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A Potts model for the herringbone transition

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Abstract. A generalisation of the three-state Potts model is introduced, which couples spin and lattice directions. The model allows, in addition to the usual ferromagnetic and antiferromagnetic phases, striped phases which reflect competition between different parameters in the model. One of these is the well-known herringbone phase. Detailed calculations of the phase boundaries are made, using mean-field and other methods.

1. Introduction

The ground state of nitrogen adsorbed on graphite, at suitable densities, is the so-called herringbone phase. In this phase the underlying graphite surface has a hexagonal structure; one third of the unit cells are occupied by nitrogen molecules which form a triangular superlattice. The molecules then orientationally order. The ordering consists of stripes with the molecules in alternate stripes at angles of $\pm\frac{1}{4}\pi$ with respect to the stripes. The pictorial effect is that of a set of fish backbones; hence the descriptive name (some diagrams are given later).

The phase has been studied experimentally (e.g. Chung and Dash 1977, Diehl *et al* 1982), computationally (e.g. O'Shea and Klein 1977, Mouritsen and Berlinsky 1982) and theoretically (e.g. Migone *et al* 1983, Schick 1983). It seems reasonably clear that the driving mechanism is the quadrupolar interaction between nitrogen molecules on neighbouring sites. This interaction prefers neighbouring molecules to form a 'T' like structure, i.e. perpendicular to each other with the end of one molecule pointing at the centre of its neighbour. The molecules are kept in the surface plane by the potential of the graphite substrate. A molecule on a given site can, however, only point at two of its neighbours, and be pointed at by another two. Two others are left. However, the four neighbours whose orientations are given, together with repetitions of this process, are sufficient to build up an unfrustrated ordered ground state. This is the herringbone structure.

The herringbone structure also seems to occur in substances other than nitrogen. Hydrogen, a quantum liquid, exhibits the phase at low temperatures (Harris and Berlinsky 1979). The smectic E liquid crystal is a layered phase, in which the molecules within each layer adopt the herringbone structure (Meyer 1975, 1976). There have also been reports of herringbone structures adopted by systems of large molecules adsorbed on graphite. It seems quite a general phenomenon (Taub 1988).

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The herringbone ground state is sixfold degenerate. We seek a spin model with such a ground state (and perhaps others). Some theoretical works, especially in the chemistry literature, seek an accurate mapping between the input potentials and the resulting ground state. This will not be our aim, partly because it obscures what is common between all herringbone-like structures. A suitable idealisation is to pin the particles to their sites, and to ignore out of plane fluctuations, whether translational or rotational. Models which allow continuous spin degrees of freedom can be used, as for instance by Schick (1983) or Meyer (1975, 1976). The finite degeneracy of the ground state results from the coupling of the continuous degrees of freedom with the (finite number of) lattice directions. We seek rather a model with discrete spin directions, which has a ground state with the right symmetry, and into which the lattice direction-spin direction coupling is already built. Such a model should define the universality class of the transition.

One such model was the so-called n-component cubic model, discussed in this context by Nienhuis *et al* (1983). We propose here an alternative, based on the intuition of the basic T-like structure of nearest neighbours. This model has three states per site, corresponding to molecules pointing in the directions of the nearest neighbours. It is apparent that, for a suitable Hamiltonian function, the herringbone ground state, with its sixfold degeneracy, is a possibility. We note that in the experimental case of nitrogen, the molecules do not quite point at their neighbours in the ground state. This does not however affect the symmetry or degeneracy of the ground state.

Models which have n equivalent states were introduced by Potts (1952) many years ago. Since that time there has been much interest in the phase diagram and the nature of the phase transitions in the three-state Potts model (e.g. Nienhuis *et al* 1979). This model, depending on its parameters, has either a ferromagnetic or an antiferromagnetic ground state, for the two-dimensional triangular lattice discussed here. But in this model spin directions and lattice directions exist in different spaces. In this work we construct a Potts model which couples spin and lattice directions.

In this paper we study this model. We discover its ground states. We are predominantly, though not exclusively, interested in its applicability to understanding the herringbone phase. The plan of the paper is as follows. In § 2 we describe the model in more detail. In § 3 we determine its ground states, and investigate the phase boundaries by a number of different methods. Finally in § 4 we make some concluding remarks.

2. Model

We consider a system of Potts-like spins on a two-dimensional triangular lattice. We identify the three Potts spin directions with the three principal axes of the lattice as shown in figure 1. Symmetry considerations then allow four possible nearest-neighbour energies, as shown in table 1. The total Hamiltonian can now be written

$$H = \tfrac{1}{2}\sum_{\{ij\}} [\varepsilon_1 \delta_{\sigma_i\sigma_j}\delta_{\sigma_i r_{ij}}\delta_{\sigma_j r_{ij}} + \varepsilon_2 \delta_{\sigma_i\sigma_j}(1-\delta_{\sigma_i r_{ij}})(1-\delta_{\sigma_j r_{ij}}) + \varepsilon_3(1-\delta_{\sigma_i\sigma_j})(\delta_{\sigma_i r_{ij}}+\delta_{\sigma_j r_{ij}}) + \varepsilon_4(1-\delta_{\sigma_i\sigma_j})(1-\delta_{\sigma_i r_{ij}})(1-\delta_{\sigma_j r_{ij}})] \tag{2.1}$$

where the sum is taken over nearest-neighbour sites, r_{ij} is the vector joining the sites I and J, and the three possible directions of r_{ij} are associated with the spin directions σ_i, as shown in figure 1.

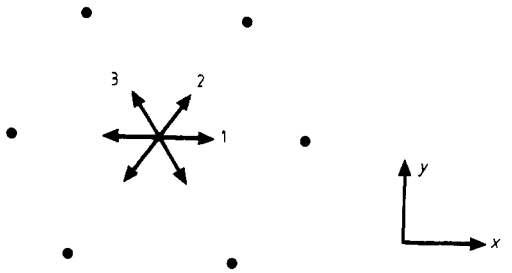

Figure 1. Triangular lattice. Double headed arrows show the three possible Potts orientations, labelled 1, 2, 3.

Table 1. Nearest-neighbour energies. The spins are on neighbouring sites in the x direction. The spins are given double arrows to emphasise that the sense is not important.

Configuration	Label	Degeneracy	Energy
↔ ↔	α	1	ε_1
↗ ↗	β	2	ε_2
↔ ↗	γ	4	ε_3
↗ ↘	δ	2	ε_4

From the point of view of the statistical mechanics of the model the four independent variables of the model ε_i can be reduced to three by choosing a zero of energy. We now show that by exploiting symmetry considerations the number of free variables can in fact be further reduced to two.

We use the sum rule

$$\tfrac{1}{2}\sum_{\{ij\}} \delta_{\sigma_i r_{ij}} = N \tag{2.2}$$

where N is the number of sites in the lattice. This result becomes evident when it is recalled that each site i with spin σ_i in an arbitrary direction has two nearest neighbours in direction σ_i.

Equation (2.1) can now be rearranged as

$$H = \tfrac{1}{2}\sum_{\{ij\}} [(\varepsilon_1 - 2\varepsilon_3 + \varepsilon_4)\delta_{\sigma_i\sigma_j}\delta_{\sigma_i r_{ij}}\delta_{\sigma_j r_{ij}}$$

$$+ (\varepsilon_2 - \varepsilon_4)\delta_{\sigma_i\sigma_j}(1 - \delta_{\sigma_i r_{ij}})(1 - \delta_{\sigma_j r_{ij}}) + (\varepsilon_3 - \varepsilon_4)(\delta_{\sigma_i r_{ij}} + \delta_{\sigma_j r_{ij}}) + \varepsilon_4] \tag{2.3}$$

which can be further transformed using the sum rule (2.2) to

$$H = N(2\varepsilon_3 + \varepsilon_4) + \tfrac{1}{2}\sum_{\{ij\}} [J_1\delta_{\sigma_i\sigma_j}\delta_{\sigma_i r_{ij}}\delta_{\sigma_j r_{ij}} + J_2(1 - \delta_{\sigma_i r_{ij}})(1 - \delta_{\sigma_j r_{ij}})\delta_{\sigma_i\sigma_j}] \tag{2.4}$$

where

$$J_1 = \varepsilon_1 - 2\varepsilon_3 + \varepsilon_4 \qquad J_2 = \varepsilon_2 - \varepsilon_4.$$

The form of the Hamiltonian (2.4) is the same as that of (2.1); the energies J_1 and J_2 correspond to renormalised energies for configurations α and β in table 1, whereas the renormalised energy for configurations γ and δ is zero. The constant energy term $N(2\varepsilon_3 + \varepsilon_4)$ does not contribute to the statistical mechanics. This form of Hamiltonian is gratifyingly close to the Potts model form, in which unlike spins on nearest-neighbour

sites couple with zero energy. The form (2.4) generalises the simple Potts model in a minimal way to allow for coupling between lattice and spin directions.

In the following sections we study some aspects of the statistical mechanics of the Hamiltonian (2.4).

3. Statistical mechanics

3.1. The ground state

The Hamiltonian (2.4) sustains four ground states, which we label: ferromagnetic (F), herringbone (HB), blanket-stitch (BS) and antiferromagnetic (AF). The respective ground-state configurations are shown in figure 2, and their ground-state energies shown in table 2.

Broadly speaking, ferromagnetism is favoured if both α and β configurations have negative energy and antiferromagnetism is favoured if they both have positive energy. The blanket-stitch and herringbone ground states result from compromises which favour α but disfavour β (BS) or vice versa (HB). More detailed analysis of the stabilities of the various ground states shows that the regions where the compromise ground states remain valid are rather narrow, and there is a wide regime where ferromagnetism obtains. The results of this analysis are shown in figure 3.

The line $J_1 = J_2$ corresponds to the well studied ordinary Potts model, which has ferromagnetic or antiferromagnetic ground states, depending on the sign of J. The HB ground state has the same symmetry and degeneracy as the herringbone states observed in nitrogen and hydrogen monolayers adsorbed on graphite surfaces. Both the BS and

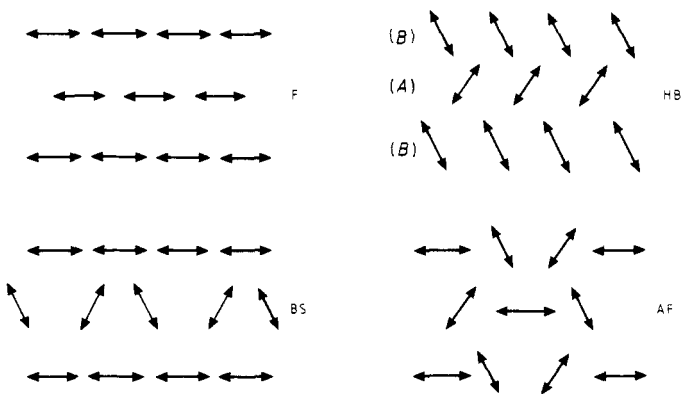

Figure 2. The ground-state configurations.

Table 2. Ground-state energies, E/N.

State	Energy per site	Degeneracy
F	$J_1 + 2J_2$	3
HB	J_2	6
BS	$\frac{1}{2}J_1$	12
AF	0	6

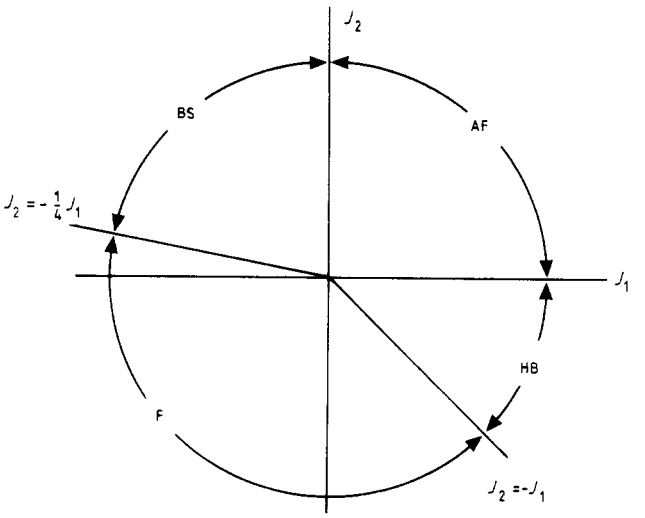

Figure 3. Regions of stability for the different ground states.

HB phases are striped phases, and as such are analogous to striped phases occurring in other models with competing interactions, such as the ANNNI model and clock models (Fisher and Selke 1980). In particular, the F-HB and F-BS transitions at $T=0$ are multiphase points, in the sense that at these transitions the ground state is degenerate with respect to change of stripe phase and wavelength.

From here on we concentrate on the statistical mechanics of the HB and F phases.

3.2. Mean-field theory

We confine our interest to the region in which the F and HB phases are competing, i.e. $J_1>0$, $J_2<0$. It will be convenient to parametrise J_1 and J_2 as follows:

$$J_1 = J(1-\alpha) \qquad J_2 = -J\alpha \tag{3.1}$$

and to measure temperatures T in terms of J:

$$\tilde{T} = K_B T/J = \beta^{-1}. \tag{3.2}$$

From now on we drop the tilde over $\tilde{T}$; equivalently $J=1$.

The phase diagram is now characterised by the parameters T, α; at $T=0$, $0<\alpha<\frac{1}{2}$ is the HB region, and $\alpha>\frac{1}{2}$ is the F region.

The ferromagnetic phase is uniform. The low-T phase is characterised by probabilities $n_i = (i=1,2,3)$ of occupation by spin direction i. Without loss of generality we assume the ordering to occur in the 1 direction. The relevant order parameter is

$$S = n_1 - \tfrac{1}{3}. \tag{3.3}$$

The free energy difference ΔA between the ordered ferromagnetic phase and the disordered phase is given in the mean-field approximation by

$$\Delta A(S) = T[(\tfrac{1}{3}+S)\ln(1+3S)+(\tfrac{2}{3}-S)\ln(1-\tfrac{3}{2}S)]+\tfrac{3}{2}S^2(1-3\alpha) \tag{3.4}$$

yielding the self-consistent equation for S

$$\tfrac{1}{3}+S = \{1+2\exp[3\beta S(1-3\alpha)]\}^{-1}. \tag{3.5}$$

There is a first-order phase transition between the disordered and ferromagnetic states along the line $T_{FD} = 0.71(3\alpha-1)$.

The herringbone phase, by contrast, is divided into two sublattices A and B, as shown in figure 2. We suppose without loss of generality that orientation 2 is predominant in A and orientation 3 is predominant in B. The low-T phase is characterised by n_i^A, n_i^B, where $n_1^A = n_1^B = p$, $n_2^A = n_3^B = q$ and $n_3^A = n_3^B = r$. There are now two relevant order parameters:

$$x = q - r \qquad y = \tfrac{1}{3} - p. \tag{3.6}$$

In the low-T limit $q = 1$, $p = r = 0$, and hence $x = 1$, $y = \frac{1}{3}$. The free energy difference between the ordered and disordered phases is

$$\Delta A(x, y) = T[(\tfrac{1}{3} - y)\ln(1 - 3y) + (\tfrac{1}{3} + \tfrac{1}{2}y + \tfrac{1}{2}x)\ln(1 + \tfrac{3}{2}y + \tfrac{3}{2}x) + (\tfrac{1}{3} + \tfrac{1}{2}y - \tfrac{1}{2}x)\ln(1 + \tfrac{3}{2}y - \tfrac{3}{2}x)] + \tfrac{3}{2}(1 - 3\alpha)y^2 - \tfrac{1}{2}(1 - 3\alpha)x^2 \tag{3.7}$$

yielding mean-field equations

$$\tfrac{1}{3} - y = \{1 + 2\cosh \beta x(1 - \alpha)\exp[-3\beta y(1 - \alpha)]\}^{-1}$$
$$x = \frac{2\sinh \beta x(1 - \alpha)}{2\cosh \beta x(1 - \alpha) + \exp 3\beta y(1 - 3\alpha)}. \tag{3.8}$$

We now obtain, for low α, a second-order phase transition from the disordered to the HB phase along the line $T_{HB} = 2/3(1 - \alpha)$. There is a tricritical point at $\alpha = \frac{3}{7}$, $T = \frac{8}{21}$. Beyond this tricritical point the transition is first order. There is a first-order transition between the F and HB phases which remains very close to $\alpha = \frac{1}{2}$, though for $T > 0$ there is a very small region of $\alpha < \frac{1}{2}$ where the F state is more stable than the HB state. We show the phase diagram thus calculated in figure 4.

3.3. Beyond mean-field theory

The mean-field theory is, however, misleading in a crucial way near $\alpha = \frac{1}{2}$, where the F and HB phases have comparable stability. Indeed, as observed above, the point

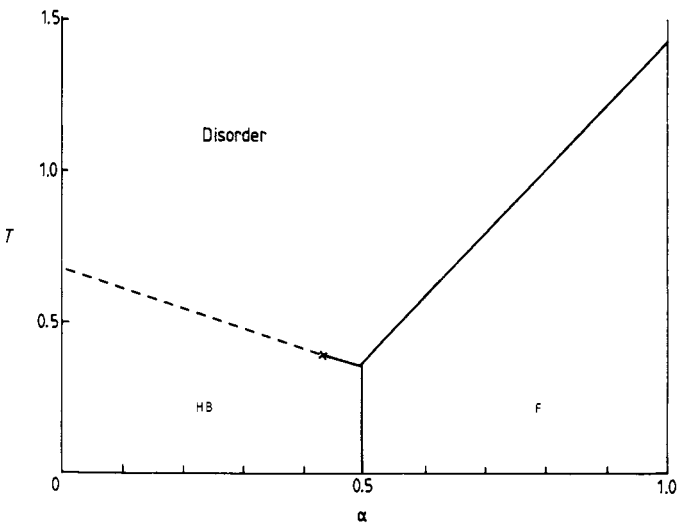

Figure 4. The mean-field phase diagram. ——, first-order transition; - - -, second-order transition, ×, tricritical point.

($\alpha = \frac{1}{2}$, $T = 0$) is a multiphase point. At this point the surface energy between two HB phases with the same glide direction but out of phase stripes, or between the HB phase and the F phase (along a suitable direction, and with suitable relative orientations) is zero. At low temperatures there is no cost in introducing domain walls (albeit in suitable directions) and hence any ordered phase is destroyed. This is the basis of the method of Müller-Hartmann and Zittarz (1977), who calculate the transition temperature of the two-dimensional Ising model by calculating the temperature at which the free energy of a domain wall between regions of opposite spins disappears. Here we use this method to construct the phase diagram near $\alpha = \frac{1}{2}$, where the mean-field transition temperatures are significantly reduced by fluctuation effects.

We first consider the ferromagnetic region, $\alpha > \frac{1}{2}$. We consider two domains in the 2 and 3 directions respectively, separated by a wall in the x direction. The basic situation is shown in figure 5. The ground state of the wall is straight; the wall is N lattice spacings = N long. A tedious though elementary calculation yields a ground-state energy of $N(2\alpha - 1)$; this is the difference between the ground-state energy of a monodomain system and that of a system with the boundaries. The wall is soft at $\alpha = \frac{1}{2}$, as remarked upon above. We make a solid on solid (SOS) model of the behaviour of the wall at finite temperatures. This model includes steps, as shown in figure 5(b). Each step has energy ($\alpha - \frac{1}{2}$). There are $2N$ possible step positions, N in each direction. In the spirit of the SOS approximation we ignore (a) fluctuations in the bulk states, such as, for instance, the possibility of spins in the 1-direction appearing at the interface, (b) the possibility of 'overhangs', i.e. the possibility of the wall position being non-monotonic in the x direction, and (c) interactions between neighbouring steps. In this approximation the surface free energy per unit length is given by

$$\gamma(T) = \gamma_0(T) - T \ln Z_{\text{step}} \tag{3.9}$$

where

$$Z_{\text{step}} = \{1 + \exp[-\beta(\alpha - \tfrac{1}{2})]\}^2 \tag{3.10}$$

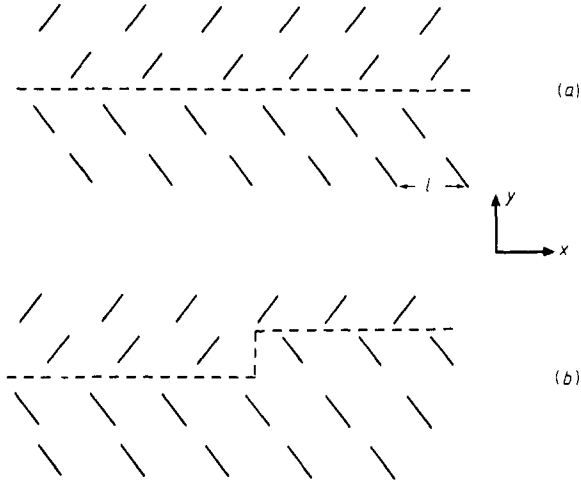

Figure 5. Domain boundaries in the ferromagnetic regime. (a) The domain wall in its ground state. This wall has energy $2(\alpha - \frac{1}{2})$ per unit length. (b) The domain wall with a step in it. Each step has energy ($\alpha - \frac{1}{2}$).

is the partition function, per unit length, associated with steps. Hence

$$\gamma(T) = 2\alpha - 1 - 2Tn\{1 + \exp[-\beta(\alpha - \tfrac{1}{2})]\}. \tag{3.11}$$

We expect a phase transition when the wall free energy goes soft, or equivalently for

$$T_F = 2.08(\alpha - \tfrac{1}{2}). \tag{3.12}$$

We now discuss the herringbone region $\alpha < \frac{1}{2}$. The crucial boundaries and walls are shown in figure 6. We make the same sos approximation as above. The wall energy is now $N(1-2\alpha)$, which as before becomes soft at $\alpha = \frac{1}{2}$. The step energy is α, which however does not soften at $\alpha = \frac{1}{2}$. The arguments of equations (3.9)-(3.11) can be repeated, yielding a wall free energy per unit length of

$$\gamma(T) = 1 - 2\alpha - 2T \ln[1 + \exp(-\beta\alpha)]. \tag{3.13}$$

The condition $\gamma(T) = 0$ yields the equation

$$\exp[\beta_c(\tfrac{1}{2} - \alpha)] = 1 + \exp(-\beta_c\alpha). \tag{3.14}$$

Close to $\alpha = \frac{1}{2}$ this has the limit

$$T_c = -\frac{1}{2\ln(\alpha - \frac{1}{2})}. \tag{3.15}$$

The modified phase diagram in the region $\alpha = \frac{1}{2}$ is shown in figure 7.

This calculation shows that, near $\alpha = \frac{1}{2}$, fluctuations substantially suppress the ordering predicted by mean-field theory, and that at $\alpha = \frac{1}{2}$ the ordered state persists down to $T = 0$. No prediction, of course, can be made by this method about the nature of the order-disorder transitions. An interesting feature is the shape of the ordering transition line near $\alpha = \frac{1}{2}$. On the ferromagnetic side ($\alpha > \frac{1}{2}$) T_c is linear in $(\alpha - \frac{1}{2})$; this reflects the fact that both the wall energy and the step energy become soft at $\alpha = \frac{1}{2}$. On the other hand, on the herringbone side ($\alpha < \frac{1}{2}$), $T_c \sim [\ln(\frac{1}{2} - \alpha)]^{-1}$, because here while the wall energy is soft, the step energy remains finite at $\alpha = \frac{1}{2}$.

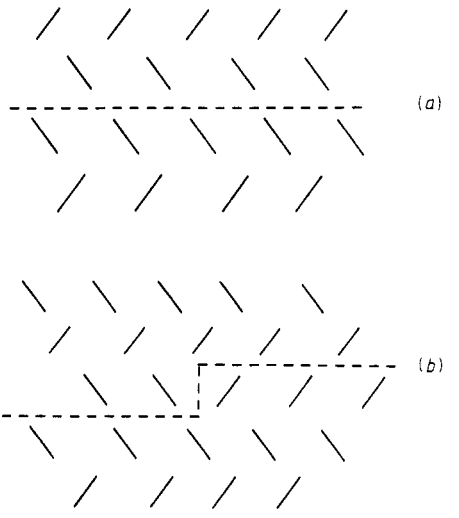

Figure 6. Domains in the HB regime. (*a*) The ground state of the domain wall, with energy $2(\frac{1}{2} - \alpha)$ per unit length. (*b*) Domain wall with step. Step has energy α.

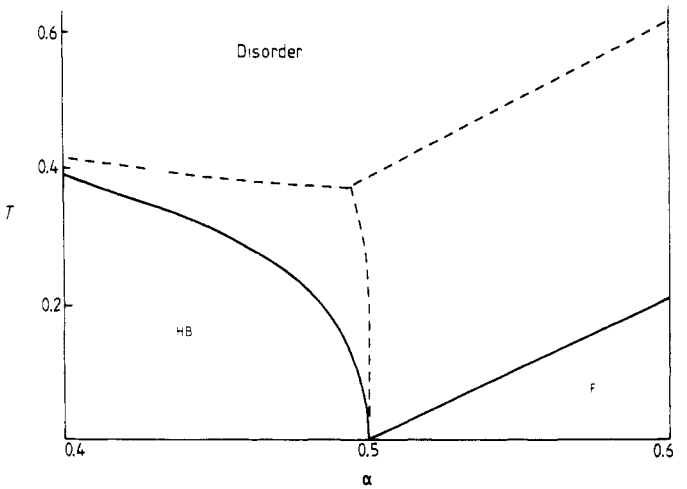

Figure 7. The phase diagram near $\alpha = \frac{1}{2}$. - - -, mean-field predictions; ——, predictions of Müller-Hartmann-Zittarz method.

4. Conclusions

We have discussed the properties of a simple two-dimensional lattice model with three states per site. The model is a simple generalisation of the much studied three-state Potts model. It was designed to describe those systems which have low-temperature herringbone phases. For a certain range of parameters of the model, there is a low-temperature herringbone phase. We speculate that from the point of view of critical properties this model may be the simplest realisation of the herringbone phase. For this reason it may well be worthwhile to investigate its properties more accurately by simulation. An exact solution may also exist.

The model also has ferromagnetic and antiferromagnetic states, like the orthodox Potts model, and another new phase, which we have labelled, for pictorial reasons, the blanket-stitch phase. As far as we know such a phase has not been observed, but it would be interesting to know what physical circumstances would be favourable for its formation. We make the general observation that the ferromagnetic and herringbone phases would be 'close packed' phases in a molecular sense, whereas the other two phases are not, which might explain why they are rarer, if not absent, in nature.

There is, in addition, competition between ferromagnetic and herringbone phases. There is a multiphase point between these two phases, and in this region the ordering phase transition is strongly suppressed. We have investigated this suppression by considering a solid on solid model of domain wall free energy.

The model we have introduced has some appealing features. In particular, it has a finite number of states. It therefore well describes the phase transition of systems which have easy axes and thus ground states with discrete symmetry, such as the herringbone phase as observed in N_2 adsorbed on graphite in a registered $\sqrt{3} \times \sqrt{3}$ phase. It it thus relatively straightforward to extend the elementary considerations of this paper to more detailed quantitative studies using, for instance, finite-size scaling with transfer matrices, or Monte Carlo simulation.

You and Fain (1985, 1986) have studied, experimentally, mixtures of N_2 and Ar, and CO and Ar, adsorbed in a registered phase on graphite. The argon atoms are

spherical and not orientationally orientable. This complicates the phase behaviour. Too many argon atoms and even at low temperatures orientational order is not favoured; if there are only a few the ground states are unchanged. However, in an intermediate regime the argon atoms and nitrogen molecules can themselves spatially order, in such a way as to avoid orientational frustration in the ground state. This occurs in the so-called pinwheel phase observed by You and Fain, in which (in the language of this paper) one site in four is occupied by argon atoms. Each argon atom is surrounded by N_2-occupied sites orientationally ordered around it in a 'pinwheel' configuration. The model introduced in this paper can easily be generalised to include 'vacancies' in such a way as to describe this phase.

On the other hand, this model has only limited applicability. It is a strictly in-plane model. Harris and Berlinsky (1979) in their description of these phenomena discussed crystal fields which aligned molecules either in, or out of, the plane of adsorption. They then derive more complicated phases, including herringbone phases in which the molecules are tilted with respect to the absorption plane. Such crystal fields can be introduced by, for instance, increasing the adsorption density above $\sqrt{3} \times \sqrt{3}$ registry so that the adsorbed phase becomes incommensurate with the underlying lattice. These phenomena are not well described by the present model, and although the model can be generalised so as to take this account, it is not clear that these efforts would lead to an economical description of the physical phenomena.

Acknowledgments

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