ordering would effect crystallization. Starting from a supercooled liquid, we applied a large enough shear to reach the string-ordering state. We then turned off the shear. The system always returned to the supercooled liquid phase and not a crystal. Thus the shear does not seem to help the system to crystallize at least for the relatively short-

range interaction,  $\lambda = 5$ , studied here.

In summary, we have observed for the first time a shear-induced alignment of colloidal particles in a Brownian-dynamics simulation. This phase which has two-dimensional order in the plane perpendicular to the flow should generally be observable for a wide range of colloidal systems provided the reduced temperature is near or below  $\tilde{T}_m$  and  $\lambda$  is not too large.

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