

Statistics of Adsorption on Top and Bridge Sites of a Square Lattice: Transfer-Matrix Approach

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Statistics of particles adsorbed on the lattice with a complex elementary cell are analyzed by employing the transfer-matrix technique. The results obtained are compared with those given by the cluster approximation and also with the experimental data for the CO/Ni(100) system. The transfer-matrix technique is shown to be very effective for studies of two-dimensional systems with complex lattices.

KEY WORDS: Lattice-gas model; lateral interactions; single-crystal surfaces.

1. INTRODUCTION

Adsorbed overlayers at finite coverages represent an example of nonideal statistical systems. To describe the phase diagrams of such overlayers and also rate processes with the participation of adsorbed particles, lattice-gas models are often used.⁽¹⁻⁴⁾ As a rule, the lattice (square, triangular, or honeycomb) is assumed to have only one fine type of site. On the other hand, there are also many real systems with two or more types of adsorption sites. For example, Fig. 1 shows the (100) face of fcc metals such as Pt, Pd, and Ni. In this case, there are at least three types of geometrically-different points (fourfold, top, and bridge) and each of them may in principle serve as an adsorption site.

In the present paper, we will consider the statistics of adsorption on a square lattice with two (top and bridge) types of sites (Fig. 2). A real prototype of this model is given by CO adsorption on the (100) face of fcc metals.⁽⁵⁾ In particular, the recent careful studies of CO adsorption on

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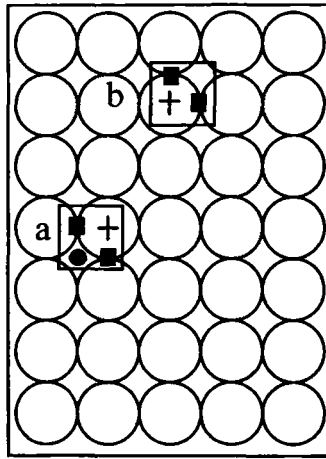


Fig. 1. The (100) face of fcc metals: (a) the elementary cell with all the possible types of geometrically different points, (b) the elementary cell for CO/Ni(100).

Ni(100) by Fourier transform infrared adsorption reflection spectroscopy (FTIRAS) show that at room temperature and below the CO molecules are located simultaneously with considerable probability both on top and bridge sites.⁽⁶⁻⁸⁾

The model under consideration was investigated by using the 12-site cluster approximation.⁽⁹⁾ Employing the transfer-matrix technique, we demonstrate below that the results provided by the cluster approximation are usually correct globally, but often miss important minor details.

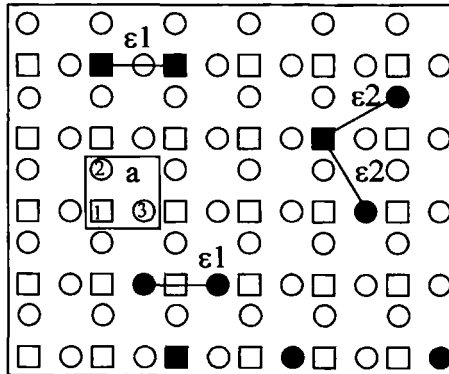


Fig. 2. Decorated lattice for the model under consideration. Empty and occupied sites are shown respectively by open and filled circles and squares. ϵ_1 and ϵ_2 indicate the energy of the nearest neighbor and next-nearest neighbor lateral interaction. (a) The elementary cell.

Concluding the introduction, we note that the lattice shown in Fig. 2 belongs to the class of so-called decorated lattices.^(10,11) For such lattices, the lattice-gas model can sometimes be exactly solved (i.e., the partition function can be represented as an explicit analytical expression). In the case under consideration, the exact solution, to our knowledge, is lacking.

2. MODEL AND METHOD

To simulate adsorption on top and bridge sites of a square lattice, we use the same assumptions as in ref. 9:

- (i) At low coverages, the energy of adsorption on top and bridge sites is considered to be zero and ΔE , respectively.
- (ii) Simultaneous adsorption of two molecules on two nearest neighbor top and bridge sites or on two nearest neighbor bridge sites is prohibited. To refer to such a restriction the term "spatial constraint" is employed below.
- (iii) We take into account the nearest neighbor and next-nearest neighbor lateral interactions, ε_1 and ε_2 (Fig. 2). Note that here and below we use the terms "nearest neighbor" and "next-nearest neighbor" with respect to pairs which become nearest neighbor and next-nearest neighbor after excluding the arrangements which do not satisfy the spatial constraint rule formulated in the paragraph above.
- (iv) In addition, we will take into account the difference in the vibrational partition functions for adsorption on top and bridge sites. Significant contribution to the partition functions arises only from low-frequency vibrations. In the case of CO adsorption on the (100) face of fcc metals, the frequencies are known to be low only for two degenerate frustrated translations on top sites and for one frustrated translation on bridge sites.

Our goal is to calculate the relative population of top and bridge sites. To solve this problem, one can in principle employ the cluster approximation, transfer-matrix technique, or Monte Carlo simulations. In practice, however, the Monte Carlo method is not effective, because the nearest neighbor lateral interactions may be large, and under such circumstances it is rather difficult to reach equilibrium. The cluster approximation with four top sites, eight bridge sites, and periodic boundary conditions (Fig. 3) was used in ref. 9. The disadvantage of this approach is known to be connected with its inability to describe formation of ordered structures with large unit cells. As shown below, this case is realized at some sets of the model

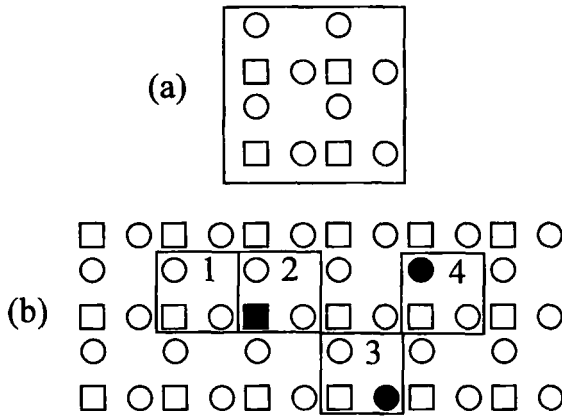


Fig. 3. (a) Cluster used for calculation of top and bridge populations in ref. 9. (b) Elementary cell and its four possible states.

parameters, and in such cases the results given by the cluster approximation are not accurate.

Let us consider now application of the transfer-matrix technique for calculating the top- and bridge-site populations. General principles on how to use this technique for describing the lattice statistics are well known^(12, 13) (for application of this approach to solving kinetic problems, see refs. 14–17). As usual in the transfer-matrix technique, we consider a strip which is infinite along the *Y* axis and finite along the *X* axis. The strip contains *M* elementary cells in the latter direction (we employed *M* = 4). The elementary cell corresponding to the model and its four possible states are shown in Fig. 3. The periodic boundary conditions are also introduced along the *X* axis. Thus, we study the lattice-gas model on the cylinder. As was shown for simpler systems, the accuracy at *M* = 4 is better than a few percent.⁽¹⁸⁾

Using a standard definition of the transfer matrix, we can write the matrix elements for such system as follows (we set $k_B = 1$)

$$T_{ij} = \exp(\frac{1}{2}v_i + \frac{1}{2}v_j + v_{ij}) \tag{1}$$

where

$$v_i = -\frac{\epsilon_1}{T} \sum_{k=1}^M (n_{1,i,k}n_{1,i,k+1} + n_{2,i,k}n_{2,i,k+1} + n_{3,i,k}n_{3,i,k+1}) - \frac{\epsilon_2}{T} \sum_{k=1}^M (n_{1,i,k}n_{2,i,k+1} + n_{2,i,k}n_{1,i,k+1}) + \frac{(\mu + 2T \ln f_i)}{T} \sum_{k=1}^M n_{1,i,k} + \frac{(\mu + T \ln f_b - \Delta E)}{T} \sum_{k=1}^M (n_{2,i,k} + n_{3,i,k}) \tag{2}$$

$$\begin{aligned}
 v_{ij} = & -\frac{\varepsilon_1}{T} \sum_{k=1}^M (n_{1,i,k}n_{1,j,k} + n_{2,i,k}n_{2,j,k} + n_{3,i,k}n_{3,j,k}) \\
 & -\frac{\varepsilon_2}{T} \sum_{k=1}^M (n_{1,i,k}n_{3,j,k} + n_{3,i,k}n_{1,j,k} + n_{2,i,k}n_{1,j,k+1} + n_{1,j,k}n_{3,i,k+1})
 \end{aligned}
 \tag{3}$$

In fact, these matrix elements are the Boltzmann factors of two nearest rings on the cylinder. Thus, indexes i and j indicate the possible states of the rings.^(12, 13, 17) Here $n_{1,i,k}$, $n_{2,i,k}$, $n_{3,i,k}$ are the occupation numbers for sites in the elementary cell (Fig. 3) which are located on the k th place in the ring and are in the i th state, and

$$f_i = 1/[1 - \exp(-\hbar\omega_i/T)] \tag{4}$$

$$f_b = 1/[1 - \exp(-\hbar\omega_b/T)] \tag{5}$$

are the vibrational partition functions for frustrated translations [the factor 2 in Eq. (2) arises from degeneracy of the vibrations on top sites].

Without spatial constraints, the number of possible states of the rings is 4^M and the transfer-matrix size is $4^M \times 4^M$. Taking into account the spatial constraints, the transfer-matrix size can be reduced compared to $4^M \times 4^M$ (from 256×256 down to 136×136 for $M = 4$).

The transfer matrix defined above is nonsymmetric and its right- and left-hand-side eigenvectors corresponding to the maximum eigenvalue are different. The calculation of the top-and bridge-site populations can be carried out as follows:

$$\theta_h = \frac{\sum_i u_{l,i} u_{r,i} n_{2,i,1}}{\sum_i u_{l,i} u_{r,i}} \tag{6}$$

$$\theta_{tot} = \frac{\sum_i u_{l,i} u_{r,i} (n_{1,i,1} + n_{2,i,1} + n_{3,i,1})}{\sum_i u_{l,i} u_{r,i}} \tag{7}$$

where $u_{l,i}$ and $u_{r,i}$ are the i th components of the left- and right-hand-side eigenvectors corresponding to the maximum eigenvalue.

To calculate the eigenvectors of the transfer matrix, we have employed the standard iteration procedure.

3. RESULTS AND DISCUSSION

As pointed out in the introduction, our goal is to calculate the relative population of top and bridge sites. At low coverage ($\theta_{tot} \ll 1$) the spatial

constraints are negligible, the lateral interactions are negligible as well, and the relative population of top and bridge sites is given by

$$\theta_t/\theta_b = (f_t^2/2f_b) \exp(\Delta E/T) \quad (8)$$

At finite coverages, the transfer-matrix calculations have been done for the same sets of parameters as in ref. 9.

The results of calculations are shown in Figs. 4–7. It is easily seen that relation (8) is fulfilled both for the transfer-matrix results and for the cluster approximation.⁽⁹⁾ In addition, one can conclude that the results given by the two approaches are close at $\theta_{\text{tot}} < 0.5$. This is explained by the absence of ordered structures with a large elementary cell at these coverages. For the lateral interactions (repulsion) shown in Fig. 2, the only ordered structure, formed on the bridge or top sites (depending on the sign of ΔE) near $\theta_{\text{tot}} = 0.5$ at relatively low temperature, has a $c(2 \times 2)$ symmetry (the corresponding elementary cell is small). (An accurate analysis of the ground state at low and high coverages for the introduced model is given in ref. 9.)

Let us consider now the statistics at $\theta_{\text{tot}} > 0.5$. In this case, the coverage dependence of the relative population of different sites predicted by the transfer-matrix technique has features which are lacking in that given by the cluster approximation. For example, the transfer-matrix technique predicts that the bridge fraction as a function of the total coverage has extremum at $\theta_{\text{tot}} = 2/3$ (often maximum or sometimes minimum). The magnitude of the extrema is equal to 0.5 at low temperatures. To understand these extrema more deeply, it is instructive to calculate the adsorption isotherms (Fig. 8). The horizontal segments on these isotherms corresponding to some “ideal” ordered structure are easily seen at $\theta_{\text{tot}} = 2/3$. The analysis of the ground state for the system under consideration indicates that with the lateral interactions shown in Fig. 2 the ordered phase with the $c(3 \times 2)$ elementary cell seems to be formed at $\theta_{\text{tot}} \simeq 2/3$. This ordered structure is exhibited in Fig. 9. The size of the elementary cell of the ordered phase is larger in this case than the cluster size used in ref. 9. This is a reason for the difference between the results obtained by the transfer-matrix technique and the cluster approximation at $\theta_{\text{tot}} > 0.5$. Here it is relevant to note that employing the transfer-matrix technique, we calculate the population of top and bridge sites in fact for the $M \times \infty$ cluster. Thus, the ordered phases with arbitrary size of the elementary cell along the Y axis are automatically taken into account in the framework of our approach.

Finally, we make a few comments on the CO/Ni(100) system. In this case, the maximum coverage measured is about 0.67.^(6–8, 19) The relative

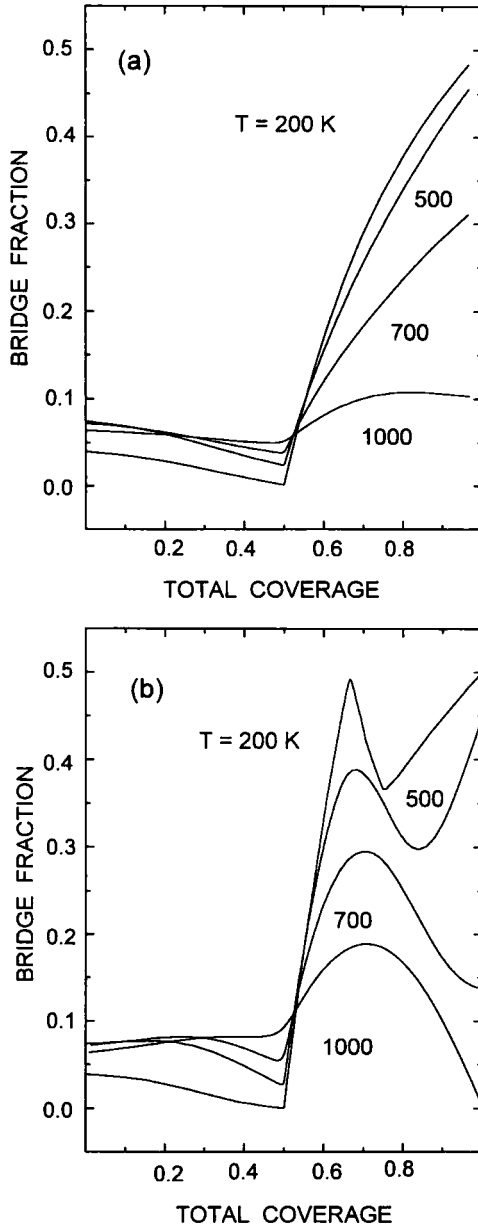


Fig. 4. Fraction of molecules adsorbed on bridge sites as a function of the total coverage for $\Delta E = 1$ kcal/mol, $\varepsilon_1 = 4$ kcal/mol, $\varepsilon_2 = 1$ kcal/mol, and $h\omega_l = h\omega_b = 5$ meV at different temperatures (as indicated in the figure): (a) the results obtained by the cluster approximation;⁽¹⁹⁾ (b) the results predicted by the transfer-matrix technique with $M = 4$.

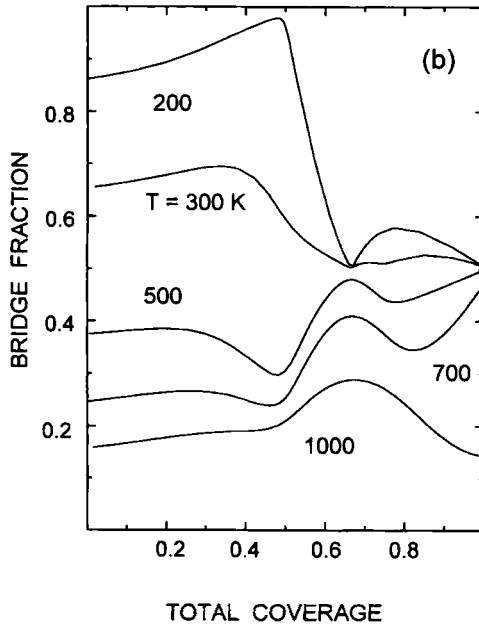
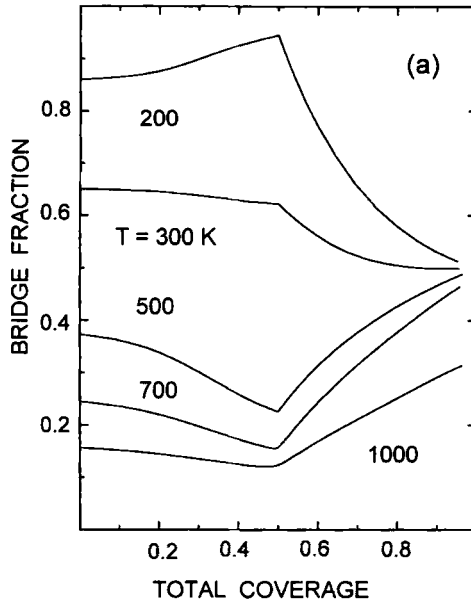


Fig. 5. As in Fig. 4, for $\Delta E = -1$ kcal/mol, $\epsilon_1 = 4$ kcal/mol, $\epsilon_2 = 1$ kcal/mol.

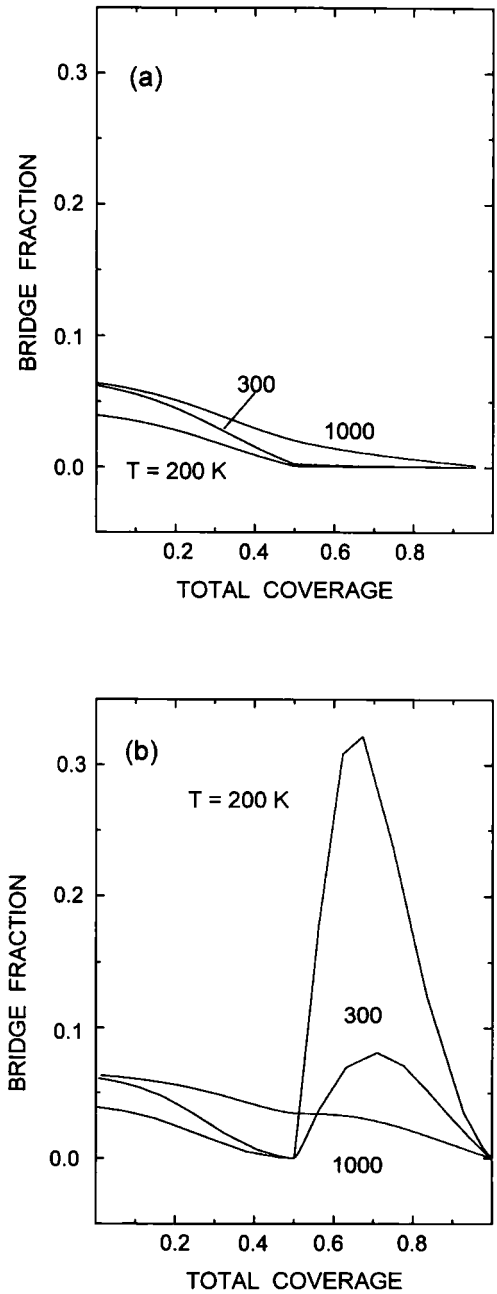


Fig. 6. As in Fig. 4, for $\Delta E = 1$ kcal/mol, $\varepsilon_1 = 3$ kcal/mol, $\varepsilon_2 = 2$ kcal/mol.

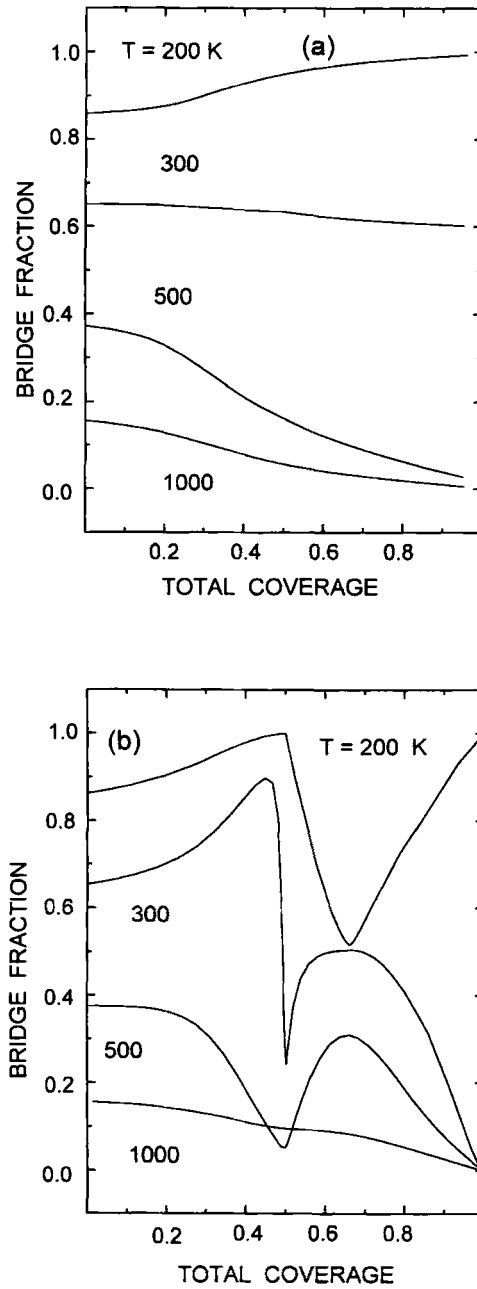


Fig. 7. As in Fig. 4, for $\Delta E = -1\text{ kcal/mol}$, $\varepsilon_1 = 3\text{ kcal/mol}$, $\varepsilon_2 = 2\text{ kcal/mol}$.

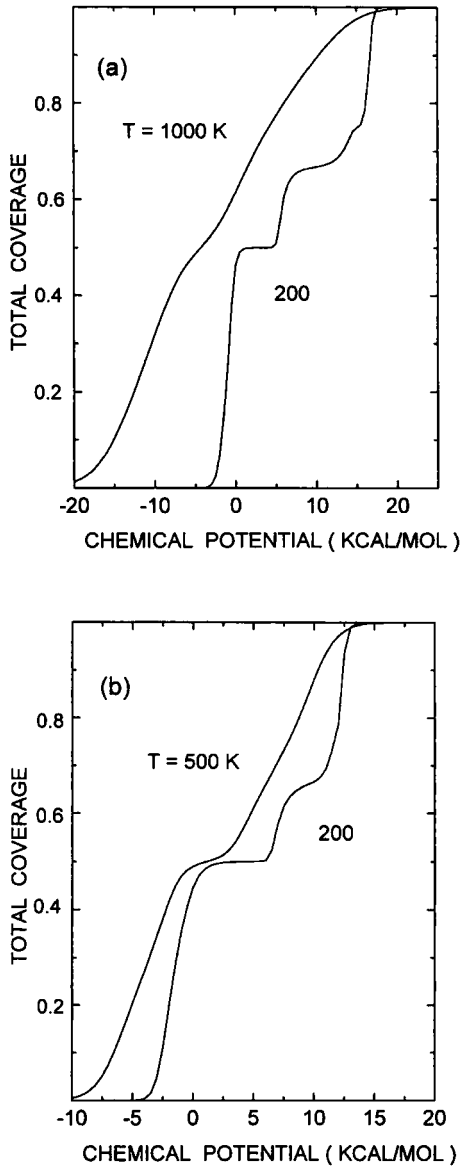


Fig. 8. Isotherms obtained by the transfer-matrix method at $M=4$ at high and low temperatures (as indicated in the figure): (a) $\Delta E=1$ kcal/mol, $\varepsilon_1=4$ kcal/mol, $\varepsilon_2=1$ kcal/mol, and $\hbar\omega_t=\hbar\omega_b=5$ meV; (b) $\Delta E=-1$ kcal/mol, $\varepsilon_1=3$ kcal/mol, $\varepsilon_2=2$ kcal/mol, and $\hbar\omega_t=\hbar\omega_b=5$ meV; (c) isotherms calculated at $T=300$ K with $\Delta E=-20$ meV, $\hbar\omega_t=3.2$ meV, $\hbar\omega_b=3.7$ meV [the notation (3, 0) means $\varepsilon_1=3$ kcal/mol and $\varepsilon_2=0$ kcal/mol, etc.].

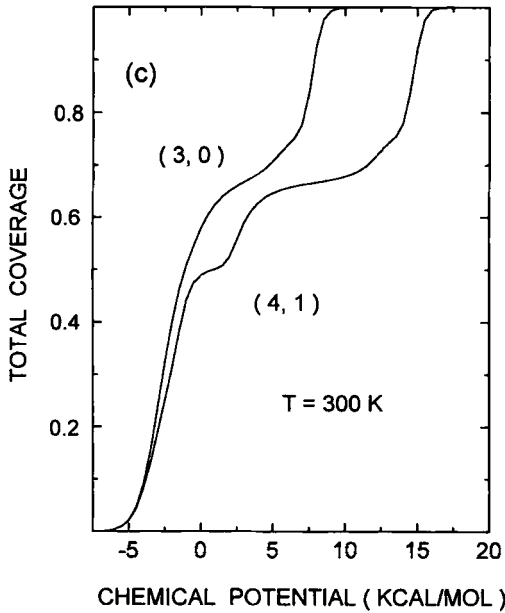


Fig. 8 (Continued)

population of top and bridge sites obtained in the experiment at $\theta_{tot} < 0.67^{(18)}$ are close to those predicted by the transfer-matrix technique for the model under consideration with the parameters proposed in ref. 9 (Fig. 10).

It is also of interest that the transfer-matrix technique yields, in agreement with the experiment, a more rapid growth of the bridge fraction at $0.5 < \theta_{tot} < 0.67$ compared to that given by the cluster approximation.

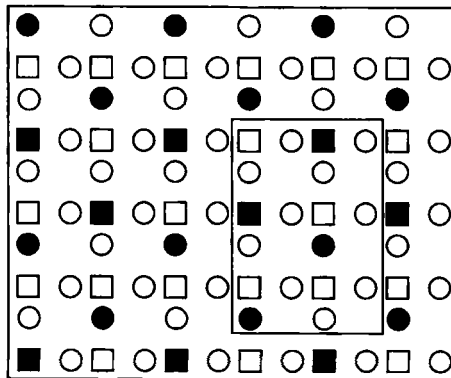


Fig. 9. Ordered $c(3 \times 2)$ structure at $\theta_{tot} = 2/3$ and $\theta_t = \theta_b = 1/3$.

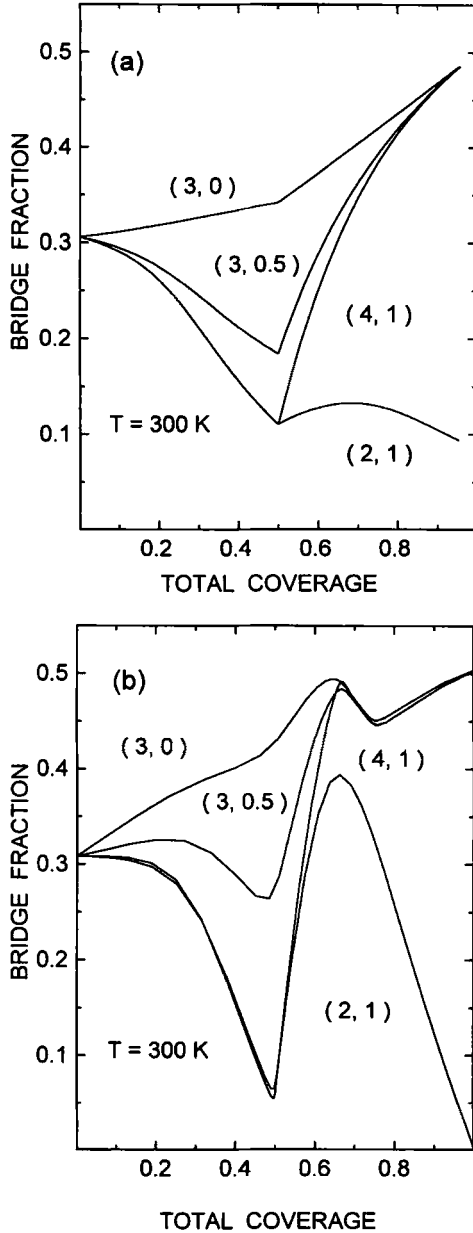


Fig. 10. Fraction of CO molecules adsorbed on bridge sites as a function of coverage calculated at $T = 300 \text{ K}$ with $\Delta E = -20 \text{ meV}$, $\hbar\omega_i = 3.2 \text{ meV}$, $\hbar\omega_b = 3.7 \text{ meV}$, and several sets of the adsorbate-adsorbate interactions [the notation $(3, 0)$ mean $\varepsilon_1 = 3 \text{ kcal/mol}$ and $\varepsilon_2 = 0 \text{ kcal/mol}$, etc.].

4. CONCLUSION

We have shown that the transfer-matrix technique is very effective for studies of the statistics of adsorption on periodic lattices with a few types of adsorption sites per elementary cell. In particular, this technique can describe rather accurately ordered phases with a large elementary cell.

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