

## Generalized Bragg-Williams Method for "Antiferromagnetic" Lattice Gases

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**Abstract** The many-sublattice Bragg-Williams approximation of statistical mechanics is applied to the two-dimensional square and triangular lattice-gas models with nearest-neighbor repulsive interactions. Each problem is solved through both the canonical and grand-canonical methods. The present treatment emphasizes the duality between concentration and chemical potential and illustrates the appearance of first- and second-order transitions in each method.

### 1. INTRODUCTION

The Ising model of binary systems can be formulated in several different "languages". Among these, the most popular descriptions are the original spin-one-half ferro- or antiferromagnet, the binary alloy, and the "lattice gas". The latter term was introduced by Yang and Lee<sup>1</sup> to describe a lattice of sites that can be either empty or occupied by at most one particle or atom. A lattice gas is thus characterized by a concentration of occupied sites  $x = N_a/N$ , where  $N_a$  is the number of atoms and  $N$  is the total number of sites in the lattice.

Lattice-gas models are of interest both as representations of real physical systems — such as intercalated layered compounds<sup>2-4</sup>, adsorbed monolayers on crystal surfaces<sup>5,6</sup>, and metal hydrides<sup>7</sup> — and for their intrinsic formal content.

In regards to the latter aspect, the lattice gas with nearest-neighbor ( $nn$ ) inter-atomic repulsion is mathematically equivalent to the Ising antiferromagnet. Occupied sites correspond to up spins and vacancies to down spins. The chemical potential plays the role of the magnetic field and the one-half-concentration lattice gas can be identified with the zero-field antiferromagnet. This isomorphism appears when the grand partition function of the lattice gas is compared to the partition function of the Ising magnetic system<sup>8</sup>.

In this paper we present two examples of two-dimensional lattice-gas models with  $m$  repulsive (i.e., antiferromagnetic) interactions. Phase diagrams are numerically calculated within a generalized mean-field, or Bragg-Williams (BW)<sup>9</sup>, approximation, which divides the original lattice into a number of equivalent sublattices that are compatible with the ground-state configuration of the system. Ordered phases are represented by the predominant occupation of one of the sublattices.

Since it neglects the possibility of short-range correlation between the occupied sites, the BW approximation is not expected to lead to accurate phase diagrams. It is, however, a useful starting point towards more sophisticated calculations, such as the renormalization-group<sup>2,5</sup> and cluster-variation<sup>3</sup> methods. Besides, due to its simple formulation, the BW approximation pedagogically illustrates, in a clear and intuitive way, several fundamental concepts of statistical mechanics. Here we emphasize the equivalence of the canonical and grand-canonical treatments, and hence the duality between concentration and chemical potential. A new method is presented for the grand-canonical treatment that reduces the problem to searching and classifying the solutions of one equation of only one variable. The concepts of first- and second-order transitions are graphically illustrated by the behavior of those solutions.

The two-dimensional square and triangular lattice-gas systems, both with  $m$  repulsion only, are examined in the next two sections, which are both organized in the following way: (A) General considerations are presented about the system, followed by the description of the BW approximations for its energy and entropy; (B) A canonical treatment is discussed based on the minimum property of the free energy; (C) Finally a grand-canonical study is developed based on the minimum property of the grand potential, followed by a comparison between methods (B) and (C).

## 2. THE SQUARE LATTICE GAS

### 2.1. General considerations

As illustrated in Fig. 1, the square lattice is divided into two interpenetrating sublattices,  $\alpha$  and  $\beta$ , such that any site in one of

them has Four nearest neighbors in the other one. This representation can be justified by the following argument: For  $T = 0$  and the concentration  $x = 1/2$  the total energy of the nn-repulsion square lattice gas is minimized by the configuration that corresponds to total occupation of one of the sublattices and null occupation of the other one. In this way, occupied pairs of nn sites are avoided.

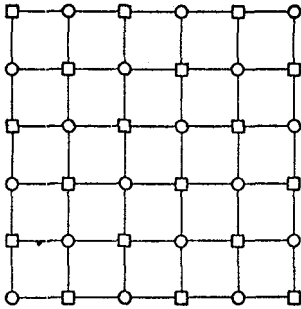


Fig.1 - Representation of the square lattice with its two interpenetrating sublattices.

We define  $n_v$  ( $v = a, \beta$ ) as the occupation number of sublattice  $v$ , i.e., the probability that a site of sublattice  $v$  be occupied by an atom. The total concentration of the lattice gas is given by

$$x = (n_\alpha + n_\beta)/2 \quad (1)$$

We define a long-range order parameter

$$\eta = \frac{n_\alpha - n_\beta}{n_\alpha + n_\beta} \quad (2)$$

such that  $\eta = 0$  in a disordered phase (when the two sublattices are equally occupied) and  $\eta \neq 0$  in an ordered phase (when one sublattice is preferentially occupied). At  $T = 0$  and  $x = 1/2$ , the maximum and minimum values  $\eta = \pm 1$  occur in a degenerate way, according to whether sublattice  $a$  or  $\beta$  is occupied. We may remove this degeneracy by assuming the  $a$  sublattice to be filled first, so that  $\eta > 0$ .

The BW approximation for the energy of a two-sublattice nn-repulsion square lattice gas is

$$E = 2 N U n_\alpha n_\beta \quad (3)$$

where  $U$  is the interaction energy of two atoms in nn sites,  $2N$  is the total number of pairs of nn sites in the lattice, and  $(n_\alpha, n_\beta)$  is the

BW approximation for the probability that such a  $mn$  pair be occupied by two atoms. This implies, of course, that the correlations between different sites are ignored.

The entropy is obtained from the total number of ways for combining the supposedly uncorrelated occupied and empty sites in each sublattice, in the form

$$S = k_B \sum_{\nu} \ln \frac{(N/2)!}{(Nn_{\nu}/2)! [N(1-n_{\nu})/2]!} \quad (4)$$

This is a straightforward two-sublattice generalization of the usual mean-field entropy of binary systems<sup>10</sup>.

## 2.2. The canonical method

According to the formalism of the canonical ensemble, the equilibrium configuration of the system is given by the minimization of the Landau (i.e., non-equilibrium) free energy  $F = E - TS$  with respect to the appropriate variational parameters at fixed temperature and number of particles. Throughout this paper the area and number of sites of the lattice gas are taken as constant. We thus fix the concentration  $x$  in the canonical formalism.

Due to the constraint of Eq. (1), only one of the two sublattice occupation numbers, say  $n_a$ , should be considered as an independent minimization parameter. Equivalently, we choose the order parameter  $\eta$  of Eq. (2) as our independent variable. The occupation numbers are then given by

$$n_{\alpha} = x(1 + \eta) \quad (5a)$$

$$n_{\beta} = x(1 - \eta) \quad (5b)$$

and the Landau free energy can be readily expressed, according to Eqs. (3) and (4), and with the use of Stirling's approximation for the factorials, as

$$F(\eta; x, T) = 2 N U n_{\alpha} n_{\beta} + \frac{Nk_B T}{2} \sum_{\nu} [n_{\nu} \ln n_{\nu} + (1-n_{\nu}) \ln(1-n_{\nu})] \quad (6)$$

In the above equation,  $n_\alpha$  and  $n_\beta$  should be considered as functions of  $\eta$ , with  $x$  as a parameter, according to Eq. (5). The minimum property of  $F(\eta; x, T)$  yields

$$8xq = \tau \ln \frac{1 - x - x\eta^2 + \eta}{1 - x - x\eta^2 - \eta} \quad (7)$$

where we defined the reduced temperature  $\tau = k_B T / U$ .

We need only to solve Eq. (7) for  $x < 1/2$ . Indeed, due to the pairwise, concentration-independent nature of the assumed interactions, the thermodynamics of the system for  $x > 1/2$  can be obtained from the results for  $x < 1/2$ . The temperature-concentration phase diagram, in particular, displays a mirror symmetry about the line  $x = 1/2$ . This particle-hole symmetry, as noted by van Baal<sup>11</sup>, is due only to the absence of many-body interactions in the model, and is independent of the approximation.

For  $x < 1/2$ , Eq. (7) can be solved by a Newton-Raphson scheme<sup>12</sup> with the only restriction  $|\eta| < 1$ . For the reduced temperature  $\tau > \tau_c \equiv 1$ ,  $\eta = 0$  (disordered phase) is the only solution. For  $\tau < \tau_c$ , the solution  $\eta = 0$  is a minimum of  $F(\eta; x, T)$  only if  $x < x_-$  or  $x > x_+$ , where

$$x_\pm = [1 \pm (1 - \tau)^{1/2}] / 2 \quad (8)$$

Otherwise, the function  $F(\eta; x, T)$  has a local maximum at  $\eta = 0$  and two symmetric minima at  $\eta < 0$  and  $\eta > 0$ . Assuming  $n_\alpha > n_\beta$ , we choose the positive solution. The behavior of  $F(\eta; x, T)$  as  $x$  crosses  $x_-$  is illustrated in Fig. 2, where the reduced Landau free energy  $f(\eta; x, \tau) \equiv F(\eta; x, T) / (N U)$  is plotted for  $\tau = 0.75$  and several values of  $x$  near  $x_- = 0.25$ . The transition is of second order, i.e., the equilibrium value of  $\eta$  is a continuous function of  $x$  near  $x_-$ .

It is interesting to investigate the behavior of the sublattice occupation numbers  $n_\alpha$  and  $n_\beta$  as functions of  $x$  at a given  $T$ . This behavior is illustrated in Fig. 3, which is symmetric with respect to an inversion about the midpoint (0.5, 0.5), for  $\tau = 0.75$ . The curves for the two occupation numbers are seen to bifurcate continuously at  $x = x_- \equiv 0.25$  and to merge again at  $x = x_+ \equiv 0.75$ .

A phase diagram is obtained in the  $(x, \tau)$  plane from Eq. (8) as shown in Fig. 4(b). A similar phase diagram can be obtained in the

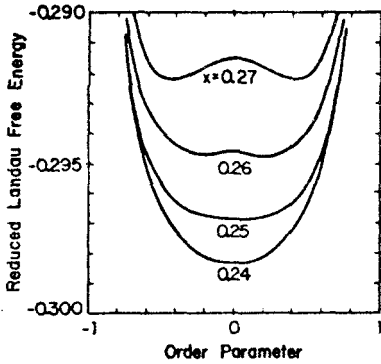


Fig.2 - Reduced Landau free energy  $f(\eta; T, x)$  as function of the order parameter  $\eta$ , for  $k_B T = 0.75 U$  and several values of the concentration  $x$ , for the nn-repulsion BW square model.

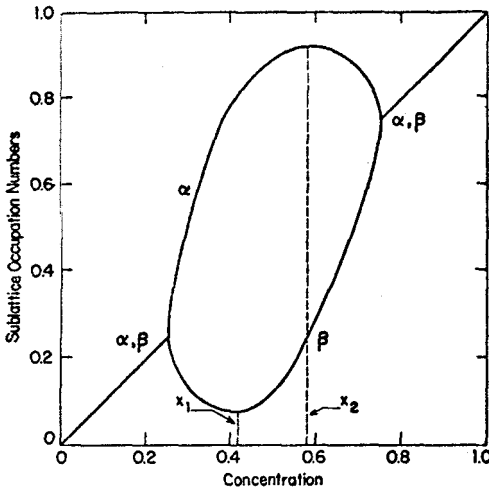


Fig.3 - Occupation numbers of sublattices  $\alpha$  and  $\beta$ , as functions of the concentration  $x$ , for  $k_B T = 0.75 U$  in the square lattice.

$(\mu, \tau)$  plane, as shown in Fig. 4(a), where  $\mu$  is the reduced chemical potential, defined by

$$\mu \equiv \frac{\mu_1}{U} = \frac{1}{NU} \frac{\partial F}{\partial x} \quad (9)$$

where  $\mu_1$  is the chemical potential of the atoms in the lattice gas.

It is needless to state that all thermodynamic properties of the system are obtained in a straightforward way once the Landau free energy of Eq. (6) has been minimized, at given  $x$  or  $T$ . The specific heat at constant  $x$ , for instance, displays a discontinuity, typical of

a mean-field second-order transition, at the corresponding order-disorder temperature, and vanishes above that temperature.

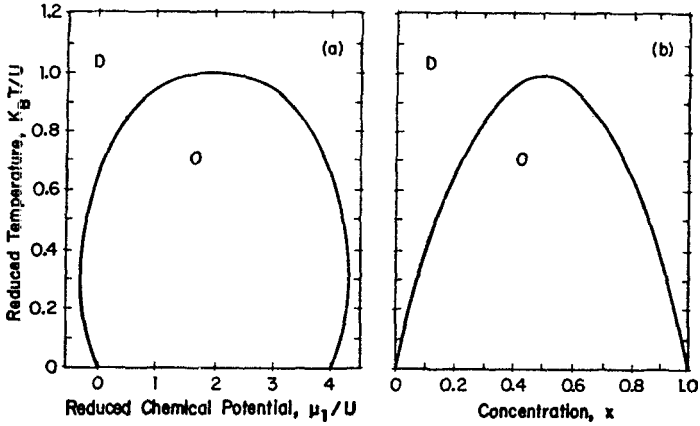


Fig.4 - Order (O)-disorder (D) phase diagrams for the  $m$ -repulsion BW square lattice in (a) the temperature v. chemical potential plane, (b) the temperature v. concentration plane.

### 23. The grand-canonical method

In the grand-canonical ensemble, the chemical potential  $\mu_1$  is a fixed thermodynamic parameter, instead of the number of particles. Now the two sublattice occupation numbers are independent variables for the minimization of the grand potential

$$\Omega = F - \mu_1 N x \tag{10}$$

The concentration  $x$  is obtained from Eq. (1) after  $\Omega$  has been minimized. The grand-canonical and canonical formalisms are expected to give the same results, of course, except in the case where we are interested in fluctuations in the number of particles, which are ignored in the canonical treatment. This aspect is not relevant to our discussion.

From Eqs. (1), (6) and (10) we can write our non-equilibrium grand potential as

$$\begin{aligned} \Omega(n_\alpha, n_\beta; \mu_1, T) = & N U(4x^2 - n_\alpha^2 - n_\beta^2) \\ & + \frac{Nk_B T}{2} \sum_V [n_V \ln n_V + (1-n_V) \ln(1-n_V)] \\ & - \frac{N\mu}{2} (n_\alpha + n_\beta) \end{aligned} \quad (11)$$

At fixed  $V$ , and  $T$ , the minimum property of  $\Omega(n_\alpha, n_\beta; \mu_1, T)$  yields the equation<sup>13</sup>

$$4x - 2n_V + \frac{\tau}{2} \ln \frac{n_V}{1-n_V} - \frac{\mu}{2} = 0 \quad (12)$$

where, as before,  $\tau = k_B T/U$ , and  $\mu = \mu_1/U$ . Eq. (12) can be solved by assigning values to

$$\lambda = \mu - 8x \quad (13)$$

and looking for the solutions of

$$g(n_V) \equiv -4n_V + \tau \ln \frac{n_V}{1-n_V} = \lambda \quad (14)$$

This equation has three different roots between 0 and 1 whenever  $h$  is such that  $g(x_+) < \lambda < g(x_-)$ , where  $x_+$  and  $x_-$  are defined in Eq. (8), for  $\tau < 1$ . (Otherwise, Eq. (14) has the only solution  $n_V = x$  corresponding to the disordered phase.) The three roots, which we call  $u_1$ ,  $u_2$  and  $u_3$  can be assigned in six different ways to the two sublattice occupation numbers. We have the pairs

$$\{n_\alpha, n_\beta\} = \{u_1, u_1\}, \{u_1, u_2\}, \{u_1, u_3\}, \{u_2, u_2\}, \{u_2, u_3\} \text{ and } \{u_3, u_3\} \quad (15)$$

It is found that  $\{u_2, u_2\}$  does not lead to a minimum of the grand potential at fixed  $\mu$ . The other five pairs appear as we scan the concentration range from 0 to 1 continuously in the following steps (see Fig. 5):

- (a)  $\lambda$  increases from  $-\infty$  to  $g(x_-)$  while  $x$  increases from 0 to  $x_-$ ;
- (b)  $\lambda$  decreases from  $g(x_-)$  to  $g(x_+)$  while  $x$  increases from  $x_-$  to  $x_1 < 1/2$ ;
- (c)  $\lambda$  increases from  $g(x_+)$  to  $g(x_-)$  while  $x$  increases from  $x_1$  to  $x_2 > 1/2$ ;



(d)  $\lambda$  decreases again from  $g(x_-)$  to  $g(x_+)$  while  $x$  increases from  $x_2$  to  $x_+$ ;

(e)  $\lambda$  finally increases from  $g(x_+)$  to  $+\infty$  while  $x$  increases from  $x_+$  to 1.

Steps (b)-(d) appear in the ordered phase. The points  $x_1$  and  $x_2$  are indicated in Fig. 3 as the positions for the minimum of  $n_\beta$  and the maximum of  $n_\alpha$ , respectively, for the ordered phase.

The phase diagrams of Fig. 5 are easily recovered by the present grand-canonical treatment. The order-disorder transition  $x_-$  is the local maximum of  $g(n_\nu)$  where the solution to Eq. (14) bifurcates. This is the transition point between steps (a) and (b) above. The fact that this transition is of second order is related to the possibility of continuously increasing the concentration through the bifurcation process. This is due to (i) the existence of exactly two equivalent variables  $n_a$  and  $n_b$  and to (ii) the shape of  $g(n_\nu)$  for  $n_\nu$  near  $x_-$ , specially the positive sign of the third derivative of  $g(n_\nu)$ . This latter factor is responsible for  $n_\alpha$  to increase faster than  $n_\beta$  decreases for  $x$  just larger than  $x_-$ . We might anticipate that first-order transitions in the BW triangular lattice, discussed in the next section, are due to requirement (i) not being satisfied.

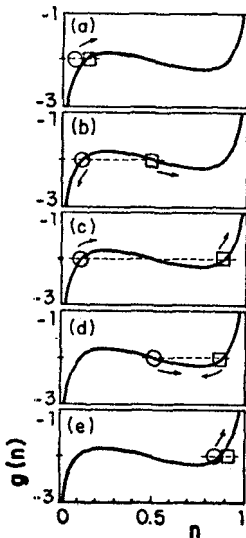


Fig.5 - Evolution of the solutions of the equation  $g(n_\nu) = A$  for  $k_B T = 0.75U$  in the square lattice as  $A$  (a) increases from  $-\infty$  to  $g(x_-)$ , (b)-(d) oscillates between  $g(x_-)$  and  $g(x_+)$ , (e) increases from  $g(x_+)$  to  $+\infty$ . From (a) to (e) the concentration  $x$  always increases.

The second-order transition between the disordered and ordered phases in the square lattice is represented schematically in Fig. 6 by  $F$ -versus- $x$  and  $\Omega$ -versus- $\mu_1$  plots. The transition point  $P$  is seen to be well determined in both plots, with continuous derivatives.

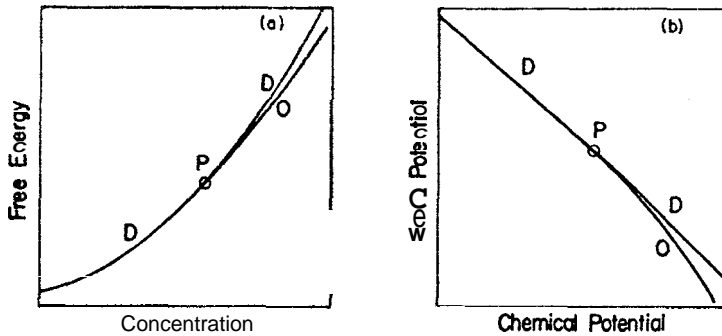


Fig.6 - Schematic representation of (a) concentration dependence of free energy and (b) chemical potential dependence of grand potential in the vicinity of the disorder-order transition in the square lattice.

### 3. THE TRIANGULAR LATTICE GAS

#### 3.1. General considerations

The triangular lattice is essentially different from the square lattice, discussed in the preceding section, since it cannot be divided into two equivalent sublattices. This fact is related to the "frustration" of the triangular-lattice Ising magnetic system, where no antiferromagnetic order is possible at zero external field. As shown in the following discussion, it is also the reason for the BW approximation for the triangular lattice to yield a first-order transition between ordered and disordered phases, in contrast to the second-order transition exhibited by the square lattice.

As illustrated in Figure 7, the triangular lattice is divided into three interpenetrating sublattices,  $\alpha$ ,  $\beta$ , and  $\gamma$ , such that any site in one of them, say  $\alpha$ , has three nearest neighbors in each of the other

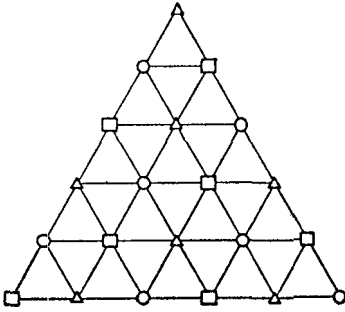


Fig.7 - Representation of the triangular lattice with its three interpenetrating sublattices.

two sublattices,  $\beta$  and  $\gamma$ . Perfectly ordered structures at  $T=0$  for the triangular lattice gas with  $m$  repulsion exist at  $x = 1/3$  ( $n_\alpha = 1, n_\beta = n_\gamma = 0$ ) and at  $x = 2/3$  ( $n_\alpha = n_\beta = 1, n_\gamma = 0$ )<sup>14</sup>. The occupation numbers  $n_\nu$  ( $\nu = \alpha, \beta, \gamma$ ) are defined as in the preceding section. The total concentration  $x$  is now

$$x = (n_\alpha + n_\beta + n_\gamma)/3 \quad (16)$$

The BW interaction energy is given by

$$E = NU(n_\alpha n_\beta + n_\beta n_\gamma + n_\gamma n_\alpha) \quad (17)$$

while the BW entropy is

$$S = k_B \sum_\nu \ln \frac{(N/3)!}{(N n_\nu/3)! [N(1 - n_\nu)/3]!} \quad (18)$$

in complete analogy to the results obtained for the square lattice.

### 3.2. The canonical method

The minimization of the Landau free energy is most easily carried out when two of the sublattice occupation numbers are considered to be equal, e.g.,  $n_\beta = n_\gamma$ . We then have only one independent variable, at fixed  $x$ . The most general case of three different sublattice occupation numbers is treated in the next sub-section.

As in section 2, we may define a long-range order parameter

$$\eta = \frac{n_\alpha - n_\beta}{n_\alpha + 2 n_\beta} \quad (19)$$

so that

$$n_{\alpha} = x(1 + 2\eta) \quad (20a)$$

$$n_{\beta} = x(1 - \eta) \quad (20b)$$

The Landau free energy is now

$$\begin{aligned} F(\eta; x, T) = & NU(2n_{\alpha} n_{\beta} + n_{\beta}^2) + \frac{N k_B T}{3} \left[ n_{\alpha} \ln n_{\alpha} \right. \\ & + (1 - n_{\alpha}) \ln(1 - n_{\alpha}) + 2 n_{\beta} \ln n_{\beta} \\ & \left. + 2(1 - n_{\beta}) \ln(1 - n_{\beta}) \right] \end{aligned} \quad (21)$$

where  $n_{\alpha}$  and  $n_{\beta}$  are functions of  $\eta$ , with  $x$  as a parameter, according to Eq. (20). The minimum property of  $F(\eta; x, T)$  yields

$$9x\eta = \tau \ln \frac{1 - x - x\eta + 2x\eta^2 + 2\eta}{1 - x - x\eta + 2x\eta^2 - \eta} \quad (22)$$

where, again,  $\tau = k_B T / U$ .

This equation can also be solved by the Newton-Raphson iteration method. The disordered phase ( $\eta=0$ ) is the solution for  $\tau > \tau_c \equiv 3/4$ . Similarly to the case of section 2.2,  $\eta = 0$  is at least a local minimum of  $F(\eta; x, T)$  if  $x < x_-$  or  $x > x_+$ , where

$$x_{\pm} = \frac{1}{2} \pm \left( \frac{1}{4} - \frac{\tau}{3} \right)^{1/2} \quad (23)$$

Let us now consider the region  $0 < x < 1/2$ . The local minimum at  $\eta = 0$  for  $x < x_-$  turns out to be a global minimum only if  $x < x_0$ , where  $x_0$  is within 0.02 smaller than  $x_-$ . Such behavior is illustrated in Fig. 8, for  $\tau = 0.5$ , when  $x_- = 0.21132$  and  $x_0$  lies between 0.20 and 0.195. Inside the narrow interval  $x_0 < x < x_-$ , the global minimum corresponds to a positive value of  $\eta$ , in the same branch of the solution for  $x > x_-$ . If only one phase were allowed, we would thus witness a discontinuous change of the order parameter at  $x = x_0$ .

When the disordered (D) and the two-sublattice ordered ( $0_2$ ) phases are allowed to coexist, the concentration interval of coexistence is determined, for each  $\tau$ , by the common tangent to the equilibrium free energy curves of the two phases<sup>10</sup>.

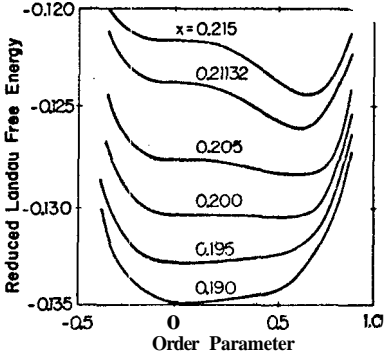


Fig.8 - Reduced Landau free energy  $f(\eta; T, x)$  as function of the order parameter  $\eta$ , for  $k_B T = 0.5U$  and several values of the concentration  $x$ , for the nn-repulsion BW triangular lattice.

Equivalently, as illustrated in Fig. 9(b), the coexistence interval is determined by the crossing point A between the grand potential curves for the two phases. The two derivatives at A,

$$\frac{\partial \Omega}{\partial \mu_1} = -Nx \quad (24)$$

one for each phase, determine the values of  $x$  [A and A' in Fig. 9(a)] that define the interval of coexistence. In this way, the phase diagram of Fig. 10 is computed. The three-sublattice ordered phase (O3) is discussed in the next sub-section in the context of the grand-canonical ensemble.

### 3.3. The grand-canonical method

We now return to the general case when the three sublattice occupation numbers are considered to be independent. At fixed chemical potential  $\mu_1$  our non-equilibrium grand potential is

$$\begin{aligned} \Omega(\{n_\nu\}; \mu_1, T) = & \frac{NU}{2} \left[ 9x^2 - \sum_\nu (n_\nu)^2 \right] \\ & + \frac{N k_B T}{3} \sum_\nu \left[ n_\nu \ln n_\nu + (1-n_\nu) \ln(1-n_\nu) \right] \\ & - \frac{N \mu_1}{3} \sum_\nu n_\nu \end{aligned} \quad (25)$$

The minimum property of  $\Omega(\{n_\nu\}; \mu_1, T)$  yields the equation

$$3x - n_\nu + \frac{T}{3} \ln \frac{n_\nu}{1-n_\nu} - \frac{\mu}{3} = 0 \quad (26)$$

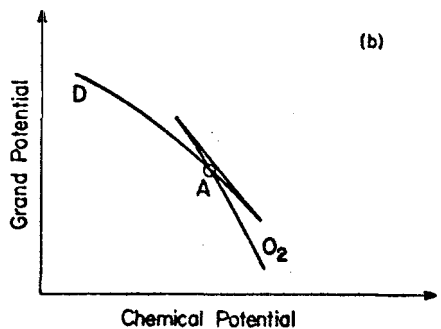
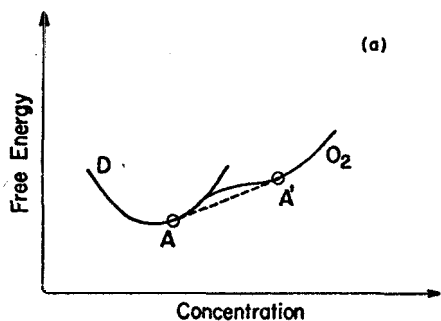


Fig.9 - Schematic representation of (a) concentration dependence of free energy and (b) chemical potential dependence of grand potential in the region of transition between the disordered (D) and the two-sublattice ordered ( $O_2$ ) phases of the triangular lattice.

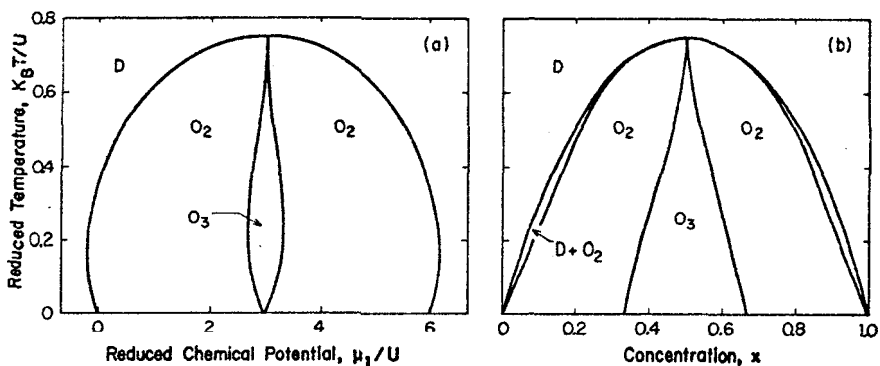


Fig.10 - Phase diagrams for the nn-repulsion BW triangular lattice in (a) the temperature v. chemical potential plane, (b) the temperature v. concentration plane, showing the disordered (D), two-sublattice ordered ( $O_2$ ) and three-sublattice ordered ( $O_3$ ) phases.

which can be solved by assigning values to

$$\lambda = \mu - 9x \tag{27}$$

and looking for the solutions of

$$h(n_V) \equiv -3n_V + \tau \ln \frac{n_V}{1-n_V} = \lambda \tag{28}$$

For  $\tau < 3/4$ , this equation has three different roots between 0 and 1 whenever  $\lambda$  is such that  $h(x_+) < \lambda < h(x_-)$ , where  $x_+$  and  $x_-$  are given by Eq. (23). The three roots,  $u_1, u_2$  and  $u_3$ , can be assigned in ten different ways to the three sublattice occupation numbers. For instance, we can have the triplets

$$\{n_\alpha, n_\beta, n_\gamma\} = \{u_1, u_1, u_1\}, \{u_1, u_1, u_2\}, \text{ etc.} \tag{29}$$

It is found that the three triplets  $\{u_1, u_2, u_2\}$ ,  $\{u_2, u_2, u_2\}$  and  $\{u_2, u_2, u_1\}$  do not lead to minima of the grand potential at fixed  $\mu$ . The seven remaining triplets are found when the concentration range is scanned from 0 to 1 (but not in a continuous way), as evident in Fig. 11.

The first D-0<sub>2</sub> transition corresponds to the transition between steps (a) and (b). Since the curve  $h(n)$  is, to lowest order, symmetric about the maximum at  $h = x_-$ , and two sublattice occupations,  $n_\beta$  and  $n_\gamma$ , decrease in (b), it is obvious that  $x$  must initially decrease after the (a)-(b) transition. This tendency is eventually overcome by the lower inclination of the middle branch of  $h(n)$ , occupied by  $n_\alpha$ , making  $x$  to increase again. This provokes a discontinuity in the sublattice occupation numbers as functions of the concentration, thus making the transition to be of first order.

An analogous reasoning applies to the 0<sub>2</sub>-0<sub>3</sub> transition between the two different ordered phases, which corresponds to the transition between steps (c) and (d), when, again,  $x$  must initially decrease, since  $n_a$  decreases in step (d). The discontinuity in  $x$  is, however, so small that the 0<sub>2</sub>-0<sub>3</sub> coexistence region is not apparent in the phase diagram of Fig. 10(b). The resulting phase diagram in the  $(\mu, \tau)$  plane is shown in Fig. 10(a).

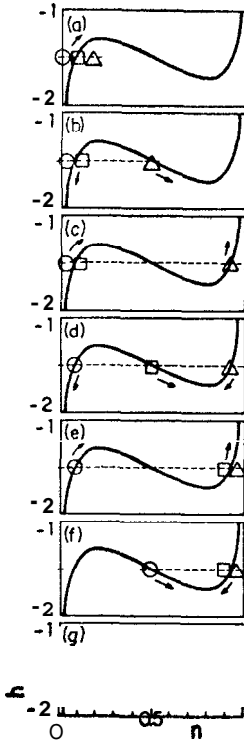


Fig.11 - Evolution of the solutions of the equation  $h(n_v) = \lambda$ , for  $k_B T = 0.5 U$  in the triangular lattice, as  $\lambda$  (a) increases, from  $-\infty$  to  $g(x_-)$ , (b)-(f) oscillates between  $g(x_-)$  and  $g(x_+)$ , (g) increases from  $g(x_+)$  to  $+\infty$ .

We finally display in Fig. 12 the behavior of the sublattice occupation numbers  $n_\alpha$ ,  $n_\beta$  and  $n_Y$  as functions of the concentration  $x$  at  $\tau = 0.5$ .

#### 4. CONCLUSIONS

We have shown how the canonical and grand-canonical statistical mechanical treatments are applied to the generalized (many- sublattice) Bragg-Williams approximation for two examples of two-dimensional lattice-gas models with nearest-neighbor repulsive interactions. The two treatments illustrate how order-disorder phase diagrams and equilibrium thermodynamic functions are obtained by initially fixing either the concentration of occupied sites or their chemical potential. This duality will persist, of course, in more sophisticated treatments. It is analogous to the one between magnetization and magnetic field in mag-



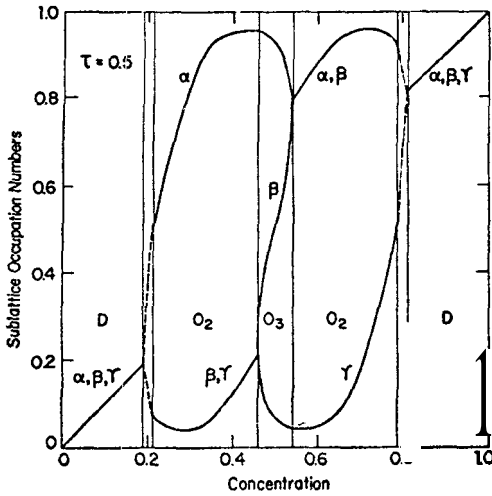


Fig.12 - Occupation numbers of sublattice  $\alpha$ ,  $\beta$  and  $\gamma$ , as functions of the concentration  $x$ , for  $k_B T = 0.5$  in the triangular lattice.

netic systems, or the one between volume and pressure in classical (e.g., van der Waals) liquid-gas systems. In a more general sense, either the response to a generalized force or the generalized force itself are good fixed thermodynamic parameters for the minimization of the appropriate thermodynamic potential.

The main qualitative differences between the results for the square and the triangular lattices are due to the different numbers of equivalent sublattices into which each lattice can be divided. As evident in the grand-canonical treatment, the appearance of first-order transitions in the triangular lattice in our model is due to the fact that the triangular lattice cannot be divided into two interpenetrating equivalent sublattices. Incidentally, this is also the reason for the existence of "frustration", leading to the impossibility of a perfect antiferromagnetic ordering (with all nearest-neighbors of anti-parallel spins) in the equivalent Ising model. In the lattice-gas language, this implies that the disordered phase is the correct solution at  $x = 1/2$ , even at  $T = 0$ . In spite of this discrepancy, the Bragg-Williams approximation is an instructive model, which has led to interesting illustrations of concepts of statistical mechanics, specially the duality between concentration and chemical potential and the possibility of first- and second-order transitions.

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13. It is interesting to notice that Eq. (12) can be written in a Fermi-Dirac form  $n_v = \{\exp[(\epsilon_v - \mu)/T] + 1\}^{-1}$ , where  $\epsilon_v = 8x - 4n_v$  (e.g.,  $\epsilon_\alpha = 4n_\beta$ ) is the BW approximation for the reduced energy of one atom in sublattice v. This is easy to understand, since each site can be occupied by either zero or one particle, thus playing the role of the one-particle energy states in a non-interacting Fermi-Dirac system (see, e.g., Ref. 10).
14. This can be shown in an analogous way to the treatment of the ground-state structure in the square lattice. Ground-state structures for the triangular lattice with various pairwise interactions were obtained by M. Kaburagi and J. Kanamori, J. Phys. Soc. Jap. 44, 718 (1978).

## Resumo

A aproximação estatística de Bragg-Williams, generalizada para várias sub-redes, é aplicada aos modelos de gás de rede quadrada e triangular (em duas dimensões) com interações repulsivas entre primeiros vizinhos. Cada problema é resolvido duplamente através dos métodos canônico e grã-canônico. O presente tratamento enfatiza a dualidade entre concentração e potencial químico e ilustra o aparecimento de transições de fase de primeira e segunda ordem em cada método.