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# Non-classical pathways of crystallization in colloidal systems

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Colloidal systems offer the ideal conditions to study the nucleation process, both from an experimental viewpoint, due to their relative large size and long time-scales, and from a modeling point of view, due to the tunability of their interactions. Here we review some recent works that study the process of colloidal crystallization from a microscopic perspective. We focus in particular on non-classical pathways to nucleation where the appearance of the solid crystals involves fluctuations of two (or more) order parameters. We interpret the non-classical behavior as a decoupling of positional and orientational symmetry breaking. We then consider how the nucleation pathway determines which polymorph is selected upon nucleation from the melt. Moreover we show how the study of nucleation pathways not only sheds new light on the microscopic mechanism of nucleation, but also provides important information regarding its avoidance, thus suggesting a deep link between crystallization and vitrification.

## I. INTRODUCTION

Nucleation is an important process both for our understanding of the dynamics of first-order phase transitions, and for its practical applications, ranging from the semiconductor, metal, chemical, pharmaceutical, and food industry, and to studies of climate change. Despite a century of studies on nucleation (for a review see Ref. [1]) the process is still not entirely understood, especially at a microscopic level. By far the biggest problem with our classical understanding of nucleation is the small size of the crystalline nuclei involved in the transition (of the order of 10-1000 molecules in usual conditions). Their small size cast doubts on the use of macroscopic thermodynamic properties in describing these crystalline nuclei, as for example the use of surface tensions in presence of small and highly curved interfaces. At the same time, it makes the observation of crystalline nuclei impractical for most atomic and molecular systems.

A notable class of systems in which the crystallization process is more easily accessible are colloidal suspensions. The size and the slow dynamics of typical colloidal suspensions, allows for direct single-particle-level observation with confocal microscopy experiments [2–6]. Moreover, the tunability of their interactions makes direct comparisons with simple Soft Matter models, like the hard-sphere system, possible. Colloidal systems can thus be considered as an ideal benchmark for testing our understanding of the nucleation theories. Here we review some of the recent progress made in the field of colloidal crystallization, focusing on non-classical pathways. These are identified as pathways in which different order parameters take distinct roles during the transition.

## II. BEYOND CNT

The simplest and most general understanding of nucleation is embodied in Classical Nucleation Theory (CNT), which provides a successful framework to understand and

analyze data from nucleation for a large variety of processes. Yet, its predictions are experimentally very difficult to test, especially given the exponential nature of the transition, which makes the results very prone to small changes in the experimental conditions. This difficulty is exemplified in nucleation studies of systems that, despite their simple interactions, have nucleation rates that are at odds with CNT. The first example is the condensation of Argon [7], where CNT predictions and experimentally measured rates differ by approximately 26 orders of magnitude. The second example involves the prototypical colloidal system, hard spheres, where the discrepancy between predicted nucleation rates and experimental measurements is about 10 orders of magnitude. Numerical simulations found that the nucleation rate increases dramatically with the colloid volume fraction  $\phi$ , growing by more than 15 orders of magnitude from  $\phi = 0.52$  to  $\phi = 0.56$ , where it has a maximum [8–15]. On the other hand, experiments found the nucleation rate to be much less sensitive to the volume fraction [16, 17], whose precise determination is also a challenging problem [18]. There have been several attempts at solving this inconsistency, but no consensus has been found yet. Two recent explanations have emerged. In the first one [19], the discrepancy is attributed to experiments, after noting that the gravitational lengths of many of the colloidal samples are still very short compared to the size of the colloids. The basic idea is that the gravitational field coupled to long range interactions (such as hydrodynamic interaction), can cause an increase of density fluctuations in the sample, then triggering crystallization at a higher rate of the gravitation free simulations. The second explanation instead attributed the discrepancy on simulations, which neglect hydrodynamic interactions [20]. In the latter simulations, hydrodynamic interactions have the effect of increasing the nucleation rate of colloids, thus potentially explaining the difference with the experiments.

Classical Nucleation Theory rests on two main assumptions. The first one is the so-called *capillarity approximation*, which is the assumption that small crystalline nuclei have the same thermodynamic properties of the

bulk solid, like specific volume or surface tension. Many results contradict these assumption [21, 22]. Several attempts have tried to go beyond the capillarity approximation and an account of these is beyond the scope of this review; see for example Ref. [21–25].

The second assumption upon which CNT rests is that the process can be described by just one reaction coordinate. Under this assumption, all order parameters involved in the transition proceed simultaneously. Also this assumption has been shown to fail to capture the dynamics of the transition, especially in simulation works where different reaction coordinates can be followed during nucleation [26–31]. Also recent theoretical investigations are focusing on the extension of classical nucleation theory to more than one dimension [32, 33].

Another assumption is that a supercooled liquid is homogeneous and the nucleation happens randomly in space. Recent studies showed that this is not the case even for quasi-single-component systems [34]. Effects of spatial heterogeneity also plays an important role near a critical point if it exists [35]. Thus, the effects of spatial heterogeneity of the melt should be taken into account.

### III. TWO-STEP NUCLEATION AND PRECURSORS

The inability of CNT to distinguish different pathways to crystallization, in which two or more order parameters evolve independently during the transition, has come to prominence with the discovery of two-step nucleation pathways. Two-step crystallization refers to a nucleation pathway where, instead of direct nucleation from the gas phase (one-step crystallization), the system is found to crystallize inside disordered liquid droplets. These droplets are usually formed due to the presence of a metastable phase separation [36–38]. In colloidal systems, the process has been studied both experimentally [39, 40], and theoretically [35, 41–44]. The number and variety of solutions that have been found to crystallize from dense liquid precursors lead to the idea that two-step crystallization pathways are quite universal crystallization processes. For example, two-step crystallization processes have been suggested for systems outside the region of stability of the dense fluid phase [38, 41, 45–48].

Perhaps the most surprising result is the suggestion that nucleation via dense amorphous regions can occur even in systems where a dense fluid phase does not exist. The best known example of such a system is given by colloidal models of hard spheres, whose crystallization behaviour has been studied extensively [2, 8, 10, 13, 49–52]. For hard-spheres, several observations have suggested that the presence of a metastable fluid-fluid demixing transition is not a necessary condition for a dense precursor-mediated crystallization process [14, 16, 53–58]. The role of density fluctuations, and their priority over structural fluctuations are still subject to investigation, and for the moment the importance of both

contributions cannot be ruled out [59]. In the following we focus more on works that, for colloidal systems with short range-interactions, point to an alternative nucleation pathway, where the dominant role is taken by structural fluctuations instead of density fluctuations.

Two fundamental symmetries are broken at the liquid-to-solid transition: translational and orientational symmetry. Translational order is a measure of the positional order between pair of particles in the system, while orientational order expressed the degree of angular order between three or more particles in the system. According to Classical Nucleation Theory, the crystallization process occurs in one-step, with all the relevant order parameters changing at the same time across the transition. Two-step crystallization processes, instead, are at odds with the classical description, as they describe a scenario in which densification precedes structural ordering. Indeed, also the opposite scenario is possible, with structural order fluctuations preceding the increase of density.

In order to study this process from a microscopic perspective, one should follow the nucleation process from the nucleation event to the growth of the crystalline nucleus over its critical nucleus size. By using local order parameters, describing the degree of translational [31, 60] and orientational [8, 31, 61–63] order around individual particles, it is then possible to construct a statistical map of the microscopic pathway to crystallization. While most of our knowledge comes from molecular simulations on model systems [11, 12, 19, 31, 58, 64], recent confocal microscope experiments have also started to shed light on this process in colloidal systems [65, 66].

Several works have suggested that the crystallization in hard sphere-like particles is first triggered by a structural (bond orientational order) fluctuation, then followed by a densification of the ordered region. Evidence comes from the study of the correlation length of fluctuations [11, 12, 31, 60, 67, 68], the lifetime of the fluctuations [12, 67–71], the radial profile of crystalline nuclei [24, 72], the Landau free energy profile [31], and translational vs orientational curves [31, 60, 65, 66].

Evidence of bond orientational foreshadowing of crystallization has been suggested for colloidal systems both in simulations [11, 12, 31, 60, 64, 73] and experiments [65, 66, 74]. Interestingly, the role of structural fluctuations has been investigated also in a variety of different systems, like metallic melts [75, 76], anisotropic particles [77–79], and polymers [80, 81]. The idea of studying crystallization under external fields by studying the effects of the field on the bond orientational order is also a new direction for future research, whose power has been shown for example in Ref. [82] for the case of crystallization in sheared suspensions.

### IV. POLYMORPH SELECTION

Polymorph selection plays a fundamental role in many applications, and has been the subject of many investi-

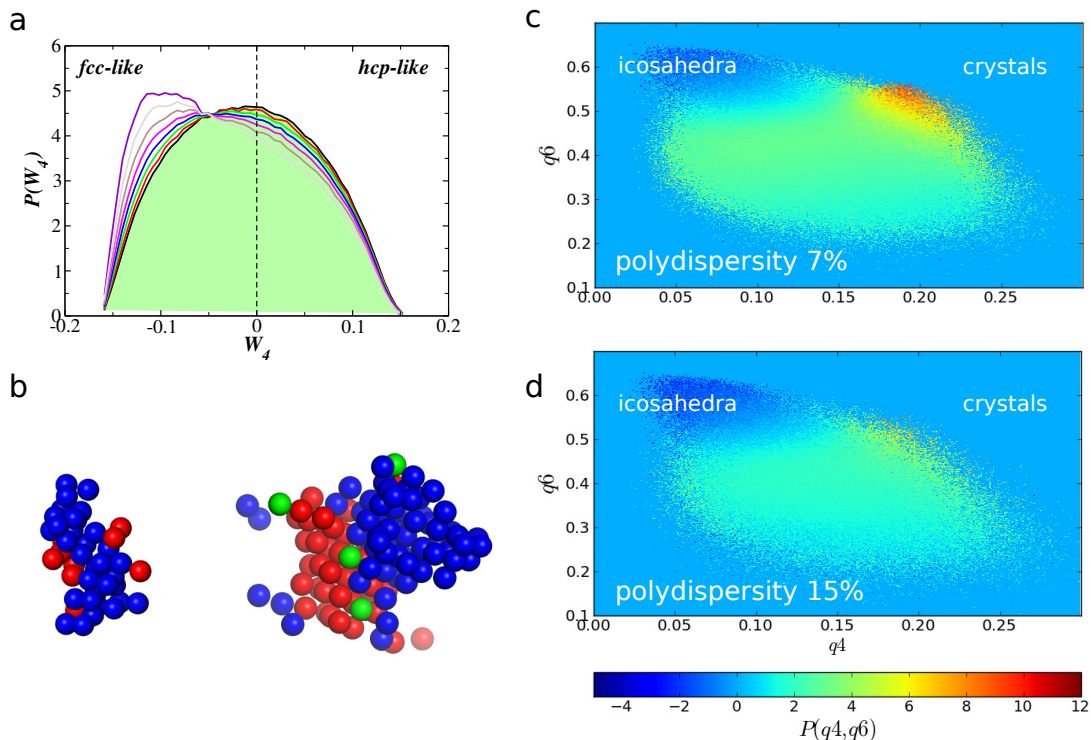


FIG. 1. **Polymorphs and glassiness.** **a.** Hard spheres at  $\beta P\sigma^3 = 17$ : probability distribution of the order parameter  $W_4$  for sets of particles with increasing values of  $Q_6$ ; the full area is the distribution for the melt, while increasing values of  $Q_6$  skew the distribution towards the *fcc* symmetry. **b.** Gaussian Core Model at  $P = 0.05$ : two-snapshots of the same nucleus at different times; blue particles are *bcc* particles, red particles are *fcc* particles. **c.** Polydisperse hard spheres at  $\beta P\sigma^3 = 23$ : joint probability distribution  $P(q_4, q_6)$  for 7% polydispersity. **d.** Polydisperse hard spheres at  $\beta P\sigma^3 = 23$ : joint probability distribution  $P(q_4, q_6)$  for 15% polydispersity. Full figures can be found in Refs. [31, 60, 64].

gations [31, 52, 64, 83, 84].

The observation that nucleation starts in regions of high bond orientational order within the metastable fluid has important consequences in determining which polymorph is being nucleated. We expect the structure of a particular crystal to reflect the symmetry of the precursor region from which it was nucleated. This idea was first tested in the hard spheres fluid [31]. In hard spheres, the free energy difference between the *fcc* and *hcp* polymorphs is almost indistinguishable. (around 0.1% of the thermal energy in favour of *fcc*) [85, 86]. This means that there is a comparable driving force for the nucleation of either the *fcc* or *hcp* crystal. Since the *fcc* and *hcp* crystal are polytypes (meaning that they differ only in the stacking sequence along the direction perpendicular to the hexagonal planes), thermodynamics predicts random stacking between *fcc* and *hcp* planes (a crystal structure known as *rhcp*, random close packed structure). But many studies, both experimental [2, 6, 49, 87] and simulations [10, 31, 88], have found that the *fcc* phase is much more abundant than the *hcp* phase. The preference for *fcc* nucleation can be understood by looking at the symmetry of the regions where nucleation occurs. Indeed, a study of the structural properties of supercooled

hard-spheres, shows that the population of *fcc*-like precursor regions is bigger than the *hcp*-like precursor regions [31]. A convenient order parameter which distinguishes between *fcc*-like and *hcp*-like orientational symmetry is  $W_4$  (for its definition we refer to Ref. [5, 31]): the *fcc* structure is characterized by negative values of  $W_4$ , while the *hcp* structure by positive values of  $W_4$ . Fig. 1a shows the probability distribution of the  $W_4$  order parameter for precursor regions characterized by increasing values of bond orientational order  $Q_6$ . While the supercooled melt has a symmetric distribution of  $W_4$ , precursor regions progressively peak around negative values of  $W_4$ , indicating an *fcc*-like symmetry. The *hcp*-to-*fcc* transition would then occur at much longer timescales, due to the negligible free energy difference between the two different polytypes.

Polymorph selection was also tested in the Gaussian Core Model (GCM), a good model for the effective interaction between the centers of mass of polymers dispersed in a good solvent [89]. The GCM has two different stable crystalline phases, a low pressure *fcc*-phase and a high-pressure *bcc* phase. The nucleation process in the GCM model was first considered in Ref. [52], where it was shown that the description of the transition is en-

hanced by taking into account the prestructured particles surrounding the crystalline nucleus. Ref. [64] then established a clear link between the precursor regions and the crystal phase which was nucleated from them, also noting a kinetic preference for the bcc phase, even in regions where the stable phase is fcc. Ref. [84] then found that the nuclei have a mixed nature, not consisting of a single polymorph, and that the kinetic pathway selected during nucleation persists even when the nucleus is many times above its critical size. Fig. 1b shows an example of a mixed-phase nucleus. All these results suggest that polymorph selection is already made in a supercooled state before nucleation starts, and that it is connected with the symmetry of the precursor regions formed by structural fluctuations.

## V. SLOW DYNAMICS AND EXTERNAL FIELDS

It is interesting to note that regions of high bond orientational order have not only been linked to nucleation, but also to its absence, i.e. glass formation. It was observed that, over the time scale of heterogeneous dynamics, extended regions of high bond orientational order displayed a slower dynamics than disordered regions [12, 60, 67, 68, 90]. Apart from bond-orientational ordered regions, also highly packed regions are characterized by slow dynamics [5, 60]. The most notable of these structures is the icosahedral-packing which, since the pioneering work of Frank, is the archetypal model of amorphous structures. However, on approaching the glass transition, the icosahedral order does not grow in size, whereas bond-orientational order grows [5, 60]. A link between slow dynamics and regions of extended bond-orientational order has been found both in polydisperse hard spheres [5, 12, 60, 68] hard disks [67, 90, 91], and colloidal ellipsoids [92].

In Ref. [31] it was shown that, at high density, the population of solid particles is outgrown by particles with icosahedral orders. Even a small fraction of icosahedral particles strongly suppresses the crystallization process [93, 94]. The effect becomes more prominent with the introduction of polydispersity in particle sizes: in Ref. [60] it is shown that the size asymmetry favors the formation of icosahedral environments, while suppressing the crystalline ones. Fig. 1c-d shows the joint probability map of the order parameters  $q_4$  and  $q_6$ . This map is convenient because crystalline particles are located in the upper-right corner of the map, while icosahedral-like environments in the upper-left corner. We can see that, going from a system with 7% polydispersity (Fig. 1c) to a system with 15% polydispersity (Fig. 1d) the ex-

tent of crystalline regions is highly suppressed, while icosahedral-environments grow. It is interesting to note that disorder (in this case polydispersity) does not always destabilize the crystal. For example, in the case of particles with angular (patchy) interactions, it was shown that angular disorder does not compromise the crystallizability of the system [95]. Glasses are thermodynamically unstable, and, despite the slow dynamics, they can crystallize. The study of both the static [96] and dynamic [97] properties of the devitrification process holds great promises for the understanding of the glass transition.

To conclude, we consider how an external field can couple with the orientational order in the fluid and affect its dynamics and crystallizability. Ref. [98] studied this relationship in a vertically vibrated quasi-two-dimensional granular liquid, and with polydisperse and bidisperse liquids Brownian simulations. It showed that the walls induce additional glassy order to the fluid, but that this effect can be encapsulated in a bare correlation length dependent on the distance from the wall. This also suggests a link between bond orientational order and slow dynamics. Ref. [19] instead considered the effect of rough walls on colloidal suspensions under the effects of gravity. It was shown that, while rough walls do not perturb the density field, they strongly suppress bond orientational order up to distances comparable to the bond-orientational correlation length. This suppression of bond orientational order is then reflected in a strong suppression of nucleation close to the walls.

Another interesting external field is shear, which has been considered in detail in Ref. [82], showing that shear suppresses the development of crystallization precursor regions, but favors the growth of crystal nuclei once they are formed. This offers a compelling explanation of the non-monotonous dependence of the crystallization rate on the shear rate. The response of colloids to external fields, makes them ideal candidates to uncover their effect on crystallization [99]

## VI. CONCLUSIONS

To conclude, we have reviewed recent progress on non-classical pathways to crystallization in colloidal systems. Besides advancing our understanding of the nucleation process on a microscopic scale, these studies have shed light on interesting phenomena, such as polymorph selection, glassiness, and devitrification. Especially interesting is the study of the effect of external fields on the nucleation process. up to now, the case of external walls and uniform shear have been considered, but many other directions are open to investigation.

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