Monte Carlo study of linear chain submonolayer structures.
Application to Li/W(112)

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The lattice gas model for adsorption of alkaline elements on W(112) surface is studied by Monte Carlo simulations. The model includes dipole–dipole interaction as well as long-range indirect interaction. The numerical results show that truncation of the indirect interaction even at 200 Å may change a phase diagram, i.e., new phases containing domain walls might occur. It is demonstrated that a defected phase can exist at high temperatures even if it is not stable at T=0. The phase diagram for Li/W(112) is constructed and long periodic chain structures (9×1), (6×1), (4×1), (3×1), and (2×1) are found to be stable at low temperatures. Role of thermal fluctuation is discussed by comparison of Monte Carlo results with mean field approximation results.

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I. INTRODUCTION

Chemisorption on metal surfaces has been studied for over 30 years.
1,2,3,4,5,6,7,8,9
. One of interesting problems concerns with structures and phase transitions in chemisorbed submonolayers. In particular alkaline, alkaline-earth, and rare-earth elements adsorbed on W(112) and Mo(112) form linear chain structures.
8,9 In case of low coverages (θ < 0.5), the commensurate phases with chains normal to the troughs of the substrate are observed. The period of these structures changes from 2 to 9.

It is intention of this paper to study phase diagrams by Monte Carlo simulations. This method was successfully applied to lattice gas models with short range interactions.
1,2,3,4,5,6,7,8,9 On the other hand, one can expect more difficult problems in case of long range interactions, e.g., occurrence of complicated structures.
18,19,20,21
. The paper is organized as follows. In section 2 the lattice gas model is described. Two difficulties connected with application of Monte Carlo simulations to this model are discussed in section 3. In section 4 phase diagrams are presented and section 5 contains discussion and conclusions.

II. THE MODEL

In the previous paper
22 we introduced the lattice gas model of linear chain submonolayer structures on the (112) surface of W and Mo. Adsorption sites form the rectangular lattice (see Fig. 1) with \( a_x = a \sqrt{2} \) and \( a_y = a \sqrt{3}/2 \), where \( a \) denotes the lattice constant of the bcc elementary cell. The model Hamiltonian within the grand canonical ensemble, is defined as

\[
H = \frac{1}{2} \sum_{i,j; i \neq j} V_{ij} n_i n_j - \mu \sum_i n_i,
\]

where \( n_i \) is the occupation variable at each adsorption site \( i \) with \( n_i = 1 \) if the \( i \)th site is occupied by an adatom and \( n_i = 0 \), if not. The chemical potential is denoted by \( \mu \) and \( V_{ij} = V(|r_i - r_j|) \) is the pairwise interaction consisting of electrostatic and indirect interactions

\[
V(|r|) = \frac{2d^2}{|r|^3} \left\{ \begin{array}{ll}
A \cos(2k_F |y| + \varphi) & \text{for } y \neq 0 \\
E_0 \delta(|x|, a_x) & \text{for } y = 0
\end{array} \right.
\]

The first part of Eq. (2), \( 2d^2/|r|^3 \), describes a repulsive dipole–dipole interaction between two adatoms with identical dipole moments \( d \). The second term in Eq. (2) represents an asymptotic part of the indirect interaction between adatoms via conduction electrons of the substrate. This particular interaction is highly anisotropic...
and is closely related to the existence of nearly flattened segments of the Fermi surface being perpendicular to the [111] axis directed along the atomic troughs of the substrate[13,14]. It is also possible that contribution to this interaction comes from quasi-one-dimensional surfaces states[22]. Very recently, G. Godzik et al[14] suggested that oscillatory indirect interaction of this form is, in case of Sr/Mo(112), induced by charge density waves involving surfaces states. An amplitude $A$ and a phase $\varphi$ can be treated as phenomenological parameters and $k_F$ denotes a wavenumber of electrons at the Fermi surface. Finally, for $y = 0$ there is an attractive indirect interaction $E_b$ between the nearest neighbours along the x-direction which is responsible for the chain formation.

In this work we choose the set of model parameters the same as proposed in the previous paper[10] for adsorption of lithium on W(112) surface, i.e., $d = 1.5D$, $A = -0.137eV\AA$, $k_F = 0.41A^{-1}$, $\varphi = 1.26\pi$, $E_b = -0.05eV$, and $a = 3.16A$. We will use a reduced chemical potential $\mu/\mu_0$ with $\mu_0 = k_BT$, $T = 100K$. Although the interaction described by Eq. (2) is long-range we introduce finite range of this interaction in Monte Carlo study. The dipole-dipole interaction is accounted for distances between adatoms smaller than $R_m$ and the indirect interaction along the y-direction for distances smaller than $Y_m$ (see Fig. 1).

The adatom coverage $\theta$ is defined as

$$\theta = \frac{1}{N} \sum_i < n_i >,$$

where $N$ is the number of adsorption sites and angle brackets mean a thermodynamic average.

It is convenient to transcript the lattice gas model as

Ising model by introducing spin variables $s_i = 1 - 2n_i$,

$$H = \frac{1}{8} \sum_{i,j} V_{ij} s_i s_j - H \sum_i s_i,$$

where the magnetic field $H$ is expressed by the chemical and interaction potentials:

$$H = -\frac{\mu}{2} + \frac{1}{4} \sum_{ij} V_{ij}.$$

Using Ising Hamiltonian, Eq. (4), we can perform simulation in the canonical ensemble which is equivalent to simulation of the lattice gas, Eq. (1), in the grand canonical ensemble. Of course, the former method is much easier.

III. MONTE CARLO METHOD

In Monte Carlo simulation we employ standard Metropolis algorithm to Ising Hamiltonian, Eq. (4), on finite rectangular lattice of $L_x \times L_y$ sites with periodic boundary conditions (PBC). Quantities such as magnetisation $M$, specific heat $C_H$, and energy $E$ are obtained as

$$M = \frac{1}{N} \sum_i < s_i >,$$

$$C_H = \frac{1}{Nk_BT^2} \left( < H^2 > - < H >^2 \right),$$

$$E = \frac{1}{N} < H >,$$

where $N = L_x L_y$ is the number of spins. We will use the relation between coverage $\theta$ and the magnetisation $M : \theta = (1 - M)/2$. Since we are interested in linear chain structures we measure also magnetisation at each row of the lattice

$$M_j = \frac{1}{L_x} \sum_i < s_{i,j} >,$$

where

$$r_i^{(j)} = (ia_x, ja_y),$$

Having $M_j$ one can calculate coverage at $j$th lattice row $\theta_j = (1 - M_j)/2$.

To study phase diagram we calculate the correlation function $< s_j s_l >$ and the structure factor defined as

$$S(q) = \frac{1}{N^2} \sum_{j,l} < s_j s_l > \exp(iq(r_j - r_l)),$$

where $q$ is a wavevector from reciprocal space. This function is used to recognize an ordered phase.

We encountered two difficulties in examination of phase diagrams by Monte Carlo method:
FIG. 2: Ground states in the chemical potential / lattice size $\mu/\hbar\omega$ plane for range of indirect interaction $Y_m = 72$. Regions denoted by 2 and 3 correspond to phases $(2 \times 1)$ and $(3 \times 1)$. For detailed description of states 2a and 2b see the text.

1. The dependence of the results on range of the indirect interaction.

2. The dependence of the resulting spin structure, at low temperatures, on an initial spin configuration.

In the previous paper we studied this model within the molecular field approximation (MFA) finding several ordered phases of $(p \times 1)$ type in phase diagrams. The $(p \times 1)$ structure at $T = 0$, has every $j$th row (for $j = 1, 2, \ldots, L_y/p$) occupied by adatoms and remaining rows empty. Therefore, coverage in this structure $\theta = 1/p$ and the structure factor $S(q)$ reaches maximum at $q = (0, 2\pi/(p\omega))$. The phase diagram constructed for the Li/W(112) system contains the $(2 \times 1)$, $(3 \times 1)$, $(4 \times 1)$, $(6 \times 1)$, and $(9 \times 1)$ linear chain structures. Performing Monte Carlo simulations we observed that additional ordered structures can occur in a phase diagram. It may happen when the range of indirect interaction $Y_m$ is shorter than the linear lattice size along the y-direction $L_y$. We start investigation of this problem by checking the influence of indirect interaction range on the ground states. As an example we present in Fig. 2 a part of ground-state diagram for constant range of interaction $Y_m = 72$ and different values of the lattice size $L_y$. We see that only two phases, $(2 \times 1)$ and $(3 \times 1)$, are present in this part of phase diagram when the interaction range $Y_m$ is close to the lattice size ($L_y < 108$). An additional phase denoted as (2a) appears for $L_y > 108$. This is linear chain structure consisting of two domains of the $(2 \times 1)$ phase and separated by two empty rows. Thus it has coverage $\theta = (L_y - 2)/(2L_y)$. It is worth noting that the $(2 \times 1)$ phase has two domains: one with adsorbate chains placed in even lattice rows and the second with chains in odd rows. The configuration of the (2a) phase at $L_y = 144$ may be represented by sequence of distances between subsequent chains in the following way $\{2_{31}, 3_{1}, 2_{34}, 3_{1}\}$, where $l_j$ denotes sequence of $j$ identical distances $l$. When range of interaction is nearly $1/4$ of $L_y$ then another phase (2b), containing four domain walls, occurs in the phase diagram (see Fig. 2). It looks like double (2a) phase, e.g., the (2b) phase can be represented by following sequences of distances $\{2_{34}, 3_{1}, 2_{34}, 3_{1}, 2_{31}, 3_{1}, 2_{27}, 3_{1}\}$ for $L_y = 264$. In a part of diagram corresponding to lower coverage (not shown in Fig. 2) there are also phases containing walls and domains of $(4 \times 1)$, and $(6 \times 1)$ long periodic structures but detailed discussion will not be presented here. It worth to mention at this place, that the (2a) phase can occur in the temperature phase diagram, even if the (2a) phase is not a ground state. In order to check the role of the boundary conditions, we performed additional calculation of the ground states using free edge boundary condition along the y-direction. The same defected phases where obtained but the number of domain walls was reduced by one. Above discussion shows that truncation of long-range indirect interaction in our model causes some technical difficulties in applying Monte Carlo method, e.g. it can be impossible to study finite-size scaling. On the other hand, the truncation of the interaction interpreted as screening effect might be important from physical point of view because it generates defected phases containing domain walls.

The second problem observed in our Monte Carlo calculation, dependence of resulting configuration on the initial spin configuration, is due to presence of short range attractive interaction between the nearest neighbours along the x-direction. When linear chain structure is formed at low temperature, it is difficult to change the period of such structure by changing temperature or chemical potential using single spin flip Metropolis algorithm. We study a phase diagram performing MC runs at constant magnetic field (or chemical potential) by cooling down or heating up the sample. The simulation start from high temperature in the cooling down process and after thermalization and measurement temperature is lowering the by $\Delta T$ then such procedure is repeated till $T = 0$. At each temperature, all quantities are measured after $2 \times 10^4$ MC steps per spin during subsequent 5000 MC steps. The final spin configuration at $T$ is used as initial one at $T - \Delta T$. For some values of $H$ the cooling down process finishes at $T = 0$ with configuration having energy greater than energy of ground-state. Hence this way can produce metastable phases. To overcome this problem we use heating up process which starts at temperature $\Delta T$ with ground-state configuration as the initial spin configuration. In subsequent temperature steps, $T_i = T_{i-1} + \Delta T$, the specific heat $C_H$ and the mean energy $\langle H \rangle$ are measured. This allow us to calculate the entropy

$$S(T) = \int_0^T \frac{C_H(T')}{T'} \,dT',$$

by numerical integration. Then the free energy can be
obtained as 

\[ F(T) = \langle H \rangle - TS(T) \].

Repeating simulations at given \( H \) with different ground-state configurations as initial configurations, we can find a phase with the lowest free energy at temperature \( T \).

IV. PHASE DIAGRAMS

To study phase diagrams by Monte Carlo simulations we used method described in the previous section, i.e., simulations at constant chemical potential (or magnetic field) with variable temperature. The phase transition between ordered phases is determined by examination of free energies of appropriate phases. Temperature of transition from disordered phase to an ordered one is determined from behaviour of the structure factor \( S(q) \), specific heat \( C_H \) or sublattice magnetisation \( M_j \). Lattice sizes \( L_x, L_y \) used in our simulations are rather small due to long-range interaction and large number of MC runs needed to construct phase diagrams. Most simulations were performed for \( 20 \times 72 \) lattice sites, but some calculations were performed on \( 40 \times 72 \) and \( 20 \times 144 \). Periodic boundary conditions were assumed, therefore \( L_y \) was chosen as multiplicity of 36 in order to allow formation of ideal chain structures with period 2, 3, 4, 6, and 9, which exist in the ground-state phase diagram.

It has been shown in the previous section that defected ordered structure can occur when \( Y_m < L_y \). We now discuss the thermal stability of such structure for two sets of parameters \( L_y \) and \( Y_m \). We see in Fig. 3a that the \( (2a) \) phase dominates the part of phase diagram corresponding to intermediate coverage and it pushes down the phase \( (2 \times 1) \). Hence, it is impossible to pass directly from the ordered \( (2 \times 1) \) phase to the disordered phase. More interesting case is shown in Fig. 3b where the \( (2a) \) phase occurs at high temperatures, although it is not stable at \( T=0 \). In this case, the \( (2a) \) phase is also placed between the \( (2 \times 1) \) phase and the disordered phase. We think, that this is important result because it shows that analysis of the ground states is not sufficient to find all ordered phases. The phase \( (2a) \) has two interesting features

1. The wavevector \( q = (0, 2\pi(L_y - 2)/(2L_ya_y), at which the structure factor has maximum, does not depend on temperature.

2. The sublattice order parameters vanish at some temperatures whereas the behaviour of \( S(q) \) indicates the existence of ordered structure.

The first feature indicates that the phase \( (2a) \) is not an incommensurate phase. In order to understand the second feature we performed simulations with different Monte Carlo measurement times. If the time of measurement is not too long (e.g., \( 5 \times 10^6 \) MC time steps at \( T = 300K \)) we observe (see Fig. 3b) that order in this structure changes spatially along \( y \)-direction. The disorder appears near domain walls but as one moves form the wall the chain structure emerges with increasing ordering. On the other hand we found that domain walls and the whole structure are moving along the \( y \) direction during simulation. This is a reason why the sublattice order parameters vanish if averaging time is long enough (see Fig. 4 where results of simulations with different averaging time are presented) but the structure factor remains finite.

A. Application to Li/W(112)

Linear chain structures \( (2 \times 1), (3 \times 1), \) and \( (4 \times 1) \) were observed in the experiment of adsorption of lithium atoms on W(112) surface. Using MFA method, we have shown that lattice gas model, Eq. 1, describes such sequence of structures. Now we present results of Monte Carlo simulations. To avoid occurrence of phases with domain walls of \( (2a) \) type, we chose the range of indirect interaction equal to the linear size of the lattice along \( y \) direction, i.e., \( Y_m = L_y \). Most simulations were performed on \( 20 \times 72 \) lattice and sometimes the lattice of \( 40 \times 72 \) sites was used. The range of dipole-dipole interaction was \( R_m = 12a_y \). The ranges of these interactions used in previous MFA studies were both equal to \( 36a_y \). Therefore we also repeated the MFA calcula-
smaller than MFA critical temperature (the MFA critical ordered linear chains structures at temperatures much ent. Thermal fluctuations, not present in MFA, destroy the upper part of the diagram situation is quite differ-
diagram does not depend on the method. However in (T, Fig. 5 we plot results of MFA and MC methods in the
potential plane for \( \theta \). As previously, MFA calculation were performed compare the MFA results with Monte Carlo simulation
tions for present values of interaction ranges in order to
MFA results with Monte Carlo simulation results. As previously, MFA calculation were performed for all structures of \((p \times 1)\) type with \(p\) up to 12. In Fig. 5, we plot results of MFA and MC methods in the
(\(T,\mu\)) phase diagram. A low temperature part of the diagram does not depend on the method. However in the upper part of the diagram situation is quite different. Thermal fluctuations, not present in MFA, destroy ordered linear chains structures at temperatures much smaller than MFA critical temperature (the MFA critical
temperature for the \((2 \times 1)\) phase can be even two times greater). Moreover, MFA results do not allow to reach long periodic phases \((4 \times 1)\) and \((6 \times 1)\) directly from the disordered phase. On the other hand results of MC simulations show that all ordered phases can be reached from disordered phase in wide range of chemical potential. It is interesting to look at results of MC study presented in the (temperature - coverage) phase diagram (see Fig. 6).

Ordered phases of \((p \times 1)\) are separated by mixed phases \((p, p')\) which denotes mixture of \((p \times 1)\) phase and \((p' \times 1)\) phase. It is worth noting that ordered chain structures with period 6 and 9, present in the phase diagram, were not observed in experiments which were performed at temperatures above 77K. We expect that these phases could be observed experimentally at temperatures below 77K.

Now, we are going to discuss the order of the phase transitions. The phase transitions between the ordered phases, e.g., \((2 \times 1) \to (3 \times 1)\), are of the first order because sublattice order parameters and structure factors change discontinuously at the transition points. The analysis of the phase transition from an ordered phase to the disordered phase is much more complicated. Checking temperature dependence of the structure factor and heat capacity (some results are shown in Fig. 4) we found that the transition to \((9 \times 1)\) and \((6 \times 1)\) phases is the first-order phase transition because of discontinuity of the structure factor. The transition to the \((3 \times 1)\) and \((4 \times 1)\) phases seems to be continuous transition. It is difficult to state the order of the phase transition form the disordered phase to the \((2 \times 1)\) phase. Although, the structure factor seems to be continuous function of temperature, the heat capacity is smeared near the transition temperature indicating the first-order phase transition. On the other hand, in the MFA calculation this phase transition is of the second order. One of possible explanation of this discrepancy is based on observation of additional, very weak maxima of the structure factor with the wave vector close to \(q = (0, \pi / (a_y))\) and temperature in the

FIG. 4: The deviation of row coverage \(\theta_i\) from the lattice coverage \(\theta\) (denoted by bars) calculated at \(T = 300K, \mu = 22\mu_0, Y_m = 72, L_y = 144\), and for averaging time (a) \(5 \times 10^4\) (b) \(10^6\) MC steps per spin.

FIG. 5: Phase diagram in the temperature / the chemical potential plane for \(Y_m = L_y = 72\). Mean-field results are denoted by thick lines and Monte Carlo results are represented by circles (a thin line serve as guide for an eye).

FIG. 6: Monte Carlo phase diagram in the temperature / coverage plane for \(Y_m = L_y = 72\). Results of simulations are represented by circles.
narrow range of the transition temperature. This can suggest that defected phases like the 2(a) phase are still present close to the transition temperature. In order to answer whether this problem is connected with the finite range of indirect interaction one should performed finite-size calculation with infinite range of the interaction. It can be done by employing a numerical method to accelerate the convergence of a Fourier series.

V. DISCUSSION AND CONCLUSIONS

Our Monte Carlo analysis revealed that truncation of the indirect interaction changes a phase diagram even if the interaction range is very large. New phases containing domain walls occur at high temperatures between the disordered phase and the (p x 1) phase. This problem complicates study of critical behaviour via finite-size scaling. One possible solution of such problem is accounting for infinite range of indirect interaction. It can be carried out by employing a numerical method to accelerate the convergence of a Fourier series in the same way as in earlier paper. However, it would be time consum-

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