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LETTER

Vanishing of configurational entropy may not imply an ideal glass transition in randomly pinned liquids

The paper by Ozawa et al. (1) presents numerical results for the configurational entropy density, s_c, of a model glass-forming liquid in the presence of random pinning. The location of a "phase boundary" in the pin density (c) − temperature (T) plane, which separates an "ideal glass" phase from the supercooled liquid phase, is obtained by finding the points at which $s_c(T, c) \to 0$. According to the theoretical arguments in ref. 2, an ideal glass transition at which the α-relaxation time τ_α diverges takes place when s_c goes to zero.

We have studied the dynamics of the same system using molecular dynamics simulations. In Fig. 1, *Left*, we show the time dependence of the self intermediate scattering function, $F_s(k, t)$, calculated at three state points in the $(c − T)$ plane where $s_c(T, c) \simeq 0$ according to Ozawa et al. (1). It is clear from the plots that the relaxation time is finite (τ_α is of the order of 10^6) at these state points. Similar conclusions have been obtained in ref. 3, where an overlap function was used to calculate τ_α at these state points.

If the numerical results for $s_c(T, c)$ reported in Ozawa et al. (1) are correct, then our explicit demonstration of the fact that τ_α does not diverge at state points where $s_c = 0$ according to Ozawa et al. (1) would have fundamental implications for theories of the glass transition. The well-known random first-order transition (RFOT) description of the glass transition is based on the premise that the vanishing of s_c causes a divergence of τ_α. The prediction (2) of the existence of a line of ideal glass transitions in the $(c − T)$ plane for randomly pinned liquids was based on the RFOT description. Our results for τ_α would imply that the RFOT description is not valid for pinned liquids. Because a divergence of τ_α is the defining feature of the glass transition, the entropy-vanishing "transition" found in Ozawa et al. (1) at which τ_α does not diverge should not be called a glass transition.

If, however, we disregard the results for $s_c(T, c)$ reported in Ozawa et al. (1), then all available data for the dynamics of this system (3, 4) can be understood from a description that is consistent with RFOT and the requirement that the presence of pinning must decrease s_c. This description (3) is based on the assumption that $s_c(T, c) = B(c)s_c(T, 0)$ for small values of c, where $B(c)$ is a smooth function that decreases with increasing c, with $B(0) = 1$. This assumption, when combined with the Adam–Gibbs relation, predicts that the logarithm of $\tau_\alpha(T, c)$ should be a linear function of $1/[Ts_c(T, 0)]$ with a coefficient that increases with c. The data for $\tau_\alpha(T, c)$ in ref. 3 are consistent with this prediction (Fig. 1, *Right*). We have verified that the data for $\tau_\alpha(T, c)$ and $s_c(T, 0)$ in Ozawa et al. (1) are also consistent with this prediction (Fig. 1, *Middle*). This observation provides a way of reconciling the behavior of $\tau_\alpha(T, c)$ with RFOT, but it also implies that the data for $s_c(T, c)$ reported in Ozawa et al. (1) are not quantitatively accurate.

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Fig. 1. (*Left*) Plots of the time dependence of the self intermediate scattering function, $F_s(k, t) = (1/N_m)[\langle \sum_{i=1}^{N_m} e^{i\vec{k} \cdot (\vec{r}_i(t) - \vec{r}_i(0))} \rangle]$, where k is the wavenumber at the first peak of the static structure factor, $\langle \ldots \rangle$ implies an average over thermal history, $[\ldots]$ represents an average over different realization of the pinned particles, and N_m is the number of unpinned mobile particles. Results are shown for three state points at which $s_c(T, c) \simeq 0$ according to Ozawa et al. (1). The α-relaxation time τ_α is calculated using a fit to the form $F_s(k, t) = A \exp[-(t/\tau_1)^2/2] + (1 - A)\exp[-(t/\tau_\alpha)^\beta]$. The fits are shown by solid lines. The relaxation times for these state points are $\tau_\alpha(T = 0.50, c = 0.16) \simeq 3.7 \times 10^6$, $\tau_\alpha(T = 0.55, c = 0.20) \simeq 2.4 \times 10^6$, and $\tau_\alpha(T = 0.70, c = 0.30) \simeq 9.0 \times 10^5$. (*Middle*) $\tau_\alpha(T, c)$ versus $1/[Ts_c(T, 0)]$ for data extracted from Ozawa et al. (1). (*Right*) $\ln[\tau_\alpha(T, c)]$ versus $1/[Ts_c(T, 0)]$ for the data in ref. 3.