Comment on “Generalized localization model of relaxation in glass-forming liquids”

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Recently, Simmons et al. reported on the correlation between the structural relaxation time $\tau_s$ and the picosecond short-time mean square displacement $\langle u^2 \rangle$ (ST-MSD) by presenting experimental and simulation results, and developing a localization model (LM).

The authors stated that, due to the influence of the fast beta relaxation “any fixed universal relationship between $\tau$ and $\langle u^2 \rangle$ is unlikely” and “an additional parameter would seem to be required to capture this relationship”. To support the claim, it was shown that the scaling, proposed in ref. 2, between $\tau_s$ and the reduced variable $\langle u^2 \rangle = (\langle u^2 \rangle)/(\langle u^2 \rangle)$ at the glass transition), which does not depend on local relaxation (LR) explicitly, apparently fails for the studied systems (Fig. 1, ref. 1). To test the scaling, Simmons et al. imposed the best possible collapse of the data in the high temperature range claiming this as being the approach of ref. 2. In contrast, we never used this procedure in that $\langle u^2 \rangle$ could be contributed by spurious relaxation effects at high temperature. Actually, our procedure defines $\langle u^2 \rangle$ according to the usual definition of the glass transition temperature $T_g$ ($\log (\eta(T_g)) = 12 \pm 0.5$ or $\log (\tau_s(T_g)) = 2 \pm 0.5$ in SI units), sets the reduced variable $\langle u^2 \rangle$ and proceeds to the scaling by adjusting the conversion factors of the time, $\tau_{CF}$, and the viscosity, $\eta_{CF}$, from the molecular-dynamics (MD) units to the actual SI units to favor the best possible collapse of the data of all the systems close to $T_g$ in the low temperature range. The list of the conversion factors is in Table 1 of ref. 3. Fig. 1a shows the reported scaling about several glass formers in a wide range of fragility. The same procedure applied to the new data of ref. 1 leads to Fig. 1b. Then, even if in principle LR may affect $\langle u^2 \rangle$, as discussed by two of us elsewhere, the results by ref. 1 do not provide strong evidence that LR breaks down the scaling by $\langle u^2 \rangle$ proposed in ref. 2. We ascribe most deviations to the data paucity increasing the

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uncertainty of $\langle u_g^2 \rangle$ and then $\langle \overline{u^2} \rangle$. Indeed, if larger datasets are available, like for glycerol, the deviations decrease (compare empty and filled squares in Fig. 1b).

Furthermore, in spite of purported large deviations from the scaling (Fig. 1 of ref. 1), Fig. 1b shows that the “pure polymer” model (PPM) is indistinguishable from other well-known scaling-compliant polymer models differing only for insignificant changes in the bond stiffness, i.e. the FENE (very high stiffness) and the rigid-bond (infinite stiffness) models. This suggests that the unphysical negative value of the mean square escape distance parameter $a^2$, which results from fitting the master curve of our scaling – eqn (1) of ref. 1 – to the PPM data (see the negative slope of the best-fit curve of the PPM data at $\langle u^2 \rangle_T/(\overline{u^2}) = 0$ in Fig. 1 of ref. 1), is an artifact due to the improper scaling procedure by the authors of ref. 1.

Two final remarks are in order: (i) the LM master curve has three adjustable parameters (Table 1, ref. 1) whereas the scaling by $\langle \overline{u^2} \rangle$ adjusts one parameter (the conversion factor $\tau_{CF}$ or $\eta_{CF}$, see Table 1, ref. 3) since $\langle u_g^2 \rangle$ is taken from the experimental data. (ii) Fig. 1 demonstrates the scaling by $\langle \overline{u^2} \rangle$ in the log-linear plot to disprove the statement by Simmons et al. that it is a deceptive consequence of using log-log plots.

References