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Perturbative density functional theory for phase transitions in a two-dimensional antiferromagnetic fluid

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We study the temperature-density phase diagram of a fluid in two dimensions consisting of hard disks which, in addition, possess an internal (Ising) spin degree of freedom. The Ising spin of each disk couples with those of its neighbors via a short-ranged antiferromagnetic (AF) interaction. Recent Monte Carlo simulations have shown that this system undergoes a gas-liquid transition followed by a gas–AF-ordered-square-solid sublimation transition at low temperatures. Using a perturbative density functional approach we obtain, in addition to the observed transitions, a freezing transition at high density to a frustrated triangular solid phase. Interestingly, the calculated phase diagram suggests that at low temperatures, this transition is suppressed so that over a range of parameters, the system refuses to crystallize. [S1063-651X(97)07902-6]

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In this Brief Report we present a density functional [1,2] theory for phase transitions in a system of hard disks in two dimensions with Ising internal states which couple antiferromagnetically to their neighbors. This antiferromagnetic (AF) fluid, which is essentially equivalent to an ordering binary alloy studied [3–5] in an ensemble where the chemical potential difference of the two species is held fixed and equal to zero, is expected to have a rich phase diagram due to an interplay between the tendencies to order and to pack as densely as possible. In two dimensions the closest packed structure is a triangular lattice, which, however, cannot show an Ising antiferromagnetic transition because of frustration effects. Monte Carlo results [6] show the presence of a gas-liquid transition driven by short-ranged AF order in the liquid, followed by a gas–almost-fully-AF-ordered-*square*-solid transition at low temperatures. The antiferromagnetic interaction therefore favors an ordered square lattice solid over a disordered triangular lattice at low temperatures. At high density, the effects of close packing are expected to be dominant and at the close packing density the triangular solid is expected to be the stable phase at all temperatures. Indeed, a study of the competition between these effects promises to be interesting.

We describe below a calculation where the effects of short- and long-range AF order have been kept perturbatively over the hard disk contribution to yield a complete phase diagram of this system. Our calculated phase diagram (see Fig. 1) shows stable regions corresponding to all the phases seen in the simulation [6]. For low temperatures and high densities we obtain an intriguing suppression of the freezing transition to the triangular solid within our perturbative calculation. This may signal a breakdown of standard perturbation theory in this regime, leading to the interesting possibility of the presence of nontrivial (and nonperturbative) phases without long-ranged positional order.

To begin, consider the following N-particle Hamiltonian for the AF fluid:

$$H=-\sum_{i<j}^{N} J(\mathbf{r}_i-\mathbf{r}_j)S_iS_j+\sum_{i<j}^{N} U(\mathbf{r}_i-\mathbf{r}_j), \tag{1}$$

where $U(r)$ is the hard disk potential for particles of diameter σ, S_i are spin variables ($S_i=\pm 1$), and $J(r)$ is given by

$$J(r)=\begin{cases} -\epsilon, & \sigma<r<\Delta \\ 0, & r>\sigma. \end{cases} \tag{2}$$

For Δ we chose the value $\Delta=1.4\sigma$ which restricts the AF interaction to nearest neighbors thus eliminating complications due to frustration in the AF-ordered square lattice structure. The strength of the AF interaction ϵ fixes the energy scale of the problem and the hard disk diameter σ supplies a

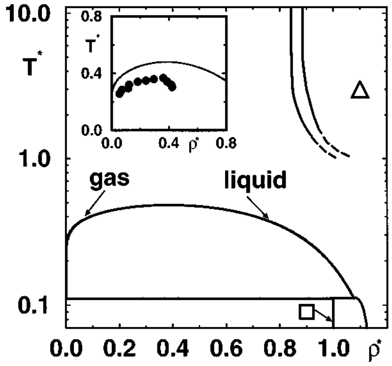

FIG. 1. Temperature (T^*) and density (ρ^*) phase diagram of the antiferromagnetic fluid as obtained from density functional theory. The square lattice has density $\rho^*=1$ and is denoted by □. The region where the triangular lattice is stable is denoted by △. The dotted lines represent the extrapolated coexistence boundary between the liquid and the triangular lattice. Our perturbative density functional theory breaks down for low temperatures and high densities so that we do not observe a freezing transition in this range of values for T^* and ρ^*. Inset shows our calculated gas-liquid phase boundary together with Monte Carlo results from Ref. [6]. The Bethe-Peierls approximation overestimates the short-range AF ordering in the fluid, leading to a higher gas-liquid critical point temperature. The horizontal line is the triple line.

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length scale. The full interaction between the disks thus consists of a hard disk part and a square-well (step) part if the spins point in opposite (same) directions.

Within the density functional formalism [1] the Helmholtz free energy per unit volume at temperature $T^{*}:=T/\varepsilon=\beta^{-1}/\varepsilon$ and density $\rho^{*}=\rho\sigma^{2}$ is taken to be a functional of the time averaged number density $\rho(\mathbf{r})$. The equilibrium value of this free energy is obtained by minimizing this functional for choices of $\rho(\mathbf{r})$. For magnetic systems which show long-ranged magnetic order, this functional was generalized [7] to include the magnetization density $m(\mathbf{r})$ such that, in addition, one needs to minimize in the space of $m(\mathbf{r})$ also. In general, we decompose the free energy of the fluid and the solids into the reference hard disk part, $f_{\mathrm{HD}}([\rho])$, and terms containing the contribution of the magnetic interaction. Perturbative treatments of attractive interactions are known to yield essentially correct results for the freezing transition of Lennard-Jones [8] and square-well [9] fluids. We discuss below this perturbative density functional theory for the fluid, triangular solid, and the square solid, respectively.

In contrast to the ferromagnetic case [10,11,7], the inclusion of the magnetic interactions for the AF system is nontrivial. The main difference lies in the fact that the fluid and the triangular solid phases *do not* possess long-ranged AF ordering [6]. However, the effect of short-range AF order in both the fluid and the triangular solid is expected to be important. In the former case, this leads to a liquid-gas transition as observed in Monte Carlo simulations [6]. A mean field treatment for the magnetic part, on the other hand, will completely neglect this effect. In order to include the free energy contribution of local short-ranged AF ordering, we would have to go beyond mean field theory. For the fluid case this may be achieved by going over one order higher in a systematic, but approximate, cluster expansion [12] and using a Bethe-Peierls [13] formalism to keep the dominant nontrivial contribution from short-ranged AF order. In the spirit of the ferromagnetic calculation [11,7] we use

$$\beta f_{f}(\rho)=\rho^{*}\ln[\rho^{*}]-\rho^{*}-\rho^{*}\ln[1-\eta]+\rho^{*}\frac{\eta}{[1-\eta]} -\rho^{*}\ln[\cosh(\beta\varepsilon)]J_{\mathrm{eff}}, \qquad (3)$$

where the packing fraction $\eta=\pi\rho^{*}/4$ in two dimensions and the effective interaction strength in the fluid can be approximated by $J_{\mathrm{eff}}=\int_{\sigma}^{\sigma+\Delta}d^{2}r\rho g(r)$ with $g(r)$ taken to be the pair distribution function of the *reference* hard disk fluid. For the calculations reported in this paper, we have obtained this quantity by numerically Fourier transforming the accurate and convenient analytic form for the Ornstein-Zernike direct correlation function [14] for the hard disk fluid in two dimensions due to Rosenfeld [15].

In the case of the triangular solid the magnetic contribution to the free energy is somewhat more accurately known. The Ising AF interaction is frustrated in a triangular lattice at any nonzero temperature. The triangular lattice, like the fluid, has only short-ranged AF correlations. As the temperature is lowered these short-ranged AF correlations diverge, leading to a zero temperature phase transition in the nearest neighbor Ising AF model on a perfect triangular lattice [16]. In our case, since the pair interaction range is limited to nearest neighbors we may use the *exact* expression for the excess free energy due to these short-ranged AF correlations for the nearest neighbor AF Ising model on a triangular lattice [16,17],

$$\beta f_{t}([\rho])=\beta f_{\mathrm{HD}}([\rho])+\rho^{*}\ln(2)-\rho^{*}\ln(e^{-3\beta\varepsilon}+e^{\beta\varepsilon}) +\rho^{*}\frac{1}{8\pi^{2}}\int_{0}^{2\pi}\int_{0}^{2\pi}\ln\{1+2\kappa[\cos\omega_{1}+\cos\omega_{2}+\cos(\pi-\omega_{1}-\omega_{2})-1]\}d\omega_{1}d\omega_{2}, \qquad (4)$$

where we have subtracted the high temperature entropy [ln(2)] from the magnetic part, and $\kappa=(\exp[-4\beta\varepsilon]-1)/(\exp[-4\beta\varepsilon]+1)^{2}$.

The square lattice exists only at extremely low temperatures. In addition, we find that the square lattice is almost completely AF ordered. In this case we expect a mean field treatment of the magnetic part to be exact. The unfrustrated, nearest neighbor AF square solid, however, maps exactly to its ferromagnetic counterpart which has been studied earlier in Ref. [7] within a mean field approach. To simplify the calculation, we have here further restricted the average density of the square lattice to $\rho^{*}=1$. This is justified by the observation that the square lattice in the, equivalent, ferromagnetic case [7], was found to be stable only for a tiny region centered around density $\rho^{*}=1$. The free energy functional in this approximation is given by

$$\beta f_{s}([\rho])=\beta f_{\mathrm{HD}}([\rho])+\frac{\beta}{2}\int\frac{d\mathbf{r}}{V}m(\mathbf{r})\xi_{m}(\mathbf{r}) -\int\frac{d\mathbf{r}}{V}\rho(\mathbf{r})\ln[2\cosh\{\beta\xi_{m}(\mathbf{r})\}]. \qquad (5)$$

The integrals are over the full two-dimensional ''volume'' V. The magnetic molecular field $\xi_{m}(\mathbf{r})$ is given by $\xi_{m}(\mathbf{r})=-\int d\mathbf{r}'m(\mathbf{r}-\mathbf{r}')J(\mathbf{r}')$. The staggered magnetization density $m(\mathbf{r})$, for the antiferromagnetic case that we consider here, is proportional to the number density, i.e., $m(\mathbf{r})=\pm m_{0}\rho(\mathbf{r})$, where the number m_{0} determines the staggered magnetization of the lattice at any temperature and density and has to be obtained self-consistently.

For the hard disk contribution to the free energy for the solid phases, we use the functional $\beta f_{\mathrm{HD}}([\rho])$ of the *nonuni-*

form density $\rho(\mathbf{r})$. In this calculation, for the hard disk free energy functional we have used the Ramakrishnan-Yussouff functional [1] in the form introduced by Ebner, Krishnamurthy, and Pandit [18]. Using any other free energy functional [1] for the hard disk part gives more or less identical results as long as it reproduces the two-dimensional hard disk freezing transition (for $T^* \to \infty$) accurately. For both the solids, the free energy functional needs to be minimized with respect to choices of (nonuniform) densities $\rho(\mathbf{r})$ to obtain the Helmholtz free energies of the solid phases. For the AF square lattice, in addition, one has to minimize the free energy functional Eq. (5) with respect to choices of m_0. To this end, we approximate the one body density $\rho(\mathbf{r})$ at position $\mathbf{r}$ by a set of nonoverlapping Gaussians with width α/a^2 centered on lattice sites $\mathbf{R}$ in a lattice of lattice parameter a:

$$\rho(\mathbf{r}) = \frac{\rho_0 A_n \alpha}{a^2 \pi} \sum_{\mathbf{R}} \exp[-\alpha(\mathbf{r}-\mathbf{R})^2/a^2], \tag{6}$$

where ρ_0 is the average density of the solid and A_n denotes the area of the unit cell. This ansatz for the density now reduces the free energy functional to a *function* of α (and in addition, m_0 for the square lattice structure). The global minimum of this function in the space of α (and m_0, if applicable) for a choice of $\{\mathbf{R}\}$ gives the Helmholtz free energy of the chosen lattice. Knowing the free energies of the fluid from Eq. (3), triangular solid [Eq. (4)], and the square solid [Eq. (5)] one can construct the full phase diagram in the temperature-density plane after obtaining the coexistence densities (by constructing the convex hull—''Maxwell's construction'') at any given temperature.

Our central result, the phase diagram of Hamiltonian (1), is presented in Fig. 1. We obtain a gas-liquid coexistence region with a critical point at temperature $T_c^* = 0.47$ and density $\rho_c^* = 0.4$, which is somewhat higher than the Monte Carlo results of Ref. [6]. This is due to the fact that the Bethe-Peierls approximation for short-ranged correlations in the AF fluid overestimates the effect of these correlations. It is well known [19,20] that the convergence of cluster [12] expansions for lattice models with competing interactions is poor and oscillatory. At high temperature the magnetic part in the Hamiltonian becomes less important and the fluid freezes to a triangular solid without AF order with freezing parameters ($\rho_f^* = 0.84$) which are in good agreement with results obtained in previous studies [21,22] for the freezing of hard disks. When the temperature is lowered, however, the AF interaction becomes more and more important. Since the AF interaction is frustrated in the triangular lattice, there is no additional incentive for the system to freeze so that the coexistence densities *increase* with decreasing temperature. For temperatures below $T^* = 1.5$ the frustration effects become so pronounced that the triangular solid structure becomes metastable and we fail to observe freezing. However, at these low temperatures and high densities most probably our approximation for the fluid phase is untenable (the free energy has been extrapolated for densities above $\rho^* = 0.875$, which is above the hard disk freezing density). We comment on this aspect below.

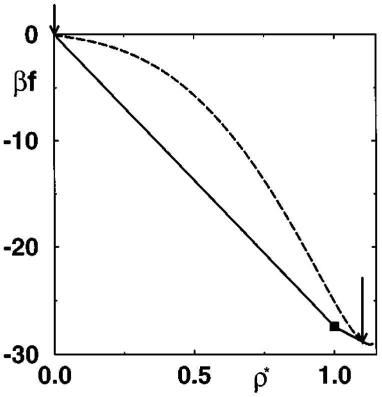

FIG. 2. Free energy versus density at $T^* = 0.1$ in the case of gas–square-solid coexistence. The square-solid density is fixed at $\rho^* = 1$, see text, the square-solid free energy is marked by a filled square, and arrows show the coexistence densities for the gas–square-solid coexistence and for the square-solid–liquid coexistence. The dashed line is the fluid free energy, the solid line is the convex envelope of the free energies (fluid and square solid).

At low temperatures the stability of a square lattice structure at fixed density $\rho^* = 1$ is examined. At temperature below $T^* = 0.11$ we find stable free energy minima [Eq. (5)] with realistic values for the Gaussian width parameter $\alpha > 10$ so that the density $\rho(\mathbf{r})$ consists of nonoverlapping Gaussians centered on lattice sites. The square lattice structure is stabilized solely by the appearance of the staggered magnetization due to the AF interaction. The coexistence densities to the gas phase and the high density liquid phase were computed with the double tangent construction (see Fig. 2). Interestingly, the square lattice phase is found to be in coexistence with a low density gas for $\rho^* < 1$ and a high density liquid phase for $\rho^* > 1$ in this temperature range whereas the triangular solid phase is consistently metastable. This is in direct contrast to the ferromagnetic case [7] where the square lattice structure was seen to be in coexistence with a low density gas and a triangular solid.

Our study thus raises the following interesting question: What happens to an AF fluid at low temperatures and high densities? Although the initial increase of the coexistence densities for the fluid to triangular solid freezing transition can be understood in terms of frustration effects in the triangular solid, it is possible that the effects of AF correlations are being incorrectly estimated within our theory at high densities and low temperatures. One way to improve upon the Bethe-Peierls treatment (in this range of temperature and density) for the short-ranged correlations is the inclusion of higher order clusters. However, for fluids this procedure is severely restricted by the fact that nontrivial higher order distribution functions of the fluid which are required in order to carry out such a calculation are not known. In order to get a feel for the importance of these higher order correlations for the relative stability of the fluid and the triangular solid phases, we have repeated the calculation with a Bethe-Peierls approximation of the short-ranged correlations in the triangular solid. This produces, however, an incorrect phase diagram where the gas-liquid critical point is metastable and at high densities the triangular solid remelts. The answer may also lie in the way the short-ranged AF correlations are accommodated by the fluid. Namely, it is possible that in this range of T^* and ρ^* the system may not tend to remain either a liquid or a triangular solid, but may make use of the short-ranged AF correlations by going over to a *tetratic* structure [23] with no long-ranged positional order but with strong fourfold long-ranged orientational order. An equilibrium structural ‘‘glass’’ may be another possibility. Indeed, analogous *pressure induced amorphization* transitions are experimentally observed [24] in real systems. In any case, a perturbative theory for the AF ordering in this phase may not be sufficient and new ideas are required. We are, at present, carrying out detailed, large scale Monte Carlo simulations in this regime to settle the issue.

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