Edge effects on low temperature surface adsorption phases and phase transitions on finite-width square terraces

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Abstract

A transfer matrix approach is used to conduct a thorough investigation of all possible adsorbate configurations or phases on terraces of various widths M including edge effects, and limited to first- and second-neighbor adsorbate–adsorbate interactions. Figures showing the configurations that occur within this model are presented for $M = 3$ and 4, and detailed tables provide the phase sequences corresponding to all possible ranges of values for the interaction energies. Higher width terrace results have also been completed and are available upon request. As such, the model calculations provide a useful reference for experimentalists leading to predictions of the values of the interaction energies from the observed phase sequence and the conditions prevailing at the transition between phases. A few experimental results are interpreted using the model. One suggests specific experiments, which would make the observations more amenable to direct comparison with the calculations.

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1. Introduction

In a recently proposed model of low temperature preferential adsorption on the steps of long finite-width square terraces [1], lattice–adsorbate interactions on edge-sites were assumed to be different from that in the interior or bulk of the surface. The substrate consists of long terraces with the edge-sites being first-neighbors, forming an array parallel to the bulk-sites. Agreement was obtained with the experimental data satisfying the constraints of the model, such as adsorption of cobalt on silver(1 0 0) [2] and bromine

on Cu(11 1 0) [3], which in Lang et al.'s notation for high Miller index surfaces [4] corresponds to Cu (s)-[10(1 0 0) $\times$ 1(0 0 1)]. Here, the model is applied to study the effect on the adsorption phases and phase transitions by changing the orientation of the edges, so that adjacent edge-sites are second-neighbors, for which experimental data is available. We have completed the study of terraces of width M up to six atomic sites. We were also able to find a number of analytic extensions of these results for any M , which were numerically verified up to $M = 11$. Here we are reporting the complete results for the first non-trivial terraces with $M = 3$ and 4, and only provide the configurations of all possible phases for $M = 5$. The discussion of higher width terraces is very brief and just sufficient to exhibit a sample of analytic

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generalizations for any M . The compilation of the data not presented in this paper is available upon request.

No a priori assumptions are made as to whether forces are attractive or repulsive, or as to their relative strength. By changing the orientation of the steps, many more structural orderings are observed, including clustering on the edges, domain walls, staircase patterns, square, and hexagonal patterns. The patterns are also found to depend on whether the width of the terrace is even or odd. As in previous investigations, we will show that the occupational characteristics at the transitions between phases are often found to fit exact analytic expressions in terms of the golden ratio. A method of conducting adsorption experiments is again suggested. (1) Record the structural ordering of the phases, as the pressure of the gas is gradually increased. (2) Determine the pressures at which transitions between phases occur, starting from empty to full coverage. When there is no surface reconstruction, and if first- and second-neighbor interactions are predominant, our model predicts a number if not all the interaction energies, adsorbate–adsorbate, and adsorbate–substrate at the edge-sites and in the bulk. Our results are compared with the available experimental observations.

2. The model

The general features of our lattice model and comparison with others have been described at length in a series of articles published in the past 9 years [5–13]. For completeness, the following summary intends to make the article self-contained, providing the appropriate references for those interested in pursuing the details. The long terraces considered are made of a square lattice, with the arrays of edge-sites oriented at 45° with the arrays of sites in the bulk, as shown in Fig. 1. Adsorption takes place at sites forming a lattice commensurate with that of the substrate; for this reason we do not make any distinction between these two lattices. The notation used here is the same as that of [1]. The chemical potential per particle in the gas phase, μ' , depends on the gas pressure. The adsorbate–substrate interaction energy at edge-sites is V_e , and V_0 is the adsorbate–substrate interaction energy at bulk-sites. Lateral interactions are limited to first- and second-neighbors with energies V and W , respectively.

Fig. 1. Square lattice terrace with edge-sites being second-neighbors.

Positive energies correspond to attraction and negative energies to repulsion. At thermodynamic equilibrium, θ_0 is the coverage of the lattice, θ and β are the numbers per site of first- and second-neighbor monomers, and finally γ is the number per site of monomers at the edges of the terrace. Therefore the number of monomers per site in the bulk is $(\theta_0 - \gamma)$, and, at thermodynamic equilibrium, the energy per site E_{site} is:

$$E_{\text{site}} = \mu'\theta_0 + V_0(\theta_0 - \gamma) + V_e\gamma + V\theta + W\beta \\ = (\mu' + V_0)\theta_0 + (V_e - V_0)\gamma + V\theta + W\beta. \quad (1)$$

It is then convenient to define the quantities,

$$\mu = \mu' + V_0, \quad U = V_e - V_0, \quad (2)$$

where U is zero when the adsorbate–substrate interaction is the same at the edges as in the bulk. For convenience, U is referred to as the “edge-interaction” and to μ simply as the “chemical potential.” With T the absolute temperature and k_B , Boltzmann’s constant, the absolute activities associated with μ , V , W , and U are:

$$x = \exp\left(\frac{\mu}{k_B T}\right); \quad y = \exp\left(\frac{V}{k_B T}\right); \\ z = \exp\left(\frac{W}{k_B T}\right); \quad u = \exp\left(\frac{U}{k_B T}\right). \quad (3)$$

Unlike the case for which edge-sites are first-neighbors [10], here the recursive construction of the transfer matrix, T_M^1 , for a terrace of M sites in width, and with $U = 0$, involves eight block-matrices, as follows:

$$T_M^1 = \begin{pmatrix} T_{M-1}^1 & xP_{M-1}^1 \\ T_{M-1}^2 & xzP_{M-1}^2 \end{pmatrix}; \\ T_M^2 = \begin{pmatrix} T_{M-1}^3 & xyP_{M-1}^3 \\ T_{M-1}^4 & xyzP_{M-1}^4 \end{pmatrix}; \quad (4a)$$

$$T_M^3 = \begin{pmatrix} T_{M-1}^1 & xzP_{M-1}^1 \\ T_{M-1}^2 & xz^2P_{M-1}^2 \end{pmatrix};$$

$$T_M^4 = \begin{pmatrix} T_{M-1}^3 & xyzP_{M-1}^3 \\ T_{M-1}^4 & xyz^2P_{M-1}^4 \end{pmatrix}; \quad (4b)$$

$$P_M^1 = \begin{pmatrix} T_{M-1}^1 & xyP_{M-1}^1 \\ T_{M-1}^2 & xyzP_{M-1}^2 \end{pmatrix};$$

$$P_M^2 = \begin{pmatrix} T_{M-1}^3 & xy^2P_{M-1}^3 \\ T_{M-1}^4 & xy^2zP_{M-1}^4 \end{pmatrix}; \quad (4c)$$

$$P_M^3 = \begin{pmatrix} T_{M-1}^1 & xyzP_{M-1}^1 \\ T_{M-1}^2 & xyz^2P_{M-1}^2 \end{pmatrix};$$

$$T_M^4 = \begin{pmatrix} T_{M-1}^3 & xy^2zP_{M-1}^3 \\ T_{M-1}^4 & xy^2z^2P_{M-1}^4 \end{pmatrix}. \quad (4d)$$

The initial conditions are $T_0^1 = T_0^2 = T_0^3 = T_0^4 = P_0^1 = P_0^2 = P_0^3 = P_0^4 = 1$, and the rank of any of the block-matrices with lower index M is 2^M . Once matrix T_M^1 is constructed for $U = 0$ (or $u = 1$), it is generalized for any u in exactly the same manner it is done in [10], where edge-sites are first-neighbors. For example, for the non-trivial case $M = 3$, the transfer matrix is:

$$T_3^1 = \begin{pmatrix} 1 & xu & x & x^2yu & xu & x^2u^2 & x^2yu & x^3y^2u^2 \\ 1 & xzu & x & x^2yzu & xu & x^2zu^2 & x^2yu & x^3y^2zu^2 \\ 1 & xyu & xz & x^2y^2zu & xu & x^2yu^2 & xyzu & x^3y^3zu^2 \\ 1 & xyzu & xz & x^2y^2z^2u & xu & x^2yzu^2 & x^2yzu & x^3y^3z^2u^2 \\ 1 & xzu & xy & x^2y^2zu & xzu & x^2z^2u^2 & x^2y^2zu & x^3y^3z^2u^2 \\ 1 & xz^2u & xy & x^2y^2z^2u & xzu & x^2z^3u^2 & x^2y^2zu & x^3y^3z^3u^2 \\ 1 & xyzu & xyz & x^2y^3z^2u & xzu & x^2yz^2u^2 & x^2y^2z^2u & x^3y^4z^3u^2 \\ 1 & xyz^2u & xyz & x^2y^3z^3u & xzu & x^2yz^3u^2 & x^2y^2z^2u & x^3y^4z^4u^2 \end{pmatrix}. \quad (5)$$

In general, all elements in even-numbered columns are multiplied by u . An additional factor of u is added to all elements in even-numbered columns in the second half of the matrix.

The partition function, Z , of the adsorption system on a terrace of width M and finite length N , at thermal equilibrium, is computed from the knowledge of all the eigenvalues of the transfer matrix. The Frobenius–Perron theorem states that the eigenvalue of largest modulus of a matrix, whose elements are real and

non-negative, is real and positive. This is the case of our transfer matrix. Let R_{le} be this largest eigenvalue. In the thermodynamic limit as the length of the terrace becomes infinite, R_{le} becomes the only contribution to Z , and $Z = R_{le}^{1/M}$ [14]. In this limit, the coverage θ_0 , the numbers per site of first- and second-neighbors, θ and β , and the number per site of monomers on the edges, γ , are obtained as:

$$\theta_0 = \frac{x}{MR_{le}} \frac{\partial R_{le}}{\partial x}; \quad \theta = \frac{y}{MR_{le}} \frac{\partial R_{le}}{\partial y};$$

$$\beta = \frac{z}{MR_{le}} \frac{\partial R_{le}}{\partial z}; \quad \gamma = \frac{u}{MR_{le}} \frac{\partial R_{le}}{\partial u}. \quad (6)$$

The occupational characteristics of the terrace are specified by the set $\{\theta_0, \theta, \beta, \gamma\}$. Referring to phases, zero coverage or empty phase, $\{0, 0, 0, 0\}$, will be called “ E .” Full coverage will be denoted “ F ” and corresponds to $\{1, 2(M-1)/M, 2(M-1)/M, 2/M\}$. The entropy per site divided by Boltzmann’s constant, S_{ent} , will be called entropy, and it is given by:

$$S_{ent} = \left(\frac{1}{M} \right) \ln R_{le} - \left(\frac{E_{site}}{k_B T} \right). \quad (7)$$

All numerical calculations were done on the Cray J90 of the Pittsburgh Supercomputing Center using the

EISPACK software for determining the largest eigenvalue R_{le} and its partial derivatives with respect to the various activities. The numerical accuracy achieved in computing the occupational characteristics is better than eight figures, and that in computing the entropy is better than six figures. Keeping the temperature relatively low, and for a given set of values of V , W , and U , all adsorption phases are determined by varying μ . At low chemical potential, or low gas pressure, there is no adsorption and the terrace is empty, $\{0, 0, 0, 0\}$. As μ is

gradually increased, adsorption begins to take place, the entropy increases to a maximum, then decreases and reaches a plateau, which lasts for a relatively wide range of values of μ . If the plateau is at $S = 0$, we have reached a perfectly ordered phase; if S is not zero we have reached a partially ordered phase. After a series of peaks and plateaus, and beyond a certain value of μ , the terrace is completely covered. The transition between phases is the point at which the entropy reaches a local maximum. As has always been the case in the past, the value of μ at which a transition occurs is numerically found to satisfy the condition:

$$\mu = -V\left(\frac{\Delta\theta}{\Delta\theta_0}\right) - W\left(\frac{\Delta\beta}{\Delta\theta_0}\right) - U\left(\frac{\Delta\gamma}{\Delta\theta_0}\right), \quad (8)$$

where $\Delta\theta_0$, $\Delta\theta$, $\Delta\beta$ and $\Delta\gamma$ are the changes in the characteristics between the phases on either side of the transition. Equivalently stated, throughout the transition region between phases, there is no change in the total energy per site ($\Delta E_{\text{site}} = 0$). In the boundary region between any two phases, the quantities θ , β and γ are each linearly related to the coverage θ_0 , with the end-points of the line matching the occupational characteristics of the phases on either side, as verified in all previous studies. Therefore, these linear relations and Eq. (8) are additional checks of the validity of our numerical results.

The results obtained for terraces of width $M = 3$ and the corresponding analysis of the available experimental data, are presented in Section 3. We are not aware of experimental data for terraces of higher order widths, which could be analyzed using our model.

The results for terraces with $M = 4$ are fully presented in Section 4. Section 5 provides all the phases with their occupational characteristics and configurations for $M = 5$, but without the detailed energy regions and sequences in which these phases occur. A brief discussion is also included on higher order width terraces. Section 6 is the summary and conclusion.

3. Terraces of width $M = 3$

In addition to the trivial empty and full coverage phases, there are seven other possible phases only when first- and second-neighbor interactions are taken into account. The occupational configuration of a phase corresponds to a given distribution of occupied sites, with the remaining sites being vacant. The dual of a phase is the one for which its vacant sites are occupied, and its occupied sites are vacant. With this convention, we found that the phases appear in pairs, with the exception of one being its own dual, as shown in Fig. 2. The three pairs of phases in this figure are $(S_1, \bar{S}_1)$, $(S_2, \bar{S}_2)$ and $(S_3, \bar{S}_3)$, and the single phase S_4 being its own dual. In this and the following sections, we have ordered the phases first by increasing coverage, followed by increasing first-neighbors, then increasing second-neighbors, and last increasing occupied edge-sites. The occupied sites of phases S_i are the black circles and the vacancies are the white circles. Since the vacancies of S_i are the occupied sites of the dual phase $\bar{S}_i$, we have connected these vacant sites to highlight the dual phase. There are 26

Fig. 2. Occupational characteristics and configurations of the phases and their duals on terraces with $M = 3$.

energy regions with first-neighbor repulsion, and 28 energy regions with first-neighbor attraction. The sequence of the phases encountered in each of these regions are exhibited in Tables 1 and 2. The value of the chemical potential, coverage, and entropy at the transition between any two phases are listed in Table 3. There is no need to provide the values of θ , β , and γ as they are each linearly related to the coverage, as explained in Section 1. One notes that most of these values are obtained in closed form, where $\varphi = (1 + \sqrt{5})/2$.

It has been established that the surface structure of the $(2\sqrt{2} \times \sqrt{2})R45^\circ$ -O phase adsorbed on Cu(1 0 0) is missing row-type with oxygen coverage 0.5 ML [15]. Fig. 3 reproduces the observed copper-oxide chain

Table 1

Energy regions and phase sequences on square terraces with $M = 3$ and first-neighbor repulsion ($V < 0$), allowing second-neighbors to be attractive ($W > 0$) or repulsive ($W < 0$), while the differential energy U between adsorbate–substrate in the bulk and the edges being positive or negative

$W < V$	
$U < 2W$	$E \rightarrow S_1 \rightarrow S_2 \rightarrow \bar{S}_3 \rightarrow F$
$2W < U < -V + 2W$	$E \rightarrow S_1 \rightarrow S_2 \rightarrow S_4 \rightarrow \bar{S}_3 \rightarrow F$
$-V + 2W < U < V$	$E \rightarrow S_1 \rightarrow S_4 \rightarrow \bar{S}_3 \rightarrow F$
$V < U < 0$	$E \rightarrow S_1 \rightarrow S_3 \rightarrow S_4 \rightarrow \bar{S}_3 \rightarrow F$
$0 < U < V - W$	$E \rightarrow S_3 \rightarrow S_4 \rightarrow \bar{S}_3 \rightarrow F$
$V - W < U < 2V - 3W$	$E \rightarrow S_3 \rightarrow S_4 \rightarrow \bar{S}_1 \rightarrow F$
$2V - 3W < U$	$E \rightarrow S_3 \rightarrow \bar{S}_2 \rightarrow \bar{S}_1 \rightarrow F$
$V < W < 2V/3$	
$U < 2W$	$E \rightarrow S_1 \rightarrow S_2 \rightarrow \bar{S}_3 \rightarrow F$
$2W < U < W$	$E \rightarrow S_1 \rightarrow S_2 \rightarrow S_4 \rightarrow \bar{S}_3 \rightarrow \bar{S}_1 \rightarrow F$
$W < U < 2V - 2W$	$E \rightarrow S_1 \rightarrow S_3 \rightarrow S_4 \rightarrow \bar{S}_3 \rightarrow \bar{S}_1 \rightarrow F$
$2V - 2W < U < 0$	$E \rightarrow S_1 \rightarrow S_3 \rightarrow S_4 \rightarrow \bar{S}_2 \rightarrow \bar{S}_1 \rightarrow F$
$0 < U < 2V - 3W$	$E \rightarrow S_3 \rightarrow S_4 \rightarrow \bar{S}_2 \rightarrow \bar{S}_1 \rightarrow F$
$2V - 3W < U$	$E \rightarrow S_3 \rightarrow \bar{S}_2 \rightarrow \bar{S}_1 \rightarrow F$
$2V/3 < W < V/2$	
$U < 2W$	$E \rightarrow S_1 \rightarrow S_2 \rightarrow \bar{S}_3 \rightarrow F$
$2W < U < 2V - 2W$	$E \rightarrow S_1 \rightarrow S_2 \rightarrow S_4 \rightarrow \bar{S}_3 \rightarrow \bar{S}_1 \rightarrow F$
$2V - 2W < U < W$	$E \rightarrow S_1 \rightarrow S_2 \rightarrow S_4 \rightarrow \bar{S}_2 \rightarrow \bar{S}_1 \rightarrow F$
$W < U < 0$	$E \rightarrow S_1 \rightarrow S_3 \rightarrow \bar{S}_2 \rightarrow \bar{S}_1 \rightarrow F$
$0 < U$	$E \rightarrow S_3 \rightarrow \bar{S}_2 \rightarrow \bar{S}_1 \rightarrow F$
$V/2 < W < 0$	
$U < 2V - W$	$E \rightarrow S_1 \rightarrow S_2 \rightarrow \bar{S}_3 \rightarrow F$
$2V - W < U < 2V - 2W$	$E \rightarrow S_1 \rightarrow S_2 \rightarrow \bar{S}_3 \rightarrow \bar{S}_1 \rightarrow F$
$2V - 2W < U < W$	$E \rightarrow S_1 \rightarrow S_2 \rightarrow \bar{S}_2 \rightarrow \bar{S}_1 \rightarrow F$
$W < U < 0$	$E \rightarrow S_1 \rightarrow S_3 \rightarrow \bar{S}_2 \rightarrow \bar{S}_1 \rightarrow F$
$0 < U$	$E \rightarrow S_3 \rightarrow \bar{S}_2 \rightarrow \bar{S}_1 \rightarrow F$
$0 < W$	
$U < 2V - W/2$	$E \rightarrow S_2 \rightarrow F$
$2V - W/2 < U < -W/2$	$E \rightarrow S_2 \rightarrow \bar{S}_2 \rightarrow F$
$-W/2 < U$	$E \rightarrow \bar{S}_2 \rightarrow F$

Table 2

Energy regions and phase sequences on square terraces with $M = 3$ and first-neighbor attraction ($V > 0$), allowing second-neighbors to be attractive ($W > 0$) or repulsive ($W < 0$), while the differential energy U between adsorbate–substrate in the bulk and the edges being positive or negative

$W < -2V$	
$U < -2V + 2W$	$E \rightarrow S_1 \rightarrow S_2 \rightarrow \bar{S}_3 \rightarrow F$
$-2V + 2W < U < V + 2W$	$E \rightarrow S_1 \rightarrow \bar{S}_3 \rightarrow F$
$-V + 2W < U < -V$	$E \rightarrow S_1 \rightarrow S_4 \rightarrow \bar{S}_3 \rightarrow F$
$-V < U < 2V$	$E \rightarrow S_4 \rightarrow \bar{S}_3 \rightarrow F$
$2V < U < -W$	$E \rightarrow S_3 \rightarrow S_4 \rightarrow \bar{S}_3 \rightarrow F$
$-W < U < V - 3W$	$E \rightarrow S_3 \rightarrow S_4 \rightarrow F$
$V - 3W < U$	$E \rightarrow S_3 \rightarrow \bar{S}_1 \rightarrow F$
$-2V < W < -V$	
$U < -2V + 2W$	$E \rightarrow S_1 \rightarrow S_2 \rightarrow \bar{S}_3 \rightarrow F$
$-2V + 2W < U < V + 2W$	$E \rightarrow S_1 \rightarrow \bar{S}_3 \rightarrow F$
$V + 2W < U < -V$	$E \rightarrow S_1 \rightarrow S_4 \rightarrow \bar{S}_3 \rightarrow F$
$-V < U < -W$	$E \rightarrow S_4 \rightarrow \bar{S}_3 \rightarrow F$
$-W < U < 2V$	$E \rightarrow S_3 \rightarrow S_4 \rightarrow F$
$2V < U < V - 3W$	$E \rightarrow S_3 \rightarrow S_4 \rightarrow F$
$V - 3W < U$	$E \rightarrow S_3 \rightarrow \bar{S}_1 \rightarrow F$
$-V < W < -V/2$	
$U < -2V + 2W$	$E \rightarrow S_1 \rightarrow S_2 \rightarrow \bar{S}_3 \rightarrow F$
$-2V + 2W < U < -2V - W$	$E \rightarrow S_1 \rightarrow \bar{S}_3 \rightarrow F$
$-2V - W < U < 2V + 3W$	$E \rightarrow \bar{S}_3 \rightarrow F$
$2V + 3W < U < -W$	$E \rightarrow S_4 \rightarrow \bar{S}_3 \rightarrow F$
$-W < U < 2V$	$E \rightarrow S_4 \rightarrow F$
$2V < U < -4W$	$E \rightarrow S_3 \rightarrow S_4 \rightarrow F$
$-4W < U < 4V$	$E \rightarrow S_3 \rightarrow F$
$4V < U$	$E \rightarrow S_3 \rightarrow \bar{S}_1 \rightarrow F$
$-V/2 < W < 0$	
$U < -2V + 2W$	$E \rightarrow S_1 \rightarrow S_2 \rightarrow \bar{S}_3 \rightarrow F$
$-2V + 2W < U < -2V - W$	$E \rightarrow S_1 \rightarrow \bar{S}_3 \rightarrow F$
$-2V - W < U < -2V - 5W$	$E \rightarrow \bar{S}_3 \rightarrow F$
$-2V - 5W < U$	$E \rightarrow F$
$0 < W$	
$U < -2V - W/2$	$E \rightarrow S_2 \rightarrow F$
$-2V - W/2 < U$	$E \rightarrow F$

with the missing rows as reported in [15]. This clearly shows that the surface exhibits terraces of three atomic sites in width, with interstitial adsorption forming a lattice commensurate with the substrate. Oxygen adsorption sites correspond to the phase $\bar{S}_2$. According to our model, the only energy regions where such a phase may occur are: (1) $W < V < 0$ and $U > 2V - 3W$; (2) $V < W < 0$ and $U > 2V - 2W$; or (3) $V < 0 < W$ and $U > 2V - W/2$. Further reduction in the range of interaction energies is possible, if one knows whether this phase is the only one observed.

Table 3
Conditions at all possible transitions between phases on square terraces with $M = 3$

Transition	μ	θ_0	S
$E \rightarrow S_1$	0	$1/3(\varphi + 2)$	$(1/3)\ln \varphi$
$E \rightarrow S_2$	$-W$	$1/6$	0
$E \rightarrow S_3$	$-U$	$1/6$	$(1/3)\ln(1 + \sqrt{2})$
$E \rightarrow S_4$	$-2(V + U)/3$	0.282191805	0.203126
$E \rightarrow \bar{S}_2$	$-3W/2 - U$	$1/3$	0
$E \rightarrow \bar{S}_3$	$-V - (W + U)/2$	0.259005338	0.127415
$E \rightarrow F$	$-4(V + W)/3 - 2U/3$	$1/2$	0
$S_1 \rightarrow S_2$	$-2W$	$(\varphi + 1)/3(\varphi + 2)$	$(1/3)\ln \varphi$
$S_1 \rightarrow S_3$	$-2U$	0.239269398	0.203126
$S_1 \rightarrow S_4$	$-V - U$	$1/3$	$(1/3)\ln(1 + \sqrt{2})$
$S_1 \rightarrow \bar{S}_3$	$-2(2V + W + U)/3$	0.384474861	0.203126
$S_2 \rightarrow \bar{S}_2$	$-2W - 2U$	$1/2$	0
$S_2 \rightarrow \bar{S}_3$	$-2V - U$	$1/2$	$(1/3)\ln(1 + \sqrt{2})$
$S_2 \rightarrow S_4$	$-2(V - W + U)$	0.427397269	0.203126
$S_2 \rightarrow F$	$-2V - 3W/2 - U$	$2/3$	0
$S_3 \rightarrow S_4$	$-2V$	$(\varphi + 3)/3(\varphi + 2)$	$(1/3)\ln \varphi$
$S_3 \rightarrow \bar{S}_2$	$-3W - U$	$1/2$	$(1/3)\ln(1 + \sqrt{2})$
$S_3 \rightarrow \bar{S}_1$	$-(4V + 2U)/3 - 2W$	0.615525139	0.203126
$S_3 \rightarrow F$	$-2(V + W) - U/2$	0.740994660	0.127415
$S_4 \rightarrow \bar{S}_1$	$-V - 3W - U$	$2/3$	$(1/3)\ln(1 + \sqrt{2})$
$S_4 \rightarrow \bar{S}_2$	$2V - 6W - 2U$	0.572602732	0.203126
$S_4 \rightarrow \bar{S}_3$	$-2V - 2W$	$(2\varphi + 3)/3(\varphi + 2)$	$(1/3)\ln \varphi$
$S_4 \rightarrow F$	$-2V - 2(4W + U)/3$	0.717808193	0.203126
$\bar{S}_2 \rightarrow \bar{S}_1$	$-4V$	$(2\varphi + 5)/3(\varphi + 2)$	$(1/3)\ln \varphi$
$\bar{S}_2 \rightarrow F$	$-4V - W$	$5/6$	0
$\bar{S}_3 \rightarrow \bar{S}_1$	$-4W - 2U$	0.760730594	0.203126
$\bar{S}_3 \rightarrow F$	$-2V - 3W - U$	$5/6$	$(1/3)\ln(1 + \sqrt{2})$
$\bar{S}_1 \rightarrow F$	$-4V - 2W$	$(3\varphi + 5)/3(\varphi + 2)$	$(1/3)\ln \varphi$

Then, the model indicates that it occurs if and only if $V < 0 < W$ and $U > -W/2$, which corresponds to the last row of Table 1. The characteristics of the transitions $E \rightarrow \bar{S}_2$ and $\bar{S}_2 \rightarrow F$ are listed in Table 3, which occur at $\mu_1 = -3W/2 - U$ and $\mu_2 = -4V - W$, respectively. As mentioned in previous publications, when the

Fig. 3. Missing row reconstruction of oxygen adsorbed on Cu(1 0 0) exhibiting terraces with $M = 3$, as reported in [15].

entropy at a transition is zero, this expresses the fact that at the transition there is a mixture of the phases appearing on either side. This is the case in the example being considered. Thus, at the first transition one should observe a mixture of empty patches and patches of $\bar{S}_2$. Similarly, at the second transition, one should observe a mixture of patches with full coverage and patches of $\bar{S}_2$. If it is possible to determine experimentally the pressures at which the transitions occur, this in turn will provide the values of μ_1' and μ_2' , leading to the relationships: $\mu_1' = -3W/2 - V_e$ and $\mu_2' = -V_0 - 4V - W$. If in addition, the adsorbate–substrate interactions, V_e and V_0 , at the edge and in the bulk of the terrace are also known, one may then deduce the values of first- and second-neighbor interaction energies as $V = (1/6)(\mu_1' + V_e) - V_0/4$, and $W = -(2/3)(\mu_1' + V_e)$. Since W is expected to be positive and V negative, one predicts $V_e < -\mu_1'$ and $V_0 > (2/3)(\mu_1' + V_e)$.

Fig. 4. (a) Partial listing of the occupational characteristics and configurations of the phases and their duals on terraces with $M = 4$. (b) Continuation of the listing of the occupational characteristics and configurations of the phases and their duals on terraces with $M = 4$.

Another example of adsorption on reconstructed Cu(1 0 0) leading to terraces of $M = 3$ is the “Surfactant effect of oxygen in epitaxial γ -Fe/Cu(0 0 1)–O($2\sqrt{2} \times \sqrt{2}$)R45°” [16]. This experiment shows that oxygen can be used to prepare the surface, which then stabilizes the epitaxial growth of the γ -Fe film. Still another example of preparing the Cu(1 0 0) surface is by adsorption of lithium followed by magnesium leading to Mg/Cu(1 0 0)–Li($2\sqrt{2} \times \sqrt{2}$)R45° [17]. There, the authors use a tensor LEED analysis to conclude that their “model 9” provides the best interpretation of the data. This “model 9” correspond to our phase S_2 . Without additional information, one cannot set limits on the possible interaction energies as this phase occurs in a large number of energy regions.

The deposition of molecular oxygen on Ag(4 1 0) corresponds to adsorption on terraces of three atomic sites in width [18]. This is a molecular beam experiment, where the authors show that adsorption takes place first at the steps, and gradually in the bulk at 105 K. This is interpreted as the sequence, $E \rightarrow S_3 \rightarrow \bar{S}_2 \rightarrow \bar{S}_1 \rightarrow F$. From Table 1, there are several energy regions for which this occurs, corresponding to repulsive first- and second-neighbors ($V < 0$, $W < 0$), and $U > 0$; that is, adsorbate–sub-

strate interaction at the step is larger than that in the bulk of the terrace. This is in agreement with [18] which reports a barrier activation energy of 0.25 eV on the step, and 0.60 eV in the bulk.

We have found references on structural changes of fcc(1 0 0) surfaces occurring during the adsorption process, creating grooves and domain walls with periodicity of 5 and 6 molecular units wide, such as ethanethiol on Au(1 0 0) [19]. While such a system may be treated as made of terraces with $M = 5$ and 6, the experimental data could not be interpreted using our model. The remaining sections summarize the theoretical results for higher width terraces, showing a very rich variety of phases including domain walls.

4. Terraces of width $M = 4$

As we have limited our study to first- and second-neighbor interactions, we found only 11 pairs of phases called $(R_i, \bar{R}_i)$, two phases that are self-dual, R_{12} and R_{13} , and two other phases, R_6 and R_{15} which occur without their dual. This leads to a total of 26 phases. Their occupational characteristics and configurations are shown in Fig. 4a and b.

Table 4

Partial listing of the energy regions and phase sequences on square terraces with $M = 4$ and first-neighbor repulsion

Terraces with $M = 4$ and repulsive first-neighbors: $V < 0$

(a)

$W < 7V/4$

$U < V + 2W$
 $V + 2W < U < V/2 + 2W$
 $V/2 + 2W < U < -V/2 + 2W$
 $-V/2 + 2W < U < 3V$
 $3V < U < 2V$
 $2V < U < 3V/2$
 $3V/2 < U < V$
 $V < U < V/2$
 $V/2 < U < 0$
 $0 < U < -V$
 $-V < U < 5V/2 - 2W$
 $5V/2 - 2W < U < 3V/2 - 2W$
 $3V/2 - 2W < U < V - 2W$
 $V - 2W < U$

$E \rightarrow R_1 \rightarrow R_4 \rightarrow R_7 \rightarrow \bar{R}_{11} \rightarrow \bar{R}_2 \rightarrow F$
 $E \rightarrow R_1 \rightarrow R_4 \rightarrow R_7 \rightarrow \bar{R}_{11} \rightarrow \bar{R}_9 \rightarrow \bar{R}_2 \rightarrow F$
 $E \rightarrow R_1 \rightarrow R_4 \rightarrow R_7 \rightarrow R_{13} \rightarrow \bar{R}_9 \rightarrow \bar{R}_2 \rightarrow F$
 $E \rightarrow R_1 \rightarrow R_4 \rightarrow R_{13} \rightarrow \bar{R}_9 \rightarrow \bar{R}_2 \rightarrow F$
 $E \rightarrow R_1 \rightarrow R_4 \rightarrow R_{13} \rightarrow \bar{R}_9 \rightarrow \bar{R}_5 \rightarrow \bar{R}_2 \rightarrow F$
 $E \rightarrow R_1 \rightarrow R_4 \rightarrow R_{13} \rightarrow \bar{R}_9 \rightarrow \bar{R}_5 \rightarrow \bar{R}_1 \rightarrow F$
 $E \rightarrow R_1 \rightarrow R_4 \rightarrow R_6 \rightarrow R_{13} \rightarrow R_{15} \rightarrow \bar{R}_5 \rightarrow \bar{R}_1 \rightarrow F$
 $E \rightarrow R_1 \rightarrow R_5 \rightarrow R_6 \rightarrow R_{13} \rightarrow R_{15} \rightarrow \bar{R}_4 \rightarrow \bar{R}_1 \rightarrow F$
 $E \rightarrow R_1 \rightarrow R_5 \rightarrow R_9 \rightarrow R_{13} \rightarrow \bar{R}_4 \rightarrow \bar{R}_1 \rightarrow F$
 $E \rightarrow R_1 \rightarrow R_5 \rightarrow R_9 \rightarrow R_{13} \rightarrow \bar{R}_4 \rightarrow \bar{R}_1 \rightarrow F$
 $E \rightarrow R_2 \rightarrow R_5 \rightarrow R_9 \rightarrow R_{13} \rightarrow \bar{R}_4 \rightarrow \bar{R}_1 \rightarrow F$
 $E \rightarrow R_2 \rightarrow R_9 \rightarrow R_{13} \rightarrow \bar{R}_4 \rightarrow \bar{R}_1 \rightarrow F$
 $E \rightarrow R_2 \rightarrow R_9 \rightarrow R_{13} \rightarrow \bar{R}_7 \rightarrow \bar{R}_4 \rightarrow \bar{R}_1 \rightarrow F$
 $E \rightarrow R_2 \rightarrow R_9 \rightarrow R_{11} \rightarrow \bar{R}_7 \rightarrow \bar{R}_4 \rightarrow \bar{R}_1 \rightarrow F$
 $E \rightarrow R_2 \rightarrow R_{11} \rightarrow \bar{R}_7 \rightarrow \bar{R}_4 \rightarrow \bar{R}_1 \rightarrow F$

$7V/4 < W < 5V/4$

The first two sub-regions in the range $U < V/2 + 2W$ are identical to those of region $W < 7V/4$
 $V/2 + 2W < U < 3V$
 $3V < U < -V/2 + 2W$
 $-V/2 + 2W < U < 2V$

$E \rightarrow R_1 \rightarrow R_4 \rightarrow R_7 \rightarrow R_{13} \rightarrow \bar{R}_9 \rightarrow \bar{R}_2 \rightarrow F$
 $E \rightarrow R_1 \rightarrow R_4 \rightarrow R_7 \rightarrow R_{13} \rightarrow \bar{R}_9 \rightarrow \bar{R}_5 \rightarrow \bar{R}_2 \rightarrow F$
 $E \rightarrow R_1 \rightarrow R_4 \rightarrow R_{13} \rightarrow \bar{R}_9 \rightarrow \bar{R}_5 \rightarrow \bar{R}_2 \rightarrow F$

$$E \rightarrow R_2 \rightarrow R_5 \rightarrow R_{11} \rightarrow \bar{R}_7 \rightarrow \bar{R}_4 \rightarrow \bar{R}_1 \rightarrow F$$

Terraces with $M = 4$ and repulsive first-neighbors: $V < 0$ [illegible]

Table 4 (Continued)

Terraces with $M = 4$ and repulsive first-neighbors: $V < 0$		
$0 < W$	$U < 2V - W$	$E \rightarrow R_3 \rightarrow \bar{R}_{11} \rightarrow F$
	$2V - W < U < 2V + W$	$E \rightarrow R_3 \rightarrow R_{12} \rightarrow F$
	$2V + W < U < -W$	$E \rightarrow R_3 \rightarrow R_{12} \rightarrow \bar{R}_3 \rightarrow F$
	$-W < U < W$	$E \rightarrow R_{12} \rightarrow \bar{R}_3 \rightarrow F$
	$W < U$	$E \rightarrow R_{11} \rightarrow \bar{R}_3 \rightarrow F$
Terraces with $M = 4$ and attractive first-neighbors: $V > 0$		
$W < -V$	$U < 2W$	$E \rightarrow R_4 \rightarrow \bar{R}_{11} \rightarrow \bar{R}_2 \rightarrow F$
	$2W < U < 3V/2 + 2W$	$E \rightarrow R_4 \rightarrow \bar{R}_{14} \rightarrow \bar{R}_2 \rightarrow F$
	$3V/2 + 2W < U < -V/2$	$E \rightarrow R_4 \rightarrow R_{13} \rightarrow \bar{R}_2 \rightarrow F$
	$-V/2 < U < V/2$	$E \rightarrow R_{13} \rightarrow \bar{R}_2 \rightarrow F$
	$V/2 < U < 3V/2$	$E \rightarrow R_{13} \rightarrow F$
	$3V/2 < U < 5V/2$	$E \rightarrow R_2 \rightarrow R_{13} \rightarrow F$
	$5V/2 < U < V/2 - 2W$	$E \rightarrow R_2 \rightarrow R_{13} \rightarrow \bar{R}_4 \rightarrow F$
	$V/2 - 2W < U < 2V - 2W$	$E \rightarrow R_2 \rightarrow R_{14} \rightarrow \bar{R}_4 \rightarrow F$
	$2V - 2W < U$	$E \rightarrow R_2 \rightarrow R_{11} \rightarrow \bar{R}_4 \rightarrow F$
$-V < W < -V/2$	The first two sub-regions with $U < -3V/2 - W$ are the same as those of region $W < -V$	
	$-3V/2 - W < U < 3V/2 + W$	$E \rightarrow \bar{R}_{14} \rightarrow \bar{R}_2 \rightarrow F$
	$3V/2 + 2W < U < V/2$	$E \rightarrow R_{13} \rightarrow \bar{R}_2 \rightarrow F$
	$V/2 < U < 3V/2$	$E \rightarrow R_{13} \rightarrow F$
	$3V/2 < U < V/2 - 2W$	$E \rightarrow R_2 \rightarrow R_{13} \rightarrow F$
	$V/2 - W < U < 7V/2 + W$	$E \rightarrow R_2 \rightarrow R_{14} \rightarrow F$
$-V/2 < W < 0$	$7V/2 + W < U < 2V - 2W$	$E \rightarrow R_2 \rightarrow R_{14} \rightarrow \bar{R}_4 \rightarrow F$
	$2V - 2W < U$	$E \rightarrow R_2 \rightarrow R_{11} \rightarrow \bar{R}_4 \rightarrow F$
	$U < -V$	$E \rightarrow \bar{R}_{11} \rightarrow \bar{R}_2 \rightarrow F$
$0 < W$	$-V < U < -V - 3W$	$E \rightarrow \bar{R}_2 \rightarrow F$
	$-V - 3W < U$	$E \rightarrow F$
	$U < -V - W$	$E \rightarrow \bar{R}_{11} \rightarrow F$
	$-V - W < U$	$E \rightarrow F$

There, we have chosen the same conventions as in Fig. 2 corresponding to $M = 3$. The black circles are the occupied sites of phase R_i , and if R_i has a dual, its vacant sites represented by white circles are connected to indicate that they are the occupied sites of the dual $\bar{R}_i$. Unlike the case $M = 3$, there are two partially ordered phases, R_9 and $\bar{R}_9$, for which the entropy is $(1/8)\ln 2$; they correspond to the last diagram of Fig. 2a. The arrow in this diagram indicates the freedom of moving an occupied site to a neighboring vacant site without changing the characteristics of phase R_9 . Similarly, the reverse is possible without changing the characteristics of $\bar{R}_9$. Table 4 parts (a)–(c) provide the complete listing of all the energy regions and the sequence of phases occurring in each of them. For repulsive

first-neighbors ($V < 0$), 11 regions of W have been identified ranging from $W < 7V/4$ to $W > 0$. For repulsive first-neighbors ($V < 0$), four regions of W have also been identified, ranging from $W < -V$ to $W > 0$. These regions are further divided into sub-regions of values of U depending on V and W , each one corresponding to the occurrence of a given sequence of phases by increasing chemical potential. There is a total of 142 sub-regions for $V < 0$, and 23 for $V > 0$. Table 5 provides the conditions at which all possible transitions occur. There are two cases where we could not get the coverage and the entropy with sufficient numerical accuracy and left the corresponding entries blank. In a few cases, the numerical results are obtained in closed form with an accuracy exceeding eight figures. For the first time,

Table 5

Partial listing of the conditions at all possible transitions between phases on square terraces with $M = 4$

Transition	μ	θ_0	S
(a)			
$E \rightarrow R_1$	0	0.097127002	0.191122543
$E \rightarrow R_2$	$-U$	$1/2(\varphi + 2)$	$(1/2)\ln \varphi$
$E \rightarrow R_3$	$-W$	1/8	0
$E \rightarrow R_4$	$-V/2$	0.150837341	0.161142
$E \rightarrow R_{11}$	$-W - U$	1/4	0
$E \rightarrow R_{12}$	$-3W/2 - U/2$	1/4	0
$E \rightarrow R_{13}$	$-3V/4 - U/2$	0.269871321	0.145719
$E \rightarrow \bar{R}_{14}$	$-V - (W + U)/3$	1/4	0
$E \rightarrow \bar{R}_{11}$	$-V - W$	1/4	0
$E \rightarrow \bar{R}_2$	$-(4V + U)/3 - W$	3/8	0
$E \rightarrow F$	$-3(V + W)/2 - U/2$	1/2	0
$R_1 \rightarrow R_3$	$-3W$	0.205747794	0.140600
$R_1 \rightarrow R_4$	$-3V/2$	0.210170089	0.099730
$R_1 \rightarrow R_5$	$-3U/2$	0.237874234	0.140600
$R_1 \rightarrow R_6$	$-V/2 - U$	0.257766093	0.207771
$R_2 \rightarrow R_5$	U	0.275855250	0.077348
$R_2 \rightarrow R_9$	$-V$	0.325640613	0.164217
$R_2 \rightarrow R_{11}$	$-2W - U$	$(\varphi + 1)/2(\varphi + 2)$	$(1/2)\ln \varphi$
$R_2 \rightarrow R_{13}$	$-3V/2$	3/8	$(1/8)\ln 2$
$R_2 \rightarrow R_{14}$	$-(4V + 2W + U)/3$	0.369489732	0.099730
$R_3 \rightarrow R_7$	$-2V + W$	0.294252206	0.140600
$R_3 \rightarrow R_8$	$-W - U$	0.31909	0.121
$R_3 \rightarrow R_{12}$	$-2W - U$	3/8	0
$R_3 \rightarrow \bar{R}_{11}$	$-2V - W$	3/8	0
$R_4 \rightarrow R_6$	$-V/2 - 2U$	0.293922196	0.111516
$R_4 \rightarrow R_7$	$-V/2 - 2W$	0.289829910	0.099730
$R_4 \rightarrow R_{13}$	$-V - U$	3/8	$(1/4)\ln 2$
$R_4 \rightarrow \bar{R}_{14}$	$-3V/2 - 2(W + U)/3$	0.369489730	0.099730
$R_4 \rightarrow \bar{R}_{11}$	$-3V/2 - 2W$	0.349162659	0.161142
(b)			
$R_5 \rightarrow R_6$	$-5V/2 + U$	0.317132645	0.063195
$R_5 \rightarrow R_8$	$-5W + U$	0.344560946	0.123678
$R_5 \rightarrow R_9$	$-5V/3 - 2U/3$	0.350530484	0.127573
$R_5 \rightarrow R_{11}$	$-(5W + 3U)/2$		
$R_6 \rightarrow R_{10}$	$-V/4 - 9W/2 + U$	0.365734710	0.063195
$R_6 \rightarrow R_{13}$	$-7V/4 - U/2$	0.411495588	0.140600
$R_7 \rightarrow R_{10}$	$V - 2W - 3U/2$	0.369268755	0.088595
$R_7 \rightarrow R_{13}$	$-5V/4 + W - 3U/2$	0.420340177	0.099730
$R_7 \rightarrow \bar{R}_{11}$	$-2V - 2W$	0.402872994	0.191121
$R_8 \rightarrow R_{10}$	$-4V + 3W + U$	0.387927625	0.077348
$R_8 \rightarrow R_{12}$	$-3W - U$	0.430900	0.122
$R_9 \rightarrow R_{11}$	$V - 4W - 2U$	0.414373104	0.217088
$R_9 \rightarrow R_{13}$	$-2V$	5/12	$(1/8)\ln 3$
$R_{10} \rightarrow R_{12}$	$V - 9W/2 - 3U/2$	0.443059537	0.106145
$R_{10} \rightarrow R_{13}$	$-11V/4 + 3W - 3U/2$	0.448289499	0.077348
$R_{10} \rightarrow \bar{R}_{11}$	$-4V - 2W + U$	0.438115715	0.140600

Table 5 (Continued)

Transition	μ	θ_0	S
$R_{11} \rightarrow \bar{R}_7$	$-2V - W$	0.597127002	0.191123
$R_{11} \rightarrow \bar{R}_4$	$-5V/2 - W$	0.650837341	0.161142
$R_{12} \rightarrow \bar{R}_{10}$	$2V + 3W/2 - U/2$	0.556940463	0.106145
$R_{12} \rightarrow \bar{R}_8$	$2V - U$	0.569	0.121
$R_{12} \rightarrow \bar{R}_3$	$-2V - W - U$	5/8	0
$R_{12} \rightarrow F$	$-3V - 3W/2 - U/2$		
$R_{13} \rightarrow R_{15}$	$-5V/4 - 3W - U/2$	0.588504410	0.140600
$R_{13} \rightarrow \bar{R}_{10}$	$7V/4 - 6W - 3U/2$	0.551710501	0.077348
$R_{13} \rightarrow \bar{R}_9$	$-2V - 3W$	7/12	$(1/5)\ln 2$
$R_{13} \rightarrow \bar{R}_7$	$V/4 - 4W - 3U/2$	0.579659810	0.099730
$R_{13} \rightarrow \bar{R}_4$	$-V - 3W - U$	5/8	$(1/4)\ln 2$
$R_{13} \rightarrow \bar{R}_2$	$-V/2 - 3W$	5/8	$(1/8)\ln 2$
$R_{13} \rightarrow F$	$-9V/4 - 3W - U/2$	0.730128681	0.145719
(c)			
$R_{14} \rightarrow \bar{R}_{14}$	$-7V/6 - 7W/3 - 2U/3$	0.630510270	0.099730
$R_{14} \rightarrow F$	$-7V/3 - 8W/3 - U/3$	3/4	0
$R_{15} \rightarrow \bar{R}_5$	$-7V/2 - 3W + U$	0.682867354	0.063195
$R_{15} \rightarrow \bar{R}_4$	$-V/2 - 3W - 2U$	0.706077803	0.111512
$R_{15} \rightarrow \bar{R}_1$	$-3V/2 - 3W - U$	0.742233908	0.207771
$\bar{R}_{14} \rightarrow \bar{R}_2$	$-2V - 7W/3 - U/3$	0.630510270	0.099730
$\bar{R}_{11} \rightarrow \bar{R}_9$	$-V + W - 2U$	0.585626896	0.217087
$\bar{R}_{11} \rightarrow \bar{R}_7$	$-2V - W$	0.402872994	0.191121
$\bar{R}_{11} \rightarrow \bar{R}_5$	$-V - W/2 - 3U/2$	0.623768570	0.140600
$\bar{R}_{11} \rightarrow \bar{R}_2$	$-2V - W - U$	$3/4 - 1/4\sqrt{5}$	$(1/2)\ln \varphi$
$\bar{R}_{11} \rightarrow F$ (low T)	$-2V - 2W - U$	3/4	0
$\bar{R}_{11} \rightarrow F$ (high T)	$-2V - 2W - U$	7/8	$(1/4)\ln 2$
$\bar{R}_{10} \rightarrow R_{15}$	$-23V/4 + 3W/2 + U$	0.634265290	0.063195
$\bar{R}_{10} \rightarrow \bar{R}_8$	$-2V - 6W + U$	0.612072375	0.088595
$\bar{R}_{10} \rightarrow \bar{R}_7$	$-2V - W - 3U/2$	0.630731246	0.140600
$\bar{R}_9 \rightarrow \bar{R}_5$	$-V - 3W - 2U/3$	0.649469516	0.127573
$\bar{R}_9 \rightarrow \bar{R}_2$	$-3V - 3W$	2/3	$(1/5)\ln 2$
$\bar{R}_8 \rightarrow \bar{R}_5$	$-6V + 2W + U$	0.655439056	0.123678
$\bar{R}_8 \rightarrow \bar{R}_3$	$-2V - 2W - U$	0.68088	0.1116
$\bar{R}_7 \rightarrow \bar{R}_4$	$-7V/2 - W$	0.710170089	0.099730
$\bar{R}_7 \rightarrow \bar{R}_3$	$-2V - 4W$	0.705747794	0.140600
$\bar{R}_5 \rightarrow \bar{R}_2$	$-6V - 3W + U$	0.724144750	0.077348
$\bar{R}_5 \rightarrow \bar{R}_1$	$7V/4 - 6W - 3U/2$	0.762125767	0.140600
$\bar{R}_4 \rightarrow \bar{R}_1$	$-5V/2 - 3W$	0.789829910	0.099730
$\bar{R}_4 \rightarrow F$	$-7V/2 - 3W$	0.849162659	0.161142
$\bar{R}_3 \rightarrow \bar{R}_1$	$-4V$	0.794252205	0.140600
$\bar{R}_3 \rightarrow F$	$-4V - 2W$	7/8	0
$\bar{R}_2 \rightarrow F$ (low T)	$-2V - 3W - U$	7/8	0
$\bar{R}_2 \rightarrow F$ (high T)	$-2V - 3W - U$	$3/4 + 1/4\sqrt{5}$	$(1/2)\ln \varphi$
$\bar{R}_1 \rightarrow F$	$-4V - 3W$	0.902872998	0.191123

Fig. 5. (a) Partial listing of the occupational characteristics and configurations of the phases and their duals on terraces with $M = 5$. The occupied sites of the phases are the black circles which are connected. Dual phases when they exist have not been highlighted as in Figs. 2 and 4a and b. Phases Q_1 , Q_4 , Q_{10} and Q_{11} exhibit staircase patterns. Preferential edge adsorption appears in Q_2 and Q_6 , clustering at the edges in Q_9 and $\overline{Q}_{11}$, ladder pattern in Q_7 , and triangular pattern in Q_5 . (b) Continuation of the listing of the occupational characteristics and configurations of the phases and their duals on terraces with $M = 5$. Here, Q_{13} is a ladder pattern with alternating vacant and occupied sites in the middle, while Q_{14} is a combination of ladder and partial edge adsorption. Q_{15} and Q_{16} have a combination of squares and triangles, decorated and partially decorated.

Fig. 6. An example of domain wall formation on even-width M terraces with edge-sites being second-neighbors. Here the drawing is for a terrace with $M = 10$.

we have observed transitions which occur at different coverage and entropy depending on temperature, for $\bar{R}_{11} \rightarrow F$ and $\bar{R}_2 \rightarrow F$. This change occurs abruptly at a given critical temperature which itself depends on the energy region.

5. Terraces of width $M > 4$

We have completed the compilation of all the energy regions and phases for $M = 5$ and 6, and obtained partial results for higher width terraces up to and including $M = 11$. For $M = 5$, there are 10 pairs of phases ($Q_i, \bar{Q}_i$), one self-dual phase Q_{12} , and five phases appearing without their dual, $Q_5, Q_{10}, Q_{14}, Q_{15}$ and Q_{16} , for a total of 26 phases, as in the case $M = 4$. The occupational characteristics and configurations are shown in Fig. 5a and b. For repulsive first-neighbors, there are 8 energy regions for W , ranging from $W < V$ to $W > 0$, with 98 sub-regions for U . For attractive first-neighbors, there are 16 energy regions for W ranging from $W < -7V/3$ to $W > 0$, with 178 sub-regions for U .

For $M = 6$, there are 13 pairs of phases, 2 self-dual phases, and 26 phases occurring without their dual, for a total of 54 phases. For repulsive first-neighbors, there are 24 energy regions for W , with 462 sub-regions for U . For attractive first-neighbors, there are two energy regions for W , $W < 0$ and $W > 0$,

with nine sub-regions for U . All of this information is available upon request. However, the given diagrams for $M = 5$ should be a sufficient guide for the experimentalists, and gives some hints on how we were able to achieve the analytical extension for any M of a number of phases.

Generalization of the results for higher width terraces have been obtained. Namely, preferential adsorption on the edges correspond to two phases: (1) every other edge-site is occupied, $\{1/M, 0, 0, 1/M\}$, generalizing S_3, R_2 , and Q_2 ; and (2) all edge-sites are occupied, $\{2/M, 0, 0, 2/M\}$, generalizing R_{11} and Q_6 . These phases also appear with their duals. Cluster formation on the edges has also been found, namely $\{2/M, 4/3M, 2/3M, 4/3M\}$, which is the generalization of phases R_{14} and Q_9 , as well as a number of phases with domain walls. For example, phase $\{(M+2)/4(M+1), 0, 0, 1/(M+1)\}$ occurring on even width terraces is the generalization of R_5 . It consists of a staircase of vacancies separating triangular patches of $p(2 \times 2)$. Phase $\{(3M^2 - 6M - 8)/4M(M-3), (M^2 - 2M - 2)/M(M-3), (M^2 - 2M - 2)/M(M-3), 2/M\}$ for even-width terraces, $M > 4$, is another example of a domain wall pattern. Fig. 6 makes the domain wall more explicit with $M = 10$. For any even $M > 4$, the periodicity of the domain walls is $M - 3$. To give a flavor of some of the generalizations we have achieved, the following is a sequence of phases generalized for $M > 4$ and

corresponding to repulsive first- and second-neighbors with $U < 2V + 3W$:

phases and the complete set of energy regions in which a given phase sequence is observed. This work

$$\begin{aligned}
 E \xrightarrow{\mu=0} & \left\{ \frac{M-2}{4(M-1)} \quad 0 \quad 0 \quad 0 \right\} \xrightarrow{\mu=\frac{2(M-1)V}{M}} \left\{ \frac{M-2}{4(M-1)} \quad 0 \quad 0 \quad 0 \right\} \\
 & S = \left(\frac{1}{2M} \right) \ln \left(\frac{M-2}{2} \right) \xrightarrow{\mu=-2V} \left\{ \frac{M-2}{2M} \quad \frac{M-3}{2M} \quad 0 \quad 0 \right\} \\
 & \xrightarrow{\mu=-V-3W} \left\{ \frac{1}{2} \quad \frac{M-1}{2M} \quad \frac{3}{M} \quad 0 \right\} \xrightarrow{\mu=\frac{(2M-7)V}{M-4} - \frac{2(2M-9)W}{M-4}} \left\{ \frac{2(M-1)}{3M} \quad \frac{5(M-2)}{6M} \quad \frac{2}{3} \quad 0 \right\} \\
 & \xrightarrow{\mu=\frac{(2M-5)V}{M-4} - \frac{4(M-3)W}{M-4}} \left\{ \frac{(M-2)(3M-8)}{4M(M-3)} \quad \frac{M^2-6M+10}{M(M-3)} \quad \frac{M-2}{M} \quad 0 \right\} \\
 & \xrightarrow{\mu=-4V-\frac{2(M-3)W}{M-4}} \left\{ \frac{3M^2-18M+16}{4M(M-5)} \quad \frac{M^2-6M+6}{M(M-5)} \quad \frac{M^2-6M+6}{M(M-5)} \quad 0 \right\} \\
 & \xrightarrow{\mu=-4V-4W} \left\{ \frac{M-2}{M} \quad \frac{2(M-3)}{M} \quad \frac{2(M-3)}{M} \quad 0 \right\} \xrightarrow{\mu=-2V-W-U} \left\{ \frac{M-1}{M} \quad \frac{2(M-2)}{M} \quad \frac{2M-5}{M} \quad \frac{1}{M} \right\} \xrightarrow{\mu=-2V-W-U} F.
 \end{aligned}$$

From Figs. 4a–b and 5a–b, referring to terraces of width $M = 4$ and 5, respectively, we have also found adsorption on sites forming, squares, ladders, and triangles. For $M = 6$, we have also observed irregular hexagons of different orientations, as well as combination of hexagons and squares. There are a number of phases appearing without their dual partners, and rarely does the sequence of phases in a given energy region exhibit particle-hole symmetry, normally expected for pair-wise interactions.

6. Conclusion

The model is applicable at thermal equilibrium and relatively low temperature (may be as high as 1000 K in some cases). The surface structure is assumed to remain unchanged during adsorption. However, in some cases, surface reconstruction occurs during the adsorption of certain elements, such as oxygen and alkali metals, adsorption on the reconstructed surface may then be analyzed using this model. The interaction energies are coverage independent and the only ones considered are: adsorbate–substrate in the bulk being different from that at the edges; and adsorbate–adsorbate limited to first- and second-neighbors.

Since no a priori assumptions are made as to whether forces are attractive or repulsive, or as to their relative strength, we have obtained all possible

has shown the effect of the orientation of the edge-sites of square lattice terraces. Unlike the previous study [1] of square lattice terraces with edge-sites being first-neighbors, when edge-sites are second-neighbors, a richer collection of structural orderings are observed. With the edge-sites being first-neighbors we only found square and rectangular adsorption patterns, and their various combinations. Here, we highlighted clustering on the edges and domain walls, and for the first time, we have observed conditions of certain transitions between two phases to depend on temperature. The changes in these conditions occur at a critical temperature, which depends on the energy region.

For a given adsorption system, while keeping a relatively low temperature, we suggest one gradually increases the external gas pressure and records, at thermodynamic equilibrium, the phases and conditions at which the transition between phases occur. The phases and the order in which they appear depend on the interaction energies. Thus, with this information, one can deduce the various interaction energies in the manner described in Section 3 for $M = 3$. If there are experimental data available for square terraces with $M = 4$, we have provided Tables 4 and 5 to allow for the analysis of the data and obtain some, if not all of the interaction energies, provided first- and second-neighbor interactions are predominant. Should experimental data become available

for terraces with $M = 5$ and 6, the equivalent of Table 4 and parts (a)–(b) of Table 5 will be provided upon request.

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