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Localization and the glass transition

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Abstract. We explore the role of disorder-induced localization in the dynamics of glasses and supercooled liquids using instantaneous normal mode (INM) analysis. This study is motivated by the fact that such localized excitations (tunnelling states and soft harmonic vibrations) are believed to be important in the thermodynamics and dynamics of amorphous systems at very low temperatures. The results are presented for two simple model systems that show the existence of a temperature below which all unstable INMs become localized. The relationship of this temperature to the glass transition is discussed.

1. Introduction

Amorphous materials at very low temperatures possess a variety of properties that are quite distinct from those of crystals. For example, the heat capacities of amorphous materials below about 1 K increase linearly with increasing T and are significantly larger than their crystalline counterparts (which vary generically as T^3) [1]. Similar anomalous behaviour is found for a variety of other properties, such as thermal conductivity. Although many issues remain unresolved, these anomalies are, at present, best explained by the presence of disorder-induced localized excitations that coexist with and dominate the sound waves at low frequencies. At very low temperatures these states are primarily tunnelling modes (two-level systems (TLSs)) [2, 3]. At higher temperatures there is evidence [4, 5] that the dominant excitations here are low-frequency quasi-localized (resonant) harmonic vibrations.

Recent experiments indicate a correlation between the nature of the glass transition and the relative concentration of TLSs and the quasi-localized harmonic modes [6, 7]. Given this correlation and the dominance of localized modes at very low temperatures, it is natural to speculate as to the role of localization at higher temperatures in the vicinity of T_g. In this work, we explore this question in two model systems using the technique of instantaneous normal mode (INM) analysis.

2. Instantaneous normal modes

Like standard normal modes, INMs [8, 9] are defined by expanding the potential energy of an N-particle system about a chosen configuration and diagonalizing the second-derivative (force-constant) matrix; the resulting eigenvectors and eigenvalues are the modes and the squared mode frequencies, respectively. The configurations used to determine the INM spectrum are not potential minima, as in normal mode analysis, but are taken directly from the trajectory at a given temperature. The force-constant matrix thus produced

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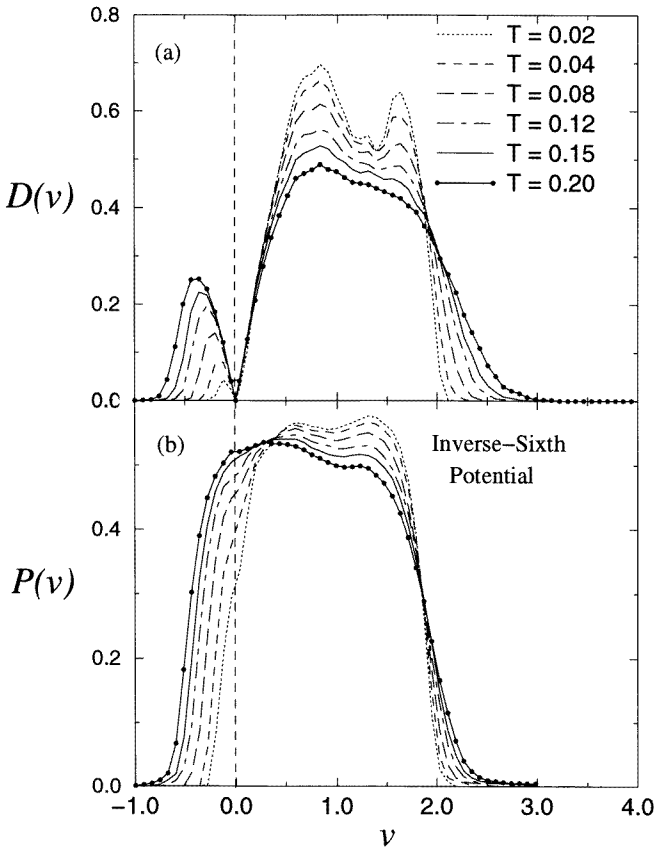

Figure 1. The average INM (a) DOS and (b) participation ratio for the inverse-sixth power system at several reduced temperatures as functions of frequency (in units of $(\epsilon/m\sigma^2)^{1/2}$. For display purposes, the imaginary frequencies are shown as negative frequencies.

is not necessarily positive definite, and negative eigenvalues (imaginary frequencies) occur for eigenvectors representing directions with negative energy-surface curvature. The configurationally averaged INM density of states (DOS) gives a trajectory-weighted representation of the curvature of the many-body potential energy surface.

The INM approach has been shown to give an accurate description of short-time dynamics in liquids [9]. By assuming that the imaginary frequency modes in the INM spectrum represent 'unstable' directions in configuration space and that their relative fraction is correlated to the number of barriers in the system that are accessible at the given temperature, researchers have also had success in developing quantitative theories for dynamics at long times (diffusion) in liquids, even into the supercooled regime [8].

Here, we are primarily interested in the degree to which the INMs are spatially localized (or extended). This can be quantified for a given eigenvector in terms of the participation ratio $p_\alpha \equiv [N \sum_i (\boldsymbol{e}_\alpha^i \cdot \boldsymbol{e}_\alpha^i)^2]^{-1}$, where $\boldsymbol{e}_\alpha^i$ is the projection of the eigenvector (labelled by α) onto atom i. For extended modes, p is of order unity. For localized modes, it will scale inversely with the system size.

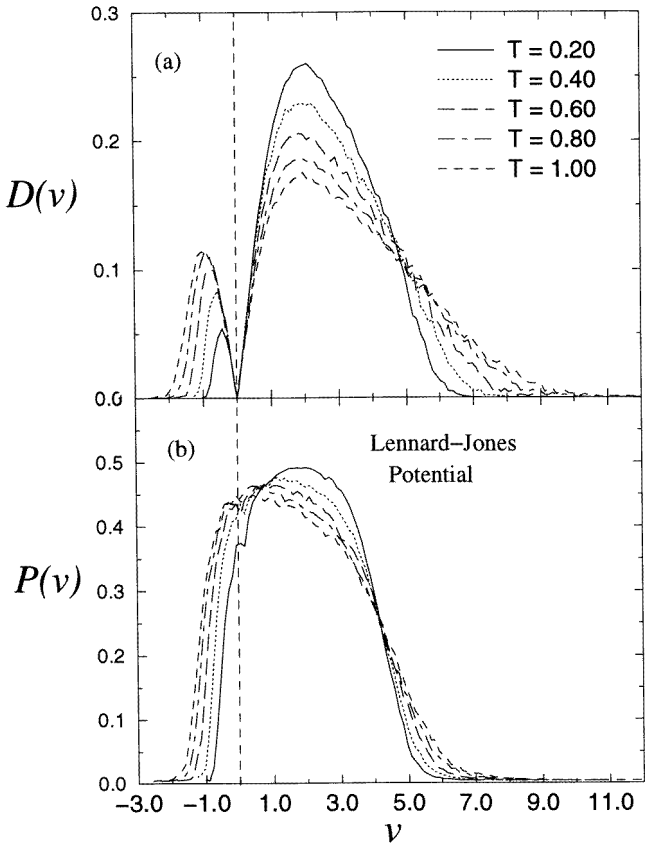

Figure 2. Same as figure 1, except for the LJ system.

3. Results and discussion

We present results for two model interaction potentials: an inverse-sixth power repulsion $v(r) = \epsilon(\sigma/r)^6$ and a Lennard-Jones (LJ) potential $v(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. For both systems, all simulations and INM analyses were done by varying the reduced temperature kT/ϵ at fixed reduced density $\rho^* = \rho\sigma^3 = 1.0$. Except where otherwise indicated, the systems consisted of 500 particles. For specific details of the simulations and INM configuration analysis, see [10].

For this reduced density, we estimate the limiting T_g^* for the inverse-sixth power system to be between 0.05 and 0.08 [10]; the lower value is from a fit of the diffusion constant data using a Vogel–Fulcher (VF) form and the upper value is from a power-law fit motivated by results from mode-coupling theory [11]. For the LJ system at this density, T_g^* has been estimated previously [8] to be in the range 0.35–0.40.

Figures 1(a) and 1(b) show the configurationally averaged INM DOS and participation ratios, respectively, for the inverse-sixth power system as a function of frequency for several temperatures. The same quantities for the LJ system are shown in figure 2. As expected, the density and average magnitude of imaginary frequencies increase with increasing temperature. Note that the fraction of imaginary frequency modes remains non-

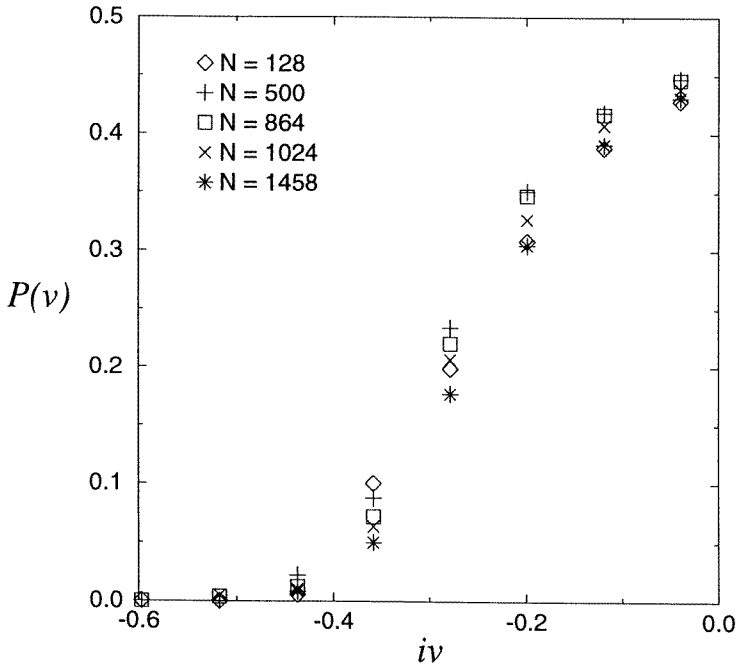

Figure 3. Size dependence of the participation ratio (for the inverse-sixth power system) $p(v)$ is shown for a reduced temperature of 0.08 in the imaginary frequency regime. The system sizes include $N = 128$ (◇), 500 (+), 864 (□), 1024 (×) and 1458 (∗). The error bars are less than or equal to the size of the symbols in magnitude and have therefore been omitted for clarity.

zero even well within the glass phase, and the postulated relationship between these modes and the diffusion constant must break down at low temperatures.

We then divide the imaginary frequency modes into three categories: stable modes (modes that simply reflect an inflection point at the side of an otherwise single-well potential and could not be properly classified as 'unstable'), unstable extended modes and unstable localized modes. The modes that are unstable but spatially localized would not contribute to liquid-like flow, since any associated barrier crossing would be confined to local rearrangement but could still lead to overall diffusion via a hopping mechanism.

The stable and unstable imaginary frequency modes are differentiated by examining the energy profiles generated by advancing the system along a particular eigenvector. Double and single wells are labelled 'unstable' and 'stable', respectively. We have determined that no unstable INMs are found with frequency magnitudes below a critical value $0.15(\epsilon/m\sigma^2)^{1/2}$ and $0.25(\epsilon/m\sigma^2)^{1/2}$ for the inverse-sixth and LJ potentials, respectively [10].

To distinguish between localized and extended modes we examine the participation ratio. Figures 1 and 2 show that the modes in the tails of the INM spectra are localized and those near the centre are extended, having participation ratios of order unity, but a precise determination of the localized–extended boundary ('mobility edge') requires an analysis of system size dependence. Figure 3 shows the participation ratio for the imaginary frequency part of the INM spectrum for the inverse-sixth power system at $T^* = 0.08$ for a variety of system sizes. In this figure, we see that the participation ratio becomes significantly size

dependent below a participation ratio of about 0.35 (for $N = 500$); this could be viewed as an upper bound on the mobility edge, for which a more accurate determination would require further analysis using much larger systems. Using a participation ratio of 0.35 to determine the mobility edge for the $N = 500$ systems together with the above stability criteria for the imaginary frequency modes, analysis of figure 1(b) yields a transition temperature for the inverse-sixth system of about 0.06, below which all unstable INMs are localized. This value falls within the estimated range of glass transition temperatures for this system and could provide an explanation for the observation that below T_g there is no diffusion even though the overall fraction of unstable modes is non-zero. Below the critical temperature, diffusion could proceed only via a series of localized hops. When extended unstable modes appear at higher temperatures, then a continuous flow mechanism for diffusion would be possible.

In summary, we have shown that, as the temperature is lowered and the INM spectra shift toward real frequencies, the mobility edge crosses the boundary between stable and unstable modes. This indicates that there exists a temperature below which all unstable modes become localized. From our analysis this temperature appears to be closely associated with the glass transition and we speculate that it is a possible origin of the proposed change in the mechanism of diffusion in fragile glasses at a temperature slightly above T_g [12, 13].

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