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Comment on “Direct Observation of Stretched-Exponential Relaxation in Low-Temperature Lennard-Jones Systems Using the Cage Correlation Function”

Rabani, Gezelter, and Berne (RGB) report [1] “direct observation” of stretched exponential relaxation of the cage correlation function, which [2,3] describes the motion of atoms out of the first shell of neighbors, in disordered (Lennard-Jones) LJ solids [4]. Their fit is

$$C_{\text{cage}}(t) = e^{-(\gamma t)^\beta}, \quad (1)$$

with $\beta \approx 1/2$. For temperatures $T^* = 0.5, 0.41$, and 0.33 , $\gamma = 1.9, 0.83$, and 0.43 ns^{-1} , respectively. RGB note that β is uncertain since $C_{\text{cage}}(t)$ has decayed only by a single decade on the observed time scale (7 ns). They derive a static distribution of relaxation rates, $\rho(k)$, and use Zwanzig’s theory [5] to obtain diffusion constants D in “reasonable agreement” with simulation.

Single particle hopping and vibrational motion are two distinct mechanisms for cage dynamics. Vibrations are responsible for the rapid ($<1 \text{ ps}$) decay of neighborhood lists in glasses [6]. RGB argue that vibrations do not contribute to irreversible changes since for longer times, the cage will reconstitute itself. However, in condensed phases, vibrational lines are *homogeneously* broadened, typically in the GHz range. We thus expect the reconstitution of cages to be incomplete on ns time scales even in the absence of hopping, leading to the ansatz,

$$C_{\text{cage}}(t) = \kappa(p e^{-t/\tau_v} + e^{-t/\tau_h}). \quad (2)$$

Here, p is the relative weight of the vibrational mechanism and κ is chosen to match the two fits at $t = 0.1 \text{ ns}$. Equation (2) is an excellent fit,

T^*	τ_v (ns)	τ_h (ns)	p
0.5	0.4	2.5	1.43
0.41	0.4	3.7	0.77
0.33	0.4	4.8	0.45

and [cf. Fig. 1] describes $C_{\text{cage}}(t)$ as well as Eq. (1) over the observed time range. Thus, vibrational dynamics gives rise to a fast, T -independent β process, while the slow, T -dependent α process is due to particle hopping, or structural relaxation [7].

Vibrational frequencies are of the order ps^{-1} , so the low hopping rate limit [4] of Zwanzig’s theory applies, $D/T^* \sim \langle k \rangle$. Since $\langle k \rangle = -dC_{\text{cage}}/dt|_{t \rightarrow 0} = \frac{1}{2} \sqrt{\gamma/t} \rightarrow \infty$, $\langle k \rangle$ diverges and RGB introduce an upper cutoff $k_{\text{max}} = 390 \text{ ns}^{-1}$ so that $\langle k \rangle \sim \sqrt{\gamma k_{\text{max}}}$. Although $C_{\text{cage}}(t)$ is observed on ns time scale, D is determined by hopping rates $\sim \text{ps}^{-1}$. Rates $\sim \text{ns}^{-1}$ yield D which are far too small. RGB’s calculations follow our estimate $D/T^* \sim \sqrt{\gamma}$; $(D_{\text{cage}}/T^*)^2/\gamma = 1.15, 1.26$, and 1.23 at

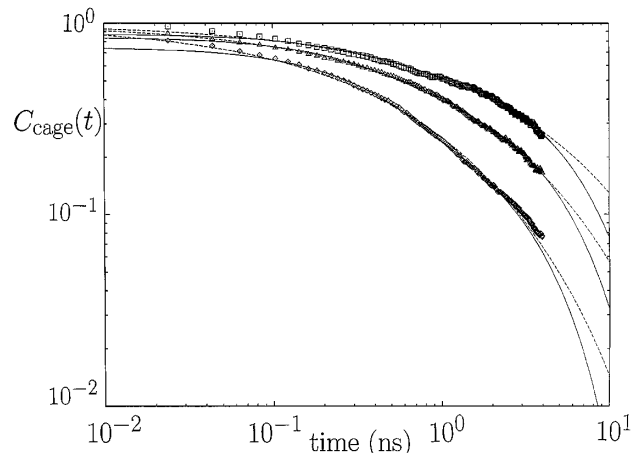


FIG. 1. A log-log plot of the two fits for $C_{\text{cage}}(t)$. Dashed lines are stretched exponentials, Eq. (1), and full lines are linear superpositions of two exponentials, Eq. (2). The open diamonds are for $T^* = 0.5$, the open triangles for $T^* = 0.41$, and the open squares for $T^* = 0.33$ (data provided by the authors of Ref. [1]). Note that the parameters in Eq. (2) are chosen such that the fits coincide at $t = 0.1 \text{ ns}$.

$T^* = 0.5, 0.41$, and 0.33 . However, the theory estimates of D are “in the ballpark” only because of the contribution of rates orders of magnitude faster than the time scale of observation, governed by the adjustable cutoff.

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