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Phase transitions in lattice gases of orientable molecules

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An extension of the Peierls argument due to Heilmann is used to prove the existence of an ordered phase in two lattice-gas models of orientable molecules. The first model is a lattice gas of tetrahedral molecules on a body-centered-cubic lattice. The second model is a lattice gas of trigonal planar molecules on a triangular lattice. A lattice site in either model can be vacant or occupied by a molecule in either of the two orientations in which the molecular bonds point toward neighboring lattice sites. Two neighboring molecules attract if one points a bond toward the other and repel if both molecules point bonds toward one another. The ordered phase in the three-dimensional model has the same orientational ordering that has been proposed to exist in liquid carbon tetrachloride. The ordered phase in the two-dimensional version has the structure indicated by Monte Carlo studies to exist in a system of methane adsorbed on graphite.

I. INTRODUCTION

Phase transitions in lattice gases composed of molecules having nonspherical molecular shapes have been the subject of several recent investigations. Systems of linear molecules have been studied as models for liquid crystals.[1-8] Lattice gases of orientable molecules have been used to model the properties of water,[9-16] hydrogen-bonded solvents,[17] carbon tetrachloride,[18] and adsorbed monolayers.[19-21]

In the present paper, we prove the existence of ordered phases in two lattice gas models. Model 1 consists of a three-dimensional lattice gas of tetrahedral molecules on a body-centered-cubic (bcc) lattice. Model 2, a two-dimensional analog of model 1, consists of trigonal planar molecules on a triangular lattice. In both models, a lattice site can be either vacant or occupied by a molecule in either of the two orientations in which the molecular bonds point toward neighboring lattice sites.[18-21] One such orientation is illustrated for model 1 in Fig. 1 and for model 2 in Fig. 2. Two molecules on neighboring sites attract with an energy $\epsilon \leq 0$ if one molecule points a bond toward the other, and repel with a steric bond-bond repulsion energy $\gamma \geq 0$ if both molecules point bonds toward each other.

The ground state for sufficiently large chemical potential μ consists of an ordered structure in which every lattice site is occupied by a molecule in a single orientation. For both models 1 and 2, the special case of hard-core repulsion ($\gamma \rightarrow \infty$ and $\epsilon = 0$) has been studied by series techniques[18,19] and has been previously proved to undergo an order-disorder transition.[20]

On the basis of x-ray diffraction studies, liquid carbon tetrachloride has been recently proposed to exhibit local orientational ordering in a body-centered-cubic (bcc) structure in which the carbon atoms occupy lattice sites and the chlorine atoms point toward carbon atoms of neighboring molecules.[22-25] As such, model 1 should provide a reasonable model for liquid-vapor equilibrium in carbon tetrachloride. The ground-state structure models the local orientational ordering proposed to exist in liquid carbon tetrachloride, except that the complete translational order, which is present in the lattice gas, is of course absent in the true liquid. (Recently, however, lattice-gas models for liquid

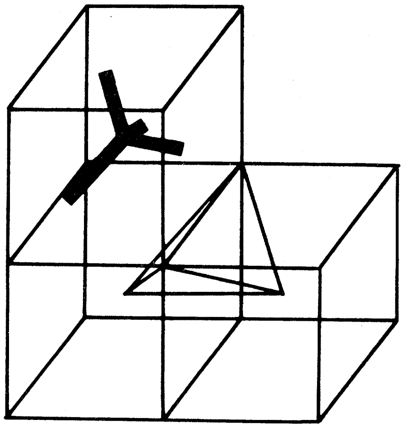

FIG. 1. One possible orientation of a tetrahedral molecule on the bcc lattice is shown. A tetrahedron is illustrated which contains one vertex from each of the four fcc sublattices of the bcc lattice.

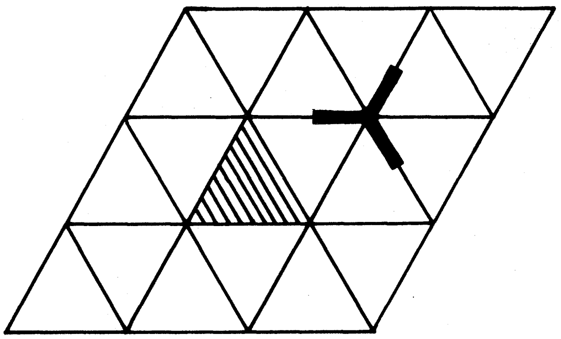

FIG. 2. One possible orientation of a trigonal planar molecule on the triangular lattice is shown. The shaded triangular region is referred to in the Peierls argument.

crystals have been introduced which have orientational order without the translational order of a crystal.[26])

Model 2 has also been studied using renormalization-group methods.[21] The ordered structure in model 2 was recently indicated by Monte Carlo studies to exist in a system of methane adsorbed on graphite.[27]

In the next section we will use an extension of the Peierls argument,[28] due to Heilmann,[29] to prove the existence of an ordered phase in the two models at sufficiently low temperature and sufficiently high chemical potential. The Ruelle theorem[30] can be used to show that the models are transition free, both at sufficiently high temperature and at sufficiently low chemical potential. As such, the models exhibit order-disorder phase transitions.

II. PEIERLS'S ARGUMENT

Since the notion of a contour is a central part of the Peierls argument, we shall now define what we mean by a contour segment in each of the two models.

The bcc lattice is composed of four interlocking face-centered-cubic (fcc) sublattices. The lattice is also composed of tetrahedra, each having one vertex from each of the four fcc sublattices. One such tetrahedron is illustrated in Fig. 1. Two of the edges are of second-neighbor length, and the other four edges are of first-neighbor length.

The 15 different molecular configurations which can border a tetrahedron in the lattice-gas model are illustrated in Fig. 3. The tetrahedra are represented as squares, an edge representing a first-neighbor distance, and a diagonal representing a second-neighbor distance. The ground state for model 1 is composed entirely of tetrahedra of type 1, as illustrated in Fig. 3.

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. One such triangle is illustrated in Fig. 2.

The seven different types of molecular configurations which can occur about a given triangle are illustrated in Fig. 4. The ground state for model 2 is composed entirely of triangles of type 1, as illustrated in Fig. 4.

These triangles and tetrahedra are examples of ν-dimensional simplexes. We shall consider simplexes of type $i \neq 1$ 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 1. Otherwise, the face is said to be disordered. An inspection of Figs. 3 and 4 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.

The use of such simplexes as contour segments has been previously used in a Peierls argument for phase transitions in lattice-gas models for water.[13] In the models for water, however, the ordered ground-state structures were translates of one another. In the present models, the ground-state structures are related by reflection.

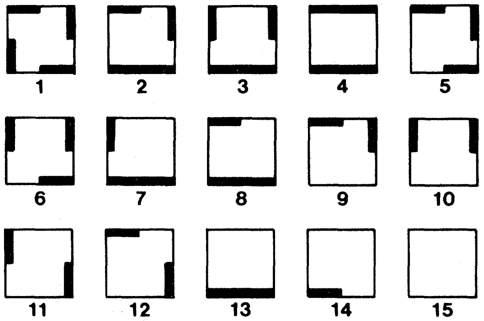

FIG. 3. Fifteen principally different types of molecular configurations which can border a given tetrahedron (see Fig. 1) on the bcc lattice. Tetrahedra are represented as squares, an edge representing a first-neighbor distance, and a diagonal representing a second-neighbor distance.

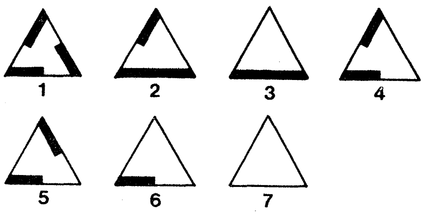

FIG. 4. Seven different types of molecular configuration which can border a given triangle (see Fig. 2) on the triangular lattice.

Certain models which contain exactly two ordered structures related by reflection can be proved to have an ordered phase using an extension of the Peierls argument[28] due to Heilmann.[29] The argument requires that a specification of the contours must uniquely specify the configuration, and that the contours must have a Hamiltonian such that the total Hamiltonian is a sum of the Hamiltonians of the contours.

In the present models, if the outer boundary of the lattice is composed of one of the two ordered ground-state structures, then regions consisting of molecules in either of the two ordered ground-state structures are separated by closed contours. Moreover, a configuration is uniquely specified by a specification of the contours.

We associate with each of the tetrahedra of model 1 a quantity H_i equal to the sum of $-\mu/24$ for each molecular bond, $\epsilon/6$ for each attractive interaction, and $\gamma/6$ for each repulsive interaction. The values of H_i are given in Table I for each of the 15 types of tetrahedra, as illustrated in Fig. 3.

Similarly, we associated with each of the triangles of model 2 a quantity H_i equal to the sum of $-\mu/6$ for each molecular bond, $\epsilon/2$ for each attraction, and $\gamma/2$ for each repulsion. The values of H_i are given in Table II for each of the seven types of triangles, as illustrated in Fig. 4.

For either model, the Hamiltonian $H(\xi)$ for a configuration ξ is then given as the sum of the H_i for each simplex in the lattice Λ. The grand-canonical partition function for the system is given as

$$\Xi=\sum_{\xi}\exp\left[\frac{-H(\xi)}{kT}\right].$$

If, instead, the quantity H_i-H_1 is associated with each simplex in a configuration, then the Hamiltonian (except for a constant term $|\Lambda|H_1$) is given as the sum of the H_i-H_1 for each contour segment in the configuration.

In either model, closely spaced reflection planes (lines) exist which map the lattice onto itself while interchanging the orientation of the molecules in a configuration.

The above properties ensure that the reflection principle of Heilmann[28] can be used to show that an outer contour occurs with sufficiently low probability to prove that there is an ordered phase at sufficiently low temperature if

$$\alpha=\min H_i-H_1>0\ ,\quad i\neq 1\ .$$

A consideration of Tables I and II indicates

$$\alpha=\begin{cases}\min(\mu/6-2\epsilon/3,\mu/24-\epsilon/3,\gamma/6-\epsilon/3), & \text{model 1}\\ \min(\mu/2-3\epsilon/2,\mu/6-\epsilon,\gamma/2-\epsilon), & \text{model 2}\end{cases}\ .$$

As such, $\alpha>0$ if $\mu>4\epsilon$ in model 1, and $\alpha>0$ if $\mu>3\epsilon$ in model 2.

III. DISCUSSION

The Peierls argument indicates that at sufficiently low temperature and sufficiently high chemical

TABLE I. Values of the Hamiltonian restricted to tetrahedra of type i as illustrated in Fig. 3.

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

TABLE II. Values of the Hamiltonian restricted to triangles of type i as illustrated in Fig. 4.

i	H_i
1	$3\epsilon/2-\mu/2$
2	$\epsilon/2+\gamma/2-\mu/2$
3	$\gamma/2-\mu/3$
4	$\epsilon/2-\mu/3$
5	$-\mu/3$
6	$-\mu/6$
7	0

potential, the models exist in an ordered structure in which all the lattice sites are occupied by molecules in a single orientation.

Using an analysis essentially the same as given previously for a lattice-gas model for water,[13] the Ruelle theorem[30] can be used to show that the two models are analytic (transition free), both at sufficiently high temperatures and at sufficiently low chemical potential. As such, an order-disorder transition is present in each of the two models.

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