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LETTER TO THE EDITOR

# Onset of bulk behaviour in a finite-thickness slab

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**Abstract.** The behaviour of an Ising antiferromagnet which is known to undergo a continuous transition in two dimensions and a first order transition in three is considered in a slab geometry of finite thickness. We note that the phase behaviour is intimately related to the surface boundary conditions which govern wetting. For the interesting case in which wetting phenomena are not important, we find that the bulk behaviour is already manifest when the slab is only eleven layers thick.

Given a system which is known to undergo a continuous transition in two dimensions, and a first-order transition in three, what sort of transition will a finite-thickness slab of the material undergo? This question has application to films of numerous materials which display common types of ordering transitions between solid and liquid phases, paramagnetic and ferromagnetic phases [1] or other related states. Shnidman and Domany [1] considered the question and argued as follows. If the three-dimensional transition had been continuous so that the bulk correlation length $\xi$ diverged as the bulk transition temperature was approached, then the finite thickness of the slab would become apparent at a temperature at which this correlation length was comparable to the thickness of the slab; a continuous transition, characteristic of the two-dimensional model, would then occur. However, as the bulk transition is first order, the correlation length never diverges, but attains some finite value $\xi(T_c)$ at the bulk transition temperature $T_c$. This establishes for the slab a characteristic width, $L^x \simeq \xi(T_c)$; for thicknesses $L > L^x$, the system behaves like bulk and a first-order transition is expected, while for $L < L^x$, it acts two dimensionally and a continuous transition should occur. A tricritical point, also characteristic of the two-dimensional system, separates the two regimes. This analysis was supported by an approximate position space renormalisation group calculation on a three-state Potts model which did indeed produce such a crossover in the order of the transition, but could only place the characteristic thickness within a very large range, $2^5 < L^x < 2^{13}$.

It must be noted that both the analysis and calculation of Shnidman and Domany ignore surface effects related to wetting phenomena [2], effects which can completely alter their scenario. For example, suppose that the slab were semi-infinite and that the boundary conditions at the surface of the slab were such that, as coexistence between bulk phases was approached from the disordered side by decreasing some field or chemical potential, the ordered phase wet the surface. At a sufficiently low temperature, this complete wetting would proceed via distinct first-order layering transitions, while at higher temperatures it would proceed continuously. In a finite

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slab with the same boundary conditions at both surfaces, one expects the ordered phase to appear in just the same way. At low temperatures, the ordered state would appear via a series of layer transitions beginning at the surfaces and working inward until the entire slab was ordered; at higher temperatures, the order would propagate continuously from the surfaces. Thus the Shnidman–Domany scenario, in which the entire slab undergoes either one continuous or first-order transition, can occur only with boundary conditions such that complete wetting of the surface of the semi-infinite slab by either phase does not take place. Even if these conditions are met, there can be a modification of the scenario in which a few surface layers undergo their own transitions, followed by all the rest of the layers which make a single transition.

We have investigated a system which displays continuous and first-order transitions in two and three dimensions respectively and which lends itself to study by means of the cluster variational method (CVM) [3]. In addition to its relative simplicity, the CVM has the virtue that effects of the surface, omitted in [1], can be included (see e.g. [4]). The system consists of Ising spins, $\sigma_i$ located on the sites of a slab of a face-centred cubic lattice, which interact antiferromagnetically with their nearest neighbours. The Hamiltonian is

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - H \sum_i \sigma_i$$

where $J < 0$, and the first sum is over nearest-neighbour pairs. The slab is made up of $L = 2l+1$ $(1,0,0)$ planes. The transition studied is that from the paramagnetic phase, which exists for sufficiently strong uniform external fields $H$, to the $A_3B$ ordered phase. In this phase, the spins on one of the four sublattices into which the FCC lattice can be decomposed are aligned opposite to the field, while spins on the other three sublattices remain aligned with the field. In three dimensions this transition, which has the same symmetry as that of the four-state Potts model [5], is known to be first order [6–10], a result given correctly by the CVM [6–9]. On the other hand, a single (100) layer of the system has only two of the four sublattices, and the ordered array consists of two sets of spins of which one is aligned parallel and the other antiparallel to the field. Therefore the transition has the symmetry of the Ising model and will be continuous, a result also given by the CVM. This particular system has been chosen for study precisely because the relatively simple CVM gives the second- and first-order transitions in two and three dimensions and can therefore be expected to show the crossover between these behaviours.

The boundary conditions of the slab are that it has neither additional fields acting at the surface nor additional strength in the surface bonds. Under these conditions, the completely ordered state of the slab consists in alternating (100) layers of spins; the surface layers, and every second layer from them, are paramagnetic having all spins aligned with the field. (We assign them layer numbers $l, l-2, \ldots, -(l-2), -l$, where layer 0 is the centre.) The other interleaved layers are antiferromagnetic (layers $l-1, l-3, \ldots, -(l-3), -(l-1)$) having the two sublattices of spins antiparallel to one another. We find that this ordered state is obtained from the pure paramagnetic phase via the following sequence of transitions as the external field is reduced at low temperatures. At some value, $H_1(T, l)$, layers $(l-1)$ and $-(l-1)$, which are related by symmetry, undergo a continuous Ising transition. At a second and smaller value, $H_2(T, l)$, layers $(l-3)$ and $-(l-3)$, also symmetry related, undergo a continuous Ising transition. Finally, at a still smaller value, $H_3(T, l)$, *all* layers, $(l-5)$, $(l-7), \ldots, -(l-7)$, $-(l-5)$, undergo a single first-order transition. As $l \to \infty$, $H_3(T, l) \to H_c(T)$,

the bulk phase boundary. If $l$ is sufficiently small, only the relevant portion of this sequence will be observed (e.g. for $2l+1=7$, layers 2 and $-2$ make a continuous transition at $H_1$ and layer 0 at $H_2$). Thus, under these surface conditions, we observe the kind of scenario envisaged by Shnidman and Domany and can identify the thickness $L^x$ beyond which the slab evinces bulk-like behaviour to be $L^x = 11$. This is a thin slab indeed!

Our calculation employs the CVM in the tetrahedron approximation [7-9], an approximation which gives very good bulk phase boundaries when evaluated by comparison [10, 11] with Monte Carlo simulations [10]. Because our calculation for the slab geometry is rather close to that of [8] for the bulk, our description can be brief. The aim of the CVM is to write a tractable approximate form for the entropy in terms of the entropies of clusters. These cluster entropies are defined in terms of the reduced density matrices $\rho_\alpha$, which depend only on the spins contained in the cluster $\alpha$, according to $S_\alpha/k_B \equiv -\mathrm{Tr}\,\rho_\alpha \ln(\rho_\alpha)$, where $k_B$ is Boltzmann's constant. In the tetrahedron approximation, the entropy of the slab has the form

$$S \approx S^{\mathrm{tetra}} - S'^{\mathrm{pair}} + 5S'^{\mathrm{point}} + S^{\mathrm{surfpoint}} \tag{1}$$

where $S'^{\mathrm{pair}}$ contains no contribution from pairs in the surface and $S'^{\mathrm{point}}$ contains no contribution from surface points. The parameters which are varied to minimise the approximate free energy are the elements of the reduced density matrices, which can be viewed as the probabilities of observing various configurations of the cluster when in thermodynamic equilibrium. There are sixteen independent configurations of a tetrahedron. We do not deal with this number of independent parameters for each tetrahedron since it is sufficient for our purposes to study the dimensional crossover at a single low temperature. Increasing the temperature merely shifts the location of the bulk transition to the $A_3B$ ordered state and eventually eliminates it, but does not alter its first-order nature when it occurs. We choose, therefore, a temperature, $T/|J| = 0.5$, which is low enough that configurations in which more than one spin in a cluster is oriented against the external field can be ignored. Due to the loss of translational symmetry brought about by the presence of the two parallel and identical surfaces, clusters of points in the surface must be distinguished from other points, and pairs which lie in the surface from other pairs. The cluster configuration probabilities which are needed are as follows: $z_{n,a}$ is the probability that, in a tetrahedron between planes $n$ and $n-1$, a spin on sublattice $a$ which is in the plane $n$ is down, antiparallel to the external field†; $z_n$ is the probability that, in this same tetrahedron, all spins are up; $y_n$ is the probability that both spins are up in a nearest-neighbour pair in the plane $n$; $y_{n,a,b}$ is the probability that nearest-neighbour spins are up, one spin in plane $n$ on sublattice $a$, the other in plane $n-1$ and sublattice $b$; $x_{n,a}$ is the probability that a spin in plane $n$ on sublattice $a$ is up. The probability of observing a single down spin in plane $n$ and on sublattice $a$ is independent of the kind of cluster it is in and is equal to the previously defined $z_{n,a}$.

The various cluster contributions to the entropy are now written in terms of these variables. As the function $x\ln(x)$ appears repeatedly, we denote it as $L(x)$. Then

$$-S^{\mathrm{tetra}}/Nk_B = 4\sum_{n=1}^{l}\left(L(z_n) + 2\sum_a L(z_{n,a})\right) - 4\sum_a (L(z_{l,a}) - L(z_{0,a})) \tag{2}$$

† The probability that a down spin occurs in this same tetrahedron on a sublattice in the same $n-1$ plane is clearly equal to $z_{n-1,a}$.

$$-S'^{\text{pair}}/Nk_B = 4\sum_{n=1}^{l-1}\left(L(y_n)+\sum_a L(z_{n,a})\right)+2\left(L(y_0)+\sum_a L(z_{0,a})\right)$$
$$-2\sum_1^l\left(\sum_{a,b} L(y_{n,a,b})+4\sum_a L(z_{n,a})\right)+4\sum_a (L(z_{0,a})-L(z_{l,a})) \tag{3}$$

$$-S'^{\text{point}}/Nk_B = \sum_{n=1}^{l-1}\sum_a (L(x_{n,a})+L(z_{n,a}))+\tfrac{1}{2}\sum_a (L(x_{0,a})+L(z_{0,a})) \tag{4}$$

$$-S^{\text{surfpoint}}/Nk_B = \sum_a (L(x_{l,a})+L(z_{l,a})) \tag{5}$$

where $N$ is the number of sites per plane. It is understood that terms involving sums over $n$ from 1 to $l-1$ are absent if $l=1$.

Because the Hamiltonian involves only one- and two-body terms, the thermodynamic expectation value of the energy can be expressed in terms of the probabilities of finding points and pairs in various configurations. One obtains within the approximation

$$-E/N = 2J\sum_{n=1}^{l}\sum_{a,b}(y_{n,a,b}-z_{n,a}-z_{n-1,b})+4J\sum_{n=1}^{l-1}(y_n-z_{n,a}-z_{n,\bar{a}})$$
$$+2J(y_0-z_{0,a}-z_{0,\bar{a}})+4J(y_l-z_{l,a}-z_{l,\bar{a}}\Big)$$
$$+H\sum_{n=1}^{l-1}(z_{n,a}-x_{n,a})+\tfrac{1}{2}H\sum_a (z_{0,a}-x_{0,a})+H\sum_a (z_{l,a}-x_{l,a}) \tag{6}$$

where $\bar{a}$ is the sublattice other than $a$ on the specified plane. The free energy within the approximation, $F=E-TS$, is now completely specified by (1)-(6). The number of variables on which it depends is reduced to those only of the tetrahedron by the use of the property of reduced density matrices $\rho_\beta = \mathrm{Tr}_{\alpha-\beta}\rho_\alpha$ which yields

$$y_n = \begin{cases} \tfrac{1}{2}\left(z_n+z_{n+1}+\sum_a (z_{n-1,a}+z_{n+1,a})\right) & n\neq 0,\ l \\ z_1+\sum_a z_{1,a} & n=0 \\ z_l+\sum_a z_{l-1,a} & n=l \end{cases}$$

$$y_{n,a,b} = z_n + z_{n,\bar{a}} + z_{n-1,\bar{b}} \qquad n=1,2,\ldots,l$$

$$x_{n,a} = z_{n,\bar{a}} + y_n \qquad n=0,1,\ldots,l.$$

Lastly, the tetrahedron variables themselves are constrained by the requirement that

$$z_n+\sum_a (z_{n,a}+z_{n-1,a}) = 1 \qquad n=1,2,\ldots,l.$$

The free energy is minimised, subject to these constraints, by the introduction of Lagrange multipliers and the resulting equations are solved numerically by Kikuchi's natural iteration method [9].

Results from this procedure are shown in figure 1 in which the values of the magnetic fields at which transitions occur at $T/|J|=0.5$ in slabs of thicknesses $2l+1$ are shown for values of $l=0,1,\ldots,11$. The value for $l=0$, a single plane, was calculated via the CVM for consistency using a pair as the basic unit. Note that the large difference

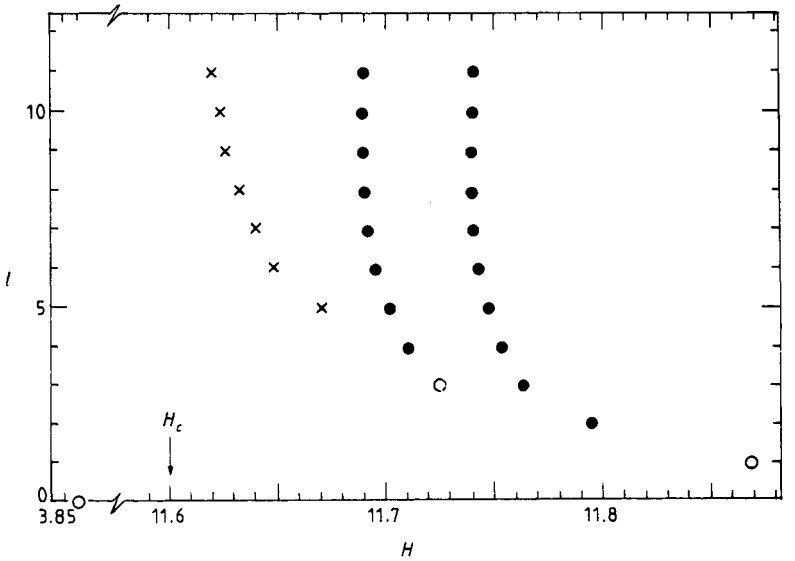


**Figure 1.** Values of the external field $H$ at which transitions occur at a temperature $T/|J| = 0.5$ in a slab of thickness of $2l+1$ layers. An open circle denotes a single continuous transition; a full circle denotes the transition of two layers which, because they are symmetry related, become critical at the same value of $H$; a cross denotes a single first-order transition at which $l-4$ layers order together. The bulk ordering field is denoted by $H_c$. Note the break in the scale of $H$.

between the critical values of the magnetic field for a single layer and for any other thickness is simply a reflection of the difference between four and twelve nearest neighbours. Continuous transitions are shown with circles. At the single first-order transition, denoted by a cross, $l-4$ layers order together. From the figure we see that for the surface conditions we have employed (no surface fields or bond enhancement), no wetting of the surface of a semi-infinite bulk by either phase would occur. Further, under these conditions, the first-order nature of the transition of the three-dimensional system already begins to influence the behaviour of the slab when it is only eleven layers thick. The only remnant of the continuous nature of the transition of the two-dimensional system is the presence of two continuous surface transitions.

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