Comment on "Microscopic Theory of Network Glasses"

In a recent Letter, Hall and Wolynes [1] (HW) ask whether a microscopic theory of network glasses can be developed starting from a model of dense spherical fluids. To do so, they constrain the number of nearest neighbors and count their central force interactions separately. They obtain the dynamical transition temperature T_A (below which the system is nonergodic and the motion is landscape determined), and the entropy crisis (Kauzman) temperature T_K as functions of n_b, the average number of nearest neighbor bonds/atom. A Lindemann melting criterion on the amplitude of nearest neighbor vibrations defines the glass transition temperature T_G. The model shows that T_A/T_G and T_K/T_G monotonically increase and decrease, respectively, as functions of n_b. For $n_b = 2.4$, $T_A/T_G = 100$, an unreasonable result. Mode coupling theory defines a critical nonergodicity temperature T_c beyond which a radical change in the long time limit of the density-density correlation function occurs. T_c has been plausibly estimated for vitreous silica in molecular dynamics simulations [2] as $T_c/T_G = 2$. Even this temperature is presently outside the reach of experimental investigations [2].

How do these results compare with experiments? There are standard procedures for extrapolating specific heats to obtain T_K, but identifying the onset of nonergodicity at T_A (or T_c) is much more difficult. Chalcogenide glasses are ideal test systems because one can synthesize them over a wide range of n_b by chemical alloying group IV additives in Se base glass. Fortunately, glass transitions of these systems have been recently reinvestigated [3] using T-modulated scanning calorimetry (MDSC), a new method which permits separating the usual DSC heat flow endotherm $\dot{H}_T$ into a reversing part $\dot{H}_{\rm rev}$ which is ergodic (and which follows the modulated T profile) from the nonreversing part $\dot{H}_{\rm nr}$ which is nonergodic (arising from underlying temperature dependent activated processes) as illustrated in Fig. 1(a). MDSC permits one to establish this temperature T_A at which dynamics become landscape dominated (i.e., in MDSC language dominated by a T-dependent $\dot{H}_{\rm nr}$) in contrast to the linear response regime (i.e., at high temperatures when the heat flow is $\dot{H}_{\rm rev}$ dominated by a constant activation energy).

In binary Ge_xSe_{1-x} glasses, observed variations in T_A/T_G and T_K/T_G as a function of $n_b = 2 + 2x$ are compared to HW predictions in Fig. 1(b). The $T_K/T_G(n_b)$ results were obtained from a Vogel-Fulcher analysis of viscosity measurements [4]. One finds the observed and predicted variations in $T_K/T_G(n_b)$ ratio to be in reasonable accord with each other showing a general reduction starting from a value of about 0.9 at $n_b = 2$ to a value of 0.6 near $n_b = 2.7$. Note, however, that the broad global minimum in the observed T_K/T_G ratio near $n_b = 2.4$ is not reproduced by the HW approach. More serious is the fact that observed T_A/T_G values are (i) 2 orders of magnitude lower than the HW predictions and (ii) show a global minimum near $n_b = 2.4$ that is in sharp contrast to the almost linear increase [Fig. 1(b)] predicted by HW. The global minima in T_K/T_G and T_A/T_G ratios are features related to self-organization of glasses that are missing in the HW approach. Clearly, features such as inclusion of local structures [3,5], structural self-organization [5,6], and noncentral forces (bond bending) are missing in the theory. Bond-bending forces constitute $(4n_b - 6)/(5n_b - 6)$ of the global number of network constraints (e.g., 0.6 at the ideal $n_b = 2.4$) indicating that the noncentral (angular) forces have to be included in a successful theory of network glasses.

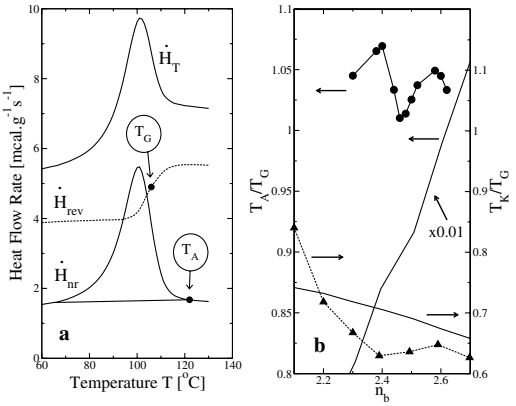

FIG. 1. (a) MDSC scan of $As_{20}Se_{80}$ bulk glass; T_G is defined as the inflexion point of $\dot{H}_{\rm rev}$ while T_A is the end point of the $\dot{H}_{nr}$ endotherm. (b) T_A/T_G (●) and T_K/T_G (▲) for Ge-Se glasses. Lines without symbols are HW predictions [1].

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