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LETTER TO THE EDITOR

Low-temperature series analysis of multilayer adsorption at surfaces

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Abstract. We show that a low-temperature series analysis, taken to all orders by selecting important graphs at each stage, can be used to demonstrate that an Ising system with an interface forced upon it exhibits an infinite sequence of first-order layering transitions as a function of applied magnetic field. We also discuss a model with a short-range surface potential, the Abraham model, and show that it exhibits at least one layering transition at low temperatures.

Surface and interface problems are of wide ranging physical importance. Properties such as wetting, interfacial adsorption and surface reconstruction are of relevance to many biological and technological systems (Rowlinson and Widom 1982, Binder 1983).

Recently a great deal of effort has been devoted to the study of interfaces in simple spin models (see Binder 1983 and Pandit *et al* 1982 for reviews). In this work we consider Ising models which are, at zero temperature, constrained to have an interface which is pinned in the vicinity of a surface. We show that series expansions taken to all orders (Fisher and Selke 1981) can be used to study the behaviour of the interface as the temperature is increased.

The geometry we consider is a three-dimensional simple cubic lattice with periodic boundary conditions in two directions and free surfaces in the third as shown in figure 1. An interface is introduced by applying an infinite surface field of opposite sign on the two free surfaces (Abraham 1980). If one makes it energetically favourable for the interface to be pinned at the surface, either by introducing a row of weak bonds (Abraham 1980) or a bulk field (Pandit and Wortis 1982), then on increasing the

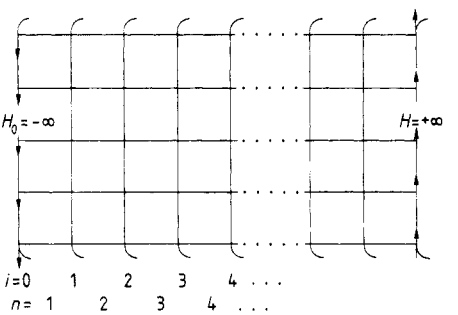

Figure 1. The geometry of the interface model considered. At zero temperature the interface is sharp and may lie in any position, n, parallel to the free surfaces.

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temperature there will be a competition between the entropy, which wants the interface to lie in the middle of the system, and the energy, which wants it to remain pinned to the surface. This can lead to a phase transition, through which the interface becomes unbound, called a surface wetting or depinning transition (Cahn 1977, Abraham 1980, Kroll and Lipowsky 1982).

If the depinning occurs at a temperature above the roughening temperature, T_R, it is expected that the transition will not be affected by the lattice structure. This is the situation in two bulk dimensions, where $T_R = 0$ and the transition is continuous.

In three dimensions, however, T_R is finite and the discreteness of the lattice is expected to be important. That this is indeed the case was first shown by de Oliveira and Griffiths (1978) in a mean-field analysis of a lattice gas model with a long-range attractive surface potential. They found that for an appropriate choice of parameters the surface underwent an infinite sequence of first-order layering transitions. The mean-field analysis has since been refined and extended (Pandit and Wortis 1982, Pilorz and Sokolowski 1984) and Monte Carlo, variational and renormalisation group methods have been applied to the problem (Ebner *et al* 1985, Weeks 1982, Huse 1985).

We consider the geometry shown in figure 1 with infinite fields on the boundary layers and allow Ising spins on each site to interact through the Hamiltonian

$$\mathcal{H} = -\tfrac{1}{2}J_0 \sum_{i,j,j'} S_{i,j}S_{i,j'} - aJ \sum_j S_{0,j}S_{1,j} - J \sum_{i>0} S_{i,j}S_{i+1,j} - H \sum_{i,j} S_{i,j}, \tag{1}$$

where the pair interactions are ferromagnetic and extend over nearest-neighbour sites. The subscript i labels the layers with $i = 0$ being the surface layer (see figure 1) and the subscript j distinguishes between sites in a given layer. We first take the case $a = 1$. The bulk field, H, constrains the interface to lie next to the free surface at zero temperature. In mean field theory this model is expected to depin through an infinite sequence of first-order transitions (Pandit and Wortis 1982). We show here that such a sequence of transitions is also obtained within a low-temperature series approximation.

We first note that at $H = 0$ the ground state is infinitely degenerate as the interface can lie in any position parallel to the surface. We must therefore perform a low-temperature expansion about each of the possible interface positions at ($T = 0$, $H = 0$), and compare the free energies to determine whether any layers are adsorbed onto the surface at finite fields and temperature. Using n to label the position of the interface, with $n = 1$ describing the position immediately adjacent to the surface, as shown in figure 1, we find to first order the following reduced interface free energies per site (with respect to a pinned interface)

$$\begin{aligned} f_n - f_1 &\equiv -\beta(F_n - F_1) \\ &= -2(n-1)\beta H + [y^{-1} + (n-2)y^{-1}t^2 - (n-1)yt^2]\omega^{q_\perp} + O(\omega^{2q_\perp - 2}), \\ &\quad n \geq 2 \end{aligned} \tag{2}$$

where the Boltzmann factors used in the expansion are

$$y = \exp(-2\beta H), \qquad t = \exp(-2\beta J), \qquad \omega = \exp(-2\beta J_0) \tag{3}$$

and $q_\perp$ is the coordination number of the lattice in the planes parallel to the surface (in the calculations described here we use a simple cubic lattice and so $q_\perp = 4$).

Assuming that for a layering transition to occur $H \sim O(\omega^{q_\perp})$ we may take $y = 1$ and consider the sign of the free energy difference given in (2) to show that the first layering

transition, between $n = 1$ and $n = 2$, occurs at

$$H_{12} = \tfrac{1}{2}(1 - t^2)\omega^{q_\perp} + O(\omega^{2q_\perp - 2}). \tag{4}$$

The comparison is indicated graphically in figure 2(a). The $n = 2$ phase is stable between $H = H_{12}$ and $H = 0$ where the interface depins from the surface. On $H = 0$ the phases $n \geqslant 2$ remain degenerate and their stability can only be determined by a higher-order calculation.

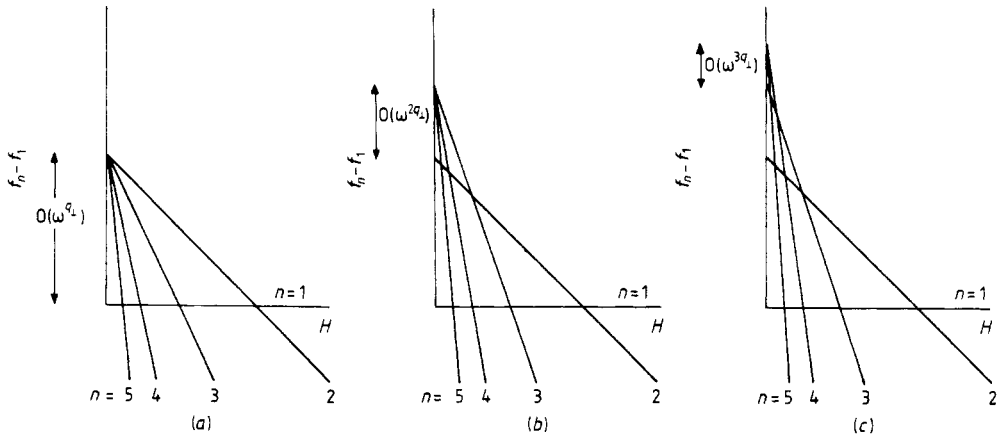

Figure 2. Comparison of reduced interface free energy differences per site ($f_n - f_1$) at (a) first- (b) second- and (c) third-order of the low temperature series expansion.

Taking the calculation to second order shows that the $n = 3$ phase appears between $n = 2$ and the wet phase. The reduced free energies are given to this order by

$$f_2 - f_1 = -2\beta H + (y^{-1} - yt^2)\omega^{q_\perp} + 2(y^{-2} - y^2t^4)\omega^{2q_\perp - 2} + (t^2 - y^2t^2 - \tfrac{5}{2}y^{-2} - 1 + \tfrac{7}{2}y^2t^4)\omega^{2q_\perp} + 6(y^{-3} - y^3t^6)\omega^{3q_\perp - 4} + O(\omega^{3q_\perp - 2}) \tag{5}$$

$$f_n - f_2 = 2(n-2)t^4(y^{-2} - y^2)\omega^{2q_\perp - 2} + [(n-4)y^{-2}t^2 + y^{-2} - (n-2)y^2t^2 - (\tfrac{7}{2}n - 8)y^{-2}t^4 + (\tfrac{7}{2}n - 7)y^2t^4]\omega^{2q_\perp} + 6(n-2)t^6(y^{-3} - y^3)\omega^{3q_\perp - 4} + O(\omega^{3q_\perp - 2}), \qquad n \geqslant 3 \tag{6}$$

leading to phase boundaries

$$\beta H_{12} = \tfrac{1}{2}(1 - t^2)\omega^{q_\perp} + (1 - t^4)\omega^{2q_\perp - 2} - \tfrac{5}{2}(1 - t^4)\omega^{2q_\perp} + 3(1 - t^6)\omega^{3q_\perp - 4} + O(\omega^{3q_\perp - 2}) \tag{7}$$

$$\beta H_{23} = \tfrac{1}{2}(1 - t^2)^2\omega^{2q_\perp} + O(\omega^{3q_\perp - 2}) \tag{8}$$

$$\beta H_{3\infty} \sim O(\omega^{3q_\perp - 2}). \tag{9}$$

A full calculation of the low-temperature series rapidly becomes very complicated with increasing order. However, the phase diagram can be built up inductively by considering the leading order graphs which differentiate between the free energies of the phases n and $n' > n$ (Fisher and Selke 1981). Some thought indicates that these

will occur at order n and are long graphs consisting of a chain of spins perpendicular to the interface with no kinks, together with the corresponding disconnected graphs. When the free energy difference is taken only two such sets of graphs remain (see table 1 for an example). Allowing breaks at all possible points of the chain, and associating a minus sign with each of the disconnections (Fisher and Selke 1981), contributions from all the graphs can be summed using the binomial theorem to give

$$f_{n'} - f_n = -2\beta(n'-n)H + (1-t^2)^n \omega^{nq_\perp} + O(\omega^{(n+1)q_\perp}), \qquad n' > n \tag{10}$$

where, to this order, we have taken $y = 1$. For H sufficiently small the difference in reduced free energies is positive and hence, at order n, the phase $n+1$ appears between n and the wet phase. The phase boundaries are given by

$$\beta H_{n,n+1} = \tfrac{1}{2}(1-t^2)^n \omega^{nq_\perp} + O(\omega^{(n+1)q_\perp}) \tag{11}$$

$$\beta H_{n+1,\infty} \sim O(\omega^{(n+1)q_\perp}). \tag{12}$$

Table 1. Leading-order graphs contributing to $f_4 - f_3$. A caret denotes a flipped spin and a vertical line that the neighbouring spins are disconnected.

Graph	Count	Boltzmann weight ($y = 1$)
$-\hat{-}\hat{-}\hat{-}+++\ldots$	1	1
$-\hat{-}\vert\hat{-}\hat{-}+++\ldots$	−1	t^2
$-\hat{-}\hat{-}\vert\hat{-}+++\ldots$	−1	t^2
$-\hat{-}\vert\hat{-}\vert\hat{-}+++\ldots$	1	t^4
$---+\hat{+}\hat{+}\hat{+}+\ldots$	−1	t^2
$---+\hat{+}\vert\hat{+}\hat{+}+\ldots$	1	t^4
$---+\hat{+}\hat{+}\vert\hat{+}+\ldots$	1	t^4
$---+\hat{+}\vert\hat{+}\vert\hat{+}+\ldots$	−1	t^6

The higher-order phases remain degenerate at $H = 0$. However the phase $n+2$ will appear at the next order of the expansion and so on building up an infinite sequence of layers. The mechanism through which the inductive argument proceeds is indicated schematically in figure 2 for $n = 1, 2$ and 3. The resulting phase diagram is given in figure 3. H_{12} is plotted quantitatively to second order for $J_0 = J_1 = 1$; the width of the other phases is exaggerated for clarity.

We now address the subtle question of whether a system with a short-range surface potential can exhibit an infinite sequence of layering transitions in the absence of a magnetic field. We consider the Abraham model (Abraham 1980) on a simple cubic lattice, that is, the Hamiltonian (1) with $H = 0$ and a allowed to vary. The phase boundary between the pinned and unpinned phases of the interface will lie at a temperature which decreases with increasing a from the transition temperature of the three-dimensional Ising model at $a = 0$ to $T = 0$ at $a = 1$. At $a = 1$ the ground state is infinitely degenerate with every position of the interface having the same energy.

We have found that this problem is considerably more complicated and that it is necessary to go to third order in the low temperature expansion to show that the $n = 2$ phase does appear. The corresponding phase boundaries are given by

$$\beta J(1-a_{12}) = \tfrac{1}{2}(1-t^2)\omega^{q_\perp} + (1-t^4)\omega^{2q_\perp - 2} - \tfrac{1}{4}(1-t^2)(3+7t^2)\omega^{2q_\perp} + 3(1-t^6)\omega^{3q_\perp - 4} + O(\omega^{3q_\perp - 2}) \tag{13}$$

$$\beta J(1-a_{2\infty}) = \tfrac{1}{2}(1-t^2)\omega^{q_\perp} + 2t^2(1-t^2)\omega^{2q_\perp - 2} + \tfrac{1}{4}(1-t^2)(1-11t^2)\omega^{2q_\perp} + (1-t^2)(1+8t^4)\omega^{3q_\perp - 4} + O(\omega^{3q_\perp - 2}) \quad (14)$$

resulting in the phase diagram shown in figure 4.

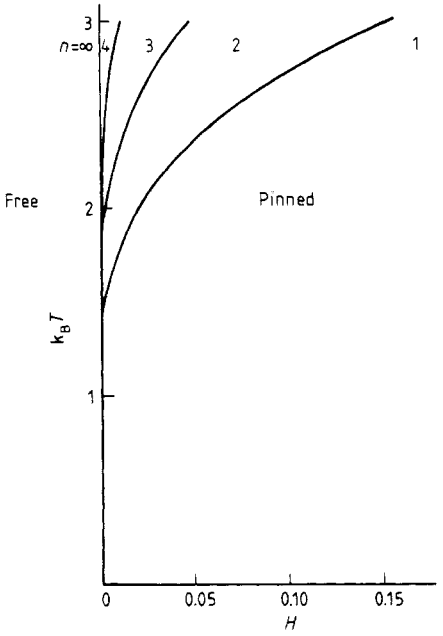

Figure 3. Phase diagram of multilayer adsorption of an Ising system with a bulk field, H, pinning the interface to the surface. The boundary between the $n=1$ and $n=2$ phases is quantitatively correct to second order for $J_0 = J_1 = 1$. The width of the higher-order phases is exaggerated for clarity.

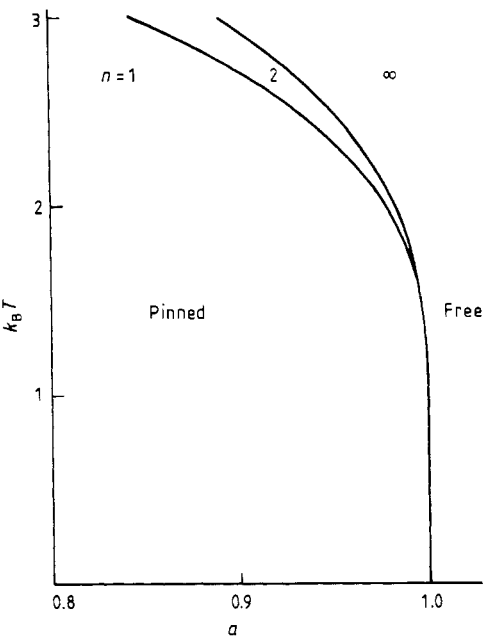

Figure 4. Low-temperature phase diagram of the Abraham model on a simple cubic lattice from low-temperature series calculations taken $O(\omega^{4q_\perp - 2})$ for $J_0 = J_1 = 1$. To this order all phases with $n \geq 2$ remain degenerate on the boundary between the phases $n=2$ and $n=\infty$.

To this order all phases with $n \geq 3$ remain degenerate on the boundary between $n=2$ and the wet phase. Because a given phase is only stabilised at a relatively high order compared to the distance of the interface from the surface, many diagrams contribute to the free energy difference of phases n and $n' \geq n$ to leading order. Therefore a general calculation is very difficult. An explicit calculation of the reduced free energy to $O(\omega^{4q_\perp - 2})$ does not lift the degeneracy on $a_{2\infty}$. Therefore we are at present unable to conclude whether further layering transitions occur before the interface depins. The details of this calculation, together with mean-field results for this model, will be presented elsewhere.

In conclusion, we have shown that low-temperature series methods enable us to predict an infinite sequence of layering transitions as a function of an external field. A short range surface potential can stabilise at least one layering transition at low temperatures.

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