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Reply to “Comment on ‘Origin of the excess wing and slow β relaxation of glass formers: A unified picture of local orientational fluctuations’ ”

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Here I reply to the comment of Ngai on my recent publication [H. Tanaka, Phys. Rev. E **69**, 021502 (2004)]. Some of my comments made on the coupling model were not accurate. In relation to this, I discuss the following three fundamental problems: (i) whether the slow β mode continues to exist above the melting point T_m, (ii) whether there is a continuity of the slow β mode and the α one across T_m, and (iii) whether the slow β mode can be fully decoupled from the α mode above the glass transition temperature T_g. I also propose a method of the analysis of dielectric relaxation data and a key experiment to resolve these important remaining issues.

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As pointed out by Ngai in his comment [1] on my paper [2], I was not aware of papers [3–5] that described the new interpretation of the slow β (or Johari-Goldstein) mode based on the extended coupling model, even though Ref. [3] was published before the submission of my paper. Thus I made comments in my paper [2] on the old interpretation [6] without knowing the new one. On the references in my paper, I should also have quoted the papers by Olsen and others [7,8], which first suggested that the excess wing is due to an underlying slow β process.

On the issue of whether the slow β mode continues to exist above the so-called T_A (or the melting point T_m), I agree that this is, in practice, very difficult to solve experimentally. In relation to this, I explain the similarities and the differences between the coupling model and our model. In the coupling model, the slow β mode merges to the α relaxation with an increase in the temperature and becomes indistinguishable from the α mode above T_A since the coupling parameter n becomes small there, as explained in Ngai's comment [1]. In this model the slow β mode is the independent or primitive relaxation, which is the main relaxation process above T_A. Note that above T_A no cooperativity is involved in the structural relaxation. Thus, the slow β mode is the continuation of the primitive relaxation. In our model, on the other hand, the slow β mode should be absent above T_A since the dynamic heterogeneity (or the existence of solidlike metastable islands) is prerequisite for the existence of the slow β mode [2]. It is the highly restricted orientational vibrational motion, which exists only in solidlike metastable islands. Thus, our model suggests that (a) the α mode keeps the continuity across T_A although it changes the character from the independent to the cooperative one around T_A but (b) the slow β mode emerges only below T_A. In our model, the rotational vibrational motion of molecules in metastable islands is followed by full rotation. This scenario of the two-step sequential rotational relaxation is consistent with the extended coupling model [3–5]. Thus, the two models are similar in the sense that both suggest that cooperativity is necessary for the decoupling between the slow β mode and the α one. The difference between the two models stems from whether the slow β mode exists above T_A or not.

I agree with Ngai [1] that this difference itself is rather conceptual and may not have a practical meaning. However, this problem is related to another important question on the continuity of the α mode and slow β mode across T_A [9], which is, in practice, more important. Resolving this issue experimentally is also quite difficult. Instead of considering the above rather conceptual problem, we consider this more realistic problem and propose a way to solve it. This might open up a possibility to answer the above naive, conceptual problem. For polymers, there are some detailed analyses that focus on this naive problem; they seem to support the continuity between the α mode above T_A (called “ a mode”) and the slow β one [9,10]. However, this conclusion might be affected by the way of the analysis of the overlapped slow β and α modes (see Ref. [11] and the discussion below). On the other hand, for spherical particles, which is the case for colloidal suspensions and computer simulations, there is no slow β mode and thus there is clear continuity of the α mode across T_A. I expect that this basic feature should not be altered by the introduction of anisotropy into the particle shape (see below).

This problem of the continuity of the two modes may be solved by focusing on the fact that the α relaxation involves two types of motion: structural relaxation (escape motion of molecules from their cages) and full rotational relaxation (their full rotation upon the escape). Thus, the α relaxation can be measured by measuring either the decay of the correlation of density fluctuations (e.g., polarized light and neutron scattering experiments) or the rotational relaxation (e.g., depolarized light scattering and dielectric relaxation experiments). When we measure the temporal correlation of density fluctuations, there is no effect of the slow β mode; in this case, the α relaxation follows the fast β relaxation instead of the slow β relaxation. This tells us that the α relaxation itself should be continuous across T_A and not affected by the emergence of the slow β mode. The temperature dependence of the viscosity η also supports this fact. When we directly measure the rotational relaxation by using dielectric spectroscopy or depolarized light scattering, however, both the α and slow β modes can be seen in the spectra below T_A. This is simply because both modes possess rotational character (full rotation in the α relaxation and rotational vibration in the slow β relaxation). Thus, the total relaxational spectrum consists of the contributions from the two modes. The overlapping between the two modes makes the analysis quite difficult when the two modes are not well separated in the frequency (or time) domain. However, the above fact indicates that there is a way to reduce the ambiguity coming from the overlapping of the two modes. I propose the following procedure. By assuming the continuity of the α relaxation time τ_α, we can extrapolate τ_α across the crossover region by using a smooth function such as the Vogel-Fulcher relation. Alternatively, we can use the data of η or those of τ_α obtained from the density correlation function. Similarly, we can also estimate the stretching parameter $\beta_K(=1-n)$ in the crossover region. In this way, we can obtain the smooth temperature dependences of τ_α and β_K across the crossover region. By using these τ_α and β_K, we can then estimate $\tau_{slow\beta}$ and the relaxational strength of each mode. I believe that the reduction of the number of the fitting parameters increases the physical reliability of the fitting significantly compared to the usual fitting method. Thus, I expect that the continuity problem may be solved by this procedure. I also suggest that simulations of a liquid made of anisotropic particles [12] may be useful for solving this issue.

Here we should note that whether the contributions of the α and slow β relaxations are convoluted or added still remains a key question (see, e.g, Ref. [11]). William and Watts [13] considered that the slow β motion is the restricted motions in a fixed environment, which allow a partial relaxation, and this environment is broken by the α relaxation. This is basically the same as our picture if we regard the fixed environment as a metastable island. For this case, the whole relaxation function is given by

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

where $\phi_\alpha(t)$ and $\phi_\beta(t)$ correspond to the normalized relaxation function of the α and slow β processes, respectively, and f_α is the fraction of the α relaxation. This is called "convolution ansatz." Only when the α and slow β modes are well separated, the relaxation function is approximated by

$$\phi(t) = f_\alpha\phi_\alpha(t) + (1 - f_\alpha)\phi_\beta(t). \tag{2}$$

This is called "addition ansatz." The detailed comparison of these two ansatz were made by Gómez *et al.* [11]. They concluded that the convolution ansatz is physically more reasonable. The convolution ansatz was also supported by a free-energy landscape model [14]. Our picture also supports the convolution ansatz. However, it also suggests that some modifications due to the dynamic heterogeneity are necessary. In our model, each metastable island has its own lifetime τ_α and slow β relaxation time. The former is the origin of the distribution of the structural relaxation time (τ_α); that is, the dynamic heterogeneity. The degree of coupling between the slow β and α mode is also different among metastable islands. This situation may be approximated by introducing the relaxation function for each metastable island i as

$$\phi^i(t) = \phi^i_\alpha(t)[f^i_\alpha + (1 - f^i_\alpha)\phi^i_\beta(t)]. \tag{3}$$

The whole relaxation function is then expressed as

$$\phi(t) = \frac{1}{N}\sum_{i=1}^{N} \phi^i(t), \tag{4}$$

where N is the number of metastable islands per unit volume. To reveal the detail characteristics of the relaxation such as the correlation between the broadness of the slow β relaxation and that of the α relaxation, further theoretical studies are highly desirable along this line.

Finally, the issue of whether the slow β mode can be fully decoupled from the α mode or not is also difficult to settle, as suggested by Ngai in his comment, because of the problem of resolving the slow β mode from the nearby α mode near the crossover temperature T_{cross} (see also above). This issue may be rephrased as whether the crossover temperature T_{cross} between the coupled and the decoupled regime [2] can exist separately from the glass transition temperature T_g (or above T_g) or not. According to the coupling model, the slow β relaxation time $\tau_{slow\beta}$ and the primitive relaxation time τ_0 are related to the α relaxation time as

$$\tau_{slow\beta} \cong \tau_0 = (t_c)^n(\tau_\alpha)^{1-n}, \tag{5}$$

where t_c is the crossover time $(\sim 2\times 10^{-12}$ s) [1]. Thus, there should not be any sharp change in the temperature dependence of $\tau_{slow\beta}$, provided that there is no sharp change in the temperature dependence of n between T_A and T_g. Thus, $\tau_{slow\beta}$ should exhibit the non-Arrhenius behavior above T_g, reflecting the Vogel-Fulcher behavior of τ_α. Indeed, such behavior is observed in some glass formers [4,15]. On the other hand, our model suggests that the slow β mode should exhibit the crossover from the non-Arrhenius behavior in the coupled regime to the Arrhenius one in the decoupled regime at T_{cross}. If T_{cross} is located above T_g, we should see such a crossover above T_g. For $T_{cross} < T_g$, on the other hand, there is no practical difference in the two models. Here I point out that some data analyses seem to support the existence of T_{cross} above T_g, or the Arrhenius behavior even above T_g, for supercooled liquids (see, e.g., Refs. [11,16–21]) and also for plastic crystals [22]. In relation to this issue, it is worth mentioning that it was suggested [7,23,24] that the slow β peak frequency even decreases (τ_β increases) with increasing temperature above T_g for tripropylene glycol and sorbitol. Thus, the situation is unfortunately not clear at all, for example, for sorbitol [25]. To settle this difficult issue, we should carefully check (i) whether the slow β mode analyzed in these papers is a genuine slow β mode or not and also (ii) whether the analysis of the overlapped spectra in the crossover region is unambiguous or not. We propose to apply the above-mentioned strategy of the fitting to this problem as well. The comparison of the activation energy of the slow β mode between T_{cross} and T_g with that of the α mode above T_A is also useful. Further careful studies on this problem are highly desirable. From this respect, I suggest that a very fragile liquid with large R_l (see Ref. [2] on its definition and Ref. [15] on its effect) may be suitable for checking whether T_{cross} can in principle exist above T_g or not. This is because for a more fragile liquid with larger R_l, τ_α can more easily become much longer than $\tau_{slow\beta}$ even near T_A [2].

As suggested by Ngai, there is no firm experimental evidence to draw any reliable conclusion on the issues at present. Thus, my statements, which were made on the coupling model in relation to the above issues in my paper [2], were not accurate. Although these issues are quite difficult to settle in a clear manner, they certainly deserve further investigation since the resolutions of these issues should contribute to our deeper understanding of the origin and nature of the slow β mode. In particular, further experimental studies of the slow β process above T_g are highly desirable.

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[1] K. L. Ngai, preceding Comment, Phys. Rev. E **70**, 063501 (2004).
[2] H. Tanaka, Phys. Rev. E **69**, 021502 (2004).
[3] K. L. Ngai, J. Phys.: Condens. Matter **15**, S1107 (2003).
[4] K. L. Ngai and M. Paluch, J. Phys. Chem. B **107**, 6865 (2003).
[5] K. L. Ngai and M. Paluch, J. Chem. Phys. **120**, 857 (2004).
[6] K. L. Ngai, P. Lunkenheimer, C. Le'on, R. Brand, and A. Loidl, J. Chem. Phys. **115**, 1405 (2001).
[7] N. B. Olsen, J. Non-Cryst. Solids **235–237**, 399 (1998).
[8] The first attempt to explain the excess wing by assuming the existence of a second process was made even earlier; e.g., A. Hoffmann, F. Kremer, E. W. Fischer, and A. Schönhals, in *Disorder Effects on Relaxational Processes*, edited by R. Richert and A. Blumen (Springer, Berlin, 1994), p. 309.
[9] E. Donth, *The Glass Transition* (Springer, Berlin, 2001).
[10] M. Beiner, Macromol. Rapid Commun. **22**, 869 (2001).
[11] D. Gómez, A. Alegria, A. Arbe, and J. Colmenero, Macromolecules **34**, 503 (2001).
[12] M. Higuchi, J. Matsui, and T. Odagaki, J. Phys. Soc. Jpn. **72**, 178 (2003).
[13] G. Williams and C. D. Watts, in *NMR, Basic Principles and Progress*, edited by P. Diehl, E. Fluck, and R. Kosfeld (Springer, Berlin, 1971); G. William, Adv. Polym. Sci. **33**, 60 (1979).
[14] G. Diezemann, U. Mohanty, and I. Oppenheim, Phys. Rev. E **59**, 2067 (1999).
[15] T. Blochowicz and E. A. Rössler, Phys. Rev. Lett. **92**, 225701 (2004).
[16] E. Rössler, Phys. Rev. Lett. **65**, 1595 (1990).
[17] S. Corezzi, E. Campani, P. A. Rolla, S. Capaccioli, and D. Fioretto, J. Chem. Phys. **111**, 9343 (1999).
[18] M. M. Margulies, B. Sixon, L. David, G. Vigier, R. Dolmazon, and M. Albrand, Eur. Phys. J. E **3**, 55 (2000).
[19] M. Vogel and E. Rössler, J. Chem. Phys. **114**, 5802 (2001).
[20] T. Fujima, H. Frusawa, and K. Ito, Phys. Rev. E **66**, 031503 (2002).
[21] A. Minoguchi, K. Kitai, and R. Nozaki, Phys. Rev. E **68**, 031501 (2003).
[22] C. Tschirwitz, S. Benkhof, T. Blochowicz, and E. Rössler, J. Chem. Phys. **117**, 6281 (2002).
[23] N. B. Olsen, T. Christensen, and J. C. Dyre, Phys. Rev. E **62**, 4435 (2000).
[24] J. C. Dyre and N. B. Olsen, Phys. Rev. Lett. **91**, 155703 (2003).
[25] Furthermore, there can be other causes that may affect the analysis of the slow β mode. For example, it was suggested [G. Power and J. K. Vij, J. Chem. Phys. **120**, 5455 (2004)] that conflicting results on the slow β process of sorbitol reported in literature may be caused by the incomplete melting due to the extremely slow melting of the crystal and/or the existence orientationally disordered crystal.