

## Theory of Shear-Induced Melting of Colloidal Crystals

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We propose a theory of shear-induced melting of colloidal crystals based on a nonequilibrium generalization of first-order freezing theory. The results agree qualitatively with experiment.

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Shear-induced melting<sup>1-5</sup> is one of the most puzzling of the many beautiful phenomena observed when a crystalline (lattice spacing  $a \sim 5 \times 10^3 \text{ \AA}$ , shear modulus  $G \sim 10^2 \text{ dyne cm}^{-2}$ ) suspension of charged ( $Z = 300-1000$ ) submicron polystyrene spheres ("polyballs") is subjected to a velocity gradient  $\epsilon$ . In these systems, Bragg scattering persists even in the presence of shear flow, and disappears only when the shear rate  $\epsilon$  exceeds a critical value  $\epsilon_{\text{melt}}$ . Moreover,  $\epsilon_{\text{melt}}$  seems to go continuously to zero as the equilibrium melting transition of the crystal is approached.<sup>3,4</sup> Note that, for reasons discussed elsewhere,<sup>6,7</sup> equilibrium melting is effected here by the addition of hydrochloric acid to decrease the screening length of the interactions. At a critical acid concentration  $n_*$ , a liquid state results. Attempts<sup>1,8</sup> have been made to describe shear melting as a purely mechanical instability of sliding layers of crystal, governed by the competition between the disruptive interlayer forces and the restoring elastic response within a layer. Since the latter forces, and hence the threshold rate of shear, would then be proportional to typical shear moduli of the crystal, which remain nonzero at the equilibrium first-order melting transition,<sup>3</sup> it is hard to see how this approach could give  $\epsilon_{\text{melt}} \rightarrow 0$  as the acid concentration  $n \rightarrow n_*$ .

We show here that the transition can be understood as an extension of equilibrium melting by deriving a generalized Hansen-Verlet (HV)<sup>9</sup> criterion. That is, we show that even in the presence of shear flow, freezing should set in when the maximum height  $S_m$  of the structure factor  $S(\mathbf{q})$ , where  $\mathbf{q}$  is at a fixed direction in the flow plane, reaches a certain critical value. In three dimensions, for freezing into a bcc lattice, this value is

$$S_{\text{freeze}}(\epsilon, 45^\circ) = S_{\text{HV}} \left[ 1 - \frac{1}{24} (\epsilon\tau)^2 (q_0/\Delta)^2 \right] \quad (1)$$

when measured in the shear plane at  $45^\circ$  to the flow. Here  $\tau$  is a microscopic diffusion time  $\sim 10^{-2}$  sec for polyballs,  $q_0$  is the radius in reciprocal space of the most prominent ring of maxima of  $S(q)$  at equilibrium, and  $\Delta$  is its full width at half maximum at freezing.  $S_{\text{HV}}$  is the value of  $S_m$  at freezing in the absence of shear. In addition, we find that the shift in the

coexistence curve is given by

$$n_*(n_p; \epsilon) = n_*(n_p; \epsilon = 0) - \frac{1}{12} \left( \frac{q_0}{\Delta} \right)^2 \frac{(\epsilon\tau)^2}{|d \ln S_m / dn_a|} \quad (2)$$

in three dimensions, where  $n_p$  is the average polyball density. To test (2) one needs an estimate, from experiment or microscopic theory, of the dependence of  $S_m$  on the acid concentration  $n_a$ . Equation (1), however, can be tested directly in light scattering or small-angle x-ray scattering.

Note that these effects are of order  $(\epsilon\tau)^2$ , and are hence not likely to be seen at reasonable shear rates in ordinary liquids, where  $\tau$  is of order  $10^{-12}$  sec. For polyballs, the necessary shear rates of around 100 Hz are easily obtained. A well-known consequence of this is that a substantial distortion of the Debye-Scherrer ring of maxima of the static structure factor  $S(q)$  of the polyball liquid can be observed<sup>1</sup> at shear rates of  $\sim 10$  Hz.

We now describe our theory and calculations. Recall that the equilibrium transition from liquid to crystal occurs when the free energies for the two phases become equal. In order to obtain a similar criterion for shear melting, we need the generalization of a free-energy functional.<sup>10</sup> Since we are not at equilibrium this cannot be constructed by simple means. Instead we calculate the distribution  $P[\rho]$  for the polyball density fluctuations in a shear flow from a Fokker-Planck equation<sup>11</sup> and extract the free energy from it.

To this end, let us consider a polyball suspension at equilibrium in the liquid phase, but near crystallization. The static structure factor  $S(q) = \langle \rho_{\mathbf{q}} \rho_{-\mathbf{q}} \rangle$ , where  $\rho$  is the polyball density, has a sharp maximum on a wave-vector shell  $|\mathbf{q}| = q_0$ , and weaker peaks at larger  $q$ . For  $q \approx q_0$ , we can write

$$S(q) = k_B T / [r + c(q^2 - q_0^2)^2], \quad (3)$$

so that  $S(q_0) = k_B T / r$ . Since  $S(q)$  is the Fourier transform of the density-density correlation function, a simple phenomenological Landau free energy<sup>12</sup> which will describe the liquid-solid transition as a density-

wave instability is

$$F = \frac{1}{2} \int d^d x d^d x' A(\mathbf{x} - \mathbf{x}') \delta\rho(\mathbf{x}) \delta\rho(\mathbf{x}') + \int d^d x \{ -g [\delta\rho(\mathbf{x})]^3 + u [\delta\rho(\mathbf{x})]^4 \} + F_0, \quad (4)$$

where

$$A(\mathbf{x}) = \int (2\pi)^{-d} d^d q A_{\mathbf{q}} \exp(i\mathbf{q} \cdot \mathbf{x}), \quad (5a)$$

with

$$A_{\mathbf{q}} = r + c(q^2 - q_0^2)^2 \quad (5b)$$

near  $q = q_0$ . Here  $F_0$  is the free energy of the uniform liquid,  $\delta\rho = \rho(\mathbf{x}) - \rho_0$  is the departure of the density at  $\mathbf{x}$  from its quiescent value  $\rho_0$ , and  $g$  and  $u$  are phenomenological parameters. This free energy can be used to determine, for instance, the likely symmetries of crystals near equilibrium melting.<sup>13</sup>

Now suppose that a plane shear flow  $\mathbf{v} = \epsilon y \hat{\mathbf{x}}$  is imposed on the suspension. Provided that one neglects the effect of density fluctuations on the velocity field (i.e., that one assumes passive convection) one can describe the density fluctuations using the Langevin equation

$$(\partial_t + \epsilon y \partial_z) \rho(\mathbf{x}) - \Gamma \nabla^2 \delta F / \delta \rho(\mathbf{x}) = f(\mathbf{x}, t), \quad (6a)$$

with

$$\langle f(\mathbf{x}, t) f(\mathbf{x}', t') \rangle = 2k_B T \delta(t - t') (-\Gamma \nabla^2) \delta^d(\mathbf{x} - \mathbf{x}'), \quad (6b)$$

or equivalently<sup>11</sup> using the Fokker-Planck equation

$$\partial_t P = - \int d^d x [\delta / \delta \rho(\mathbf{x})] \{ \nabla \cdot [\rho(\mathbf{x}) \epsilon y \hat{\mathbf{x}}] - \Gamma \nabla^2 [\delta P / \delta \rho(\mathbf{x}) + \beta^{-1} P \delta F / \delta \rho(\mathbf{x})] \}. \quad (7)$$

Here the last term on the left-hand side in (6a) represents the diffusion of the interacting polyballs,  $\Gamma$  is a kinetic coefficient,  $\beta = (k_B T)^{-1}$ , and  $f(\mathbf{x}, t)$  is a thermal noise source whose statistics guarantee that at equilibrium ( $\epsilon = 0$ ),  $P[\rho] = \exp(-\beta F[\rho])$  is a stationary solution of (7). Note that when  $\epsilon \neq 0$ ,  $\exp(-\beta F)$  is no longer a solution to (7).

Our method of solution is very simple. We seek stationary solutions  $P[\rho]$  to (7) by expanding  $\ln P$  in a functional Taylor series in  $\delta\rho$ . Schematically, we write

$$-\beta^{-1} \ln P = \frac{1}{2} \delta\rho K_2 \delta\rho + K_3 (\delta\rho)^3 + K_4 (\delta\rho)^4 \quad (8)$$

as in equilibrium Landau theory, and determine the  $K_i$ 's, which are to be interpreted as operators, by calculating correlation functions<sup>14</sup> from the Langevin equation (6).  $K_2$ , for example, is just the inverse of  $G(\mathbf{x} - \mathbf{x}') = \langle \delta\rho(\mathbf{x}) \delta\rho(\mathbf{x}') \rangle / k_B T$ , the bare equal-time autocorrelation of the density in the presence of a shear flow. Its Fourier transform  $G(\mathbf{q})$ , as can be seen from Eq. (6), satisfies

$$\left[ \frac{1}{2} \epsilon q_x \partial / \partial q_y + \Gamma q^2 A_{\mathbf{q}} \right] G(\mathbf{q}) = k_B T \Gamma q^2, \quad (9a)$$

so that

$$G(\mathbf{q}) = \left[ 1 + \frac{\epsilon q_x}{2\Gamma q^2 A_{\mathbf{q}}} \partial_{q_y} \right]^{-1} k_B T A_{\mathbf{q}}^{-1} \quad (9b)$$

$$= \left[ 1 - \frac{\epsilon q_x}{2\Gamma q^2 A_{\mathbf{q}}} \partial_{q_y} + \left( \frac{\epsilon q_x}{2\Gamma q^2 A_{\mathbf{q}}} \partial_{q_y} \right)^2 - \dots \right] k_B T A_{\mathbf{q}}^{-1}. \quad (9c)$$

Here we have imposed stationarity ( $\partial_t G = 0$ ) and, in the spirit of mean-field theory, ignored fluctuation corrections to  $G(\mathbf{q})$  generated by the nonquadratic terms in  $F$ . In this way, we can also calculate  $K_3$  and  $K_4$ . In this simple model where the nonquadratic terms in  $F$  are purely local and the renormalizations are ignored, we find that the vertices retain their equilibrium values:

$$K_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) = g (2\pi)^d \delta(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3), \quad (10)$$

$$K_4(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4) = u (2\pi)^d \delta(\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 + \mathbf{q}_4). \quad (11)$$

However, if  $K_3$  or  $K_4$  had a more complex dependence on  $q_i$ 's, then nontrivial  $\epsilon$  dependence would be generated.

The equal-time density correlations in the shearing suspension are thus, to leading order in  $\epsilon$ , those given by the

probability distribution

$$P[\rho; \epsilon] \propto \exp(-\beta \Omega[\rho; \epsilon]), \quad (12a)$$

which solves (7) with

$$\Omega[\rho; \epsilon] = \frac{1}{2} \int (2\pi)^{-d} d^d q k_B T G^{-1}(\mathbf{q}) |\delta\rho_{\mathbf{q}}|^2 + \int d^d x [-g(\delta\rho)^3 + u(\delta\rho)^4], \quad (12b)$$

with  $G(\mathbf{q})$  given by (9b). We can thus treat  $\Omega$  as the Landau free energy for the liquid-solid transition in the presence of shear. Note that for  $q \rightarrow 0$ ,  $G(\mathbf{q}) \rightarrow k_B T/A_{\mathbf{q}}$ , as is seen from the fact that for  $q_x = 0$  the shear term drops out of (9a). Thus  $\Omega$  evaluated for the uniform liquid is still  $F_0$ .  $\Omega$  differs from the equilibrium free energy  $F$  [Eq. (4)] only in its quadratic term, that is, in  $G(\mathbf{q})$ , the shear-dependent static susceptibility. From (9c), one obtains (after some straightforward algebra) the maximum value of  $\beta G(\mathbf{q})$ :

$$r_{\epsilon}^{-1}(\theta) = \beta G_m(\theta, \epsilon) = r^{-1} [1 - (\epsilon\tau)^2 (cq_0^4/r) \cos^2\theta \sin^2\theta] + O((\epsilon\tau)^4), \quad (13)$$

which occurs at

$$q = q_m(\theta, \epsilon) = q_0 [1 + \frac{1}{2} \epsilon\tau \sin\theta \cos\theta] + O((\epsilon\tau)^3), \quad (14)$$

where  $\theta$  is the angle between the  $y$  axis and the projection of  $\mathbf{q}$  into the  $xy$  plane, and  $\tau = (\Gamma q_0^2 r)^{-1}$ . This maximum value is less than  $r^{-1}$ , the equilibrium value, except at  $\theta = 0, \pi/2, \pi, 3\pi/2$ ; shear reduces equal-time correlations in the fluid. The distortion of the ring of maxima can be removed by a simple change of coordinate:  $\mathbf{q} \rightarrow \mathbf{q} + \frac{1}{2} \epsilon\tau q_x \hat{\mathbf{y}}$ . This means that we must determine the nature of the density-wave instability in a fluid whose structure factor has an angle-dependent maximum  $G_m(\theta, \epsilon)$ , on the sphere  $|\mathbf{q}| = q_0$ , given by (13).

The condition for the occurrence of this density-wave instability is obtained from the Landau free energy

$$\Omega[n] = \frac{1}{2} \int [r_{\epsilon}(\theta) + c(q^2 - q_0^2)^2] |n_{\mathbf{q}}|^2 (2\pi)^{-d} d^d q + \int d^d x [-gn^3(\mathbf{x}) + un^4(\mathbf{x})], \quad (15)$$

with  $r_{\epsilon}(\theta)$  given by (13). Here  $n_{\mathbf{q}} = \delta\rho(\mathbf{q} - \frac{1}{2} \epsilon\tau q_x \hat{\mathbf{y}})$ . Suppose we are at the coexistence curve of the unsheared liquid. The analysis of Alexander and McTague<sup>13</sup> tells us that the liquid will freeze into the crystalline structure which minimizes the free energy (viz., bcc in 3D and hcp in 2D). These structures have the largest number of triangles of the reciprocal lattice and therefore maximize the (negative) contribution of the cubic term in  $F$ . Now consider the effect of a small shear flow  $\mathbf{v} = \epsilon\mathbf{y}\hat{\mathbf{x}}$ . The free energy for the transition is now (15), which has the same cubic and quartic terms as the equilibrium  $F$  but a larger quadratic term. We can therefore simply use Alexander and McTague's<sup>13</sup> results to find that the phase into which the system will first freeze, in terms of the order parameter  $n_{\mathbf{q}}$ , is a hexagonal lattice in two dimensions and bcc in three. In terms of the physical order parameter  $\delta\rho_{\mathbf{q}}$  the reciprocal lattice is deformed in accordance with (14). Using (15) one readily obtains the free energy  $\Omega$  of the distorted crystal relative to the liquid to leading order in  $\epsilon$ :

$$\Omega[\rho; \epsilon] = \frac{1}{2} r_{\text{eff}}(\epsilon) |\rho_G|^2 + O(\rho_G^3), \quad (16a)$$

where  $\rho_G$  is the amplitude of the undistorted density wave, and

$$r_{\text{eff}} = \frac{1}{3} [2r + r_{\epsilon}(\theta = 45^\circ)] > r \quad (16b)$$

for a 3D bcc lattice.

Thus, in the absence of shear the system was on

the coexistence curve, then in the presence of shear it will be in the liquid phase. Equivalently, shear causes freezing to be postponed until  $r^{-1}$  exceeds the value at which freezing occurred in the absence of shear. The transition is still governed by a free energy with a cubic term and hence remains first order.

Since the free energy for the uniform liquid remains unchanged,  $\Omega$  has to decrease to the same critical value for freezing to occur as it did in equilibrium. In other words, a density wave should set in when  $r_{\text{eff}}(\epsilon) = S_{\text{HV}}^{-1}$ . This leads to Eq. (1), which can be tested directly by experiment.

The data available at present give the acid concentration at melting,  $n_*$ , as a function of  $\epsilon$ . From (16b) we can say that

$$d \ln n_* / d \epsilon^2 = -\frac{1}{12} (cq_0^4/r) (d \ln n_* / d \ln r) \tau^2 \quad (17)$$

in three dimensions, leading to Eq. (2). We therefore need the dependence of the equilibrium maximum height  $r^{-1}$  of the structure factor on the concentration  $n_*$  of acid. As a rough estimate,<sup>15</sup>  $r^{-1}$  drops from the HV value of 2.8 to about 1 when  $n_a$  is increased from  $n_*$  to  $2n_*$ . We take experimentally observed<sup>1,2</sup> values of  $\tau$  (16 ms for 0.109- $\mu\text{m}$  polyballs at 0.16% volume fraction) rescaled assuming  $\tau \sim q_0^{-2} \sim (\text{vol. fract.})^{2/3}$  to give a value for  $\tau$  appropriate for available data which are at 4% volume fraction. Molecular-dynamics simulations<sup>16</sup> of  $S(q)$  at freezing give  $cq_0^4/r \approx 30$  for

both a hard-sphere liquid and a one-component plasma. Combining these numbers we estimate that  $d \ln n_*/d\epsilon^2 \approx 2 \times 10^{-5} \text{ sec}^2$ . Preliminary data<sup>15</sup> give a value of  $5 \times 10^{-5} \text{ sec}^2$  which is the correct order of magnitude.

Finally, a few words of caution. First, our theory works with strictly stationary states and cannot in its present form treat the complex, nonstationary, partially ordered states seen by Ackerson and Clark,<sup>1,2</sup> who study shear melting at stresses  $\sigma > \sigma_l$ , the ideal strength of the crystal. Lindsay and Chaikin<sup>3,4</sup> work at  $\sigma < \sigma_l/3$ , and it is with their data that we compare our predictions. Secondly, we probably overestimate the effect of shear since for  $\sigma < \sigma_l$  the appearance of density waves will affect the velocity profile, thus violating the approximation of passive convection.

It should now be clear that further work needs to be done to determine how successfully the theory compares with experiment. Detailed measurements of the behavior of  $\epsilon_{\text{melt}}$  when  $n_a \approx n_*$  need to be performed to verify the  $n_* \sim \epsilon^2$  law. Better still would be a direct test of Eq. (1) based on structure-factor measurements. The need to linearize  $r(n_a)$  could be eliminated by use of an accurate microscopic calculation<sup>16,17</sup> of  $S(q)$ . This would result in an  $n_*$  accurate beyond  $O(\epsilon^2)$ . Finally, since mode coupling away from equilibrium gives rise to shear dilatancy<sup>18</sup> and alters static correlations,<sup>19</sup> a study of its effect on the shear melting transition would be most worthwhile. These calculations are now in progress.

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