Frustration of the isotropic-columnar phase transition of colloidal hard platelets by a transient cubic phase

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Using simulations and theory, we show that the cubic phase is metastable for three model hard platelets. The locally favored structures of perpendicular particle stacks in the fluid prevent the formation of the columnar phase through geometric frustration resulting in vitrification. Also, we find a direct link between structure and dynamic heterogeneities in the cooperative rotation of particle stacks, which is crucial for the devitrification process. Finally, we show that the life time of the glassy cubic phase can be tuned by surprisingly small differences in particle shape.

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Nucleation is the process whereby a metastable phase transforms into a stable one, via the spontaneous formation of a cluster of the stable phase. According to classical nucleation theory, the free-energy barrier that separates the metastable phase from the stable state decreases with increasing supersaturation, and for quenches in the spinodal regime, the phase transformation proceeds via spinodal decomposition and coarsening. However, at sufficiently high supersaturations the motion of the particles can slow down so dramatically that the metastable state enters a glass regime.

Vitrification hampers the phase transformation as the particles cannot rearrange diffusively to form the stable phase. However, some glasses can evolve into the stable phase despite the arrested motion. The mechanism behind this so-called "devitrification" process is not well-understood, and neither the origin of the glass transition and its interplay with nucleation. An intriguing scenario based on geometrical frustration has been proposed, where the local order in the liquid phase is incompatible with the long-range order of the crystal phase [1]. Hence, the formation of locally favored structures in the liquid, a concept proposed by Frank to explain the transient ground state of this model [2], prevents the crystallization. This scenario has been investigated using a two-dimensional lattice-free spin glass model, where the degree of frustration against crystallization can be tuned by an additional anisotropic potential that locally favors five-fold symmetry which is incompatible with the crystalline ground state of this model [1].

In this Letter, we investigate the interplay between nucleation, geometrical frustration, and devitrification in a simple (more realistic) 3D model system of colloidal hard platelets using computer simulations. The most common model systems for colloidal platelets are hard cut spheres (HCS), which consist of the middle section of thickness $L$ of a sphere of diameter $D$, and oblate hard spherocylinders (OHSC), comprising of a flat cylindrical core with diameter $D$ and height $L$, and a toroidal rim with tube diameter $L$. OHSC are more rounded than HCS (see Fig. 1a), and are therefore expected to better model the shape of colloidal disks, such as polymer-coated clay platelets [3] or charge-stabilised Gibbsite platelets [4]. Interestingly, for $L/D = 0.2$, the phase diagram of OHSC displays an isotropic–columnar (IC) phase transition [5], whereas a very peculiar cubatic phase was reported in between the isotropic and the columnar phase for HCS [6]. In this phase, the particles form small stacks of almost cube-like dimensions, which tend to align perpendicular to each other. Recently, it was shown that larger system sizes tend to destabilize the cubic phase [7, 8]. However, it remains an open question whether or not the cubic phase is thermodynamically stable for colloidal hard platelets.

Here, we show that the cubic phase of different model hard platelets is not stable, but should be considered as a transient phase in the IC phase transformation. In addition, we show that the degree of geometric frustration

![FIG. 1. (Color online) (a) Three model platelets: oblate hard spherocylinders (OHSC), hard cut spheres (HCS) and "double hard cut spheres" (DHCS). The volumes of the particles are given by $v_{\text{OHSC}} = \pi L^3/6 + \pi^2 \sigma L^2/8 + \pi\sigma^2 L/4$ with $\sigma = D - L$, $v_{\text{HCS}} = \pi L(3D^2 - L^2)/12$, and $v_{\text{DHCS}} = \pi L(3D^2 - (L/2)^2)/12$ with $L$ and $D$ the (total) thickness and diameter of the particles, respectively. (b) A typical configuration of a cubic phase of OHSC with $L/D = 0.2$ and $P^* = 11.25$ ($\eta \simeq 0.57$). Different colors denote different orientations.](image)

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FIG. 2. (Color online) (a) The size of the largest columnar cluster \( n \) in an MD simulation of an isotropic fluid of \( N = 10000 \) OHSC with \( L/D = 0.2 \) at packing fraction \( \eta = 0.56 \) and \( \eta = 0.57 \). (b) and (d) Typical configurations of the largest columnar clusters, when the size of the largest cluster is around 300 particles (post-critical) for \( \eta = 0.56 \) (b) and \( \eta = 0.57 \) (d). Different colors of the particles denote different orientations. Swiftly rotating fluid particles are denoted by arrows pointing into the direction of the rotation; the other fluid particles are not shown at all. (c) The rotational non-Gaussian parameter \( \beta \) as a function of the time \( t \) in units of \( \tau_{\text{MD}} \) (see text) for \( \eta = 0.5 \) and \( \eta = 0.56 \).

We first consider a suspension of \( N \) OHSC with aspect ratio \( L/D = 0.2 \) in a volume \( V \) or at a pressure \( P \). This system displays a bulk transition from an isotropic phase with packing fraction \( \eta_I \equiv v_{\text{OHSC}} N/V = 0.5050 \) to a columnar phase with \( \eta_{\text{IC}} = 0.5691 \) at pressure \( P^* = \beta P v_{\text{OHSC}} = 8.27 \), where \( \beta = 1/k_B T \) and \( v_{\text{OHSC}} \) is the volume of the OHSC particle [5].

In order to study the spontaneous formation of the columnar phase from the isotropic fluid phase, we require a cluster criterion that enables us to identify the columnar clusters. Unfortunately, the cluster criterion that was introduced to nucleation of the nematic, smectic, and crystal phase in systems of colloidal hard rods [10–12], is not strict enough to identify columnar clusters. We therefore developed a new cluster criterion that enables us to detect hexagonal columnar clusters, which goes beyond the indentification of single columns [13]. Particles are considered eligible for inclusion into a columnar cluster if they have sufficient neighbors with columnar order. Neighbors are considered to have columnar order when they have sufficient hexagonal order, as measured by a standard order parameter, but do not show high ordering with another symmetry. See [14] for details.

We use event driven Molecular Dynamics (MD) simulations of relatively large system sizes (\( N = 1500, 3000, \) and 10000) to study the kinetics of the \( \text{IC} \) phase transformation. Time is measured in units of \( \tau_{\text{MD}} = \sqrt{3 m D^2} \), where \( m \) is the mass of an OHSC. For \( \eta \geq 0.56 \), we observe the immediate formation of short stacks of OHSC in the supersaturated isotropic fluid phase, which subsequently tend to orient perpendicular to each other to optimize the packing. The symmetry of these locally favored structures in the resulting cubic phase is incompatible with that of the columnar phase, and hence the cubic orientational order can be seen as geometric frustration against the formation of the columnar phase. The cubic order is more pronounced for higher \( \eta \) and smaller system sizes (\( N = 1500 \) and 3000). A typical configuration of such a cubic phase is shown in Fig. 1(b) for \( \eta = 0.57 \). However, in very long simulations the cubic phase always transforms into a columnar phase. In order to analyze the phase transformation, we show the time evolution of the largest columnar cluster identified by our cluster criterion in Fig. 2a for \( \eta = 0.56 \) and 0.57. We clearly observe that the cluster grows much slower for lower \( \eta \) due to the lower supersaturation. In addition, we present typical configurations of post-critical columnar clusters in Fig. 2b and d. At a packing fraction of \( \eta = 0.56 \), we observe one columnar cluster that grows further to form the stable columnar phase, while for \( \eta = 0.57 \) three post-critical clusters are observed as the nucleation barrier is much lower. Interestingly, the nematic directors of the columnar clusters are aligned along the three preferred axes of the cubic phase, where it originated from, see Fig. 2d. We conclude that the \( \text{IC} \) phase transformation proceeds via a transient cubic phase and corresponds to a nucleation and growth scenario in which a spontaneously formed columnar cluster grows out to form the stable columnar phase. During MD simulations with
$N = 10000$, we observe the appearance of columnar clusters before long-range cubic order appeared after quick compression. In fact, this was to be expected, as the time it takes for the cubic order to spread throughout the system increases with system size, while the time for a nucleus to form in a fixed volume is size system independent. Therefore, the behavior observed in experiments, such as the Cryo-TEM experiments in which the cubic phase was observed [3], is largely dependent on the sample volume, which for Cryo-TEM is rather small to allow sufficiently fast shock-freezing of the sample. This suggests that the cubic phase may be stabilized by confinement.

Additionally, we investigated the translational and orientational dynamics of the particles in the supersaturated fluid of OHSC. To this end, we calculate the mean square translational displacement $\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$ and the mean square rotational displacement $\langle |\Delta \mathbf{\varphi}(t)|^2 \rangle$ (not shown), where the angular brackets indicate an ensemble average, $\mathbf{r}(t)$ and $\Delta \mathbf{\varphi}(t) = \int_0^t \mathbf{\omega}(t) \, dt$ are the position and the angular displacement [9], respectively, of particle $i$ at time $t$ with $\mathbf{\omega}$ the angular velocity. The corresponding translational and rotational diffusion constants measured in event-driven MD simulations [14] show a clear slowing down of the translational and rotational dynamics by about a factor of $\sim 5$ when the packing fraction is increased from $\eta = 0.5$ to 0.56. The simultaneous slowing down of the translational and rotational dynamics should be contrasted with the decoupling of the freezing of the translational and rotational degrees of freedom that is found for hard ellipsoids [15, 16], as well for the attractive-repulsive Gay-Berne ellipsoids [17, 18]. We expect that the translational and rotational dynamics are strongly coupled in all systems that form stacks or columns in the isotropic fluid. This very likely includes those experimental discotic systems that display direct heterogeneous dynamics cannot be easily related to the local structure [21]. Similarly, the growth of a columnar phase often proceeds by collective attachment of small stacks rather than single particles [14]. Interestingly, the rotation of stacks also plays a crucial role in the late-stage development of the columnar cluster. Fig. 3 shows a form of defect-healing in which a stack of mis-aligned particles in the columnar cluster first breaks up into smaller stacks and, subsequently, these smaller stacks reorient to conform with the director of the cluster.

As nucleation of a columnar phase from a glassy state with cubic order is hardly studied, it is interesting to determine the nucleation barrier associated for this devitrification process. Since the equilibration can only proceed via collective rearrangement of small clusters, the formation of the columnar phase is severely hampered by slow dynamics. We determine the nucleation barrier by employing the umbrella sampling technique in Monte Carlo (MC) simulations [10]. The resulting Gibbs free energy barrier $\triangle G(n)$ as a function of columnar cluster size $n$ for OHSC with $L/D = 0.2$ and packing fraction $\eta = 0.550$ and 0.569 (squares). The dashed line is a fit [22] to classical nucleation theory. Configurations of the critical nucleus are shown obtained from MC for $\eta = 0.550$ and 0.569 in the main panel and from MD simulations at $\eta = 0.56$ in the inset.

![Diagram](http://dx.doi.org/10.1103/PhysRevLett.108.206101)
OHSC is metastable with respect to an IC phase transition. In this light, it is interesting to study the effect of particle shape on the stability of the cubic phase. To this end, we measure the cubic order parameter \[ \eta \] as a function of pressure for the three particle shapes depicted in Fig. 1 using NPT MC simulations with \( N = 3000 \) particles. The shapes (ordered from more curved to more cylinder-like) are OHSC, HCS, which resemble recently synthesized particles of Ref. [24], and double hard cut spheres (DHCS). The latter model consists of two superimposed HCS and is essentially a cylinder. All three models have the same height-to-diameter ratio of \( L/D = 0.2 \). The onset of cubic order, as defined by the packing fraction \( \eta_{\text{cub}} \) at which the cubic order parameter suddenly increases, is shown as the dashed, blue line in Fig. 5. We observe clearly that \( \eta_{\text{cub}} \) decreases upon decreasing the particle curvature. Furthermore, \( \eta_{\text{cub}} \) for \( N = 3000 \) HCS is essentially equal to that of the largest system size, \( N = 1728 \), of Ref. [7], indicating that finite size effects beyond \( N = 3000 \) are small.

In addition, we study the stability of the cubic phase using a high-order virial theory. In Ref. [7], it was shown that a 8th-order expansion is required to predict a stable isotropic-cubic phase transition for HCS with \( L/D = 0.2 \). Here, we apply this theory to predict the isotropic-cubic phase transition for OHSC, HCS (with higher precision than in Ref. [7]), and DHCS. The results for the bulk density of the cubic phase in coexistence with the isotropic phase are denoted by the dashed, red lines in Fig. 5c at the 8th virial level. Although, the agreement with the simulations results is not satisfactory, surprisingly, the trend of the bulk density of the cubic phase with particle curvature is very similar to that of the NPT MC simulations.

Finally, we determine the stability of the cubic phase with respect to the columnar phase for HCS and DHCS. The apparent stability of the cubic phase for HCS could be due to dynamic arrest. Inspired by the particle stack rotations as observed in our MD simulations, we introduce a new cluster move in the MC simulations to speed up equilibration [14]. In order to investigate more precisely the location of the phase coexistence between the isotropic or cubic fluid phase with the columnar phase, we perform NPT MC simulations of the two coexisting phases in a simulation box that is large enough that the interfacial free energy is sufficiently small [25, 26].

The coexistence pressure can be determined as the pressure at which neither of the phases grows at the expense of the other phase [14, 26]. The corresponding coexistence densities for HCS and DHCS are shown in Fig. 5. Clearly, the pressure at which the columnar phase becomes more stable than the isotropic phase is lower than the pressure at which long-range cubic order was found, which unambiguously shows that the cubic phase is unstable for all three shapes considered. The strong decrease of \( \eta_{\text{cub}} \) as the particle shape changes from OHSC to HCS causes a strong decrease in \( \Delta \mu \) and, therefore, a strong increase in the life-time of the cubic phase, see also Fig. S4 [14].

In conclusion, we find that the cubic phase is metastable with respect to an IC phase coexistence for all three model platelets, and can be regarded as a transient phase in the IC phase transformation. The locally favored structures of perpendicularly oriented particle stacks in the cubic phase leads to geometric frustration that prevents the formation of the columnar phase thereby yielding vitrification. Additionally, we find a direct link between structural order and dynamic heterogeneities provided by the cooperative rotation of particle stacks in the cubic phase. Such a link is often assumed to be characteristic for glassy behavior, but is not easy to demonstrate in e.g., colloidal hard sphere glasses. We also show that the cooperative stack rotations play an important role in the devitrification process and that the life time of the cubic phase can be tuned by confinement and by surprisingly small differences in the particle shape. Interestingly, our results explain recent experimental observations on suspensions of gibbsite platelets which enter a kinetically arrested glass regime upon increasing the particle concentration and in which small iridescent grains of the columnar phase were formed after periods of months to years [4].

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[20] The particles do not rotate around their symmetry axis in our EDMD. Therefore, the diffusion at short times seems two-dimensional, while our definition of $\alpha_2(t)$ is for three dimensions. As a result, $\lim_{t \to 0} \alpha_2(t)$ is larger than zero.
[23] M. Moszyńska, Selected topics in convex geometry (Birkhäuser, Boston, 2006).