Interplay between steps and nonequilibrium effects in surface diffusion for a lattice-gas model of O/W(110)

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The authors consider the influence of steps and nonequilibrium conditions on surface diffusion in a strongly interacting surface adsorbate system. This problem is addressed through Monte Carlo simulations of a lattice-gas model of O/W(110), where steps are described by an additional binding energy E_B at the lower step edge positions. Both equilibrium fluctuation and Boltzmann-Matano spreading studies indicate that the role of steps for diffusion across the steps is prominent in the ordered phases at intermediate coverages. The strongest effects are found in the $p(2 \times 1)$ phase, whose periodicity L_p is 2. The collective diffusion then depends on two competing factors: domain growth within the ordered phase, which on a flat surface has two degenerate orientations [$p(2 \times 1)$ and $p(1 \times 2)$], and the step-induced ordering due to the enhanced binding at the lower step edge position. The latter case favors the $p(2 \times 1)$ phase, in which all adsorption sites right below the step edge are occupied. When these two factors compete, two possible scenarios emerge. First, when the terrace width L does not match the periodicity of the ordered adatom layer (L/L_p is noninteger), the mismatch gives rise to frustration, which eliminates the effect of steps provided that E_B is not exceptionally large. Under these circumstances, the collective diffusion coefficient behaves largely as on a flat surface. Second, however, if the terrace width does match the periodicity of the ordered adatom layer (L/L_p is an integer), collective diffusion is strongly affected by steps. In this case, the influence of steps is manifested as the disappearance of the major peak associated with the ordered $p(2 \times 1)$ and $p(1 \times 2)$ structures on a flat surface. This effect is particularly strong for narrow terraces, yet it persists up to about $L \approx 25 L_p$ for small E_B and up to about $L \approx 500 L_p$ for E_B, which is of the same magnitude as the bare potential of the surface. On real surfaces, similar competition is expected, although the effects are likely to be smaller due to fluctuations in terrace widths. Finally, Boltzmann-Matano spreading simulations indicate that even slight deviations from equilibrium conditions may give rise to transient peaks in the collective diffusion coefficient. These transient structures are due to the interplay between steps and nonequilibrium conditions and emerge at coverages, which do not correspond to the ideal ordered phases. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2713100]

I. INTRODUCTION

Metal surfaces are essentially never ideally flat but rather characterized by various kinds of imperfections such as impurities and defects, including steps and kinks. However, this is by no means an undesired matter, since in many cases, steps and kinks, for example, are highly useful as they promote chemical reactions and enhance molecular dissociation.[1–4] These properties that are rather unique to steps have elicited substantial experimental activity focused on understanding the role of stepped surfaces in potential applications. What is rather surprising, though, is that theoretical and computational studies of stepped surfaces have received considerably less attention. This is particularly true

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with regard to surface diffusion, which plays a crucial role in a variety of surface processes such as surface growth, lubrication, as well as reactions between individual particles.[5–10] The related single-particle (tracer) and collective diffusion processes have been investigated rather extensively on flat (idealized) systems,[11–14] but the challenge of addressing step-induced effects on surface diffusion is still a topical issue.

The first systematic study of the influence of regular arrays of steps on diffusion was done by Natori and Godby,[15] who treated the tracer diffusion of a single particle within the lattice-gas model. Recently, Durukonaglu *et al.*[16] considered the effect of step-step separation on surface diffusion using molecular dynamics simulations, with focus on single-particle dynamics. Another recent study is by Olsen *et al.*[17], who employed density functional theory to determine the influence of steps on the diffusion of hydrogen on Pt(211). Concerning collective diffusion, the first comprehensive theoretical analysis in equilibrium was carried out by Merikoski and Ying.[18,19] They considered the simple Langmuir lattice-gas model and established that additional binding at the step edge has a pronounced influence. Further, they were able to establish a criterion for crossover from terrace dominated to step dominated diffusion in terms of the additional binding energy at the step edge and the Ehrlich-Schwoebel barrier.[19] Over the last few years, the present authors have carried out a series of systematic studies of collective diffusion and spreading on vicinal surfaces,[20–25] in most cases by considering a lattice-gas model of a stepped surface through Monte Carlo simulations. These studies have focused on the role of various generic properties such as the distinctly different energetics along and across the steps and strengthened binding at the step edge positions in determining the coverage dependence of collective diffusion (for a review of some of the work, see Ref. 24). The enhanced binding at the step edge is often the rate limiting step in terms of the diffusion rate across the steps (though enhanced diffusion across steps compared to a flat surface has also been observed[26]).

However, despite this considerable body of work, there is one important issue that remains unexplored. This is the role of steps in diffusion within *spatially ordered phases* of surface adsorbate systems, which is characteristic of many strongly interacting surface systems at low enough temperatures. Thus, to clarify the role of steps in systems where ordered phases among adsorbed adatoms emerge from interparticle interactions under given thermodynamic conditions, we consider here a lattice-gas model of oxygen adatoms diffusing on a stepped W(110) surface. We also address the influence of nonequilibrium conditions in this context through simulations of spreading of density profiles of oxygen adatoms.

II. MODEL

We consider here a system of strongly interacting adatoms on a static vicinal surface. For this purpose, we employ a model of oxygen atoms diffusing on a W(110) surface, which has been cleaved to a desired terrace width (step-step distance) L. All terraces are of equal width and the steps are
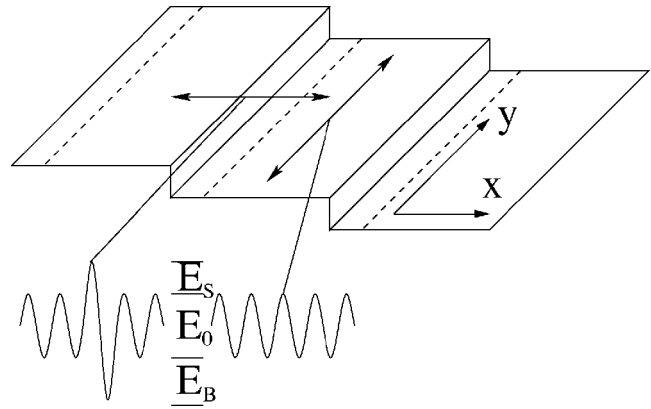

FIG. 1. Geometry and relevant activation barriers for the model used here for a stepped surface. In the direction across the steps, there is an additional barrier at the step edge position known as the Ehrlich-Schwoebel barrier E_S. The E_B denotes an additional binding energy at the lower step edge, and E_0 characterizes the diffusion barrier of a single adatom in the dilute limit on a flat surface. The diffusion tensor for adatoms has its principal axes in the x direction across the steps and in the y direction along the steps.

straight, i.e., there are no kinks. On a flat surface, the lattice-gas Hamiltonian for this model is given by[27,28]

$$H = \sum_{m=1}^{5} \sum_{\langle ij \rangle} J_m n_i n_j + \sum_{m=1}^{2} \sum_{\langle ijk \rangle} J_{tm} n_i n_j n_k - \mu \sum_i n_i. \quad (1)$$

The Hamiltonian includes pair interactions up to fifth nearest neighbors as well as certain three-body interactions. Here $n_i = 0, 1$ is the occupation number of the lattice site i, and $\langle ij \rangle$ and $\langle ijk \rangle$ denote pair and three-body interactions, respectively. The strengths of the respective interactions are denoted by J_m and J_{tm}; see Ref. 28 for details. Following Refs. 27 and 28, we have chosen $J_2 = J_3 = -0.390 J_1$, $J_5 = 0.690 J_1$, and $J_{t1} = J_{t2} = -0.720 J_1$. To set the scales for temperature and energy, we have chosen $J_1 = -58.3$ meV, which reproduces the phase transition temperature of $T_c \approx 710$ K between the disordered high-temperature phase and the ordered $p(2 \times 1)$ phase at a coverage of $\theta \approx 0.45$; see Ref. 28. The number of adatoms in our simulations is fixed; thus we set the chemical potential $\mu = 0$.

As depicted in Fig. 1, steps on the surface are characterized by several parameters. There is an Ehrlich-Schwoebel barrier E_S controlling rates over step edges and an additional binding energy at the lower step edge E_B. The activation barrier of a single adatom (in the limit $\theta \rightarrow 0$) associated with a jump on a terrace is given by E_0.

To numerically study diffusion, we have performed standard Monte Carlo simulations using the transition dynamics algorithm (TDA) of Ref. 29, in which the thermally activated nature of diffusion processes is accounted for. In essence, in the TDA a jump from an initial state i with energy E_i to a final state f with energy E_f proceeds through an intermediate saddle point or transition state I with energy $E_I = \Delta + (E_i + E_f)/2$. Then the transition rate from the initial to the final state is subsequently $w_{i,f} = w_{i,I} w_{I,f}$, where the rates have a Metropolis form $w_{i,j} = \min[1, \exp(-(E_j - E_i)/k_B T)]$ and the additional barrier $\Delta > 0$ characterizes the effect of the (bare) saddle point of the adiabatic substrate potential together with step-induced effects. Here, since our objective is to gauge the

influence of steps on surface diffusion for this model system, we have described Δ in terms of E_0 and E_B as follows:

$$E_I = \frac{E_i + E_f}{2} + E_0 + E_B. \tag{2}$$

Note that here E_0 does not influence the qualitative behavior of diffusion but only scales the magnitude of diffusion coefficients. The additional binding energy E_B is nonzero only at the lower step edge position, and its strength is varied in our simulations; see Sec. III for discussion.

In equilibrium simulations, we determine the collective surface diffusion coefficient $D_c(\theta)$ by decomposing it in a standard way[14,30,31] into the center-of-mass diffusion coefficient (mobility) $D_{cm}(\theta)$ and the thermodynamic factor $K_d(\theta)$, which together yield

$$D_c(\theta) = K_d(\theta) D_{cm}(\theta). \tag{3}$$

Here,

$$K_d(\theta) = \frac{1}{S_0(\theta)}, \tag{4}$$

where the static structure factor S_0 is calculated as the zero wave-vector limit of the full dynamic structure factor $S(\mathbf{q}, t)$ at $t=0$ as

$$S_0 = \lim_{\mathbf{q} \to 0} S(\mathbf{q}, t=0). \tag{5}$$

To compute S_0, we used a large system comprised of 500×500 lattice sites, from which S_0 was calculated for subsystems of linear sizes 50, 100, 150, 200, 220, and 240 lattice sizes, hence employing finite-size analysis to extract the final value for S_0.

The mobility is calculated from the center-of-mass displacement

$$D_{cm} = \lim_{t \to \infty} \frac{1}{2Ntd} \langle |\mathbf{R}(t) - \mathbf{R}(0)|^2 \rangle, \tag{6}$$

where $\mathbf{R} = (1/N) \Sigma_i \mathbf{r}_i$, and $\mathbf{r}_i$'s are the coordinates of the N particles, and $d=2$ is the spatial dimension. As usual, we have computed $D_{cm}(\theta)$ by using the memory expansion method.[14,32] To this end, systems of sizes 100×100 sites were used. Our data for D_{cm} were typically averaged over 5×10^7 Monte Carlo steps.

To find the full coverage dependence of $D_c(\theta)$, we have determined it through the well-established Boltzmann-Matano (BM) method.[6,33] The BM method is widely used for analysis of collective diffusion in spreading experiments. We have recently employed the same approach to elucidate the influence of nonequilibrium conditions and impurities on surface diffusion coefficients.[20,23,34–36] The BM method is based on an assumption that, in the long time limit, the coverage profiles $\theta(x,t)$ along the spreading direction x collapse to a single scaling function when scaled with $\theta(x/\sqrt{t})$. Using the transformation $\eta = x/\sqrt{t}$, we can find $D_c(\theta)$ as a solution of the nonlinear diffusion equation as[37]

$$D_c(\theta) = -\frac{1}{2t} \left(\frac{dx}{d\theta} \right)_\theta \int_0^\theta x(\theta') d\theta'. \tag{7}$$

In practice, spreading simulation has been conducted for a system of size $L_x \times L_y$ lattice sites. Typical values chosen in this work are $L_x = 1500$ and $L_y = 200$, though they depend slightly on the number of steps and the terrace width, see below. The initial adatom distribution corresponds to a sharp steplike interface profile where all sites for $x < L_x/2$ are occupied ($\theta = 1$), while the other half of the system is empty ($\theta = 0$). Hence the density gradient gives rise to diffusive spreading in the $+x$ direction. Periodic boundary conditions are employed in both directions. However, in all the cases studied here, the system size has been chosen to be large enough in the x direction such that the adatoms never reach the boundary of the system during the simulation. As an example, for spreading across the steps separated by five lattice sites ($L=5$), the system has been chosen to contain 300 steps and thus for spreading across the steps $L_x = 1500$.

Following our previous works,[20,23] we can use Eq. (7) as an operational definition to obtain effective, time-dependent diffusion coefficients $D_c^t(\theta)$ from coverage profiles scaled at well-separated limited time intervals, where the system is still evolving towards its equilibrium state. In practice this is done by averaging coverage profiles from independent spreading simulations at fixed time periods. The data are typically averaged over 50–60 independent simulations. Based on our tests, there are no observable finite-size effects in our data.

The model used for O/W(110) has been previously studied extensively for the case of a flat surface under equilibrium[28,38,38] and nonequilibrium conditions.[40] The parametrization of steps, though, is less obvious because we are not aware of any experimental or first-principles studies to shed light on the values of E_S and E_B. The only somewhat related study is the one by Jardin et al.,[41] who considered the energetics of oxygen on a stepped bcc (110) surface using a tight-binding scheme with approximations, where the specific nature of the surface was not accounted for. Despite its generic nature, Ref. 41 concludes that the binding of oxygen at the lower step edge position is more favorable than on a terrace ($E_B > 0$), E_S is small, and that diffusion parallel to the ledge is rather insensitive to the presence of the step. Consequently, in our simulations we have used a parametrization which is consistent with these findings. The Ehrlich-Schwoebel barrier was set at $E_S = 0$, because that does not change the nature of the results but only slows down diffusion here. The value of $E_B > 0$ was varied during the simulations to consider its influence on diffusion. Finally, the bare potential was chosen to be $E_0 = 50$ meV, which is consistent with previous studies.[28]

All calculations were done at the temperature of $T = 590$ K. On the one hand, this temperature is sufficiently low to observe all the important ordered phases of this system. On the other hand, it is also high enough to facilitate getting good statistics for collective diffusion. In the chosen temperature, the phase behavior[39] is characterized by many phases starting from the disordered phase at low coverages, from which one crosses continuously over to the $p(2 \times 1)$ phase at $\theta \approx 0.35$. At higher coverages, there is another transition of second order to the $p(2 \times 2)$ phase at $\theta \approx 0.59$, which in turn crosses continuously over to the disordered
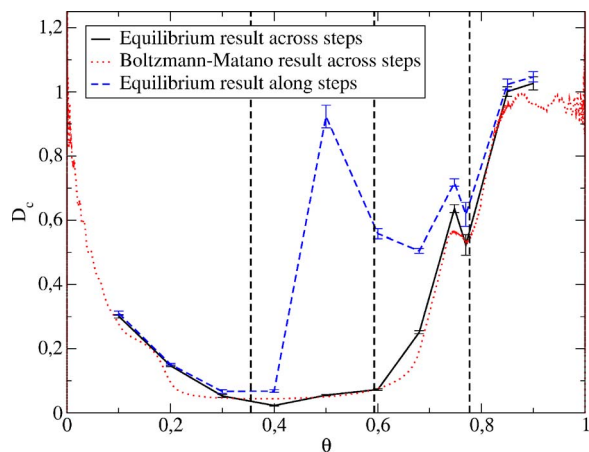
FIG. 2. Equilibrium (solid line) and BM (dotted) results for $D_c(\theta)$ for diffusion across the steps, using $L=4$ and $E_B=5$ meV. For comparison, the dashed line represents $D_c(\theta)$ for diffusion along the steps. The case along the steps is qualitatively similar to the equilibrium results for a flat surface (Ref. 39) Vertical lines indicate the positions of phase boundaries in equilibrium for a flat surface (see text for details).

phase around $\theta \approx 0.78$. The phase diagram is in line with experimental findings; see Ref. 28 for discussion on this matter. In the figures below, these phase boundaries as determined from equilibrium simulations for a system without steps have been shown by dashed lines, where appropriate.

III. RESULTS

A. Equilibrium results and equilibration of Boltzmann-Matano profiles

Let us first consider the equilibrium behavior of collective diffusion. While these studies are computationally more time consuming than BM simulations, which rather readily result in the full coverage dependence of $D_c(\theta)$, the equilibrium data allow us to determine the conditions when the BM profiles are sufficiently close to equilibrium conditions. Having done this, we can employ BM simulations to thoroughly elucidate the influence of steps on surface diffusion.

Comparison between equilibrium and BM simulations with $L=4$ and $E_B=5$ meV is given in Fig. 2. The focus here is on the data for diffusion across the steps. They indicate that the time period of 250 000–300 000 Monte Carlo steps (MCS) used for the analysis of BM simulations is sufficiently long in order to find the correct equilibrium behavior of collective diffusion. The deviations from equilibrium are minor. They are observable only in the high-coverage ordered $p(2\times2)$ phase close to $\theta=0.75$, where the BM simulations slightly reduce the peak height of $D_c(\theta)$ as the ordering of the adatom phase is not fully developed. Hence, unless mentioned otherwise, the BM results discussed below have been analyzed from the same time window, that is, for 250 000–300 000 MCS after the initiation of the spreading process.

Figure 2 illustrates the prominent role of steps on diffusion and, in particular, the role of step orientation with respect to diffusion. The diffusion tensor can be decomposed into two principal components: one component characterizing diffusion along the steps and another describing diffusion
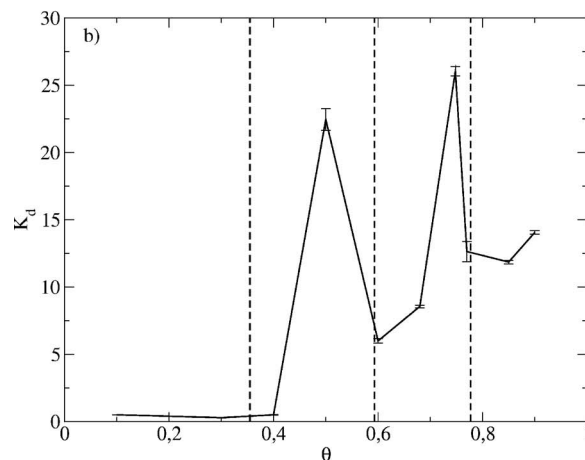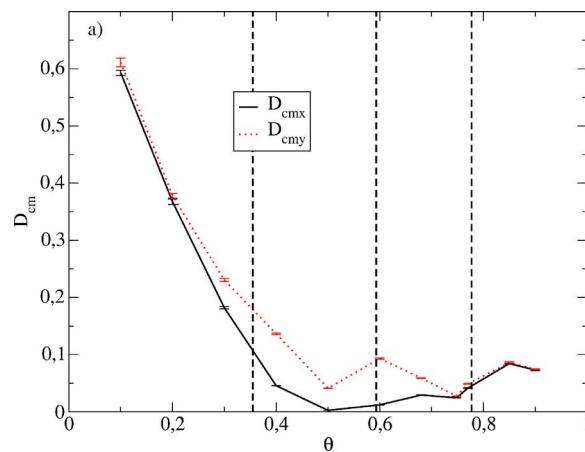

FIG. 3. (a) Equilibrium mobility $D_{cm}(\theta)$ across (solid line) and along (dotted line) the steps. Here $D_{cmx}(\theta)$ $[D_{cmy}(\theta)]$ stands for diffusion across (parallel to) the steps. (b) Thermodynamic factor as determined through equilibrium simulations. The results are for $L=4$ and $E_B=5$ meV. Vertical lines indicate the positions of phase boundaries in equilibrium for a flat surface.

perpendicular to them. The data in Fig. 2 highlight the fact at small coverages, diffusion along and across steps is essentially similar. In the ordered $p(2\times1)$ phase, however, the situation is completely different. In this highly ordered anisotropic phase, the diffusion coefficients along and across the steps are significantly different. This difference is due to the center-of-mass diffusion coefficient (see Fig. 3), which is strongly suppressed for diffusion across the steps. The attenuation essentially eliminates the main peak in $D_c(\theta)$ around $\theta=0.5$. As $D_{cm}(\theta)$ competes with the thermodynamic factor and $K_d(\theta)$ displays a strong peak at $\theta=0.5$ (see Fig. 3), it is obvious that the steps reduce the diffusive motion substantially across the steps.

It is interesting to compare the present result with the results of collective diffusion for the same model on a flat surface.[35] We find that $D_{cx}(\theta)$ and $D_{cy}(\theta)$ perfectly match those found for $D_{c,\perp}(\theta)$ and $D_{c,\parallel}(\theta)$, where $D_{c,\perp}$ and $D_{c,\parallel}$ are the collective diffusion coefficients across and along the chains of adatoms in the $p(2\times1)$ phase, respectively. This means that the specific orientation of the $p(2\times1)$ phase in this stepped system is induced by the steps, that is, the binding energy E_B. This is demonstrated in Fig. 4, which for $\theta \approx 0.5$ clearly shows how the adatoms close to steps prefer to
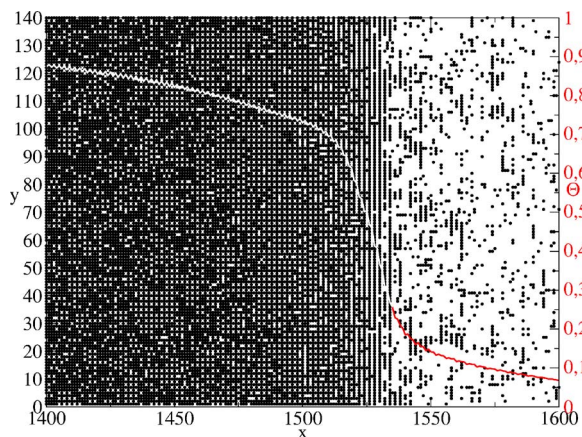
FIG. 4. Snapshot of the system after 300 000 MCS for $L=4$ and E_B $=50$ meV. Note that only part of the system is shown here in the y direction. The density profile $\theta(x)$ vs x is also shown by the continuous line across the system (see the right panel for the coverage scale).

FIG. 6. Example of the system configuration after 300 000 MCS for L $=16$ and $E_B=5$ meV. Only part of the system is shown in the y direction. The density profile is also shown by the continuous line.

form rows right under the step edge. This in turn dictates the orientation of the $p(2 \times 1)$ phase and results in the slow center-of-mass diffusion across the steps.

In the $p(2 \times 2)$ phase, $D_{cm}(\theta)$ is also affected to some degree, but the difference is considerably smaller than in the $p(2 \times 1)$ phase.

B. Boltzmann-Matano spreading: Even terrace widths

The above results highlight the distinct difference between diffusion along and across the steps. However, the terrace width considered above was small and matched the ordered phases of this system. Next we consider the case where the terrace width is varied over a large range, subject to a condition that it still coincides with the size of the $p(2 \times 1)$ and $p(2 \times 2)$ phases; that is, we consider even values of L. The objective is to assess the changes in diffusion associated with a crossover from narrow to wide terraces. The case of odd L is discussed separately below.

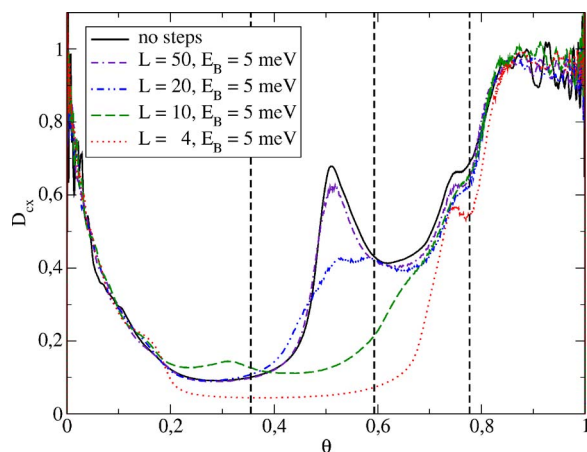Figure 5 shows the collective diffusion coefficient across

FIG. 5. Results for the collective diffusion coefficient across steps, $D_{cx}(\theta)$, for different terrace widths $L=4$, 10, 20, and 50. The additional binding energy at the lower step edge has been chosen as $E_B=5$ meV. $D_c(\theta)$ on a flat surface (solid line) is shown for reference. Vertical dashed lines denote the phase boundaries of the $p(2 \times 1)$ and $p(2 \times 2)$ phases for a system without steps.
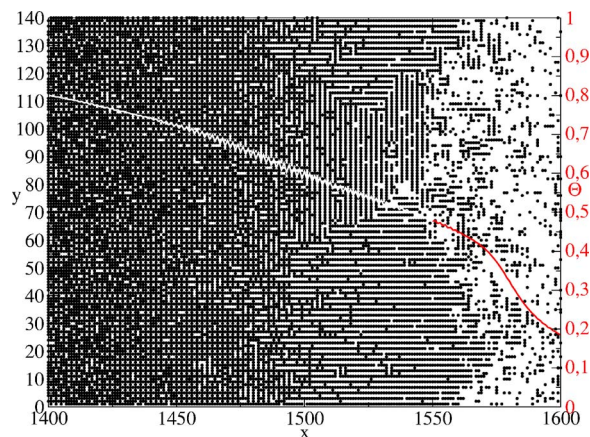
the steps, $D_{cx}(\theta)$, for several even terrace widths. We also show the results for a flat surface in the absence of steps (see also Ref. 39). The results for a flat surface show how closely the collective diffusion reflects changes in phase behavior and, in particular, the ordered nature of the adatom layer. This is evidently close to the ideal coverages of 1/2 and 3/4 of the $p(2 \times 1)$ and $p(2 \times 2)$ phases, respectively, where we find prominent peaks due to the strongly enhanced thermodynamic factor in the ordered regions. What is remarkable, though, is the influence of steps on diffusion data. For wide terraces (large L), $D_{cx}(\theta)$ is essentially similar to the data for a flat surface. In the other limit of a narrow terrace ($L=4$), the minor peak at $\theta=0.75$ is still found but the main peak around $\theta=0.5$ is completely absent. The reasons for this behavior were discussed in the previous section, the main point being the increased binding at the lower step edge. The enhanced binding at the step edge fixes the orientation of the $p(2 \times 1)$ phase, blocking mass flow as almost all sites right below the step edge are occupied, which in turn implies that the collective diffusion across the steps is substantially reduced. This effect is most prominent for narrow terraces. As the terrace width is increased, the role of steps and the additional binding at the step edge become less important, and the behavior approaches that of the flat surface. There, both orientations of the $p(2 \times 1)$ phase contribute equally to the collective diffusion. In the present case, the crossover between the "narrow" and "wide" terrace behavior is around $L_{co} \approx 16$. Under these conditions, both orientations of the $p(2 \times 1)$ phase are present, see Fig. 6. For $L > L_{co}$, we found data supporting the presence of a (small) peak around $\theta =0.5$, while for $L < L_{co}$, such behavior was not evident.

The cases corresponding to narrow terraces pose a challenge for simulations, since the equilibration times become very large. This is due to the large concentration of steps and the resulting binding at the step edges. As an example, the minor peaks in Fig. 5 for $L=10$ at $\theta \approx 0.3$ and for $L=4$ at $\theta \approx 0.15$ are actually transient features and due to the fact that these systems are not in complete equilibrium. When these simulations were extended to much longer times (beyond 10^6 MCS), these minor peaks vanished while all other structures in the data remained unchanged. What makes this
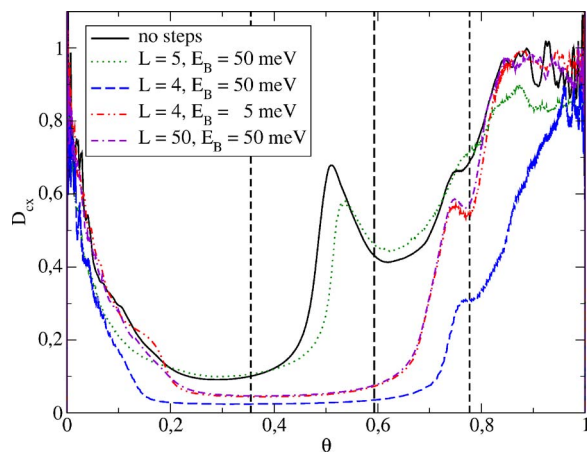
FIG. 7. Collective diffusion coefficients across the steps, $D_{cx}(\theta)$, for odd ($L=5$) and even ($L=4$) terrace widths. The result for a flat surface is also given for comparison. For the even terrace width ($L=4$), the data demonstrate the effect of two different binding energies at the lower step edge position ($E_B=5$ and 50 meV). Also shown is the case of a wide terrace ($L=50$) with a strong binding energy ($E_B=50$ meV). In the case of the odd terrace width ($L=5$), we only show the results for strong binding ($E_B=50$ meV). The $D_{cx}(\theta)$ for $L=5$ with a small binding energy $E_B=5$ meV is essentially identical to the flat surface behavior and is hence not plotted here. Vertical dashed lines denote the locations of phase boundaries for a flat system without steps.
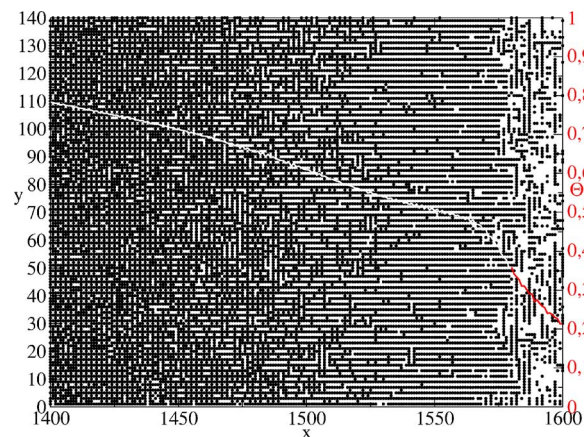

FIG. 8. Snapshot of the system configuration after 300 000 MCS for a case with $L=5$ and $E_B=50$ meV. Only part of the system is shown in the y direction. Continuous line indicates the density profile.

finding interesting is the fact that Butz and Wagner[42] have conducted BM spreading experiments to consider the diffusion of oxygen on a W(110) surface. While their studies are not fully comparable to ours due to the temperature range of 760–880 °C in their study (corresponding to the disordered phase), some features of their findings may be compared to ours. Butz and Wagner found that $D_c(\theta)$ displayed a maximum near $\theta \approx 0.45$ and a decrease beyond $\theta=0.6$. The studies in Ref. 42 were conducted over large times (4–45 min) and large distances (several micrometers). Hence the experimental data are presumably influenced by nonequilibrium conditions (see Fig. 6 in Ref. 42) as well as steps, which are essentially unavoidable over such large scales (see also Ref. 43). In our simulation data, we have found the emergence of transient peaks at coverages less than 0.5, originating from the interplay of steps and nonequilibrium conditions. In particular, the data in Fig. 5 for $L=20$ show that for the present stepped system the main peak close to $\theta=0.5$ is more shallow and considerably broadened with respect to the flat surface, and there is some structure on the low-coverage side of the main peak. All these features are in qualitative agreement with the data in Ref. 42.

C. Boltzmann-Matano spreading: Odd terrace widths

In real samples, where the terrace widths are not necessarily identical to each other, it is likely that the unit cell corresponding to an ordered adatom layer does not always coincide with the step-step distance but gives rise to local frustration. In the present case, that happens when L is an odd number. To this end, let us first consider the cases $E_B=5$ and 50 meV together with $L=5$, see Fig. 7. We find that for weak binding at the step edge ($E_B=5$ meV), $D_{cx}(\theta)$ is practically the same as in the flat surface case (data not shown). Further, even for strong binding at the lower step

edge, $E_B=50$ meV, the collective diffusion coefficient is affected by steps only very weakly. Clearly, the even and odd terrace widths give rise to distinctly different behavior, see Fig. 7 for comparison. This difference is further emphasized by the fact that for $L=4$, the step-induced effects are very prominent, while an increase of L from 4 to 5 drastically changes the behavior of $D_{cx}(\theta)$.

The significance of odd L is demonstrated in Fig. 8. Even though L is small, we find only region with orientations of the $p(2 \times 1)$ phase with chains perpendicular to steps close to $\theta=0.35-0.59$. For comparison, a similar snapshot for $L=4$ shown in Fig. 4 indicates only the orientations with chains parallel to persist in that case. It is evident that an odd L gives rise to frustration, which in turn breaks the step-induced ordering manifested as a specific orientation of the $p(2 \times 1)$ phase.

D. Boltzmann-Matano spreading: Influence of step edge binding

Finally, let us briefly discuss the role of E_B in more detail. One of the issues related to the present model is the strength of this additional binding parameter at the lower step edge. In the absence of *ab initio* or experimental data, we prefer not to make strong arguments in favor of any particular value of E_B. Usually, on the basis of changes in the coordination number as adatoms diffuse from terraces to the step edge, it is justified to expect enhanced binding at the lower step edge position. This generic property is here complemented by studies where we vary the value of E_B and hence aim to clarify the resulting trends. The results presented below are mainly for $E_B=5$ and 50 meV. The significance of these numbers is best understood by comparing them to the bare potential value $E_0=50$ meV: see Sec. II.

For even terrace widths, Fig. 7 shows that E_B has a significant effect on $D_{cx}(\theta)$ for narrow terraces. Then, the stronger the binding energy E_B is, the more suppressed the ordering effects are in $D_{cx}(\theta)$. When the terrace width is increased with strong binding up to $L=50$, we find that the influence of steps is alleviated in the sense that the data are very close to the case of weak step binding with a narrow terrace width ($L=4$ and $E_B=5$ meV), see Fig. 7. Here, Fig. 5 indicates that
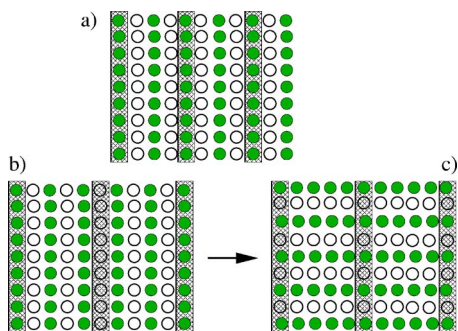
FIG. 9. Schematic structures for occupied (filled circles) and vacant (open circles) sites on the W(110) surface, where the first rows of adsorption sites under the step edge are shown as dashed boxes. (a) The ordered $p(2 \times 1)$ phase has a periodicity of 2 and hence matches the periodicity of a vicinal surface with even L (here $L=4$). (b) In the case of an odd L (here $L=5$), the periodicity of the $p(2 \times 1)$ phase does not match the periodicity of the vicinal surface. (c) Consequently, for odd L (here $L=5$), the orientation perpendicular to steps is also possible and may emerge spontaneously.

for $E_B = 5$ meV, the terrace width has to change from $L=4$ to $L \approx 50$ to recover the main peak at $\theta = 0.5$. Using this as a rough estimate, we can conclude that for $E_B = 50$ meV in Fig. 7, the terrace width should increase to about $L = 1000$ to find the peak at $\theta = 0.5$ in a manner similar to the flat surface. This highlights the prominent role of steps on diffusion: the strong binding ($E_B = 50$ meV) used here is of the same magnitude as the bare potential of the surface, E_0. Thus, the stronger E_B is, the more prominent its effects are on collective diffusion. For odd terrace widths, the situation is clearly different. Then weak binding ($E_B = 5$ meV) has no effect at all, and even for strong binding the effect is surprisingly small, see Fig. 7.

Summarizing the above results, we may conclude that there are two competing factors which both give rise to ordering along the surface. First, as also shown in previous works,[18–24] the lower step edge acts as a trap for adatoms which diffuse across the steps. This favors enhanced occupancy of adsorption sites at the lower step edge position, and for sufficiently strong binding at the step edge all adsorption sites in the first row below the step would be occupied. In order to adapt to this condition, the $p(2 \times 1)$ phase should orient itself accordingly. Second, due to the symmetric nature of the Hamiltonian, the two orientations of the $p(2 \times 1)$ phase are energetically equivalent in the flat surface case: thus the self-ordering of the adlayer promotes both orientations to a similar extent. The competition between the two factors dictates the ordering of the system. The key parameters in this respect are L and E_B characterizing steps and the adatom interaction Hamiltonian.

As shown in Fig. 9, the competing factors dominate under different conditions. For even and small L, the step-induced effect is important even for small E_B. For even and large L, the influence of steps on diffusion is important only if E_B is large compared to typical adatom-adatom interactions. When L is odd, however, the self-ordering dominates as L in this case does not match the periodicity of the $p(2 \times 1)$ phase and hence reduces the impact of the additional binding energy at the step edge. Thus, for odd L, steps play a major role in collective diffusion only if E_B is very large.

IV. SUMMARY AND DISCUSSION

Nanoscale engineering of surfaces offers new possibilities for controlling various kinetic processes such as growth or chemical reactions. One particularly simple and effective way to achieve this is to create regular arrays of steps on single crystal substrates by cleaving or through growth techniques. It has been demonstrated that such arrays of steps can be indeed used to control surface kinetics and, in particular, spreading, adatom mobility, and collective diffusion.

In the present work, we have extended our previous studies[20–25] on the influence of regular arrays of steps to the important case where strong interactions between the surface adatoms lead to the formation of ordered phases at finite coverages. This leads into an interesting interplay between step and nonequilibrium effects due to the competition between intrinsic phase ordering and step-induced symmetry breaking in ordering. In particular, using a lattice-gas model for the O/W(110) adsorbate system, we demonstrate that the collective diffusion then depends on two competing factors: domain growth within the ordered phase and step-induced ordering due to enhanced binding at the lower step edge position. The latter case favors an ordered phase, in which all adsorption sites below the step edge are occupied. In the case of O/W(110), this means that strong step edge binding selects one of the degenerate phases around $\theta = 0.5$ when the step spacing matches its intrinsic periodicity. In this case collective adatom transport is strongly affected by steps in the ordered phase. However, if the matching condition is not met, there is frustration that largely eliminates the effect of steps provided that step edge binding is not exceptionally large. Under these circumstances, the collective diffusion coefficient behaves largely as on a flat surface.

As already briefly mentioned in Sec. III C, under realistic experimental conditions, there is always some variation in the distribution of the terrace widths due to miscut errors, impurities, thermal fluctuation effects, etc. In the present case, such variation can cause significant changes in the ideal scenario presented above. This effect should be most pronounced in the $p(2 \times 1)$ phase, where mass transport is efficiently reduced at terraces with even (and small) L due to the matching condition with ordering. If we consider the case where we assume that the steps are ideally straight and the intended miscut corresponds to high-mobility steps (e.g., $L = 5$) and there is a small concentration of low-mobility steps ($L = 4$ or $L = 6$), the latter hinder the mobility of adatoms very efficiently. However, in the opposite case where a system with mostly low-mobility steps is diluted with high-mobility steps, there should be very little change in diffusion. In the more realistic case where step widths fluctuate in time and in space, the above scenario is too simplistic because the high- and low-mobility patches do not percolate through the system but are small. It would be an interesting problem to study these effects with more detailed simulations.

Additionally, our Boltzmann-Matano spreading simulations indicate that even slight deviations from equilibrium conditions may give rise to transient peaks in the collective diffusion coefficient. These transient structures are due to the interplay between steps and nonequilibrium conditions and

emerge at intermediate coverages. The detailed role of domain growth on stepped surfaces will be studied in future works.

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