

## Phase Transitions in Binary Lattice Gases\*

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We prove the existence of phase transitions in several kinds of two-component lattice gases: Some of these are isomorphic to spin systems and/or to fluids composed of asymmetrical molecules which can have different orientations. Among the models studied is one with infinite repulsion between particles of different species (hard cores), extending over arbitrarily many neighboring lattice sites. Some of these systems have been investigated previously in the mean field approximation and numerically.

### 1. INTRODUCTION

Among the most striking aspects of the behavior of macroscopic systems are the ubiquity and variety of the phase transitions they undergo. The demonstration that the nonsmooth behavior of the thermodynamic functions, which characterizes phase transitions, follows from the rules of statistical mechanics for the computation of these quantities is one of the most interesting aspects of the latter study.

The first demonstration of this kind was Peierls' proof of the existence of spontaneous magnetization in a two-dimensional Ising spin system with nearest-neighbor ferromagnetic interactions.<sup>1</sup> Peierls' results have been made rigorous and his method generalized and used to prove the existence of phase transitions for various lattice systems without having (or being able) to compute the thermodynamic functions explicitly.<sup>2</sup> In recent work along this line Dobrushin was able to prove the existence of a phase transition in a  $\nu$ -dimensional lattice gas,  $\nu \geq 2$ , with hard cores which exclude the occupancy, by any particle, of the  $2\nu$  nearest-neighbor sites of an occupied site.<sup>3</sup> This required a new extension of the Peierls' method since this system does not have the symmetry (between "up" and "down" spins) of the spin system.<sup>4</sup>

In this paper we extend the Peierls' method further and prove the existence of phase transitions in four binary lattice-gas models described below. In one of these models the particles have arbitrarily extended hard cores: a type of system for which the existence of a phase transition has not been proven rigorously before.

### 2. DESCRIPTION OF MODELS

Consider a  $\nu$ -dimensional square lattice  $Z^\nu$ ,  $\nu \geq 2$ , and let  $V$  be a cubic box containing  $|V|$  lattice points. Suppose that the sites of  $V$  can be occupied by two types of particles called A and B.

*Model 1* is described by the activities  $z_A, z_B$ , and the following interaction potentials:

$$\varphi_{AA}(\mathbf{r}) = \varphi_{BB}(\mathbf{r}) = \begin{cases} 0 & \text{for } \mathbf{r} \neq 0 \\ +\infty & \text{for } \mathbf{r} = 0 \end{cases} \quad (2.1)$$

and

$$\varphi_{AB}(\mathbf{r}) = \begin{cases} 0 & \text{for } |\mathbf{r}| > d \\ +\infty & \text{for } |\mathbf{r}| \leq d \end{cases}, \quad (2.2)$$

where  $\mathbf{r}$  is a vector between lattice sites occupied by different particles and  $d$  is the lattice spacing. We shall call *model 2* the generalization of model 1 obtained by allowing  $\varphi_{AB}(\mathbf{r}) = +\infty$  for  $\mathbf{r}$  in some symmetric convex set.

Let  $\alpha$  be a configuration containing  $N_A(\alpha)$  and  $N_B(\alpha)$  particles of type A and B, respectively. If  $\alpha$  is allowed, i.e., if on each lattice site there is at most one particle and no A particle is within the hard core of any B particle, then the Boltzmann factor for  $\alpha$  is simply

$$z_A^{N_A(\alpha)} z_B^{N_B(\alpha)}. \quad (2.3)$$

We can observe that the line  $z_A = z_B$  is a symmetry line for the problem, and we may expect that as  $z_A = z_B = z \rightarrow \infty$ , this symmetry is spontaneously broken and that there are two distinct equilibrium states, one A-rich and the other B-rich. If this happens, the system will show a first-order phase transition when one passes from the  $z_A > z_B$  region to the  $z_B > z_A$  region through a point  $z$  on the diagonal  $z_A = z_B$  with  $z$  large enough.

The technique for showing the spontaneous breakdown of the symmetry will be the Peierls' technique of introducing a nonsymmetric "surface term" in the Boltzmann factor of a configuration and showing that its influence will not disappear even for very large systems when  $z$  is large enough.

Calling  $D$  the "diameter" of the hard cores in model 2, we find an upper bound on the lattice gas fugacity above which there is some phase transition. This upper bound tends to zero, as it should, when  $D \rightarrow \infty$ . Unfortunately, however, it only goes to zero as  $D^{-1}$ , which means that if one tries to go to the limit of a continuum gas by keeping the hard core length  $D$  fixed while letting the lattice spacing  $d$  go to zero, the upper bound on the critical continuum fugacity would go to infinity as  $d^{-(\nu-1)}$  since the

continuum fugacity  $z_c$  behaves as  $zd^{-\nu}$  ( $z$  the lattice gas fugacity) in the lattice  $\leftrightarrow$  continuum transformation. We are thus unable to prove the existence of a phase transition at some finite fugacity, in a continuum system: a proof sadly lacking at the present time. (The only proofs of the existence of phase transitions for continuum systems available at present are for systems with infinite range "Kac potentials" which exhibit classical van der Waals type phase transitions.<sup>5</sup>) Whether the kind of technique employed in this paper will eventually prove useful for continuum systems remains to be seen.

Model 1 may also be interpreted as a model for orientational phase transitions in two dimensions. To do this, we imagine a two-dimensional square lattice where molecules with two different orientations "horizontal" and "vertical" can be situated at the center of each bond. Some sites (bonds) may also be empty. When there is a particle in a horizontal (vertical) position on some site, then it excludes vertical (horizontal) particles from its four neighbor sites. We may picture the molecules as narrow rods of the same length as the bonds with their centers pivoted at the midpoints of the bonds, and require that there be no overlap of the rods (Fig. 1). Identifying the vertical and horizontal particles as species A and B, we go back to the two-component lattice gas described before with  $z_A = \exp[\beta(\mu + E_v)]$ ,  $z_B = \exp[\beta(\mu + E_h)]$ , where  $\mu$  is the chemical potential and  $E_v$  and  $E_h$  are vertical and horizontal components of the "electrical field." A phase transition in this system would correspond to a spontaneous "lining up" of the molecules parallel to each other (perhaps somewhat similar to what may happen in liquid crystals).

It is also possible to think of model 1 as the limit of an Ising spin system: We suppose that on each site of our lattice sits an Ising "spin-1" particle  $S = 0, +1, -1$  and that the energy of a configuration is

$$H_3\{S\} = -J \sum_{\langle i,j \rangle} S_i S_j (1 - S_i S_j) + h \sum_i S_i - \mu \sum_i S_i^2, \quad (2.4)$$

where  $\sum_{\langle i,j \rangle}$  means sum over the pairs of nearest neighbors; then, if we let  $J \rightarrow +\infty$  and if we interpret  $S_i = 0, +1, -1$  as meaning, respectively, that the site  $i$  is empty or occupied by an A or B particle, we realize that (2.4) defines a model equivalent to model 1 with  $z_A = e^{\beta(\mu+h)}$  and  $z_B = e^{\beta(\mu-h)}$ . The phase transition means, in this case, that for large  $\mu$  there is spontaneous magnetization when  $h = 0$ .

We shall define *model 3* to be the system described by the Hamiltonian in Eq. (2.4) but with  $0 \leq J < +\infty$ . This system and some variations of it have been

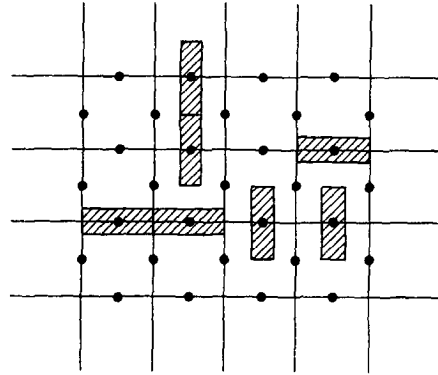


FIG. 1. An allowed configuration of orientable rods.

studied extensively by Wheeler and Widom<sup>6</sup> in various approximations as a model for the separation of solutes in a solution.

*Model 4* will be a system similar to model 3 but with a Hamiltonian defined as

$$H_4\{S\} = -J \sum_{\langle i,j \rangle} S_i S_j + h \sum_i S_i - \mu \sum_i S_i^2. \quad (2.5)$$

This model has been studied in the literature in the mean field approximation<sup>7</sup> and used to interpret the magnetic properties of  $\text{UO}_2$ . It can also be interpreted as a model for an annealed alloy of magnetic and non-magnetic atoms. The magnetic atoms have spins  $S_i = \pm 1$ , and  $\mu$  measures their concentration. The sums in (2.5) are then interpreted as going only over sites occupied by magnetic atoms. For a quenched alloy (where the distribution of magnetic atoms is random, independent of the temperature), the existence of spontaneous magnetization at high concentrations of magnetic atoms and low temperatures has been proven previously by Griffith and Lebowitz.<sup>8</sup>

### 3. EXISTENCE OF PHASE TRANSITION IN MODELS 1 AND 2

Let  $\alpha = \{x_i\}$ ,  $i = 1, \dots, |V|$ , be a configuration in the box. As a boundary condition we shall assume that all lattice sites outside  $V$  are occupied by A particles. Each lattice site is the center of a  $\nu$ -dimensional unit cube. If a lattice site  $x$  is occupied by an A particle (B particle), we shall color that cube centered on  $x$  red (black). We shall denote by  $C(x, A)$  [ $C(x, B)$ ] the union of all cubes from which B particles (A particles) are excluded by the hard core of the particle located at  $x$ . The cubes in  $C(x, A)$  [ $C(x, B)$ ] outside the cube centered at  $x$  will be colored pink (gray). The remaining cubes will be colored white. Each cube in the lattice will thus, for a permissible configuration, have one of the following colors: red, pink, black, gray, pink-gray, or white

(red-pink = red, black-gray = black). The cells outside  $V$  will all be red for the boundary condition we are considering.

Without describing the shapes of the particles in detail, we shall assume (looking at a single A particle on the lattice at  $x$ ) that  $C(x, A)$  is invariant under rotations by  $\pi/2$  and that its convex hull does not contain in its interior the center of any cell which is not pink, i.e., any lattice point where a black particle may be placed. We shall assume further that when the lattice spacing is unity, then there exists an integer  $\delta$  such that, starting from any surface of  $C(x, A)$ , it is possible to move in a direction perpendicular to this surface into the interior of  $C(x, A)$  for a distance  $\delta$  passing through pink cells only. For our model 1,  $\delta = 1$ , while for "cubical" particles the side of the cube is  $2\delta + 1$ . To investigate the limit in which the lattice spacing  $d \rightarrow 0$ , we define the hard core for different  $d$ 's to be the union of all the cubes whose centers lie inside the convex hull of the  $C(x, A)$  for  $d = 1$ , i.e., the convex hull of  $C(x, A)$  does not change as  $d \rightarrow 0$ . With this definition  $\delta$  increase as  $d^{-1}$  when  $d \rightarrow 0$ . [A similar description holds of course also for  $C(x, B)$ ].

The union of all  $C(x, B)$ , i.e., the union of all black, gray, and gray-pink cubes is separated from the rest of the lattice by a  $(\nu - 1)$ -dimensional surface  $S(\alpha)$  which decomposes as a union of closed connected polyhedra, which we call contours. To avoid ambiguity in this decomposition when all four faces adjacent to the same edge belong to  $S(\alpha)$ , we may imagine the corners of the cubes clipped off.

Let  $G$  be an outer contour, i.e., it is possible to draw a path from  $G$  to the surface of  $V$  without crossing any other contour, and let  $|G|$  denote the area of this contour measured in units of  $d^{\nu-1}$ . We have that  $|G|$  is an integer. The probability of such a contour  $G$  for  $z_A = z_B = z$  is given by

$$P(G) = \sum_{\alpha \supset G} z^{[N_A(\alpha) + N_B(\alpha)]} / \sum_{\alpha} z^{[N_A(\alpha) + N_B(\alpha)]}, \quad (3.1)$$

where  $\alpha \supset G$  means a configuration in which there is a contour  $G$ . We shall now obtain an upper bound on  $P(G)$  from which will follow an upper bound on the probability  $\pi_B(x)$  that a site  $x$  is occupied by a B particle by the standard argument that if  $x$  is occupied by a B particle it must be inside some contour  $G$ , so that

$$\pi_B(x) \leq \sum_{|G|} K(|G|) \hat{P}(|G|), \quad (3.2)$$

where  $\hat{P}(|G|)$  is an upper bound on  $P(G)$  and

$$K(|G|) = (|G|/2\nu)^{\nu-1} 3^{|G|-\nu} \quad (3.3)$$

is the Peierls' upper bound<sup>1-4</sup> on the number of contours of area  $|G|$  which contain a site  $x$ . It will then be seen that the density of B particles  $\rho_B \leq \max_x \pi_B(x)$  is bounded by a decreasing function of the fugacity  $z$  for sufficiently large  $z$ . Since, however, the total density of particles  $\rho_A + \rho_B$  is a nondecreasing function of  $z$ , being the derivative with respect to  $\ln z$  of the grand canonical pressure which is a convex function of  $\ln z$ , there will exist a  $z'$  such that, for  $z > z'$ ,  $\rho_B < \rho_A$ . By symmetry, the opposite will be true for a boundary condition in which all the sites outside  $V$  are occupied by B particles. This will show the nonuniqueness of the infinite volume "Gibbs state"<sup>2-4</sup> for  $z > z'$ . It follows further from the uniqueness of the state at low values of the fugacity<sup>4</sup> that there will be some nonanalyticity in the correlation functions for some  $z < z'$ . We may also deduce from the equality of the pressure (in the thermodynamic limit) for the different boundary conditions that there will be a discontinuity in the densities  $\rho_A$  and  $\rho_B$  whenever the fugacities  $z_A$  and  $z_B$  cross each other at a value of  $z > z'$ .

To get an upper bound on  $P(G)$ , we shall restrict the sum in the denominator of (4.1). Before doing that, we need the following definition: A set of lattice points  $x_i, i = 1, \dots, n$ , occupied by A or B particles is said to form a cluster if, by the rules of the hard-core exclusion, these particles have to be all of the A type or all of the B type, i.e., we can label the particles in such a way that  $x_i \in C(x_{i+1}, \cdot)$  for all  $i$ . Consider now a configuration  $\alpha \supset G$ . Moving from any point on  $G$  into the interior in a direction perpendicular to  $G$ , one will find  $\delta$  gray or gray-pink cubes; i.e., given  $G$ , we know that these cubes cannot have any other colorings. Let  $G_\delta$  be the set of all these cubes. Their number  $|G_\delta| \geq |G| \delta/2\nu$ . The pinkness of these cubes may be due to red particles exterior to  $G$  or to red particles interior to  $G$  or both. For each configuration  $\alpha \supset G$  there will be another configuration  $T_0(\alpha)$  in which all the B particles at positions  $x_j$  in the interior of  $G$  whose cores  $C(x_j, B)$  contain any of the cubes in  $G_\delta$ , as well as all B particles which are in the same cluster with any of these, are replaced by A particles. The transformation  $\alpha \rightarrow T_0(\alpha)$  is not always a one-to-one transformation as there may be more than one  $\alpha \supset G$  going into the same  $T_0(\alpha)$ . It is clear, however, from our definition of  $C(x, \cdot)$  that there will be a bound of the form  $m^{|G|}$  on the number of such  $\alpha$ 's with  $m$  independent of the lattice spacing  $d$ . [For  $\nu = 2$  and  $C(x, \cdot)$  a square of side  $(2\delta + 1)$ , there will at most  $2^n$  of these, where  $n$  is the number of "corners" of  $G$  whose angle in the interior of  $G$  is  $3\pi/2$ .] It is clear that in the configuration  $T_0(\alpha)$  all the cubes in  $G_\delta$  will be colored pink. Let

$T_l(\alpha)$ ,  $l = 1, \dots, |G_\delta|$ , be the configuration where there are A particles in  $l$  cubes of  $G_\delta$ , i.e.,  $T_l(\alpha)$  is a configuration obtained from  $\alpha \supset G$  by first changing  $\alpha$  to  $T_0(\alpha)$  and then putting  $l$  A particles in the region  $G_\delta$ . We then have as a lower bound on the denominator in (3.1)

$$\begin{aligned} & \sum_{\alpha} z^{[N_A(\alpha)+N_B(\alpha)]} \\ & \geq m^{-|G|} \sum_{\alpha \supset G} z^{[N_A(\alpha)+N_B(\alpha)]} \sum_{l=0}^{|G_\delta|} z^l \binom{|G_\delta|}{l} \\ & \geq m^{-|G|} (1+z)^{|G| \delta/2\nu} \sum_{\alpha \supset G} z^{[N_A(\alpha)+N_B(\alpha)]}, \end{aligned} \quad (3.4)$$

where we have used the upper bound  $|G_\delta| \geq |G| \delta/2\nu$ . Substituting (3.4) into (3.2), we get an upper bound on the density of B particles, for the boundary condition used,

$$\rho_B \leq \sum_{k=k_{\min}}^{\infty} 3^{-\nu} \binom{k}{\nu}^{v/v-1} (3m)^{2k} (1+z)^{-\delta k/\nu} = \hat{\rho}_B(z). \quad (3.5)$$

Here  $k = |G|/2$  is an integer and  $k_{\min} = \frac{1}{2} |G_{\min}|$ , where  $G_{\min}$  is the surface area of  $C(x, A)$  in units of  $d^{v-1}$ . For large values of  $z$ ,  $\hat{\rho}_B(z)$  is a decreasing function of  $z$ . Hence, as discussed earlier, there will exist a  $z'$  such that, for  $z > z'$ ,  $\rho_B < \rho_A$ , and thus there will be some kind of phase transition for  $z < z'$ .

If the lattice spacing  $d$  is decreased,  $\delta$  will increase as  $(D/d)$  while  $\rho_B$  and  $\rho_A$  will decrease as  $(d/D)^v$ , where  $D$  is the "diameter" of the hard cores, which remains fixed. As mentioned in the Introduction, the passage to the continuum involves the replacement of  $z$  by  $z_c d^\nu$  and  $\rho$  by  $\rho_c d^\nu$  so that the right side of (3.5) would not give any bound on the continuum density of B particles for any finite  $z_c$ .

#### 4. EXISTENCE OF PHASE TRANSITION IN MODELS 3 AND 4

We now color the cubes which contain A particles red and those containing B particles black and the empty ones white (no pink or gray) and fill all the cubes outside  $V$  with A particles. For a configuration  $\alpha$  we consider the union of all the white and black cubes and let  $G$  be an outer contour of such a region. Then all the cubes adjacent to  $G$  from the outside are colored red while the cubes adjacent to  $G$  from the inside are either black or white. Suppose that there are  $l(G)$  cubes adjacent to  $G$  from the inside,  $l(G) \geq |G|/2\nu$ , and  $k$  of these, labeled  $\xi_1, \dots, \xi_k$ , are black. The probability of a contour  $G$  with specified  $\xi_1, \dots, \xi_k$  is given by

$$\begin{aligned} & P(G: \xi_1, \dots, \xi_k) \\ & = \sum_{\alpha \supset (G: \xi_1, \dots, \xi_k)} e^{\beta[\mu N(\alpha) - U(\alpha)]} / \sum_{\alpha} e^{\beta[\mu N(\alpha) - U(\alpha)]}, \end{aligned} \quad (4.1)$$

where  $N(\alpha) = N_A(\alpha) + N_B(\alpha)$  is the total number of particles in this configuration,  $\mu$  is the chemical potential which is the same for the A and B particles and  $U(\alpha)$  is the potential energy of this configuration. To obtain a lower bound on the denominator in (4.1), we restrict the sum there to configurations  $T(\alpha)$ , where  $\alpha \supset (G: \xi_1, \dots, \xi_k)$  and  $T(\alpha)$  is a configuration obtained from  $\alpha$  by interchanging all the A and B particles inside  $G$  and filling all the empty  $(l-k)$  cubes adjacent to the interior of  $G$  with A particles. We then have for model 3

$$N(T(\alpha)) = N(\alpha) + (l-k) \quad (4.2)$$

and

$$U(T(\alpha)) \geq U(\alpha) - Jk + J(2\nu - 1)(l-k), \quad (4.3)$$

the last term in (4.3) arising from the possibility that an empty site after being filled with an A particle may find itself surrounded on  $(2\nu - 1)$  sides with B particles. This transformation  $\alpha \rightarrow T(\alpha)$  is one to one since we are specifying the positions of the sites adjacent to  $G$  which contain B particles. Hence we have

$$\begin{aligned} & P(G: \xi_1, \dots, \xi_k) \\ & \leq \exp \{ -\beta Jk - \beta[\mu - (2\nu - 1)J](l-k) \}, \end{aligned} \quad (4.4)$$

and thus

$$\begin{aligned} P(G) & = \sum_{k=0}^l \sum_{(\xi_1, \dots, \xi_k)} P(G: \xi_1, \dots, \xi_k) \\ & \leq [\exp(-\beta J) + \exp\{-\beta[\mu - (2\nu - 1)J]\}]^l \\ & \leq [\exp(-\beta J) + \exp\{-\beta[\mu - (2\nu - 1)J]\}]^{|G|/2\nu}, \end{aligned} \quad (4.5)$$

where the last inequality holds when the term in the bracket is less than unity since  $l \geq |G|/2\nu$ .

We can now find an upper bound on the sum of the probabilities  $\pi_0(x) + \pi_B(x)$  that a lattice site  $x$  is empty or occupied by a B particle since in either case  $x$  will have to be inside some outer contour  $G$  because of our boundary conditions. Using the same bound as in Sec. 3 on the number of contours of area  $|G|$  which can contain  $x$ , we have

$$\begin{aligned} \pi_0(x) + \pi_B(x) & \leq \sum_{k=\nu}^{\infty} 3^{-\nu} \binom{k}{\nu}^{v/v-1} 3^{2k} \\ & \quad \times [\exp(-\beta J) + \exp\{-\beta[\mu - (2\nu - 1)J]\}]^{k/\nu}. \end{aligned} \quad (4.6)$$

For a given  $J > 0$  there will be a region in the  $(\beta, \mu)$  plane bounded by some curve  $\beta(\mu)$  (see Fig. 2), such that whenever  $\beta$  and  $\mu$  are in that region the right

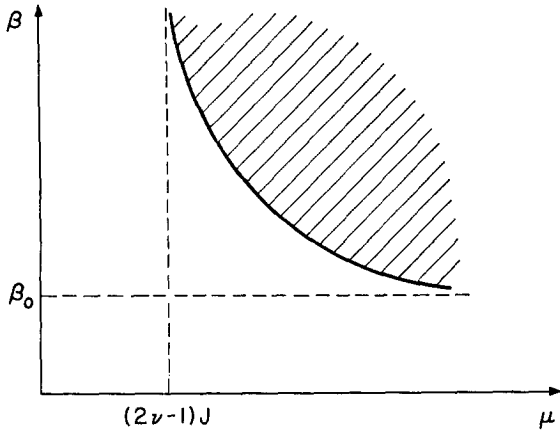


FIG. 2. The dashed area is contained in the two-phase region for model 3. The  $J$  dependence of  $\beta_0$  is roughly  $\propto J^{-1}$ . A similar picture holds for model 4.

side of (4.6) will be less than  $\frac{1}{2}$ . But, since

$$\pi_A(x) = 1 - \pi_0(x) - \pi_B(x), \tag{4.7}$$

we will have

$$\pi_A(x) > \pi_B(x) \text{ whenever } \pi_0(x) + \pi_B(x) < \frac{1}{2}, \tag{4.8}$$

and thus the equilibrium state will depend on the boundary conditions and not be unique. The existence of a phase transition then follows from the same arguments as in Sec. 3.

Model 4 can be treated as model 3 but (4.3) is replaced by

$$U(T(\alpha)) \leq U(\alpha) - 2Jk + J(2\nu - 1)(l - k); \tag{4.9}$$

therefore, the conclusions of model 3 can be drawn also for model 4.

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