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Impact of fragility on enthalpy relaxation in glass

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The macroscopic properties of a glass are continually relaxing toward their equilibrium supercooled liquid values. Experimentally, the shape of the relaxation function in a glass is known to depend on the fragility of the supercooled liquid. In this paper, we investigate the impact of fragility on the relaxation behavior of glasses in the enthalpy landscape framework. We show that the fragility of a supercooled liquid is a direct result of the interplay of enthalpic and entropic effects in the enthalpy landscape. Through proper adjustment of the transition barriers in an enthalpy landscape, the fragility of a system can be adjusted while maintaining the same glass transition temperature. By modeling a set of systems with identical glass transition temperatures but varying values of fragility, we show that supercooled liquid fragility has a significant impact on the enthalpy relaxation behavior of a glass. In particular, the magnitude of enthalpy relaxation decreases dramatically with increasing fragility. Finally, we discuss how in the limit of infinite fragility the glass transition becomes an ideal second-order phase transition where no relaxation is possible in the glassy state.

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I. INTRODUCTION

A fundamental understanding of the behavior of glass can be obtained only through study of the nonequilibrium physics involved in the glass formation and relaxation processes [1,2]. As a nonequilibrium system, a glass continually relaxes toward an equilibrium supercooled liquid state. This relaxation process is essentially frozen at low temperatures, where the dynamics of the system are too slow to observe relaxation on a laboratory time scale. The relaxation process is accelerated during heat treatments when the glass is exposed to temperatures approaching the transition range. As the temperature changes during the heat treatment, the equilibrium supercooled liquid state is also changing, providing a "moving target" toward which the glass relaxes. When the heat treatment is finished and the glass brought back to low temperatures, the physical properties of the glass likely have relaxed with respect to those before the heat treatment.

Recent investigations by Niss and co-workers [3] and by Hornbøll and Yue [4] found an empirical correlation between the relaxation behavior of glass and the fragility of the corresponding supercooled liquid. The term "fragility," coined by Angell [5–8], refers to the scaling behavior of viscosity with temperature. Angell plotted the logarithm of viscosity ($\log_{10}\eta$) of various supercooled liquids as a function of T_g/T, where T is the absolute physical temperature and T_g is the glass transition temperature of the particular composition. The glass transition temperature is taken at the annealing point viscosity (10^{12} Pa s, or 10^{13} P), assuming a typical laboratory cooling rate. Using such a plot of $\log_{10}\eta$ versus T_g/T, Angell noted two distinct scaling behaviors. Certain supercooled liquids, such as silica and germania, exhibit a near-Arrhenius dependence of viscosity on temperature, while others show a significant departure from Arrhenius behavior. Angell thus classified supercooled liquids as either "strong" or "fragile," depending on whether they exhibit an Arrhenius (strong) or non-Arrhenius (fragile) scaling of viscosity with temperature. Fragility itself is defined as the slope of the $\log_{10}\eta$ versus T_g/T curve at the glass transition temperature [9]:

$$m \equiv \left.\frac{d\log_{10}\eta}{d(T_g/T)}\right|_{T=T_g}. \tag{1}$$

A greater value of fragility m indicates a larger departure from Arrhenius behavior. (A strong liquid has $m \approx 17$.) Please note that fragility is a property of the supercooled liquid state and not of the glassy state; hence, the fragility is independent of the thermal history of the system.

The work of Niss and co-workers [3] shows that the relaxation function of a glass becomes increasingly nonexponential as the fragility of the glass-forming liquid is increased. Their investigation builds on work by Böhmer and co-workers [9], who had previously demonstrated the nonexponential relaxation behavior of fragile systems, as compared to the simple exponential relaxation behavior observed in strong systems. Researchers have also demonstrated a connection between fragility and (a) the intensity of the boson peak in glass [10], (b) the vibrational properties of energy minima and the distribution of these minima [11,12], (c) the difference between harmonic and anharmonic vibrational heat capacities [13], (d) the sharpness of the glass transition in terms of change in heat capacity [14], (e) the ratio of elastic to inelastic scattering in the Brillouin spectra [15], (f) Poisson's ratio [16,17], and (g) the temperature scaling of the elastic shear modulus [18].

In this paper, we show that the value of the supercooled liquid fragility has a large impact on the magnitude of enthalpy relaxation observed in a glass. An increase in the fragility of a system leads to a greater free energy barrier for structural relaxation below the glass transition temperature.

This results in a sharper glass transition and a significant reduction in enthalpy relaxation upon subsequent heat treatments. In the limit of infinite fragility, the glass transition becomes perfectly sharp, yielding an ideal second-order thermodynamic phase transition. In this case, no relaxation is possible below the glass transition temperature.

Our paper is organized as follows. In Sec. II we give an overview of our modeling approach, which is based on the concept of an enthalpy landscape. In Sec. III we derive an expression for fragility within the enthalpy landscape formalism and show how the fragility of the landscape can be adjusted while maintaining a constant glass transition temperature. In Sec. IV we show that an increase in the fragility of a system can lead to a significant reduction in the magnitude of enthalpy relaxation in a glass. Finally, in Sec. V we discuss the implications of a hypothetical infinitely fragile system, where no relaxation is possible in the glassy state.

II. ENTHALPY LANDSCAPES AND THE GLASS TRANSITION

The study of supercooled liquid and glassy systems can be facilitated using the enthalpy landscape approach [19–22]. The zero-temperature enthalpy landscape of an N-atom system is

$$H = U(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N,L) + PL^3, \tag{2}$$

where the potential energy U is a function of the atomic position vectors $\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N$ and the length L of the simulation cell. The pressure P of the system is constant, and the simulation cell is assumed to be cubic. The H hypersurface is, in effect, a $(3N+1)$-dimensional landscape containing a multitude of local minima. Each of these minima corresponds to a mechanically stable configuration of atoms known as an "inherent structure" [23–28]. The volume of configurational space that drains to a particular minimum via steepest descent is called a basin; hence, there is one basin for every inherent structure.

The utility of the enthalpy landscape approach lies in the ability to separate the fast vibrations within a basin, i.e., the vibrations about a particular inherent structure configuration, from the slower interbasin transitions ("basin hopping"). While the enthalpy landscape itself is independent of temperature, the way in which the system samples the phase space depends on its kinetic energy, and hence on the temperature of the system. At high temperatures, the system can flow freely among basins, corresponding to the case of an ergodic, equilibrium liquid. As the system is cooled, the interbasin transitions occur less frequently owing to the loss of thermal energy. Finally, the glassy state at low temperatures corresponds to a breakdown of ergodicity where the system becomes trapped in a subset of the overall phase space known as a "metabasin" [2].

Recently, we have developed a rigorous physical model for the glass transition of selenium, a simple but realistic glass-forming system [22]. Our model combines the enthalpy landscape approach above with nonequilibrium statistical mechanics techniques [29–32]. Our approach involves first mapping the continuous enthalpy landscape to a discrete set of inherent structures and transition points, which can be accomplished using eigenvector following [21,33] or another method such as the activation-relaxation technique of Barkema and Mousseau [34,35]. A separate calculation is required to compute the inherent structure density of states [36]. Finally, the dynamics of the glass-forming system can be computed using the master equation solver of Mauro, Loucks, and Gupta [37], which employs a coarse-graining approach to access laboratory time scales.

For our model of selenium we employ the interatomic potentials of Mauro and Varshneya [38], derived from quantum mechanics using Møller-Plesset perturbation theory [39] and the Dunning basis set [40]. The transition points in selenium involve elementary bond angle and torsion angle transitions, which have a nearly constant enthalpy barrier of $\Delta H \approx 1$ eV [22,41]. The degeneracy of the inherent structures—and hence the transition points—varies exponentially with enthalpy [22]. Using a recursive counting argument, we compute a maximum number of accessible transition points of $g = e^{180}$ $(\ln g = 180)$ [22]. Figure 1(a) shows an enthalpy-temperature diagram for selenium computed with our model and assuming a typical laboratory cooling rate of 1 K/min. The glass transition temperature, here based on the intersection of the extrapolated glassy and supercooled liquid lines, is 318 K, in agreement with the experimental value [42]. Figure 1(b) shows the enthalpy-temperature diagram of this same glass after undergoing a subsequent thermal cycle. The relaxation behavior is clearly visible in this figure.

III. FRAGILITY IN THE ENTHALPY LANDSCAPE APPROACH

As derived previously [22], the viscosity of a glass can be computed in the enthalpy landscape approach by

$$\eta(t_{\text{obs}}) = CNT\left[\sum_{\alpha=1}^{\Omega} p_\alpha \sum_{\beta\neq\alpha}^{\Omega}\left(\sum_{\gamma\neq\beta}^{\Omega} K_{\gamma\beta} f_{\alpha\gamma}(t_{\text{obs}}) - \sum_{\gamma\neq\beta}^{\Omega} K_{\beta\gamma} f_{\alpha\beta}(t_{\text{obs}})\right)\right]^{-1}, \tag{3}$$

where t_{obs} is the observation time (i.e., the measurement time), C is a constant related to the magnitude of the structural transitions, $K_{\beta\gamma}$ is the transition rate from basin β to basin γ, and $f_{\alpha\beta}(t_{\text{obs}})$ is the conditional probability of occupying basin β after starting in basin α and evolving for exactly t_{obs}. These conditional probabilities account for the continuous breakdown of ergodicity that occurs in the glass transition regime [43]. If we assume that the viscosity measurement is fast compared to the internal relaxation time scale of the glass, then the conditional probability $f_{\alpha\beta}$ reduces to a Kronecker δ function,

$$\lim_{t_{\text{obs}}\to 0} f_{\alpha\beta}(t_{\text{obs}}) = \delta_{\alpha\beta}, \tag{4}$$

and the viscosity expression becomes

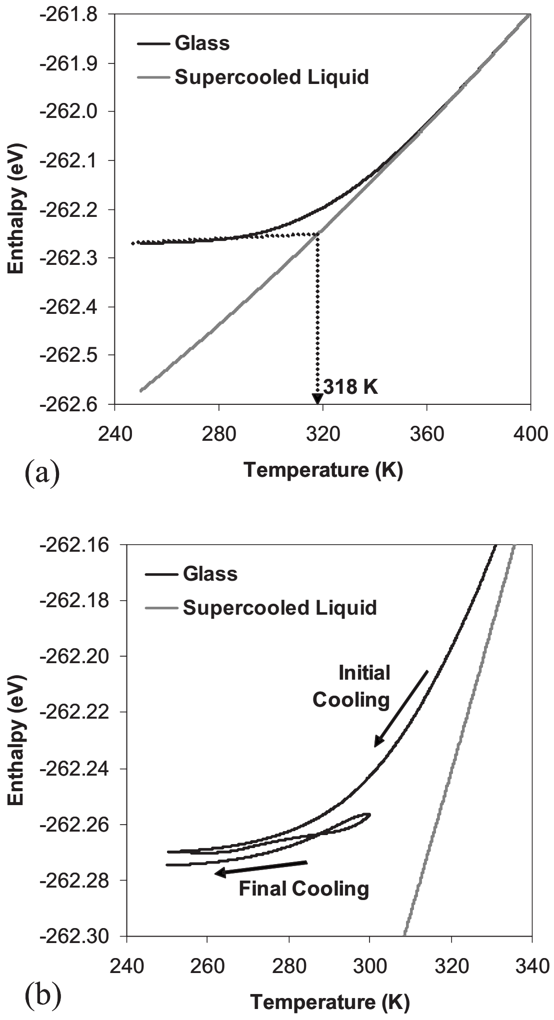

FIG. 1. (a) Computed enthalpy-temperature diagram for selenium using a cooling rate of 1 K/min. The glass transition temperature is T_g=318 K. (b) The glass in (a) is reheated to 300 K and subsequently cooled back to 250 K. The reheating and recooling rate is 1 K/min, identical to the initial cooling rate. The heat treatment results in relaxation of the glass enthalpy.

$$\lim_{t_{\mathrm{obs}}\to 0} \eta(t_{\mathrm{obs}}) = CNT\left(\sum_{\alpha=1}^{\Omega} p_\alpha \sum_{\beta\neq\alpha}^{\Omega} K_{\alpha\beta}\right)^{-1}. \tag{5}$$

Using the definition of fragility in Eq. (1), the constant prefactors drop out, giving

$$m = -\frac{1}{\ln 10} - \frac{d\log_{10}(\Sigma_{\alpha=1}^{\Omega} p_\alpha \Sigma_{\beta\neq\alpha}^{\Omega} K_{\alpha\beta})}{d(T_g/T)}\Bigg|_{T=T_g}. \tag{6}$$

A simpler form for fragility can be obtained in the case of a single activation enthalpy, such as we can assume for selenium [44], where the transition rate can be written as [37]

$$K(T) = \nu g(T)\exp\left(-\frac{\Delta H}{k_B T}\right) = \nu\exp\left(-\frac{\Delta H - kT\ln g(T)}{kT}\right). \tag{7}$$

Here, ν is the attempt frequency, $g(T)$ is the total number of accessible transition points at temperature T, ΔH is the enthalpy barrier, and k is Boltzmann's constant. In this case, the fragility can be expressed as

$$m = -\frac{1}{\ln 10} - \frac{d\log_{10}[\nu g(T)\exp(-\Delta H/kT)]}{d(T_g/T)}, \tag{8}$$

which reduces to

$$m = -\frac{1}{\ln 10}\left(1 + \frac{d\ln g(T)}{d(T_g/T)}\right) + \frac{\Delta H}{kT_g \ln 10}. \tag{9}$$

Suppose now we wish to adjust the fragility of a supercooled liquid while maintaining a constant equilibrium enthalpy vs temperature curve, and also while maintaining a constant glass transition temperature T_g for a given cooling rate. Since the shape of the $\ln g(T)$ curve has a direct impact on the enthalpy and volume curves of the supercooled liquid, the first term in Eq. (9) must be held constant. This leaves only ΔH as a free parameter for adjusting fragility. However, adjustment of ΔH also affects the glass transition temperature, since a greater enthalpy barrier would lead to a higher T_g.

To maintain a constant glass transition temperature, the transition rate (or, inversely, the structural relaxation time) must be held constant at $T=T_g$. (Recall that the glass transition occurs when the internal relaxation time scale of the system equals an external time scale defined by the inverse of the cooling rate [2]. Hence, for a constant cooling rate, the structural relaxation time is a constant at T_g.) Therefore,

$$K(T_g) = \nu\exp\left(-\frac{\Delta H - kT_g\ln g(T_g)}{kT_g}\right) \tag{10}$$

should be held constant while simultaneously adjusting ΔH to vary the fragility:

$$\Delta H \to \Delta H + \delta H. \tag{11}$$

This can be accomplished by adding a constant to $\ln g(T)$,

$$\ln g(T) \to \ln g(T) + \delta\ln g, \tag{12}$$

where δH and $\delta\ln g$ are chosen to obtain a constant Gibbs free energy barrier, $\Delta G = \Delta H - kT_g\ln g(T_g)$, at the glass transition temperature:

$$\delta H = kT_g\delta\ln g. \tag{13}$$

Hence, Eq. (13) provides a relation for adjusting fragility while preserving a constant glass transition temperature and without altering the enthalpy curve of the supercooled liquid. Figure 2(a) shows a plot of $\ln g$ versus ΔH, using selenium as the base landscape (T_g=318 K).

Figure 2(b) plots the values of fragility obtained by adjusting the ΔH and $\ln g$ values of selenium as above. In the limit of $\Delta H\to 0$, Eq. (9) predicts a lower limit of fragility that is determined by the slope of the $\ln g(T)$ curve. For an enthalpy landscape based on our model of selenium, this lower limit is m=33.84. [A lower fragility could be obtained with a flatter $\ln g(T)$ curve.] There is no theoretical upper limit to fragility:

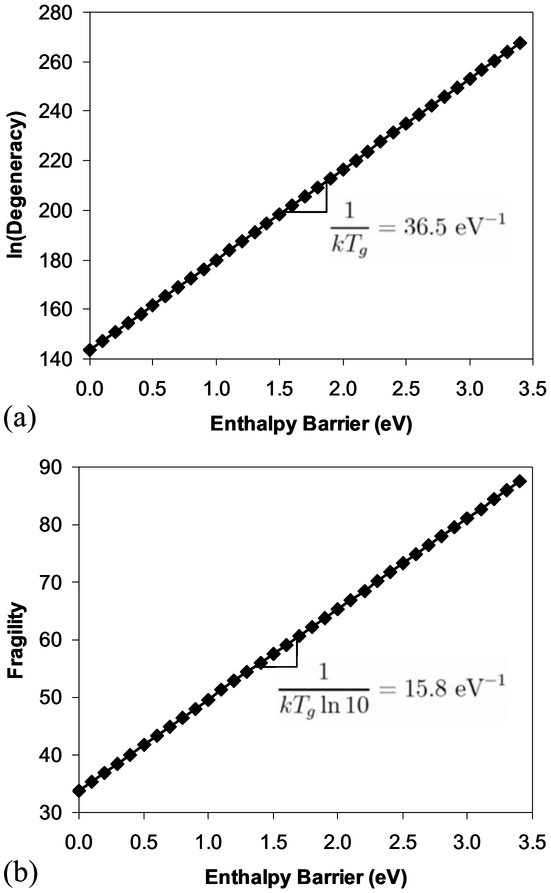

FIG. 2. (a) Variation of $\ln g$ with ΔH to adjust fragility while maintaining the same glass transition temperature as selenium. (b) Variation of fragility with enthalpy barrier.

$$\lim_{\Delta H \to \infty} m \to \infty. \tag{14}$$

As indicated in Eq. (9) and in Fig. 2(b), the slope of the m vs ΔH curve is governed solely by the glass transition temperature:

$$\frac{dm}{d\Delta H} = \frac{1}{kT_g \ln 10}. \tag{15}$$

Figure 3 plots the enthalpy-temperature diagrams for three systems with identical glass transition temperature but different values of fragility. Here we find that increasing the fragility of the system leads to a sharper, more well-defined glass transition. With a higher fragility, the effective free energy barrier for structural relaxation increases more rapidly as the system is cooled through the glass transition. In a highly fragile system, the dynamics above the glass transition are governed by entropy effects (i.e., the high number of available transition states); at temperatures below the glass transition, the dynamics are governed by the enthalpic activation barrier (ΔH). In a system with lower fragility, there is no distinct crossover from entropy-dominated to enthalpy-dominated dynamics as the system is cooled through the glass transition; here, the glass transition is more gradual.

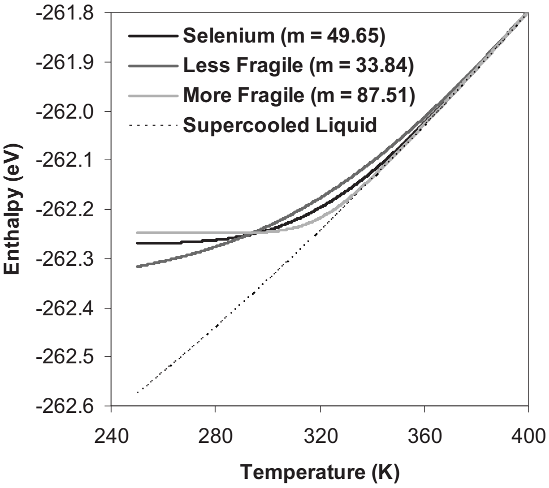

FIG. 3. Computed enthalpy-temperature curves for three glass-forming systems with different values of fragility. The cooling rate for all systems is 1 K/min. Increase in the fragility of the supercooled liquid results in a sharper glass transition.

This relationship between fragility and the sharpness of the glass transition was noted previously by Angell [14], based on experimental heat capacity curves. We discuss this feature of fragility and the implications for relaxation behavior more thoroughly in the ensuing sections.

IV. FRAGILITY AND ENTHALPY RELAXATION

To quantify the impact of fragility on enthalpy relaxation in glass, we vary the enthalpy barrier ΔH up to 3.4 eV while adjusting the total number of transition points as in Fig. 2(a). As shown in Fig. 2(b), we cover a range of fragility values from 33.84 to 87.51. The lower limit of fragility is obtained using an enthalpy barrier of 0.01 eV. The glasses are formed by cooling from 400 to 250 K at a rate of 1 K/min. They are then subjected to a linear heat treatment, where the maximum temperature of the heat treatment is varied from 260 to 320 K. We consider three reheating and recooling rates: 1 K/min (equal to the initial cooling rate), 1 K/s (faster than the initial cooling rate), and 0.01 K/s (slower than the initial cooling rate). A schematic diagram of the temperature path is provided in Fig. 4. The enthalpy relaxation is computed as

$$\frac{|\Delta H|}{H_0} = \frac{|H' - H_0|}{H_0}, \tag{16}$$

where H_0 is the enthalpy of the initially cooled glass and H' is the enthalpy after completing the subsequent thermal treatment and returning to 250 K. Since we plot the data in logarithmic units, an absolute value is used to ensure a positive value of relaxation. (Here, "relaxation" can refer to a positive or negative change in enthalpy.)

Figure 5 shows three contour plots of $\log_{10}(|\Delta H|/H_0)$ versus fragility and heat treatment temperature. The three plots (a)–(c) show results for the three reheating and recooling rates. The magnitudes of the enthalpy relaxation values vary by six orders of magnitude across the figures, from 10^{-3} to

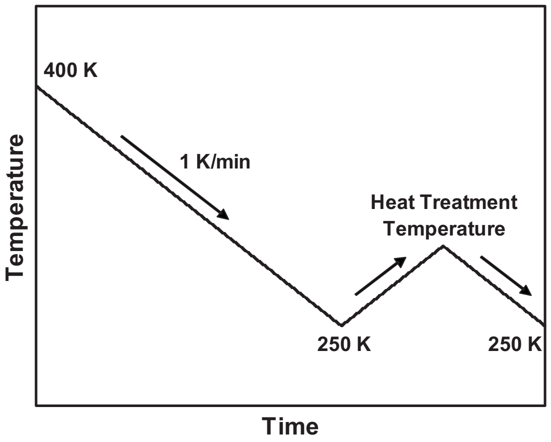

FIG. 4. Temperature path for the relaxation simulations. The glass is formed initially by cooling from 400 to 250 K at a rate of 1 K/min. The initially cooled glass is then heated to the heat treatment temperature and subsequently recooled to 250 K. The reheating and recooling rates are equal. We consider reheating and cooling rates of 1 K/s (faster than the initial cooling rate), 1 K/min (equal to the initial cooling rate), and 0.01 K/s (slower than the initial cooling rate).

10^{-9} levels. For all reheating and recooling rates, increasing the fragility of the supercooled liquid leads to a significant decrease in relaxation, by several orders of magnitude for the range of fragility values under study.

To a first-order approximation, the contour plots in Fig. 5 are fairly symmetric about the diagonal from the upper left to the lower right corners of the figure. This leads us to the following rule of thumb regarding the impact of fragility on relaxation behavior: increasing the fragility by one unit has a similar effect as decreasing the heat treatment temperature by 1 K. Of course, this is just a first-order approximation, and the value of 1 K will have to be normalized by the glass transition temperature, in this case 318 K. (For a glass with $T_g = 1272$ K, increasing the fragility by one unit should have a similar impact as decreasing the heat treatment temperature by 4 K.)

Why is increasing fragility so effective at reducing enthalpy relaxation in glasses? Let us take a closer look at the enthalpy-temperature curves for a less fragile ($m = 36.98$) and a more fragile ($m = 87.51$) system as they undergo heat treatment and subsequently return to 250 K. Figure 6 shows that, as expected from the discussion in Sec. III, increasing the fragility of the supercooled liquid leads to a much sharper glass transition since the free energy barriers to structural relaxation increase more rapidly as the system is cooled. At temperatures above the glass transition the free energy barriers are lower for the higher-fragility system (due to entropic effects); hence, it can more closely follow the supercooled liquid line. However, below the glass transition temperature the free energy barriers are greater in the higher-fragility system (due to enthalpic effects), leading to a sharper departure from the supercooled liquid line and a more sudden vitrification. Since the free energy barriers below T_g are higher with greater fragility, it is more difficult for the system to relax during heat treatment. Consequently, relaxation is significantly inhibited by fragility for any heat treatment below T_g.

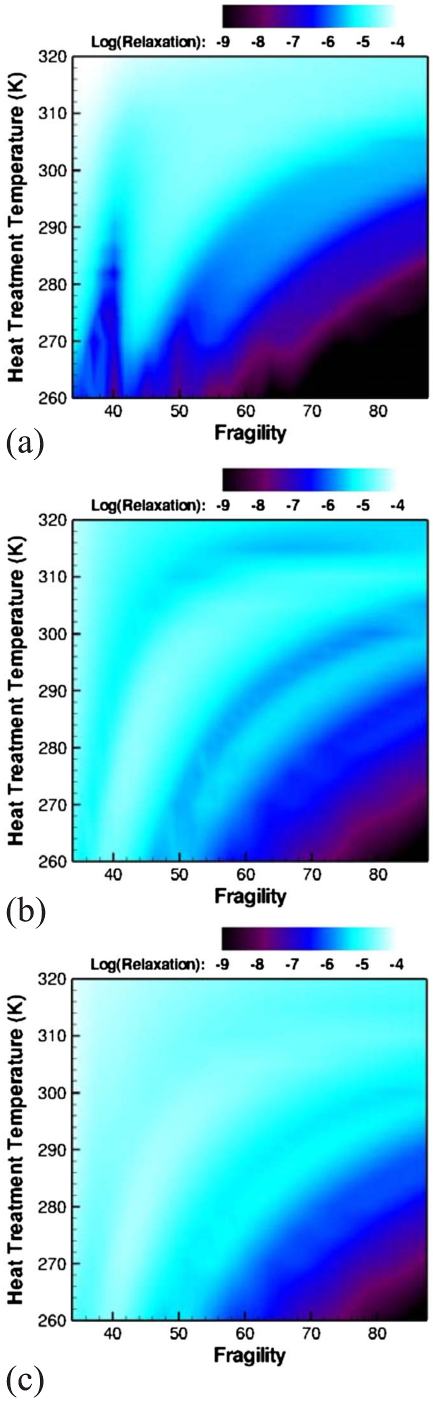

FIG. 5. (Color online) Enthalpy relaxation using a reheating and recooling rate of (a) 1 K/s, (b) 1 K/min, and (c) 0.01 K/s.

This can also be understood, at least qualitatively, in terms of the Adam-Gibbs model of cooperative relaxations [45], where the relaxation time is related to the configurational entropy $S_{\mathrm{conf}}(T)$ of the system via

$$\tau(T) \propto \exp\left(\frac{C}{T S_{\mathrm{conf}}(T)}\right), \tag{17}$$

where C is a constant. Below the glass transition temperature, the configurational entropy can be computed using the

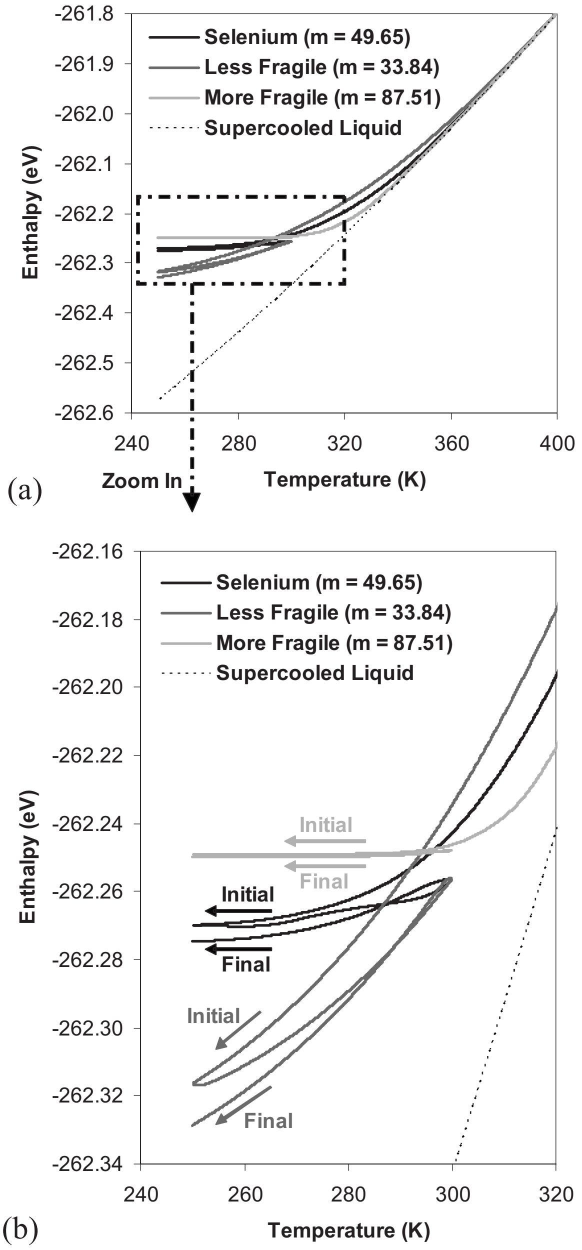

FIG. 6. (a) Enthalpy-temperature curves for three glasses with different values of fragility but the same glass transition temperature. (b) A closer view of the relaxation curves. The magnitude of relaxation decreases dramatically with increasing fragility.

continuously broken ergodicity framework of Mauro, Gupta, and Loucks [43]. For $T<T_g$ the higher-fragility system, which is dominated by enthalpy effects, will be able to visit fewer states compared to a similar system with lower fragility. This leads to a lower configurational entropy $S_{\mathrm{conf}}(T<T_g)$ with increasing fragility, and hence a longer relaxation time via the Adam-Gibbs relation.

V. FRAGILITY AND THE IDEAL GLASS TRANSITION

As discussed in Sec. III, there is an inherent lower limit of fragility governed by the slope of the $\ln g(T)$ curve; however, there is no theoretical upper limit to fragility. This raises the interesting question of what happens in the limit of infinite fragility. As we have shown in Figs. 3 and 6 and discussed above, an increase in the fragility of a supercooled liquid increases the sharpness of the glass transition. Therefore, in the limit of infinite fragility we should observe an infinitely sharp glass transition. Above the glass transition temperature there would be an effectively zero free energy barrier to relaxation, so the system would trace the supercooled liquid line perfectly. Below the glass transition temperature, the free energy barrier would be effectively infinite, prohibiting *any* structural relaxation. Hence, no relaxation would occur for any heat treatment below the glass transition temperature. As shown schematically in Fig. 7, such an ideal glass transition would yield a discontinuity in the slopes of the enthalpy and volume curves.

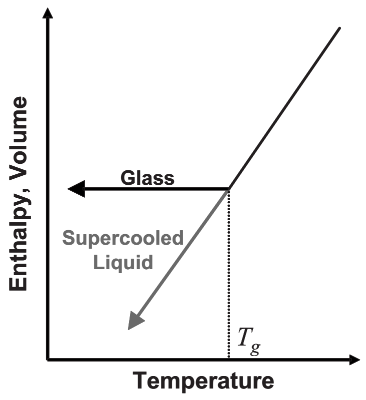

FIG. 7. Schematic diagram of an ideal glass transition, where there is a discontinuity in the slope of the enthalpy and volume curves at the glass transition temperature. An ideal glass transition is obtained in the limit of infinite fragility.

Such an ideal glass transition has been considered previously by Gibbs and DiMarzio [46] and others seeking to develop a thermodynamic model of the glass transition [1]. The appeal of the ideal glass transition is that it represents an ideal second-order Ehrenfest phase transition. With an ideal glass transition, the full thermal history of the glass can be accounted for using just a single order parameter. While this allows for a greatly simplified picture of the glassy state, an ideal glass transition can occur *only* in the limit of infinite fragility. Hence, a thermodynamic model of the glassy state that uses just a single order parameter is insufficient to capture accurately the full effect of thermal history on glass properties.

An ideal glass transition also implies a complete and discontinuous breakdown of ergodicity at the glass transition temperature. In this case, the statistical mechanics of the glassy state can be described within the broken ergodic framework of Palmer [47]. However, a finite value of fragility necessarily implies a *continuous* breakdown of ergodicity at the glass transition. The statistical mechanics of such a system can be described using the continuously broken ergodicity formalism [43].

VI. CONCLUSIONS

Whereas a strong liquid exhibits a constant free energy barrier for structural relaxation, for fragile liquids the free energy barrier increases as the system is cooled. As a result, a fragile system has a more sudden breakdown of ergodicity at the glass transition. Due to the higher free energy barriers below the glass transition temperature, glasses formed from fragile liquids exhibit less relaxation. Both the fragility of a supercooled liquid and its glass transition temperature are governed by the interplay of entropy and enthalpy effects. The fragility of an enthalpy landscape can be adjusted while maintaining a constant glass transition temperature if the transition point enthalpies are increased while simultaneously increasing the total number of available transitions. In this manner, the Gibbs free energy barrier for structural relaxation can be held constant at the glass transition, ensuring a constant glass transition temperature. While there is no theoretical upper limit to fragility, the lower limit is governed by the density of states curve.

An infinitely fragile system leads to an ideal glass transition with a sharp discontinuity in the heat capacity and thermal expansion curves (i.e., the slopes of the enthalpy and volume curves). Such an ideal glass transition involves a discontinuous breakdown of ergodicity as the small transition barriers at high temperature become effectively infinite below the glass transition. In the limit of infinite fragility, no relaxation can occur at temperatures below the glass transition.

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