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Presence of racemic phases at low temperatures in a three-dimensional lattice gas of enantiomers

Abdel K Belkasri and Dale A Huckaby

Department of Chemistry, Texas Christian University, Fort Worth, TX 76129, USA

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Abstract. A lattice gas on the body-centred cubic lattice containing a pair of enantiomers is studied for a domain of orientation-dependent interactions in which the ground-state configurations are infinitely degenerate, each containing a racemic mixture of enantiomers. A finite number of these configurations are dominant, meaning they have a maximum number of lowest-energy excitations. An extension of the Pirogov–Sinai theory of phase transitions due to Bricmont and Slawny is used to show that the low-temperature phases for this domain of interactions have the structure of the dominant ground-state configurations, together with a number of defects or excitations. This is the first proof of the existence of racemic phases at low temperatures in a lattice model.

1. Introduction

A molecule is said to be chiral if it has the property of being nonsuperimposable upon its mirror image. A chiral molecule and its nonsuperimposable mirror image are called enantiomorphs, d and l , and together they constitute an enantiomeric pair. An equal (50–50) mixture of two enantiomorphs is called a racemic mixture.

Living systems are very sensitive to the enantiomeric type of a chiral molecule; in fact, only one of the two enantiomorphs of chiral amino acids and sugars are actually present in an organism. The pharmaceutical industry is very much involved in the production of enantiomorphs [1].

The spontaneous phase separation of a racemic mixture of enantiomorphs into enantiomerically pure d and l crystals was first accomplished in 1848 by Pasteur [2]. The great majority of racemic mixtures, however, form racemic crystals and do not undergo enantiomeric phase separation.

In 1985 Huckaby *et al* [3] published the first proof of the existence of enantiomeric phase separation in a model system. They introduced a two-dimensional lattice gas model [3–5] in which the two enantiomorphs of a tetrahedral molecule, consisting of a carbon atom bonded to four different groups, can occupy the sites of a triangular lattice such that a certain one of the groups points away from the plane of the lattice, the other three groups pointing toward neighbouring lattice sites. For intermolecular interactions such as those present between the zwitterion forms of an amino acid, they proved that a racemic mixture will undergo enantiomeric phase separation at sufficiently low temperature and sufficiently large chemical potential. Examples of enantiomeric phase separation in two dimensions have recently been observed on the surfaces of water [6, 7], graphite [8], and mica [9].

The phenomenon of chiral discrimination, both heterochiral discrimination which favours a racemic mixture, and homochiral discrimination, favouring enantiomeric

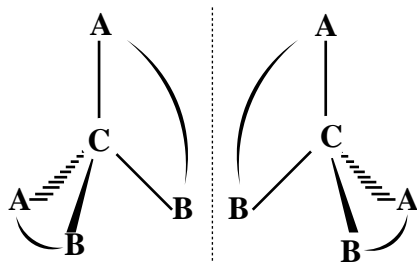


Figure 1. An enantiomeric pair of molecules, *d* and *l*, consisting of a molecule $C(AB)_2$ together with its nonsuperimposable mirror image.

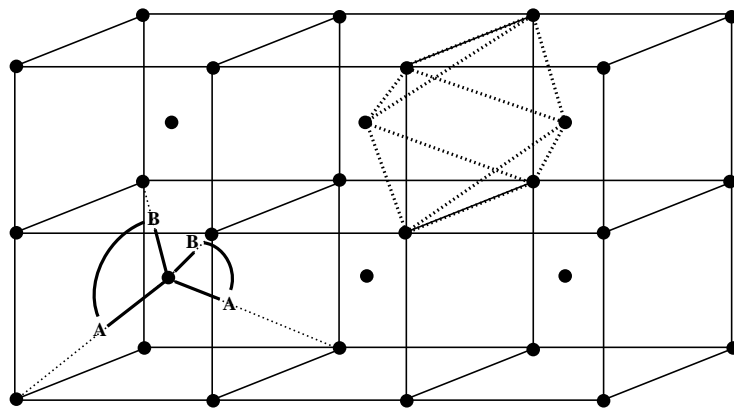


Figure 2. Illustration of the bcc lattice with the molecule $C(AB)_2$ at a site. The octahedron and its translates are used in the construction of the *m*-potential.

separation, was studied in 1988 by Andelman and de Gennes [10] and again in 1989 by Andelman [11] using a model for a two-dimensional Langmuir–Blodgett film. As in the model considered earlier by Huckaby *et al* [3,4], the molecules in their model consist of a carbon atom bonded to four different groups, with one group, here a hydrocarbon chain, pointing away from the water surface. The other three groups are on the water surface, with two groups on one molecule interacting with two groups on a neighbouring molecule. They found that some types of interactions favour homochiral discrimination, and other types of interactions favour heterochiral discrimination.

In order to study both enantiomeric phase separation and the formation of racemic crystals in three dimensions, in 1994 Huckaby *et al* [12] introduced a three-dimensional lattice gas model containing the two enantiomorphs having the molecular structure $C(AB)_2$, where C is a carbon atom tetrahedrally bonded to each end of an AB group (see figure 1). A molecule in the model can occupy the sites of a body-centred cubic (bcc) lattice in any of the 12 orientations in which the bonds from C to A and B point toward neighbouring sites (see figure 2).

In section 2 the orientation-dependent intermolecular interactions are defined for the model, and the structures of the various ground-state configurations are described. For one domain of interaction parameters and chemical potential, described in section 2, the model has 24 ground-state configurations, in which every site is occupied by a molecule of the same enantiomeric type, *d* or *l*, and in which every molecule has the same molecular orientation.

In [12] the Pirogov–Sinai theory [13, 14] was used to prove that the low-temperature phases in this domain, except for defects, have the same structure as the enantiomerically pure ground-state configurations. The model thus exhibits enantiomeric phase separation in that domain of interaction parameters.

For another domain of interaction parameters and chemical potential, the ground-state configurations are infinitely degenerate, each such configuration having a *layered structure*, each layer consisting of an ordered racemic mixture of d and l enantiomorphs (see figure 4). Since the ground states are infinitely degenerate, the Pirogov–Sinai theory [13, 14] cannot be used to determine the structure of the low-temperature phases in this domain of parameters. In the present paper we use an extension of the Pirogov–Sinai theory due to Bricmont and Slawny [15] to determine the structure of the racemic phases which occur at low temperature in this domain.

In section 3 we show that a finite number of the ground-state configurations in this domain are *dominant*, in that they can have a maximum number of lowest-energy excitations. Moreover, each (simply connected) excitation of a ground state in this domain is shown to satisfy a *regularity condition*, in that the excitation energy goes to infinity as the size of the excitation extends to infinity. In addition, any configuration ξ^* containing an excitation is shown to have a *retouch property*, meaning that associated with ξ^* is a unique configuration ξ which differs from ξ^* only in that the excitation is replaced by a local configuration of lowest energy. Since the ground-state configurations in this domain have a layered structure and a finite number of them are dominant, and since the excitations satisfy a regularity condition and have a retouch property, then the Bricmont–Slawny theory [15] can be used to prove that in this domain of the interaction parameters, the low-temperature phases, except for excitations, have the structure of the dominant ground-state configurations.

Thus, in the present paper we have used the Bricmont–Slawny theory to obtain the first proof of the existence of ordered racemic phases in a model system, and in so doing we have demonstrated that the theory can be successfully applied to models having many orientational states and several interaction parameters. In addition to a number of models considered by Bricmont and Slawny [15], the theory has also been used to aid in the elucidation of the low-temperature phase diagram of a spin-1 model of microemulsions [16].

2. The model

In [12] the present model was introduced, and the structure of the ground-state configurations in each of two domains of the interaction parameters was derived. In this section we define the interactions in the model and give a description of the structure of the ground-state configurations in these two domains. This description is given in a fashion which will be useful in section 3 for demonstrating that the model in one domain satisfies the special conditions required in order to use the Bricmont–Slawny theory [15].

We consider a lattice gas on the bcc lattice in which each lattice site can be either vacant or occupied by one of the two enantiomorphs, d or l , having the structure $C(AB)_2$ as illustrated in figure 1. If a site is occupied by a molecule, the central C atom is at the site and the four bonds from C to groups A and B point toward neighbouring sites (see figure 2).

We consider the case in which the overall system contains equal numbers of the two enantiomorphs. Then, due to symmetry of the phases present at equilibrium, the chemical potentials of d and l molecules are equal in all phases, $\mu_d = \mu_l \equiv \mu$. A molecule at a given site is characterized by the orientation of its X groups ($X = A, B$) and by its enantiomeric

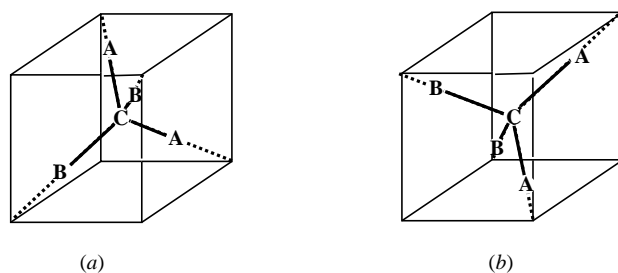


Figure 3. A given orientation for the molecule $C(AB)_2$ consists in placing the groups A, A, B, and B near four of the corners of a cube. The orientation in (a) and its six permutations are said to be in the same ‘CX-bond orientation’ and the ones in (b) are in the other CX-bond orientation.

form (d or l). There are exactly 12 possible ‘X-group orientations’, hereafter called simply ‘orientations’. Six of them are in one ‘CX-bond orientation’, i.e. their CX bonds ($X = A, B$) can be superimposed by translation regardless of the A or B nature of the ends, and the other six are in the other CX-bond orientation (see figure 3). Thus a configuration of a molecule at site i is specified by

$$\xi_i \equiv (\theta, e_\theta)_i \quad (1)$$

where θ is its orientation, i.e. $\theta \in \{\theta^{(1)}, \theta^{(2)}, \dots, \theta^{(6)}, \bar{\theta}^{(1)}, \bar{\theta}^{(2)}, \dots, \bar{\theta}^{(6)}\}$ and e_θ specifies the enantiomeric form: $e_\theta \in \{d, l\}$. Thus there are 25 different configurations possible at a lattice site, including the vacancy.

The Hamiltonian for the configuration $\xi = \{\xi_l\}$ (l runs over the sites of the bcc lattice) has the form

$$H(\xi) = \sum_{i,j} E_{i,j}(\xi) - \mu N(\xi) \quad (2)$$

where $N(\xi)$ is the total number of molecules, and $E_{i,j}(\xi) = E(\xi_i, \xi_j)$ is the intermolecular pair-interaction energy between a molecule at site i with configuration ξ_i and a molecule at site j with configuration ξ_j .

The model incorporates physically realistic pair interactions between first- and second-neighbour molecules. The interaction energies depend on the orientations and the types of the pair of molecules. As is the case in many models containing molecules with realistic molecular shapes, an asymmetry in the interaction results because of the asymmetry of the molecular shapes. In particular, if molecules at i and j are switched in configurations ξ and ξ' ($\xi_i = \xi'_j$ and $\xi_j = \xi'_i$), then $E_{i,j}(\xi)$ is not necessarily equal to $E_{i,j}(\xi')$.

Due to extreme steric repulsion, we assume that a pair of first-neighbour molecules are excluded from being in relative orientations in which each molecule points a group (A or B) toward a group of the other molecule. Before defining the other pair interactions, it is helpful to first define the ‘AB-bond line’ of a molecule. The AB-bond line is the line bisecting the two AB bonds in the molecule (see figure 4).

Let X and Y refer to A or B groups on neighbouring molecules, let a subscript 1 or 2 refer to whether the pair of molecules are first- or second-neighbours, and let the absence or presence of a prime (') indicate, respectively, whether the molecules are in the same or opposite CX-bond orientations. The pair interaction energy $E_{i,j}$ between molecules on sites i and j is then the sum of the interactions between the closest pairs of X and Y groups (each such interaction denoted as ϵ_1^{XY} , ϵ_2^{XY} , $\epsilon_1^{XY'}$ or $\epsilon_2^{XY'}$), plus the steric repulsion between

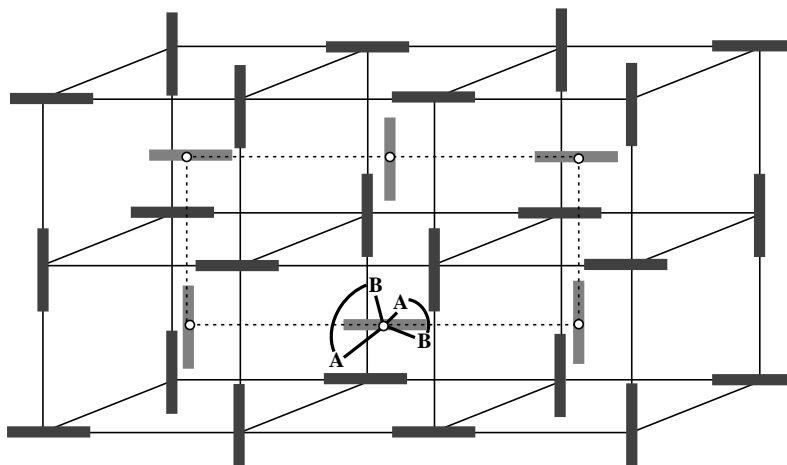


Figure 4. A ground-state configuration for three planes. The AB bond is illustrated for a molecule. The two enantiomers d and l have perpendicular AB-bond lines. The front plane is in the configuration P while the plane in the rear is in the configuration \bar{P} .

the closest pair of AB bonds (equal to γ_1 or γ'_1 if the first-neighbour pair have perpendicular AB-bond lines, to γ_2 or γ'_2 if the second-neighbour pair have colinear AB-bond lines, and to 0 otherwise).

We shall assume that the AB bond is polar, i.e. that the interactions between X and Y groups are electrostatic, given as

$$\epsilon_i^{AB(\prime)} = -\epsilon_i^{AA(\prime)} = -\epsilon_i^{BB(\prime)} = \epsilon_i^{(\prime)} < 0 \quad (3)$$

where $i = 1$ or 2 , and (\prime) indicates either the absence or presence of a prime. The model thus contains the nine parameters $\epsilon_1, \epsilon_2, \epsilon'_1, \epsilon'_2, \gamma_1, \gamma_2, \gamma'_1, \gamma'_2$ and μ . For sufficiently large μ , the ground-state configurations have every site occupied by a molecule, all the molecules being in the same CX-bond orientation [12].

Consider the set \mathcal{O} of lattice translations of the octahedron o illustrated in figure 2. Since the Hamiltonian in equation (2) is a sum of terms associated with each occupied site and with each occupied first- or second-neighbour pair of sites, then each of these terms can be partitioned equally among the octahedra in \mathcal{O} which contain the respective site or pair of sites. This partition defines the Hamiltonian restricted to an octahedron o , $H_o(\xi)$. The Hamiltonian can then be written as a sum of restricted Hamiltonians

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

For the domain \mathcal{D} of interactions in which $\epsilon_1 < \epsilon_2 < 0$, $\gamma_1, \gamma_2 > 0$ and μ is sufficiently large, it has been shown [12] that

$$\min_{\xi} H_o(\xi) = H_0 = 4\epsilon_1 + 4\epsilon_2 + \min\{\gamma_2, 2\gamma_1\} - \mu \quad (5)$$

and that configurations exist in \mathcal{D} in which every octahedron in \mathcal{O} has a restricted Hamiltonian equal to H_0 . The restricted Hamiltonian thus constitutes an m -potential in \mathcal{D} [17].

The structure of the ground-state configurations in \mathcal{D} can be described as follows. First, imagine the molecules without AB bonds. There are then 12 orientations possible. In a ground state in \mathcal{D} , every site is occupied by a molecule in the same orientation.

In \mathcal{D} , if $0 < \gamma_2 < 2\gamma_1$, the AB bonds are such that every molecule in a ground-state configuration is of the same enantiomeric type, d or l , and in the same molecular orientation. There are thus 24 ground-state configurations, and the Pirogov–Sinai [13, 14, 18] theory is sufficient to prove that multiple equilibrium states exist at sufficiently low temperatures, these states corresponding to d -rich or l -rich phases which are small perturbations of the ground states. Enantiomeric phase separation thus occurs at low temperature in this domain of interactions [12].

In \mathcal{D} , if $0 < 2\gamma_1 < \gamma_2$, in addition to all the molecules in a ground-state configuration being in the same one of the 12 possible orientations, each of these configurations contains a racemic mixture of d and l molecules. A ‘characteristic direction’ appears in each ground-state configuration. The AB-bond lines of all the molecules are perpendicular to this direction and are contained in one of the three sets of parallel planes (200), (020) or (002). Within each plane (see figure 4), molecules which are second neighbours are of opposite enantiomeric type, d or l , and have perpendicular AB-bond lines. For a given orientation of all the molecules in a ground-state configuration, there are thus two possible configurations of AB-bond lines in a plane, P and \bar{P} , related by the symmetry $d \rightleftharpoons l$. All of the ground-state configurations can be obtained from the 12 configurations $[PPPP \dots]_i$, in which all of the parallel planes (which are perpendicular to the characteristic direction) are in the P configuration, by simply changing one or more planes from P to \bar{P} . The index i runs over the 12 molecular orientations.

If there are p planes in the lattice there will be 12×2^p ground-state configurations, each corresponding to a racemic mixture of molecules. Hence, even if the number of ground states is infinite ($2^p \rightarrow \infty$ when $p \rightarrow \infty$) there is no residual entropy. As we shall show in section 3, the model in this domain satisfies the conditions of the Bricmont–Slawny [15] extension of the Pirogov–Sinai theory, and there are a finite number of racemic phases at sufficiently low temperatures.

3. Existence of racemic phases at low temperatures

In a domain of parameters in which there are an infinite number of ground states, an extension of the Pirogov–Sinai theory due to Bricmont and Slawny [15] can be used to determine the structure of the low-temperature phases if the ground states and excitations satisfy certain special conditions. First, the ground states must have a *layered structure* in that they can all be obtained from a finite number of ground states by simply changing the configurations in a set of planes. Second, the number of *dominant ground states*, those which allow the maximum number of lowest-energy excitations, must be finite. Third, the excitations must satisfy a *regularity condition* in that the amount by which the energy of an excitation exceeds that of a ground state must go to infinity as the size of the excitation extends to infinity. Fourth, a configuration containing an excitation must have a *retouch property* in that the excitation can be replaced by a unique local configuration of lowest energy. If these four conditions are satisfied, then theorem A of [15] ensures that the low-temperature phases in this domain have the structure of the dominant ground states, together with some excitations.

For the domain $\mathcal{D}_R \subset \mathcal{D}$ in which $\epsilon_1 < \epsilon_2 < 0$, $0 < 2\gamma_1 < \gamma_2$, and μ is sufficiently large, the ground states, described in section 2, are infinitely degenerate. Any ground-state configuration in \mathcal{D}_R can be obtained by simply changing all molecules $d \rightleftharpoons l$ in a set of planes starting from the ground-state configurations $[PPPP \dots]_i$, where i refers to one of the 12 molecular orientations. The ground-state configurations in \mathcal{D}_R thus have the *layered structure* assumed in the Bricmont–Slawny theory.

Since the Hamiltonian restricted to an octahedron forms an m -potential in \mathcal{D}_R , the energy of each octahedron in an excitation exceeds that of each octahedron in a ground-state configuration. If an excitation extends to infinity, it must either do so by extending to an infinite number of planes or by having an infinite perimeter in at least one plane. Either way, there are an infinite number of octahedra in the excitation and a resulting infinite energy. Hence the *regularity condition* is satisfied.

The local exterior of an excitation within a plane coincides necessarily with a ground state, P or \bar{P} , restricted to that plane. Thus, an excitation can be uniquely replaced in each plane by the extension of the local ground-state configuration at its exterior. The excitations thus have the *retouch property*.

We now proceed to determine the structure of the *dominant* ground-state configurations, those which afford a maximum number of lowest-energy excitations. Because of the local symmetry in the layers of the ground-state configurations, it is clear that any discriminating excitation, meaning one which occurs in a different number of ways in some ground-state configurations than in the others, must necessarily extend to at least three parallel planes of the configuration. As illustrated in figure 5, such excitations must extend from plane I to plane III. Thus to determine which ground states are dominant, we shall attempt to determine which sequence, $P \square P$ or $P \square \bar{P}$ (the \square represents the middle plane which may be in either the P or \bar{P} configuration), has more elementary excitations with lower energy.

Since any excitation involving only a single molecule cannot extend to three planes, a discriminating excitation must involve two or more molecules which are first or second neighbours. Excitations involving two molecules which extend from plane I to plane III are illustrated in figure 5(a) for $P \square P$ and in figure 5(a') for $P \square \bar{P}$. These excitations have the same energy and the same counting and therefore do not differentiate between $P \square P$ and $P \square \bar{P}$. In fact, no differentiation between $P \square P$ and $P \square \bar{P}$ occurs due to excitations involving only two molecules.

For the case of excitations involving three molecules, the excitation of $P \square P$ in figure 5(b) differs in energy from the corresponding one involving molecules at the same sites in $P \square \bar{P}$ and, at first glance, appears to effect a differentiation; however, the excitation in figure 5(b') of $P \square \bar{P}$ has the same energy and the same counting. Hence, no net differentiation results because of these excitations.

There are, however, excitations involving three molecules which do differentiate between $P \square P$ and $P \square \bar{P}$. The one with the lowest energy, illustrated in figure 5(c), has the energy $E_3^* = 3\gamma_2 + 6\gamma_1 - 16\epsilon_1 - 12\epsilon_2$ and occurs in $P \square P$ but not in $P \square \bar{P}$. (The corresponding excitation involving molecules at the same sites in $P \square \bar{P}$ is illustrated in figure 5(c') and exceeds E_3^* in energy by $2\gamma_1$.) Since this excitation forms a 'loop', a cancellation of its discriminating effect by a similar excitation in $P \square \bar{P}$, as occurred with the excitations of figure 5(b) and figure 5(b'), does not occur.

The differentiating excitation with lowest energy which includes four molecules contains a loop and is illustrated in figure 5(d). It occurs in $P \square P$ but not in $P \square \bar{P}$ and has the excitation energy $E_4^* = 8\gamma_2 - 8\gamma_1$. (The corresponding excitation involving molecules at the same sites in $P \square \bar{P}$ exceeds E_4^* in energy by $8\gamma_1$.) We also checked the excitations involving five molecules, and none with energy lower than $\min\{E_3^*, E_4^*\}$ causes a differentiation between $P \square P$ and $P \square \bar{P}$.

If no other excitations with energy less than or equal to $\min\{E_3^*, E_4^*\}$ occur which differentiate between $P \square P$ and $P \square \bar{P}$, then the 48 ground-state configurations $\mathcal{G}_R = \{[PPPP \dots]_i, [\bar{P}\bar{P}\bar{P}\bar{P} \dots]_i, [P\bar{P}P\bar{P} \dots]_i, [\bar{P}P\bar{P}P \dots]_i; i = 1 - 12\}$ are the dominant ground-state configurations.

As in the case with other models [15, 16], proving that these are in fact the lowest-energy

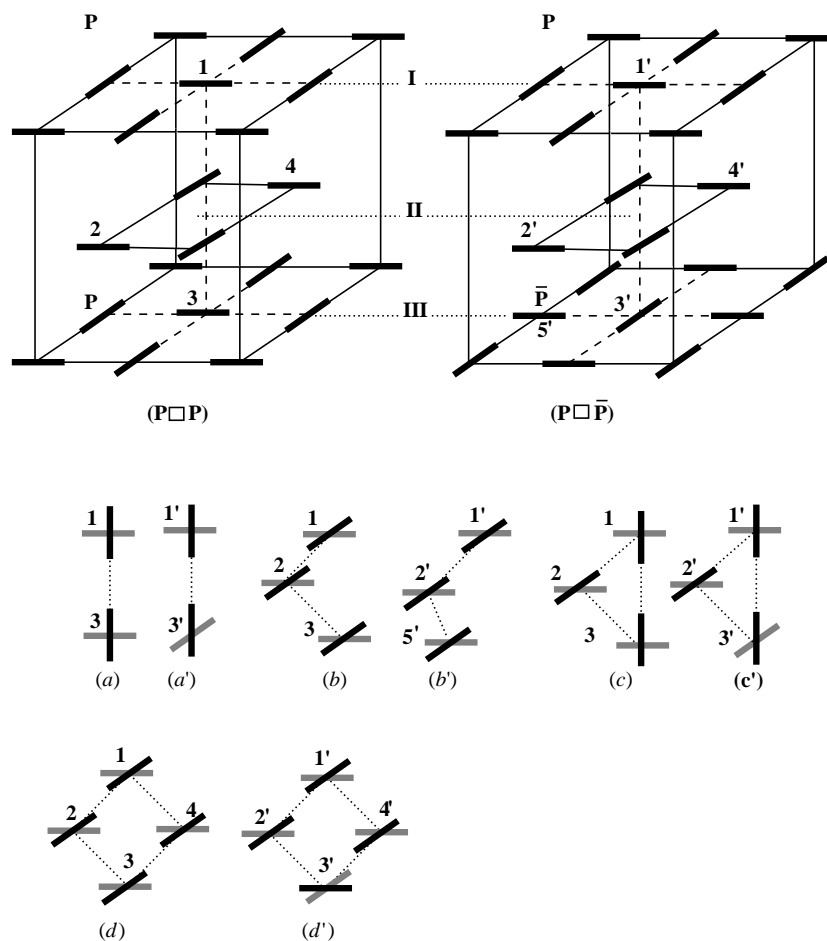


Figure 5. Illustration of the first-order excitations for the sequences $P \square P$ and $P \square \bar{P}$. The AB-bond lines in the excitation are represented by heavy short lines. A grey AB-bond line indicates the initial position before the excitation.

excitations which occur as excitations in more ways in some ground states than in others has not been accomplished, for it has not been ruled out that some excitations involving six or more molecules could have lower energy than $\min\{E_3^*, E_4^*\}$ and occur as excitations in some ground states in more ways than in other ground states. This is unlikely, however, for since the Hamiltonian restricted to an octahedron constitutes an m -potential, the excitation energy generally increases with the size of the excitation. It is interesting to point out that the dominant ground states we found are the most symmetric among the infinite set of ground states, which is also the case for other models studied by this technique [15, 16]. A heuristic explanation would be the following: since in general an excitation has a ‘shape’, it will usually have more ways to occur in a perfectly symmetric configuration than in one with lesser symmetry.

We thus conclude that the 48 configurations in \mathcal{G}_R are the dominant ground-state configurations. Within \mathcal{G}_R , the 24 configurations $[PPPP\dots]_i$ and $[\bar{P}\bar{P}\bar{P}\bar{P}\dots]_i$ are related to a single configuration R by physical rotations and translations; likewise, the 24

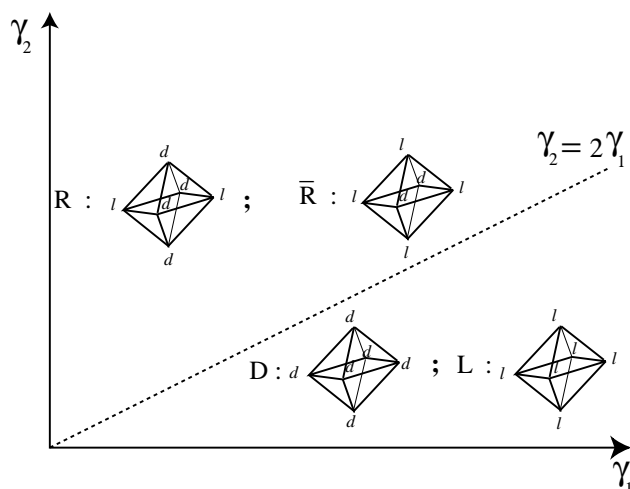


Figure 6. Low-temperature phase diagram of the three-dimensional enantiomeric model.

configurations $[P\bar{P}P\bar{P}\dots]_i$ and $[\bar{P}P\bar{P}P\dots]_i$ in \mathcal{G}_R are related by rotations and translations to a single configuration \bar{R} in which the molecules are in the same orientation as those in R . The configuration \bar{R} can be converted to R by a 90° rotation about an axis in the characteristic direction, followed by a reflection in a plane containing the axis. Thus, all the configurations in \mathcal{G}_R are related by symmetries of the Hamiltonian.

Since the ground-state configurations have the layered structure, the excitations satisfy the regularity condition and have the retouch property, and there are a finite number of symmetry-related dominant ground-state configurations, then using theorem A of [15], we conclude that at sufficiently large chemical potential the low-temperature phases of the three-dimensional enantiomeric model in the racemic regime ($2\gamma_1 < \gamma_2$) are small perturbations of the 48 ground-state configurations in \mathcal{G}_R .

It is interesting to note that if $2\gamma_1 < \gamma_2$, there are two physically different phases at low temperatures which are perturbations of the ground-state configurations R and \bar{R} , just as there are two physically different phases, one d rich and one l rich, at low temperatures if $2\gamma_1 > \gamma_2$. The d -rich and l -rich phases are small perturbations of two ground states, D and L , which are related by symmetry in the same way as are R and \bar{R} . The phase diagram is illustrated in figure 6.

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