Stable Solution of the Simplest Spin Model for Inverse Freezing

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We analyze the Blume-Emery-Griffiths model with disordered magnetic 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 and spinodal lines for the model are computed using the Full Replica Symmetry Breaking Ansatz that always yields a thermodynamically stable phase. 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, including the right thermodynamic behavior.

In the recent past the phenomenon of “inverse melting”, already hypothesized by Tammann a century ago, has been found experimentally in very different materials, ranging from polymeric and colloidal compounds to high-$T_c$ superconductors, proteins, ultra-thin films, liquid crystals and metallic alloys. 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 counter intuitive 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 P4M1P 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 between glass and crystals and between fluid and glass (“inverse freezing”).

A reentrance in the transition line can due both to the existence of a liquid phase with an entropy lower than the one of the solid and/or because the liquid is more dense than the solid (like in the water-ice transition). 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, $s_2$, becomes equal to the one of the solid, $s_1$, according to the Clausius Clapeyron equation for first order phase transitions. From this point a whole iso-entropic line, $\Delta s = s_2 - s_1 = 0$, can be continued both inside 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 hypothesized a transition to an “ideal” glass at the temperature at which $\Delta s = 0$, in order to avoid the paradox that an under-cooled 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 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. [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.

The aim of this paper is to study a simple mean-field model for the inverse transition in a spin-glass, in order to heuristically represent the inverse fluid-amorphous transition. The model we consider displays quenched randomness as 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 unresolved competition among many similar states in the system evolution, but the source of frustration can be of different nature, e.g. geometric. The kind of frustration can actually lead to different amorphous phases (a glass or a spin-glass) but it is not the quenched randomness the discriminant factor. Indeed, spin-glass models can be found without quenched disorder as well as structural glass models with quenched disorder (e.g. the “discontinuous spin-glasses” 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.
It includes the Blume-Capel\cite{12} and the Blume-Emery-Griffiths\cite{13} models, when the couplings are ferromagnetic, and the Ghatak-Sherrington (GS) model\cite{14} when the couplings are random variables and no biquadratic interaction occurs (see Ref.\cite{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\cite{15,16} Schupper and Shnerb introduced a generalization of the GS model to theoretically represent the phenomenon of inverse freezing. They computed the phase diagram of such a model in the Replica Symmetric (RS) approximation presenting evidence that a reentrance occurs if the degeneracy of the magnetically interacting sites is larger than the one of the holes. 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, this time considering the thermodynamically stable spin-glass 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.\cite{11} in a non pathological 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 model Hamiltonian we consider is

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

where $S = 1, 0, −1$, $D$ is the crystal field, $J_{ij}$ are quenched random variables (Gaussian) of mean zero and variance $1/N$. The parameter $K$ represents the strength of the biquadratic interaction. We call $k$ the degeneracy of the filled in sites of one type ($S = 1$ or $S = −1$) and $l$ the degeneracy of the empty sites ($S = 0$). The relevant parameter is $r = k/l$.\cite{12} 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.\cite{15} is recovered, for which no reentrance was observed.\cite{10,11}

Schupper and Shnerb bring about the idea that a larger degeneracy of the interacting sites yields a qualitative change of the phase diagram up 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 up to display a reentrance in the $T − D$ plane, as they show in the RS case.\cite{12} This solution turns out to be unphysical in any phase that is not the PM one\cite{12} 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 up to developing a reentrance.

We discuss the physically stable solution for both the GS model\cite{14,15} ($K = 0$) and the model with attractive biquadratic interaction\cite{14} ($K/J = 1$), whose phase diagrams are plotted in Fig.\ref{fig:1} and we compare it with the RS results (see Fig.\ref{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.\cite{2}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{The $D-T$ 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 ($D_c = 1.19315$). In the inset the same diagram is plotted when $K = 1$ (attractive biquadratic interaction).}
\end{figure}

Having a model with variables displaying a relative degeneracy $r$ ($D = D_r$), in order to describe the partition 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 ther-
FIG. 2: $D$-$T$ phase diagrams at $K = 0$ of the Ising spin glass on lattice gas (left), of the GS 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 latter model the reentrance occurs above the tricritical point.

modynamic potential with respect to the temperature (e.g. entropy and internal energy) that will, instead, receive contributions from additional terms. Identifying $D_{1/2} = -\mu$ one can recover the case of magnetic spins on a lattice gas of chemical potential $\mu$.\cite{10,11}

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,\cite{20} whereas they slightly differ at very low temperature (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 absence of biquadratic interaction. In the inset the difference between the FRSB and the RS free energies ($|\Delta F | = F_{\text{frsb}} - F_{\text{rs}}$) is plotted. In the coexistence region we have a subregion where the stable phase is PM (r.h.s. of fig. 3), i.e. $F_{\text{pm}} < F_{\text{sg}}$, and a complementary subregion where $F_{\text{sg}} < F_{\text{pm}}$. 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)\cite{18} and we can see in the inset that $F_{\text{frsb}} > F_{\text{rs}}$. 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 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 $F_{\text{rs}}(D)$ and $F_{\text{frsb}}(D)$. (see Fig. 2). One can infer, however, that it remains above $D_{1/2}(T)$.

We show the $D$-$T$ phase diagrams for $K = 0$ and $K = 1$ in Fig. 4 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 at difference with 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.\cite{16,17}

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:

$$\frac{dD}{dT} = \frac{s_{\text{pm}} - s_{\text{sg}}}{\rho_{\text{pm}} - \rho_{\text{sg}}} = \frac{\Delta s}{\Delta \rho}$$

This formula is valid for any $r$. We stress that in passing from $r$ to $r'$ also the entropy changes of a term $\rho \log r/r'$, in agreement with the crystal field shift given above. Going down along the transition line, as $\Delta s$ changes sign the slope becomes positive. The $\Delta s = 0$ point is called a Kauzmann locus.\cite{21}

Looking at the phase diagram in the spin-1 case one can observe that the RS first order phase transition line
tropy as a function of the temperature is shown across in the inverse order. In Fig. 4 the behavior of the en-
freezing transitions are possible. In particular a transi-
tion line and both a first and a second order inverse
lines. In the inset $s(D)$ is plotted at $T = 0.23$.
also displays a second turning as the temperature be-
comes 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 a first and a second order inverse
freezing transitions are possible. In particular a transition
with exchange of latent heat can occur exclusively in
the inverse order. In Fig. 1 the behavior of the en-
tropy 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 para-
magnet becomes an amorphous magnet (i.e. “freezes”)
aquiring latent heat from the heat bath.

Introducing a biquadratic interaction term and vary-
ing it from attractive to repulsive the situation does not
change 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 re-
region is reduced (the tricritical temperature tends to zero
as $K \to -\infty$).

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 mod-
els can be built starting from this one, introducing an
attractive or repulsive biquadratic interaction (the last
term in Hamiltonian $\mathbf{H}$) and/or tuning the relative de-
genrety of the value $S = 0$ and $S^2 = 1$ of the spin
variable (the Schupper-Shnerb “spin” but the GS one
already contains all features needed to qualitatively rep-
resent the experimental results.

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