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Spontaneous bond orientational ordering in liquids: An intimate link between glass transition and crystallization

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Abstract. The origin of slow dynamics near glass transition and the mechanism of crystal nucleation are two unsolved fundamental problems associated with the metastable supercooled state of a liquid. So far these phenomena have been considered rather independently, however, we have revealed an intimate link between them. Recently we found that crystal-like bond orientational order develops in the supercooled state of (nearly) single-component systems such as spin liquids and weakly polydisperse colloidal liquids. In these liquids, low free-energy configurations in a supercooled liquid have a link to the rotational symmetry which is going to be broken upon crystallization. We argue that this is a direct consequence of that the same free energy governs both glass transition and crystallization at least in this type of liquids. We found that it is such structural ordering at least in this type of liquids that causes glassy slow dynamics and dynamic heterogeneity. Furthermore, we revealed that such structural order also plays a crucial role in crystal nucleation: Crystallization is a process of the enhancement of spatial coherence of crystal-like bond orientational order and ‘not’ driven by translational order at least in the nucleation stage. These results clearly indicate that the theoretical description at the two-body level is not enough to describe these phenomena and it is crucial to take into account many body correlations, particularly, bond orientational correlations. We argue that there is an intrinsic link between glass transition and crystallization if crystallization does not accompany other processes such as phase separation. If crystallization involves phase separation, on the other hand, such a direct link may be lost. We speculate that even in such a case glassy structural order may still be associated with low free-energy local configurations.

Keywords: Glass transition, slow dynamics, crystallization, nucleation, and bond orientational order

PACS: 61.20.Gy; 64.70.P-; 64.70.Q-; 64.70.dg

INTRODUCTION

In general, when a liquid is cooled, it either crystallizes or vitrifies. Except liquids with quenched disorder, such as atactic polymers, a single-component liquid can in principle crystallize below the melting point T_m without accompanying inhomogenization (phase separation). Glass transition is thus observed only when crystallization is ‘kinetically’ avoided. This is suggestive of a deep link between crystallization and vitrification. However, most of previous approaches did not consider crystallization to be important for the physical description of vitrification itself. In these approaches, either a purely kinetic origin for dynamic arrest is sought or the special free energy describing the vitrification branch is newly introduced. In both cases, the crystallization branch has been ignored, or purely kinetic avoidance of crystallization has been assumed. Then the main focus has been put on the origin of slow dynamics in the vitrification branch [1]. One reason for this may come from the fact that because people who are interested in glass transition are not interested in the crystallization branch but only in the glass transition branch. Another reason may come from our intuition linked to a different, but related phenomenon, jamming transition. When we consider slow-

ing down of motion of people in a packed train, we do not care about crystallization. This is also related to the fundamental question concerning the link between glass transition and jamming transition [2, 3, 4, 5].

The above problem is also related to the most fundamental question of what is the origin of slow dynamics near glass transition. There are a few different scenarios: purely dynamical scenarios [6, 7, 8, 9], scenarios based on dynamical correlations due to dense packing [10], and scenarios based on growing static order ((i) exotic amorphous order [11, 12, 13, 14], (ii) icosahedral order [15, 16, 17], and (iii) crystal-like bond orientational order [18, 19, 20, 4, 3]). We are going to show that at least for nearly single-component liquids glassy slow dynamics and dynamical heterogeneity are caused by the development of critical-like fluctuations of static crystal-like bond orientational order.

Glass transition takes place if crystallization is avoided upon cooling or increasing density. However, the physical factors controlling the ease of vitrification and the nature of glass transition remain elusive. Among various glass forming systems, colloidal liquids are one of the most ideal because of the simplicity and controllability of the interactions. We tackled both of these long-standing questions by using numerical simulations and

experiments of monodisperse and polydisperse colloidal systems.

For polydisperse systems, we systematically control the polydispersity, which can be regarded as the strength of frustration effects on crystallization [21, 22]. We revealed that crystal-like bond orientational order grows in both size and lifetime and icosahedral order also develops but without increasing its size when increasing the colloid volume fraction [23]. We confirmed that it is the former and not the latter that is relevant to slow dynamics. We stress that bond orientational ordering in hard-sphere-like systems is a direct consequence of dense packing and a manifestation of low configurational entropy. Our study suggests an intriguing scenario that the strength of frustration against crystallization controls both the ease of vitrification and the nature of glass transition. Vitrification may be a process of hidden crystal-like ordering under frustration [18, 24, 25, 26, 19]. We confirmed that this scenario also works in driven granular matter [27].

We also found that the degree of frustration effects on crystallization controls not only the glass-forming ability but also the fragility of liquid [18] for both colloidal liquids [21, 22] and spin liquids [26, 28]. Despite the difference in the origin of frustration effects on crystallization (geometrical vs energetic), the behavior is remarkably similar between them: Hidden glassy structural ordering may be the common origin of dynamic heterogeneity and slow dynamics in these systems and the degree of frustration on ordering controls the fragility [19]. We note that bond orientational order is related to structures of low local free energy. Thus, we may say that there is an intrinsic link between structure and dynamics in glass-forming materials: slow dynamics may be a consequence of ‘glassy structural ordering’ toward low local free energy in a liquid [21, 26, 19, 4, 3].

The above picture is further supported by our study on crystal nucleation, which reveals an intimate link between bond orientational order fluctuations in a liquid and crystals nucleated from it [22, 29, 30].

In this article we will show firm evidence supporting an intrinsic link between glass transition and crystallization and discuss possible mechanisms of these fundamental phenomena.

EXPERIMENTAL AND SIMULATION METHODS AND STRUCTURAL ANALYSIS

Experimental methods

We used PMMA (poly(methyl methacrylate)) colloids sterically stabilized with methacryloxypropyl terminated

PDMS (poly(dimethyl siloxane)) and fluorescently labeled with rhodamine isothiocyanate chemically bonded to the PMMA. The polydispersity was estimated to be slightly larger than 6% [31]. This amount of polydispersity allows us to avoid or at least delay crystallization [32] but is too low for fractionation to happen. The colloids were suspended in a solvent mixture of cis-decalin and cyclohexyl-bromide for both optical index and density matching. Electrostatic interactions were screened by adding tetrabutylammonium bromide salt. The data were collected on a Leica SP5 confocal microscope, using 532 nm laser excitation. The temperature was controlled on both stage and objective lens, allowing a more precise density matching.

Simulation methods

Here we explain our simulation method. We employ polydisperse colloidal systems interacting with the Weeks-Chandler-Andersen (WCA) repulsive potential [33]: $U_{jk}(r) = 4\epsilon \{(\sigma_{jk}/r)^{12} - (\sigma_{jk}/r)^6 + 1/4\}$ for $r < 2^{1/6}\sigma_{jk}$, otherwise $U_{jk}(r) = 0$, where $\sigma_{jk} = (\sigma_j + \sigma_k)/2$ and σ_j represents the size of particle j . We introduce the Gaussian distribution of particle size σ_j . Its standard deviation is regarded as polydispersity; $\Delta = \sqrt{(\langle\sigma^2\rangle - \langle\sigma\rangle^2)}/\langle\sigma\rangle$. We use standard Brownian dynamics simulations. For all simulations shown below, the particle number is $N = 4096$ and we employed a periodic boundary condition. The temperature is fixed at $k_B T/\epsilon = 0.025$.

The volume fraction is given by $\phi = 1/(6L^3) \sum_{j=1}^N \pi(\sigma_j^{\text{eff}})^3$, where L is the box size and σ_j^{eff} is the effective diameter of the particle j . $\sigma_{jk}^{\text{eff}} = (\sigma_j^{\text{eff}} + \sigma_k^{\text{eff}})/2$ is characterized as $U_{jk}(\sigma_{jk}^{\text{eff}}) = k_B T$. We use these effective (scaled) diameters for comparing our results with those of hard sphere systems and estimating the volume fraction.

We carefully attain the quasi-equilibrium state for each ϕ and Δ by the following protocol. First we prepare an initial particle configuration by setting the coordinate of the center of mass of each particle almost randomly while avoiding the overlap with other particles. Then we prepare the steady quasi-equilibrium state by running a simulation for more than for about 10 times of the equilibrium structural relaxation time ($10\tau_\alpha$) after the preparation of the initial state.

In our system, crystal nucleation takes place at $\Delta = 6\%$ as a rare event, but for $\Delta = 12$ and 16% , we never observe crystal nucleation during our simulation [22]. This is consistent with experimental results that a polydisperse colloidal system with $\Delta \geq 10\%$ is practically regarded as an ideal glass forming system free from crystallization

Analysis methods for dynamics and glassy structural order

We characterize the structure of a liquid by the radial distribution function: $g(r) = 1/(\rho N)\langle\rho(\vec{r})\rho(\vec{0})\rangle$, where ρ is the average density and $\rho(\vec{r})$ is the local density at \vec{r} . The dynamics is, on the other hand, characterized by the intermediate scattering function (ISF): $F(q_p, t) = \frac{1}{N} \sum_j \exp\{i\vec{q}_p \cdot (\vec{r}_j(t) - \vec{r}_j(0))\}$, where \vec{r}_j is the position vector of particle j , $i = \sqrt{-1}$ and q_p corresponds to the wave number of the first peak of the structure factor.

The time-averaged l -th order coarse-grained bond orientational order parameter of particle k is calculated as $\bar{Q}_l^k = \frac{1}{\tau_\alpha} \int_{t_0}^{t_0 + \tau_\alpha} dt \left(\frac{4\pi}{2l+1} \sum_{m=-l}^l |Q_{lm}^k|^2 \right)^{1/2}$. The time average is taken for a period of τ_α . Here $Q_{lm}^k = 1/N_b^k \sum_{j=1}^{N_b^k} q_{lm}(\vec{r}_{kj})$ and N_b^k is the number of the nearest neighbors of particle k including particle k itself. $q_{lm}^k = 1/n_b^k \sum_{j=1}^{n_b^k} Y_{lm}(\vec{r}_{kj})$ where $Y_{lm}(\vec{r}_{kj})$ is a spherical harmonic function of degree l and order m . n_b^k is the number of bonds of particle k . This spatial coarse-graining added to the standard Steinhardt bond orientational order parameter [41, 42] has tremendous significance not only in detecting local ordering explicitly by reducing noises [43, 44], but also in avoiding the contribution of icosahedral order and picking up only extendable bond orientational order [23, 30]. Here we mainly use \bar{Q}_6^k which is $l = 6$ of \bar{Q}_l^k .

SLOW DYNAMICS AND STRUCTURAL ORDERING IN A SUPERCOOLED LIQUID

First we focus on the glass transition behavior to seek the origin of slow dynamics associated with the glass transition. In our polydisperse colloids, the degree of polydispersity Δ is a key control parameter to avoid crystallization. The monodisperse system rather quickly crystallizes once the volume fraction ϕ exceeds 54%. Even for this system, we can access dynamics and structural order in a metastable supercooled liquid for $\phi \leq 54.5\%$ [45]. In our simulation, above $\Delta = 6\%$, we can practically avoid crystal nucleation during our simulation period and thus study glassy slow dynamics. We also note that phase separation (fractionation) does not take place in our systems in the time scale of our simulations.

Effects of polydispersity on the glass-transition behavior

Here we summarize the effects of the polydispersity Δ on the ϕ -dependences of the structural relaxation time τ_α and the translational diffusion constant D_t (see Fig. 1). We can see a weak decoupling between τ_α and D_t [4]. We estimate the ideal glass transition point ϕ_0 and the fragility index D by making the VFT fitting to the data of τ_α : $\tau_\alpha = \tau_0 \exp(D\phi/(\phi_0 - \phi))$. Here we note that smaller D means ‘more fragile’. We found that both ϕ_0 and D monotonically increase with an increase in Δ (see Table 1 and Fig. 1). The stronger frustration increases the glass transition volume fraction ϕ_g , which we define ϕ where $\tau_\alpha = 10^6$, and the volume fraction ϕ_0 , above which configurational entropy hypothetically disappears (see Table 1). It also increases D , or makes the liquid stronger. This result is consistent with our previous results in two-dimensional (2D) glass-forming systems, 2D spin liquid [26] and 2D polydisperse colloidal liquid [21], suggesting some universality of the roles of frustration in the glass transition behavior. This agrees well with the prediction of our two-order-parameter model [18, 24, 25, 46, 47, 48, 3] that the increase in the strength of ‘frustration against crystallization’ makes a liquid stronger.

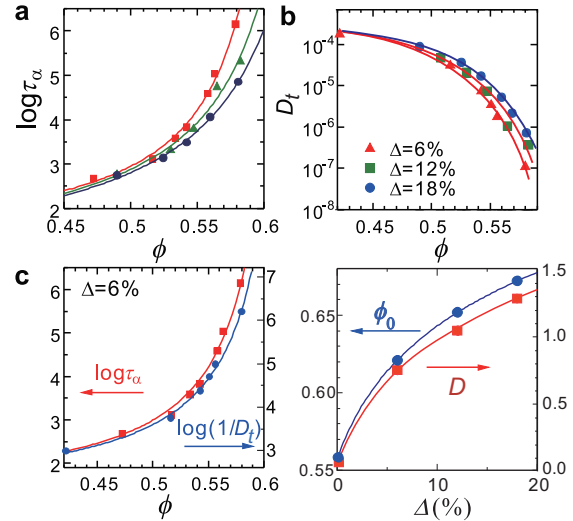


FIGURE 1. Effects of the polydispersity Δ on the ϕ -dependences of the structural relaxation time τ_α (a) and the translational diffusion constant D_t (b). (c) Weak decoupling between τ_α and D_t for $\Delta = 6\%$. (d) The Δ -dependences of the ideal glass transition volume fraction ϕ_0 (blue circles) and the fragility index D (red squares).

TABLE 1. Δ -dependence of D , ϕ_0 , and ϕ_g .

Δ	D	ϕ_0	ϕ_g
0%	0.074	0.557	0.555
6%	0.754	0.621	0.588
12%	1.048	0.653	0.610
18%	1.287	0.673	0.619

A signature of structural ordering in the structure factor and the absence of its link to density fluctuations

We calculated the structure factor $S(q)$ in a supercooled liquid state from its definition $S(q) = 1/(\rho N) \langle \rho(q) \rho(-q) \rangle$, where $\rho(q) = \int \sum_{j=1}^N \delta(\vec{r} - \vec{r}_j) e^{i\vec{q} \cdot \vec{r}} d\vec{r} = \sum_{j=1}^N e^{i\vec{q} \cdot \vec{r}_j}$. Figure 2 shows $S(q)$ at $\phi = 0.577$ and $\Delta = 6\%$. As will be shown later, we find that at this ϕ the correlation length ξ of crystal-like bond orientational order becomes of medium-range. In the low q region, however, there is little excess scattering, indicating little density-density correlations in the lengthscale of ξ . This means that this medium-range crystal-like order (MRCO) accompanies little density change. Thus we may say that MRCO possesses bond orientational order, but little translational order. Here we note that the splitting of the second peak of $S(q)$ reflects the existence of this MRCO. This subpeak grows with an increase in ϕ , reflecting the growth of crystal-like bond orientational order in a supercooled liquid. The similar behaviors were also found also in 2D colloidal liquids [21] and 2D driven granular matter [27].

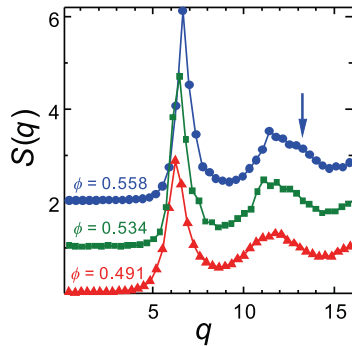


FIGURE 2. Structure factor $S(q)$ for three volume fractions for $\Delta = 6\%$. In the low q region, there is little excess scattering. On the other hand, there is the growth of a shoulder, or a subpeak, in the second peak (see the red arrow).

The ϕ -dependence of solidity and the degree of dynamic heterogeneity

We estimate the Debye-Waller (DW) factor A and the Kohlrausch-Williams-Watts (KWW) exponent β in a supercooled liquid at $\Delta = 6\%$ and $\phi = 0.577$, by fitting the following function to the intermediate scattering function (ISF): $F(q_p, t) = (1 - A) \exp[-(t/\tau_\beta)] + A \exp[-(t/\tau_\alpha)^\beta]$. Figure 3 shows the ϕ dependence of A and β . The Debye-Waller factor A increases with an increase in ϕ , suggesting the increase in solidity toward ϕ_g . We believe that this is related to the growth of bond orientational order which is also a consequence of dense packing. On the other hand, β decreases with an increase in ϕ , which is characteristic of a fragile glass former. This is consistent with the fact that the system becomes structurally and dynamically more heterogeneous while approaching ϕ_g . This supports that the stretched structural relaxation is due to dynamic heterogeneity, which may be further linked to structural heterogeneity: Particles in more ordered and spatially extended regions relax more slowly [21, 27, 19, 23].

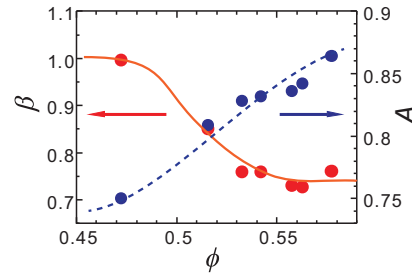


FIGURE 3. ϕ -dependence of the DW factor A and the KWW exponent β for $\Delta = 6\%$. A increases and β decreases with an increase in ϕ .

Growth of the spatial correlation length of the bond orientational order parameter

To estimate the spatial correlation length of the bond orientational order parameter, ξ_6 , we calculated the spatial correlation function $G_6(r)$:

$$G_6(r) = \frac{4\pi}{13} \left\langle \sum_{m=-6}^6 Q_{6m}(r) Q_{6m}^*(0) \right\rangle / g(r).$$

Figure 4(a) shows the ϕ -dependence of $G_6(r)$. $G_6(r)$ is well fitted by the Ornstein-Zernike function as $G_6(r) \propto r^{-1} \exp(-r/\xi_6)$. From this fitting, we obtain the spatial correlation length ξ_6 . This ξ_6 grows as a system approaches the ideal glass-transition point $\phi_0 = 0.62$ as

$\xi = \xi_0[(\phi^{-1} - \phi_0^{-1})/\phi_0^{-1}]^{-2/3}$. This particular fitting can contain an error of ± 0.1 for the determination of ν , but our previous study provides a much higher accuracy (see Fig. 4 of Ref. [19]). This behavior is confirmed to be the same as that of the so-called dynamical correlation length ξ_4 [22], which is determined by using the four-point density correlator [49].

The above exponent for critical-like divergence of ξ_6 is $\nu = 2/3$, which is suggestive of that the critical-like behavior observed in glass-forming liquids belongs to the 3D Ising universality [19]. It is worth noting that the same power law divergence of a static correlation length was reported by Mosayebi et al. [50, 51] for binary Lennard-Jones and soft sphere mixtures. To obtain static glassy order they analyzed the response of the inherent structure to static shear perturbation, focusing on the degree of the affine deformation. They interpreted this exponent to be that predicted by the random-first-order-transition (RFOT) theory [11, 13, 14]. However, we consider that this critical-like behavior is rather consistent with glassy critical phenomena (see below).

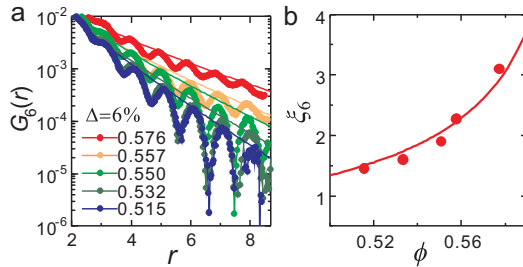


FIGURE 4. ϕ -dependence of the spatial correlation for $\Delta = 6\%$. (a) ϕ -dependence of the spatial correlation function $G_6(r)$ for $\Delta = 6\%$. The solid lines are fittings of the Ornstein-Zernike function $G_6(r) \propto r^{-1} \exp[-r/\xi_6]$. (b) ϕ -dependence of the spatial correlation length ξ_6 for $\Delta = 6\%$. The solid curves are the fitted functions, $\xi_6 = \xi_{60}[(\phi^{-1} - \phi_0^{-1})/\phi_0^{-1}]^{-2/3}$, with $\xi_{60} = 0.518$ and $\phi_0 = 0.621$.

Correlation between structural fluctuations and dynamic heterogeneity

Here we show evidence suggesting the correlation between structural order and dynamics in Fig. 5 (for a more quantitative comparison, see Ref. [23]). We can see that particles with large displacements have less crystal-like bond orientational order (or, low Q_6). This suggests a correlation between the degree of crystal-like bond orientational order and slowness of particles. Such a correlation can be more clearly observed visually in 2D glass forming systems [21, 27, 26, 19]. A more statistically relevant analysis on the structure-dynamics correlation in 3D will be reported elsewhere.

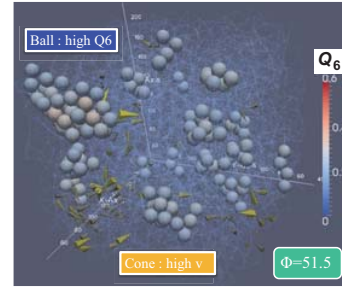


FIGURE 5. Correlation between crystal-like bond orientational order and particle displacements at $\phi = 0.515$ (polydispersity of about 6%). Large particles have high crystal-like bond orientational order and arrows (cones) indicate displacements. This figure is made on the basis of three-dimensional confocal microscopy observation of a colloidal suspension [23].

Lifetime of fluctuations of crystal-like bond orientational order

In Fig. 6 we show a time sequence of thermal fluctuations of MRCO (highly ordered regions). Although MRCO might look like microcrystallites or crystal (pre-) nuclei, we conclude that it is not the case. This can be confirmed by observing the temporal change of MRCO. Figure 6 indicates a series of snapshots of MRCO over $3\tau_\alpha$ for $\Delta = 12\%$. At $t = t'$ there exist islands of MRCO, but at $t = t' + 3\tau_\alpha$ some of them already disappear. Furthermore, fluctuations of bond orientational order have no direct link to density fluctuations [19] (see also Fig. 2 and the related discussion). These clearly tell us that MRCO is ‘not’ a crystal nucleus itself, although it contains small transient nuclei, whose sizes are below the critical nucleus size (see also Ref. [23]). These transient nuclei should be regarded as a part of bond order parameter fluctuations. Unlike growing crystal nuclei, MRCO has a finite lifetime: a few times of τ_α in this case. The lifetime becomes longer with an increase in ϕ .

We emphasize that for $\Delta = 12\%$, we never see crystal nucleation in our simulation time and this system behaves as a model glass former, as in a real experimental system. For example, we note that a polydisperse colloidal system with $\Delta = 10\%$ was used in Ref. [35] and it behaves as an ideal glass forming system free from crystallization. Thus, we conclude that MRCO is an intrinsic structural feature of a supercooled liquid, which steadily exists as structural fluctuations.

We found that the lifetime of MRCO is slightly longer than the structural relaxation time τ_α for a deeply supercooled liquid, which is comparable to the characteristic timescale of dynamical heterogeneity, τ_H , measured by four-point density correlation functions [19, 3] (see Fig.

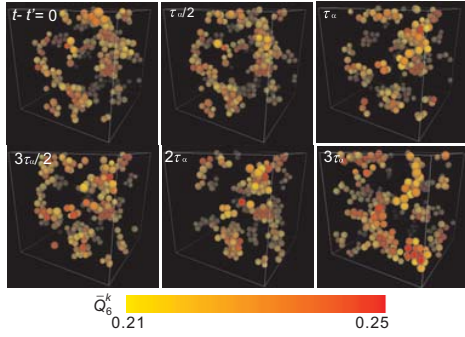


FIGURE 6. Snapshot of MRCO for a period of $4\tau_\alpha$ at $\phi = 0.559$ and $\Delta = 12\%$. At $t = t'$ there exist MRCO clusters, but at $t = t' + 3\tau_\alpha$ some of them already disappear. This indicates that MRCO is temporally fluctuating and has a finite lifetime, and thus it is nothing to do with crystal nuclei.

7). Since dynamic heterogeneity is measured on the basis of single particle diffusive motion, it is regarded to disappear if particles move ‘together’ by an amount of the threshold distance, even though there is no relative motion among these particles. In this sense, we believe that the lifetime of crystal-like bond orientational order has a physically more significant meaning. We also showed [19, 3] that the fluctuations of MRCO obeys the dynamics of the dynamical universal class Model A [52].

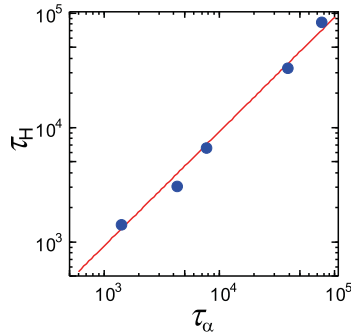


FIGURE 7. The relation between τ_α and τ_H for $\Delta=6\%$. We can clearly see $\tau_\alpha \cong \tau_H$.

In relation to roles of bond orientational order in crystallization (see below), we note that the long lifetime of MRCO may play a crucial role in crystal nucleation since it takes some incubation time for nuclei to be formed.

Roles of icosahedral ordering

For a 3D polydisperse system, there are at least two origins of frustration against crystallization: One is local icosahedral ordering tendency and the other is random disorder effects originating from the polydispersity

of particles. Note that for 3D hard spheres a particle having 12 nearest neighbors can have three types of bond orientational order (fcc, hcp, and ico). Among them, local icosahedral ordering is not a major cause of slow dynamics due to its intrinsically localized nature and the dominant one is crystal-like (fcc-like) bond orientational order [23]. This tells us that only spatially extendable structural order is responsible for slow dynamics. So the scenario that icosahedral ordering is a major and unique underlying ordering behind vitrification may not be valid at least for a hard sphere system. Nevertheless, local icosahedral structures are formed in hard sphere liquids [23, 53, 54], and their number density increases with an increase in ϕ , which leads to stronger frustration effects on crystal-like ordering [23, 30]. In this sense, even a monodisperse hard sphere system is not free from frustration effects on crystallization and suffers from self-generated internal frustration controlled by entropy [19, 30, 3]. This situation may be similar to metallic glass formers [55, 56], although the tendency of icosahedral ordering can be more pronounced for these systems due to the chemical nature of bonding [57] and the matching of atomic sizes [58].

Glassy critical dynamics or RFOT scenario

According to the RFOT scenario [59, 14], transport near glass transition is driven by activated processes, the driving force for which are ‘entropic’ in nature. Because the entropy vanishes linearly near the Kauzmann temperature T_K the size of the domains is predicted to grow as $\xi \sim ((T - T_K)/T_K)^{-2/d}$. This is at least apparently consistent with our observation. However, we note that the RFOT theory is based on two-body density correlation (see, e.g., Ref. [60]) and thus does not explicitly include many-body correlations, in particular, in the form of bond orientational correlations. Thus this theory may not explain the development of bond orientational order in a supercooled liquid. The droplet theory, constructed by balancing the entropic driving force and the opposing cost of creating an interface between two glassy states leads to the Vogel-Fulcher-Tammann equation [59, 14]. More importantly, droplets are excitation of ‘amorphous order’. This is not consistent with what we observed in nearly single-component systems, where crystal-like order develops upon cooling. We also point out that in our simulation and experiments, spatial fluctuations of the crystal-like bond orientational order parameter are not like ‘droplets’ but rather continuous critical-like fluctuations, whose spatial correlation is well described by the Ornstein-Zerinke function. The dynamics of the order-parameter fluctuations is also found to be well described by model A (non-conserved order-parameter dynamics)

[52]. So the behavior is more second-order-like rather than first-order-like. At this moment, thus, we prefer to interpret glassy slow dynamics as a consequence of ‘glassy critical dynamics’ [3, 19, 61], although further study is certainly necessary on this point.

CRYSTAL NUCLEATION FROM A SUPERCOOLED LIQUID

So far we focus on the growth of crystal-like bond orientational order in the supercooled state of a hard-sphere system. On this basis, here we consider how a supercooled liquid is destabilized by crystallization and crystal nuclei are formed.

Crystallization, more strictly, crystal nucleation in a supercooled liquid, is a process in which a new ordered phase emerges from a disordered state. It is important not only as a fundamental problem of nonequilibrium statistical physics, but also as that of materials science [62, 63, 64, 65, 66]. Crystallization has been basically described by the classical nucleation theory. However, nature provides intriguing ways to help crystallization beyond such a simplified picture. An important point is that the initial and final states are not necessarily the only players. This idea goes back to the step rule of Ostwald [67], which was formulated more than a century ago. He argued that the crystal phase nucleated from a liquid is not necessarily the thermodynamically most stable one, but the one whose free energy is closest to the liquid phase. Stranski and Totomanow [68], on the other hand, argued that the phase that will be nucleated should be the one that has the lowest free energy barrier. Later Alexander and McTague [69] argued, on the basis of the Landau theory, that the cubic term of the Landau free energy favors nucleation of a body-centered cubic (bcc) phase in the early stage of a weak first order phase transition of a simple liquid. Since then there have been a lot of simulation studies on this problem, but with controversy (see, e.g., [70, 42] and the references therein). Here we show a new scenario of crystal nucleation beyond the above classical scenarios, focusing on structural ordering intrinsic to the supercooled state of liquid.

Crystal nucleation process in a monodisperse system

Here we show a typical crystal nucleation process in a monodisperse colloidal liquid in Fig. 8. We can clearly see crystal nuclei are selectively formed in regions of high crystal-like bond orientational order. After a quench, thermal fluctuations of crystal-like bond orientational order are developed and this stage shows

a typical behavior of the supercooled state of a glass-forming liquid [45]. In this stage very small crystal nuclei are created and annihilated in regions of high crystal-like bond orientational order, but they have a finite lifetime and thus are transient. After some time, a nucleus whose size is larger than the critical nucleus size is formed and starts to grow. Such a nucleus is always born only in a region of high crystal-like bond orientational order [45]. This is a consequence of the fact that the initial stage of crystallization is the enhancement of the spatial coherence of the phase of crystal-like bond orientational order [30]. This means that crystallization is triggered by bond orientational ordering and ‘not’ by positional ordering. Once crystals are nucleated, fluctuations of bond orientational order are pinned due to wetting to crystals.

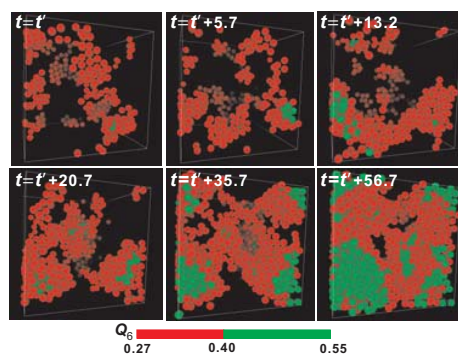


FIGURE 8. Birth of a crystal nucleus from medium-range structural order. The process of nucleation of a crystal at $\phi = 0.537$ ($N = 4096$). Particles with intermediate Q_6 ($0.27 \leq Q_6 \leq 0.40$) are colored red (dark gray), whereas those with high Q_6 ($Q_6 \geq 0.4$) are colored green (light gray). The time unit is the Brownian time of a particle, τ_B . We can see the birth of a crystal and its growth. $t = t'$ is the time when a supercooled liquid reaches a sort of quasi-equilibrium steady state after the initiation of simulations from a random disordered state.

Our scenario of crystal nucleation

Our physical scenario of crystallization can be summarized as follows [45, 29, 30, 3]. After a quench from an equilibrium liquid state to a supercooled state, medium-range bond orientational order whose symmetry has a connection to an equilibrium crystal structure (fcc or hcp in hard-sphere colloids with more weight in fcc [23, 30, 3]) first develops as spontaneous thermal fluctuations. When regions of high crystal-like bond orientational order accidentally have high local density as a consequence of thermal density fluctuations, crystal nucleation is initiated with a high probability by accompanying the increase in the spatial coherence of bond orientational order without a discontinuous density jump [30]. Here we note that the bond-orientational field and

the density field are almost completely decoupled (as shown in Ref. [30]), and that the only necessary condition for crystallization is the nucleation from regions of high bond orientational order. So, the roles of high density and high bond order are not equal. This is because high density can rather easily be attained by fast density fluctuations, but high bond order is realized by much slower critical-like fluctuations. We note [30] that regions of high bond order have on average a higher density, but the opposite is not true. Thus, the factor triggering crystallization are the fluctuations of bond orientational order.

The sequence of crystallization from melt induced by a temperature or density quench is thus summarized as follows: An initial homogeneous equilibrium liquid at a high temperature is transformed into an ‘inhomogeneous’ supercooled liquid with crystal-like bond orientational order fluctuations after the quench. Then the phase coherency of crystal-like bond orientational order in a region of high density starts to increase continuously. Finally, a crystalline phase is formed by the development of translational order induced by the growth of crystal-like bond orientational order. We emphasize that these processes ‘continuously’ take place at the microscopic level.

Since the Ostwald’s seminal argument, intermediate states between the initial liquid and the final crystal state has been searched from the crystal side [67, 68, 69, 70, 42]. However, our study demonstrates that it is crucial to consider hidden structural ordering in a supercooled liquid. We point out that the slowness of these structural fluctuations is also crucial for nucleation to efficiently take place.

Recently it was suggested that crystal nuclei are not formed spontaneously in one step from random fluctuations, but rather in a two step through preordered precursors of high density with structural order [71, 72]. This two-step crystal nucleation scenario now becomes very popular [73, 74, 75, 76, 71, 72, 77]. The importance of locally high density regions as precursors was also pointed out by ref. [72] on the basis of numerical simulation of hard-sphere crystallization.

Thus, we consider which of bond order parameter fluctuations and density fluctuations is crucial for crystal nucleation. We revealed that crystallization starts from crystal-like bond orientational ordering and then density ordering (positional ordering) comes into play later [30]: Microscopically, crystallization starts from locally high density regions inside the regions of high bond orientational order, both of which are spontaneously formed by thermal fluctuations [30]. We note that density fluctuations whose amplitude is determined by isothermal compressibility K_T , can often allow a system to locally access the lower bound of crystal density. Contrary to the two-step crystallization scenario, our study [30] shows

that high local density is a necessary condition for crystal nucleation, but not a sufficient condition. On a microscopic scale it is bond order parameter and neither density nor translational order that triggers crystal nucleation. As emphasized above, we note that the process of crystal nucleation is ‘continuous’ rather than made of ‘discrete’ steps. Our finding is markedly different from the conventional view based on macroscopic observation where we can see a discontinuous change in the density upon crystal nucleation. This clearly indicates the crucial role of bond orientational ordering in crystallization.

Crystal nucleation is triggered by the enhancement of the phase coherence of bond orientational order in high density regions in a metastable liquid and then translational order follows afterwards [30]. This looks natural, considering that crystal nucleation starts from a very small size: It is difficult to define translational order for such a small region, since it is characterized by periodicity over a long distance. Translational order can be attained in the growth process of nuclei, but not in the nucleation process. The theory of crystallization may need to be fundamentally modified to incorporate these findings. How universal this scenario is to more complex liquids remains for future investigation, but our preliminary studies on soft sphere and water suggests the universality [29, 30].

INTIMATE LINK BETWEEN GLASS TRANSITION AND CRYSTALLIZATION

In the above, we showed that (i) there is critical-like enhancement of crystal-like bond orientational ordering in supercooled polydisperse colloidal liquids, which is the origin of glassy slow dynamics and dynamical heterogeneity, and (ii) crystal nucleation is also triggered by the enhancement of the spatial coherence of this ordering. This finding strongly suggests an intimate link between crystallization and glass transition [3]. Namely, a supercooled liquid is intrinsically heterogeneous and, in this sense, homogeneous nucleation may necessarily be “heterogeneous”. The state of a supercooled liquid is prepared, or self-organized, for future crystallization. This feature may generally be seen in glass-forming liquids: although crystal nuclei whose size exceed the critical nucleus size are usually not formed in a good glass former, small transient nuclei are spontaneously formed selectively in regions of high crystal-like bond orientational order [23]. Frustration on crystallization controls the barrier for crystallization, and thus, plays a crucial role in the glass-forming ability. Our study suggests a necessity to develop a theory of glass transition and crystallization based on the free energy including bond orientational order (effects of many body correlations, particularly, bond

angle correlations) as an important factor in addition to the two-body density correlation [18, 20, 4, 3].

SUMMARY

In this article, we show that the rotational symmetry which is going to be broken upon crystallization is already broken ‘locally’ in a supercooled liquid. Growth of its spatio-temporal fluctuations under frustration is the origin of glassy slow dynamics and dynamic heterogeneity at least in weakly polydisperse hard spheres. Furthermore, crystal-like bond orientational order triggers crystal nucleation with a high probability if regions of high order can reach a density required for crystallization by spontaneous thermal density fluctuations. Frustration on crystallization (polydispersity in colloidal liquids) lowers the probability of crystal nucleation significantly since it reduces the degree of crystal-like bond orientational ordering and increases the degree of icosahedral ordering which has strong frustration effects on crystallization. This strongly suggests an intrinsic link between glass transition and crystallization. Furthermore, this indicates that a supercooled liquid is not a homogeneous state, but has mesoscopic spatio-temporal structures (see Fig. 9). This may be due to a consequence of glassy critical phenomena [19, 3].

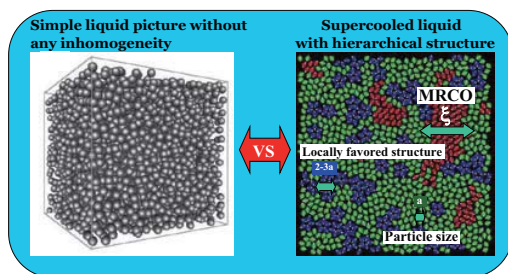


FIGURE 9. Schematic figure showing the difference between a classical picture of a supercooled liquid (the homogeneous liquid picture) and a picture based on our study (the spatio-temporally inhomogeneous liquid picture). The former situation may be described by two-point density correlations alone, whereas the latter situation requires many-body correlations (e.g., bond orientational order parameter) for its physical description. For the latter we used a typical structure of a supercooled two-dimensional spin liquid [26, 28].

Bond orientational order may be a relevant structure measure for slow dynamics only in nearly one-component systems and not necessarily a general measure. In systems where phase separation is necessary for crystallization taking place, which is the case for some binary mixtures and highly polydisperse colloidal systems, bond orientational order no longer has a link to the symmetry of the crystal. But there may still exist some

(unknown) glassy structural order causing slow dynamics, which may be associated with low local free-energy configurations in the ‘homogeneous’ metastable liquid branch before phase separation [4, 20, 3]. The validity of this physical picture is to be checked carefully for various glass-forming systems. In relation to this, we should note other measures for detecting static structural correlations [78, 79, 80, 81, 82]. The relationship between these static measures and bond orientational order is an interesting issue relating to what structural features are responsible for slow dynamics and whether there is really a general link between structure and dynamics or not.

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