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1985 J. Phys. A: Math. Gen. 18 3585

(http://iopscience.iop.org/0305-4470/18/18/020)

J. Phys. A: Math. Gen. 18 (1985) 3585-3591. Printed in Great Britain

Existence of phase transitions in a model three-component solution

Dale A Huckaby, Jacek M Kowalski† and Masato Shinmi
Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, USA

Received 10 May 1985

Abstract. A model three-component solution is considered in which the bonds of the lattice $\mathbb{Z}^d$ ($d=2$ or 3) are covered by rod-like molecules of types AA, BB or AB. The ends of molecules near a common lattice site interact with energies ε_{AA}, ε_{BB}, and ε_{AB}. The model is equivalent to an Ising model on a line graph with coupling constants $J_1=(\varepsilon_{AA}+\varepsilon_{BB}-2\varepsilon_{AB})/4$ and $\mu_1=(2\mu_{AB}-\mu_{AA}-\mu_{BB})/4$, and with a field $h_1=(2d-1)(\varepsilon_{BB}-\varepsilon_{AA})/4-(\mu_{BB}-\mu_{AA})/4$. The Peierls argument is used to prove that demixing into a pure AA and a pure BB phase occurs at sufficiently low temperatures if $J_1<0$, $\mu_1<0$ and $h_1=0$. If $J_1<0$ and $\mu_1>|h_1|$, an ordered phase consisting of only AB molecules is proved to exist at sufficiently low temperatures.

1. Introduction

Wheeler and Widom (1968) introduced a lattice model of a three-component solution containing rod-like molecules of types AA, BB and AB. Each bond of the lattice is covered by a single molecule. The ends of molecules near a common lattice site interact with energy ε_{AA} if both ends are of type A, ε_{BB} if both ends are of type B and ε_{AB} if one end is of type A and the other end is of type B. A typical configuration for such a system is illustrated in figure 1 for $\mathbb{Z}^2$.

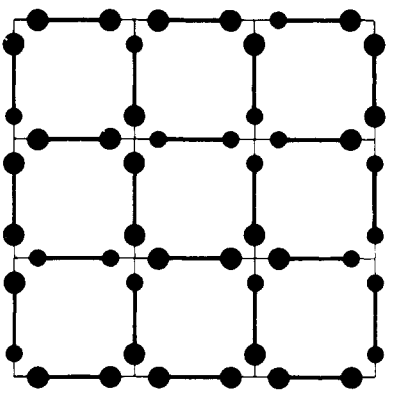

Figure 1. Configuration of molecules on $\mathbb{Z}^2$.

† Present address: Department of Physics, University of Texas at Arlington, Arlington, Texas 76019, USA.

0305-4470/85/183585+07$02.25

Under the simplifying assumption that a type A and a type B molecular end near a common site repel infinitely ($\varepsilon_{AB} \to \infty$), and that like ends do not interact ($\varepsilon_{AA} = \varepsilon_{BB} = 0$), the model has only two reduced activities as thermodynamic variables and can be easily mapped onto the standard Ising model on the same lattice. The bulk and interfacial properties of the model in this special case have been investigated by Wheeler and Widom (1968) and Widom (1984).

We consider the model with general finite interactions ε_{AA}, ε_{BB} and ε_{AB}. We (Huckaby and Kowalski 1984) studied the zeros of the grand partition function for this model and, using some results of Heilmann (1971) and Ruelle (1973), proved that there are no phase transitions if $\varepsilon_{AB} \leqslant (\varepsilon_{AA} + \varepsilon_{BB})/2$. In this paper we shall prove that if $\varepsilon_{AB} > (\varepsilon_{AA} + \varepsilon_{BB})/2$, then ordered phases exist at sufficiently low temperatures for certain ranges of the chemical potential differences $\mu_{AB} - \mu_{AA}$ and $\mu_{AB} - \mu_{BB}$. Since vacant sites are not allowed, the model is considered in the limit in which the chemical potentials μ_{AA}, μ_{BB} and μ_{AB} all tend to infinity; however, differences such as $\mu_{AB} - \mu_{AA}$ or $\mu_{AB} - \mu_{BB}$ are finite thermodynamic variables which determine the relative concentrations of the three molecular species at equilibrium.

2. Ising representation of the model

As mentioned by Wheeler and Widom (1968), the general model with finite interactions can be formulated as an Ising model on a decorated lattice. Although we previously treated the model as a lattice gas (Huckaby and Kowalski 1984), it is convenient in the present context to consider instead the Ising representation. For simplicity, we shall consider the model only on $\mathbb{Z}^d$ ($d = 2$ or 3). The decorated lattice Λ_2 corresponding to the model on $\mathbb{Z}^2$ is illustrated in figure 2. The d-dimensional lattice Λ_d is a line graph, i.e. it can be covered by a set of complete graphs such that each vertex of Λ_d is covered by exactly two complete graphs. (A complete graph C_v is a graph containing v vertices together with links joining every pair of vertices.) The complete graphs C_2 and C_{2d} form covering sets for the line graph Λ_d associated with the model on $\mathbb{Z}^d$, where each site of Λ_d is covered by a vertex from one C_2 and from one C_{2d} graph.

If we let $S_i = +1$ ($S_i = -1$) indicate that site $i \in \Lambda_d$ is occupied by a type A (type B) molecular end, then we can formally write the grand canonical partition function

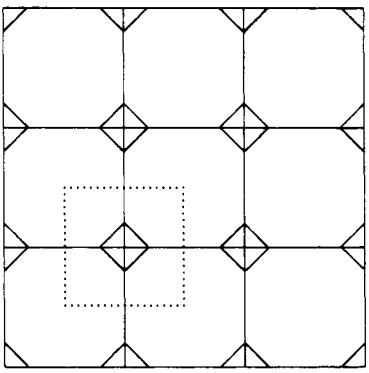

Figure 2. Line graph Λ_2 associated with the model on $\mathbb{Z}^2$. The square region enclosed by a dotted line is referred to in the Peierls argument of § 4.

for the model on Λ_d as

$$\Xi_{\Lambda_d} = \sum_{\{S_i\}} \exp(-H_{\Lambda_d}(\{S_i\})/kT), \tag{1}$$

where the Hamiltonian is given as

$$\begin{aligned} H_{\Lambda_d}(\{S_i\}) = & \sum_{(i,j)\subset C_{2d}} \{\varepsilon_{AA}(1+S_i)(1+S_j)+\varepsilon_{BB}(1-S_i)(1-S_j) \\ & +\varepsilon_{AB}[(1-S_i)(1+S_j)+(1+S_i)(1-S_j)]\}/4 \\ & -\sum_{(i,j)\subset C_2} \{\mu_{AA}(1+S_i)(1+S_j)+\mu_{BB}(1-S_i)(1-S_j) \\ & +\mu_{AB}[(1-S_i)(1+S_j)+(1+S_i)(1-S_j)]\}/4. \end{aligned} \tag{2}$$

Collecting terms in equation (2), we see that the Hamiltonian, except for a constant term, can be written as

$$H^{I}_{\Lambda_d}(\{S_i\}) = J_I \sum_{(i,j)\subset C_{2d}} S_iS_j + \mu_I \sum_{(i,j)\subset C_2} S_iS_j - h_I \sum_{i\in\Lambda_d} S_i, \tag{3}$$

where $J_I = (\varepsilon_{AA}+\varepsilon_{BB}-2\varepsilon_{AB})/4$, $\mu_I = (2\mu_{AB}-\mu_{AA}-\mu_{BB})/4$ and $h_I = (2d-1)(\varepsilon_{BB}-\varepsilon_{AA})/4-(\mu_{BB}-\mu_{AA})/4$. Hence, the Wheeler-Widom model is equivalent to an Ising model on a line graph composed of complete graphs C_2 and C_{2d}, each of which has a different coupling constant.

We have previously shown (Huckaby and Kowalski 1984) that the model has no phase transition if $J_I \geq 0$. The Lee-Yang circle theorem (Lee and Yang 1952) suffices to show that there are also no phase transitions if $J_I < 0$, $\mu_I < 0$ and $h_I \neq 0$.

In § 3 we shall show that, for a range of the parameters J_I, μ_I and h_I, the ground states of the Hamiltonian of equation (3) correspond to ordered structures which are two-fold degenerate. In § 4 we use the Peierls argument to prove the existence of ordered phases for low-temperature regions of (J_I, μ_I, h_I, T) space for which the ground states ($T=0$) are two-fold degenerate. The original treatment of Peierls (1936) has been generalised and modified to treat a large class of lattice models (Griffiths 1964, Dobrushin 1968, Heilmann 1972, 1974, Sinai 1982, Holsztynski and Slawny 1978, Fröhlich *et al* 1980). Since the ground states we consider are related either by spin inversion or by translation, then the methods described by Griffiths (1964) and Dobrushin (1968) are sufficient to prove the existence of ordered phases in the present model. Since the model is disordered at sufficiently high temperatures, then there are order-disorder phase transitions in the model.

3. Ordered ground-state structures

A portion of Λ_d which consists of one C_{2d} graph together with the C_2 graphs which border it will be called a 'star', $\mathcal{S}_d$. Stars for $d=2$ and for $d=3$ are illustrated in figure 3. We shall consider Λ_d to be a union of stars. This allows us to impose on Λ_d any of a large class of boundary conditions, including periodic boundaries. Since Λ_d is a union of stars, the Hamiltonian on Λ_d can then be written as a sum of Hamiltonians restricted to each star portion of Λ_d. The Hamiltonian restricted to a star $\mathcal{S}_d$ is given as

$$H_{\mathcal{S}_d}(\{S_i\}) = J_I \sum_{(i,j)\subset C_{2d}} S_iS_j + (\mu_I/2) \sum_{(i,j)\subset C_2} S_iS_j - (h_I/2) \sum_{i\in\mathcal{S}_d} S_i. \tag{4}$$

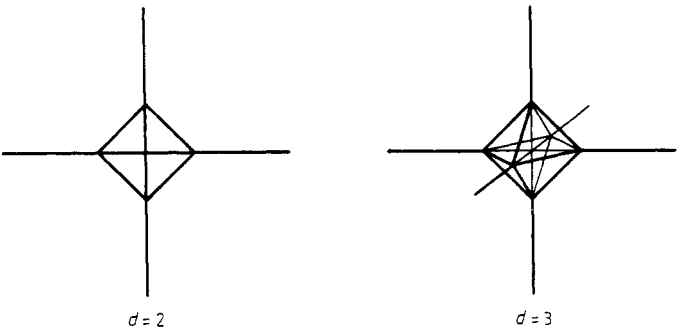

Figure 3. A star portion of Λ_d for which a restricted Hamiltonian is defined by equation (4). A star consists of one C_{2d} graph together with the C_2 graphs which border it.

In equation (4), the factor of $\frac{1}{2}$ which preceeds the second and third summations should be replaced by unity if site i or site j is on the boundary of Λ_d.

Let H_0 denote the lowest value of the restricted Hamiltonian for a star portion of a configuration. Stars with this value will be called 'ground-state stars'. Stars with higher values of the restricted Hamiltonian, H_*, will be called 'excited-state stars'. The value $\alpha_d = \min(H_* - H_0)$ will be of importance in the construction of the Peierls argument in § 4.

We see from equation (4) that a star composed of all AA molecules has the same value of the restricted Hamiltonian as a star composed of all BB molecules if and only if $h_1 = 0$. If $h_1 = 0$, then changing the configuration from an all AA star or an all BB star adds $-J_1 a - \mu_1 b$ to the value of the restricted Hamiltonian, where a and b are both non-negative and not both zero. Therefore, a sufficient condition for an all AA star or an all BB star to be a ground-state star is that $h_1 = 0$, $J_1 < 0$ and $\mu_1 < 0$.

Conversely, suppose the all BB and all AA configurations are ground states of Λ_d. Comparing the Hamiltonian for the all BB configuration with one which is identical except that one BB molecule is replaced by an AA molecule, we see that $J_1 < 0$ necessarily. By comparing the all BB configuration to one which is identical to it except that the type B molecular ends at the vertices of one C_{2d} graph are replaced by type A molecule ends, we see that $\mu_1 < 0$ necessarily. Hence, $h_1 = 0$, $J_1 < 0$ and $\mu_1 < 0$ are the necessary and sufficient conditions for the ground states of Λ_d to consist of all AA or all BB molecules.

A consideration of the possible configurations on a star indicates that if $h_1 = 0$, $J_1 < 0$ and $\mu_1 < 0$, then

$$\alpha_d = \min\{-\mu_1, -(4d-2)J_1\} > 0. \tag{5}$$

We shall next determine the region of (J_1, μ_1, h_1) space for which Λ_d has a two-fold degenerate ground state corresponding to ordered configurations consisting of only AB molecules, where the vertices of each C_{2d} graph are occupied by either all type A or all type B molecular ends. It is clear from equation (3) that these two configurations on Λ_d have the same value of the Hamiltonian. Suppose these configurations are ground-state configurations. By comparing the Hamiltonian for one such configuration to that for a configuration which differs only in that the orientation of one AB molecule is switched, we see that $J_1 < 0$ necessarily. Comparing one of the two configurations

to one in which the type A or type B molecular ends at the vertices of one C_{2d} graph are replaced by the other type of end, we find that $\mu_1 > |h_1|$ necessarily.

In addition, we see from equation (4) that the two stars which are composed of AB molecules, such that the C_{2d} graph is occupied by only one type of molecular end, have the same value of the restricted Hamiltonian. Changing such a star configuration adds $-J_1 a + (\mu_1 \pm h_1) b$ to the value of the restricted Hamiltonian of equation (4), where a and b are both non-negative and not both zero. Therefore, sufficient conditions for a ground-state star to contain all AB molecules with the C_{2d} graph occupied by only one type of molecular end are that $J_1 < 0$ and $\mu_1 > |h_1|$. These are then the necessary and sufficient conditions for the ground-state configurations on Λ_d to consist of only AB molecules, such that the vertices of each C_{2d} graph are occupied by either all type A or all type B molecular ends.

A consideration of the possible configurations on a star indicates that if $J_1 < 0$ and $\mu_1 > |h_1|$, then

$$\alpha_d = \min\{\mu_1 - |h_1|, -(4d-2)J_1\} > 0. \tag{6}$$

In the next section the values of α_d given by equations (5) and (6) will be used in a Peierls argument to prove that the ordered ground-state structures discussed above persist as ordered phases at sufficiently low temperatures.

4. Existence of ordered phases

In this section we shall construct a Perierls argument to prove that ordered phases exist in the model at sufficiently low temperatures in regions of (J_1, μ_1, h_1, T) space for which the corresponding ground states ($T = 0$) have the ordered structures discussed in § 3.

Since the notion of a contour is central to the Peierls argument, we now define what we mean by a contour in a configuration. For the two-dimensional lattice Λ_2, the square region r_2 outlined by dots in figure 2 is said to be associated with the star $\mathcal{S}_2$ which has its C_4 portion interior to r_2. Analogously in three dimensions, a cubic region r_3 is associated with each star $\mathcal{S}_3$ in Λ_3. If $\mathcal{S}_d$ is an excited-state star, then the associated region r_d is said to be a contour segment. Two contour segments are said to be connected in the two-dimensional case if they share a common vertex and in the three-dimensional case if they share a common edge. A simply connected set of contour segments constitutes a contour. A contour is said to be closed if its outer border does not intersect the border of Λ_d. A closed contour which is not surrounded by another closed contour is said to be an outer contour.

Let O_{AA} (O_{BB}) denote the ordered structure in which every bond of $\mathbb{Z}^d$ contains an AA molecule (BB molecule). Let O_{AB} denote the structure in which every bond of $\mathbb{Z}^d$ contains an AB molecule such that each C_{2d} of Λ_d is occupied by either all type A or all type B molecular ends and such that the origin is occupied by a type A molecular end. Then let O_{BA} denote the structure which is related to O_{AB} by a unit translation of $\mathbb{Z}^d$.

If N_δ is the number of bonds of $\mathbb{Z}^d$ which contain molecules which belong to an ordered structure O_δ on a lattice containing $|\Lambda_d|/2$ such bonds, then as discussed by Dobrushin (1968) and Griffiths (1972), there is an ordered phase in the thermodynamic limit if $\langle N_\delta \rangle / (|\Lambda_d|/2) > \frac{1}{2}$, where there are two symmetrically related ordered structures, and where the thermal average is taken only over configurations in which the outer

boundary of the lattice contains the ordered structure O_δ. Convergence proofs of series expansions suffice to show that the model is disordered at high temperatures, thereby proving the existence of an order-disorder transition in the model.

If the stars on the boundary are occupied by one of the four structures O_δ discussed above, then all bonds of $\mathbb{Z}^d$ containing molecules not belonging to O_δ are enclosed by (or embedded within) an outer contour γ. As a consequence,

$$|\Lambda_d|/2 - \langle N_\delta \rangle < \sum m_{|\gamma|} n_{|\gamma|} P_\gamma, \tag{7}$$

where $m_{|\gamma|}$ is the maximum number of molecules enclosed by (or embedded in) a contour of length $|\gamma|$, $n_{|\gamma|}$ is the number of contours containing $|\gamma|$ segments, and P_γ is an upper bound to the probability that a given contour of length $|\gamma|$ occurs in a configuration.

The maximum number of molecules $m_{|\gamma|}$ contained within a contour of length $|\gamma|$ is not greater than the number of molecules contained within a d-dimensional isoperimetric spherical region. A maximum of three edges of a contour segment r_2 can be on the outer border of a contour in Λ_2, and a maximum of five faces of a contour segment r_3 can be on the outer border of a contour in Λ_3. The number of molecules enclosed by a closed contour does not exceed half the number of sites of Λ_d enclosed by the contour. A simple calculation then gives $m_{|\gamma|} < (9/2\pi)|\gamma|^2$ in two dimensions and $m_{|\gamma|} < (5^{3/2}/2\pi^{1/2})|\gamma|^{3/2}$ in three dimensions.

To obtain an upper bound to $n_{|\gamma|}$, first assign a number to each region r_d in Λ_d. There are at most $|\Lambda_d|/(2d)$ such regions at which a contour can be begun. To continue the contour, add any segments which are connected to the segment of the growing contour which has the lowest number assigned to it. Without regard to the molecular configurations of the contour, there are 2^8 ways to continue a contour in Λ_2 and 2^{18} ways to continue a contour in Λ_3. The process is terminated when the contour contains $|\gamma|$ segments. There are at most $2^{4d|\gamma|}$ configurations for a contour containing $|\gamma|$ segments. Hence, $n_{|\gamma|} < [|\Lambda_d|/(2d|\gamma|)]2^{-8}2^{16|\gamma|}$ in two dimensions, and $n_{|\gamma|} < [|\Lambda_d|/(2d|\gamma|)]2^{-18}2^{30|\gamma|}$ in three dimensions. The division by $|\gamma|$ results since the choice of the first segment is arbitrary. Substituting for $m_{|\gamma|}$ and $n_{|\gamma|}$ in equation (7) yields

$$2\langle N_\delta \rangle / |\Lambda_d| > 1 - a_d \sum_{|\gamma|} b_d^{|\gamma|} |\gamma|^{1/(d-1)} P_\gamma, \tag{8}$$

where a_d and b_d are constants.

We now proceed to calculate an upper bound to P_γ. Suppose the boundary is composed of a ground-state structure O_δ. Let C_γ be the set of configurations which contain an outer contour γ. With each configuration $\xi \in C_\gamma$ we associate a configuration $\xi^* \in C_\gamma^*$ (this is a 1-1 correspondence) generated in the following manner. If $O_\delta = O_{AA}$, change all O_{BB} regions (together with their interiors) that border γ by replacing all type A (type B) molecular ends with type B (type A) molecular ends. If $O_\delta = O_{AB}$, change all O_{BA} regions (together with their interiors) that border γ by translating each such region by a unit lattice spacing in $\mathbb{Z}^d$. After performing one or the other of the above operations, then replace the contour γ with structure O_δ. The resulting configuration ξ^* has the property that

$$H_{\Lambda_d}(\xi) - H_{\Lambda_d}(\xi^*) \geqslant \alpha_d |\gamma|, \tag{9}$$

where α_d is given by equation (5) if $O_\delta = O_{AA}$ or $O_\delta = O_{BB}$ and by equation (6) if $O_\delta = O_{AB}$ or $O_\delta = O_{BA}$.

Hence

$$P_\gamma \equiv \Xi_{\Lambda_d}^{-1} \sum_{\xi \in C_\gamma} \exp(-H_{\Lambda_d}(\xi)/kT)$$

$$< \sum_{\xi \in C_\gamma} \exp(-H_{\Lambda_d}(\xi)/kT) \Big/ \sum_{\xi^* \in C_\gamma^*} \exp(-H_{\Lambda_d}(\xi^*)/kT)$$

$$\leqslant \exp(-\alpha_d|\gamma|/kT). \tag{10}$$

Equations (8) and (10) ensure that $\langle N_\delta \rangle / (|\Lambda_d|/2) > \frac{1}{2}$ at sufficiently low temperatures.

Therefore, there are pure AA and pure BB phases in the model at sufficiently low temperatures if $J_1 < 0$, $\mu_1 < 0$ and $h_1 = 0$. In addition, if $J_1 < 0$ and $\mu_1 > |h_1|$, there is an ordered pure AB phase in the model at sufficiently low temperatures.

Acknowledgment

This research was supported by the Robert A Welch Foundation, grant P-446.

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