Physica A 160 (1989) 148–156
North-Holland, Amsterdam

# LOW-TEMPERATURE IMPURITY PAIRING IN THE FRUSTRATED 2D ISING MODEL*

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Received 7 July 1989

We present exact results on the low-temperature behavior of the square lattice $\pm J$ Ising model, with a concentration $c$ of ferromagnetic bonds and a concentration $1-c$ of antiferromagnetic bonds. We find that for $T$ below a characteristic temperature $T_0$, the system is "frozen" in the sense that its ground state properties coincide with measured quantities for systems of macroscopic size. We find that $T_0$ is remarkably large, being roughly room temperature if $J/k_B \approx 1000$ K. We also study the effect on the free energy of various spatial arrangements of the ferromagnetic bonds.

There has been renewed interest in models of randomly dilute magnetism. This interest stems from many sources. For example, it is becoming appreciated that some features of high-temperature superconductivity (HTSC) may be related to the magnetic properties of the CuO layers [1]. For the "2–1–4" compounds, with the general chemical formula $La_{2-x}(Sr, Ba)_xCuO_{4-y}$, it is known that the Cu ions form a plane square lattice antiferromagnet with a nearest neighbor coupling $J$ that is on the order of 1300 K [2]. The interactions *between* planes are considerably weaker. Moreover, it is believed that the effect of nonstoichiometric doping by Sr or Ba is to remove electrons from the oxygens [2]. Since the oxygens reside on the bonds between the Cu ions in the square lattice, considerable theoretical interest has focussed on the effect of these holes on the magnetic behavior of the $CuO_2$ planes [3–5]. It has been proposed that the spin of the hole interacts strongly with the Cu on either end of the bond, thereby creating an effective ferromagnetic interaction between these Cu ions [5] which give rise to magnetic frustration. Although for these materials the spins are more likely to be Heisenberg quantum spins, the qualitative physics displayed by classical Ising spins may provide some relevant physical insight.

* This work is based in part on the Ph.D. thesis of Borko Stošić (Univ. of Belgrade).

An open question, of possible relevance to elucidation of the HTSC phenomena, is the mechanism of real space pairing of the holes on the oxygen ions, which are responsible for carrying the supercurrent [3]. Initial studies focussed on calculating the reduction in magnetic energy if these holes became paired in real space [5]. Recently, Oliveira and Penna performed an interesting set of Monte Carlo calculations at *non-zero* temperature, which showed the potential importance of comparing the entropies of various hole distributions [6].

Our purpose here is to provide information complementary to that of Oliveira and Penna by performing analytic calculations on the low-temperature behavior of the Ising model with a concentration $1-c$ of antiferromagnetic (AF) bonds between nearest-neighbor (nn) spins, and a concentration $c$ of ferromagnetic (F) bonds of the same strength. We first study the pure case, $c=0$, and find that up to unexpectedly high temperatures the spins are effectively "frozen" in the ground state, and that only the first term in the low-temperature expansion of the partition function contributes to the thermodynamic behavior. Although the same effect is observed for $c>0$, we find that in the temperature region of interest for HTSC pairing of F bonds increases the overall entropy of the system, thus reducing the free energy. This in turn indicates that even in such a simpe model there is a tendency of low-temperature impurity pairing.

Consider an Ising antiferromagnet on a $L \times L$ square lattice with periodic boundary conditions. We write the partition function in the form

$$Z = \mathrm{e}^{\beta|J|N_\mathrm{b}} \sum_{l=0}^{N_\mathrm{b}} D_l \, \mathrm{e}^{-2l\beta|J|} \,. \tag{1a}$$

Here $\beta \equiv 1/k_\mathrm{B}T$, $N_\mathrm{b} = 2L^2$ is the number of bonds, $J = -|J|$ the interaction energy of nn spins, and $D_l$ the degeneracy of energy level $E_l$. Thus

$$E_l = |J|(-N_\mathrm{b} + 2l) \,, \qquad l = 0, 1, \ldots, N_\mathrm{b} \,. \tag{1b}$$

The $l=0$ term in (1a) correspond to the two Néel spin configurations. The next non-zero term arises from the $2L^2$ configurations corresponding to the first excited state, obtained by flipping any spin. Thus at low temperature (large values of $\beta|J|$),

$$Z = 2\,\mathrm{e}^{2\beta|J|L^2}(1 + L^2\,\mathrm{e}^{-8\beta|J|} + \mathcal{O}(\mathrm{e}^{-12\beta|J|})) \,. \tag{2a}$$

From the partition function, we obtain the dimensionless free energy per

spin

$$\frac{F}{|J|L^2} = -2 - \frac{\ln 2}{\beta|J|L^2} - \frac{e^{-8\beta|J|}}{\beta|J|} + \mathcal{O}(e^{-12\beta|J|}), \tag{2b}$$

and the dimensionless entropy per spin

$$\frac{S}{k_B L^2} = \frac{\ln 2}{L^2} + (1 + 8\beta|J|)\, e^{-8\beta|J|} + \mathcal{O}(e^{-12\beta|J|}). \tag{2c}$$

To find the range of validity of (2b) and (2c), we compare in fig. 1 these curves with the corresponding curves obtained from the exact Onsager solution. Both the zeroth order and first order approximations coincide with the exact solution up to surprisingly large values of $T$. In order to make a quantitative estimate of the temperature boundary below which the system is effectively frozen in the ground state, let us consider macroscopically large systems (with, e.g., $L \sim 10^9$) for which the size-dependent terms in (2b) and (2c) are negligible. Let $\epsilon$ denote the best accuracy to which a given quantity can be measured. The exponential correction term in (2b) may then be neglected for all values of temperature satisfying the inequality

$$\frac{e^{-8\beta|J|}}{\beta|J|} \leqslant \epsilon .$$

The analogous result for (2c) is

$$(1 + 8\beta|J|)\, e^{-8\beta|J|} \leqslant \epsilon .$$

Both inequalities are satisfied for $T < 300\,\mathrm{K}$ if we choose $J \approx 1000\,\mathrm{K}$ and $\epsilon = 10^{-10}$. Thus for an Ising system at a temperature less than 10% of $T_c$, both the free energy and the entropy are within 1 part in 10 billion of the values predicted by consideration of the ground state alone.

Next we consider a system with $c > 0$. Since we are not attempting to make a quantitative estimate of the contributions of all particular F bond configurations, but instead just to establish if there is a pairing tendency of F bonds, we further consider three distinct categories of configurations of F bonds (cf. fig. 2):

(i) unpaired configurations (UC),
(ii) paired configurations (PC), and
(iii) parallel paired configurations (PPC).

An UC is defined by the condition that spins belonging to different F bonds are not neighbors of each other. A PC is defined as a configuration in which

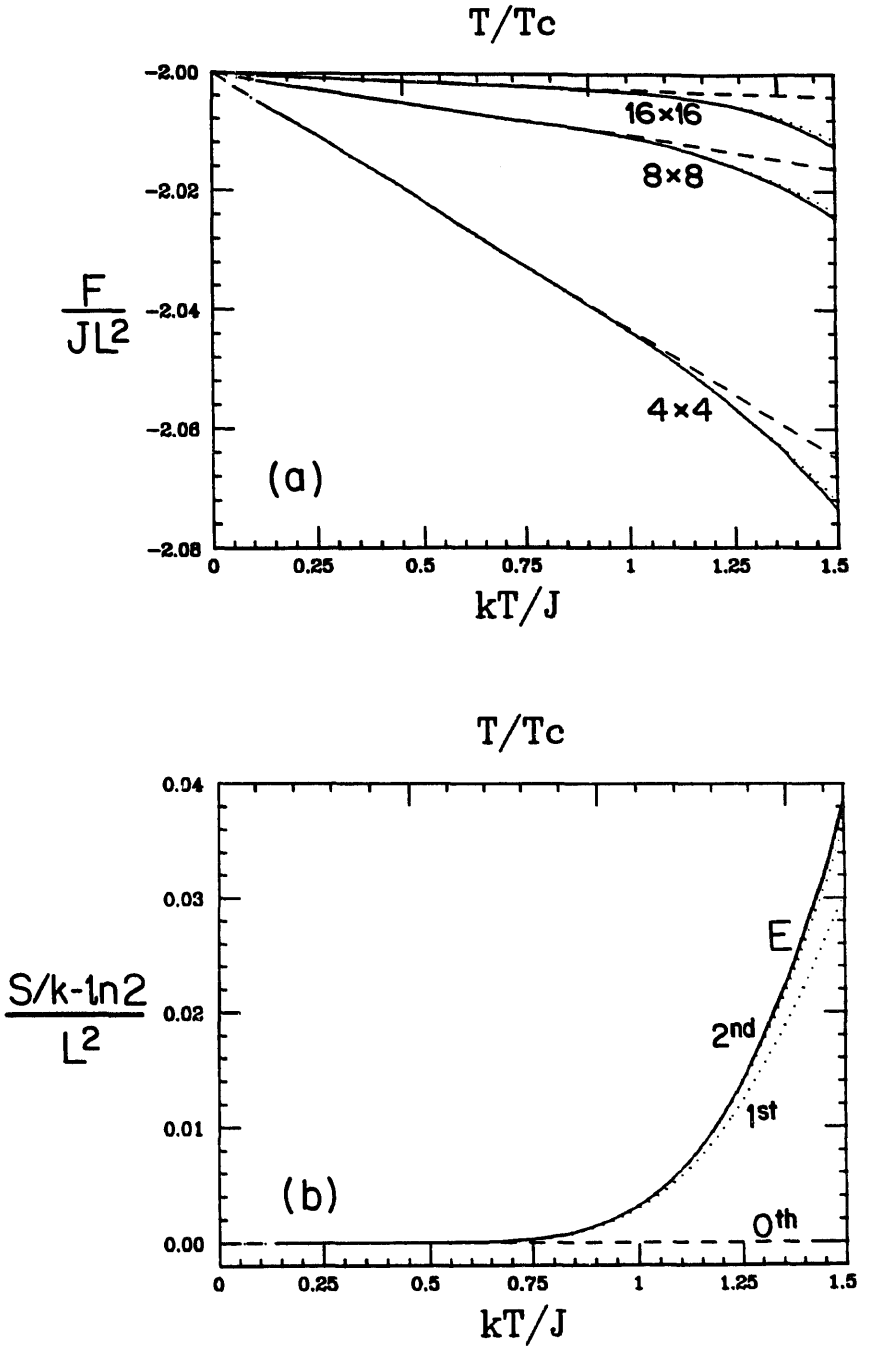
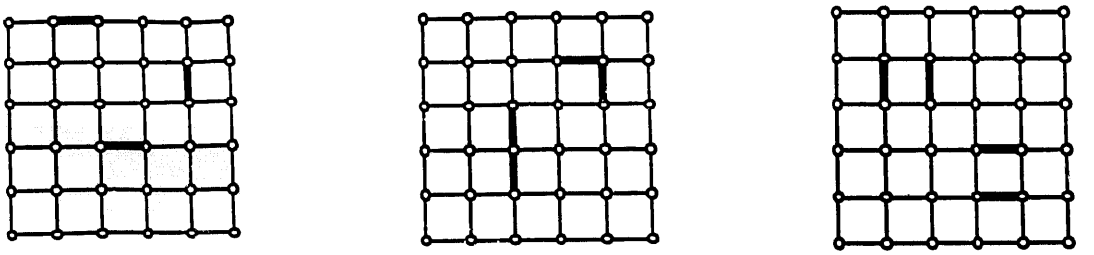



Fig. 1. Dependence on $kT/|J|$ of (a) the dimensionless free energy per spin and (b) the dimensionless entropy per spin for the $c = 0$ case. The full lines represent the exact Onsager solution, the dotted lines the first order approximation as given by (2), and the dashed lines the zeroth order approximation obtained by neglecting exponential terms in eq. (2). In (a), the bottom set of curves are for $L = 4$, the middle set for $L = 8$, and the top set for $L = 16$. The cases $L = 4$, 8, and 16 cannot be distinguished in (b). In (b) we also show as a dotted curve the second order approximation.



(a) (b) (c)

Fig. 2. Typical configurations for $c \neq 0$, distinguishing the cases of (a) unpaired configurations (UC), (b) paired configurations (PC) and (c) parallel paired configurations (PPC). The F bonds are represented by heavy lines, and the AF bonds by light lines.

two F bonds share a single spin, but each pair is spatially separated from all other pairs by at least one spin. In a PPC two neighboring F bonds are parallel to each other. All three types of configurations are macroscopically homogeneous and are well defined only for small concentrations (roughly up to $c \approx 0.2$). All three of them also have the same ground state energy $E_0 = |J|(-N_b + 2N_F)$ with $N_F$ "unsatisfied" bonds. Although the assumption of a random distribution would seem to favor UCs, we shall see that in the temperature range of interest PCs display a larger entropy and hence a lower free energy. No such effect is found for PPCs; in contrast, ref. [6] reports that the PPC is entropically the most favorable case.

Since in all three cases, there are no large clusters of F bonds, the analog of (1) becomes

$$Z = e^{(N_b - 2N_F)\beta|J|} \sum_{l=0}^{N_b - 2N_F} D_l e^{-2l\beta|J|} . \tag{3a}$$

Here $N_F = 2L^2 c$ is the number of F bonds, and

$$E_l = |J|(-N_b + 2N_F + 2l) , \qquad l = 0, 1, \ldots , N_b - 2N_F , \tag{3b}$$

is the energy for $N_F + l$ "unsatisfied" bonds.

In the UC case, the ground state again has degeneracy $D_0 = 2$, while the first excited state now corresponds to $l = 2$, that is to all the spin configurations that can be obtained from the Néel configuration by flipping just one spin that belongs to one of the F bonds. The degeneracy of the first excited state is thus $D_2 = 4N_F$, where the factor of two arises from the up-down symmetry. In terms of the concentration of F bonds, we have $D_2 = 8cL^2$. The low temperature expansion of $Z$ is thus

$$Z = 2 e^{2L^2(1-2c)\beta|J|}(1 + 4cL^2 e^{-4\beta|J|} + \cdots) , \tag{4a}$$

and the analogs of (2b) and (2c) are

$$\frac{F}{|J|L^2} = -2(1-2c) - \frac{\ln 2}{\beta|J|L^2} - \frac{4c}{\beta|J|}\,e^{-4\beta|J|} + \cdots \tag{4b}$$

and

$$\frac{S}{kL^2} = \frac{\ln 2}{L^2} + 4c(1+4\beta|J|)\,e^{-4\beta|J|} + \cdots . \tag{4c}$$

Compared to the $c = 0$ case, the temperature region in which (4b) and (4c) are valid is now reduced by a factor of 2. Nonetheless, for $|J| \approx 1000\,\mathrm{K}$ and an accuracy $\epsilon = 10^{-10}$, the exponential factors in (4b) and (4c) may be neglected for temperatures below 150 K.

While for an UC the ground state corresponds to only two possible Néel spin configurations, in the paired case flipping any combination of the spins shared by two F bonds will not change the energy of the system. The ground state is thus highly degenerate. Since there are $N_p = N_F/2$ pairs and since there are $\binom{N_p}{l}$ ways to choose a subset of $l$ spins to be flipped, the ground state degeneracy is

$$D_0 = 2\sum_{l=0}^{N_p}\binom{N_p}{l} = 2^{N_p+1} . \tag{5a}$$

The first excited state again corresponds to spin configurations with $N_F + 2$ unsatisfied bonds; they can be obtained from the ground state configuration by flipping any of the spins that belong to just a single F bond and are not neighbors to already flipped spins. Since for each of the $2\binom{N_p}{l}$ ground state configurations with $l$ flipped spins there are $2(N_p - l)$ ways to choose a spin satisfying the above conditions, where the factor of two arises from the fact that each of the bond pairs has two ends, we have a contribution to the first excited state degeneracy of

$$4\sum_{l=0}^{N_p}\binom{N_p}{l}(N_p - l) = N_p 2^{N_p+1} .$$

The same energy is also obtained from any of the $2\binom{N_p}{l}$ ground state configurations with $l$ flipped spins by flipping any of the spins which belong to one of the $2l$ unsatisfied AF bonds and do not belong to the F bonds. The corresponding contribution is $4\Sigma_{l=0}^{N_p}\binom{N_p}{l}l$. The degeneracy of the first excited state is

$$D_2 = 4\sum_{l=0}^{N_p}\binom{N_p}{l}N_p = N_p 2^{N_p+2} . \tag{5b}$$

The analog of (2a) is thus

$$Z = 2\,e^{2L^2(1-2c)\beta|J|} 2^{cL^2}(1 + 2cL^2\,e^{-4\beta|J|} + \cdots), \tag{6a}$$

while (2b) and (2c) become

$$\frac{F}{|J|L^2} = -2(1-2c) - \frac{\ln 2}{\beta|J|}\left(c + \frac{1}{L^2}\right) - \frac{2c}{\beta|J|}\,e^{-4\beta|J|} + \cdots \tag{6b}$$

and

$$\frac{S}{kL^2} = \left(c + \frac{1}{L^2}\right)\ln 2 + 2c(1 + 4\beta|J|)\,e^{-4\beta|J|} + \cdots . \tag{6c}$$

We see that the correction terms in (6b) and (6c) are two times smaller, for the same value of $B|J|$ than the corresponding correction terms in (4b) and (4c) for the unpaired case. This means that PC freezes in the ground state at temperatures higher than UC. Unlike the unpaired case, there is a nonvanishing residual entropy $c \ln 2$, and the free energy will be lower by a factor $c \ln 2/\beta|J|$ for $L \gg 1$ in the entire temperature region of interest. In fig. 3, we compare curves defined in eqs. (4b) and (4c) with those from (6b) and (6c) for the special choice $L = 10^9$ and $c = 0.1$, and notice that a PC is entropically more favorable than a UC.

Finally, in the PPC case considered extensively in ref. [6], the ground state degeneracy is again $D_0 = 2$, while the first excited state corresponds to all the spin configurations that can be obtained the same way as in the UC case, or by flipping simultaneously two neighboring spins belonging to different F bonds of a pair. The degeneracy of the first excited state is thus $D_2 = 4N_F + 4N_p = 12cL^2$. This yields the same first order equations for $Z$, $F$, and $S$ as (4) for the UC, the exponential term now being multiplied by an additional factor 3/2. This new factor, however, does not change the ground state contributions to these quantities, nor does it significantly influence the range of temperatures below which the system is frozen in the ground state. The PPC case is thus not entropically more favorable than the UC case.

In summary, we have calculated thermodynamic properties at low temperatures for the square lattice Ising model with AF bonds of strength $J$ and F bonds of strength $K = -J$. We find that the system is frozen in the ground state up to surprisingly high temperatures. We find no evidence of preferential pairing of parallel bonds, as suggested by ref. [6]; rather, for the entire temperature range of interest we find paired configurations in which each pair shares a single site, which exhibit a non-zero residual entropy and a lower free energy than unpaired configurations. Hence there is a tendency for real space

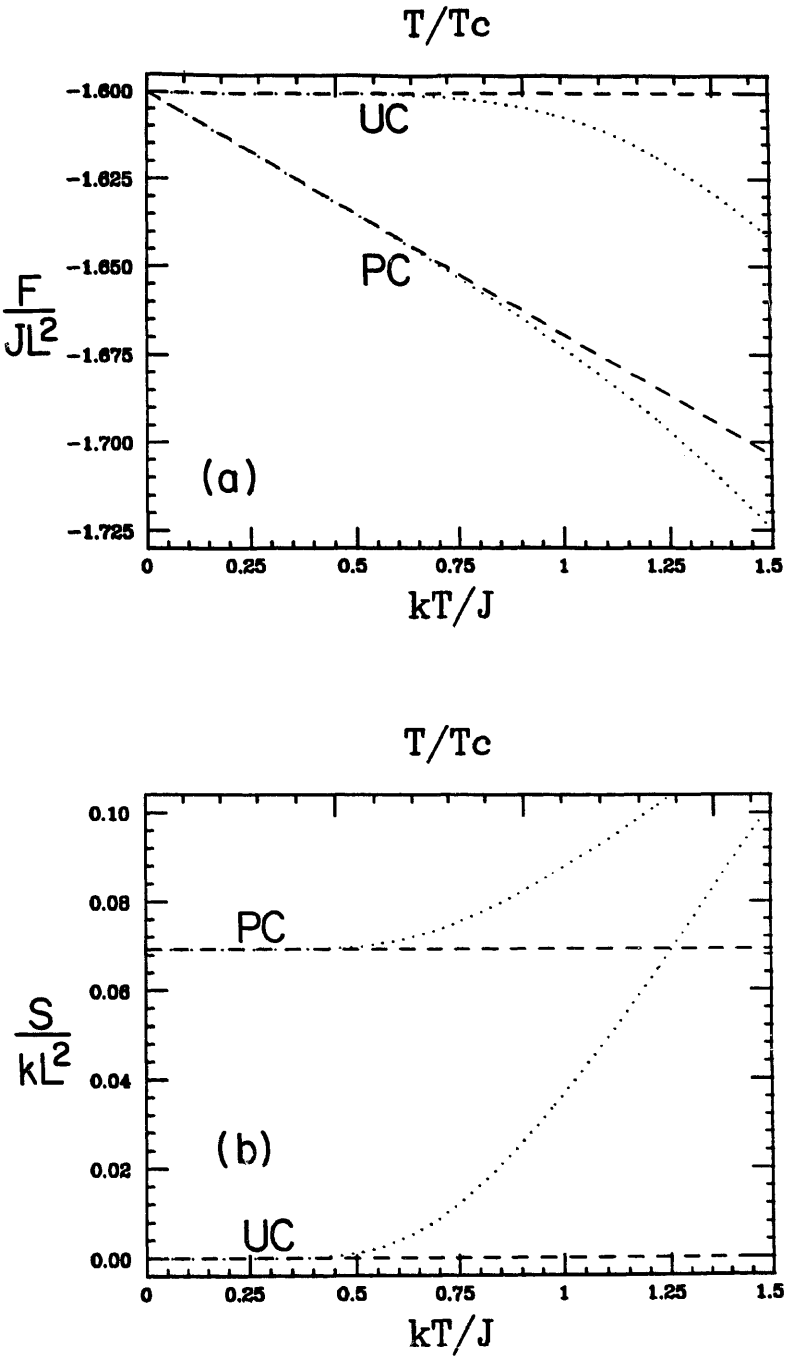



Fig. 3. Comparison of (a) free energy and (b) entropy as functions of $kT/|J|$ for an unpaired configuration (UC) and a paired configuration (PC) of frustrated bonds for a special choice $L = 10^9$, $c = 0.1$. The dashed lines represent zeroth order approximations obtained by neglecting the exponential terms in (2) and (6), respectively, while the dotted lines represent the first order approximation as given by these equations The first order correction for a PC is less than that for a UC by a factor of 2 for all temperatures in the region of interest. In (a), the top set of curves is for the UC case while the bottom curves is for the PC case; in (b), the reverse is true.

pairing of impurities. To be more relevant to HTSC phenomena, similar studies should be performed for the classical and quantum mechanical Heisenberg models [2], for [5] $K > |J|$, and for temperature dependent coupling [7, 8] $K(T)$.

## Acknowledgements

We wish to thank P. Alstrøm, A. Coniglio, I. Fittipaldi, J. Lee, S. Milošević and R. J. Vasconcelos dos Santos for sharing with us their many physical insights into this problem. We also wish to thank Professor Amnon Aharony for helpful correspondence and generous constructive criticism, and Professor S. Milošević for his continued guidance in many aspects of physics. This work has been supported in part through funds provided by the Yugoslav–USA Joint Scientific Board under Project No. 534 (NSF) and by the Serbian Science Foundation under Project No. 1.2.

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