Microphase Separation and modulated phases in a Coulomb frustrated Ising ferromagnet

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Abstract. – We study a 3-dimensional Ising model in which the tendency to order due to short-range ferromagnetic interactions is frustrated by competing long-range (Coulombic) interactions. Complete ferromagnetic ordering is impossible for any nonzero value of the frustration parameter, but the system displays a variety of phases characterized by periodically modulated structures. We have performed extensive Monte-Carlo simulations which provide strong evidence that the microphase separation transition between paramagnetic and modulated phases is a fluctuation-induced first-order transition. Additional transitions to various commensurate phases may also occur when further lowering the temperature.

In a variety of systems a tendency to order induced by short-range interactions is frustrated by long-range competing effects. In diblock copolymer melts, cross-linked polymer mixtures and interpenetrating networks, short-range forces between mutually incompatible components would drive a phase transition at low enough temperature, but total segregation is forbidden by constraints due to covalent bonds or crosslinks. Instead, a microphase separation transition may occur, where the system forms phases with periodically modulated structures such as lamellar, hexagonal, or cubic phases[1, 2, 3]. Similarly, self-assembly in water-oil-surfactant mixtures results from the competition between the tendency of oil and water to phase separate and the stoichiometric constraints due to the presence of the surfactant molecules that act as the electroneutrality condition in a system of charged particles[4, 5]. In supercooled liquids, the dramatic slowing down of the structural relaxation which leads to the glass transition has been ascribed to the presence of frustration-limited domains whose formation comes from the inability of the locally preferred arrangement of the molecules in the liquid to tile space periodically[6]. Others examples include frustrated phase transition in doped antiferromagnets[7] and metal-ammonia solutions[8], or else pattern formation in various nonequilibrium systems[9].

The physics of the above mentioned situations appears to be reasonably well described by lattice or continuum models in which both short-range ordering and long-range Coulombic...
frustrating interactions are present. In this letter, we consider a Coulomb frustrated Ising ferromagnet whose Hamiltonian is given by

$$H = -J \sum_{<i,j>} S_i S_j + \frac{Q}{2} \sum_{i \neq j} \frac{S_i S_j}{r_{ij}},$$

(1)

where $J, Q > 0$, $S_i = \pm 1$, $<i,j>$ indicates a sum restricted to nearest neighbors, and $r_{ij}$ is the distance between the sites $i$ and $j$ on a three-dimensional cubic lattice. The two main questions that we address here by combining analytical results and Monte-Carlo simulations are the following: (i) what is the nature of the microphase separation transition from the paramagnetic to the “modulated” phases and how does it vary with varying frustration, i.e. varying ratio $Q/J$? (ii) What is the nature of the modulated phases?

The mean-field approximation to the Coulomb frustrated model is easily derived. We introduce $\tau_k(Q)$ as the Fourier transform of the full pair interaction potential in Eq. (1), e.g., for small wave vectors and a $3-d$ cubic lattice, $\tau_k(Q)$ is approximatively given by

$$\tau_k(Q) \simeq -6 + \Delta(k) + \frac{4\pi Q}{\Delta(k)} \left(1 + b \Delta(k) + c \sum_{\alpha=x,y,z} \Delta^2(k_\alpha) \Delta^2(k_\alpha) + \cdots\right),$$

(2)

where $\Delta(k) = \sum_{\alpha=x,y,z} \Delta(k_\alpha) = 2 \sum_{\alpha=x,y,z} (1 - \cos(k_\alpha))$ is the Fourier transform of the lattice Laplacian, $b$ and $c$ are constants, and $J$ has been set equal to 1. For $Q \neq 0$, $\tau_k(Q)$ attains its minimum, $\tau_m(Q) = \min_k \{\tau_k(Q)\}$, for a set of nonzero values of the wave vector, $\{k_m(Q)\}$. The mean-field treatment predicts the occurrence with decreasing temperature of a second-order phase transition at $T_c(Q) = -\tau_m(Q)$; $T_c(Q)$ goes continuously to $T_c^0$, the critical temperature of the unfrustrated ferromagnet, as $T_c^0 - T_c(Q) \sim Q^{1/2}$ when $Q \to 0$. At the transition, the ordering is characterized by a nonzero wave vector, corresponding to one of the $k_m(Q)$’s, which for small enough values of $Q$ is zero in two directions and behaves as $Q^{1/4}$ in the third one. The mean spherical version of Eq. (1), in which the spins are taken to be real numbers with the global constraint that their mean square value is equal to one, leads to a quite different behavior. The most significant feature is the existence of an “avoided” critical point at $T_c^0$. The microphase separation transition is again of second-order and the ordering wave vector is one of the $\{k_m(Q)\}$’s; but the critical temperature is now given by $T_c^{-1}(Q) = \int d^3k/(2\pi)^3 (\tau_k(Q) - \tau_m(Q))$, and when $Q \to O^+$ it goes to a temperature which is much less than $T_c^0$. Actually, within the mean spherical treatment, the transition is very sensitive to the form of the long range interaction: whereas a $1/r$ interaction leads to $T_c(Q) > 0$, a slightly different form obtained by retaining only the leading $1/\Delta(k)$ term in Eq. (2) drives $T_c(Q)$ to zero for $Q < 16$. This latter feature results from the fact that the minimizing wave vectors $k_m(Q)$ form a $2-d$ surface in $k$-space (they form a finite set for the $1/r$ interaction). A similar feature is encountered in the Landau-Ginzburg-Wilson Hamiltonian that describes symmetric diblock copolymers. It has been argued by Brazovskii, on the basis of a self-consistent Hartree approximation, that such systems display a fluctuation-induced first-order transition that takes place at a nonzero temperature $T_0(Q)$, with $T_0 - T_0(Q) \sim Q^{1/4}$ when $Q \to O^+$. Additional support to this prediction has been given by renormalization group analyses.

In order to check the relevance of these various predictions, we have performed extensive Monte-Carlo simulations of the $3-d$ dimensional Coulomb frustrated Ising ferromagnet. Our results provide, we believe for the first time, direct numerical evidence supporting the Brazovskii scenario of a fluctuation-induced first-order transition for such a model. The simulations have been done for many values of the frustration parameter $Q$. Long-range interactions lead to
very time-consuming runs and we have considered lattices of $L^3$ sites for $L$ ranging from 4 to 24 with periodic boundary conditions (anisotropic lattices of various sizes up to $12 \times 12 \times 30$ have been also used). To treat properly the Coulomb interactions Ewald sums have been used; the site-site pair terms are calculated once for all at the beginning of the run and are stored in an array for the entire run: therefore, a large number of reciprocal vectors can be included in the Ewald sum to ensure a very good accuracy for the calculation of the Coulomb potential. The constraint of zero total magnetization has been enforced by always considering the simultaneous flip of a pair of up and down spins (note that the presence of long-range interactions and the relatively fast equilibration for system sizes studied reduce the advantage of considering cluster algorithms). Each run consists then of $2-6 \times 10^4$ Monte-Carlo Sweeps (MCS) per lattice site for equilibration followed by $6 \times 10^4 - 10^5$ MCS to calculate the equilibrium quantities. In order to verify that the equilibrium state is indeed reached and that the results do not depend upon the initial configuration, each run is performed by starting both from a high-temperature configuration and from the ground state.

In Fig. 1, we display the microphase separation transition from paramagnetic to modulated phases in the (scaled) temperature-frustration diagram for a dozen of values of $Q$. Also shown on the same diagram are the mean-field and mean-spherical predictions. Transitions associated with very small values of $Q$ are of course inaccessible to simulations in finite-size boxes (at least two lamellae characterized by opposite magnetizations must be present in the simulation box to satisfy the constraint of zero total magnetization, which limits the width of the lamellae and by consequence the smallness of the frustration); however, the results are compatible with a power-law behavior,

$$T^0_c - T_0(Q) \sim Q^\kappa$$

with $\kappa \simeq 0.25 - 0.35$, and the period of the lamellar structures is in good agreement with

$$2\pi/|k_m(Q)|.$$ As stressed before, the transition is first-order. To locate the transition and determine its order, we have monitored as a function of both decreasing and increasing temperature the heat capacity $C_v = \langle (E - \langle E \rangle)^2 \rangle$ and the Binder cumulants; we have also studied the (potential) order parameter $|M_k| = \langle |S_k| \rangle$, where $S_k$ is the Fourier transform of the spin variable along the three directions of the lattice. Results for $Q = 0.4$ are shown in Fig. 2. A hysteresis loop between heating and cooling runs is observed in $E$ versus $T$ (Fig. 2a), and the distribution of the energy histograms around the transition temperature $T_0$ exhibits a forbidden region for the energy (Fig. 2b); they both indicate a first-order transition. Also supporting this conclusion is the apparent jump in the order parameter and the strong system size-dependence of the heat capacity (e.g. $\max_T C_v(T) \sim L^p$ with $p > 1$). Similar behavior is observed for the other values of $Q$. However, the transition becomes more and more weakly first-order as the frustration decreases.

To provide a more complete investigation of the phase diagram, we have also studied analytically and numerically the $T = 0$ properties of the system. In doing so, we have assumed, as indeed observed in our Monte-Carlo simulations and also in several related two-dimensional models\[3, 4\] and in the three-dimensional Ising model with dipolar competing interactions\[4\], that the ground states consist in periodically modulated structures. When $Q \to +\infty$ the ground state is an anti-ferromagnetic (Néel) state ($1 \times 1 \times 1$) and it is stable for $Q \geq 15.3$. For $15.3 \geq Q \geq 14.6$, the system passes though a succession of "anisotropic checkerboard" phases of the form $(1 \times 1 \times n)$ with $n$ a positive integer. A "tubular" phase $(1 \times 1 \times \infty)$ is stable for $14.6 \geq Q \geq 6.2$, and in a narrow range of $Q (6.2 \geq Q \geq 5.2)$, one obtains a second infinite sequence of $(1 \times n \times \infty)$ phases. For smaller values of $Q$, the ground state is found by lamellar phases whose width increases with decreasing $Q$. We have checked that
more complicated phases involving mixtures of lamellae with different widths are not stable at zero temperature. When $Q \to 0$ and for the purpose of calculating the energy, the Fourier transform of the Coulomb potential can be well approximated by $1/\Delta(k)$. For a lamellar phase of period $2m$ in the $z$-direction, the only nonzero values of $|S_k|$ are for $k = (0, 0, k_z)$ and $|S_{k_z}| = 1/(m \sin(k_z/2))$ with $k_z = \pi(2n + 1)/m$ and $n = 0, ..., m - 1$. Therefore, after some calculation, one obtains an explicit expression for the corresponding energy per spin,

$$E(m) = -J(3 - 2/m) + Q \left( \frac{\pi}{6} m^2 + \frac{\pi}{3} \right),$$

showing that the lamellar width $m$ goes as $(\pi Q/6)^{1/3}$ when $Q \to 0$. This dependence is analogous to that derived for symmetric diblock copolymer systems in the so-called strong segregation limit\cite{1, 2}, whereas the behavior at the transition line to the paramagnetic state rather corresponds to the weak-segregation limit result\cite{1, 2}.

At nonzero temperatures, one may expect that the system undergoes a series of transitions to various commensurate, and at temperatures close to $T_0(Q)$ incommensurate, phases just like in the ANNNI model\cite{16}. Such a behavior is indeed observed in the mean-field theory\cite{9}, but a sequence of modulated phases is hard to detect in Monte-Carlo simulations of finite-size systems. We have focused our study on $Q = 0.144$ for which the ground state is a lamellar structure of half-period 2 and the ordering at the microphase separation transition is characterized by a modulation half-period close to 2.5. (Other modulations could also occur at intermediate temperatures.) To observe at least these two types of order in a simulation where only restricted values of the wave vectors are allowed, we have used anisotropic lattices. For instance, with a $12 \times 12 \times 24$ lattice, phases with modulation of half-period of 2.4 are allowed in the $z$-direction. Figure 3 illustrates at the level of the order parameter $|M_k|$ the passage from the low-temperature state formed by periodic lamellae of width 2 ($k_z = \pi/2$) to a mixed or incommensurate phase characterized by an average half-period of 2.4 ($k_z = 5\pi/12$) for $1.85 \leq T \leq 1.75$. For $T \geq 1.85$, the system is disordered and all components of $|M_k|$ are zero. Corresponding spin configurations are displayed in Fig.4.

In this letter, we have studied the properties of the microphase separation transition and of the modulated phases observed in a three dimensional Coulomb frustrated Ising model.
Fig. 2. – Monte-Carlo results for (a) the total energy per spin $E$ as a function of $T$ (open and filled circles correspond to heating and cooling runs, respectively); (b) energy histograms around $T = 1.5$ (full line in (a)) for a frustration parameter $Q = 0.4$.

Fig. 3. – Variation with $T$ of the $|M_k|$ with $k = (0,0,k_z)$ for (a) $k_z = \pi/2$ and (b) $k_z = 5\pi/12$ from the Monte-Carlo simulations (for $Q = 0.144$ and a box size $=12 \times 12 \times 24$). The microphase separation transition occurs for $T_0 \simeq 1.84$ and it is signaled by the appearance of a nonzero value of $|M_{k_z}|$ for $k_z = 5\pi/12$. At a lower temperature $T \simeq 1.77$, a second transition occurs to a lamellar phase characterized by a nonzero $|M_{k_z}|$ for $k_z = \pi/2$ (all other $M_k$’s are zero).

Our Monte-Carlo results provide strong evidence that the transition from the paramagnetic phase is a fluctuation-induced first-order one, in contrast to the Ising ferromagnet with dipolar interactions for which the transition is second-order[15]. The only (second-order) critical point in the temperature-frustration phase diagram is at $T_c^0$. The transition line approaches $T_c^0$ from below in a nonanalytic fashion as $Q \kappa$ with $\kappa \sim 0.25 - 0.35$, avoided critical behavior can still dominate the physics of weakly frustrated system above the transition line, thereby leading to frustration-limited domain structures in this region. Additional simulation studies of the paramagnetic state will however be necessary to confirm this prediction. We have also shown that the model gives rise to a variety of modulated phases whose characteristics vary both with temperature and frustration. The Laboratoire de Physique Théorique des Liquides is UMR No 7600 au CNRS. We are grateful to D. Kivelson, S. Kivelson, Z. Nussinov, A. Lesne,
Fig. 4. – Spin configurations corresponding to the different phases observed in the Monte-Carlo simulations at $Q = 0.144$ (box size $12 \times 12 \times 24$): (a) disordered (paramagnetic) phase, (b) modulated phase with averaged half-period of 2.4 lattice units; (c) lamellar structure with a half-period of 2 (this is also the ground state). Up and down spins are represented by diamonds and dots, respectively.

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