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Ergodicity-breaking transition and high-frequency response in a simple free-energy landscape

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We present a simple dynamical model described by a Langevin equation in a piecewise parabolic free-energy landscape, modulated by a temperature-dependent overall curvature. The zero-curvature point marks a transition to a phase with broken ergodicity. The frequency-dependent response near this transition is reminiscent of observations near the glass transition. [S1063-651X(99)51007-6]

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Supercooled liquids can undergo an ergodicity-breaking transition at which the time required to adequately sample the allowed phase space becomes longer than observation times [1,2] and the liquid freezes into a glassy state [1]. Recent experiments indicate that the approach to this glass transition has some universal features [3] when viewed in terms of the frequency-dependent response of the system. In both supercooled liquids [3] and spin glasses [4], the approach to the glass transition is characterized by two generic features, a frequency-independent behavior at high frequencies and the presence of three distinct regimes in the relaxation spectrum. These features are different from those observed near a critical point where the high-frequency response is thought to be uninteresting [5]. Existing theories of the glass transition [1,6] offer no satisfactory explanation of the unusual frequency-dependent response. In this Rapid Communication, we present a simple, dynamical model which is able to describe the frequency-dependent response observed near the glass transition.

Time-dependent fluctuations in a system approaching a critical point are described, within the spirit of Landau theory, by a Langevin equation for the order parameter [5]. Adopting a similar framework for describing the fluctuations near a glass transition, we study the Langevin dynamics of a collective variable, ϕ, relaxing in a multivalleyed free-energy landscape. This collective variable is envisioned to be one of the slow variables in a viscoelastic liquid, such as a density fluctuation mode [6] or a component of the average strain field [7]. The multivalleyed free-energy surface is modulated by a temperature-dependent overall curvature. The introduction of this curvature was inspired by simulations of a frustrated spin system in which the role of ϕ is played by an elastic strain field, and the curvature arises from a coupling between the frustrated spin variables and the strain field [8]. The vanishing of the overall curvature is identified in our model with the glass transition.

A schematic picture of the free energy is shown in Fig. 1. All valleys (including the megavalley) in the free-energy surface are assumed to be parabolic. Each valley is parametrized by its curvature r_n, width Δ_n, position of the center ϕ_n^0 and position of the minimum C_n. Consequently, each valley is characterized not only by the time it takes to escape from it but also by its internal relaxation time. The set of $\{C_n\}$ is fixed by the requirement that the free energy, $F(\phi)$, is a continuous function. To simplify the picture even further, we set all $\Delta_n=\Delta$, which then automatically fixes $\phi_n^0=n\Delta$. The curvatures of the valleys are taken to be independent random variables picked from a distribution $P(r,n)$. This defines a free-energy function

$$F(\phi)=\frac{1}{2}R\phi^2+\frac{1}{2}\sum_{n=-\infty}^{\infty}\mu_n\{r_n(\phi-\phi_n^0)^2+C_n\}. \quad (1)$$

Here $\{\mu_n\}$ is the set of functions specifying the range of each subwell, i.e., $\mu_n=1$ if $\phi_n^0-\Delta/2\leqslant\phi\leqslant\phi_n^0+\Delta/2$ and zero otherwise. The curvature of the megavalley is denoted by R.

The dynamics is modeled by relaxation in this free-energy surface and is defined by the Langevin equation

$$\frac{\partial\phi}{\partial t}=-R\phi-\sum \mu_n r_n(\phi-\phi_n^0)+\eta(t), \quad (2)$$

where η is a Gaussian noise with zero average and variance $\langle\eta(t)\eta(t')\rangle=\Gamma\delta(t-t')$. The temperature scale is set by $\beta=\Delta^2/\Gamma$. In the absence of any subvalley structure, (all $r_n=0$), Eq. (2) results in a Debye relaxation spectrum with a

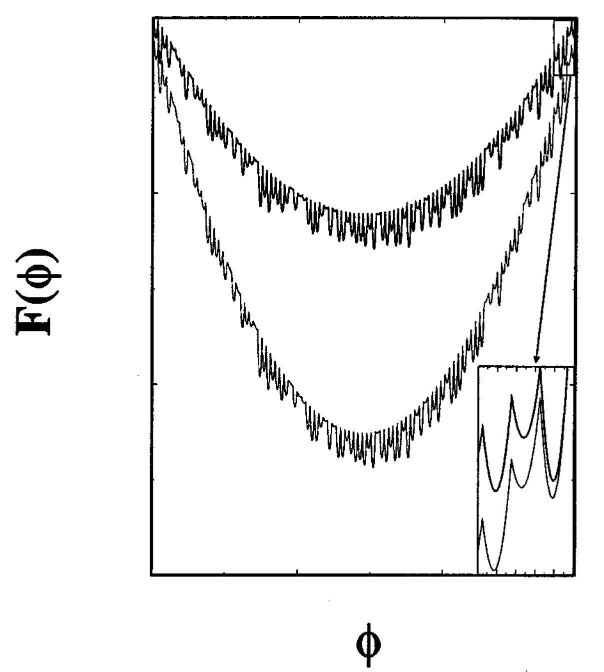

FIG. 1. Free-energy landscape for two different values of R with a fixed distribution of $\{r_n\}$. The inset shows how the overall curvature modifies the heights of the barriers between the valleys.

relaxation time of $1/R$. If R is taken to be of the form assumed in Landau theory, such that it vanishes linearly at the critical temperature, then Eq. (2) provides a mean-field description of critical slowing down [5]. The effect of the subvalley structure on the relaxation spectrum, and the nature and existence of phase transitions in the two-dimensional space spanned by R and β are the subjects of this paper.

The dynamics of systems approaching the glass transition has been modeled previously by random walks in the environment of traps [9]. What distinguishes our model is the presence of an overall curvature modulating the landscape and the description of the dynamics *within* the valleys. As shown below, both these features have nontrivial effects on the relaxation spectrum.

Specific features of the distribution $P(r,n)$ affect the detailed nature of the response. The assumption that the curvature of each valley is uncorrelated with its position, $P(r,n) \sim P(r)$ is the easiest to implement and is the scenario that we examine in detail. A natural candidate for $P(r)$ is an exponential distribution $P(r)=e^{-\beta_0 r}/\beta_0$, observed in many spin-glass models [9]. The frustrated spin model that motivated the introduction of the overall curvature also indicated an exponential distribution of barrier heights [8].

The occurrence of an ergodicity-breaking transition in our model can be demonstrated explicitly [11]. The equilibrium probability distribution, predicted by Eq. (2), is $\exp[-\beta F(\phi)]$ as long as the integral of this function over ϕ remains finite [10]. A simple calculation [11] shows that this integral diverges as $1/(\beta_0-\beta)\sqrt{R}$. As $R\to 0$, an equilibrium distribution can no longer be defined [10] and correlation functions become power law in nature with no characteristic time scale. The point $R=0$, $\beta=\beta_0$ is special in that the power-law correlations no longer decay to zero and the system falls out of equilibrium. The approach to this special point, where ergodicity is broken, can be studied by analyzing the equilibrium correlation function, $C(t)=\langle\phi(0)\phi(t)\rangle$, and the response function associated with it through the fluctuation dissipation relation [5]. In the absence of the overall curvature, the $1/\sqrt{R}$ factor gets replaced by the system size, the probability *density* diverges as $\beta\to\beta_0$, and the correlation functions are always characterized by power laws [9]. The line with $R=0$ is, therefore, special and in the present work, we are mainly interested in studying the $R=0$, $\beta=\beta_0$ point as it is approached along a generic line in the (R,β) space.

The dynamical processes contributing to the correlation function can be roughly subdivided into the internal relaxation within each subvalley and the activated motion between subvalleys, modulated by the presence of the overall curvature R. The correlation functions along the $R=0$ line can be calculated by using the well known mapping of the Langevin equation to a quantum mechanical model [10] and leads to [11],

$$C(t)=\sum_n e^{\beta r_n}\left(\frac{e^{-r_n t}}{r_n}+e^{-(t/\beta)e^{-\beta r_n}}\right). \tag{3}$$

Physically, the first term within the parentheses represents the superposition of independent relaxations within each valley, while the second term represents activated motion.

Generalization of these results to nonzero R involves evaluating the eigenvalue spectrum of the quantum Hamiltonian as modified by the overall curvature. Taking the curvature into account perturbatively leads to the following generalization of $C(t)$:

$$C^{trap}(t)=\sum_n \theta(\Delta F_n)e^{-\beta F_n^{min}}\left(\frac{e^{-R_n t}}{R_n}+e^{-(t/\beta)e^{-\beta\Delta F_n}}\right). \tag{4}$$

Here $R_n=r_n+R$, $F_n^{min}=n^2R-r_n$, and the θ-function excludes the valleys for which the effective free-energy barrier, $\Delta F_n=(R_n/2)(1/2-nR/R_n)^2$, becomes zero due to the presence of the overall curvature. The contribution of these zero-barrier valleys cannot be calculated perturbatively. The time evolution of ϕ involves hopping over barriers, relaxation within the subvalleys, and, in the ''free'' regions, relaxation in response to only the overall curvature. Since the free region is expected to be small in the vicinity of $R=0$, we have simplified this complex relaxation process by including the free relaxation within a mean-field type approximation that neglects the positional relationship between the free valleys and the valleys with barriers. The total correlation function then reduces to a sum of C^{trap} and C^{free} with

$$C^{free}(t)=\sum_n \theta(-\Delta F_n)\frac{e^{-\beta n^2 R-Rt}}{R}. \tag{5}$$

One of the most interesting aspects of our model is the high-frequency response. The origin of this can be understood from an analysis of the results along the $R=0$ line [cf. Eq.(3)]. The hopping term in $C(t)$ is then identical to the one analyzed in [9], and in frequency domain, leads to an imaginary part of the susceptibility, $\chi''(\omega)=\omega\overline{C}(\omega)$, of the form $\omega^{(\beta_0-\beta)/\beta}$ at low frequencies and decaying as $1/\omega$ at high frequencies. There is, however, a new feature that arises from the internal dynamics and drastically changes the high-frequency behavior. The internal relaxation part of $\overline{C}(\omega)$ is given by

$$\overline{C}^{int}(\omega)=\int_{r*}^{\infty}dr\,\frac{e^{-(\beta_0-\beta)r}}{\omega^2+r^2}. \tag{6}$$

The contribution of this term to $\chi''(\omega)$ behaves as $[\pi/2-\arctan(r^*/\omega)]$ [12] for $\omega\leqslant 1/(\beta-\beta_0)$; a function that decays extremely slowly with frequency as $\beta\to\beta_0$. The total frequency-dependent response, therefore, behaves as $\omega^{(\beta_0-\beta)/\beta}$ for $\omega\to 0$ and is a slowly decaying function at high frequencies.

The overall curvature changes the effective barriers heights and the effective distribution of r. The parameter space of our model is spanned by R and β. In order to simplify the analysis, we study the response along the family of lines defined by $a(\beta_0-\beta)=\beta_0\beta R$, with $a=1$ for most of the calculations. The relaxation spectrum, obtained from $C^{trap}(t)$, is given by

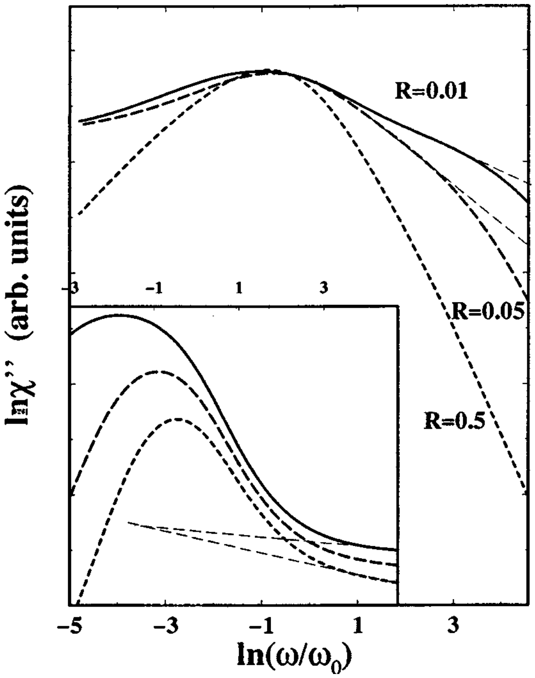

FIG. 2. Imaginary part of the susceptibility, $\chi''(\omega) = \omega \overline{C}^{trap}(\omega)$ [cf. Eq. (7)] for different values of R. The peak intensities have been matched. Frequencies have been normalized to ω_0, a microscopic frequency scale determined by the parameters of the model. The inset shows the full relaxation spectra, *including* the contribution from the ''free'' valleys for $R=0.1$, 0.05 and 0.01. The long-dashed lines show the high-frequency power law extending up to $\omega \simeq a/R$. The parameter $a=1$ in the main figure but $a=100$ in the inset.

$$\overline{C}^{trap}(\omega) = \sum_n e^{-\beta n^2 R} \int_{nR}^{\infty} dr e^{-(\beta_0 - \beta)r} \times \left(\frac{1}{\omega^2 + r^2} + \frac{e^{-\beta \Delta F_n}/\beta}{\omega^2 + e^{-2\beta \Delta F_n}/\beta^2} \right). \quad (7)$$

This expression in not analytically tractable and the complete frequency-dependent response can be obtained only from a numerical calculation. The basic features can, however, be understood from a simplified analysis. For small R, the primary effect of the overall curvature is to introduce an upper and a lower cutoff to the distribution $P(r)$. The $e^{-\beta n^2 R}$ term of Eq. (7) makes the system finite with an ''effective'' number of wells $\simeq 1/\sqrt{R}$, which in turn leads to an upper cutoff of $r_{max} = -\log R$ [11]. The lower cutoff arises from the elimination of the zero-barrier valleys that is the source of the lower limit on the integral in Eq. (7). The primary effect of the upper cutoff is to alter the exponent of the low-frequency power law from $(\beta_0 - \beta)/\beta$ to one which goes to zero more rapidly with R. The high-frequency response is affected by the overall width of the distribution of r which increases as $R \to 0$ and leads to an essentially frequency-independent response for $\sqrt{R} \ll \omega \ll 1/R$. A less significant effect of R is to alter the exponent of the power law in this frequency range.

The results from a complete numerical analysis of Eq. (7) are shown in Fig. 2. It is clear from these results that there is a slowly decaying high-frequency response. The exponent characterizing this high-frequency power law is a function of R and approaches zero as $R \to 0$. It is also evident that the response is characterized by a low-frequency power law with the exponent approaching zero as $R \to 0$.

The free part of the relaxation spectrum is given by

$$\overline{C}^{free}(\omega) = \frac{1}{R^2 + \omega^2} \sum_n e^{-\beta n^2 R} \int_0^{nR} dr e^{-\beta_0 r}, \quad (8)$$

and leads to a Debye spectrum with peak at $\omega = R$. There is a tradeoff between the hopping dynamics and free relaxation, with the hopping contribution decreasing as R increases, and more valleys become effectively ''free.'' The inset of Fig. 2 demonstrates the effect of the free part with a shift in peak frequency as well as the appearance of an intermediate regime.

Three distinct regimes of the response emerge: a low-frequency power law, associated with hopping between different valleys; a Debye-like peak coming from barrierless relaxation; and a high-frequency power-law decay resulting from the superposition of many single-relaxation-time processes. The high-frequency power law is intimately related to the fact that the system explores more valleys as the curvature decreases. The low-frequency power law is controlled by the effective distribution of barriers, which also depends on R. The curvature, therefore, controls both the high- and low-frequency behavior of the dynamical response. This picture of the dynamical response is very similar to the experimentally observed response in spin glasses [4], with the response flattening out at both high- and low-frequency ends and the peak moving to zero, but slower than exponentially.

In supercooled liquids, only the high-frequency response flattens out, and the peak shifts towards zero according to a Vogel-Fulcher law [1,3]. In our model, this difference could be ascribed to a difference in the nature of correlations in the distribution $P(r,n)$. In a structural glass, the crystalline state is the absolute global free-energy minimum. The valleys of our model correspond to metastable states and the megavalley represents the states accessible in the supercooled phase, with the crystalline minimum lying outside this region. This suggests that the depth of a valley and its position are correlated, with the deeper valleys situated further away from the minimum of the megavalley. A correlation of this form in $P(r,n)$ alters the R dependence of the upper cutoff in the distribution of barrier heights and leads to a maximum escape time $t_{esc} \sim \exp(1/R^{\alpha})$. Here $\alpha > 0$ is the exponent of a power law describing the correlation between the depth and the position of valleys. For times longer that t_{esc}, there is only barrier-free motion in our model. At frequencies lower than $\omega_c = (t_{esc})^{-1}$, we, therefore, predict that $\chi''(\omega) \sim \omega$, with no flattening out of the low-frequency response. The upper cutoff does not have a large influence on the response arising from the internal dynamics of the valleys. The high-frequency cutoff is still $\approx 1/R$, as seen from Eq. (6).

The original motivation for constructing the dynamical model came from observations in a nonrandomly frustrated spin system whose phenomenology is remarkably similar to structural glasses [8]. Simulations of this system indicated a free-energy surface with an overall curvature, and the vanishing of this curvature was accompanied by the appearance of broken ergodicity and ''aging'' [8]. The dynamics was effectively one dimensional, with the shear strain playing the role of ϕ. This frustrated spin system, can, therefore, be viewed as a microscopic realization of the dynamical model presented here, and could provide the connection between our simple toy model and the dynamics of real glasses.

In conclusion, we have demonstrated that the basic features of the frequency-dependent response near a glass transition can be understood on the basis of a multivalleyed free-energy surface with an overall curvature, which goes to zero at the glass transition. This is reminiscent of models where the glass transition is associated with an instability [13]. In our model, the spectrum crosses over from being pure Debye at large curvatures to one with three distinct regimes. The asymptotic, high-frequency power law is characterized by an exponent approaching zero as the curvature approaches zero. Our analysis also suggests that the relaxation spectra of spin glasses and structural glasses can be described by the same underlying model with different correlations in the distribution of valleys.

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