

Stable Solution of the Simplest Spin Model for Inverse Freezing

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We analyze the Blume-Emery-Griffiths-Capel model with disordered interaction that displays the inverse freezing phenomenon. The behavior of this spin-1 model in crystal field is studied throughout the phase diagram, and the transition lines are computed using the full replica symmetry breaking ansatz. We compare the results both with the formulation of the same model in terms of Ising spins on lattice gas, where no reentrance takes place, and with the model with generalized spin variables recently introduced by Schupper and Shnerb [Phys. Rev. Lett. **93**, 037202 (2004)], for which the reentrance is enhanced as the ratio between the degeneracy of full to empty sites increases. The simplest version of all these models, known as the Ghatak-Sherrington model, turns out to hold all the general features characterizing an inverse transition to an amorphous phase.

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In the recent past the phenomenon of “inverse melting,” already hypothesized by Tammann a century ago [1], has been found experimentally in very different materials, ranging from polymeric and colloidal compounds to high- T_c superconductors, proteins, ultrathin films, liquid crystals, and metallic alloys [2–5]. This kind of transition includes, e.g., the solidification of a liquid or the transformation of an amorphous solid into a crystal upon heating. The reason for this counterintuitive process is that a phase usually at higher entropic content happens to exist in very peculiar patterns such that its entropy is decreased below the entropy of the phase usually considered the most ordered one. An example taking place in the widely studied polymer P4MIP [2] is the one of a crystal state of *higher* entropy that can be transformed into a fluid phase of *lower* entropy on cooling, thus allowing, e.g., the melting of a crystal as the temperature (or pressure) is decreased. Inverse transitions, in their most generic meaning (i.e., both thermodynamic or occurring by means of kinetic arrest), have been observed between fluid and crystal phases [3], between glass and crystal [2], and between fluid and glass (“inverse freezing”) [4].

A reentrance in the transition line can be due to both the existence of a liquid phase with an entropy lower than the one of the solid and/or the fact that the liquid is more dense than the solid (as in the water-ice transition). According to the Clausius-Clapeyron equation, when an entropic “inversion” accounts for the phase transition, the equilibrium transition line changes slope in a point where the entropy of the fluid phase, s_l , becomes equal to the one of the solid, s_s . From this critical point a whole isoentropic line, $\Delta s = s_l - s_s = 0$, can be continued inside both the solid and the liquid phases, as the thermodynamic parameters (temperature and pressure, for instance) are varied. This is a particularly interesting observation since, in the context of glass formers, Kauzmann [6] hypothesized a transition to an “ideal” glass at the temperature at which $\Delta s = 0$, in

order to avoid the paradox that an undercooled liquid might possess less entropy than the associated crystal at the same values of the thermodynamic parameters. From an experimental point of view the Kauzmann temperature would be the temperature of the glass transition (that is, not a true phase transition because it is strictly kinetic in origin) in an idealized adiabatic cooling procedure. Since the astronomically long relaxation time needed to actually perform such an experiment makes such a procedure unfeasible, the evidence in favor of the existence of a thermodynamic glass transition mainly comes from analytical and numerical investigations (see, e.g., Refs. [7,8]). The fact that a $\Delta s = 0$ line turns out naturally in the description of the behavior of materials with inverse transition avoids, at least for these substances, the Kauzmann paradox and breaks the connection between $\Delta s = 0$ extrapolation and the existence of an ideal amorphous phase [2,3].

The aim of this Letter is to study a simple mean-field model for the inverse transition in spin glasses, heuristically representing the inverse fluid-amorphous transition. The model we consider contains quenched randomness as a basic ingredient. We stress, however, that such a disorder is not necessary to induce the spin-glass transition. Truly relevant is the frustration caused by it, i.e., the unresolvable competition among many similar states in which the system can find itself. The source of frustration can be of a different nature, e.g., random impurities or geometrical constraints. The *kind* of frustration can actually lead to different amorphous phases (a glass or a spin glass). The quenched randomness, instead, is not a discriminant factor. Indeed, spin-glass models can be found without quenched disorder [9] as well as structural glass models with quenched disorder (e.g., the “discontinuous spin glasses” [7] sharing the physical properties of a true glass rather than of an amorphous magnet).

We have been analyzing the Blume-Emery-Griffiths-Capel (BEGC) model with quenched disorder using the

full replica symmetry breaking (FRSB) scheme of computation that yields the exact stable thermodynamics. The interested reader can find details about the computation of the thermodynamics of this kind of model in Refs. [10,11]. The BEGC model includes the Blume-Capel [12] and the Blume-Emery-Griffiths [13] models, when the couplings are ferromagnetic, and the Ghatak-Sherrington (GS) model [14], when the couplings are random variables and no biquadratic interaction occurs (see Ref. [11] for a more complete literature report). The model we have been extensively analyzing in the past is the one with Ising spins ($S = \pm 1$) on a lattice gas (with site occupation numbers $n = 0, 1$). In that case the value associated with a single site can be 1, 0, or -1 , but zero has a double degeneracy with respect to 1 (or -1). The original BEGC model consists, instead, of spin-1 variables $S = 1, 0, -1$, with 1 (or -1) being as degenerate as 0. In their recent work [15,16] Schupper and Shnerb introduced a generalization to theoretically represent the phenomenon of inverse freezing. They computed the phase diagram of the GS model in the replica symmetric (RS) approximation, presenting evidence that a reentrance occurs if the degeneracy of the magnetically interacting sites ($S^2 = 1$) is larger than the one of the holes ($S = 0$). Stimulated by their work we have been looking at the phase diagram of the random BEGC model in terms of the variables introduced by them, but considering the thermodynamically stable spin-glass solution obtained by means of the FRSB ansatz, instead of the RS approximation. The aim of this work is (i) to check the validity of the idea introduced in Ref. [15] in a nonpathological case and (ii) to determine the simplest model in which the inverse freezing phenomenon is qualitatively well reproduced, including the presence of latent heat.

The Hamiltonian of the model is

$$\mathcal{H} = \sum_{ij} J_{ij} S_i S_j + D \sum_{i=1}^N S_i^2 - \frac{K}{N} \sum_{i < j} S_i^2 S_j^2, \quad (1)$$

where $S = 1, 0, -1$, D is the crystal field, and J_{ij} are quenched random variables (Gaussian) of mean zero and variance $1/N$. The parameter K represents the strength of the biquadratic interaction.

We denote by k the degeneracy of the filled sites ($S = 1$ or $S = -1$) and l the degeneracy of the empty sites ($S = 0$). The relevant parameter is $r = k/l$ [15]. When $r = 1$, the spin-1 model is obtained. If, furthermore, $K = 0$, the model is the GS one. When, otherwise, $r = 1/2$ and $D \rightarrow \mu = -D$, the lattice gas formulation of Ref. [17] is recovered, for which no reentrance was observed [10,11].

Schupper and Shnerb introduce the idea that a larger degeneracy of the interacting sites yields a qualitative change of the phase diagram to develop a reentrance in the T - D phase diagram, thus allowing for a phase transition from the paramagnetic (PM) to the spin-glass (SG) phase as temperature is *increased*. Their statement is that, if the ratio r is large enough, the phase diagram changes so much

that it displays a reentrance in the T - D plane, as they show in the RS case [15]. This solution turns out to be unphysical in any phase that is not the PM one [18], and the shape of the transition line and of the SG spinodal line might then be sensitive to the thermodynamic instability intrinsic in such approximation. Therefore, moving to the right RSB scheme of computation, there is no guarantee that the first order transition and the spin-glass spinodal lines would remain the same. On the other hand, not even the certainty exists that the first order phase transition line between the PM and the SG phase computed in the RS scheme has to be displaced with respect to the PM/SG(FRSB) transition line to develop a reentrance.

We discuss the physically stable solution for both the GS model [14,19] ($K = 0$) and the model with attractive biquadratic interaction [11] ($K/J = 1$), whose phase diagrams are plotted in Fig. 1, and we compare it with the RS results (see Fig. 2). We study the behavior of the phase diagram for (a) the lattice gas case ($r = 1/2$), for which no inverse transition occurs anywhere in the parameter space; (b) the spin-1 case ($r = 1$), where the first order transition line displays a reentrance soon below the tricritical temperature; (c) the generalized cases as $r > 1$; in particular, we plot the results of the model with variables taking values $S = \{1, 1, 0, -1, -1\}$ for which the reentrance takes place above the tricritical point, along the second order phase transition line.

Having a model with variables displaying a relative degeneracy r (and $D = D_r$), in order to describe the par-

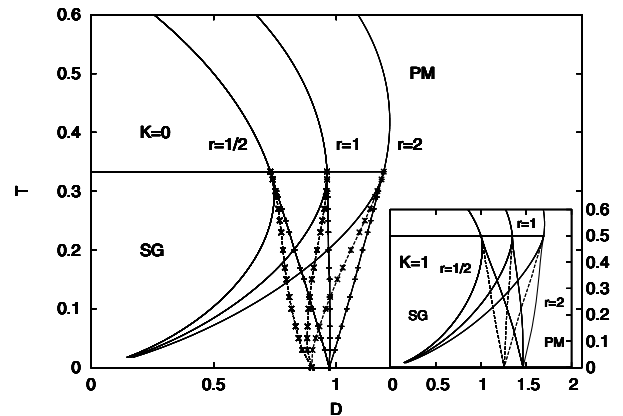


FIG. 1. The T - D phase diagram in absence of biquadratic interaction. Three models with different behaviors are plotted: $r = 1/2, 1, 2$. For each model three curves are represented, each departing from the same tricritical point: the full curve on the left is the spinodal of the PM phase, the dashed one in the middle is the first order transition line, and the right one is the SG spinodal line. The group of three curves on the left are for the Ising spins on lattice gas ($r = 1/2$, $T_c = 1/3$, $D_c = 0.73105$). The group of curves in the middle represent the lines of the GS model ($r = 1$, $D_c = 0.96210$). The curves on the right correspond to the $r = 2$ model ($D_c = 1.9315$). In the inset the same diagram is plotted when $K = 1$ (attractive biquadratic interaction).

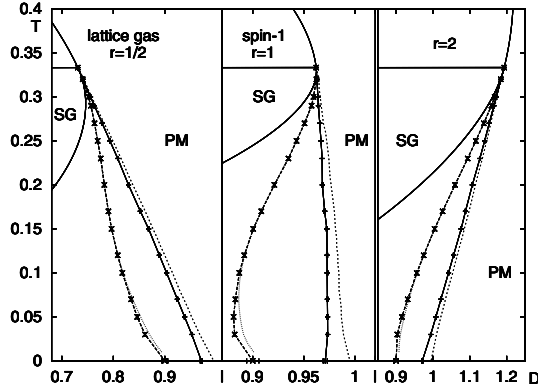


FIG. 2. T - D phase diagrams at $K = 0$ of the Ising spin glass on lattice gas (left), of the spin-1 model (center), and of the random BEGC model with $r = 2$ (right). Both the RS and the FRSB solution (the latter with error bars) are plotted. In the first case no reentrance takes place, disregarding the approximation. A reentrance occurs, instead, below the tricritical point in the spin-1 model along the first order transition line, and a second reentrance seems to be there for $T < 0.03$. In the model with $r = 2$ the reentrance occurs above the tricritical point.

tion function of another model whose variables have degeneracy r' it is enough to vary the crystal field as $D_{r'} + T \log r' = D_r + T \log r$. This does not hold, however, for the state functions obtained deriving the thermodynamic potential with respect to the temperature (e.g., entropy and internal energy) that will, instead, receive contributions from additional terms. Identifying $D_{1/2} \equiv -\mu$, one can recover the case of magnetic spins on a lattice gas of chemical potential μ [10,17].

The analysis leads us to the conclusion that the transition lines are not very much dependent on the ansatz used to compute the quenched average of the free energy. Actually, for not extremely low T , the first order transition lines yielded by the RS and the FRSB ansatz coincide down to the precision of our numerical evaluation of the FRSB antiparabolic Parisi equation [20] (see Fig. 2). For what concerns the spinodal lines, the RS ones are shifted by a small amount inside the pure PM phase. In order to clarify this point, the behavior of the free energy vs D at fixed temperature ($T = 0.23$) is displayed in Fig. 3 for the spin-1 model in the absence of biquadratic interaction. In the inset the difference between the FRSB and the RS free energies ($\Delta F \equiv F_{\text{sg}}^{\text{frsb}} - F_{\text{sg}}^{\text{rs}}$) is plotted. In the coexistence region we have a subregion where the stable phase is PM (right-hand side of Fig. 3), i.e., $F_{\text{pm}} < F_{\text{sg}}^{\text{frsb}}$, and a complementary subregion where $F_{\text{sg}}^{\text{frsb}} < F_{\text{pm}}$. The free energy of the stable spin-glass phase is, of course, the FRSB one. In the SG phase any approximation of this free energy yielded by means of a finite number of RSB leads to a *lower* value (and an unstable phase) [20], and we can see in the inset that $F_{\text{sg}}^{\text{frsb}} > F_{\text{sg}}^{\text{rs}}$. The two free energies merge around the first order transition (compatibly with the numerical uncertainty). At $T = 0.23$ in the phase coexistence region the

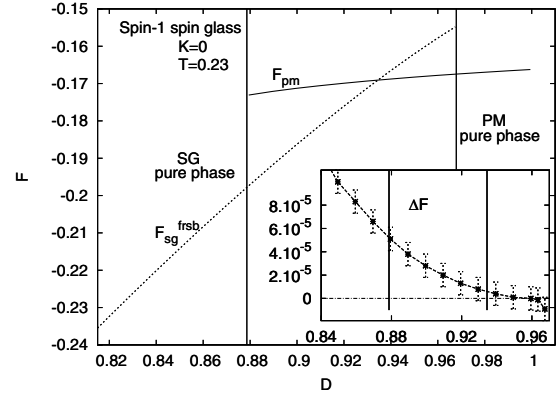


FIG. 3. The free energy F_{pm} and $F_{\text{sg}}^{\text{frsb}}$ versus the crystal field D at $T = 0.23$ in the GS model ($K = 0$). The left side vertical line is at the spinodal point of the PM phase, the right one at the spinodal point of the SG phase. The first order transition occurs at $D_1 = 0.9344$. In the inset $\Delta F = F_{\text{sg}}^{\text{frsb}} - F_{\text{sg}}^{\text{rs}}$ is displayed. At this temperature the two functions merge very near to the tricritical point (right side vertical line).

two ansatz yield very similar values (as opposed, e.g., to the behavior deep in the SG pure phase), so that it is not possible to determine exactly the merging point of $F_{\text{sg}}^{\text{rs}}(D)$ and $F_{\text{sg}}^{\text{frsb}}(D)$ (see Fig. 2). One can infer, however, that it remains above $D_1(T)$.

We show the D - T phase diagrams for $K = 0$ and $K = 1$ in Fig. 1 and inset, at different values of r . The diagram of the model with Ising spins on lattice gas is here represented as a function of the parameter $D = -\mu$, in order to simplify the comparison with the spin-1 model and the $r > 1$ cases. We find that the reentrance in the D - T plane is present already in the spin-1 GS model. As a consequence, this implies that there is no need for the intuition of Ref. [15] in order to have a model for inverse freezing from low temperature liquid to high temperature amorphous solid. This is different from the liquid-crystal inverse transition (“inverse melting”) for the description of which the original Blume-Capel model is not adequate and $r > 1$ is needed [15,16].

The slope of a first order line is given by the Clausius-Clapeyron equation. For the BEGC model it can be written in terms of the crystal field D (playing the role of a chemical potential), instead of the pressure that is not defined in our model:

$$\frac{dD}{dT} = \frac{s_{\text{pm}} - s_{\text{sg}}}{\rho_{\text{pm}} - \rho_{\text{sg}}} = \frac{\Delta s}{\Delta \rho}. \quad (2)$$

This formula is valid for any r . We stress that in passing from r to r' also the entropy shifts of a quantity $\rho \log r/r'$, in agreement with the crystal field shift given above. Going down along the transition line, as Δs changes sign the slope becomes positive. The $\Delta s = 0$ point is called a Kauzmann locus [3].

Looking at the phase diagram in the spin-1 case, one can observe that the RS first order phase transition line also

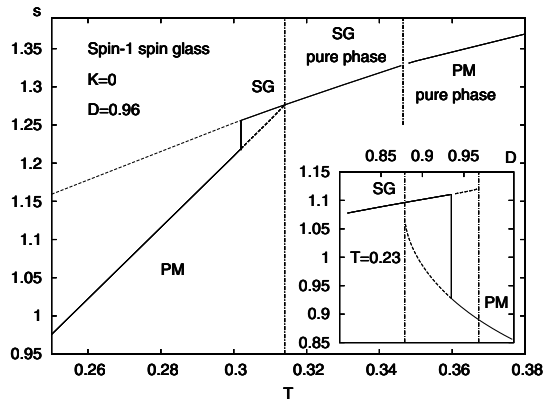


FIG. 4. Entropy vs T at the crystal field value of $D = 0.96$ for the GS model. $T_1 = 0.302$. The two vertical dashed lines mark the SG ($T_{SG} = 0.314$) and PM ($T_{PM} = 0.3465$) spinodal points. In the inset $s(D)$ is plotted at $T = 0.23$.

displays a second turning as the temperature becomes lower and lower (see Fig. 2). Such a turning is less evident as the FRSB solution is considered, but it does not disappear. The low temperature turning is not there, instead, for $r = 2$. We notice also that in this last case the reentrance is already in the second order phase transition line and both first and second order inverse freezing transitions are possible. In particular, a transition with an exchange of latent heat can occur exclusively in the inverse order. In Fig. 4 the behavior of the entropy as a function of the temperature is shown across an inverse transition (as a function of the crystal field D in the inset) for the spin-1 model. The entropy of the PM phase *below* the first order transition line is *smaller* than the entropy of the SG: heating the system, the paramagnet becomes an amorphous magnet (i.e., “freezes”) acquiring latent heat from the heat bath.

Introducing a biquadratic interaction term and varying it from attractive to repulsive does not change the situation much (see, e.g., inset of Fig. 1). For any value of K no reentrance of the phase transition line occurs in the D - T phase diagram of the lattice gas model, whereas it is *always* there for the spin-1 model. The only consequence of reducing K is that the area of the phase coexistence region is reduced (the tricritical temperature tends to zero as $K \rightarrow -\infty$).

In conclusion, we have shown that the Ghatak-Sherrington model, i.e., the Blume-Capel model with quenched disordered magnetic interactions, computed in the exact FRSB ansatz, undergoes the inverse freezing phenomenon acquiring latent heat from the heat bath as the paramagnet becomes a spin glass. Many other models can be built starting from this one, introducing an attractive

or repulsive biquadratic interaction [the last term in Hamiltonian (1)] and/or tuning the relative degeneracy of the value $S = 0$ and $S^2 = 1$ of the spin variable (the Schupper-Shnerb “spin” [15]), but the GS one already contains all features needed to qualitatively represent the experimental results.

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