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Comment on ''Fast dynamics of glass-forming glycerol''

K. L. Ngai and C. M. Roland
Naval Research Laboratory, Washington, D.C. 20375-5000

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The coupling model predicts the existence of a prominent fast α process at times <2 ps in fragile glass-forming liquids such as polymers. A further prediction is that this process will be only weakly apparent in intermediate and strong liquids such as glycerol. In light of these predictions, we have reexamined the neutron scattering data of glycerol published by Wuttke, Petry, Coddens, and Fujara (WPCF) [Phys. Rev. E **52**, 4026 (1995)], leading to the conclusion that the fast α process is indeed quite weak therein. Thus, the coupling model predictions are fully consistent with the glycerol data, notwithstanding WPCF's statement to the contrary. [S1063-651X(97)03502-2]

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In a paper that has appeared in this journal [1], Wuttke, Petry, Coddens, and Fujara (WPCF) reported data on the vibrational and relaxational dynamics of glycerol obtained by incoherent neutron scattering (INS) experiments. The $S(q,t)$ data of glycerol are quite different from that of polymers [2,3]. WPCF pointed out that ''The data analysis in Refs. 5 and 7 [[2] and [3] in this paper] was motivated in part by the coupling approach of Ngai [29].'' Referring to the fast α process, $\exp(-t/\tau_D)$ for $t<t_c$, of the coupling model, they stated: ''This ansatz predicts an Arrhenius behavior for t_D. No such temperature dependence can be found in glycerol. Instead, the short-term limit of $S(q,t)$ is temperature independent in shape; only its amplitude increases roughly proportionally to temperature.'' This statement implies that the coupling model is inconsistent with the fast dynamics of glass-forming liquids. Their contention was even more forcefully made in Ref. [4].

Since WPCF did not remove the vibrational contribution from their intermediate scattering function, the relaxational component was not isolated. Hence, no rigorous comparison can be made of the glycerol data to the predictions of any theory concerned with the relaxational dynamics, such as the coupling model. Moreover, an important result of the coupling model, overlooked by WPCF, is the prediction that the prominence of the fast α process depends on the magnitude of the parameters, τ^* and β, describing the slow α process, $\exp[-(t/\tau^*)]^\beta$ for $t>t_c$. This prominence, reflected in the amount of decay, $1-\exp(-t_c/\tau_D)$, of the fast process which occurs up to the crossover time, is governed by the fact that at $t=t_c$, $\exp(-t_c/\tau_D)=\exp[-(t/\tau^*)]^\beta$. Since t_c is temperature insensitive, we can see that the prominence of the fast process diminishes for larger τ^* and/or larger β. This property of fast relaxation has been amply demonstrated in Figs. 1(a)–1(c) of Ref. [5]. It has been experimentally found that most polymers have significantly smaller β's than even the fragile small-molecule glass-forming liquids, and also than glycerol, which is only an intermediate liquid. This finding is consistent with the coupling model, since intrachain cooperativity of the repeat units along the polymer backbone enhances intermolecular constraints, leading to a larger coupling parameter, n $(=1-\beta)$. The prominence of the fast process in polymers is a consequence of their larger n [2,3]. While the difference between the short-time behavior of glycerol and polymers is readily understood from the coupling model, other theories, such as mode coupling theory, offer no guidelines concerning the relationship between the prominence of the fast β process (the mode coupling theory's counterpart to the fast α process of the coupling model) and chemical structure or other measurable parameters such as the Kohlrausch exponent. We have reexamined the data of WPCF using the coupling model [6], and indeed confirm that the fast α process of glycerol lacks sufficient prominence, whereby it was misconstrued as nonexistent from their rudimentary fitting to the stretched exponential [1].

According to the coupling model, the q dependence of the τ^* at a fixed T is related to that of τ_D by $\tau^*(q)\propto\tau_D(q)^{1/\beta}$. To test this prediction, the q dependence of τ_0 must be determined, since it is not predicted by the coupling model. When the ''Gaussian approximation'' holds [2,3], we have $\tau_D \propto q^{-2}$, whereby the coupling model predicts that $\tau^*\propto q^{-2/\beta}$. In polymers, since the fast α process is prominent, τ_0 and its dependencies on q and T can be readily determined from experimental data. For some polymers, such as polyvinylchloride, it was found that $\tau_D\propto q^{-2}$ at fixed T, and the predicted $\tau^*\propto q^{-2/\beta}$ was indeed observed [2]. In other polymers, such as polyisoprene and polybutadiene, it was found that $\tau_D(T)\propto q^{-\gamma}$ at any fixed T, with $\gamma<2$ [3]. As discussed by Zorn [7] and Colmenero [8], an exponent $\gamma<2$ reflects a breakdown of the Gaussian approximation. Under this circumstance, the coupling model predicts $\tau^*\propto q^{-\gamma/\beta}$ which, depending on the value of γ, can be considerably weaker than $q^{-2/\beta}$, as was experimentally found. Pending determination of the q dependence of τ_D, this deviation of τ^* from $q^{-2/\beta}$ could be a verification of, not at odds with, the coupling model. WPCF's declaration that ''our data contradict the relation $\kappa=2/\beta$'' is misleading, since this is expected only when the Gaussian approximation applies. Of course, the validity of WPCF's stated q dependence itself is open to question, given their reliance on t-T superpositioning.

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