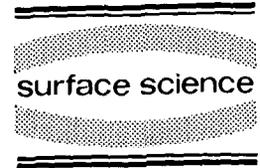




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# Measuring surface mass diffusion coefficients by observing step fluctuations

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## Abstract

To show how experiments probing the equilibrium fluctuations of steps can be used to explore the mechanisms of surface mass self-diffusion, we study the equilibrium fluctuations of vicinal surfaces in the solid-on-solid model using standard Monte Carlo kinetics with no special barriers to attachment at step edges. By examining the wavelength dependence of the time constants of the fluctuations, we find that in this simple model the step fluctuations are determined by how fast adatoms and vacancies can diffuse away from step edges. This result is contrasted with the case where step-edge attachment becomes the rate-limiting process. The result of the former case is used to understand how steps diffuse when their configuration is out of equilibrium. In particular, we compute how a bunch of steps breaks apart, due to the entropic repulsions between them, to form a uniform step array. Using the theory of Rettori and Villain, we show that the surface mass diffusion coefficient deduced from characterizing the step fluctuations accurately accounts for the evolution of the step bunch.

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## 1. Introduction

The question we address in this paper is the relationship between the thermal fluctuations in step-edge positions and surface mass diffusion. Steps fluctuate (in time) because atoms are continually attaching to and detaching from the step edges, or moving along them. The nature of the fluctuations depends on many details of the steps and the way in which adatoms and vacancies on the terraces interact with them. Ref. [1] catalogs the different ways steps can fluctuate, depending on the ways in which adatoms or vacancies are distributed and move across the surface. If the

step-edge position is far from its thermal equilibrium position, these fluctuations can eventually lead to a net motion of the overall position of the step edge. How the surface mass diffusion coefficients, which are determined by this motion, are related to step properties has been discussed by many authors, mostly on the basis of heuristic arguments and in the context of the flattening of grooved surface profiles [2–4]. Here we discuss the behavior of steps in a complete microscopic model, the solid-on-solid (SOS) model, with Monte Carlo kinetics. Our approach is first to study the equilibrium fluctuations of the steps (i.e., their “Brownian motion” [5]) and then to use these fluctuations to try to understand the equilibration of step configurations which are initially out of equilibrium.

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Our primary motivation for looking at this problem is the advances in microscopy which make possible direct observation of step fluctuations (even at the atomic level!) [6–12]. In this paper we show how an experimentalist might go about using these fluctuations to probe the atomic mechanism responsible for the flow of atoms which occurs during the evolution of surface morphology: we explicitly show how observations of step fluctuations can be used to deduce surface mass diffusion coefficients in one particular model, a simple solid-on-solid model in which atoms are constrained to move along the surface.

For the simplest SOS kinetics, for which no special activation barriers to atomic motion are assigned to the step edge, we find that the adatom diffusion on the terraces controls how steps fluctuate and diffuse. This model certainly does not encompass all possibilities for surface diffusion. For example, if emission of atoms from the step edge is much slower than diffusion on the terraces, the nature of the fluctuations of the step edge will be distinctly different. (This case is discussed in Refs. [1,13], and briefly below.) Thus, in a spirit very similar to experiments which determine mechanisms responsible for changes in surface morphology from examining the decay of sinusoidal surface groves [14], examination of step fluctuations can yield information about the mechanisms of step diffusion. The analysis of the special case presented in this paper gives an idea of what is possible from the careful interpretation of experimental data.

## 2. The solid-on-solid model

Fig. 1 depicts an SOS model [15] with a step. The energy of this system is defined by  $\epsilon \sum_{nn} |h_i - h_j|$ , where  $h_i$  is the height of the surface at square-lattice site  $i$ ,  $\epsilon$  is the nearest-neighbor bond energy, and the sum is over nearest-neighbor sites  $i$  and  $j$ . All of the present simulations were done at  $kT = 0.9\epsilon$ . This temperature was chosen so that the density of adatoms on the terraces is significant, yet well below the terrace roughening temperature ( $kT_R \approx 1.2\epsilon$ ). Periodic boundary conditions were used in the  $y$  direction.

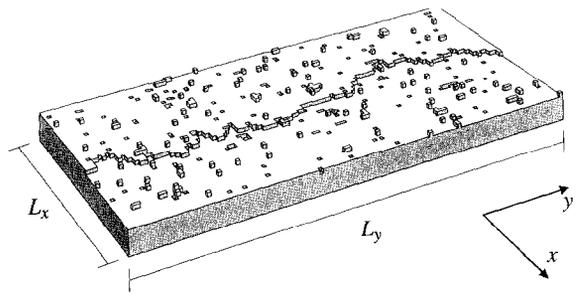


Fig. 1. A step in the SOS model at a temperature of  $kT = 0.9\epsilon$ . The concentration of vacancies and of adatoms on the terraces is approximately  $0.02/\Omega$ .

To introduce  $N_s$  steps, screw boundary conditions were used in the  $x$  direction: the height of the lattice at  $x = 0$  was fixed to be  $N_s$  sites above the surface at  $x = L_x$ . All the surfaces considered had dimensions  $L_x \times L_y = 60a \times 120a$ .

The choice of kinetics is based on the desire to study processes dominated by surface diffusion. Accordingly, we assume that the energy barrier for an atom leaving the surface is much greater than the barriers associated with moving along the surface. Thus, we use the standard Metropolis Monte Carlo algorithm with the number of atoms conserved (i.e., with “Kawasaki dynamics”) [16]. The sites of the surface are chosen at random. At each iteration, a randomly chosen atom tries to hop to a random nearest-neighbor site. If the energy change of the lattice in making the hop is negative or zero, then the hop is made. If the hop increases the surface energy, the hop is made with the usual Boltzmann probability. All sites, including step edge sites, are treated equivalently. Thus, in the model being used, the activation barriers for atomic diffusion are implicitly assumed to be the same for diffusion on the terraces and diffusion across and along the step edges.

In what follows it is necessary to have some definition of the step-edge position  $x$  as a function of  $y$ . Because of the possibility of overhangs along the step edges, this definition is not completely trivial. The choice we make is analogous to the “Gibbs dividing surface” between two phases: for each value of  $y$ , the position of the

step separating a terrace of height  $na$  and a terrace of height  $(n + 1)a$  is  $L_x - N_{n+1}(y)a$ , where  $N_{n+1}(y)$  is the number of atoms (with specified  $y$ ) of height equal to  $n + 1$ . At the temperature of the simulations, the resulting location of the step edge along column  $y$  is usually within a lattice constant or so of the position one would intuitively select. However, a difficulty with this approach is that a component of the step fluctuations is due to the fluctuations in the concentration of adatoms on the terraces. Fortunately, as described below, this component is easily computed by considering the case with no steps. (Note, however, near and, of course, above the roughening temperature, when one does not really expect step positions to be accurately described by single-valued functions  $x(y)$ , even this procedure breaks down.) These subtleties should not be important in analyzing experimental data: any other consistent choice of the location of the step edge would work as well [17].

### 3. The equilibrium fluctuations of a single step edge

To characterize the fluctuations of the step edges, we follow Ref. [11] and study the correlations in the spatial Fourier components of each step edge. Clearly, long-wavelength fluctuations of the step edge will decay much more slowly than small-wavelength fluctuations. The precise functional form of the dependence of decay time on wavelength provides a diagnostic of the nature of the processes important in determining the fluctuations, and ultimately the processes important for mass diffusion.

The Fourier components  $x_q(t)$  are defined by

$$x(y, t) = \sum_q x_q(t) \exp(iqy). \quad (1)$$

The correlation function we examine is

$$G_q(t - t') = \langle |x_q(t) - x_q(t')|^2 \rangle - G_q^0(t - t'), \quad (2)$$

where  $G_q^0(t - t')$  describes the fluctuations in the step-edge position caused by terrace fluctuations.

Fig. 2 shows  $G_q(t)$  for  $N_s = 1$  for several values of  $q$ , averaging over  $10^7$  Monte Carlo steps per site (discarding the first  $10^6$  for equilibration). On the basis of the analysis of the Langevin equations describing the extreme cases of completely random atom attachment and detachment at the step edge or completely random hops along the step edges, one expects  $G_q$  to saturate exponentially [13]: on time scales of more than a few changes, one should have

$$G_q(t) = A(q)[1 - \exp(-|t|/\tau(q))]. \quad (3)$$

The dotted lines in Fig. 2 show least-squares fits to Eq. (3) with  $A(q)$  and  $\tau(q)$  adjustable parameters for each  $q$ . Fig. 3 shows the  $A(q)$  and  $\tau(q)$  deduced from the fits (essentially identical results were obtained for  $N_s$  as large as 5). The amplitudes  $A(q)$  depend only on the equilibrium fluctuations of the step edge. From general considerations [18], one expects their size decreases with increasing step-edge stiffness  $\tilde{\beta}$  according to

$$A(q) = \frac{2kT}{L_y \tilde{\beta} q^2}. \quad (4)$$

Fig. 3a shows the expected  $q^2$  dependence: from the amplitude we deduce that  $\tilde{\beta} \approx 0.56kT/a$ . For

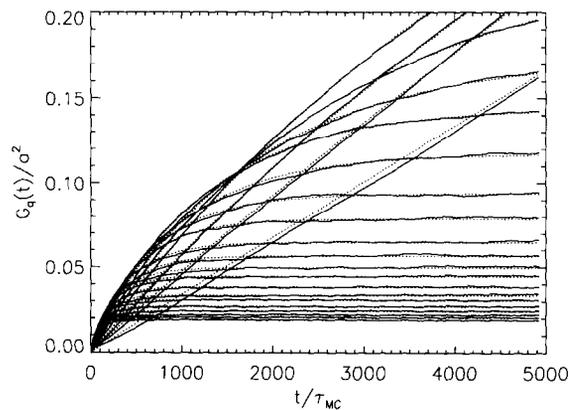


Fig. 2. Time correlation function of the Fourier components of the step-edge position for a range of  $q$ . As  $q$  increases, the initial slope (the inverse time constant  $\tau(q)$ ) increases: the curve with the smallest initial slope has  $q = 8\pi/L_y$ . On each subsequent curve,  $q$  increases by  $2\pi/L_y$ .

comparison, the terrace–step–kink (TSK) approximation to the step-edge stiffness [19] is

$$\tilde{\beta}_{\text{TSK}} = \frac{2kT}{a} \sinh^2(\epsilon/2kT). \quad (5)$$

At  $kT = 0.9\epsilon$ ,  $\tilde{\beta}_{\text{TSK}} \approx 0.68kT/a$ . Given that the TSK model neglects step-edge overhangs, adatoms, and vacancies, it is not surprising that it overestimates  $\tilde{\beta}$ . (The more thermal excitations possible, the less stiff the step edge.)

Fig. 3b shows the inverse time constant as a function of  $q$  for two different average terrace widths. If the step motion is governed by random attachment/detachment at the step edges, the time constant of the fluctuations  $\tau(q)$  should vary as  $q^{-2}$ , for step-edge hopping  $\tau(q)$  should vary as  $q^{-4}$  [11]. The extreme cases of  $q^{-2}$  and  $q^{-4}$  do not well describe the step-edge fluctuations! Instead (as shown by the solid line) they are well-described by a  $q^{-3}$  law.

#### 4. The nature of step fluctuations when terrace diffusion is slow

We now discuss what the behavior of Fig. 3b, in particular the  $q^{-3}$  law, tells us about the mechanism of step motion. Motivated by the work of Mullins [20] and of Pimpinelli et al. [1], we suppose that the diffusion on the terraces is the

rate-limiting step in our model. This is reasonable because our model has no kinetic barriers to attachment at the step edge – the sticking coefficient is large.

To see what the consequences of terrace-diffusion-controlled step motion are, imagine a curved step in a uniform sea of adatoms, as schematically shown in Fig. 4a. Because of the positive bulge of the step edge, the step edge will emit adatoms (or absorb vacancies) so that it can become straighter and lower its free energy. If diffusion on the terraces is sufficiently rapid that the rate of emission is not hindered by how fast the adatoms diffuse away, the step-edge curvature will quickly equilibrate, as described by the Langevin equation discussed in Ref. [13], and as found [11] to describe steps on Si(111) at 900°C. This process gives a relaxation time which varies as  $q^{-2}$ , which, as mentioned above, is inconsistent with the Monte Carlo simulations.

Suppose, however, that although the step edge can emit atoms or absorb vacancies very rapidly, atoms or vacancies can only slowly diffuse away from the step edge. In the situation of Fig. 4a, the concentration of adatoms near the step edge would increase, as seen in Fig. 4b, until the chemical potential change of an atom being emitted from the step edge is zero. From the Gibbs–Thomson equation, this occurs when  $c_s$ , the con-

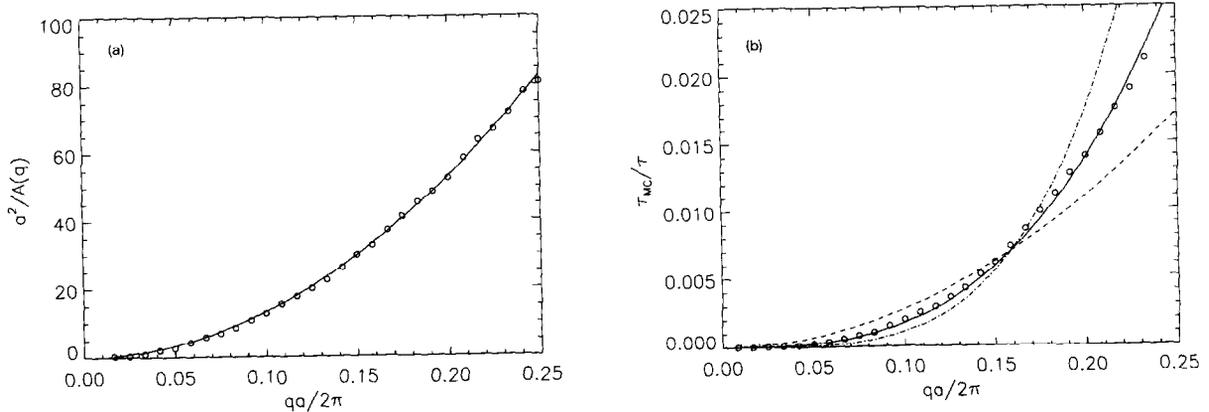


Fig. 3. (a) The circles show the values of  $A(q)$  deduced from fits to the data in Fig. 2. The solid line shows the fits to Eq. (4), from which we deduce  $\tilde{\beta} = 0.56kT/a$ . (b) The dependence of the relaxation time  $\tau$  on wavenumber  $q$  for average terrace width  $60a$ . The solid line is a fit to  $q^3$ . As discussed in the text, the prefactor can be interpreted in terms of the diffusion coefficient  $D_s$  for adatoms and vacancies on the terraces. The dashed and dot-dashed lines show fits to  $q^2$  and  $q^4$ , respectively.

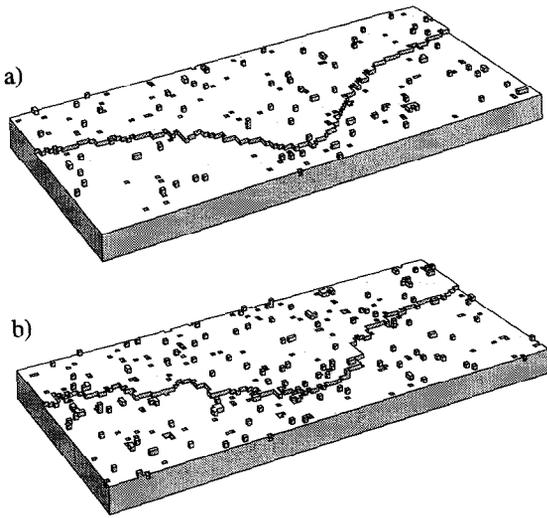


Fig. 4. (a) A curved step in a uniform sea of adatoms will begin to straighten quickly by emission of adatoms. (b) If diffusion of adatoms on the terraces is slow, then the concentration of adatoms on the terraces will increase (as indicated by the darkened terraces) until the step nearly stops. Any subsequent motion of the step edge waits on the diffusion of adatoms away from the bulge.

centration of adatoms near the step edge, reaches a value which depends on the local curvature of the step edge [20–22]:

$$c_s = c_0 - c_0 \Omega \frac{\tilde{\beta}}{kT} \frac{\partial^2 x}{\partial y^2}, \quad (6)$$

where  $c_0$  is the equilibrium concentration of adatoms, and  $\Omega = a^2$  is the atomic area. (For vacancy concentrations,  $-\Omega$  replaces  $\Omega$ .)

Any subsequent motion of the step edge is governed by the diffusion of the excess adatoms toward regions of lower chemical potential *along* or away from this edge. This problem was treated by Mullins [20,23] in the context of the decay of grooved surface profiles, and more recently by Bales and Zangwill [22] and Uwaha and Saito [24] in studies of step morphology during growth. Here we repeat these arguments, and then apply them to our results in Figs. 2 and 3. We should say at the outset that it is not obvious that an analysis based on macroscopic equations such as Eq. (6) should work well on the length scale of thermal

fluctuations – comparisons with simulations of microscopic models are thus important.

Imagine one started with a sinusoidal step profile:

$$x(y, t) = x_q(t) \cos(qy). \quad (7)$$

By Eq. (6), this form implies a concentration gradient of adatoms along and away from the step edge. We assume that local slopes of the step edge are always small, so that the concentration field is essentially given by assuming that the concentration is  $c_0$  very far from the step edge and  $c_s(y)$  along the line of the average step position (here taken to be at  $x = 0$ ). Supposing the step edge to be the predominant source and sink of adatoms,  $\nabla^2 c(x, y) = 0$  away from the step edge. Because of Eq. (6), we have the boundary condition

$$c(0, y) = c_0 + c_0 \Omega \frac{\tilde{\beta}}{kT} q^2 x_q \cos(qy). \quad (8)$$

The solution to these equations for  $x > 0$  is simply

$$c(x, y) = c_0 + c_0 \Omega \frac{\tilde{\beta}}{kT} q^2 x_q \exp(-|q|x) \times \cos(qy). \quad (9)$$

The current of adatoms *approaching* the step edge is then

$$j_s = \frac{1}{\Omega} \frac{\partial x}{\partial t} = 2D_s \frac{\partial c}{\partial x} \Big|_{x=0^+} = - \frac{2D_s c_0 \tilde{\beta} \Omega}{kT} |q|^3 x_q \cos qy, \quad (10)$$

where  $D_s$  is the diffusion coefficient of adatoms on the terraces. The factor of two arises because the diffusion occurs away from both sides of the step edge. Thus,

$$\frac{dx_q}{dt} = - \frac{2D_s c_0 \tilde{\beta} \Omega^2}{kT} |q|^3 x_q. \quad (11)$$

This equation is completely deterministic, describing the decay of existing fluctuations. How one adds (random) thermal fluctuations in the step-edge position is to a certain degree phe-

nomenological. We make a conventional choice which is mathematically simple and try to justify it in retrospect. First, we simply add a noise term  $\eta_q(t)$  to Eq. (11):

$$\frac{dx_q}{dt} = -\frac{2D_s c_0 \tilde{\beta} \Omega^2}{kT} |q|^3 x_q + \eta_q(t). \quad (12)$$

We assume that  $\eta_q(t)$  is random in the sense that it is uncorrelated in  $t$  and  $q$ :

$$\langle \eta_q(t) \eta_{q'}^*(t') \rangle = \frac{1}{L_v} f(q) \delta(t-t') \delta_{q,q'}. \quad (13)$$

Given this choice for the form of the noise, the function  $f(q)$  is determined by the requirement that the equilibrium fluctuations are those specified by equilibrium statistical mechanics. To be more precise, from Eqs. (12) and (13), it is straightforward to show [25] that

$$\begin{aligned} \langle x_q(t) x_{q'}^*(t') \rangle &= e^{-\alpha(q)(t+t')} \int_0^t d\tau' \int_0^{t'} d\tau \langle \eta_q(\tau) \eta_{q'}^*(\tau') \rangle \\ &\times e^{\alpha(q)(\tau'+\tau)}, \end{aligned} \quad (14)$$

where  $\alpha(q) = 2D_s c_0 \tilde{\beta} |q|^3 \Omega^2 / kT$ . This is only consistent with the prefactor of Eq. (3) (which, again, is characteristic of the *equilibrium* structure of the step edge) if

$$f(q) = 4D_s c_0 \Omega^2 |q|. \quad (15)$$

From Eq. (14) we recover Eq. (3), with the time constant [26]

$$\tau(q) = \alpha^{-1}(q) = \frac{kT}{2D_s c_0 \Omega^2 \tilde{\beta} |q|^3}. \quad (16)$$

The real-space Langevin equation associated with terrace-diffusion-controlled step motion, showing a “non-local” character of the rule-governing local step velocities, as well as the time correlations of the position of a single point on the step edge, is described in the Appendix.

We are now in a position to interpret the fits of Fig. 3. If  $\tau_{MC}$  is the Monte Carlo unit of time, then from the fits of  $\tau^{-1}(q)$ , we find

$$\frac{2D_s c_0 \Omega^2 \tilde{\beta}}{kT} \approx 0.0070 \frac{a^3}{\tau_{MC}}. \quad (17)$$

Using the estimate from Fig. 3a that  $\tilde{\beta} \approx 0.56kT/a$ , we thus conclude that

$$c_0 D_s \approx \frac{0.0063}{\tau_{MC}}. \quad (18)$$

(Since the vacancies and adatoms are largely diffusing independently of each other because their density is low,  $c_0$  should be interpreted as the sum of the vacancy and adatom concentrations: by counting the number of defects on a step-free surface at our  $T = 0.9\epsilon/k_B$  we find that  $c_0 \approx 0.041/a^2$ .) The accuracy of this estimate of the diffusion coefficient can be directly evaluated. For atoms hopping on a square lattice of sites, the diffusion coefficient is given by [27]  $D_s = a^2/4t_h$ , where  $t_h$  is the time between hops on the terraces. By observing that 2.4% of the surface atoms hop on a step-free surface during one Monte Carlo sweep (i.e.,  $c_0/t_h = 0.024/a^2 \tau_{MC}$ ), we thus deduce that  $D_s c_0 \approx 0.0060/\tau_{MC}$ . Given the many assumptions leading to Eq. (16), this level of agreement is satisfying!

## 5. Case of fast terrace diffusion

To provide some idea of the limits of the validity of Eq. (16), we now give an explicit example of its failure by modifying the kinetics of the Monte Carlo algorithm. A basic assumption leading to Eq. (16) is that the rate at which fluctuations of the step-edge position decay (or are built up) is determined by the diffusion rate on the terraces. If the sticking coefficient for an atom to be incorporated into the step edge is sufficiently small, this will no longer be the case. If the thermal noise of attachments and detachments is uncorrelated, then it is easy to show [11] that

$$\tau(q) = \frac{kT \tau_a}{\Omega^{3/2} \tilde{\beta} q^2}, \quad (19)$$

where  $\tau_a$  is the time between attachment/detachment events.

To produce the crossover between Eq. (16) and (19) explicitly, we modified the Monte Carlo algorithm in the following manner: if a trial hop lowered the system energy, it was accepted with a

probability of 1/10. Since an isolated adatom hopping onto the step edge typically lowers its energy, this makes the sticking coefficient  $s \approx 0.1$  [28]. To satisfy detailed balance, and thus not to change the equilibrium properties of the surface, the probabilities for hops which increased the surface energy (such as, for example, adatom emission from the step edge) were also divided by 10. Trial atomic hops which did not change the surface energy were always accepted. Since most of the adatoms on the terraces do not change their energy during a hop, this means that one expects the diffusion constant  $D_s c_0$  not to be changed much – indeed, explicit computation on a step-free surface shows that  $D_s c_0$  has changed only from  $0.0060/\tau_{MC}$  to  $0.0056/\tau_{MC}$ . The equilibrium averages have not, of course, changed at all with the change in kinetics: the amplitudes of the step fluctuations shown in Fig. 3a are identical.

To gauge the change in the nature of the step fluctuations with the change in sticking coefficient, we define the step “mobility” by

$$\Gamma_q = L_y A(q) / 2\tau(q). \quad (20)$$

For the case of diffusion limited by step-edge attachments (Eq. (19)),  $\Gamma_q$  should be  $a^3/\tau_a$  independent of  $q$ , while for the case of diffusion limited by atomic motion on the terraces (Eq. (16)) it should be linear in  $q$ . Fig. 5 compares the step mobility for the original and modified Monte Carlo algorithm. The dependence of  $\Gamma_q$  on  $q$  has changed considerably: for the case with small sticking coefficient,  $\Gamma_q$  saturates to a constant value at large  $q$ . There are two points of quantitative interest in Fig. 5:

(1) The saturated value of  $\Gamma_q$  for the case  $s = 0.1$  is around  $0.003a^3/\tau_{MC}$ . To check the consistency of this result with Eq. (19), we note that the time between changes in the step edge is twice the time between attachments, and the time between attachments is determined by the sticking coefficient and the rate of collisions of adatoms and vacancies with the step. Thus,

$$\tau_a^{-1} \approx 4sD_s c_0. \quad (21)$$

Using the directly determined values of  $D_s c_0$  and Eqs. (4), (19), and (20), Eq. (21) gives a value of

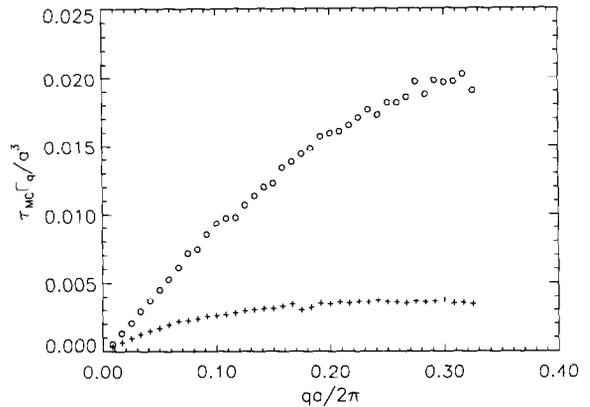


Fig. 5. The  $q$  dependence of the step mobility  $\Gamma_q$  defined in Eq. (20). This dependence shows how the fundamental nature of step fluctuations changes when the rate-limiting process changes from terrace diffusion to step-edge attachment. The upper curve (circles) is for the diffusion-limited case of Fig. 3b. The lower curve (crosses) is for the case when the sticking coefficient at the step edge is roughly 1/10. As discussed in the text, the saturation at large  $q$  of the lower curve is characteristic of step-edge attachment-limited fluctuations.

$\tau_a$  of  $420\tau_{MC}$  and of  $\Gamma_q$  of around  $0.002a^3/\tau_{MC}$ , roughly consistent with Fig. 5.

(2) For the small-sticking-coefficient case,  $\Gamma_q$  only saturates when  $qa/2\pi$  is greater than around 0.1. This is roughly the  $q$  at which the fluctuations determined by the local attachments of Eq. (19) are slower than fluctuations determined by the diffusion field given by Eq. (16): equating the two time constants and using Eq. (21) gives the expected crossover wavenumber as  $q_{\text{crossover}} a/2\pi \approx (2/\pi)s \approx 0.064$  [29].

## 6. Simulations of step diffusion

To probe surface mass diffusion, we used the simulation to study the following situation. We started with a non-equilibrium configuration of 5 straight steps ( $N_s = 5$ ) with nearest-step separation of 6 lattice spacings (Fig. 6a). Because  $L_x$  is 60 spacings, the equilibrium spacing is  $12a$ . Thus, as time progresses the steps diffuse apart (see Figs. 6b and 6c). The jagged lines in Fig. 7 show the time dependence of the average step-edge positions (averaged over 20 distinct runs). The

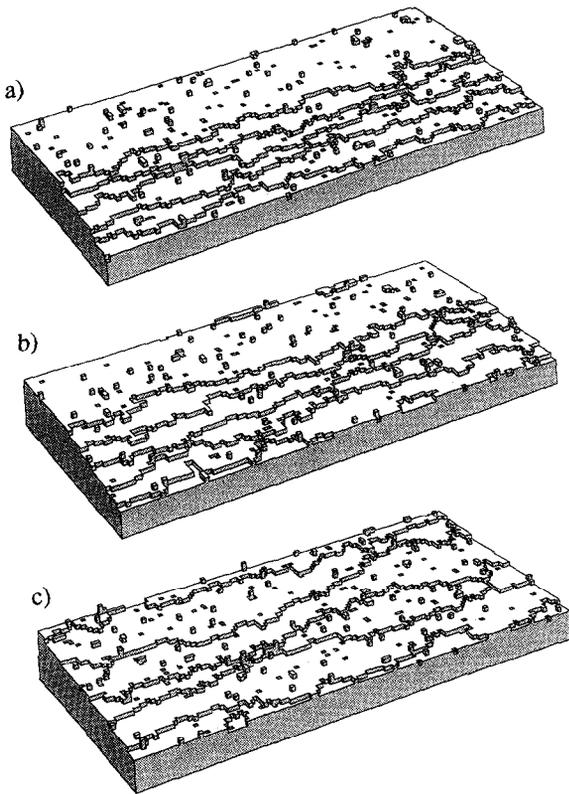


Fig. 6. Sample configurations of the surfaces used to study step motion. (a) The initial configuration of 5 steps separated by 6 lattice constants. (b) The surface after  $10^6$  Monte Carlo steps per site. (c) The final configuration after  $3 \times 10^6$  MCS/site.

question is, can we understand this motion on the basis of the results of the preceding section?

Since we have found that the fluctuations of the steps are limited by slow terrace diffusion, one might suspect that the theory of Rettori and Villain [2] for the evolution of surface morphology is appropriate. We thus work out the prediction of this theory for our case.

Rettori and Villain make the assumption that a chemical potential can be associated with each step edge. This chemical potential is determined by the size of the neighboring terraces. If the chemical potentials are different for neighboring steps, that is if the surface is curved, there will be a flow of atoms across the intervening terrace. If

this flow is determined by the diffusion rate of the atoms on the terraces, then Rettori and Villain show that the current from the  $n$ th to the  $(n-1)$ th step is given by (in their notation)

$$j_n = -K(\mu_n - \mu_{n-1})/l_n, \quad (22)$$

where

$$K \approx \frac{D_s c_0}{kT}, \quad (23)$$

and  $l_n$  is the width of the terrace between steps  $(n-1)$  and  $n$ . (As an aside, it is perhaps worth repeating here that in the continuum limit this equation reduces to Mullins' classical equation describing surface self-diffusion:

$$j(x) = -\frac{D_s c_0}{kT} \frac{\partial \mu}{\partial x}. \quad (24)$$

Eq. (24) assumes that surface mass diffusion is limited by terrace diffusion – if there are large kinetic barriers associated with step-edge attachment/detachment, this equation will not be correct [18,30], leading to values of  $D_s$  which vary with the average terrace width  $\langle l \rangle$ .)

Assuming the dependence of the projected surface free energy per unit area,  $f$ , on a surface with average terrace width  $\langle l \rangle$  takes the usually assumed form for a vicinal surface [31]:

$$f(T, \langle l \rangle) = f^0(T) + \frac{\beta(T)}{\langle l \rangle} + \frac{g(T)}{\langle l \rangle^3}, \quad (25)$$

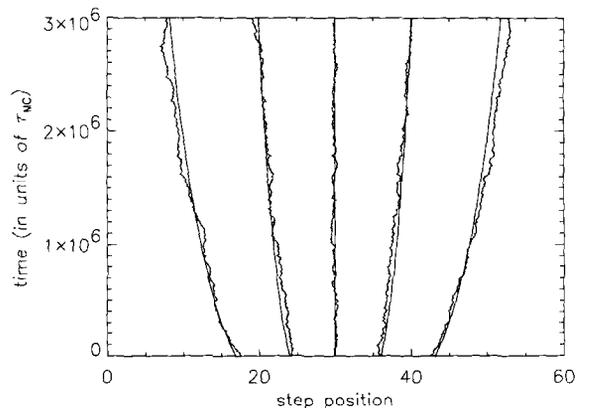


Fig. 7. The fluctuating lines show the time dependence of the average step position of the process shown in Fig. 6. The smooth lines show the predictions of the theory of Rettori and Villain [2].

the chemical potential is

$$\mu_n = 3g(l_n^{-3} - l_{n+1}^{-3})\Omega. \quad (26)$$

(Again, in the continuum limit, this equation reduces to the standard Gibbs–Thomson formula.) For our steps with only entropic and no energetic interactions between them, we expect [31]

$$g \approx \frac{\pi^2 (kT)^2}{6 \tilde{\beta}}. \quad (27)$$

The velocity of each step edge is then

$$v_n = \frac{\partial x_n}{\partial t} = \Omega(j_{n+1} - j_n),$$

$$j_n = \frac{-3D_s c_0 \Omega g}{kT l_n} \left( \frac{2}{l_n^3} - \frac{1}{l_{n-1}^3} - \frac{1}{l_{n+1}^3} \right). \quad (28)$$

These equations can be easily integrated numerically. Fig. 7 shows the result, choosing the value of  $D_s c_0$  to best fit our observations. The predicted functional form agrees well with the simulations. The result

$$D_s c_0 = 0.006/\tau_{MC}, \quad (29)$$

in excellent accord with what we deduced in Eq. (18)! Thus, although the two-dimensional fluctuations of the steps are essential to their motion, a one-dimensional calculation in which the driving force is the entropic interactions between steps is sufficient to describe their motion.

## 7. Conclusions

First, the fluctuations of the steps in the SOS model with Monte Carlo kinetics are governed by a different mechanism from the extreme cases of random adatom emission and of hopping along the step edges, discussed in Ref. [11]. The wavelength dependence of the step fluctuations suggest that diffusion on the terraces dominates morphological changes. We have explicitly shown that the simple change of reducing the sticking coefficient at the step edges to 1/10 (i.e. incorporating a higher activation barrier for step-edge attachment than for terrace diffusion) changes the nature of step fluctuations *qualitatively*.

The case considered here is perhaps the simplest in the sense that the kinetic properties of the steps do not play much of a role in the evolution of the surface morphology: the surface mass diffusion coefficient is simply the terrace adatom diffusion coefficient. It gives, however, a complete example of how mass diffusion coefficients can be deduced from observations of step fluctuations and be used to predict the rate of changes in surface morphology. For instance, the situation described in Section 6 is directly relevant to the *unfaceting* of surfaces or to the decay of metastable (artificially prepared) structures on surfaces. As an example of the former, we mention recent scanning tunneling microscopy experiments on the unfaceting transformation of stepped Ag(110) [32]. When exposed to oxygen, these surfaces break up into regions of bunched steps and large (110) terraces. Examination of the terrace-width distribution of the unbunched steps suggests that, as in our model, the interaction between steps has a large entropic component [33]. Exposure of the surface to CO reverses the faceting by removing the oxygen: the entropy of step wandering presumably drives the steps back to fill the large (110) terraces. If the rate-limiting step in such processes is diffusion of Ag atoms across the terraces, then comparison with the results of Eq. (28) could directly yield estimates of diffusion constants, which could be compared with parallel observations of the attachment/detachment processes at the step edges.

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## Appendix

For the sake of comparison with the equations in Ref. [13], we here: (1) write down the real-space

Langevin equation for the process described in Section 4, and (2) derive the equation governing the fluctuations of one point on the step edge.

(1) Converting Eq. (12) to real space, we find that

$$\frac{\partial x}{\partial t} = -\frac{4D_s c_0 \tilde{\beta} \Omega^2}{kT} \int_{-\infty}^{\infty} \frac{\partial^2 x}{\partial y'^2} \Big|_{y'} \times \frac{b^2 - (y - y')^2}{[b^2 + (y - y')^2]^2} dy' + \eta(y, t), \quad (30)$$

where  $b$  is a convergence factor on the order of a lattice constant. Thus, the local velocity of the step edge depends on the curvature of the step edge over a *range* of  $y$ , a manifestation of the couplings in the vibrations in the step edge caused by the diffusion field of adatoms. The weighting function is strongly peaked at  $y = 0$ , becomes negative, and then becomes small as  $y$  becomes large. The form of this function reflects the fact that for attachments to occur to lower the step free energy, they must deplete the adjoining sea of adatoms, making motion of adjoining regions of the step edge more difficult. This process is also evident in the correlations of the noise implied by Eq. (13):

$$\begin{aligned} &\langle \eta(y, t) \eta(y', t') \rangle \\ &= 8D_s c_0 \Omega^2 \frac{b^2 - (y - y')^2}{[b^2 + (y - y')^2]^2} \delta(t - t'). \end{aligned} \quad (31)$$

(2) The expression for the mean square displacement of a single point on the step edge is obtained by summing  $\langle x_q(t) x_q^*(0) \rangle$  over  $q$ : in the limit of  $L_y$  very large this sum leads to

$$\begin{aligned} &\langle (x(t) - x(0))^2 \rangle \\ &= \frac{L_y}{2\pi} \int_{-\infty}^{\infty} A(q) [1 - \exp(-|t|/\tau(q))] dq. \end{aligned} \quad (32)$$

Substituting Eqs. (3) and (16), this gives

$$\begin{aligned} &\langle (x(t) - x(0))^2 \rangle \\ &= \frac{4}{\sqrt{3} \Gamma(1/3)} \left( \frac{kT}{\tilde{\beta}} \right)^{2/3} (2D_s c_0 \Omega^2 t)^{1/3}. \end{aligned} \quad (33)$$

This  $t^{1/3}$  divergence is intermediate between the  $t^{1/2}$  divergence expected for adatom-attachment-limited fluctuations and the slow  $t^{1/4}$  divergence associated with step-edge hopping [12].

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