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Possible resolution of the Kauzmann paradox in supercooled liquids

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Generally, the entropy of the supercooled liquid decreases more rapidly than that of the crystal. Thus, the former, if we extrapolate it smoothly below the glass-transition temperature T_g, becomes equal to the latter at the so-called Kauzmann temperature T_K. Further extrapolation below T_K leads to the unphysical situation that the entropy of disordered liquid is lower than the ordered crystal, which results in the violation of the third law of thermodynamics. This is known as the ''Kauzmann paradox'' which has been the key problem of liquid-glass transition for a long time. Here we propose a simple resolution of the Kauzmann paradox by answering a fundamental question of how deeply we can supercool a liquid. We argue that the lower metastable limit T_{LML}, below which a liquid should crystallize before its structural relaxation, is located above the Kauzmann temperature T_K. Thus, the entropy crisis at T_K is naturally avoided by crystallization. We suggest that it is dynamic heterogeneity that destabilizes a deeply supercooled ''equilibrium'' liquid state as well as a glassy state against crystallization. This may have a significant implication on the stability of a glassy state, which is of industrial importance in relation to the storage of glassy material.

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I. INTRODUCTION

Liquid-glass transition phenomena are universally observed in various types of liquids, including molecular liquids, ionic liquids, metallic liquids, oxides, and chalcogenides [1–4]. A liquid is always in a metastable state below its melting point T_m. Thus, whether it becomes a glassy state at T_g upon cooling or crystallizes critically depends upon the cooling rate. If the cooling rate is sufficiently slow, any liquid crystallizes [5]. Thus, there is a critical cooling rate above which a liquid can be vitrified. Provided that we can successfully avoid crystallization, we are allowed to discuss the nature of a supercooled liquid state at very low temperatures, which is fundamentally quite interesting. However, this supercooled liquid state far below melting point T_m is not well understood. For example, it is known that the entropy of the supercooled liquid decreases more rapidly than that of the crystal and thus the former becomes equal to the latter at the so-called Kauzmann temperature T_K (see Fig. 1). Further extrapolation below T_K leads to the unphysical situation that the entropy of disordered liquid is lower than the ordered crystal, which results in the violation of the third law of thermodynamics, provided that the crystal is stable upon cooling until 0 K and thus its entropy approaches zero as $T \to 0$ K [6]. This is known as the ''Kauzmann paradox'' [7] which has been one of the most fundamental problems of liquid-glass transition for more than 50 years [1–4,8–11].

Kauzmann considered this important problem in depth [7,11]. He noticed that the extrapolation of liquid entropy toward lower temperatures leads to the unphysical situation that the entropy of the hypothetical ''equilibrium'' [12] liquid becomes less than that of the crystal, as described above. However, Kauzmann [7] had focused on the fact that at low temperatures the free-energy barrier for crystal nucleation, ΔF^c, can become much lower than that for structural relaxation, since the former decreases with decreasing T while the latter increases. Thus, he concluded that the characteristic time of nucleation and crystallization τ_x should become shorter than that of structural relaxation, τ_α, before reaching T_K and therefore, an extrapolation of the ''equilibrium'' liquid's entropy to much lower temperatures is ''operationally meaningless.''

This conclusion of Kauzmann was, however, challenged by the following argument based on the modern knowledge on the supercooled liquid (see Secs. 4.1 and 4.3.1 of Ref. [1]). It is now well established [1,13] that the nucleation of a crystal is controlled not only by ΔF^c, but also by the kinetic factor, namely, the characteristic time of material transport τ_t. Thus, the above conclusion, derived by Kauzmann, which neglects this fact, cannot be justified. As shown below, if we adopt $\tau_t = \tau_\alpha$, which is now widely believed to be valid, we reach the conclusion that $\tau_x \gg \tau_\alpha$ [see a dotted curve (τ_α branch) in Fig. 2 and later discussions], contrary to Kauzmann's argument. This implies that we can continue to cool a liquid while keeping a condition that the equilibration time is longer than τ_α and avoiding crystallization. Thus, it is now widely believed [1–4] that the Kauzmann paradox still remains paradox, despite that various efforts have been made to resolve it [8–11]. Since the Kauzmann paradox is deeply related to the nature of glass transition and the origin of the slow dynamics, it has had strong influences on our understanding of glass-transition phenomena.

There can be three types of approaches to resolve the Kauzmann paradox.

(a) The first type of approach is to introduce an ''ideal glass transition'' to avoid this paradox [1–4] [see Fig. 1(a)]. For example, Gibbs and DiMarzio [14] first pointed out from their consideration of uncrystallizable atactic polymers that this paradox would vanish if a second-order phase transformation occurs at T_K. In this scenario, at T_K the equilibrium liquid transforms in the Ehrenfest sense to an ''ideal glass'' of the same entropy and heat capacity as the crystal but a higher energy than that of the crystal. Adam and Gibbs [15] extended this approach and provided a configurational en-

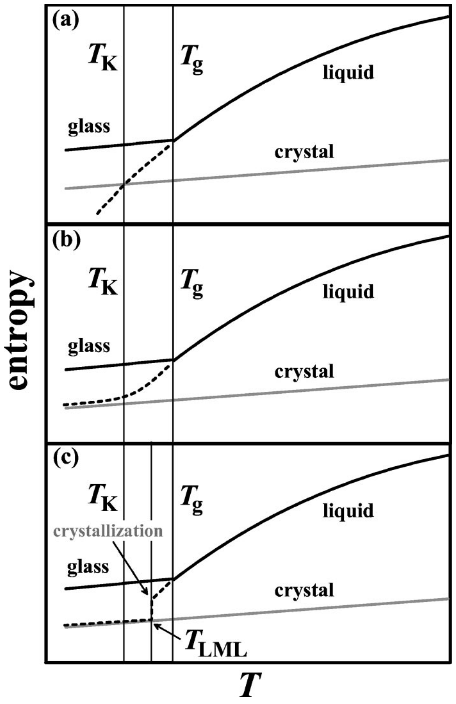

FIG. 1. Three scenarios to resolve the Kauzmann paradox. (a) Ideal glass-transition scenario. In this case, a supercooled liquid is supposed to transform into an ideal glass state at T_0, which is the second-order phase transition. Accordingly, the structural relaxation time diverges at T_0. (b) Smooth extrapolation scenario. In this scenario, the excess entropy smoothly goes to zero toward $T=0$ K. Thus, there is no divergence of the structural relaxation time at T_0. This is the singularity-free scenario. (c) Crystallization scenario. In this scenario, a supercooled liquid becomes unstable against crystallization and thus it transforms into a crystalline state as a result of the first-order phase transition (crystallization) before the excess entropy becomes zero.

tropy theory, which connects the configurational entropy to the viscosity with a Vogel-Fulcher-like relation. This idea is further developed into a more microscopic theory based on a spin-glass picture [16–19]. However, the existence of such an ideal glass transition itself is still a matter of debate [1,8–11].

(b) The second type of approach is to reconsider the way of extrapolation carefully [see Fig. 1(b)]. For example, Stillinger [8] demonstrated on the basis of the inherent structure theory that (i) an ideal glass transition cannot occur for substances of limited molecular weight and with usual intermolecular interactions, (ii) the entropy of liquid smoothly approaches that of crystal toward $T=0$ K, and (iii) particle rearrangements of finite free-energy cost are always available at any positive temperature to mediate flow at a finite rate under applied stress. Similarly, Johari [10] also pointed out on the experimental basis that the configurational entropy smoothly goes to zero toward $T=0$ K and thus there is no paradox.

(c) The third type of approach is to consider the stability of the supercooled liquid against crystallization [see Fig. 1(c)]. This is the original approach of Kauzmann himself, but there have been few further efforts along this direction after its validity was questioned as explained above.

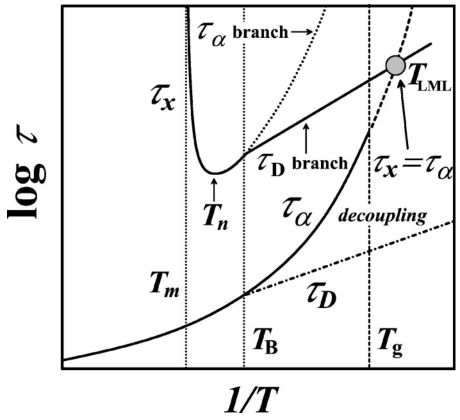

FIG. 2. Schematic figure representing the temperature dependence of the characteristic times (τ_α, τ_D, and τ_x) of a glass-forming liquid. Structural relaxation time τ_α obeys the Vogel-Fulcher equation [see Eq. (3)] and diverges while approaching T_0. Translational diffusion mode τ_D is, on the other hand, decoupled from structural relaxation mode τ_α at T_B upon cooling. Below melting point T_m, a liquid tends to crystallize and thus the characteristic time of nucleation and crystallization τ_x becomes finite below T_m. Reflecting the decoupling of τ_D from τ_α at T_B, τ_x also changes its temperature dependence at T_B. Since the relevant transport process of crystallization is not the structural relaxation mode, but the translational diffusion one, the true τ_x (τ_D branch) is considerably shorter than τ_x estimated with the assumption that $\tau_t=\tau_\alpha$ (τ_α branch).

The difficulty of this problem arises from the fact that the Kauzmann temperature exists in an experimentally inaccessible temperature range. This is the primary reason why there is no consensus on this issue of how the configurational entropy decreases to zero upon cooling.

In this paper, we reconsider the Kauzmann paradox from the above standpoint (c), focusing on the stability of a supercooled liquid against crystallization. In other words, we reconsider how deeply we can supercool a liquid while equilibrating it. Thus, we will not touch the above-mentioned issue of whether an ideal glass transition exists or not. On the basis of the recent findings [20–22] of the decoupling of a translational diffusion mode from a structural relaxation one and the resulting change in the crystallization kinetics, we argue that it is intrinsically impossible to cool an ‘‘equilibrium’’ liquid until T_K without crystallization. Thus, we show that the Kauzmann paradox, or the entropy crisis, can be avoided by crystallization. We also suggest that there is a possibility of experimentally accessing the instability point of a supercooled liquid against crystallization and directly checking the validity of our scenario.

II. BRIEF REVIEW OF THE CLASSICAL THEORY OF NUCLEATION

First we briefly review the classical theory of nucleation [1,13]. Although it is not a first-principle theory, it is well established that it describes the nucleation and growth pro-

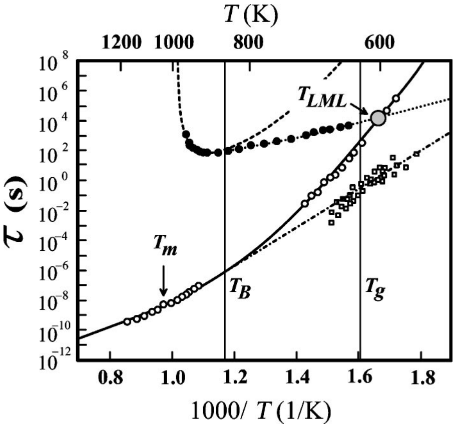

FIG. 3. Temperature dependences of τ_α, τ_D, and τ_x for a metallic glass former [20] $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$. Open circle, τ_α; filled circle, τ_x; and open square, τ_D. All the data are taken from Ref. [20]. The solid line is the Vogel-Fulcher law, the dot-dashed line is the Arrhenius law, and the dashed line is the prediction of Eq. (5). For this material, it is experimentally found that τ_D obeys the Arrhenius law. $f(\phi,T)$ can be estimated to be 10^7-10^8 around the nose temperature T_n. At $T=600$ K, which is slightly below T_g, τ_x ($\tau_t=\tau_D$) is comparable to τ_α. Thus, τ_x should become smaller than τ_α below temperature T_{LML}, which is located around 600 K for this material. Thus, it is impossible to supercool this liquid further below T_{LML} while allowing the full structural relaxation. Note that the characteristic relaxation time at T_{LML} is in the order of 10^4 s, which may be accessible experimentally. The key temperatures of this material are as follows: $T_m=1026$ K, $T_n=895$ K, $T_B=850$ K, $T_g=623$ K, and $T_0=413$ K. Fragility index D_f is 18.5.

cess of crystal on a satisfactory level (see, e.g., Fig. 3). Thus, we consider the stability of a supercooled liquid against crystallization on the basis of this classical theory. The frequency of homogeneous nucleation (i.e., nucleation that occurs in a liquid without assistance of impurity particles) was considered as a key physical factor characterizing the stability of a supercooled state. Nucleation frequency I is given by

$$I=\frac{k_n}{\tau_t}\exp[-\Delta F^c/k_BT], \tag{1}$$

where k_n is a constant specified by the model. Here ΔF^c, which is the free-energy barrier for nucleation of a critical nucleus, is a key thermodynamic factor governing I. According to the standard theory of the first-order phase transition, the size of a critical nucleus is estimated as $r_c=2\gamma/\delta\mu$, where $\delta\mu$ is the free-energy difference per unit volume between a supercooled liquid and a crystal and γ is the interface tension between them. Note that $\delta\mu$ is usually an increasing function of the degree of supercooling. Approximately, $\delta\mu\cong\Delta H_f(1-T/T_m)$ near T_m, where ΔH_f is the enthalpy of fusion. Then, the free-energy barrier for its nucleation is given by

$$\Delta F^c=\frac{16\pi\gamma^3}{3\,\delta\mu^2}. \tag{2}$$

On the other hand, a kinetic factor governing I is τ_t, which is the characteristic time of material transport controlling crystallization. τ_t is usually believed to be structural relaxation time τ_α, which is proportional to viscosity η and obeys the Vogel-Fulcher law for a supercooled state at low temperatures (see Fig. 2 and Sec. III for its theoretical basis):

$$\tau_\alpha=\tau_0\,\exp\left(\frac{D_fT_0}{T-T_0}\right), \tag{3}$$

where τ_0 and D_f are constants and T_0 is the so-called Vogel-Fulcher temperature. Since T_0 is located very near T_K, at least for fragile glass formers, it is usually assumed that $T_0=T_K$, following the Adam-Gibbs picture [15,23,24]. D_f is known as the fragility index, which is negatively correlated with the fragility. Namely, the viscosity of a more fragile liquid with smaller D_f increases more steeply with decreasing temperature [1–4].

After nucleation, a nucleated crystal grows. This growth velocity is given by

$$V=\frac{k_v}{\tau_t}[1-\exp(-v_m\delta\mu/k_BT)], \tag{4}$$

where k_v is a constant and v_m is volume per atom or molecule. Thus, the characteristic time required for crystallization of a certain small volume fraction ϕ of a supercooled liquid, τ_x, is given below T_m by

$$\tau_x=\left(\frac{3\phi}{\pi IV^3}\right)^{1/4}=\tau_t\left(\frac{3\phi}{\pi k_nk_v}\,\frac{\exp\left[\dfrac{\Delta F^c}{k_BT}\right]}{\left[1-\exp\left(-\dfrac{v_m\delta\mu}{k_BT}\right)\right]^3}\right)^{1/4}$$
$$=\tau_tf(\phi,T). \tag{5}$$

This τ_x has a minimum at the so-called nose temperature T_n which is located slightly below T_m, as a result of the competition between an increasing driving force for crystallization $\delta\mu$ and a decreasing mobility ($1/\tau_t$) upon supercooling (see Fig. 2). This fastest rate of crystallization at T_n determines the critical cooling rate R_c, or the glass formability. Then, the conditions to vitrify are rather straightforwardly obtained [13]: (i) larger ΔF_c and (ii) larger η in a supercooled region. It is usually believed that if we can successfully pass through the most dangerous temperature region around T_n without crystallization upon cooling, a supercooled state at a lower temperature may be stable, or free from crystallization. This last conclusion is a direct consequence of the assumption of $\tau_t=\tau_\alpha$, whose validity will be reconsidered carefully below.

III. THEORETICAL BASIS OF THE VOGEL-FULCHER LAW

Slow dynamics of supercooled liquid and the relevance of the Vogel-Fulcher law are worth considering in more detail, since our argument relies on its (at least apparently) diverging character at T_0. There are various models describing the slow dynamics associated with glass transition. There has been no consensus on this issue, which is directly related to the problem of whether an ideal glass transition exists or not: For example, the theories based on a spin-glass picture predict the Vogel-Fulcher-type divergence [16–19], the frustration-limited domain theory proposes the power law T dependence of the activation energy [25], and some theories predict nondivergent behavior at a finite temperature [26]. It is beyond the scope of this paper to discuss the origin of the slow dynamics itself in detail [27,28]. Here we note that the coincidence of T_0 and T_K for fragile glass formers [1,2,23,29] and the numerical simulations suggestive of the close connection between thermodynamic and kinetic singularity [30] are more consistent with the Vogel-Fulcher law than the other predicted behaviors. Although the singularity at T_0 must be considered more carefully [4], the Vogel-Fulcher law is a reasonable approximation. This scenario is supported by the notion that the universal behavior of supercooled liquids arises from an underlying random first-order transition [16–19], which is found in mean-field theories of spin glass without reflection symmetry, and in mode-coupling and density functional approaches to the structural glass transitions [17,19].

A theoretical argument based on random first-order transition, which supports the validity of the Vogel-Fulcher law, is as follows [16,19]. Below T_A the system has to overcome some free-energy barrier to reach another metastable state. The driving force for this process to occur is the configurational entropy of the other states to which the region might hop. Thus, the mosaic structure made of metastable islands emerges below T_A, which results in dynamic heterogeneity. Dynamic coherence length ξ, which is the characteristic size of metastable islands, diverges toward the spin-glass-like transition temperature T_0 as $\xi \cong a[(T-T_0)/T_0]^{-2/3}$ (a being molecular size) and the free-energy barrier diverges as $\Delta F = k_B T[D_f T_0/(T-T_0)]$. Thus, the Vogel-Fulcher law can be derived on the basis of a microscopic theory (see Refs. [16,19] for the details).

As discussed by Stillinger [8], the configurational entropy would not vanish in any realistic model with finite-range forces. This is because point defects are always present and they lead to a finite contribution to the configurational entropy. However, even if rounding of the transition were to occur below the laboratory glass transition, the above argument should be relevant to the supercooled state except for the very vicinity of T_0 [16]. Thus, we use the Vogel-Fulcher law for τ_α in our discussion.

Here we note that whether we can extrapolate the Vogel-Fulcher law into and beyond T_g is a matter of debate [26]. However, we believe that if we fit the Arrhenius law to τ_α above T_m and fit the Vogel-Fulcher law only below T_m, there should be little deviation from the Vogel-Fulcher law near and below T_g [28]. The validity of the Vogel-Fulcher law even below T_g can indeed be seen in Fig. 3, at least for a metallic glass former studied here. More importantly, what we consider here is a hypothetical "equilibrium liquid" before vitrification. Thus, we believe that we can use the Vogel-Fulcher law in our argument even below T_g determined for a rather fast cooling rate.

Finally, we note that the above theory [19] also predicts that the distribution of the free-energy barrier height ΔF, induced by the fluctuation in the configurational entropy, gives rise to the heterogeneity in relaxation time τ_α. Accordingly, relaxation in supercooled liquids is expressed by the stretched exponential as [1,2]

$$\phi(t) = \exp[-(t/\tau_\alpha)^{\beta_K}], \tag{6}$$

where β_K is the stretched exponent ($0 < \beta_K \leqslant 1$). Note that a smaller β_K means wider distribution of the relaxation time. As will be discussed in the following section, this distribution of τ_α is the origin of the translational-rotational decoupling, or the violation of the Stokes-Einstein relation. We note that the degree of dynamic heterogeneity, which is characterized by β_K, is controlled by the fragility. More fragile liquids with smaller D_f have stronger dynamic heterogeneity (smaller β_K) [1,2,19,31].

IV. TRANSLATIONAL-ROTATIONAL DECOUPLING AND CRYSTALLIZATION KINETICS

Magill and Plazek [32] found in their pioneering work that the material transport of crystallization in a deeply supercooled liquid is not controlled by viscosity and the crystal growth rate decouples from viscosity below T_m. Very recently, it has been suggested [20–22] that for a deeply supercooled liquid the crystallization is not controlled by the structural relaxation mode, but is controlled by the translational diffusion mode (see Fig. 2), which naturally explains the above finding of Magill and Plazek. For metallic glass formers, Masuhr *et al.* [20] found that the translational diffusion decouples from the structural relaxation (or viscosity) below bifurcation temperature T_B [33] and translational diffusion constant D_T follows the Arrhenius law there (see Fig. 3). They also confirmed that the crystallization kinetics is controlled by the translational diffusion and not by the viscosity. For molecular liquids, on the other hand, Swallen *et al.* [22] demonstrated by the study of deeply supercooled tris-naphthylbenzene near T_g that translational diffusion constant D_T is proportional to $\eta^{-0.77}$ (fractional Stokes-Einstein relation) and enhancement of translational diffusion relative to viscosity or rotation by a factor of 400 at T_g. This decoupling behavior is quite consistent with that derived from the crystallization growth rate data of the same material [21,32]. These studies indicate that by decreasing the crystallization temperature, the crystallization kinetics changes from viscosity-dominated to diffusion-dominated one at T_B, reflecting the translational-rotational decoupling [20–22].

Thus, we can say that it is translational diffusion that controls the rate of material transport for crystallization at any temperature. The crucial point is that the translational diffusion mode is decoupled from the structural relaxation one below T_B [33] (see Fig. 2), violating the Stokes-Einstein relation [1–4,34,35]. Although there is no firm microscopic basis why the Stokes-Einstein-like relation should hold for molecular diffusion, it is well established experimentally that it holds for a "true" equilibrium liquid above T_m over a wide temperature range. This decoupling is ascribed to the existence of dynamic heterogeneity [34,35]: A deeply supercooled liquid is not a usual liquid any more but is a dynamically heterogeneous liquid [16,19,31]. The most intuitive explanation for the rotational-translational decoupling based on the dynamic heterogeneity is as follows. The characteristic time scale of rotational motion is governed by the slower contributions of the distribution of relaxation times, $D_r \propto \langle \tau_\alpha \rangle^{-1}$ (D_r being rotational diffusion constant), while the average translational time is governed by faster times, $D_t \propto \langle \tau_\alpha^{-1} \rangle$ (D_t being translational diffusion constant) [19,25,34,35]. For a liquid with a very narrow distribution of the relaxation time, which is characterized by $\beta_K \cong 1$, it is obvious that $\langle \tau_\alpha \rangle^{-1} \cong \langle \tau_\alpha^{-1} \rangle$ and thus $D_r \propto D_t$. For this case, the Stokes-Einstein relation holds. This is the case for a liquid above T_m. Below T_m [28] (or T_A [16–19]), the relaxation time distribution becomes wider with decreasing T, or β_K starts to decrease from 1. This tendency is stronger for more fragile liquids (note that more fragile liquids have stronger cooperativity, or stronger dynamic heterogeneity). Thus, the degree of the decoupling is larger for more fragile liquids. For such a case, τ_x can be significantly shorter than that estimated on the basis of relation $\tau_t = \tau_\alpha$ (see Fig. 2).

V. A POSSIBLE RESOLUTION OF THE KAUZMANN PARADOX

A. Our scenario

Now we are ready to provide a resolution to the Kauzmann paradox. The very assumption made upon considering the entropy crisis is that a supercooled liquid continues to be an ‘‘equilibrium’’ liquid, at least until T_0, once it is deeply supercooled below the dangerous temperature region around T_n. The validity of this assumption itself must be checked carefully. The key physical parameter determining whether we can supercool a liquid while allowing its structural relaxation is the ratio of τ_x / τ_α which can be quantitatively expressed as

$$\frac{\tau_x}{\tau_\alpha} = \frac{\tau_t}{\tau_\alpha} f(\phi, T). \tag{7}$$

If we assume $\tau_t = \tau_\alpha$, we obtain $\tau_x / \tau_\alpha = f(\phi, T)$. Here, $f(\phi, T)$ is the slowness factor associated with nucleation and crystallization [see Eq. (5)]. Since it is known to be large for ‘‘good’’ glass formers (see the caption of Fig. 3), τ_x / τ_α can also be large. However, since the material transport for crystallization is controlled by the translational diffusion of an individual atom or a molecule (τ_t) and not by the structural relaxation (τ_α), the correct relation to be used is $\tau_t = \tau_D$, and ‘‘not’’ $\tau_t = \tau_\alpha$. Reflecting the decoupling of the τ_D mode from the τ_α one below T_B, thus, τ_t below T_B is described by either (i) the Arrhenius-type temperature dependence [20] or (ii) the fractional Stokes-Einstein relation [34,35]. For rather strong metallic glass formers, it is well established that the diffusion process is well described by the Arrhenius law [36,37]. For fragile molecular glass formers, on the other hand, it is often described by the fractional Stokes-Einstein relation [34,35]. Namely, τ_t changes the temperature dependence around T_B from Eq. (3) to either (i) $\tau_t \cong \tau_0 \exp(\Delta E / k_B T)$, where ΔE is the activation energy and often similar to that of the viscosity above T_m or (ii) $\tau_t = \tau_\alpha^n$ $(n<1)$. The situation for case (i) is schematically shown in Fig. 2. Below T_B, thus, we should use

$$\frac{\tau_x}{\tau_\alpha} \cong \exp\left(\frac{\Delta E}{k_B T} - \frac{D_f T_0}{T - T_0} \right) f(\phi, T) \tag{8}$$

or

$$\frac{\tau_x}{\tau_\alpha} = \tau_\alpha^{n-1} f(\phi, T). \tag{9}$$

Note that both $\exp[(\Delta E / k_B T) - (D_f T_0 / T - T_0)]$ and τ_α^{1-n} become zero (or at least very small) at T_0, while $f(\phi, T)$ is rather insensitive to T except near these temperatures and almost constant around T_0, although it diverges at either $T = T_m$ or $T = 0$ K [38]. Thus, either of the above relations leads to the conclusion that τ_x / τ_α should become quite small (less than 1) for deep supercooling before reaching T_0. We call temperature T_{LML}, where τ_x becomes equal to τ_α, ‘‘lower metastable limit,’’ following Kauzmann [7]. Note that T_{LML} should always be located above T_0. We stress that it is not meaningful to consider an ‘‘equilibrium’’ liquid below T_{LML} since a liquid should crystallize below T_{LML} during the equilibration (or structural relaxation) time, which must be longer than τ_α by definition. The distance between T_{LML} and T_0 may be smaller for stronger liquids due to a weaker decoupling. However, even for strong liquids, such as SiO_2 and GeO_2, the temperature dependence of τ_α or η changes from the Arrhenius to the Vogel-Fulcher-type below T_m [39]. This implies the existence of the cooperativity and the resulting dynamic heterogeneity, even though they are weak. For example, T_0's of SiO_2 and GeO_2 are estimated as 529 and 199 K, respectively [39]. Provided that a translational-rotational decoupling also occurs in these liquids, our argument should also apply to these strong liquids, although T_{LML} may be located rather near T_0. It is worth stressing that no matter how close T_{LML} is to T_0, the fact that $T_{LML} > T_0$ is crucial for the avoidance of the Kauzmann paradox. Finally, for a hypothetical ‘‘strong-limit’’ liquid, whose τ_α obeys the Arrhenius law, its T_0 is located at 0 K by definition. Thus, there is no violation of the third law of thermodynamics. In any case, the unphysical situation of the Kauzmann paradox can naturally be avoided by our scenario [see Fig. 1(c)].

B. Experimental supports

In Fig. 3, we show the behavior of τ_α, τ_D, and τ_x for a metallic glass former [20] to provide the readers with a quantitative support about what is described above. It clearly shows that τ_x can indeed become less than τ_α with decreasing T. We stress that the temperature extrapolation of τ_x, which is necessary to draw this conclusion, is only about 30 K. More importantly, there is no need of extrapolation for τ_α, which means that we need not worry about whether there is an ideal glass transition or whether τ_α really goes to infinity. It can be easily confirmed in Fig. 3 that up to 590 K the Vogel-Fulcher relation describes the experimental data of τ_α well. T_{LML} is located around 600 K, which is only -20 K below T_g and the structural relaxation time is 10^4 s there. Thus, it may be possible to experimentally approach T_{LML} while equilibrating the liquid and checking whether the liquid really loses its stability against crystallization there. We note that T_{LML} (~ 600 K) is located far above T_0 (~ 413 K). The rather close distance between T_g and T_{LML} and the not so long relaxation time ($\sim 10^4$ s) at T_{LML} suggests a possibility that the relevance of our scenario resolving the Kauzmann paradox may be checked experimentally for such a system.

We expect that the same conclusion should also be reached for molecular liquids (see, e.g., Ref. [21]). Unfortunately, however, there are few molecular liquids for which τ_x (crystal growth rate G and nucleation rate I) and τ_t under deep supercooling are available. Thus, extensive check of our scenario for various glass-forming liquids remains a future task.

C. Consideration on the non-mean-field effects of crystallization

Here we consider whether the mean-field treatment of crystallization affects our main conclusion. The dynamic heterogeneity and the resulting translational-rotational decoupling are induced by the non-mean-field effects due to fluctuations of configurational entropy. Fluctuation effects on kinetics are effectively included by using $\tau_t = \tau_D$ instead of $\tau_t = \tau_\alpha$. Inclusion of such non-mean-field effects would also affect the evaluation of $f(\phi,T)$. For example, there is a possibility that the critical size of a nucleus r_c may become smaller than dynamic coherence length ξ near T_0 since the former decreases with an increase in the degree of supercooling while the latter increases. However, the nondiverging character of $f(\phi,T)$ at T_0 should not be changed by these effects since we do not expect any singularity of ΔF_c and $\delta\mu$ at T_0. Thus, we believe that our conclusion would not be affected by the non-mean-field effects, at least on a qualitative level. More explicitly, the effects may change the location of T_{LML}, but should not affect our basic conclusion that T_{LML} should be located above T_0. In relation to this issue, it is worth noting that the crystallization behavior in deeply supercooled liquids is quite well described by the expression for τ_x [see Eq. (5) and Fig. 3], whose validity has been experimentally confirmed for metallic glass formers [20] and also for molecular liquids [21].

VI. STABILITY OF A GLASSY STATE: CRYSTALLIZATION BELOW T_g

Finally, we discuss the stability of a metastable liquid state against crystallization at low temperatures. Since the decoupling of τ_α and τ_D modes is the origin of crystallization at low temperatures in our model, we suggest that a very fragile liquid may crystallize even below T_g. Such crystallization below T_g is indeed reported by Oguni and his coworkers [40] for several fragile liquids. Although crystallization below T_g was ascribed to the slow-β (Johari-Goldstein) relaxation mode in Ref. [40], we suggest that it can be induced by the translational diffusion mode. Note that the slow-β mode, which is usually assigned to be the rotational librational motion [2], should not exist in metallic glass formers made of spherical atoms and thus it cannot explain the change in their crystallization kinetics below T_B (see Ref. [20]). Since both modes start to decouple from the structural relaxation mode around T_B upon cooling, our assignment can also explain the interesting observation of Oguni and his co-workers on crystallization below T_g [40].

Next we consider the case of a strong liquid. Different from a fragile liquid, we expect that a strong liquid should be more difficult to crystallize than a fragile one below T_g since its kinetics is almost controlled by τ_α due to the very weak decoupling, which means $\tau_t = \tau_D \cong \tau_\alpha$, and thus τ_x/τ_α should be large. In other words, a *stronger liquid*, which suffers from *stronger disorder effects* [28], is *more homogeneous dynamically*. This is indeed the case for silica: Silica glass continues to be amorphous even after thousands of years. This prediction that a stronger glass former should be more stable against crystallization has an important implication on the storage of glassy material below T_g. It is of practical significance to keep glassy functional materials, such as photo-printing films, in the glassy state without crystallization during the storage period. We argue that the reduction of fragility should enhance the stability of glassy material against crystallization below T_g. This prediction may be useful for improving the long-term stability of glassy material during the storage.

In relation to this problem, we point out that crystal formation in a glassy material should induce extensional stress (negative pressure) around a nucleated crystal due to the volume contraction upon crystallization, which should provide the free volume to the particles surrounding the crystal, increase their mobility, and help further crystallization. This feature should become quite important especially below T_g, where τ_x becomes comparable to τ_α. The effects of negative pressure may not exist for a supercooled liquid state and may be unique to a glassy state. We speculate that this scenario may explain a sudden increase in the growth speed below T_g, observed by Hikima, Hanaya, and Oguni [40], which is apparently counterintuitive and cannot be expected from the conventional theory of crystallization. This problem will be considered in more detail elsewhere.

VII. SUMMARY

In summary, we propose that a supercooled liquid should crystallize before reaching T_0 if it is cooled slowly enough to satisfy the condition that the equilibration time is longer than structural relaxation time τ_α. This indicates that there exists a lower metastable limit T_{LML}, below which an ‘‘equilibrium’’ supercooled liquid cannot exist. Thus, the Kauzmann paradox is naturally resolved. This conclusion may apparently look the same as that derived by Kauzmann himself more than 50 years ago [7]. However, we stress that the physics behind them is entirely different: The decoupling of the translational diffusion mode from the structural relaxation one, which was not known at the time of Kauzmann, is a key to deriving our conclusion. We suggest that it is *dy-*

namic heterogeneity that destabilizes an ‘‘equilibrium’’ supercooled liquid state as well as a glassy state against crystallization at low temperatures.

It should also be noted that our resolution removes the physical foundation for the necessity of an ideal glass transition at T_0. At the same time, however, our resolution does not necessarily exclude the existence of such a hidden dynamic singularity associated with T_0. Note that theoretical extrapolation is always possible. Our study indicates that this is a separate problem and we cannot use the Kauzmann paradox to justify the existence of an ideal glass transition. Further study is necessary to elucidate this problem, which is deeply connected with the physical nature of liquid-glass transition and conceptually important [8–10,14,41].

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