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Ordered Structure of Adatoms in the Extended Range Lattice Gas Model

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The ordered structure of adatoms is discussed in the light of a theory which determines rigorously the ground state of the extended range lattice gas model. Several examples are discussed to show that an appearance or absence of an ordered structure at a particular density yields informations about the adatom interaction. The intermediate phase which may appear at finite temperatures is discussed briefly.

§1. Introduction

Ordered arrays of adatoms are found in many cases of the adsorption process of simple gases.[1] For example, Na atoms on the W (110) surface are found to be arranged in order when the ratio of Na atoms to W atoms on the surface is equal to 1/6, 1/4 and 1/3.[2] In the present paper we discuss the condition for the appearance of ordered structures with the classical lattice gas model in which we assume that the sites where adatoms sit in are equivalent to each other and form a two dimensional lattice. We introduce pairwise interactions between adatoms whose range is finite, but extended beyond the nearest neighbor sites. Determining the structure of lowest energy of the model for arbitrary density of adatoms, we shall show that ordered structures appear at several characteristic values of the density which are determined by the lattice geometry and relative magnitudes of 1st, 2nd,$\cdots$ neighbor interactions. Thus we can deduce a certain amount of informations about the adatom interaction from the experimental observation of appearance or absence of an ordered structure at these characteristic values of density.

The rapid decrease of the magnitude of the adatom interaction concluded by Einstein and Schrieffer[3] in the case of the neutral chemisorption may support the above-mentioned assumption of a finite interaction range. As will be discussed later, the analysis which assumes a sufficiently extended range will be meaningful even in the case of the ionic chemisorption. We carry out the analysis by use of a method used in the discussion of the magnetization process of the Ising antiferromagnet which can determine the ground state rigorously in most cases.[4] Emphasizing the principle and general consequences of the analysis rather than details of individual cases, we discuss several simple examples such as the triangular and square lattices with 1st and 2nd neighbor interactions in this paper. The effect of the 3rd neighbor interaction will be mentioned briefly. We discuss also the face-centered rectangular lattice with up to 7th neighbor interactions which may correspond to the Na on W (110) case. Also the phase transitions at finite temperatures is discussed briefly at the end.

§2. Determination of the Ground State of the Model Hamiltonian

We start with the Hamiltonian given by

$$H=\sum_{\mathrm{k}}J_{\mathrm{k}}p_{\mathrm{k}}, \tag{1}$$

where J_{k} which can be either positive (repulsive) or negative (attractive) is the interaction constant of the k-th neighbor interaction; p_{k} is the total number of the k-th neighbor pairs of adatoms. In order to eliminate the edge effect, we assume that the lattice is on the surface of the three dimensional torus. We assume that J_{k}'s are independent of the density. Though this assumption may not be justified always, the analysis with fixed constants will be useful even for elucidating the significance of the density dependence of the interaction constants.

There exist several geometrical inequalities which restrict the lowest possible values of certain linear combinations of p_{k}'s for a given value of the density. By use of these inequalities we can determine the lowest possible value

Table I. Examples of geometrical inequalities for the triangular lattice. N is the total number of lattice sites; θ is the ratio of the number of adatoms to N. Inequalities are referred in the text by use of notations shown in the second column.

Inequalities		Definition of M's
$D_1 \equiv p_1+p_2 \geqq M(40)$	(d1)	$M(40)=0$ for $\theta \leqq 1/4$, $N(4\theta-1)$ for $1/4 \leqq \theta \leqq 1/2$,
$D_2 \equiv 5p_1+p_2 \geqq 3M(40)$	(d2)	$N(8\theta-3)$ for $1/2 \leqq \theta \leqq 3/4$,
$F_1 \equiv p_1 \geqq M(30)$	(f1)	$N(12\theta-6)$ for $3/4 \leqq \theta \leqq 1$.
$F_2 \equiv p_2 \geqq M(30)$	(f2)	$M(30)=0$ for $\theta \leqq 1/3$, $N(3\theta-1)$ for $1/3 \leqq \theta \leqq 2/3$,
$G_1 \equiv -p_1+p_2 \geqq M(31)$		$N(6\theta-3)$ for $2/3 \leqq \theta \leqq 1$.
$H_1 \equiv -p_2 \geqq 3M(21)$		$M(31)=-N\theta$ for $\theta \leqq 1/2$, $N(\theta-1)$ for $1/2 \leqq \theta \leqq 1$.
$H_2 \equiv -2p_1+p_2 \geqq 3M(21)$		$M(21)=-N\theta$ for $\theta \leqq 1$.

of H as a function of the density. Table I shows some of the inequalities pertaining to p_1 and p_2 of the triangular lattice. These inequalities are derived quite straightforwardly by a general method which we discuss about elsewhere.[5] If $J_1>0$, $J_2>0$ and $J_k=0$ for $k \geqq 3$, we rewrite the Hamiltonian given by eq. (1) by use of the lhs. of inequalities (d1) and (d2) in the Table I as

$$\begin{aligned} &H=(J_1-5J_2)p_1+J_2D_2 \\ \text{or } &H=(5J_2-J_1)(D_1/4)+(J_1-J_2)(D_2/4) \\ \text{or } &H=J_1D_1+(J_2-J_1)p_2. \end{aligned} \tag{2}$$

The quadrant $J_1>0$ and $J_2>0$ in the J_1-J_2 plane can be divided into three regimes, $J_1>5J_2>0$, $5J_2>J_1>J_2>0$, and $J_2>J_1>0$. One of the energy expressions given by eq. (2) has positive coefficients for p's or D's in each regime. With Such an energy expression the inequalities (d1), (d2), (f1) and (f2) tell us the lowest limit of the energy for a given density θ. For example, we obtain in the case of $J_2>J_1>0$

$$H \geqq J_1M(40)+(J_2-J_1)M(30), \tag{3}$$

where the definitions of θ, N and M's are given in Table I. The structures $S(1/4)$, $S_2(1/3)$, $S_3(1/3)$ and $S_1(1/2)$ shown in Fig. 1 satisfy the equality in the inequalities for H as well as in the inequalities (d1) and (f2) at $\theta=1/4$, $1/3$ and $1/2$. $S_2(1/3)$ and $S_3(1/3)$ are degenerate in energy in this case. We can see easily then that a mixture of $S(1/4)$ and $S_{2\text{ or }3}(1/3)$ with appropriate ratio satisfies the equality in the limit of $N\to\infty$ for the range $1/4<\theta<1/3$; similarly a mixture of $S_{2\text{ or }3}(1/3)$ and $S_1(1/2)$ will be the state of lowest energy for the range $1/3<\theta<1/2$.

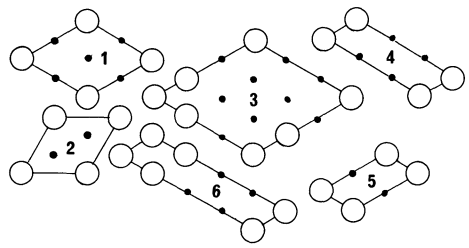

Fig. 1. Unit cells of the ordered structures in the case of the triangular lattice with 1st and 2nd neighbor interactions. Open circles represent the sites occupied by adatoms; small black spons are vacant sites. In the text and Table II the structure 1 is referred as $S(1/4)$ (note that it appears at $\theta=1/4$), 2 as $S_1(1/3)$, 3 as $S_2(1/3)$, 4 as $S_3(1/3)$, 5 as $S_1(1/2)$ and 6 as $S_2(1/2)$. Structures with $\theta>1/2$ are omitted (see text).

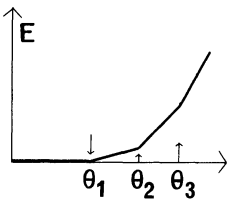

Fig. 2. A schematic representation of the energy vs θ curve.

We can carry out the analysis for the whole ranges of J_1 and J_2, using appropriate inequalities. Generally the ground state energy vs θ curve is represented by a broken line such as shown in Fig. 2. At each inflection point of the curve an ordered structure appears; note that the inflection points correspond to those θ values at which the rhs. of the inequalities used in the analysis change their θ dependence. The restrictions imposed on the values of p_k's by the inequalities help us greatly to find the ordered structures satisfying the equality condition. It is

Table II. The ordered structures in the case of the triangular lattice with 1st and 2nd neighbor interactions. Those appearing in the region $\theta > 1/2$ are omitted (see text).

Regime	Ordered Structures
$J_1 > 5J_2 > 0$	$S(1/4)$, $S_1(1/3)$, $S_1(1/2)$
$5J_2 \geqq J_1 \geqq J_2 > 0$	$S(1/4)$, $S_1(1/2)$
$J_2 > J_1 > 0$	$S(1/4)$, $S_{2or3}(1/3)$, $S_1(1/2)$
$J_2 > -J_1 \geqq 0$	$S_{2or3}(1/3)$, $S_2(1/2)$*
$-J_1 \geqq J_2 > -J_1/2 > 0$	$S_2(1/2)$
$-J_1/2 \geqq J_2$, $J_1 \leqq 0$	no structure
$J_1 > 0$, $J_2 \leqq 0$	$S_1(1/3)$

*If $J_1 = 0$, no structure is expected at $\theta = 1/2$.

to be noted also that whenever on ordered structure appears at $\theta = \theta_0$, we find another ordered structure at $\bar{\theta}_0 = 1 - \theta_0$ because of the particle-hole symmetry. The structure at $\bar{\theta}_0$ is obtained by interchanging the sites occupied by adatoms with vacant sites in the structure at θ_0. Table II together with Figs. 1 summarizes the result of the analysis for the triangular lattice with the 1st and 2nd neighbor interactions. When the 3rd neighbor interaction is introduced, the result becomes quite complicated. A (5×5) structure, for example, may appear in the process. Details of the analysis will be published elsewhere.[5]

In the case of the square lattice with 1st and 2nd neighbor interactions the $c(4 \times 2)$ and $p(2 \times 2)$ structures which are degenerate in energy appear at $\theta = 1/4$ if $J_1 > 0$ and $J_2 > 0$, being followed by $c(2 \times 2)$ in the regime $J_1 > 2J_2 > 0$ and by $p(1 \times 2)$ in the regime $2J_2 > J_1 > 0$. In the cases, $2J_2 > -J_1 \geqq 0$ and $J_1 > 0$, $J_2 \leqq 0$, the ordered structure appears at $\theta = 1/2$ only, with the $p(1 \times 2)$ in the former case and $c(2 \times 2)$ in the latter case. When $-J_1 \geqq 2J_2$, $J_1 \leqq 0$ (J_2 can be either positive or negative), no ordered structure appears for $\theta < 1$. When the third neighbor interaction is introduced, we have the possibility of finding ordered structures at $\theta = 1/5$, 1/4, 1/3, 2/5, 3/7, 1/2 and their counterparts in the regime $\theta > 1/2$. For example, in the case where both conditions, $J_1 > 2J_2 > 4J_3 > 0$ and $J_1 > (2J_2 + 2J_3)$, are satisfied, the ordered structures appear at $\theta = 1/5$, 1/4, 1/3 and 1/2 for $\theta \leqq 1/2$; the structure at $\theta = 1/5$ is $p(\sqrt{5} \times \sqrt{5})$ with basis vectors pointing in the directions [21] and [12] and the one at $\theta = 1/3$ is such that every three rows in the directions parallel to a diagonal of the square are occupied by adatoms; those at $\theta = 1/4$ and 1/2 are $c(4 \times 2)$ and $c(2 \times 2)$. From the analysis for the whole ranges of J_1, J_2 and J_3, we conclude that $c(4 \times 2)$ appears in the regime $J_1 > 2J_2 > 4J_3 > 0$ only. Details of the analysis will be given elsewhere.[5]

§3. Face-Centered Rectangular Lattice with up to 7th Neighbor Interactions

The Na atoms on W (110) case may be discussed with the face-centered rectangular lattice. Since the adatom interaction in this case may arise partly from the electric dipolar interaction, the applicability of the model which assumes a finite interaction range is questionable. Nevertheless we may suppose that near neighbor interactions are mainly responsible for the formation of an ordered structure, since the contribution made by far neighbor interactions will be almost independent of the structure. From this point of view we carry out first the analysis of a finite range model.

Figure 3 shows the observed structures and the definitions of up to 7th neighbor interactions which are numbered in order of distance. If we assume $J_k > 0$ for $k = 1, 2, \cdots 7$ and neglect farther interactions, the $c(2 \times 4)$ structures appears at $\theta = 1/8$ (see Fig. 3 for definition of the basis vectors). We can show than that if $J_1 >$

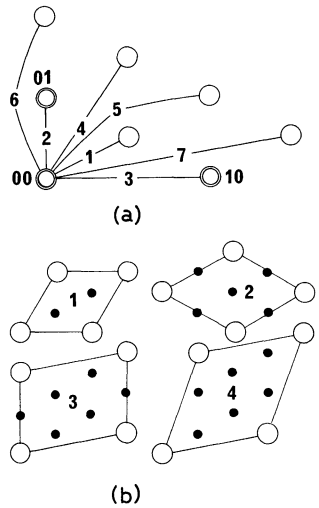

Fig. 3. (a) The coordinates of sites and k-th neighbors ($k = 1, 2, \cdots, 7$) of a site of the face-centered rectangular lattice on the W(110) surface. (b) Structures in the Na on W(110) case. Structures 1, 2 and 3 are observed at $\theta = 1/3$, 1/4 and 1/6, respectively.[2] Structure 4 is a possible one at $\theta = 1/7$.

$(5/2)(J_6+J_7)$, $J_2>2(J_6+J_7)$, $J_3>(J_6+2J_7)$, $J_4>(J_6+J_7)$, $J_5>(J_6+J_7)$ and $J_7>J_6$ are satisfied, the observed structure at $\theta=1/6$ (see Fig. 3) follows the structure at $\theta=1/8$. If one of these conditions is violated, a different ordered structure will be the next one. In particular, if $J_6>J_7$ as expected in the dipolar interaction, the structure shown in Fig. 3 will appear at $\theta=1/7$. This conclusion is supported also by our calculation of the dipolar energies of the structures at $\theta=1/6$, $1/7$ and $1/8$ which includes far neighbor interactions. Thus if the absence of the $\theta=1/7$ structure is established experimentally, we can conclude that an indiredt interaction should be present to reverse the order of J_6 and J_7 in magnitude. Between $\theta=1/6$ and $\theta=1/4$ there are possibilities of finding ordered structures at $\theta=1/5$ and $2/9$, though the dipolar calculation seems to support the direct transition from the structure at $\theta=1/6$ to that at $\theta=1/4$ shown in Fig. 3. Further details will be reported in future.[5]

§4. Concluding Remarks

We may conclude that if we can establish the sequence of ordered structures in the adsorption process experimentally, we can determine the regime into which the interaction constants fall in. Even the appearance or absence of a particular structure may provide us with an information; we have mentioned the case of the $c(4\times2)$ structure of the square lattice and the $\theta=1/7$ structure in the face-centered rectangular lattice as examples. Since experiment is done at finite temperatures, however, we have to be aware of the possibility that the transition temperature of an ordered structure is below the temperature where experiment is done. The transition temperature of an ordered structure at a low value of θ is expected generally to be relatively low because of the high entropy of the disordered state. There is another possibility that a new structure may appear at finite temperatures as an intermediate phase between the ordered structure and the disordered one. For example, the $\theta=1/4$ structure in the face-centered rectangular lattice may undergo a transition to the structure in which the lattice is divided into two sublattices, one consisting of the corner sites and another of the face-centered sites, with a uniform distribution of adatoms within each sublattice, but with different occupation probability between the two sublattices. Adopting the mean field approximation,* we can show that this intermediate phase exists if the ratio

$$R=2(2J_1-J_2-J_3+2J_4-2J_5-J_6+2J_7)/(J_2+J_3-2J_5-J_6)$$

exceeds 2.33. When R is equal to 5 which is rather close to the value 4.38 estimated by assuming the dipolar interaction, this intermediate phase undergoes the transition to the disordered phase at $T\cong1.9T_{c1}$, where T_{c1} is the transition temperature between the $\theta=1/4$ structure shown in Fig. 3 and the intermediate one.

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*In this argument, the effect of vibration of adatoms is neglected.