We present results for collective diffusion of adatoms on a stepped substrate with a submonolayer coverage. We study the combined effect of the additional binding at step edge, the Schwoebel barrier, the enhanced diffusion along step edges, and the finite coverage on diffusion as a function of step density. In particular, we examine the crossover from step–dominated diffusion at high step density to terrace–dominated behavior at low step density in a lattice–gas model using analytical Green’s function techniques and Monte Carlo simulations. The influence of steps on diffusion is shown to be more pronounced than previously anticipated.

PACS numbers: 68.35.Fx, 05.40.+j

The importance of surface steps in dynamical processes such as growth and ordering is widely recognized [1]. Among other effects, there exist extra activation barriers at the steps leading to a different mobility for adsorbates there as compared to the flat terrace region [2]. In recent years, several new techniques have been employed to measure the diffusion rate of adsorbate on well–defined low index surfaces [3–6]. However, since most of these experiments involve studies of density fluctuations over a length scale much larger than the average distance between steps on the surface, it is important to ascertain whether the measured diffusion constant corresponds to the intrinsic value for the wide terrace region, or whether it is strongly influenced by the rates near the step edges. While many theoretical studies on the extra barriers at step edges exist, only a few consider the effect of steps on measurable diffusion constants [7,8], and criteria for the crossover from step–dominated to terrace–dominated diffusion with increasing terrace width are not well established [9].

In this Letter, we present a study of the effect of various microscopic modifications of adatom jump rates due to surface steps on macroscopically observable collective diffusion. We describe the system of adsorbates on a substrate with a periodic array of steps by a lattice–gas model. We use a combination of analytical approach and Monte Carlo simulations to analyze the dependence of diffusion on step density in this model. We discuss the implications of our results on the experimental determination of diffusion constants, and the recent measurements by Xiao et al. [10] using optical diffraction techniques in particular.

Following an earlier work dealing with the zero coverage limit [11], we introduce several energy barriers in our model characterizing the adsorption on the stepped substrate. These are the additional binding energy $E_B$ at lower step edge, the Schwoebel barrier $E_S$ for motion across step edges, the diffusion barrier on terraces $E_0$, and the barrier for jumps along lower step edges $E_2$ [2]. The corresponding potential profile in direction perpendicular to step edges (x direction) is shown in Fig. 1(a).

The substrate surface has a periodic array of steps separated by terraces of width $L$ lattice sites [see Fig. 1(c)]. Thus each adsorption site in the lattice gas model can be labelled by the coordinate $(x, y)$ of the unit cell together with a site index $s = 1, 2, \ldots, L$ within the unit cell. We assume hard–core interactions between the adatoms. For each lattice site we then define a stochastic occupation variable $n_{xy}^s(t)$, which can take only the values 0 and 1. To analyze collective diffusion, we define the Green’s functions $G_{xy,x'y'}^{s,s'}(t) = -2\pi i \theta(t) (u_{xy}^s(t) u_{x'y'}^{s'}(0))$, where $s, s' = 1, 2, \ldots, L$, the fluctuation variables $u_{xy}^s(t)$ are defined by $u_{xy}^s(t) = n_{xy}^s(t) - \langle n_{xy}^s \rangle$, and $\theta(t)$ is the Heaviside step function [12].

The equations of motion for $G_{xy,x'y'}^{s,s'}(t)$ follow from the rate equations for $u_{xy}^s(t)$ [2]. After Fourier transforming with respect to the time and cell coordinates, we can obtain a closed set of equations for the Green’s functions $G_k^{s,s'}(\omega)$ in $(k, \omega)$ space by decoupling the higher order Green’s functions. In this mean–field approximation, $G_k^{s,s'}(\omega)$ turn out to be inversely proportional to the determinant of an almost tridiagonal $L \times L$ matrix $A(k, \omega)$. The interior elements of $A$,

$$A_{ss} = i \omega + 2\Gamma_0 \cos k_y b - 4\Gamma_0$$
$$A_{s,s+1} = \Gamma_0,$$  \hspace{1cm}  (2)

are related to terrace jumps, and the modified elements at the corners of $A$,
\( A_{11} = i\omega + 2\Gamma_2 \cos k_y b - \Gamma_1 - \Gamma_2 - (\Gamma_0 - \Gamma_1 + \Gamma_d - \Gamma_u)c_t \)
\( A_{22} = i\omega + 2\Gamma_0 \cos k_y b - 4\Gamma_0 - (\Gamma_1 - \Gamma_0)c_e \)
\( A_{1L} = i\omega + 2\Gamma_2 \cos k_y b - 3\Gamma_0 - \Gamma_d - (\Gamma_u - \Gamma_d)c_e \)
\( A_{2L} = \Gamma_0 - (\Gamma_1 - \Gamma_0)c_e \)
\( A_{1L} = \Gamma_u + (\Gamma_d - \Gamma_u)c_e e^{-iLk_x a} \)
\( A_{L1} = \Gamma_d + (\Gamma_u - \Gamma_d)c_e e^{-iLk_x a} \)
\( (3) \)

are related to jumps near step edges. All the other elements of \( A \) are identically zero. Here \( a \) and \( b \) are the nearest-neighbour distances in \( x \) and \( y \) directions, respectively. By symmetry, the average occupation numbers \( \langle n_{xy}^s \rangle \) depend only on the row index \( s \). In the present model, we have only two distinct row coverages \( c_e \) and \( c_t \), defined by \( c_e = \langle n_{xy}^1 \rangle \) for the lower edge row and \( c_t = \langle n_{xy}^2 \rangle = \ldots = \langle n_{xy}^L \rangle \) for terraces. The value of total coverage \( c = c_e + (c_t - c_e)/L \) together with the detailed balance condition

\[ \frac{c_e(1 - c_t)}{c_t(1 - c_e)} = e^{E_B/kT} \]
\( (4) \)

completely determine the values of \( c_e \) and \( c_t \).

The diffusion tensor \( D \) can be extracted from the diffusive poles of the Green’s functions, i.e. from the zeros of \( \det A \) in the hydrodynamic limit \( \kappa \to 0 \) and \( \omega \to 0 \) at \( \omega = -i \kappa \cdot D \cdot \kappa \). By expanding the determinant and collecting the leading terms for small \( \omega \) and \( \kappa \), we find the diagonal elements of \( D \) to be

\[ D_{xx} = \frac{(1 - c_e)(1 - c_t)\Gamma_0 L^2 a^2}{\kappa [L - 2(1 - c_e) + (1 - c_t)(1 + e^{E_B/kT})]} \]
\[ D_{yy} = \frac{\kappa}{L - 1}(1 - c_t)\Gamma_0 + (1 - c_e)c_e \Gamma_2 b^2 \]
\[ \kappa = (L - 1)(1 - c_t)c_t + (1 - c_e)c_e. \]
\( (5) \)

By symmetry, the nondiagonal elements of \( D \) are identically zero.

To test the mean-field result of Eq. \( 3 \), we have performed standard Monte Carlo (MC) simulations \( 13 \) for the same model. In the MC simulations, the collective diffusion constant has been calculated using the Green–Kubo relation \( 3 \)

\[ D_{\nu\nu} = f \lim_{t \to \infty} \frac{1}{4Nt} \left( \sum_{i=1}^{N} \left| r^{(i)}_\nu(t) - r^{(i)}_\nu(0) \right|^2 \right), \]
\( (6) \)

where the sum is over all particles and \( \nu = x, y \). For our model, the ‘thermodynamical factor’ \( f \), which is inversely proportional to particle number fluctuations \( 3 \), can be calculated exactly yielding the result \( f = Lc/\kappa \) with \( \kappa \) defined in Eq. \( 5 \). The coverage dependence of \( D \) as given by Eq. \( 4 \) together with the simulation results are shown in Fig. \( 2 \) for a temperature comparable to the various activation barriers in the system: \( kT = 1/2 \) with \( E_B = E_S = E_0 - E_2 = 1 \). Typical simulation parameters were \( 10^6 \) MC steps per atom for thousand atoms in the system. We conclude that the mean-field theory agrees very well with the MC result, with no discernible systematic deviation \( 14 \). At low temperatures \( f \) has a maximum at \( c \approx 1/L \) due to the suppression of fluctuations when lower edge rows get filled \( (c_e \approx 1) \) and terraces are almost empty \( (c_t \approx 0) \), resulting in a maximum of \( D_{xx} \) at \( c \approx 1/L \). In the case of \( D_{yy} \), this effect of reduced fluctuations is cancelled out by the enhanced blocking of jumps along the lower step edges.

We now focus on the dependence of the diffusion constant on the width of the terrace as given by the expression in Eq. \( 3 \). In this regard, \( D_{yy} \) has a relatively weak dependence on the width, since diffusion in the direction parallel to the step edge has to proceed through the terrace region as soon as the step edge row is filled. Below we shall concentrate on \( D_{xx} \), i.e. diffusion perpendicular to the steps. At very high temperature or for very wide terraces, the diffusion constant \( D_{xx} \) would approach the value \( D_\infty = \Gamma_0 a^2 = e^{-E_0/kT}a^2 \) appropriate for a single terrace, and the effect of the steps vanishes. In the other limit of low temperature and narrow terrace width, diffusion is dominated by the steps, and \( D_{xx} \propto e^{E_B/kT} \), where the total barrier \( E_{sd} \) is now \( E_0 + E_S + E_B \). The crucial question is how the system crosses over from one limit to another. The crossover behaviour can be understood most easily in the limit \( c e^{E_B/kT} \gg 1 \) and \( c \gg 1/L \) \( 15 \), in which the expression of \( D_{xx} \) in Eq. \( 5 \) simplifies to the form

\[ D'_{xx} = \frac{\Gamma_0 a^2}{L + c(1 + e^{E_B/kT})e^{E_B/kT}}, \]
\( (7) \)

from which we see immediately that the crossover occurs at \( L \approx c e^{(E_B + E_S)/kT} \). For large values of \( (E_B + E_S)/kT \), this implies that the effect of steps could be substantial even for terrace widths up to several hundred lattice spacings.

Recently the diffusion of CO on clean Ni(110) was studied by Xiao et al. \( 16 \). From a measurement on a sample with high step densities \( 16 \), they deduce the value of the step-dominated barrier \( E_{sd} \) for diffusion to be 239 meV. The activation barrier for CO diffusion along (001) on a good sample with average step separation of \( L \approx 170 \) was determined to be 120 meV. For diffusion along (110), a barrier of 95 meV was measured. These authors then use a heuristic argument to arrive at the following crossover criterion: \( L^2 \approx e^{(E_B + E_S)/kT} \). Based on this formula they conclude that in the experimental temperature range of 100 to 200 K, the influence of the steps should be negligible \( 16 \). The measured value of 120 meV is then assigned to be the value of the barrier \( E_0 \) appropriate for CO diffusion along (001) on clean Ni(110).

We now apply our results to analyze whether the effect of steps is indeed negligible under these conditions in this system. We take as input the measured value for \( E_{sd} \) of
239 meV and the estimated values of \( L = 170, \ E_0 = 120 \) meV for the (001) direction and \( L = 520, \ E_0 = 95 \) meV for the (110) direction, and set \( E_S = 0 \) \[10\]. For simplicity, we have also taken all the prefactors of the various jump rates to be equal \[13\]. We calculate the effective extra barrier due to the steps, \( \Delta E(T,L) \), for diffusion perpendicular to the steps, defined as the local slope of the Arrhenius plot of \( D_{xx}/D_\infty \) using Eq. \[5\] for coverage \( c = 0.5 \). In Fig. \[3\] we show the result as a function of temperature for diffusion along the two directions. In both cases, below 300 K, \( \Delta E \) is sizable and the effective barrier is not just the terrace value \( E_0 \) but considerably affected by steps. Clearly the heuristic crossover criterion in Ref. \[4\] underestimates the influence of the steps.

In a more recent experiment \[6\] the effect of sulphur as an impurity on diffusion of CO on Ni(110) was studied. It was proposed that the main effect of sulphur is to increase the effective step barrier dramatically. A barrier of 323 meV was measured for diffusion along both the main orientations. These authors conclude that in this case, the diffusion is dominated by the sulphur–poisoned step edges, and the measured value of 323 meV is then assigned to be \( E_{\text{ad}} \), i.e. the step–dominated barrier. We have also applied our analysis to this system and find that here with \( L = 520 \) assuming \( E_S = 0 \), the steps indeed dominate for \( E_0 \leq 200 \) meV. So the determination of the sulphur–modified step barrier in Ref. \[4\] is reasonableness consistent with the starting assumption in this case.

In this Letter, we have presented a theoretical analysis of collective diffusion on stepped substrates, and studied the dependence of the diffusion constant on the terrace width, coverage and temperature. In particular, we have established a criterion for crossover from terrace dominated diffusion to step dominated diffusion. Compared with a heuristic criterion used before \[13\], our theory predicts a much stronger influence of the steps on the diffusion barrier. The experiments of CO on Ni(110) in Refs. \[4\] \[6\] represent a situation characteristic of diffusion on smooth metal surfaces with steps as far as few hundred lattice spacings apart and temperature range of 100 to 200 K. Our results show that under these conditions, the influence of the steps on the measured diffusion barrier can be considerable, and a careful theoretical analysis is needed to interpret the measured barrier value. In this study, the only interaction effect taken into account is the exclusion of double occupation on the same site. The effect of additional interaction between adatoms on the influence of the steps remains to be investigated.

This work has been supported by the Academy of Finland (J. M.), Emil Aaltonen Foundation (J. M.), and by a grant from the Office of Naval Research (S. C. Y. and J. M.). Computational resources of the Theoretical Physics Computing Facility at Brown University are gratefully acknowledged.

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[15] Other limits of \( D_{xx} \) as well as those of \( D_{yy} \) will be discussed in detail in forthcoming work \[12\].

[16] For this system the Schwobel barrier is believed to be very small; P. J. Feibelman, private communication.

[17] In case of different prefactors for jumps on terraces and at step edges, \( \nu_{\text{e}} \) and \( \nu_{\text{c}} \), respectively, the effect of prefactors on crossover can be taken into account by using the form \( L \approx c e^{(E_B+E_S)/kT} \nu_{\text{e}}/\nu_{\text{c}} \), from which we see that the effect of the prefactors on the crossover temperature is only logarithmic.
FIG. 1. Geometry and jump rates of the lattice model for diffusion on a stepped substrate. (a) The potential profile in x direction. (b) Side view of the model showing the various hopping rates for jumps in x direction near step edges. (c) Top view of the model showing the size of one unit cell with the indices $s = 1, 2, \ldots, L$ of each lattice site within the cell.

FIG. 2. Mean field and Monte Carlo results for $D_{xx}$ and $D_{yy}$ as a function of coverage at temperature $kT = 1/2$ for the hard-core model with $E_S = E_B = E_0 - E_2 = 1$. Lines show the mean field solution of Eq. (5), and plotting symbols denote the results of Monte Carlo simulations with errorbars less than the size of the symbols. Here diffusion coefficients are shown in units of $D_\infty$ that is the value for infinite terrace width and coverage in units of one monolayer.

FIG. 3. The effective extra activation barrier due to the steps for diffusion of CO along the (001) and (110) directions on Ni(110). See text for parametrization.