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Roles of bond orientational ordering in glass transition and crystallization

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Abstract

It is widely believed that crystallization in three dimensions is primarily controlled by positional ordering, and not by bond orientational ordering. In other words, bond orientational ordering is usually considered to be merely a consequence of positional ordering and thus has often been ignored. This one-order-parameter (density) description may be reasonable when we consider an equilibrium liquid–solid transition, but may not be enough to describe a metastable state and the kinetics of the transition. Here we propose that bond orientational ordering can play a key role in (i) crystallization, (ii) the ordering to quasi-crystal and (iii) vitrification, which occurs under rather weak frustration against crystallization. In a metastable supercooled state before crystallization, a system generally tends to have bond orientational order at least locally as a result of a constraint of dense packing. For a system interacting with hard-core repulsions, the constraint is intrinsically of geometrical origin and thus the basic physics is the same as nematic ordering of rod-like particles upon densification. Furthermore, positional ordering is easily destroyed even by weak frustration such as polydispersity and anisotropic interactions which favour a symmetry not consistent with that of the equilibrium crystal. Thus we may say that vitrification can be achieved by disturbing and prohibiting long-range positional ordering. Even in such a situation, bond orientational ordering still survives, accompanying its critical-like fluctuations, which are the origin of dynamic heterogeneity for this case. This scenario naturally explains both the absence of positional order and the development of bond orientational order upon cooling in a supercooled state. Although our argument is speculative in nature, we emphasize that this physical picture can coherently explain crystallization, vitrification, quasi-crystallization and their relationship in a natural manner. For a strongly frustrated system, even bond orientational order can be destroyed. Even in such a case there may still appear a structural signature of dense packing, which is linked to slow dynamics.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Liquid–glass transition is one of the most fundamental problems in condensed matter physics [1–3]. Glass transition takes place if we can successfully avoid crystal nucleation upon cooling. Thus it is intrinsically a cooling rate (or, time) dependent nonequilibrium phenomenon. In this sense, crystallization is an underlying thermodynamic transition which always exists behind glass transition, implying that there must be an intrinsic link between crystallization and glass transition phenomena. However, when one considers the problem of glass transition and the associated slow dynamics,

the fact that a supercooled liquid can crystallize has often been ignored or presupposed, and accordingly most existing theories of glass transition have been constructed on the basis of a liquid state theory. In this scenario, it is assumed that crystallization is bypassed ‘purely’ kinetically. This relies on the fact that there is no evident change in the two-point density correlator of a supercooled liquid from the melting point to the glass transition point: the absence of growth of positional order. This has been regarded as an indication of the absence of any structural change in a supercooled liquid state. One of the most successful quantitative theories along this line is the mode-coupling theory of liquid–glass transition [4]. This

theory successfully describes slow dynamics in supercooled colloidal liquids (see, e.g., [5]). Its further extension to incorporate cooperative activated dynamics has also been made [6]. Contrary to the above-mentioned common belief that there is little structural change in a supercooled liquid, we have recently revealed that some model glass-forming systems exhibit temporal medium-range bond orientational order, whose correlation length appears to diverge towards the ideal glass transition temperature T_0 [7–13]. We emphasize that such bond orientational order is not easy to detect by the two-point density correlator, which may be a reason why this structural signature has not been recognized so far.

About a decade ago, we proposed that there should be a deep link between crystallization and vitrification, and frustration against crystallization is a key to understanding glass transition behaviour including slow dynamics, fragility, and glass-forming ability [14–16]. On the basis of this physical picture, we recently studied one of the simplest glass-forming liquids, polydisperse hard sphere liquids (strictly speaking, the Weeks–Chandler–Andersen (WCA) liquids [17]), focusing on a link between crystallization and vitrification [9–13, 18]. We confirmed that with an increase in the polydispersity Δ (i.e., frustration), a system can be more easily vitrified for both two- (2D) and three-dimensional (3D) systems. We found that in a supercooled liquid there appears bond orientational order with spatio-temporal fluctuations, the size and lifetime of which both increase with an increase in the packing fraction ϕ . It was revealed that this structural order is characterized by hexagonal close packing (hcp) symmetry for 3D [12, 13]. This bond orientational ordering exhibits a critical-like divergence towards the ideal glass transition packing fraction ϕ_0 and its critical behaviour turns out to belong to the 3D Ising universality class. We also observed essentially the same behaviour in 2D spin liquids [7, 8], where a spin on a particle tends to induce the formation of pentagons and this tendency leads to frustration against crystallization because of the inconsistency of the five-fold symmetry with the crystal symmetry, and also in 2D binary hard disks, and in 3D polydisperse Lennard-Jones particles [12]. However, unlike ordinary critical phenomena, it is difficult to approach the hypothetical critical point ϕ_0 (or T_0) due to the dramatic slowing down of the dynamics. This intrinsic inaccessibility to ϕ_0 (or T_0) makes an unambiguous check of the critical scaling extremely difficult. Nevertheless, our study clearly shows that at least in these model glass-forming systems there is growing structural order (e.g., bond orientational order), which has a link to dynamic heterogeneity in a supercooled liquid state. We also note that similar crystal-like order was also observed in a supercooled state of 2D magnetic colloids both experimentally and numerically [19].

We also found that for monodisperse and weakly polydisperse systems ($\Delta \leq 6\%$), crystal nucleation takes place during a simulation time. Interestingly, crystals always nucleate from the regions of high hcp order in a supercooled hard-sphere-like liquid, which is reminiscent of critical wetting phenomena [13, 18]. This indicates a strong link between the structural feature of bond orientational order in a supercooled liquid state and that of a nucleated crystal [12], consistent with

our two-order-parameter model [14–16, 20–24]. Furthermore, this is also consistent with a recent study by Pedersen *et al* on structural fluctuations in a Wahnström mixture [25]. On the basis of colloidal experiments, van Meegen and his co-workers also showed the possibility of an intrinsic link between crystallization and glass transition [26–28].

In this paper, we consider this link between a crystal structure and hidden order in a supercooled liquid in more detail, putting a special focus on hard-sphere-like systems. This is related to the very fundamental question of whether we can specify a supercooled liquid state and crystallization by a single order parameter (density ρ) alone or we need a new additional order parameter. In our original two-order-parameter model of glass transition [14–16, 20–24], we did not consider the roles of bond orientational order associated with the symmetry of the equilibrium crystal in an explicit manner. Here we are going to show that bond orientational order, which is a consequence of the constraint of dense packing and/or due to directional bonding, plays a crucial role in crystallization and the liquid–glass transition, both of which usually take place in a densely packed metastable liquid. At this time, our discussion is speculative, but we hope that this will contribute to deeper understanding of the nature of a metastable supercooled liquid as well as crystallization.

2. Experimental and numerical evidence supporting our basic picture

First we explain experimental and numerical evidence supporting our physical picture [14–16]. It is widely recognized that if we can avoid crystallization in any way, a system continuously transforms from a liquid state to a nonergodic glassy state upon cooling or densification. For example, water is known as a very poor glass-former, whereas glycerol as a good glass-former. For ordinary single-component organic liquids, there is no physical variable to control the glass-forming ability except for pressure, and thus we simply classify liquids into glass-forming and non-glass-forming liquids. This classification itself is rather ambiguous and the critical cooling rate required for vitrification varies from material to material. Many atomic liquids are very easily crystallized and usually we need $R_c > 10^6 \text{ K s}^{-1}$ to vitrify them. However, by mixing a few components we can increase the glass-forming ability significantly. This is common in both chalcogenide and metallic glasses. For chalcogenide glasses, it has been established that the glass-forming ability is maximized by balancing the number of constraints due to covalent bonding with the number of degrees of freedom. Furthermore, a concept of self-organized network formation explains the composition window of the high glass-forming ability [29]. This concept allows us to provide a guide to predict the glass-forming ability of chalcogenide glasses. For metallic glasses, mixing of more than a few atoms also leads to a drastic increase in the glass-forming ability [30]. Metallic alloys with a high glass-forming ability are now widely recognized as bulk metallic glass-formers. In both chalcogenide and metallic glasses, an increase in the number of components is an important factor to increase

Table 1. Types of frustration in various glass-forming liquids. Here ‘Disorder’ means random disorder effects and ‘Frustration’ means energetic (or entropic) frustration. MC stands for multi-components, LFS stands for locally favoured structures whose local symmetry are not consistent with the symmetry of the equilibrium crystal. Here ico stands for icosahedral structures, and SI stands for stereo-irregularity.

Material	Oxide	Chalcogenide	Metal	Organic	Colloid	Polymer
Disorder	MC	MC	MC	MC	MC	SI + MC
Frustration	LFS	LFS	LFS (ico)	LFS	LFS (ico)	LFS

the glass-forming ability. However, this is not the only cause. In chalcogenide glasses, the importance of local bond orientational ordering by directional covalent bonding is well established, as described above. In metallic glasses, the importance of local icosahedral ordering in vitrification [31] is also well accepted [20, 21, 30]. In the field of soft matter, atactic polymers are known as very good glass-formers (or, uncrystallizable materials). This is induced by stereo-irregularity, i.e., quenched-in structural disorder effects. Finally, in colloidal glasses, mixing of particles with different sizes or increasing the degree of polydispersity is known as crucial for avoiding crystallization [32–35].

In numerical simulations of a supercooled liquid, the situation is quite similar. Usually we mix particles with different sizes and the size ratio is chosen so as to most efficiently avoid crystallization [36]. A systematic study on the effects of the size ratio of binary particle mixtures were also performed by Hamanaka and Onuki [34]. Anisotropic potentials with specific symmetry, such as the Dzugutov potential [37], are also used to avoid crystallization [7]. Recently, it was shown that even a model system designed for avoiding crystallization can crystallize if the simulation time is long enough [38]. This is suggestive of a link between vitrification and crystallization: a liquid always tends to crystallize.

All these experimental and numerical examples strongly suggest that frustration against crystallization is a key to vitrification. These examples indicate that the glass-forming ability is not only controlled by a kinetic factor, but also by a thermodynamic factor, since all the above-mentioned factors are included in the Hamiltonian of a system. The Hamiltonian should include not only a part describing crystallization but also a part describing frustration and/or random disorder effects against crystallization. The latter reflects a tendency of a liquid to form locally favoured structures (whose symmetry is not necessarily consistent with the symmetry of the equilibrium crystal) or random disorder effects (e.g., mixing of molecules or atoms, polydispersity of colloidal particles, and stereo-irregularity of polymers). So it may be natural to put the phenomena of crystallization as the most fundamental physical basis for understanding the liquid–glass transition. This is the basis of our two-order-parameter model of the liquid–glass transition [14–16, 20–22]. According to this model, various features characterizing glass transition behaviour, such as glass-forming ability and fragility, are all controlled by the degree of frustration against crystallization: for example, stronger frustration makes a liquid less fragile and a better glass-former. Such behaviour is indeed confirmed for a 2D spin liquid [7, 8] and polydisperse hard-sphere-like systems [9, 12, 13]. The types of frustration

against crystallization can be grouped into the following two categories: energetic frustration and random disorder effects. These are summarized in table 1 for various types of materials.

3. Crystallization of hard spheres

Each of the above-mentioned material groups has interesting features concerning frustration and its consequences. Here, however, we focus our attention on the simplest, but very important ideal system, i.e., hard-sphere-like liquids (colloidal liquids [39]).

3.1. Entropy-driven positional ordering

Here we discuss structural ordering in hard sphere liquids (more generally, particles interacting with pure repulsions) and its link to crystallization. So we first review the theory of freezing of hard sphere liquids, following a clear intuitive description given by Baus [40]. In the framework of density functional theory, the freezing of hard spheres is described as a competition between two forms of entropy: a loss in configurational entropy when particles are ordered and a gain in correlational entropy resulting from the particle localization. The difference $\Delta f = f(\rho_S) - f(\rho_L)$ in free energy per unit volume between the solid (S) and liquid (L) at constant average density ($\rho_S = \rho_L = \rho$) can be written as

$$\Delta f = k_B T \frac{1}{V} \int d\mathbf{r} \rho(\mathbf{r}) \ln \frac{\rho(\mathbf{r})}{\rho} - \frac{k_B T}{2V} \int d\mathbf{r} \int d\mathbf{r}' c(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}(\rho)) \Delta\rho(\mathbf{r}) \Delta\rho(\mathbf{r}'), \quad (1)$$

where k_B is Boltzmann’s constant, T the temperature, and V the volume. Here $\Delta\rho = \rho - \bar{\rho}$, and $c(\mathbf{r}, \mathbf{r}'; \bar{\rho}) = c(|\mathbf{r} - \mathbf{r}'|; \bar{\rho})$ is the direct correlation function of the liquid at the average density $\bar{\rho}$. The first term in the right-hand side is $-T\Delta s_{\text{conf}}$, where Δs_{conf} is the difference in configurational entropy between the solid and the liquid. The second term is the difference $\Delta\tilde{u}$ in the effective internal energy $\tilde{u} = u - Ts_{\text{corr}}$, where s_{corr} is the correlational entropy. In the case of hard spheres there is no internal energy ($u = 0$) and thus $\tilde{u} = -Ts_{\text{corr}}$. The hard sphere freezing can thus be described as a competition between the two forms of entropy, s_{conf} and s_{corr} . Then the solid can be interpreted as the state of the highest correlational entropy.

This scenario implies, although not directly, that even a liquid tends to gain correlational entropy by attaining a (orientationally) more regular packing to reduce the total free energy of the system. This feature, which is absent in an (undriven) athermal system, is crucial in the following argument.

3.2. Selection of a crystalline structure

The next question relating to crystallization is which crystal structure is selected upon nucleation. Thermodynamically, the formation of metastable phases might be explained by differences in interfacial free energies. The formation of a bcc–liquid interface might cost less energy than that of an fcc–liquid interface. For hard spheres, it is known that the fcc phase is the stable structure, but the free-energy difference between the fcc and the hcp structure is very small ($<10^{-3}k_B T$) [41], indicating that thermal fluctuations of the order of $k_B T$ could transform a cluster of 10^3 particles from fcc to hcp or cause stacking faults. The only difference between the fcc and the hcp structure is the stacking of 2D close-packed hexagonal crystal planes. For the fcc structure the stacking is ABC, whereas for the hcp structure the stacking is AB. If the interfacial free energies of a crystal fcc–liquid, hcp–liquid, or an rhcp–liquid interface are different, then this picture could completely be altered. Here, rhcp refers to a random stacking of close-packed hexagonal crystal planes. Whether small crystal nuclei are more like fcc or hcp is not so clear. Experiments by Pusey *et al* [42] and Elliot *et al* [43] indicate that the fcc structure is favoured. However, microgravity experiments by Zhu *et al* [44] showed that, initially, small crystal nuclei have an rhcp structure. Our structural analysis of crystal nuclei formed in numerical simulations suggests that the structure of nuclei is rhcp, consistent with the results of Auer and Frenkel [45]. More precisely, the averaged crystal structure gradually transforms from hcp-like to more fcc-like in the growth process [13, 18].

4. Is bond orientational ordering universally expected?

In a 2D hard disk system, the ordering is proposed to take place via two sequential continuous transitions in the order of bond orientational ordering and translational ordering upon densification. This is known as the Kosterlitz–Thouless–Halperin–Nelson–Young scenario [46]. In a 3D hard sphere system, on the other hand, the freezing is often described by the above described density functional theory (see, e.g., [47]). So the role of bond orientational ordering in 3D crystallization is not so clear. This may be due to the fact that in 2D the bond orientational ordering temperature T_Q is higher than the translational ordering temperature T_ρ , whereas in 3D T_Q may be lower than T_ρ even if it exists, except for the case of quasi-crystal formation [48]. This difference may arise from the difference in the strength of the constraint from dense packing between 2D and 3D: the constraint is weaker in 3D than in 2D due to the freedom associated with the extra dimension. It should monotonically decrease with an increase in the space dimension d . Reflecting this feature, bond orientational ordering may be hidden behind crystallization, e.g., for a 3D hard sphere system, unlike the case of 2D hard disks.

However, we stress that bond orientational ordering is a consequence of a very general geometrical constraint coming from ‘dense packing’ for a system interacting with hard-core repulsions. The basic physics is the same as nematic

ordering of rod-like particles. Thus it is natural to expect that it always plays a significant role in any ‘dense’ system in which crystallization and vitrification usually take place. For a monodisperse system, the natural average number of nearest neighbour particles is 6 for 2D disks, whereas it is 12 for 3D spheres. This should lead to the tendency of bond orientational ordering associated with the symmetry linked to these numbers of average nearest neighbours (see below on the details of types of preferred bond orientational order). Thus, for 2D hard disks hexatic order is preferred, whereas for 3D hard spheres hcp, fcc, or icosahedral bond orientational order are favoured. Since hcp has a lower symmetry than fcc, the most probable local arrangements of particles may be hcp and icosahedral for hard spheres.

The constraint from dense packing is stronger in 2D than in 3D, but the effect is still quite important even for a 3D system. For attractive systems interacting with an anisotropic potential, real attractive bonds (e.g., covalent bonds and hydrogen bonds) formed with the surrounding particles should select the type of bond orientational order. For example, for liquids such as water, Si, Ge, SiO₂, the tetrahedral order [1] characterized by Q_3 is the key bond orientational ordering [49, 50].

In rather weakly polydisperse colloids, we observe hcp-like bond orientational order in a supercooled liquid state [12, 13]. However, if the strength of disorder becomes very strong, there is no reason to believe that the same type of ordering should be seen. The natural number of nearest neighbours is no longer necessarily 6 for 2D and 12 for 3D, and it should strongly fluctuate. Indeed, in a 2D binary system with a size ratio of ~ 1.4 , it turns out that hexatic order, which is a good measure for weakly polydisperse 2D hard disks [9], is no longer a suitable structural indicator capable of characterizing the slow dynamics. We found that local structural entropy $s_2(\mathbf{r})$ is a reasonable indicator even for such a case [12]. In these purely repulsive systems, a system always tends to maximize the total entropy of the system by gaining correlational entropy.

5. The nature of hcp-like ordering: metastable crystal nuclei or critical-like fluctuations of bond orientational order

We found a clear indication for the growth of hcp-like bond orientational order upon densification in a supercooled liquid state of a 3D hard-sphere-like (WCA) liquid [12, 13, 18]. We stress that this is a natural consequence of dense packing. However, the nature of such order may be a matter of discussion. One might think that it is merely a consequence of pre-nuclei, or metastable crystals. Before nucleation, the existence of such pre-nuclei whose size is smaller than a critical nucleus size cannot be ruled out. Hereafter we explain why we do not take such a view.

- (i) The region of high hcp-like order almost has the same density as that of low hcp-like order. This means that hcp-like bond orientational order is almost completely decoupled from positional (translational)

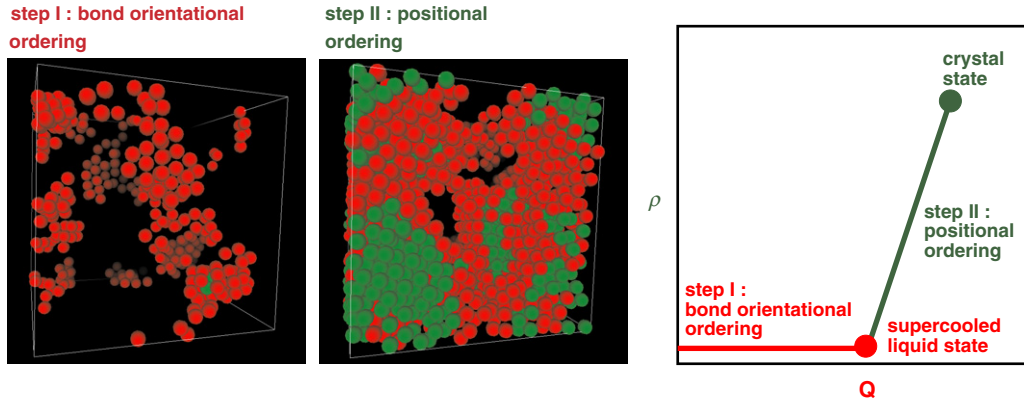


Figure 1. A scenario of two-step ordering of crystallization. Step I (left): in a supercooled liquid state before crystal nucleation, a system attains only bond orientational ordering, which has a finite lifetime. Step II (middle): crystal nucleation preferentially occurs in a region of high bond orientational order and accompanies positional ordering. The kinetic pathway of crystal nucleation is drawn in a two-order-parameter plane (left). For simplicity, we consider only one type of bond orientational order Q . In reality, this process may occur in a multi-dimensional space. According to the conventional picture, formation of pre-nuclei should accompany the density change from a liquid state and thus leads to fluctuations along the ρ axis. Such behaviour was not observed in our simulations [12, 13, 18].

ordering [12, 13, 18]. However, one might still argue that this is simply because pre-nuclei are too small to have a measurable density difference. We stress that the structural fluctuations we observe in a supercooled liquid do not occur along the density ρ axis but along the bond orientational order Q axis (see figure 1). This seems at least to rule out a scenario of pre-nuclei based on the classical nucleation theory, where the lowering of the free energy upon crystallization comes from density ordering. Note that the classical nucleation theory assumes that a crystal nucleus has the same structure as the equilibrium crystal, including the density and symmetry.

- (ii) The size of a critical nucleus r_c is smaller than the characteristic size of high hcp-like regions ξ . Here we define the size of a critical nucleus as the size of a crystal of high Q_6 and high density [13, 18]. If we consider the high hcp order region surrounding a critical nucleus as a part of the nucleus, the fact that $r_c < \xi$ may not be used as the evidence against pre-nuclei scenario. Then, however, we have to alter our physical picture that a crystal nucleus is separated from a liquid phase with a rather sharp interface. Or we need to regard the high hcp order region as a solid rather than a liquid. The former is against what is assumed in the classical nucleation theory, whereas the latter is inconsistent with the usual definitions of solid and liquid.
- (iii) In a system of higher polydispersity ($\Delta \geq 7\%$), we never observe crystallization in our simulation time. However, there always appears such structural ordering in a less pronounced way [12, 13, 18]. We confirm that structural fluctuations in a supercooled liquid are fluctuations of hcp-like bond orientational order and not those of density. This indicates that the hcp-like order is intrinsic to a metastable supercooled hard-sphere-like liquid.
- (iv) More importantly, hcp-like bond orientational order appears as spatially correlated critical-like fluctuations. This is confirmed by the fact that the spatial correlation of

Q_6 is well described by the Ornstein–Zernike correlation function with the correlation length ξ [12, 13, 18]. This feature is not usually expected if the high Q_6 regions are formed by nucleation events, which are barrier-overcoming random events and thus expected not to be so strongly correlated spatially.

- (v) The growth of the size and amplitude of hcp-like bond orientational correlation upon densification is very consistent with the Ising-like criticality [12]. Such a feature is not expected, at least from the current knowledge of crystal nucleation.

For these reasons, we argue that structural order observed in a supercooled state is not due to pre-nuclei in the sense of the classical nucleation theory, but something new. However, this issue is probably not so important. What is important is that a supercooled liquid is metastable against crystallization and thus affected by it in a direct and an indirect manner. Our study [13, 18] indicates that dynamic heterogeneity may be a manifestation of such effects, at least for several systems we studied.

6. Bond orientational ordering behind crystallization

6.1. Density (translational) ordering

First we consider a Landau-type free energy associated with translational ordering [48, 51, 52].

$$F_\rho = F_\rho^{(2)} + F_\rho^{(3)} + F_\rho^{(4)} + \dots \quad (2)$$

where $F_\rho^{(2)}$ is the quadratic term having the form

$$F_\rho^{(2)} = \int dq A(q) \rho(q) \rho(-q). \quad (3)$$

Near the transition into a translationally ordered state, the minimum of $A(q)$ selects the magnitude of the fundamental wavevectors. Then the symmetry, i.e., which particular set of

directions $\pm\hat{q}_i$ will be chosen, depends on the third and fourth order terms, provided that we can neglect the higher order terms in the vicinity of the transition. The discrete versions of these terms, for fixed q , are

$$F_\rho^{(3)} = B \Sigma \rho(\hat{q}_i) \rho(\hat{q}_j) \rho(\hat{q}_k), \quad \hat{q}_i + \hat{q}_j + \hat{q}_k = 0, \quad (4)$$

and

$$F_\rho^{(4)} = \Sigma C(\hat{q}_i \cdot \hat{q}_j, \hat{q}_j \cdot \hat{q}_k) \rho(\hat{q}_i) \rho(\hat{q}_j) \rho(\hat{q}_k) \rho(\hat{q}_l), \quad \hat{q}_i + \hat{q}_j + \hat{q}_k + \hat{q}_l = 0. \quad (5)$$

The rotational and translational symmetries are fully implemented by these expressions. Alexander and McTague [52] assumed that the isotropic component of C dominates the quartic term. Under this assumption, the free energy F_ρ is minimized by a set of $\rho(\pm\hat{q}_i)$ which maximizes $|F_\rho(3)|/|\rho|^3$. Then they considered $\pm\hat{q}_i$ parallel to the edges of a triangle, an octahedron (tetrahedron), and an icosahedron. We can add to this list a tetrahedral bipyramid and an idealized pentagonal bipyramid. These correspond to 2D hexagonal lattice (2Dhex), bcc, icosahedral edge model (ieqc), 3D hexagonal lattice (3Dhex), and idealized closed packing of tetrahedra (ideal), respectively. The result is $F_\rho^{\text{bcc}} < F_\rho^{\text{3Dhex}} < F_\rho^{\text{ideal}} < F_\rho^{\text{2Dhex}} < F_\rho^{\text{ieqc}}$. This leads to the conclusion that bcc is most favoured, whereas icosahedral edge model quasi-crystalline ordering is least favoured.

This conclusion is a direct consequence of the fact that the lower order term in the free energy (equation (2)) plays a more important role in the early stage of growth of density fluctuations. However, we argue below that there is an additional important selection rule from the constraint of dense packing, under which crystallization usually takes place (except for a system interacting with rather long-range (or soft) repulsions).

For example, we need some additional mechanism stabilizing icosahedral order to explain the formation of icosahedral crystals. Introduction of bond orientational ordering is one possible resolution [48]. Below we argue that bond orientational order may play a crucial role not only in quasi-crystal formation, but also in crystallization and glass transition in general.

6.2. Bond orientational order linked to the equilibrium crystal

We observe the growth of hcp-like bond orientational order in a supercooled state toward ϕ_0 . This is not expected from the standard density functional theory described above¹. Furthermore, crystals nucleated first have hcp or fcc structures rather than bcc structure. This result is not consistent with the prediction of the seminal argument (see above) given by Alexander and McTague [52] based on the Landau theory [51], although the degree of supercooling might already be too large for us to apply their theory. How to understand these phenomena is an issue we want to discuss here.

¹ Here we note that we are not claiming that the classical density functional theory cannot describe crystallization itself. What we propose here is that bond orientational ordering is hidden behind crystallization, and it plays an important role in a supercooled state where crystallization does not yet take place and may affect the kinetic pathway of crystallization.

Crystallization of spherical particles is usually described by the density (or translational order) as the order parameter. However, the above-mentioned observation seems to indicate that the density may not be the only order parameter controlling crystallization, but we need an additional order parameter to describe the behaviour of a supercooled liquid as well as crystallization. The most probable candidate is the bond orientational order parameter(s).

The importance of bond orientational ordering was pointed out for crystal ordering [53–56] as well as for orientational ordering [57, 58]. Nelson and Toner [59] also considered a possible existence of a residual bond angle order analogous to that found in a two-dimensional hexatic phase. They pointed out that a bulk phase with bond orientational order (‘cubic’ liquid crystal) might be observable in supercooled liquids.

In relation to this, there is also an interesting approach to quasi-crystal formation, which puts a focus on both translational and orientational orderings, including their couplings. Jaric [48] showed that a quartic orientational free energy leads to long-range icosahedral order which stabilizes the icosahedral quasi-crystalline state through a coupling with a translational order parameter. The description of quasi-crystal formation was made on the basis of a few different ideas. Bak [60], Mermin and Troian [61], and Kalugin *et al* [62] considered this problem on the basis of the Landau theory of solidification formulated by Alexander and McTague [52]. In order to bypass the original conclusion that a bcc structure should be generally favoured (see above), they either include higher order terms or an additional component to the density. Unlike these approaches, Jaric [48] proposed to introduce an orientational order parameter which stabilizes the quasi-crystalline phase. He provided an interesting view of solidification as an interplay between orientational order and translational order parameters in a similar spirit to the above approach by Nelson and Toner [59].

On the basis of our observation, we propose [20] that bond orientational ordering generally plays a crucial role also in three-dimensional crystallization and quasi-crystal formation, in line with [48]. We stress that theories of crystallization solely based on translational ordering miss an important physical constraint coming from dense packing, which leads to bond orientational ordering for a system interacting with hard-core repulsions. Instead of going to the details, here we draw an intuitive physical picture, which may explain our observation.

We describe crystallization by two types of orderings: positional and bond orientational ordering. Now we consider the distribution of bonds joining a particle located at \mathbf{r} to its nearest neighbours. Expanding the density $\rho(\mathbf{r}, \omega)$ of points pierced by these bonds on a small sphere inscribed about \mathbf{r} , we have [46]

$$\rho(\mathbf{r}, \Omega) = \Sigma_{l=0}^{\infty} \Sigma_{m=-l}^{m=l} Q_{lm}(\mathbf{r}) Y_{lm}(\Omega), \quad (6)$$

where the $Y_{lm}(\Omega)$ are spherical harmonics. Densely packed spherical particles with the same size usually possess 12 nearest neighbours. So a natural bond orientational order should be associated with hcp, fcc, and icosahedral (ico) symmetries. As discussed above, the most important ones

are hcp and ico order. The hcp order is represented by a combination of Q_{6m} and Q_{4m} , whereas ico order is by Q_{6m} ordering (involving no Q_{4m} ordering).

Now we consider couplings between orderings of ρ and Q . The lowest order coupling between Q and ρ is given by the rotationally and translationally invariant energy. Up to the lowest order, ρ does not couple linearly to Q , and $\rho(\mathbf{q})\rho(-\mathbf{q})$ couples to it [48]. Consequently the equilibrium ρ need not have the symmetry of the equilibrium Q . This particular type of coupling leads to an asymmetric coupling between the orderings. If the translational ordering temperature T_ρ is higher than the bond orientational ordering temperature T_Q then, because the Q - ρ interaction is linear in Q , the ordering of ρ at T_i will necessarily induce an ordering in Q . On the other hand, if $T_Q > T_i$ then, because the Q - ρ interaction is quadratic in ρ , the ordering of Q at T_Q will have the effect of renormalizing the quadratic coupling without necessarily inducing an ordering of ρ . Jaric proposed that this case of $T_Q > T_\rho$ may correspond to quasi-crystal formation [48].

In our problem of crystallization, $T_\rho > T_Q$. However, due to a rather strong first order nature of liquid–solid transition, a system can enter into a long-lived metastable state, where a liquid–glass transition can take place. In this branch we may forget the ordering of ρ , even for $T < T_\rho$, until crystal nucleation starts. Because of the strong first order nature of the translational ordering, there is little growth of density fluctuations: there is almost no change in the positional correlation length. So the only remaining ordering is that of Q . There bond orientational ordering towards hcp and ico compete, which leads to frustration [7, 20, 21]. For simplicity, we consider the following free energy associated with bond orientational ordering Q :

$$F_Q = \int dr (a t Q^2 + I_3(Q) + O(Q^4) + \frac{1}{2} K (\nabla Q)^2) + \dots \quad (7)$$

where a is a positive constant, t is the reduced temperature $\tilde{t} = 1/\phi - 1/\phi_0^b$ (or $\tilde{t} = T - T_0^b$), and \dots represents frustration originating from competing bond orientational orderings (e.g., Q_6 versus Q_4) or random disorder effects. Here ϕ_0^b (or T_0^b) is the bare transition point. Even though the third order invariant I_3 is suggestive of the first order nature of the transition, the transition might be almost continuous. The situation may be similar to a liquid–cubic–liquid crystal transition [59], where low-energy Goldstone modes associated with the ordering may lead to large fluctuations and destroy the first order nature. Furthermore, frustration effects originating from competing Q_4 and Q_6 orderings and/or random disorder effects due to polydispersity may change the nature of the transition from a continuous (characteristic to a tensorial order parameter) to a discrete Ising symmetry (characteristic to a scalar order parameter). We speculate that renormalization of frustration effects changes the symmetry of the transition from the continuous to the discrete Ising symmetry and also shifts the critical point from T_0^b (or ϕ_0^b) to T_0 (or ϕ_0).

6.3. Difference in frustration effects on translational and bond orientational ordering

Translational order is rather easily destroyed by frustration effects, whereas bond orientational order is rather resistant

to them. This difference in the fragility against frustration between the two types of order can be understood by noting the following fact: by their definitions translational order is ‘global’ whereas bond orientational order is ‘local’. This difference makes evident the important roles of bond orientational ordering in crystallization, which are usually hidden behind crystallization, i.e., long-range translational ordering. As stressed above, bond orientational ordering stems from a constraint of dense packing. This may be a reason why it is rather resistant to the disorder effects of polydispersity. As long as the degree of the polydispersity is modest, the random disorder effects destroy only translational ordering, but bond orientational ordering may still survive, and may play a crucial role in a metastable supercooled liquid state.

7. Cooperative bond orientational ordering in a supercooled liquid

7.1. Critical-like behaviour

Critical-like behaviour of dynamic heterogeneity was first pointed out in seminal papers by Yamamoto and Onuki [63, 64]. They found that accumulated broken bonds in a certain time interval closely resemble the critical fluctuations of Ising systems. This conclusion was deduced from, e.g., the Ornstein–Zernike form of their structure factor and a dynamical scaling relation between the relaxation time and the correlation length. In this case, the critical-like behaviour was observed for a dynamic quantity.

We recently found that some glass-forming liquids exhibit critical-like behaviour of a ‘static’ structural quantity [7–13]. For example, our 3D hard-sphere-like (WCA) system exhibits Ising-like criticality of a hcp-like bond orientational order parameter, including the diverging correlation length $\xi_Q \sim t^{-\nu}$, where $t = (T - T_0)/T_0$ (or $t = (\phi_0 - \phi)/\phi$) and the diverging susceptibility $\chi_Q \sim t^{-\gamma}$, where $\nu = 0.63$ and $\gamma = 1.22$ for 3D [12]. At least apparently, such criticality towards ϕ_0 suggests its link to the liquid–glass transition. Since the range over which we can observe critical behaviour is rather narrow, it is also unclear whether the link is only apparent or essential. If such a link is essential to the glass transition, it indicates that the glass transition of a hard-sphere-like system is a consequence of a hypothetical thermodynamic transition occurring in a metastable state. Here it is worth noting that a hard-sphere-like system also suffers from frustration due to the tendency for local icosahedral ordering even for a monodisperse system. This may be viewed as competing orderings of Q_6 and Q_4 . As mentioned above, the hcp ordering can be viewed as cooperative ordering of Q_6 and Q_4 , whereas ico ordering is Q_6 ordering (without Q_4 ordering).

Although the very origin of critical-like behaviour observed in our system is still elusive, frustration effects on bond orientational ordering may be the origin of the Ising-like discrete symmetry of the critical behaviour [12]. However, this point needs further detailed study. In relation to this, it is worth mentioning other examples of the transformation from a continuous to a discrete Ising symmetry induced by frustration effects in spin systems [65, 66], implying the generality of

frustration and random disorder effects on the nature of the ordering.

7.2. Do the correlation length and the relaxation time really diverge?

Although we revealed hidden structural ordering in several model supercooled liquids [12, 13], there remain many open questions. For example, it is not clear at this moment whether ξ really diverges at T_0 (or ϕ_0) or not, which can never be checked practically. Some researchers proposed that there is no singularity above $T = 0$ K [67–69]. In relation to this, we should note that the validity of the VFT relation, or the presence of the singularity at a finite temperature, has been questioned [70, 71]. In our scenario, this problem may also be related to whether the ordering transition is second order, rounded, or weakly first order. We emphasize that the power-law divergence of ξ at least practically describes the observed change of ξ very well in the accessible ϕ (or T) regions. Since the ideal glass transition point T_0 is intrinsically an inaccessible critical point, further careful studies are necessary. We should also note that a physical mechanism which connects the diverging length and slow dynamics remains elusive. This problem lies at the heart of the origin of the glass transition.

In relation to the above, it may be worth mentioning the following point. We showed that MRCO has a distinct connection to dynamic heterogeneity. We can say that particles in higher MRCO regions are slower than those in lower MRCO regions. However, the opposite is not necessarily true. For example, in 2D spin liquids [7, 8], we found that particles of high MRCO having antiferromagnetic order (red particles in figure 2) have slower dynamics. However, locally favoured structures (blue pentagons in figure 2) also have slow dynamics. A similar situation may also be seen in hard sphere liquids. Particles in high hcp bond orientational order are slower, but particles in high icosahedral order are also slow. Thus, at this moment, it is not very clear whether the static correlation length and the structural relaxation time are coupled with each other until T_0 (or ϕ_0) or they are decoupled eventually.

7.3. Crossover between critical (low temperature) and non-critical (high temperature) behaviour

Here we consider a possible crossover between critical (low temperature) and non-critical (high temperature) behaviour. Our scenario of a hidden critical point at the ideal glass transition point ϕ_0 suggests that the glass transition volume fraction ϕ_g is located far below ϕ_0 . In other words, we cannot access the vicinity of the hypothetical critical point, which is markedly different from the situation of usual critical phenomena. This implies that we are almost always quite far from the critical point and the accessible reduced temperature t is rather large. Recently, we found for gas–liquid critical phenomena of a colloid–polymer mixture that the crossover of the correlation length from a critical to a non-critical, classical regime can be expressed by replacing the ordinary $t = (T - T_c)/T_c$ by $t = (T - T_c)/T$ (T_c : the critical point) [72]. This expression avoids an unphysical behaviour

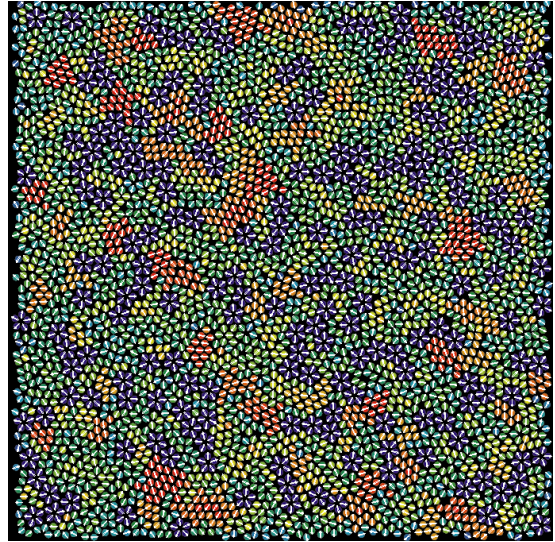


Figure 2. A typical structure of a supercooled 2D spin liquid [7]. Red particles have high MRCO (antiferromagnetic bond orientational order) and blue particles have local order with five-fold symmetry. These two types of order compete with each other and are the origin of frustration in this system. This situation may be similar to monodisperse hard spheres and metallic liquids [20, 21].

that $\xi \rightarrow 0$ for $T \rightarrow \infty$, and guarantees $\xi \rightarrow \xi_0$, where ξ_0 is the bare correlation length reflecting a characteristic length of microscopic interactions, for $T \rightarrow \infty$. This expression was also theoretically proposed for magnetic systems [73]. So we should be able to describe the crossover from a critical to a non-critical regime by replacing $t = (\phi_0 - \phi)/\phi$ by $t = (\phi_0 - \phi)/\phi_0$ in a natural manner. In hard sphere colloids, it is known that for $\phi \leq 0.45$ the relaxation time is almost independent of ϕ [26], which implies that there is no cooperativity for that ϕ range. For ordinary molecular liquids, this relation may describe a crossover from a high temperature Arrhenius to a low temperature super-Arrhenius behaviour. This point needs further studies. This crossover marks the onset of the criticality, which induces all sorts of characteristic glassy behaviours, such as dynamic heterogeneity and translational–rotational decoupling (the violation of the Stokes–Einstein relation).

7.4. Mapping between T and ϕ

The control parameter in colloidal systems is the volume fraction of colloids ϕ . Then it is often assumed that $1/\phi$ plays a similar role to T in molecular or atomic systems and is used as an effective temperature. This mapping was initiated in applying the mode-coupling theory to colloidal glassy systems. In such a case, we deal with a small parameter $\epsilon = (T - T_c)/T_c$ or $\epsilon = (\phi_c - \phi)/\phi$, as in critical phenomena. For $\epsilon \ll 1$ we may safely assume $T \propto 1/\phi$. Note that the mode-coupling T_c is located in a liquid regime and thus accessible. However, when we consider $t = (T - T_0)/T_0$ or $t = (\phi_0 - \phi)/\phi$ in glass transition, this parameter is usually not so small because of the intrinsic inaccessibility to T_0 or ϕ_0 , as discussed above. So the use of $1/\phi$ as an effective temperature cannot be justified on firm ground.

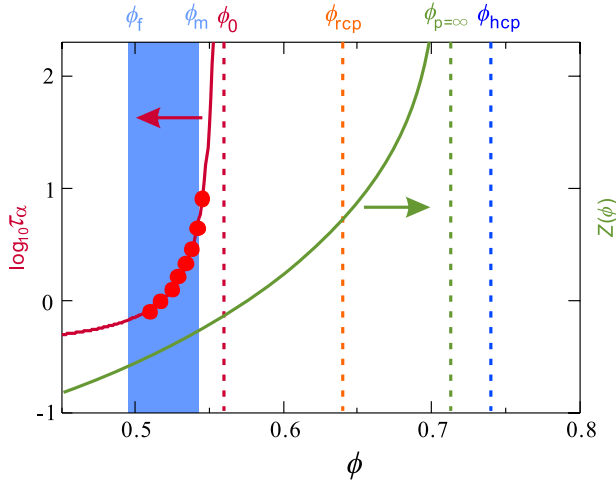


Figure 3. Key volume fractions for monodisperse hard-sphere-like liquids. Red points and lines are the ϕ dependence of τ_α for a monodisperse WCA liquid. The farthest left vertical red dashed line is ϕ_0 , where τ_α hypothetically diverges following the VFT relation. The green curve schematically represents the ϕ dependence of $Z(\phi)$. We speculate that it diverges at $\phi_{p=\infty}$, which may be located between $\phi_{rcp} \sim 0.64$ and the hexagonal close packing volume fraction $\phi_{hcp} \sim 0.74$ (see above). The volume fraction of freezing and melting points, ϕ_f and ϕ_m are also indicated.

This problem, which may be crucial, particularly for particles interacting with soft potentials [74, 75], was recently addressed by Berthier and Witten [74] and also by Xu *et al* [76]. It was proposed that the dimensionless control parameter is $T/p\sigma^3$, where σ is the particle diameter and p is the pressure, and thus the relevant parameter for colloids is $1/p$ rather than $1/\phi$. Berthier and Witten analysed the ϕ dependence of $Z(\phi) = p/\rho k_B T$ for hard spheres and harmonic spheres. It was found that the result is inconsistent with the free volume prediction $Z(\phi) = d/(1 - \phi/\phi^*)$, where d is the dimensionality and ϕ^* is the critical packing fraction, which is often called the random close packing fraction ϕ_{rcp} . Their result is not consistent with any power-law divergence at $\phi < 0.65$. We speculate that on noting that hard-sphere-like liquids have a tendency to have medium-range bond orientational order, the dynamic transition occurs at ϕ_0 , which is far below the diverging point of Z , $\phi_{p=\infty}$. The validity of this scenario needs to be checked carefully, including a detailed analysis of the dependence on the rate of densification. This ϕ dependence of $Z(\phi)$ has an important practical consequence: in the region of $0.51 < \phi < 0.65$ the ϕ dependence of $Z(\phi)$ can be rather well approximated by a relation like $Z(\phi) = a_0 + a_1\phi$ (a_0 and a_1 are constants). This range of ϕ we often use to study glassy dynamics of colloidal liquids. The above rather simple relation between Z and ϕ allows us to use $1/\phi$ as an effective temperature, at least approximately.

We stress that such an approximate relation crucially relies on a non-divergent increase of Z with an increase in ϕ , at least below $\phi = 0.65$. As schematically shown in figure 3, in our scenario, the hypothetical divergence of the structural relaxation time τ_α occurs at ϕ_0 (for a monodisperse system $\phi_0 = 0.56$) much lower than $\phi_{p=\infty}$, where the pressure diverges. Furthermore, the pressure divergence may

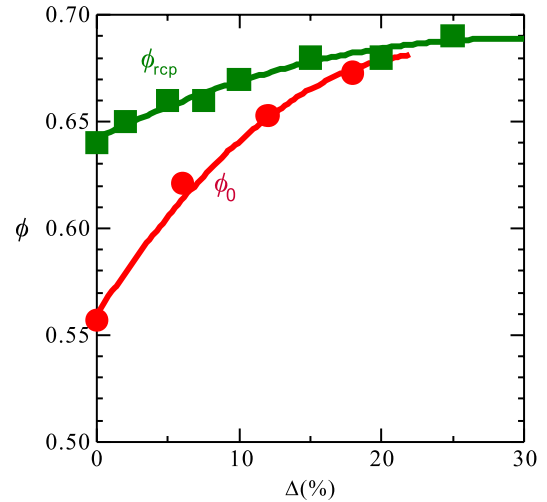


Figure 4. The dependence of ϕ_0 [13] and ϕ_{rcp} [77] on the polydispersity Δ .

also occur at a volume fraction higher than $\phi_{rcp} = 0.64$ because of a tendency of medium-range bond orientational ordering in a supercooled liquid. This is a consequence of the entropy maximization unique to a thermal system, which makes the glass transition distinct from the jamming transition in athermal systems (see also below).

7.5. Comparison between a thermal and an athermal system

The fact that particles tend to have hcp-like bond orientational order with an increase in the packing fraction ϕ seems not to be consistent with a scenario that the ideal glass state of hard spheres is linked to the random close packing (rcp) structure. To see this, in figure 4 we compare the ideal glass transition point ϕ_0 obtained from our analysis with ϕ_{rcp} estimated by Schaertl and Sillescu [77] for various degrees of polydispersity Δ . We can clearly see that ϕ_0 is always lower than ϕ_{rcp} and the difference between ϕ_0 and ϕ_{rcp} becomes smaller with an increase in Δ . For a monodisperse system, $\phi_0 \sim 0.56$ is significantly lower than ϕ_{rcp} or $\phi_{p=\infty}$. This seems to be inconsistent with a scenario that the ideal glass transition volume fraction ϕ_0 is associated with the volume fraction at which the pressure diverges, $\phi_{p=\infty}$ [78, 79], at least in 3D. This point needs further careful study, since the estimation of ϕ_0 for $\Delta = 0\%$ may involve a large error because of a large extrapolation: we cannot access a high ϕ region due to rapid crystallization. Our finding suggests that MRCO of hcp-like bond orientational order leads to a faster decrease of the configurational entropy than a system with a random structure upon densification. The distance ($\phi_{rcp} - \phi_0$) may be correlated with the degree of bond orientational order in a system. For $\Delta > 25\%$, $\phi_0 \sim \phi_{rcp}$ (see figure 4). This implies that the mechanism in which bond orientational ordering leads to a gain in the total entropy no longer works for such a large Δ , which indicates that the strong link between bond orientational order and mobility may be lost for a system of large Δ (see below).

We argue that the hypothetical ideal glass state is a state where the configurational entropy has vanished but

considerable correlational entropy still remains. In other words particles do not necessarily freeze there, unlike the state of random close packing, where particle positions are severely constrained geometrically (the nature of the isostatic jamming transition [79]). The importance of the entropic contribution may make the glass transition of a thermal system distinct from the jamming transition of an (undriven) athermal system (see also figure 3 and the related discussion), although a deep link might still remain between them [80]. This problem is also linked to the nature of ‘amorphous’ packings of hard spheres [78]. Our study suggests that packings in an amorphous state are not necessarily a perfectly random state (with exotic amorphous order) but possess bond orientational order for hard spheres as long as the polydispersity is not too large.

8. Dynamic heterogeneity and its link to bond orientational ordering

8.1. Origin of dynamic heterogeneity

Our simulation and experimental results both indicate that regions of high hcp order have slower dynamics than those of low hcp order. There is almost a one-to-one correspondence between the degree of high hcp order and the slowness of the particle dynamics [12, 13]. This is consistent with a physical picture in which a region of high hcp order has low configurational, but high correlational entropy, provided that the degree of configurational entropy is the measure of mobility [81]. A region of low hcp order has larger configurational entropy, which is manifested by the presence of voids (or defects) that allow local particle collective motion [12]. These void structures are characterized by a number of constraints smaller than that of the degrees of freedom and thus have also floppy modes that may contribute to the excess of the vibrational density of states [8].

Our study shows that in a hard-sphere-like system, dynamic heterogeneity has a structural, or thermodynamic, origin rather than a kinetic origin, at least in the range of the volume fraction studied. How general this is remains for future study, but we confirm a similar static origin of dynamic heterogeneity for a few different systems [12]. For weakly disordered systems, slow regions are characterized by high bond orientational order, which has a link to the bond orientational order of the equilibrium crystal structure. For strongly disordered systems, a local version of the structural entropy defined by the two-point density correlation, $s_2(\mathbf{r})$, turns out to be a good static (or structural) measure of dynamic heterogeneity. A similar conclusion was also derived by Krekelberg *et al* for a binary mixture of hard spheres (the size ratio = 1.3) [82]. We should note that this measure may generally be applied to a variety of systems, including polydisperse hard-sphere-like systems, although it does not provide us with detailed information on structural features. Immobile particles exhibit stronger average pair correlations to their neighbours than mobile particles. The spatial distribution of local s_2 should also be correlated with that of voids [12]. So the local number density of voids can be a general and

common measure of the local mobility of particles. It may be worth mentioning that we can make a connection between a stronger local positional correlation and slower dynamics there if we adopt the local version of mode-coupling theory. The above results seem to suggest that a liquid–glass transition is controlled by the part of the free energy of the system, but in a non-trivial manner. Its physical link to slow dynamics is not yet clear.

8.2. Roles of voids or defects in less ordered regions

Now we consider how particle mobility is coupled to the degree of bond orientational order from a more microscopic viewpoint. As described above, there is a one-to-one correspondence between the mobility and the degree of local disorder. For a 2D colloidal system, we apply the Delaunay triangulation to analyse a structure in real space [12] (see figure 5). This method was originally developed by Glaser and Clark [83] to study 2D melting of hard disks. We introduced a characteristic distance between neighbouring particles, beyond which a bond is regarded as broken. Then, bonds between neighbouring particles predominantly form triangles, but sometimes form squares, pentagons, ... At a high density, the population of polygons beyond pentagons is negligible. A region of high bond orientational order is mostly made by rather regular triangles, whose area is about equal to the average size of triangles of the system. On the other hand, in a region of low order, there are often squares, which are surrounded by triangles, whose area is smaller than the average. This defective structure (square), which is excited ‘thermally’ under a constraint of packing, has an extra free volume. We note that this method can naturally be extended to 3D structures.

The above observation leads to the following picture. Defects (or voids) are thermally excited in a supercooled liquid in a spatially and temporally correlated manner. Defects are anti-correlated with fluctuations of bond orientational order. This is very natural if one notes that both are related to the degree of particle packing: voids are a strong manifestation of the local violation of packing constraints, whereas bond orientational order is a consequence of packing constraints. A defect (or void) in a less ordered region dresses a high density compressed region around it, which compensates the density fluctuations. The existence of such a compressed region suggests that defects are elastically coupled with each other, which may also be related to the concept of cooperative rearrangement. This elastic interaction may lead to (irreversible) particle motion outside ordered regions: directional motion driven by self-induced stress fields. The number density of such defects monotonically decreases towards ϕ_0 in proportional to $(\phi_0 - \phi)$ [12] (see figure 5). This is again consistent with the hypothetical transition of bond orientational order occurring at ϕ_0 . Here we note that an alternative way to define defects and their roles in slow dynamics was discussed by Aharonov *et al* [84]. The decrease in these defects upon cooling or densification may be the origin of the slowing down of the dynamics towards ϕ_0 . Since an ordered region has few defects in it, there is basically

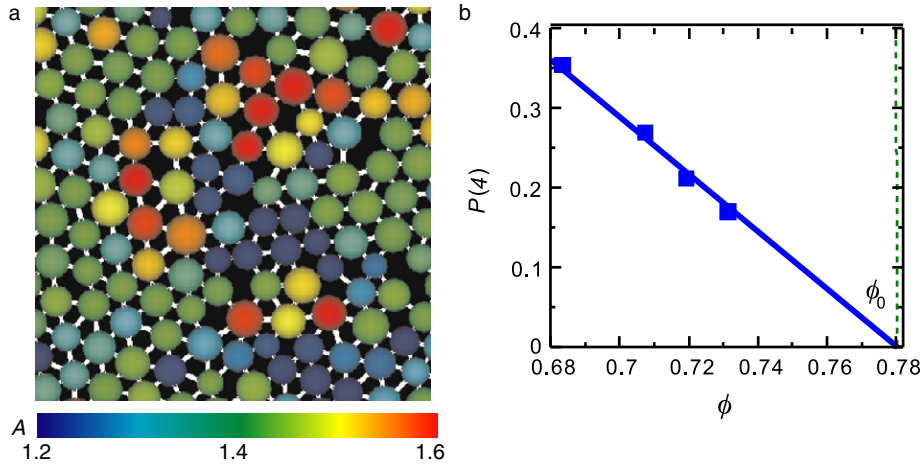


Figure 5. (a) Correlation of a local volume (area) per particle, A , calculated from the area of a Voronoi polygon to a tiling unit (triangles, squares, pentagons, . . .), or geometrical defects, for 2DPC. Geometrical defects, or voids (red particles), accompany densely packed triangles (blue particles) nearby, and thus density fluctuations are suppressed over a long range. See the colour bar for the meaning of the particle colour. (b) ϕ -dependence of the fraction of squares, $P(4)$ which are averaged over $10\tau_\alpha$ for each ϕ . Squares (geometrical defects) decrease, or transform to triangles, with an increase in ϕ and tend to completely disappear around ϕ_0 . We can see that $P(4) \propto (\phi_0 - \phi)$. Here we note that ϕ_0 is independently determined from the VFT fitting to τ_α .

little cage breaking motion in it. In this sense, an ordered region is rather free from mechanical stress and is in a relaxed state. This explains the correlation between the degree of bond orientational order, the degree of residual mechanical stress, and the degree of solidity (low mobility), which may be the origin of dynamic heterogeneity. Interestingly, the characteristic length scale of all these quantities is given by the correlation length ξ .

Finally we discuss the nature of a hypothetical ideal glass below T_0 . It may be a state of the absence of voids which leads to its nonergodicity. For 2D, thus, it may be a state tiled only by compact triangles. The long-range coherency of the directions of triangles may be absent because of frustration effects. This loss of the phase coherence of the complex hexatic bond orientational order parameter may be the origin of the Ising-like discrete symmetry of the transition.

8.3. Decoupling between structural relaxation and diffusion

Here we briefly discuss a consequence of dynamic heterogeneity, i.e., decoupling between structural relaxation τ_α and diffusion. In figure 6 we plot a scaled structural relaxation time $\tau_\alpha/\tau_\alpha^0$ and the inverse of a scaled diffusion constant D_0/D . The latter was taken from the paper by Zaccarelli *et al* [85]. Since both the structural relaxation time τ_α and the diffusion constant are difficult to measure for $\Delta = 0\%$ for a high volume fraction, because of interference by crystallization, the data are rather limited. Nevertheless, we can clearly see that $\tau_\alpha/\tau_\alpha^0$ increases much more steeply than D_0/D , which is a clear indication of the decoupling between structural relaxation (or viscosity) and diffusion: the violation of the Stokes–Einstein relation. The degree of decoupling becomes weaker with an increase in the degree of polydispersity Δ [86]. Since we merely compare results of different simulations here, however, a more detailed comparison is highly desirable. The Stokes–Einstein relation relies on $D = k_B T / (6\pi\eta a)$, where η is the viscosity and a

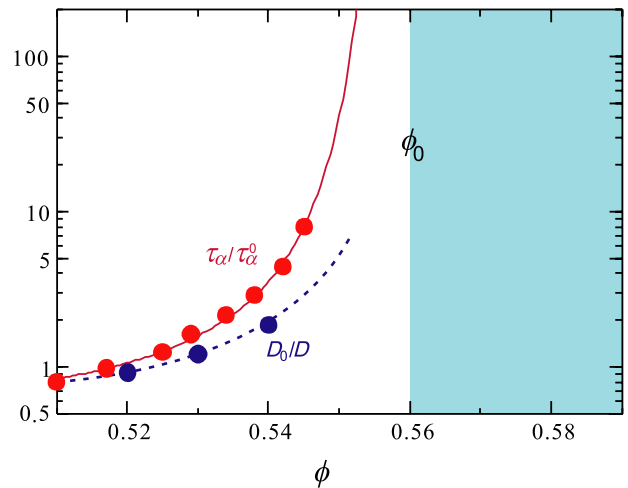


Figure 6. The relation between a scaled structural relaxation time, $\tau_\alpha/\tau_\alpha^0$, and the inverse of a scaled diffusion constant, D_0/D . The solid (red) curve is the VFT fitting to $\tau_\alpha/\tau_\alpha^0$ with $\phi_0 = 0.56$. The dashed (blue) curve is a guide to eye.

is the particle radius. We note that even this relation does not have a firm basis. The proportionality between η and τ_α is also assumed to compare τ_α and D . Such a decoupling is known to be associated with dynamic heterogeneity [1, 2, 77, 87].

Apparently, the structural relaxation time τ_α diverges long before the divergence of $1/D$ (although it is not clear whether these quantities really diverge or not). The diffusion constant has been known to apparently diverge at a relatively high volume fraction [88]. The above result for the violation of the Stokes–Einstein relation is a strong manifestation of the presence of a growing dynamic correlation length for monodisperse colloidal systems [18]. This decoupling is also suggested to be related to the resolution of the Kauzmann paradox [89]. This scenario was recently confirmed by

Saika-Voivod *et al* [90] for silica. Furthermore, the roles of dynamic heterogeneity in pattern evolution during crystal growth were also revealed [91, 92].

8.4. Link between dynamic heterogeneity and Debye–Waller factor

Slow regions with high hcp-like order are characterized by high correlational entropy, which should lead to a high Debye–Waller factor or a large Edwards–Anderson order parameter at an intermediate timescale just before the structural relaxation takes place [9]. This may also explain the finding of Widmer-Cooper and Harrowell on a negative correlation between the Debye–Waller factor and the propensity of motion [93–95]. The Debye–Waller factor is a measure of solidity. The increase of the Debye–Waller factor with an increase in ϕ or a decrease in T may reflect the development of structural order such as bond orientational ordering in a supercooled liquid [24]. It is also natural to expect that the (local) Debye–Waller factor is negatively correlated with the (local) number density of voids.

9. Link of bond orientational ordering (dynamic heterogeneity) to crystal nucleation

9.1. Enhanced crystal nucleation by critical-like structural fluctuations

A supercooled state of a hard-sphere-like liquid does not have a homogeneous random structure, contrary to common belief, but has transient MRCO with hcp-like bond orientational order. We showed [13, 18] that MRCO involves little density change and should not be regarded as pre-nuclei or small crystallites²: MRCO is an intrinsic structural feature of a supercooled state, which is also confirmed from the presence of MRCO even in a system of $\Delta > 7\%$, which never crystallizes in a simulation period (see also section 5). Furthermore, our result shows the important role of MRCO in crystallization [13, 18] (see figure 1). A crystal nucleus is formed by thermal fluctuations preferentially inside regions of high MRCO because of the following reason: nucleation in a region of high MRCO leads to a small free-energy gain upon crystal ordering, but more importantly decreases the crystal–liquid interfacial energy drastically, which in total results in a large decrease in the nucleation barrier, i.e., the enhancement of the nucleation probability. We note (see figure 1) that a crystal nucleus is almost perfectly embedded in a high MRCO region (coloured red), or perfectly wet to it. We stress that the roles of transient structural ordering (MRCO) in crystal nucleation have been overlooked so far. This preferential crystal nucleation in regions of high hcp bond orientational order [13, 18] may be consistent with the above described view that crystallization is a consequence of simultaneous translational and bond orientational ordering. Because of the rather strong first order nature of the translational ordering, a system easily becomes metastable against it, bond orientational ordering develops first after a temperature quench. Then translational ordering takes

place as nucleation by overcoming the barrier associated with the creation of a new interface, which is mainly associated with $|\nabla\rho|$ and $|\nabla\rho_q|$. Nucleation preferentially takes place in a region of high hcp order since the interfacial energy cost associated with $|\nabla Q|$ can be much lower there.

This can be viewed as wetting-induced crystal nucleation, which may further be interpreted as enhanced crystal nucleation (positional ordering) by critical fluctuations associated with bond orientational ordering at ϕ_0 . Such effects of critical fluctuations on crystal nucleation were originally proposed for crystallization in protein solutions [96]. We note that in protein solutions there often exists a critical point associated with phase separation between protein and water below the melting point of the crystal. Thus, near a critical point in the one-phase region, critical concentration fluctuations may enhance nucleation of protein crystals. So, if we adopt that glass transition accompanies critical-like fluctuations of bond orientational order, which diverge towards the hypothetical ideal glass transition point T_0 [7, 9, 11, 12], we can explain preferential nucleation of crystals in a region of high hcp order in a hard-sphere-like liquid within the same scenario, providing that bond orientational ordering is an important ingredient of crystallization.

Here we consider why the nucleation frequency predicted by the existing theories is much lower (by many orders of magnitude in certain conditions) than that observed experimentally for hard-sphere-like systems [45, 97–101]. In relation to this, we note that in various systems the classical nucleation theory often underestimates the crystal nucleation frequency by many orders of magnitude [102]. Recently Pusey *et al* [103] proposed that the above-mentioned discrepancy between experiments and simulations reported by Auer and Frenkel [97] can largely be removed by taking into account the fact that the experimental volume fractions are (inappropriately) calculated assuming freezing to occur at $\phi = 0.494$, which is the value for a system of $\Delta = 0\%$ and should be replaced by 0.508 for the system of $\Delta = 5\%$ used in the experiments. This certainly reduces the discrepancy, but the ϕ -dependence of the nucleation frequency is still much steeper for simulations than for experiments.

Recently we showed that the crystal nucleation frequency estimated by brute-force Brownian dynamics simulations of monodisperse WCA particles is much higher than the prediction of Auer and Frenkel for monodisperse hard spheres [97]. Very recently, however, Filion *et al* [104] confirmed the results obtained by Auer and Frenkel by a few different methods, including brute-force event-driven MD simulations of hard spheres with the NPT ensemble. Since brute-force MD simulations are expected to contain effects of bond orientational ordering automatically, the origin of the discrepancy may not necessarily be related to the enhancement of crystal nucleation by pre-existing hcp-like order. We use NVT ensemble [13, 18], BD simulations, and WCA particles, whereas Auer and Frenkel [97] and Filion *et al* [104] employed NPT ensemble, event-driven MD, and the hard sphere potential. Thus, the possible causes of the difference may be NPT or NVT, event-driven MD or BD, or the hard sphere potential or the WCA potential. Concerning

² However, this issue might be a matter of the definition of pre-nuclei.

the interaction potential, we previously confirmed that the results of driven granular hard spheres [11] match those of BD simulations of WCA particles well [9], after making a size correction for WCA particles: we regarded the diameter at which the potential is equal to $k_B T$ as the effective diameter. This value is consistent with an effective particle diameter for the WCA particle, $\sigma_e = 2^{1/6}/(1 + \sqrt{T})^{1/6}$, proposed by Heyes and Okumura [105], which leads to the collapse of the compressibility factor for several isotherms. We also confirm that ϕ_f of our WCA particles after the size correction is about 0.498, which is reasonably close to the values for hard spheres, $\phi_f = 0.494$. Whether we can regard WCA particles after the size correction as hard spheres still needs to be checked more carefully. For example, there remains a possibility that although the phase behaviour is not so different between WCA and hard spheres the crystal nucleation barrier is significantly different between them. In relation to this, it may be worth mentioning that Auer and Frenkel showed that the introduction of weak repulsive interactions due to surface charges on colloid surfaces leads to a drastic increase in the crystal nucleation rate [106]. There is also a possibility that the difference in the ensemble between NVT and NPT may lead to a difference in the kinetic pathway of crystallization. In NVT the (osmotic) pressure in the supercooled liquid branch decreases towards the coexistence pressure upon crystallization, whereas in NPT the pressure is kept constant. At this moment we do not have any clear answer to explain the above-mentioned discrepancy. We are now studying possible origins of the discrepancy.

Recently Pusey *et al* [85, 103] confirmed an interesting kinetic route to crystals at high ϕ [107], which only requires a small rearrangement of the particle positions for crystallization to take place. We speculate that this mode of crystallization may be related to the novel kinetic pathway of crystal nucleation we found [13, 18], i.e., preferential positional ordering in a region already having high hcp-like bond orientational order, since it should not require large rearrangement of particles: densification and repulsive interactions may automatically lead to crystal nucleation since there is already a hcp-like bond orientational order. This mode may particularly be important where there is a high degree of supercooling.

9.2. Relation to other numerical works suggesting two-step-like crystallization

Here we mention other works which are related to our claim that MRCO plays a significant role in crystal nucleation. Recently van Megen [26] pointed out a possible link between dynamic heterogeneity (immobile clusters) and crystallization on the basis of their detailed study of crystallization processes by light scattering measurements. van Megen *et al* [27, 28] also recently found that there is an essential difference in the dynamics below and above ϕ_f . As ϕ is increased from ϕ_f , a partial arrest of the number density fluctuations spreads from the position of the main structure factor peak to other wavevectors. The resistance to flow increases not just because density fluctuations become slower, as for a system in thermodynamic equilibrium, but also because of a decrease

in the number of spatial modes by which thermal energy can dissipate. For $\phi > \phi_f$, there are structural impediments to the diffusive momentum currents by which the particles dissipate their instantaneous thermal energy. They also suggest that these features are associated with the intrinsically irreversible nature of a metastable supercooled state. Although our scenario does not predict that an essential change takes place exactly at ϕ_f , the correlation length ξ and the structural relaxation time τ_α (see figure 3) start to increase steeply around ϕ_f , and we speculate that the characteristics found by van Megen *et al* may be explained by bond orientational ordering in a metastable supercooled liquid: bond orientational order causes the resistance to flow and acts as a structural impediment to the diffusional momentum currents.

It was suggested on the basis of colloidal experiments that a crystallization process consists of two steps [108]. Following this observation, Schilling *et al* [109] observed that some precursors appear before crystallization in simulations. They reported that the precursors have a higher density than a supercooled liquid, unlike our MRCO. Further detailed study on the elementary process of crystal nucleation and its link to dynamic heterogeneity would be highly desirable.

9.3. Spatial correlation in nucleation events

Because of the conserved nature of the number density of colloidal particles, crystal nucleation necessarily accompanies depletion of colloidal particles around crystal nuclei. This itself can lead to some spatial correlation between nucleation events if the crystal nucleation rate is enough high. Furthermore, since the bond orientational order parameters have spatial correlation characteristic of critical fluctuations, whose correlation length is given by ξ , this may also lead to the spatial correlation of crystal nuclei. If crystal nucleation is completely random, the resulting point pattern should be a Poisson pattern and its structure factor may not produce a distinct peak at a finite wavenumber because of the absence of the spatial correlation of crystal nucleation events. Thus we believe that bond orientational ordering also plays a crucial role in producing the spatial correlation. Schätzel and Ackerson [110] showed that the scattering peak exhibits a distinct low q peak, which indicates the spatial correlation of the position of crystal nuclei. Their finding is consistent with the above scenario that (i) crystal nucleation selectively takes place in regions of high hcp order, which have spatial correlation, or (ii) it is spatially correlated because of the conserved nature of the density order parameter under a constraint of the constant volume of the system and a high nucleation rate helped by bond orientational order.

10. Summary

Here we proposed that crystallization in a three-dimensional hard-sphere-like system is controlled not only by positional (density) ordering, but also by bond orientational ordering. This may generally be true for other systems. In a metastable supercooled state before the first order positional ordering, i.e., crystallization, takes place, a system tends to have bond

orientational order, which has spatio-temporal fluctuations reminiscent of critical fluctuations. For a hard-sphere-like system, medium-range bond orientational order has a symmetry of hcp-like order, which may be preferred by the correlational entropy under a constraint of dense packing. Because of the same reason, icosahedral order also develops with an increase in the volume fraction, but it cannot grow in the size, unlike hcp-type order, because of the internal geometrical frustration. It may tend to align with mirror-related orientational correlation, as discussed by Tomida and Egami [111], although this remains to be checked. This icosahedral ordering may act as impurities against hcp-like bond orientational ordering, which may change the symmetry of the phase transition from a continuous to a discrete Ising (Z_2) symmetry [12]. This situation may be very similar to that in metallic glass-formers [7, 8, 20, 21], along the lines of Frank's original argument [31]. Here we emphasize that the major ordering in hard-sphere-like systems may be hcp type and not icosahedral type. We speculate that the same scenario of competing orderings applies to other glass-forming liquids [14–16, 22].

This physical picture implies that a supercooled liquid state of a hard-sphere-like system which suffers from rather weak frustration effects against crystallization tends to have hcp-like bond orientational ordering accompanying critical-like fluctuations, which may be the origin of dynamic heterogeneity. After a quench from an equilibrium liquid state, crystal nucleation takes place according to the following sequence [18]: (i) initial homogeneous equilibrium liquid \rightarrow (ii) 'inhomogeneous' supercooled liquid with bond orientational order \rightarrow (iii) intermediate ordered phase [52, 112–114] \rightarrow (iv) final crystalline phase. In the conventional scenario, step (ii) is replaced by 'homogeneous disordered supercooled liquid'. Our finding may fundamentally alter the conventional picture of the state of liquid, in which a (supercooled) liquid is spatially homogeneous and possesses no structural order (at most short-range order). Since Ostwald's seminal argument, intermediate states between the initial liquid and the final crystal state has been sought from the crystal side [52, 112–114]. However, our study demonstrates that it is equally important to consider hidden ordering in a supercooled liquid. This may be regarded as an intermediate state formed from the liquid side.

We also note that the initial crystal has an hcp structure, but the structure gradually changes to a more fcc structure. This nucleation process may be viewed as 'heterogeneous nucleation', although it is usually categorized as homogeneous nucleation. This is a manifestation of the importance of bond orientational order in crystallization.

We stress that bond orientational order is an intrinsic consequence of dense packing for hard-sphere-like systems. Because of this nature, the degree of bond orientational order should be anti-correlated with the number density of voids, which may be regarded as free volume. Voids elastically interact with each other, which may induce spontaneous collective particle motion in regions of low order.

Such bond orientational order may be destroyed under strong frustration (e.g., for binary mixtures of particles whose

size ratio is ~ 1.4). Even in such a case, there may exist structural signatures linked to dynamic heterogeneity [12], which should be linked to the spatial distribution of voids. However, the link is much more subtle and further careful studies are necessary to elucidate the origin of dynamic heterogeneity in such systems.

At this time, it is not easy to clarify how bond orientational ordering, its correlation length, correlated voids, and the free volume associated with voids are related to slow dynamics in a quantitative manner. This is central to the origin of glassy dynamics. We hope that structural fluctuations in a supercooled liquid and its link to bond orientational ordering and crystallization will provide us with a new route to understand crystallization, vitrification, and the link between them.

Finally, we note that the importance of bond orientational ordering in a liquid is not limited to the problems of crystallization, quasi-crystal formation, and vitrification, upon which we have concentrated in this paper. The fact that we need at least two order parameters (density and bond orientational order parameter) to describe the state of a liquid is also crucial for understanding the thermodynamic and kinetic anomaly of water-type liquids [49, 50, 115, 116] as well as liquid–liquid transitions [117, 118], which may be characteristic of liquids with directional bondings (e.g., covalent and hydrogen bonding). It is highly desirable to develop a theory which describes, in a unified manner, the state of liquids ranging from hard spheres to a liquid such as water, as well as phenomena including crystallization, quasi-crystal formation, liquid–glass transitions, water-like anomalies, and liquid–liquid transitions.

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