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# General view of a liquid-liquid phase transition

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We present a general view of a liquid-liquid phase transition, based on a simple physical picture that there is ''cooperative medium-range bond ordering'' for any liquids. Contrary to the common belief, we argue that liquid is not homogeneous and in any liquid there exist locally favored structures, which are frustrated with normal-liquid structures. The cooperative excitation of locally favored structures leads to a gas-liquid-like critical point of bond ordering. This picture naturally leads to the conclusion that liquid-liquid transition is not specific to special materials, but can in principle exist in any liquids. Our model suggests a new possibility that (i) even an ordinary molecular liquid can have a hidden liquid-liquid phase transition and (ii) it may be the origin of a second amorphous phase (e.g., ''glacial phase'') and critical-like, large-scale fluctuations (''Fischer clusters'') observed in supercooled molecular liquids.

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## I. INTRODUCTION

A single-component liquid may have more than two kinds of isotropic liquid states and the transition between these different states is called ''liquid-liquid phase transition'' [1–3]. It is one of the most interesting challenging problems in the field of liquid science. There is much experimental evidence suggestive of its existence for a variety of liquids covering atomic to molecular liquids [3]. For example, liquid carbon (C) is one of the most well-studied materials and the existence of a high-pressure liquid-liquid phase transition is experimentally suggested and theoretically predicted [4–8]. Recently, Katayama *et al.* [9] studied the first-order liquid-liquid phase transition in phosphorus (P) by *in situ* x-ray diffraction observation. The coexistence of two forms of liquids during the transformation was directly observed. Thus, the existence of a first-order liquid-liquid phase transition is strongly suggested for phosphorus. The behavior of Si and Ge [10] is similar to that of C and P. Se, Te, Rb, Cs, and other atomic liquids are also suggested to be candidates of liquids with liquid-liquid phase transition [3,11]. Network-forming liquids such as $SiO_2$, $GeO_2$, and $H_2O$ are also expected to have a liquid-liquid phase transition [12–14]. For example, liquid water, which is one of the most familiar network-forming liquids, has solid-state amorphous-amorphous transitions [15] and is suggested to have a liquid-liquid phase transition below its melting point [16–19]. Furthermore, Aasland and McMillan [20] recently reported a striking experimental finding: In a supercooled state of $Al_2O_3$-$Y_2O_3$, they directly observed with optical microscopy the coexistence of two glassy liquids, which have completely the same composition but different density. This surprising finding indicates that even a (quasi-) single-component liquid can phase separate into two liquid phases [2]. Similar phenomena have also been reported by a number of researchers in various liquids (see Refs. [2,20]). However, such a transition seems not to have been widely accepted as a convincing fact and its existence itself remains as an interesting research subject. This situation partly comes from (i) the counterintuitive nature of the phenomena and (ii) the experimental difficulties; namely, in most cases the transition is located at high temperatures and high pressures (e.g., for C, P, Si, Ge, Te, . . . ) or hidden by solidification (e.g., for water).

In addition to these counterintuitive phenomena of liquid-liquid transitions, there are other mysterious phenomena in supercooled liquids. One is the phenomenon, which is widely known as ''Fischer clusters'' [22] in the molecular glass community. According to the standard theory of simple single-component liquids [1,23], the structure factor at a wave number $q=0$, $S(0)$, is determined by the isothermal compressibility $K_T$ as $S(0)=\rho k_B T K_T$ ($\rho$ is the density; $k_B$ is Boltzmann's constant; $T$ is temperature). Contrary to this common sense, however, Debye and Bueche found excess light scattering far beyond this prediction and the existence of long-range density fluctuations with a correlation length $\xi_{cl}$ of 200 nm in a glassy polymer [21]. Furthermore, it was recently demonstrated by Fischer and his coworkers [22,24] that strong excess light scattering due to large-scale fluctuations is commonly observed near the glass-transition temperature $T_g$ in both molecular liquids [e.g., ortho terphenyl, bis-methyl-phenyl-cyclohexane, and bis-methyl-methoxy-phenyl-cyclohexane] and polymeric liquids [e.g., poly(methyl methacrylate) and polysiloxane]. These surprising results strongly suggest that large-scale fluctuations, which are called ''Fischer clusters,'' *quite commonly* exist in various ordinary liquids under deeply supercooled conditions. Another example is the existence of a second amorphous phase (''glacial phase'') in triphenyl phosphite (TPP) [25]. Kivelson *et al.* [25] recently found a first-order phase change from deeply supercooled liquid (TPP) at 1 atm to a rigid amorphous phase called the ''glacial phase,'' which is clearly distinguished from an ordinary glassy phase. It should be noted that supercooled TPP also exhibits excess light scattering peculiar to Fischer clusters. Although there has been no firm consensus [26,27], the possible existence of the liquid-liquid transition was suggested [25,28]. The physical origin of these phenomena is still quite far from being even qualitatively understood.

Although there have been a number of examples suggestive of the existence of liquid-liquid phase transition, it has not been clarified how universal such a transition is, or what is the necessary condition for it. A liquid-liquid transition has so far been discussed in a rather specific way about a particular substance. The possible general nature was sometimes suggested [2,3], but restricted to a rather special family of liquids (network-forming liquids).

In this paper, we reconsider this problem from a fundamental viewpoint, focusing on how we should describe liquid physically. We argue that packing effects and specific symmetry-selective interactions generally lead to *cooperative medium-range ordering* in any liquid [29–33] and it is this bond ordering that is the origin of liquid-liquid phase transition. Our model, thus, suggests that liquid-liquid phase transition can, in principle, exist in any liquid in its stable, metastable, or unstable state. On the basis of this model, the above-described phenomena such as ''glacial phase'' and ''Fischer clusters'' can reasonably be explained by the existence of hidden spinodal of a liquid-liquid phase transition and its pretransitional effects, although this scenario has yet to be proven. We believe that such a simple physical view is quite useful for the understanding of these counterintuitive, mysterious phenomena.

In Sec. II, we explain our physical picture of liquid. In Sec. III, we describe a two-state model with cooperativity. In Sec. IV, we propose a few possible types of liquid-liquid phase transitions. In Sec. V, we discuss critical phenomena near a gas-liquid-like critical point of bond ordering. In Sec. VI, we show that our model can also provide a simple physical explanation for the phenomena of a liquid-glass transition. In Sec. VII, we summarize our paper.

## II. A SIMPLE PHYSICAL PICTURE OF LIQUID

To understand the phase behavior of any material physically, we must clarify what are the relevant order parameters to describe it. It is widely believed that liquid can be described by just one order parameter density $\rho$, which beautifully describes a gas-liquid phase transition. However, we have recently proposed that this is not the case for any liquid near its crystallization point, or the lower stability limit of liquid [29–33] and thus at least two order parameters, which we call density and bond order parameters, are necessary for the physical description of liquid. A density order parameter tries to maximize the density (or packing) to lower the attractive interaction energy and leads to the long-range ordering (crystallization). At the same time, however, any molecules locally favor a certain packing symmetry that is different from the symmetry favored by a density order parameter. The formation of these locally favored structures can be viewed as a consequence of specific many-body interactions. Thus, we proposed the following physical picture of liquid: (i) there exist rather well-defined, unique locally favored structures (medium-range order) in any liquids and (ii) such local structures are ''cooperatively'' excited in a sea of another disordered background structure (normal-liquid structures), and their number density increases upon cooling since they (in a ground state) are energetically more favorable than normal-liquid structures (in an excited state). This cooperativity is a natural consequence of frustration between density and bond ordering. The relevance of this two-order-parameter model of liquid is supported by the successful description of water's anomalies [31–33].

Here we demonstrate some examples of such medium-range order (locally favored structure) to gain a deeper insight into the hidden ordering in liquid. For spherical molecules, for example, it is widely recognized that they locally favor an icosahedral arrangement [1], whose symmetry is inconsistent with the crystallographic symmetry. Molecules such as water, on the other hand, have a strong ability to form hydrogen bonding that favors a local symmetry of tetrahedral arrangements. The most probable candidates of the locally favored structure are an ''octameric unit'' or a ''six-member ring'' [32,33], which are elementary structural units of ice Ih. A similar idea can be applied to atomic liquids such as carbon [4–8]. Carbon is known to favor the sp, $\mathrm{sp}_2$, $\mathrm{sp}_3$ type of bonding sequentially with an increase in pressure. We introduce three bond order parameters $Si$ $(i=1-3)$ in addition to the density order parameter, to express the locally favored structure selected by $\mathrm{sp}_i$ bonding in our language. The specific volume increases with a decrease in $i$. An important point is that with an increase in pressure $P$ the denser configuration is sequentially selected in the order of $S1$, $S2$, $S3$, and $\rho$.

Hereafter we consider only a case of two order parameters $\rho$ and $S$, for simplicity, although we can straightforwardly generalize our model to a case of $m$ order parameters. Here we note that a system of $m$ order parameters can in principle have $m$ critical points corresponding to the ordering associated with each order parameter. A critical point of density $(\rho)$ ordering is, of course, a usual gas-liquid critical point.

Next we consider how to define our bond order parameter in a more rigorous manner. A locally favored structure can be viewed as a minimum structural unit (a ''symmetry element''), which has an excluded volume effect. Thus, our ''bond order parameter'' $S(\boldsymbol{r})$ can be defined as the ''local fraction of locally favored structures'' in a small volume around a point $\boldsymbol{r}$. Formally, for example, $S(\boldsymbol{r})$ can be defined by using the so-called bond-orientational order parameter $Q_{lm}$ [34]:

$$Q_{lm}(\boldsymbol{R})=Y_{lm}(\theta(\boldsymbol{R}),\phi(\boldsymbol{R})), \tag{1}$$

where the $Y_{lm}(\theta,\phi)$ are the spherical harmonics, and $\theta(\boldsymbol{R})$ and $\phi(\boldsymbol{R})$ are the polar angles of the bond measured with respect to some reference coordinate system, and $\boldsymbol{R}$ is the midpoint of a bond. The local average of their rotationally invariant combination can be used as the definition of the local bond order parameter $S(\boldsymbol{r})$. Thus we take the average of $Q_{lm}$ over a small volume located at $\boldsymbol{r}$. We redefine the locally averaged, or coarse-grained, quantities $\overline{Q_{lm}}$ as $\overline{Q_{lm}}(\boldsymbol{r})=\langle Q_{lm}(\boldsymbol{R})\rangle_{\boldsymbol{r}}$. Then, the rotationally invariant combination $Q_l(\boldsymbol{r})$ can be defined as

$$Q_l(\boldsymbol{r})=\left[\frac{4\pi}{2l+1}\Sigma_{m=-l}^{l}|\overline{Q_{lm}}(\boldsymbol{r})|^2\right]^{1/2}. \tag{2}$$

For icosahedrons, for example, we can use $Q_6(\boldsymbol{r})$ as the definition of the local bond order parameter $S(\boldsymbol{r})$. We can apply such representation of the symmetry using spherical harmonic expansions (or higher-rank tensors) for the definition of $S$, to express the symmetry of any types of locally favored structures.

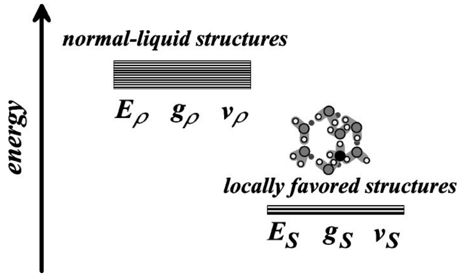

FIG. 1. Schematic figure representing the energy levels of normal-liquid and locally favored structures. Note that $E_S<E_\rho$, $v_S>v_\rho$, and $g_S \ll g_\rho$. A possible example of locally favored structures for water is schematically shown. It has a specific packing symmetry and also has a core volume into which other molecules cannot enter.

## III. A TWO-STATE MODEL WITH COOPERATIVITY

First we estimate the $T,P$ dependence of the bond order parameter $S$ on the basis of a simple two-state (or multistate) model. A two-state model with cooperativity was first developed by Strässler and Kittel [35] and applied to the problem of a liquid-liquid transition by Rappoport [36] and then by many researchers for a variety of materials. We argue that such a multistate model can be applied to any liquid without any exception, provided that *the formation of local structures (medium-range ordering) is a universal feature of liquids*. First we characterize the state of normal-liquid structures ($j=\rho$) and that of locally favored structures ($j=S$). $E_j$, $v_j$, and $g_j$ are the energy, specific volume, and degeneracy of the $j$ state, respectively (see Fig. 1). Note that $E_S<E_\rho$ and $g_S \ll g_\rho$. The last relation is a direct consequence of the uniqueness of locally favored structures and the existence of many possible configurations of normal-liquid structures. This means the large loss of entropy $\Delta\sigma = k_B \ln(g_\rho/g_S)>0$ upon the formation of a locally favored structure.

The entropy $\sigma$ of a system can be calculated as

$$\sigma(S) = -k_B\left[S\ln\frac{S}{g_S}+(1-S)\ln\frac{1-S}{g_\rho}\right]. \tag{3}$$

Without cooperative (interaction) effects, the energy is given by

$$U=SE_S+(1-S)E_\rho. \tag{4}$$

Here we consider the effect of cooperative excitation. Since the two types of elementary structures are frustrated with each other, it is natural to expect that the excitation probability of each structure is higher for a higher local concentration of like species. Including this effect up to the second order, we obtain the following energy:

$$U=SE_S+(1-S)E_\rho+JS(1-S). \tag{5}$$

Here $J>0$ because of the frustration, which indicates that the excitation of the same type of structure as its neighbor is energetically more favored than that of the different type. The free energy $f$ is, thus, given by

$$\begin{aligned} f(S) &= U-T\sigma+[Sv_S+(1-S)v_\rho]P \\ &= SE_S+(1-S)E_\rho+[Sv_S+(1-S)v_\rho]P \\ &\quad + k_BT\left[S\ln\frac{S}{g_S}+(1-S)\ln\frac{1-S}{g_\rho}\right]+JS(1-S). \end{aligned} \tag{6}$$

The above type of model is sometimes called a mixture model. However, both normal-liquid and locally favored structures are temporally created and annihilated and the lifetimes of these structures are rather short. Thus, we point out that the concept of a mixture of two components is misleading; for example, the bond order parameter $S$ should be treated as a ‘‘nonconserved’’ order parameter [30] (see Sec. V), in contrast to the fact that in a usual mixture model it is treated as a conserved variable.

We now consider a possible liquid-liquid phase transition, or *cooperative medium-range bond ordering*, on the basis of the above free energy *f*. The equilibrium value of $S$ is determined by the condition $\partial f/\partial S=0$, or

$$\beta[-\Delta E+\Delta v P+J(1-2S)]+\ln\frac{g_\rho S}{g_S(1-S)}=0, \tag{7}$$

where $\Delta E=E_\rho-E_S>0$, $\Delta v=v_S-v_\rho$, and $\beta=1/k_BT$. It is worth noting that the degeneracy of each state, or the entropy difference between the two states, strongly affects the phase behavior. A critical point is determined by the conditions $f_S'(S_c)=0$, $f_S''(S_c)=0$, $f_S^{(3)}(S_c)=0$, and $f_S^{(4)}(S_c)>0$, as

$$S_c=1/2, \tag{8}$$

$$T_c=J/(2k_B), \tag{9}$$

$$P_c=[\Delta E-T_c\Delta\sigma]/\Delta v. \tag{10}$$

A first-order phase-transition temperature $T_t$ is obtained as

$$T_t=(\Delta E-P\Delta v)/\Delta\sigma. \tag{11}$$

Note that a first-order transition occurs only if $T_t<T_c$. $\Delta v$ may be positive in most cases (e.g., for water), but it can also be negative in principle. The sign of $\Delta v$ determines the slope of $T_t(P)$.

## IV. POSSIBLE TYPES OF LIQUID-LIQUID PHASE TRANSITION

The examples of possible phase diagrams are shown in Figs. 2–4. The type of a phase diagram is classified by the values of $J$ and $\Delta E$. The phase diagrams include both liquid-solid and liquid-liquid transitions. As shown in these figures, we propose that liquid-liquid phase transition, in principle, exists in any liquids including even ordinary molecular liquids. The necessary conditions are (i) the existence of locally favored structures and (ii) their cooperative excitation ($J>0$). For materials of large $J$ and $\Delta E$, a liquid-liquid transition exists in a stable liquid state (see Fig. 2), while it is hidden by crystallization for materials of intermediate $J$ and $\Delta E$ (see Fig. 3) or it is located in a glassy state for materials of small $J$ and $\Delta E$ (see Fig. 4).

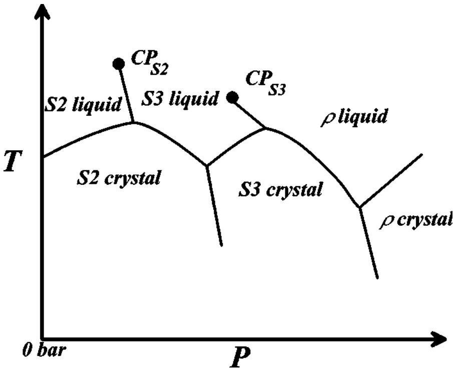

FIG. 2. Schematic $P-T$ phase diagram of a liquid with large $\Delta E$ and $J$ such as liquid carbon. The gas-liquid critical point ($\mathrm{CP}_\rho$) is not shown in this figure.

### A. Liquid with large $J$ and $\Delta E$

First we consider the case of large $J$ and $\Delta E$. Carbon and phosphorus may be examples of materials having large $J$ and $\Delta E$ (see Fig. 2). Carbon is, for example, known to have a few candidates of locally favored structures, reflecting sp ($S1$), $\mathrm{sp}_2$ ($S2$), and $\mathrm{sp}_3$ ($S3$) bonding. Figure 2 demonstrates a possible phase diagram of such a liquid, which starts from a situation that $\mathrm{sp}_2$-type bonding is dominant at ambient pressure. There should exist $S1$ liquid in a negative pressure region. $\mathrm{CP}_{S2}$ and $\mathrm{CP}_{S3}$ are critical points associated with $S2$ and $S3$ ordering, respectively. Above the critical points, the type of liquid changes in a continuous manner. In this case, the liquid-liquid transition lines and the associated critical points exist in an equilibrium liquid state. Note that the relation among the density of each phase is as follows: $S2$ liquid $<S2$ crystal $<S3$ liquid $<S3$ crystal $<\rho$ liquid $<\rho$ crystal. For carbon, the $S2$ crystal is graphite and the $S3$ crystal is diamond. The sign of the slope of a melting line is determined by the Clausius-Clapeyron relation $dT_\mathrm{m}/dP=\Delta v_\mathrm{m}/\Delta\sigma_\mathrm{m}$, where $T_\mathrm{m}$ is the melting point, and $\Delta\sigma_\mathrm{m}$ and $\Delta v_\mathrm{m}$ are the changes in entropy and volume upon melting, respectively. Since $\Delta\sigma_m>0$, the sign of $dT_m/dP$ is determined solely by $\Delta v_m$. The melting lines in Fig. 2 are drawn by using this fact and the above relation among the density of each phase. The phase diagram shown in Fig. 2 is basically consistent with that of liquid carbon obtained by experiments [7] and simulations (see, e.g., Fig. 2 of Ref. [6]) in a low pressure region. More quantitative comparisons require the information on physical quantities such as $\Delta E$, $\Delta v$, $\Delta\sigma$, and $J$. Our model predicts the existence of an additional critical point ($\mathrm{CP}_{S3}$) at a high pressure region of the phase diagram. Experimental studies in this high pressure region are highly desirable.

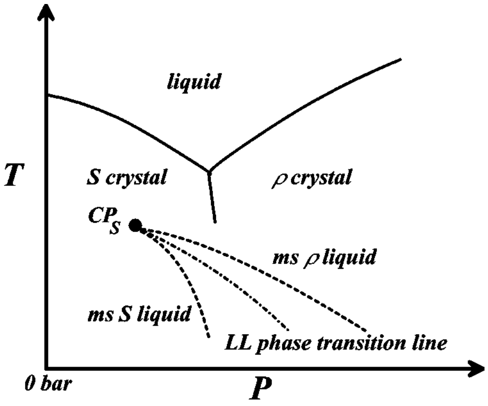

FIG. 3. Schematic $P-T$ phase diagram of a liquid with intermediate $\Delta E$ and $J$ such as liquid water. $\mathrm{CP}_S$ is a critical point of $S$ ordering. The gas-liquid critical point ($\mathrm{CP}_\rho$) is not shown in this figure. ms stands for "metastable." The dashed and dot-dashed lines are spinodal and first-order transition lines, respectively.

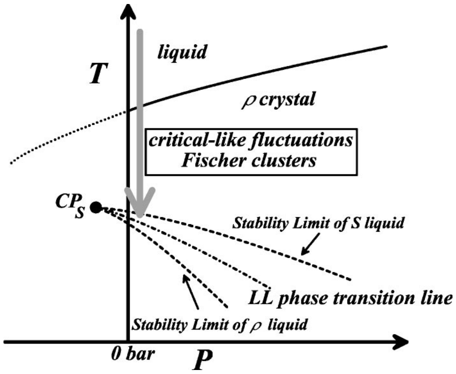

FIG. 4. Schematic $P-T$ phase diagram of a liquid with small $\Delta E$ and $J$ for a case of $\Delta v>0$. $\mathrm{CP}_S$ is a critical point of $S$ ordering and located at negative pressure. The gas-liquid critical point ($\mathrm{CP}_\rho$) is not shown in this figure.

### B. Liquid with intermediate $J$ and $\Delta E$

Water may be an example of a material having intermediate $J$ and $\Delta E$ (see Fig. 3). In this case, the liquid-liquid transition line and the associated critical point exist in a metastable state below the melting line [17]. Actually, recent experimental [18] and molecular dynamics simulations [16,14] have indicated evidence of a first-order liquid-liquid transition in a metastable state of water. For water, for example, ice Ih is identified as $S$ crystal, while ices III, V, ... are identified as $\rho$ crystal. The liquid density should be higher than $S$ crystal, but lower than $\rho$ crystal, which is consistent with what is known for the real water.

Liquid water is also known to exhibit unusual thermodynamic behaviors, which are very much different from those of other molecular liquids [1,2,19]: volume expansion upon its freezing at 0 °C, density maximum at 4 °C, and the anomalous increase of compressibility and heat capacity upon cooling. According to our model, the volume expansion upon the freezing into ice Ih can be explained by the fact that water crystallizes into $S$ crystal, and not into $\rho$ crystal, at ambient pressure. Water may be the only molecular liquid that can crystallize into $S$ crystal at positive pressures. This fact makes water a very special liquid. For example, water is extremely difficult to vitrify. This can be explained by the fact that $S$ ordering (crystallization into ice Ih) is free from frustration effects, since the energy of the $S$ state is lower than that of the $\rho$ state. We emphasize that our two-order-parameter model can also reasonably explain water's thermodynamic and dynamic anomalies by the increase in the medium-range order ($S$) upon cooling [31–33]. It is straightforward to estimate the temperature and pressure dependence of $S$ for a case of $S\ll 1$ from Eq. (7):

$$S \cong \frac{g_S}{g_\rho} \exp[\beta(\Delta E - P\Delta v)]. \tag{12}$$

Thus, the excitation probability of $S$ should be given by the Boltzmann factor. By using this relation, we can explain the density anomaly of water. The locally favored structure has a more specific volume by $\Delta v$ than the normal-liquid structure does. This is simply because hydrogen bonding has a strong tendency of ‘‘symmetry selection’’ and leads to the formation of the locally favored structure, which has a core volume (or void) in it, while van der Waals interactions simply favor a denser configuration. This is the origin of the competition between $\rho$ and $S$. Without the formation of locally favored structures, $\rho$ should monotonically increase with decreasing $T$ due to van der Waals attractions, as in ordinary liquids. However, the increase in $S$ upon cooling leads to the decrease in $\rho$ via their couplings. With decreasing $T$, a volume increase due to medium-range bond ordering starts to overcome a volume decrease due to density ordering, since the temperature dependence of the former is much stronger than that of the latter. This competition is primarily responsible for the unusual decrease in $\rho$ upon cooling below 4 °C in water. In our model, the specific volume $v_{\mathrm{sp}}$ and the density $\rho$ are, respectively, given by

$$v_{\mathrm{sp}}(T,P) = v_{\mathrm{sp}}^{\mathrm{B}}(T,P) + \Delta v \overline{S}, \tag{13}$$

$$\rho(T,P) \sim \rho_{\mathrm{B}}(T,P) - \rho_{\mathrm{B}}(T,P)\frac{\Delta v}{v_{\mathrm{sp}}}\overline{S}, \tag{14}$$

where $\rho_{\mathrm{B}}(T,P) = M/v_{\mathrm{sp}}^{\mathrm{B}}(T,P)$ ($M$ is the molar mass). The subscript and superscript $B$ denote the background (normal) part. We found that the above relation very well explains the temperature and pressure dependence of the density of water [31–33]. The anomalies of isothermal compressibility, heat capacity, and viscosity can also be explained in the same framework of the model [31–33]. These facts support the relevance of our physical picture.

### C. Liquid with small $J$ and $\Delta E$

Finally, we argue that even an ordinary liquid, which has small $J$ and $\Delta E$, may have a liquid-liquid transition (see Fig. 4). For this case, $P_c$ may be negative. This picture provides us with a possible scenario of ‘‘Fischer clusters.’’ With approaching to the mean-field spinodal, there should be the critical enhancement of $S$ fluctuations, which causes the excess scattering. This can happen at ambient pressure if a critical point of $S$ ordering is located at a negative pressure and $\Delta v > 0$ (see Fig. 4) or if it is located at a positive pressure and $\Delta v < 0$. Thus, ‘‘Fischer clusters’’ can be viewed as critical-like fluctuations of $S$ near a hidden mean-field spinodal of a gas-liquid-like phase transition of locally favored structures ($S$ ordering). This conclusion is a natural consequence of our picture that *cooperative medium-range ordering exists in any liquid*. Dynamic anomaly associated with Fischer clusters can also be reasonably explained by our model [30], as shown in Sec. V. If our scenario is correct, these phenomena should be ideal for the experimental study of the nature of a liquid-liquid phase transition since they occur at ambient pressure. Note that such a study usually suffers from experimental difficulties due to high temperatures and high pressures for most of materials that have so far been expected to have a liquid-liquid phase transition.

The following predictions can be made on the basis of our model: (i) Liquids having ‘‘Fischer clusters’’ should have a liquid-liquid phase transition at a lower temperature. This transition may be hidden by a liquid-glass transition. (ii) Applying a higher pressure at the same temperature should weaken the critical-like anomaly for $\Delta v > 0$, while strengthening it for $\Delta v < 0$ [37]. Here it is worth noting that our discussion is based on the mean-field approximation. The critical-like anomaly near a spinodal line exists only in the mean-field limit. This may explain why ‘‘Fischer clusters’’ are characterized by a long bare correlation length and are commonly observed in many polymeric glass formers [22,24], on noting that the Ginzburg criterion is safely satisfied in a system with a long-range interaction as in polymer systems.

## V. COUPLING BETWEEN DENSITY AND BOND ORDER PARAMETERS

### A. Relevant Hamiltonian

The Hamiltonian of ideal liquids associated with density fluctuations is approximately given by

$$\beta H_\rho = \int d\boldsymbol{r} \frac{\tau}{2} \delta\rho^2 = \int d\boldsymbol{r} f(\delta\rho),$$

where $\tau = \beta(\overline{\rho}^2 K_T)^{-2}$ and it is always positive. Here $\overline{\rho}$ is the average density and a decreasing function of $T$ (note that $\rho = \overline{\rho} + \delta\rho$). In a real liquid, however, the bond order parameter plays essential roles, as explained above. Using $\delta S = S - \overline{S}$, we introduce the following minimal Hamiltonian, which governs $S$ fluctuations near a gas-liquid-like critical point or mean-field spinodal lines of bond ordering:

$$\beta H_S = \int d\boldsymbol{r} \left[ \frac{\kappa}{2} \delta S^2 + \frac{b_4}{4} \delta S^4 \right] = \int d\boldsymbol{r} g(\delta S),$$

where $\kappa = b_2(T - T_S^*)$ ($T_S^*$ is a critical or spinodal temperature of bond ordering without the coupling to $\rho$) and $b_2$ and $b_4$ are positive constants. By further including the gradient terms and the lowest-order (bilinear) couplings between $\delta\rho$ and $\delta S$, we obtain the following Hamiltonian that we believe is relevant to the physical description of liquid near a gas-liquid-like transition of locally favored structures [30]:

$$\beta H_{\rho S} = \int d\boldsymbol{r} \left[ h(\delta\rho, \delta S) + \frac{K_\rho}{2} |\nabla \delta\rho|^2 + \frac{K_S}{2} |\nabla \delta S|^2 \right], \tag{15}$$

$$h(\delta\rho, \delta S) = f(\delta\rho) + g(\delta S) - c_{1\rho} \delta\rho (\overline{S} + \delta S) - c_{1S} (\overline{\rho} + \delta\rho) \delta S. \tag{16}$$

Note that $f$, $g$, and $h$ are dimensionless free-energy densities. For $\Delta v > 0$, which is a usual case, an increase in $S$ leads to a decrease in $\rho$ and an increase in $\tau$, while an increase in $\rho$ leads to a decrease in $S$ and $T_S^*$. Hence, all the coupling constants $c_i$ in Eq. (16) should be negative for most cases.

### B. Kinetic equations

Next we consider how the dynamics of $\delta\rho$ and $\delta S$ should be described near the critical point of bond ordering. At a liquid instability point, it is known that a supercooled liquid as a whole becomes intrinsically unstable with respect to density fluctuations of wave number $q_0$ ($q_0$ is the first scattering peak wave number). This causes the softening of a nonpropagating soft mode with $q\sim q_0$ [38], which leads to the breakdown of the incompressibility assumption. Thus, we should regard a supercooled liquid to be compressible. More generally, a liquid should be treated as ''compressible'' when we consider *isothermal* spontaneous density fluctuations with long wavelengths, although adiabatic ones propagate as a sound mode. For such compressible liquids, it is known [23] that $\delta\rho_q \propto -\delta Q_q$ ($Q$ is the heat mode), as long as we consider slow dynamics at small $q$. Since the heat mode is a conserved mode, $\delta\rho$ should be treated as a conserved order parameter obeying a diffusion-type equation. On the other hand, $\delta S$ should be treated as a nonconserved order parameter. Thus, we have the following dynamic equations [30], if we neglect convective terms:

$$\frac{\partial \delta\rho(\boldsymbol{r},t)}{\partial t} = L_\rho \nabla^2\left[-K_\rho \nabla^2 \delta\rho + \frac{\partial h(\delta\rho,\delta S)}{\partial \delta\rho(\boldsymbol{r},t)}\right], \tag{17}$$

$$\frac{\partial \delta S(\boldsymbol{r},t)}{\partial t} = -L_S\left[-K_S \nabla^2 \delta S + \frac{\partial h(\delta\rho,\delta S)}{\partial \delta S(\boldsymbol{r},t)}\right], \tag{18}$$

where $L_\rho$ and $L_S$ are kinetic coefficients. Here the Gaussian noise terms are not written explicitly. We propose that Eqs. (15)–(18) are the fundamental equations universally describing ultraslow critical-like dynamics of supercooled liquids. These dynamic equations are basically the same as those of the so-called ''model C'' [39–41].

### C. Critical phenomena under the couplings between two order parameters

Within the framework of a linearized theory [40,41], we study slow dynamics of large-scale fluctuations near the critical point of density ordering. First we introduce a vector notation

$$\boldsymbol{x} = \begin{bmatrix} \delta\rho \\ \delta S \end{bmatrix} \quad \text{and} \quad \boldsymbol{x}_0 = \begin{bmatrix} \langle \delta\rho \rangle \\ \langle \delta S \rangle \end{bmatrix}.$$

The average values of the order parameters $\overline{\rho}$ and $\overline{S}$, are shifted due to their bilinear coupling compared to those without the coupling, respectively, by

$$\langle \delta\rho \rangle \sim \frac{c_{1\rho}\overline{S}}{\tau} \quad \text{and} \quad \langle \delta S \rangle \sim \frac{c_{1S}\overline{\rho}}{\kappa}.$$

After linearization with respect to small deviations

$$\boldsymbol{x}^* = \begin{bmatrix} \delta\rho^* \\ \delta S^* \end{bmatrix} \tag{19}$$

from $\boldsymbol{x}_0$, Eqs. (17) and (18) reduce to the following eigenvalue problem by using

$$\boldsymbol{x} = \boldsymbol{x}_0 + \boldsymbol{x}^* \exp(i\boldsymbol{q}\cdot\boldsymbol{r} + \omega t), \tag{20}$$

where $\boldsymbol{q}$ is the wave vector:

$$\boldsymbol{A}\boldsymbol{x}^* = -\omega \boldsymbol{x}^*, \tag{21}$$

where $\boldsymbol{A} = \boldsymbol{T}(\boldsymbol{H} + q^2\boldsymbol{K})$ with

$$\boldsymbol{T} = \begin{bmatrix} L_\rho q^2 & 0 \\ 0 & L_S \end{bmatrix}, \quad \boldsymbol{K} = \begin{bmatrix} K_\rho & 0 \\ 0 & K_S \end{bmatrix}, \tag{22}$$

and

$$\boldsymbol{H} = \begin{bmatrix} h_{\delta\rho\delta\rho} & h_{\delta\rho\delta S} \\ h_{\delta S\delta\rho} & h_{\delta S\delta S} \end{bmatrix} = \begin{bmatrix} \tau & c_{1\rho}+c_{1S} \\ c_{1\rho}+c_{1S} & \kappa \end{bmatrix}, \tag{23}$$

where $\boldsymbol{H}$ is the so-called Hesse matrix and the derivatives $h_{xy} = \partial^2 h/\partial x \partial y$ are taken at $\boldsymbol{x}_0$. In the limit of small $q$, the two dispersion branches are straightforwardly obtained as

$$\omega_1 \sim -L_\rho \left[\frac{\det \boldsymbol{H}}{h_{\delta S\delta S}}\right] q^2 + O(q^4), \tag{24}$$

$$\omega_2 \sim -L_S\left[h_{\delta S\delta S} + \left(K_S + \frac{L_\rho h^2_{\delta\rho\delta S}}{L_S h_{\delta S\delta S}}\right) q^2\right] + O(q^4). \tag{25}$$

In the limit of large $q$, on the other hand, $\omega_1 \sim -L_\rho q^4$ and $\omega_2 \sim -L_S K_S q^2$.

#### 1. Critical-like phenomena in a stable state

The stable state is characterized by $\kappa>0$ and $\det \boldsymbol{H}>0$. Critical-like fluctuations grow with approaching to a temperature, which is determined from the condition $\det \boldsymbol{H} = \tau\kappa - (c_{1\rho}+c_{1S})^2 = 0$ as

$$T_c = T_S^* + \frac{(c_{1\rho}+c_{1S})^2}{b_2 \tau}. \tag{26}$$

Hereafter we use $T_c$ to represent both the critical temperature and the mean-field spinodal temperature. The mode, which slows down with approaching to $T_c$, is characterized by $\omega_1$. The decay rate $\Gamma_q$ is given by $\omega_1 = -L_\rho(\det \boldsymbol{H}/\kappa)q^2$. Thus, the critical mode has diffusional nature and the lifetime of fluctuations increases with approaching to $T_c$ in proportion to $(T-T_c)^{-1}$ within the mean-field approximation. The possible effects of such critical-like fluctuations are discussed in Sec. V D. It should be noted here that polydispersity effects such as the distribution of $E_\rho$ and $E_S$ may weaken the critical effects.

#### 2. Early-stage phase ordering in an unstable state

The unstable state is characterized by $\det \boldsymbol{H}<0$. This is classified into two cases by the sign of $\kappa$. (i) For a case of $\kappa>0$, we have one unstable branch characterized by $\omega_1$. In this case, the eigenvector of the unstable branch is of mixed character for all $q$ [see Eq. (24)] and, thus, fluctuations of both $\delta\rho$ and $\delta S$ grow simultaneously. Note that $\boldsymbol{x}_0$ becomes a saddle point in this case. At $q=0$, the components $\delta\rho^*$ and $\delta S^*$ of the eigenvector $\boldsymbol{x}^*$ satisfy $\delta\rho^*/\delta S^* = -h_{\delta S\delta S}/h_{\delta\rho\delta S}$. (ii) For a case of $\kappa<0$, one branch characterized by $\omega_2$ (for small $q$) becomes unstable. This mode at $q=0$ corresponds to the growth of bond order. If there is no coupling to density, this mode is characteristic of the ordering of the nonconserved order parameter, which is the case of the so-called ''model A'' [39]. For nonzero $h_{\delta\rho\delta S}$, the term $L_\rho h^2_{\delta\rho\delta S}/L_S h_{\delta S\delta S}$ can be negative. Thus the fastest growth mode with finite $q$ emerges similarly to the case of the ordering of the conserved order parameter, but with a nonzero growth rate at $q=0$. Differently from the above case, the bond ordering first proceeds nearly on the constant density line in the $(\rho,S)$ space and then the order parameters relax to their equilibrium values.

### D. Fischer clusters

#### 1. A possible origin of excess scattering

Here we consider the origin of excess light scattering in supercooled liquids on the basis of the above model. The refractive index $n$ is a function of not only $\rho$, but also $S$, since $n$ of locally favored structures is smaller than that of normal-liquid structures. It may be reasonable to assume that the local bond ordering directly (not via density) affects the polarizability, or the refractive index $n$, on considering its unique local symmetry and the electronic nature of bonding. Here it should be noted that if this is not the case, the light scattering intensity $I(q)$ should be expressed solely by density fluctuations and thus no excess scattering is expected. We stress that *in many liquids the refractive index n cannot be expressed by a function of only density*. For example, this fact is particularly well-established for liquid water [42]. In our model, thus, $I(q)$ is given by

$$I(q)\propto\left(\frac{\partial n}{\partial\rho}\right)^2\langle|\delta\rho_q^*|^2\rangle+2\left(\frac{\partial n}{\partial\rho}\right)\left(\frac{\partial n}{\partial S}\right)\langle\delta\rho_q^*\delta S_{-q}^*\rangle+\left(\frac{\partial n}{\partial S}\right)^2\langle|\delta S_q^*|^2\rangle. \tag{27}$$

These correlation functions at small $q$ can be straightforwardly obtained as

$$\langle|\delta\rho_q^*|^2\rangle=(\kappa+K_Sq^2)/A(q), \tag{28}$$

$$\langle\delta\rho_q^*\delta S_{-q}^*\rangle=(c_{1\rho}+c_{1S})/A(q), \tag{29}$$

$$\langle|\delta S_q^*|^2\rangle=(\tau+K_\rho q^2)/A(q), \tag{30}$$

where

$$A(q)=(\tau+K_\rho q^2)(\kappa+K_Sq^2)-(c_{1\rho}+c_{1S})^2 \sim\det\boldsymbol{H}+[\tau K_S+\kappa K_\rho]q^2. \tag{31}$$

According to the standard theory of pure liquids, the structure factor at a wave number $q=0$, $S(0)$, is determined by the isothermal compressibility $K_T$ as $S(0)=\rho k_BTK_T$. If density is the only order parameter, the light scattering intensity at $q=0$ should be given by $I_\rho(0)=(\partial n/\partial\rho)^2S(0)$. This is actually the case for many pure liquids. Contrary to this common sense, however, excess scattering far beyond the above prediction was observed for various glass formers [21,22,24]. In our model, this excess scattering can be explained by the fact that $\kappa\ll c_{1\rho}+c_{1S}$ and/or $\kappa\ll\tau$ near $T_c$, where $\kappa\to0$. These conditions guarantee the dominance of Eqs. (29) and (30) over Eq. (28) near the spinodal lines. This is a direct consequence of the fact that there is instability for bond fluctuations (a gas-liquid-like transition of locally favored structures) but not for density fluctuations in a liquid state.

Fischer *et al.* [22,24] also found the Ornstein-Zernike form of light scattering function $I(q)\sim1/[1+\xi_{cl}^2q^2]$. This is also consistent with the $q$ dependence of Eqs. (29) and (30). In our model, $\xi_{cl}$ is given by $\xi_{cl}^2\sim(\tau K_S+\kappa K_\rho)/\det\boldsymbol{H}$, which diverges as $T\to T_c$. Within the mean-field approximation, $\xi_{cl}\sim(T-T_c)^{-1/2}$. This is also consistent with a divergent increase in $\xi_{cl}$ near a glass-transition temperature $T_g$ [22], which is suggestive of the existence of a hidden critical point $T_c$ or spinodal temperature $T_{sp}$. Fischer clusters are also characterized by the $q^2$ dependence of the decay rate $\Gamma_q\propto q^2$, and also by the fact that $\Gamma_q\to0$ with $T\to T_c$ [22]. The former is suggestive of simple diffusion. These experimental findings can be explained as follows. In our model, both $\delta\rho_q^*$ and $\delta S_q^*$ can be expressed by a linear combination of two eigenmodes characterized by $\omega_1$ and $\omega_2$. In particular, the ''slow'' critical mode decays as $\exp(\omega_1t)$, and the decay rate of this mode, $\Gamma_q=-\omega_1$, is proportional to $q^2$, as described in Sec. V C 1. Further, $\Gamma_q\propto\det\boldsymbol{H}\propto(T-T_c)\to0$ with $T\to T_c$. Thus, our model can well explain all essential features of the anomalous excess light scattering observed in supercooled liquids (''Fischer clusters'') [22,24] at least on a qualitative level.

#### 2. Apparent violation of the compressibility sum rule

Next we consider why the compressibility sum rule is apparently violated. This can naturally be explained by comparing Eq. (27) with

$$K_T=\frac{1}{k_BT\rho^2}\int d\boldsymbol{r}\langle\rho^r(\boldsymbol{r})\rho^r(\boldsymbol{0})\rangle, \tag{32}$$

where $\delta\rho^r=\delta\rho^*+c_{1\rho}/\tau\delta S^*$ is the real fluctuation of density under the coupling to bond ordering. Since $|c_{1\rho}/\tau|$ is small, the major contribution to $K_T$ comes from the direct density-density correlation. On the other hand, the scattering intensity mainly comes from fluctuations of bond order parameters [see Eq. (27)], which may be dominant near the mean-field spinodal. Thus, we suggest that the apparent violation of the compressibility sum rule is due to (a) the existence of an additional hidden order parameter, namely, bond order parameter, which has critical-like fluctuations, and (b) its direct coupling to the refractive index $n$.

### E. Phase separation of a single-component liquid into two phases

#### 1. Phase-separation kinetics

Next we consider phase separation of a single-component liquid into two phases below $T_c$. Because of the existence of a new order parameter $S$ and the resulting coupling between $\rho$ and $S$, phase separation can proceed on the $(\rho,S)$ plane even for a one-component liquid. The details of the phase-separation kinetics are described in Sec. V C 2. Our model predicts the negative correlation between the two order parameters: a high-density region has less bond order, while a low-density region has more bond order. This is a direct consequence of negative coupling between the two order parameters ($c_{1\rho}, c_{1S} < 0$). It can, thus, naturally explain why the two-phase coexistence is possible in a single-component liquid [2]. It should be noted that glass-forming liquids automatically satisfy the necessary condition for the existence of such a gas-liquid-like transition, since vitrification itself is caused by the existence of *locally favored structures* in our picture [29] (see Sec. VI).

#### *2. Phase coexistence and phase transformation*

Aasland and McMillan [20] found the evidence of the coexistence of two phases in liquid $Al_2O_3$-$Y_2O_3$ by direct microscopic observation. For liquid phosphorus, furthermore, Katayama *et al.* [9] succeeded in observing the process of the transformation from a less dense to a denser liquid including the coexistence of the two phases by *in situ* x-ray diffraction measurements. These behaviors including the density change during the transformation are naturally explained by our model. The kinetics of the transformation can be described by the coupled Langevin equations (see Sec. V B).

Further, Kivelson *et al.* [25] found that supercooled TPP slowly transforms into a glacial phase in a temperature range between 213 K and 225 K. It was identified as a new amorphous phase, although its amorphous nature is still a matter of debate [26,27]. The possibility of liquid-liquid phase transition is suggested [25,28]. If this is the case, the phenomena can be explained as follows. According to our model, this transformation can be viewed as the transition between $\rho$ liquid and $S$ liquid. It was suggested that the glacial phase is denser than the supercooled liquid, however, no direct data of the density is available. At this moment, thus, the sign of $\Delta v$ for this system is not yet known in an unambiguous manner. This information is crucial for revealing the nature of the transition, and the precise density measurement is highly desirable. It should be mentioned that supercooled TPP exhibits dynamic features characteristic of Fischer clusters [25]. The coexistence of Fischer clusters and liquid-liquid phase transformation is also consistent with our picture (see Fig. 4). Before going to the details, however, we definitely need further careful studies on the more fundamental problem of whether the glacial phase is really a new amorphous phase [25,28] or it has some orientational order [26,27].

## VI. CONNECTION OF OUR MODEL TO THE PHENOMENA OF LIQUID-GLASS TRANSITION

Finally, we mention that our model provides natural explanations not only for liquid-liquid phase transition, but also for liquid-glass transition and the thermodynamic and dynamic anomalies of water, in a coherent manner. For the water's anomalies, we already explain them in Sec. IV B. The details on this problem were described in Refs. [31–33]. So we briefly explain how our two-order-parameter model of liquid can explain another poorly understood phenomenon in liquids, namely, a liquid-glass transition (see Ref. [29] on the details).

Recently, we proposed a simple physical model for the universal description of glass-transition phenomena covering from the strong to fragile limit [29]. The model is essentially the same as that described in this paper. In our model, locally favored structures with finite, but long lifetimes are randomly distributed in a sea of normal-liquid structures. Thus, even simple liquids suffer from random disorder effects of thermodynamic origin. We argue that locally favored structures act as impurities and produce the effects of ‘‘fluctuating interactions’’ and ‘‘symmetry-breaking random fields’’ against density ordering, in much the same way as magnetic impurities for magnetic ordering in spin systems. Similarly to random-spin systems, thus, we predict the existence of two key temperatures relevant to glass transition, the density ordering (crystallization) point $T_m^*$ of the corresponding pure system without frustration and the Vogel-Fulcher temperature $T_0$. Glass transition is then characterized by these two transitions: (A) a transition from an ordinary-liquid state to a Griffiths-phase-like state at $T_m^*$, which is characterized by the appearance of high-density metastable islands with medium-range order, and (B) another transition into a spin-glasslike nonergodic state at $T_0$ and the resulting divergence of the lifetime of metastable islands, namely, the $\alpha$ relaxation time. Between $T_m^*$ and $T_0$, a system has a complex free-energy landscape characteristic of the Griffiths-phase-like state, which leads to the non-Arrhenius (cooperative) behavior of $\alpha$ relaxation and dynamic heterogeneity below $T_m^*$. This simple physical picture provides us with a universal scenario of glass transition covering the strong to fragile limit. For example, our model predicts that stronger random-disorder effects make a liquid ‘‘stronger,’’ or ‘‘less fragile’’ [29]. Namely, liquids with large $S$ (or large $\Delta E$) should be ‘‘stronger.’’ According to our model, stronger disorder effects lead to the larger distance between the onset temperature of cooperativity $T_m^*$, and the temperature of divergence $T_0$. Thus, a stronger liquid should have a weaker (more Arrhenius) temperature dependence of viscosity, which is consistent with what is widely known.

To summarize, the locally favored structures have three different roles, depending upon the length scale: (i) In a large length scale, the cooperativity in their excitation leads to critical-like phenomena and liquid-liquid phase transitions. (ii) In a small length scale, on the other hand, they play a similar role as magnetic impurities in spin glass and lead to a liquid-glass transition. (iii) Further, the average fraction of locally favored structures directly affect the thermodynamic quantities of a liquid, such as density, heat capacity, and compressibility. Correspondingly, thus, our two-order-parameter model of liquids may provide reasonable physical pictures not only for (i) liquid-liquid phase transition, but also for (ii) liquid-glass transition and (iii) the thermodynamic and dynamic anomalies of liquids such as water.

## VII. SUMMARY

In summary, we propose that contrary to the common belief, liquid is not homogeneous in the intermediate length scale and any liquid has medium-range bond order, which is excited cooperatively in the background normal-liquid structures. This feature originates from many-body interactions. Thus, we need at least two order parameters to express this feature of liquids. This picture naturally leads to a conclusion that a liquid-liquid transition can, in principle, exist in any liquids, including atomic liquids such as C, P, Si, Ge, Se, Rb, and Cs, network-forming liquids such as water, $SiO_2$, and $GeO_2$, and ordinary molecular liquids. In particular, our model provides us with reasonable physical explanations for mysterious phenomena found in supercooled molecular liquids such as ''Fischer clusters'' and ''glacial phase,'' although they have yet to be proven. We need further studies to confirm the existence of liquid-liquid transition of an ordinary glass-forming liquid (hidden in the glassy region) and to establish its relation to the so-called ''Fischer clusters'' and ''glacial phase.''

We stress that our model may explain liquid-liquid phase transitions, liquid-glass transitions, and the thermodynamic and dynamic anomaly of liquids such as water in a ''unified'' manner and reveal the relationship among these phenomena, which have so far been considered not to be related to each other. Further studies are desirable to check the validity of this physical picture. In particular, it is important to check the existence of a long-lived locally favored structure and reveal its structure for each liquid. We believe that the locally favored structure should have unique vibrational modes and the detection of such soft vibrational modes may be the easiest way to prove its existence. In relation to this, we propose that the so-called boson peak comes from such vibrational modes unique to locally favored structures. This model quite naturally explains the fact that the boson peak exists even in an equilibrium liquid state above the melting point for some glass formers, which is difficult to explain by conventional models of the boson peak. The details on the possible relation between locally favored structures and the boson peak will be discussed elsewhere [43].

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