

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

Cite this: *Soft Matter*, 2013, **9**, 7890

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Received 21st January 2013

Accepted 2nd July 2013

DOI: 10.1039/c3sm50227a

www.rsc.org/softmatter

Recently, Simmons *et al.* reported on the correlation between the structural relaxation time τ_α 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).¹ The authors stated that, due to the influence of the fast beta relaxation “any fixed universal relationship between τ 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 τ_α and the reduced variable $\overline{\langle u^2 \rangle} \equiv \langle u^2 \rangle / \langle u_g^2 \rangle$ ($\langle u_g^2 \rangle$ denotes $\langle u^2 \rangle$ 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.³ Actually, our procedure defines $\langle u_g^2 \rangle$ according to the usual definition of the glass transition temperature T_g ($\log \eta(T_g) = 12 \pm 0.5$ or $\log \tau_\alpha(T_g) = 2 \pm 0.5$ in SI units), sets the reduced variable $\overline{\langle u^2 \rangle}$ and proceeds to the scaling by adjusting the conversion factors of the time, τ_{CF} , and the viscosity, η_{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.² 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.^{2,3} 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,³ the results by ref. 1 do not provide strong evidence that LR breaks down the scaling by $\overline{\langle u^2 \rangle}$ proposed in ref. 2. We ascribe most deviations to the data paucity increasing the

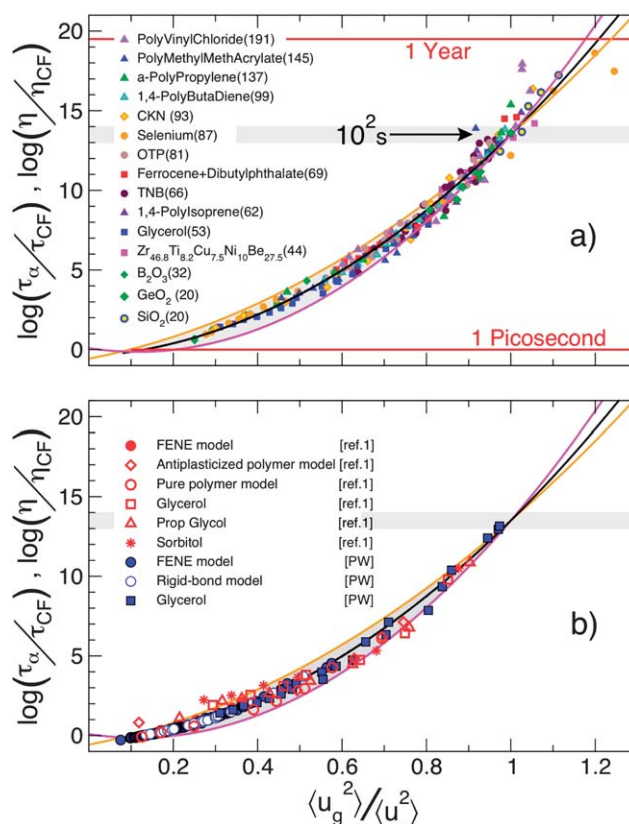


Fig. 1 Correlation between the reduced relaxation time (or viscosity) vs. the reduced ST-MSD. τ_{CF} and η_{CF} are the conversion factors from the time and viscosity MD units to the corresponding SI units, respectively. (a) Current status (numbers in parentheses denote the fragility, the list of the conversion factors is in Table 1 of ref. 3); (b) update by Simmons *et al.* (red symbols)¹ and the present work (PW) (blue symbols). The black line is the master curve found in ref. 2 with accuracy bounded by the colored curves. “Pure polymer” data from Fig. 5 of ref. 1. The conversion factor used for the experimental data of ref. 1 is $\log \tau_{CF} = -11.75 \pm 0.25$.

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uncertainty of $\langle u_g^2 \rangle$ and then $\overline{\langle u^2 \rangle}$. Indeed, if larger datasets are available, like for glycerol,^{2,3} 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 stiffness²) 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 $\langle u^2 \rangle_{T_g} / \langle u^2 \rangle = 0$ 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 $\overline{\langle u^2 \rangle}$ adjusts *one* parameter (the conversion factor τ_{CF} or η_{CF} , see Table 1, ref. 3) since $\langle u_g^2 \rangle$ is taken from the experimental data.² (ii) Fig. 1 demonstrates the scaling by $\overline{\langle u^2 \rangle}$ 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

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