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A series approach to wetting and layering transitions: I. Potts models

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Abstract. Our aim in a triad of papers is to show that series methods provide a complementary approach to mean-field theories in the study of interface wetting and unbinding transitions.

In this paper we consider a q-state Potts model, which contains an interface bound to a surface by a bulk field. Low-temperature and high-q series expansions are used to show that, as the field tends to zero, the interface unbinds from the surface through a sequence of first-order layering transitions. We discuss the various regions of the phase diagram where the different expansions are expected to be valid and compare our results with those obtained in the mean-field approximation.

1. Introduction

In the past few years there has been a spate of publications dealing with the properties of interfaces in, for example, solids, fluids and magnets. Theoretical approaches, such as mean-field theory (Widom 1972), numerical work (Selke 1984) and phenomenological arguments (Fisher 1986), have been used to explain such diverse physical phenomena as the shape of fluid-fluid interfaces, wetting and the role of interfaces in phase transitions. Recent reviews on both the structure of interfaces and interfacial wetting transitions have been published by Pandit *et al* (1982), Sullivan and Telo da Gama (1985) and Abraham (1986). Also of recent interest are papers by Bricmont and Slawny (1985) and Bricmont and Lebowitz (1987); earlier work is referenced in the reviews. The dynamics of interfacial transitions is a large topic in itself and will not be considered here (de Gennes 1985).

In this series of three papers we shall focus upon three-dimensional models in which a discrete underlying lattice influences the behaviour of a two-dimensional interface. The simplest example would be a semi-infinite Ising model with an interface introduced via a suitable choice of boundary conditions. Previous authors (de Oliveira and Griffiths 1978, Pandit *et al* 1982, Pilorz and Sokolowski 1984) have shown that in such systems an interface bound to a surface by, for example, a bulk field or local pinning potential, may unbind through a series of first-order layering transitions as the field or potential tends to zero. However, their results have been based upon mean-field theories. Our aim here is to extend work by Duxbury and Yeomans (1985) and Armitstead *et al* (1986) showing that series expansions can be usefully used to describe such layering transitions. We find results which are usually, but not always, qualitatively similar to those obtained in the mean-field limit.

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In this, the first of the three papers, we describe the unbinding transitions of an interface in a q-state Potts model which is bound to the surface by a bulk field. We use both low-temperature and high-q expansions to show that the interface unbinds from the surface through a series of first-order layering transitions as the bulk field tends to zero, that is, as coexistence is approached. Results of the two different types of expansion, which are expected to hold in different regions of parameter space, are compared. We then discuss the mean-field limit of the same problem by solving the mean-field equations numerically and also by taking the mean-field limit of the low-temperature series (Thompson 1974, Szpilka and Fisher 1986). No qualitative differences in the interface phase diagrams are found.

In the second paper of the series we will show that the same method is applicable to a group of models which have been usefully used as simplified, and hence more tractable, representations of interfaces: the solid-on-solid models. In these systems overhangs of the interface and bulk fluctuations are suppressed. We study a model in which the interface is attracted to the surface by a local pinning potential and demonstrate a sequence of layering transitions as the pinning potential approaches zero. These models have been studied in previous publications using renormalisation group methods (Nightingale *et al* 1984) and extrapolations from numerical results on strips of finite width (Luck *et al* 1983).

The third paper will continue some earlier work (Armitstead *et al* 1986) in which the wetting of an interface in the three-state chiral clock model was studied using a low-temperature series. We examine the same model through a numerical solution of the mean-field theory and, surprisingly, find qualitatively different results. We investigate this further by taking the mean-field limit of the low-temperature series, obtaining results in agreement with the numerical work. We show that there is a crossover to mean-field behaviour as the coordination number of the lattice is increased and demonstrate that mean-field theory underestimates fluctuations which are important in driving the transitions for the simple cubic lattice.

The experimental data required to observe layering transitions is very difficult to gather because the low-temperature work requires long equilibration times and good resolution is needed to distinguish between possible layers. Qualitative comparisons with specific systems are hampered by limited knowledge of many atom-substrate potentials. However, layering transitions have been observed in systems of a gas adsorbed on a solid substrate; a classic example is the Kr-on-graphite work of Singleton and Halsey (1954). Further experiments, and possible interpretations of their results, are described in the reviews already cited (Pandit *et al* 1982, Sullivan and Telo da Gama 1985).

We now introduce the model which will be studied in this paper: the Potts model with an interface. The geometry we consider is a simple cubic lattice with periodic boundary conditions in two directions and free surfaces in the third. A general site is labelled (i,j) where i labels the layers parallel to the surfaces, with $i=1$ being the surface layer, and j distinguishes sites within a layer. This geometry is shown in figure 1. At each lattice site there is a q-state Potts spin $\sigma_{i,j}=1,2,\ldots,q$. An interface is introduced into the system by applying infinite surface fields favouring states $\sigma_{1,j}=1$ and $\sigma_{\infty,j}=2$ in layers 1 and ∞ respectively. The Hamiltonian of the system is then taken to be

$$H=-\tfrac{1}{2}J_0\sum_{\substack{ij\\ij'\\i>1}}\delta(\sigma_{i,j},\sigma_{i,j'})-J\sum_{\substack{ij\\i>0}}\delta(\sigma_{i,j},\sigma_{i+1,j})-h\sum_{\substack{ij\\i>1}}\delta(\sigma_{i,j},2). \tag{1.1}$$

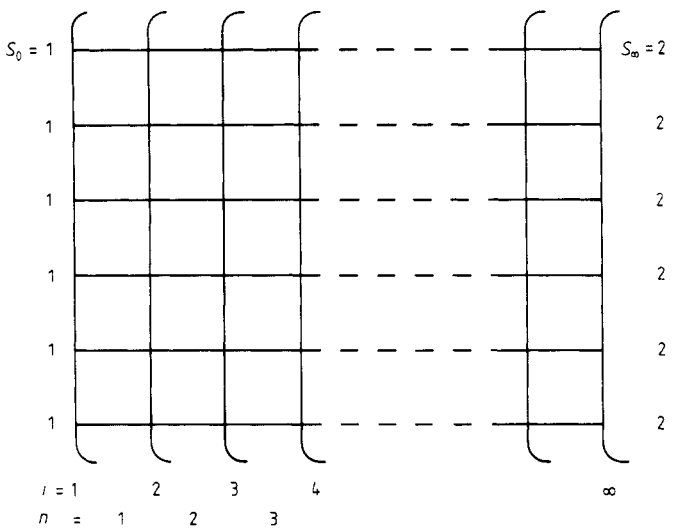

Figure 1. Interface geometry considered for the Potts model on a simple cubic lattice. n denotes the position of the interface.

The pair interactions are ferromagnetic and act between nearest neighbours. Note that we have distinguished in-layer and interlayer couplings—this will be useful in the low-temperature series analysis which follows.

For $h > 0$, at zero temperature, $T = 0$, the interface is constrained to lie next to the surface. We shall use n to label the position of the interface with $n = 1$ describing the position immediately adjacent to the surface, as indicated in figure 1. For $h < 0$ the interface is unpinned from this surface and lies at $n = \infty$. For $h = 0$, all positions of the interface, given that it remains parallel to the surfaces, are degenerate in energy.

Our aim is to explore what happens in the vicinity of $h = 0$ for $T > 0$. To this end we shall use two different expansion methods: firstly, a low-temperature series which is described in § 2 and, secondly, a large-q expansion elucidated in § 3. In both cases the low orders of the series expansion are considered explicitly. We then show how it is possible to pick out the important terms at general order and hence to predict a large, and possibly infinite, sequence of layering transitions. The methods have different ranges of validity and demonstrate that different fluctuations are important in driving the transition in the two regimes.

In § 4 the same problem is studied using the mean-field approximation. Section 4.1 shows how the mean-field limit of the low-temperature series may be taken by considering an infinite coordination number. The layering sequence is qualitatively unchanged by this limiting procedure. A numerical solution of the mean-field equations, presented in § 4.2, confirms this result. Finally § 5 contains brief concluding remarks.

2. Low-temperature expansions

2.1. Setting up the expansion

As low-temperature expansions will be used throughout this series of papers, and as the Potts model provides one of the easiest examples, we shall discuss the calculation

in some detail. The work extends that of Duxbury and Yeomans (1985) who treated the Ising model ($q=2$). Our results agree with theirs in this limit.

To study the phase diagram at non-zero temperatures consider spin flips about all possible degenerate ground states. The standard low-temperature expansion (Domb 1960) follows from a decomposition of the partition function

$$Z_n(N) = \exp(-NE_n^0/k_B T)\left(1 + \sum_{m=1} \Delta Z_n^m(N)\right) \tag{2.1}$$

where n labels the position of the interface at $T=0$, E_n^0 is the ground-state energy per spin, N is the number of spins in the lattice and $\Delta Z_n^m(N)$ is the total contribution from states with m overturned spins. The reduced free energy per spin is then given by

$$F_n = -F_n(N)/Nk_B T \tag{2.2}$$

$$= -E_n^0/k_B T + \sum_{m=1}' \Delta Z_n^m(N)/N \tag{2.3}$$

where, using the linked-cluster theorem (Domb 1960), $\Sigma'_{m=1} \Delta Z_n^m(N)$ now only contains terms linear in N.

The Boltzmann factors appearing in the expansion are:

$y = \exp(-\beta h)$, the contribution from the bulk field for spin flips from $\sigma = 2$ to any other state,

$t = \exp(-\beta J)$, for introducing a wrong bond perpendicular to the interface, and

$w = \exp(-\beta J_0)$, for introducing a wrong bond parallel to the interface,

where $\beta = 1/k_B T$.

The aim is to find the interface position n which, for a given h and T, maximises the reduced free energy. The summation in (2.3) may be expressed as a power series in the parameter w. For small enough w we may deduce the qualitative form of the phase diagram from the leading-order terms of the expansion, with higher-order corrections giving only a small shift in the phase boundaries. We consider first the lowest-order contributions to the free energy to demonstrate how the sequence of interface phases may be built up inductively.

2.2. Low-order terms

From diagrams where one spin is flipped relative to the ground state we obtain

$$F_n - F_1 = -(n-1)\beta h + [y^{-1} + (q-2)t + (n-2)(y^{-1} + q - 2) \times t^2 - (n-1)(q-1)t^2 y]w^{q_\perp} + O(w^{2q_\perp - 2}) \tag{2.4}$$

where $q_\perp$ is the number of nearest neighbours within a layer. Putting $\beta h \sim O(w^{q_\perp})$ for a phase transition gives

$$F_n - F_1 = -(n-1)\beta h + [1 + (q-2)t - (q-1)t^2]w^{q_\perp} + O(w^{2q_\perp - 2}) \tag{2.5}$$

$$F_{n'} - F_n = -(n'-n)\beta h + O(w^{2q_\perp - 2}) \qquad n', n \geq 2. \tag{2.6}$$

Equations (2.5) and (2.6) show that for $O(w^{2q_\perp - 2}) < h < h_{1:2}$ defined by

$$\beta h_{1:2} = [1 + (q-2)t - (q-1)t^2]w^{q_\perp} + O(w^{2q_\perp - 2}) \tag{2.7}$$

then $F_2 - F_n > 0$, $n = 1, 3, 4 \ldots$. Hence $n = 2$ appears as a stable phase and first-order calculations have been sufficient to determine the 1:2 phase boundary. However, it is apparent from (2.6) that phases with $n \geqslant 2$ remain degenerate within $O(w^{2q_-})$ of $h = 0$. This is shown diagrammatically in figure 2(a).

To break this degeneracy it is most convenient to evaluate $F_n - F_2$, which is first non-zero at the second-order of the low-temperature expansion. It proves consistent (see (2.9)) to take $\beta h \sim O(w^{2q_-})$ giving

$$F_n - F_2 = -(n-2)\beta h + (1-t)^2[1+(q-1)t]^2 w^{2q_-} + O(w^{3q_-}). \tag{2.8}$$

Therefore $n = 3$ is the stable phase for $O(w^{3q_-}) < h < h_{2:3}$ where

$$\beta h_{2:3} = (1-t)^2[1+(q-1)t]^2 w^{2q_-} + O(w^{3q_-}). \tag{2.9}$$

Interface phases with $n \geqslant 3$ remain degenerate within $O(w^{3q_-})$ of $h = 0$. This is shown in figure 2(b).

2.3. Transfer matrix calculations

The first- and second-orders of the low-temperature series presented above suggest that the interface phase $n+1$ will first be identified as stable at the nth order of the expansion. To prove this it is necessary to write down the leading term in the expansion at general order. This is less imposing than it might first appear because if reduced free energy differences, $F_{n'} - F_n$, $n' > n$, are considered then many combinations of spin flips contribute in the same way to both $F_{n'}$ and F_n and hence cancel out when the difference is taken. An obvious example is shown in figure 3(a). What is perhaps not so obvious is that other diagrams which differ from one another by factors of y, such as that shown in figure 3(b), will also cancel to leading order in the vicinity of a phase boundary. This occurs because, when the dependence of h on w^{q_-} is considered, it becomes apparent that it is consistent to take $y = 1$ to leading order.

Some thought shows that the lowest-order diagrams which do contribute to $F_{n'} - F_n$ in the vicinity of a phase boundary are chains of length n. The chain which is of lowest order in t is shown in figure 3(c). These are indeed the physical fluctuations one would expect to distinguish between the free energy of an interface at position n

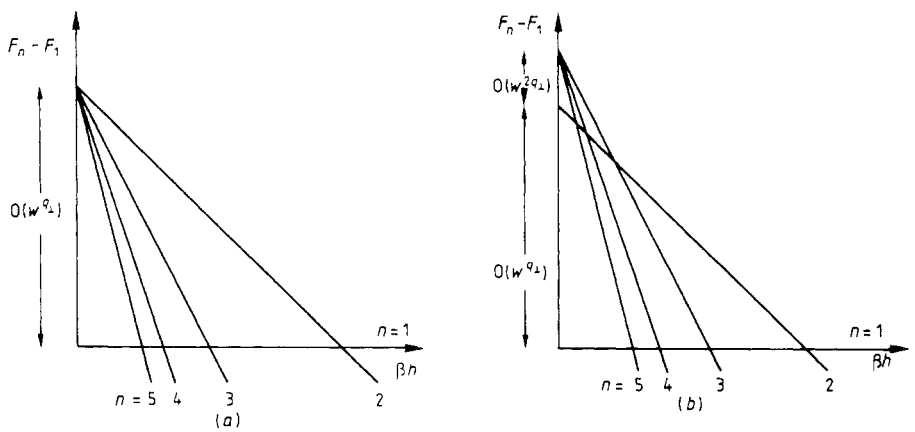

Figure 2. Qualitative comparison of the reduced free energy differences per interface spin, $F_n - F_1$, at (a) first-order and (b) second-order of the low-temperature expansion.

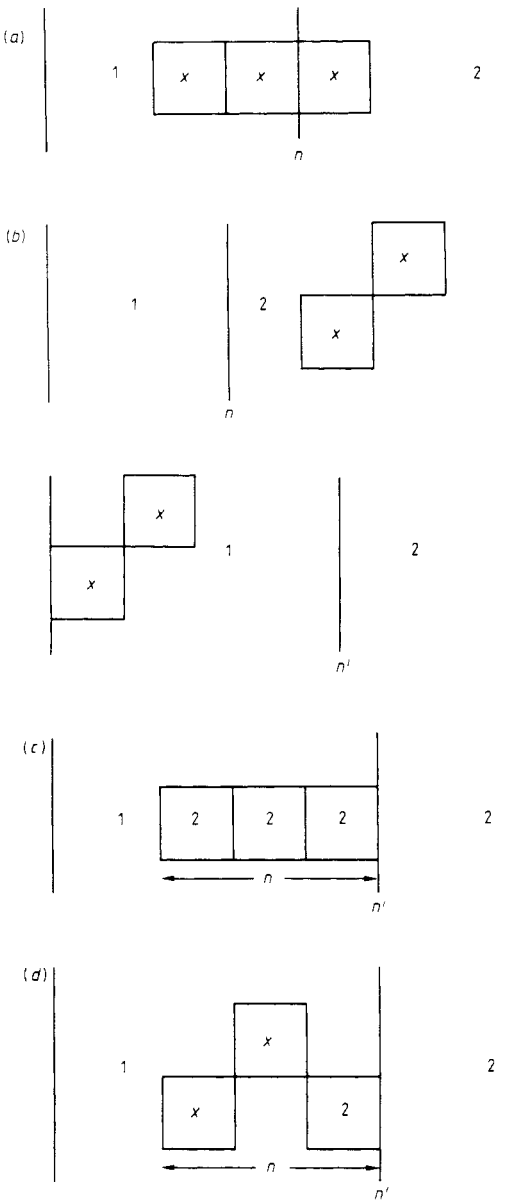

Figure 3. Graphs which need to be considered in calculating the reduced free energy difference $F_{n'} - F_n$, $n' > n$, in the low-temperature expansion. The surface and the interface are denoted by vertical lines and the flipped spins are enclosed by a box. The symbol inside the box shows the final spin state; x denotes that the spin is different from any of its neighbours. (*a*) Graph occurring in both phases n' and n, and therefore not contributing to $F_{n'} - F_n$. (*b*) Graphs with the same Boltzmann factor in the vicinity of a phase boundary, which cancel out in $F_{n'} - F_n$. (*c*) Graph giving rise to the lowest-order contribution to $F_{n'} - F_n$. (*d*) A typical disconnected graph which must also be included.

and one at n'. Also disconnections of such a chain, for example, that shown in figure 3(d), must be included. Each disconnection contributes a counting factor of -1 (Fisher and Selke 1981).

The problem of evaluating the leading-order reduced free energy difference is therefore a matter of building up the contribution from long thin diagrams. This is essentially a one-dimensional problem and may be treated using transfer matrices. The method is explained in appendix 1 and leads to the result

$$F_{n'} - F_n = -(n'-n)\beta h + [1+(q-2)t-(q-1)t^2]^n w^{nq_-} + \mathrm{O}(w^{(n+1)q_- - 2}) \qquad n' > n. \tag{2.10}$$

We are now in a position to argue inductively that the interface wets through a series of first-order phase transitions. Assume that at the $(n-1)$th order of the expansion the phase n has been established as stable for

$$[1+(q-2)t-(q-1)t^2]^{(n-1)} w^{(n-1)q_-} + \mathrm{O}(w^{nq_- - 2}) > \beta h > \mathrm{O}(w^{nq_- - 2}) \tag{2.11}$$

and, from (2.10), that all phases $n' \geq n$ remain degenerate at $\beta h = 0 + \mathrm{O}(w^{nq_- - 2})$. (Figure 2($b$) shows the situation for $n = 3$.) To break this degeneracy it is necessary to consider higher-order terms, $\mathrm{O}(w^{nq_-})$, in the expansion. The reduced free energy difference $F_{n'} - F_n$, $n' > n$, is given by (2.10). This equation shows immediately that for

$$[1+(q-2)t-(q-1)t^2]^n w^{nq_-} + \mathrm{O}(w^{(n+1)q_- - 2}) > \beta h > \mathrm{O}(w^{(n+1)q_- - 2}) \tag{2.12}$$

position $(n+1)$ is stable compared to n and $n' > n+1$. All phases $n' \geq n+1$ remain degenerate at $\beta h = 0 + \mathrm{O}(w^{(n+1)q_- - 2})$.

As we have explicitly demonstrated the appearance of phases $n = 1, 2, 3$, iterating this argument recursively leads to a sequence of layering transitions. However, for large n or q, correction terms may become important in determining the phase sequence, as will be commented upon later.

3. High-q expansions

3.1. Setting up the expansion

In § 2 we demonstrated how to build up a series expansion using a temperature-dependent variable as the small parameter. This should predict the correct phase sequence for finite q and sufficiently small temperatures. However, for q large the series will need reordering and will eventually break down. Therefore in order to examine this region of the phase diagram we shall use another small variable, $(1/q)^a$, where a is a parameter to be determined such that successive terms of the series can be ordered in decreasing size.

In setting up the expansion we follow Ginsparg *et al* (1980) who studied the bulk-phase diagram of the q-state generalisation of the Ising gauge theory with matter fields in the Lagrangian form. Goldschmidt (1981) later extended this work to include the effects of an applied field.

Our first aim is to describe the expansion and to explain what constitutes a sensible small parameter. Then, in § 3.2, the lowest orders of the high-q series are presented explicitly. In § 3.3 we examine the phase diagram to general order, revealing that the system still undergoes a sequence of layering transitions. Finally, in § 3.4, we compare the low-temperature and high-q expansions, noting that there are two regions in which different diagrams drive the transitions.

At sufficiently low temperatures or high fields the bulk phase is ferromagnetic for all q and this is the region in which our expansion is valid. As in the previous section, we consider all possible ground states and expand the free energy about them. We shall take the case $J = J_0$ because, although the calculations can easily be generalised to the non-isotropic model, we do not gain any further insight by doing so.

The standard expansion uses $\exp(-\beta J)$ as a small variable. In order to define a sensible large-q limit it is convenient to parametrise the theory in terms of new couplings, v and f, defined by

$$e^{\beta J} = 1 + q^a v \tag{3.1}$$

$$e^{\beta h} = 1 + q^b f \tag{3.2}$$

where a and b will be shown to satisfy certain inequalities by requiring that the terms of the expansion can be ordered in decreasing size as $q \to \infty$ for v and f fixed. Indeed, if a high-temperature expansion is also performed in terms of the same couplings, a and b are unambiguously determined if both series are to have sensible limits. Here we are free within certain constraints to choose those values which prove to be the most useful.

The bulk fluctuations will be considered first and limits on a and b will then be derived. These limits will be shown to still hold when there is an interface in the system and, choosing suitable values for a and b, the expansion will be demonstrated explicitly to lowest orders. We shall discuss later the effects of taking a different value of a.

The terms in the summation in (2.1) may be written

$$\Delta Z_n^m(N) = \sum_{\substack{\text{diagrams} \\ \text{with } m \\ \text{spin flips}}} (\text{weight}) \exp(-\beta L) \exp(-\beta h S) \tag{3.3}$$

where S is the net number of spins flipped from the state $\sigma_{i,j} = 2$ in a given diagram and L is the extra number of wrong bonds created by the m spin reversals.

To ensure that the q-dependent contributions from bulk diagrams of a given size decrease as the size increases, we identify the diagrams which, for a given m, contribute to the series with the highest power of q. These are diagrams with m spins flipped from $\sigma_{i,j} = 2$, occupying minimum volume, such that all neighbours are in a different state and they contribute a factor

$$q^S(1+q^a v)^{-L}(1+q^b f)^{-S} \sim \begin{cases} q^{S(1-ad-b)} & e^{\beta h} \gg 0 \\ q^{S(1-ad)} & e^{\beta h} \sim O(1) \end{cases} \tag{3.4}$$

where d is the dimensionality. Therefore terms in the series will decrease in size with increasing m if

$$\begin{aligned} &a + b/d \geqslant 1/d && e^{\beta h} \gg 0 \\ &a \geqslant 1/d && e^{\beta h} \sim O(1). \end{aligned} \tag{3.5}$$

It is now important to check whether (3.5) still holds when the system contains an interface. For a given m the contribution with the highest power of q comes from a $(d-1)$-dimensional compact diagram where all spins lie in the '2' phase next to the interface and all neighbours flip to a different state. Such diagrams again lead to condition (3.4).

In the work which follows we shall choose $a = \frac{1}{3}$. This allows the expansion to be used at higher temperatures as will be remarked upon further in § 3.4. It will be demonstrated in the next section that we are working near $h = 0$ and that the choice of b is irrelevant to leading order. Therefore, for convenience, we now put $b = 0$.

3.2. Lowest-order calculations

We now present explicitly the lowest-order terms of an expansion in $z = 1/q^{1/3}$ and show how, just as in the case of the low-temperature series, there is a sequence of interface phases with new phases appearing as higher orders of the expansion are considered.

For large βh, $n = 1$ is stable and therefore to find a possible phase boundary as βh decreases we calculate $F_n - F_1$. All contributions from single-spin-flip diagrams are listed in table 1. Adding these together gives (note this is the same as equation (2.4) but written in terms of the new parameters v and f):

$$\begin{aligned} F_n - F_1 = &-(n-1)\beta h + (1+z^{-1}v)^{-4}(1+f) + z^{-3}(1-2z^3)(1+z^{-1}v)^{-5} \\ &+ (n-2)(1+z^{-1}v)^{-6}(1+f) + (n-2)z^{-3}(1-2z^3)(1+z^{-1}v)^{-6} \\ &- (n-1)z^{-3}(1-z^3)(1+z^{-1}v)^{-6}(1+f)^{-1}. \end{aligned} \tag{3.6}$$

Retaining only the leading-order term we obtain

$$F_n - F_1 = -(n-1)\beta h + z^2 v^{-5} + \mathrm{O}(z^3) \qquad n \geqslant 2. \tag{3.7}$$

This demonstrates that for a phase transition βh must be small; hence we may put $f = 0$ and our choice of b, as stated above, becomes irrelevant. As βh decreases, $n = 2$ becomes stable when

$$\beta h_{1:2} = z^2 v^{-5} + \mathrm{O}(z^3). \tag{3.8}$$

To this order in the expansion, all $n \geqslant 2$ are degenerate for $\beta h = 0 + \mathrm{O}(z^3)$. Note that we have implicitly assumed that v is not too large so that the series can still be ordered in terms of powers of z. This point will be discussed further in § 3.4.

Now consider the terms $\mathrm{O}(z^3)$. These will arise from:

(a) single-spin-flip diagrams, from the last two terms of equation (3.6) and also from the expansion of the Boltzmann factor in the lowest-order term, and

Table 1. Contributions to $F_n - F_1$, $n \geqslant 2$, from single-spin-flip diagrams in the high-q expansion. The flipped spin is denoted by a caret; $x \neq 1, 2$. L is the extra number of wrong bonds created by the spin reversal and S is the net number of spins flipped from $\sigma_{ij} = 2$.

Spin flipped	Number of diagrams per interface spin	L	S
$1\hat{1}2 \to 1\hat{2}2$	1	4	−1
$1\hat{1}2 \to 1\hat{x}2$	$(q-2)$	5	0
$1\hat{1}1 \to 1\hat{2}1$	$(n-2)$	6	−1
$1\hat{1}1 \to 1\hat{x}1$	$(q-2)(n-2)$	6	0
$2\hat{2}2 \to 2\hat{1}2$	$-(n-1)$	6	1
$2\hat{2}2 \to 2\hat{x}2$	$-(q-2)(n-1)$	6	1

(b) the lowest-order two-spin-flip diagram, as shown in figure 4(a), which contributes

$$2z^3v^{-9}(1-2z^3)(1-3z^3)(1+zv^{-1})^{-9} \sim 2z^3v^{-9}. \tag{3.9}$$

Adding (a) and (b) gives

$$F_n - F_1 = -\beta h(n-1) + z^2v^{-5} + z^3(-6v^{-6}+2v^{-9}) + O(z^4) \qquad n \geqslant 2. \tag{3.10}$$

Hence $n \geqslant 2$ remain degenerate for $\beta h = 0 + O(z^4)$ at this order. Note that it is evident from the lowest-order calculations that once a given diagram contributes at a given order it will also contribute at higher orders from the expansion of the Boltzmann factor. This does not occur in the low-temperature series.

The lowest-order graph which does contribute to $F_n - F_2$ is shown in figure 4(b). This gives

$$F_n - F_2 = -\beta h(n-2) + z^4v^{-10} + O(z^5). \tag{3.11}$$

There are no contributions from single-flip diagrams in the vicinity of the n:2 boundary. Hence the interface phase $n = 3$ becomes stable for

$$\beta h_{2:3} = z^4v^{-10} + O(z^5). \tag{3.12}$$

Consideration of the lowest-order calculations enables us to deduce the form of the important diagrams at general order. We shall use this information in the next section to enable us to propose an inductive argument to obtain a sequence of layering transitions.

3.3. General-order diagrams

To explore the effect of higher-order terms in z on the phase diagram it is necessary to identify the lowest-order diagrams which contribute to $F_{n'} - F_n$, $n' > n$. These are, as in the case of the low-temperature series, axial chains of length n as shown in figure 5(a). However, only configurations in which each spin flips to a different state to its neighbours need be considered in leading order. Moreover, disconnected graphs give higher-order contributions. Hence

$$F_{n'} - F_n = -(n'-n)\beta h + (z/v)^{5n}z^{-3n}(1-2z^3)^n(1+zv^{-1})^{-5n} + O(z^{2n+1}) \tag{3.13}$$

$$= -(n'-n)\beta h + z^{2n}v^{-5n} + O(z^{2n+1}). \tag{3.14}$$

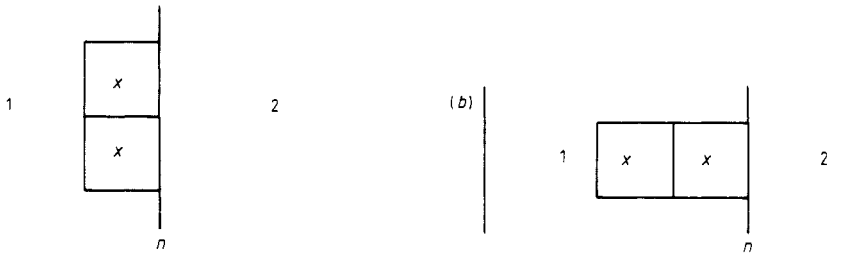

Figure 4. Important diagrams appearing in the high-q expansion. (a) Lowest-order two-spin-flip graph. (b) Lowest-order graph contributing to $F_n - F_2$, $n \geqslant 3$.

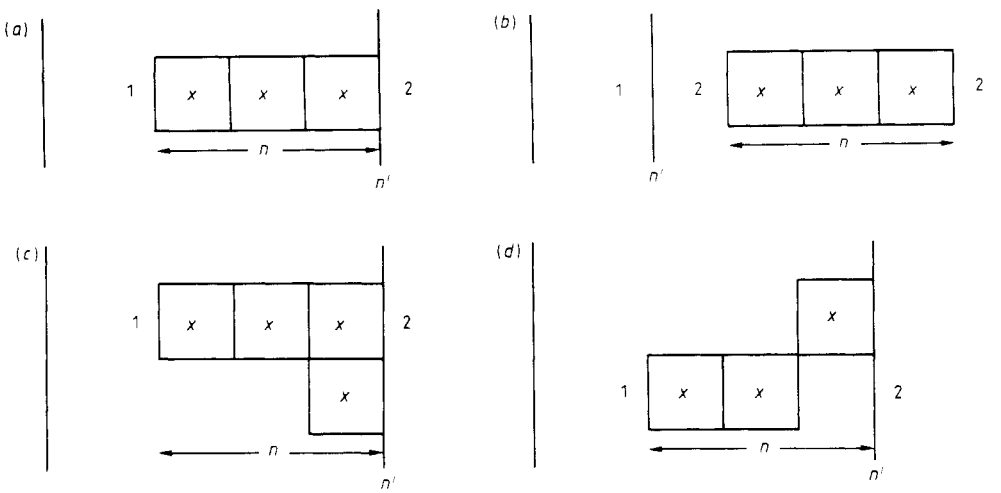

Figure 5. Diagrams which contribute to $F_{n'}-F_n$, $n'>n$, in the high-q expansion. (a) Lowest-order contribution. (b), (c) and (d) First correction terms.

We have also calculated the correction terms to this expression as a guide to where the ordering of the series breaks down. All contributions to $O(z^{2n+1})$ are listed below.

(i) $-5nz^{2n+1}v^{-(5n+1)}$ from the expansion of $(1+zv^{-1})^{-5n}$ in the leading-order term.

(ii) $-z^{2n+1}v^{-(5n+1)}$ from connected axial chains which do not border the interface in the '2' phase with all neighbours flipping to different states as shown in figure 5(b).

(iii) $4z^{2n+1}v^{-(5n+4)}$ from graphs as shown in figure 5(c), again with all neighbours flipping to different states. The factor of 4 arises from the possible orientations of the graphs.

(iv) $-(n-1)z^{(2n+1)}v^{-(5n+1)}$ from the axial chains which contribute in leading order but with a single disconnection as shown in figure 5(d). The factor $(n-1)$ arises from counting the $(n-1)$ possible positions of the disconnection.

Adding these contributions gives

$$F_{n'}-F_n=-(n'-n)\beta h+z^{2n}v^{-5n}-z^{(2n+1)}(6nv^{-(5n+1)}-4v^{-(5n+4)})+O(z^{2n+2}). \tag{3.15}$$

It is now possible to use an inductive argument, analogous to that presented in § 2.3, to show that a sequence of layering transitions is stable. Assume that at the $2(n-1)$th order of the expansion the phase n has been established as stable for

$$z^{2(n-1)}v^{-5(n-1)}+O(z^{2n-1})>\beta h>O(z^{2n-1}) \tag{3.16}$$

and that all phases $n'\geqslant n$ remain degenerate for $\beta h=0+O(z^{2n-1})$. The higher-order terms in the expansion which break this degeneracy are, from (3.15), $O(z^{2n})$. The reduced free energy difference $F_{n'}-F_n$, $n'>n$, is given by (3.15), which shows that for

$$z^{2n}v^{-5n}+O(z^{2n+1})>\beta h>O(z^{2n+1}) \tag{3.17}$$

position $(n+1)$ is stable compared to n and n', with $n'>n+1$. All phases $n'\geqslant n+1$ remain degenerate at $\beta h=0+O(z^{2n+1})$.

Iterating this argument recursively leads to a sequence of layering transitions until the value of n appearing in the correction terms in (3.15) becomes important. Note that, in contrast to the expansion used in § 2.3, the phase boundaries predicted will be more accurate for larger values of q. However, the value of v, related to the

temperature, may be important in the ordering of the series. This is commented upon further in the next section.

3.4. Crossover between the high-q and low-temperature regions

From both the high-q and low-temperature expansions we have demonstrated a sequence of layering transitions. However, from the derivation of the general-order diagrams, it is apparent that different diagrams dominate in each case. Therefore there must be a crossover between the regions of validity of the two expansions. In order to understand this crossover it is helpful to concentrate first on the significance of the value of v.

In the $q \to \infty$ limit in zero field, the critical point is given by $v = 1$ (Goldschmidt 1981). $v > 1$ defines the ferromagnetic region in which our high-q expansion is valid; therefore $v \geq 1$ in the expression for the reduced free energy. Increasing v, at fixed q, corresponds to decreasing the temperature.

Notice in (3.6) that $O(z^4)$ includes a contribution $z^4 v^{-4}$. If v is very large then this term will dominate $z^2 v^{-5}$, that is, v rather than z is important in determining the ordering of the series. At general order, v is important when $z^2 v \sim O(1)$. The diagrams which eventually dominate when the series is ordered in terms of v have a contribution of $O(z/v)^{4n}$; these are also the diagrams, shown in figure 3(c), which dominate in the low-temperature expansion. $z^2 v \sim O(1)$ signals a crossover between the high-q diagrams and the low-temperature diagrams providing the leading term at each order of the series expansion.

The same phenomenon is evident from the general term in the low-temperature expansion given in (2.10). When $qt \sim 1$ the dominant term in the square brackets is qt rather than 1, and the ordering of the terms in the series must be changed. Indeed for $qt > 1$, it is not clear from this approach whether the correct leading-order terms could be identified or even that the series does not diverge. The high-q expansion is

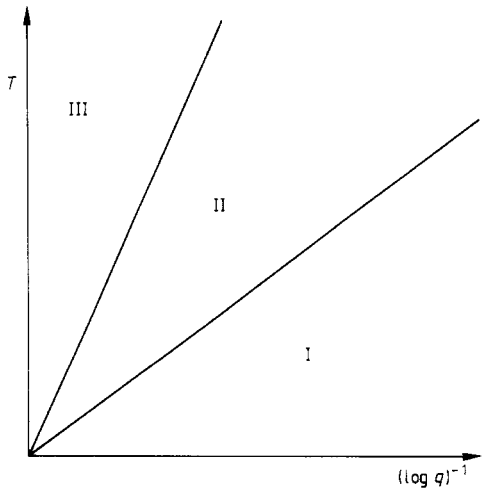

Figure 6. The regions of validity of the expansions in the q-T plane. Region I: low-temperature diagrams dominate. Region II: high-q diagrams dominate. Region III: neither series is valid ($v < 1$).

needed to show that the q dependence in itself does not cause a divergence. (Note that $qt \sim z^{-2}v^{-1}$ as expected.)

Identifying the diagrams which give rise to the leading-order terms indicates that the important fluctuations in the low-temperature limit are, as shown in § 2.3, axial diagrams in which all spins are flipped to state 2, that is, the bulk phase extends locally towards the surface. In the high-q limit however, these are replaced by diagrams of the same shape but with all spins flipping to a state different from their neighbours, as illustrated in figure 5(a). In figure 6 we show the boundary between the two regimes in the q-T plane.

We now make some comments on the choice of a. In § 3.1 the limit $a \geq 1/d$ was derived, and we chose the value corresponding to the lower bound. Taking different values of a would cause different terms in the expansion to dominate. For example, for $a > 1$, the low-temperature diagrams dominate for all v, whereas for $1 > a \geq 1/d$ high-q diagrams dominate for suitable v. We chose the lower limit as this automatically probes the highest possible temperatures before the series breaks down as $v \to 1$. (Note that $v = 1$ is below the bulk critical temperature $T_c(q)$ for all $q < \infty$.)

4. Mean-field theory

Most previous work on layering transitions in Ising systems has been based on mean-field approximations (de Oliveira and Griffiths 1978, Pandit *et al* 1982). Therefore we devote this section to comparing the results of mean-field theory and low-temperature series calculations to check the validity of the mean-field approximation in three dimensions and to follow which fluctuations are important as the mean-field limit is approached. In the Potts case considered here mean-field theory and low-temperature series do, as expected, give the same sequence of layering transitions. However, this is not always the case as will be demonstrated for the chiral clock model in the third paper of this series.

We take two approaches. Firstly, following Szpilka and Fisher (1986) we perform the low-temperature series expansion for general coordination number $q_\parallel$, $q_\perp$, the number of nearest neighbours parallel and perpendicular to the normal to the wall respectively, and take the mean-field limit, $q_\parallel, q_\perp \to \infty$, with $q_\parallel J$ and $q_\perp J_0$ fixed. This allows us to follow the evolution of the low-temperature series as the mean-field limit is approached. Secondly, we perform a more conventional numerical mean-field theory which is valid at higher temperatures but which must be solved numerically.

4.1. Low-temperature series in the mean-field limit

We perform a low-temperature expansion with arbitrary coordination number and, having obtained an expression for the phase boundaries, $\beta h_{n:n+1}$, take the mean-field limit, $q_\parallel, q_\perp \to \infty$ with $q_\parallel J$ and $q_\perp J_0$ constant (Thompson 1974). The lattice does not have to be regular or tied to a particular spatial dimension for this result to hold.

Consider first the Ising case, $q = 2$. The way in which the number of axial neighbours affects the Boltzmann factor involved in creating an axial chain is illustrated in figure 7. Observe that each flipped spin can occupy $q_\parallel/2$ positions relative to the flipped spin in the preceding layer. Including the contributions from initial and final bonds, and using an iterative argument as in § 2.3 to demonstrate a sequence of layering

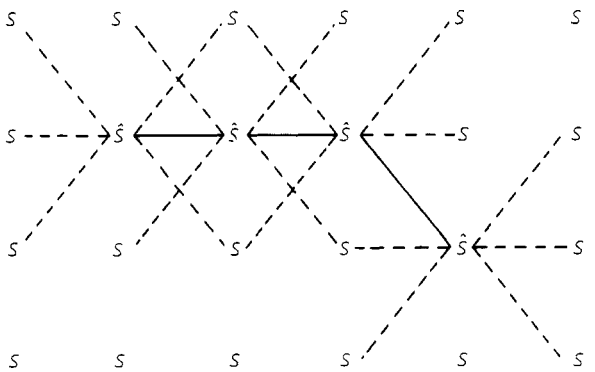

Figure 7. Possible appearance of an axial chain of flipped spins for the Ising model when the axial coordination number exceeds 2 (here $q_{\|}=6$). Layers are denoted by columns of spins S. In each layer one spin (marked $\hat{S}$) is flipped. It is coupled to a flipped spin in an adjacent layer by a full line and also to $(\frac{1}{2}q_{\|}-1)$ unflipped spins by broken lines. In-layer broken bonds (q_{-} per flipped spin) are not shown.

transitions, leads to the phase boundaries

$$\beta h_{n;n+1}=[q_{\|}(t^{q_{\|}-2}-t^{q_{\|}})/2]^{n-1}(1-t^{q_{\|}})w^{nq_{-}}+O(w^{(n+1)q_{-}-2}). \tag{4.1}$$

Hence the mean-field limit, $t^{q_{\|}}=\tau=$ constant, $t^2\to 1$, is

$$\beta h_{n;n+1}=(1-\tau)[\tau\ln(1/\tau)]^{n-1}w^{nq_{-}}+O(w^{(n+1)q_{-}}). \tag{4.2}$$

Note that all the connected and disconnected diagrams are needed to obtain this result with the contributions from the disconnections becoming increasingly important as the mean-field limit is approached.

We now turn to the more general case of the q-state Potts model. The leading-order diagrams are again axial graphs and the easiest way of calculating their contribution is to extend the transfer matrix method described in appendix 1 to a general coordination number. The form of the necessary matrices are given in appendix 2. The resulting phase boundary is

$$\begin{aligned}\beta h_{n;n+1}=&[t^{q_{\|}-2}+(q-2)t^{q_{\|}-1}-(q-1)t^{q_{\|}})]^{n-1}(q_{\|}/2)^{n-1}\\&\times[1-t^{q_{\|}}+(q-2)(t^{q_{\|}/2}-t^{q_{\|}})]w^{nq_{-}}+O(w^{(n+1)q_{-}-2})\end{aligned} \tag{4.3}$$

which in the mean-field limit becomes

$$\beta h_{n;n+1}=[q\tau\ln(1/\tau)/2]^{n-1}(1-\tau^{1/2})[1+(q-1)\tau^{1/2}]w^{nq_{-}}+O(w^{(n+1)q_{-}}). \tag{4.4}$$

This form of the phase boundary demonstrates that the mean-field result depends strongly on the q states of the model. Moreover, in the mean-field limit the distinction between connected and disconnected graphs is lost because each spin is connected to all spins in the neighbouring layers. Therefore, for an axial graph, it does not matter which spin within the layer is reversed.

Mean-field theory underestimates the effects of thermal fluctuations (Buff *et al* 1965). The interface unbinds from the surface because of entropic repulsion; hence we should expect the phase boundaries at a given field to occur at a higher temperature in mean-field theory compared with the low-temperature series result. The first few phase boundaries demonstrate this and are compared qualitatively in figure 8.

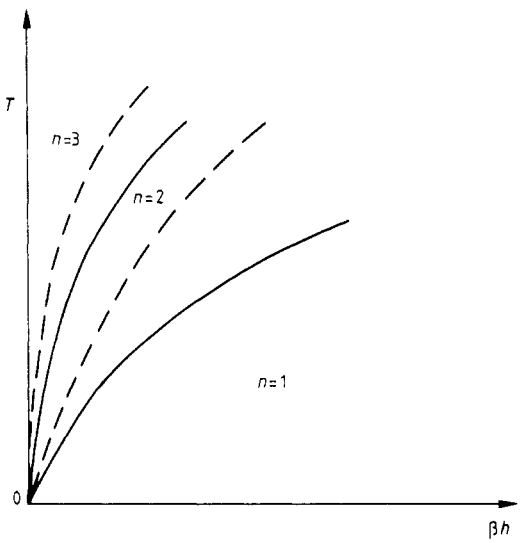

Figure 8. Qualitative comparison of the phase diagram obtained from low-temperature series (full curves) with that obtained from mean-field theory (broken curves) for the q-state Potts model.

Note that if $q\tau \geqslant O(w^{q-})$ then the low-temperature result (4.4) may no longer be used. This difficulty at high q was that discussed in §§ 2 and 3. Further work would be required to demonstrate layering transitions for all q.

4.2. A numerical mean-field theory

For completeness we compare the mean-field limit of the low-temperature series to the more conventional numerical mean-field theory for layered systems (Pandit *et al* 1982). We restrict our attention to the Ising model because it proved very difficult to obtain satisfactory numerical solutions for the Potts case. The advantage of this approach to mean-field theory is that it can be used at all temperatures—although it does not always predict the correct phase diagram, for example, above the roughening temperature.

To obtain the mean-field equations we use the Bogoliubov inequality (Yokoi *et al* 1981) for the mean-field free energy, F_{mf}, in a system with N layers of spins containing $N_\perp$ spins per layer:

$$F \leqslant F_{mf} = \min_{\eta_i}(F_0 + \langle H - H_0 \rangle_0) \tag{4.5}$$

where H is the Ising Hamiltonian

$$H = -\tfrac{1}{2}J_0 \sum_{\substack{ij \\ i>1}} S_{i,j}S_{i,j'} - J \sum_{\substack{ij \\ i>0}} S_{i,j}S_{i+1,j} - h \sum_{\substack{ij \\ i>1}} \delta(S_{i,j}, 1) \qquad S_{i,j} = \pm 1. \tag{4.6}$$

F is the exact free energy

$$F = -k_B T \ln[\mathrm{Tr}(e^{-\beta H})] \tag{4.7}$$

and $\langle\ \rangle_0$ are thermodynamic averages taken with respect to a trial Hamiltonian

$$H_0 = \sum_{i=2}^{N-1} \sum_j \eta_i S_{i,j}. \tag{4.8}$$

Because of the lack of translational invariance the mean field, η_i, must be allowed to vary with layer i.

Minimising with respect to the mean fields, η_i (Yokoi *et al* 1981), gives the usual expression for the free energy (ignoring constant terms)

$$F_{mf} = N_\perp \sum_{i=2}^{N-1} [k_B T \log(2 \cosh \beta\eta_i) + 2J_0\langle S_i\rangle^2 + J\langle S_i\rangle\langle S_{i-1}\rangle] - J\langle S_1\rangle\langle S_2\rangle \tag{4.9}$$

where the mean spin, $\langle S_i\rangle$, $2 \leq i \leq N-1$, satisfies

$$\eta_i = 4J_0\langle S_i\rangle + J(\langle S_{i+1}\rangle + \langle S_{i-1}\rangle) + h \tag{4.10}$$

$$\langle S_i\rangle = \tanh \beta\eta_i \tag{4.11}$$

and $\langle S_1\rangle$, $\langle S_N\rangle$ are fixed by the initial conditions to be -1 and $+1$ respectively.

Equations (4.10) and (4.11) were solved by choosing an initial configuration and iterating until self-consistency was achieved. It may be the case that for a given T and h there are many solutions corresponding to local minima of the free energy, with the solution obtained numerically depending on the initial conditions. Within the mean-field approximation each solution may be identified as giving a distinct metastable film; the solution for which F_{mf} is an absolute minimum gives the stable configuration of the interface. Although a search through initial configurations does not guarantee that the global minimum has been found, a plot of the free energies of the metastable states, which were approximately straight lines over the region of interest, gave us confidence in our results.

The results agreed with our previous approaches, that is, a sequence of layering transitions. We found no indication that the sequence would terminate for large n. In table 2 we compare values for the 2:3 phase boundary resulting from the different methods addressed in this paper to allow a quantitative comparison. The mean-field methods are in good agreement with one another: their discrepancy is due to the effect of ignoring higher-order terms in the low-temperature expansion.

Table 2. Values for the phase boundary, $(\beta h)_{2:3}$, obtained by the different methods considered in this paper.

T	Low-temperature series	Numerical mean-field theory	Low-temperature mean-field theory
1.0	5.6×10^{-8}	4.1×10^{-9}	4.1×10^{-9}
1.5	1.8×10^{-5}	3.2×10^{-6}	3.0×10^{-6}
2.0	3.4×10^{-4}	9.2×10^{-5}	7.9×10^{-5}

5. Summary and discussion

Our aim in this paper has been to show that series methods can be used to predict a sequence of layering transitions as an interface unbinds from a surface. The model considered has been a q-state Potts model, extending previous work by Duxbury and Yeomans (1985) on the Ising model ($q = 2$). We have shown that layering transitions can be predicted by utilising both low-temperature and high-q expansions. The

sequence of phases must be established inductively by considering the leading-order contributions to the free energy at successive orders of the expansion. These arise from axially connected chains of flipped spins whose Boltzmann factors can, because of their one-dimensional nature, be calculated using a transfer matrix method described in the appendices.

The dominant fluctuations responsible for driving the transitions are different in the low-temperature and high-q limits. In the former case, a chain of spins, extending from the interface towards the surface, in which each spin flips to the bulk phase to the right of the interface is important, whereas in the latter case the chain comprises spins which have all transformed to states which differ from their neighbours.

To compare our results to previous work, the mean-field theory of the model has also been studied, both by taking the infinite coordination number limit of the low-temperature series and by a numerical solution of the mean-field equations. We find that the sequence of layering transitions is qualitatively unchanged in this approximation. We have shown that there is no distinction between connected and disconnected chains in this limit. The underestimation of thermal fluctuations by mean-field theory affects the phase boundaries as illustrated in figure 8.

The n dependence of the correction terms, such as that proportional to n in (3.15), means that we cannot conclude that there is an infinite sequence of phases. Initially the correction terms arise in the low-temperature series from axial graphs with bumps, such as that shown in figure 9. These will have an extra factor $O(nt^2w^{nq_--2})$ compared with an axial chain, hence for sufficiently large n the correction terms may dominate the leading-order term which we have used to establish the phase sequence. This point is discussed in detail by Szpilka (1985).

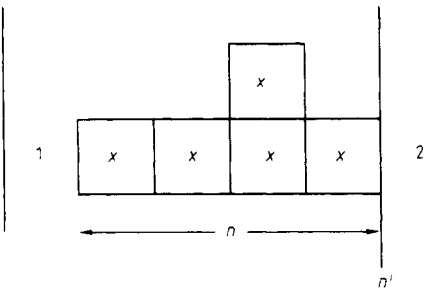

Figure 9. A diagram in the low-temperature expansion which, when all the possible positions of the protruding spin are considered, may dominate the leading-order terms for large n.

Above the roughening temperature, T_R, the layering transitions must be destroyed (Sullivan and Telo da Gama 1985). The first-order boundaries are expected to terminate at a sequence of critical points which accumulate at T_R. Although low-temperature series methods have been used in both Ising (Weeks *et al* 1973) and Potts (Schmidt and Pesch 1984) models to obtain a value for T_R, they necessarily involve extrapolating the series using Padé analysis. The first few terms presented here do not, by themselves, give any measure of T_R but the series certainly fails to converge as w increases. In the large-q series there is no obviously similar effect. We conjecture that this indicates that in the $q \to \infty$ limit roughening is not observed. Indeed, Pearce and Griffiths (1980) proved that in the $q \to \infty$ limit mean-field theory, which neglects roughening, is exact (Widom 1972).

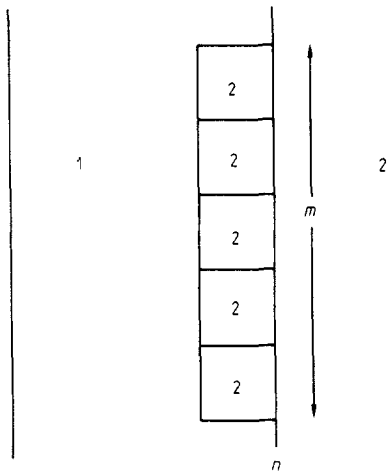

Figure 10. A diagram where m^2 adjoining spins next to the interface are flipped to the '2' state. For sufficiently large m and $h>0$ this diagram decreases the energy.

It should be noted that there exist high-order excitations which decrease the energy. An example is shown in figure 10, where m^2 neighbouring spins with $O(m)$ edge spins are flipped next to the interface in the '1' phase. The Boltzmann weight for this diagram is of order

$$\exp[\beta m(hm - J_0)]. \tag{5.1}$$

For sufficiently large diagrams the field term dominates and leads to a divergence in the Boltzmann weight.

The problem arises because the states are only degenerate at a point; as soon as $h>0$, however small, there is only one ground state and the expansions we have performed are about metastable states. Therefore the convergence of our expressions for the interface free energy is not obvious; however, it is a useful computational aid in finding the phase boundaries. This point has also been commented upon by Bricmont and Lebowitz (1987) in their consideration of the Blume-Capel model.

Despite these problems, series expansions provide a powerful method for studying interface phase transitions. In two further papers we will extend the techniques described here to consider two rather different problems. Firstly, we will study solid-on-solid models where the interface is bound to the surface by a local pinning potential. We will then extend previous work on the chiral clock model (Armitstead *et al* 1986) to show that in this case the mean-field limit is not in agreement with series expansions in three dimensions.

Appendix 1

The transfer matrix method was introduced by Yeomans and Fisher (1984) to count all contributions from axial graphs of general length together with their decompositions (Fisher and Selke 1981). This allows the chain of flipped spins to be built up step by step with the appropriate Boltzmann factor for a connected or disconnected spin being included at each stage.

Consider first the contribution from overturning two axially adjacent spins in the '1' phase. The Boltzmann factors contributed by the new bond depend on the final excited states of the two neighbouring spins. There are $(q-1)^2$ possible final combinations of spins, many of which will carry the same factor; if the two final states are different a factor of tw^{q_-} will be introduced whilst if they are the same the factor is w^{q_-}. We are considering the region near a phase boundary, and therefore, as explained in § 2.3, may take $y \sim O(1)$. The possible contributions may be recorded as a $(q-1) \times (q-1)$ matrix, $\mathbf{M}'$, where the (x, y)th element representing the Boltzmann factor for a spin flip from the initial state (σ_i, σ_{i+1}) to the final state $(\sigma_i + x, \sigma_{i+1} + y)$ (where we assume arithmetic modulo q throughout) is given by

$$M'_{xy} = \begin{cases} w^{q_-} & x = y \\ tw^{q_-} & x \neq y. \end{cases} \tag{A1.1}$$

In order to take account of decompositions of the axial graphs, it is then necessary to include the possibility of a break between the two flipped spins (that is, to consider the spins to lie on different rows of the lattice). In this situation, the Boltzmann factors corresponding to the $(q-1)^2$ excited states form the matrix

$$M''_{xy} = t^2 w^{q_-} \tag{A1.2}$$

where the Boltzmann factor does not depend on the final states as two wrong bonds perpendicular to the interface are always formed. Thus recalling that a decomposition must be accompanied by a factor of -1 (Fisher and Selke 1981, Yeomans and Fisher 1984) we can write the elements of the full matrix, $\mathbf{M}$, which adds a bond between two '1' spins as

$$M_{xy} = \begin{cases} (1-t^2)w^{q_-} & x = y \\ (t-t^2)w^{q_-} & x \neq y. \end{cases} \tag{A1.3}$$

As $y \sim O(1)$, this is also the matrix which adds a bond between two axial spins in the same initial state irrespective of that state—we shall need the case $\sigma_i = \sigma_{i+1} = 2$.

We also need a row vector to represent adding the first bond at the extreme left of the chain. If the initial bond is ferromagnetic then the yth element of this row vector, u_y, corresponding to the Boltzmann factor for flipping the initial spin to state $(\sigma_i + y)$ is given by

$$u_y = tw^{q_-} \tag{A1.4}$$

for all y.

The final broken bond can be accounted for by a column vector. In the ensuing calculations two vectors will be needed corresponding to the initial configurations and spin flips:

(*a*) $(1, 2) \rightarrow (1 + x, 2)$

$$v_x^a = \begin{cases} t^{-1} & x = 1 \\ 1 & x \neq 1 \end{cases} \tag{A1.5}$$

(*b*) $(2, 2) \rightarrow (2 + x, 2)$

$$v_x^b = t \qquad \text{for all } x.$$

To obtain the leading-order contribution to the reduced free energy difference, $F_{n'} - F_n$, $n' > n$, we need to evaluate the axial diagrams shown in figures 3(*c*) and 3(*d*). These can be constructed using the matrices listed above as follows:

$$\begin{aligned} &\text{(i)} \quad \boldsymbol{u}\mathbf{M}^{n-1}\boldsymbol{v}^a \\ &\text{(ii)} \quad \boldsymbol{u}\mathbf{M}^{n-1}\boldsymbol{v}^b. \end{aligned} \tag{A1.6}$$

Hence the leading-order contribution to $F_{n'} - F_n$ is given by

$$F_{n'} - F_n = -(n'-n)\beta h + \boldsymbol{u}\mathbf{M}^{n-1}(\boldsymbol{v}_a - \boldsymbol{v}_b) \tag{A1.7}$$

$$= -(n'-n)\beta h + [1+(q-2)t-(q-1)t^2]^n w^{nq_\perp} + \mathrm{O}(w^{(n+1)q_\perp - 2}). \tag{A1.8}$$

This reduces to the result obtained by Duxbury and Yeomans (1985) in the Ising case, $q = 2$.

Appendix 2

In this appendix we write down the transfer matrices needed to calculate the Boltzmann factors for flipping an axial chain of spins with an arbitrary number of parallel and perpendicular nearest neighbours, $q_\parallel$ and $q_\perp$. The notation used is the same as in appendix 1 so it will be sufficient to list the matrix elements which are further elucidated by referring to figure 7.

$$M'_{xy} = \begin{cases} \frac{1}{2}(q_\parallel t^{q_\parallel - 2} w^{q_\perp}) & x = y \\ \frac{1}{2}(q_\parallel t^{q_\parallel - 1} w^{q_\perp}) & x \neq y \end{cases} \tag{A2.1}$$

$$M''_{xy} = \tfrac{1}{2}(q_\parallel t^{q_\parallel} w^{q_\perp}) \tag{A2.2}$$

$$M_{xy} = \begin{cases} \frac{1}{2}[q_\parallel t^{q_\parallel - 2}(1-t^2) w^{q_\perp}] & x = y \\ \frac{1}{2}[q_\parallel t^{q_\parallel - 1}(1-t) w^{q_\perp}] & x \neq y \end{cases} \tag{A2.3}$$

$$u_x = t^{q_\parallel/2} w^{q_\perp} \qquad \text{for all } x \tag{A2.4}$$

$$v^a_y = \begin{cases} t^{-q_\parallel/2} & y = 1 \\ 1 & y \neq 1 \end{cases} \tag{A2.5}$$

$$v^b_y = t^{q_\parallel/2} \qquad \text{for all } y. \tag{A2.6}$$

Using these elements to calculate the products (A1.6) leads immediately to (4.3).

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