Relation between Thermodynamics and Kinetics of Glass-Forming Liquids

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Vitrification of a supercooled liquid is often characterized by the hypothetical kinetic instability point, the Vogel-Fulcher temperature T_0, and the thermodynamic one, the Kauzmann temperature T_K. The widely believed relation $T_0 \cong T_K$ is regarded as the supporting evidence of a direct connection between the thermodynamics and kinetics of glass-forming liquids. Here we demonstrate that T_K/T_0 systematically increases from unity with a decrease in the fragility, contrary to the common belief. This systematic deviation may be explained by a synergistic effect between the weaker cooperativity and the stronger tendency of short-range ordering in stronger glass formers.

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Liquid-glass transition phenomena are universally observed in various types of liquids, including molecular liquids, ionic liquids, metallic liquids, oxides, and chalcogenides [1–3]. There are three key temperatures that are often used to characterize vitrification of a supercooled liquid: glass-transition (T_g), Vogel-Fulcher (T_0), and Kauzmann (T_K) temperatures. T_g is a measurable temperature, below which a liquid becomes a glassy state upon cooling, while T_0 and T_K are, respectively, "hypothetical" kinetic and thermodynamic instability points. To determine T_0 and T_K, we need to extrapolate the data of the viscosity (or the structural relaxation time) and the entropy of a liquid below T_g, respectively. The former is determined by fitting the so-called Vogel-Fulcher law, $\eta = \eta_0 \exp(\frac{B}{T-T_0})$, where η_0 and B are constants and T is the temperature, to the viscosity. The latter is, on the other hand, determined by the temperature where the extrapolated liquid entropy becomes lower than the entropy of the equilibrium crystal. Since it is in principle impossible to confirm the very existence of these hypothetical instabilities experimentally, it is a matter of debate whether such kinetic and thermodynamic instability points are necessary properties of a supercooled liquid or not [4,5]. Nevertheless, it is empirically established that the relation $T_K \cong T_0$ holds for many liquids [6]. This fact is often regarded as the supporting evidence of a direct connection between the thermodynamics and kinetics of glass-forming liquids [7,8] as well as the existence of "ideal glass transition" [1–3]. The fact that the relation $T_K \cong T_0$ holds for various types of liquids also implies a possibility of the universal physical description of glass transition for all types of glass formers covering from fragile to strong ones [9].

In this context, we stress that this connection between entropy crisis and viscosity divergence is the basis of some key theories of glass transition, such as the Adam-Gibbs theory [10], the spin-glass theories [11,12], and the energy-landscape pictures [3,13,14]. Here we briefly review a popular argument that connects the configurational entropy of a glass-forming liquid with its slow dynamics. According to the Adam-Gibbs theory [10], $\eta = \eta_0 \exp(C/T\sigma_{\mathrm{conf}})$, where C is a constant and σ_{conf} is the configurational entropy. If we assume that the heat capacity difference between the liquid and the solid is given by $\delta C_P = K/T$ and the entropy difference between them, $\delta\sigma$, vanishes ($\delta\sigma = 0$) at T_K, we immediately obtain [6] $\delta\sigma = K(1/T_K - 1/T)$. If we assume $\delta\sigma = \sigma_{\mathrm{conf}}$ [15], the above equation reduces to the Vogel-Fulcher equation, $\eta = \eta_0 \exp[DT_0/(T - T_0)]$, with $T_0 = T_K$. Thus, the relation $T_0 = T_K$ is necessary for the direct link between the thermodynamic singularity and the kinetic one. The above argument leads to the relation $D = C/\delta C_P(T_0)$, which is consistent with the well-known experimental fact [6,8] that for many liquids except for some alcohols and bulk metallic glass formers, the heat capacity jump upon the glass transition at T_g, $\delta C_P(T_g)$ ($= K/T_g$), is smaller for a stronger liquid, or for larger D. This argument is often used to support a direct connection between thermodynamics and kinetics and the relation $T_K \sim T_0$.

However, there are some exceptions for the relation $T_K \cong T_0$ (see Ref. [16] and tables in Refs. [1,6]), which have been overlooked so far and have not attracted much attention. Since this relation is of significant fundamental importance for our physical understanding of glass transition, as reviewed above, it is meaningful to investigate the relation between T_K and T_0 in more detail. In this Letter, thus, we make an extensive survey on the values of T_K and T_0 for various types of glass formers. Surprisingly, a positive correlation between T_K/T_0 and the fragility index D [17] has been found, contrary to the often-assumed relation $T_K \cong T_0$. We propose a plausible scenario of this correlation.

First we show the results of our survey on T_K, T_0, and the fragility index D, and their relationship (see Table I). Glass formers investigated here contain molecular liquids, metallic glass formers [18], and oxide glass formers. The values of T_K/T_0 are plotted against D for 18 liquids in Fig. 1. This clearly tells us that the widely believed and often-assumed relation [9] $T_K \cong T_0$ is severely violated for strong liquids and it holds only for rather fragile liquids. Furthermore, it reveals that there is

TABLE I. Relation among the key temperatures, T_m, T_K, and T_0, and the fragility index D for various glass formers. All the data that are not labeled are taken from Ref. [6].

No.	Material name	T_K (K)	T_0 (K)	T_K/T_0	D	No.	Material name	T_K (K)	T_0 (K)	T_K/T_0	D
1	GeO_2	418[a]	199[a]	2.1	113[a]	10	Ethylene glycol	115	109	1.05	16.0
2	SiO_2	876[a]	529[a]	1.66	63[a]	11	$Cu_{47}Ti_{34}Zr_{11}Ni_8$	573[k]	500[e]	1.15	12[e]
3	$ZnCl_2$	250	180–236	1.39–1.06	32	12	Glycerol	135	127	1.07	10.6[l]
4	Butyronitrile	81.2	58	1.26	32	13	Sorbitol	236	224	1.05	8.6
5	Vit4[b]	560[c]	372[d]	1.5	22.7[e]	14	Toluene	96	103	0.93	5.6
6	$Mg_{65}Cu_{25}Y_{10}$	325[f]	260[f]	1.25	22.1[f]	15	*o*-terphenyl	200	184	1.09	5.0
7	Vit1[g]	558[h]	413[h]	1.35	20.4[e]	16	Propylene carbonate	125.8	130	0.97	2.9
8	$Pd_{40}Ni_{40}P_{20}$	500[i]	390[j]	1.28	18.1[j]	17	Triphenyl phosphite	166	183	0.91	2.9
9	1,2-propane diol	127	114	1.11	17.8	18	Sucrose	283	290	0.98	0.154

[a] Reference [29]. [b] $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ [c] Reference [30]. [d] Reference [31]. [e] Reference [32]. [f] Reference [33].
[g] $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ [h] Reference [34]. [i] Reference [35]. [j] Reference [36]. [k] Reference [37]. [l] Reference [38].

a strong positive correlation between T_K/T_0 and D. Namely, T_K systematically deviates from T_0 more significantly for a less fragile, or stronger, liquid.

Our finding suggests that the above popular argument is not enough to understand the relation between thermodynamics and kinetics of glass-forming liquids. Here we propose a plausible scenario for this relation, focusing on the tendency of short-range bond ordering in liquids. It has often been assumed in glass-transition theories such as the free-volume theory that a liquid is in a completely disordered state and the state of liquid can be expressed solely by its density, namely, the state of packing. Contrary to this, we have recently proposed a two-order-parameter model of liquid [19–21]. Our model is based on the physical picture that (a) there exist rather well-defined, unique locally favored structures in any liquids and (b) such structures are created in a sea of normal-liquid structures and its number density increases upon cooling since they are energetically more favored by ΔE than normal-liquid structures. Namely, a liquid is in a disordered state in the long range, but it locally possesses the short-range bond order. This short-range order is due to specific interactions between liquid atoms or molecules that have the symmetry-selective nature. They may stem from the shape of molecules (van der Waals interactions), hydrogen bonding, covalent bonding, or electrostatic interactions. Most typical examples of such short-range order is a tetrahedral structure for silica [1] and an icosahedral structure for metallic glass formers [1,22], which have been confirmed by both experiments and simulations [1]. We identify such a locally favored structure as a minimum structural unit [symmetry (or volume) element]. The average fraction of locally favored structures are straightforwardly calculated as $\bar{S}(T) \cong \exp(\frac{\Delta E - T\Delta\sigma - P\Delta v}{k_B T})$, for the case of $\bar{S} \ll 1$ [19–21]. Here k_B is the Boltzmann's constant, P is the pressure, Δv is the difference in specific volume between a locally favored structure and the corresponding normal-liquid structure, and $\Delta\sigma$ is the difference in entropy between them. Since there are many different configurations for normal-liquid structures, while there is a unique locally favored structure that satisfies the condition to be a symmetry element, the former has larger entropy than the latter. At a low temperature, however, the above assumption $\bar{S} \ll 1$ is no longer valid especially for a strong liquid. Furthermore, the cooperativity in formation of locally favored structures may lead to a liquid-liquid phase transition [1,21].

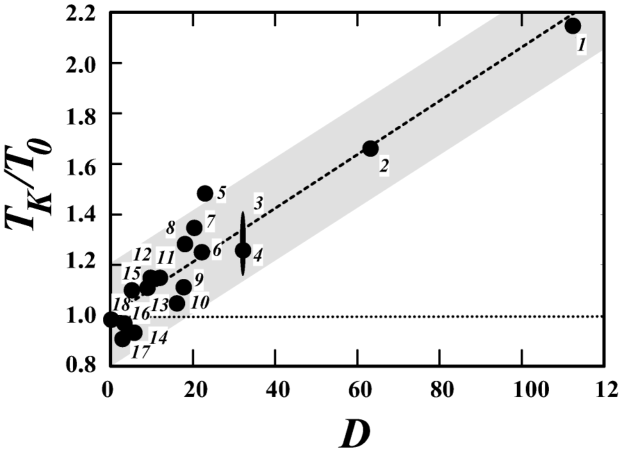

FIG. 1. Correlation between T_K/T_0 and the fragility index D for materials listed in Table I. The horizontal dotted line is a line of $T_K/T_0 = 1$. Note that (i) the deviation of T_K from T_0 is considerable, which is sometimes more than 100 K for strong liquids, and (ii) it systematically increases with an increase in D for various types of glass formers. Thus, we believe that the observed systematic increase in T_K/T_0 with D is far beyond errors and meaningful, despite the fact that the extrapolations of T_K and T_0 inevitably contain large ambiguity especially for strong liquids.

We propose that such short-range bond ordering in liquid is a key to understanding the thermodynamic behavior for a variety of glass-forming liquids such as covalent, metallic, and van der Waals liquids, in a unified manner. Along with this idea, here we explain the larger deviation of T_K/T_0 from unity with a decrease in the fragility as follows: (i) Short-range bond ordering in a liquid leads to an extra decrease of entropy of the liquid, which leads to the upward shift of T_K from T_0 upon extrapolations (see Fig. 2). (ii) Such short-range ordering is not *directly* associated with the divergence of the viscosity at T_0, or cooperativity. In other words, it does not have any singularity at T_0. Because of its different temperature dependence, it should be regarded as the source of an "extra" decrease [see (i)]. (iii) Stronger liquids are characterized by a stronger tendency of short-range ordering. Since the energy scale of interactions determines the energetic gain of short-range bond ordering, it is quite natural to expect that the degree of short-range bond ordering ($\bar{S}$) increases in the order of van der Waals, hydrogen-bonded, and covalent-bonded liquids, which leads to a decrease in fragility (an increase in D). These three points naturally explain the positive correlation between T_K/T_0 and D through the degree of short-range bond ordering ($\bar{S}$). Hereafter we consider these points (i)–(iii) in more detail.

First we consider the effects of this short-range bond ordering in a liquid on the thermodynamic properties of a supercooled liquid. With including the entropy associated with short-range bond ordering, $\sigma_{\rm SRO} = \Delta\sigma_{\rm SRO}(1-\bar{S})$ ($\Delta\sigma_{\rm SRO}$ is the total entropy change associated with short-range bond ordering), the excess entropy $\delta\sigma$ can be expressed as $\delta\sigma = \sigma_{\rm conf} + \Delta\sigma_{\rm SRO}(1-\bar{S}) + \sigma_{\rm vib}^e$. Here $\sigma_{\rm vib}^e$ is the excess vibrational entropy of a liquid over the crystal. Note that similarly to $\sigma_{\rm conf}$, the above $\Delta\sigma_{\rm SRO}$ should also become zero at T_0, where a system is supposed to become nonergodic even for infinitely slow cooling. Thus, the following approximate relation is obtained: $\delta\sigma(T) = \frac{C'}{D}(\frac{1}{T_0} - \frac{1}{T}) - \Delta\sigma_{\rm SRO}\bar{S}(T) + \sigma_{\rm vib}^e(T)$, where C' is a constant.

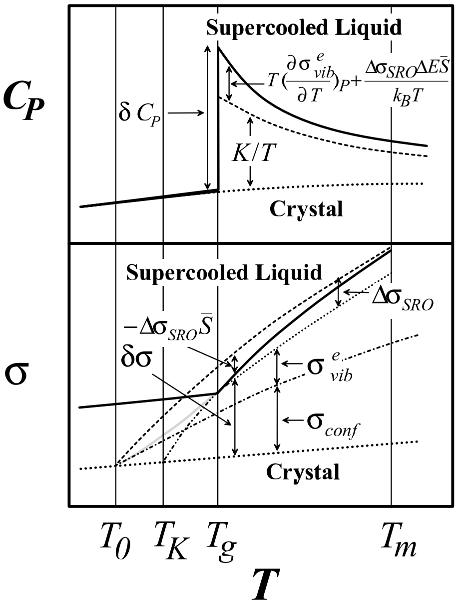

FIG. 2. Temperature dependence of C_P (top) and σ (bottom). Short-range bond ordering results in the deviation of T_K from T_0 toward the high-temperature side and the extra contribution to the C_P jump at T_g, δC_P. The latter may explain unusually large $\delta C_P(T_g)$ for alcohols and metallic glass formers [2].

Now we are ready to explain the observed discrepancy between T_K and T_0. According to the above argument, T_K is determined as the extrapolated zero-crossing temperature of the above $\delta\sigma$ estimated from the heat capacity (C_P) measurements, while T_0 is determined as that of $\sigma_{\rm conf}$ estimated from kinetic measurements of the viscosity or the structural relaxation time (see Fig. 2). This means that the Kauzmann temperature T_K, where the extrapolated entropy of liquid becomes equal to that of the crystal, does not necessarily coincide with T_0 kinetically determined. We can straightforwardly obtain the relation between T_K and T_0 from $\delta\sigma(T_K) = 0$:

$$\frac{T_K}{T_0} \cong 1 + \frac{T_K[\Delta\sigma_{\rm SRO}\bar{S}(T_K) - \sigma_{\rm vib}^e(T_K)]}{C'} D. \qquad (1)$$

Thus, our model predicts that T_K/T_0 should increase from unity with an increase in the strong nature of liquid, or D [23]. This D dependence reflects the fact that a stronger liquid with larger D has a smaller configurational entropy [24], namely, weaker cooperativity. This prediction is consistent with the tendency observed experimentally for various glass formers (see Fig. 1).

What remains to be done is to clarify the relation between the degree of short-range bond ordering ($\bar{S}$) and the strong nature of liquid (D). According to our two-order-parameter model of liquid-glass transition [19], the anisotropic part of interactions inevitably induces frustration between different local symmetries favored by interactions (more specifically, between a part consistent with the symmetry of the equilibrium crystal and that inconsistent with it), which plays major roles in vitrification. In our model, thus, it is the degree of short-range bond ordering in a liquid, $\bar{S}$, that controls the fragility. More precisely, the short-range bond order induces the disorder effects on crystallization, which are similar to effects of random fields in spin glass, if the symmetry of short-range bond order is not consistent with that of the long-range crystalline order [25]. The strength of the effective random fields, which is characterized by $\bar{S}$, is a key physical factor controlling the fragility. In our model, thus, a stronger liquid, which is characterized by larger ΔE, suffers from stronger disorder effects on crystallization and leads to a larger distance between the onset of frustration, which is related to T_m, and the transformation to the spin-glass-like state at T_0. Note that the larger T_m/T_0 means the larger D. Thus, our model predicts a positive correlation between $\bar{S}$ and D. This correlation is also consistent with the well-recognized fact [1–3] that network-forming covalent liquids, which have a strong tendency of short-range bond ordering, are strong glass formers. We also note that the positive correlation between the degree of icosahedral ordering and D is also well known for metallic glass formers [16,26,27]. On a phenomenological level, thus, it is quite reasonable to correlate the degree of short-range bond ordering with the strong nature of liquid, or the fragility index D, *even without the help of the above argument based on* *the two-order-parameter model.* This strongly supports a positive correlation between $\bar{S}$ and D. To clarify this correlation on a more quantitative level, however, further studies are necessary. In this context, Jund *et al.* [28] recently made an interesting simulation in which the tendency of tetrahedral ordering in a covalent-bonding liquid (SiO_2) is systematically controlled. They found a clear positive correlation between the degree of short-range tetrahedral ordering and the fragility index D. This study supports our physical picture and may provide a quantitative check of our proposal.

To summarize, we demonstrated that there are many glass formers for which the relation $T_0 = T_K$ is severely violated, and found a positive correlation between T_K/T_0 and D for the existing data. A possible scenario for this correlation was proposed on the basis of our two-order-parameter model of liquid. Further careful and systematic studies on the relation between T_0 and T_K for many glass formers with various fragility are highly desirable to confirm the correlation more unambiguously, since the results might be affected by the way of extrapolations made, especially for strong liquids. Finally, we stress that our finding does not necessarily deny a direct connection between thermodynamics and kinetics itself. For example, the behavior of σ_{conf} shown in Fig. 2 is consistent with a direct connection between thermodynamics and kinetics. Finally, we note that our thermodynamic model is not specific to any models of glass transition and quite generic in the sense that it assumes only short-range bond ordering in liquids and the resulting decrease in the entropy.

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[18] Although the compositions of the crystals can be different from that of the liquid for multicomponent systems, it should not cause a large error in estimating T_K because the C_P values of many stable solid solutions or compounds are approximately equal to those of the mixture of metals according to the Neumann-Kopp rule [Q. Jiang, M. Zhao, and X. Y. Xu, Philos. Mag. B **76**, 1 (1997)].

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