

Phase Transitions in Lattice Gas Models for Water

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Water-like lattice gases on the triangular and body-centered cubic lattices are investigated. Molecules may reside on the lattice sites in either of two possible orientations, a hydrogen bond being formed between molecules on neighboring sites if they have the proper orientation with respect to one another. For a range of chemical potential at sufficiently low temperatures, the models are shown to have an ordered phase consisting of an open, hydrogen-bonded, icelike structure. The models are shown to be transition-free at sufficiently high temperature, indicating the existence of a critical point.

KEY WORDS: Water; ice; phase transitions; lattice gas; Peierls' argument.

1. INTRODUCTION

A statistical mechanical theory which in a satisfactory way describes the properties of liquid water seems still to be a distant goal. One way to gain insight is to study simplified models of "water-like" molecules. In the present article we consider a very simple lattice model which might be classified as water-like; actually, we consider two models, one version on the ($\nu = 2$)-dimensional triangular lattice and another version on the ($\nu = 3$)-dimensional body-centered cubic (bcc) lattice.

The two-dimensional model is the same as a lattice gas model studied by Bell and Lavis.^(1,2) A continuum version of the model has been considered by Ben-Naim.⁽³⁾ The main idea in the model is to disregard the asymmetry (but not the direction) of the hydrogen bond; i.e., one does not distinguish

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between the hydrogen atom and the lone pair of electrons. In the lattice gas version, besides limiting the positions of the molecules to the lattice sites, the rotation of the molecules is restricted so as to allow only two different orientations.

The three-dimensional version of the two-orientation model is similar to a lattice gas model considered by Bell and Salt⁽⁴⁾ and by Fleming and Gibbs,^(5,6) the essential difference being that in their model the distinction between lone pairs and hydrogen atoms is retained. As such, a water molecule is allowed 12 possible orientations in their model.

The object of the present article is to establish that the models considered simulate water in the sense that they undergo a phase transition to an ordered phase which is characterized by an open structure (density approximately $2/3$ in the two-dimensional version and $1/2$ in the three-dimensional version) similar to the structure of ice.

To be more precise, the two orientations allowed in the models may be *pictured* as orientations of trigonal-planar molecules on the triangular lattice and as orientations of tetrahedral molecules on the bcc lattice, where the center of a molecule occupies a lattice site and the bonds point toward neighboring lattice sites. This pictorial representation has the following meaning: if two molecules occupy neighboring sites such that the bonds of the pictorial representations overlap, a hydrogen bond with energy $\epsilon < 0$ is said to form.

As such, three translationally related hydrogen-bonded structures P_1 , P_2 , and P_3 can exist on the triangular lattice, each occupying an open honeycomb structure. Similarly, four translationally related hydrogen-bonded structures P_1 , P_2 , P_3 , and P_4 can exist on the bcc lattice, each occupying an open diamond structure. The triangular lattice can be filled with only one of the ordered structures, but two interlocking diamond structures can simultaneously fill the bcc lattice.

Since we wish to show that under certain conditions an open, icelike crystalline state can exist at equilibrium on the bcc lattice, a repulsion $\gamma \geq 0$ will be added between two molecules on neighboring sites if neither molecule points a bond toward the other. This repulsion will disfavor the configuration composed of two interlocking diamond structures compared to the case where only one diamond lattice is filled. A repulsion $\gamma' \geq 0$ will also be added between a pair of molecules on first-neighbor sites if only one of them points a bond toward the other. This repulsion γ' is added in order to avoid necessarily favoring occupancy of noninterlocking structures over the occupancy of interlocking structures. In fact, if $2\gamma'$ is less than $\gamma + \epsilon$, we shall find that at closest packing an ordered structure can exist in which all of the molecules are in a single orientation. This is the same high-density ordered structure

which exists for a model in which the hydrogen-bonded attraction is replaced by a hard-core repulsion.⁽⁷⁾

For each of the two lattices we shall use the Peierls argument⁽⁸⁻¹¹⁾ in order to prove that at equilibrium an ordered phase exists at sufficiently low temperature. In the bcc lattice, we shall find it convenient to consider separately each of the two types of ordered, hydrogen-bonded structures mentioned above. The presence or absence of phase transitions for the models at the close-packed limit will then be determined by first showing the models at closest packing to be equivalent to Ising models. The Ruelle theorem^(12,13) will then be used to prove the existence of critical points for the models and to show that the models have no transitions at sufficiently low chemical potential μ .

2. ORDER-DISORDER TRANSITIONS: PEIERLS' ARGUMENT

In this section we shall apply Peierls' argument⁽⁸⁻¹¹⁾ in order to prove the existence of an ordered phase in the two models considered. Since the notion of a contour plays a central role in the Peierls argument, we shall first define what we shall mean by a contour in a configuration.

The triangular lattice is composed of three triangular sublattices. The lattice is also composed of triangles having edges of first-neighbor length and a vertex from each of the three sublattices. The bcc lattice is composed of two simple cubic sublattices, each of which is composed of two face-centered cubic (fcc) sublattices. The lattice is also composed of tetrahedra having one vertex from each of the fcc sublattices. Two of the edges of each tetrahedron are of second-neighbor length and connect two vertices from the same simple cubic sublattice. Each of the other four edges connects a vertex from each of the two simple cubic sublattices and is of first-neighbor length.

In Fig. 1 are listed the seven principally different types of molecular configuration which can occur about a given triangle in the triangular lattice. Only triangles of type $i_0 = 1$ are bordered by a configuration which belongs to only one ordered hydrogen-bonded structure.

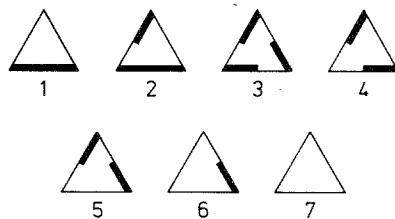


Fig. 1. The seven principally different types of molecular configuration which can occur about a given triangle in a configuration on the triangular lattice.

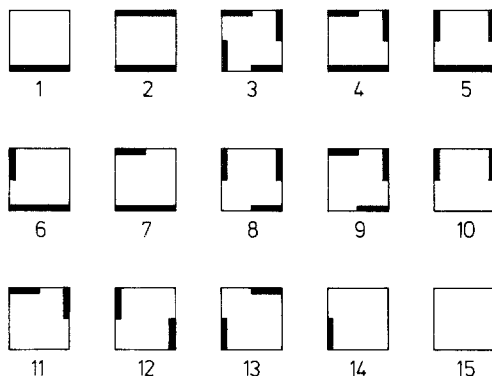


Fig. 2. The 15 principally different types of molecular configuration which can border a given tetrahedron in a configuration on the bcc lattice. The tetrahedra are represented as squares, an edge representing a first-neighbor distance, and a diagonal representing a second-neighbor distance.

In Fig. 2 are listed the 15 principally different types of molecular configuration which can occur about a tetrahedron in the bcc lattice. These tetrahedra are represented as squares, the diagonals corresponding to the tetrahedral edges of second-neighbor length. For the bcc lattice we shall show that two different types of hydrogen-bonded phase can exist, type 1, which consists of an open hydrogen-bonded diamond structure, and type 2, which consists of two interlocking hydrogen-bonded diamond structures. In addition, we shall show in Section 3 that there exists at closest packing a third type of ordered structure, type 3, having no hydrogen bonding, in which all of the molecules are in a single orientation.

Each of these three types of ordered structure is composed entirely of tetrahedra of a single type. In fact, we have numbered in Fig. 2 the different types of configurations about a tetrahedron so that an ordered structure of type i_0 consists only of tetrahedra of type i_0 , where $i_0 = 1, 2, \text{ or } 3$.

These triangles and tetrahedra are examples of ν -dimensional simplices. We shall consider simplices of type $i \neq i_0$ to be contour segments. A $(\nu - 1)$ -dimensional surface element of a simplex (an edge for $\nu = 2$ and a triangle for $\nu = 3$) will be called a *face* of a simplex. A face will be said to be ordered if the molecular configuration at the ν vertices of the face could be the same as the configuration of ν vertices of a face of a simplex of type i_0 . Otherwise, the face is said to be disordered. An inspection of Figs. 1 and 2 indicates that a contour segment can contain at most one ordered face. Two contour segments will be said to be connected if they share a disordered face. A simply connected set of contour segments shall constitute a contour. A contour shall be said to be closed if its border contains only ordered faces.

If N_α is the number of sites which have an ordered structure P_α in a configuration on a lattice Λ having $|\Lambda|$ sites, then as discussed by Dobrushin,⁽¹⁰⁾ there is an order-disorder transition in the thermodynamic limit if $\langle N_\alpha \rangle / |\Lambda| > 1/p$, where p is the number of ordered structures which can be superimposed by the operation of an element of the space group of the lattice, and where the thermal average is taken only over configurations in which the outer boundary is composed of the ordered structure P_α .

In the triangular lattice, P_α will be one of the $p = 3$ ordered hydrogen-bonded honeycomb structures. In this case, each vacant site can be said to belong to a specified one of the three ordered structures. For ordered structures of type 1 on the bcc lattice, P_α will be one of the $p = 4$ hydrogen-bonded diamond structures. In this case a vacancy that borders a simplex of type $i_0 = 1$ can be said to belong to a specified ordered structure, whereas a vacant site bordered by only contour segments can be said to belong to both of two different ordered structures. For ordered structures of type 2 on the bcc lattice, P_α will be one of the $p = 2$ sets of interlocking diamond structures. In this case a vacant site belongs to neither of the $p = 2$ ordered structures.

In the cases considered, if the boundary is occupied by structure P_α , then all sites not belonging to P_α are enclosed by a closed contour which is also an outer contour. Then for any such configuration,

$$|\Lambda| - N_\alpha \leq \sum_{L=L_0}^{\infty} N(L) \sum_{j=1}^{m(L)} X_L^{(j)} \quad (1)$$

where $N(L)$ is the maximum number of sites which can be enclosed by a contour of L segments, $m(L)$ is the maximum number of types of closed contours of L segments, and

$$X_L^{(j)} = \begin{cases} 1 & \text{if contour } j \text{ is present in the configuration} \\ 0 & \text{otherwise} \end{cases}$$

A closed contour can consist of no fewer than L_0 segments, where $L_0 = 6$ for the triangular lattice and $L_0 = 24$ for the bcc lattice.

We shall now obtain an upper bound to $N(L)$. Since at most one face of a contour segment can border a closed contour, then a closed contour of L segments can have no more sites interior to the contour than can a ν -dimensional sphere with volume V and surface SL , where S is the $(\nu - 1)$ -dimensional surface area of a face of a contour segment which has a volume V_0 . Since a site interior to a contour is a vertex of L_0 simplices enclosed by the contour, each simplex having $\nu + 1$ vertices, then $N(L) \leq (V/V_0)(\nu + 1)/L_0$. A simple computation then gives

$$N(L) \leq \begin{cases} 3^{-1/2}(2\pi)^{-1}L^2 & \text{triangular lattice} \\ 12^{-1}(2\pi^2)^{-1/4}L^{3/2} & \text{bcc lattice} \end{cases} \quad (2)$$

Hence, for either lattice,

$$N(L) < (1/6)L^{v/(v-1)} \quad (3)$$

We next obtain an upper bound to $m(L)$. Since there are three possible configurations at each site, there are then at most 3^{v+1} possible choices for the first simplex of the contour. We shall number successively the disordered faces of the growing contour, adding the next simplex of the contour to the disordered face with the lowest number. Since each added simplex introduces at most one new vertex to the contour, then there are less than 3^{L+v} contours of L simplices which include a given simplex. Since each vertex in a closed contour must be shared by at least s simplices, where $s = 2$ for the triangular lattice and $s = 4$ for the bcc lattice, then no new vertices will be introduced by the last $s - 1$ simplices added to form a closed contour. Since each lattice considered is composed of at most $L_0|\Lambda|/(v + 1)$ simplices, then there are less than $3^{L+v-s+1}L_0|\Lambda|/[L(v + 1)]$ closed contours composed of L simplices, the division by L resulting since the choice of the first segment is arbitrary. Since $3^{v-s}L_0/(v + 1) = 2$, then for either lattice,

$$m(L) < 6 \cdot 3^L |\Lambda|/L \quad (4)$$

Combining Eqs. (1), (3), and (4), it follows that

$$1 - \langle N_a \rangle / |\Lambda| < \sum_{L=L_0}^{\infty} 3^L L^{1/(v-1)} \langle X_L^{(j)} \rangle_{\max} \quad (5)$$

We now proceed to obtain an upper bound to $\langle X_L^{(j)} \rangle$. We associate with each of the seven types of triangle listed in Fig. 1 a corresponding quantity ω_i equal to the sum of $\mu/3 - \epsilon/2$ for each hydrogen bond bordering the triangle and $\mu/6$ for each "incomplete" hydrogen bond bordering the triangle. We associate with each of the 15 types of tetrahedron in Fig. 2 a corresponding quantity ω_i equal to the sum of $\mu/12 - \epsilon/6$ for each hydrogen bond bordering the tetrahedron, $\mu/24$ for each "incomplete" hydrogen bond, $-\gamma/6$ for each pair of occupied first-neighbor sites in the tetrahedron neither of which points a bond toward the other, and $-\gamma'/6$ for each pair of occupied first-neighbor sites in the tetrahedron, one of which points a bond toward the other. The ω_i for the triangular lattice are listed in Table I, and the ω_i for the bcc lattice are listed in Table II. Then in any configuration C containing N molecules,

$$(\mu N - E)_C = \sum_i n_i(C) \omega_i \quad (6)$$

where the sum extends over the seven types of triangle or the 15 types of tetrahedron. Here $n_i(C)$ is the number of simplices of type i in the configuration C .

Table I. Quantities ω_i Associated with the Corresponding Configurations Illustrated in Fig. 1 for the Triangular Lattice

i	1	2	3	4	5	6	7
ω_i	$\frac{1}{3}\mu - \frac{1}{2}\epsilon$	$\frac{1}{2}\mu - \frac{1}{2}\epsilon$	$\frac{1}{2}\mu$	$\frac{1}{3}\mu$	$\frac{1}{3}\mu$	$\frac{1}{6}\mu$	0

Let λ be the set of all configurations which contain a contour \mathcal{L} , which is an outer contour of length L . With each configuration $C \in \lambda$ we associate a configuration $C^* \in \lambda^*$ (this association is a 1-1 correspondence) generated in the following manner. Let T_r be a unit translation which converts structure P_r to structure P_α . Translate by T_r all $P_r, r \neq \alpha$, regions (together with their interiors) that border \mathcal{L} . Then replace all contour segments of \mathcal{L} with simplices of type i_0 having structure P_α . The result is to form a configuration C^* such that

$$(\mu N - E)_C - (\mu N - E)_{C^*} = \sum_{i \neq i_0} n_i(\mathcal{L})(\omega_i - \omega_{i_0}) \leq -L\epsilon_\mu \tag{7}$$

where $n_i(\mathcal{L})$ is the number of contour segments of type i in the contour \mathcal{L} and

$$\epsilon_\mu = \min_{i \neq i_0} (\omega_{i_0} - \omega_i) = \omega_{i_0} - \max_{i \neq i_0} \omega_i \tag{8}$$

Hence,

$$\begin{aligned} \langle X_L^{(\mathcal{L})} \rangle &= \sum_{C \in \lambda} \exp \beta(\mu N - E)_C \Big/ \sum_C \exp \beta(\mu N - E)_C \\ &\leq \sum_{C \in \lambda} \exp \beta(\mu N - E)_C \Big/ \sum_{C^* \in \lambda^*} \exp \beta(\mu N - E)_{C^*} \leq \exp(-\beta\epsilon_\mu L) \end{aligned} \tag{9}$$

where $\beta = 1/(kT)$.

Table II. Quantities ω_i Associated with the Corresponding Configurations Illustrated in Fig. 2 for the BCC Lattice

i	ω_i	i	ω_i
1	$\mu/12 - \epsilon/6$	9	$\mu/8 - \gamma'/3$
2	$\mu/6 - \epsilon/3 - \gamma/3$	10	$\mu/12 - \gamma/6$
3	$\mu/6 - 2\gamma'/3$	11	$\mu/12 - \gamma'/6$
4	$\mu/6 - \epsilon/6 - \gamma/6 - \gamma'/3$	12	$\mu/12$
5	$\mu/6 - \epsilon/6 - \gamma/6 - \gamma'/3$	13	$\mu/12$
6	$\mu/8 - \epsilon/6 - \gamma'/6$	14	$\mu/24$
7	$\mu/8 - \epsilon/6 - \gamma/6$	15	0
8	$\mu/8 - \gamma/6 - \gamma'/6$		

Combining Eqs. (5) and (9), we then obtain

$$1 - \langle N_\alpha \rangle / |\Lambda| < \sum_{L=L_0}^{\infty} L^{1/(v-1)} (3e^{-\beta\epsilon_\mu})^L \tag{10}$$

which converges if $3 \exp(-\beta\epsilon_\mu) < 1$. Let t_p be the solution of the equation

$$\sum_{L=L_0}^{\infty} L^{1/(v-1)} (3e^{-1/t_p})^L = (p - 1)/p \tag{11}$$

If $\epsilon_\mu > 0$, then $\langle N_\alpha \rangle / |\Lambda| > 1/p$ if $kT \leq t_p \epsilon_\mu$, proving the existence of an ordered phase for this temperature range.

For the triangular lattice the values of ϵ_μ can be obtained from Eq. (8) and the quantities in Table I. There is an ordered phase if $\epsilon_\mu > 0$, which occurs if $3\epsilon/2 < \mu < \epsilon$. This phase exists in the region

$$\frac{kT}{|\epsilon|t_3} \leq \begin{cases} 1/2 - \mu/3\epsilon & \text{if } 3\epsilon/2 < \mu \leq \epsilon \\ \mu/6\epsilon & \text{if } \epsilon \leq \mu < 0 \end{cases} \tag{12}$$

This region of the (μ, T) plane is illustrated in Fig. 3.

For the bcc lattice, the values of ϵ_μ can be obtained from Eq. (8) and the quantities in Table II. If $\gamma > 0$, there is an ordered phase of type 1 for the range $2\epsilon < \mu < \min\{(2\epsilon + 4\gamma), 4\gamma'\}$. In addition, if

$$\mu > \max\{(2\epsilon + 4\gamma), (4\epsilon + 8\gamma - 4\gamma')\},$$

there is an ordered phase of type 2 if $2\gamma' > \gamma + \epsilon$. In particular:

If $\gamma = 0$, there exists type 2 if $\mu > 2\epsilon$.

If $0 < \gamma < \gamma' - \epsilon/2$, there exists type 1 if $2\epsilon < \mu < 2\epsilon + 4\gamma$ and type 2 if $\mu > 2\epsilon + 4\gamma$.

If $\gamma' - \epsilon/2 \leq \gamma < 2\gamma' - \epsilon$, there exists type 1 if $2\epsilon < \mu < 4\gamma'$ and type 2 if $\mu > 4\epsilon + 8\gamma - 4\gamma'$.

If $\gamma \geq 2\gamma' - \epsilon$, there exists type 1 if $2\epsilon < \mu < 4\gamma'$.

For the case $\gamma' = 0$, the regions of the (μ, T) plane for which ordered

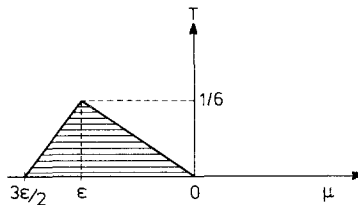


Fig. 3. Region of the (μ, T) plane given by Eq. (12) in which an ordered phase exists on the triangular lattice. The temperature coordinate is in units of $|\epsilon|t_3/k$.

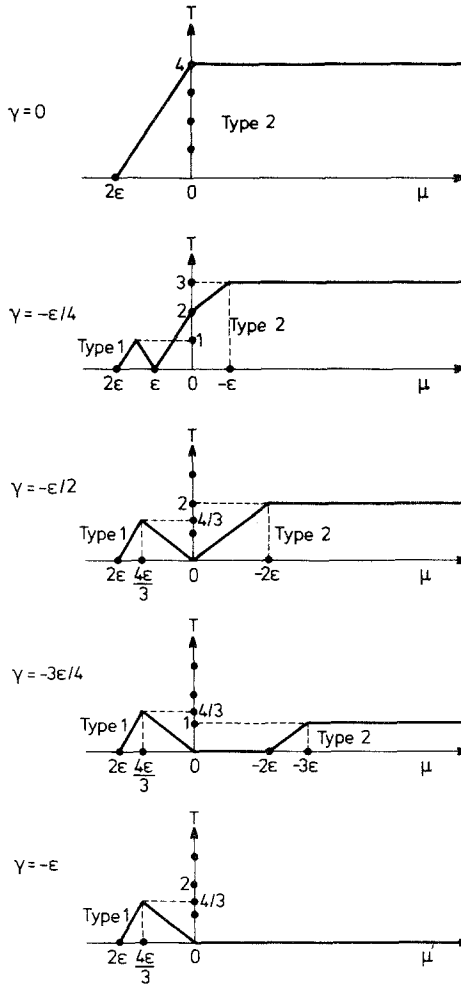


Fig. 4. Regions of the (μ, T) plane in which ordered phases of type 1 or type 2 are shown to exist on the bcc lattice for the case when $\gamma' = 0$ and γ is varied from zero to infinity. The temperature coordinate is in units of $24|\epsilon|t_p/k$, where $p = 4$ for the type 1 structure and $p = 2$ for the type 2 structure.

phases are proved to exist are illustrated in Fig. 4 for five different values of γ . At $\gamma = 0$, only type 2 is shown to exist. As γ is increased, type 1 is shown to be present at larger and larger (but negative) values of μ . Increasing γ tends to destabilize the type 2 structure. In fact, as γ is increased, type 2 is shown to be present at only larger and larger values of μ . For $\gamma > -\epsilon$, type 2 is not shown to be present at all.

If γ is kept constant and γ' is increased, type 1 can be shown to exist for

larger and larger values of μ , and type 2 can be proved to exist at smaller and smaller values of μ . This results since increasing γ' destabilizes noninterlocking diamond structures.

3. EQUIVALENCE AT CLOSEST PACKING TO ISING MODELS

We shall now show that the models at closest packing are equivalent to Ising models. This equivalence has been given previously for the two-dimensional lattice model by Bell and Lavis.⁽¹⁾

As mentioned in Section 2, the triangular lattice can be decomposed into three triangular sublattices A , B , and C such that each triangular simplex with edges of first-neighbor length and vertices at lattice sites has a vertex from each of the three sublattices. We shall denote the two orientations of a molecule as $+$ and $-$, such that an $(A, B, C) = (+, +, +)$ configuration corresponds to configuration $i = 3$ in Fig. 1.

Letting $S_i = +1$ if site i is occupied by a molecule in the $(+)$ -orientation, and $S_i = -1$ if site i is occupied by a molecule in the $(-)$ -orientation, then at closest packing, the energy of a configuration can be written as

$$E = \sum_{(i,j)} \frac{1}{4} \epsilon (1 + S_i)(1 - S_j) \quad (13)$$

where the sum extends over all first-neighbor pairs taken in the following standard ordering according to sublattices: $(i, j) = (A, B)$, (B, C) , or (C, A) . Since each site appears in the sum equally often as i and as j , then

$$\sum_{(i,j)} (S_i - S_j) = 0 \quad (14)$$

and the model is equivalent at closest packing to an antiferromagnetic Ising model on the triangular lattice with $J = -\epsilon/4 > 0$ and zero magnetic field,⁽¹⁾ which has no phase transition as a function of temperature.⁽¹⁴⁾

Similarly, the bcc lattice can be decomposed into four fcc sublattices A , B , C , and D such that each irregular tetrahedral simplex with four edges of first-neighbor length and two edges of second-neighbor length and vertices at lattice sites has a vertex from each of the four sublattices. The two edges of second-neighbor length, say \overline{AB} and \overline{CD} , are represented in Fig. 2 as the diagonals of a square. We shall denote the two orientations of a molecule as $+$ and $-$, such that an $(A, B, C, D) = (+, +, +, +)$ orientation corresponds to configuration $i = 3$ in Fig. 2. If S_i is defined as above, then the energy of a close-packed configuration can be written as

$$E = \sum_{(i,j)} \left\{ \frac{1}{4} \epsilon (1 + S_i)(1 - S_j) + \frac{1}{4} \gamma (1 + S_j)(1 - S_i) + \frac{1}{2} \gamma' (1 + S_i S_j) \right\} \quad (15)$$

where the sum extends over all first-neighbor pairs taken in the following

standard ordering according to sublattices; $(i, j) = (C, A), (A, D), (B, C),$ or (D, B) . Since Eq. (14) holds for this case as well, then the model is equivalent to an Ising model on the bcc lattice with $J = -\epsilon/4 - \gamma/4 + \gamma'/2$ and zero magnetic field.

If $2\gamma' > \gamma + \epsilon$, then $J > 0$ and the model is equivalent to an anti-ferromagnetic Ising model which has a transition⁽¹¹⁾ to a low temperature phase which corresponds to the ordered type 2 structure. If $2\gamma' < \gamma + \epsilon$, then the model is equivalent to a ferromagnetic Ising model which has a transition⁽¹¹⁾ to a phase corresponding to the type 3 structure. If $2\gamma' = \gamma + \epsilon$, there is no transition at closest packing.

4. REGIONS OF THE (μ, T) PLANE WHICH ARE FREE OF TRANSITIONS

Consider the lattice Λ_s formed by "splitting" each lattice site of a two-orientation lattice gas into two separate sites, the occupancy of each of the two sites so formed being equivalent to occupancy of a site on the original lattice by a molecule in a certain one of the two possible orientations.⁽⁷⁾ The two-orientation lattice gas is then equivalent to a one-orientation lattice gas on Λ_s . The Ruelle Theorem^(12,13) can then be applied to the lattice gas on Λ_s in order to locate regions of the (μ, T) plane in which the original two-orientation lattice gas is free of transitions.

For the two models considered here, a molecule on the equivalent split lattice Λ_s interacts via a hard-core repulsion with a molecule on one other site of Λ_s . In addition, it interacts via a hydrogen bond with a molecule on any one of n_ϵ sites, where $n_\epsilon = 3$ for the triangular lattice and $n_\epsilon = 4$ for the bcc lattice. A molecule on the bcc lattice also interacts via repulsions γ and γ' with molecules on $n_\gamma = 4$ and $n_{\gamma'} = 8$ sites, respectively.

Letting $z = \exp(\beta\mu)$, $z = (z_1, \dots, z_{|\Lambda_s|})$, and letting $A \sim$ denote the complement of the set A , then the Ruelle Theorem^(12,13) ensures that the grand partition function $\Xi(z) \neq 0$ in $D = \{D_x\}_{x \in \Lambda_s}$, where

$$D_x = - [(-R)(-\Delta_\epsilon)^{n_\epsilon}(-\Delta_\gamma)^{n_\gamma}(-\Delta_{\gamma'})^{n_{\gamma'}}] \sim \tag{16}$$

Here $R = \{z: \text{Re}(z) \leq -1/2\}$,

$$\Delta_u = \begin{cases} z: |z + 1| \leq (1 - C_u)^{1/2} & u < 0 \\ z: |z + C_u| \leq [C_u(C_u - 1)]^{1/2} & u > 0 \end{cases}$$

and $C_u = \exp(\beta u)$.

It is easy to see that D_x contains the nonnegative real axis if

$$n_\epsilon \sin^{-1}(1 - e^{\beta\epsilon})^{1/2} + n_\gamma \sin^{-1}(1 - e^{-\beta\gamma})^{1/2} + n_{\gamma'} \sin^{-1}(1 - e^{-\beta\gamma'})^{1/2} < \pi/2 \tag{17}$$

This inequality is certainly satisfied at sufficiently small β , proving the models

are analytic (transition free) at sufficiently high temperatures. An upper bound on the critical temperature T_c is given by Eq. (17) as

$$kT_c < -a \left[2 \ln \cos \frac{\pi}{2(n_\epsilon + n_\gamma + n_{\gamma'})} \right]^{-1} \quad (18)$$

where $a = \max(|\epsilon|, \gamma, \gamma')$.

Using Grace's Theorem,⁽¹⁵⁾ one can show that Δ_ϵ in Eq. (16) could also be replaced by $\Delta = \{z: |z| \geq C_\epsilon^{1/2}\}$. Then $D_{x \sim}$ contains no element with modulus less than

$$\frac{1}{2} C_\epsilon^{n_\epsilon/2} \{C_\gamma - [C_\gamma(C_\gamma - 1)]^{1/2}\}^{n_\gamma} \{C_{\gamma'} - [C_{\gamma'}(C_{\gamma'} - 1)]^{1/2}\}^{n_{\gamma'}}$$

If $C > 1$, then $C - [C(C - 1)]^{1/2} > 1/2 - 1/(8C) > 3/8$. Hence there is no transition if

$$\mu < \epsilon n_\epsilon/2 - kT[\ln 2 + (n_\gamma + n_{\gamma'}) \ln(8/3)] \quad (19)$$

5. DISCUSSION

At sufficiently low temperature, the simple two-orientation lattice gas models considered here have been shown to have an ordered phase consisting of an open hydrogen-bonded, "icelike" structure. For the bcc lattice the introduction of a repulsion γ was necessary in order to obtain the existence of such a phase. The resulting ordered phase, type 1, consisting of an open hydrogen-bonded diamond structure, is similar to the ice phase known as ice Ic.⁽⁴⁾ For the bcc lattice a dense ordered phase, type 2, consisting of two interlocking hydrogen-bonded diamond structures, was also shown to exist. This phase is essentially the same as the ice phase known as ice VIII.⁽⁴⁾

At closest packing ($\mu \rightarrow \infty$) the models were shown to be equivalent to Ising models with zero magnetic field. For the bcc lattice a dense phase of either type 2 or type 3 was shown to exist at closest packing, depending on whether the equivalent Ising model was antiferromagnetic or ferromagnetic, respectively. The type 3 phase has no hydrogen bonding and consists of molecules all in a single orientation.

For the triangular lattice the model is equivalent in the close-packed limit to an antiferromagnetic Ising model and therefore has no ordered phase.⁽¹⁾ If repulsions similar to those introduced in the bcc lattice had been introduced in the triangular lattice, the model would be equivalent at closest packing to an Ising model with $J = -\epsilon/4 - \gamma/4 + \gamma'/2$. If $2\gamma' < \epsilon + \gamma$, the Ising model is ferromagnetic and has an ordered phase at low temperatures corresponding to a structure with no hydrogen bonding in which all of the molecules are in a single orientation. The structure would be composed entirely of triangles of type $i = 3$ as illustrated in Fig. 1. This structure is

identical to the high-density phase which exists for a model in which the hydrogen-bonded attraction is replaced by a hard-core repulsion.⁽⁷⁾

In addition, the two models have been shown to be transition free at sufficiently low chemical potential. Moreover, the models were shown to be analytic at sufficiently high temperature, indicating the existence of a critical point.

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