

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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In a recent paper [Phys. Rev. E **69**, 021502 (2004)], Tanaka commented on an old coupling model interpretation of the Johari-Goldstein (JG) secondary relaxation [J. Chem. Phys. **115**, 1405 (2001)]; namely, that it implies not all molecules contribute to the JG relaxation. In this Comment, I point out to the readers that this old interpretation has been revised in recent publications [J. Phys.: Condens. Matter **15**, S1107 (2003); J. Phys. Chem. B **107**, 6865 (2003); J. Chem. Phys. **120**, 857 (2004); Macromolecules **37**, 8123 (2004)]. In the new interpretation, essentially all molecules contribute to the JG relaxation. Another comment of Tanaka that applies to both the old and the new interpretation is discussed and shown to be of no practical significance.

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In a recent paper, Tanaka [1] reviewed some existing data on the excess wing and the slow β or Johari-Goldstein relaxation [2–4] of glass formers, and presented his own model explanation of their origins and relation to the α relaxation. The paper also made comments on my coupling model (CM) interpretation of the Johari-Goldstein (JG) relaxation. His comment (see Sec. H of his paper) was on a defunct interpretation given in a work published three years ago [5]. Since then, the interpretation in Ref. [5] had been revised. The new interpretation was given in more recent works [6–8] to replace the old one in Ref. [5]. In reading Tanaka’s paper, the readers should be aware of my new interpretation of the (JG) relaxation, and the fact that Tanaka’s comments on the old interpretation in Ref. [5] do not apply to the new interpretation [6–8]. As far as the CM interpretation of the JG relaxation is concerned, attention should be on the new interpretation [6–8] and its applications [9–12]. The new interpretation was already embedded in Refs. [6–8]. Here, I briefly restate its essence to show that essentially all molecules contribute to the JG relaxation in the new interpretation, in agreement with Tanaka’s own model, and to answer some other comments by Tanaka.

The independent or primitive relaxation of the CM is the precursor of the cooperative (i.e., intermolecularly coupled) α relaxation. It entails the motion of all parts of the molecule [13–15], but is a local process. These attributes of the primitive relaxation are clearly shared by the JG relaxation of rigid molecular glass formers, and are true also for all glass formers if the JG relaxation is suitably defined, as demonstrated in Ref. [8]. Thus, it can be expected that the primitive relaxation time τ_0 is approximately located near the most probable relaxation time τ_β of the JG relaxation at all temperatures T and pressures P [6–12]. A relation in the CM,

$$\tau_0 = (t_c)^n (\tau_\alpha)^{1-n}, \quad (1)$$

enables τ_0 to be calculated from the parameters τ_α and n in the Kohlrausch function, as

$$\phi(t) = \exp[-(t/\tau_\alpha)^{1-n}], \quad (2)$$

used to fit the time dependence of the α relaxation. In Eq. (1), t_c is the crossover time from independent relaxation to

cooperative relaxation and has the approximate value of 2×10^{-12} s for small molecular liquids [15]. It was found that

$$\tau_0(T, P) \approx \tau_\beta(T, P) \quad (3)$$

holds in many glass formers that have genuine JG relaxations. Since all molecules have τ_0 of their own, it can be inferred from the beginning that none of the molecules is excluded from contributing to the JG relaxation.

The new interpretation in Refs. [6–8] recognized the findings of solvation dynamics experiments on liquid D-sorbitol [16] to indicate that the JG β -relaxation process is spatially uniform, and of the deuteron NMR studies of several liquids [17] which have led to the conclusion that *essentially* all molecules contribute to the JG β relaxation by small-angle reorientation. It is consistent with these findings because, while not all molecules succeed in relaxing independently at the same time, all molecules will eventually contribute to the JG relaxation at later times. In the new interpretation, the JG relaxation transpires in the time scales beginning with the onset of independent local relaxation and extending to longer times where there is increasing development of many-molecule relaxations (i.e., “cooperativity”), and thus essentially all molecules contribute to the JG relaxation. In this respect, the new interpretation is in agreement with the view from Tanaka’s model [1] that essentially all molecules contribute to the JG relaxation. Overall, their dynamics viewed from the CM are heterogeneous, consistent with experiment [18]. The JG relaxation regime is terminated at some later time ($\gg \tau_\beta$ or τ_0) when fully cooperative molecular dynamics is finally reached, and, thereafter, the α -relaxation correlation function is well described by the Kohlrausch function.

Tanaka made another comment on the JG relaxation that is relevant for not only the defunct interpretation [5] but also the new interpretation [6–8]. He stated that “... 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 .” Let me answer this comment of Tanaka on my model. From Eqs. (1)–(3), the separation between the α - and β -peak frequencies ($\log \nu_\beta - \log \nu_\alpha$), is approximately equal to

$$\begin{aligned}
 (\log \nu_\beta - \log \nu_\alpha) &\approx (\log \nu_0 - \log \nu_\alpha) = n[\log \nu_c - \log \nu_\alpha] \\
 &= n[10.9 - \log \nu_\alpha]. \quad (4)
 \end{aligned}$$

The frequencies ν_0 , ν_α , ν_β , and ν_c , all in Hz, are defined by $1/(2\pi\tau_0)$, $1/(2\pi\tau_\alpha)$, $1/(2\pi\tau_\beta)$, and $1/(2\pi t_c)$, respectively. Dielectric and light scattering data of small molecular glass-forming liquids show that the coupling parameter n , appearing in Eqs. (1), (2), and (4), decreases towards zero with increasing temperature [5,6,13,19]. At temperatures above T_A , n is typically less than 0.1 [13,19] and $\log \nu_\alpha$ is not much smaller than $\log \nu_c = 10.9$. Hence, both factors on the right-hand side of Eq. (4) are small, and the separation ($\log \nu_\beta - \log \nu_\alpha$) is practically zero. The two relaxations have merged into one relaxation, as observed experimentally. Moreover, when n becomes small, there is hardly any degree of cooperativity left in the α relaxation, meaning that there is little difference in character between it and the independent relaxation or the JG relaxation. Thus, the comment made by Tanaka, although technically not incorrect, is like splitting hairs.

Determining the exact temperature dependence of what Tanaka called $\tau_{slow\beta}$ at temperatures near and above T_A is a difficult undertaking because of the overlap of the α and β processes, and the need to use some arbitrary procedure to deduce $\tau_{slow\beta}$. One procedure is to use the Williams-Watts hypothesis that the entire correlation function of the two processes can be written as the sum [$f_\alpha\varphi_\alpha(t) + (1-f_\alpha)$

$\varphi_\alpha(t)\varphi_\beta(t)$], where f_α is a fitting parameter, and $\varphi_\alpha(t)$ and $\varphi_\beta(t)$ are taken to be the same as the functions at lower temperatures where the two processes are well separated from each other. The other procedure is based on the assumption that overlapping α and β processes can be represented in the frequency domain as the superposition of two additive relaxation processes, a Havriliak-Negami (HN) function for the α -process and another HN function or a Cole-Cole (CC) function for the β process. Multiple parameters are introduced along with this assumption. The deduced values of $\tau_{slow\beta}$ by either procedure have large uncertainties arising from either the *ad hoc* assumption made or the multiple parameters used in the fit. Thus, it is impossible to either verify or falsify the existence of the *delicate* crossover of temperature dependence of $\tau_{slow\beta}$ at T_{cross} above T_g proposed by Tanaka. Nonetheless, Tanaka believes such highly uncertain values of $\tau_{slow\beta}$ deduced by others support the existence of T_{cross} and went on to make the comment that this "... seems to be difficult to be explained by Ngai's model which predicts $\tau_{slow\beta} \propto \tau_\alpha^{\beta k}$." This comment is irrelevant because the new interpretation considers only the most probable τ_β , obtained from the frequency ν_β at the maximum of resolved JG loss peak, and comparing it with that calculated by $(t_c)^n(\tau_\alpha)^{1-n}$ [6,7]. Nowhere in the new interpretation [6,7] have I compared this calculated value with the highly uncertain values of $\tau_{slow\beta}$ deduced by others using either the Williams-Watts ansatz or the superposition of HN and CC methods.

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