Cluster Crystals under Shear

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We show that a distinct class of colloidal crystals, which consist of mutually overlapping particles, has a novel and universal response to steady shear. After a shear-banding regime at low shear rates, strings parallel to the flow direction form as shear grows, which order on a hexagonal crystal in the gradient-vorticity plane. At even higher shear, lateral fluctuations of the strings, enhanced by hydrodynamics, lead to a disordered, fluid state. Our results are based on appropriate simulation techniques that correctly account for hydrodynamics. We also find that shear vastly accelerates the nucleation rates of supercooled fluids into the cluster crystals.

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Complex, non-Newtonian fluids demonstrate an enormously rich rheological behavior under steady or oscillatory shear, which leads to a variety of nonequilibrium structures. This nonlinearity makes complex fluids extremely challenging to understand from the fundamental point of view. They show shear banding [1], thixotropy [2], and shear thinning [3,4] as well as, in many cases, shear thickening [3]. In addition, these materials bear high importance for a wide variety of applications in, e.g., nanotechnology and micropatterning [5], microfluidics [6], or shock absorption [7]. On one side, shear can induce order, in the form of sliding planes, to a colloidal dispersion that is disordered in equilibrium, bringing about thixotropy and shear thinning. Reversely, shear can cause a shear-induced disorder (SID) transition of a crystal to a flowing, uniform phase.

In this Letter, we focus on steady shear of colloidal crystals [8]. The topic has attracted a great deal of attention also in the context of atomic systems [9], aiming at understanding the sequence of states that lead from an equilibrium crystal at zero shear to a shear-molten state at high shear. The hitherto explored scenarios on the succession of steady states at increasing shear are dependent on the type of interparticle interactions, on crystal orientation in the cell, on concentration, and, for the case of charge-stabilized colloids, on salinity. Ackerson and Clark [10] have performed a combination of shear and small-angle neutron-scattering measurements on charge-stabilized colloids both for body-centered cubic (bcc) and for face-centered cubic (fcc) lattices. The generic scheme under which the SID comes about is a succession, with increasing shear rate, proceeding from the equilibrium crystal to a strained solid in which either twin bcc or zigzag motions of successive close-packed planes are observed, to a sliding layer structure with two-dimensional order, and finally to a fluid [11]. Subsequent experiments have confirmed the salient features of this scenario, both for charged colloids [12,13] and for hard spheres [8,14]. A particularly

intriguing finding of the experimental investigations on charged colloids is the emergence of short stringlike correlations between the colloids close to the SID transitions [10,13] without spatial ordering of the same. Butler and Harrowell [15] found in their simulations of Yukawa crystals that, although these strings had no particular correlation in the flow-vorticity plane, they showed hexagonal order in the gradient-vorticity plane, which was absent in the experiments. It was subsequently argued that this ordering might be a simulation artifact arising either from the absence of walls in the original simulation [15] or from the emergence of a pseudo-oscillatory shear profile due to the periodic boundary conditions in the flow direction [16].

The subject of this work is shear of colloidal cluster crystals, whose equilibrium structure and dynamics have been the subject of intensive investigations since their discovery in computer simulations a few years ago [17]. The interaction potential of these colloids is bounded; i.e., it allows for full and multiple particle overlaps, a condition fulfilled for suitable polymer-based colloids [18]. A necessary and sufficient condition for the stability of cluster crystals is the existence of negative components in the Fourier spectrum of the effective interaction potential [19]. The resulting cluster crystals are characterized by an accumulation of N_c particles on each lattice site, where N_c scales proportionally to the density, so that a cluster crystal with a concentration-independent lattice constant emerges [17,19,20]. Most recently, the quantum version of such systems, termed there as droplet crystals, has been analyzed [21]. The equilibrium dynamics of cluster crystals is also highly unusual, featuring a superposition of phononic oscillations and activated hopping dynamics [22,23], the latter resulting in a finite long-time diffusivity that scales as $\exp(-\rho/T)$, where ρ is the density and T the absolute temperature.

Though the equilibrium properties of these novel phases are by now very well understood, nothing is known about their nonequilibrium behavior. We discover here that

cluster crystals respond to shear through a novel scenario: Shear banding occurs at low shear rates, followed by string formation, in which the flow-aligned strings formed by the interpenetrating particles order in a hexagonal lattice on the gradient-vorticity plane. At a critical shear rate $\dot{\gamma}_c \propto \sqrt{\rho}$, the string phase melts into a disordered fluid with a concomitant increase of the viscosity. This form of self-organization arises from penetrability: In contrast to hard colloids [11], no zigzag or sliding planes are necessary to relax the stresses, since particles can go over one another. The correspondence of our model with experimental realizations of cluster crystals is discussed in the Supplemental Materials [24].

We considered a fcc cluster crystal, formed by clusters of overlapping particles which interact via the generalized exponential model (GEM)-8 potential $U(r) = \epsilon \exp[-(r/\sigma)^8]$, ϵ and σ being energy and length scales, respectively. This crystal is exposed to shear forces via parallel shearing walls that are parallel to the z (flow) direction, the x axis being the gradient and the y axis the vorticity directions. The walls are separated by a distance L_x (see Supplemental Materials for details of the simulation). The system was sheared along the crystallographic [100] or along the [111] plane at temperature $k_B T/\epsilon = 0.2$ and at three different state points with densities $\rho\sigma^3 = 2.6$, 3.9, and 5.9 (corresponding to average cluster occupation numbers $N_c = 4$, 6, and 9, respectively). In the bulk phase, the system forms stable fcc cluster crystals at these state points [19,22].

As we expose the system to the shearing forces, we find the following striking form of self-organization: Within a certain range of shear rate $\dot{\gamma} \in [\dot{\gamma}_{\min}, \dot{\gamma}_c]$ (to be specified below), the cluster crystal transforms into an arrangement of parallel strings, which align in the flow direction and form a two-dimensional hexagonal lattice in the gradient-vorticity plane. Along the strings, the particles display a disordered, liquidlike structure (see Fig. 1). In Brownian dynamics simulations in which hydrodynamics is ignored, this string formation occurs for arbitrarily small $\dot{\gamma}$, whereas in the multiparticle collisional dynamics (MPCD) simula-
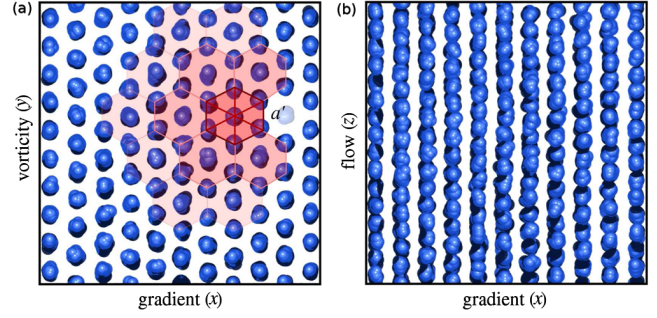

FIG. 1 (color online). (a) Vorticity-gradient and (b) flow-gradient views of the strings formed in an cluster crystal under shear with a shear rate $\dot{\gamma} \in [\dot{\gamma}_{\min}, \dot{\gamma}_c]$ (see the text). Blue spheres (not drawn to scale) represent GEM particles. In (a), a few centers of mass of the strings are connected by straight lines, and the red shading of the resulting hexagonal tiles reflects the distance from the arbitrarily chosen central string; a' is the lattice constant of the triangular lattice formed by the strings.

tions, we obtain a nonlinear velocity profile and wall slip (shear banding) for $\dot{\gamma} < \dot{\gamma}_{\min} \cong 0.05$, since the shear flow is shielded by the outer layers of the crystals.

The formation of strings is independent of the initial conditions, since it occurs both for ordered and for disordered starting configurations. More details about the transformation process are revealed by shearing with fixed $\dot{\gamma}$ at the two different orientations of the crystal specified above: For shear along the [100] direction, the cluster crystal completely melts shortly after shear is applied. The melting process starts from the center of the crystal and then expands gradually towards the outer layers. Eventually, the strings form out of this transient melt. When shearing along the [111] direction, the system takes advantage of the fact that the ABC stacking encountered in the cluster crystal is very similar to the final ordering of the strings [Fig. 1(a)]. Thus, the crystal melts only along the (111) planes which, themselves, remain well-separated from each other during the entire process. The fact that the transformation process is "easier" in the latter case is reflected by the fact that the yield stress σ_0 (see Table I)

TABLE I. Simulation results from shearing of GEM-8 cluster crystals at $T = 0.2$ for different cluster occupation numbers N_c and crystal orientations in the shear cell, indicated in the first column. Listed are the Bingham yield stress σ_0 and the shear viscosities η_1 (of the string phase) and η_2 (of the molten phase at high shear). The value $\dot{\gamma}_{c,1}$ is an estimate for string melting according to the Bingham plastic model, while $\dot{\gamma}_{c,2}$ is obtained by identifying the minimum of $d\Phi/d\dot{\gamma}$ (see the text).

N_c	σ_0 [ϵ/σ^3]	η_1 [$\tau\epsilon/\sigma^3$]	η_2 [$\tau\epsilon/\sigma^3$]	$\dot{\gamma}_{c,1}$ [τ^{-1}]	$\dot{\gamma}_{c,2}$ [τ^{-1}]
4 [100]	7.60 ± 0.13	32.12 ± 0.41	39.81 ± 0.44	0.33	0.34
4 [111]	7.51 ± 0.12	30.94 ± 0.42	40.32 ± 0.34	0.30	0.35
6 [100]	10.81 ± 0.27	40.32 ± 0.68	50.97 ± 0.56	0.36	0.42
6 [111]	8.49 ± 0.31	39.86 ± 0.53	50.67 ± 0.51	0.35	0.42
9 [100]	16.30 ± 0.26	50.13 ± 0.68	69.70 ± 0.77	0.40	0.47
9 [111]	11.04 ± 0.14	49.60 ± 0.73	66.98 ± 0.93	0.42	0.47

is lower when shearing in the [111] direction. We invite the reader to watch short videos (see [24]) which we produced from our simulations. They provide an impression of the dynamical process of the string formation in the two different crystal orientations.

The formation of the strings, i.e., the loss of ordering parallel to the flow direction and the subsequent triangular ordering perpendicular to the flow direction, can be understood as follows. The physical mechanism that stabilizes the GEM particles in a three-dimensional crystal is self-sustaining: The restoring force for any particle towards a lattice site is provided by the neighboring clusters [19]. An applied shear distorts the clusters in the flow direction, reducing thereby the magnitude of the restoring force. Since this process is self-amplifying, a higher shear rate distorts the clusters even more and reduces the restoring force concomitantly, leading to melting along the flow direction, and clusters start to flow. This process is unique to penetrable colloids, since the presence of a hard core prohibits particle overlap. In the string phase, each particle separated from a string of line density Λ by a distance R experiences a repulsive potential $U_{2d}(R) = \Lambda \int_{-\infty}^{\infty} U(r)dz$. The string-string interaction potential per unit length is then given by $\Lambda U_{2d}(R)$, which is a bounded repulsion in two dimensions. Applying the analysis of Ref. [19], we find that, under their mutual repulsion, these strings now form a triangular crystal. For the case of the GEM-8 potential at hand, the interstring potential has a Fourier transform with a negative minimum located at $K_{min}/k_{min} \cong 1.28$, where k_{min} and K_{min} are the locations of the minima of the Fourier transforms of $U(r)$ and $U_{2d}(R)$, respectively. This implies that the lattice constant of the ensuing triangular crystal is smaller than that of the original fcc crystal, a fact confirmed in our simulations by the emergence of additional layers of strings for shear in the [100] direction.

If the shear rate then exceeds the density-dependent critical value of $\dot{\gamma}_c$, the system melts and its shear viscosity η increases significantly (shear thickening). Again, melting starts in the center of the simulation box. The underlying mechanism that is responsible for this melting process becomes evident from the MPCD simulations: For sufficiently high $\dot{\gamma}$ values, particles are able to overtake each other as they move along the strings, a phenomenon that is strongly supported by hydrodynamic interactions since a tagged particle can move in the wake of its preceding particle [25]. In conjunction with the two-dimensional particle-string interaction $U_{2d}(R) \propto \Lambda$, this allows us to estimate the critical shear rate $\dot{\gamma}_c$ as follows. The typical time scale $t_\perp$ for any particle to deviate from the string in the perpendicular direction by a distance a is $t_\perp \cong 2\pi/\omega$, where ω is the oscillation frequency due to the superposition of the potentials $\sum_i U_{2d}(|\mathbf{R} - \mathbf{R}_i|)$, $\{\mathbf{R}_i\}$ being the vectors of the (nearest) neighbors in the hexagonal lattice and a being the amplitude of the oscillations [19]. The

corresponding time $t_\parallel$ for it to move along the same distance parallel to the string, once it has been displaced from it laterally by a, is given by $t_\parallel \cong a/(a\dot{\gamma}) = \dot{\gamma}^{-1}$. As long as the shear rate is sufficiently small and $t_\parallel \gg t_\perp$ holds, shear does not destroy the strings. However, when $t_\parallel \cong t_\perp$, particles start overtaking and string correlations are destroyed. Taking the above expressions for $t_\perp$ and $t_\parallel$, the estimate $\dot{\gamma}_c = \omega/(2\pi)$ is obtained. Since $\omega^2 \propto \Lambda \propto N_c$ [19], we obtain $\dot{\gamma}_c = b\sqrt{N_c}$, where b is a numerical coefficient that depends on $U(r)$ (here $b = 0.18 \pm 0.04$).

From the simulations, the value of $\dot{\gamma}_c$ can be estimated via two different routes: First, we employ a macroscopic Bingham plastic model describing a viscoplastic material that behaves as a rigid body at low stress but flows as a viscous fluid at high stress. Here, the shear stress σ_{xz} is given by $\sigma_{xz}(\dot{\gamma}) = \eta\dot{\gamma} + \sigma_0$, η being the shear viscosity and σ_0 being the yield stress. Fitting these results to this model leads to the values for σ_0 and η summarized in Table I. Furthermore, from the intersection of the fitted curves in the two different regimes (see Fig. 2), we obtain results for $\dot{\gamma}_c$. The approximate character of the model is reflected in the fact that the identified values for $\dot{\gamma}_c$ differ markedly for different crystal orientations at the same N_c; nevertheless, the model serves as a good indicator.

Second, we consider the free volume fraction $\Phi(\dot{\gamma})$, which decreases as the system melts out of the strings. During this transition, more particles are suddenly exposed to the flow, leading to a dramatic increase in the fluid resistance. This is a unique property of this cluster crystal, since usually the shear viscosity drops at shear melting. Here, we considered each GEM particle as a sphere of
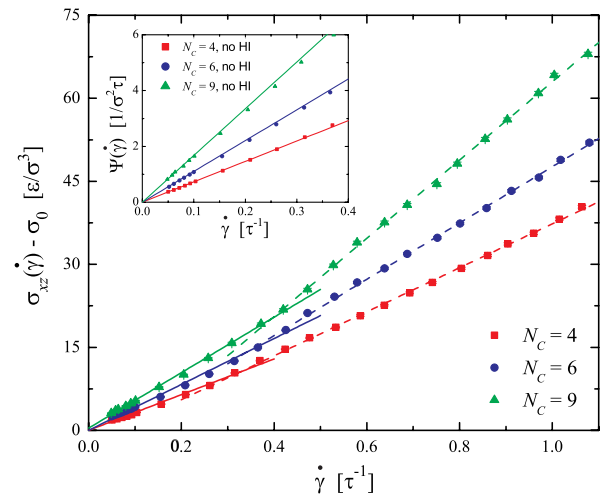

FIG. 2 (color online). Shear stress $\sigma_{xz}(\dot{\gamma})$, reduced by the yield stress σ_0, as obtained from the MPCD simulations, for shear at the [100] orientation. The full lines (string state) and the dashed lines (molten state) are fits according to the Bingham plastic. The inset shows the flux $\Psi(\dot{\gamma})$ of particles across the simulation box, as obtained from full MPCD (lines) and from Brownian dynamics without hydrodynamics (symbols).
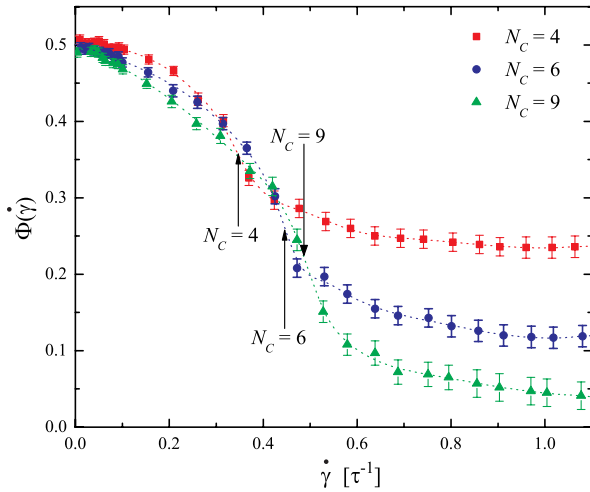
FIG. 3 (color online).   Free volume fraction of the GEM particles, $\Phi(\dot{\gamma})$, for the three systems investigated (as labeled). Minima in $d\Phi/d\dot{\gamma}$ are indicated by vertical arrows.

diameter σ and calculated the free volume Φ in each state by straightforward counting. Results are shown in Fig. 3. By identifying the minimum of $d\Phi/d\dot{\gamma}$, we obtain an additional estimate for $\dot{\gamma}_c$ (see Table I). We find remarkable agreement with the theoretical estimate $\dot{\gamma}_c = b\sqrt{N_c}$ above; e.g., for $N_c = 4$ we obtain $\dot{\gamma}_c = 0.36\,(0.34)$ from theory (simulations), and the latter are consistent with the $\dot{\gamma}_c \sim \sqrt{N_c}$ scaling for the remaining N_c values. In the string phase, the $\Phi(\dot{\gamma})$ curves exhibit almost no N_c dependence, similarly to the equilibrium case, where the free volume is also density-independent (at a given temperature) due to the fixed lattice constant [19]. As $\dot{\gamma}$ exceeds $\dot{\gamma}_c$, the strings fluidize, which manifests itself in the rapid, N_c-dependent decrease of $\Phi(\dot{\gamma})$. The curves decay faster for higher N_c, and the inflection points shift, as predicted by the theory, to higher shear rates.

Finally, we note that the formation of a cluster crystal out of a melt is dramatically accelerated via shearing. Without shear, disordered metastable systems remain fluid in the simulation. Shearing the same with $\dot{\gamma} < \dot{\gamma}_c$ leads to string formation: When switching off the shear flow, the strings immediately split into distinct clusters, located at the positions of an fcc cluster crystal, with its (111) planes being parallel to the shearing walls.

We have put forward a novel scenario for the shear response of cluster crystals, which is unique to this novel class of systems and universal for all of them, i.e., independent of the details of their interparticle interactions. The salient features are the formation and ordering of long strings oriented parallel to the flow and a subsequent shear-induced fluidization of the same at high shear rates. The phenomena found are robust with respect to the interwall separation and offer a new paradigm for structure formation out of equilibrium. Our findings are free of any artifacts associated with the simulation technique [15,16], since we consider explicit walls and our steady shear rates do not cause pseudo-oscillations. The formation of strings is rather reminiscent of findings in simulations of sheared colloidal fluids, in which flow-aligned strings that order hexagonally on the gradient-vorticity plane have been found [26–28], though these have not been seen in experiments; see, e.g., Ref. [29] and the discussion in Ref. [13]. Cluster crystals emerge thereby as novel materials that show unique and universal characteristics not only in equilibrium but also under external drive. The formation of triangularly ordered strings bears striking similarities to the Abrikosov lattice of superconductors. Further, the emergence of long, connected "wires" under shear can be seen as a type of a transition from an isolating (clusters) to a shear-induced conducting material (strings). Finally, the enormous acceleration of the crystal nucleation rates can be associated with a particular transition pathway, in which three-dimensional order emerges, after cessation of shear, out of disorder via the intervening formation of two-dimensionally ordered patterns.

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[24] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.107.068302 for the relation to experiments and simulation details.

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however, we expect it to take place at some higher shear rate.

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