

Distinct behaviors of the two stages of heterogeneous crystallization under different supercooling degrees

Junfeng Zhou,¹ Zhen Chen^{1,*} and Lei Xu^{1,2,†}

¹Department of Physics, The Chinese University of Hong Kong, Shatin, Hong Kong, China

²Shenzhen Research Institute, The Chinese University of Hong Kong, Shenzhen, Shenzhen, China



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Crystallites form in supercooled liquids as particles rearrange into ordered structures, driven by thermal fluctuations or external stimuli. While the thermodynamics of heterogeneous crystallization under boundary constraints is well described by classical nucleation theory, the kinetics of symmetry formation—particularly in systems far from the transition point—remains poorly understood. In this study, we investigate the heterogeneous crystallization of a colloidal system across a wide range of effective supercooling degrees by varying the volume fraction. Using confocal microscopy, we capture the motion and local structures of particles *in situ* with high spatial and temporal resolution. Our results reveal a consistent crystallization pathway across different supercooling levels: Rotational symmetry forms prior to translational symmetry, with normal modes of local structures playing distinct roles in each stage of crystallization. Notably, the liquid-to-precursor transformation is robust even under deep supercooling, suggesting minimal influence of supercooling on rotational order development. In contrast, the precursor-to-solid transformation is significantly accelerated in denser systems, indicating that translational order is strongly governed by the degree of supercooling. These findings provide insights into the interplay between thermodynamics and kinetics in heterogeneous crystallization and offer guidance for controlling phase transitions across a broad range of disciplines.

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I. INTRODUCTION

The transition between phases of matter involves a structural reorganization that leads to the formation of symmetries from the parent phase, playing a pivotal role in diverse physical contexts, including condensed matter [1–4], biology [5–7], and cosmology [8–10]. When cooled below the transition point, liquids are often trapped in a supercooled state [11,12] before transforming into crystalline solids. During this transition, transient solid seeds emerge from the disordered surroundings, driven by thermal fluctuations [13,14] or external stimuli such as impurities [15], external fields [16], and boundaries [17,18]. While the solid phase is thermodynamically more stable than the liquid, the nucleation and growth of crystal nuclei are controlled by the degree of supercooling and the interplay between surface energy and chemical potentials. According to classical nucleation theory (CNT), small nuclei typically dissolve unless they surpass a critical size [19,20], where the nucleation energy barrier reaches its maximum.

As the degree of supercooling increases, the nucleation rate rises due to a reduced energy barrier (CNT). However, under deep supercooling, particle mobility is severely restricted, hindering the growth of nuclei as neighboring particles struggle

to form a crystalline structure [21]. Additionally, near a substrate, particle motion is further constrained [22], irrespective of thermodynamic conditions, which can significantly influence phase transition dynamics [23], polymorphic selection [24], and even obstruct heterogeneous crystallization under specific boundary conditions [25,26]. Thus, both the degree of supercooling and boundary conditions critically impact the growth kinetics of the crystalline phase, affecting the size, shape, and distribution of crystals. These processes, however, remain incompletely understood.

During the transition from a supercooled liquid to a solid phase, the particle configuration undergoes significant reorganization due to the incompatibility of symmetries between the two phases [27,28]. However, CNT only provides a thermodynamic description of structural transformation but not explicitly address how local structural symmetry changes. Since crystals are characterized by particles arranged in periodic patterns, distinct rotational and translational symmetries must first emerge within localized regions of the supercooled liquid, typically near boundaries. Over the past decade, extensive research has focused on uncovering the fundamental mechanisms governing symmetry transformation in supercooled liquids. Studies have shown that the liquid-solid transition occurs in two distinct stages, consistent with Ostwald's rule [29–31]: first, relative order emerges within local clusters, referred to as precursors; second, these precursors align to form long-range translational order, resulting in crystalline structures. Thus, these multiple pathways can be well addressed by rate process theory [32,33] via decomposing crystallization into a sequence of activated events with transition rates governed by local energy barriers, thereby

*Contact author: chenzhen_physics@163.com

†Contact author: xuleixu@cuhk.edu.hk

quantitatively describing the multistep dynamical evolution of structural symmetry breaking that CNT cannot resolve.

Computational studies [34,35] of the free-energy landscape reveal that the asynchronous generation of short-range rotational order and long-range translational order reduces the energy barrier compared to the single-step transformation described by CNT—whether occurring in the bulk or near boundaries. However, an important question remains unresolved: How do the kinetics of symmetry formation during these two stages evolve under varying thermodynamic conditions? Furthermore, which stage of the phase transition is most affected by changes in the degree of supercooling or boundary conditions?

In recent years, colloidal suspensions have emerged as a compelling model system, analogous to atomic systems, for investigating the kinetic pathways of phase transitions [14,36]. Unlike atomic systems, where transitions are typically driven by temperature changes, liquid-solid transition of colloidal systems is driven by increasing the volume fraction ϕ beyond the equilibrium freezing point [37,38], which serves an analogous role to temperature in atomic phase transitions. The motion of Brownian particles in colloidal systems can be directly observed via microscopy [39], enabling the thermodynamic and kinetic processes of structural transformation to be resolved with high temporal and spatial resolution during crystallization. Moreover, colloids can assemble into various crystalline phases [40,41], including body-centered cubic (bcc), face-centered cubic (fcc), and hexagonal close-packed (hcp) structures, providing a versatile platform for exploring the mechanisms of symmetry transformations under different thermodynamic conditions.

In this study, we investigate the kinetic process of heterogeneous crystallization by varying the effective supercooling degree (ϕ) using a monodisperse colloidal suspension. Specifically, we examine the effects of supercooling degree and boundary conditions on the two distinct stages of the crystallization process, leveraging a confocal microscopy system for *in situ* observations. To gain deeper insight into the crystallization mechanism, we analyze the normal modes of local particle structures, which reveal the origins of rotational and translational symmetries. Additionally, we interpret the kinetic processes of symmetry transformation within the framework of rate process theory.

Our findings show that the formation of rotational symmetry is largely unaffected by the degree of supercooling, in contrast to the strong dependence observed for translational symmetry development. This distinction provides valuable insights into the fundamental mechanisms governing dynamic behavior during heterogeneous crystallization and contributes to a more comprehensive understanding of the interplay between thermal conditions and structural symmetry in crystallization processes.

II. RESULTS AND DISCUSSION

A. Formation of crystalline symmetry at different degrees of supercooled

Here, we employ a monodisperse colloidal system composed of poly(methyl methacrylate) (PMMA) particles

dispersed in polar organic solvents as a simplified model to investigate the kinetic dynamics of heterogeneous crystallization under varying degrees of supercooling. Our systems are prepared below the crystallization threshold ($\phi^* \sim 2\%$) and further reach the deep supercooled state [42] by increasing ϕ from 3% to 20%. The effective supercooling degree of colloidal system is determined via the Lindemann criterion [43], which relates the effective supercooling degree to the vibrational amplitude of particles in their local crystalline cages. Over our experimental volume fractions, effective supercooling degree ranges from $0.06T_m$ to $0.63T_m$, covering a broad regime from shallow to deep supercooling. In the supercooled liquid, colloidal particles are randomly distributed without any local crystalline order. However, the confinement by the hard wall enriches precursor clusters near the boundary [36], facilitating solid nuclei preferentially nucleating at the substrate rather than in the bulk [Fig. 1(a)]. In contrast, particles in the bulk remain disordered due to the high energy barrier for nucleation, making it difficult for ordered precursors to form. Over time, these nuclei grow into solid grains along the boundary, subsequently serving as a substrate for bulk crystallization, leading to the supercooled liquid above these solid layers transforming into precursors before solidifying, propagating the phase transition into deeper regions. As ϕ increases, the supercooled system becomes increasingly unstable, accelerating the crystallization process due to a reduction in the energy barrier (Fig. 6).

Heterogeneous crystallization involves not only local density increases but also a symmetry transition from liquid disorder to crystalline order. Following Ostwald's step rule [29], the phase transition proceeds from liquid to precursor and then to solid. Using the bond-orientational order parameters [44] (q_{lm} and w_{lm}), we identify distinct structural phases (liquid, three precursor types, and solid) despite supercooled degrees (Fig. 7). To highlight the differences between disordered and ordered structures, we project the local configurations of particles onto the (111) crystal plane, as shown in Fig. 1(b). In the liquid phase, neighboring particles are randomly distributed around the central particle, reflecting the isotropic nature of the liquid state. In contrast, precursors exhibit symmetric axes in the first shell, indicating the emergence of rotational symmetry, while translational symmetry remains absent [middle panel of Fig. 1(b)]. For solid particles, both rotational and translational symmetries are fully established, with particles in multiple neighbor shells precisely occupying lattice points, demonstrating that translational symmetry forms during the precursor-to-solid transition.

To quantify the evolution of translational and rotational symmetries during crystallization, we define two order parameters: $Q_6 = \sum_i q_6^i$ and $\bar{Q}_6 = \sum_i \bar{q}_6^i$, representing the degree of rotational and translational order of system, respectively. As illustrated in Fig. 1(c), Q_6 increases steadily during the early stages of crystallization, while $\bar{Q}_6$ remains constant until Q_6 exceeds a critical value, after which both parameters increase. This decoupling of rotational and translational symmetry formation further confirms the two-stage kinetic process of crystallization.

The asynchronous formation of rotational and translational symmetries suggests distinct particle dynamics during the

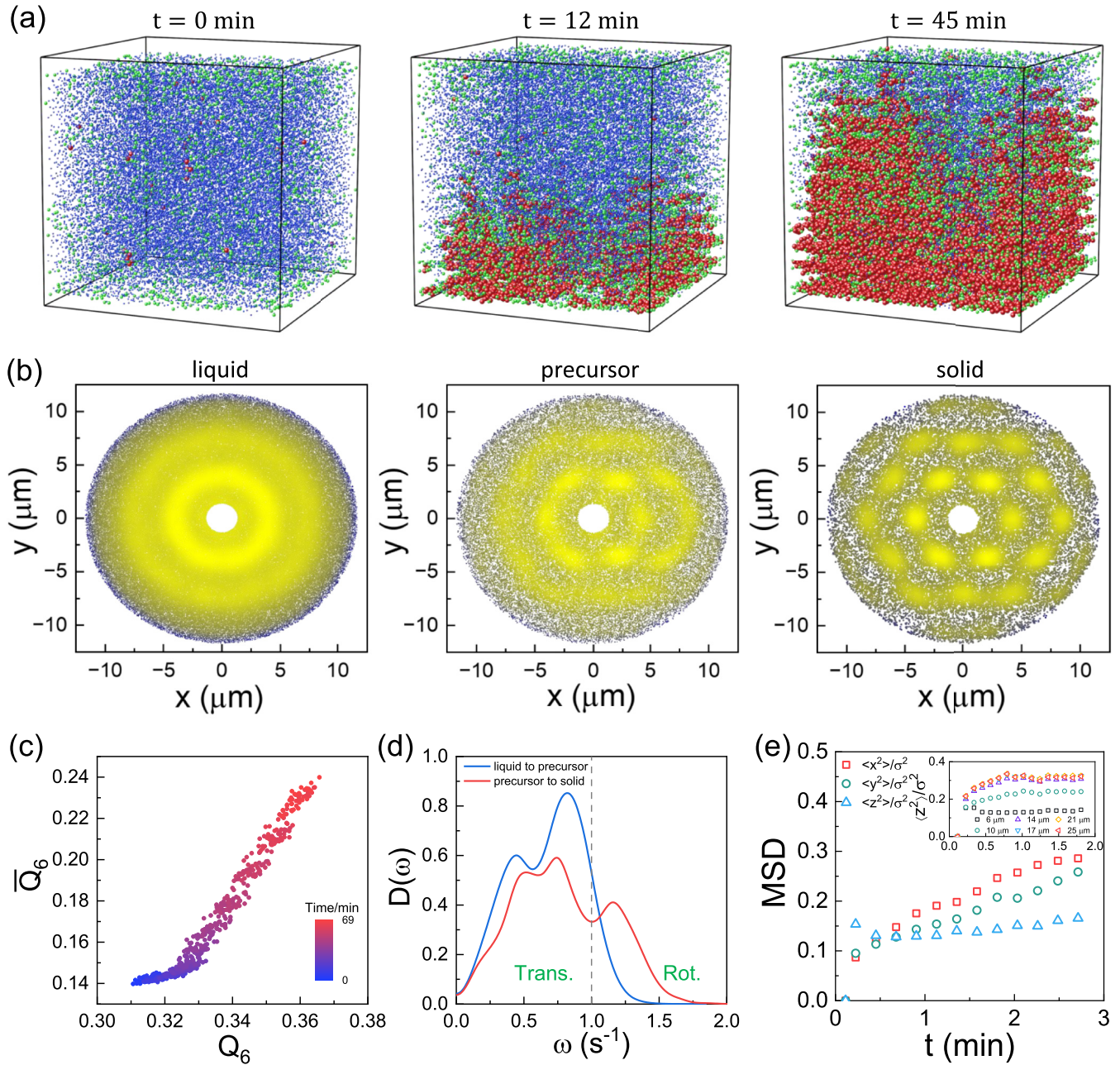


FIG. 1. Formation of crystalline symmetry during the heterogeneous crystallization in monodisperse colloidal system, $\phi = 10\%$. (a) Three-dimensional snapshots of the heterogeneous crystallization. The black spheres indicate liquid phase and the green/red spheres represent precursors/solids. (b) Configuration of neighbors around the particle with different structures. The hole in the center indicates the size of a single particle. (c) Evolution of the rotational and translational symmetries, depicted by the two order parameters Q_6 and $\bar{Q}_6$. (d) Density of states (DOS) for local structures during the two stages of crystallization. (e) Mean-squared displacement (MSD) of particles at $z = 6 \mu\text{m}$. Particle motion is significantly constrained along the z axis near the substrate ($z \leq 10 \mu\text{m}$), as evidenced by the anisotropic mean-square displacement, while for particles farther away ($z > 10 \mu\text{m}$) the boundary effect vanishes, which set the criterion to separate the boundary and bulk regions.

two stages of crystallization. To explore these dynamics, we calculated the normal modes of clusters before structural transitions and analyzed the [45–48] DOS associated with these transitions [Figs. 1(d) and 11]. In the liquid-to-precursor stage, most normal modes occur at low frequencies $\omega < 1 \text{ s}^{-1}$, whereas plenty of normal modes with high frequency ($\omega > 1 \text{ s}^{-1}$) are emerged during the precursor-to-solid transition. In addition, a two-band structure of DOS for the

precursor-to-solid transition indicates that normal modes in the two bands provoke different symmetries since both rotational and translational symmetries must be formed in the precursor-solid transition while only rotational symmetry is needed in the liquid-precursor transition. Furthermore, previous studies [45] demonstrate that low-frequency modes correspond to translational motions, while high-frequency modes involve rotational motions. These findings reveal that

rotational symmetry is initially driven by translational modes, which displace particles toward lattice sites to form local crystalline symmetry, while rotational modes align particle orientations to extend crystalline order in the second stage. Remarkably, this dynamic mechanism governs symmetry formation across a wide range of supercooling conditions, as depicted in Fig. 8.

Besides, to investigate the spatial extent of boundary effects on symmetry transformation, we analyzed the dynamics of particles near the substrate by calculating the MSD in space, as illustrated in Fig. 1(e). Clearly, the presence of the substrate imposes a geometric constraint on particle motion, leading to a significant suppression of the z component of MSD for particles in the vicinity of the wall ($z \leq 10 \mu\text{m}$). In contrast, for particles located farther from the substrate (Fig. 5, $z > 10 \mu\text{m}$), the z component converges with the in-plane components, and the MSD becomes essentially isotropic in all three spatial directions, indicating that the boundary effect has effectively vanished. Therefore, we divide the space into two parts, boundary region ($z \leq 10 \mu\text{m}$) and bulk region ($z > 10 \mu\text{m}$), to clearly investigate the boundary effects on the structural transformations.

B. Kinetic transformations in the two stages of crystallization

In our colloidal system, diverse ordered structures manifest distinct rotational symmetries characterized by $\overline{w}_4$ and $\overline{w}_6$, specifically bcc-like, fcc-like, and hcp-like symmetries (Fig. 7). However, upon densifying the system to $\phi = 20\%$, the thermodynamically stable phase consistently emerges as the bcc solid phase. Consequently, the formation of bcc crystals as the final structure predominantly occurs through two sequential stages: the transition from liquid to bcc-like precursor and subsequently from bcc-like precursor to bcc solid. To clearly elucidate the kinetic behavior of these structural transformations, we focus on the principal pathways within each transition stage, examining both boundary and bulk regions without loss of generality.

According to the rate process theory [32], the dynamics of phase transition can be depicted as a process of climbing the free-energy landscape, akin to chemical reactions where reactants and products are governed by reaction rates. In our framework, disordered states are pointed as the “reactant” and ordered structures as the “product.” Thus, the forward transition rate k^+ represents the rate at which disordered structures transition to ordered ones, while the reverse transition rate k^- denotes the opposite process. Then, transition rates are expressed as $k = \frac{1}{N_i} \frac{dN_i}{dt} \sim \frac{1}{N_i} \frac{\delta N_{ij}}{\delta t}$, where N_i is the number of particles at state i , δN_{ij} signifies the number of particles transitioning from state i to state j , and δt is the short observing time (~ 6.2 s, far less than the crystallization time of tens of minutes). Since the environment is slowly evolving during phase transition [Fig. 1(c)], we employ Q_6 to identify the system’s state and track the evolution of $k^\pm$ under different thermodynamic conditions. In the initial stage of phase transition, crystallization is triggered within the boundary region.

In the first stage of crystallization, few liquid particles transition into bcc-like precursors in a disordered environment at the initial time, and these precursors are easily destructed under thermal fluctuations, as indicated by $k^+ < k^-$ [Fig. 2(a)].

However, as more ordered structures emerge in the boundary region, k^+ increases and k^- decreases with increasing Q_6 . A critical state is eventually reached where bcc-like precursors persist and further refine the environmental order, marked by $k^+ = k^-$. Beyond this threshold, a larger proportion of liquid undergoes local structural changes to form precursors. Notably, both k^+ and k^- are minimally affected by ϕ , suggesting that the formation of rotational symmetry is universal across different supercooled degrees. In the second stage, where bcc-like precursors transform into bcc solids, we also calculated the transition rates evolving with the global order parameter Q_6 , as depicted in Fig. 2(b). Again, the transformation between bcc-like precursors and bcc solids is hindered ($k^+ < k^-$) in a disordered environment ($Q_6 < 0.3$), indicating that translational symmetry within the boundary region stabilizes only when neighboring particles exhibit a high degree of order. Consequently, translational symmetry of bcc is easily disrupted in a disordered environment. Only when the global order surpasses a certain threshold ($Q_6 > 0.3$) does the transformation from bcc-like precursor to bcc solid become continuous, as $k^+ > k^-$. Additionally, as the supercooled degree is increased, k^+ remains relatively unchanged, while k^- decreases at higher ϕ . These different influences of supercooled degree on the two stages of crystallization underscore that the formation of translational symmetry, rather than rotational symmetry, is primarily governed by ϕ .

To eliminate the boundary effects on structural transformations, we also examined the kinetic processes in the bulk region, which actually exhibit similarities to those in the boundary region. Notably, the crossing point of transition rates in the first stage occurs later in the bulk region ($Q_6^c > 0.35$), demonstrating that substrate-imposed constraints on the vertical motion of particles facilitate the refinement of local orientational order [Fig. 2(a)]. Consistent with the boundary region, all data points of k^+ and k^- are almost overlapped with increasing ϕ during the liquid to bcc-like precursor transition. However, the intersection point of $k^\pm$ during the bcc-like precursor to bcc transition occurs in a more disordered environment compared to the boundary region, demonstrating that translational symmetry formation is impeded in the boundary region due to limited particle motion. Furthermore, $k^\pm$ curves are elevated with increasing ϕ , with k^+ magnitudes larger and k^- lower in denser systems. The disparate evolution observed in the two stages of heterogeneous crystallization demonstrates that the formation of rotational symmetry is less influenced by the degree of supercooling, since it primarily relies on the arrangement of nearest neighbors. Conversely, the establishment of translational symmetry, a crucial characteristic of crystalline structures, is heavily affected by supercooled degree during the second stage of crystallization. Consequently, the differences on the kinetic process of heterogeneous crystallization with increasing ϕ are caused by the great impacts of supercooled degree on the second stage in the bulk, while the boundary constraint just changes the initial condition and the equilibrium point.

C. Thermodynamic properties of heterogeneous crystallization

According to CNT, the energy barrier governing phase transition is typically determined by the deviation from the

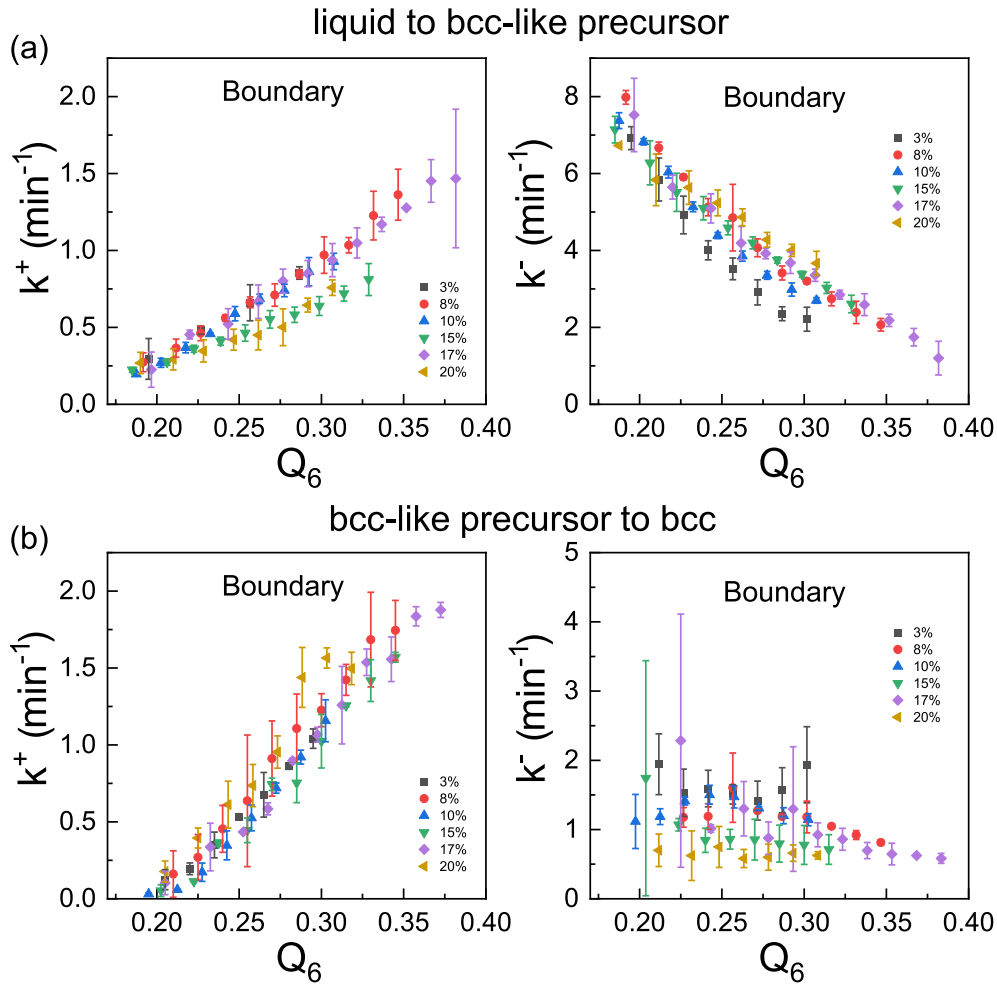


FIG. 2. Kinetic transitions of two stages of crystallization across different ϕ in the boundary region. (a) Transition rates of liquid to bcc-like precursor stage. (b) Transition rates of bcc-like precursor to bcc stage. Remarkably, the kinetic behavior of two stages within the boundary region is less influenced by ϕ .

transition point and is presumed independent of initial thermal conditions. However, as illustrated in Figs. 2 and 3, structural transformation pathways are significantly influenced by the environment order. To elucidate the intrinsic mechanism of crystallization under different effective supercooling degrees, we quantified the effective free-energy difference along these pathways while varying the system's volume fraction. Since transition rates provide insight into the energy landscape's uphill and downhill segments during structural transformation, the kinetic equilibrium constant $K = \frac{k^+}{k^-}$ is linked to the effective free energy ΔG^{eff} as $\frac{\Delta G^{\text{eff}}}{k_B T} = -\ln K$. In the first stage of heterogeneous crystallization, the free-energy difference between liquid and bcc-like precursor is positive in a disordered environment [Fig. 4(a)], indicating that bcc-like precursors are in a higher-energy state and more likely to revert to the liquid state. Beyond the crossing point ($k^+ = k^-$), the free energy of bcc-like precursors becomes lower than that of the liquid, driving the phase transition forward. Remarkably, ΔG^{eff} for the liquid-to-precursor transition is nearly independent of ϕ , as evidenced by the overlapping curves (Fig. 12). In the absence of boundary constraints, the evolution of ΔG^{eff} is similar to that in the

boundary region but exhibits a narrower variation across ϕ [Fig. 4(b)].

During the second stage of crystallization, the evolution of ΔG^{eff} between bcc-like precursor and bcc in both boundary and bulk regions diverges compared to the first stage [Figs. 4(c) and 4(d)]. As the system becomes increasingly ordered, bcc forms from a higher-energy state to a stable state, contrasting with bcc-like precursors. Notably, this pathway's evolution varies with ϕ , indicating that particle order extending to neighbors is strongly influenced by the supercooled degree. Within the boundary region, particles struggle to refine their structure to long-range order due to vertical motion constraints, thereby constraining their trajectories on the energy landscape. Consequently, the free-energy difference between disordered and ordered structures is higher in the boundary region than in the bulk at equivalent order levels. Moreover, the evolution of ΔG^{eff} for other pathways exhibits similar behavior, with the second stage being sensitive to ϕ (Fig. 12). The evolution of ΔG^{eff} in the two crystallization stages reveals that the energy decline in the first stage is minimally affected by supercooled degree, whereas the formation of translational symmetry in the second stage is strongly

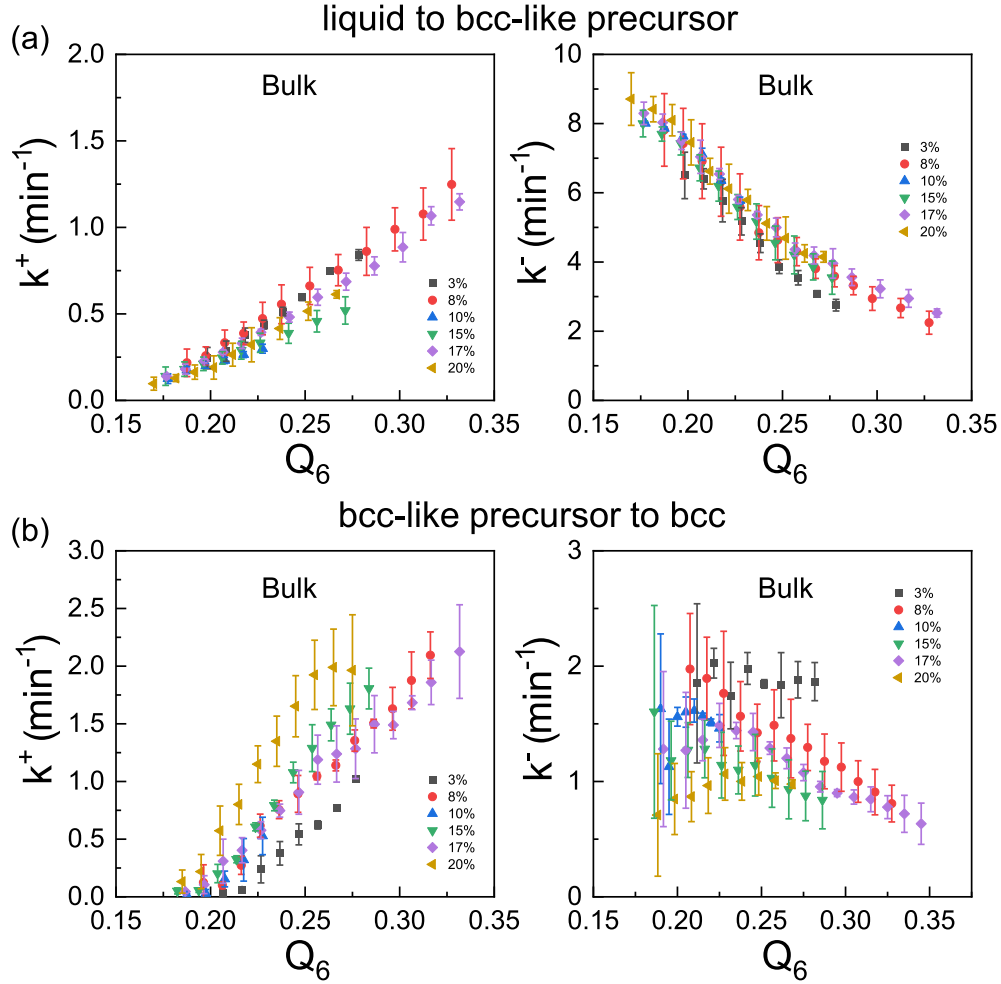


FIG. 3. Kinetic transitions of two stages of crystallization across different ϕ in the bulk region. (a) Transition rates of liquid to bcc-like precursor stage. (b) Transition rates of bcc-like precursor to bcc stage. Remarkably, the data points of the first stage are almost collapsed across different ϕ ; however, the kinetic behavior of the second stage is intensively affected by the supercooled degree.

dependent on ϕ . This dependency is the primary factor driving differences in the dynamic process of heterogeneous crystallization when far from the transition point.

III. CONCLUSION

In this study, we investigate the heterogeneous crystallization of colloidal system with different volume fraction by virtue of the confocal microscopy to observe the kinetic pathway during structural transformation at the single-particle level. During the crystallization, we find that the formations of crystalline symmetry under different supercooled degrees follow the same route; i.e., the evolutions of rotational and translational symmetries are decoupled, in which the rotational symmetry is formed prior to the translational symmetry, and then both are refined later. Remarkably, we observe divergent impacts of the supercooled degree on the two stages of heterogeneous crystallization: The kinematic process of liquid transforming into precursor is robust even when the system far away from the transition point, implying that the formation of the rotational order is slightly affected by the supercooled degree; however, the transformation between precursor and solid

is significantly enhanced in dense systems, which demonstrates that the development of translational order is controlled by the supercooled degree. As for the boundary constraints, the formation of precursors is easier than that of a solid in the boundary region, as the emergence of crystalline order needs the reconfiguration of particles at large scale but the motion of particles is limited. Our study offers valuable insights into the thermodynamics and kinetics of heterogeneous crystallization, offering a pathway to uncovering intrinsic mechanism controlling the dynamic process of phase transition.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

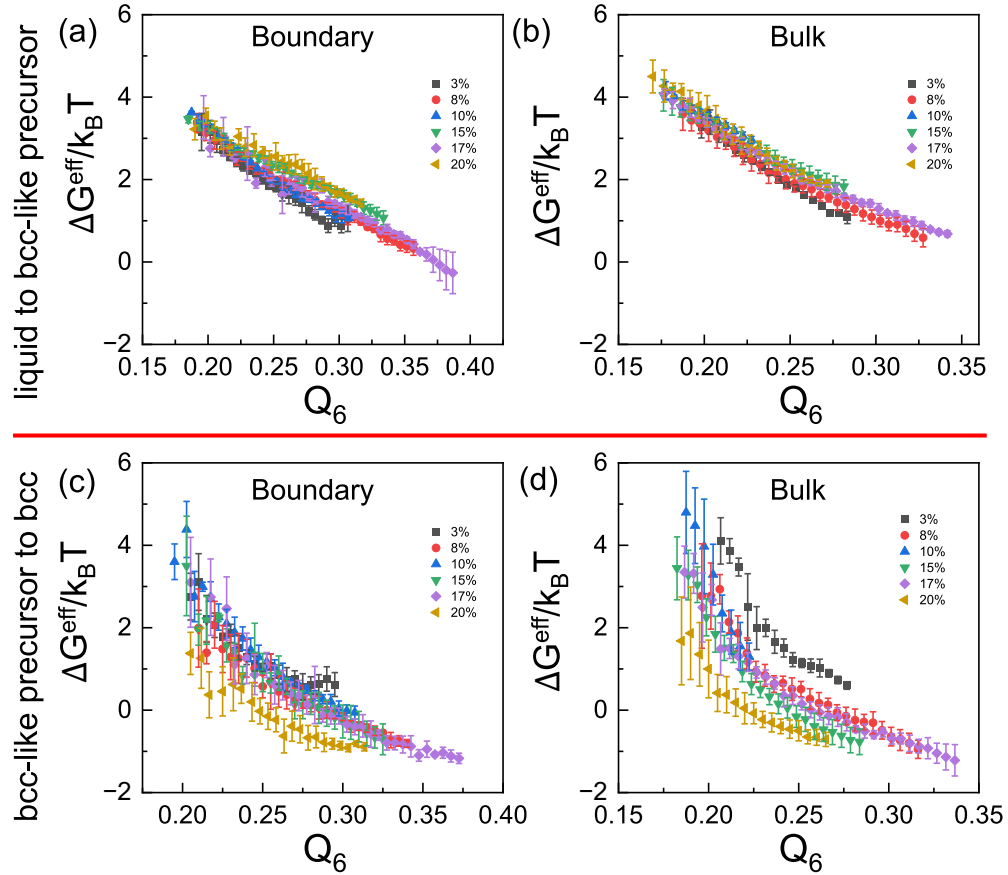


FIG. 4. Free-energy differences of two crystallization stages in the boundary and bulk regions. Evolution of the free-energy difference between liquid and bcc-like precursor during the crystallization with varying ϕ in the boundary region [panel (a)] and bulk region [panel (b)]. At the same orderness of environment, the variation of ΔG^{eff} is within $1k_B T$ at different ϕ , showing less influence of supercooled degree on the formation of rotational symmetry. Evolution of the free-energy difference between bcc-like precursor and bcc during the crystallization with varying ϕ in the boundary region [panel (c)] and bulk region [panel (d)]. At the same orderness of environment, the variation in ΔG^{eff} exceeds $2k_B T$ across different ϕ , demonstrating that the main effect of supercooled degree is changing the formation of translational symmetry.

APPENDIX A: EXPERIMENTAL DETAILS

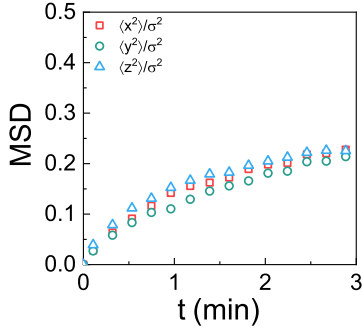
1. Properties of colloidal particles

The particles we used are nitrobenzoxadiazole-dyed PMMA colloids with diameter $\sigma = 2.3 \mu\text{m}$ and a polydispersity of less than 2.5%, which are purchased from Edinburgh Research and Innovation Ltd. (see the detailed information in [49]). These particles are dispersed in an organic solvent composed of nonpolar component (tetrahydronaphthalene, Aldrich) and polar components (mixture of iododecane and iodododecane, Aldrich). The volume ratio between three solvents is fixed at tetrahydronaphthalene:iododecane:iodododecane = 1:1.1:8.9 to achieve both the density and the refractive index match. To make sure that a good density match is achieved, we put every sample inside a centrifuge at 5000 rpm for 20 mins and observed no sedimentation. The pair interaction is well described by the Yukawa potential, that is, $u(r) = A \exp(-\kappa(r - \sigma))/(r/\sigma)$. Here, κ^{-1} is the Debye screening length, σ is the diameter of particles, and A is denoted as the strength of potential. The diameter of particles was measured from fluorescent snapshots captured by microscopy, $\sigma = 2.3 \mu\text{m}$. With a fixed $\phi = 0.1\%$, the screening length $\kappa^{-1}/\sigma = 0.67 \pm 0.02$ and the strength

of interaction $A = 623 \pm 48 k_B T$ are captured from the radial distribution function according to the simple liquid theory.

2. Sample preparation

We use confocal fluorescence microscopy with 63X oil objective to study the crystallization of colloidal particles sealed in rectangular capillary tubes (VitroCom, 5010S) with a cross section of $2 \text{ mm} \times 200 \mu\text{m}$. The imaging volume is $147 \mu\text{m} \times 147 \mu\text{m} \times 40 \mu\text{m}$, containing from several thousand to tens of thousands of particles depending on the volume fraction, which ranges from 3% to 20% in our experiments. In confocal microscopy, only the thin slice of the sample at the focal plane is imaged with high contrast, as fluorescence emission from out-of-focus regions is blocked by the confocal pinhole. This allows us to reconstruct the three-dimensional positions of individual particles by acquiring a stack of two-dimensional image slices at consecutive heights, with a voxel size of $0.2 \times 0.2 \times 0.3 \mu\text{m}$ and a temporal resolution of 6.2 s per full three-dimensional scan. Since the diameter of fluorescent colloidal particles is $2.3 \mu\text{m}$, each particle will be captured in several sequential images with different spot sizes as it is sliced at different positions. Fluorescent spots

FIG. 5. Mean-squared displacement of particles at $z = 14 \mu\text{m}$.

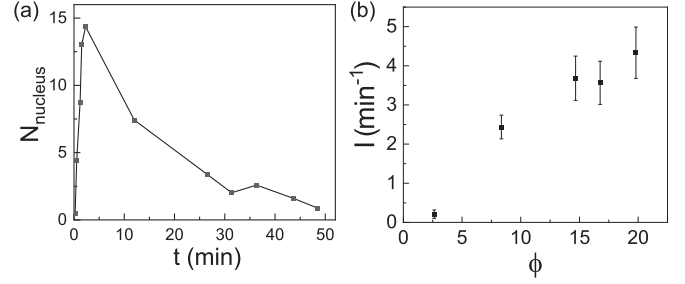
belonging to the same particle are identified and linked based on spatial continuity across adjacent slices, and the centroid of each spot is determined as the three-dimensional position of the corresponding particle. This procedure enables us to directly track particle trajectories and resolve the structural evolution of the colloidal system during crystallization. The volume fraction ϕ is calculated from the total volume of all detected particles N divided by the imaging volume, and its uncertainty is estimated to be approximately 0.3% based on repeated measurements. For each volume fraction, we have repeated the crystallization experiments at least five times to ensure statistical reproducibility.

3. Boundary constraints on colloidal particles

It is well established that particle motion is strongly influenced by the local environment. To quantify the boundary effect induced by the substrate, we calculated the MSD of particles at different heights along three Cartesian directions, as described in Fig. 5. Near the substrate ($z = 6 \mu\text{m}$), the motion of colloidal particles is isotropic in the xy plane, as evidenced by the overlap of the x and y components of MSD [see Fig. 1(e)]. At short times, both $\langle x^2 \rangle / \sigma^2$ and $\langle y^2 \rangle / \sigma^2$ increase linearly with t , indicating diffusive behavior characteristic of the supercooled liquid. In contrast, the motion of particles along z axis is greatly restricted due to the geometric confinement imposed by the wall. Far from the substrate, however, particles recover their full mobility, and the three MSD components overlap throughout the entire time window (Fig. 5), indicating isotropic motion in the bulk. To further characterize the spatial range of the boundary effect, we examined the z component of the MSD at different heights [inset of Fig. 1(e)]. When particles are far away from the substrate ($z > 10 \mu\text{m}$), the restricted behavior of $\langle z^2 \rangle / \sigma^2$ gradually disappears. It demonstrates that the effects of boundary constraint on the dynamic motion of particles is quite short ranged ($z < 10 \mu\text{m}$). Therefore, we divide the system into the boundary ($z \leq 10 \mu\text{m}$) and the bulk regions ($z > 10 \mu\text{m}$).

4. Nucleation rates

To quantitatively characterize the kinetics of crystallization, we measure the nucleation rate $I = \frac{dN_{\text{nucleus}}}{dt}$ under different volume fractions, where N_{nucleus} is the cumulative number of postcritical nuclei identified during the nucleation stage. The nucleation rate I is extracted from the linear slope

FIG. 6. (a) Number of nuclei during the crystallization, $\phi = 8\%$. (b) Nucleation rates of colloidal system with varying ϕ .

of N_{nucleus} versus time in the nucleation stage, as shown in Fig. 6(a), and its dependence on ϕ is presented in Fig. 6(b). At low volume fractions near the equilibrium freezing point ($\phi \sim 3\%$, close to the transition point at $\sim 2\%$), the formation of solid nuclei is extremely rare. This is because the thermodynamic driving force is weak, and the height of the nucleation barrier ΔG^* remains large, making it energetically unfavorable for subcritical clusters to cross the barrier and grow into postcritical nuclei. As the volume fraction increases, the system is driven deeper into the metastable supercooled regime, and the nucleation rate rises sharply. This trend is consistent with the CNT expression, $I \sim \exp(-\frac{\Delta G^*}{k_B T})$. The decrease of ΔG^* with increasing ϕ arises from the larger chemical potential difference between the liquid and solid phases, which reduces the critical nucleus size and lowers the free-energy barrier. The error bars in Fig. 6(b) represent the standard deviation of the measured nucleation rates obtained from at least five independent experimental runs at each volume fraction, ensuring statistical reliability of the reported values.

APPENDIX B: LOCAL SYMMETRY IDENTIFICATION

1. Structural classification

The local symmetry of particles is characterized by a series of bond-orientational order parameters (BOPs). To measure these BOPs, nearest neighbors are determined by locating their position within a sphere around particle i . The radius of surrounding sphere, r_c , is chosen as the first minimum valley of the radial distribution function $g(r)$. The number of nearest neighbors of particle i is denoted as $N_b(i)$. Then, a bond-orientational order parameter of particle i , $q_l(i)$, can be calculated as $q_l(i) = (\frac{4\pi}{2l+1} \sum_{m=-l}^{m=l} |q_{l,m}(i)|^2)^{1/2}$, where $q_{l,m}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{l,m}(\theta_{ij}, \phi_{ij})$. Here, $Y_{l,m}(\theta_{ij}, \phi_{ij})$ are the spherical harmonics functions with $m \in (-l, l)$. The orientation of neighboring particles relative to particle i is denoted as the polar angle θ_{ij} and the azimuthal angle ϕ_{ij} . As the solid phase has a good translational symmetry, we use the coarse-gained bond order parameters, $\bar{q}_l(i) = (\frac{4\pi}{2l+1} \sum_{m=-l}^{m=l} |\bar{q}_{l,m}(i)|^2)^{1/2}$, with $\bar{q}_{l,m}(i) = \frac{1}{N_b(i)} \sum_{k=0}^{N_b(i)} q_{l,m}(k)$, to precisely distinguish ordered structure from liquid. The sum over k runs from 0 to $N_b(i)$ to include the particle i itself ($k = 0$) and the $N_b(i)$ neighbors. We take the same criteria in our previous work to identify liquid ($\bar{q}_6(i) \leq 0.28$) and more ordered structures that include precursors and solids

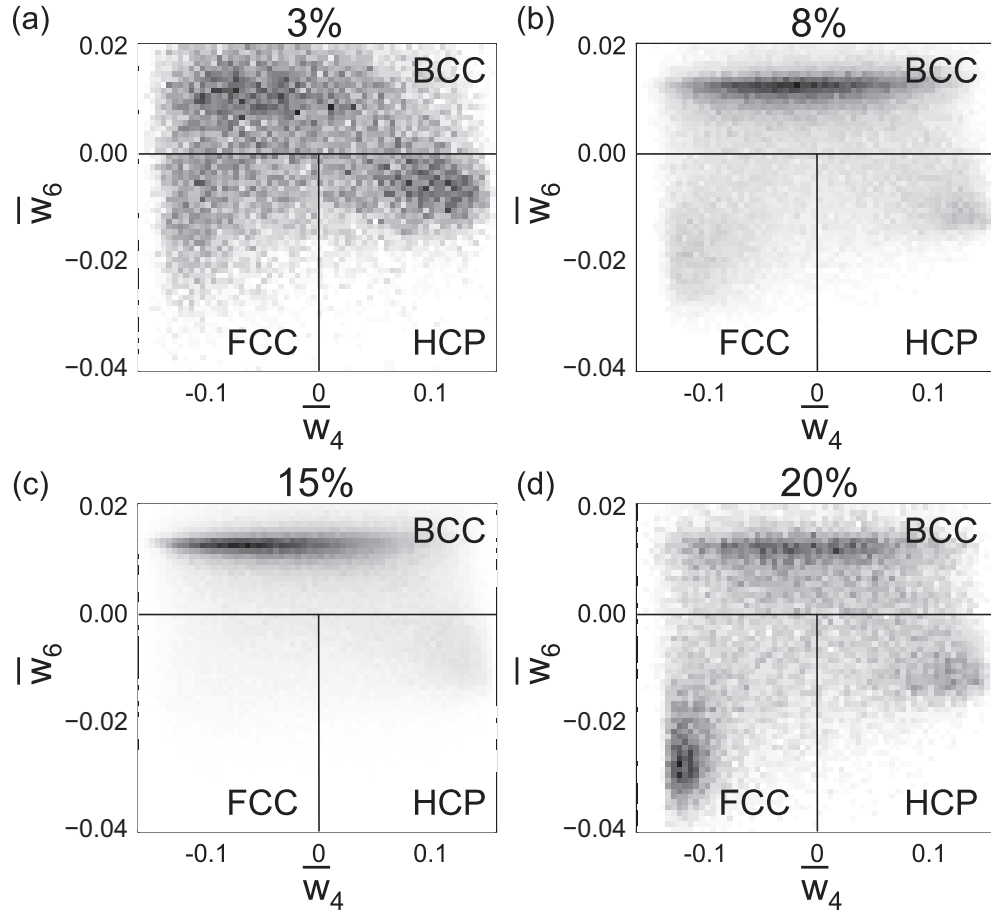


FIG. 7. Population of particles with different symmetries spanned by the bond-orientational order parameters.

($\bar{q}_6(i) > 0.28$). Furthermore, we quantify the crystalline order of system during crystallization by averaging the order parameter of particles in the local region of interest, $Q_6 = \sum_{i=1}^N \bar{q}_6(i)/N$. To distinguish different symmetries in our system, we also use the rotational invariant order parameters $\bar{w}_l(i) = \sum_{m_1, m_2, m_3=0}^l \binom{l}{m_1} \binom{l}{m_2} \binom{l}{m_3} \frac{\bar{q}_{l, m_1}(i) \bar{q}_{l, m_2}(i) \bar{q}_{l, m_3}(i)}{|\bar{q}_l(i)|^3}$. The bcc, hcp, and fcc symmetries can be clearly distinguished in the $\bar{w}_4$ and $\bar{w}_6$ planes (Fig. 7), and this classification remains robust across the entire range of volume fractions investigated ($\phi = 3\%$ to 20%). To distinguish solid from precursor, we use a dot product, $d(i, j) = \sum_{m=-l}^l q_{l, m}(i) q_{l, m}^*(j)$, between particle i and its neighbor j to identify a solid bond with $d(i, j) > 0.7$. We pick out particles with relatively high order ($\bar{q}_6 > 0.28$) but small solid bond number ($\xi < 7$) as precursors, and define particles with large solid bond number ($\xi \geq 7$) as solid structures.

2. Robustness of the structural classification criterion

To systematically test the robustness of our results against the choice of structural classification, we varied the $\bar{q}_6$ cut-off separating liquid and ordered (precursor/solid) structures from 0.27 to 0.29, while keeping the solid-bond-number criterion fixed at the standard literature value. Over this physically reasonable range, we first examined the local morphological characteristics of the three identified structural

types—liquid, precursor, and solid. As shown in Fig. 8, the representative configurations remain qualitatively unchanged across the threshold variation: For liquid particles, neighboring particles are uniformly distributed around the central particle with no apparent angular correlation; for precursor particles, the first coordination shell exhibits incipient orientational ordering, while the outer shells remain disordered; and for solid particles, multiple shells of crystalline symmetry are clearly resolved, indicating the full establishment of both translational and rotational order. This morphological consistency confirms that the structural assignment is not sensitively dependent on the precise $\bar{q}_6$ value.

Furthermore, we performed a quantitative comparison by computing the effective free-energy differences ΔG^{eff} associated with the two sequential kinetic stages—liquid-to-precursor and precursor-to-solid transitions, respectively—under different $\bar{q}_6$ thresholds, as presented in Fig. 9. It is evident from the comparison that the free-energy cost for forming the precursor phase remains largely insensitive to the supercooling degree, indicating that the first stage is primarily governed by establishing local rotational symmetry. In contrast, the effective free-energy difference for the second stage, corresponding to the formation of solids from precursors, exhibits a strong dependence on supercooling: Higher supercooling significantly reduces ΔG^{eff} , thereby accelerating the crystallization process. Most importantly, both the qualitative trends and the quantitative separations between the two stages

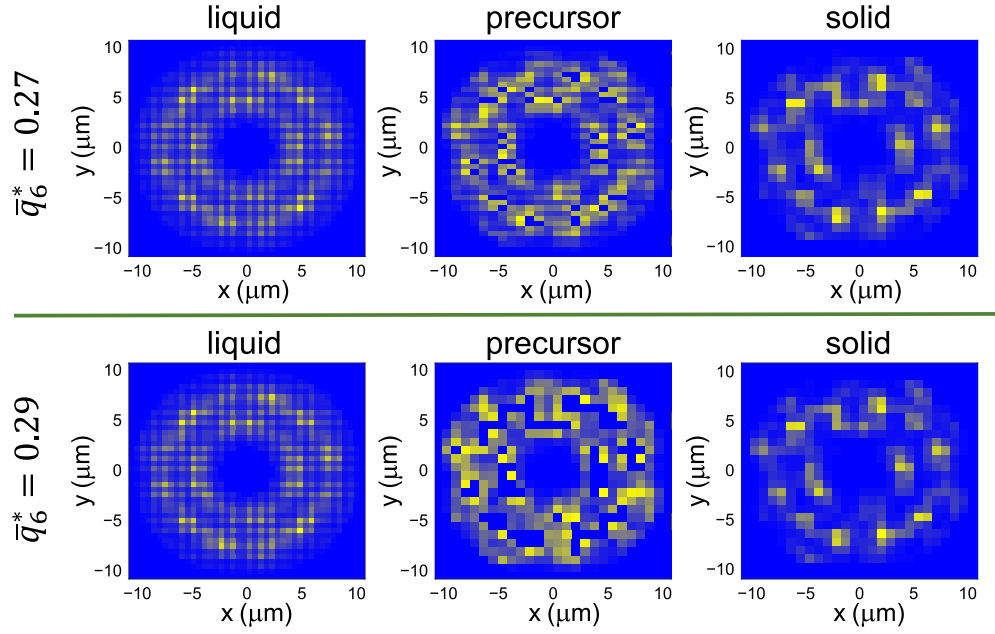


FIG. 8. Distribution probability of neighboring particles around the particle with different structures under varied structural classification criterion.

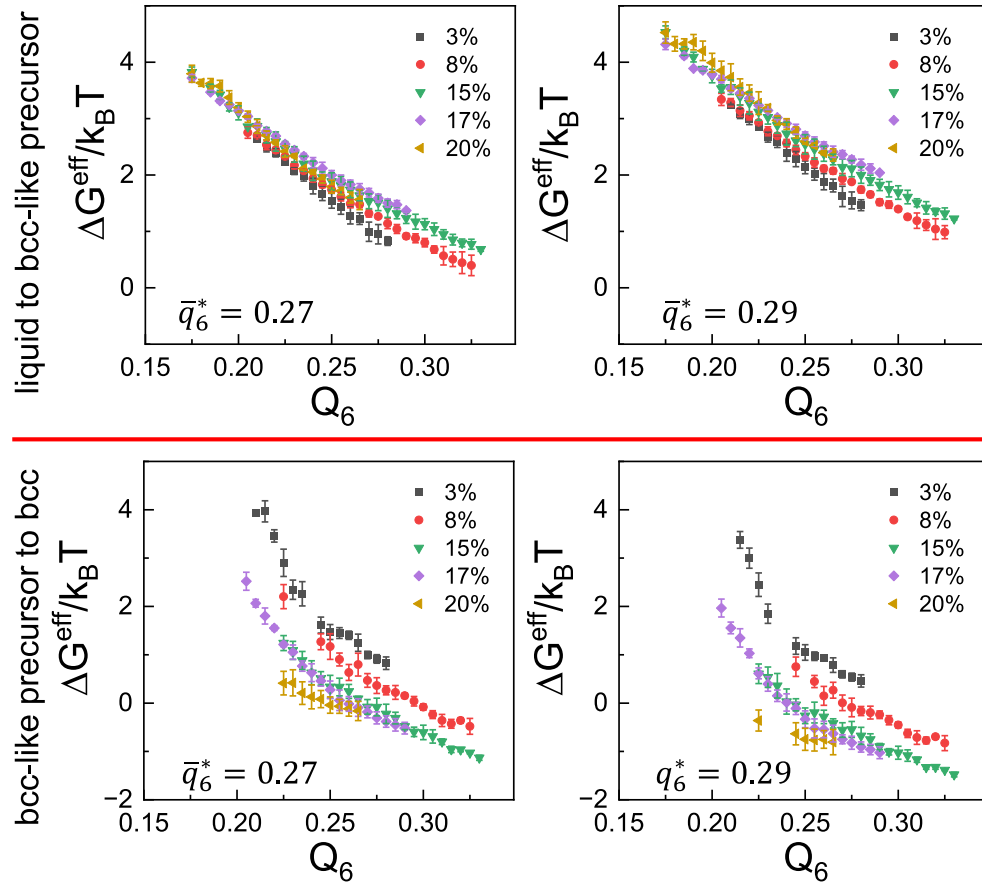


FIG. 9. Effective free-energy differences of two crystallization stages under different structural classification criterion.

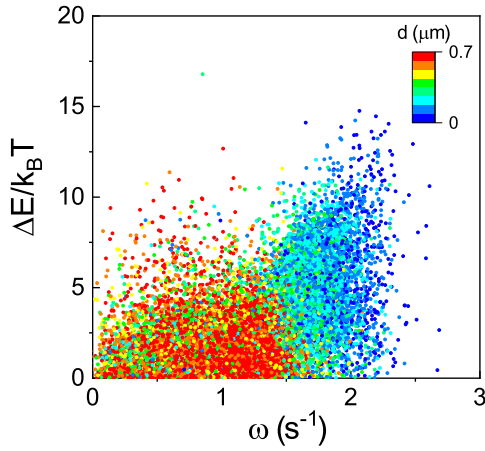


FIG. 10. Displacements of the structural centroid of local cluster under different normal modes.

remain unchanged when the $\bar{q}_6$ cutoff is varied from 0.27 to 0.29, demonstrating that our conclusions are robust and independent of the specific threshold choice.

APPENDIX C: DENSITY OF STATES

1. Theory

To elucidate the role of normal modes in symmetry transformation, we calculate the density of states (DOS) based on the local clusters undergoing symmetry changes. The local cluster consists of a central particle and its neighbors within the first two coordinate shells, totalling n particles. The $n - 1$ particles belong to the same ordered structure, while the central particle is in a disordered state but will transition to the same ordered structure at the next time step $t + \Delta t$. We use the configuration of the cluster before the transition to compute the DOS, capturing the dynamic behavior of the system during the symmetry transformation process. Following Ostwald's rule of stages, which governs heterogeneous crystallization, we focus on two primary pathways: liquid to precursor and precursor to solid. These pathways allow us to investigate the properties of normal modes during structural transitions. For example, we select a precursor cluster containing n particles, where only one particle undergoes a symmetry change to be

solid after a short time interval Δt . The configuration of the cluster before the transition is used to construct the dynamic matrix H , defined as:

$$H = \nabla_{i\alpha} \nabla_{j\beta} U(\mathbf{R}), \quad (\text{C1})$$

where U represents the total potential energy of the cluster, and $\mathbf{R} = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n\}$ denotes the coordinates of all particles within the cluster. Here, $i, j = 1, 2, \dots, n$ index the particles, and $\alpha, \beta = x, y, z$ represent the spatial dimensions. The dynamic matrix H captures the harmonic interactions between particles in the cluster. By diagonalizing the dynamic matrix, we obtain the eigenvalues ω_k^2 and eigenvectors $\mathbf{v}_k$, which satisfy the equation:

$$H\mathbf{v}_k = \omega_k^2 \mathbf{v}_k, \quad (\text{C2})$$

where ω_k is the frequency of the normal mode $\mathbf{v}_k$. The density of states is then derived from the distribution of these normal mode frequencies. To ensure statistical robustness, we analyze thousands of such clusters, each containing one particle that undergoes the same structural transition, and compute the DOS for the two pathways mentioned above. This approach allows us to systematically study the influence of normal modes on symmetry transformations and crystallization dynamics.

2. Translational and rotational normal modes

To substantiate the assignment of low- and high-frequency modes to translational and rotational motions, respectively, we have performed a detailed mode-characterization analysis by examining the displacement field associated with each eigenmode. Specifically, for each normal mode, we compute the displacement of the structural centroid of the local cluster. As shown in Fig. 10, normal modes in the low-frequency regime exhibit a significant centroid displacement (shown by the red color), indicating that these modes predominantly involve collective translational motion of the entire cluster. In contrast, for modes in the high-frequency regime, the centroid displacement is negligibly small, while the constituent particles undergo relative displacements that preserve the cluster's center of mass—a signature of predominantly rotational or orientational fluctuations. This distinct behavior directly demonstrates that the low-frequency DOS captures

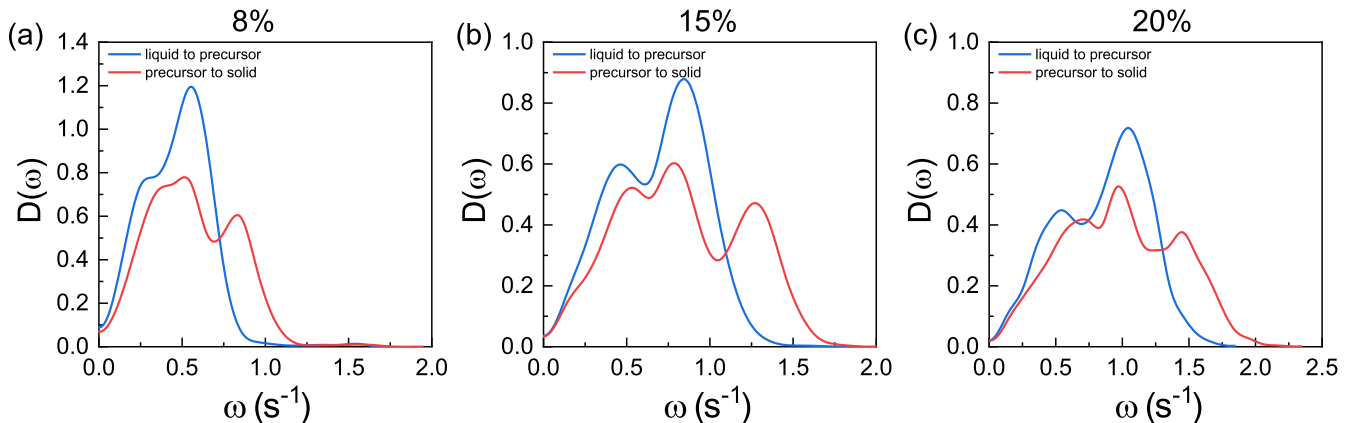


FIG. 11. Density of states at two stages of crystallization for (a) $\phi = 8\%$, (b) $\phi = 15\%$, and (c) $\phi = 20\%$.

translational symmetry dynamics, whereas the high-frequency DOS reflects local rotational rearrangements.

3. DOS at different volume fractions

We also examine the evolution of the DOS associated with the two sequential kinetic stages—liquid to precursor and precursor to solid—under varying volume fractions, as presented in Fig. 11. When the volume fraction increases from 8% to 20%, a distinct difference emerges between the two stages: The DOS of the second stage (precursor to solid) develops an additional peak in the high-frequency region compared to that of the first stage (liquid to precursor). Given that low-frequency modes correspond to translational motions while high-frequency modes reflect rotational rearrangements, this spectral difference carries direct physical implications for the symmetry-breaking mechanisms governing each stage. Specifically, the formation of the solid phase during the second stage requires the simultaneous activation of both translational and rotational modes—the former to establish long-range translational order and the latter to orient the emerging crystalline domains and enhance rotational symmetry. In contrast, the first stage, which involves the formation

of the precursor phase, primarily relies on low-frequency translational modes to adjust local packing and orientational correlations, without the need for significant rotational excitations. Furthermore, at low volume fractions ($\phi = 8\%$), the two distinct peaks originally observed in the low-frequency region coalesce into a single broad peak, suggesting that the separation between different translational relaxation channels becomes less pronounced under weaker driving forces. This merging of low-frequency features likely reflects the reduced structural rigidity and the more liquidlike character of the system at shallow supercooling, where the energy landscape is less corrugated and the distinction between different translational modes is blurred.

APPENDIX D: RATE PROCESS THEORY

1. Theory

Rate process theory forms the fundamental basis of our physical understanding of many phenomena with an energy barrier, such as chemical reaction, nucleation, stimulated radiation, and nervous impulse. The process could be a simple transformation $A \rightleftharpoons B$, such as our liquid-solid transition that involves one original state or “reactant” A and one final state

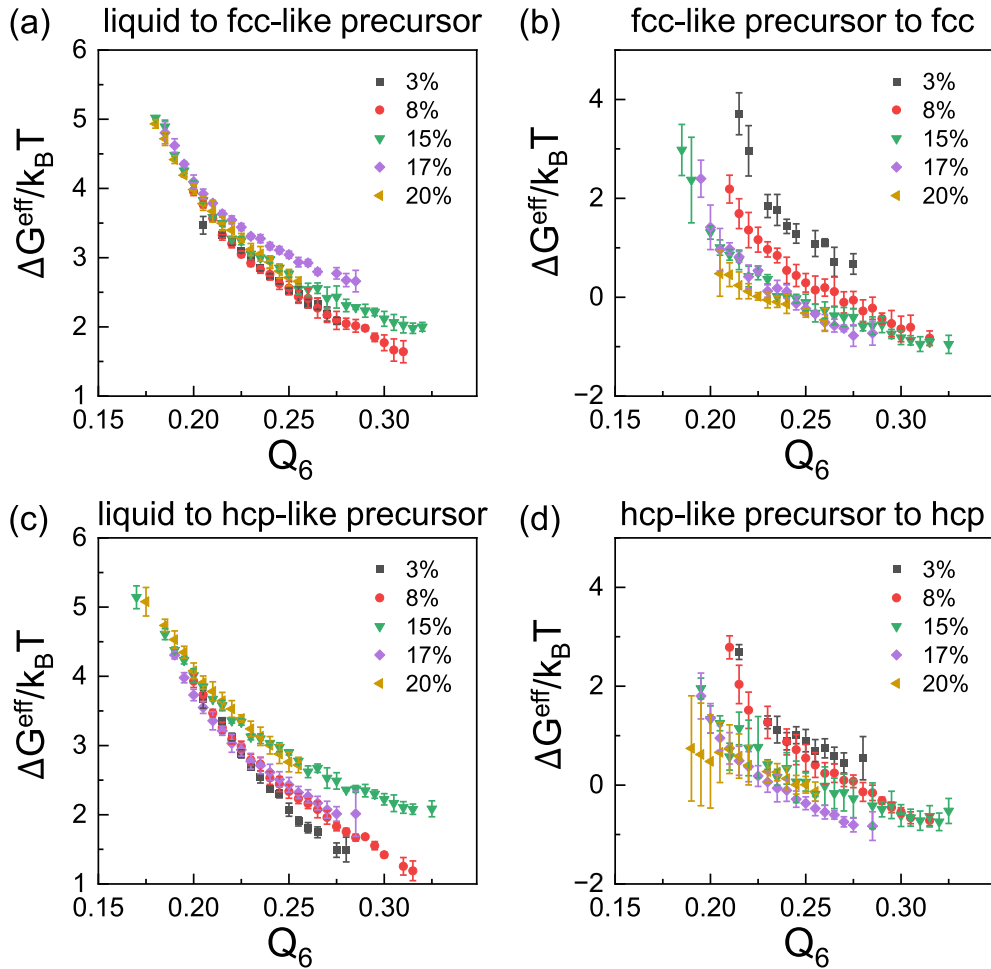


FIG. 12. Energy differences for FCC and HCP symmetry formation during two stages of crystallization across different ϕ in the bulk region.

or “product” B . The reactant needs to cross the energy barrier to become the product along a reaction pathway on the free-energy landscape. Since the transition process is bidirectional, the production rate is determined by the competition between the forward and reverse transitions. From a thermodynamic point of view, the forward transition rate is linked to the energy barrier looked from state A : $k^+ \sim e^{-(G_{\max}-G_A)/k_B T}$, while the reverse reaction rate is linked to the energy barrier looked from state B : $k^- \sim e^{-(G_{\max}-G_B)/k_B T}$. Here, $G_{\max}$ is the maximum energy along the reaction path (i.e., the energy barrier), and the free energy of the initial and final states are G_A and G_B , respectively. At equilibrium, the particle numbers at states A and B are constants and their ratio is governed by the equilibrium constant, $K = k^+/k^- = e^{-(G_B-G_A)/k_B T}$. This is the basic idea behind the chemical reaction constant. In a more general nonequilibrium situation, such as our phase transition, the transition rate can be experimentally obtained from the instantaneous number variation of the reactant A and the product B during the transition, $k^+ = \frac{1}{N_A} \frac{dN_A}{dt}$ and $k^- = -\frac{1}{N_B} \frac{dN_B}{dt}$. From these two rates, we can further get: $K = k^+/k^- = e^{-(G_B-G_A)/k_B T}$, which gives the instantaneous energy difference between states A and B from experiment.

2. Formation of FCC and HCP symmetry

In addition to the dominant BCC pathway discussed in the main text, we also examined the kinetic behavior of the minor pathways—namely, the formation of fcc-like and

hcp-like structures—to assess whether the influence of supercooling on crystallization kinetics is general across different symmetry types. As shown in Fig. 12, we computed the effective free-energy differences ΔG^{eff} for both the liquid-to-precursor and precursor-to-solid stages as functions of the global order parameter Q_6 , for the fcc and hcp channels. For the first stage, i.e., the transition from the liquid to fcc-like or hcp-like precursors, the effective free-energy differences exhibit only weak dependence on volume fraction across the entire range from 3% to 20%. This indicates that the formation of locally ordered precursors with different rotational symmetries is governed primarily by local structural fluctuations rather than by the global thermodynamic driving force, and is therefore largely insensitive to the degree of supercooling. In contrast, the second stage—transforming fcc-like precursor to fcc and hcp-like precursor to hcp—is strongly affected by the effective supercooling degree. As ϕ is increased, the effective free-energy differences for both pathways decrease significantly. At shallow supercooling (low volume fractions), the second-stage transition is kinetically hindered and rarely observed, whereas at deep supercooling (high volume fractions), ΔG^{eff} is substantially reduced, allowing the solidification process to proceed more readily. These results are fully consistent with the behavior observed for the BCC pathway in the main text, confirming that the asymmetric response of the two kinetic stages to supercooling is a general feature of the crystallization kinetics, independent of the specific crystalline symmetry ultimately formed.

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