Self-Poisoning of Crystal Nuclei in Hard-Rod Liquids

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We report a Monte Carlo study of the pathway for crystal nucleation in a fluid of hard, colloidal rods. In the earliest stages of nucleation, a lamellar crystallite forms. Subsequent thickening of this lamella is hampered by the fact that the top and bottom surfaces of this crystallite are preferentially covered by rods that align parallel to the surface. As a consequence, subsequent growth of individual crystals is stunted. Experimental evidence for such stunted crystal growth has recently been reported by Maeda and Maeda in experiments on suspensions of colloidal rods [Phys. Rev. Lett. **90**, 018303 (2003)]. The simulations suggest that, in experiments, the growth of multilayer colloidal crystals can be selectively enhanced by the application of an external aligning field.

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When spherical particles crystallize, the crystal nuclei that form tend to be roughly spherical [1,2]. In contrast, nonspherical molecules may form crystals that are strongly anisometric. The reason is twofold: First of all, the solid-liquid interfacial free-energy density may be very different for crystal faces parallel and perpendicular to the molecular axes. As a consequence, the equilibrium shape of small crystal nuclei is nonspherical. In addition, once crystals grow beyond the size of the critical nucleus, the rate at which molecules are incorporated into the crystal may depend strongly on the nature of the crystal face. In some extreme cases, this may lead to the formation of extremely elongated (liquid) crystal fibers [3,4].

Sometimes the growth rate of one or more crystal facets can be inhibited by the addition of an impurity that strongly adsorbs onto the growth front and thereby "poisons" the incorporation of new molecules into that facet. In fact, the molecules that lead to poisoning of a growth surface need not be impurities in the chemical sense. They can simply be misaligned or misfolded specimens of the crystallizing species (see, e.g., [5,6]). In either case, one can argue that the crystal growth is blocked by incorporation of defects in the crystal. In this Letter, we report a numerical study that reveals a different kind of self-poisoning: the crystal nucleus itself is free of defects, but it is covered by a liquid layer of molecules that do not have the correct orientation to be incorporated in the crystal. This has consequences both for crystal nucleation and for subsequent crystal growth.

The system that we studied is a model for a colloidal suspension of hard, rodlike particles. These particles are modeled as hard spherocylinders with a diameter D and a cylindrical segment of length L. In our simulations, we considered 2400 rods with an aspect ratio $L/D = 2$. These particles have a relatively simple phase diagram [7]: at low pressures, the system forms an isotropic fluid. At a pressure $p = 5.64\ k_BT/D^3$, the isotropic fluid coexists with an orientationally ordered crystal phase. (In the following the unit of energy is k_BT and the unit of length is D.) We are interested in crystal nucleation from the metastable fluid; i.e., we would like to study how crystallites are formed in the liquid, what their interfacial tension is with respect to the fluid, and how they cross the free-energy barrier, which is caused by the interplay between free-energy loss due to interfacial tension and gain due to formation of crystallite volume.

To study this phenomenon, we compressed the fluid beyond coexistence, to a pressure of $p = 6$. At this pressure, the chemical potential difference between the (metastable) fluid and the solid phases is approximately $0.2\ k_BT$ per particle. In spite of the fact that, at this pressure, the solid is more stable than the liquid, spontaneous crystallization never occurred on the time scales of our (quite long) simulations. However, at higher supersaturations (e.g., $p = 8$, $\Delta\mu = 1.3\ k_BT/\text{particle}$) spontaneous crystallization did occur on the time scale of a simulation (see Fig. 2). By working at $p = 6$, a pressure where spontaneous crystallization is suppressed, we can study the free energy and the structure of small crystal nuclei (see Fig. 1), using the biased sampling techniques described in Refs. [1,2].

In order to follow the formation of crystallites from solution, we need an order parameter that distinguishes particles in a crystalline environment from those in the liquid phase. In the crystal phase, all particles within one crystal tend to be strongly aligned. We employed this fact to define our crystallinity criterion: two particles i and j are said to belong to the same crystallite if: (i) their surface-to-surface distance is less than $0.5\ D$ and (ii) the dot product of the unit vectors along their respective axes satisfies $|\mathbf{u}_i.\mathbf{u}_j| > 0.995$. With this criterion, 99.8% of all particles in an equilibrium crystal are recognized as belonging to that crystal. As the criterion only considers the relative orientation of neighboring particles, it does not distinguish between crystalline, smectic, and (dense) nematic structures. This means that we do not impose strong constraints on the structure of the crystal nucleus. A side effect of this rather loose criterion is that many

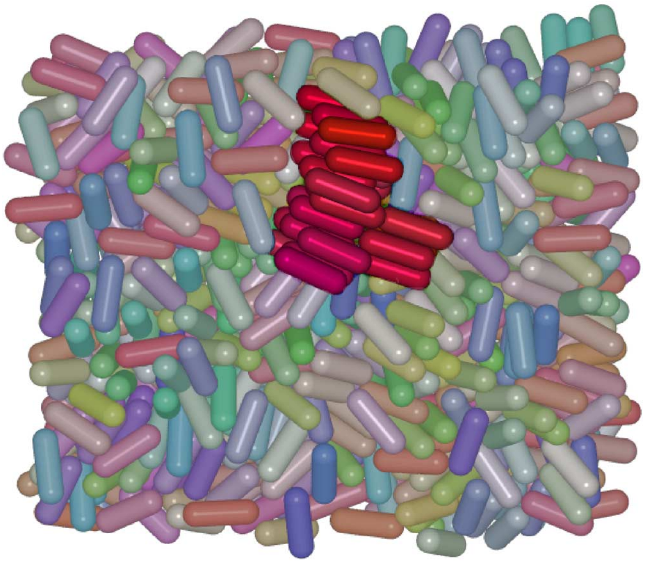

FIG. 1 (color online). A metastable liquid configuration at $p = 6$, containing a (subcritical) crystalline cluster (dark shading or red). Shading or color is used to distinguish between different orientations of the rods.

particles in the liquid are identified as belonging to small crystallites. However, we found that the number of rods in these crystallites was rarely larger than 2: about 5% of all particles belong to "crystal" dimers and less than one in a thousand belongs to a larger cluster. We never observed spontaneous fluctuations that resulted in crystalline clusters containing more than ten particles.

We denote the average number of clusters consisting of n particles by N_n. A good measure for the probability to find a cluster of size n is the ratio $P(n) \equiv N_n/N$, where N is the total number of particles in the system. We define an intensive free-energy barrier for the formation of a crystal nucleus of n particles as $\Delta G(n) = -k_B T \ln P(n)$. Only small clusters ($n \leq 10$) form in normal simulation. To probe $P(n)$ for larger n, we use biased, multihistogram simulations (for details, see Ref. [2]).

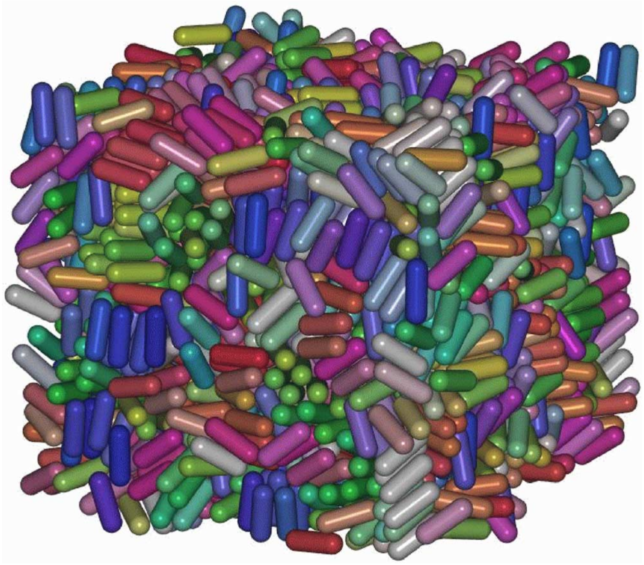

FIG. 2 (color online). When compressing an isotropic suspension of rods to a reduced pressure $p = 8$, crystallization is fast and the system becomes polycrystalline.

When we perform such a multihistogram simulation, we find that we can grow large, ordered clusters. However, somewhat surprisingly, we find that most particles in the ordered cluster are located in a single hexagonally ordered layer. As we bias the cluster-size distribution towards larger crystallites, we observe no tendency to form crystallites that contain multiple layers. To be more precise: a few particles may order on top of the crystallite, but these embryonic new layers quickly dissolve again. All growth of the cluster concentrates on the edges, and the free energy of the cluster rises monotonically with size (see Fig. 3). In other words: the system never crossed a nucleation barrier beyond which crystallites would grow spontaneously.

Interestingly, a rough analysis of the data shown in Fig. 3 suggests that a flat crystallite is not the most stable one. If we assume that the crystallite is cylindrical, with a thickness $h \equiv L + D$ and a radius r, then we can approximate the free energy of this cluster by

$$\Delta G(r) = 2\pi r h \gamma_{\parallel} + \pi r^2 (2\gamma_{\perp} - h\rho_s |\Delta\mu|), \qquad (1)$$

where $\gamma_{\parallel}$ and $\gamma_{\perp}$ are, respectively, the free-energy

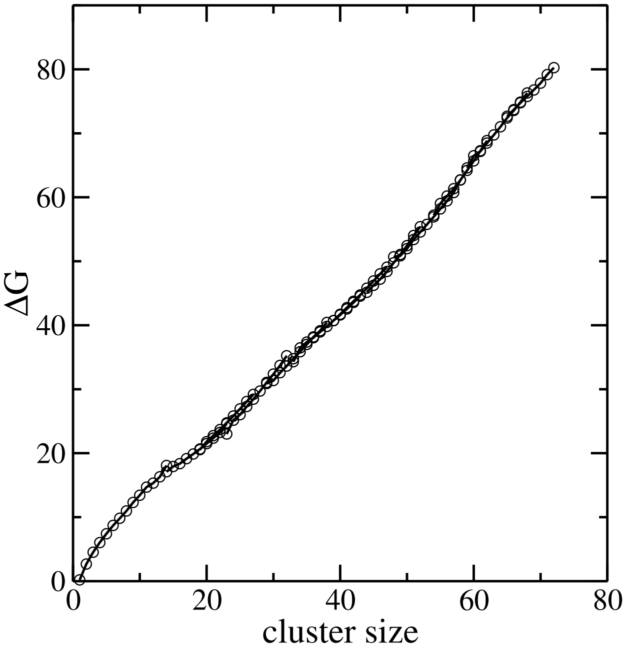

FIG. 3. Size dependence of the free energy of a small crystal nucleus. For the low supersaturations that we studied, ΔG for a single crystalline layer grows monotonically with cluster size. In order to nucleate a stable crystal, a multilayer nucleus must first form.

densities of the side and of the top/bottom surfaces. ρ_s is the density of the crystalline phase.

It is hardly surprising that we see no evidence for a critical size beyond which lamellae grow spontaneously: in a lamellar crystal, both the bulk free energy and the (dominant) surface free-energy scale with the cross-sectional area. A lamella can only grow spontaneously when $(2\gamma_\perp - \rho_s|\Delta\mu|) < 0$. At the low supersaturation that we use ($|\Delta\mu| = 0.2$), this condition is not satisfied. In fact, a fit of Eq. (1) to the free-energy barrier in Fig. 3 yields $\gamma_\perp = 0.6$. Moreover, we find that $\gamma_\parallel \ll \gamma_\perp$. (In Fig. 3 ΔG is almost linear in cluster size. Therefore the contribution from $\gamma_\parallel$ must be very small.) This is interesting, because in this case, we should expect multilayer clusters to be more stable than flat disks. The fact that, in our simulations, we observe the formation of disklike crystallites suggests that there are *kinetic* reasons that inhibit the formation of multilayer crystallites. The simplest assumption is that multilayer growth is difficult because every new layer has to nucleate on top of an existing layer [4]. To test this, we used the same biased Monte Carlo procedure to compute the free energy of a crystallite that forms on top of an ordered crystalline substrate. However, before we discuss these simulations, it is instructive first to look at the ordering in the liquid near the crystal surface.

Figure 4 shows the angular distribution of particles in the liquid close to the top surface (the surface perpendicular to the director field) and the side surface (the surface parallel to it) of a perfect crystal of hard spherocylinders. The peaks at $|\cos\theta| = 1$ for the side surface and at $\cos\theta = 0$ for the top surface indicate that a large fraction of the particles align parallel to the surface. In addition, for the top surface, the angular distribution also peaks for orientations perpendicular to the surface.

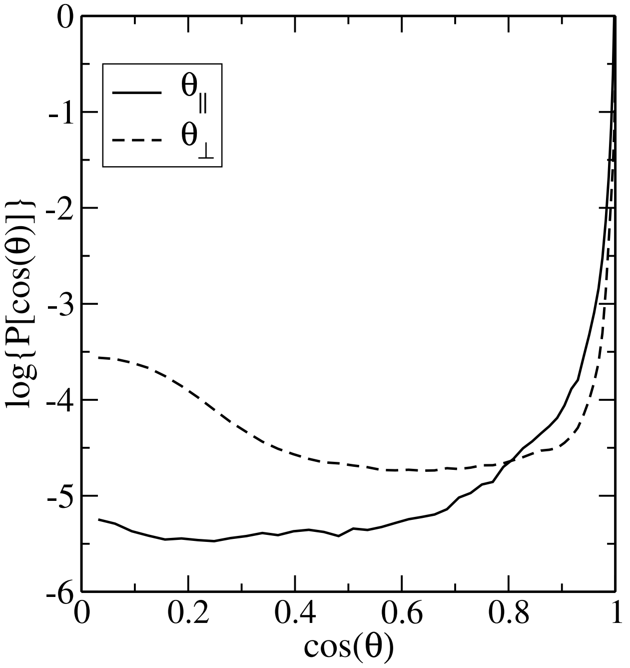

FIG. 4. Angular distribution of liquid particles close to a surface of a hard-rod crystal. $\theta_\parallel$ denotes the surface parallel to the director field (“side surface”), $\theta_\perp$ the surface perpendicular to it (“top surface”).

The preference of particles to lie flat on the crystal surface facilitates growth of the side surface, but it makes growth of the top/bottom surface difficult. Particles have to overcome a barrier of roughly 2 kT/particle in order to stand up on the surface and align with the director. In contrast, incorporation of particles on the side face of a crystal is relatively easy. Indeed, we find no inhibition of the lateral growth of spherocylinder crystals, even when the growth of additional layers is effectively suppressed.

The discussion above suggests that, in order to form a second crystal layer, an appreciable fraction of the particles on the top or bottom surface must spontaneously align parallel to the surface normal. The “reaction” path for second-layer formation would then be orientational alignment, followed by crystallization. To explore this possible route, we performed simulations where we introduced a second biasing parameter that facilitates the alignment of the particle orientation $\vec{u}_i$ with the surface normal $\vec{n}$, for particles close to the (top or bottom) surface.

$$S_{\text{liquid}} = \langle (\vec{n} \cdot \vec{u})^2 \rangle.$$

Unlike the order parameter that we used to measure crystallinity, S increases continuously with alignment. In contrast, particles are counted as crystalline only if they are already well aligned. This implies that S is sensitive to the prealignment that is, presumably, a prerequisite for crystallization.

Indeed, we find that applying an orientational bias greatly facilitates the growth of a second crystal layer.

There is, however, another effect, that slows down the growth of a second layer. Figure 5 shows the free-energy barrier associated with the formation of a compact crystalline island on top of a lamellar substrate. In the same figure, we also show the free-energy cost associated with the addition of the same number of crystalline (i.e., well-aligned) particles, N_{total}, anywhere in the second layer. Clearly, the random distribution of crystalline particles in the second layer has a higher entropy than the arrangement in a single cluster. This means that if a small number of crystalline particles is added to a second layer, it is entropically favorable to distribute them randomly over the surface. Once their number exceeds a certain threshold (12 for the case plotted in Fig. 5), surface tension wins from positional entropy and they aggregate into a cluster. This aggregation is, itself, a nucleation event. It is therefore a slow process. Hence, second-layer growth is difficult for two reasons: it costs free energy to prealign the particles that are to be incorporated in the crystal, and

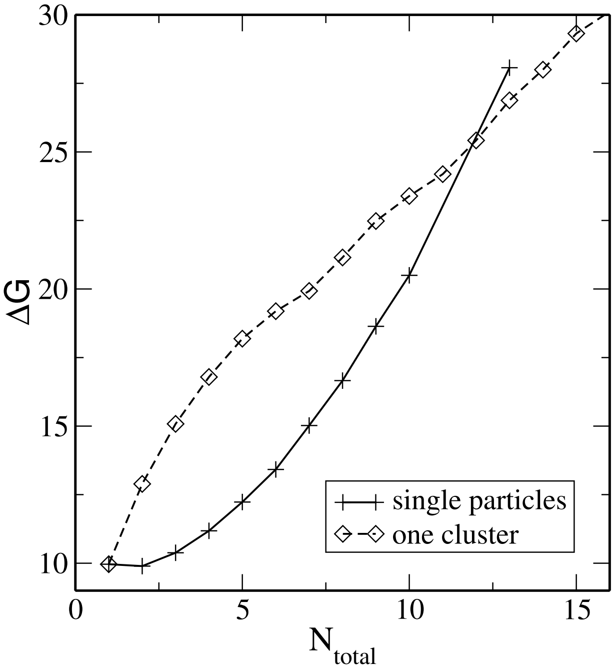

FIG. 5. Free energy dependence on particle distribution in the new layer: all particles in the new layer form one single cluster (dashed line) and all particles are in clusters of size 1 (solid line).

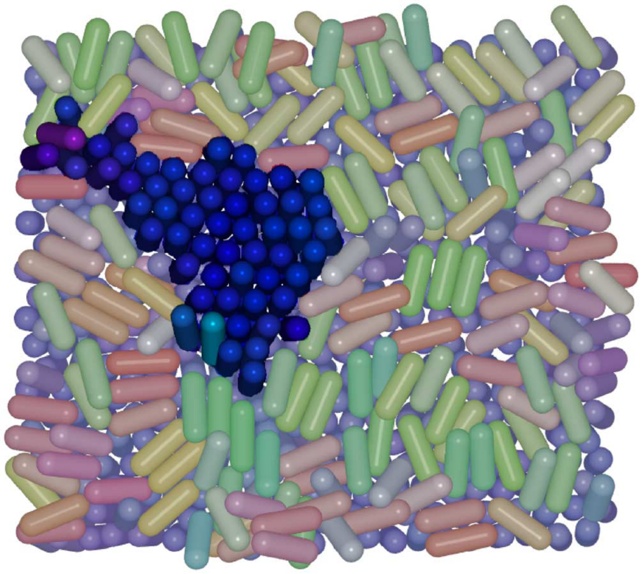

FIG. 6 (color online). Configuration snapshot of second-layer growth: only those particles are shown that are adjacent to the top surface of a lamellar crystal close to a solid surface (seen from the top). Most particles lie flat (light shading or colors). But, in addition, a crystalline cluster of about 50 rods has formed (dark shading or blue).

then a nucleation event is needed to create a compact cluster that can grow to a larger size. In Fig. 5 we do not show the complete nucleation barrier as, for the small supersaturation used in our simulations, the critical cluster size is rather large, $N_{\mathrm{cluster}} \simeq 200$. (A cluster this size would, of course, require a substrate of at least this size. It is unlikely that such substrates will form spontaneously in the bulk.) By introducing a bias on N_{cluster} it is possible to grow a complete second layer on top of a first one. Figure 6 shows a configuration snapshot of those particles which are close to the first layer (looking down onto the layer through the invisible liquid). Most particles lie flat on the first layer (light shading or colors), but there is also a cluster of roughly 50 particles standing (dark shading or dark blue).

Recent experiments by Maeda and Maeda [8] on the isotropic-to-smectic transition in colloidal hard rods of β–FeOOH rods, showed that these particles tend to form disklike crystallites. The present simulations suggest that this experimental observation is a logical consequence of the fact that, at sufficiently high supersaturation, multilayer growth is still kinetically inhibited, due to orientational "self-poisoning" of the top and bottom growth surfaces, whereas lateral growth proceeds relatively unhampered. It is tempting to speculate that the same factors are responsible for the morphology of the raftlike protein crystal nuclei observed by Yau and Vekilov [9]

The present simulations suggest that, experimentally, the growth of colloidal crystals of rodlike particles can be greatly enhanced by applying a field that prealigns the rods. A strong, static magnetic field should have this effect. In particular, it should facilitate the growth of multilayer crystals under conditions where a single-layer lamellar crystal is thermodynamically unstable.

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