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Low-temperature phases obtained by linear programming: An application to a lattice system of model chiral molecules

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ABSTRACT

A convenient, Peierls-type approach to obtain low-temperature phases is to use the method of an *m*-potential. In this paper we show that, for more complex systems where it may be rather difficult to rewrite the Hamiltonian as an *m*-potential and whose configurations are subject to linear constraints, the verification of the Peierls condition can be reformulated as a linear programming problem. Before introducing this novel strategy for a general lattice system, we compare it with the *m*-potential method for a specific model molecular system consisting of an equimolar mixture of a chiral molecule and its non-superimposable mirror image that occupy all the sites of a honeycomb lattice. In one range of interactions, we prove that a racemic low-temperature phase occurs (containing equal numbers of each enantiomer). However, in a neighboring range of interactions, we show that a homochiral low-temperature phase (containing a single enantiomer) exists, and thus chiral segregation occurs in the system. Our linear programming technique yields these results in wider ranges of interactions than the *m*-potential method.

1. Introduction

Extending the famous Peierls argument [1,2], Pirogov and Sinai [3,4] were first to study the low-temperature phases and phase diagram for an asymmetric Ising model. Later, this approach was successfully generalized to a theory [5,6] enabling one to obtain phases, phase diagrams, and first-order phase transitions at low temperatures for a wide class of lattice systems in which symmetry need not be present. It is only necessary that (a) there are just finitely many (hence, periodic) ground states from which stable low-temperature phases can arise, and (b) in any configuration the energy of a boundary separating two ground-state regions is at least proportional to the size of this boundary (the Peierls condition). Then a low-temperature phase is associated with each of the ground states. In addition, the structure of a typical microscopic configuration of the phase is very similar to that of the associated ground state: in an overwhelming majority of the lattice the configuration coincides with the ground state, and there are only small and sparse regions (of non-zero volume density, though) where the two differ. More details concerning the theory can be found, for example, in a review [7] and the references given there.

Holsztynski and Slawny [8] provided a straightforward method to verify the Peierls condition and thus obtain low-temperature phases by rewriting the system Hamiltonian as an *m*-potential. An interaction potential, Φ, is called an *m*-potential if there is a lattice configuration σ and a finite segment, S, of the lattice such that σ minimizes Φ on every S, i.e.,

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$\Phi(\sigma_S) \leqslant \Phi(\omega_S)$ for all configurations ω. However, if the system is complex, it may be necessary to consider a large segment S so that $\Phi(\omega_S)$ may have a huge number of distinct values and the minimization of Φ becomes very complicated.

In this paper we propose a novel way to verify the Peierls condition in the case when the configurations of a lattice system are subject to linear constraints. We motivate the technique by first applying it to a specific lattice system containing an equal number of two enantiomers on a honeycomb lattice in the close-packed regime (see Sections 2 and 3). The molecular structures require that the configurations of the system at closest packing must satisfy linear equations (constraints).

Using triangular lattice segments T composed of four sites (a site plus its three closest neighbors), we first obtain the ground states of the system in two ranges of interactions by using the m-potential method. In one range ($\mathcal{R}_1^{\mathrm{mp}}$) there is a single racemic ground state (with equal numbers of each enantiomer), while in the other range ($\mathcal{R}_2^{\mathrm{mp}}$) there is a single homochiral ground state (containing a single enantiomer). In two other ranges of interactions, no ground states are obtained. We then apply our technique, resulting in a minimization equivalent to a linear programming problem, and we obtain the ground states in all ranges of interactions. The racemic ground state is obtained in the same range $\mathcal{R}_1^{\mathrm{mp}}$, the homochiral ground state is obtained in a range ($\mathcal{R}_2^{\mathrm{lp}}$) significantly larger than $\mathcal{R}_2^{\mathrm{mp}}$, and an infinite number of ground states are obtained in the remaining range.

Subsequently, we verify the Peierls condition in the cases when the racemic and homochiral ground states exist. In ranges $\mathcal{R}_1^{\mathrm{mp}}$ and $\mathcal{R}_2^{\mathrm{mp}}$ this is implied by the existence of the m-potential. However, in the portion of range $\mathcal{R}_2^{\mathrm{lp}}$ that is beyond $\mathcal{R}_2^{\mathrm{mp}}$, the triangular segments T yield no m-potential. In that region, we verify the Peierls condition explicitly, which results in yet another minimization equivalent to a linear programming problem. Verifying the Peierls condition and realizing that typical configurations of a low-temperature phase are very similar to the associated ground state, we will be able to conclude that our system has a racemic as well as a homochiral low-temperature phase.

After treating a specific system, we extend our technique to a general lattice system. In Section 4, we introduce such a general system and assume that certain linear constraints are present. Then, in Section 5, we describe how the ground states of the system can be obtained. Namely, like Holsztynski and Slawny [8], we use the assumption that a periodic configuration is a ground state if and only if it has the lowest specific energy. Then we observe that the specific energy may be written as a convex combination of the energies, g_j, corresponding to a finite domain, D, of the lattice (the g_j are values of the Hamiltonian in D). Hence, in order to obtain the ground states, one needs to minimize convex combinations of g_j with convex coefficients subject to linear constraints. This is a linear programming problem that can be readily solved by standard methods (such as the simplex method [9]). Only when D is taken sufficiently large does one get the situation equivalent to the method of an m-potential. For smaller domains D the present approach can be more convenient.

Finally, in Section 6, we show that the verification of the Peierls condition can be formulated as a linear programming problem closely related to the above one: the minimization of convex combinations of g_j subject to the same linear constraints, excluding those convex combinations whose values are close to the ground-state specific energy. In particular, if there is a single g_j equal to the ground-state specific energy, then this g_j is excluded. Supplementary developments are placed in the Appendix.

2. Motivation: a lattice system of model chiral molecules

In order to motivate our technique inspired by linear programming, we first introduce a specific system on a honeycomb lattice and then treat it by the standard method of an m-potential, using triangular segments (T) of the lattice. We shall show that this approach yields ground-state configurations and low-temperature phases in some regions of interactions. However, in the remaining regions the lowest energy segments do not satisfy global restrictions, and thus cannot yield ground states. In Section 3, the model is treated by our technique based on linear programming that finds the lowest energy triangular segments T that do satisfy the global restrictions, and these yield the ground states in the regions where the m-potential fails. Simultaneously, the technique reproduces the results of the m-potential in regions where the m-potential works.

2.1. The system

As an example of a lattice system, we introduce the following two-dimensional system of model chiral molecules. A molecule contains three groups, A, B, and C, equidistant from the molecular center and from each other. Thus, we depict a molecule by a tripod (see Fig. 1). The chirality of a molecule is represented by a clockwise or counterclockwise ordering of the three groups: in the former case, one speaks of an l molecule; in the latter case, one speaks of a d molecule.

We place the molecules on a regular honeycomb lattice, $\mathbb{H}$, so that each site of the lattice is occupied by a single molecular tripod center (the close-packed regime). For simplicity, we allow only one orientation of each molecular tripod, as shown in Fig. 1(a), so that the set of configurations of a single tripod are the six permutations of the groups A, B, and C. Moreover, we let the interaction between molecules be limited to nearest neighbors, assuming that two neighboring molecules interact only via the pairs of their first and second closest groups, as shown in Fig. 1(b). Namely, we consider the Hamiltonian

$$H_{\Lambda}^{\mathrm{ch}}(\omega_{\Lambda}) = \sum_{XY} \varepsilon_{XY} N_{\Lambda,XY}(\omega_{\Lambda}), \tag{1}$$