

## Brownian motion of steps on Si(111)

N. C. Bartelt, J. L. Goldberg,\* T. L. Einstein, and Ellen D. Williams  
*Department of Physics, University of Maryland, College Park, Maryland 20742-4111*

J. C. Heyraud and J. J. Métois  
*CRMC2-CNRS, Case 913, Campus Luminy, F-13288 Marseille Cedex 9, France*

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Step motion on surfaces can now be measured quantitatively. We present a formalism for analyzing equilibrium step fluctuations and apply it to real-time reflection electron microscope observations of step motion on Si(111). The time correlation functions of the step positions and of their Fourier components are compared with predictions from Langevin equations for two extreme mechanisms for step motion: edge diffusion and terrace exchange. At 900 °C, the dominant mechanism is terrace exchange with a time constant  $\tau_a$  of  $\sim 1 \mu\text{s}$ . The significance of  $\tau_a$  for atomic mechanisms of surface mass transport is discussed.

The use of direct imaging capabilities to measure statistical distributions among the states of a system has revolutionized our ability to understand the equilibrium structure of surfaces.<sup>1-3</sup> Similar advances in understanding kinetic processes are at hand due to the development of real-time *in situ* imaging capabilities such as reflection electron microscopy,<sup>4</sup> low-energy electron microscopy,<sup>5</sup> and high-temperature scanning tunneling microscopy.<sup>6</sup> One of the important applications of this emerging capability will be in understanding the kinetics of step motion on surfaces, which is important in growth<sup>7-9</sup> and in the equilibration of surface structure.<sup>10-14</sup> The simplest conditions under which step motion can be observed are equilibrium conditions in which the step position is fluctuating under thermal excitations. Such thermal fluctuations resulted in the ragged appearance of the step edges in scanning tunneling microscopy observations of Ag(111),<sup>15-17</sup> which are due to the thermal motion of atoms along the step edge on the same time scale as the scanning process.<sup>17</sup> In principle, it should be possible to analyze such thermal fluctuations to obtain the fundamental mechanisms and rates of step motion. We describe in this work the experimental signatures expected for two extreme models for step motion and demonstrate the experimental feasibility of distinguishing these two models. We show how analysis of the time and wavelength dependence of the step fluctuations gives the fundamental "step mobility" or step diffusion coefficient which governs how a step responds to being out of equilibrium. Our approach is a modification of a Langevin formalism which we had previously applied to the problem of the rate of step equilibration.<sup>18</sup>

Specifically, we demonstrate this approach by analyzing *time-dependent* reflection electron microscope (REM) of step motion. The data were obtained for Si(111) surfaces at 900 °C, and the *static* images were previously analyzed by Alfonso *et al.*<sup>3</sup> to determine the nature of the step-step interactions. At the temperature of measurement, the surface is above the (7×7) to (1×1) reconstructive transition, but below the temperature where sublimation (and thus net step motion) is appreciable. The REM technique, which allows *in situ* observations of the steps, is described elsewhere.<sup>3,19,20</sup> The data are an-

alyzed here in detail for a vicinal surface with an average step separation of 1400 Å. Figure 1 shows a sample image of one of these surfaces. Such images were recorded at video rates (30 frames/s). We used a digital frame averager to average over 2-4 frames. Next, regions of interest were digitized and stored with a time resolution of 10 frames/s. To analyze the step motion, an automatic procedure was developed to measure the positions of the steps in each frame. Typically 40 points were marked on each step edge. To correct for the distortion caused by the glancing incidence of the electron beam, we transformed coordinates as described in Ref. 3. Figure 2 shows the time dependence of the position of one point on one of the step edges. Notice that during one second the steps can fluctuate on the order of 100 Å. [The interatomic spacing on the (111) surface is 3.84 Å.] Approximately 800 such data sets were extracted from the video images and averaged to determine the correlation functions discussed below.

There are two extreme cases of the many microscopic mechanisms<sup>21</sup> which can cause step motion: (1) the exchange of atoms at the step edge with adatoms or va-

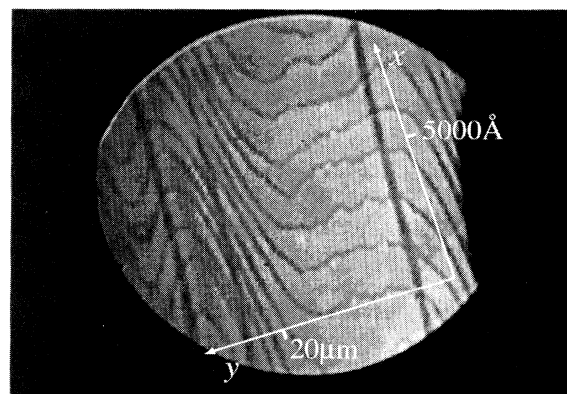


FIG. 1. A reflection electron microscope image of a stepped Si surface at 900 °C. The dark lines are single atomic layer high steps. The average step separation is  $\sim 1400 \text{ \AA}$ . As indicated on the superimposed axes, because of the glancing incidence of the electron beam, the dimension along the step edges is  $\sim 35$  times the perpendicular dimension.

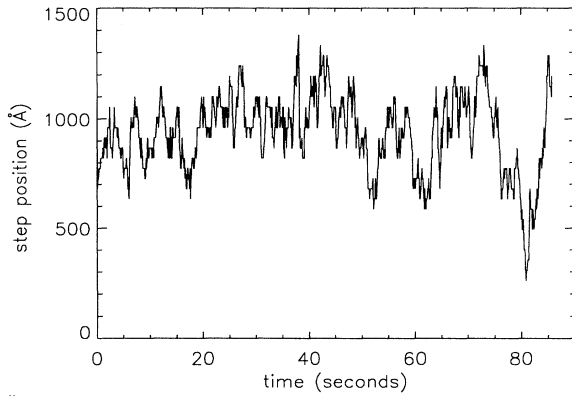


FIG. 2. The time dependence of the position of a single point on one of the step edges in Fig. 1. The data set was extracted from video-tape REM images. Many such sets of data allow us to determine the step mobility.

cancies on the terraces; (2) the motion of atoms hopping from one step site to another on the *same* step [as suspected to dominate for stepped Ag(111) and Cu(100),<sup>17</sup> for example]. As we shall show, the two classes are clearly distinguishable by analysis of the correlations in the fluctuations shown in Fig. 2. We stress at the outset that these correlation functions will depend on the step edge stiffness  $\tilde{\beta}$ , which is a measure of the step's tendency to remain straight,<sup>22</sup> as well as on the atomic kinetics. To understand the role of  $\tilde{\beta}$ , imagine the case (1) of atoms continually attaching and detaching at the step edge. If this happened completely randomly, the roughness of the step edge would quickly increase. But because rough step edges have high energy, the net detachment or attachment rate at any point of the step edge will be influenced by the local roughness in such a way as to smooth the step edge. The balance between the thermal "noise" of atoms attaching and detaching and the tendency of the step to minimize its curvature energy can be expressed in terms of a Langevin equation. If one mimics the interactions due to neighboring steps by a constraining potential of the form  $cx^2$ ,<sup>23</sup> the Langevin equation governing the fluctuations for case (1), random exchange, is<sup>18</sup>

$$\frac{\partial x}{\partial t} = \frac{\Gamma_a \tilde{\beta}}{kT} \frac{\partial^2 x}{\partial y^2} - \frac{2\Gamma_a cx}{kT} + \eta_a(y, t), \quad (1)$$

where  $\Gamma_a$  is the "step mobility" and  $\eta_a$  is the random thermal noise. From straightforward analysis of this equation,<sup>9,18,24</sup> we find that when the step is in thermal equilibrium the correlation  $G(t - t') = \langle x^2 \rangle - \langle x(t)x(t') \rangle$  of the fluctuations at any particular point on the step edge will be given, at early times, by

$$G(t) = \left( \frac{2kT\Gamma_a}{\pi\tilde{\beta}} \right)^{1/2} t^{1/2}. \quad (2)$$

This functional form is independent of the details of the attachment kinetics and step free energy. In principle it should be valid on time scales greater than a few attachment/detachments,<sup>18</sup> but short compared to the time between step collisions. Equation (2) can be immediately compared with the data. Figure 3 plots  $G(t)$ , determined from the data. The fit to the square

root time dependence is reasonably good, suggesting that the step motion is predominately due to adatom attachment/detachment. From the fit shown in Fig. 3, we estimate  $kT\Gamma_a/\tilde{\beta} \approx 3 \times 10^8 \text{ \AA}^4$ . The significance of this number will be discussed below.

For comparison, if the observed step motion were produced only by atoms hopping along the step edges, then the temporal correlations would be given by a different Langevin equation:<sup>18</sup>

$$\frac{\partial x}{\partial t} = -\frac{\Gamma_h \tilde{\beta}}{kT} \frac{\partial^4 x}{\partial y^4} + \frac{2\Gamma_h cx}{kT} \frac{\partial^2 x}{\partial y^2} + \eta_h(y, t). \quad (3)$$

(Now the noise  $\eta_h$  conserves the average step edge position.<sup>18</sup>) The correlations of a single point on the step edge at early times are now given by

$$G(t) = (0.46 \dots) \left[ \frac{(kT)^3 \Gamma_h}{\tilde{\beta}^3} \right]^{1/4} t^{1/4}. \quad (4)$$

This form is also compared with the data in Fig. 3. The fit is poor, evidently ruling out hopping along the step edge as the dominant contribution to the step motion.

To analyze the data in more depth, we consider the analogy of the steps to vibrating strings, recently discussed, for example, by Nozières.<sup>22</sup> Again, the basic question is whether the steps are "vibrating" because of the random attachment/detachment of atoms with the step edge (local random pushes on the "string") or because of the mass flow along the step edge (local twists of the string). One very striking feature of the experimental observations of the steps is that large-wavelength fluctuations decay slowly while short-wavelength fluctuations decay quickly. It is thus natural to study the time dependence of the Fourier components of the step edge. Taking  $y$  to be the coordinate along a step and  $x$  the coordinate perpendicular to the step edge, we define the Fourier components of the step edge  $x_q$  through

$$x(y, t) = \sum_q x_q \exp(iqy). \quad (5)$$

Using *either* Eq. (1) or Eq. (3) to compute the correlation

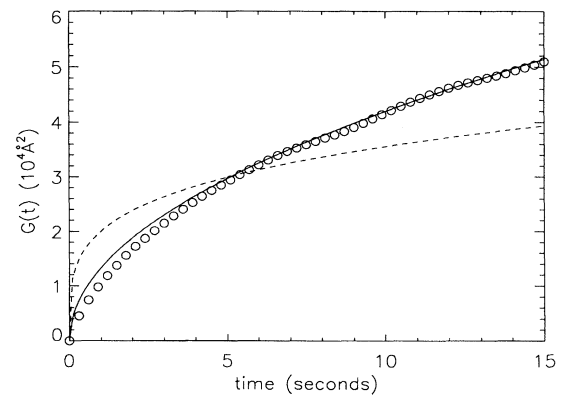


FIG. 3. The circles show the correlation function  $G(t)$  deduced from averaging over  $\sim 800$  data sets such as shown in Fig. 2. We have only included the correlation functions for times shorter than 15 s, because for longer times, the statistical noise becomes large. The solid line is a fit to Eq. (2); the dashed line is a fit to Eq. (4).

function  $G_q(t - t') = \langle |x_q(t) - x_q(t')|^2 \rangle$  yields<sup>9</sup> the prediction that each Fourier component will be correlated through

$$G_q(t) = \frac{2kT}{L(\tilde{\beta}q^2 + c)} \left( 1 - \exp[-|t|/\tau(q)] \right), \quad (6)$$

where  $L$  is the length of the analyzed step. For the case of adatom attachment/detachment, one finds the time constant decreases with increasing  $q$  according to

$$\tau(q) = \frac{kT}{\Gamma_a(\tilde{\beta}q^2 + c)}. \quad (7)$$

For the case of atoms hopping along the step edge, one finds

$$\tau(q) = \frac{kT}{\Gamma_h q^2(\tilde{\beta}q^2 + c)}. \quad (8)$$

The wavelength dependencies of Eqs. (7) and (8) are in agreement with the analysis of Pimpinelli *et al.*<sup>21</sup> for these two mechanisms of step wandering. In addition, we have performed Monte Carlo simulations which show that Eqs. (6)–(8) do indeed describe well the fluctuations of a step in the terrace-step-kink and solid-on-solid model over distinct ranges of  $T$  and  $q$ .<sup>25</sup>

Figure 4 shows  $G_q(t)$  deduced from the data, along with the fits to the exponential function of Eq. (6). From Fig. 4 it is evident that the time constant of the fluctuations does indeed increase with decreasing wavelength, as expected. Figure 5 quantifies this dependence by showing the  $q$  dependence of the inverse of the time constant, along with fits to Eqs. (7) and (8). The fit is clearly more consistent with the quadratic dependence of the attachment/detachment mechanism of Eq. (7) than the quartic dependence of Eq. (8), as anticipated by the analysis of Fig. 2. There is no evidence that diffusion along the step edge plays *any* role here, although it could well be important at larger  $q$  than probed in this experiment.

Thus, in summary, we find that the fluctuations of steps on Si(111) have the characteristics of Brownian motion: a simple Langevin process in which terrace adatoms or vacancies are allowed to attach and detach randomly from the step edges. What are the implications of the particular form of Eq. (1)? Given that atoms are attaching and detaching from the step edges, the principal assumption made in Eq. (1) is that the adatoms/vacancies

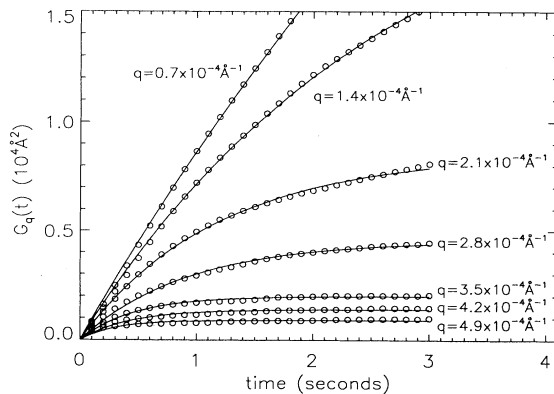


FIG. 4. The time correlations  $G_q(t)$  for a range of Fourier components (circles). The solid lines show the fits to Eq. (6).

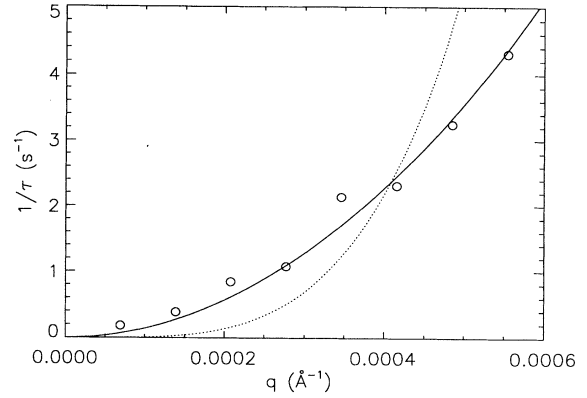


FIG. 5. The inverse of the time constant as a function of wave vector determined from the fits of Fig. 4. The solid and dotted lines show the fits to Eqs. (7) and (8), respectively. By examining terrace length distributions, Alfonso *et al.* (Ref. 3) find that the interaction between steps is consistent with an  $A/l^2$  repulsion, with  $A \approx 280 \text{ meV } \text{Å}$ . Because  $c \approx 6A/l^4$  (Ref. 23), the effect of  $c$  is negligible on the scale of this figure. From the fit to Eq. (7), we deduce a step mobility  $\Gamma_a = 5 \times 10^7 \text{ Å}^3 \text{ s}^{-1}$ .

can diffuse so quickly that they provide an infinite reservoir for step attachments and detachments. (This assumption is analogous to the assumption in traditional Brownian motion experiments that the mass of the observed particle is much greater than that of the molecules of the fluid.) One can easily envision physical situations where this assumption fails. For example, if the adatom diffusion rate on the terraces is slow compared to the adatom emission rate from the step edge, the density of adatoms can vary<sup>8,10</sup> along the step edge, leading to a time constant which varies as  $|q|^{-3}$  (Refs. 10, 21, and 25) rather than  $q^{-2}$  as we deduce from the experimental data. In such a microscopic description of step motion containing several different atomic processes with different activation energies, one can expect crossovers between the different characteristic step behaviors as a function of temperature. In addition, Pimpinelli *et al.*<sup>21</sup> have shown that the  $q^{-3}$  behavior, expected when terrace diffusion is rate limiting, can cross over to  $lq^{-2}$  behavior when the step separation  $l$  is sufficiently small. The conditions for such crossovers have not been thoroughly quantified theoretically, however. Further experiments studying the temperature and terrace-width dependence of the fluctuations are clearly warranted.

In addition to yielding information on the mechanism of step fluctuations, this analysis provides a concrete measure of the step mobility  $\Gamma_a$ . As discussed in Ref. 18, given the validity of Eq. (1), if the average position of a step is displaced from its neighbors, this step mobility describes how the net position of the step diffuses towards equilibrium (a manifestation of the Einstein relation). Thus,  $\Gamma_a$  is important in theories of how surface morphologies equilibrate through step motion.<sup>26,27</sup> To estimate the step mobility  $\Gamma_a$  from Fig. 5, we use the value of  $\tilde{\beta} \approx 30 \text{ meV}/\text{Å}$ , which we deduced from fits to the amplitude of Eq. (6). (This number is lower than the best estimate of  $68 \text{ meV}/\text{Å}$  quoted in Ref. 3; however, it

is in the range of quoted numbers.) From the fit shown in Fig. 5, we then estimate from Eq. (7) that

$$\Gamma_a \approx 5 \times 10^7 \text{ \AA}^3 \text{ s}^{-1}. \quad (9)$$

This yields  $kT\Gamma_a/\tilde{\beta} \approx 2 \times 10^8 \text{ \AA}^4$ , roughly consistent with the value deduced from Fig. 3.

Although  $\Gamma_a$  is an important quantity in its own right, we now discuss its microscopic interpretation. For uncorrelated noise in Eq. (1) (as we have assumed),

$$\langle \eta_a(y, t) \eta_a(y', t') \rangle = \frac{2\Gamma_a}{kT} \delta(y - y') \delta(t - t'). \quad (10)$$

Interpreting the noise  $\eta_a$  as due to random attachments and detachments of *single* atoms, one finds

$$\Gamma_a \approx a^3/\tau_a, \quad (11)$$

where  $a$  is an atomic dimension, and  $\tau_a$  is the average time between attachments/detachments. From Eqs. (9) and (11) we deduce that  $\tau_a$  is on the order of  $10^{-6}$  s. Is this number plausible? As a lower limit on what is reasonable, suppose the terrace atoms/vacancies which collide with the step edges are completely mobile, i.e., that they form a two-dimensional gas. Then the number of collisions per unit length of step edge per second will be of order  $nv_{\text{rms}}/\pi$  where  $n$  is the density of atoms on the terrace, and  $v_{\text{rms}}$  is the root-mean-square velocity. Taking  $v_{\text{rms}} = \sqrt{2kT/m}$ , the average density would only have to be on the order of  $10^{-6}/a^2$  to explain the

observed  $\tau_a$ . Of course, for the physical model under consideration, step attachment should be the rate limiting step. In other words, only some fraction of the step collisions should result in a successful attachment. If we treat step attachment as a simple activated process, the time constant can be related to the activation energy through  $1/\tau = n\nu \exp(-E_a/kT)$ . If  $n$  lies between 0.1 and 1, and  $\nu$  has a typical value of  $10^{13} \text{ s}^{-1}$ , the activation energy would be 1.4–1.6 eV. These magnitudes of  $n$  and  $E_a$  are comparable to values deduced from other experimental observations.<sup>28–30</sup>

An alternative explanation of the observed  $q^{-2}$  dependence of the time constant, as proposed by Pimpinelli *et al.*,<sup>21</sup> is that the step motion is determined by adatoms emitted by neighboring steps. In this case there would be a linear dependence of the time constant on terrace width. We cannot of course determine there is such a linear dependence of the time constant using the single data set analyzed here ( $l = 1400 \text{ \AA}$ ).<sup>31</sup> However, if we reinterpret our value of  $\Gamma_a$  in this model, the time constant for terrace diffusion is consistent with the values of Pimpinelli *et al.* of  $10^{-8} \text{ s}^{-1}$ . In a simple activation model for terrace diffusion, this value yields  $E_a$  in the range of 0.9–1.1 eV for  $n$  varying between 0.1 and 1.0.

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\* Permanent address: Dept. of Physics, Colorado College, Colorado Springs, CO 80903.

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<sup>31</sup> We have also analyzed less extensive data for steps separated by 1000 Å containing 300 data sets such as in Fig. 2. The  $q$  dependence of the time constant of the relaxations is the same, within uncertainty, as for the 1400 Å spaced steps. However, the larger errors prohibit checking the  $l$  dependence proposed by Pimpinelli *et al.* (Ref. 21).

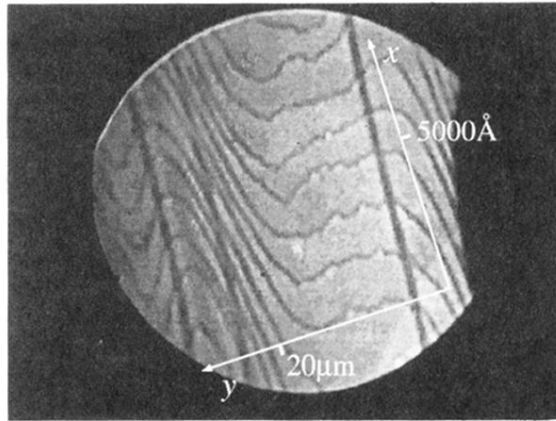


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