Relaxation Spectra at the Glass Transition: Origin of Power Laws

Michael Ignatiev, Lei Gu and Bulbul Chakraborty
The Martin Fisher School of Physics
Brandeis University
Waltham, MA 02254, USA
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We propose a simple dynamical model of the glass transition based on the results from a non-randomly frustrated spin model which is known to form a glassy state below a characteristic quench temperature. The model is characterized by a multi-valleyed free-energy surface which is modulated by an overall curvature. The transition associated with the vanishing of this overall curvature is reminiscent of the glass transition. In particular, the frequency-dependent response evolves from a Debye relaxation peak to a function whose high-frequency behavior is characterized by a non-trivial power law. We present both an analytical form for the response function and numerical results from Langevin simulations.

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In supercooled liquids, the glass transition is heralded by anomalously slow relaxations \(^1\). The phase below the glass transition temperature is non-ergodic and the dynamics is characterized by “aging” \(^1\). Recent experiments indicate that the approach to the glass transition has some universal features \(^2\) when viewed in terms of the frequency-dependent response of the system. Some of these features are also shared by spin glass transitions \(^2\). Theoretical research has focussed on spin-glass-like phenomena in nonrandom systems \(^4\) and some of these models have been shown to be equivalent to mean-field spin-glass models \(^4\). The dynamics of certain frustrated XY models have also been shown to exhibit glassy behavior \(^2\).

In this paper, we present a dynamical model of the glass transition and analyze the trends in its frequency dependent response. The model is characterized by a multi-valleyed free-energy surface modulated by an overall curvature and the glass transition is associated with the vanishing of this overall curvature. A multi-valleyed free-energy surface has long been associated with glasses \(^1\). The features of the present model were deduced from simulations of a nonrandomly frustrated spin model \(^8\). The frequency-dependent response of the system can be calculated in closed form, and its low temperature approximation becomes exact in the high-frequency limit. The results show that, as the overall curvature approaches zero, the frequency-dependent susceptibility changes from a characteristic Debye relaxation peak to a power-law spectrum reflecting the distribution of curvatures of the valleys. The predicted changes agree qualitatively with the generic features identified in experiments \(^2\).

We begin with a description of the results of simulations of the frustrated spin system. The model considered is an Ising antiferromagnet on a deformable triangular lattice. Detailed analysis of this model has shown that there is a first-order transition from the disordered paramagnetic state to an ordered “striped” phase \(^9\). Frustration plays a crucial role in this phase transition \(^1\). The model is characterized by two order parameters: a staggered magnetization with Ising symmetry and a shear distortion with three-state Potts symmetry.

Monte Carlo simulations \(^6\) have demonstrated that the time evolution of various physical quantities, such as the average energy, undergoes a qualitative change as the system is quenched below a characteristic temperature \(T^*\), below the ordering transition \(\nu\). To investigate the nature of the transition at \(T^*\), we computed the fluctuation metric, \(\Omega(t)\). This function has been shown to be sensitive to ergodicity breaking and has been used to study the glassy phase in Lennard-Jones systems \(^1\). The metric is defined by:

\[
\Omega(t) = \langle (\nu(t) - \bar{\nu})^2 \rangle = \left\langle \frac{1}{T} \int_0^T dt' E(t') \right\rangle
\]

Here \(\bar{\nu}\) is the ensemble average of the energy. If a system is ergodic, the fluctuation metric decays to zero at times longer than the equilibration time and behaves as \(1/t\) for exponential relaxations \(^1\). Breaking of ergodicity is signaled by the appearance of a non-zero long-time limit and a trajectory dependence \(^1\). Fluctuation metrics obtained from our simulations (Fig. \(1\)) show that the supercooled state at temperatures above \(T^*\) is ergodic but the state below \(T^*\) exhibits broken ergodicity.

A free-energy function was obtained from the probability distribution of energy \(^8\) assuming that quasi-equilibrium is reached in each of the valleys \(^5\). The resulting function is a one-dimensional projection of the actual, multidimensional free-energy surface. As seen in Fig. \(5\), at temperatures above \(T^*\), there is a well defined valley centered at an energy corresponding to zero shear \(^5\). The curvature of this valley decreases and sub-valley structures become more pronounced as \(T^*\) is approached and, at the ergodicity-breaking transition, one is left with a multi-valleyed free energy landscape. These observations are consistent with the idea of a shear instability, which is known to exist in this model \(^1\), oc-
curving at \( T^* \). The temperature \( T^* \) separates a high-temperature regime where the valleys with finite shear distortions are not accessible from a low-temperature regime where these valleys become accessible. The loss of ergodicity is associated with divergence of the average trapping time in these valleys and is reminiscent of weak-ergodicity breaking [1-4].

\[
\phi(t) = \frac{\delta H[\phi]}{\delta \phi(t)} + \eta(t), \quad (3)
\]

with the Gaussian noise
\[
< \eta(t)\eta(t') > = \Gamma \delta(t - t'). \quad (4)
\]

We are interested in studying the frequency dependent response of this system as the overall curvature is tuned to zero. The response can be calculated by constructing an appropriate generating function. Integrating over the Gaussian noise, leads to the dynamical action [13]
\[
S[\phi] = \int dt \left[ \frac{\partial}{\partial t} \phi(t) + \frac{\delta H[\phi]}{\delta \phi(t)} \right]^2, \quad (5)
\]

which defines the generating function
\[
Z[h] = \int \mathcal{D}\phi(t) \left[ \frac{\partial}{\partial t} \phi(t) + \frac{\delta H[\phi]}{\delta \phi(t)} \right] \exp \left\{ -\frac{1}{2\Gamma} S[\phi] + \int dt \phi(t) \right\} . \quad (6)
\]

For an ergodic system, the response can be related to a correlation function through the fluctuation dissipation theorem. Approaching the glass transition temperature from above, we can use this relationship to calculate the imaginary part of the frequency-dependent susceptibility \( X(\omega) \) from a knowledge of the correlation function \( \chi \) [8-13]:
\[
\chi = \frac{\delta}{\delta h'} < \phi[h] > ; < \phi[h] > = \frac{\delta}{\delta h} \ln Z[h].
\]

Introducing the “centered” order parameter, \( x_n = \phi - \phi_0 \) and “effective” subwell curvature \( R_n = r_n + R \), and using the non-overlapping property: \( \mu_m \mu_n = \delta_{mn} \mu_n \), the dynamic action can be rewritten as:
\[
S[\phi] = \int dt \sum_{n=0}^{n_{\text{max}}} \left( \frac{\partial}{\partial t} + R_n \right) x_n(t) + R \phi_0 \left[ \mu_n \right]^2, \quad (7)
\]

The non-overlapping property also leads to the generating function being written as a sum of functions belonging to each segment: \( Z[h] = \sum_{n=0}^{n_{\text{max}}} Z_n[h] \), where the subwell generating functions are given by:
\[
Z_n[h] = \int \mathcal{D}x_n \mu_n ||\omega_n|| \exp \left\{ -\frac{1}{2\Gamma} \int dt \left( \omega_n x_n - \Gamma \omega_n^{-1} H_n \right)^2 \right\} \exp \left( \int dt Q_n + \frac{\Gamma(\omega_n^{-1} H_n)^2}{2} \right) \equiv Z_n^0[h] \exp \left( \int dt Q_n + \frac{\Gamma(\omega_n^{-1} H_n)^2}{2} \right). \quad (8)
\]

In the above equation, we have introduced the variables:
\[ H_n = h - \frac{RR_n \phi_n^0}{2\Gamma}, \]
\[ \omega_n^2 = \frac{\partial^2}{\partial r^2} + R_n^2, \]
\[ Q_n = h\phi_n^0 - \frac{(R\phi_n^0)^2}{2\Gamma}. \]

If the subwells were not constrained to exist in finite regions of the order parameter space, then \( Z_n^{0[h]} \) would be a constant and the response of the system obtained from the resulting generating function would be a sum of Lorentzians. It will be shown below that this is very nearly the case in the limit of large frequency (scale set by the noise strength \( \Gamma \)).

Because of the non-overlapping property (cf Eq. (8)), the susceptibility can be expressed in terms \( \chi_n \) and \( \phi_n \) which denote the susceptibility and average order parameter of the individual, decoupled wells. The calculation of \( \chi_n \) defies any simple analytic approach, because of the finite region of functional integration in the partition function. However, if the noise is small enough and the system never escapes its subwell, we can neglect all these effects of finiteness of the wells. It can be shown that the error vanishes as we increase \( \xi_n = \omega_n^2 \Delta_n^2 / 2\Gamma \). In the zero noise limit all \( Z_n^{0[h]} \) are the same and do not depend on \( h \). For finite noise, the same effect can be achieved by increasing the frequency associated with the response function and therefore, the low-noise approximation is less restrictive for high frequencies.

The simplest case is when the overall curvature, \( R \) vanishes. In this limit, which we associate with the glass transition, the frequency-dependent response \( \chi_n \) is given by:

\[ \chi_n(\omega) = \frac{\Gamma}{\omega_n^2}. \]  

(9)

Here, \( \omega_n^2 = \omega^2 + R_n^2 \). The “effective” susceptibility \( \chi = \langle \chi_n \rangle \) is given by the weighted sum over all the subwells:

\[ \chi = \sum_n p_n \chi_n, \quad p_n = \frac{Z_n}{Z}. \]

Since \( \chi_n \) depends on \( n \) only through the curvature \( r_n \) \((R = 0)\), the susceptibility \( \chi \) can be expressed in terms of the probability of encountering a given curvature:

\[ \chi = \int dr \frac{P(r)}{\omega^2 + r^2}; P(r) \equiv \sum_n p_n \delta(r - r_n) \]  

(10)

In general, \( P(r) \) depends on the distribution of curvatures and the ‘time’ spent in a well with given curvature. The latter is determined by the depth of the well and the overall curvature. However, in the low-noise regime, where we have argued that \( p_n \) is independent of \( n \), \( P(r) \) reflects the ‘intrinsic’ distribution of curvatures in the model Hamiltonian. If this distribution is described by a power law: \( r^\alpha \), then within our approximation which is exact in the high-frequency limit, the response of the system reflects this power law.

\[ \chi(\omega) = \int dr \frac{r^\alpha}{\omega^2 + r^2} \sim \omega^{n-1} \]  

(11)

When the curvature \( R \) is non-zero, the probabilities, \( p_n \), get multiplied by \( \exp(-R^2\phi_n^2/2\Gamma) \) and even for extremely small overall curvature, \( R \), the distribution \( P(r) \) changes considerably due to a different sampling of the wells. As \( R \) increases only subwells centered close to \( \phi = 0 \) are sampled appreciably and, in the limit of large \( R \), the response of the system is dominated by a single parabolic well (Debye response). The intrinsic distribution of curvatures is reflected in the susceptibility only in the limit of \( R = 0 \). This result shows that by tuning the overall curvature of a multi-valleyed free-energy surface the high-frequency response of the system can be changed from a pure Debye spectrum \((\chi \sim \omega^{-2})\) to a nontrivial power law which reflects the distribution of curvatures of the subwells.

To demonstrate these features explicitly and to analyze the effect of large noise, we performed simulations of the Langevin equation (3). The subwells were chosen to be distributed uniformly \((\alpha = 0)\) and the largest subwell curvature was determined by considering the numerical stability of the system which required that in each well \( \phi \delta t < 2\Delta_n \). In each run the starting point was near the bottom of a randomly chosen subwell. We calculated the susceptibility as an average over a large number \((\sim 1000)\) of runs and each run was \( \sim 10000 \) Monte Carlo Steps long. The results are shown in the Fig (3).

For zero overall curvature, irrespective of the noise
strength, the susceptibility reflects the distribution of the subwell curvatures (Fig. 2d).

For a non-zero overall curvature, one can distinguish between two distinct regimes (a) low noise such that there is no escape from wells and (b) noise large enough to make escape possible. The behavior in the (a) regime is summarized in Figs. 2(a) and 2(b). At these noise strengths, a finite value of the overall curvature leads to a large damping of the contributions from all subwells centered away from \( \phi = 0 \), and one observes a superposition of very few Lorentzian peaks (Fig. 2). If the noise strength is increased, at small \( R \), the susceptibility starts to pick up contributions from all the subwells and the response becomes non-Debye like (cf Fig. 2a).

The response of the system is qualitatively different in regime (b), as illustrated in Fig 2a. The finiteness of the wells becomes a crucial factor and, at some minimum value of \( R \), escape from the most distant wells became possible. The dominant contribution to the susceptibility arises from the relaxation towards \( \phi = 0 \) and at large \( R \) there is a crossover to a single Debye peak with no evidence of the internal structure. In the intermediate regime, the susceptibility reflects a superposition of both probing the distribution and relaxation towards the center. In this case the shape of the curve is sensitive to the details of all the distributions: centers of subwells, their widths (depths) and curvatures.

The numerical and analytical results demonstrate that by tuning \( R \) or the noise strength \( \Gamma \), one can reach a special “glassy” phase with a frequency-dependent susceptibility obeying a non-trivial power law (Eq. 1). For large noise and curvature, one observes a Debye peak determined by the overall curvature \( R \). Starting from this liquid-like phase, the power-law regime is reached by decreasing the curvature. In the low-noise limit (regime (a)), the phase with the Debye-like response resembles a frozen amorphous or polycrystalline state since there is no escape from subwells. The location of the Debye peak is determined not by the overall curvature \( R \) but by the average curvature of the subwells located near \( \phi = 0 \). This frozen phase is unusual since the system still relaxes in a multitude of subwells and is far from equilibrium. The frozen phase can be made to approach the “glassy” phase by increasing the noise strength. The power-law behavior characterizes the glass and is not observed in either the liquid or the frozen phase.

The transition from the “liquid” to the “glassy” phase, as depicted in Fig. 2), is similar to experimental observations in supercooled liquids. In both theory and experiment, the shift of the Debye peak towards lower frequencies is accompanied by a change in the power law which characterizes the high-frequency response. The scaling features observed in experiments are intriguing and probably reflect some interesting physical features of glass formers. This physics would dictate the type of distributions of curvatures and heights which enter our theoretical model. As mentioned before, all these distributions are crucial in determining the behavior of \( \chi(\omega) \) in the regime intervening between the large \( R \) and \( R = 0 \) phases. We have made no attempt to tailor these distributions to reproduce the scaling behavior observed in experiments.

In conclusion, we have shown that our model of the glass transition predicts changes in the high-frequency response of a system approaching the glass transition. This model can be taken only as a schematic picture of a real glass transition but suggests that a multi-valleyed free-energy surface with an overall curvature can be taken as a useful template for glassy systems. The transition associated with the vanishing of the curvature is a new type of critical point and our analysis shows that this “phase transition” is characterized by a non-trivial, high-frequency response.

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