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Origin of the excess wing and slow β relaxation of glass formers: A unified picture of local orientational fluctuations

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Here we consider the relation between the excess wing and the slow β relaxation, focusing on the degree of the coupling between cooperative rotational motion associated with creation and annihilation of metastable islands (α mode) and local rotational jump motion in a cage (slow β mode). For a strongly coupled case the slow β mode appears as the excess wing having the character of the α mode, while for a fully decoupled case as an independent local mode having the Arrhenius temperature dependence. We argue that the degree of the coupling between the two modes is controlled by the following two factors: (i) the relation between the characteristic size of metastable islands and the cage size and (ii) the disparity between the high-temperature Arrhenius behavior of the α mode and the Arrhenius behavior of the slow β mode.

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I. INTRODUCTION

Structural relaxation of glass-forming liquids, which is known as α relaxation, enormously slows down upon cooling while approaching the glass-transition temperature T_g [1]. This slowing down of the α relaxation is a key feature of the liquid-glass transition. There have been a number of attempts to explain this slow dynamics theoretically [1]. They include (a) theories based on the cooperativity of the motion [2,3], (b) mode-coupling theory [4], (c) spin-glass theory [3,5], and (d) theories based on frustration [6,7]. Although these approaches are based on the different physical pictures, they are sometimes closely related with each other. Experimentally, on the other hand, Stickel *et al.* [8] demonstrated that the temperature dependence of the α relaxation time τ_α changes from Arrhenius-type to Vogel-Fulcher-type at T_A, which is located near the melting point T_m, and further to another Vogel-Fulcher-type at T_B, reflecting the appearance of cooperativity upon cooling. In this scenario, τ_α is assumed to diverge at the so-called Vogel-Fulcher temperature T_0. It is also well established that, in addition to the α relaxation, there exists another slow mode, which is rather universally observed in many glass formers near or below T_g and known as the slow β (Johari-Goldstein) mode. This mode appears around T_A and often becomes a distinct mode below T_B [1,9–11]. The average relaxation time of the slow β mode $\tau_{slow\beta}$ usually obeys the Arrhenius law below T_B:

$$\tau_{slow\beta}=\tau_{0\beta}\exp\left(\frac{E_\beta}{k_BT}\right), \tag{1}$$

where $\tau_{0\beta}$ is the preexponential factor, E_β is the average activation energy of the slow β process, and k_B is the Boltzmann constant. It is also known that the distribution of the activation energy E of the slow β motion is usually very broad and can be approximated by the symmetric Gauss distribution [12]

$$g(E)=\frac{1}{\sqrt{2\pi}\sigma}\exp\left[-\frac{1}{2}\left(\frac{E-E_\beta}{\sigma}\right)^2\right], \tag{2}$$

where σ^2 is the variance. This slow β mode continues to exist below T_g. Johari and Goldstein [10] proposed that this mode may be a universal and intrinsic feature of glass-forming liquids at low temperatures, since it is observed even for rigid molecules having no intramolecular modes.

This universality is, however, apparently weakened by the following fact. There are many glass formers that do not exhibit a well-resolved slow β mode in the dielectric loss spectrum $\epsilon''(\nu)$ (ν being frequency). Their $\epsilon''(\nu)$ usually exhibits the so-called excess wing on the high-frequency side of the α-relaxation peak, which is described by the high-frequency power law $\epsilon''\sim\nu^{-\beta_K}$, where $\beta_K(\leqslant 1)$ is the so-called Kohlrausch stretched exponent. This wing can be reasonably well described by a second power law $\epsilon''\sim\nu^{-b}$, where $0<b<\beta_K$. It is known that the so-called Nagel scaling leads to a collapse of $\epsilon''(\nu)$ curves for different temperatures and various materials into a single master curve [13]. Although there are some efforts to describe the excess wing theoretically [14], there has so far been no consensus on its microscopic origin. There are two different basic views on the nature of the excess wing. Dixon *et al.* [13] proposed on the basis of the above Nagle scaling that the excess wing is an intrinsic feature of the α relaxation and thus universal to all the glass formers. Ngai [15], on the other hand, proposed on the basis of his coupling model that the excess wing is just the high-frequency flank of the slow β peak, whose low-frequency part is fully covered (or hidden) by the dominant α peak.

According to the above-mentioned difference in the dynamic features of the high-frequency side of the α relaxation, glass-forming liquids has often been classified into two types: type *A* materials with the excess wing (e.g., glycerol) and type *B* ones with a distinct slow β peak (e.g., toluene and sorbitol) [1,16,17]. The validity of such classification is now a matter of active debate. Here we summarize recent important experimental contributions concerning this problem.

(1) Schneider *et al.* [18] and Ngai *et al.* [19] made interesting experiments and analyses on type *A* materials. They expected that the slow β mode should be better resolved at a

lower temperature because its temperature dependence is weaker than that of the α mode. Indeed they successfully observed a well-resolved slow β peak at a low temperature even in type A materials (glycerol and propylene carbonate) after the long-time annealing of the samples below T_g. They also found that for these materials $\tau_{slow\beta}$ obeys the Vogel-Fulcher law instead of the Arrhenius one. They concluded that the slow β relaxation and the excess wing should have the same origin.

(2) Döß *et al.* [20] recently demonstrated by a systematic study on polyalcohols that the appearance of the slow β mode gradually changes from an excess wing to a pronounced peak from glycerol ($m=57$) to thretol ($m=79$), xylitol ($m=94$), and sorbitol ($m=128$). Here m is the so-called fragility (or steepness) index defined as [21,22]

$$m=\frac{1}{T_g}\left.\frac{d\log_{10}X(T)}{d(1/T)}\right|_{T=T_g}, \tag{3}$$

where X is τ_α or η (viscosity). Note that the larger m is, the more fragile the liquid is. They concluded that their observation strongly supports the assumption that the excess wing is the high-frequency flank of the slow β relaxation. Furthermore, they found from nuclear magnetic resonance (NMR) experiments that the slow β motion is slower and its vibration amplitude is smaller for glycerol than for sorbitol.

(3) From a systematic study of oligomers with different lengths, Mattsson *et al.* [23] concluded that the difference in type A and B stems from the difference in τ_α at the merging temperature. With a decrease in τ_α at the merging temperature, the behavior of a system changes from type A to type B.

(4) Casalini and Roland [24] recently reported the lack of correlation between the α relaxation and the excess wing and suggested that the two phenomena are distinct.

(5) Hensel-Bielowka and Paluch [25] investigated the pressure dependence of the excess wing of type A materials and the slow β mode of type B ones. They found that the effects of temperature and pressure on the excess wing relative to the α process is equivalent, while the effect of pressure on the slow β relaxation is considerably weaker than that on the α relaxation. They concluded that this supports the validity of the above classification into type A and B materials and that the origin of the excess wing is different from that of the slow β relaxation.

Some of these results apparently look contradictory with each other and thus there has so far been no consensus on this problem even on a qualitative level.

Finally we mention recent works on the merging behavior of the α and the slow β mode. Gómez *et al.* [26] studied the merging behavior of several type B polymers. They demonstrated that the merging behavior can be well explained by Williams-Watts approach [27] using the following rotational relaxation function:

$$\phi(t)=\phi_\alpha(t)[f_\alpha+(1-f_\alpha)\phi_\beta(t)], \tag{4}$$

where $\phi_\alpha(t)$ and $\phi_\beta(t)$ correspond to the normalized relaxation function of the α and slow β processes, respectively, and $1-f_\alpha$ represents the fraction of slow β relaxation. We note that in this approach both processes are assumed to be "statistically independent." Margulies *et al.* [28] also studied the merging behavior in sorbitol and maltitol by NMR and discussed the difference in the merging behavior between the two materials on a molecular level. Fujima *et al.* [29], on the other hand, revealed by the careful analysis of dielectric spectra of sorbitol and *m*-fluoroaniline in the merging region that (i) the slow β mode starts to decouple from the α mode around T_A, (ii) its temperature dependence is Vogel-Fulcher-like for $T_A>T>T_{cross}$, but (iii) below T_{cross} it becomes Arrhenius-like. This sequential change in the temperature dependence should also be explained.

In this paper, we propose a simple physical scenario that at least qualitatively accounts for all the above experimental facts in a coherent manner. We argue that the physical origins of the excess wing and slow β mode are essentially the same and the apparent difference comes from the difference in the degree of the decoupling of the slow β mode from the α one, which is mainly controlled by (a) the fragility and (b) the disparity between the high-temperature Arrhenius behavior of the α relaxation and the Arrhenius behavior of the slow β mode. Thus, we propose that the difference between type A and type B materials stems solely from this difference in the degree of the decoupling between the two modes.

II. MICROSCOPIC ORIGIN OF THE SLOW β MODE

Despite the long history of research, there has been no agreement on the microscopic origin of the slow β mode [30]. However, the most plausible interpretation may be the small-amplitude rotational jump motions of molecules [1,9,31,32]. This interpretation is strongly supported by recent multidimensional NMR studies [33].

A. Assignment of the slow β mode

We draw the following simple picture based on this interpretation. Upon cooling, the cooperativity sets in below T_A [34]. This leads to the gradual change in the temperature dependence of τ_α from Arrhenius-type to Vogel-Fulcher-type (see Sec. III A and III B for the details). Below this temperature, there is a cooperative rearranging region, which we call "metastable islands" (see Sec. III A and Ref. [35] for the details of our model). The average lifetime of metastable islands is, thus, τ_α. This island continues to exist for a time duration of $\sim\tau_\alpha$. For densely packed metastable islands, the rotational motion of a molecule is sterically or energetically hindered by the surrounding molecules. Thus, the thermal activation overcoming this barrier is necessary for the rotational jump motion. During the lifetime of a metastable solidlike island, thus, each molecule in it can neither translationally escape from its local environment ("cage"), which is composed of the neighboring molecules, nor make a full rotation due to the topological constraints; it can make only rotational jump motion in its cage. This small-amplitude orientational fluctuation mode should be the slow β mode. More specifically, it is multistate rotational jumping motion overcoming the average barrier height E_β with the attempt frequency of $\sim 1/\tau_{0\beta}$ [see Eq. (1)]. After some rotational jumps, a molecule can escape from its cage and make full rotation upon the reorganization of the metastable islands. These two modes start to decouple around T_A (the onset of cooperativity), reflecting the appearance of long-lived metastable islands. Note that above T_A all molecules can easily escape from its cage and make full rotation simply by overcoming an energy barrier E_α and thus there is no slow β mode. We call this temperature region above T_A the single-mode Arrhenius regime. Thus, it is natural to consider that the existence of metastable islands is prerequisite for the emergence of the slow β mode [1]. It is the existence of metastable islands that provides a situation that the lifetime of rotational jump sites is longer than the slow β relaxation time $\tau_{slow\beta}$.

B. Specific features of slow β relaxation

1. Nonuniversal features

In relation to the above microscopic origin, it is worth noting that the strength of the slow β mode relative to the α mode largely differs from material to material. Döß *et al.* [20] recently proposed that the amplitude of the rotational jump motion, which is characterized by the body angle $\delta\Omega$ of the motion, determines the dielectric strength of the slow β mode. The decrease in the dielectric relaxation strength of the slow β mode upon cooling can be explained by the decrease of $\delta\Omega$ with a decrease in *T*. The material specific features of the relative strength of the slow β mode can also be naturally explained by the scenario that the strength of the slow β relaxation peak in dielectric spectra depends upon $\delta\Omega$. Thus, if $\delta\Omega$ is very small, the dielectric intensity of the slow β mode should be very weak and may not be observed, which was indeed confirmed for glycerol by Döß *et al.* [20]. This material specific feature of $\delta\Omega$ may be the origin of nonuniversal amplitude of a slow β mode [36].

In relation to the above, we note that small $\delta\Omega$ can be one of the causes for fragile type *A* materials. Strictly speaking, such fragile type *A* materials should be treated separately from strong type *A* materials since the physical origin may be different between them. We expect that there should be a difference in the temperature dependence of $\tau_{slow\beta}$ between fragile and strong type *A* materials, although it may be difficult to distinguish them experimentally due to the weak intensity of the slow β peak.

2. Dynamic heterogeneity of the slow β process

Our picture is consistent with the recent experimental findings [33,37] suggesting that essentially all molecules contribute to the slow β motion. At the same time, however, the amplitude of the slow β motion should be larger for looser metastable islands. The size and density distribution of metastable islands (dynamic heterogeneity) should lead to heterogeneity in the tightness of cage (not distinct as ‘‘islands of mobility’’ [10]), which should cause the dynamic heterogeneity of the slow β mode. According to our picture, the lifetime of the slow β heterogeneity should be of the order of that of metastable islands τ_α, which is consistent with the recent NMR finding [38]. Molecules in tight cages can make only small-amplitude rotational vibration, while those in loose cages can make rather large-amplitude one before the reorganization of the cages. In this sense, our picture should be placed between the two extremes (homogeneous and heterogeneous limits), which were recently discussed in depth by Johari [31]. In our model, the degree of the dynamic heterogeneity of the α mode, which is characterized by β_K, is one of the major factors controlling the broadness of the distribution of $\tau_{slow\beta}$. Thus, we propose that the broadness of the distribution of $\tau_{slow\beta}$, which is characterized by σ [see Eq. (2)], should increase with a decrease in β_K; namely, σ is larger for more fragile liquids and also for a lower temperature. The latter is consistent with the experimental results (see, e.g., Ref. [29]). The validity of these predictions should be checked more carefully in the future.

III. SIMPLE MODEL OF DECOUPLING OF THE SLOW β MODE FROM α ONE

Stickel *et al.* [8] clearly demonstrated that τ_α changes its temperature dependence from Arrhenius to Vogel-Fulcher-type around T_A. Here we present a possible scenario of such a change in the temperature dependence of τ_α.

A. Two-order-parameter model of liquid-glass transition

We recently proposed a two-order-parameter (TOP) model of liquid-glass transition [35,39,40]. In our view, most liquids intrinsically have short-range bond order, which is favored by symmetry-selective parts of interactions: Locally favored structures are created and annihilated randomly in both space and time in a sea of normal-liquid structures. We argue that a liquid-glass transition, which occurs in a metastable liquid branch, is caused by energetic frustrations hidden in the interaction potential. We express this frustration by the competition between long-range density ordering (crystallization) and short-range bond ordering (formation of locally favored structures). When these two types of ordering favor different symmetries, which are not compatible with each other, the frustration leads to spin-glass-like behavior. This is the basic physical picture of our model of liquid-glass transition. There is also a possibility that the local symmetry favored by bond ordering is compatible with the crystallographic symmetry of the equilibrium crystal. Such a case is discussed in Ref. [41].

According to this model, there exist two key temperatures relevant to glass transition: (a) a transition from the ordinary-liquid to the Griffiths-phase-like state around T_m^*, which is characterized by the appearance of metastable solidlike islands and the resulting appearance of the cooperative nature of the α relaxation, and (b) another transition into the spin-glass-like state and the resulting divergence of the α relaxation time at T_0. T_m^* is a density-ordering (melting) point of the corresponding hypothetical pure system that is free from disorder effects of short-range bond ordering. It may be located near the melting point of the real system, $T_{\rm m}$. Above T_m^*, the only global state of a system is a liquid state. Between T_m^* and T_0, the system has the complex free-energy landscape characteristic of the Griffiths-phase-like state, and metastable solidlike islands coexist and fluctuate dynamically. Below T_m^*, thus, the α relaxation time is the lifetime of metastable islands. The driving force of the formation of metastable islands is entropic, which is characteristic of the so-called ''random first order'' transition [3]. This entropic driving force decreases upon cooling and hypothetically disappears at T_0, which leads to the divergence of τ_α while approaching T_0. In our model, T_g is defined as a temperature, below which metastable islands whose characteristic lifetime is longer than the observation time are percolated.

In the mean-field dynamic theory, a glassy freezing occurs for all $T<T_A=T_m^*$ and a system may exhibit a Griffiths-like singularity, which leads to the critical-like divergence of τ_α at T_A (similarly to the behavior near the mode-coupling T_c predicted by the schematic mode-coupling theory [4]). For a system of finite-range interactions, however, fluctuation effects smear out such a singularity. Thus, long-time dynamical processes (cooperativity) associated with metastable islands ''gradually'' appear around T_A upon cooling [42].

As described above, we assign the slow β mode to the restricted ''rotational'' jump motion of molecules in metastable islands, which exist only below T_A $(=T_m^*)$.

B. What determines the degree of the decoupling?

It is natural to consider that the relation between the α relaxation time and the slow β one is a key to understanding the origin of the slow β mode and resolving the controversy associated with type *A* and type *B* glass formers. We propose that the degree of the decoupling of the two modes below T_A depends solely upon the ratio $\tau_\alpha/\tau_{slow\beta}$.

According to the above TOP model of liquid-glass transition [35], there may be two important temperatures T_m^* and T_m^c (see Ref. [35] for the definition of the latter), which, correspond to T_A and T_B, respectively, in the terminology of Stickel *et al.* [8]. Hereafter we use T_A and T_B to avoid confusion. Thus, we interpret T_A as the temperature characterizing a gradual onset of cooperativity, below which the system have a complex free-energy landscape. The temperature region between T_A and T_B can be regarded as the crossover region [35].

1. Onset of cooperativity: Temperature dependence of τ_α

Here we focus our attention on the fact that cooperativity of molecular motion should appear below T_A upon cooling. For critical phenomena, the characteristic size of order-parameter fluctuations *continuously* diverges while approaching the critical point. Contrary to this, the cooperativity plays an important role only below T_A; that is, the characteristic coherence length (or, the characteristic size of metastable islands) ξ exceeds the molecular size *a* only below T_A for liquid-glass transition. Above T_A, the only length scale of the system is the molecular size *a*. Thus, we cannot describe ξ as $\xi=a[(T-T_0)/T_0]^{-\mu}$ (μ being exponent) above T_A; instead, we need to pay special attention to the onset temperature around which cooperativity starts to play an important role in the structural relaxation. Here we emphasize that ξ is a measure of the typical size of the cooperatively rearranging region and is not associated with any static spatial heterogeneity. Thus, it cannot be detected in the static density correlation function. To express such a gradual crossover from the noncooperative to the cooperative regime around T_A and the resulting Arrhenius-to-Vogel-Fulcher crossover ''analytically,'' we introduce the following crossover function, although it is artificial rather than physical:

$$f(T)=\frac{1}{\exp[\gamma(T-T_C)]+1}, \tag{5}$$

where T_C is the middle temperature of the crossover region $[T_C\sim(T_A+T_B)/2]$ and γ is the positive constant that controls the sharpness of the transition of $f(T)$ from 0 to 1 upon cooling. The larger γ is, the sharper the transition is. $1/\gamma$ is a measure of the width of the crossover region, which is characterized by the temperature distance between T_A and T_B, namely, T_A-T_B.

Above T_A, τ_α is determined by the barrier to overcome upon the translation and rotation of a molecule; as in usual equilibrium liquids, the only constraint to the translational and rotational motion of molecules stems from the interactions between molecules. Above T_A, thus, τ_α should obey the Arrhenius law as

$$\tau_\alpha=\tau_{0\alpha}\exp\left(\frac{E_\alpha}{k_BT}\right), \tag{6}$$

where $\tau_{0\alpha}$ is the preexponential factor and E_α is the average activation energy of the α process. Below T_A, on the other hand, the cooperative rearranging motion is required for both translational and rotational motion of molecules in addition to the breakup of bonds. Thus, the characteristic time τ_α should be given by the product of the Arrhenius law and the Vogel-Fulcher-type temperature dependence. We propose that the effective barrier dominating the structural relaxation E_b should be given by (a) $E_b=E_\alpha$ above T_A and (b) $E_b=E_\alpha+BT/(T-T_0)$ below T_B. We assume that the ''gradual'' transition between the above two cases can be expressed by using the smooth crossover function given by Eq. (5). Thus, the temperature dependence of τ_α should obey the following modified Vogel-Fulcher (VF) law [35]:

$$\tau_\alpha=\tau_{0\alpha}\exp\left(\frac{E_\alpha}{k_BT}\right)\exp\left[\frac{Bf(T)}{k_B(T-T_0)}\right]. \tag{7}$$

This modified VF law can naturally describe the crossover from the Arrhenius to the Vogel-Fulcher behavior between T_A and T_B and also the divergence of τ_α at T_0. The fitting of the traditional VF law to experimental data in a low-temperature range often produces an unrealistic attempt frequency $\tau_{0\alpha}^{-1}$ (see, e.g., Ref. [43]). This problem can be avoided by using Eq. (7).

Here we show an example of the fitting in Fig. 1. The result is quite satisfactory. The Arrhenius-to-Vogel-Fulcher crossover is naturally expressed by Eq. (7). The results for various glass-forming liquids will be shown elsewhere.

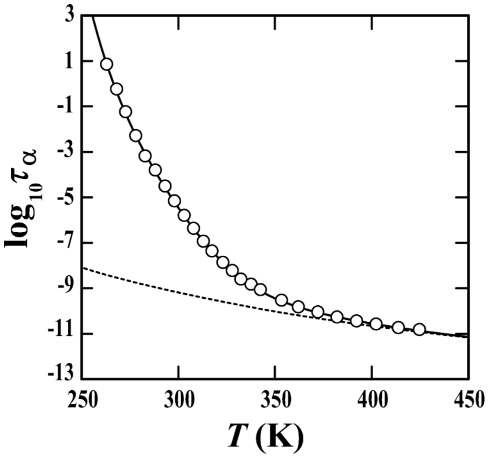

FIG. 1. Fitting of our modified Vogel-Fulcher law to the temperature dependence of the viscosity data of bis-methyl-methoxy-phenyl-cyclohexane (BMMPC). Data are taken from Ref. [43]. The solid line is the fitted theoretical curve [see Eq. (7)]. The dashed line is the extrapolation of the high-temperature Arrhenius behavior expressed by $\tau_\alpha = \tau_{0\alpha}\exp(E_\alpha/k_B T)$. The fitting parameters are determined as follows: $\tau_{0\alpha} = 10^{-14.2}$ s, $T_0 = 211$ K, $T_C = 312$ K, $E_\alpha/k_B = 3300$ K, $B/k_B = 1280$ K, and $\gamma = 0.044$. We note that the value of $\tau_{0\alpha}$ is comparable to that of $\tau_{0\beta}$ (see Table I). We also note that $T_g = 261$ K and $T_m = 346$ K for BMMPC.

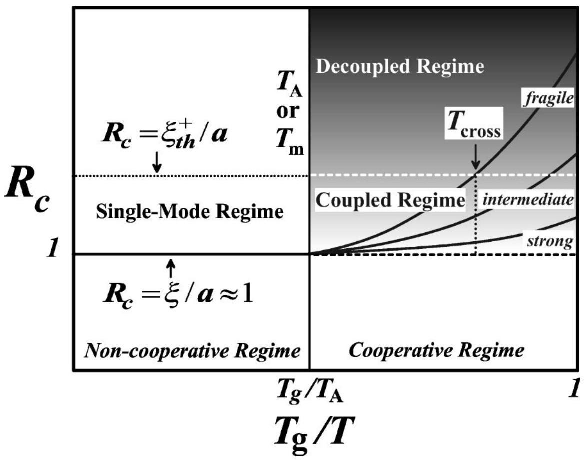

FIG. 2. Temperature dependence of $R_c = \xi/a$. ξ starts to increase only below T_A as $\xi \sim a[(T-T_0)/(T_A-T_0)]^{-2/3}$. It increases more rapidly below T_A upon cooling for a more fragile liquid since the distance between T_A and T_0 is closer. The crossover temperature T_{cross} is defined as a temperature at which ξ becomes larger than ξ_{th}^{+}. Note that T_{cross} may have a distribution, reflecting the distribution of ξ (or τ_α) (see also Fig. 4).

2. Physical factors controlling the decoupling of the two modes

Now we consider what determines $\tau_\alpha/\tau_{slow\beta}$, which controls the degree of the decoupling of the two modes below T_A. From Eqs. (1) and (7), we obtain the following expression for $\tau_\alpha/\tau_{slow\beta}$ below T_A [44]:

$$\frac{\tau_\alpha}{\tau_{slow\beta}} = \frac{\tau_{0\alpha}}{\tau_{0\beta}}\exp\left[\frac{E_\alpha - E_\beta}{k_B T}\right]\exp\left[\frac{Bf(T)}{k_B(T-T_0)}\right]. \tag{8}$$

In the case of type A material, it is difficult to estimate $\tau_{0\beta}$ and E_β experimentally since the slow β mode is not decoupled from the α mode and thus it cannot be observed as an independent mode. Here, however, we consider the hypothetical intrinsic slow β mode, whose temperature dependence is of Arrhenius type. This is the slow β mode that should be observed if only the α mode is frozen and switched off (fully decoupled limit). Such a condition might be satisfied at very low temperatures.

According to the random first-order transition scenario of glass transition [3], the cooperative activation energy ΔF is determined by the dynamic coherence length ξ via the following scaling relation:

$$\Delta F \sim \epsilon \xi^{-d}, \tag{9}$$

where $\epsilon = (T-T_0)/T_0$ and d is the spatial dimension. The scaling relation for the size of metastable islands, $\xi \sim \epsilon^{-\mu}$ ($\mu = 2/d$), yields the Vogel-Fulcher-like activation energy $\Delta F \propto 1/(T-T_0)$ [3]. Thus, we can map the time scale associated with cooperativity onto the dynamic coherence length ξ. The change of dynamics around T_A can be expressed by the change in the temperature dependence of ξ. ξ starts to increase from a (a being the size of molecule or particle) below T_A (see Ref. [35] for the details): $\xi \cong a$ for $T > T_A$, while $\xi \cong a[(T-T_0)/(T_A-T_0)]^{-2/3}$ [3] for $T < T_A$. Thus, we can conclude that $\tau_\alpha/\tau_{slow\beta}$ is controlled by the following two factors:

$$R_c = \xi/a, \tag{10}$$

$$R_l = \frac{\tau_{0\alpha}}{\tau_{0\beta}}\exp\left[\frac{E_\alpha - E_\beta}{k_B T}\right]. \tag{11}$$

Here we note that in most cases R_c is a dominant factor determining the degree of the decoupling of individual cages from metastable islands because R_c diverges with approaching T_0. R_l can, on the other hand, be the origin of nonuniversal behavior. The increase of ξ with decreasing T should be steeper for more fragile liquids since the distance between the onset of cooperativity T_A and the diverging temperature T_0, $T_A - T_0$, is smaller; in other words, $T_A - T_0$ is negatively correlated with the fragility index m [35,40]. Thus, R_c increases more rapidly for more fragile liquids (see Fig. 2). On the other hand, R_l is determined by local dynamics and thus material specific.

C. Decoupling between the α and the slow β mode

Here we consider how the two physical factors controlling the decoupling behavior, R_c and R_l, affect the appearance of the slow β mode.

1. Roles of R_c on the decoupling behavior

First we consider the case where the degree of the decoupling is primarily controlled by R_c (see Fig. 2). Before starting discussion, we define two threshold values of ξ for convenience: ξ_{th}^{-} is the threshold value of ξ, above which the slow β mode can exist but it appears as the excess wing due to its strong coupling to the α mode. ξ_{th}^{+} is, on the other hand, the threshold value of ξ, above which the slow β mode can exist as a distinct independent mode. Here it should be noted that no sharp changes would not occur at these values.

(i) For the case of $\xi \sim a$, there is no cooperativity and thus there is no separation between the two modes. This results in the absence of the slow β mode. This is the case of $T \geqslant T_A$.

(ii) Below T_A but near T_A, R_c is only slightly larger than 1 (see Fig. 2). More precisely, ξ is larger than ξ_{th}^-, but smaller than ξ_{th}^+. For this case, the slow β mode can exist, but it is not decoupled from the α one because of the small frequency separation between them. This leads to the strong overlap of the dielectric spectra of the two modes. In this case, molecules fully rotate after oscillating only a few to several times in the cage, which itself is dynamically fluctuating with the rate of α relaxation. Thus, the slow β mode, which is strongly modulated by the α mode, should possess the nature of the α mode. Thus, $\tau_{slow\beta}$ should have the temperature dependence of Vogel-Fulcher type, reflecting the cooperative nature. It should also be sensitive to pressure, reflecting the nature of the α mode.

(iii) For the case of $R_c \gg 1$ (or, $\xi > \xi_{th}^+$), the local environment of a molecule (cage) is well defined and continues to exist for a time much longer than $\tau_{slow\beta}$ and thus the slow β mode is fully decoupled from the α mode. In this case, the temperature dependence of $\tau_{slow\beta}$ should be of Arrhenius type and its pressure dependence should be weak, reflecting its intrinsically local nature. For fragile liquids, this situation can be realized for deep supercooling. The crossover from regime (ii) to (iii) takes place at the crossover temperature T_{cross}, where $\xi \sim \xi_{th}^+$ (see Fig. 2). Note that this crossover temperature of the slow β mode, T_{cross}, is different from that of the α mode, T_B. Usually, T_{cross} is located below T_B. This crossover phenomenon reasonably explains the merging behavior of α and slow β modes observed by Gómez *et al.* [26], Margulies *et al.* [28], and Fujima *et al.* [29] (see Fig. 3).

(iv) For rather strong liquids, the slow β mode cannot be fully decoupled from the α one even for deep supercooling since ξ does not increase so much (namely, $\xi \leqslant \xi_{th}^+$) (see Fig. 2). This is simply because the singular point, the Vogel-Fulcher temperature T_0, is located far below T_g for a strong liquid [35]. The slow β mode should, thus, possess the α-mode nature [see also case (v)]. For a very strong liquid, however, it would not be observed as a separate mode due to the very small time separation between the two modes and should be observed as the excess wing [see Fig. 3(b)], provided $R_l \sim 1$. Finally, we note that our model naturally predicts that *the excess wing should disappear above* T_A, consistently with the experimental result [45].

(v) When the slow β and α modes are strongly coupled with each other as in cases (ii) and (iv), we expect that $\tau_{slow\beta}$ is related to τ_α: A possible relation may be [15,19]

$$\tau_{slow\beta} \sim \tau_\alpha^{\beta_K}. \tag{12}$$

Since β_K should be equal to 1 above T_A (note that there is no cooperativity above T_A), the above relation gives us a natural bifurcation of the slow β mode from the α mode at T_A. Note that this particular relation leads to the Nagle scaling, which was demonstrated by Ngai [19]. However, further theoretical studies are necessary to elucidate the temperature dependence of $\tau_{slow\beta}$ for the strongly coupled case.

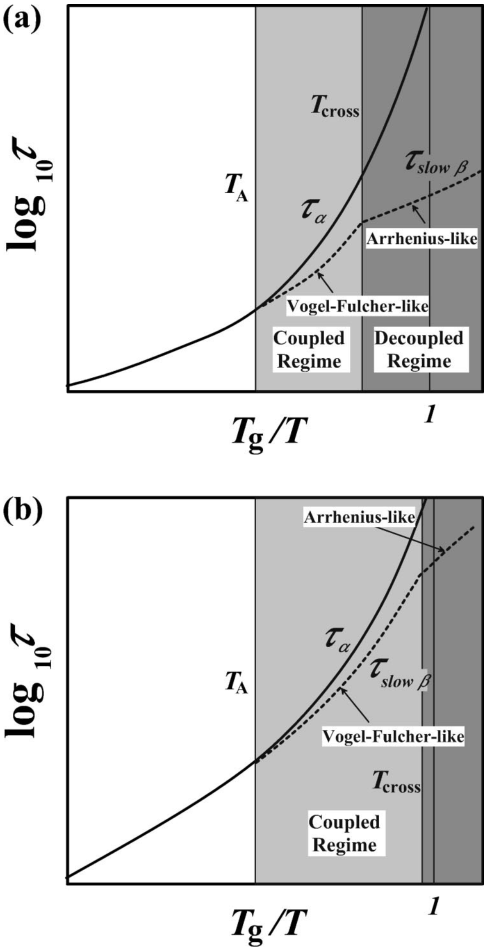

FIG. 3. Relation between τ_α and $\tau_{slow\beta}$ for a fragile liquid (a) and a rather strong liquid (b) in the so-called Angell plot. For case (a), the slow β mode is decoupled from the α mode at a temperature T_{cross}, which is not so far below T_A. For case (b), on the other hand, the decoupling occurs only at very low temperatures: The slow β mode modulated by the α mode, which has the Vogel-Fulcher-like temperature dependence, covers the wide temperature region between T_A and T_{cross}. For a very strong liquid, decoupling would never be observed. The distance between T_{cross} and T_A should increase with a decrease in the fragility (see Fig. 2). Finally, we stress that both τ_α and $\tau_{slow\beta}$ have wide distributions, although they are represented by thin lines.

In the above discussion, we neglect the effects of the broad distributions of τ_α and $\tau_{slow\beta}$. The broadness of the relaxation time distributions and its relation to a possible coexistence of the excess wing and the slow β mode [17] will be discussed in Sec. III E.

2. Roles of R_l on the decoupling behavior

Next we consider the case that R_l plays an important role in the decoupling behavior. R_l is determined by local dynam-

TABLE I. Relation between the fragility and the slow β characteristics. All the data are taken from Ref. [1]. Here we list only low molecular-weight molecular liquids. BMMPC: bis-methyl-methoxy-phenyl-cyclohexane; BMPC: bis-methoxy-phenyl-cyclohexane; ODE: 4,4-(octahydro-4,7-metano-5H-indene-5-ylidene)-bisphenol-dimethylether ($C_{24}H_{28}O_2$); CDE: cresol-phthalate-dimethylether; PDE: phenyl-phthalate-dimethylether; FDE: flourene-9,9-bisphenol-dimethylether.

Name of glass former	m	$\log_{10}[(2\pi/\tau_{0\beta})/(\text{rad/s})]$	E_β (kJ/mol)	type
1-butyl bromide	44			*A*
Propylene glycol	48			*A*
Glycerol	49			*A*
Isobutyl bromide	49			*A*
2-butyl bromide	52			*A*
3-bromopentane	56	14.8	23.1	*B*
BMMPC	59			*A*
BMPC[a]	63	14.0	50.1	*B*
m-tricrestyl phosphate	63			*A*
Propyl benzene	70			*A*
ODE	71			*A*
Ortho-terphenyl	74	16.0	48.9	*B*
CDE	75			*A*
PDE	78	13.2	17.4	*B*
FDE	84	10.4	4.7	*B*
Salol	89			*A*
Propylene carbonate	91			*A*
Methyltetrahydrofurane	93			*A*
Benzoin isobutylether	94	16.3	55	*B*
Triphenyl phosphite	97			*A*
Toluene	98	16.1	25.3	*B*
Cresyl glycidyl ether	135	13.2	18.4	*B*
Butyl benzene	172			*A*
Isopropyl benzene	189	15.0	25.9	*B*

[a] The secondary mode listed in this table may not be the slow β mode, but the rotational mode of the methoxyphenol moiety [G. Meier, B. Gerhartz, D. Boese, and E. W. Fischer, J. Chem. Phys. **94**, 3050 (1991)].

ics and can thus be material specific. For example, specific interactions may affect significantly the activation energy E_β and thus $\tau_{slow\beta}$. The molecular size may also affect the value of $\tau_{0\beta}$ [23]. If R_l is small due to these reasons, it is possible that even for fragile liquids $\tau_{slow\beta}$ is too slow to be decoupled from the α mode and thus strongly modulated by it. Thus, the situation similar to the above case (iv) can be realized for liquids of $R_l \ll 1$, irrespective of the fragility. Thus, even fragile liquids may belong to type A. In this case, the slow β mode is hidden by the α one. For example, this may be the case of polypropylene carbonate in Table I. Similarly, if $R_l \gg 1$, even a strong liquid can have a distinct slow β mode. We note that studies on a more microscopic level are necessary for revealing what physical factors determine R_l.

Here we mention fact (3) in the Introduction in relation to the roles of R_l. Mattsson *et al.* [23] demonstrated that the difference in type *A* and *B* stems from the difference in τ_α at the merging temperature, from their systematic experimental study of oligomers with different lengths. The larger molecular size leads to the longer $\tau_{0\beta}$. Their result indicates that with the decrease in R_l the system changes from type *B* to type *A*. Thus, this can be regarded as an example of the above-described effects of R_l on the decoupling behavior.

We also note that a similar behavior was observed in a series of neat polyalcohols [20]. For these polyalcohols, it was revealed that the less fragile liquid has the smaller $\tau_{0\alpha}/\tau_{0\beta}$ (or smaller R_l) and the smaller $\delta\Omega$. It may be worth studying the microscopic origins of this correlation among the fragility R_l and $\delta\Omega$ for these materials.

D. Correlation between the fragility and the decoupling behavior

When the degree of the decoupling is primarily controlled by R_c, there should be a simple correlation between the fragility and the decoupling behavior. If we neglect the effects of R_l, our model suggests that strong liquids should belong to type *A*, while fragile ones to type *B* [36]. This is consistent with the known difference in the fragility between type *A* and *B* materials [46]. For example, Ngai reported that there is no slow β mode for rather strong glass formers, whose β_K at T_g is greater than 0.7. As can be seen in Table I, there is indeed a clear tendency that type *A* materials are less fragile than type *B* ones: Stronger liquids whose fragility index *m* is smaller than 70–80 belong to type *A* materials. Here it should be noted that this threshold value of *m* may not have a significant meaning since the estimation of *m* usually contains a large error and there are exceptions for this correlation (see below).

We note that the effects of R_l may explain why there are many exceptions for the above correlation (see Table I). A system with small R_l may belong to type *A* (fragile type *A* material) even though its fragility is high. The opposite case (strong type *B* material) may also be possible for large R_l, namely, if E_β is considerably lower than E_α. It is also possible in principle if $\tau_{0\beta}$ is shorter than $\tau_{0\alpha}$, but this would be unlikely. In usual cases where $E_\beta \sim E_\alpha$, strong liquids should belong to type *A*. Our picture tells us that for small R_c (namely, for $\xi < \xi_{th}^{+}$) the slow β mode is modulated by the α mode due to their strong coupling. These considerations lead us to a conclusion that there should not exist strong type *B* materials. Thus, we speculate that the secondary process observed in strong type *B* materials is not the slow β mode in the strict sense but another local mode, as in the case of BMPC [30] (see the caption of Table I). This point should be checked carefully in the future.

Finally, we note that small $\delta\Omega$ can also be the origin of fragile type A material, as pointed out in Sec. II B 1.

E. Possible coexistence of the excess wing and the slow β mode

Next we briefly consider the problem of the coexistence of the excess wing and the slow β peak, which is observed for a few glass-forming liquids. This is sometimes regarded as the evidence supporting that the excess wing is independent of the slow β mode [17]. The most natural explanation can be given by assuming the existence of two local modes. For example, one of them is the slow β mode, while the other may be the intramolecular local mode such as methyl rotation. Although we believe that this simple explanation may account for most cases, we note that in our scenario the coexistence is possible for a certain situation [see Fig. 4(c)] even for the case that there exists only a single slow β process. The wide distribution of ξ can lead to the situation that the slow β mode in smaller metastable islands with shorter τ_α is strongly coupled with the α mode, while that in larger ones is decoupled from it. According to the definitions of $\xi_{th}^{\pm}$, we can draw the following picture. Molecules belonging to metastable islands, whose characteristic size ξ satisfies the condition $\xi_{th}^{-} < \xi < \xi_{th}^{+}$, contribute to the excess wing that possesses the α-mode-like character, while those belonging to metastable islands, whose characteristic size ξ satisfies the condition $\xi > \xi_{th}^{+}$, contribute to the slow β peak. We note that the character should change *continuously* from excess-wing-like to slow-β-peak-like with an increase in the degree of the decoupling. Figure 4 schematically shows how the distribution of ξ changes with temperature. This coexistence of the excess wing and the slow β mode, which is possible for Fig. 4(c), is schematically shown in Fig. 5.

F. Effects of aging on the slow β mode

It was shown by Schneider *et al.* [18] that aging below T_g makes the slow β peak more distinct. During the aging, it is expected that characteristic size of metastable islands ξ increases with the waiting time t_w, which leads to the increase in τ_α (or ξ) with t_w. According to our model (see Fig. 4), this means that the slow β mode becomes more decoupled from the α mode with t_w, which should lead to (a) the transformation of the slow β mode from excess-wing-like to peaklike and (b) the larger frequency separation between the two modes. This is consistent with what was observed experimentally [18].

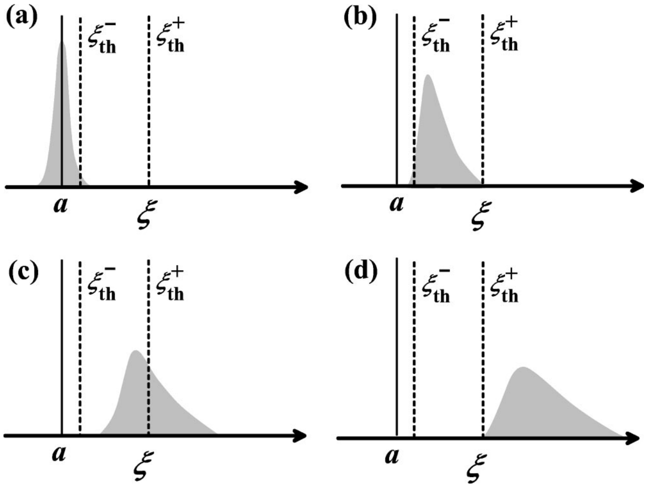

FIG. 4. Schematic figures showing how the distribution of the characteristic size of metastable islands ξ changes with temperature *T*. (a) Above T_A, (b) just below T_A, (c) in the merging region, and (d) below T_{cross}. For case (c), the excess wing and the slow β mode can coexist (see Fig. 5).

G. Comparison of our model with experimental facts

Here we stress that our model can explain all the experimental facts (1)–(5) reviewed in the introduction, some of which apparently look contradictory with each other, in a coherent manner. In our picture the excess wing and the slow β mode share the common microscopic origin and the dif-

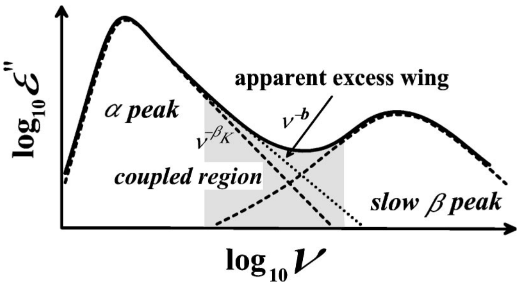

FIG. 5. A simple explanation for the coexistence of the excess wing and the slow β peak. There may exist a considerable frequency region where these two modes are strongly coupled and the slow β mode possesses the character of α mode. Note that for larger (more dense) metastable islands of the longer lifetime the slow β mode can be decoupled from the α mode, while for smaller (less dense) ones of the shorter lifetime it is strongly modulated by or coupled with the α mode. The former appears as the slow β peak, while the latter appears as the excess wing.

ference between them arises from the degree of the coupling between the α and the slow β mode. Thus, our model is consistent with facts (1) [18,19] and (2) [20] (see also the above discussion about the aging effects). Our model is also consistent with fact (3) [23], as explained in Sec. III C 2. In our picture, these two modes are essentially distinct from the α mode: Both modes primarily stem from the slow β mode, although the excess wing possesses some character of the α mode, reflecting the coupling of the slow β mode to the α one. Thus, our model is also consistent with fact (4) [24]. The difference in the pressure dependence between the excess wing and the slow β mode [fact (5)] [25] can also be naturally explained by our model (see Sec. III C 1). Note that in our model the excess wing possesses the character of the α mode due to the strong coupling (or mixing) between the α and the slow β modes, while the slow β mode decoupled from the α mode is of intrinsically local nature and its pressure dependence should be weak. The fact that the slow β mode in type B material is insensitive to pressure [25] seems to be more consistent with our model rather than the models based on the idea of islands of mobility. Finally, we point out that our model can naturally explain the merging (or bifurcation) behavior of the α and the slow β mode [26,28,29] [see also Fig. 3(a)], as discussed in Sec. III C 1.

H. Relation to Ngai's coupling model

Finally it may be worth comparing the present model with Ngai's model [19] since both are based on a picture of coupling between modes. Ngai *et al.* [19] ascribed the slow β mode to a primitive (unconstrained) relaxation process, which is devoid of intermolecular coupling, and thus to the motion of molecules in the boundary regions between cooperative rearranging regions, following the Johari's idea of islands of mobility [10,31]. On the other hand, we ascribe it to the constrained rotational jump motion inside a cage in a metastable island. Thus, it exists only below T_A in our model, differently from the Ngai's model, in which the primitive mode continues to exist far above T_A. Our model suggests that a majority of molecules take part in the slow β process, which looks consistent with the recent experimental finding [33,37]. In our model, the slow β mode can be a local mode independent of the α mode in the fully decoupled regime. This results in the existence of T_{cross} [see Fig. 3(a)], which separates the coupled and decoupled regimes. Such crossover behavior at T_{cross} [26,28,29] and the complete decoupling of the slow β mode from the α one, which results in the Arrhenius temperature dependence of the slow β mode, seem to be difficult to be explained by Ngai's model, which predicts $\tau_{slow\beta} \propto \tau_\alpha^{\beta_K}$. At the same time, however, we speculate that this relation derived by Ngai, which naturally explains the Nagel scaling, might even hold in our case, but only when the two modes are strongly coupled. We also note that our model seems to be more consistent with the fact that E_β is often different from E_α. Since our model is qualitative and experimental data that can be used to check the validity of the models are rather limited, however, further careful studies are necessary to clarify what is the physical mechanism governing the behavior of the slow β mode.

IV. SUMMARY

In this paper, we discuss the origin of the excess wing and the slow β relaxation of glass formers and the relation between them, which have been a matter of active debate. We propose a simple physical scenario that can at least qualitatively account for the recent experimental findings, which apparently look contradictory with each other, in a coherent manner. We argue that whether liquid has the excess wing or the slow β mode is primarily determined by the degree of the coupling between the cooperative translational and rotational motion associated with creation and annihilation of metastable islands (α mode) and the local rotational jump motion in a cage (slow β mode). Furthermore, we propose that the relation between the characteristic size of metastable islands and the cage size is one of the major factors controlling the degree of the coupling between the two modes. For example, this naturally explains why the slow β mode is usually observed only for rather fragile liquids. We also discuss the physical origin that leads to the violation of this correlation between the fragility and the degree of the decoupling. Finally, our model suggests that the slow β mode, which is constrained rotational jump motion in a cage, is a generic and intrinsic feature [10] of supercooled liquid (below T_m) and glassy (below T_g) states of molecules (or particles) with anisotropy.

We hope that our simple model would contribute to our understanding of the nature of the excess wing and the slow β mode, which has been discussed over many years. Since our discussion is qualitative and speculative in nature, however, further quantitative studies are highly desirable.

Note added in proof. Very recently, Minogruchi *et al.* [47] reported the detailed study on dielectric relaxation of polyols (sorbitol and xylitol and their mixtures) and concluded that the origin of the slow β process is essentially the same among the polyols. This is consistant with our proposal.

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