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LETTER TO THE EDITOR

Critical behaviour at surfaces: variational approach for the free energy†

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Abstract. The variational approach based on the Bogoliubov's inequality for the free energy is used in order to study the thermodynamical properties of the semi-infinite Ising model with modified exchange interactions $J_s = J(1+\Delta)$ on a free surface. The critical temperature of the surface ordering, as well as the extrapolation length are obtained as a function of Δ for the two- and three-dimensional models.

In this letter we treat the semi-infinite Ising model with modified exchange interaction on a free surface. This system can be viewed as a d-dimensional Ising film of N_l layers ($N_l \to \infty$) with periodic boundary conditions along the direction parallel to the film. The exchange interaction between all nearest-neighbour spins is assumed to be J, except for spins on the surface where the interaction is assumed to be $J_s = J(1+\Delta)$. The Hamiltonian model of the system can then be written as

$$\mathcal{H} = -J_s \sum_{(\boldsymbol{\rho},\boldsymbol{\rho}')} \sigma_{1,\boldsymbol{\rho}}\sigma_{1,\boldsymbol{\rho}'} - J\sum_{n=2}^{N_l}\sum_{(\boldsymbol{\rho},\boldsymbol{\rho}')} \sigma_{n,\boldsymbol{\rho}}\sigma_{n,\boldsymbol{\rho}'}$$
$$-J\sum_{\boldsymbol{\rho}}\sum_{n=1}^{N_l} \sigma_{n,\boldsymbol{\rho}}\sigma_{n+1,\boldsymbol{\rho}} - h\sum_{n,\boldsymbol{\rho}}\sigma_{n,\boldsymbol{\rho}} - h_1\sum_{\boldsymbol{\rho}}\sigma_{1,\boldsymbol{\rho}}, \qquad (1)$$

where n labels the $(d-1)$-dimensional layer and $\boldsymbol{\rho}$ is the $(d-1)$-dimensional coordinate parallel to the surface. h is a uniform field acting throughout the system and h_1 is a field acting on the surface layer located at $n = 1$.

On the basis of mean-field theory (Mills 1971, Binder and Hohenberg 1974, Binder 1983 and references therein) it has been shown that for Δ greater than a critical value Δ_c the system orders on the surface before it orders in the bulk, whereas for $\Delta < \Delta_c$ the surface orders when the bulk does. For very large values of Δ the surface behaves like a $(d-1)$-dimensional Ising model and the bulk can be neglected.

Clearly, these mean-field results are in disagreement with the expected results for $d = 2$, since there is no ordering on the one-dimensional surface at finite temperatures. Actually, Au-Yang (1973) has exactly shown that the critical temperature, as well as the critical exponents for the two-dimensional model are independent of Δ. However, since a two-dimensional surface exhibits a finite critical temperature, it is reasonable

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to assume that for $d=3$ there exists a critical value J_{sc} above which the surface orders at a temperature T_c greater than the bulk transition temperature.

In order to sutdy the thermodynamical properties of the model (1) we employ a variational method based on the Bogoliubov's inequality (see, for example, Falk 1970):

$$F(\mathscr{H}) \leq F_0(\mathscr{H}_0) + \langle \mathscr{H} - \mathscr{H}_0 \rangle_0 = \phi(\gamma), \tag{2}$$

where $F(\mathscr{H})$ is the free energy of the system described by $\mathscr{H}$, $F_0(\mathscr{H}_0)$ is the free energy associated with a trial Hamiltonian $\mathscr{H}_0 = \mathscr{H}_0(\gamma)$, γ standing for the variational parameters, and $\langle \ldots \rangle_0$ means an average taken over the ensemble defined by $\mathscr{H}_0$. An approximated free energy is obtained by minimising the RHS of (2) with respect to the variational parameters and assuming that $F(\mathscr{H}) \equiv \phi_{\min}(\gamma)$.

According to the present variational approach, the usual mean-field approximation (Binder and Hohenberg 1974, Binder 1983) can be obtained by choosing

$$\mathscr{H}_0 = \sum_{n,p} \gamma_{n,p} \sigma_{n,p}, \tag{3}$$

with $\gamma_{n,p} = \gamma_n$, since the magnetisation within each layer is assumed to be uniform (i.e., the system is translationally invariant along the directions parallel to the surface).

In order to improve the approximation, we choose the following trial Hamiltonian

$$\mathscr{H}_0 = \sum_{n=1}^{N_1} \sum_{\substack{\text{linear} \\ \text{chains}}} \mathscr{H}_{\mathrm{LC}}^n, \tag{4}$$

where

$$\mathscr{H}_{\mathrm{LC}}^n = -J_n \sum_i \sigma_i \sigma_{i+1} - \gamma_n \sum_i \sigma_i \tag{5}$$

is the Hamiltonian of a linear Ising chain and $J_n = J$ for $n \geq 2$ and $J_1 = J_s$. The second sum in (4) extends over all linear chains parallel to the surface (and parallel to each other) within the layer n. With this choice for the trial Hamiltonian all the interactions along one specific direction parallel to the surface can be taken into account exactly, while the interactions between linear chains are taken into account in a mean-field way.

The RHS of equation (2) can then be written as

$$\phi(\gamma) = \sum_{n=1}^{N_1} f_0(\gamma_n) - \frac{z_s - 2}{2} J_s m_1^2 - \frac{z_s - 2}{2} J \sum_{n=2}^{N_1} m_n^2 - J \sum_{n=1}^{N_1} m_n m_{n+1}$$
$$- h_1 m_1 - h \sum_{n=1}^{N_1} m_n + \sum_{n=1}^{N_1} \gamma_n m_n, \tag{6}$$

where $f_0(\gamma_n)$ is the free energy per spin of the linear Ising chain, z_s is the coordination number within each $(d-1)$-dimensional layer and we have assumed a uniform magnetisation

$$m_n = -\frac{\partial f_0(\gamma_n)}{\partial \gamma_n} = \frac{\sinh \beta\gamma_n}{(\sinh^2 \beta\gamma_n + \mathrm{e}^{-4\beta J_n})^{1/2}}, \qquad \beta = 1/k_B T \tag{7}$$

within each laer. Minimisation of equation (6) with respect to the variational parameters leads to

$$\gamma_1 = h_1 + h + (z_s - 2) J_s m_1 + J m_2, \tag{8}$$

$$\gamma_n = h + (z_s - 2) J m_n + J(m_{n+1} + m_{n+1}), \qquad n \geq 2. \tag{9}$$

Above the critical temperature and for small fields h and h_1, equations (7)-(9) can be linearised and we find

$$m_1 = e^{2\beta J_s}[H + H_1 + (z_s - 2)\beta J_s m_1 + \beta J m_2], \tag{10}$$

$$m_n = e^{2\beta J}[H + (z_s - 2)\beta J m_n + \beta J(m_{n+1} + m_{n-1})], \qquad n \geqslant 2, \tag{11}$$

where $H = \beta h$ and $H_1 = \beta h_1$.

The bulk magnetisation, $m_b = m_{n\to\infty}$, can be obtained from (11) and one finds

$$m_b = H/(e^{-2\beta J} - z_s\beta J). \tag{12}$$

The phase transition in the bulk of the film will then occur when the denominator of (12) vanishes, i.e.,

$$e^{-2\beta_{cb}J} = z_s\beta_{cb}J, \tag{13}$$

which is precisely the same critical temperature as for a fully infinite system (de Carvalho and Salinas 1978, Plascak and Silva 1982).

As in the usual mean-field approximation, the system given by (10) and (11) can be solved by setting

$$m_n = m_b + \delta\, e^{-q(n-1)}. \tag{14}$$

The magnetisation m_1 then becomes

$$m_1 = \chi_{1,1}H_1 + \chi_1 H, \tag{15}$$

where

$$\chi_{1,1} = e^{2\beta J(1+\Delta)}/D(\beta, \Delta), \tag{16}$$

$$\chi_1 = e^{2\beta J(1+\Delta)}\beta J(y-1)/D(\beta, \Delta)(e^{-2\beta J} - z_s\beta J), \tag{17}$$

and

$$D(\beta, \Delta) = 1 + \beta J\, e^{2\beta J(1+\Delta)}[y - (z_s - 2)\Delta] - e^{2\beta J\Delta}, \tag{18}$$

$$y = e^q = \frac{1}{2\beta J}\{e^{-2\beta J} - z_s\beta J + 2\beta J + [(e^{-2\beta J} - z_s\beta J)(e^{-2\beta J} - z_s\beta J + 4\beta J)]^{1/2}\}. \tag{19}$$

For $\Delta < \Delta_c$, where Δ_c is given by

$$D(\beta_{cb}, \Delta_c) = 0, \tag{20}$$

and $T > T_{cb}$ one has $D(\beta, \Delta) > 0$ so the system orders on the surface at a temperature which is the same as the bulk critical temperature. For $T \gtrsim T_{cb}$ equations (13) and (19) lead to

$$q \sim [z_s(1 + 2\beta_{cb}J)(T - T_{cb})/T_{cb}]^{1/2}, \tag{21}$$

which shows that this transition is to a state where the bulk is ordered ($q^{-1} \to \infty$). From equations (16) and (17) one can also obtain the extrapolation length λ (Binder 1983) which in this case, can be written as

$$\lambda = \beta_{cb}J\, e^{2\beta_{cb}J(1+\Delta)}/D(\beta_{cb}, \Delta). \tag{22}$$

At $\Delta = \Delta_c$ the extrapolation length goes to infinity.

For $\Delta > \Delta_c$ the surface orders at a shifted temperature given by the solution of

$$D(\beta_c, \Delta) = 0. \tag{23}$$

The transition temperature for the surface of the two-dimensional model as a function of Δ is shown in figure 1. In this case we have $\beta_{cb}J = 3.52$ and $\Delta_c = 1.22$ while the usual mean-field approximation gives $\beta_{cb}J^{MF} = 4$ and $\Delta_c^{MF} = 0.5$. Although the linear Ising chain has no finite critical temperature, for very large values of Δ the surface still orders at a temperature greater than T_{cb}. This result reflects the fact that in the present approximation the interactions between the surface and the inner layer are taken into account in a mean-field way. However, as can be seen in figure 1, the behaviour of T_c as a function of Δ is much closer to the exact one than that found in the usual mean-field approximation (the exact result is $\beta_{cb}J = 2.27$ independent of Δ).

Figure 2 shows the transition temperature for the surface of the three-dimensional Ising model as a function of Δ. The critical value of the surface interaction is, in this case, $\Delta_c = 0.30$. This value should be compared with $\Delta_c = 0.6$ obtained from high-temperature series expansion up to eighth order for $d = 3$ (Binder and Hohenberg 1974). The usual mean-field approximation gives $\Delta_c^{MF} = 0.25$. For large values of Δ equation (23) leads to

$$1 \sim e^{2\beta J\Delta} 2\beta J\Delta \sim e^{2\beta J_s} 2\beta J_s, \tag{24}$$

which is the critical temperature given by (13) for the two-dimensional model, as expected. The extrapolation length as a function of Δ is shown in figure 3. In this case, a similar behaviour is obtained for $\Delta < 0$, the difference being that $\lambda^{-1} < \lambda_{MF}^{-1}$.

Finally, it can be shown that the critical exponents γ_1 and $\gamma_{1,1}$ obtained from equations (16) and (17) are exactly the same as those given by the usual mean-field approximation, with only the coefficients of the susceptibilities being different.

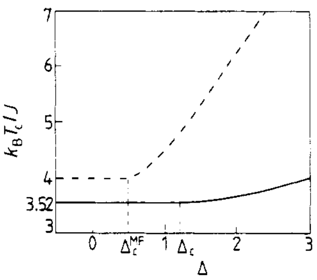

Figure 1. Transition temperature for the surface as a function of Δ for the two-dimensional model. The full curve represents the present approximation and the chain curve the usual mean-field approximation.

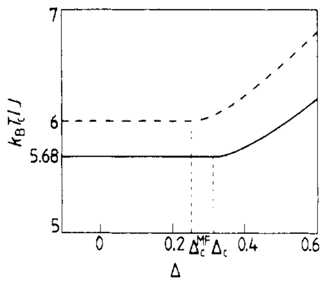

Figure 2. The same as figure 1 for the three-dimensional model.

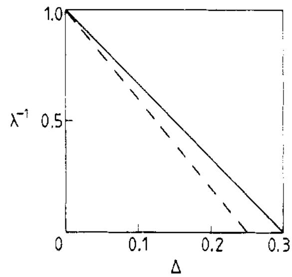

Figure 3. Extrapolation length as a function of Δ for the three-dimensional model. The full curve represents the present approximation and the chain curve the usual mean-field approximation.

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