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# Adsorption on surfaces with molecular-scale heterogeneities

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The Ono–Kondo lattice model for the density gradient near a surface is applied to surfaces where the adsorbate–adsorbent interactions are not homogeneous. While solving the general equations would be quite complex, relatively simple solutions can be obtained for periodic surfaces such as a checkerboard. It is shown that the adsorption behavior on surfaces with molecular-scale heterogeneities is very different from adsorption on surfaces where the surface heterogeneities are much larger than the size of the adsorbent molecules. © *1996 American Institute of Physics.* [S0021-9606(96)04610-7]

## I. INTRODUCTION

The behavior of adsorption on heterogeneous surfaces has been discussed widely.[1–14] Surface inhomogeneities have been classified[9] as having patchwise, random, medial, or regular (periodic) distributions of adsorption sites on the surface. These are illustrated in Fig. 1.

Previous theoretical treatments of this subject have considered patchwise[9,10] and random[12–14] surfaces by assuming a distribution function describing the strength of the adsorbate–adsorbent interactions. Then the adsorption isotherm for the entire surface is calculated by averaging (or integrating) over this distribution function.[4] This implies that adsorption on areas with different energies are independent, i.e., lateral interactions between adsorbate molecules on surface sites with different energies are not taken into consideration. This approximation is reasonable if the regions with the same energies are large compared to the molecular size (i.e., the patchwise model[9]). It also is reasonable when the adsorbate–adsorbate interactions are small. However, many real systems do not satisfy these conditions. Even seemingly homogeneous surfaces (like faces of monocrystals or surfaces of liquids) have periodic variations in the surface potential. To our knowledge there are no previous analytic treatments of adsorption behavior on periodic heterogeneous surfaces or on surfaces where the heterogeneities are of molecular size.

In principle, a general statistical mechanical treatment should allow one to take into account multiple potential functions for adsorbate–adsorbent interactions. However, this leads to complicated integral equations which do not result in explicit expressions for the adsorption isotherm. Even for the simplest systems (which also give very interesting results[15]) analytical solutions have not been possible. Therefore, simplified models, like the lattice model presented here, can provide important insights because analytic solutions are possible.

## II. LATTICE MODEL FOR DENSITY GRADIENTS

Here we consider lattice theory for a one-component adsorbate where $i$, $j$, and $k$ are the three dimensions of the lattice coordinates. We assume the lattice fluid is in contact with a flat surface at the plane of $i=0$ and that the first layer of adsorbed molecules is in the plane of $i=1$. There are interactions between nearest neighbors with $\epsilon$ being the energy of adsorbate–adsorbate interactions, and $\epsilon_s$ is the energy for adsorbate–surface interactions. The classical Ono–Kondo equations[16,17] of thermodynamic equilibrium for this system relate the density in each layer to the densities in the adjacent layers and to the density in the bulk through the mean-field approximation. The one-dimensional Ono–Kondo lattice theory has been used to describe homogeneous surfaces.[17–20] For a general treatment of surface heterogeneities it is necessary to consider the Ono–Kondo equations in three dimensions and to couple them to boundary conditions that describe the surface (energy) topology. Though the three-dimensional Ono–Kondo theory has been implied previously,[17] to our knowledge these equations have not been solved.

The Ono–Kondo equations are based on relatively simple mean-field assumptions. Consider taking an adsorbate molecule at a site with coordinates $i$, $j$, $k$ and moving it to an empty site infinitely distant from the surface. This is equivalent to the exchange of a molecule with a vacancy,

$$A_{i,j,k}+V_{\infty}\rightarrow V_{i,j,k}+A_{\infty}, \tag{1}$$

where $A$ is the adsorbate molecule, and $V$ is the vacancy (empty site) that it fills (and vice versa). If this exchange occurs at equilibrium, then

$$\Delta H-T\Delta S=0, \tag{2}$$

where $\Delta H$ and $\Delta S$ are the enthalpy and entropy changes, and $T$ is the absolute temperature.

The value of $\Delta S$ can be represented in the form,

$$\Delta S=k_B \ln W_1-k_B \ln W_2, \tag{3}$$

where $W_1$ is the number of configurations where the site with coordinates $i$, $j$, $k$ is occupied by an adsorbate molecule and the infinitely distant site is empty, and $W_2$ is the number of configurations where the infinitely distant site is occupied by an adsorbate molecule and the site with coordinates $i$, $j$, $k$ is empty. Here $k_B$ is Boltzmann's constant.

If the overall number of configurations for the system is $W_0$, then in mean-field lattice approximation

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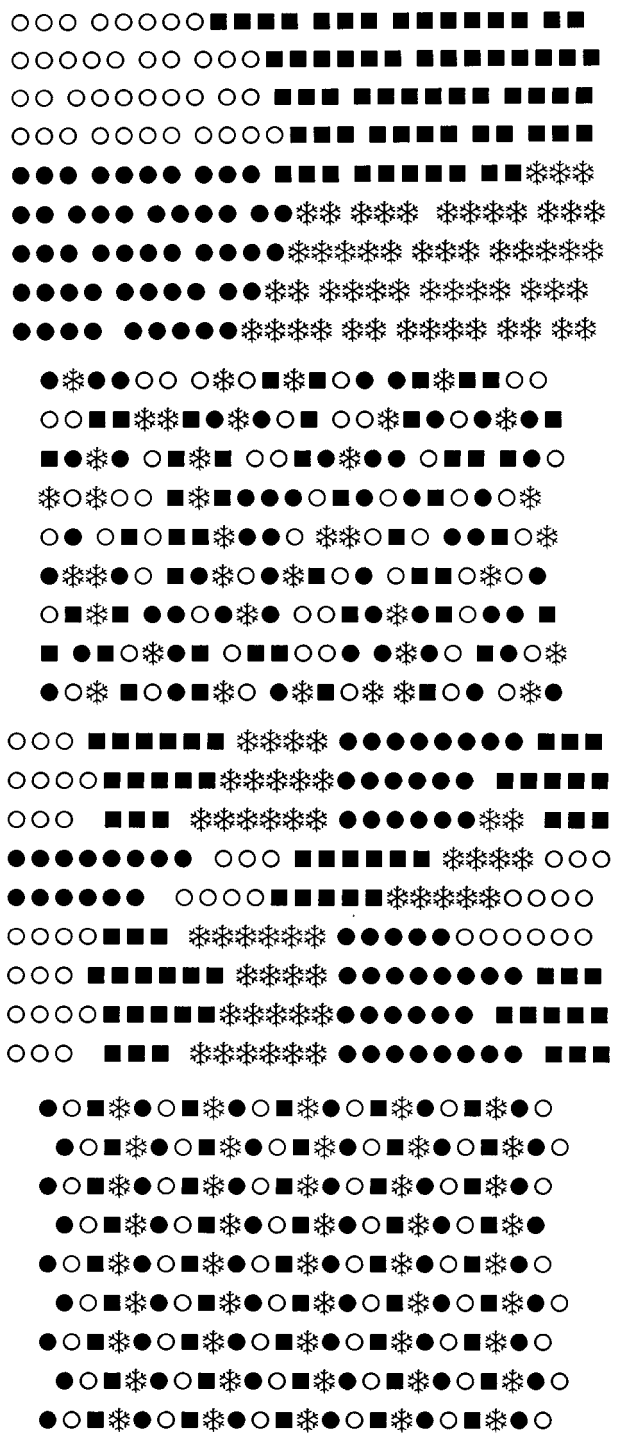


FIG. 1. Different types of surface inhomogeneities.

$$W_1/W_0 = x_{i,j,k}(1-x_\infty) \tag{4}$$

and

$$W_2/W_0 = (1-x_{i,j,k})x_\infty, \tag{5}$$

where $x_{i,j,k}$ is the probability that the site with coordinates $i$, $j$, $k$ is occupied by an adsorbate molecule, and $x_\infty$ is the bulk mole fraction of adsorbate.

Substituting Eqs. (4) and (5) into Eq. (3) we have

$$\Delta S = k_B \ln\{[x_{i,j,k}(1-x_\infty)]/[(1-x_{i,j,k})x_\infty]\}. \tag{6}$$

The change in enthalpy can be calculated in the mean-field approximation for a simple cubic lattice by considering the number of neighboring sites that are occupied near the surface compared to the bulk. Then,

$$\Delta H = -(x_{i+1,j,k}+x_{i-1,j,k}+x_{i,j+1,k}+x_{i,j-1,k}+x_{i,j,k+1} + x_{i,j,k-1}-6x_\infty)\epsilon. \tag{7}$$

From Eq. (2) and Eqs. (6) and (7) it follows that

$$\ln\{[x_{i,j,k}(1-x_\infty)]/[(1-x_{i,j,k})x_\infty]\} + (x_{i+1,j,k}+x_{i-1,j,k}+x_{i,j+1,k}+x_{i,j-1,k}+x_{i,j,k+1} + x_{i,j,k-1}-6x_\infty)\epsilon/k_BT = 0. \tag{8}$$

Equation (8) is the Ono–Kondo equation[17] for three dimensions. It relates the local density in each site $(i,j,k)$ to the density in the bulk. It is applicable to all molecular layers with $i \geqslant 2$.

## III. HOMOGENEOUS SURFACE

Before considering the general three-dimensional case for a heterogeneous surface, it will be useful to discuss the predictions of Eq. (8) for a homogeneous surface. In this case, the value of $x_{i,j,k}$ depends only on $i$ and Eq. (8) becomes one-dimensional,

$$\ln\{[x_i(1-x_\infty)]/[(1-x_i)x_\infty]\} + (x_{i+1}+x_{i-1}+4x_i-6x_\infty)\epsilon/k_BT = 0. \tag{9}$$

This equation relates the density in each layer (i) to the densities in the adjacent layers and to that in the bulk.

In order to solve Eq. (9) for values of $i \geqslant 2$, we must specify a boundary condition for $i=1$. For a homogeneous surface, this is

$$\ln\{[x_1(1-x_\infty)]/[(1-x_1)x_\infty]\} + (x_2+4x_1-6x_\infty)\epsilon/k_BT + \epsilon_s/k_BT = 0, \tag{10}$$

where $\epsilon_s$ is the adsorbate–surface interaction energy.

The one-dimensional Ono–Kondo equations [Eqs. (9) and (10)] have been used previously to describe homogeneous surfaces.[17–21] When there are no adsorbate–adsorbate interactions, $\epsilon=0$, and it follows from Eq. (10) that

$$x_1 = x_\infty/[x_\infty+(1-x_\infty)\exp(\epsilon_s/k_BT)], \tag{11}$$

which is the Langmuir isotherm.[22] If $x_2=x_\infty$ (monolayer adsorption) and $x_\infty \ll x_1$ then Eq. (10) gives

$$x_1 = x_\infty/[x_\infty+(1-x_\infty)\exp(\epsilon_s/k_BT+4\epsilon/k_BT)]. \tag{12}$$

This is the Frumkin adsorption isotherm.[23,24] Equations (11) and (12) become the conventional forms of Langmuir and Frumkin equations if the pressure is proportional to the density.

The Langmuir, Frumkin, and other isotherms have been used to calculate adsorption on heterogeneous adsorbents by integrating over the distribution function describing the range of adsorbate–adsorbent energies.[8–10,14,25]

## IV. ENERGY DISTRIBUTION FUNCTION

The traditional approach to adsorption on heterogeneous surfaces is to use the ''fundamental integral equation''[9] for adsorption on heterogeneous surfaces, i.e.,

$$a=\int a_{\epsilon s}F(\epsilon_s)d\epsilon_s, \tag{13}$$

where $a$ is the total amount adsorped on the heterogeneous surface, $a_{\epsilon s}$ is the amount adsorped on a homogeneous surface with the adsorbate–surface interaction energy $\epsilon_s$, and $F(\epsilon_s)$ is the distribution function describing the strength of adsorbate–surface interactions. Reference 8 reviews many of the adsorption isotherms that have been applied to heterogeneous surfaces using Eq. (13).

While the ''fundamental integral equation'' [Eq. (13)] often is presented as a general description of adsorption on heterogeneous surfaces, this equation is rigorous only in certain limits. In general, if the surface is heterogeneous on a molecular scale, the value of $a_{\epsilon s}$ cannot be taken as that for a homogeneous surface. Instead, the value of $a_{\epsilon s}$ inside the integral is not just a function of $\epsilon_s$; it also depends on $F(\epsilon_s)$ and on the geometric pattern on the surface.

To illustrate the limitations of the ''fundamental integral equation'' for adsorption on heterogeneous surfaces, we begin by discussing adsorption on a surface that has a checkerboard pattern of adsorption energies. For a checkerboard surface, each white site is surrounded by black sites and vice versa. In addition, this periodicity can be treated by considering only two types of sites (black and white). This allows the three-dimensional equations to be reduced to two coupled one dimensional equations. Due to the symmetry of the problem, these can be written in terms of a single lattice coordinate, $n=j+k$,

$$\begin{aligned}&\epsilon_s=\epsilon_1 \quad \text{if } j+k \text{ is odd},\\ &\epsilon_s=\epsilon_2 \quad \text{if } j+k \text{ is even}.\end{aligned} \tag{14}$$

To solve Eq. (8), a boundary condition for the concentrations, $x_{1,j,k}$, in the first monolayer is required. This is

$$\begin{aligned}&\ln\{[x_{1,j,k}(1-x_\infty)]/[(1-x_{1,j,k})x_\infty]\}\\ &\quad+(x_{2,j,k}+x_{1,j+1,k}+x_{1,j-1,k}+x_{1,j,k+1}+x_{1,j,k-1}\\ &\quad-6x_\infty)\epsilon/k_BT+\epsilon_s(j+k)/k_BT=0,\end{aligned} \tag{15}$$

where $\epsilon_s(j+k)$ is the energy of interaction with surface at location $(j+k)$.

For the two types of adsorption sites given in Eq. (14), the boundary condition given in Eq. (15) can be transformed into the following two equations:

$$\begin{aligned}&\ln\{[x_{1,j,k}(1-x_\infty)]/[(1-x_{1,j,k})x_\infty]\}\\ &\quad+(x_{2,j,k}+x_{1,j+1,k}+x_{1,j-1,k}+x_{1,j,k+1}+x_{1,j,k-1}\\ &\quad-6x_\infty)\epsilon/k_BT+\epsilon_1/k_BT=0\end{aligned} \tag{16}$$

for odd $j+k$, and

$$\begin{aligned}&\ln\{[x_{1,j,k}(1-x_\infty)]/[(1-x_{1,j,k})x_\infty]\}\\ &\quad+(x_{2,j,k}+x_{1,j+1,k}+x_{1,j-1,k}+x_{1,j,k+1}+x_{1,j,k-1}\\ &\quad-6x_\infty)\epsilon/k_BT+\epsilon_2/k_BT=0\end{aligned} \tag{17}$$

for even $j+k$.

For $i\to\infty$ we require that

$$x_{i,j,k}\to x_\infty \tag{18}$$

for all $j$ and $k$. Also due to periodicity we have

$$x_{i,j+2,k}=x_{i,j,k}, \tag{19}$$

$$x_{i,j,k+2}=x_{i,j,k}. \tag{20}$$

Equation (8) and conditions (16)–(20) describe the Ono–Kondo model for a checkerboard surface.

## V. ANALYTIC SOLUTIONS

Equation (8) can be rewritten as

$$x_{i,j,k}=x_\infty/[x_\infty+(1-x_\infty)\exp(\lambda\epsilon/k_BT)], \tag{21}$$

where

$$\begin{aligned}\lambda=&x_{i+1,j,k}+x_{i-1,j,k}+x_{i,j+1,k}+x_{i,j-1,k}+x_{i,j,k+1}\\ &+x_{i,j,k-1}-6x_\infty.\end{aligned} \tag{22}$$

When $\lambda\epsilon/k_BT$ is small, i.e.,

$$|\lambda\epsilon/k_BT|\ll 1, \tag{23}$$

Eq. (21) can be linearized and transformed to

$$\begin{aligned}&\delta_{i+1,j,k}+\delta_{i-1,j,k}+\delta_{i,j+1,k}+\delta_{i,j-1,k}+\delta_{i,j,k+1}\\ &\quad+\delta_{i,j,k-1}-k_BT\delta_{i,j,k}/[x_\infty(1-x_\infty)\epsilon]=0,\end{aligned} \tag{24}$$

where

$$\delta_{i,j,k}=x_{i,j,k}-x_\infty. \tag{25}$$

The inequality in Eq. (23) is valid in two cases; for small values of $\epsilon/k_BT$ (at any distribution of concentrations) and for low levels of adsorption (small $\delta_{i,j,k}$) for any $\epsilon/k_BT$.

Using the variable $n=j+k$ and taking into account the periodic symmetry of the checkerboard, the three-dimensional equation (24) can be rewritten in equivalent two-dimensional form

$$\begin{aligned}&\delta_{i+1,n}+\delta_{i-1,n}+2\delta_{i,n+1}+2\delta_{i,n-1}\\ &\quad-k_BT\delta_{i,n}/[x_\infty(1-x_\infty)\epsilon]=0.\end{aligned} \tag{26}$$

This two-dimensional Eq. (26) can be transformed into two one-dimensional equations,

$$\alpha_{i+1}+\alpha_{i-1}+4\beta_i-\alpha_ik_BT/[x_\infty(1-x_\infty)\epsilon]=0, \tag{27}$$

$$\beta_{i+1}+\beta_{i-1}+4\alpha_i-\beta_ik_BT/[x_\infty(1-x_\infty)\epsilon]=0, \tag{28}$$

where

$$\alpha_i=\delta_{i,n} \tag{29}$$

and

$$\beta_i=\delta_{i,n+1}. \tag{30}$$

The summation of Eqs. (27) and (28) gives

$$y_{i+1}+y_{i-1}+y_i\{4-k_BT/[x_\infty(1-x_\infty)\epsilon]\}=0, \tag{31}$$

where

$$y_i=\alpha_i+\beta_i. \tag{32}$$

The general solution of Eq. (31) is of the form

$$y_i=C_1\omega_1^i+C_2\omega_2^i, \tag{33}$$

where $C_1$ and $C_2$ are arbitrary constants, $\omega_1$ and $\omega_2$ are roots of the following characteristic equation:

$$\omega^2+\{4-k_BT/[x_\infty(1-x_\infty)\epsilon]\}\omega+1=0 \tag{34}$$

so that

$$|\omega_1|<1 \tag{35}$$

and

$$|\omega_2|>1. \tag{36}$$

From Eqs. (18), (33), and (36) it follows that $C_2=0$. Therefore the solution to Eq. (31) can be rewritten in the form

$$y_i=(\alpha_1+\beta_1)\omega_1^{i-1}. \tag{37}$$

The value of $y_i/2=(\delta_{i,n}+\delta_{i,n+1})/2$ is the average composition in layer $i$. To find the local compositions $\alpha_i$ and $\beta_i$ we substitute $\beta_i$ from Eqs. (32), (37) into Eq. (27). This gives

$$\alpha_{i+1}-\alpha_i[4+k_BT/[x_\infty(1-x_\infty)\epsilon] +\alpha_{i-1}+4(\alpha_1+\beta_1)\omega_1^{i-1}=0. \tag{38}$$

The general solution of the inhomogeneous Eq. (38) is the sum of a partial solution $(\alpha_i)_{\text{part}}$ and a general solution $(\alpha_i)_h$ of the homogeneous equation

$$\alpha_{i+1}-\alpha_i\{4+k_BT/[x_\infty(1-x_\infty)\epsilon]\}+\alpha_{i-1}=0. \tag{39}$$

The partial solution of Eq. (38) can be written as

$$(\alpha_i)_{\text{part}}=B\omega_1^{i-1}. \tag{40}$$

Substituting Eq. (40) into Eq. (38) gives the following expression for $B$:

$$B=4(\alpha_1+\beta_1)/\{4\omega_1+k_BT\omega_1/[x_\infty(1-x_\infty)\epsilon]-\omega_1^2-1\}. \tag{41}$$

The general solution of Eq. (39) is

$$(\alpha_i)_h=C_3p_1^i+C_4p_2^i, \tag{42}$$

where $C_3$ and $C_4$ are arbitrary constants, $p_1$ and $p_2$ are the roots of the following characteristic equation:

$$p^2-\{4+k_BT/[x_\infty(1-x_\infty)\epsilon]\}p+1=0 \tag{43}$$

so that

$$|p_1|<1 \tag{44}$$

and

$$|p_2|>1. \tag{45}$$

From Eqs. (18) and (45) we have $C_4=0$. Therefore, the solution of Eq. (38) is

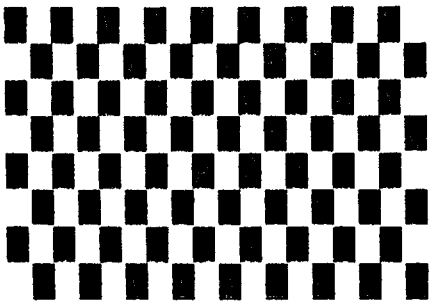
$$\alpha_i=C_3p_1^i+4(\alpha_1+\beta_1)\omega_1^{i-1}/\{4\omega_1+k_BT\omega_1/[x_\infty(1-x_\infty)\epsilon]-\omega_1^2-1\}, \tag{46}$$

where

$$C_3=(\alpha_1-B)/p_1. \tag{47}$$

## VI. GENERAL EQUATIONS FOR DIFFERENT TYPES OF PERIODIC SURFACES

### A. Simple checkerboard surface



For this type of surface, Eq. (8) with Eqs. (19) and (20) is equivalent to the following two equations:

$$\ln\{[g_i(1-x_\infty)]/[(1-g_i)x_\infty]\} +[g_{i+1}+g_{i-1}+4h_i-6x_\infty]\epsilon/k_BT=0 \tag{48}$$

and

$$\ln\{[h_i(1-x_\infty)]/[(1-h_i)x_\infty]\} +[h_{i+1}+h_{i-1}+4g_i-6x_\infty]\epsilon/k_BT=0, \tag{49}$$

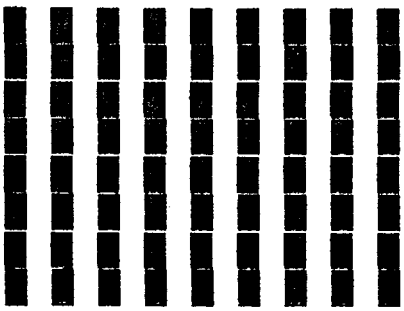
where

$$g_i=x_{i,j,k} \tag{50}$$

and

$$h_i=x_{i,j+1,k}=x_{i,j,k+1}. \tag{51}$$

### B. Striped surface



For this case Eqs. (19) and (20) are

$$x_{i,j+1,k}=x_{i,j,k} \tag{52}$$

and

$$x_{i,j,k+2}=x_{i,j,k}, \tag{53}$$

and the three-dimensional Eq. (8) reduces to the following two equations:

$$\ln\{[g_i(1-x_\infty)]/[(1-g_i)x_\infty]\} + [g_{i+1}+g_{i-1}+2g_i+2h_i-6x_\infty]\epsilon/k_BT=0, \quad (54)$$

$$\ln\{[h_i(1-x_\infty)]/[(1-h_i)x_\infty]\} + [h_{i+1}+h_{i-1}+2h_i+2g_i-6x_\infty]\epsilon/k_BT=0, \quad (55)$$

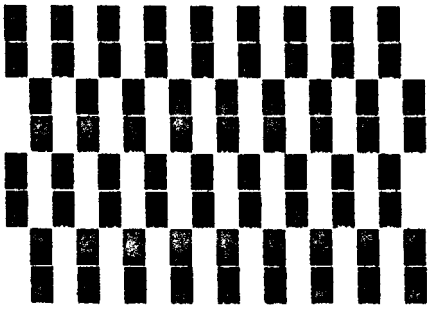
where

$$g_i=x_{i,j,k} \quad (56)$$

and

$$h_i=x_{i,j,k+1}. \quad (57)$$

### C. Two-site checkerboard surface



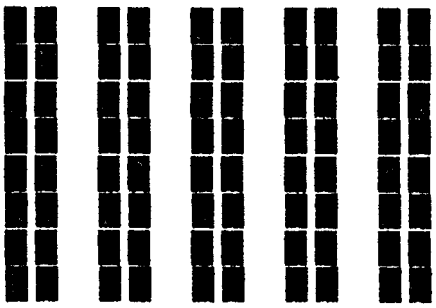
For this boundary Eq. (8) becomes

$$\ln\{[g_i(1-x_\infty)]/[(1-g_i)x_\infty]\} + [g_{i+1}+g_{i-1}+g_i+3h_i-6x_\infty]\epsilon/k_BT=0, \quad (58)$$

$$\ln\{[h_i(1-x_\infty)]/[(1-h_i)x_\infty]\} + [h_{i+1}+h_{i-1}+h_i+3g_i-6x_\infty]\epsilon/k_BT=0, \quad (59)$$

where $g_i=x_{i,j,k}$ for black sites and $h_i=x_{i,j,k}$ for white sites.

### D. Two-site striped surface



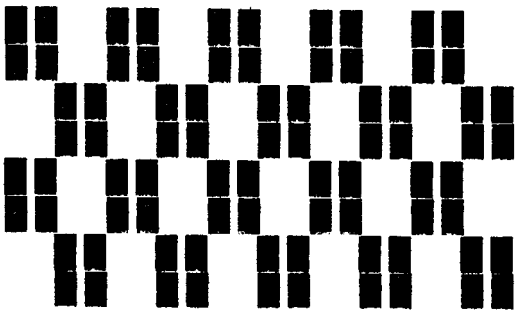
For this boundary Eq. (8) becomes

$$\ln\{[g_i(1-x_\infty)]/[(1-g_i)x_\infty]\} + [g_{i+1}+g_{i-1}+3g_i+h_i-6x_\infty]\epsilon/k_BT=0, \quad (60)$$

$$\ln\{[h_i(1-x_\infty)]/[(1-h_i)x_\infty]\} + [h_{i+1}+h_{i-1}+3h_i+g_i-6x_\infty]\epsilon/k_BT=0, \quad (61)$$

where $g_i=x_{i,j,k}$ for black sites and $h_i=x_{i,j,k}$ for white sites.

### E. Four-site checkerboard surface



For this type of boundary, Eq. (8) with Eqs. (19) and (20) are equivalent to Eqs. (54) and (55) for striped surface. These two surfaces have the same numbers of black and white neighbors for each black and each white site.

### F. Any periodic surface with $r_1$ black and $s_1$ white neighbors for each black site and $s_2$ black and $r_2$ white neighbors for each white site

Analysis of the equation pairs (48)–(49), (54)–(55), (58)–(59), (60)–(61) shows that they differ only in coefficients $r$ and $s$ in the linear terms $r_1g_i+s_1h_i$ and $r_2h_i+s_2g_i$. Here $r$ is the number of black sites around a black site or the number of white sites around a white site; $s$ is the number of black sites around a white site or number of white sites around a black site. The subscript 1 refers to the neighbors around black sites, and the subscript 2 refers to the neighbors around white sites. Since for the simple cubic lattice $s=4-r$, a general set of equations can be written in the form

$$\ln\{[g_i(1-x_\infty)]/[(1-g_i)x_\infty]\} + [g_{i+1}+g_{i-1}+r_1g_i+(4-r_1)h_i-6x_\infty]\epsilon/k_BT=0, \quad (62)$$

$$\ln\{[h_i(1-x_\infty)]/[(1-h_i)x_\infty]\} + [h_{i+1}+h_{i-1}+r_2h_i+(4-r_2)g_i-6x_\infty]\epsilon/k_BT=0, \quad (63)$$

where $g_i=x_{i,j,k}$ for black sites and $h_i=x_{i,j,k}$ for white sites.

The analytical solution presented in Eq. (46) can be generalized to the case of arbitrary $r_1$ and $r_2$ in Eqs. (21)–(46). In particular, instead of Eqs. (27) and (28) we have

$$\alpha_{i+1}+\alpha_{i-1}+r_1\alpha_i+(4-r_1)\beta_i-\alpha_i k_BT/[x_\infty(1-x_\infty)\epsilon]=0, \quad (64)$$

$$\beta_{i+1}+\beta_{i-1}+r_2\beta_i+(4-r_2)\alpha_i-\beta_i k_BT/[x_\infty(1-x_\infty)\epsilon]=0. \quad (65)$$

For $r_1=r_2$ (this is true for the surfaces considered above) the summation of Eqs. (64) and (65) results in Eq. (31).

## VII. INFLUENCE OF LATTICE TYPE

Equation (8) is written for a simple cubic lattice. However, it is a simple matter to write these equations for other types of lattices. Here we give expressions for face-centered, volume-centered, and hexagonal lattices.

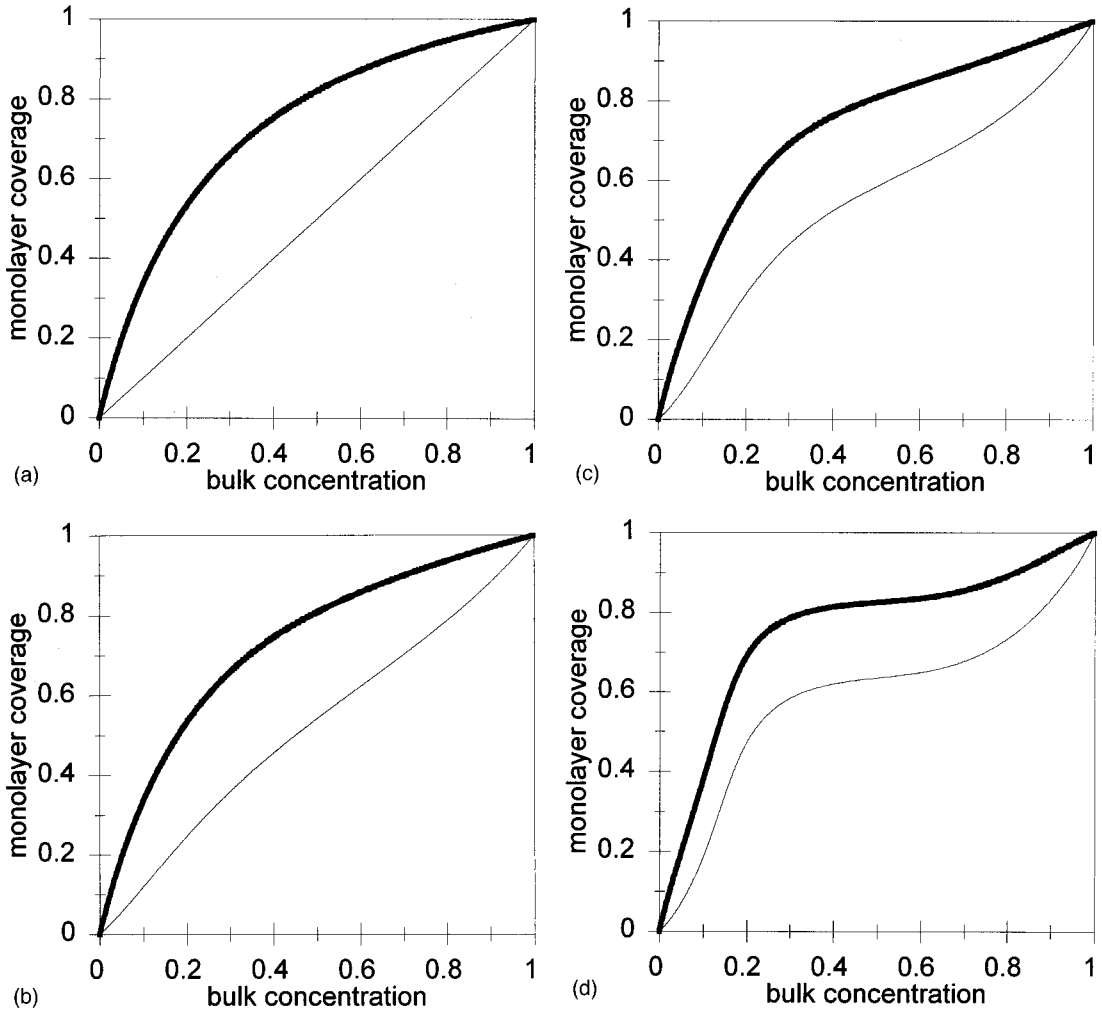



FIG. 2. Dependence of monolayer coverage for black sites, $x_{1,n}$ (light line), and for white sites, $x_{1,n+1}$ (heavy line) on bulk concentration. Here $\epsilon_1/k_BT=0$ and $\epsilon_2/k_BT=-1.5$ but $\epsilon/k_BT$ changes from 0 (a) to $-0.75$ (d). For black sites with zero energy of adsorbate–adsorbent interactions monolayer coverage is significant due to the lateral interactions.

### A. Face-centered

In this case we have

$$\ln\{[x_{i,j,k}(1-x_\infty)]/[(1-x_{i,j,k})x_\infty]\} + [x_{i+1,j+1,k}+x_{i+1,j,k+1}+x_{i,j+1,k+1}+x_{i-1,j-1,k} + x_{i-1,j,k-1}+x_{i,j-1,k-1}+x_{i-1,j+1,k}+x_{i-1,j,k+1} + x_{i,j-1,k+1}+x_{i+1,j-1,k}+x_{i+1,j,k-1}+x_{i,j+1,k-1} - 12x_\infty]\epsilon/k_BT=0. \quad (66)$$

### B. Volume-centered

For this lattice Eq. (8) transforms to

$$\ln\{[x_{i,j,k}(1-x_\infty)]/[(1-x_{i,j,k})x_\infty]\} + [x_{i-1,j-1,k-1}+x_{i+1,j-1,k-1}+x_{i-1,j+1,k-1} + x_{i-1,j-1,k+1}+x_{i-1,j+1,k+1}+x_{i+1,j-1,k+1} + x_{i+1,j+1,k-1}+x_{i+1,j,k+1}-8x_\infty]\epsilon/k_BT=0. \quad (67)$$

### C. Hexagonal

For these cases the Ono–Kondo equation has the following form:

$$\ln\{[x_{i,j,k}(1-x_\infty)]/[(1-x_{i,j,k})x_\infty]\} + [x_{i+1,j,k}+x_{i-1,j,k}+x_{i,j+1,k}+x_{i,j-1,k}+x_{i,j,k+1} + x_{i,j,k-1}+x_{i-1,j+1,k}+x_{i+1,j-1,k}+x_{i,j-1,k+1} + x_{i,j+1,k-1}+x_{i+1,j,k-1}+x_{i-1,j,k+1}-12x_\infty]\epsilon/k_BT=0. \quad (68)$$

## VIII. MONOLAYER ADSORPTION

The influence of surface heterogeneities is most significant in the first monolayer. Therefore, describing the behavior of monolayer adsorption on these heterogeneous surfaces will illustrate most of the important phenomena predicted by the model. We have monolayer adsorption when

$$x_{2,j,k}=x_\infty \quad (69)$$

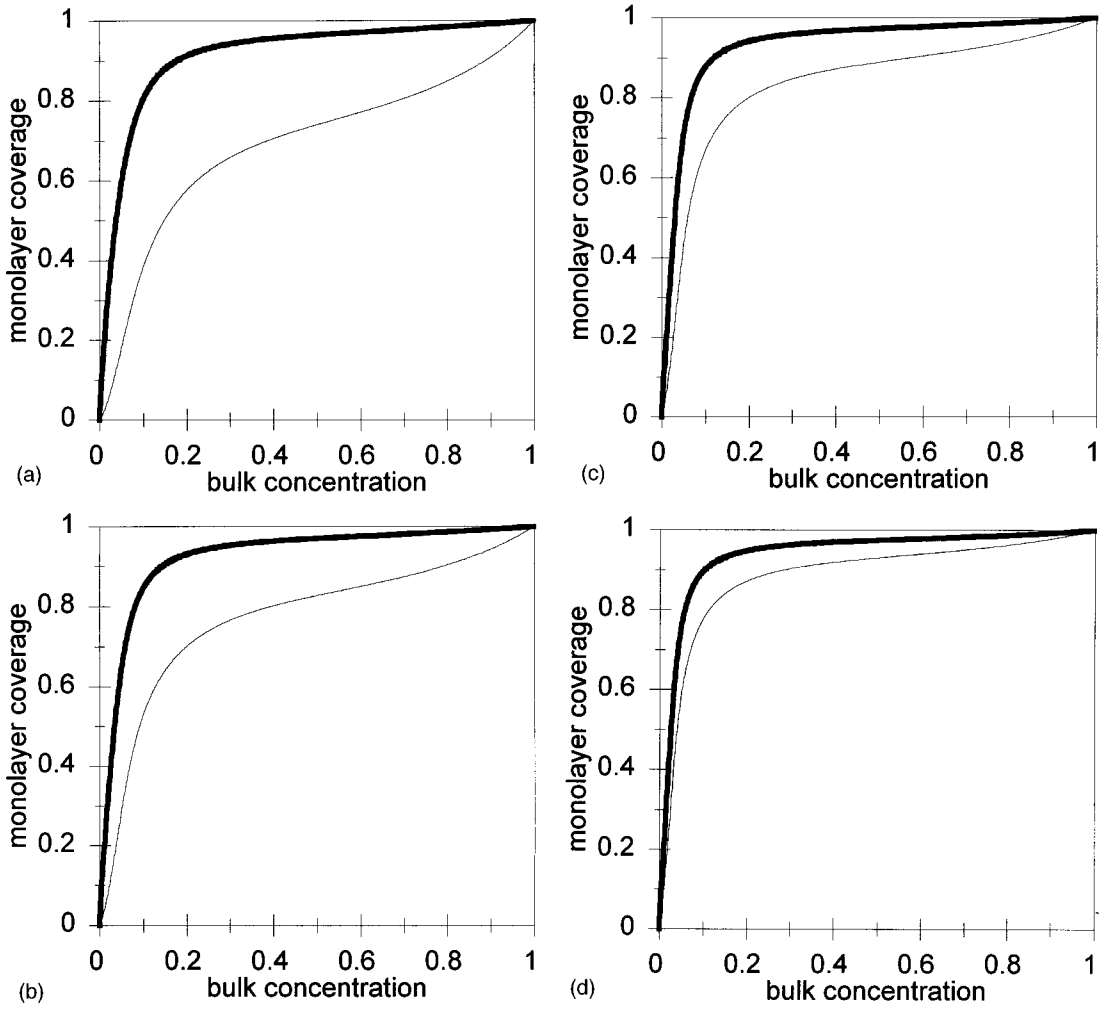



FIG. 3. Dependence of monolayer coverage on bulk concentration for $\epsilon/k_BT=-0.5$, $\epsilon_2/k_BT=-3$, and different values of $\epsilon_1/k_BT$: $-0.5$ (a), $-1$ (b), $-1.5$ (c), $-2$ (d). In case of $\epsilon_1/k_BT=-2$ and $\epsilon_2/k_BT=-3$ coverages of black (light line) and white (heavy line) sites are very close.

for any $j$ and $k$.

With condition (69), Eqs. (16) and (17) are equivalent to the following set of equations:

$$\ln\{[x_{1,n}(1-x_\infty)]/[(1-x_{1,n})x_\infty]\} + (4x_{1,n+1}-5x_\infty)\epsilon/k_BT+\epsilon_1/k_BT=0, \tag{70}$$

$$\ln\{[x_{1,n+1}(1-x_\infty)]/[(1-x_{1,n+1})x_\infty]\} + (4x_{1,n}-5x_\infty)\epsilon/k_BT+\epsilon_2/k_BT=0, \tag{71}$$

where $x_{1,n}$ is the monolayer coverage on the black sites and $x_{1,n+1}$ is the monolayer coverage on the white sites. Equations (70) and (71) are nonlinear. However, for given values of $\epsilon/k_BT$, $\epsilon_1/k_BT$, and $\epsilon_2/k_BT$, the dependence of $x_{1,n}$ and $x_{1,n+1}$ on $x_\infty$ can be calculated numerically.

Figure 2 shows dependence of $x_{1,n}$ and $x_{1,n+1}$ on $x_\infty$ for $\epsilon_1/k_BT=0$, $\epsilon_2/k_BT=-1.5$, and different values of $\epsilon/k_BT$. As shown in Fig. 2, a checkerboard surface can have significant adsorption due to the lateral interactions even on sites with zero energy of adsorption. Figure 3 presents the same dependence for $\epsilon/k_BT=-0.5$, $\epsilon_2/k_BT=-3$, and different values of $\epsilon_1/k_BT$. It can be seen that for $\epsilon_1/k_BT=-2$ monolayer coverages for black and white sites are almost equal despite the very different values $\epsilon_1/k_BT$ and $\epsilon_2/k_BT$.

Equations (70) and (71) can be generalized for any $r_1$ and $r_2$,

$$\ln\{[x_{1,n}(1-x_\infty)]/[(1-x_{1,n})x_\infty]\} + [r_1x_{1,n}+(4-r_1)x_{1,n+1}-5x_\infty)\epsilon/k_BT+\epsilon_1/k_BT=0, \tag{72}$$

$$\ln\{[x_{1,n+1}(1-x_\infty)]/[(1-x_{1,n+1})x_\infty]\} + [r_2x_{1,n+1}+(4-r_2)x_{1,n}-5x_\infty)\epsilon/k_BT+\epsilon_2/k_BT=0. \tag{73}$$

Figure 4 shows dependence of $x_{1,n}$ and $x_{1,n+1}$ on $x_\infty$ for $\epsilon_1/k_BT=-0.5$, $\epsilon_2/k_BT=-3$, $\epsilon/k_BT=-0.5$, and different types of periodic surfaces with $r_1=r_2$. As shown in Fig. 4, decreasing $r$ from four (for patched surface) to zero (for simple checkerboard) results in slightly decreasing $x_{1,n+1}$ and drastically increasing $x_{1,n}$ through lateral interactions.

The examples above have been for periodical surfaces with $r_1=r_2$, i.e., surfaces with equal numbers of black and

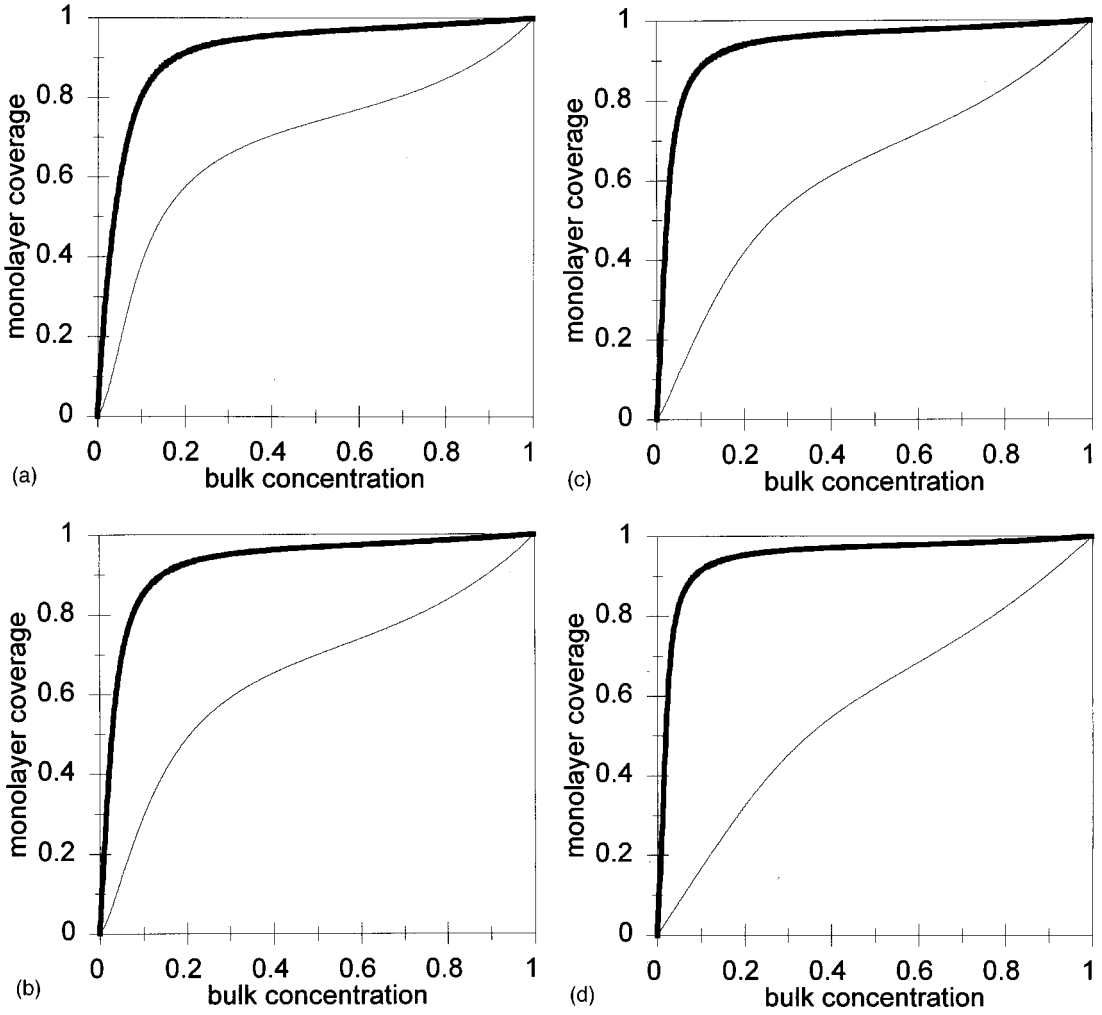



FIG. 4. Dependence of monolayer coverage on bulk concentration for $\epsilon_1/k_BT=-0.5$, $\epsilon_2/k_BT=-3$, $\epsilon/k_BT=-0.5$, and different types of periodic surfaces; (a) simple checkerboard ($r_1=r_2=0$), (b) striped surface ($r_1=r_2=2$), (c) two-site checkerboard ($r_1=r_2=3$), and (d) patched surface ($r_1=r_2=4$).

white sites. To illustrate influence of black site fraction, $\phi$, on monolayer coverage we consider the following surfaces:

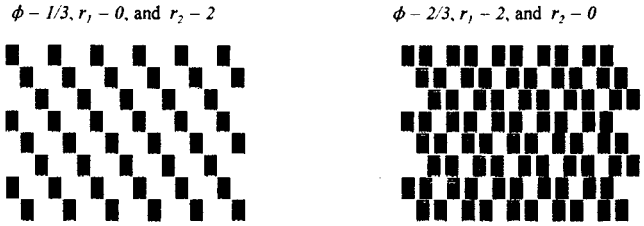
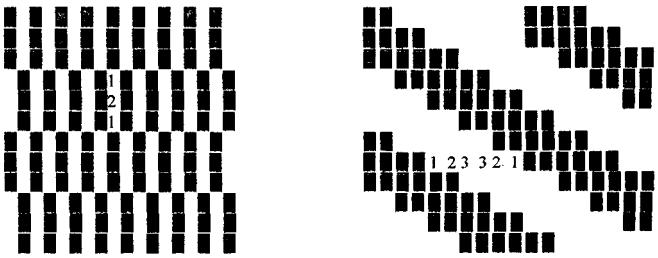



Figure 5 shows the dependence of monolayer coverage for black and white sites on bulk concentration for surfaces with $\phi=1/3$, $\phi=1/2$ (simple checkerboard), and $\phi=2/3$. Here $\epsilon_1/k_BT=0$, $\epsilon_2/k_BT=-3$, and $\epsilon/k_BT=-0.5$. As shown in Fig. 5, the monolayer coverage for both black and white sites goes up as $\phi$ goes down. For white sites the difference between adsorption with $\phi=1/3$ and $\phi=1/2$ is much greater than for black sites. For black sites, this difference is much greater between $\phi=2/3$ and $\phi=1/2$ than it is between $\phi=1/3$ and $\phi=1/2$.

## IX. GENERALIZATION FOR ARBITRARY PERIODIC SURFACE

Above, we have considered surfaces with two different types of sites. Surfaces with a greater number of different sites can be treated as well, but this increases the number of equations that must be solved simultaneously. Examples of other interesting surfaces include




For such systems, the general equation for $i \geqslant 2$ can be written in the form

$$\ln\{[g_{i,l}(1-x_\infty)]/[(1-g_{i,l})x_\infty]\}$$

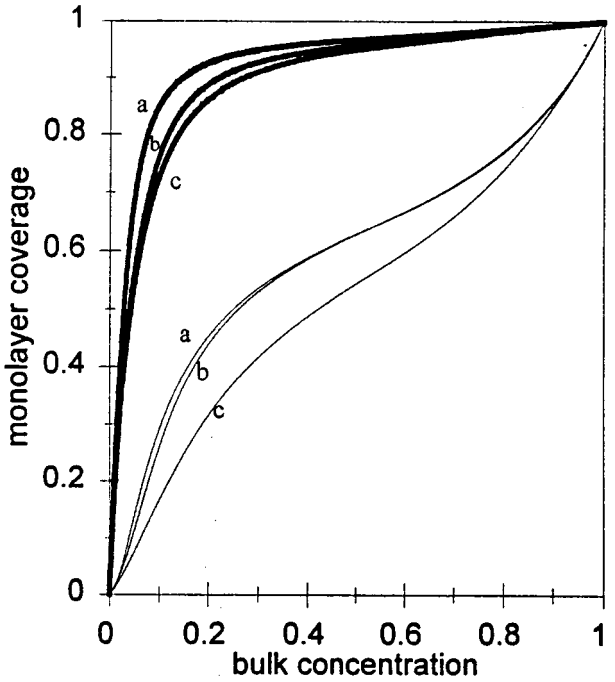



FIG. 5. Dependence of monolayer coverage for black sites (light line) and for white sites (heavy line) on bulk concentration for surfaces with different fraction of black sites; 1/3 (a), 1/2 (b), and 2/3 (c). Here $\epsilon_1/k_BT=0$, $\epsilon_2/k_BT=-3$, $\epsilon/k_BT=-0.5$.

$$+\left\{\sum_{m-1}^{M}\left[s_{lm}(g_{i+1,m}+g_{i-1,m})+r_{lm}g_{i,m}\right.\right.$$

$$\left.\left.-(2s_{lm}+r_{lm})x_{\infty}\right]\right\}\epsilon/k_BT=0, \tag{74}$$

where $g_{i,l}$ is $x_{i,j,k}$ for site of type $l$, $r_{lm}$ is the number sites of type $m$ that are adjacent to site $l$ in the monolayer, $s_{lm}$ is the same number with respect to adjacent monolayer, and $M$ is the number of different sites (including both black and white).

The boundary condition for $i=1$ is

$$\ln\{[g_{1,l}(1-x_{\infty})]/[(1-g_{1,l})x_{\infty}]\}$$

$$+\left\{\sum_{m=1}^{M}\left[s_{lm}g_{2,m}+r_{lm}g_{1,m})-(s_{lm}+r_{lm})x_{\infty}\right]\right\}\epsilon/k_BT$$

$$+\epsilon_l/k_BT=0, \tag{75}$$

where $\epsilon_l$ is the energy of adsorbate–surface interaction for site of type $l$.

Equations (74) and (75) for $l=1,2,\ldots,M$ determine $M$ unknown functions $g_{i,1}, g_{i,2},\ldots,g_{i,M}$.

## X. CONCLUSION

The three-dimensional version of the Ono–Kondo equations presented here can be used to describe the adsorption on heterogeneous surfaces. These three-dimensional equations predict different results for different types of periodic surfaces where the size of the surface heterogeneities are molecular scale.

Analysis of the adsorption behavior on a checkerboard surface shows that lateral interactions strongly influence the adsorption behavior. This is demonstrated by high levels of adsorption even on sites with zero adsorbate–surface interaction energy.

## ACKNOWLEDGMENT

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