Instantaneous Normal Modes and the Glass Transition

Scott D. Bembenek and Brian B. Laird*

Department of Chemistry, University of Kansas, Lawrence, Kansas 66045

(Received 28 June 1994)

The "instantaneous" normal mode (INM) spectrum for a model soft-sphere system is calculated via molecular-dynamics computer simulation for a variety of temperatures both above and below the observed glass transition temperature. In such spectra, the modes can be classified as either real or imaginary frequency. Results indicate that the liquid → glass transition is associated with the temperature below which all "unstable" INM's become localized and that the crossover from unstable to stable INM's occurs at a finite imaginary frequency and not at zero as is generally assumed. Two possible mechanisms for the glass transition are discussed that are consistent with the present data.

PACS numbers: 61.43.Fs, 61.20.Lc, 63.20.Pw, 64.70.Pf

The glass phase is the most poorly understood of the fundamental phases of matter. Unlike freezing, the transition from a liquid to a glass is not a well-defined thermodynamic transition, since the glass transition temperature T_g depends upon the nature of the cooling process, implying a primarily kinetic mechanism. However, whether this transition is driven (or accompanied) by some underlying thermodynamic transition is at present an open question. In addition, at very low T, glasses and amorphous solids [1] in general exhibit thermodynamic and transport behavior that is both quantitatively and qualitatively different than crystals, indicating far richer microscopic dynamics.

The anomalous thermodynamic behavior of glasses at low T can be explained by assuming that the dominant low-frequency contributions to the vibrational density of states are localized excitations. Such localization is a consequence of the structural disorder of the system. Below about 1 K the dominant excitations are postulated to be localized two-level tunneling states [2,3]. This model successfully reproduces the observed unusual thermodynamic properties of amorphous systems at very low temperatures, including the linear temperature dependence of the heat capacity, which is a universal property of amorphous systems below about 1 K [4].

At higher temperatures (between 1 and 20 K), this two-level state (TLS) model breaks down, failing to explain the observed plateau region of the thermal conductivity [4,5] in amorphous systems at about 10 K as well as pronounced nonlinearities in the heat capacity above 1 K [4]. Experiments [6,7] and computer simulations [8,9] show that, in this region, low-frequency localized harmonic modes become important. There is some indication that these modes and the TLS have a common structural origin [10,11]. Recent experiments also show a correlation between the nature of the glass transition and the relative concentration of TLS and the localized harmonic modes [12,13].

The purpose of this present work is to study the role of disorder-induced localized excitations in the glass transition. To do this, we make use of the concept of "instantaneous" normal modes (INM) [14–16]—an extension to the liquid and glassy state of the harmonic normal-mode technique that has been so valuable in understanding the solid state. By analyzing the localization of these instantaneous normal modes in a simulation of a model system both above and below the glass transition temperature, an interesting picture emerges.

Instantaneous normal modes are defined in analogy to the standard normal modes. For a system consisting of N identical spherically symmetric particles at temperature T and volume V, we expand the total potential Φ about an $3N$-dimensional configuration $\mathbf{R}_0$ (chosen arbitrarily from the trajectory), yielding

$$\Phi(\mathbf{R}) = \Phi(\mathbf{R}_0) - \mathbf{F} \cdot (\mathbf{R} - \mathbf{R}_0) + \frac{1}{2}(\mathbf{R} - \mathbf{R}_0) \cdot \mathbf{K} \cdot (\mathbf{R} - \mathbf{R}_0) + \cdots , \tag{1}$$

where the force vector and dynamical matrix are given by

$$(\mathbf{F})_{i\alpha} \equiv \left.\frac{\partial \Phi(\mathbf{R})}{\partial R_{i\alpha}}\right|_{\mathbf{R}=\mathbf{R}_0} , \tag{2}$$

and

$$(\mathbf{K})_{i\alpha,j\beta} \equiv \left.\frac{\partial^2 \Phi(\mathbf{R})}{\partial R_{i\alpha} \partial R_{j\beta}}\right|_{\mathbf{R}=\mathbf{R}_0} , \tag{3}$$

respectively. Diagonalization of the force-constant matrix $\mathbf{K}$ yields the instantaneous normal modes (eigenvectors) and corresponding squared normal-mode frequencies ω^2 (eigenvalues). Since at $T \neq 0$ an arbitrary configuration will not be at the potential minimum, the linear term $\mathbf{F}$ will not be zero and the matrix $\mathbf{K}$ will not be necessarily positive definite, but will have negative eigenvalues yielding imaginary frequencies. We can therefore classify the instantaneous normal modes as stable (real frequencies) or "unstable" (imaginary frequencies). Averaging over many configurations at a given temperature and density, we obtain the normalized INM density of states

$$\mathcal{D}(\omega) \equiv \left\langle \frac{1}{3N} \sum_{i=1}^{3N} \delta(\omega - \omega_i) \right\rangle \tag{4}$$

of the motion.

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The INM spectrum gives a map of the average curvature potential surface region visited by the dynamical trajectories, and as such is a static equilibrium property of the system. In studies on liquids and clusters, such spectra have been shown to give a very good description of the short-time dynamics [16–21]. One important quantity in these studies is the fraction of unstable modes, f_u, which can be easily obtained from the density of states, and has been found to be closely connected to the self-diffusion constant [16,17,19,22].

The amount of localization can be quantified in terms of the normalized eigenvectors $\mathbf{e}_j^\alpha$ of each INM, where j runs over all the particles in the sample and α labels the modes. The fraction of the kinetic energy of mode α located on a given atom j is then given by $(\mathbf{e}_j^\alpha \cdot \mathbf{e}_j^\alpha)$. A standard measure of localization of mode is the participation ratio

$$p_\alpha \equiv \left(N \sum_j (\mathbf{e}_j^\alpha \cdot \mathbf{e}_j^\alpha)^2 \right)^{-1}. \tag{5}$$

For extended modes p is of order unity. For localized or quasilocalized modes, it will scale inversely with the system size. Recently, the participation ratio has been used in a study of localization of INM's in liquid water [23] in which all imaginary frequency modes were reported to be delocalized.

For convenience and ease of comparison, the system chosen here is the same as that used in earlier work by Laird and Schober [8,9] on quenched ($T = 0$) normal modes, namely, one interacting via a modified inverse sixth-power repulsive potential

$$v(r) = \epsilon\left(\frac{\sigma}{r}\right)^6 + A\left(\frac{\sigma}{r}\right)^2 + B. \tag{6}$$

From here on the following standard reduced units will be used: $r^* = r/\sigma, \rho^* = \rho\sigma^3$, and $T^* = kT/\epsilon$. The potential was cut off at $r_c^* = 3.0$, and the parameters A and B were chosen so that both the potential and the force vanished at r_c^*. This form of the shifting potential was chosen so that its effect near $r^* = 1.0$ was small. In the previous study, this potential form was selected because it exhibited a larger concentration of soft localized modes than other systems studied (e.g., Lennard-Jones), which facilitated the statistical analysis.

At the density studied here, $\rho^* = 1.0$, the thermodynamic melting temperature of this system has been determined to be $T_m = 0.19$ [24] and the limiting glass transition temperature, determined by the vanishing point of a power-law fit to the diffusion constant, as $T_{0g} \approx 0.085$ [9]. The temperature T_{0g} is an inaccessible point in the liquid state and is generally considered to be the glass transition temperature in the limit of infinitely slow cooling [25].

The liquid and glass configurations used here were created using constant temperature molecular-dynamics (MD) computer simulation on a system of 500 soft spheres. For the simulations we used the velocity-Verlet algorithm [26] with a time step of 0.02—in units of $(m\sigma^2/\epsilon)^{1/2}$—and a density of $\rho^* = 1.0$. For the liquid systems above T_{0g}, the system was equilibrated at the desired temperature and then configurations separated by 100 time steps were extracted for the INM analysis. An average of 20–40 configurations were used to create the results shown below. The glass configurations (below T_{0g}) were created by first quenching a well-equilibrated liquid ($T^* = 0.5$) to the desired temperature, followed by an equilibration run of about 1000 time steps. The glass configurations were then extracted from the trajectory in the same manner as for the liquid, except that after every five configurations a new liquid starting point was chosen. Care was taken to exclude configurations for which crystallization had occurred. Also, the results were found to be insensitive to quench rate, although slower quench rates resulted in a greater tendency to crystallize.

Figure 1 shows the calculated average INM density of states (DOS) as a function of frequency $\nu \equiv \omega/(2\pi)$ for a variety of temperatures in the liquid ($T^* > 0.19$), the supercooled liquid ($0.085 < T^* < 0.19$), and the glass ($T^* < 0.085$) regimes. For convenience, we have followed the convention of earlier INM studies and multiplied the imaginary frequencies by i so that they appear on the negative real frequency axis. As seen in earlier INM studies (and as expected), the number of unstable modes and the average magnitude of the imaginary frequencies decrease continuously with decreasing temperature. Except for this general decrease, no sharp or discontinuous change is apparent in the DOS as the glass transition temperature is crossed. (The fraction of the imaginary frequency modes, f_u, as a function of T does show a change in curvature as the experimental glass transition temperature is crossed, but the significance of this is unclear.) It

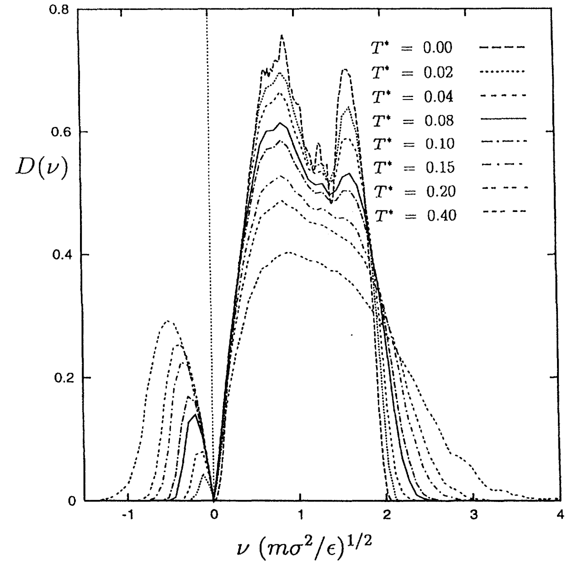

FIG. 1. Average INM density of states as a function of frequency for a variety of temperatures. For display purposes the unstable (imaginary frequency) modes are shown as negative frequencies.

should be noted, and has been pointed out earlier [15], that the bimodal appearance of the $\mathcal{D}(\nu)$ is entirely an artifact of the Jacobian factor $2\nu^2$ used in the conversion of the actual eigenvalue density $\tilde{\mathcal{D}}(\lambda = \nu^2)$ to a density of frequencies.

In previous work on liquids, f_u has been found to be closely correlated to the self-diffusion constant, a fact that seems reasonable if one interprets the imaginary frequency modes as representing motional "channels" that lead to barrier crossing. It is obvious, however, that not all such channels can lead to diffusion motion, since f_u is nonzero even well below the observed glass transition temperature. There are two possible cases in which an imaginary frequency mode would not contribute to diffusion. First, the mode could simply represent the presence of an inflection point at the side of an otherwise single-well region of the potential surface and would not represent an unstable mode at all. Second, the mode could be localized and any barrier crossing would lead to simply a local rearrangement and not overall diffusion.

To examine localization, the average INM participation ratio as a function of frequency, $p(\nu)$, is plotted in Fig. 2 for the same temperatures shown in Fig. 1. The individual $p(\nu)$ plots are typical of disorder-induced localization of a single excitation band [27]; namely, extended states [large $p(\nu)$] at the center of the band with strong localization [small $p(\nu)$] in the band tails. Qualitatively similar observations have been made for the Lennard-Jones system using visual inspection of the eigenvectors to determine the degree of localization [14]. From Fig. 2 we see that at $T^* = 0.15$ the value of $p(0)$ begins to drop rapidly with decreasing temperature, indicating that as the system approaches the glass transition temperature, the imaginary frequency modes become more localized in character. To make this result more quantitative, it is necessary to determine the value of the participation ratio that represents the dividing point between extended and localized modes. This is done by examining the size dependence of $p(\nu)$—truly localized modes will scale as $1/N$ whereas extended modes should show little, if any, dependence on size. In Fig. 3(a) is shown $p(\nu)$ for a temperature of $T^* = 0.08$ (just below T_{0g}) for systems of size $N =$ 128, 500, 864, and 1024. This plot indicates that the boundary between localized and extended modes occurs somewhere between $i\nu =$ -0.2 and about $-0.15(m\sigma^2/\epsilon)^{1/2}$, corresponding to $p \approx$ $0.35 - 0.38$ for a 500 particle system. Also shown in Fig. 3(a) is $p(\nu; T^* = 0.12)$ for $N = 500$. Assuming that the value of p at the localization boundary is the same for this temperature gives a localized/extended boundary between about $i\nu = -0.25$ and $-0.30(m\sigma^2/\epsilon)^{1/2}$.

The results above indicate that even at $T^* = 0.08$ (below the glass transition temperature) there is a nonzero fraction of extended imaginary frequency INM's. The question now is whether or not these modes can really be labeled as unstable. To answer this requires a detailed examination of the energy profile of each INM (labeled by α)

$$E_\alpha(\lambda) \equiv \Phi(\mathbf{R}_0 + \lambda \mathbf{e}_\alpha), \tag{7}$$

where Φ and $\mathbf{R}_0$ are as defined in Eq. (1), $\mathbf{e}_\alpha$ is the eigenvector for mode α, and λ is a charging parameter. For both $T^* = 0.08$ and 0.12, this examination shows that $E_\alpha(\lambda)$ for modes with the largest imaginary frequency are double-well potentials, whereas those with the smallest imaginary frequency are single wells. To quantify this we plot in Fig. 3(b) the average dimensionless barrier height, $\beta\Delta\bar{E}$ for those modes with double-well potentials as a function of frequency for $T^* = 0.08$ and 0.12,

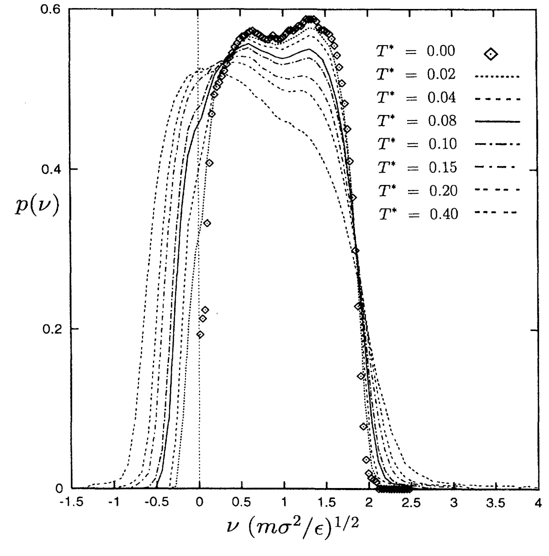

FIG. 2. The average participation ratio $p(\nu)$ as a function of frequency for the various spectra shown in Fig. 1. Again, the unstable (imaginary frequency) modes are shown as negative frequencies.

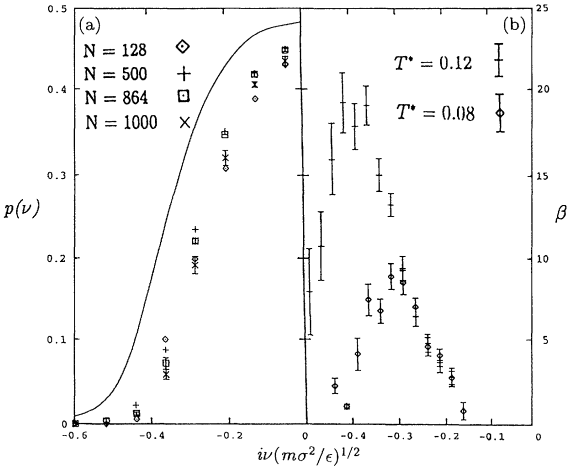

FIG. 3. (a) $p(\nu; T^* = 0.08)$ in the imaginary frequency regime for $N =$ 128 (diamonds), 500 (crosses), 864 (squares), and 1024 (X's) (the latter two also include 2σ error bars). Also shown is $p(\nu; T^* = 0.12)$ for $N = 500$. (b) Average dimensionless barrier height $[\beta = (kT)^{-1}]$ for the double-well INM energy profiles as a function of frequency for $p(T^* = 0.08)$ and 0.12.

using 10 and 7 configurations for the averaging, respectively. The principal features of this plot are the nonexistence of double wells above $i\nu \approx -0.15(m\sigma^2/\epsilon)^{1/2}$ and the fact that the two curves are identical between -0.15 and $-0.30(m\sigma^2/\epsilon)^{1/2}$. (Such a cutoff has recently been postulated for unstable INM's in liquids [28].) Therefore, the boundary between unstable and stable INM's is about $-0.15(m\sigma^2/\epsilon)^{1/2}$ not at 0 as traditionally assumed and is independent of temperature, at least in the vicinity of the glass transition. We see that at $T^* = 0.08$, which is slightly below the observed glass transition, the boundary between stable and "unstable" INM's is within error nearly coincident with the boundary between localized and extended modes. For $T^* = 0.12$, the stable and unstable boundary is still within the region of extended modes (at least as measured for $T^* = 0.08$). This gives weight to the hypothesis that the glass transition is associated with the temperature below which all unstable modes become localized.

With the error of the data presented here it is only possible to say that the "unstable" modes become completely localized below some temperature near T_{0g}—which transition occurs first is unclear. One possibility is that the two temperatures coincide and the limiting glass transition temperature is identified with the disappearance of extended unstable INM's—precisely those modes generally expected to lead to diffusive behavior. Another possible mechanism that is consistent with this data has been proposed [29,30] involving a dynamical transition occurring at a temperature *above* the glass transition. This transition represents a change in the primary diffusion mechanism in supercooled liquids from continuous flow to localized hopping steps. A connection of the hopping diffusion process to unstable INM's has been previously speculated [31] and evidence that such a transition may exist has been found in computer simulations on truncated Lennard-Jones atoms [30] and Lennard-Jones mixtures [32]. Such a mechanism has also been incorporated in mode-coupling theories of the glass transition [33].

This investigation has shown that, for a model system of monatomic soft-sphere particles, the glass transition appears to be associated with the temperature below which all unstable INM's become localized. The boundary between stable and unstable INM's is found to be at a nonzero value of $i\nu$, contrary to what is usually postulated and confirming recent speculation [28]. There is much more to be done. Are such instabilities related to "defects" in the glass, as has been shown to be the case for low-frequency harmonic vibrations in this same system [9]? A more accurate determination of the temperature at which extended unstable modes begin to appear is needed in order to determine which of these two (if either) proposed mechanisms is correct for this system. Further work to address these and other questions for a variety of systems is currently underway.

This work has been supported by the Petroleum Research fund under Grant No. 27847-G5 and by the University of Kansas General Research fund. The authors wish to thank Professor James Skinner for a critical reading of the manuscript and the referee for several constructive suggestions.

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*Author to whom correspondence should be addressed.

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