Effect of fragility on relaxation of density fluctuations in glass

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ABSTRACT

Density fluctuations play a crucial role in governing the optical, mechanical, thermodynamic, and kinetic properties of glass. The relaxation of density fluctuations displays an inherently nonmonotonic behavior, yielding a minimum in fluctuations following a quench and isothermal hold. Here we investigate the impact of liquid fragility on the relaxation of density fluctuations in the nonequilibrium glassy state. While fragility has a direct impact on the kinetics of the relaxation process, the minimum level of density fluctuations is unaffected by changes in fragility alone. The magnitude of density fluctuations can be minimized by tailoring the thermal history of the glass.

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1. Introduction

Density fluctuations are an apparently universal feature of the topologically disordered glassy state. These fluctuations are responsible for optical scattering [1–3] and are a major contributor to spatially heterogeneous dynamics in glass and glass-forming liquids [4–7]. The magnitude of density fluctuations is known to be dependent on the thermal history of the glass [6,8–11] as quantified through its fictive temperature [12]. Density fluctuations may also serve as a source of nonexponential relaxation in glass [13,14]. More recently, it has been suggested that density fluctuations may act as a precursor to polyamorphism [15] and may play a crucial role in governing the strength and fracture behavior of glass [16].

Following the pioneering work of Angell [17–21], glass-forming liquids may be classified as either "strong" or "fragile," depending on whether they display an Arrhenius or non-Arrhenius dependence of dynamics on temperature, respectively. Fragility itself is defined as the slope of the $log\tau$ versus T_g/T curve at the glass transition temperature [21],

$$m \equiv \frac{dlog_{10}\tau}{d\left(T_g/T\right)} \bigg|_{T=T_g}, \tag{1}$$

where τ is relaxation time or viscosity, T is absolute temperature, and T_g is the standard glass transition temperature. A greater value of fragility m indicates a larger departure from Arrhenius scaling. A strong liquid such as silica has $m \approx 17$. Fragility is a property of the liquid state and hence is an equilibrium property independent of

thermal history. However, fragility is known to have a large impact on the relaxation behavior of the nonequilibrium glassy state [22–29].

While density fluctuations have been studied in both strong systems (such as silica [3]) and fragile systems (such as orthoterphenyl [30]), there has been no systematic study of the impact of fragility on the relaxation behavior of density fluctuations. In this paper, we calculate the relaxation behavior of density fluctuations using an enthalpy landscape approach where the fragility of the system can be varied independently of other parameters. Our results show that the relaxation of density fluctuations is inherently nonmonotonic, independent of the particular value of fragility. However, fragility has a direct impact on the kinetics of the relaxation process, giving a delayed minimum in density fluctuations for higher values of fragility. This is caused by the more highly fragile systems having a greater free energy barrier for relaxation at temperatures below T_g. The magnitude of the density fluctuations is unaffected by fragility directly but can be indirectly affected by influencing the dynamics of glasses with different thermal histories.

2. Enthalpy landscapes and long-time dynamics

The simulation of long-time dynamics is a long-standing problem in the molecular dynamics community. This problem is especially important for glass-forming systems, since the glass transition is a dynamical transition occurring on a laboratory time scale. This time scale, of course, is much longer than what can be accessed through traditional atomistic simulation techniques [31], which are limited by a time step on the order of 1 fs. The solution to this problem is twofold: (a) separating the vibrational and configurational degrees of freedom via the enthalpy landscape formalism [32–40] and (b) accessing the long-time scale dynamics by accounting for the broken ergodic nature of the configurational transitions [41–46]. In this manner, dynamics can be calculated on any arbitrary time scale.

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The potential enthalpy landscape of an N-atom system is given by

$$H = U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, V) + PV, \tag{2}$$

where the potential energy U is a function of the atomic position vectors $\mathbf{r}_1$, $\mathbf{r}_2$, ..., $\mathbf{r}_N$, and the volume V of the simulation cell. The pressure P of the system is constant. The H hypersurface yields a $(3N+1)$-dimensional enthalpy landscape containing a multitude of local minima, each of which corresponds to a mechanically stable configuration of atoms called an "inherent structure." The volume of configurational space that drains to a particular minimum via steepest descent is referred to as a "basin." The advantage of the enthalpy landscape approach over traditional atomistic simulation techniques is that it allows for a separation of the fast vibrations within a basin from the slower inter-basin transitions corresponding to configurational changes of the system. The inter-basin transitions themselves span a wide range of time scales, including the fast β relaxation and the slower α relaxation phenomena [47].

The simulations begin in equilibrium at time $t=0$ and temperature $T=T_{\mathrm{eq}}$,

$$p_i(0) = \frac{1}{Y(T_{\mathrm{eq}})} g_i \exp\left(-\frac{H_i}{kT_{\mathrm{eq}}}\right), \tag{3}$$

where p_i is the probability of occupying basin i, k is Boltzmann's constant, g_i is the degeneracy of basin i, H_i is its enthalpy, and Y is the isothermal–isobaric partition function:

$$Y(T_{\mathrm{eq}}) = \sum_i g_i \exp\left(-\frac{H_i}{kT_{\mathrm{eq}}}\right). \tag{4}$$

The dynamics of the system are calculated using a set of coupled master equations,

$$\frac{dp_i(t)}{dt} = \sum_{j \neq i} K_{ji}[T(t)]p_j(t) - \sum_{j \neq i} K_{ij}[T(t)]p_i(t), \tag{5}$$

where the transition rates $K_{ij} = \tau_{ij}^{-1}$ are defined parametrically in terms of an arbitrary temperature path, $T(t)$. Assuming transition state theory,

$$K_{ij}[T(t)] = \nu g_j \exp\left[-\frac{H_{ij} - H_i}{kT(t)}\right], \tag{6}$$

where ν is the attempt frequency and H_{ij} is the transition point enthalpy [44]. For a sufficiently long isothermal hold, the solution of the master equation satisfies the detailed balance condition, and the system equilibrates giving a Boltzmann distribution of occupation probabilities.

The set of master equations is solved accounting for the broken ergodic nature of the system following the method of Mauro et al. [44]. With this approach, the basins of the enthalpy landscape are grouped into "metabasins" satisfying the condition of internal ergodicity. The grouping of basins into metabasins is recalculated at each time step to ensure that the criterion of internal ergodicity is always satisfied. The slow dynamics of the system are then calculated using a reduced set of master equations between metabasins, where the inter-metabasin transition rates are computed as described in Ref. [44]. With this approach, the dynamics of the system can be exactly calculated on any arbitrary time scale.

3. Isolating fragility in the enthalpy landscape formalism

Our simulations are based on the enthalpy landscape of selenium [45], calculated using classical two- and three-body interatomic potentials [48] that were derived from quantum mechanics using

Møller–Plesset perturbation theory [49] and the Dunning basis set [50]. Transition points in the selenium enthalpy landscape involve elementary bond angle and torsion angle transitions, which have a nearly constant enthalpy barrier of $\Delta H_{ij} = H_{ij} - H_i \approx 1$ eV (for $H_i > H_j$) [45,51]. Since the activation enthalpies in selenium satisfy $\Delta H_{ij} \approx 1$ eV, this leads to a simplified analytical form for the equilibrium transition rate that we can use to isolate the features of the enthalpy landscape that control fragility:

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

where $g(T)$ is the average number of accessible transition paths at temperature T. Combining this equation with the definition of fragility in Eq. (1), 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

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

This equation is used to isolate the impact of fragility on the relaxation behavior of glass. Based on Eq. (9), we construct a series of enthalpy landscapes having identical properties as selenium except with varying degrees of fragility. These new landscapes are used to simulate hypothetical glass-formers that are identical to selenium in every respect except with different values of fragility. In other words, we wish to adjust the fragility of the system while maintaining the same equilibrium enthalpy and volume vs. temperature curves and also a constant glass transition temperature T_g. In this manner, the impact of fragility on the relaxation of density fluctuations can be separated from the influence of other properties such as T_g. Eq. (9) provides two possible terms for adjusting fragility. However, the first term in Eq. (9) must be held constant since the shape of the $g(T)$ function has a direct impact on the equilibrium enthalpy and volume curves. Hence, any change in $g(T)$ will directly affect other properties of the supercooled liquid besides the fragility. This leaves only ΔH as a free parameter for adjusting fragility, but variation in 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 must be held constant at $T = T_g$. Hence,

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

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

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

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

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

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 equilibrium