

# Role of many-body correlation in slow dynamics of glass-forming liquids: intrinsic or perturbative

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**Abstract.** Upon cooling or densification, a supercooled liquid shows drastic slowing down toward its glass-transition point. The physical mechanism behind this slow glassy dynamics has been a matter of discussion for a long time, but there has still been no consensus on its origin. Recently, we have found that for systems mainly interacting with steric repulsions, glassy structural order (or, angular order) generally develops upon cooling and its correlation length,  $\xi$ , grows as  $\xi = \xi_0[(T - T_0)/T_0]^{-2/d}$  ( $\xi_0$  is the bare correlation length,  $T$  is the temperature,  $T_0$  is the hypothetical ideal glass transition, and  $d$  is the spatial dimensionality). This ordering is difficult to detect by two-body density correlation since it is a consequence of sterically-induced (entropically-driven) many-body correlation that lowers local free energy. Interestingly, the power-law growth of  $\xi$  with the exponent of  $2/d$  is reminiscent of the Ising criticality. We also find that the structural relaxation time  $\tau_\alpha$  diverges as  $\tau_\alpha = \tau_\alpha^0 \exp(K\xi^{d/2}/k_B T)$  ( $\tau_\alpha^0$ : the microscopic relaxation time,  $K$  is a fragility index,  $k_B$  is the Boltzmann constant), suggesting that glass transition is a consequence of Ising-like criticality with growing activation energy. Unlike ordinary critical phenomena, the activation energy of particle motion increases in proportion to the root of the correlation volume of  $\xi^d$ , implying that the particle motion is strongly correlated in that volume. This relation indicates that the impact of spatial fluctuations of the order parameter on slow dynamics is not perturbative but intrinsic. Although we need further study to confirm our claim, we hope that the discussion in this article would provide a good starting point for further consideration of the physical nature of glass transition.

**Keywords:** dynamical heterogeneities, glasses (colloidal, polymer, etc), glasses (structural), slow relaxation, glassy dynamics, aging

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## 1. Introduction

Glass transition takes place upon cooling or densification whenever crystallization is avoided. Liquid-crystal transition, or crystallization, is the most fundamental phase transition that takes place in any liquids upon cooling if the cooling speed is slow

enough. The critical fact is that both crystallization and vitrification take place for the same Hamiltonian, and the bifurcation is introduced only by the kinetic factor. This fact has not been taken seriously, and thus, most of the existing theories of glass transition have been developed independently from crystallization, focusing only on the vitrification branch. Our fundamental standpoint is that the theories of crystallization and vitrification should be developed on the same ground [1–5]. Thus, our approach is based on thermodynamics. Here it should be noted that there are also theories of glass transition purely based on the kinetic aspect [6–8].

Since crystallization is easier to understand compared to vitrification, we first consider the crystallization branch. In the liquid phase, the density  $\rho$  is spatially homogeneous and only weakly fluctuating around its average  $\langle \rho(\vec{r}) \rangle$  due to the finite compressibility. In contrast, in the crystalline state, the density periodically oscillates with a Fourier series expansion in terms of reciprocal lattice vectors  $\vec{G}$ , reflecting the long-range translational order [9]:

$$\langle \delta \rho(\vec{r}) \rangle = \langle \rho(\vec{r}) \rangle - \rho_0 = \sum_{\vec{G}} \rho_{\vec{G}} \exp(i\vec{G} \cdot \vec{r}), \quad (1)$$

where  $\rho_0$  is the average density and the vectors  $\vec{G}$  represent the relevant reciprocal lattice of the crystal. Since  $\langle \rho(\vec{r}) \rangle$  must be a real quantity, it must satisfy the relation  $\rho_{\vec{G}}^* = \rho_{-\vec{G}}$ . The critical feature distinguishing the liquid and solid phases is translational (or, positional) order with periodic spatial modulations.

The density fluctuations in the liquid phase, which grow weakly reflecting thermodynamic instability towards the crystal, have a maximum at non-zero wavenumber. Accordingly, the static structure factor of a liquid,  $S(k)$ , has a distinct peak at a wavenumber of  $k_0 = 2\pi/\ell$ , where  $\ell$  is the average interatomic distance. As the temperature  $T$  is lowered towards the freezing point, the magnitude of  $S(k_0)$  increases. Thus, the key wave number characterizing the liquid structure is  $k_0$ . Even with this simplification, an appropriate set of lattice vectors  $\vec{G}$  associated with the crystal from the liquid still has to be selected upon crystal nucleation. That is, the free energy must be minimized for  $\rho_{\vec{G}}$  among all possible lattice candidates. It is a complicated task to find such a set of lattice vectors, but a plausible answer was derived by Alexander and McTague [10].

Although this type of approach to liquid-solid transition, focusing on translational ordering, ‘apparently’ looks very natural, we point out that there remains a very fundamental question: What is the role of orientational ordering in crystallization? For two-dimensional (2D) hard disks, it has been widely accepted that liquid-to-solid transition sequentially takes place in the order of hexatic ordering and translational ordering upon densification. This phenomenon is known as the Kosteritz–Thouless–Halperin–Nelson–Young (KTHNY) scenario [11]. Here we note that it was recently shown convincingly that the first liquid-to-hexatic transition is weakly of first order [12]. Bond orientational order, or hexatic order, can be expressed by the distribution of bonds joining a particle located at  $\vec{r}$  to its nearest neighbors [11]. Expanding the density  $\rho(\vec{r}, \omega)$  of points pierced by these bonds on a small sphere inscribed about  $\vec{r}$ , we have [11]

$$\rho(\vec{r}, \Omega) = \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} Q_{lm}(\vec{r}) Y_{lm}(\Omega), \quad (2)$$

where  $Y_{lm}(\Omega)$  are spherical harmonics.

We stress that the origin of bond orientational ordering is fundamentally different from that of translational ordering. We need at least three-body correlation to define orientational (or, angular) order, and thus, it intrinsically has many-body nature. In contrast, positional (or, distance) order can be described by two-body correlation. The bond orientational ordering originates from the geometrical constraint due to dense packing of disks (or spheres), which primarily interact with steric repulsions. We may say that this ordering is induced entropically (note that we may consider that the free energy of hard spheres consists only of entropy). For 2D hard disk systems, the most probable number of nearest neighbor particles under dense packing is six, and thus the relevant bond orientational order is represented by a hexatic order parameter. This example tells us that bond orientational order should always play an essential role in a densely packed liquid state, in which crystallization or vitrification usually takes place, provided that the particle size distribution is reasonably small.

The bond orientational ordering of hard-sphere-like systems is driven by steric repulsions (or, entropically) and accompanied by the loss of local configurational entropy of the neighboring particles. Thus, it is natural to expect that its significance decreases with an increase in the spatial dimensionality  $d$ . For  $d=2$ , the number of nearest neighbors under dense packing is 6, but for  $d=3$ , it increases to 12. For  $d=\infty$ , it becomes infinity. This fact means that the loss of the configurational entropy upon the formation of the angular order of neighboring particles steeply increases with an increase in  $d$  [13–15] and eventually exceeds the gain of vibrational entropy obtained by forming a configuration of high packing capability. This tendency makes crystallization more difficult at higher dimensions [14]. Since the liquid density is homogeneous and its fluctuation is controlled by the compressibility, a configuration of high packing capability means a large room for particle vibrations, leading to the gain of vibrational entropy. So the critical question is at which dimension  $d_c$  the loss of the configurational entropy prevails the gain of vibrational entropy. From the  $d$ -dependence of the configurational entropy, we conclude that at least  $d_c \geq 4$ . Thus, for  $d \leq 3$ , angular ordering should play a crucial role in determining the structure of a supercooled liquid. For  $d=3$ , it is established that the density functional theory does an excellent job for an equilibrium liquid, indicating that angular ordering may play a crucial role only in a supercooled liquid state. It is consistent with what we found for hard-sphere-like liquids [16, 17]: the static correlation length of bond orientational order,  $\xi$ , exceeds the particle size only in a supercooled state above the freezing volume fraction  $\phi_f \sim 0.494$ .

Here we emphasize that the angular ordering, or bond orientational ordering, in a supercooled liquid is a consequence of many-body steric repulsions since it is induced to increase the local packing capability, which cannot be detected by the two-body density correlation. We can easily understand this fact from that we need three particles to define an angle, whereas only two to define a distance. Thus, this type of order cannot be detected by the two-body density correlator, such as  $S(k)$  and the radial distribution function  $g(r)$ . Here it is worth noting that there is often a splitting of the second peak of  $g(r)$  (see, e.g. [16–19]), which is a consequence of many-body correlation. However, we cannot infer what kind of order forms, from  $g(r)$  alone, because of the intrinsic information loss upon the dimensional reduction from  $d$  to 1. Concerning the above point, it is worth noting that the mean-field theories of glass transition such as the mode-coupling theory [20] and the random first-order transition (RFOT) theory

[21–27] are constructed based on the two-point density correlation, or translational order. Although this approximation becomes exact in the limit of infinite dimensions  $d = \infty$ , their validity to realistic systems ( $d = 2$  and  $3$ ) is questionable, and thus, needs to be carefully examined.

In this article, we consider the role of many-body correlation in slow dynamics of glass-forming liquids and argue that the impact of the resulting structural fluctuations on the dynamics of a liquid is not perturbative, but intrinsic.

## 2. Nature of frustration in glass transition

The importance of frustration in glass transition has been recognized for a long time, particularly in connection to spin glass. However, the physical meaning of frustration has to be considered carefully. Here we discuss what the origin of frustration relevant for glass transition is.

### 2.1. Approach based on frustration of the single order parameter

In his seminal paper, Frank noticed that icosahedral structures are ‘locally’ more favored than crystal structures for Lennard-Jones liquids. Since icosahedral ordering intrinsically suffers from the geometrical frustration, the importance of this type of ‘internal’ frustration has attracted considerable attention, in analogy to the frustration in a spin system leading to spin glass. Steinhardt *et al* [28] proposed a theory of glass transition, based on the internal frustration of the bond orientational order parameter  $Q_6$ , which represents icosahedral ordering. Along the same line, Tarjus *et al* [29] proposed the frustration-limited domain theory, in which the critical point of the ordering transition is avoided by frustration. The idea based on such internal frustration of the single order parameter, or spin-glass physics, has been developed into the random first-order transition (RFOT) theory, which is currently one of the most popular theories of glass transition [21–27]. It should be mentioned that this theory has been shown to have a fundamental link to the density functional theory [30], on which the mode-coupling theory [20] is based.

### 2.2. Our approach based on frustration against crystallization, or competing ordering

The above approach assumes that the source of frustration in a supercooled liquid free from quenched disorder is the internal frustration of a glassy order parameter itself. This view may be a consequence that people put focus only on the liquid branch and put the crystallization branch out of consideration (i.e. assume ‘purely’ kinetic avoidance of crystallization).

As we stressed in the above, we believe that the significant frustration leading to glass transition is against crystallization. This idea is quite natural on noting that if we can avoid crystallization, any system vitrifies upon cooling or densification. So, we regard crystallization as the main ordering and identify the tendency of local structural ordering incompatible to the crystalline order as the source of frustration against crystallization. This is the fundamental spirit of our two-order-parameter model

[1–5, 31–33]. The source of frustration can be energetic [34] and/or geometrical (e.g. polydispersity and binalization) [16, 18]. Hereafter we describe our scenario of glass transition based on this physical picture.

### 3. Role of many-body correlation in crystallization

First, we briefly review what we have found on the role of many-body correlation in crystallization so far. We found for monodisperse hard spheres that in a supercooled state the bond orientational order coarse-grained up to the neighbors [35],  $Q_6$ , which is linked to fcc and hcp crystals, grows with an increase in the degree of supercooling, or the volume fraction  $\phi$  [36]: the correlation length of  $Q_6$ ,  $\xi_6$ , is found to increase as  $\xi_6 = \xi_6^0 [(\phi_0 - \phi)/\phi]^{-2/d}$  ( $\xi_6^0$  is the bare correlation length,  $\phi_0$  is the hypothetical ideal glass-transition volume fraction) and the structural relaxation time  $\tau_\alpha$  diverges as  $\tau_\alpha = \tau_\alpha^0 \exp(K\xi_6^{d/2}/k_B T)$  ( $\tau_\alpha^0$ : the microscopic relaxation time,  $K$  is the fragility index,  $k_B$  is the Boltzmann constant, and  $T$  is the temperature). As will be described later, we found the same relations for polydisperse [16–19] and bidisperse hard-sphere-like systems [37, 38], which vitrify instead crystallize upon densification. Interestingly, the glassy slowing down and the growth of structural order is most prominent for the monodisperse system with the weakest frustration. Here it is worth noting that even for monodisperse systems, icosahedral structures are formed, which is the source of frustration against crystallization. However, the amount of the icosahedral structures is smaller than that of polydisperse systems [39]. We note that the growth of crystal-like angular order is strongest for monodisperse systems, because of both the absence of geometrical frustration originating from the particle-size distribution and the smallest fluctuations of the number of nearest neighbors.

When the angular order developing in a supercooled liquid shares the same rotational symmetry as the equilibrium crystals, it lowers the free energy barrier for crystal nucleation and thus promotes crystal nucleation [36, 40, 41]. We indeed found that crystal nucleation always takes place in pre-ordered regions with high crystal-like orientational order. Later, it was proven that this is exclusively due to the reduction of the interfacial tension  $\gamma$  due to the symmetry matching [42]. As mentioned above, even in monodisperse hard spheres, icosahedral order also forms spontaneously [43, 44], but because of its intrinsic internal geometrical frustration, its correlation length never grows [45]. It acts as a source of frustration against crystallization, but its effect is not strong enough to prevent crystallization for monodisperse hard spheres.

Here we note that the local version of the bond orientational order parameter of a particle,  $q_6$ , is sensitive to both crystal and icosahedral symmetries. However, the one coarse-grained up to its neighbors,  $Q_6$ , is sensitive to crystal-like symmetries but not to icosahedral order because icosahedral order cannot extend beyond its neighbors due to the internal geometrical frustration. This leads to the growth of the correlation length upon cooling for  $Q_6$  [16, 17], but not for  $q_6$  [46] because of spatially random distribution of icosahedral clusters [45]. This difference between  $Q_6$  and  $q_6$  leads to opposite conclusions on the role of the structural order in the slow glassy dynamics: the structural analysis using  $Q_6$  indicates the growth of structural order in a supercooled state upon

densification [16, 17], whereas the one using  $q_6$  suggests little growth [46]. This example tells us that we need special care on the choice of the structural order parameter to detect glassy structural order responsible for slow dynamics [35].

#### 4. Role of many-body correlation in the glass-forming ability

The glass-forming ability is, by definition, linked to the ease of crystallization, and both are determined by the free-energy barrier for crystal nucleation  $\Delta G$ . According to the classical nucleation theory [47],  $\beta\Delta G \propto (\beta\gamma)^3/(\beta\delta\mu)^2$  ( $\beta = 1/k_B T$ ) for  $d = 3$ . We use the interfacial tension  $\gamma$  and the chemical-potential difference between the crystal and the liquid,  $\delta\mu$ , scaled by the thermal energy  $k_B T$  in the above expression of  $\beta\Delta G$ . It is because the physical factors competing in the adimensional free energy difference  $\beta\Delta G$  is  $\beta\gamma$  and  $\beta\delta\mu$ , and not the bare  $\gamma$  and  $\delta\mu$ . In other words, these quantities should be considered relative to the available thermal energy  $k_B T$ . On the details of the justification of this claim, please refer to our original paper [42].

We found that the glass-forming ability is controlled predominantly by  $\beta\gamma$  for two systems, a liquid with tunable tetrahedrality and a binary mixture of hard disks, in which the glass-forming ability is maximized around the melting-point minimum as a function of tetrahedrality and composition, respectively [42]. We correlated the increase of  $\beta\gamma$  negatively with the degree of angular order linked to crystalline orders in a supercooled-liquid state: if the supercooled liquid tends to have angular orders similar to those of crystals,  $\beta\gamma$  is small, and thus the barrier to crystal nucleation is low, leading to the poor glass-forming ability. In contrast, if it does not have angular orders similar to crystals, or has random disordered structures,  $\beta\gamma$  becomes large, and thus the barrier also becomes high, leading to the high glass-forming ability. We note that the degree of crystalline order developed in a supercooled liquid state is negatively correlated with the configurational entropy of the liquid [42].

The above result can also be naturally understood in the two-order-parameter model [4] from the following general relation between  $\beta\gamma$  and the order parameter gradients:

$$\beta\gamma = \int dx \left[ \frac{1}{2} K_\rho \left( \frac{\partial \rho}{\partial x} \right)^2 + \frac{1}{2} K_Q \left( \frac{\partial Q}{\partial x} \right)^2 \right], \quad (3)$$

where  $\rho$  and  $Q$  are the density and structural order parameters, respectively,  $x$  is the coordinate perpendicular to the interface, and  $K_\rho$  and  $K_Q$  are positive coefficients associated with the free-energy cost due to the spatial gradients of  $\rho$  and  $Q$ , respectively. Our result also clearly indicates the crucial impact of orientational ordering developed in a supercooled liquid on crystallization: we cannot explain the behavior of  $\beta\gamma$  by a density change across the interface alone. The above scenario of glass-forming ability can also explain the experimental results on the glass-forming ability of aqueous salt solutions naturally [48, 49].

Our physical picture leads to a simple, yet appealing scenario of the glass-forming ability of liquids [42]: if angular orders similar to those of equilibrium crystals are developed in a supercooled state, the glass-forming ability is low; otherwise, high. We speculate that this scenario may be universally valid to any system, which is supported

by the fact that for many systems, the glass-forming ability is maximized around the melting-point minimum. However, this is not always a case. For example, for some metallic glass formers, the glass-forming ability is not maximized around the melting-point minimum, i.e. a deep eutectic point. In the two examples mentioned above, we consider the case in which the primary source of frustration is the competition between different types of crystalline orders. Some metallic glass formers are known to tend to form icosahedral order upon cooling, which can also act as the source of frustration against crystallization. In such a case, we should take this ordering into account in addition to crystalline orderings [50, 51]. For a system tending to form icosahedral order, if the tendency is not too strong, icosahedral ordering tends to prevent crystallization, but if it is too strong, it may even lead to the formation of quasi-crystals and some of the Frank–Kasper (FK) phases [4, 50, 51].

We can also explain by this scenario why water is a poor glass former, but silica is a good glass former despite that both tend to have similar tetrahedral orientational ordering [52]. We found that water’s tetrahedral order is much more regular than silica’s one. This difference reflects the difference in the stability of the elementary structure between  $\text{H}_2\text{O}$  and  $\text{SiO}_2$ . The molecular structure of  $\text{H}_2\text{O}$  is rigid, and the fluctuation of the H–O–H angle (close to the tetrahedral angle) is small since it is stabilized by covalent bonding that is far stronger than hydrogen bonding forming tetrahedral order. This feature leads to a high tetrahedral order. In contrast, the structure of  $\text{SiO}_2$  is much more flexible, and the fluctuation of the O–Si–O angle is more substantial since it is stabilized by the same type of interactions of covalent and ionic nature, which lead to tetrahedral order. Thus, the local tetrahedral structure of liquid water is much more regular and thus closer to the crystal structure compared to that of silica. This difference in the regularity of tetrahedral order also leads to the difference in the liquid-state anomalies. Please see [52] on the details.

These studies unambiguously demonstrate the existence of a deep intrinsic link between crystallization and vitrification, which can be characterized by the degree of frustration between crystal structures and low-free-energy structural motifs spontaneously formed in liquid. These findings support our claim that vitrification should not be discussed independently from crystallization. Thus, we should pay special attention to this link when developing a theory of glass transition [4, 34]. The link is of significant importance to understand the physics behind the glass-forming ability, which is crucial in the fields of pharmaceuticals, metallic glasses, and phase-change materials.

## 5. Role of many-body correlation in slow dynamics near glass transition

### 5.1. General growth of static structural order when approaching glass transition

Now we consider a central question on the very origin of slow dynamics near the glass-transition point [23, 53, 54]. We studied this problem based on the expectation that glass transition should have a link to crystallization, particularly for a system where the degree of frustration against crystallization is rather weak. As such systems, we studied model systems for which we can control the degree of frustration against crystallization in a systematic manner: 2D spin liquids favoring pentagonal order in various degrees

[34, 55] and weakly polydisperse hard spheres [16–19, 45]. In both systems, we found that when the degree of frustration is weak, angular order linked to the symmetry of the equilibrium crystal grows when approaching the glass-transition point. The correlation length of the angular order,  $\xi$ , increases as  $\xi = \xi_0[(X - X_0)/X_0]^{-2/d}$  ( $\xi_0$  is the bare correlation length,  $X_0$  is the value of  $X$  at the hypothetical ideal glass transition) and the structural relaxation time  $\tau_\alpha$  diverges as  $\tau_\alpha = \tau_\alpha^0 \exp(K\xi^{d/2}/k_B T)$ . Here  $X$  is  $T$  for 2D spin liquids and  $1/\phi$  for polydisperse hard spheres (both  $d = 2$  and  $3$ ). We define the hypothetical ideal glass-transition point as the diverging point of the structural relaxation time  $\tau_\alpha$ , i.e. the correlation length of  $\xi$ . However, its real presence is highly questionable, as will be discussed later.

We also found the same relations for polydisperse Lennard-Jones liquids [16]. The power-law divergence with the exponent of  $2/d$  is reminiscent of Ising criticality. It should be noted that similar Ising-like behavior was also observed for binary Lennard-Jones system by Mosayebi *et al* [56].

In these studies, we also confirmed that the static correlation length  $\xi$  grows in the same manner as the dynamical one  $\xi_4$ , which characterizes the spatial scale of the dynamical heterogeneity [57, 58]:  $\xi \cong \xi_4$ . We also found the negative correlation between the degree of coarse-grained angular order and the particle mobility. This correlation suggests that the dynamical slowing down is a consequence of angular ordering with spatial coherence.

Later, we made a non-trivial extension of structural (or, angular) order parameter to make it applicable to any systems interacting mainly with steric repulsions, including strongly frustrated systems, e.g. binary mixtures of particles with the size ratio of 1.4 [37, 38]. Under strong geometrical frustration, structural order growing in a supercooled liquid may not have a link to that of the equilibrium crystals. For example, for binary mixtures of spherical particles with a rather large size ratio (e.g. 1.4, which is often used to study the problem of glass transition [59]), phase separation is necessary for crystallization to take place. This fact means that there is no direct thermodynamic link between a supercooled state and a crystalline state since it is cut by another thermodynamic transition, i.e. phase separation [4]. More practically, standard bond-orientational order parameters are not useful for such a system since its validity relies on small fluctuations of the number of nearest neighbor particles: in binary systems, the number of nearest neighbors strongly fluctuates depending upon the composition of neighboring particles, i.e. how many large and small particles are in the neighbors around a particle.

The central idea behind the introduction of the new structural order parameter is that the local free energy is a decreasing function of local vibrational entropy, which is determined by the packing capability of the configuration of neighboring particles around a central particle [37]. The basic physics is the same as that behind the introduction of a bond-orientational order parameter, and thus, the bond-orientational order parameter can be regarded as a special case of our generalized order parameter, i.e. local packing capability  $\Psi$ . We can define this order parameter for both  $d = 2$  and  $3$ . By using this order parameter, we have extracted the static correlation length,  $\xi$ , by comparing the spatially coarse-grained order-parameter field with the mobility field obtained by the isoconfigurational ensemble. We found that the correlation between the two fields has a distinct maximum for a particular coarse-graining length,  $\xi$ , and a

particular elapsed time,  $\tau$  [37]. Interestingly, we again obtained the relations of  $\xi \cong \xi_4$  and  $\tau \cong \tau_\alpha$ . Although we used the mobility field to estimate the static correlation length  $\xi$ , the operation to obtain  $\xi$  itself is purely static, and thus we argued that the correlation length  $\xi$  should be regarded as the static correlation length.

The physics behind this argument is as follows: the critical structural feature determining the future development of dynamic heterogeneity after  $\tau_\alpha$  already exists in the static structure at  $t = 0$ ; in other words, the development of the mobility field as a function of time is already determined by the static order parameter field at  $t = 0$ . Particles with the lowest packing capability (i.e. the lowest structural order) start to move first (we may refer these regions to defective regions), and then the mobility field evolves following the structural order-parameter field. These defective regions may correspond to the so-called soft spots [60]. However, this mobility field does not ‘locally’ follow the order parameter field, since the motion of particles in a region of relatively high packing capability should be correlated spatially: the motion of particles cannot take place independently but cooperatively, since a configuration of high packing capability is stabilized entropically, or by steric repulsions.

On the other hand, the amplitude of the local vibrational mode (i.e. cage-rattling) known as the fast  $\beta$  relaxation was found to be negatively correlated with the local packing capability in a direct (or, local) manner [37]: a particle with higher packing capability has higher local Debye–Waller factor (or, more solid-like). This fact implies that the intrinsic link between the fast  $\beta$  relaxation and the structural (or,  $\alpha$ ) relaxation through local structures, as suggested previously [18, 19, 61, 62]. This direct negative correlation between the local packing capability and the amplitude of the fast  $\beta$  motion at the local level casts doubt on the validity of the mean-field approximation in the sense that the spatial fluctuations are essential in both the fast and slow dynamics of a supercooled liquid.

For both 2D and 3D binary mixtures, we also discovered the same relations for the growth of  $\xi$  and  $\tau_\alpha$  when approaching the glass-transition point as for the weakly frustrated systems mentioned above [37]: the correlation length of local packing capability  $\Psi$ ,  $\xi$ , is found to increase as  $\xi = \xi_0[(X - X_0)/X_0]^{-2/d}$  and the structural relaxation time  $\tau_\alpha$  diverges as  $\tau_\alpha = \tau_\alpha^0 \exp(K\xi^{d/2}/k_B T)$ . Thus, we almost universally found the same scaling relations to any glass-forming systems interacting with spherically symmetric potentials, covering from weakly frustrated (e.g. polydisperse systems) to strongly frustrated systems (e.g. binary mixtures). Thus, we may say that the order parameter  $\Psi$  is ‘order-agnostic’.

Very recently, we have applied the above order parameter  $\Psi$  characterizing the packing capability to an instantaneous liquid structure at a finite temperature instead of its inherent structure at zero temperature [38]. Then, we find that this order parameter  $\Psi$  effectively acts as an intensive thermodynamic variable (temperature or pressure):  $(\Psi - \Psi_0)/\Psi_0 \propto (T - T_0)/T_0$ , where  $\Psi_0$  is the value of  $\Psi$  at the hypothetical ideal glass-transition temperature  $T_0$ . Thus, a Vogel–Fulcher–Tammann (VFT)-like relation generally holds between the structural relaxation time  $\tau_\alpha$  and the order parameter  $\Psi$ , at least for any supercooled liquids whose interparticle interactions are isotropic. More importantly, we discover that such a VFT-like relation between  $\Psi$  and  $\tau_\alpha$  is statistically valid even at a particle level if we spatially coarse-grain  $\Psi$  over the correlation length  $\xi$ .

This fact suggests that the spatial correlation of structural order is the origin of the cooperativity of dynamics, providing the physical mechanism connecting a growing length scale with the dynamical slowing down at a particle level. We stress that this physical mechanism behind slow glassy dynamics, where the spatial fluctuations of the structural order parameter are coupled with the local dynamics (or, transport), is fundamentally different from that of critical slowing down in ordinary critical phenomena, where the local dynamics is not affected by order-parameter fluctuations.

The point-to-set length, which is based on translational correlation, was also claimed to be order-agnostic [63–66], but it was shown that orientational order developed in weakly polydisperse hard disks cannot be detected by it [67]. For solving this problem, some modifications were proposed [68, 69]. However, the necessity of some modifications depending upon a system means that it is not order-agnostic any more. Here it should be noted that in general, the decorrelation of the static length scale detected by a particular method with the dynamic one (see, e.g. [65, 70–72]) does not necessarily mean that the decorrelation of the static and dynamic length scales: it might be only because the relevant static structural order is not captured by that particular method [4, 73]. Thus, we argue that such a decorrelation is a necessary condition for the irrelevance of static structural order to slow dynamics, but not a sufficient condition.

## 5.2. The nature of the spatial correlation of static structural order

Here we consider the nature of the spatial correlation of static structural order. When we calculate the spatial correlation length of static structural order,  $\xi$ , for weakly polydisperse systems, we use the correlation function of the ‘complex’ orientational order parameter in both  $d = 2$  and 3 [16–19, 45]. Thus, this length reflects the coherence length of the angular part of the order parameter rather than the correlation length of its amplitude. For the order parameter characterizing the local packing capability, we employ spatial coarse-graining to detect its correlation with dynamic heterogeneity. Both operations suggest that what controls slow glassy dynamics is the spatial coherency of packing capability. Such spatial coherency may be responsible for the high activation barrier for particle motion since it is the source of cooperativity of particle motion: under such spatial coherency, the motion of a particle must involve correlated motion of its neighbors, which further requires the same for their neighbors. In this way, the spatial coherency may determine the characteristic size of the dynamical correlation. The fact that the particles in such a correlation volume  $\delta V$  with a linear size of  $\xi$  must move coherently may be the origin of the high activation barrier in proportion to  $\delta V^{1/2} = \xi^{d/2}$ , as will be discussed in the next section.

We also note that even though we use the complex orientational order parameter, the rotational symmetry cannot be broken by the hypothetical ideal glass transition. It is because geometrical frustration does not allow a system to have a particular angular order upon the transition. So, the ideal glass-transition point may be regarded as an avoided critical point. Such transformation of the phase ordering from (Heisenberg-type) continuous to Ising ( $Z_2$ ) symmetry due to frustration and random disorder effects has also been known for spin systems [74–76], implying the generality of frustration and random disorder effects on the nature of the ordering. Langer [77, 78] also proposed

a simple argument supporting Ising nature. However, this problem remains for future investigation.

It is crucial to realize that the glassy order parameter intrinsically suffers from frustration effects since the stabilization of a glassy state is a consequence of frustration against frustration-free crystalline ordering. This fact implies that the critical-like behavior may be only ‘apparent’, and the ideal glass transition may be avoided by the frustration effects. Once the frustration effects stop the growth of  $\xi$ , the dynamics should become Arrhenius-like. Concerning the Kauzmann paradox [54, 79], we note that the ideal glass transition may never be visited in reality since crystallization (or, in some cases, phase separation) should always take place before the supercooled liquid state is equilibrated [80].

### 5.3. Role of static structural ordering in slow dynamics: intrinsic or perturbative

*5.3.1. Spatial correlation of steric (or, entropic) origin.* In the above, we have described that we find the universal relation between the static correlation length  $\xi$  and the structural relaxation time  $\tau_\alpha$  in the form of  $\tau_\alpha = \tau_\alpha^0 \exp(K\xi^{d/2}/k_B T)$ . This relation implies that the activation energy of the structural relaxation increases in proportion to  $\xi^{d/2}$ . Then, it can be derived from a straightforward argument that the typical amplitude of fluctuations of the free energy of a system,  $\delta G$  is controlled by the characteristic correlation volume of  $\delta V$ . Here,  $\delta G$  is measured from the reference of a homogeneous liquid of  $\xi = \xi_0 = a$  ( $a$ : the particle radius). Then, we have the following relation from the general statistical-mechanics formula:

$$\langle \delta G^2 \rangle_{\delta V} = \rho k_B T^2 c_V \delta V, \quad (4)$$

where  $c_V$  is the heat capacity at constant volume. Then, we assume that the average activation barrier  $\Delta$  should be related to  $(\langle \delta G^2 \rangle_{\delta V})^{1/2}$  with  $\delta V \sim \xi^d$ . Faster/slower relaxation with a small/large correlation volume should be controlled by the lower/higher barrier. Then, we obtain

$$\Delta \propto (\rho k_B T^2 c_V)^{1/2} \xi^{d/2}, \quad (5)$$

implying  $K \propto (\rho k_B T^2 c_V)^{1/2}$ . This relation indicates that a liquid with a more significant rate of the entropy decrease upon cooling, or the larger  $c_V$ , should be more fragile.

The above relation indicates that the spatial fluctuations of structural ordering, or many-body correlation, is not perturbative, but intrinsic at least for  $d = 2$  and 3. The physical message of the relation is as follows: the motion of particles suffers from a high activation barrier associated with a large correlation volume of  $\xi^d$  because particles there must move coherently. Although the structure order itself fluctuates around its average, the impact of the structural fluctuations looks intrinsic and not perturbative. Which of the increase of the average structural order or the spatial correlation of structural order plays a more dominant role in slow glassy dynamics is the crucial remaining question, although the above relation itself is suggestive of the latter. This question is also related to the relevance of the mean-field approach to the glass-transition problem. As mentioned above, at high dimensions, there is little growth of angular order, and thus the mean-field theory may be relevant; for example, at  $d = \infty$ , the two-body

description becomes exact. However, at low dimensions ( $d = 2$  and  $3$ ), the contribution of the mean-field background may be much smaller than that of structural order parameter fluctuations [4]. This point needs to be clarified in the future.

*5.3.2. Spatial correlation of energetic origin.* Recently we studied the dynamics of water [81–85], which shows the dynamic anomaly known as ‘fragile-to-strong transition’ [86–92]. At high temperatures, water ‘apparently’ exhibits strongly non-Arrhenius behavior typical of fragile liquids. In contrast, at low temperatures, it shows the Arrhenius-like behavior typical of strong liquids. We revealed [83–85] that the origin of this anomaly is nothing to do with the glass transition, but a consequence of the Arrhenius-to-Arrhenius crossover reflecting the two-state feature of water: at high temperatures, liquid water has disordered normal liquid structures, whereas, at low temperatures, it predominantly has locally favored tetrahedral structures. At intermediate temperatures, water can be regarded as a dynamical mixture of these two structures [81, 82, 93]. Here it is worth mentioning that the onset of the non-Arrhenius behavior is located far above  $T_g$  (for water, it occurs around  $\sim 2T_g$ ), which is a clear indication that it is not associated with glass transition. We also showed that the violation of the Stokes–Einstein–Debye relation in supercooled water can be explained in terms of the simple two-state model without relying on glass-transition phenomenology [84, 85].

We argue that this crossover behavior is a generic feature of any liquids that tend to form directional energy-driven locally favored structures, which are, for example, tetrahedral structures for oxide (see, e.g. [87, 94]) and chalcogenide liquids (see, e.g. [95, 96]). Unlike entropy-driven structures discussed above, the formation of directional energy-driven structures is generally accompanied by the significant loss of entropy, and thus these structures cannot easily grow to increase their correlation length. In extreme cases, such as water and silica, such local structures do not possess an angular correlation between them and are localized, leading to the lack of cooperativity in motion. In such cases, since the motion is controlled locally and not cooperatively, directional energy-driven local structural ordering makes liquid stronger. However, in the intermediate case, the orientational order may be able to grow in its correlation length even if energetic directional interactions induce structural ordering, and the balance between energetic and entropic contributions may determine the liquid fragility [34]. If the static structural order stops growing below a particular temperature due to the entropic penalty or the internal frustration, the activation energy may also stop growing. Then, the structural relaxation time should obey the Arrhenius law below that temperature.

Similarly, icosahedral structures cannot grow their size because of a different reason, i.e. geometrical frustration. If quasi-crystals or some of the Frank–Kasper phases are not formed, the system may show a two-state feature as in water and silica. We speculate that the fragile-to-strong transition claimed for metallic glass-formers (see, e.g. [91, 97–100]) may also be explained by the two-state model. This point needs further study.

*5.3.3. Mean-field background for the dynamics.* In the above, we have argued that for liquids with entropy-driven structural ordering, the static correlation length grows, and the dynamics becomes more cooperative when approaching the glass-transition point. In contrast, for liquids with directional energy-driven structural ordering, the static correlation does not grow, and the dynamics is controlled locally. In other words, the spatially extensive heterogeneity of static structural order is intrinsic to the former, but not for the latter. Even for the former, there should be a contribution of the mean-field nature, but we speculate that its contribution is much weaker than the contribution coming from spatial structural heterogeneity, at least for hard-sphere-like systems at  $d \leq 3$ .

In real liquids such as molecular liquids, there should be contributions from both entropic and energetic structural ordering, which may lead to intermediate behaviors between the fragile- and strong-limit. Such behavior was observed in 2D frustrated spin liquids [34]. For example, directional bonding should automatically lead to an increase in the activation energy of the Arrhenius behavior and effectively make liquids stronger [4]. In 2D spin liquids, we can control the liquid fragility over a wide range just by changing the strength of directional interactions [34]. For this type of liquid, the mean-field contribution can be revealed as the Arrhenius behavior above the onset temperature, below which the cooperativity starts to play an important role. The activation energy of the high-temperature Arrhenius behavior is just controlled by the energetic local interactions between particles at a two-body level.

## 6. Structural ordering above the so-called mode-coupling critical point

Concerning the above question, here we mention that significant structural ordering is already observed above the mode-coupling  $T_c$  or below the mode-coupling  $\phi_c$ , which are empirically determined by the power-law fitting to the temperature dependence of  $\tau_\alpha$  [23]. Here we do not touch a problem of whether the mode-coupling criticality has physical relevance or not. In particular, for colloidal suspensions, or hard-sphere systems, it is often argued that  $\phi_c$  is located at  $\phi \sim 0.58$ . In the context of the RFOT theory, this volume fraction is interpreted as  $\phi_d$ , below which metastable liquid is made by a single state but above which many metastable glassy states appear. The crucial point is that our structural ordering takes place already below  $\phi_c$  for hard-sphere systems (emerging around the freezing point  $\phi_f \sim 0.494$ ). This fact indicates that the slowing down is not due to two-body effects but a consequence of many-body effects already below  $\phi_c$  or  $\phi_d$ . The nearly one-to-one correspondence between the static correlation length  $\xi$  and the dynamic correlation length  $\xi_4$  also seems inconsistent with the prediction of the mode-coupling theory [20] and the random-first-order-transition (RFOT) theory [21–27], both of which are based on the mean-field picture of the glass-transition phenomena. The correlation between the local packing capability and the Debye–Waller factor at a particle level [37] also suggests the non-mean-field nature. Since this is a crucial point to elucidate the very origin of slow glassy dynamics, further careful study is necessary.

Here it is also worth noting that the scaling argument based on the RFOT theory [21–23] also predicts the relation of  $\tau_\alpha = \tau_\alpha^0 \exp(K\xi_{\text{mos}}^{d/2}/k_B T)$ . However, this slowing down is caused by the growth of the characteristic size of ‘mosaic structures’,  $\xi_{\text{mos}}$ , but such structures are supposed to emerge only below the mode-coupling  $T_c$  reflecting the emergence of a new metastable free-energy minimum. Since mosaic structures appear only below  $T_c$  or above  $\phi_c$  (or  $\phi_d$ ), the RFOT theory predicts a decoupling between static and dynamic length scales above  $T_c$  or below  $\phi_c$  (or  $\phi_d$ ), where a supercooled liquid is made of a single state without mosaic structures. This scenario looks like being supported by the point-to-set length analysis (see, e.g. [23, 64–66, 70–72]) and other local structure analyses (see, e.g. [101] for review); however, our studies unambiguously show that the static and dynamic lengthscales grow coherently and suggest that the spatial fluctuations of static order parameter is the origin of dynamic heterogeneity even above  $T_c$  or below  $\phi_c$  (or  $\phi_d$ ). Our study suggests that there are critical-like fluctuations of structural order in a supercooled state. We also note that the local packing capability is directly correlated with the local Debye–Waller factor, or the amplitude of the fast  $\beta$  motion. We stress that the mean-field scenario cannot explain such local structure-dynamics correlation.

Concerning this issue, we should note that there was a proposal to consider dynamic heterogeneity above  $T_c$  as a consequence of critical phenomena of the MCT order parameter, or fluctuations of the (two-body) dynamical correlation [102–104]. In this scenario, the dynamic susceptibility of the four-point density correlation diverges toward the mode-coupling  $T_c$  or  $\phi_c$  below a specific spatial dimension. However, we emphasize that in this theory, the fluctuations are purely of dynamic origin and not of static origin, and thus the physical nature of fluctuations is fundamentally different from what we observed.

## 7. Relevance of structural ordering to the dynamics of a supercooled liquid under spatial confinement effects and during aging

Here we mention that our structural ordering scenario of glass transition can also naturally explain spatial-confinement effects on slow dynamics of a supercooled liquid [105]. We found that when a weakly polydisperse hard-sphere liquid is confined between two flat parallel plates, the presence of the wall leads to the enhancement of bond-orientational order, reflecting the enhancement of the coherency of the angular order by the presence of the flat walls. The wall effects, or the penetration depth, is found to decay exponentially with the spatial correlation length of  $\xi$ : this enhancement of the correlation length near the wall along the direction perpendicular to the wall,  $\xi_\perp$ , leads to slower dynamics near the wall, just obeying the relation found above locally:  $\tau_\alpha(z) = \tau_\alpha^0 \exp(K\xi_\perp(z)^{d/2}/k_B T)$ , where  $z$  is the distance from the wall. When we use a circular confinement with a rather large curvature for 2D weakly polydisperse systems, on the other hand, the wall curvature is not consistent with the bond-orientational order, i.e. impose geometrical frustration on hexatic order [11]. Thus, the wall effects decay much quickly compare to the flat wall case with the decay length of the

translational (or, positional) correlation  $\xi_p$ , which is almost insensitive to the degree of supercooling. In this case, we also have the same relation for the local structural relaxation  $\tau_\alpha(z)$  and the local correlation length  $\xi_\perp(z)$  with  $\xi_\perp(z) \equiv \xi_p(z)$ . These results strongly suggest that the structural relaxation in a particular local region is always controlled by the spatial correlation length of the static glassy structural order in that region. Here we note that such a link between the curvature and the dynamics can be explained straightforwardly by considering structural order but is difficult to explain by a purely dynamical scenario.

We also studied the aging dynamics of 2D and 3D polydisperse hard-sphere systems [106]. Here we observed little change in the two-body correlation function, i.e.  $g(r)$ , but observed the temporal growth of the correlation length of the bond-orientational order parameter,  $\xi$ , with the aging time,  $t_w$ , for both  $d = 2$  and 3. Then, the structural relaxation time at the waiting time  $t_w$ ,  $\tau_\alpha(t_w)$  was found to obey the following relation:  $\tau_\alpha(t_w) = \tau_\alpha^0 \exp(K\xi(t_w)^{d/2}/k_B T)$ . Furthermore, this relation was equivalent to the one for an equilibrium supercooled state if we replace  $t_w$  by  $\phi$ . This result also suggests that the structural relaxation time is always determined by the static correlation length of  $\xi$  in the system. A recent study using machine learning [107] supported this conclusion.

These studies on the spatial confinement and aging effects on slow glassy dynamics further support our scenario that slow dynamics is a consequence of critical-like phenomena with unique activated dynamics [4, 16, 77, 78].

## 8. Non-conserved nature of glassy structural order parameter

Here we discuss the dynamical nature of glassy structural ordering. Unlike the density order parameter, glassy structural order parameters discussed above are non-conserved quantities. It is because such an order can be formed and annihilated independently without the constraint due to its conservation. For example, we confirmed that the bond-orientational order parameter (or, hexatic order parameter) in polydisperse hard discs obeys critical-like dynamics characteristic of model A, which is the dynamical universal class of a non-conserved order parameter such as magnetization in a spin system, in the Hohenberg–Halperin classification [108]. Since the density, which is a conserved quantity, is a crucial order parameter describing a liquid state, this means that the dynamics of liquids should be described by a two-order-parameter model (or, model C) [4, 109, 110]. The density field is generally subordinate to the angular order parameter. For systems of entropy-driven ordering, such as hard spheres, the only channel of local density relaxation is the cooperative particle motion of diffusive nature (particle exchange). In contrast, for systems of energetic bond-driven ordering, the local density relaxation can be accomplished by the exchange between two states (ordered and disordered states) locally [84, 85]. This difference leads to the diffusive and non-diffusive dynamics around the interparticle distance for the former and latter, respectively [111–113]. Here we note that in the low wavenumber limit, the density fluctuation should always obey the diffusive behavior due to its conserved nature.

## 9. Impact of structural ordering on slow glassy dynamics: entropy-driven versus directional energy-driven interactions

So far, we have focused mainly on systems interacting mainly with steric repulsions. In this type of system, structural ordering, or many-body correlation, is induced by steric repulsions to lower the local free energy. This ordering can also be explained by the increase of the total entropy of the system by structural ordering, which leads to an increase in vibrational entropy with the expense of configurational entropy. Since the ordering is driven entropically, its correlation length can increase without the entropic penalty. On the other hand, if the interaction between particles is directional, such directional energy-driven ordering must be accompanied by the significant loss of entropy [35]. This feature tends to prevent the growth of the correlation length of structural order. It is because spatially-extended structural ordering leads to a significant loss of entropy. We indeed confirmed this for water and silica; for both systems, structural ordering toward tetrahedral symmetry is driven by directional bonding (hydrogen bonding for the former and covalent bonding for the latter). In these systems, structural ordering is always local, and there is little growth of the spatial correlation of the structural order parameter, or little development of the spatial coherency of the order [84, 85, 114, 115]. As mentioned above, for this type of system, we found an apparent fragile-to-strong transition. This transition has often been explained in the framework of the glass-transition phenomenology. However, we found that it is actually a consequence of a crossover from a high-temperature Arrhenius behavior with low activation energy to a low-temperature one with high activation energy [83–85]. It is worth mentioning that this crossover is nothing to do with the glass-transition phenomena, but is associated with a crossover from a high-temperature liquid with little structural order to a low-temperature liquid with high local tetrahedral order.

In this way, we can understand the two extreme cases: entropically-driven (or, sterically-driven) and directional-interaction-driven structural ordering. The former corresponds to the fragile limit, whereas the latter corresponds to the strong limit. The key remaining question is what happens in the intermediate case in which both energy and entropy play essential roles in structural orderings of liquids. The most straightforward expectation is that the dynamics is controlled by both the Arrhenius-like behaviors coming from directional bonding and cooperativity due to the growth of coherency due to steric repulsions. It is an interesting problem for future investigation.

## 10. Summary

In this article, we express our opinion on the physical origin of slow glassy dynamics focusing on the universal tendency of structural ordering in a supercooled liquid, which originates from many-body correlation. Because of intrinsic many-body nature, it is not so easy to develop an analytical theory based on this idea. However, we may at least construct a phenomenological scenario: development of critical-like fluctuations with special activated dynamics. The crucial difference from ordinary critical phenomena

[47] is the origin of slow dynamics. In ordinary critical phenomena, slow critical dynamics is a simple consequence of the increase in the lifetime of growing critical fluctuations while keeping the local dynamics unchanged. In contrast, in glass-transition phenomena, slow glassy dynamics is a consequence of the slowing down of local dynamics due to the coherency of motion that is required under particle-level structural ordering in a highly packed situation.

In this article, we describe our specific physical idea to explain the origin of slow glassy dynamics, but there are many other interesting ideas. We hope that this article would stimulate further discussion on the origin of slow glassy dynamics.

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