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Existence of Several Surface-Reconstructed Phases in a Two-Dimensional Lattice Model

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The zero-temperature phase diagram is rigorously obtained for a two-dimensional lattice model with four energy parameters. It is shown that the parameter space can be divided into regions, together with their boundaries, such that in each region the ground-state configurations are of one of seven different types. These types include one which is nondegenerate, four which are doubly degenerate, one which is infinitely degenerate but with no residual entropy, and one which is infinitely degenerate and has a nonzero residual entropy. The Pirogov–Sinai extension of the Peierls argument is used to establish the existence at low temperatures of four different types of ordered surface-reconstructed phases.

KEY WORDS: Surface reconstruction; phase transitions.

1. INTRODUCTION

In the present paper we calculate the zero-temperature phase diagram and prove the existence of four different types of ordered surface-reconstructed phases in a lattice model for surface reconstruction.

The model surface consists of a rectangular lattice with periodic boundaries which has an atom associated with each of its $(2N)^2$ lattice sites (see Fig. 1). An atom associated with a lattice site may be situated either in a position on the lattice site or displaced to a position a distance Δ to the left or right of the lattice site.[1,2] An extra energy ε_R is associated with an atom which is at a position to the left or right of its associated lattice

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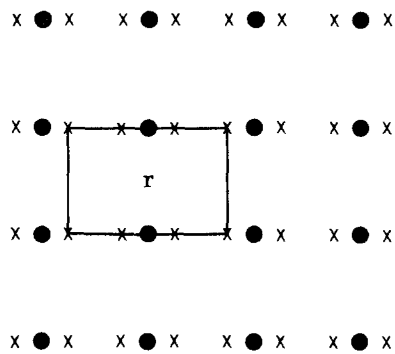

Fig. 1. The configuration in which all of the atoms, here depicted as black disks, reside on their associated lattice sites. In other configurations, atoms may be displaced either left or right of their lattice sites to one of the two neighboring positions marked by an X. The rectangle r is used to aid in the determination of the ground states and the ordered phases present in the model.

site. If a pair of atoms associated with neighboring lattice sites on the same horizontal row of sites are displaced toward one another, they interact with an energy ε_A. If a pair of atoms associated with neighboring lattice sites on the same vertical row of sites are displaced in opposite directions, they interact with an energy ε_{SS}; and if one is displaced and the other remains on its associated lattice site, the pair of atoms interact with an energy ε_S.

The model has been previously studied using a Monte Carlo technique for the case in which ε_{SS} and ε_S are repulsive interactions; i.e., $\varepsilon_{SS} > 0$ and $\varepsilon_S > 0$.[1,2] In this case, vertical rows of atoms energetically favor either all being on their lattice sites or all being displaced in the same direction, left or right of their lattice sites. Two types of ordered reconstructed phases were obtained for this case of the interaction parameters.

In Section 2 we rigorously obtain the zero-temperature phase diagram for the model for almost all possible values of the four energy parameters. We show that the parameter space can be divided into regions such that in each region the ground-state configurations are of one of seven different types, including one type which is nondegenerate, four which are doubly degenerate, and two which are infinitely degenerate. Of the two types of infinitely degenerate ground states, one has a nonzero residual entropy and one does not. We also discuss the nature of the ground states which occur on the boundaries between the regions. In Section 3 the Pirogov–Sinai theory[3] is used to prove the existence at sufficiently low temperatures of four different types of ordered surface-reconstructed phases in the model.

2. THE ZERO-TEMPERATURE PHASE DIAGRAM

The calculation of the phase diagram at zero temperature consists of a specification of the ground states of the model in the various regions and on the boundaries between regions in the space of the four interaction parameters ε_R, ε_A, ε_{SS}, and ε_S.

The Hamiltonian of a configuration ξ of atoms in the model can be written as

$$H(\{n\}) = n_R \varepsilon_R + n_A \varepsilon_A + n_{SS} \varepsilon_{SS} + n_S \varepsilon_S \tag{1}$$

where n_i is the number of interactions with energy ε_i which occur in the configuration, and where $\{n\} = (n_R, n_A, n_{SS}, n_S)$.

To each rectangle $r = 1,..., (2N)^2$ of the type pictured in Fig. 1, we assign a restricted Hamiltonian H_r defined as follows. An as yet undetermined real number x is assigned to each of the n_0^r atoms which are at the corners of r, a value $\varepsilon_R/2 - x$ to each of the n_R^r atoms which are displaced from the lattice sites at the middle of the horizontal edges of r, a value $\varepsilon_A/4$ to each of the n_A^r pairs of atoms which interact with an energy ε_A along the edges of r, and a value ε_{SS} (or ε_S) if the pair of atoms associated with the sites at the middle of the horizontal edges of r interact with an energy ε_{SS} (or ε_S). The restricted Hamiltonian can then be written as

$$H_r(\{n^r\}) = n_R^r \varepsilon_R/2 + n_A^r \varepsilon_A/4 + n_{SS}^r \varepsilon_{SS} + n_S^r \varepsilon_S + (n_0^r - n_R^r)\, x \tag{2}$$

where

$$\{n^r\} = (n_R^r, n_A^r, n_{SS}^r, n_S^r, n_0^r) \tag{3}$$

The sum of the restricted Hamiltonians of all the (overlapping) rectangles r in a configuration ξ which has $\{n\}$ yields

$$H(\{n\}) = \sum_r H_r(\{n^r\}) \tag{4}$$

The sum in Eq. (4) is independent of the parameter x, for each atom which is displaced from its associated lattice site in ξ is counted with the value x with two rectangles and with the value $-x$ with two other rectangles.

The adjustable parameter x was introduced to aid in the determination of the ground-state configurations. In particular, if there exists a configuration ξ and a value of x such that the restricted Hamiltonian for every rectangle r in ξ has the value H_r^0 of the restricted Hamiltonian, and if H_r^0 satisfies

$$H_r^0 = \min_{\{n^r\}} H_r(\{n^r\}) \tag{5}$$

in a region (or a boundary between regions) D of the space of parameters ε_R, ε_A, ε_{SS}, and ε_S, then ξ is a ground-state configuration in D, and the restricted Hamiltonian is said to constitute an "m-potential."[4] Moreover, every ground-state configuration in D is composed entirely of rectangles which have the value H_r^0.

We first seek ground-state configurations in which every rectangle r has the same type of restricted configuration ξ_r. Such restricted configurations necessarily have $n_0^r = n_R^r$, and thus have a restricted Hamiltonian H_r^0 which is independent of x. The set of inequalities

$$H_r^0 < \min_{\xi_r^* \neq \xi_r} H_r(\{n^r(\xi_r^*)\}) \tag{6}$$

is used to determine the region D and the range of values of the parameter x such that the restricted Hamiltonians for restricted configurations other than type ξ_r are all strictly larger than H_r^0. This ensures that every ground-state configuration in D is composed entirely of restricted configurations of type ξ_r.

Configurations in which every rectangle r has the same type of restricted configuration account for six different types of ground-state configurations which occur in regions of the parameter space. The other type of ground-state configuration present in a region is obtained by setting $x = 0$ and determining a region D in which a small number of restricted configurations have minimal values of the restricted Hamiltonian [see Eq. (5)]. Since $H(\{n\})$ is independent of x, and since configurations can be constructed entirely from these restricted configurations with minimal restricted Hamiltonian, then all ground-state configurations in D are composed entirely of these types of restricted configurations.

We shall now describe each of the seven types of ground-state configurations which occur in regions of the parameter space. For each type we shall define the region which corresponds to ground states of that type. We shall not, however, explicitly give the range of values of x which can be used to prove which configurations are ground states in a particular region of parameter space. These ranges of x are easily calculated using Eq. (6).

The unique "nonreconstructed" (NR) configuration which has $\{n^r\} = (0, 0, 0, 0, 0)$ is the ground state in the region

$$\varepsilon_R > \max\{0, -\varepsilon_A/2\} - \min\{0, 2\varepsilon_S, \varepsilon_{SS}\} \tag{7}$$

The NR configuration is illustrated in Fig. 1. The doubly degenerate "homogeneous paired reconstructed" (HPR) configurations having

$\{n^r\} = (2, 2, 0, 0, 2)$ are the ground states in the region defined by the inequalities

$$\begin{gathered} \varepsilon_{SS} > 0, \qquad \varepsilon_A < 0 \\ \varepsilon_R + \varepsilon_A/2 < \min\{0, 2\varepsilon_S\} \end{gathered} \tag{8}$$

An HPR configuration is illustrated in Fig. 2. The doubly degenerate "homogeneous unpaired reconstructed" (HUR) configurations having $\{n^r\} = (2, 0, 0, 0, 2)$ are the ground states in the region

$$\begin{gathered} \varepsilon_{SS} > 0, \qquad \varepsilon_A > 0 \\ \varepsilon_R < \min\{0, 2\varepsilon_S\} \end{gathered} \tag{9}$$

An HUR configuration is illustrated in Fig. 2. For the case $0 < \min\{\varepsilon_{SS}, 2\varepsilon_S\}$, the three types of configurations NR, HPR, and HUR are the only ground states which occur in regions of the zero-temperature phase diagram.[1,2] This phase diagram is illustrated in Fig. 3a.

One of the doubly degenerate "zigzag paired reconstructed" (ZPR) configurations with $\{n^r\} = (2, 2, 1, 0, 2)$ is illustrated in Fig. 2. ZPR configurations are the ground states in the region

$$\begin{gathered} \varepsilon_{SS} < 0, \qquad \varepsilon_A < 0 \\ \varepsilon_R + \varepsilon_A/2 + \varepsilon_{SS} < \min\{0, 2\varepsilon_S - \varepsilon_{SS}\} \end{gathered} \tag{10}$$

The doubly degenerate "zigzag unpaired reconstructed" (ZUR) configurations, having $\{n^r\} = (2, 0, 1, 0, 2)$, are the ground-state configurations in the region defined by the inequalities

$$\begin{gathered} \varepsilon_{SS} < 0, \qquad \varepsilon_A > 0 \\ \varepsilon_R + \varepsilon_{SS} < \min\{0, 2\varepsilon_S - \varepsilon_{SS}\} \end{gathered} \tag{11}$$

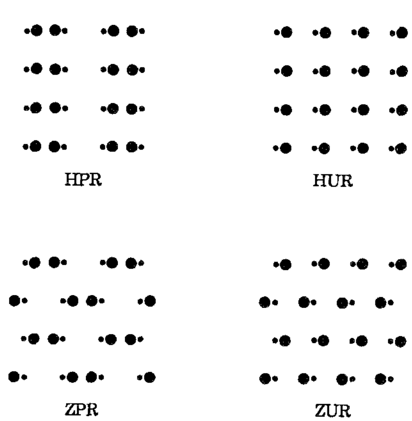

Fig. 2. Doubly degenerate ground-state configurations.

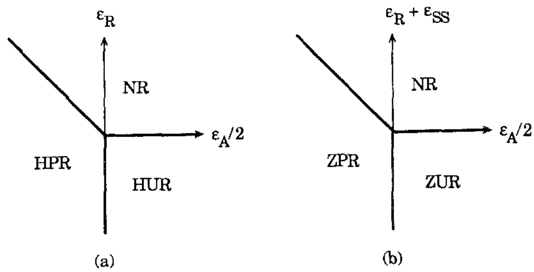

Fig. 3. Phase diagrams for the cases (a) $0 < \min\{\varepsilon_{SS}, 2\varepsilon_S\}$ and (b) $\varepsilon_{SS} < \min\{0, 2\varepsilon_S\}$.

A ZUR configuration is illustrated in Fig. 2. For the case $\varepsilon_{SS} < \min\{0, 2\varepsilon_S\}$, the NR, ZPR, and ZUR configurations are the only ground states which occur in regions of the zero-temperature phase diagram, which is illustrated in Fig. 3b.

Both of the two remaining types of ground-state configurations which occur in regions are infinitely degenerate. Configurations of one of these types, called "disordered paired reconstructed" (DPR) configurations, are composed entirely of rectangles with the single restricted configuration specified by $\{n^r\} = (1, 1, 0, 1, 1)$. One such restricted configuration is illustrated in Fig. 4. The DPR configurations are the ground states in the region defined by the inequalities

$$\begin{aligned} &\varepsilon_A < 0, \qquad 2\varepsilon_S < -|\varepsilon_R + \varepsilon_A/2| \\ &\varepsilon_R + \varepsilon_A/2 + \varepsilon_{SS} > 2\varepsilon_S - \varepsilon_{SS} \end{aligned} \tag{12}$$

The number of DPR configurations can be counted as follows. If alternate atoms on a vertical row are displaced from their lattice sites (not all in the

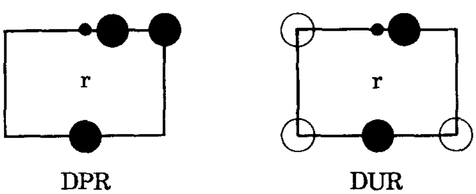

Fig. 4. The types of restricted configurations which occur on every rectangle r in each of the infinitely degenerate ground-state configurations of type DPR or DUR. The small dots represent lattice sites, the black disks represent atoms, and the white disks represent positions which can be either vacant or occupied by atoms. The restricted configurations are of a single type in the DPR ground states, and the restricted configurations can be any one of six types in the DUR ground states.

same direction), and the other atoms on the row remain on their lattice sites, the DPR configuration is completely specified by the configuration on this single vertical row. If the alternate atoms on this vertical row are all displaced in the same direction, the possible DPR configurations are composed of pairs of vertical rows of paired atoms, with two configurations possible for each such pair of vertical rows of atoms. Hence, for a lattice with $2N$ vertical and $2N$ horizontal rows of atoms, there are $4(2^N-1)$ DPR configurations. Thus the DPR ground states, although infinitely degenerate, have no residual entropy.

The infinitely degenerate ground-state configurations of the other type, called "disordered unpaired reconstructed" (DUR) configurations, are composed entirely of rectangles with configurations having one of the specifications $\{n^r\}=(1,0,0,1,n_0^r)$, where $n_0^r=0, 1$, or 2. These types of restricted configurations are illustrated in Fig. 4. The DUR configurations are the ground states in the region defined by

$$\begin{gathered} \varepsilon_A>0, \qquad 2\varepsilon_S<-|\varepsilon_R| \\ \varepsilon_R+\varepsilon_{SS}>2\varepsilon_S-\varepsilon_{SS} \end{gathered} \tag{13}$$

Without counting all of the DUR configurations, it is easy to see that they are infinitely degenerate and have a nonzero residual entropy. For example, there are $2\cdot 2^{2N^2}$ DUR configurations in which alternate atoms on every vertical and every horizontal row are all displaced from their lattice sites, the other half of the $4N^2$ atoms remaining on their associated lattice sites.

From Eqs. (12) and (13) it follows that the two types of infinitely degenerate ground states, DPR and DUR, occur in regions of parameter space only for the case $2\varepsilon_S<\min\{0,\varepsilon_{SS}\}$. The zero-temperature phase diagram for this case is illustrated in Fig. 5.

We now briefly discuss the ground states on the boundaries between the various regions in Figs. 3 and 5 and for the values of the parameters not explicitly considered in Figs. 3 and 5.

Using Eq. (5), one can show that the boundary in Fig. 3b between the regions with ground states of types NR and ZPR has a triply degenerate ground state which consists of the single NR configuration and the two ZPR configurations. All of the other boundaries between regions in Figs. 3 and 5 have infinitely degenerate ground-state configurations.

The special cases in which two of 0, $2\varepsilon_S$, and ε_{SS} are equal to each other and less than the third were not explicitly considered in Figs. 3 and 5. Although not stated, the ground states for the special case $2\varepsilon_S=0<\varepsilon_{SS}$ are correctly given both in Fig. 3a and in Figs. 5a and 5b, and the ground states for the special case $2\varepsilon_S=\varepsilon_{SS}<0$ are correctly given both in Fig. 3b and in Figs. 5c and 5d. The ground state for the special case $\varepsilon_{SS}=0\leqslant 2\varepsilon_S$

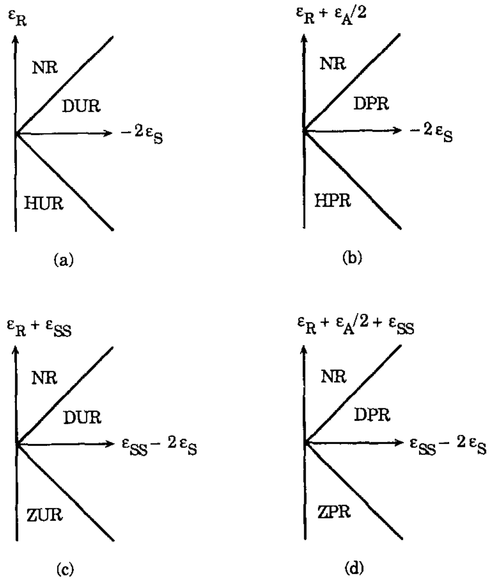

Fig. 5. Phase diagrams for the case $2\varepsilon_S < \min\{0, \varepsilon_{SS}\}$ and (a) $\varepsilon_{SS} > 0, \varepsilon_A > 0$; (b) $\varepsilon_{SS} > 0, \varepsilon_A < 0$; (c) $\varepsilon_{SS} < 0, \varepsilon_A > 0$; (d) $\varepsilon_{SS} < 0, \varepsilon_A < 0$.

is the nondegenerate NR configuration in the region given by Eq. (7) and can be shown to be infinitely degenerate otherwise. (The case $\varepsilon_S = \varepsilon_{SS} = 0$, like the case $\varepsilon_A = 0$,[2] corresponds to a one-dimensional system which has no phase transition.)

In Section 3 the Pirogov–Sinai extension[3] of the Peierls argument[5] is used to prove that ordered surface-reconstructed phases similar in structure to the four types of doubly degenerate ground-state configurations pictured in Fig. 2 exist in the model at sufficiently low temperatures.

3. EXISTENCE OF ORDERED PHASES AT FINITE TEMPERATURES

As demonstrated in Section 2, the ground-state configurations for the model are doubly degenerate in each of the four regions defined by Eqs. (8)–(11) in the space of the interaction parameters ε_R, ε_A, ε_{SS}, and ε_S. These four types of ground-state configurations, HPR, HUR, ZPR, and ZUR, are pictured in Fig. 2. In each of these four regions of parameter space, the doubly degenerate ground-state configurations are composed entirely of rectangles r having a single type of restricted configuration ξ_r

which has a value H_r^0 of the restricted Hamiltonian. For a range of values of the adjustable parameter x, H_r^0 satisfies Eq. (6); i.e., it is less than the restricted Hamiltonian for any other restricted configuration.

Since the restricted Hamiltonian is a finite-ranged m-potential[4] (see Section 2), and since the ground states are finitely degenerate in the regions defined by Eqs. (8)–(11), then Holsztynski and Slawny[6] have shown that the Pirogov–Sinai[3] extension of the Peierls argument[5] is sufficient to prove the existence of multiple equilibrium states at sufficiently low temperatures in each of these regions of the space of interaction parameters. Since the interactions in the model are finite-ranged, the equilibrium state is unique at high temperatures.[7] Consequently, a phase transition occurs at finite temperature in each of the regions of parameter space defined by Eqs. (8)–(11).[8]

These multiple equilibrium states which exist at low temperatures correspond to ordered surface-reconstructed phases which are small perturbations of the ground states in each of the four regions of parameter space defined by Eqs. (8)–(11). Since series expansion techniques can be used to show that the system is disordered at high temperatures, then the phase transitions which occur are presumably order–disorder transitions.

In addition, since the nonreconstructed (NR) configuration pictured in Fig. 1 is the unique ground-state configuration in the region of parameter space given by Eq. (7), and since the restricted Hamiltonian is an m-potential in this region, then the Pirogov-Sinai theory[3,6] proves the existence in this region of parameter space of a low-temperature phase in which nearly all of the atoms reside on their associated lattice sites.

In the regions of parameter space given by Eqs. (12) and (13), the ground-state configurations are, respectively, the infinitely degenerate DPR and DUR configurations. We have not determined the nature of the low-temperature phases which occur in these two regions of parameter space.

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