

Existence of Enantiomeric Phase Separation in a Three-Dimensional Lattice Gas Model

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A three-dimensional lattice gas model for enantiomeric phase separation is introduced. The enantiomeric molecules (*d* and *l*) are the two nonsuperimposable mirror images having the molecular structure $C(AB)_2$, where *C* is a tetrahedrally bonded carbon atom with one bond to each end of two *AB* groups. The lattice gas model consists of a body-centered cubic lattice, each site of which can be either vacant or occupied by a molecule oriented so that the *A* and *B* groups point toward neighboring lattice sites. Pairs of molecules interact with short-range, orientationally-dependent interactions. For a domain of interaction parameters, the Pirogov-Sinai extension of the Peierls argument is used to prove that *d*-rich and *l*-rich phases exist in the model at sufficiently low temperature. For another domain of interaction parameters, at sufficiently high chemical potential there is an infinite number of ground states, each containing a racemic mixture of *d* and *l* molecules.

KEY WORDS: Enantiomers; phase transitions.

1. INTRODUCTION

A molecule which has a nonsuperimposable mirror image is said to be chiral, and the two molecular forms constitute an enantiomeric pair, *d* and *l*. In the present paper we introduce a three-dimensional model for enantiomeric phase separation. For physically realistic orientationally-dependent intermolecular interactions, we prove that *d*-rich and *l*-rich phases exist in the model at sufficiently low temperature and sufficiently high chemical

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potential. This is the first three-dimensional model in which enantiomeric phase separation has been proved to occur.

This type of phase separation has been previously studied using a two-dimensional model with orientationally-dependent molecular interactions. A two-dimensional lattice gas model for enantiomeric phase separation was introduced in 1985 by Huckaby *et al.*⁽¹⁾ The sites of a triangular lattice could be occupied by either of the two enantiomeric forms of a molecule which consists of a carbon atom tetrahedrally bonded to four different groups. The molecules are situated on the lattice such that the carbon atom is above a lattice site, a certain one of the four groups points away from the lattice plane, and the other three groups, A, B, and G, point toward neighboring lattice sites. Depending on the relative orientations of the neighboring molecules, the groups can interact in either of the two ways illustrated in Fig. 1.

A special case of the model in which A and B are oppositely charged and G is a neutral group was used to model the zwitterion forms of an amino acid, where the group G characterizes the particular amino acid. The interactions were then approximated using the two parameters $\varepsilon = \varepsilon_{AB} = -\varepsilon_{AA} = -\varepsilon_{BB} < 0$ and $\gamma = \varepsilon_{AG} = \varepsilon_{BG} = \varepsilon_{GG} < 0$. For the case of equimolar concentrations of *d* and *l* molecules, symmetry requires that $\mu_d = \mu_l \equiv \mu$. For this case of the model, a modification of the Peierls argument⁽²⁾ due to Heilmann⁽³⁾ was used to prove the existence of enantiomeric *d*-rich and *l*-rich phases at sufficiently large chemical potential and sufficiently low temperature, if the energy parameters satisfy $\varepsilon < \gamma < 0$.

The phase diagram for the model was calculated⁽⁴⁾ using a cluster approximation. If the G group is so large as to sterically exclude a neighboring G group, then $\varepsilon_{GG} \rightarrow \infty$, and the phase diagram was found to exhibit a tricritical point at which a *d*-rich, an *l*-rich, and a racemic phase simultaneously become a single phase.⁽⁵⁾ A tricritical point can occur in

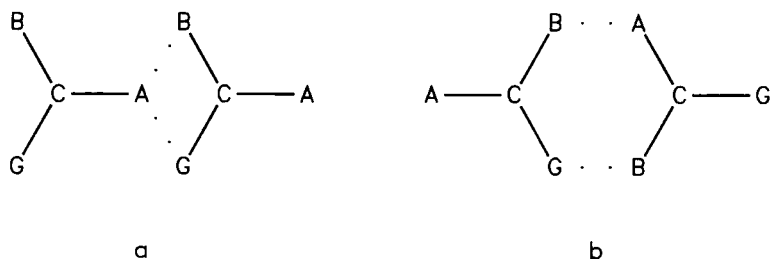


Fig. 1. The two basic types of relative orientations possible for a pair of interacting molecules in a previously studied two-dimensional lattice gas model for enantiomeric phase separation.

this two-component system because of the special symmetry present between enantiomers.

Chiral recognition in two-dimensional films has recently been a topic of considerable interest.⁽⁶⁻⁸⁾ In 1988 Andelman and de Gennes published results for a model used to study chiral discrimination between enantiomeric molecules in Langmuir–Blodgett films.⁽⁹⁾ As in the model of ref. 1, a certain group (here the hydrophobic tail) points away from the plane of the film. Neighboring pairs of molecules interact, but only if they are in the relative orientation of Fig. 1b. By considering the partition function for a pair of neighboring molecules, they studied the effects of different types of interactions on chiral discrimination. Among their conclusions were that racemization is favored if van der Waals interactions are present and enantiomeric discrimination is favored if two of the groups are oppositely charged and the third is neutral. Their work^(9,10) received a favorable critique by the editor of *Nature* magazine.⁽¹¹⁾

In the present paper we introduce a three-dimensional lattice gas model, described in detail in Section 2, in which the two enantiomeric forms, *d* and *l*, of a tetrahedral molecule (see Fig. 2) can occupy the sites of a body-centered cubic (bcc) lattice (see Fig. 3). Molecules on pairs of first- or second-neighbor sites interact with physically realistic orientationally-dependent intermolecular interactions.

For sufficiently large chemical potential, we prove in Section 3 that for a domain of interactions the ground states are finitely degenerate and consist of either all *l* or all *d* molecules, and that for another domain of interactions the ground states are infinitely degenerate and consist of a racemic mixture of *d* and *l* molecules. For the above case with a finite number of ground states, in Section 4 we use the Pirogov–Sinai extension^(12,13) of the Peierls argument⁽²⁾ to prove that *d*-rich and *l*-rich phases exist in the model at sufficiently high chemical potential and sufficiently low temperature.

2. THE MODEL

We consider a two-component lattice gas in which enantiomeric molecules occupy the sites of a bcc lattice. The enantiomers, *d* and *l*, are two nonsuperimposable mirror images, illustrated in Fig. 2, which have the structure $C(AB)_2$, where C is a central carbon atom tetrahedrally bonded to each end of two AB groups. An AB group is composed of an A and a B group bonded together by an “AB bond.” The AB bonds are depicted in Fig. 2 by curved lines. The thick straight lines represent “CX bonds,” where by X we denote an A or a B group.

Four molecules on sites of a bcc lattice are illustrated in Fig. 3. The central carbon atom of a molecule occupies a lattice site, and the molecule

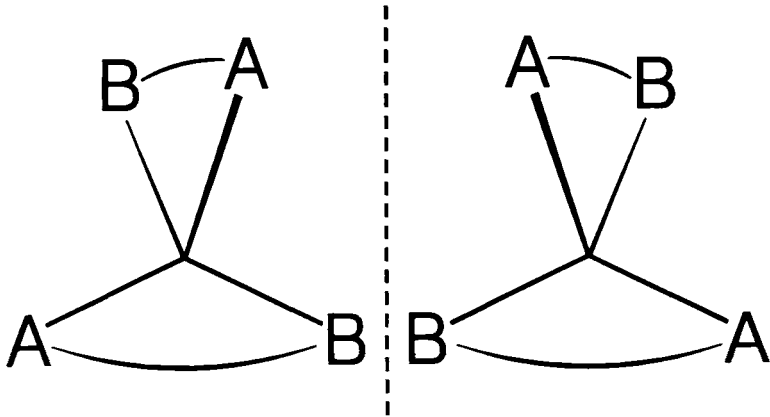


Fig. 2. An enantiomeric pair of molecules, *d* and *l*, consisting of a molecule with the structure $C(AB)_2$ together with its nonsuperimposable mirror image.

can be oriented in any one of the 12 molecular orientations in which the four CX bonds point tetrahedrally toward neighboring lattice sites. (There are thus 25 different configurations possible at a lattice site, including the vacancy and the 12 orientations possible for a *d* or *l* molecule.) Two molecules will be said to both be in the same "CX-bond orientation" if their CX bonds can be superimposed (regardless of the A or B nature of their ends) by translation of one of the molecules. A molecule in a certain one of the two possible CX-bond orientations can then be in any one of six

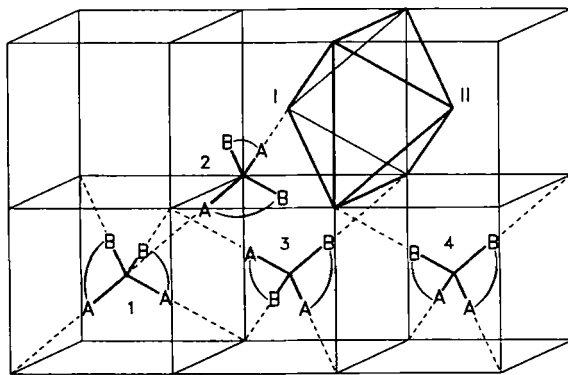


Fig. 3. Enantiomeric molecules in several different molecular orientations possible in the model. The octahedron and its translates are used in the construction of an *m*-potential in Section 3.

possible molecular orientations. In Fig. 3, molecules 1 and 2 are in one CX-bond orientation, and molecules 3 and 4 are in the other CX-bond orientation.

Our model contains the following three types of short-range interactions: a hard-core repulsion between A and B groups, electrostatic interactions between A and B groups, and steric repulsions between AB bonds. We shall now define each interaction in detail.

Let X and Y refer to A or B groups on different molecules. We shall assume the CX-bond length is less than half the first-neighbor lattice spacing, but that steric repulsion between X and Y groups is sufficiently strong to exclude more than one such group from being between two first-neighbor lattice sites. This means that first-neighbor molecules can be in different CX-bond orientations only if there is no X group on the lattice bond connecting their C atoms. Since, in a *filled lattice* there are the same number of such lattice bonds as there are X groups, then all of the molecules in a filled lattice must be in the same CX-bond orientation.

In addition, we shall assume the following interactions between X and Y groups:

- As is illustrated with molecules 1 and 2 of Fig. 3, there are three closest pairs of X and Y groups on molecules which are first neighbors and in the same CX-bond orientation. We denote the interaction of each such pair by ϵ_1^{XY} .
- As is illustrated with molecules 2 and 3 of Fig. 3, there are six pairs of closest X and Y groups on molecules which are first neighbors and in opposite CX-bond orientations. We denote the interaction of each such pair by $\epsilon_1^{XY'}$.
- As is illustrated with molecules 3 and 4 of Fig. 3, there are four closest pairs of X and Y groups on molecules which are second neighbors and in the same CX-bond orientation. The interaction of each such pair will be denoted ϵ_2^{XY} .
- As is illustrated with molecules 1 and 3 of Fig. 3, there are two closest pairs of X and Y groups on molecules which are second neighbors and in opposite CX-bond orientations. The interaction of each such pair will be denoted $\epsilon_2^{XY'}$.

We further assume the presence of charge separation such that A and B groups have opposite charges. The above interaction parameters are then assumed to satisfy, where $i = 1$ or 2 ,

$$\begin{aligned} \epsilon_i^{AB} &= -\epsilon_i^{AA} = -\epsilon_i^{BB} = \epsilon_i < 0 \\ \epsilon_i^{AB'} &= -\epsilon_i^{AA'} = -\epsilon_i^{BB'} = \epsilon_i' < 0 \end{aligned} \quad (1)$$

A subscript 1 or 2 on an energy parameter ε refers to whether the interacting groups are on molecules which are first or second neighbors, and the absence or presence of a prime on an energy parameter refers to whether the molecules are in the same or opposite CX-bond orientations. Since the interaction between groups is expected to decrease with distance, we assume further that $\varepsilon_1 < \varepsilon_2$ and that ε'_1 and ε'_2 are of the same order of magnitude as both ε_1 and ε_2 . All other pairs of X and Y groups are farther apart than the four types mentioned above and are assumed to not interact.

In addition to the electrostatic interactions between X and Y groups, we shall also assume there are short-range steric repulsions between neighboring AB bonds. There are four different relative orientations of neighboring AB bonds in which the AB bonds are closer than in other orientations. The AB bonds in these orientations should thus experience some steric repulsion. We shall assume two AB bonds

- Repel with an energy γ_1 if they are in a relative orientation symmetric to that of the closest AB bonds of molecules 1 and 2 in Fig. 3.
- Repel with an energy γ'_1 if in an orientation symmetric to that of the closest AB bonds of molecules 2 and 3 of Fig. 3.
- Repel with an energy γ_2 if in an orientation symmetric to that of the closest AB bonds of molecules 3 and 4 of Fig. 3.
- Repel with an energy γ'_2 if they are in an orientation symmetric to that of the closest AB bonds of molecules 1 and 3 of Fig. 3.

The interaction energies γ_1 , γ'_1 , γ_2 , and γ'_2 are all positive and expected to be of similar magnitude. Here we have used a notation similar to that used for the interactions between X and Y groups, a subscript 1 or 2 on an energy parameter γ referring to whether the interacting AB bonds are on molecules which are first or second neighbors, and the absence or presence of a prime on an energy parameter referring to whether the molecules are in the same or opposite CX-bond orientations. In all other relative bond orientations, even several in which the molecules are first or second neighbors, the AB bonds are farther apart and are assumed to not interact.

In Section 3 we shall rigorously obtain the ground-state configurations of the model for the case in which the chemical potentials of the molecules are sufficiently large so as to exclude the occurrence of vacancies in the ground-state structures.

3. GROUND STATES AT HIGH CHEMICAL POTENTIAL

We shall consider the case in which there are equal mole fractions of d and l molecules in the overall system. Because of the symmetry between d and l molecules, we can conclude that for this case the chemical potentials of d and l molecules are equal, $\mu_d = \mu_l \equiv \mu$. The grand canonical partition function for this case of the model on a bcc lattice with periodic boundaries is given as

$$\Xi = \sum_{\xi} e^{-H(\xi)/kT} \quad (2)$$

where the Hamiltonian for a configuration ξ is

$$H(\xi) = E(\xi) - \mu N(\xi) \quad (3)$$

Here $N(\xi)$ molecules are present in ξ and have an interaction energy $E(\xi)$.

3.1. Hamiltonian Restricted to an Octahedron

We next consider the set O of octahedra obtained by translations of the octahedron pictured in Fig. 3. The vertices of each octahedron in O include eight pairs of first-neighbor lattice sites and five pairs of second-neighbor lattice sites. Each octahedron in O has one pair of second-neighbor lattice sites which are translates of sites I and II of Fig. 3 and which are not contained in any other octahedron in O . Each of the other pairs of first- and second-neighbor sites in the bcc lattice are contained in exactly two of the octahedra in O , and each lattice site is contained in six octahedra in O .

To each octahedron $o \in O$ we shall assign a restricted Hamiltonian $H_o(\xi)$ which is equal to the sum of $-\mu/6$ for each site of o that is occupied by a molecule in ξ , plus the total interaction energy between molecules in ξ which occupy the pair of second-neighbor sites that are translates of sites I and II in Fig. 3, plus one-half of the interaction energy between molecules on other pairs of sites in o . The Hamiltonian for the configuration ξ can then be written as

$$H(\xi) = \sum_{o \in O} H_o(\xi) \quad (4)$$

If there exists a configuration ξ_G such that the restricted Hamiltonian for every octahedron $o \in O$ has the value H^0 satisfying

$$H^0 = \min_{\xi, o} H_o(\xi) \quad (5)$$

for a domain D of the parameter space $(\varepsilon_1, \varepsilon'_1, \varepsilon_2, \varepsilon'_2, \gamma_1, \gamma'_1, \gamma_2, \gamma'_2, \mu)$, then ξ_G is a ground-state configuration of the system in D , and the restricted Hamiltonian constitutes an "m-potential"⁽¹³⁾ in D , the potential being equal to $H_o(\xi)$ on octahedra $o \in O$ and equal to zero on all other subsets of the lattice. Every ground-state configuration in D is then composed entirely of octahedra with restricted Hamiltonians equal to H^0 .

Since we are interested in studying enantiomeric phase separation in condensed phases, we shall elucidate the ground-state configurations only in regions in which μ is so large ($\mu > \mu^*$) that every octahedron in a ground-state configuration has no vacant lattice sites. Later in this section we shall obtain an upper bound to μ^* . Since, as shown above, all of the molecules in a filled lattice must be in the same CX-bond orientation, then only the unprimed energy parameters $\varepsilon_1, \varepsilon_2, \gamma_1$, and γ_2 are operative in these ground-state configurations.

The restricted Hamiltonian for an octahedron in which each site is occupied by a molecule can be written as

$$H_o = E_c + E_\gamma - \mu \quad (6)$$

where E_c and E_γ are the contributions to H_o which result respectively from X-group interactions and from AB-bond interactions.

We shall calculate separately the minimum values for E_c and for E_γ and then determine the (nonempty!) set of restricted configurations on an octahedron for which both E_c and E_γ are minimal. The fact that there are configurations in which E_c and E_γ are separately minimized greatly simplifies the determination of the set of restricted configurations on an octahedron for which H_o is minimal. The set of ground-state configurations is then composed entirely of octahedra with restricted configurations for which H_o is minimal.

3.2. Determination of min E_c

We now proceed to calculate a minimum for E_c . Certain features of the structure of a configuration will be exploited to simplify this calculation. Because of our assumption that steric repulsions exclude more than one X group from the space between a pair of first-neighbor sites, then if all the vertices of an octahedron are occupied by molecules, the molecules must necessarily all be in the same CX-bond orientation. Two molecules in the same CX-bond orientation will be said to have the same "X-group orientation" if their X groups can be superimposed (A on A, B on B) by translation of one of the molecules. A molecule in a certain CX-bond orientation can be in any one of six different X-group orientations. A molecule

in a certain X-group orientation is then either a *d* or an *l* molecule, depending on which of the two possible orientations for the AB bonds is realized.

If a pair of first-neighbor molecules are in the same CX-bond orientation, three X groups on one molecule interact with a single Y group on the other molecule, yielding a total interaction energy equal to either ε_1 or $-\varepsilon_1$. If a pair of second neighbors are in the same CX-bond orientation, each of two X groups on one molecule interacts with two Y groups on the other molecule, yielding a total interaction energy equal to either $4\varepsilon_2$, 0, or $-4\varepsilon_2$.

Consider a triangle of three molecules, called a " τ -triangle," in which molecules 1 and 2 are second neighbors, molecule 3 is a first neighbor to both molecules 1 and 2, and all three are in the same CX-bond orientation (see Fig. 4). Molecules 1 and 2 must have the same X-group orientation if their X groups interact with minimum possible total energy $4\varepsilon_2$, and molecule 3 must then have the same X-group orientation as molecules 1 and 2 if it interacts with minimum possible total energy ε_1 with each of them (see Fig. 4).

Using the above observation for τ -triangles, one can easily see that $E_c = 4\varepsilon_1 + 4\varepsilon_2$ if and only if the six molecules at the vertices of the octahedron (see Fig. 3) all have the same X-group orientation. Although $4\varepsilon_1$ is the minimum possible contribution to E_c from pairs of first-neighbor molecules, the minimum possible contribution to E_c from pairs of second-neighbor molecules is $8\varepsilon_2$. However, for the octahedron of Fig. 3, if the contribution to E_c from second-neighbor molecules exceeds $4\varepsilon_2$, then the molecules at vertices I and II must necessarily be in the same X-group

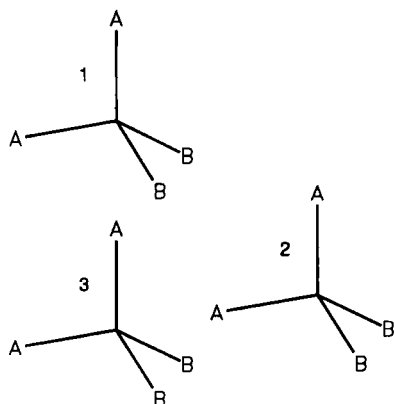


Fig. 4. A τ -triangle of three molecules referred to in the derivation of Eq. (7). Molecules 1 and 2 are second neighbors and molecule 3 is a first neighbor to both molecules 1 and 2. [The AB bonds are not shown since their positions are irrelevant for the derivation of Eq. (7).]

orientation, giving a contribution of $4\epsilon_2$ to E_ϵ . One can then see that $E_\epsilon = 8\epsilon_2 + n_1\epsilon_1$ can occur only if all four τ -triangles with vertices at I and II do not have minimal first-neighbor energy, and thus $n_1 \leq 0$. Likewise, $E_\epsilon = 6\epsilon_2 + n_1\epsilon_1$ can occur only if at least two τ -triangles with vertices at I and II do not have minimal first-neighbor energy, which requires $n_1 \leq 2$. Since we assumed $\epsilon_1 < \epsilon_2$, then

$$\min E_\epsilon = 4\epsilon_1 + 4\epsilon_2 \quad (7)$$

with all molecules on the octahedron necessarily having the same X-group orientation.

3.3. Determination of $\min E_\gamma$

After making some useful observations, we shall calculate $\min E_\gamma$. We shall call the line connecting the midpoints of the two AB bonds the "AB-bond line" of the molecule (see Fig. 5). If a pair of first-neighbor molecules have the same CX-bond orientation, their closest AB bonds do not interact if their AB-bond lines are parallel; otherwise, they interact with energy γ_1 , and their AB-bond lines are perpendicular. If a pair of second-neighbor molecules have the same CX-bond orientation, their closest AB bonds interact with energy γ_2 if their AB-bond lines are colinear; otherwise, their AB bonds do not interact.

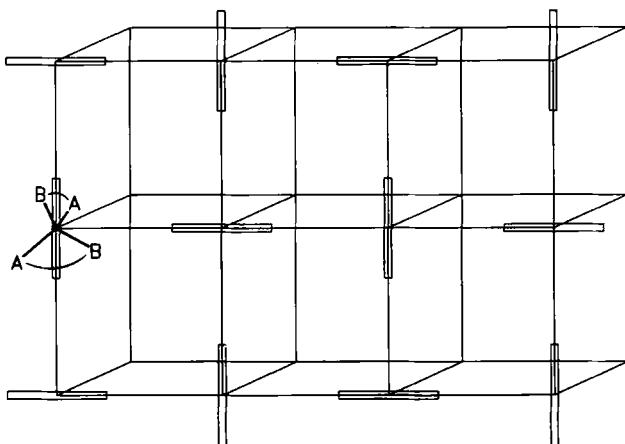


Fig. 5. The AB-bond line is illustrated for a molecule. The relative orientation of AB-bond lines in a plane is illustrated for a ground-state configuration in which there are no γ_2 interactions (see Section 3.4).

Referring to the definition of H_o given in Section 3.1, E_γ has the form $E_\gamma = n_1\gamma_1 + n_2\gamma_2$, where n_1 and n_2 are nonnegative and half-integer. If $n_1 = 0$, the AB-bond lines of all six molecules in the octahedron are necessarily parallel, which requires that $n_2 = 1$.

There are four paths of first-neighbor links which connect vertices I and II (see Fig. 3), and hence there are six closed loops of four first-neighbor links on the octahedron. It is obviously impossible for there to be exactly one pair of first-neighbor molecules on a loop which have perpendicular AB-bond lines (and hence a γ_1 interaction). Thus $n_1 = 1/2$ is impossible.

If $n_1 = 1$, every loop which contains one of the two first-neighbor pairs with a γ_1 interaction must also contain the other pair. This can occur only if both pairs contain a common molecule M, which is neither at site I nor at site II. Then the five molecules other than M must necessarily have parallel AB-bond lines. Consequently, at least one pair of second neighbors from these five molecules must have a γ_2 interaction. Thus $n_2 = 1/2$ is the minimum possible value for n_2 , given that $n_1 = 1$.

The value $n_1 = 3/2$ cannot occur, for by inspection one can see that at least one loop would be required to have exactly one pair of first neighbors with perpendicular AB-bond lines, which is impossible.

The value of $n_1 = 2$ can occur with the minimum possible value for n_2 , namely $n_2 = 0$. For example, consider the restricted configuration in which the AB-bond lines of all six molecules are parallel, and there is a γ_2 interaction between molecules at sites I and II. If the AB-bond line on the molecule at site I is changed, a restricted configuration is obtained which has $n_1 = 2$ and $n_2 = 0$.

The above analysis implies that $\min E_\gamma$ occurs with either $n_1 = 0$ and $n_2 = 1$, $n_1 = 1$ and $n_2 = 1/2$, or $n_1 = 2$ and $n_2 = 0$. We can thus conclude that

$$\min E_\gamma = \min\{\gamma_2, 2\gamma_1\} \quad (8)$$

3.4. Ground-State Configurations

If we can find configurations in which every octahedron has a restricted Hamiltonian with the value

$$H_o = \min E_e + \min E_\gamma - \mu \quad (9)$$

then at sufficiently large μ , the set of all such configurations constitutes the set of ground-state configurations, and the restricted Hamiltonian constitutes an m -potential.⁽¹³⁾

As shown above, in a restricted configuration for which E_e is minimal, all six molecules must necessarily be in the same X-group orientation.

Thus, in all restricted configurations for which H_o has the value given by Eq. (9), all molecules must have the same X-group orientation.

In a configuration for which H_o is given by Eq. (9), a molecule in a certain X-group orientation is identified as d or l according to which of the two possible orientations for the AB bonds is realized. We shall determine which of these AB-bond orientations can occur for the molecules in restricted configurations for which both E_e and E_γ are minimal. Equation (8) indicates we should consider two cases, $\gamma_2 < 2\gamma_1$ and $2\gamma_1 < \gamma_2$.

If $\gamma_2 < 2\gamma_1$, then $\min E_\gamma = \gamma_2$ and, as deduced above, the AB-bond lines of all the molecules in an octahedron are parallel. Hence, in a restricted configuration for which H_o is minimal, the molecules are either all d or all l and are all in a single molecular orientation. The only configurations which are composed of such restricted configurations are the 24 configurations in which every molecule is of a single enantiomeric type, d or l , and all are in a single molecular orientation. These 24 configurations thus constitute the set of ground-state configurations for the case $\gamma_2 < 2\gamma_1$, and the restricted Hamiltonian is an m -potential.

If $2\gamma_1 < \gamma_2$, there are no γ_2 interactions in a ground-state configuration. In order to elucidate the molecular orientations and d, l structure present in configurations which have no γ_2 interactions, consider a plane which passes through a lattice site and is perpendicular to the bisector of the ACA angle of the molecule at that site (see Fig. 5). The plane contains a square lattice of sites from the bcc lattice, the square lattice having a first-neighbor distance which is equal to the second-neighbor distance in the bcc lattice. Since the molecules all have the same X-group orientation if E_e is minimized, the AB-bond lines of all the molecules are parallel to the plane. Each AB-bond line is in one of two perpendicular directions and points toward two neighboring lattice sites of the square lattice. The AB-bond line for a d molecule points in one of these directions, and the AB-bond line for an l molecule points in the other, perpendicular direction. Since a pair of second-neighbor molecules with colinear AB-bond lines has a γ_2 interaction, there will be no γ_2 interactions in the plane if and only if one of two square sublattices of the square lattice in the plane is occupied by d molecules and the other is occupied by l molecules (see Fig. 5).

We will now show that each configuration having the above d, l structure in each of a set of parallel planes is also composed of octahedra, each of which has a minimal value of the restricted Hamiltonian. The configurations with this structure will thus constitute the set of ground-state configurations, and the restricted Hamiltonian will be an m -potential.

Every octahedron contains one square with vertices at lattice sites and edges of second-neighbor length. (See, e.g., the square formed from all but sites I and II in the octahedron of Fig. 3.) Such a square must contain a

pair of second-neighbor sites from one of the planes discussed above, the second pair coming from either the same plane or a second plane parallel to the first. In any configuration having the above d, l structure, the square will thus contain two d and two l molecules. The other two molecules in the octahedron are first neighbors to all four molecules on the square. Since d and l molecules in the same X-group orientation have perpendicular AB-bond lines, first-neighbor d, l pairs will have a γ_1 interaction, while d, d and l, l first-neighbor pairs will have no γ_1 interaction. Thus every octahedron embedded in one of these configurations has a restricted Hamiltonian with a minimal value given by Eq. (9) with $E_v = 2\gamma_1$, and there are several different restricted configurations possible for such an octahedron.

If there are p such parallel planes with alternating d and l molecules, there are 2^p ground-state configurations in which all of the molecules are in a certain one of the 12 different possible X-group orientations. Hence, if $2\gamma_1 < \gamma_2$, the ground-state configurations, each of which contains a racemic mixture of d and l molecules, are infinitely degenerate, but have no residual entropy.

3.5. Upper Bound on μ Above Which Ground States Contain No Vacancies

We are now in a position to calculate an upper bound to μ^* , the value of the chemical potential above which all restricted configurations which have a minimum value of the restricted Hamiltonian contain no vacant lattice sites.

If, at a chemical potential μ , the minimum value of the restricted Hamiltonian for an octahedron with no vacancies given by Eq. (9) is lower than is possible for any octahedron with one or more vacancies, then $\mu > \mu^*$. A lower bound on the minimum possible value of the restricted Hamiltonian for an octahedron with $n < 6$ molecules is given as the sum of $n(-\mu/6)$ plus a lower bound on the minimum possible interaction energy which can be associated with an octahedron. A crude lower bound on this minimum interaction energy is given as the sum of $4\epsilon_1$, which is the minimum interaction between molecules (or vacancies) on pairs of first-neighbor sites, plus $8\epsilon_2$, the minimum interaction between molecules or vacancies on pairs of second-neighbor sites. Therefore $\mu > \mu^*$ if, for all $0 \leq n < 6$,

$$4\epsilon_1 + 4\epsilon_2 + \min\{\gamma_2, 2\gamma_1\} - \mu < 4\epsilon_1 + 8\epsilon_2 - n\mu/6 \quad (10)$$

Therefore, if

$$\mu > 6 \min\{\gamma_2, 2\gamma_1\} - 24\epsilon_2 \quad (11)$$

the ground-state configurations contain no vacant sites and are the configurations described above.

4. EXISTENCE OF ENANTIOMERIC PHASE SEPARATION

In Section 3 we showed that if $\mu_l = \mu_d \equiv \mu$ is sufficiently large, if $\varepsilon_1 < \varepsilon_2 < 0$, and if either $0 < \gamma_2 < 2\gamma_1$ or $0 < 2\gamma_1 < \gamma_2$, then the Hamiltonian restricted to an octahedron constitutes an m -potential. Holsztynski and Slawny⁽¹⁴⁾ have proved that if a restricted Hamiltonian is a finite-ranged m -potential, and if there are only a finite number of ground-state configurations, then the extension of the Peierls⁽²⁾ argument due to Pirogov and Sinai^(12,13) is sufficient to prove the existence of multiple equilibrium states in the model. Moreover, if the ground-state configurations are symmetry-related, these multiple equilibrium states exist if the temperature is sufficiently low.^(12,13)

If $0 < \gamma_2 < 2\gamma_1$, there are 24 ground-state configurations. In each of these configurations, every lattice site is occupied by a molecule of the same enantiomeric type, d or l , and all of the molecules are in the same orientation. Since the ground-state configurations are symmetry-related, at sufficiently high chemical potential μ and sufficiently low temperature, the model has multiple equilibrium states. These low-temperature equilibrium states correspond to d - or l -rich phases which are small perturbations of one of the 24 enantiomerically pure ground-state configurations. Since the model contains only short-range interactions, there is only one equilibrium state at sufficiently high temperatures.⁽¹⁵⁾ Therefore a phase transition, corresponding to enantiomeric phase separation, occurs in this three-dimensional model system.

As shown in Section 3, if $0 < 2\gamma_1 < \gamma_2$ and μ is sufficiently large, there is an infinite number of ground-state configurations, each of which contains a racemic mixture of d and l molecules. We have not determined the nature of the equilibrium states which occur at low, but nonzero temperatures for the model in this region of parameter space.

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