

Chiral segregation in three microscopic statistical-mechanical models

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We consider three microscopic model molecular systems, each containing an equimolar mixture of a chiral molecule and its nonsuperimposable mirror image. The molecules in each model are assumed to lie on a thin film in such a way that they occupy the sites of a honeycomb lattice. Although neither enantiomorph is externally favored at low temperatures, we prove that for one range of interactions, chiral segregation into ordered phases containing a single enantiomorph occurs for two of the models and, in a second range of interactions, ordered racemic phases (containing equal numbers of each enantiomorph) occur for the two models. For a third range of interactions, each of the two models has an infinite number of ground-state configurations and, moreover, an associated residual entropy. In all three ranges of interactions considered, the third model has an infinite number of ground-state configurations and a residual entropy.

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I. INTRODUCTION

A molecule that has a nonsuperimposable mirror image is said to be chiral. A chiral molecule and its molecular mirror image are denoted as d and l enantiomorphs. Such molecules are of fundamental importance in biology, organic chemistry, and in the design of novel optically active materials. It is of great interest to be able to predict whether at low temperatures an equimolar mixture of d and l enantiomorphs will form a heterochiral (racemic) phase containing equal numbers of d and l molecules or will undergo chiral segregation and form two homochiral phases each of which contains a single enantiomorph d or l .

Initial rigorous statistical-mechanical studies of chiral segregation are due to Huckaby *et al.* [1,2]. They introduced a two-dimensional lattice gas containing two enantiomorphs and used the rigorous Peierls [3] argument to prove the existence of homochiral phases in the model at low temperatures. Later, by combining the rigorous Pirogov-Sinai theory [4,5] with the method [6] of an m potential [7], they extended their studies to a three-dimensional model system for which they established the existence of homochiral [8] as well as heterochiral [9] ordered crystalline phases, each appearing for different suitably chosen ranges of the interactions. The proof of the existence of the heterochiral (racemic) phases required the use of an extension of the Peierls argument due to Bricmont and Slawny [10].

Andelman and de Gennes studied chiral segregation in thin films at a water/air interface [11–13], using a system of tetrahedral chiral molecules (see Fig. 1). However, their approach was not truly statistical mechanical since they considered the partition functions only for a pair of neighboring molecules. Introducing a parameter Δ as the difference between the partition functions of a pair of molecules with the same chirality and a pair with the opposite chirality, they

interpreted the cases $\Delta < 0$ and $\Delta > 0$ as the tendency for the formation of heterochiral and homochiral phases, respectively. They limited their discussions to several particular examples of intermolecular interactions.

Another approach to chiral segregation is due to Nandi and Vollhardt [14,15]. In numerical studies, they used an effective pair potential theory. Rather than a pair of molecules, they considered an aggregate of molecules (all groups attached to two adjacent molecules). This mesoscopic type of approach is more advanced than that of Andelman and de Gennes, although being still far from macrophysics. Computer simulations of chiral segregation have also appeared [16], using a model similar to that of Andelman and de Gennes.

In Ref. [17], we rigorously analyzed the Andelman–de Gennes model from a statistical-mechanical point of view. We were able to rewrite the interaction potential of the model as an m potential for the whole range of intermolecular interactions. Then, similarly to the approach used in Ref. [8], we employed the Pirogov-Sinai theory to determine the

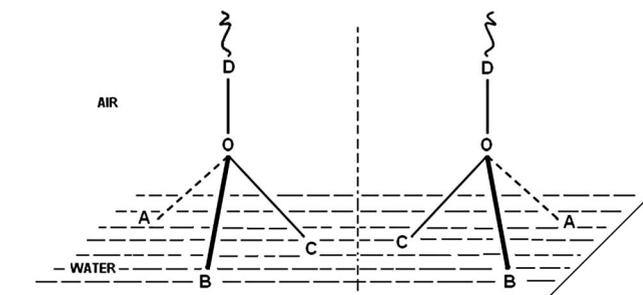


FIG. 1. A pair of tetrahedral enantiomorphs at the water/air interface considered by Andelman and de Gennes. The molecules have a center O that is connected to four different groups A , B , C , and D . The first three of them are near the interface, while the fourth one points out to the air. If, when viewed from above, the groups A , B , and C are ordered clockwise (counterclockwise), the molecule is an l molecule (a d molecule).

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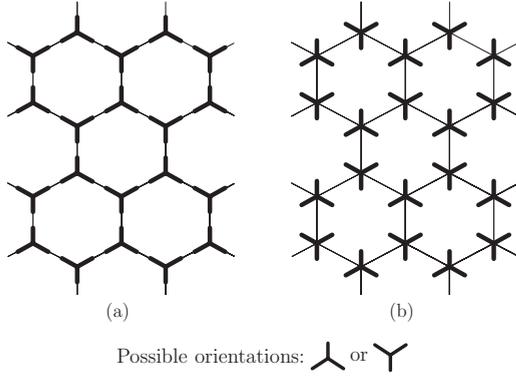


FIG. 2. Two possible arrangements of tripods on a regular honeycomb lattice.

phases of the model at sufficiently low temperatures. We proved that instead of the single parameter Δ , three parameters must be used to obtain the phases correctly. Nevertheless, when considering the several special cases of interactions studied by Andelman and de Gennes, our results showed that—perhaps surprisingly—their conjectures based on just two-molecule partition functions predicted the correct type of phases (homochiral or heterochiral) in each case.

In Sec. II we consider three model molecular systems in which equal numbers of two enantiomorphs occupy the sites of a honeycomb lattice. Then, without using the concept of an m potential, in Sec. III we construct the ground-state configurations by minimizing the specific energy of the systems. For ranges of the intermolecular interactions in which the number of ground-state configurations is finite, we show that the Peierls condition is satisfied and then employ the Pirogov-Sinai theory to obtain the structure of the low-temperature phases.

II. MODELS

In order to study chiral segregation in thin films, we consider the tetrahedral chiral molecules from Fig. 1 placed on a honeycomb lattice. Tripod centers of the molecules are supposed to occupy each site of the lattice (the close-packed regime). A configuration ω_x of a tripod with a center at the site x is one of the six permutations of $\{A, B, C\}$. For simplicity, a tripod is allowed to be only in the two possible orientations shown in Fig. 2, and two neighboring tripods must always have opposite orientations. As a result, there are only two different arrangements of the tripods on the lattice (see Fig. 2). The arrangement (a) corresponds to the model of Mao *et al.* [16] and the arrangement (b) to the Andelman–de Gennes model [11–13]. We shall use ν to distinguish between the two models: $\nu=1$ for the former model and $\nu=2$ for the latter one.

The interaction between molecules is restricted to nearest neighbors, and two neighboring molecules interact only via the closest groups A, B, C in their tripod configurations ω_x and ω_y as shown in Fig. 3. Thus, the Hamiltonians of the two models on a finite lattice Λ are

$$H_\nu(\omega_\Lambda) = \sum_{XY} \varepsilon_{XY} N_\nu^{XY}(\omega_\Lambda), \quad \nu = 1, 2. \quad (1)$$

Here ω_Λ is a collection of ω_x for all sites x in Λ ; the sum is over all six pairs $XY=AB, AC, BC, AA, BB, CC$ of closest

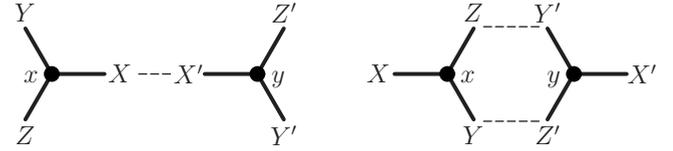


FIG. 3. Two nearest-neighbor molecules interact only via the closest pairs of groups: XX' for $\nu=1$ (left) and YZ' and ZY' for $\nu=2$ (right). The disks represent lattice sites.

groups A, B, C ; ε_{XY} are the interaction strengths between the closest groups X and Y ; and N_ν^{XY} is the number of closest group pairs XY in the configuration ω_Λ . Notice that neither the d nor the l molecules are externally favored. Since the system contains an equal number of each enantiomorph, their chemical potentials are identical $\mu_d = \mu_l \equiv \mu$; thus in the close-packed limit, the term $\mu_l N_l(\omega_\Lambda) + \mu_d N_d(\omega_\Lambda) = \mu |\Lambda|$ is configuration independent and is omitted from the Hamiltonian.

It will turn out that the Mao model ($\nu=1$) has a rather pathological behavior—its ground-state configurations are infinitely degenerate and even possess a residual entropy (see Sec. III) [18]. We will thus not be able, with the techniques employed here, to obtain the structure of its low-temperature phases and conclude whether chiral segregation occurs or not. Therefore, we shall also study a simple modification of the Mao model in which interactions between more distant group pairs XY are included. This makes the ground-state configurations finitely degenerate in some regions of interactions and allows us to study chiral segregation. The modified Mao model is

$$H_3(\omega_\Lambda) = \sum_{XY} \varepsilon_{XY} N_3^{XY}(\omega_\Lambda), \quad (2)$$

where N_3^{XY} is N_1^{XY} plus the number of third closest group pairs XY [the pairs XX', YZ' , and ZY' in Fig. 3(a)] in ω_Λ [19].

III. GROUND STATES

The periodic ground-state configurations of our three models are the periodic configurations ω that minimize the specific energy,

$$e_\nu(\omega) = \lim_{\Lambda \nearrow \infty} \frac{H_\nu(\omega_\Lambda)}{|\Lambda|}, \quad \nu = 1, 2, 3. \quad (3)$$

This is not true for any lattice system, but it holds, for example, if configurations on two sufficiently distant portions of the lattice can be chosen arbitrarily and independently of each other (see Sec. XIII in Ref [6]). This condition is obviously satisfied for the models considered here.

Clearly,

$$e_\nu(\omega) = \sum_{XY} \varepsilon_{XY} n_\nu^{XY}(\omega), \quad (4)$$

with the numbers $n_\nu^{XY}(\omega) = \lim_{\Lambda \nearrow \infty} N_\nu^{XY}(\omega_\Lambda) / |\Lambda|$. However, due to the close-packed regime, these numbers are not independent so that some of them can be eliminated as follows.

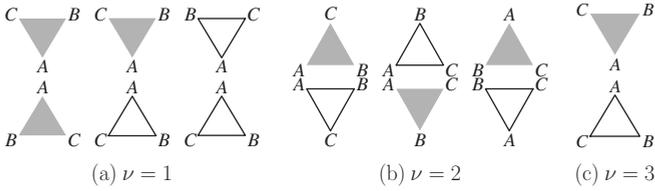


FIG. 4. The types of pair configurations ω_p containing only identical interacting group pairs. For $\nu=1, 3$, only those ω_p with AA interacting groups are shown—the others can be obtained from the three cyclic permutations of A, B , and C . Shaded (empty) triangles represent the d molecules (l molecules).

The group A , say, from a given molecule interacts in any ω_Λ with a fixed number $q=\nu$ of nearby groups $X=A, B, C$ (except near the boundary of Λ): $q=1$ for the Mao model, $q=2$ for the Andelman–de Gennes model, and $q=3$ for the modified Mao model. Hence, the total number $2N_\nu^{AA} + N_\nu^{AB} + N_\nu^{AC}$ of the groups X in Λ with which the A groups interact is equal to $\nu|\Lambda|$ (up to a Λ -boundary error). Analogous statements hold for the groups B and C . Consequently,

$$2n_\nu^{XX} + n_\nu^{XY} + n_\nu^{XZ} = \nu, \quad (5)$$

where X, Y, Z is a permutation of A, B, C . Note that Eq. (5) implies

$$0 \leq n_\nu^{XY} \leq \begin{cases} \nu, & X \neq Y \\ \nu/2, & X = Y. \end{cases} \quad (6)$$

Due to the three constraints [Eq. (5)], we may eliminate from Eq. (4) the three numbers associated with, say, interacting pairs of identical groups AA, BB, CC . We obtain

$$e_\nu = \Delta_{AB}n_\nu^{AB} + \Delta_{AC}n_\nu^{AC} + \Delta_{BC}n_\nu^{BC} + c_\nu, \quad (7)$$

where

$$\Delta_{XY} = \varepsilon_{XY} - \frac{\varepsilon_{XX} + \varepsilon_{YY}}{2}, \quad (8)$$

and the constants

$$c_\nu = \frac{\nu}{2}(\varepsilon_{AA} + \varepsilon_{BB} + \varepsilon_{CC}). \quad (9)$$

Therefore, the structure of the ground-state configurations is fully determined by the three parameters $\Delta_{AB}, \Delta_{AC}, \Delta_{BC}$ within the whole six-parameter ε space.

When minimizing the specific energies e_1, e_2, e_3 , we may distinguish four cases according to the values of the parameters Δ_{XY} .

Case 1. All three Δ_{XY} positive. The specific energy e_ν is lowest when $n_\nu^{AB}=n_\nu^{AC}=n_\nu^{BC}=0$ are the minimal possible. Then $n_\nu^{AA}=n_\nu^{BB}=n_\nu^{CC}=\nu/2$ by Eq. (5). If there exist configurations ω in which only the pairs of identical interacting groups AA, BB, CC occur, each with an equal frequency, then they must be ground-state configurations with the specific energy $e_\nu^{\min}=c_\nu$ by Eq. (7).

Figure 4 shows configurations ω_p on the pairs P of nearest-neighboring molecular tripods containing only identical interacting group pairs. Their number is 9 for the model $\nu=1$ and 3 for the models $\nu=2, 3$. Using these ω_p in such a

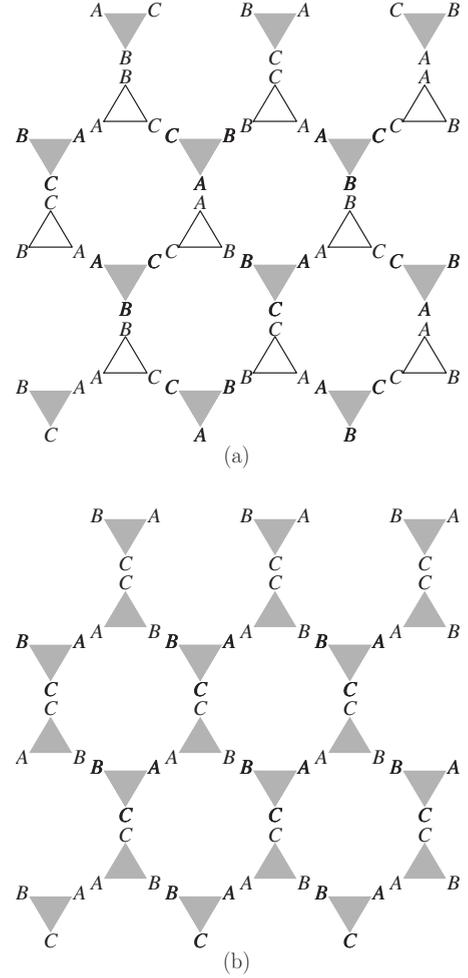


FIG. 5. Selected ground-state configurations of the Mao model and its modification in region I.

way that each of the three group pairs AA, BB, CC appears equally often, we can construct ground-state configurations for the three models.

Infinitely many ground-state configurations can be so constructed for the model $\nu=1$. First, we readily observe that Figs. 5(a) and 5(b) show two such ground-state configurations. Now, if in Fig. 5(a) we interchange, say, the A and B groups in each molecule that lies in an elementary hexagon containing no closest CC pairs, the energy of the resulting configuration remains unchanged, and we obtain another ground state. Since this interchange of A and B groups can be done independently for any number of elementary hexagons, the number of ground-state configurations that can be generated in this way approaches infinity exponentially with the lattice size, and the system thus possesses a residual entropy. Similarly, we can obtain infinitely many ground-state configurations in Fig. 5(b) by interchanging, say, all the A and B groups in each molecule that lies in an infinite row of molecules between two adjacent horizontal lines bisecting the closest CC pairs. In both cases, the switch $A \leftrightarrow B$ either turns a d molecule into an l molecule or vice versa. Hence, in (a) the number of d and l molecules remains unchanged after the switch. On the other hand, in (b) the whole row of molecules changes from d to l or vice versa. The more rows that are

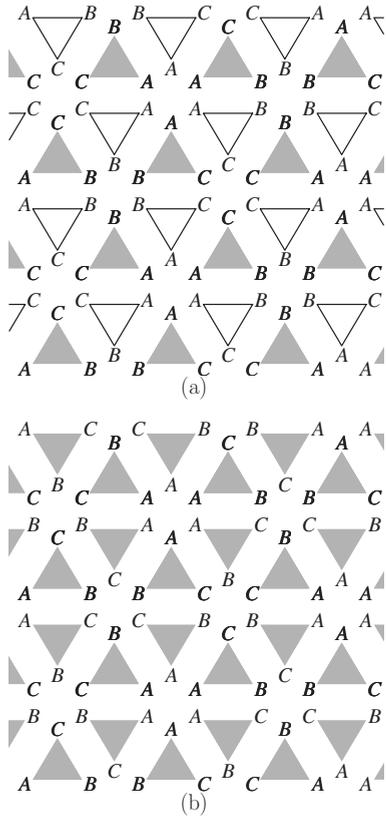


FIG. 6. Selected ground-state configurations of the Andelman–de Gennes model in regions I and II.

altered, the more molecules that are changed in this way, and thus we can construct ground-state configurations with an arbitrary macroscopic ratio of d and l molecules.

For each of the models $\nu=2$ and $\nu=3$, there exists a single sixfold degenerate periodic ground state [see Figs. 6(a) and 5(a), respectively]. Half of the molecules are of the d type and half of the l type. The sixfold degeneracy corresponds to six permutations of the groups A, B, C (i.e., rotations and flips of molecular triads).

Case 2. Two Δ_{XY} positive, one negative. Without loss of generality, let $\Delta_{BC} < 0 < \Delta_{AC} < \Delta_{AB}$ (other cases correspond to suitable permutations of A, B, C). The minimum of e_ν is attained when $n_\nu^{AB} = n_\nu^{AC} = 0$ are the minimal possible and $n_\nu^{AA} = \nu$ is the maximal possible [see Eq. (6)]. Then $n_\nu^{BB} = \nu/2$ and $n_\nu^{CC} = \nu/2$ by Eq. (5). Any ω in which only the pairs of interacting groups BC and AA occur, the BC pairs twice as often as the AA pairs, is a ground state, its specific energy being $e_\nu^{\min} = \Delta_{BC}\nu + c_\nu = \nu(2\varepsilon_{BC} + \varepsilon_{AA})/2$ by Eq. (7).

Figure 7 shows pair configurations ω_p containing AA and BC pairs of interacting groups. Their number is 7 for the model $\nu=1$ and 4 for the models $\nu=2, 3$. The ground-state configurations for the three models can be constructed by using these ω_p in such a way that the pairs BC appear twice as often as the pairs AA .

There are again infinitely many ground-state configurations for the model $\nu=1$, two of which are shown in Figs. 8(a) and 8(b). In Fig. 8(a), by independently interchanging the B and C groups in each molecule within any number of elementary hexagons that contain no AA group pairs, the

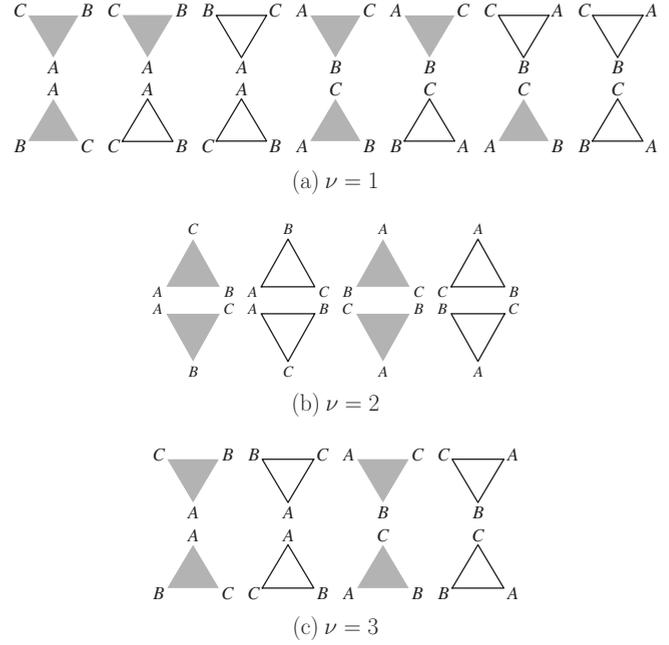


FIG. 7. The types of pair configurations ω_p containing only the interacting group pairs AA and BC .

number of ground-state configurations generated approaches infinity exponentially fast with the lattice size, and they possess a residual entropy. If the B and C groups are interchanged within each molecule in any number of infinite rows of molecules, each row being between two adjacent parallel lines bisecting the group pairs AA in Fig. 8(b), infinitely many ground-state configurations can also be constructed. In the latter case, the number of d and l molecules remains unchanged. In the former case, each molecule in the elementary hexagons changes from the d type to the l type or vice versa, and ground-state configurations can be constructed with an arbitrary macroscopic ratio of the two types of molecules.

For each of the models $\nu=2$ and $\nu=3$, only one sixfold degenerate periodic ground state can be constructed [see Fig. 6(b) and 8(a), respectively], with all the molecules being either of the d type or of the l type. The sixfold degeneracy corresponds to the two permutations of the groups B, C , and three translations of the whole state by the elementary vectors of the triangular lattice dual to the hexagonal lattice.

Case 3. One Δ_{XY} positive, two negative. Without loss of generality, let $\Delta_{BC} < \Delta_{AC} < 0 < \Delta_{AB}$. The specific energy e_ν is lowest when $n_\nu^{AB} = 0$ is minimal and thus $n_\nu^{BC} = \nu$ is the maximal possible. Hence, this case is the same as case 2 above.

Case 4. All three Δ_{XY} negative. Without loss of generality, let $\Delta_{BC} < \Delta_{AC} < \Delta_{AB} < 0$. Then e_ν is minimal only if

$$n_\nu^{AB} \leq n_\nu^{AC} \leq n_\nu^{BC}. \quad (10)$$

Using Eq. (5) to eliminate n_ν^{AB} and n_ν^{AC} in Eq. (7) yields

$$e_\nu = [\Delta_{BC} - (\Delta_{AB} + \Delta_{AC})]n_\nu^{BC} - 2\Delta_{AB}n_\nu^{BB} - 2\Delta_{AC}n_\nu^{CC} + \nu(\Delta_{AB} + \Delta_{AC}) + c_\nu. \quad (11)$$

Two subcases arise. (i) If $\Delta_{BC} < \Delta_{AB} + \Delta_{AC}$, then e_ν is mini-

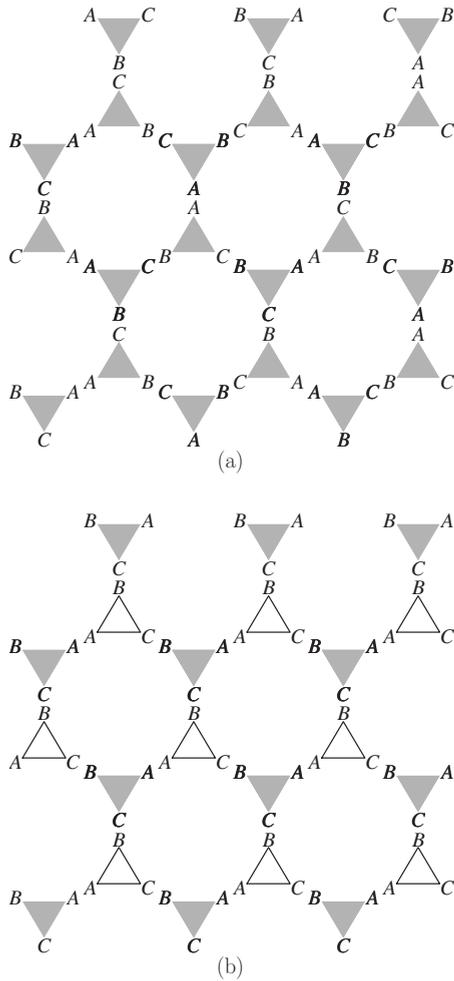


FIG. 8. Selected ground-state configurations of the Mao model and its modification in region II.

mal in Eq. (11) if $n_{\nu}^{BC} = \nu$ is maximal and $n_{\nu}^{BB} = n_{\nu}^{CC} = 0$. Equation (5) then gives $n_{\nu}^{AB} = n_{\nu}^{AC} = 0$ and then $n_{\nu}^{AA} = \nu/2$, yielding case 2 again. (ii) If $\Delta_{BC} > \Delta_{AB} + \Delta_{AC}$, then e_{ν} is minimized in Eq. (11) if $n_{\nu}^{BB} = n_{\nu}^{CC} = 0$ and n_{ν}^{BC} is minimal under the restriction of Eq. (10), yielding $n_{\nu}^{AB} = n_{\nu}^{AC} = n_{\nu}^{BC}$. Then Eq. (5) yields $n_{\nu}^{AB} = n_{\nu}^{AC} = n_{\nu}^{BC} = \nu/2$ and $n_{\nu}^{AA} = 0$, and Eq. (11) yields $e_{\nu}^{\min} = \nu(\Delta_{AB} + \Delta_{AC} + \Delta_{BC})/2 + c_{\nu} = \nu(\epsilon_{AB} + \epsilon_{AC} + \epsilon_{BC})/2$.

Figure 9 shows pair configurations ω_p containing only pairs of nonidentical interacting groups. Their number is 12 for the models $\nu=1, 2$ and 6 for the model $\nu=3$. Using these ω_p in such a way that the groups AB, AC, BC appear equally often, ground-state configurations for case 4(ii) of the three models can be constructed. Figures 10(a) and 10(b) show two ground-state configurations for the model $\nu=1$, Figs. 11(a) and 11(b) show two ground-state configurations for the model $\nu=2$, and Fig. 10(a) shows a ground-state configuration for the model $\nu=3$. For the configurations in Figs. 10(a) and 11(a), each tripod on one sublattice can be independently rotated clockwise by $2\pi/3$ without changing the configurational energy. The number of these ground-state configurations approaches infinity exponentially with the lattice size, and thus the system has a residual entropy. Since rotation does not change the chirality of a molecule, all the resulting ground-state configurations have half of the molecules of the

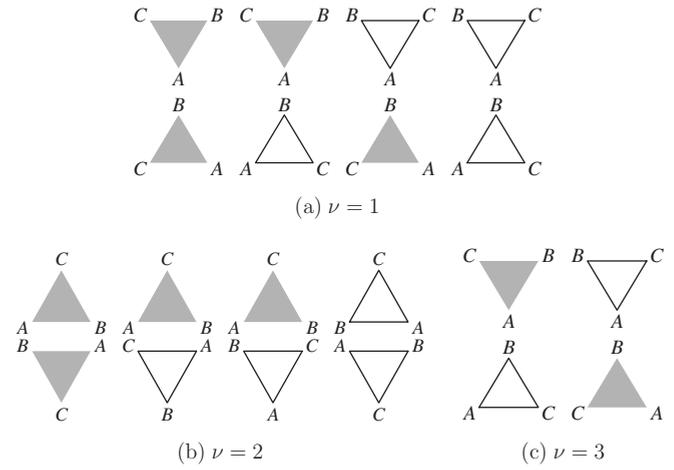


FIG. 9. Some of the pair configurations ω_p containing only non-identical interacting group pairs. The other ω_p can be obtained by taking the three cyclic permutations of A, B , and C .

d type and half of the l type. For the configurations in Figs. 10(b) and 11(b), each pair of molecules that interacts via AB groups can have the A and B groups within that pair switched, independently of other such pairs, without altering

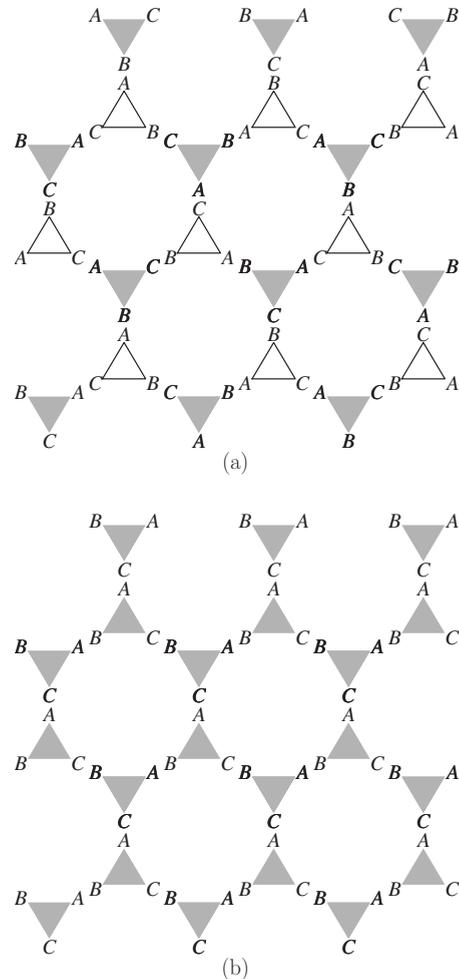


FIG. 10. Selected ground-state configurations of the Mao model and its modification in region III.

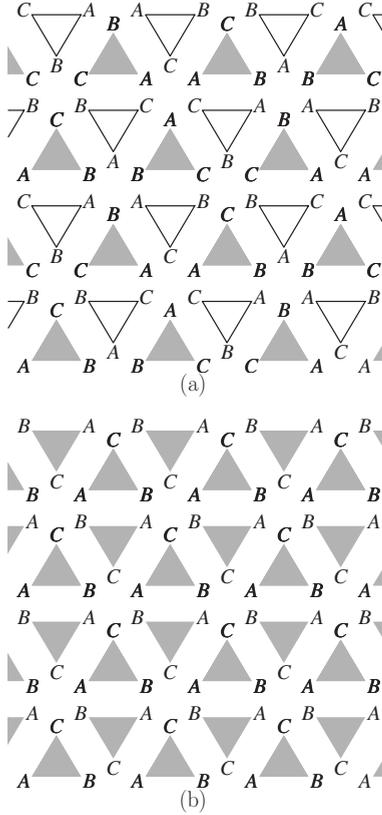


FIG. 11. Selected ground-state configurations of the Andelman–de Gennes model in region III.

the configurational energy. The number of these configurations approaches infinity exponentially in the system size, and they possess a residual entropy. Since the chirality of each molecule in these pairs is changed by the switching of A and B groups, these ground-state configurations can have an arbitrary macroscopic ratio of d and l molecules.

According to the above results, only three types of ground-state configurations can actually occur. They correspond to the following three regions in the ε space: (I) all three Δ_{XY} are positive (case 1 above); (II) the least of the three Δ_{XY} is negative and less than the sum of the other two [cases 2, 3, and 4(i) above]; and (III) the least of the three Δ_{XY} is negative and larger than the sum of the other two [case 4(ii) above].

IV. HOMOCHIRAL AND HETEROCHIRAL PHASES

For the three models, we shall now discuss the existence at low temperatures of chiral segregation into homochiral phases or the formation of racemic heterochiral phases, in dependence on the values of the intergroup interactions ε_{XY} . To this end, we describe the structure of their low-temperature phases by employing the Pirogov-Sinai theory of first-order phase transitions [4,5,20,21].

The theory enables one to rigorously determine the phases and their structures for a lattice model if the model has a finite number of ground-state configurations (all of which are then necessarily periodic), the temperature is sufficiently low, and the Peierls condition is fulfilled [22]. Then each ground state gives rise to a unique phase whose typical configuration looks as a “sea” of the corresponding ground state with isolated “islands” of non-ground-state configurations; the volume density of the islands is not equal to zero, but is on the order of $\exp(-1/kT)$.

In the present context, this leads to the conclusion that if a ground state consists of equal numbers of d and l molecules, the associated low-temperature phase is heterochiral. On the other hand, if a ground state consists of d (or l) molecules alone, the associated phase is homochiral and chiral segregation occurs.

In Sec. III we showed that the Andelman–de Gennes model ($\nu=2$) and the modified Mao model ($\nu=3$) have a finite number of symmetry-related ground-state configurations in regions I and II. Therefore, to obtain their low-temperature phases, we only need the Peierls condition to be true. This was proven in Ref. [17] for the model $\nu=2$ and is easy to show for the model $\nu=3$ as follows.

The energy $H_3(\omega_p)$ can attain only five values,

$$\begin{aligned} g_I &= \varepsilon_{AA} + \varepsilon_{BB} + \varepsilon_{CC}, \\ g_{III} &= \varepsilon_{AB} + \varepsilon_{AC} + \varepsilon_{BC}, \\ g_{YZ} &= 2\varepsilon_{YZ} + \varepsilon_{XX}, \end{aligned} \quad (12)$$

where X, Y, Z is any cyclic permutation of A, B, C . Equation (12) yields

$$\begin{aligned} g_{III} - g_I &= \Delta_{AB} + \Delta_{AC} + \Delta_{BC}, \\ g_{YZ} - g_I &= 2\Delta_{YZ}, \end{aligned}$$

TABLE I. Summary of results.

	Model	Region I All three Δ_{XY} are positive	Region II The least Δ_{XY} is negative and less than the sum of the other two	Region III The least Δ_{XY} is negative and greater than the sum of the other two
Ground states [degeneracy]	$\nu=1$	Figs. 5(a) and 5(b), [$\infty \times$]	Figs. 8(a) and 8(b), [$\infty \times$]	Figs. 10(a) and 10(b), [$\infty \times$]
	$\nu=2$	Fig. 6(a), [$6 \times$]	Fig. 6(b), [$6 \times$]	Figs. 11(a) and 11(b), [$\infty \times$]
	$\nu=3$	Fig. 5(a), [$6 \times$]	Fig. 8(a), [$6 \times$]	Fig. 10(a), [$\infty \times$]
Low temperature phases	$\nu=1$	No conclusion	No conclusion	No conclusion
	$\nu=2$	Heterochiral	Homochiral	No conclusion
	$\nu=3$	Heterochiral	Homochiral	No conclusion

$$g_{BC} - g_{III} = \Delta_{BC} - (\Delta_{AB} + \Delta_{AC}). \quad (13)$$

Thus, since $\Delta_{BC} < \Delta_{AC} < \Delta_{AB}$ (without loss of generality), g_I is the lowest of the five pair interaction energies if $\Delta_{BC} > 0$, g_{BC} is the lowest if $\Delta_{BC} < 0$ and $\Delta_{BC} < \Delta_{AB} + \Delta_{AC}$, and g_{III} is the lowest if $\Delta_{BC} < 0$ and $\Delta_{BC} > \Delta_{AB} + \Delta_{AC}$.

In Sec. III we constructed periodic ground-state configurations for the model $\nu=3$ using only those ω_P having the energy g_I (in region I), g_{BC} (in region II), and g_{III} (in region III). Thus, $H_3(\omega_P)$ is a periodic finite-ranged m potential [7] in these three regions. Since the number of ground-state configurations is finite in regions I and II, then the Peierls condition is satisfied in these two regions [6]. In fact, we used analogous although more refined arguments to verify the Peierls condition for the model $\nu=2$ in Ref. [17]. Moreover, since the ground-state configurations are symmetry related, we can apply the Pirogov-Sinai theory to conclude that the low-temperature phases of the Andelman–de Gennes model

and the modified Mao model are heterochiral in region I and homochiral in region II (see Table I).

The Pirogov-Sinai theory cannot be used to determine low-temperature phases for the models $\nu=2,3$ in region III or for the Mao model ($\nu=1$). The associated ground-state configurations are infinitely degenerate and possess a residual entropy; thus, even the Bricmont-Slawny extension [10] of the Pirogov-Sinai theory to infinitely degenerate ground-state configurations is not applicable here. Nevertheless, as our modification [Eq. (2)] of the Mao model indicates, taking into account interactions among more distant groups A, B, C , removes this pathological behavior.

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