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Crystal structure and melting in a cell model

I. Solvable lattices and isomorphisms

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Abstract. The free energy and crystal structure of some particular cases of a cell model of melting are obtained. These include (i) a class of one-dimensional cases with interactions extending to many neighbouring cells, (ii) the plane hexagonal, bcc and triangular lattices with nearest-neighbour interactions, (iii) a case of the plane, square lattice with first- and second-neighbour (diagonal) interactions, and others. The solutions for the simple cubic lattices in all dimensions were obtained in a previous paper. It is shown that some of the 2, 3, etc dimensional cases are closely related ('isomorphic') to one-dimensional cases. The detailed thermodynamics is considered in paper II.

1. Introduction

This is the first of two papers in which we consider the following questions about crystals and the ways in which they melt: (i) What is the relation between particle interactions and the resulting crystal structure? (ii) What is the relation between the structure of crystals and the nature of their melting transitions? (iii) What is the nature of metastable states in melting transitions? To study them we use the 'cell' model recently introduced by the author (Gates 1971, *An Exactly Solvable Cell Model with a Melting Transition*, to be referred to as ESCM).

At present very little is known about any of the above questions. Question (ii) was considered long ago by Landau (1937) (Landau and Lifshitz 1959). However, he concluded on the basis of a thermodynamic argument that a melting transition could not be of second order, which is contradicted by the results of ESCM, and of Gaunt and Fisher (1965) on the hard-squares lattice gas. This latter and related work represents our best answers to these questions, and is discussed further in paper II. Very recently work has begun on the general formulation of crystal properties in the framework of statistical mechanics (Ruelle 1969), but this has not yet provided answers to the three questions. The present paper deals only with the first of these; questions (ii) and (iii) are dealt with in paper II.

It was shown in ESCM that the special case of the cell model with repulsive, nearest-neighbour interactions in a cubic lattice (of any number of dimensions, including 1) gives rise to a second-order melting transition. The crystal phase has a local density with two values ρ_+ and ρ_- arranged in a sodium chloride pattern (see figure 1(a)). Some other lattices give rise to exactly the same thermodynamic behaviour, for example, the plane honeycomb lattice and the bcc lattice, each with nearest-neighbour, repulsive interactions (figure 1(b) and (c)). The reason for this similarity is that in each case one can arrange the 2 local densities ρ_+ and ρ_- on the lattice in such a way that each bond has a ρ_+ at one end and a ρ_- at the other (see figure 1). We shall not prove here that this results in the same behaviour of the systems, since the analysis is essentially that given in ESCM.

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On other types of lattice, this arrangement of ρ_+ and ρ_- is not possible: for example, on the plane triangular lattice. The simplest structure one can imagine on this lattice is that shown in figure 2(a), where the local density has three values: ρ_1 , ρ_2 and ρ_3 (not necessarily all different). In this crystal structure, each triangle of the lattice has a different density at each of its corners. We will show (§ 4) that this is in fact the crystal structure dictated by the model, and that the melting transition is,

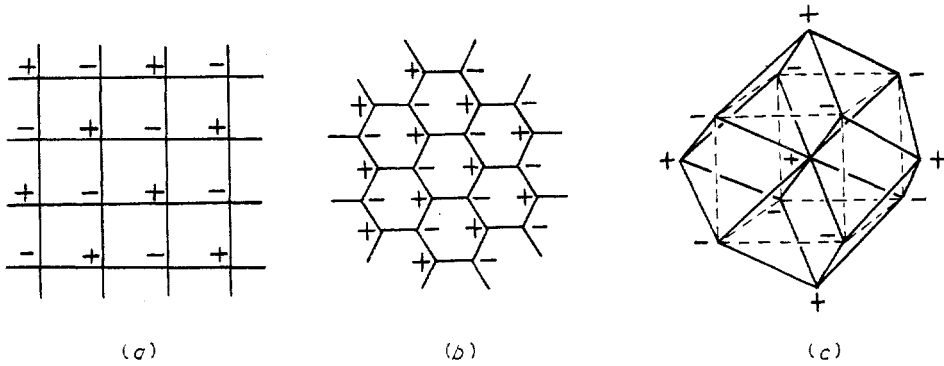


Figure 1. The arrangement of the local densities ρ_+ and ρ_- for the cell model, with nearest-neighbour repulsive interactions on (a) the ν -dimensional cubic lattice ($\nu = 2$ in the case shown), (b) a plane honeycomb lattice, and (c) the bcc lattice.

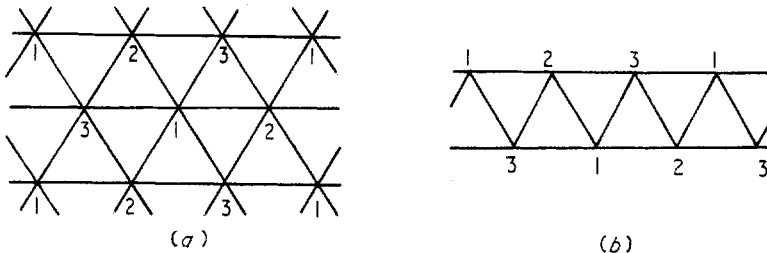


Figure 2. The arrangement of the local density values ρ_1 , ρ_2 and ρ_3 for the cell model on (a) the plane triangular lattice with first-neighbour interactions, and (b) the one-dimensional lattice with suitable second-neighbour interactions (§ 3).

unlike the previous cases, of the first order (paper II). Exactly the same behaviour is found to occur in a one-dimensional case of the model with second-neighbour interactions of suitable magnitude (figure 2(b)).

Other cases we consider (§ 4) are the simple cubic lattices (of any number of dimensions) with both nearest-neighbour and diagonal interactions. For interactions of suitable magnitude these cases can be dealt with, yielding melting transitions of the first order. Again these systems are related to a class of one-dimensional systems. Our basic results (§ 3) are the solution of the model for this class of one-dimensional systems, and (§ 4) for a related class of two, three (or more) dimensional systems. These results show how different interaction potentials influence the crystal structure and therefore provide some answers to question (i) at the beginning of this section.

2. The cell model and its basic properties

The model was defined and discussed in detail in ESCM, so we shall give only an outline of it here. In the model, particles are confined to congruent, similarly oriented,

ν -dimensional ‘cells’ of volume ω which are centred on the points of a ν -dimensional lattice $L(\gamma)$ (of any desired type) with nearest-neighbour distance $1/\gamma$. The particles can move freely from cell to cell (to make this physically plausible one can imagine very fine tubes of negligible volume connecting the cells); and each particle interacts with other particles, both in the same cell and in other cells, via the two-body potential

$$v(\mathbf{r}, \gamma, \omega) = q(\mathbf{r}) + \omega^{-1}K(\gamma\mathbf{r}) \tag{2.1}$$

where $q(\mathbf{r})$ is called the ‘short range’ or ‘reference’ potential and $\omega^{-1}K(\gamma\mathbf{r})$ the ‘long-range’ potential. The functions q and K are assumed to satisfy the stability and tempering conditions (see equations (2.14)–(2.18) of ESCM).

We consider the free energy density (per unit volume) $\tilde{a}(\rho, T, \gamma, \omega)$ defined in the usual way (see ESCM), for a system of such particles with average density ρ and temperature T , and evaluate its limit

$$a(\rho, T) \equiv \lim_{\omega \rightarrow \infty} \lim_{\gamma \rightarrow 0} \tilde{a}(\rho, T, \gamma, \omega). \tag{2.2}$$

This limiting free-energy density $a(\rho, T)$ describes a system in which the distance $1/\gamma$ between the cells and the volume ω of each cell are both very large. Since the limit $\gamma \rightarrow 0$ is taken first, the separation of the cells is much larger than their dimensions, that is

$$\gamma^{-1} \gg \omega^{1/\nu}. \tag{2.3}$$

The range of the potential $\omega^{-1}K(\gamma\mathbf{r})$ also becomes infinite as $\gamma \rightarrow 0$, so that ‘as seen by the cells’ this potential has a fixed range. The need for the factor ω^{-1} was explained in ESCM.

The basic result for the model is the following variational principle. Let $\mathcal{C}(\rho)$ be the set of functions $n(\mathbf{y})$ defined for $\mathbf{y} \in L(1)$ (i.e. on the lattice with nearest-neighbour distance unity), which are (i) non-negative, (ii) periodic in \mathbf{y} (with unspecified period), and (iii) have space average ρ , that is

$$\frac{1}{|\Gamma(n)|} \sum_{\mathbf{y} \in \Gamma(n)} n(\mathbf{y}) = \rho \tag{2.4}$$

where $\Gamma(n) \subset L(1)$ is the unit cell of n , and $|\Gamma|$ is the number of points in Γ . Let $G(n, T)$ be defined for any $n \in \mathcal{C}(\rho)$ by

$$G(n, T) \equiv \frac{1}{|\Gamma(n)|} \sum_{\mathbf{y} \in \Gamma(n)} [a^0\{n(\mathbf{y}), T\} + \frac{1}{2}n(\mathbf{y}) \sum_{\mathbf{y}' \in L(1)} n(\mathbf{y}')K(\mathbf{y}-\mathbf{y}')] \tag{2.5}$$

where $a^0(\rho, T)$ is the free energy density of the continuum system with two-body potential $q(\mathbf{r})$. Then the variational principle is (see theorem 1 of ESCM)

$$a(\rho, T) = \inf_{n \in \mathcal{C}(\rho)} G(n, T). \tag{2.6}$$

The result (2.6) simply states that to find $a(\rho, T)$ one minimizes the free energy functional $G(n, T)$ over all possible local density functions $n(\mathbf{y})$. This is similar to the well known thermodynamic principle of ‘minimizing the free energy’. One must use an infimum in (2.6) rather than a minimum, because one may need to make $\Gamma(n)$ arbitrarily large to minimize G , which would mean that the minimum could not be attained for any $n \in \mathcal{C}(\rho)$. (This happens for two-phase states.)

If suitable restrictions are made on K (for example, if $K \leq 0$), this result reduces to the result of Lebowitz and Penrose (see theorem 2 of ESCM)

$$a(\rho, T) = \text{CE}\{a^0(\rho, T) + \frac{1}{2}z\rho^2\} \tag{2.7}$$

where

$$z \equiv \sum_{s \in L(1)} K(s) \tag{2.8}$$

and CE, called the ‘convex-envelope’, means ‘take the maximal convex function of ρ which does not exceed the bracket $\{ \}$ ’. Equation (2.7) represents a fluid system, and yields a generalization of the van der Waals equation. The convex-envelope is equivalent to the Maxwell construction for the pressure, and describes the coexistence region of a first-order, gas-liquid transition.

If different restrictions are placed on K , the system has crystalline states. In particular, if the lattice is ν -dimensional cubic, and K extends to nearest neighbours, then instead of (2.7) we obtain the equation of state (4.9) of ESCM and the crystal structure shown in figure 1(a).

3. Solution for a class of one-dimensional cases

In ESCM it was mentioned that the one-dimensional cell model with many-neighbour interactions was not easy to deal with. The nearest-neighbour solution given there relied on the fact that the crystal structure is always of the form $\rho_+ \rho_- \rho_+ \rho_- \dots$; that is, the density function $n^*(y)$ which minimizes $G(n, T)$ equals ρ_+ for y odd and ρ_- for y even. If there are also second-neighbour interactions, that is, $K(2) \neq 0$ and $K(s) = 0$ for $s > 2$, the situation is more complicated. For example, one finds that, if $K(2) \leq 0$ and $K(1) > 0$, then the crystal structure is again of the form $\rho_+ \rho_- \rho_+ \rho_- \dots$, but if $K(1) = 0$ and $K(2) > 0$, the crystal structure is $\rho_+ \rho_+ \rho_- \rho_- \rho_+ \rho_+ \rho_- \dots$ (i.e. period 4) while if $K(1) = 2K(2) > 0$, the crystal structure is $\rho_1 \rho_2 \rho_3 \rho_1 \rho_2 \rho_3 \dots$ (i.e.

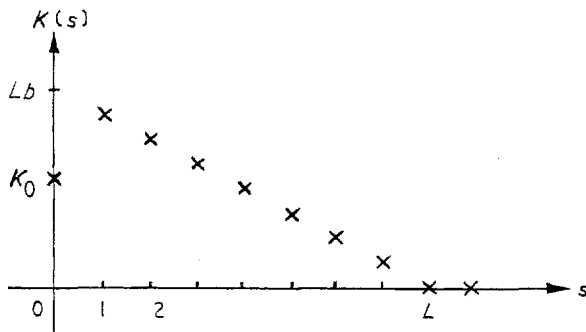


Figure 3. The long-range potential (3.1) for the solvable one-dimensional cases of the model.

period 3). We shall not prove the first two of these results since their proof is essentially the same as that given in ESCM. The third result has however an interesting generalization which we now consider. We note in passing that the general solution of all $K(1)$ and $K(2)$ seems a difficult but interesting problem because of all the different crystal structures and melting transitions which would seem to be possible.

The generalization we shall consider is a one-dimensional system with

$$K(s) = \begin{cases} K_0 & s = 0 \\ (L-s)b & s = 1, 2, \dots, L \\ 0 & s \geq L \end{cases} \quad (3.1)$$

which is illustrated in figure 3. Here b is positive, L is a positive integer and K_0 may be positive or negative. We define for any function $f(\rho)$, the ‘ L -point envelope’ $E^L f(\rho)$ by

$$E^L f(\rho) \equiv \min_{(x_1, \dots, x_L) \in \mathcal{C}(\rho)} \frac{1}{L} \sum_{i=1}^L f(x_i). \quad (3.2)$$

The special case $E^2 f$ is identical to the mid-point envelope MEF used in ESCM. Then the result we obtain is:

Theorem. For the one-dimensional cell model with potential (3.1), the free energy is

$$a(\rho, T) = \text{CE}[E^L\{a^0(\rho, T) + \frac{1}{2}(\alpha - bL^2)\rho^2\} + \frac{1}{2}bL^2\rho^2]. \quad (3.3)$$

For values of ρ and T where the bracket [] coincides with its convex envelope, one can also write

$$a(\rho, T) = G(n^*, T). \quad (3.4)$$

Here $n^*(y, \rho, T)$ minimizes $G(n, T)$ for $n \in \mathcal{C}(\rho)$, and has period L , that is

$$n^*(y+L, \rho, T) = n^*(y, \rho, T). \quad (3.5)$$

When the bracket [] differs from its convex envelope the system has two phases both with a density of the form (3.5).

The case $L = 2$ of this theorem is just a particular case of the result (theorem 3) of ESCM, that is, nearest-neighbour interactions in one dimension. Before proving the general result we first give an heuristic argument,

Consider first the nearest-neighbour case. The model can be represented by the chain in figure 4(a), where the vertices are cells and the bonds are interactions of

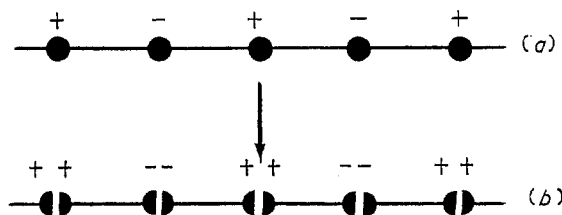


Figure 4. Illustration of the Theorem for first-neighbour interactions.

strength b . If we follow the argument of ESCM we see that equation (4.21) of that paper corresponds to splitting the chain into separate links as shown in figure 4(b) so that each vertex is halved, and then minimizing the free energy of each link. Since each link is identical, this produces densities ρ_+ and ρ_- at opposite ends of each link, and these links can be fitted together to give the density distribution $\rho_+ \rho_- \rho_+ \rho_- \dots$ shown in figure 4(a).

Now consider the $L = 3$ case. Here we have $K(1) = 2b$ and $K(2) = b$, so that the system can be represented by the network shown in figure 5(a), where again each

bond represents an interaction of strength b . It turns out (as we shall subsequently prove) that a step in the treatment of this system also corresponds to breaking the network into parts, in this case triangles whose sides 'have' strength b . The free energy of each triangle can then be minimized separately and, since all triangles have

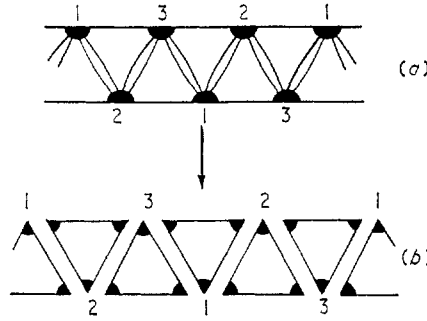


Figure 5. Illustration of the Theorem for second-neighbour interactions.

identical bonds, each has the same density distribution $\rho_1\rho_2\rho_3$. These can be arranged on each triangle so that the vertices match and the resulting network has period 3 as shown in figure 5(b).

The $L = 4$ case can be dealt with in the same way. This time we obtain a network which can be split up into equilateral tetrahedra, resulting in period 4. This should give the reader a rough idea of the reason for choosing the potential (3.1), and help with the understanding of the general proof which we now give. It may be found helpful to write out the proof for the cases $L = 2$ and 3.

Following the method of ESCM we first obtain an upper bound on $a(\rho, T)$. For the potential (3.1), the equation (2.5) for $G(n)$ (omitting T -dependence from the notation) reduces to

$$G(n) = \frac{1}{\Gamma(n)} \sum_{y=1}^{\Gamma(n)} [a^0\{n(y)\} + \frac{1}{2}K_0n(y)^2 + b \sum_{s=0}^{L-1} (L-s)n(y)n(y+s)]. \tag{3.6}$$

From the variational principle (2.6) it follows that

$$a(\rho) \leq G(n') \quad \text{for any } n' \in \mathcal{C}(\rho). \tag{3.7}$$

Choosing

$$n'(y) = \rho_y \quad \text{for } 1 \leq y \leq L \tag{3.8}$$

and

$$n'(y+L) = n'(y)$$

we obtain from (3.6) and (3.7)

$$\begin{aligned} a(\rho) \leq & \frac{1}{L} \{a^0(\rho_1) + \frac{1}{2}K_0\rho_1^2 + \dots + a^0(\rho_L) + \frac{1}{2}K_0\rho_L^2\} \\ & + \frac{b}{L} \{(L-1)(\rho_1\rho_2 + \rho_2\rho_3 + \dots + \rho_{L-1}\rho_L + \rho_L\rho_1) + (L-2) \\ & \times (\rho_1\rho_3 + \rho_2\rho_4 + \dots + \rho_{L-1}\rho_1 + \rho_L\rho_2) + (L-3)(\dots \\ & + (\rho_1\rho_L + \rho_2\rho_1 + \dots + \rho_L\rho_{L-1})\}. \end{aligned} \tag{3.9}$$

The interaction terms in this sum are obtained by considering all the pairs in the periodic series $\rho_1\rho_2 \dots \rho_L\rho_1\rho_2 \dots$, and giving the appropriate interaction to each, that is, $(L-1)b$ for nearest-neighbours etc. The terms in the bracket $\{ \}$ have the sum

$$L \times (\text{sum of all distinct pairs chosen from } \rho_1 \dots \rho_L). \tag{3.10}$$

Each pair appears only once in the bracket $()$. This result is most easily understood by going through the cases $L = 2, 3, 4$, etc. The expression (3.10) reduces to

$$\frac{1}{2}L \left\{ \left(\sum_{i=1}^L \rho_i \right)^2 - \sum_{i=1}^L \rho_i^2 \right\} = \frac{1}{2}L \left\{ (L\rho)^2 - \sum_{i=1}^L \rho_i^2 \right\}. \tag{3.11}$$

Combining (3.9) and (3.11) gives

$$a(\rho) \leq \frac{1}{L} \sum_{i=1}^L \{ a^0(\rho_i) + \frac{1}{2}K_0\rho_i^2 - \frac{1}{2}bL\rho_i^2 \} + \frac{1}{2}bL^2\rho^2. \tag{3.12}$$

Since this holds for all $\rho_1 \dots \rho_L$ with average ρ we can minimize the right side, which from (3.2) gives

$$a(\rho) \leq E^L \{ a^0(\rho) + \frac{1}{2}(K_0 - bL)\rho^2 \} + \frac{1}{2}bL^2\rho^2. \tag{3.13}$$

From (2.8) and (3.1) we have

$$\alpha = K_0 + bL^2 - bL. \tag{3.14}$$

Also, since $a(\rho)$ is convex (ESCM) we obtain

$$a(\rho) \leq CE [E^L \{ a^0(\rho) + \frac{1}{2}(\alpha - bL^2)\rho^2 \} + \frac{1}{2}bL^2\rho^2]. \tag{3.15}$$

This is half the proof of the theorem.

To obtain a lower bound on $a(\rho)$, we use in (3.6) the fact that $n(y)$ has period $\Gamma(n)$, which gives (using Γ for $\Gamma(n)$)

$$\begin{aligned} G(n) &= \frac{1}{\Gamma} \sum_{y=1}^{\Gamma} \left[\frac{1}{L} \sum_{s=0}^{L-1} [a^0\{n(y+s)\} + \frac{1}{2}K_0n(y+s)^2] \right. \\ &\quad \left. + b(\text{sum of all products } n(y+s)n(y+s') \text{ for } s \neq s' \text{ and } 0 \leq s, s' \leq L-1) \right] \\ &= \frac{1}{\Gamma} \sum_{y=1}^{\Gamma} \left[\frac{1}{L} \sum_{s=0}^{L-1} [a^0\{n(y+s)\} + \frac{1}{2}(K_0 - bL)n(y+s)^2] + b \left\{ \sum_{s=0}^{L-1} n(y+s) \right\}^2 \right]. \tag{3.16} \end{aligned}$$

We now put (cf ESCM, equation (4.23))

$$\psi(\rho) \equiv a^0(\rho) + \frac{1}{2}(K_0 - bL)\rho^2 \tag{3.17}$$

and note from (3.2) that

$$\frac{1}{L} \sum_{s=0}^{L-1} \psi\{n(y+s)\} \geq E^L \psi \left\{ \frac{1}{L} \sum_{s=0}^{L-1} n(y+s) \right\}. \tag{3.18}$$

It follows that

$$G(n) \geq \frac{1}{\Gamma} \sum_{y=1}^{\Gamma} \xi \left\{ \frac{1}{L} \sum_{s=0}^{L-1} n(y+s) \right\} \tag{3.19}$$

where

$$\xi(\rho) \equiv E^L \psi(\rho) + \frac{1}{2} b L^2 \rho^2.$$

But the definition of CE implies

$$\begin{aligned} \xi(\rho) &\geq \text{CE} \xi(\rho) \\ &= \text{CF} [E^L \{ a^0(\rho) + \frac{1}{2} (\alpha - b L^2) \rho^2 + \frac{1}{2} b L^2 \rho^2 \}] \\ &\equiv \zeta(\rho), \text{ say.} \end{aligned} \tag{3.20}$$

Hence, we have, using the convexity of $\zeta(\rho)$

$$\begin{aligned} G(n) &\geq \frac{1}{\Gamma} \sum_{y=1}^{\Gamma} \zeta \left\{ \frac{1}{L} \sum_{s=0}^{L-1} n(y+s) \right\} \\ &\geq \zeta \left\{ \frac{1}{\Gamma} \sum_{y=1}^{\Gamma} \frac{1}{L} \sum_{s=0}^{L-1} n(y+s) \right\} \\ &= \zeta(\rho) \text{ for all } n \in \mathcal{C}(\rho) \end{aligned} \tag{3.21}$$

where the equality follows from (3.1). Since (3.21) holds for all n it follows that

$$\inf_{n \in \mathcal{C}(\rho)} G(n) \geq \zeta(\rho) \tag{3.22}$$

which, together with (2.6) and (3.15), proves (3.3). The statements (3.4 and 3.5) follow from the arguments leading to (3.15). This completes the proof of the theorem.

The theorem can be generalized to ν dimensions on a cubic lattice (\mathbf{Z}^ν) by allowing interactions of the form (3.1) along each of the ν lattice directions. The result is essentially the same as (3.3) and the crystal structure is of the form shown in figure 6

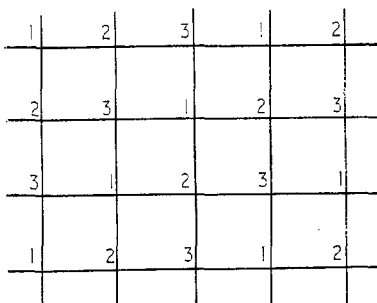


Figure 6. Arrangement of the densities ρ_1, ρ_2 and ρ_3 in the two-dimensional, $L = 3$ generalization of the Theorem.

(for $L = 3$ and $\nu = 2$). However, this is a rather artificial generalization since it does not contain any diagonal interactions.

4. Isomorphisms between different cases of the model

The cases of the model with nearest-neighbour interactions on a ν -dimensional cubic lattice all have the same free energy (equation (4.9) of ESCM) and related crystal structures (i.e. ρ_+ and ρ_- at the ends of each bond). We shall call such cases 'isomorphic'. These cubic lattices cases are also isomorphic, in the same sense,

to other lattices like the plane-honeycomb and the bcc lattices, as mentioned in the introduction. In the present section we consider further such isomorphisms.

We show firstly that the one-dimensional, $L = 3$ case of the previous section is isomorphic to the case of a triangular lattice (figure 2(a)) in which all nearest-neighbour bonds are equal. In the latter case we have

$$K(s) = \begin{cases} K_0 & s = 0 \\ K_1 & s = e_1, e_2 \text{ or } e_3 \\ 0 & \text{otherwise} \end{cases} \quad (4.1)$$

where the e_i are the unit translation vectors of the triangular lattice. Choosing an $n'(y)$ which represents the distribution of densities ρ_1, ρ_2 and ρ_3 as shown in figure 2, and using (3.7) gives

$$\begin{aligned} a(\rho) &\leq \frac{1}{3} \sum_{i=1}^3 \{a^0(\rho_i) + \frac{1}{2}K_0\rho_i^2\} + K_1(\rho_1\rho_2 + \rho_2\rho_3 + \rho_3\rho_1) \\ &= \frac{1}{3} \sum_{i=1}^3 \{a^0(\rho_i) + (\frac{1}{2}K_0 - \frac{2}{3}K_1)\rho_i^2\} + \frac{2}{3}K_1\rho^2. \end{aligned} \quad (4.2)$$

Minimizing the right side gives

$$a(\rho) \leq \text{CE}[E^3\{a^0(\rho) + \frac{1}{4}(3K_0 - \alpha)\rho^2\} + \frac{3}{4}(\alpha - K_0)\rho^2] \quad (4.3)$$

where $\alpha = K_0 + 6K_1$. The right side is also a lower bound on $a(\rho)$ as can easily be shown by the methods of the previous section (and of ESCM). Hence (4.3) is an equality. If we define here $b \equiv \frac{1}{6}(\alpha - K_0)$, then (4.3) is identical to the $L = 3$ case of (3.3), that is, the two systems are isomorphic. The basic reason for this isomorphism is that both lattices can be broken down into a set of equilateral triangles. We shall investigate the common thermodynamics of the two systems in paper II.

Next we point out that the one-dimensional, $L = 4$ case of the previous section is isomorphic to the case of a plane square lattice with nearest-neighbour and diagonal bonds such that

$$\begin{aligned} K(0, 1) &= K(1, 0) = 2b \\ K(1, 1) &= b \end{aligned} \quad (4.4)$$

that is, there are two bonds of strength b between nearest neighbours and one such bond on each diagonal (see figure 7). By the previous arguments, the free energy of this

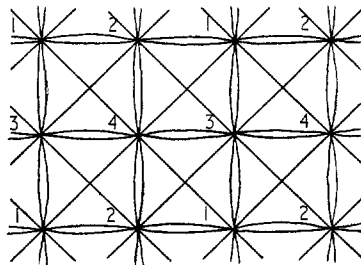


Figure 7. The arrangement of bonds and local densities ρ_1, ρ_2, ρ_3 and ρ_4 on the solvable square lattice with first- and second-neighbour interactions.

system is given by

$$a(\rho) = \text{CE}[E^4\{a^0(\rho) + (\frac{2}{3}K_0 - \frac{1}{6}\alpha)\rho^2\} + \frac{2}{3}(\alpha - K_0)\rho^2] \quad (4.5)$$

and the crystal density distribution has the form shown in figure 7. If we define here $b \equiv \frac{1}{2}(\alpha - K_0)$ then (4.5) is identical to the $L = 4$ case of (3.3); that is, the two systems are isomorphic. Here, the basic reason for the isomorphism is that both lattices can be broken down into a set of equilateral tetrahedra (see figure 7).

The $L = 8$ case of the previous section turns out, in the same way, to be isomorphic to the cubic lattice case with edge, face-diagonal and body-diagonal bonds such that

$$\begin{aligned} K(1, 0, 0) &= 4b \\ K(1, 1, 0) &= 2b \\ K(1, 1, 1) &= b. \end{aligned} \quad (4.6)$$

and

In general, the $L = 2^\nu$ case of the previous section is isomorphic to the ν -dimensional cubic lattice with the bonds

$$\begin{aligned} K(1, 0, 0, 0, \dots, 0) &= 2^{\nu-1}b \\ K(1, 1, 0, 0, \dots, 0) &= 2^{\nu-2}b \end{aligned} \quad (4.7)$$

and so on, until

$$K(1, 1, 1, 1, \dots, 1) = b.$$

We shall not consider the proof of this here since it is a straightforward generalization of the previous proofs.

A problem which we have not solved is to find lattices (if any) which are isomorphic to the $L = 5, 6, 7, 9$, etc, cases of the one-dimensional model. The sequence of lattices we have found so far is a rather curious one. It might therefore be interesting to study the whole sequence from a purely abstract, topological point of view.

5. Confirmation of a conjecture

It was shown by Gates and Penrose (1970b) that the continuous mean-field model has crystal states under certain conditions. In § 6 of this reference it was conjectured that the one-dimensional system should have a periodic crystal state with period $1/p_0$, approximately, if the Fourier transform $\hat{K}(p)$ of the long-range potential has a pronounced minimum at p_0 . We now show that this conjecture is confirmed for the previous one-dimensional cases of the cell model.

For these cases we have from (3.1)

$$\begin{aligned} \hat{K}(p) &\equiv \sum_{s=0, \pm 1, \pm 2, \dots} K(s) \exp(2\pi i p s) \\ &= K_0 + 2b \sum_{s=1}^{L-1} (L-s) \cos(2\pi p s) \\ &= K_0 + b \left(\frac{\sin \pi p L}{\sin \pi p} \right)^2 - bL. \end{aligned} \quad (5.1)$$

Hence $\hat{K}(p)$ has minima $K_0 - bL$ at

$$p = \frac{1}{L}, \frac{2}{L}, \dots, \frac{L-1}{L}, \frac{L+1}{L}, \dots, \frac{2L-1}{L}, \frac{2L+1}{L}, \dots$$

The first minimum is $p_0 = 1/L$, so that $1/p_0 = L$. This is just the period of the crystal state (theorem), so that the conjecture is confirmed.

In view of the results of § 3, one might hope that the potential

$$K(s) \equiv (L-s)b \quad s \leq L$$

$$0 \quad s \geq L \text{ (any real, positive } L) \quad (5.2)$$

for the continuum system of Gates and Penrose (1970a) might result in a crystal of period L . However, we find that

$$\tilde{K}(p) \equiv \int_{-\infty}^{\infty} ds K(s) \exp(2\pi i p s)$$

$$= b \left(\frac{\sin \pi p L}{p L} \right)^2 > 0. \quad (5.3)$$

It follows (see equation (1.7) of Gates and Penrose 1970b) that the free energy is just $a^0(\rho) + \frac{1}{2}bL^2\rho^2$, so that the system has only a fluid state. Roughly speaking, the reason for this is that the continuum case is a limit of the cell case, and the freezing transition occurs at infinite density (see paper II § 3).

6. Discussion

The cell model has been solved for a certain class of lattice and interactions. This is a very special class whose members have the property that their crystal states have a fixed periodicity. It would be interesting to try and find all such special cases, or at least to characterize them in a general way.

It is perhaps surprising that such a class does exist in the model, and one might ask whether other models also have such classes. To study this question, it might be fruitful to consider a model which resembles the cell model somewhat, namely the classical Heisenberg antiferromagnet.

Another question which arises is whether a similar class of interactions can be found for the continuum mean-field model of melting (Gates and Penrose 1970a). This model was shown to have crystal states and melting transitions, but in no case has the crystal structure been found, nor the nature of any melting transition been determined.

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