Do multilayer crystalline clusters nucleate in mixtures of Colloidal Rods and Non-adsorbing Polymer?

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We study the isotropic-to-crystal transformation in a mixture of colloidal hard rods and non-adsorbing polymer using computer simulations. We determine the height of the nucleation barrier, and we find that the critical cluster consists of a single crystalline layer that grows laterally for all polymer fugacities considered. At lower supersaturation, the free energy of a single hexagonally packed layer increases monotonically with size, while the nucleation barrier of a second crystalline layer is extremely high. Hence, the nucleation of multilayer crystals is never observed. Multilayer crystals form only in the spinodal decomposition regime, where either single crystalline membranes coalesce into multilayer clusters, or where at higher polymer fugacity smaller clusters of rods stack on top of each other to form long filaments.

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It is well known that liquids must be supercooled substantially before they start to crystallize spontaneously. The reason is that the system has to cross a free energy barrier by moving from the metastable to the stable phase. If the free energy barrier is high, spontaneous fluctuations that would result in the formation of the stable phase are unlikely and rare, and subcritical clusters that are formed will dissolve spontaneously. When spherical particles nucleate, the clusters that form, tend to be spherical: e.g., gas-bubbles in a superheated liquid, liquid droplets in a supersaturated gas, or roughly spherical crystallites in an undercooled liquid are undisputed transient clusters. On the other hand, non-spherical particles, giving rise to liquid crystalline phases with positional and orientation ordering may form anisotropic clusters. The formation of the nematic phase which possess only orientational order is well-studied experimentally [1, 2] and by theory and simulations [3–5], and proceeds via the formation of spindle-shaped elongated nematic droplets, called tactoids. This state-of-affairs should be contrasted with the formation of clusters, where both orientation and positional order plays a role. Simple transient smectic or crystalline droplets of anisotropic particles have to the best of our knowledge never been observed in experiments [1, 6] or in simulations [7, 8]. For instance, a simulation study on crystal nucleation in fluids of short hard rods shows that the growth of a single crystalline membrane is hampered by rods that are aligned parallel to the bottom and top surface of the crystallite: the surface poisons itself and hence prevents its own growth [7]. Another simulation study shows that the nucleation of the smectic phase in fluids of slightly longer rods is hampered due to slow dynamics [8]. In this Letter, we will study the interplay between orientation and positional order on the nucleation of anisotropic particles, where the cluster formation is not inhibited by kinetic effects.

To this end, we study a mixture of hard rods and non-adsorbing polymer. The addition of polymer induces an effective attraction between the rods due to the so-called depletion attraction [9]. The range and the strength of this attraction are determined by the diameter of the polymer coils and the polymer fugacity, respectively. Our model consists of hard spherocylinders (HSC) with a length-to-diameter ratio of $L^* = L/D = 5$, and a non-adsorbing ideal polymer with a radius of gyration $R_g = D/4$. The presence of the polymer is described by an empiric effective depletion potential $\beta\phi_{\rm dep} = -zV_{\rm over}(\mathbf{R}_{ij};\omega_i,\omega_j)$ that approximates the overlap volume $V_{\rm over}$ of the depletion zones of two spherocylinders, where $\mathbf{R}_{ij}$ denotes the distance between the center-of-mass of rod i and j, ω_i the orientation of rod i, $\beta = 1/k_BT$, and $z^* \equiv zD^3 = 48\eta_p^r/\pi$ the fugacity of the ideal polymer with $\eta_p^r = 4\pi R_g^3 N/3V$ the polymer reservoir packing fraction [10]. We note that the effective depletion attraction depends on the relative positions and orientations of the two rods, and is maximal for parallel and adjacent rods. The addition of non-adsorbing polymer broadens the coexistence regions, yielding broad gas-crystal coexistence at sufficiently high polymer fugacity $z^* > 2$ (see Fig. 4b of [10]). This allows us to study nucleation of clusters with positional and orientation order in a supersaturated dilute gas phase, where it is unlikely that the nucleation is hindered by self-poisoning or slow dynamics.

We study the isotropic-to-solid transition by performing Monte Carlo (MC) simulations in the isothermal-isobaric (NPT) ensemble, i.e., we fix the number of rods, temperature, and pressure. We perform simulations of 864 rods in a rectangular simulation box with periodic boundary conditions and the length of the box sides are allowed to fluctuate. When the pressure $P^* = \beta PD^3$ is slightly higher than the coexistence pressure, we have to employ special sampling techniques to study the isotropic-to-crystal transformation as nucleation is a rare event. In this case, we use the umbrella sampling technique [11] that allows us to bias the sampling

to configurations containing clusters with a certain cluster size. To this end, we employ a harmonic function $\beta W(n) = 0.5k_n(n - n_0)^2$ with n the size of the biggest cluster and the constants k_n and n_0 determine the width and the location of the phase space that is sampled, respectively [11]. The phase space enclosed around n_0 is called "window". By opening consecutive and overlapping windows of the same width and centered at increasing values of the order parameter n, we are able to compute the free energy barrier. In our simulations, we fix $k_n = 0.15$. In order to distinguish the clusters from the isotropic phase, we use the cluster criterion as described in [4]. First, we define the local orientational order of rod i by the second Legendre polynomial, $S(i) = 1/2n_i \sum_{j=1}^{n_i}(3|\omega_i \cdot \omega_j|^2 - 1)$, where n_i is the total number of rods j with a surface-to-surface distance $\rho_{ij} \leq 1.5D$ with respect to rod i. Subsequently, we employ the cluster criterion that rod i is orientationally ordered if $S(i) > 0.4$. After identifying all orientationally ordered particles in the system, we determine the solid clusters by the criterion that two orientationally ordered particles belong to the same cluster if (i) $\rho_{ij} < 0.5D$, and (ii) the dot product satisfies $|\omega_i \cdot \omega_j| > 0.85$.

We now employ the cluster criterion to study crystal nucleation at a polymer fugacity $z^* > 3.0$, which lies inside a broad gas-solid coexistence region. For $3.0 < z^* < 3.9$, we observe as expected nucleation and growth (NG) at low and spinodal decomposition (SD) at high supersaturation. For $z^* > 4.0$, we find SD for all supersaturations that we studied. In the NG regime, we calculate the Gibbs free energy ΔG as a function of cluster size using umbrella sampling. In contrast with Ref. [7], where it was found that ΔG only grows monotonically with cluster size and never crosses a barrier, we now find a Gibbs free energy barrier for different pressures and polymer fugacities. In Fig. 1, we show the Gibbs free energy barrier for $z^* = 3.0$. At this fugacity, the system exhibits a transition at $P^* = 0.002$ from an isotropic gas phase with density $\rho^* = ND^3/V = 0.0021$to a dense solid phase with density $\rho^* = 0.154$. Exemplarily, we find for $P^* = 0.0205$ that the height of the nucleation barrier is $\Delta G^* \simeq 11.7k_BT$ and the corresponding size of the critical crystal nucleus is $n^* = 28$, while for $P^* = 0.012$ we find $\Delta G^* \simeq 90k_BT$ and $n^* = 300$. Surprisingly, perhaps, we find that the clusters that are formed consist of a single hexagonally ordered layer of rods that can grow spontaneously when the cluster exceeds the critical cluster size. However, these clusters grow only laterally, i.e., particles attach from the metastable isotropic phase at the edge of the cluster, and never form crystallites consisting of multiple layers. We never observe the nucleation of additional layers in our simulations. A typical configuration of such a monolayer is shown in Fig. 1. In addition, we analyze the shape and structure of the cluster using umbrella sampling, which allows us to stabilize the cluster size around a given value, and to calculate the density and nematic order parameter profiles. Fig. 2 shows contour plots of the density profiles of the rods as a function of the distance from the center-of-mass of the cluster in the direction parallel ($r_\parallel^*$) and perpendicular ($r_\perp^*$) to the nematic director of the cluster. Three clusters are given for a system at $P^* = 0.020$ and $z^* = 3.0$: a precritical cluster consisting of 25 rods, a critical cluster with 39, and a postcritical cluster with 80 rods. Fig. 2 shows that the density is maximal in the center of the cluster, and decreases gradually towards the density of the metastable isotropic phase ($\rho^* \simeq 0.02$) from the center to the surface of the cluster. We also observe that the shape of the cluster is that of a monolayer of rods. The contour plots of the nematic order parameter profiles are very similar to the density profiles (not shown here). Also in this case, the nematic order parameter is at a maximum at the center of the cluster with a value of approximately one as expected for a solid cluster.

For high supersaturation $P^* > 0.0205$ (corresponding to $\Delta\mu > 2.2k_BT$), the nucleation barrier is very low and we observe spontaneous nucleation and growth of clusters consisting of a single crystalline layer without applying a biasing potential in our simulations. The actual nucleation pathway is shown in the attached movie [12].

For $P^* < 0.012$ ($\Delta\mu < 1.9k_BT$), we find that the free energy grows monotonically with cluster size, and hence the system never crosses a nucleation barrier beyond which the cluster can grow spontaneously. Our simulations show that the growth of these clusters proceeds again via a monolayer, and that the formation of clusters consisting of multiple crystalline layers seems to be inhibited even if we bias the cluster size distribution to larger crystallites. The inhibition of the formation of multilayer clusters has also been observed in systems of pure hard rods, and was attributed to kinetic reasons, e.g., self-poisoning or slow dynamics [7, 8]. As in the present case the metastable isotropic phase is extremely dilute, it is hard to envision that the nucleation of additional layers is hampered here by kinetic effects.

Our results do agree with the theoretical predictions for the growth of smectic filaments in suspensions of colloidal rods [13]. In this work, the free energy associated with the formation of a single circular smectic/crystalline layer with radius R and height H is approximated to be:

$$\Delta G = -\pi R^2 \rho H|\Delta\mu| + 2\pi R^2\gamma_\perp + 2\pi RH\gamma_\parallel \qquad (1)$$

with $\gamma_\perp$ and $\gamma_\parallel$ the interfacial free energy of the interface between the top and the edges of the smectic/crystalline layer and the isotropic phase, respectively. At low supersaturation, $|\Delta\mu| < 2\gamma_\perp/\rho H$, ΔG is always positive and consequently a single layer can never grow spontaneously. The free energy ΔG can only become negative by increasing the gain in bulk free energy compared to the interfacial free energy cost, and hence, only multilayer crystals may grow spontaneously [13]. Our results

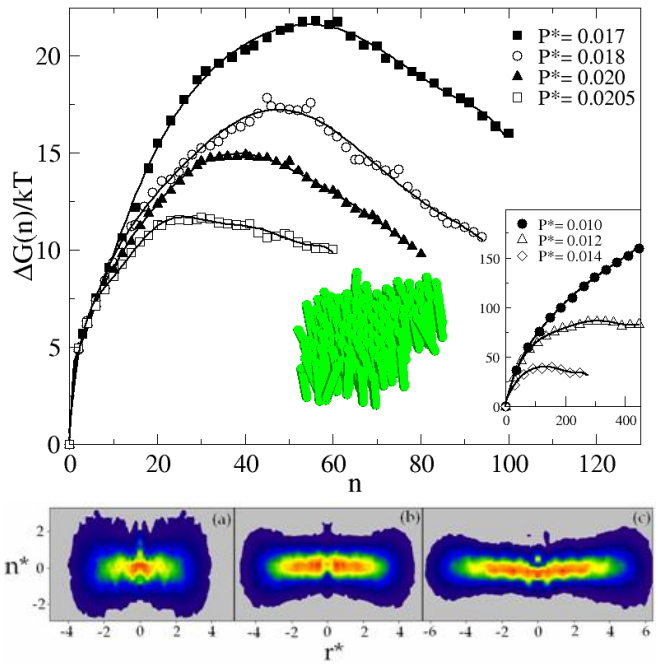

FIG. 1: (top) Gibbs free energy of a mixture of HSC with a $L/D = 5$ and non-adsorbing polymer with $R_g = D/4$ and polymer fugacity $z^* = 3.0$. The fitting lines are guides to the eye. A typical configuration of a critical cluster is shown in the inset. (bottom) Density profiles for a precritical (a), critical (b), and postcritical (c) cluster of size $n = 25, 39$, and 80, respectively, at $P^* = 0.02$ and $z^* = 3.0$. The coordinates $r^*_\parallel$ and $r^*_\perp$ are the distances per unit diameter of the rods from the center-of-mass of the cluster in the direction parallel ($r^*_\parallel$) and perpendicular ($r^*_\perp$) to the local director (color online).

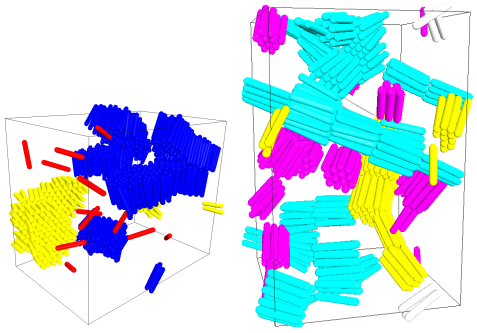

FIG. 2: (left) Crystalline membranes observed at z*=3.5 and P*=0.001 and (right) smectic filaments at z*=6.5 and P*=0.0017 (color online).

indeed show such a cross-over at $P^* \simeq 0.011$: For higher supersaturations ($P^* > 0.012$) we find a maximum in ΔG, beyond which a single membrane can grow spontaneously and for $P^* \leq 0.010$ the monolayer cannot grow as ΔG increases monotonically with n. In order to test the theoretical prediction of the crossover, we determine $\gamma_\perp$ and $\gamma_\parallel$ by fitting our free energy barriers with Eq. (1). We plot $\gamma_\perp$ and $\gamma_\parallel$ in Fig. 3a as a function of supersaturation $|\Delta\mu|$. We find that both $\gamma_\perp$ and $\gamma_\parallel$ depends weakly on P^* and that $\gamma_\perp$ is about 3-4 times larger than $\gamma_\parallel$. In addition, we plot the theoretical prediction for the crossover $\Delta\mu = 2\gamma_\perp/\rho H$ and we find that the crossover is at $|\Delta\mu| \simeq 1.6$, which is consistent with our findings that we did not find a barrier for $|\Delta\mu| = 1.57$ ($P^* = 0.010$), while there is one for $|\Delta\mu| = 1.65$ ($P^* \simeq 0.012$). In Fig. 3b, we plot the fits along with the simulation data. We observe that the precise shape of our free energy curves obtained from simulations deviates considerably with the fits, which might be due to the fact that Eq. (1) is based on the assumption that the bulk and surface properties of a small cluster can be described with those of a macroscopic crystal. In the case of a monolayer cluster, it is highly questionable whether the free energy can be divided into a bulk and a surface term, which also depends on the choice of dividing surface, and whether the line tension can be neglected. Strong finite size effects on the bulk and surface free energy of a disk-like monolayer might be expected. Recent simulation results show indeed evidence for large finite size effects in the surface free energy of NaCl crystallites, which is attributed to the faceted shape of the cluster [14].

We now study the nucleation of a second layer on a first layer, as for $P^* < 0.012$ only multilayer crystals may grow spontaneously. Above we mentioned that the growth of the clusters proceeds via a single crystalline layer that only grows laterally even if we bias the cluster size distribution to larger crystallites. In order to prevent the growth of the first layer, we equilibrate an infinite monolayer consisting of 650 rods in a periodic box at P*=0.01 and z*=3.0. By applying the same umbrella sampling technique as employed above for the nucleation of the first layer, i.e., without any orientational bias as employed in [7], we observe the formation of a second layer on the monolayer. In Fig. 5, we present the Gibbs free energy for both the formation of the first layer as well as for the second layer. Fig. 5 shows clearly that a monolayer with size n has a lower free energy than a double-layer of the same size. This explains why the monolayer only grows laterally when we bias the sampling towards larger cluster sizes. In addition, we find that the free energy barrier for the second layer is extremely high, i.e., $\beta\Delta G^* \simeq 90$ for a second layer with size $n^* = 190$. If we assume that the second layer can only be nucleated on a monolayer with at least the same size and the Gibbs free energy of a monolayer with size $n = 190$ is $\Delta G \simeq 90$, we find that the probability to find a bilayer with size $n = 380$ is $P(n = 280) \simeq \exp(-180)$, which is extremely small. In Ref. [13] , the free energy to grow a second circular smectic/crystalline layer with radius R and height H is approximated to be:

$$\Delta G_2 = -\pi R^2 \rho H |\Delta\mu| + 2\pi R H \gamma_\parallel, \qquad (2)$$

which assumes that the surface free energy for the top and bottom surface of the second circular layer is zero

as we do not create extra top surface. The inset of Fig. 4 shows, however, that the free energy for the formation of the second layer is only slightly smaller than for the first one. The discrepancy may be explained by finite size corrections of the cluster free energy and contributions of the line tension or wedge free energy that cannot be neglected. This should be investigated in future work. As we only find the nucleation of monolayers and the nucleation of additional layers is very unlikely, it is interesting to investigate how the stable crystal phase consisting of multiple crystalline layers will actually form.

To study the formation of multilayer clusters, we study the system at higher supersaturations, where we observe spinodal decomposition.

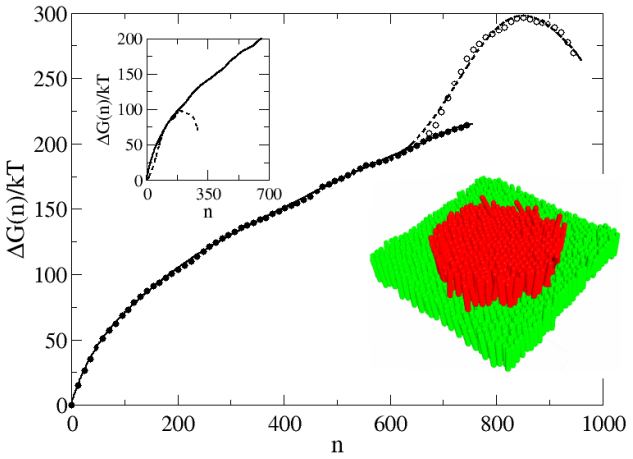

FIG. 3: Top: crystalline membranes observed at z*=3.5. P*=0.006 (left) and P*=0.01 (right). Bottom: Smectic filaments observed at z*=6.5 and P*=0.0017 (a), P*=0.0018 (b), and P*=0.0019 (c).(color online).

At low polymer fugacity, e.g. $z^* = 3.5$, we find that only a few clusters are formed at the beginning of the simulation, which tend to grow laterally as in the NG regime. Subsequently, the clusters, which grow to a considerable size, coalesce when they are sufficiently close to each other. The coalescence can give rise to bigger membranes as they merge sideways, but occasionally, two monolayers form a bilayer by top-bottom coalescence. In Fig. 4, we show a typical example where two monolayers are about to merge into a bilayer. The actual pathway is shown in the attached movie [12]. At higher fugacities, i.e. $z^* = 6.5$, we find that the number of clusters that are formed at the beginning of the simulations is much higher than that at lower fugacity, especially if the supersaturation pressure is low. These clusters pile on top of each other and form relatively long filaments consisting of many different layers with a non-uniform thickness, i.e., each layer contains a different number of rods (see [12] for a movie). Eventually, the filaments form a percolating network. Upon decreasing z^*, the thickness of the filaments increases and their length decreases, and hence, the shape of the clusters can be tuned from monolayers to long and thin filaments. Our results agree with the experimental observations of Dogic and Fraden, who studied the kinetics of the isotropic-smectic transition in mixtures of rod-like viruses and non-adsorbing polymers [1]. In this work, long thin filaments are observed at high polymer concentrations and big freely floating monolayers, which can coalesce sideways and top-bottom at low z^p. The different structures can be explained by the depletion attraction between the rods and between the surfaces of two clusters. At high polymer fugacity, many clusters are formed immediately as the depletion attraction between the rods is very high. These clusters will quickly coalesce as the attraction of the clusters is also very high. At lower z^*, only a few cluster will be formed in the beginning, which will grow laterally because the attraction of two adjacent rods is higher than two rods head to tail. For sufficient big clusters, the area of the top surface is big enough that two clusters can merge top-bottom.

In conclusion, we have studied crystal nucleation of clusters with positional and orientation order in a dilute isotropic gas phase, where it is unlikely that the nucleation is hindered by kinetic effects. We observe solely the nucleation of single crystalline layers as the nucleation of multilayer clusters is extremely rare. Structures consisting of multiple layers can only form by top-bottom coalescence of single membranes. Our findings are in agreement with experimental observations in attractive β-FeOOH rod suspensions where matlike 2D clusters are formed that subsequently merge into 3D smectic structures [6] and with experiments on fd-virus particles where huge single monolayers are formed that form multilayer structures by top-bottom coalescence [1]. We conclude that the supersaturation for which a single membrane can grow spontaneously is well-predicted by a simple free energy expression for a monolayer, while the precise free energy for the formation of small anisotropic crystallites needs further investigation.

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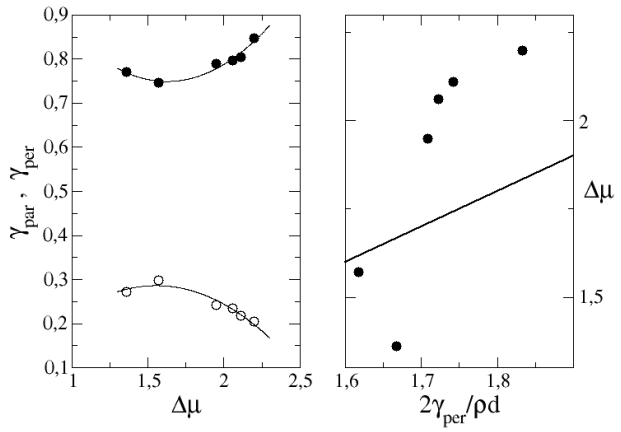

FIG. 4: Gibbs free energy of a mixture of HSC with $L/D = 5$ and non-adsorbing polymer with $R_g = D/4$ at $z^* = 3.0$ and $P^* = 0.01$. The dashed and solid curves refer to a monolayer and a double layer crystal, respectively. Snapshots (a) and (b) are monolayer clusters containing 296 and 495 rods, respectively. Snapshot (c), containing 700 rods, shows a second layer on top of an infinite monolayer (color online).

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