THE SHEAR INDUCED DISORDERING TRANSITION IN A COLLOIDAL CRYSTAL

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1.The Phenomenon

The following experiment, carried out on an aqueous suspension of charged polystyrene particles, was described by Ackerson and Clark[1] in 1983. At equilibrium the suspension adopted a crystalline structure. As an applied shear rate was increased the system underwent a sequence of reversible structural transitions: crystalline → twinned crystals → sliding hexagonal layers normal to the shear gradient → 'strings' aligned along the flow direction → complete disorder. This shear induced disordering (SID) phenomenon presents us with some fundamental puzzles. How does the imposed shear perturb the subtle configurational averaging which we know establishes the stability of the crystalline phase? How should we treat the stabilization of ordered structures in systems constrained to nonequilibrium steady states? In this paper, we shall try to address these issues through the simulation of the disordering transition using a nonequilibrium Brownian dynamics algorithm.

2. Two Pictures - "Shear Melting" vs "Mechanical Instability"

How should we think about the SID process in colloidal crystals? To make this question concrete we need some possible answers to consider. The literature currently offers two choices. One approach[2], which we shall call "shear melting", is to consider the action of the applied shear on only the short range correlations in the suspension. One then formulates an effective free energy based on these new perturbed particle correlations. In this picture, shear induced disordering occurs because increasing the shear rate leads to an increase in the effective free energy of the ordered phase. The SID process can then be regarded as the continuation of the equilibrium melting transition into the space of nonequilibrium steady states. One difficulty for this 'extended thermodynamics' is to account for the steady state structures observed by in suspensions, such as hexagonal planes and strings, which do not have an equilibrium analogue.

An alternative approach[3,4,5] involves considering the coupling of the applied shear to the collective fluctuations of the ordered phase in the form of the transverse modes. The convection of a fluctuation with amplitude along the shear gradient can result in high local strains and, hence, disordering. Hoffman's early model of torque induced disordering[6] can be expressed in terms of this picture. A weakness of these mechanical models is the neglect of the effects of shear on the elastic modulus and the amplitudes of the collective fluctuations. A distinctive feature of these theories of the mechanical instability of the shearing colloidal crystal is the important role played by long wavelength fluctuations. A consequence of this role is the prediction that the SID transition should move to lower shear rates with increasing length of the crystal along the velocity direction. We shall test for such a size dependence in the simulations.

3. Model System and Simulation Algorithm

To simulate the overdamped motion of colloidal particles in the shearing solvent we have used the following nonequilibrium Brownian dynamics algorithm to calculate the change Δr_i of the position of the ith particle in a time step Δt, $\Delta r_i = (\dot{\gamma} y_i \mathbf{e}_x + D_o F_i/k_bT)\Delta t + \mathbf{R}_i$. Here $\dot{\gamma}$ is the shear rate with the gradient parallel to the y direction and the velocity parallel to the x direction. y_i is the y coordinate of the ith particle, $\mathbf{e}_x$ is the unit vector along the x direction, F_i is the net force due to the interparticle

potential and T is the temperature. R_i is a stochastic contribution to the particle displacement chosen from a Gaussian distribution with $< R_i > = 0$ and $< R_i \cdot R_j > = 6D_o\Delta t\delta_{ij}$. We have neglected the hydrodynamic interactions between particles and so shall restrict our attention to low density suspensions at low shear rates. Standard periodic boundary conditions are applied in the velocity and vorticity directions while 'sliding box' boundary conditions apply along the shear gradient. Simulations described here ranged in particle number between 216 and 840.

The interparticle potential is the Yukawa potential, $V(r) = V_o \exp(-\kappa r)/r$. In order to model the low salt concentrations of the experiment[1], we have chosen the smallest value of κ, the inverse Debye length, our system size allows. In this case, $\kappa a = 3.1$, where $a = \rho^{-1/3}$ and ρ is the density. We have used the following reduced units: $r^* = r/a$, $T^* = 6k_BT/V_o$ and $\Delta t^* = \Delta t/(\tau_s T^*)$ where, for the structural relaxation time, we have used $\tau_s = a^2/6D_o$. This leaves us with a reduced temperature set by the stochastic bath, i.e. $<(R^*)^2> = T^*\Delta t^*$. We use the temperature rather than the Debye length to adjust the thermodynamic state of the system. Shear rates are given as Deborah numbers where $D_e = \tau_s\dot{\gamma}$.

4. Results: The Shear Induced Disordering Transition[7]

A bcc crystal was equilibrated at $T^* = 0.0237$. The shear rate was then increased gradually, with runs of over 10^5 time steps at each shear rate to establish the new steady state. The crystal was oriented with its 110 plane normal to the shear gradient and the 111 direction aligned along the flow velocity. All other orientations were found to disorder completely at the lowest shear rate studied, in agreement with the experimental observation of only this alignment. Time averaged scattering intensities were calculated in the velocity-vorticity (k_x, k_z) plane and the velocity-gradient (k_x, k_y) plane. Scattering intensities at De = 0, 0.05, 0.15 and 0.3 are shown in Figs. 1 and 2.

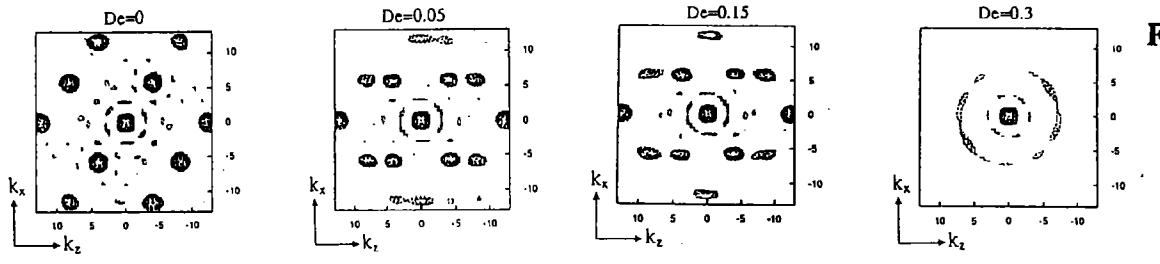


Fig.1

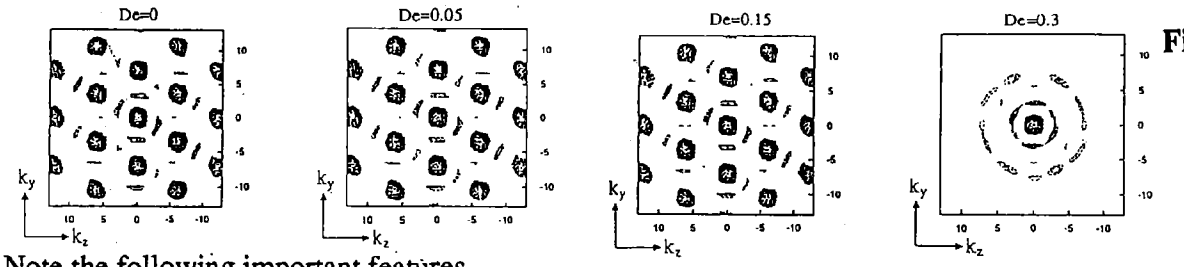


Fig.2

Note the following important features.

i) We find a shear induced disordering process which proceeds via the following sequence of steady states: bcc crystal ($D_e = 0$)→ twin bcc structure ($0 < D_e < 0.3$) → complete disorder ($D_e > 0.3$).

ii) The scattering in the velocity-vorticity plane indicates considerably less order than that in the velocity-gradient plane. This suggests that the shearing suspension resembles hexagonally packed strings, aligned along the velocity direction and with each string exhibiting only a weak registration with its neighbours.

iii) The observation of the disordering process at $D_e = 0.3$ required the full 10^5 time steps due to the long waiting time followed by the abrupt disordering near the end of hte run. This is indicative of a disordering process requiring a rare fluctuation. From animated sequences of the disordering at $D_e = 0.3$, we see the creation, motion and annihilation of interstitial-vacancy pairs. Disordering coincides with the interaction of a number of such defects to destabilize the hexagonally packed strings.

Next we look at the dependence of shear induced disordering on the temperature. To avoid the long runs required to establish the steady state, we have carried out a series of simulations using a two phase initial configuration. Runs were started with a slab of bcc crystal 8 layers thick, properly oriented, with disordered suspension on either side (504 particles in total). A number of runs (~ 10) were carried out at each set of T^* and D_e values and the fraction of runs which ordered recorded. The results are summarised on the stability diagram in Fig.3. Here the filled circles indicate that some runs ordered and the empty circles indicate 100% of the runs disordered. (Note that we never observed stable coexistence between the two shearing phases.) The solid line indicates the ordering curve. In addition to a shear induced disordering process which moves to larger shear rate as the crystal stability decreases, we also find a shear induced *ordering* process at higher shear rates. We believe this feature, frequently observed in nonequilibrium simulations, to be an artefact of the periodic boundary conditions in the velocity direction[7].

Fig.3

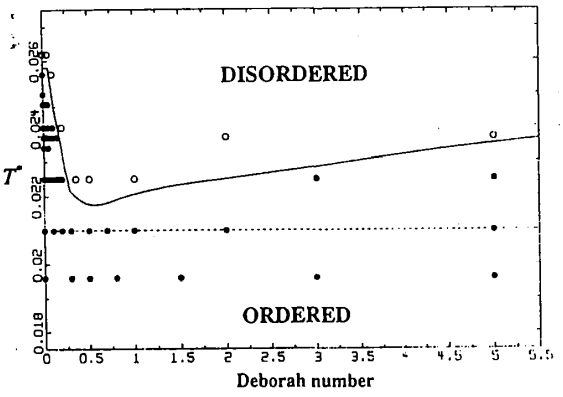
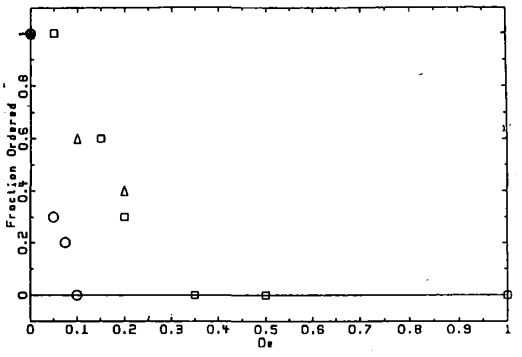


Fig.4



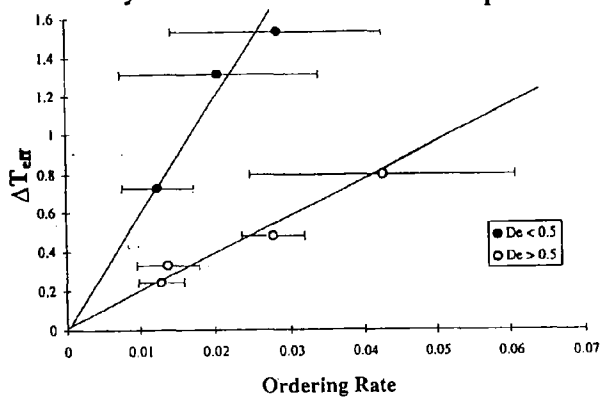
The two phase starts also allow us to examine the size dependence of the SID process. In Fig.4 we compare, at $T^* = 0.0226$, the dependence of the fraction of runs which ordered on D_e for three different systems. In units of the average interparticle spacing a, we have looked at cells with the following dimensions: ($L_{velocity}$= 6, $L_{vorticity}$ = 6,$L_{gradient}$ = 14) **squares**, ($L_{velocity}$= 6, $L_{vorticity}$ = 10,$L_{gradient}$ = 14) **triangles**, ($L_{velocity}$= 10, $L_{vorticity}$ = 6,$L_{gradient}$ = 14) **circles**. We find that increasing the cell length in the vorticity direction has no influence on the disordering transition. Increasing the length along the velocity direction, however, dramatically reduces the shear rate required to disorder the crystal. Both the anisotropy and the magnitude of this effect are very different from any equilibrium disordering transition. We conclude that the nonequilibrium disordering process involves long wavelength fluctuations with wavevectors along the velocity - in qualitative agreement with the mechanical instability model.

5. The Rate of Crystallization under shear[8]

We have monitored the rate of crystallization under shear at $T^* = 0.021$ of that fraction of the runs which ordered having started from a two phase initial configuration. These rate are plotted in Fig.5 against an effective supercooling equal to the difference between the point on the ordering curve in Fig.3 at a given shear rate and the actual temperature T^*. We find two distinct linear relationships; one, for $D_e < 0.5$, corresponds to the case of shear induced disordering, while the second, at higher

shear rates is due to the shear induced ordering process present in these calculations. At zero shear, the crystallization rate is, for small supercoolings, linear in the supercooling. Focusing on the case of the SID process, the persistence of this linear relationship in suspensions under shear provides support for some sort of a thermodynamic character in the nonequilibrium disordering process.

Fig.5



6. Conclusions - a new Model of Shear Induced Disordering[7]

We have calculated for the first time the sequence of steady states leading to the shear induced disordering of a colloidal crystal in a dilute suspension of charged particles. We find a persistent packing of string-like structures right up to the disordering transition, a feature not observed in the light scattering experiments[1]. At the start of this paper we asked how should we think of the SID process and outlined two possible scenarios: an extended thermodynamic approach and one focussing on mechanical stability. The substantial anisotropic size dependence of the critical shear rate reported here provides strong support for the involvement of mechanical coupling to long wavelength fluctuations. On the other hand, the linear relationship between crystal growth rate and th effective supercooling suggests that the latter quantity provides a useful measure of the relative stability of the ordered phase, just as it does at zero shear where thermodynamics applies. Both of these features can be accommodated in a new model based on the shear induced generation of defects. The model is as follows:

• The shear flow couples to long wavelength transverse fluctuations. The convection of these fluctuations results in the nonlinear process of defect formation, so that the rate of defect production is an *increasing* function of shear rate.

• Recombination of interstitial-vacancy pairs is inhibited in the shear crystal as the pairs are convected apart, i.e the rate of defect recombination is a *decreasing* function of shear rate.

• As the density of defects increases in the nonequilibrium crystal with increasing shear rate, defects interact leading to the destabilization of the global structure. This process is analogous to the defect induced amorphization[9] in crystals at zero shear. In these systems it is typically radiation damage or chemical process, instead of an applied shear, which generates the nonequilibrium density of defects. This collective destabilization is essentially of statistical (i.e. thermodynamic) character.

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