P H Y S I C A L   R E V I E W   L E T T E R S

Thermodynamic First Order Transition and Inverse Freezing in a 3D Spin Glass

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We present a numerical study of the random Blume-Capel model in three dimensions. The phase diagram is characterized by spin-glass–paramagnet phase transitions of both first and second order in the thermodynamic sense. Numerical simulations are performed using the exchange Monte Carlo algorithm, providing clear evidence for inverse freezing. The main features at criticality and in the phase coexistence region are investigated. We are not privy to other 3D short-range systems with quenched disorder undergoing inverse freezing.

Introduction.—We aim to investigate the phenomenon of reversible inverse transition (IT), occurring between a solid and a liquid in inverse order relation relative to standard transitions. The case of "ordering in disorder," occurring in a crystal solid that liquefies on cooling, is generally termed inverse melting. If the solid is amorphous, the IT is termed inverse freezing (IF). ITs are observed in different materials. The first examples were the low temperature liquid and crystal phases of helium isotopes He^3 and He^4 [1]. A more recent and complex material is a methyl-cellulose solution in water, undergoing a reversible inverse sol-gel transition [2]. Other examples are found in poly(4-methylpentene-1) (P4MP1) at high pressure [3], in solutions of α-cyclodextrine (αCD) and 4-methypyridine (4MP) in water [4], in ferromagnetic systems of gold nanoparticles [5], and for the magnetic flux lines in a high temperature superconductor [6]. In mentioning these cases, we stick to a definition of IT as the one hypothesized by Tammann [7] a century ago: a reversible transition in temperature at fixed pressure [8] whose low T phase is an isotropic fluid [or paramagnet (PM) for magnetic systems]. IT is not an exact synonym of reentrance. Indeed, a reentrance can be absent, as for αCD [4] or methyl-cellulose [2] solutions, where no high temperature fluid phase is detected. Moreover, not all reentrances are signatures of an IT, as for those phases with different kinds of symmetry separated by reentrant isobaric transition lines in temperature, cf., e.g., Ref. [9], in which, however, no melting to a completely disordered isotropic phase is present.

A thorough explanation of the fundamental mechanisms leading to the IT would require a microscopic analysis of the single component's behavior and their mutual interactions as temperature changes across the critical point. Because of the complexity of the structure of polymers and macromolecules acting in such transformations, a clear-cut picture of the state of single components is seldom available. For the case of methyl-cellulose [2], where methyl groups (MGs) are distributed randomly and hetero-geneously along the polymer chain [10], Haque and Morris [11] proposed that chains exist in solution as folded hydrophilic bundles in which hydrophobic MGs are packed. As T is raised, bundles unfold, exposing MGs to water molecules and causing a large increase in volume and the formation of hydrophobic links eventually leading to a gel condensation. The polymers in the folded state are poorly interacting but also yield a smaller entropic contribution than the unfolded ones. A similar behavior has been recently modeled in colloidal systems [12].

Under the assumption that this is one of the mechanisms underlying IT, we model it approximating the folded or unfolded conformation by bosonic spins: $s = 0$ representing inactive state, $s \neq 0$ interacting ones; cf. Refs. [13,14]. To represent the randomness on the position of the "interaction carrying" elements (e.g., MGs) we will introduce quenched disorder. Theoretical modeling for ITs mainly consists of heuristic reproductions of the phenomenon [13,15]. In particular, IF has been recently observed in spin-glass (SG) mean-field Blume-Emery-Griffiths-Capel (BEGC) models [16,17]. We will focus on the random Blume-Capel (BC) model [18], whose mean-field solution [19] predicts a phase diagram with both a SG-PM second order and a first order phase transition (FOPT), i.e., displaying latent heat and phase coexistence [20]. The latter is characterized by the phenomenon of IT [16,21]. This is in contrast with the behavior of the original ordered BC models, in which no IT was observed [22–24], and with the behavior of a 3D BC model with quenched disorder on a hierarchical lattice [25], yielding no IF or first order SG-PM transition. Eventually, to the best of our knowledge, the only claim of the existence of a FOPT in $D = 3$ systems in the presence of quenched disorder has been made for the 4-Potts glass [26]. In that case, though, randomness tends to strongly smooth the transition into a second order one.

Motivated by the above considerations we have, thus, numerically studied the existence of IF in a 3D random BC model with nearest-neighbor (NN) interactions.

Model.—We consider the following Hamiltonian

$$\mathcal{H}_J[s] = -\sum_{(ij)} J_{ij} s_i s_j + D\sum_i s_i^2, \qquad (1)$$

where (ij) indicate ordered couples of NN sites and $s_i = -1, 0, +1$ are spin-1 variables lying on a cubic lattice of size $N = L^3$ with periodic boundary condition. Crystal field D is a chemical potential for the magnetically active sites. Random couplings J_{ij} are independent identically distributed as $P(J_{ij}) = 1/2\delta(J_{ij} - 1) + 1/2\delta(J_{ij} + 1)$. We simulate two real replicas $\{s_i^{(1)}\}$ and $\{s_i^{(2)}\}$ of the system and define the overlap, order parameter of the SG transition, as $q^{(J)} \equiv 1/N\sum_i \langle s_i^{(1)} s_i^{(2)} \rangle$, where $\langle \cdots \rangle$ is the thermal average. If a FOPT occurs, the order parameter characterizing the transition is the density of magnetically active ($|s_i| = 1$) sites: $\rho^{(J)} = 1/N\sum_i \langle s_i^2 \rangle$ or, since we deal with finite size (FS) systems, its distribution $P_{N,J}(\rho)$. The values of the parameters depend on the particular realization of disorder ($\{J_{ij}\}$). Such dependence is self-averaging for the density probability distribution $[P_{N,J}(\rho) \sim P_N(\rho) \equiv \overline{P_{N,J}(\rho)}$ for $N \gg 1]$, but not for the overlap distribution. We denote by $\overline{\cdots}$ the average over quenched disorder.

Finite size scaling (FSS) for continuous transitions.—In order to infer the details of the critical behavior from numerical simulations of FS systems, a fundamental quantity is the four-point correlation function, i.e., the correlation between local overlaps $q_i = s_i^{(1)} s_i^{(2)}$:

$$C_4(r) \equiv \frac{1}{N}\sum_i \overline{\langle q_i q_{i+r} \rangle}. \qquad (2)$$

The information contained in C_4 can be exploited to identify the existence of a second order phase transition for FS systems, e.g., looking at a FS correlation lengthlike scaling function defined, on a 3D lattice, as [27]

$$\xi_c^2 = \frac{1}{4\sin^2 k_1/2}\left(\frac{\hat{C}_4(0)}{\hat{C}_4(k_1)} - 1\right), \qquad (3)$$

where $\hat{C}_4(k)$ is the Fourier transform of $C_4(r)$, $k_1 = |\underline{k}_1|$, and $\underline{k}_1 \equiv (\frac{2\pi}{L}, 0, 0)$ is the minimum wave vector. In the thermodynamic limit, a second order transition is characterized by a diverging correlation length, at critical temperature T_c, whose FSS behavior is the same as in Eq. (3) [28,29]. Another relevant observable is the SG susceptibility $\chi_{SG} \equiv N\overline{\langle q^2 \rangle} = \hat{C}_4(0)$, diverging at the PM-SG transition as $N \to \infty$. Because of FS, though, ξ_c and χ_{SG} cannot diverge in numerical simulations. Around the critical region, however, scale invariance survives. In fact, we can define a FS "critical" temperature T_c^L as the temperature at which the above-mentioned observables do not depend on the size. In this scaling region we have

$$\xi_c/L = \bar{\xi}_c(\xi_c/L) = \bar{\xi}[L^{1/\nu}(T - T_c)], \qquad (4)$$

$$\chi_{SG}L^{\eta-2} = \bar{\chi}(\xi_c/L) = \bar{\chi}[L^{1/\nu}(T - T_c)]. \qquad (5)$$

The critical temperature can, then, be estimated by FSS of T_c^L in the $L \to \infty$ limit.

In order to estimate the critical exponents we use the FSS quotient method [28], based on the observation that at T_c^L the correlation lengths of different linear sizes L and sL (in L units) are equal: $s\xi_c(T_c^L, L) = \xi_c(T_c^L, sL)$. For an observable A diverging as t^{x_A} ($t = T/T_c - 1$) this implies:

$$s^{x_A/\nu} = \frac{A(T_c^L, sL)}{A(T_c^L, L)} + \mathcal{O}(L^{-\omega}). \qquad (6)$$

For a SG we can obtain the exponents ν, η by means of the FSS of the quotients of $\partial_\beta \xi_c$ and χ_{SG}, scaling, respectively, with exponents $x_{\partial_\beta \xi} = 1 + \nu$ and $x_{\chi_{SG}} = (2 - \eta)\nu$.

Characterization of first order transitions.—The Clausius-Clapeyron equation for our model, where D plays the role of a pressure, reads [16]

$$\frac{dD}{dT} = \frac{s_{PM} - s_{SG}}{\rho_{PM} - \rho_{SG}} = \frac{\Delta s}{\Delta \rho}. \qquad (7)$$

When the system undergoes a FOPT, a discontinuous jump in ρ (and, thus, in q) occurs. At finite N, $P_N(\rho)$ displays two peaks in the coexistence region corresponding to PM (ρ_{PM}) and SG (ρ_{SG}) phases. The FS transition line $D_c(N, T)$ can be evaluated as the locus of points where the two phases are equally probable; i.e., the areas of the two peaks are equal [30]:

$$\int_0^{\rho_0} d\rho P_N(\rho) = \int_{\rho_0}^1 d\rho P_N(\rho), \qquad (8)$$

with $\rho_0 \in [\rho_{PM}, \rho_{SG}]$ such that $P_N(\rho_0) = 0$ (or minimal for small N next to the tricritical point).

Exchange Monte Carlo algorithm in T and D.—We simulated the equilibrium dynamics of our model using the parallel tempering (PT) algorithm, replicating the system in T and in D. For the PT in T, the swap probability of two copies between $T = T$ and $T + \Delta T$ is $P_{swap}(\Delta\beta) = \min[1, \exp\{\Delta\beta\Delta\mathcal{H}\}]$. Between D and $D + \Delta D$, it reads $P_{swap}(\Delta D) = \min[1, \exp\{\beta\Delta D\Delta\rho\}]$. We used the latter to identify the reentrance of the transition line in the T, D phase diagram; cf. Fig. 1.

We studied 3D systems with PT in T at $D = 0, 1, 1.75, 2, 2.05, 2.11$, and in D at $T = 0.2, 0.3, 0.4, 0.5$. At all D we simulated from 33 to 40 replicated thermal baths N_T at linear size $L = 6, 8, 10, 12$ (number of disordered sample, $N_J = 2000$). For $D = 0, 1, 1.75, 2$, we simulated $N_T \in [20:33]$ at $L = 16, 20$ ($N_J \in [900:1500]$) and $N_T \in [17:22]$ at $L = 24$ ($N_J \in [500:1000]$). For the PT cycles in D, $N_D \in [21:37]$, parallel replicas at different D were simulated, of $L = 6, 8, 10, 12$, and 15 ($N_J = 1000$). In the latter case varying ΔD were used, larger in the pure phases and progressively smaller approaching the coexistence region. The number of Monte Carlo steps varies from 2^{15} to 2^{21} according to L and to the lowest values of T, D reached. We checked thermalization looking at (i) the symmetry of the distributions $P_{N,J}(q)$, (ii) the t-log behavior of the energy (coincidence of the last two points), and (iii) the lack of variation of each observable (e.g., ξ, χ_{SG}) on logarithmic time windows.
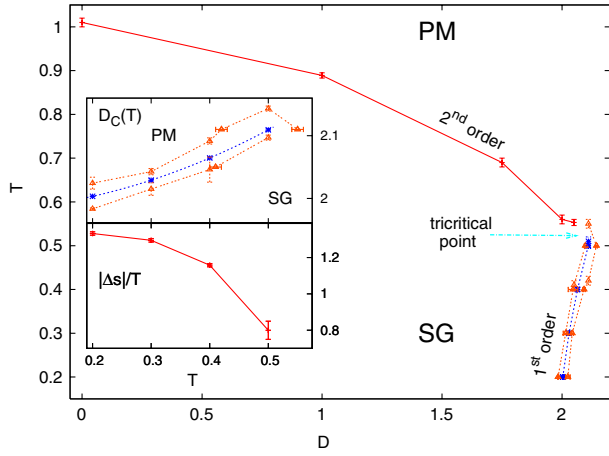
FIG. 1 (color online). Phase diagram in D, T: second order transition and an inverted FOPT occur. In the latter case also the spinodal lines are reported [gray (red) dashed lines]. Bottom inset: Latent heat $|\Delta s|/T$ along the first order line. Top inset: Detail of IF region, interpolation of transition line $D_c(\infty, T)$ [black (blue) dotted line], spinodal lines [gray (red) dashed line]. The error bars are the FSS of the minimal interval in T and D at each L needed to identify the crossings in ξ_c/L curves (for continuous transitions) or compare the areas under $P_N(\rho)$ for FOPT.

Numerical results.—In Fig. 2 we present the T behavior of ξ/L for $D = 0, 1, 2, 2.11$. From the FSS analysis of their crossing points we can determine the critical temperature and, applying the quotient method [cf. Eq. (6) with $s = 2$], we obtain estimates for the critical exponents: $\nu = 2.44(6)$, $\eta = -0.34(2)$ at $D = 0$, $\nu = 2.4(2)$, $\eta = -0.31(2)$ at $D = 1$, $\nu = 2.1(2)$, $\eta = -0.27(2)$ at $D = 1.75$. The system appears to be in the same universality class of the Edwards-Anderson model, corresponding to the $D = -\infty$ limit of our model [28,31,32]. For $D = 2$, near the tricritical point ($0.5 \lesssim T \lesssim 0.54$, $2.05 \lesssim D \lesssim 2.11$), the quotient method does not yield reliable estimates because of a crossover in the scaling functions in the range of probed sizes ($L = 6$–24). This comes about because at the tricritical point the coefficient of the fourth order term in the SG free energy action goes to zero and the sixth order term becomes relevant for the critical behavior [19], a typical behavior of BEGC-like systems [33].

At $D = 2.11$ no evidence is found for a second order phase transition whereas a FOPT is observed at $T = 0.51(1)$. This is also the reason why, as shown in the bottom right-hand panel of Fig. 2, ξ_c/L decays for $T \lesssim 0.51$.

The FOPT is determined by looking at $P_L(\rho)$ as two peaks appear and computing the (D, T) points satisfying Eq. (8). A pure phase corresponds to a single-peaked distribution, whose peak is narrower for larger systems. In Fig. 3 we show the behavior of the $P_{15}(\rho)$ through the FOPT in D at $T = 0.4$ [34]. A detail of the FSS limit of the IT line $D_c(T)$ and of the spinodal lines is plotted in the top inset of Fig. 1. The FS spinodal lines are estimated by looking at the D values at which a secondary peak first arises.
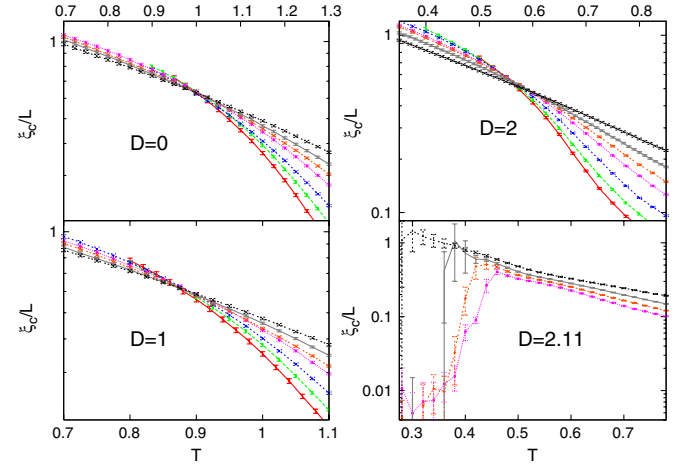

FIG. 2 (color online). Scaling functions ξ_c/L vs T for different values of the chemical potential D. For $D = 0, 1, 2$ ($L = 6, 8, 10, 12, 16, 20, 24$) a continuous phase transition is found in the region of scale invariance. At $D = 2.11$ ($L = 6, 8, 10, 12$) no crossing is observed and at low T, $\xi_c/L \to 0$.

Using Eq. (7), from the knowledge of $\Delta\rho$ and the estimate of dD/dT by numerical interpolation we compute the latent heat $|\Delta s|/T = (s_{SG} - s_{PM})/T$ employed in the transition, cf. bottom inset of Fig. 1: as T increases, the PM acquires latent heat to vitrify; SG entropy is higher than s_{PM} and the "frozen" phase is found at a higher T than the fluid one. The IF takes place between a SG of high density to an almost empty PM (e.g., at $T = 0.4$, in the coexistence region $D \in [2.046(2):2.092(5)]$, $\rho_{SG} \simeq 0.52$ and $\rho_{PM} \simeq 0.03$). The few active sites do not interact with each other but only with inactive neighbors, and this induces zero magnetization and overlap. The corresponding PM phase at high T has, instead, higher density [e.g., $\rho_{PM}(D = 2, T = 0.6) = 0.4157(2)$, $\rho_{PM}(D = 2.11, T = 0.6) = 0.596(2)$], and the paramagnetic behavior is brought about
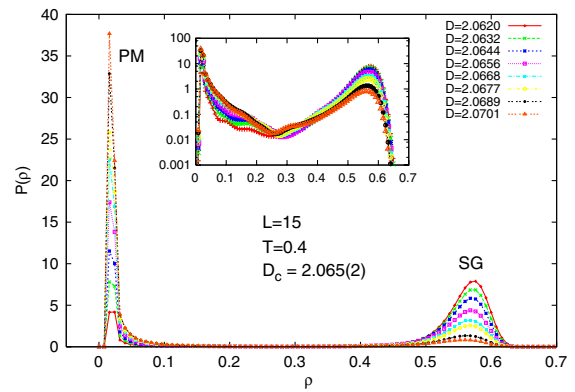

FIG. 3 (color online). Density distribution $P_L(\rho)$, $L = 15$, across the coexistence region at $T = 0.4$: two peaks develop at ρ_{PM} and ρ_{SG}. As D increases, the thermodynamically relevant phase (lowest free energy) passes from SG to PM in a first order phase transition. The dominant phase corresponds to the one with larger probability, i.e., larger integral of the peak. As the peak at ρ_{SG} vanishes, the system is in a purely PM phase. Inset: $P_{15}(\rho)$ on y-log scale.

by the lack of both magnetic order (zero magnetization) and blocked spin configurations (zero overlap).

Conclusions.—We focused on a spin-1 SG model on a 3D cubic lattice, whose features try to capture a mechanism underlying IT: the rise of inactive components at low T. We provide numerical evidence for an equilibrium inverse freezing phenomenon: at given values of an external field, heating up a paramagnet this is transformed into a SG. The whole phase diagram in temperature T and crystal field D has been studied both along the continuous transition line, where critical exponents are computed, and in the coexistence region, where FOPT line, latent heat curve, and spinodal lines are reported. This latter observation confirms the claim of Fernàndez *et al.* [26] about the existence of such transitions in quenched disordered short-range finite-dimensional systems. In the present model the FOPT can be seen by means of standard PT in the canonical ensemble, simply tuning an external pressure-elike parameter [35]. In addition to the peculiarity of FOPT, inverse freezing is also observed, for the first time, in a random short-range finite dimension system. Both features were absent in the same model on a hierarchical lattice [25], and in the ordered BC model no IT was observed [23,24].

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