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Nonequilibrium effects in diffusion of interacting particles on vicinal surfaces

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Nonequilibrium effects in diffusion of interacting particles on vicinal surfaces

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We study the influence of nonequilibrium conditions on the collective diffusion of interacting particles on vicinal surfaces. To this end, we perform Monte Carlo simulations of a lattice-gas model of an ideal stepped surface, where adatoms have nearest-neighbor attractive or repulsive interactions. Applying the Boltzmann–Matano method to spreading density profiles of the adatoms allows the definition of an effective, time-dependent collective diffusion coefficient $D_C^t(\theta)$ for all coverages θ. In the case of diffusion across the steps and strong binding at lower step edges we observe three stages in the behavior of the corresponding $D_{xx,C}^t(\theta)$. At early times when the adatoms have not yet crossed the steps, $D_{xx,C}^t(\theta)$ is influenced by the presence of steps only weakly. At intermediate times, where the adatoms have crossed several steps, there are sharp peaks at coverages $\theta<1/L$ and $\theta>1-1/L$, where L is the terrace width. These peaks are due to different rates of relaxation of the density at successive terraces. At late stages of spreading, these peaks vanish and $D_{xx,C}^t(\theta)$ crosses over to its equilibrium value, where for strong step edge binding there is a maximum at $\theta=1/L$. In the case of diffusion in direction along the steps the nonequilibrium effects in $D_{yy,C}^t(\theta)$ are much weaker, and are apparent only when diffusion along ledges is strongly suppressed or enhanced. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1924695]

I. INTRODUCTION

Far from playing an inert role as mere interfaces, solid surfaces facilitate a variety of dynamic processes. Surface diffusion, in particular, is one of the most important elementary processes, playing a crucial role in many surface-related phenomena such as surface growth, chemical reactions, and corrosion and melting. The mechanisms of surface diffusion and its properties in a variety of systems has, therefore, been studied extensively in the last few decades. Atomic diffusion on ideal solid surfaces in equilibrium is now rather well understood.[1–9] However, since most real surfaces are ideal only on relatively short length scales, it is imperative to understand the surface diffusion behavior in systems with steps and other characteristic features such as impurities and dislocations that are an inherent property of realistic surfaces. For this reason, there have been immense efforts to study, e.g., diffusion on vicinal surfaces both experimentally[10–14] and theoretically.[5,15–25] The influence of steps on surface diffusion is particularly important in spreading processes, which occur under nonequilibrium conditions.

We have recently undertaken a project to systematically study the influence of steps and impurities on surface diffusion under equilibrium[20–22] as well as nonequilibrium conditions.[19,26–28] As for nonequilibrium phenomena on stepped surfaces, the previous work[19] has been based on the Langmuir gas model, where the only interaction between adatoms is site exclusion. However, it is remarkable that despite its highly simplified nature, even the Langmuir gas model indicates nonequilibrium to play a major role, causing significant deviations for the coverage dependence of collective diffusion.[19]

Under conditions where direct interactions between the adatoms cannot be neglected, the *interplay between nonequilibrium effects, steps, and adatom interactions* is expected to further complicate the situation. To shed light on this issue, we have recently studied the equilibrium case with repulsive nearest-neighbor (NN) interactions in Refs. 20 and 21, where it was shown that the coverage dependence of the collective

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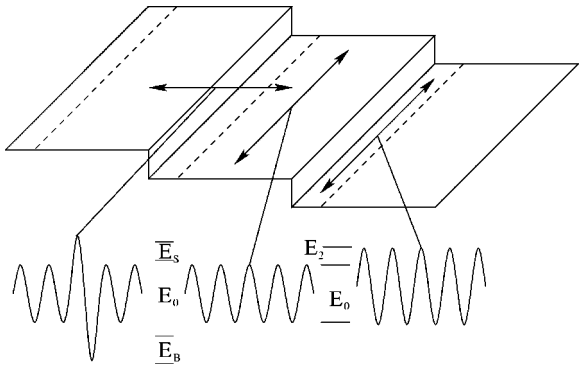

FIG. 1. Geometry and relevant activation barriers for the model of stepped surfaces. In direction across the steps the energy of the saddle point is increased by an Ehrlich–Schwoebel barrier at the step edge, E_B denotes an additional binding energy at the lower step edge, and E_2 is an additional activation energy for jumps along the lower step edge. The diffusion tensor for adatoms has its principal axes in the x direction across steps, and in the y direction along steps.

diffusion coefficient D_C is sensitive to the adatom interactions, in particular, for diffusion across the steps. In the present work, we extend these studies to the case of nonequilibrium spreading, which allows a systematic study of the influence of large coverage gradients on a stepped surface. We discuss here the case of both repulsive and attractive NN interactions in the case of relatively strong binding at the step edge, where the influence of steps is significant. We present results for diffusion across and along the steps and compare them systematically to corresponding equilibrium results.

II. MODEL

In this work we consider a system of interacting adatoms on a static vicinal surface. The interaction energy between the adatoms is given by the lattice-gas Hamiltonian

$$H/k_BT = K\sum_{\langle ij\rangle} n_i n_j, \tag{1}$$

where $K=\pm J/k_BT$ is the NN interaction strength, and J and $-J$ ($J>0$) are the coupling constants for repulsive and attractive interactions, respectively. The occupation numbers $n_i=0,1$ are summed over the NN sites of a square lattice. This model has been previously studied, e.g., in Refs. 5 and 18 in the case of an ideal surface, and we have previously used it for stepped surfaces in Refs. 19–22. On an ideal square lattice Eq. (1) is the lattice-gas representation of the two-dimensional (2D) Ising model, whose phase diagram is well known, with a critical coupling of $|K_C|=1.76$ separating the low-temperature ordered and high-temperature disordered phases.[5,18] Here we employ a value $|K|<1.76$, thus we gauge diffusion in the disordered phase.

Steps on the surface are modeled by three parameters in addition to the terrace activation energy E_0 (see Fig. 1). There is typically an Ehrlich–Schwoebel barrier E_S controlling rates over step edges, an additional binding energy at the lower step edge E_B, and an additional activation energy for jumps along the steps E_2.

Following our previous works,[19–22] we set the Ehrlich–Schwoebel barrier to zero because it does not bring any new physical phenomena here but only slows down diffusion.[15] The energy E_B increases the barrier for jumps away from step edges which act as sinks for adatoms. The activation energy is then given by $E_1=E_0+E_B$. Finally, the additional activation energy for jumps along lower step edges E_2 enhances ($E_2<0$) or suppresses ($E_2>0$) diffusion rates along the steps edges. The terraces in our model are separated by parallel steps with regular spacing L, for which we have employed the choice $L=5$ in most cases here.

We have performed standard Monte Carlo simulations with the transition dynamics algorithm (see Ref. 29). The saddle-point energy $E_{\rm sp}$ has been chosen to be always larger than the initial and final energy states E_i and E_f, respectively, i.e., $E_{\rm sp}=E_{{\rm sp},1}+E_{{\rm sp},2}$, where $E_{{\rm sp},1}=3K$ in the case of repulsive interactions, $E_{{\rm sp},1}=0$ in the case of attractive interactions, $E_{{\rm sp},2}=E_2$ in the case of fast diffusion along the steps ($E_2<0$), and $E_{{\rm sp},2}=0$ otherwise.

III. BOLTZMANN-MATANO METHOD

To determine the collective diffusion coefficient $D_C(\theta)$ as a function of coverage θ, we use the well-established Boltzmann—Matano (BM) method.[2,30] This method is widely used for analysis of the collective diffusion coefficient in spreading experiments. The method is based on an assumption that, in the long-time limit, the coverage profiles $\theta(x,t)$ 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[31]

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

Following our previous work,[19] we can use Eq. (2) 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 different calculations at fixed times, corresponding to 10–10 000 Monte Carlo steps (MCS) here. We typically average the data over 1000 simulation runs. In all the cases studied here, the system size is chosen to large enough in the direction of spreading such that the adatoms never reach the boundary of the system. For example, for spreading across the steps the system contains 300 steps, and for spreading along the steps $L_y=1500$. In the direction perpendicular to spreading we use periodic boundary conditions and system size of 140 unit cells. There are no observable finite-size effects in our data.

In our previous work in Ref. 19, it was found that starting from only one initial configuration of the system (with a fully occupied terrace corresponding to the last case in Fig. 2), there are oscillations in the coverage profiles corresponding to the periodicity of the system. To cancel out such oscillations, in the present work we have used all the configurations shown in Fig. 2 as initial configurations to obtain the

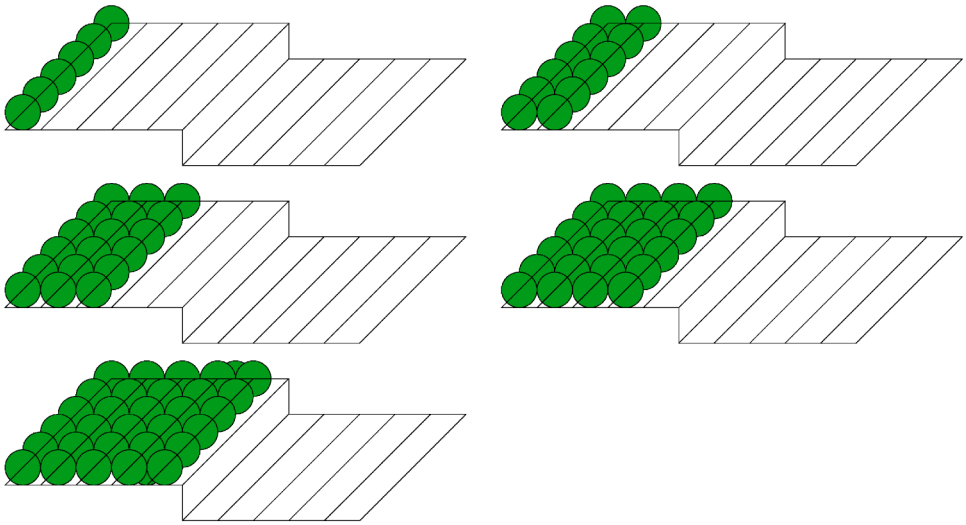

FIG. 2. Initial configurations used in the Monte Carlo simulations for the case of $L=5$. The resulting profiles are calculated as averages over simulation runs starting from these five profiles.

average profiles. This is done simply in such a way that for each initial state, half of the system is fully covered by adatoms whereas the other half is empty. This also better corresponds to the experiments where it is difficult to precisely control the boundary of the steplike profiles.

IV. RESULTS

We consider here three typical combinations of the coupling strength K, which can be either attractive or repulsive, and the binding energy at the lower step edge E_B/k_BT: (i) the case where the step binding dominates, (ii) the case where the adatom interactions dominate, and (iii) the case where both energies are roughly equal. The value of K is chosen to be small enough so that the system is always in the disordered phase. For all cases we consider separately diffusion across the steps in the x direction, and along the steps in the y direction. All the diffusion coefficients here have been normalized by the isotropic single particle diffusion coefficient on an ideal surface, $D_0 \equiv D_C(\theta \rightarrow 0)$.

A. Diffusion across steps—repulsive case

In the case of repulsive interactions it is well known that collective diffusion in equilibrium (including the adatom mobility) is enhanced.[5,18] In the present case this enhancement of diffusion competes with slowing down caused by the binding of adatoms at the lower step edges. Thus, while systems with repulsive interactions relax relatively rapidly to equilibrium, here the presence of steps slows down this process.

In particular, the large difference between diffusion rates on terraces and across the steps brings about new behavior in the nonequilibrium diffusion coefficient at early stages of spreading. This is most pronounced in the case of strong binding at lower step edge with $E_B/k_BT=4$, where we observe three different stages of evolution (see Figs. 3 and 4). At the first stage corresponding to early times (less than 100 MCS) in Fig. 3(a), $D^t_{xx,C}(\theta)$ depends only weakly on θ. It monotonically grows at low coverages and has a maximum at high coverages. This is qualitatively similar to the corresponding system of interacting particles on a flat surface.[5,18] At this stage the adatoms diffuse within one terrace only and therefore $D^t_{xx,C}(\theta)$ is influenced by the presence of steps only weakly.

At the second stage corresponding to intermediate times (up to about 500 MCS) in Fig. 3(b), the adatoms start to cross to the neighboring terraces and the role of diffusion across the steps increases. The concentration at lower step edges is significantly below its equilibrium value. Due to a high concentration gradient and a low jump probability the backflow of particles from the lower step edge to the terrace with a higher coverage is almost zero. This means that the local balance between concentrations on the terrace and its immediate step edge is reached faster than the balance between concentrations on neighboring terraces. As we can see in Fig. 5, at low coverages $d\theta/d(x/\sqrt{t})$ changes discontinuously at step positions and therefore $D^t_{xx,C}(\theta)$ is discontinuous too: at coverages below $1/L$, $D^t_{xx,C}(\theta)$ continuously grows on an interval, which corresponds to a linear region of the coverage profile (i.e., one terrace, see Fig. 5), and then jumps down. Amplitudes of the corresponding peaks decrease with increasing coverage and time, and vanish at coverage $1/L$ because above this coverage the step edge positions are almost fully occupied. The same effect observed at high coverages is due to the diffusion of vacancies on the surface.

At the third and final stage, which corresponds to times larger than about 1000 MCS in Fig. 3(c), adatom concentration at the lower step edge is almost saturated to its equilibrium value. In this regime the extra peaks disappear and $D^t_{xx,C}(\theta)$ converges to its equilibrium counterpart, as expected.

Based on our arguments above the existence of extra peaks in $D^t_{xx,C}(\theta)$ is an effect of the surface steps and it should be suppressed by repulsive interactions. To verify this we compare in Fig. 4 results for two coupling constants $K=0.5$ and $K=1$ for the case of strong step binding $E_B/k_BT=4$. The transient peaks visible in Fig. 4(a) for small cover-

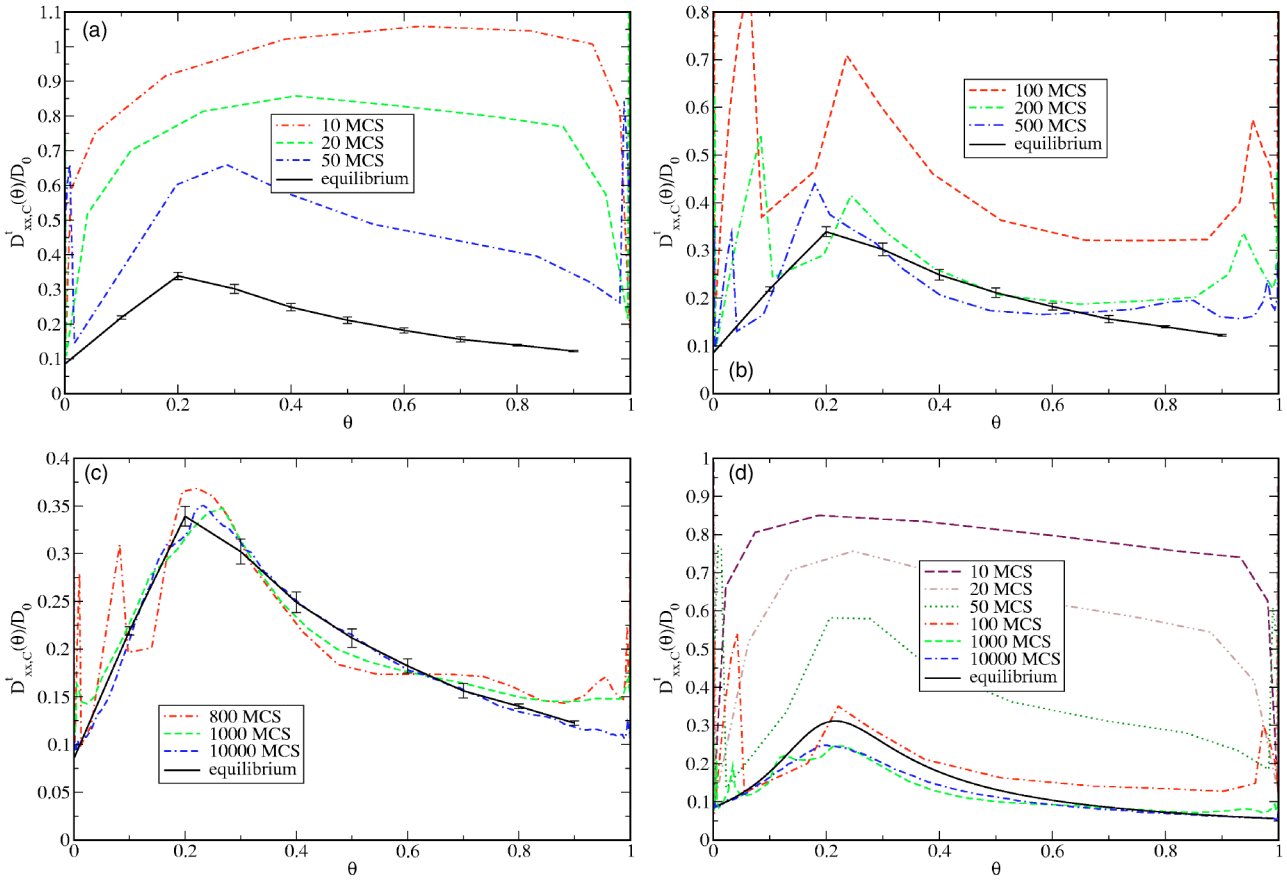

FIG. 3. Equilibrium (solid line) and time-dependent collective diffusion coefficients for a system with $E_B/k_BT=4$ and NN repulsion $K=0.2$ in three different stages (see text for details) in the case of diffusion across the steps. Reference case of the system with $K=0$ is presented in (d).

ages indeed disappear almost completely for stronger repulsive coupling due to enhanced diffusion [see Fig. 4(b)].

In the case of weak binding at the lower step edge $E_B/k_BT=1$ shown in Fig. 6, diffusion through the step is fast enough to suppress the transient peaks. Relaxation of the system towards equilibrium is also faster.

Finally, we have also studied systems with weak step binding $E_B/k_BT=1$ and even weaker couplings such as $K=0.2$ and 0.5, and as expected for such systems the nonequilibrium effects are weak. Additionally, the approach to equilibrium is also fast.

B. Diffusion across steps—attractive case

Next, we consider the case of attractive NN interactions in the model. In this case adatom attraction should slow down diffusion and lead to persistent nonequilibrium effects. In Fig. 7 we show results for the case of strong step binding and weak attraction, which is qualitatively similar to the case with weak repulsive interactions. There are again three time regimes, but the crossover times between them are shifted to longer times than in the repulsive cases. In the case of stronger attractive interaction in Fig. 8, diffusion slows down con-

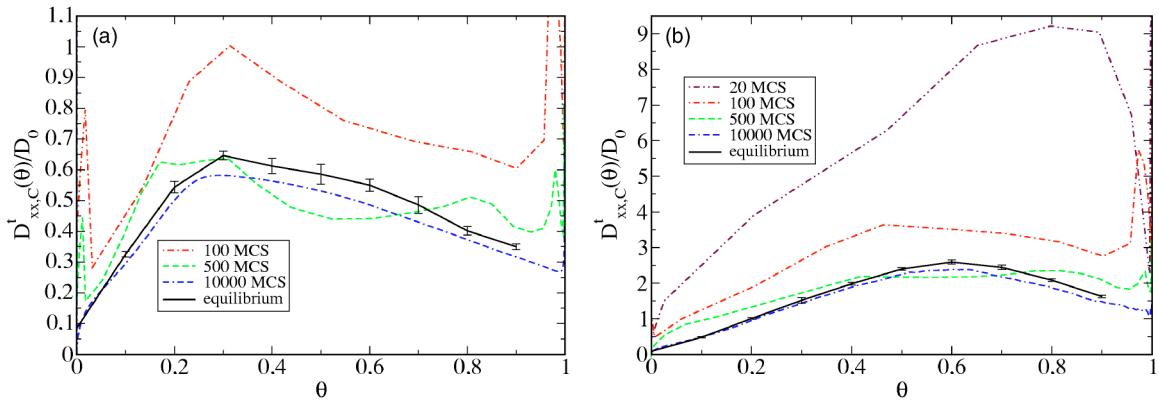

FIG. 4. Equilibrium (solid line) and time-dependent collective diffusion coefficients for a system with $E_B/k_BT=4$ and NN repulsive couplings (a) $K=0.5$ and (b) $K=1$ in the case of diffusion across the steps.

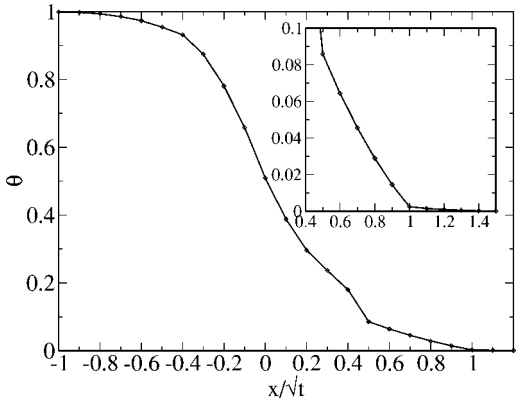

FIG. 5. Dependence of the coverage on the scaled distance $x/\sqrt{t}$. At coverages below $1/L$ the derivative $d\theta/d(x/\sqrt{t})$ has a discontinuity with periodicity L. Inset shows details of the low-coverage part of the profile.

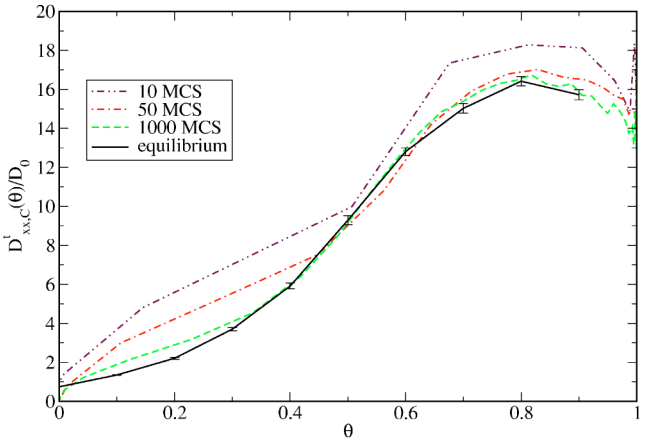

FIG. 6. Equilibrium (solid line) and time-dependent collective diffusion coefficients for a system with relatively weak step binding of $E_B/k_BT=1$ and equal NN repulsion $K=1$ in the case of diffusion across the steps.

siderably, in particular, at high coverages. For the strong step binding case, there are very sharp transient peaks in $D^t_{xx,C}(\theta)$ that persist at long times. This again indicates large differences of concentration between adjacent terraces. Peaks appear also in the case of weaker step binding with $E_B/k_BT=1$, in contrast with the repulsive case.

C. Diffusion along steps—repulsive case

Based on our previous work,[21] we expect that for the case of spreading profiles in the y direction along the ledges, nonequilibrium effects should be weak and relaxation to equilibrium fast. We find this to be the case for the present system as well, for both strong and weak step binding $E_B/k_BT=4$ and 1, respectively, and repulsive couplings $K=0.2$, 0.5, and 1. The only case where we can see strong nonequilibrium effects are systems with fast or slow diffusion along ledges, in other words in the cases where $E_2\neq 0$. Examples of such systems with a repulsive interaction $K=0.5$ are presented in Fig. 9(a) in the case of slow diffusion along the ledges ($E_2/k_BT=2$) and in Fig. 9(b) in the case of fast diffusion along the ledges ($E_2/k_BT=-2$). In the former case $D^t_{yy,C}(\theta)$ is influenced only at low coverages and relaxation is fast. In the case of fast diffusion along ledges a local maximum appears at low coverages (for discussion see Ref. 21) and strong nonequilibrium effects appear also at high coverages in the first phase of spreading. This is caused by the nonequilibrium distribution of adatoms between terraces and step edges.

D. Diffusion along steps—attractive case

In the case of attractive interactions we have studied systems with several different parameters corresponding to the previous cases, i.e., with strong and weaker binding at the lower step edge $E_B/k_BT=4$ and 1, and attractive couplings $K=-0.2$, -0.5, and -1. Again, in all these cases nonequilibrium effects are found to be weak. However, the influence of fast or slow diffusion ($E_2\neq 0$) along ledges is here more important than in the case of repulsive interactions (see Fig. 10). When diffusion along ledges is slow, $D^t_{yy,C}(\theta)$ decreases also at low coverages and a peak appears close to $\theta\approx 1/L$ (compare with the case of repulsive interaction where a similar peak appears in the case of fast diffusion along ledges). For fast diffusion along ledges, $D^t_{yy,C}(\theta)$ is simply a decreasing function of coverage and below its equilibrium values up to about 10 000 MCS. This is consistent with Ref. 32 where it was shown for attractive interactions

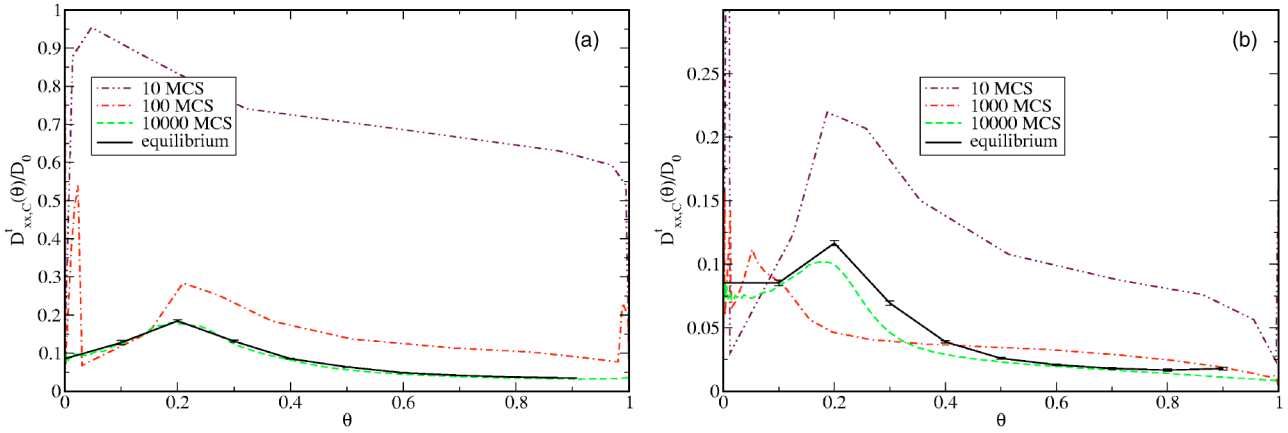

FIG. 7. Equilibrium (solid line) and time-dependent collective diffusion coefficients for a system with $E_B/k_BT=4$ and NN attractive couplings (a) $K=-0.2$ and (b) $K=-0.5$ in the case of diffusion across the steps.

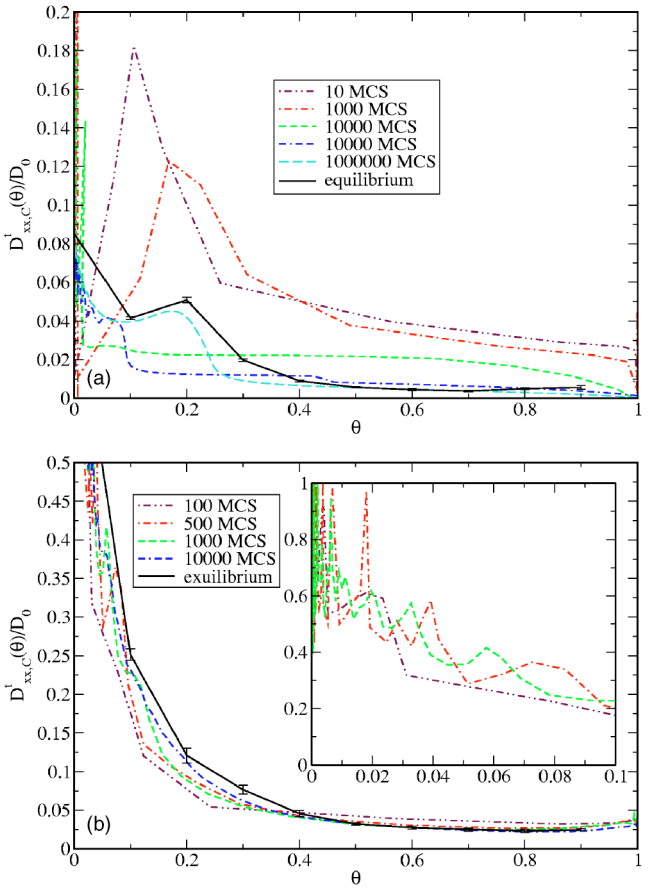

FIG. 8. Equilibrium (solid line) and time-dependent collective diffusion coefficients for a system with attractive NN coupling $K=-1$, with (a) strong step binding $E_B/k_BT=4$, and (b) comparable step binding $E_B/k_BT=1$ in the case of diffusion across the steps.

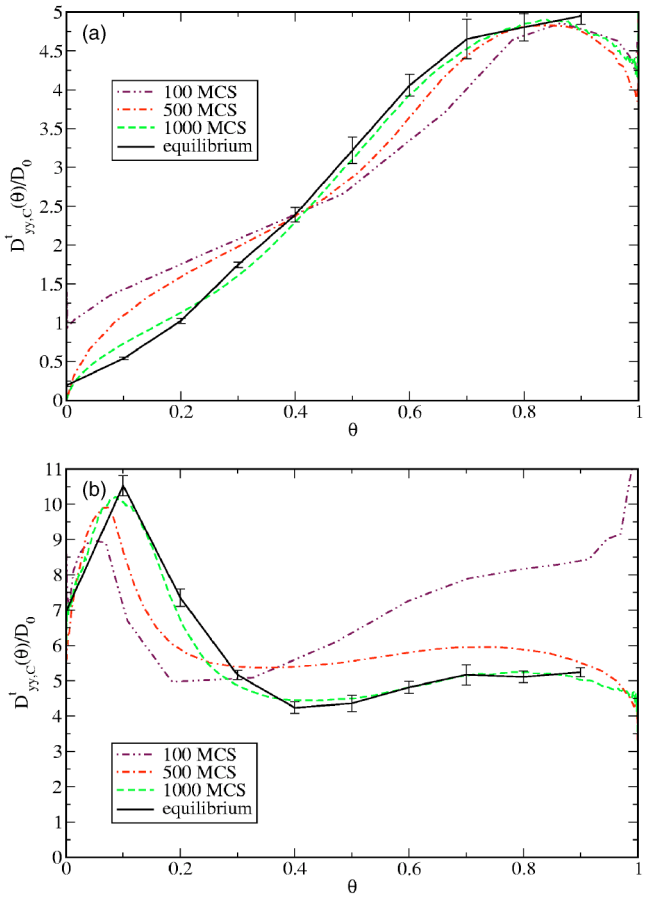

FIG. 9. Equilibrium (solid line) and time-dependent collective diffusion coefficients for a system with repulsive coupling $K=0.5$, and strong step binding $E_B/k_BT=4$ in the case of diffusion along the steps. In (a) $E_2/k_BT=2$ (slow diffusion along the steps) and in (b) $E_2/k_BT=-2$ (fast diffusion along the steps).

that diffusion at low coverages is slower than diffusion in equilibrium in the presence of large concentration gradients.

V. SUMMARY AND DISCUSSION

The present work is a contribution to an effort where our purpose is to fill the gap between experimental studies of surface diffusion and related, commonly idealized theoretical descriptions: there is a concern that theoretical models are often too simplified to correctly describe actual nonideal systems with steps, vacancies, impurities, and related imperfections. Hence, in the present work, we have employed the lattice-gas approach with adatoms interacting through repulsive or attractive NN forces in a model of vicinal surfaces to analyze surface diffusion far from equilibrium. Using Monte Carlo simulations of spreading steplike density profiles combined with the Boltzmann–Matano analysis, we have observed strong nonequilibrium effects at the early stages of spreading. We have found strong binding at a lower step edge to act as a barrier for diffusion of adatoms from each terrace to its neighboring terraces. In the case of large concentration gradients (as in the initial phase of spreading), the process of equilibration within terraces is relatively fast but equilibration between neighboring terraces is slow. This gives rise to sharp peaks in the time-dependent collective diffusion coefficient in direction across the steps for coverages below $\theta=1/L$ and above $\theta=1-1/L$. This behavior is suppressed (highlighted) by repulsive (attractive) interactions.

In the case of diffusion along the steps there are no strong nonequilibrium effects except in the case of systems with fast or slow diffusion along ledges. In such cases, the influence is greatest at low coverages. In particular, we find that for slow diffusion along ledges the time-dependent $D^t_{yy,C}(\theta)$ at a low coverage is larger than its equilibrium value $D_{yy,C}(\theta)$, while in the case of fast diffusion $D^t_{yy,C}(\theta)$ is smaller than its equilibrium counterpart. This behavior is due to the nonequilibrium distribution of adatoms between terraces and step edge positions in the initial phase of spreading. Finally, we note that although the present work considers NN interactions only, we expect many of the observed features to apply to real systems, too, as long as either attractive or repulsive short-range interactions dominate. For more complicated cases characterized by a manifold of competing interactions, it would be of great interest to study the influence of steps on adsorbate systems such as the O/W(110) system considered elsewhere.[26–28,33,34] Work in this direction is in progress.

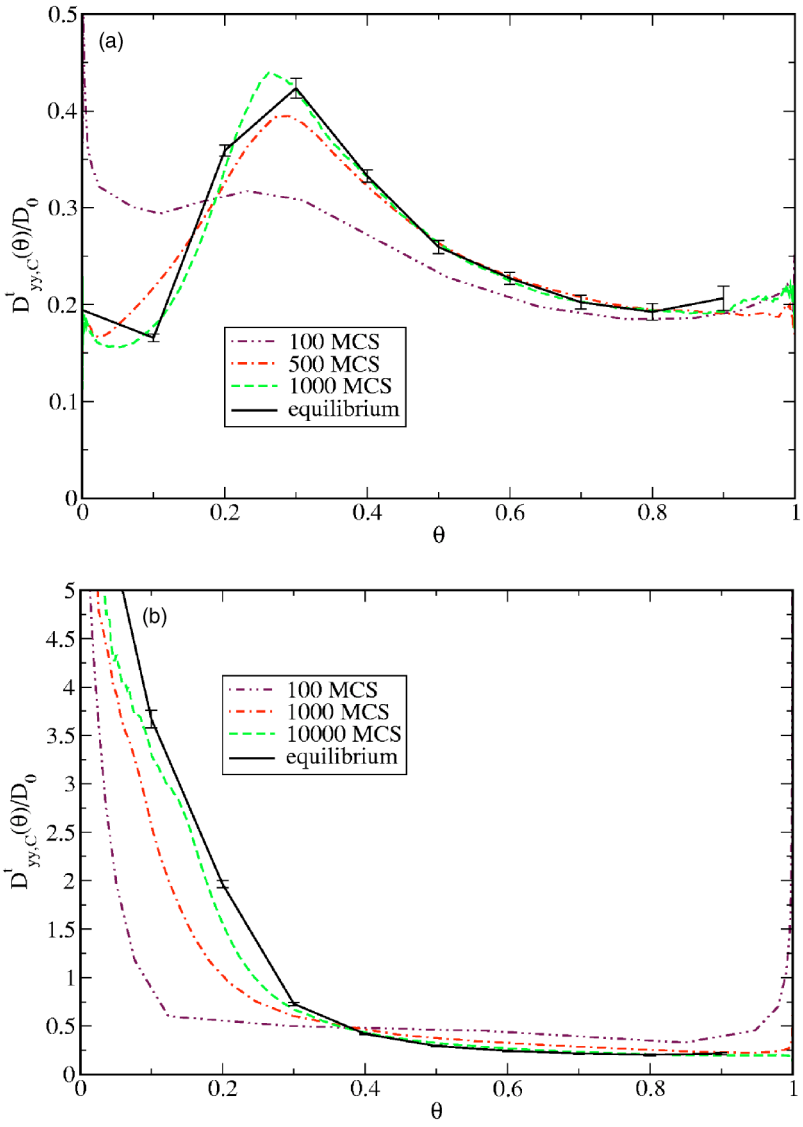

FIG. 10. Equilibrium (solid line) and time-dependent collective diffusion coefficients for a system with attractive NN coupling $K=-0.5$, and strong step binding $E_B/k_BT=4$ in the case of diffusion along the steps. In (a), $E_2/k_BT=2$ (slow diffusion along the steps) and in (b) $E_2/k_BT=-2$ (fast diffusion along the steps).

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