Inverse freezing in mean-field models of fragile glasses

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A disordered spin model suitable for studying inverse freezing in fragile glass-forming systems is introduced. The model is a microscopic realization of the "random first-order" scenario in which the glass transition can be either continuous or discontinuous in thermodynamic sense. The phase diagram exhibits a first-order transition line between two fluid phases terminating at a critical point. When the interacting degrees of freedom are entropically favored, an inverse static glass transition and a double inverse dynamic freezing appear.

Inverse melting and inverse freezing occur when a crystalline or amorphous solid reversibly transforms into a liquid upon cooling. This unusual phase behavior was first predicted by Tammann in 1903, and is generally considered to be rare because it does involve a counter-intuitive increase of thermal disorder as the temperature is lowered.[1] An example of biological relevance is provided by *elastin*.[2] In the past few years "inverse temperature transitions" of this type have attracted a renewed interest as they have been observed in a variety of soft matter systems including polymers,[3] colloids,[4] and micelles.[5] While the responsible physicochemical interactions may depend on the system under study, it has been recognized that a large enough degeneracy of the degrees of freedom interacting at low temperature provides a simple mechanism whereby inverse melting or inverse freezing may generally occur.[6]

The idea is easily described by considering an ensemble of polymers that have a low-temperature "folded" state in which they are mutually weakly interacting, and a higher-temperature "unfolded" state which is favored entropically and in which they interact strongly with each other. As temperature is increased, each polymer stretches out to reach the other polymers; the resulting entangling thus may lead to a glass transition. To obtain a minimal model of freezing by heating, one can consider[6] spins taking values $0, \pm 1$, and a Hamiltonian consisting of a term $\Sigma_i \sigma_i^2$ favoring the "folded" states $\sigma_i = 0$, and an interaction term $\Sigma_{ij} J_{ij} \sigma_i \sigma_j$ that is active in the "unfolded" states, $\sigma_i = \pm 1$. The entropic favoring of the latter is enhanced by making them *r*-fold degenerate. If the interactions matrix J is taken from the Gaussian ensemble, one then obtains a reentrant *spin-glass* phase.[6–11]

In this paper, the inverse freezing problem is addressed in the context of mean-field models of structural glasses by using the above mechanism of entropy-driven reentrance. Several reasons make such a problem interesting. The "random first-order" scenario for the glass transition[12] predicts that upon cooling fragile glass-forming liquids undergo a purely dynamic arrest before a thermodynamic singularity occurs at a lower temperature (or higher density). The dynamic arrest is the relevant one from an experimental point of view and, in order to compare observations with theoretical predictions, one should consider the effect of degeneracy on the dynamics. The point is important because a reentrant glass transition has been recently predicted by mode-coupling theory[13] and found in colloids[4] and micelles with attractive interaction.[5] The second and more general question that arises concerns the interplay of the two (static and dynamic)

glass transitions and its effect on glassy behavior[14] when a reentrance in the phase diagram takes place.

In order to answer the above questions, we consider a disordered system of N spin-1 variables with Hamiltonian

$$H = -2\sum_{ij} J_{ij}\sigma_i\sigma_j + D\sum_i \sigma_i^2, \quad \sigma_i = 0, \pm 1, \quad (1)$$

where J is a symmetric random orthogonal matrix (with $J_{ii} = 0$), and D is a crystal field playing a role similar to the chemical potential: Increasing D will favor $\sigma_i = 0$ states and reduce the effect of frustration. The case with binary spin variables ($\sigma_i = \pm 1$) corresponds to the standard random orthogonal model (ROM) studied by Marinari *et al.*,[15] which is known to be glassy at low temperature.[15–17] It should be emphasized that quenched disorder is not crucial as ROM shares the same basic phenomenology with systems having deterministic interactions.[15,18]

The free energy of the model (1) can be evaluated as in the standard ROM by using the replica method and the identity:[15] $\overline{\exp(\text{Tr } JA)} = \exp[N\text{Tr } G(A/N)]$, where A is a symmetric matrix of finite rank, the overbar is the average over the quenched disorder which is defined by the Haar measure on the orthogonal group, and

$$G(z) = \frac{\sqrt{1+4z^2}-1}{2} - \frac{1}{2}\ln\frac{\sqrt{1+4z^2}+1}{2}. \quad (2)$$

Averaging the replicated partition function gives

$$\overline{Z^n} \sim \int_{-\infty}^{\infty} \prod_{a,b} d\Lambda_{ab} dQ_{ab} \exp(-\beta f[Q,\Lambda]), \quad (3)$$

where $a, b = 1, \ldots, n$ are replica indexes, and the Parisi order parameter $Q_{ab} = \langle\sigma_a\sigma_b\rangle$ includes the diagonal terms, which correspond to the density of ± 1 spins, $Q_{aa} = \rho$. The free energy $f[Q,\Lambda]$ reads

$$-\beta f[Q,\Lambda] = \frac{1}{2}\text{Tr } G(4\beta Q) - \text{Tr}(\Lambda Q) + \ln Z_0, \quad (4)$$

where Z_0 is the single-site partition function

$$Z_0 = \sum_{\{\sigma_a\}} \exp\left(\sum_{a,b} \Lambda_{ab}\sigma_a\sigma_b - \beta D\sum_a \sigma_a^2\right). \quad (5)$$

In order to proceed one now needs to specify an ansatz for Q and Λ, and then consider the zero-replica limit $n \rightarrow 0$.

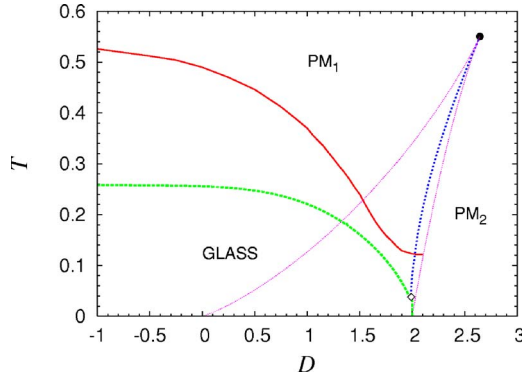*The fluid-fluid transition.* The simplest case is the replica

FIG. 1. (Color online) Phase diagram of ROM spin-1 in the temperature-crystal field plane. The continuous (red) line is the dynamic freezing, while the dashed (green) line is the static glass transition. The dotted (blue) line is the first-order transition between the two paramagnetic (PM$_1$ and PM$_2$) phases. Spinodals are shown as dotted (violet) light lines. The full dot is the critical point terminating the coexistence line. The diamond symbol is the tricritical point separating the continuous and discontinuous glass transition (at lower temperature).

symmetric ansatz: $Q_{ab}=(\rho-q)\delta_{ab}+q$, $\Lambda_{ab}=(\mu-\lambda)\delta_{ab}+\lambda$, where δ is the Kronecker symbol. In this approximation the free energy reads

$$\beta f_{RS} = -\frac{1}{2}G[4\beta(\rho-q)] - 2\beta qG'[4\beta(\rho-q)] - \lambda q + \mu\rho$$

$$- \int Dz \ln(1 + 2e^{\mu-\lambda-\beta D}\cosh(z\sqrt{2\lambda})), \qquad (6)$$

where $Dz \equiv dz e^{-z^2/2}/\sqrt{2\pi}$ and q, ρ, λ, and μ are self-consistently determined by the saddle-point equations. At sufficiently large temperature/crystal field, $q=\lambda=0$, and one recovers the annealed free energy

$$\beta f_{ann} = -\frac{1}{2}G(4\beta\rho) + \beta D\rho - s_0(\rho), \qquad (7)$$

where $s_0(\rho) = -(1-\rho)\log(1-\rho) - \rho\log\rho + \rho\log 2$ is the entropy of a noninteracting spin-1 system, and the density $\rho = \rho(\beta, D)$ satisfies the implicit equation

$$\beta D = \log\frac{2(1-\rho)}{\rho} + 2\beta G'(4\beta\rho). \qquad (8)$$

Equation (8) exhibits multiple solutions. There is an unstable phase (with negative susceptibility) and two paramagnetic fluid phases (PM$_1$ and PM$_2$) between which a first-order transition occurs. The latter terminates at a critical point located at $D_c \simeq 2.644$, $T_c \simeq 0.5506$ (see Fig. 1). The critical point does not appear in spin-1 REM (Ref. 19), showing that the two models are not equivalent in the large-D regime. Along the first-order transition line two distinct phases having equal free energy coexist, and in both it is possible to go continuously around the critical point from one coexisting phase to the other by appropriately varying D and T. This first-order transition is a general feature of spin-1 and lattice-gas systems with disordered (Gaussian or orthogonal) interactions, though it is sometimes missed. For $D \geq 2$ the density of ± 1 spins decreases upon cooling. This behavior is somehow un-
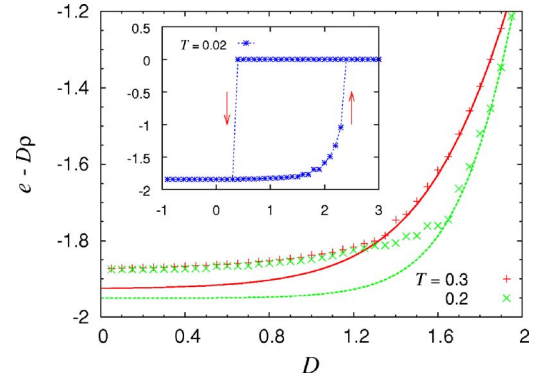

FIG. 2. (Color online) Energy density e vs crystal field D at fixed temperature T, in a slow crunching MC experiment. The lines are the analytic results of the annealed approximation.

expected if compared to what happens in the Ghatak–Sherrington model, i.e., Eq. (1) with Gaussian disorder. In the latter, the density increases upon cooling and the critical point is absent.

The static and dynamic glass transition. At low temperature/crystal field, the annealed entropy,

$$s_{ann} = s_0(\rho) + \frac{1}{2}G(4\beta\rho) - 2\beta\rho G'(4\beta\rho), \qquad (9)$$

becomes negative, suggesting that replica symmetry has to be broken. Within the one-step replica-symmetry-breaking ansatz,[20] Q and Λ are block diagonal matrices, where the blocks have size $m \times m$. Inside the blocks $Q_{ab}=(\rho-q)\delta_{ab}+q$, $\Lambda_{ab}=(\mu-\lambda)\delta_{ab}+\lambda$. Then the free energy becomes

$$\beta f_{1RSB} = \frac{1-m}{2m}G[4\beta(\rho-q)] + \lambda q(m-1)$$

$$- \frac{1}{2m}G[4\beta(\rho-q+qm)] + \mu\rho$$

$$- \frac{1}{m}\ln\int Dz(1 + 2e^{\mu-\lambda-\beta D}\cosh(z\sqrt{2\lambda}))^m. \qquad (10)$$

Expanding near $m=1$ gives $\beta f_{1RSB} \simeq \beta f_{ann} - (m-1)V$, that allows location of the static and dynamic transition through the effective potential $V = -\beta(\partial f_{1RSB}/\partial m)|_{m=1}$ (Refs. 12 and 17). The two glass transition lines $T_s(D)$ and $T_d(D)$ are shown in Fig. 1. In the Ising spin limit, $D \to -\infty$, we get $T_s \simeq 0.26$ and $T_d \simeq 0.535$, consistent with Refs. 15 and 17. Several interesting features can be observed. (i) The temperature at which the annealed entropy vanishes is very close to $T_s(D)$ for any value of D, meaning that the glassy phase of our model is similar to that of spin-1 REM (Ref. 19). (ii) There is a tricritical point at $T^* \simeq 0.036$, $D^* \simeq 2.0$ below which the nature of the glass transition changes from second to first order in the thermodynamic sense. No appreciable irreversibility effects are observed across the second-order glass-transition line when D loops start from the PM$_1$ phase, Fig. 2 (main frame), whereas there is latent heat and hysteresis across the first-order glass-transition line [see Fig. 2 (inset)]. (iii) The dynamic freezing line penetrates the PM$_2$ phase up to the spinodal line (at $D \simeq 2.1$) (see Fig. 1). For $D < 2.1$ the system is dynamically unable to reach equilibrium at low tempera-
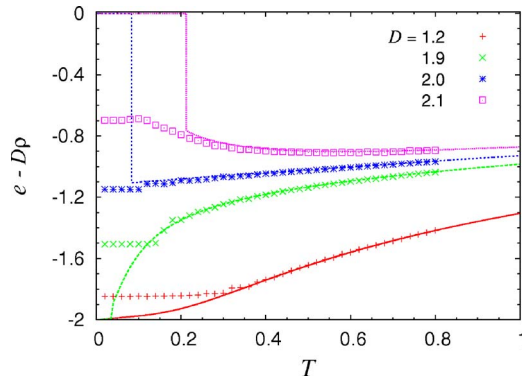
FIG. 3. (Color online) Energy density e vs temperature T at fixed crystal field D, in a slow cooling MC experiment. The lines are the analytic results of the annealed approximation.

FIG. 4. (Color online) Phase diagram of ROM spin-1 for degeneracy ratio $r=50$. Spinodal lines are not shown here.

ture even in the case in which the ground is trivial, that is for $2 < D < 2.1$ (see Fig. 3). (iv) Crunching the system from high to low D at fixed temperature, $T_d > T > T_s$, leads to a purely dynamic freezing with no underlying entropy crises. Monte Carlo (MC) results shown in Figs. 2 and 3 are for a system of size $N=512$ and a very slow annealing rate (10^7 MC sweeps per unit variation of D and T, respectively).

Inverse temperature glass transitions. To take into account inverse freezing phenomena, the interacting states, $\sigma_i = \pm 1$, are now given an entropic advantage by a degeneracy ratio $r > 1$ with respect to the noninteracting states, $\sigma_i = 0$. The opposite case in which $r < 1$ will not be discussed here: That would lead only to a reentrance of PM_1 within the PM_2 fluid phase, which, for our purpose, is less interesting. One can easily see that including degeneracy in the system corresponds to changing the crystal field in Eqs. (6)–(10) as follows: $D \rightarrow D - T \log r$ (Ref. 6). In fact, the dependence of the effective potential on the degeneracy ratio enters only through the density variable, ρ, which satisfies Eq. (8). Having the meaning of the different phases already clarified, we need only to investigate how the phase boundaries in Fig. 1 are modified accordingly. The analysis of the effective potential shows that for small r the reentrancy effect is weak, while for large enough values of r a rather interesting reentrant behavior appears. We discuss the results for the case $r = 50$, which corresponds to the phase diagram presented in Fig. 4. First of all, we see that the two glass transition lines never cross each other and that upon heating the inverse static glass-transition occurring in the range $2 < D < 2.18$ is anticipated by inverse freezing. This is due to the penetration of the dynamical arrest line in the PM_2 fluid phase. At intermediate crystal field, $2.18 < D < 2.37$, there is inverse freezing without a static glass transition. This prevents the application of the Kauzmann paradox, since in this range of crystal field the equilibrium phase at low temperature is the PM_2 fluid. Finally, at larger crystal field, $2.37 < D < 2.58$, there is a *double* inverse dynamical freezing (again with no underlying static glass transition) that goes through the PM_1 and PM_2 fluid phases (i.e., on cooling one would observe the sequence of transitions PM_1-G-PM_1-G-PM_2). In this region of the phase diagram the packing density of ± 1 spins decreases with the temperature, i.e., the glass state at lower temperature is less dense than the one at higher temperature.
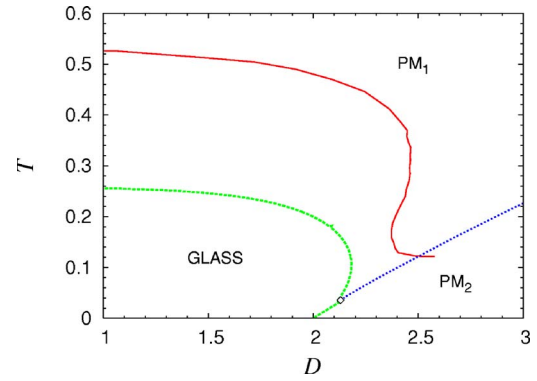
This behavior is reminiscent of that predicted by mode-coupling theory[13] and observed in experiments on attractive colloids[4] and micelles.[5]

Conclusions. To summarize, we introduced a generalization of ROM (Ref. 15) allowing investigation of inverse freezing phenomena in fragile glass-forming liquids through a mechanism of entropy-driven phase reentrance.[6] The model is a microscopic realization of the "random first-order" scenario for the structural glass transition.[12] However, in our case the glass transition can be either continuous or discontinuous in the thermodynamic sense. This is due to the presence of a first-order transition between two fluid phases. Similar results are obtained by using purely biquadratic interactions, $J_{ij}\sigma_i^2\sigma_j^2$, that would correspond to a lattice-gas ROM ($\sigma_i^2 \rightarrow n_i = 0, 1$). Notice that our results have no counterpart in the quantum version of ROM studied in Ref. 23. Rather, they have some resemblance to those obtained in Refs. 24 and 25, reproducing a number of experimental observations on the dipolar spin-glass $LiHo_xY_{1-x}F_4$ in external field.[26] In fact, the present model can be considered as the insulating limit of a generalization of the itinerant electron model (see Ref. 27) with random orthogonal interactions.

At large enough degeneracy an inverse static glass transition and a double inverse dynamic freezing occur. The latter reproduces qualitatively some features observed in recent experiments on colloidal and copolymer-micellar systems with short-range attraction.[4,5] Nevertheless, the possibility of describing the glass-glass transition[13,21,22] in the present setting remains unclear (see, however, Refs. 28 and 29) and deserves further investigation. Let us finally mention that this work can be extended by considering both bilinear and biquadratic interactions, similar to what has been done in Ref. 10. One can also include a three-body interaction term to mimic microemulsion (see, e.g., Refs. 30). Depending on the relative strength of these interactions and the nature of the quenched (Gaussian versus orthogonal) disorder, an even richer variety of phases is expected. That could lead to a better understanding of the glassy behavior of complex liquids and soft matter systems.

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