NANOSCALE FLUCTUATIONS AT SOLID SURFACES

Before you build things in the nanoworld, you'd better make sure you know how atomic fluctuations affect your structure's size and shape.

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On the nanometer scale, a seemingly smooth crystalline surface is not only bumpy, it's also in motion. Tiny mesas and depressions appear and disappear; escarpments range over the surface like waves on a beach. These thermal fluctuations are visible, thanks to advances in imaging techniques, which exploit electrons to divine the nanoscale motions (see figure 1). But although experiments can capture the spatial structure of surface fluctuations with atomic resolution, they lack the temporal resolution to follow the hops of individual atoms. Instead, observations yield a set of parameters that characterize how the surface changes on longer, millisecond timescales.

Can these parameters be derived from physical arguments to predict the nanoscopic behavior of surfaces? With so much activity at the atomic level, building a model based on the behavior of individual atoms is too difficult. Moreover, we do not know how all the atomic degrees of freedom couple to the motion of surface features formed by tens to hundreds of atoms.

Fortunately, it turns out that a thermodynamic approach—one that treats fluctuations as the larger-scale manifestations of atoms moving in equilibrium—can successfully account for the observed behavior. This approach, which is the subject of this article, has more than academic interest. As devices shrink in size to the nanometer scale, the measurement, characterization, and understanding of how tiny surface features evolve will be crucial in determining the reliability and utility of nanostructures.

Characterizing fluctuations

A key building block in the evolution of surface structure is the step—a line boundary at which the surface changes height by one or more atomic units. Steps piled on top of each other form walls, which, in turn, constitute the basic architectural elements of nanostructures. Because atoms in steps are bound to fewer atoms than are the atoms that make up flat surfaces, steps are more susceptible to thermal fluctuations than the surface as a whole. Step motion is therefore the basis for nanostructure evolution.

A step advances or retreats when atoms move along its edge or back and forth between the step and adjacent terraces. But, as suggested in figure 2, we can picture a step as a one-dimensional interface or as a massless string that can vibrate with any wavelength greater than the atomic scale. In this scheme, the restoring force that keeps step fluctuations from growing indefinitely is the free energy cost of increasing the step length, which is governed by the step stiffness, $\tilde{\beta}(T)$ (see the box on page 27).

We can quantify the tendency of a step's configuration $x(y)$ to remain straight by defining a chemical potential:

$$\mu = -\Omega\,\tilde{\beta}\,\frac{\partial^2 x}{\partial y^2}, \tag{1}$$

where Ω is the smallest increment in area by which a step moves, and the amplitude of the fluctuation is assumed to be small. When the step curves due to thermal fluctuations, the chemical potential changes, triggering atomic motion that opposes the deviations from a straight configuration (when $\mu = 0$).

At the atomic level, the physical mechanisms by which diffusing atoms give rise to step fluctuations can be put into three general classes:

▷ Periphery diffusion, in which atoms flow along the step edge.

▷ Terrace diffusion, in which an atom moves from the step to the terrace, diffuses on the terraces, and then reattaches to the step at a site some distance away.

▷ Attachment–detachment, in which atoms move between the step and terraces with no correlation between motion at different sites.

Remarkably, a simple, linearized approach based on the Langevin equation can not only describe the large-scale behavior and universal properties of fluctuating steps, but also embody the three atomic diffusion mechanisms.[1,2] According to this approach, a given location x on a step will move according to

$$\frac{\partial x}{\partial t} = -\nu(-\nabla^2)^{z/2}x + \eta, \tag{2}$$

where ν depends on the time constant, step stiffness, and temperature; z is a positive number, and η is a noise term that may depend on the diffusion mechanism. The value of z is related to the character of the atomic diffusion mechanism: $z = 4$ for periphery diffusion, $z = 3$ for terrace diffusion, and $z = 2$ for attachment–detachment.

Applying this analysis to fluctuations mediated by each of the three mechanisms yields three different classes of behavior, each described by a different power-law dependence of the fluctuations on time, temperature, and stiffness. Because we can image steps in real time, we can test whether this approach accurately describes how steps fluctuate, and, if it does, measure the key time constants and step stiffness. In particular, we can measure the temporal correlation function $G(t)$ and compare it with our model-based prediction, as given by:

$$G(t) = \langle [x(y,t) - x(y,0)]^2 \rangle \propto \left(\frac{kT}{\tilde{\beta}}\right)^{\frac{z-1}{z}} \left(\frac{t}{\tau}\right)^{\frac{1}{z}}, \tag{3}$$

where z takes the limiting value of 4 for periphery diffusion, 3 for terrace diffusion and 2 for attachment–detachment.

The first quantitative measurement of $G(t)$ for fluctu-

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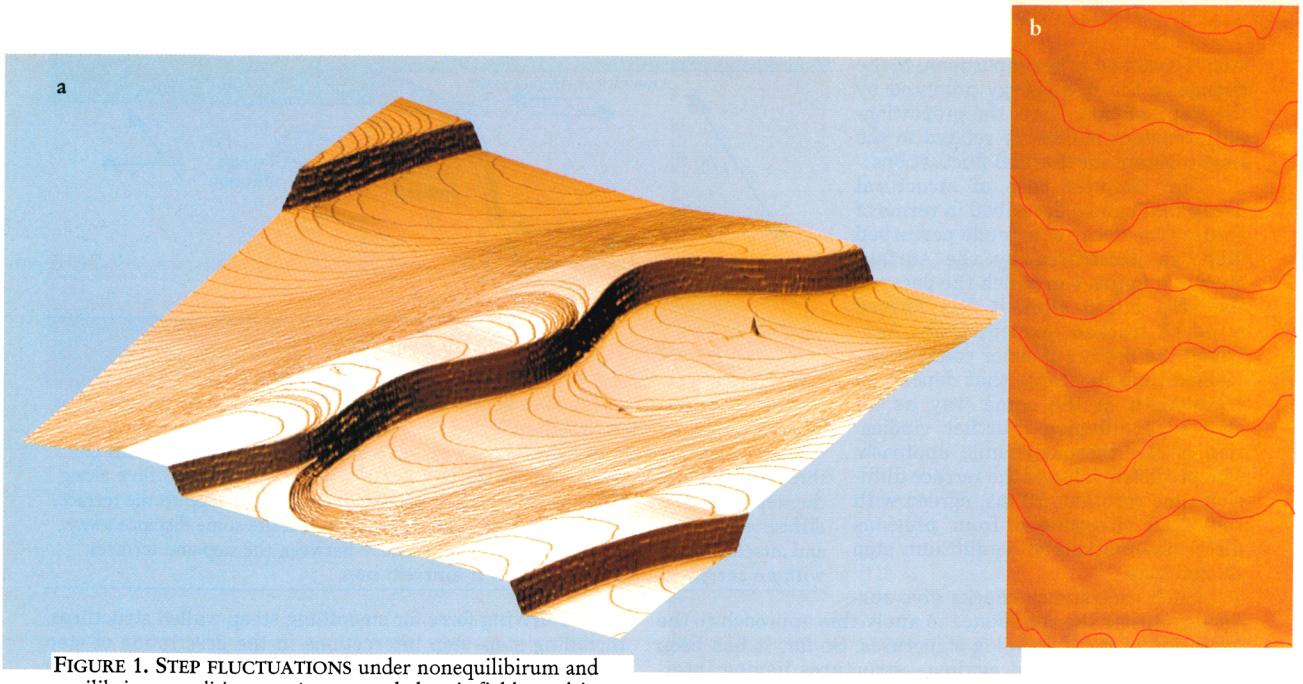

FIGURE 1. STEP FLUCTUATIONS under nonequilibirum and equilibrium conditions. **a:** An external electric field can drive a surface into complex nonequilibrium structures, such as the tight bands of single-atom steps in this 11 × 11 μm STM image. (Courtesy of Konrad Thuermer, University of Maryland.) **b:** In thermal equilibrium at 900 °C, steps fluctuate on timescales of seconds, as shown in this 1.1 × 12 μm STM image of a silicon (111) surface. The thin red lines, which are derived from a subsequent image, show where the steps (in darker orange) will be 13.7 s later. (Courtesy of J. J. Métois, CRMC2-CNRS Marseilles.)

ating steps was made by Jean-Jacques Métois's group at CNRS-Marseilles. The researchers used reflection electron microscopy (REM) to image steps on silicon (111) at temperatures in the range 900 to 1255 °C and at video rates of 30 Hz. As figure 1b shows, at these temperatures, steps shift position dramatically (by tens of nanometers) on timescales of seconds. At 900 °C, Métois's group found that $G(t)$ was clearly proportional to $t^{1/2}$.

In the wake of this first measurement, many further studies of step systems have revealed fluctuations that seem to be characterized either by periphery diffusion or by attachment–detachment. Although it is pleasing to have experiments agree well with theory, these results are actually quite puzzling. In real systems, without information to the contrary, we would probably expect several competing diffusion mechanisms to operate at the same time and to possibly contribute more or less equally to $G(t)$ under the same conditions. That, in any given system, we see just one of three theoretical limiting-case behaviors, rather than a mixture, greatly simplifies the problem of predicting fluctuations.

But why is nature so amenable? A more detailed analysis of step fluctuations that includes the possibility of competing mechanisms has answered the question. It turns out that only a small physical change in the relative importance of one mechanism is required to tip the observable fluctuation behavior into one of the three limiting-case regimes. For instance, when the time constant for attachment–detachment τ_a is large compared with the rate for periphery diffusion τ_p or terrace diffusion τ_t, attachment–detachment events limit the overall rate. In this case, z takes the limiting value of 2, which is formally expected when the rates of periphery diffusion and terrace diffusion are infinitely fast. Decreasing the ratio of τ_a to either of the other two time constants yields crossovers in observable behavior to the other two regimes, as shown in figure 3.

For example, a crossover from $z = 2$ to $z = 3$ behavior occurs with an approximately two-orders-of-magnitude change in the ratio of the time constants for diffusion and attachment–detachment. Such changes in relative rates are easily accomplished due to the tendency of rates to change exponentially with temperature. For instance, if the two processes differ in activation energy by 0.5 eV, then a change of 50 in the ratio of the rates would require about a 100 K change in temperature at 300 K.

Atomic clusters—surface islands—can be thought of as closed-loop steps, which, like open steps, can diffuse over surfaces. To address this phenomenon, experimental and theoretical studies have sought to determine the variance of the displacement of the clusters' center of mass as the clusters move about in a random-walk fashion. These random walks are expected to fall within three classes governed by the same three diffusion mechanisms introduced above.

As in the case of open steps, we can derive a measurable quantity and compare it directly to its measured value—in this case, the dependence of the diffusion coefficient D on the linear cluster size R. The experiments have shown that, usually, $D \sim R^{-\alpha}$. Furthermore, when diffusion along the periphery of the island predominates, $\alpha \simeq 3$. For the terrace diffusion mechanism, $\alpha \simeq 2$; for attachment–detachment diffusion, $\alpha \simeq 1$.

This approach to edge fluctuations has been extended by Norman Bartelt and Robert Hwang of Sandia National Laboratories to address the effects of dislocations and strain on island diffusion. Doubtless other exciting possibilities exist, too.

Fluctuations and decay

Edge fluctuations allow nonequilibrium structures to decay back toward their equilibrium state. If our interpretation of edge fluctuations is correct, then we should be able to quantitatively predict how nonequilibrium structures evolve. And if the structure is not too severely perturbed from its equilibrium configuration, then we can use the simple approach of linear kinetics, in which the velocity of a

step is assumed to be proportional to the change in the free energy produced by the step's motion. Here, the proportionality constant is directly related to the time constant for thermal fluctuations.

The simplest case of structural decay that can be described in terms of steps is the decay of a single perturbed step, as illustrated by the surface shown in figure 4 in which the decay of the step bump after it has formed could be tracked quantitatively. Analyzing the decay's Fourier components yielded time constants that depend on wavelength in the same way as for step edge diffusion. Further vindication of the thermodynamic approach: The predicted value of the terrace diffusion time constant, 10 ms, agreed with the value determined from previous direct observations of equilibrium step fluctuations.

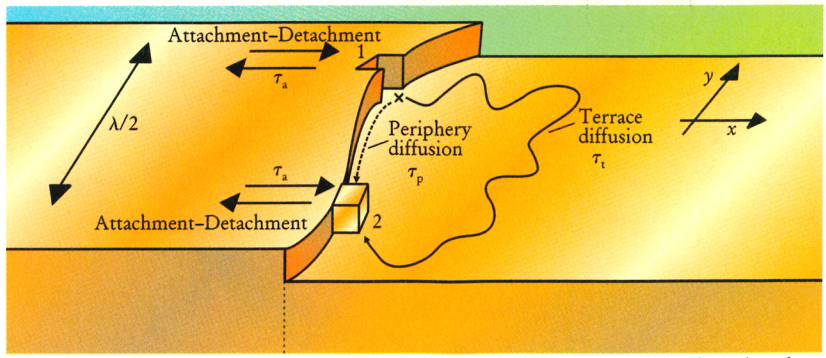

FIGURE 2. A MOVING STEP-LINE BOUNDARY on a solid surface can be thought of as a fluctuation with a wavelength of λ that successively advances or retreats through mass exchange between two sites. This mass exchange can be classified in terms of three limiting mechanisms—namely, periphery diffusion, in which atoms flow along the step edge; terrace diffusion, in which an atom moves from the step to the terrace, diffuses on the terraces, and then re-attaches to the step at a site some distance away; and attachment–detachment, in which atoms move between the step and terraces with no correlation between motion at different sites.

Such consistency checks give surface scientists the confidence to apply this approach to the evolution of more complex structures. So far, it has been applied to—and tested against—structures having interacting steps, three-dimensional forms, and variable chemical composition, as well as to structures in the presence of applied fields, such as strain or electric potential.

As an example of a complex structure, consider the stability of the pyramidal structure shown in figure 5. Whether fluctuation-driven kinetics drives the evolution of such structures can be evaluated by observing the decay of a single-layer island: If the decay rate is independent of island size (as, in fact, is the case), then detachment kinetics governs the decay.

From the measured island decay rate at any temperature (for example, 6 per second at 465 °C), the value of $\tilde{\beta}/\tau_a$ can be determined explicitly. This number in turn can be used to evaluate the decay of the pyramid, which can be thought of as being made up of sequential layers of islands, each decaying as a result of the emission of atoms from its edges. But to understand how such structures change in time, we have to model not just how steps behave by themselves, but also how they interact.

The basic physical issues are easy to understand. First, when steps are close together, step interactions (which arise from the configurational entropy of the steps and from the strain at the surface) will favor motion that maximizes the distance between steps. This tendency provides a driving force for smoothing steep-walled structures. Including step–step interactions in the description of step motion is accomplished by adding the potential energy change due to moving a step between two neighboring steps. For a steep-walled structure, the step–step repulsive interaction is strong and tends to prevent fluctuations away from the uniform slope. This process is clearly observed in the evolution of the structure in figure 5, where side walls maintain on average a constant slope as the top layers sequentially disappear.

For the simple case of such a shape-preserving decay, the coupled equations of motion of the structure's sequential layers imply that the height of the pyramid will decay as $t^{1/4}$ with an absolute rate being completely determined by the same factors that determine the decay of a single-layer island.

Analysis of many decay cycles yields extremely good agreement with these predictions. For instance, at 465 °C the measured time-exponent is 0.25 ± 0.01, and the measured absolute rate (6.1 ± 0.4 Å/s$^{1/4}$) is within a factor of two of the predicted value (3.1 ± 0.3 Å/s$^{1/4}$). This success provides further encouraging evidence that the use of measured thermodynamic parameters is a powerful tool for predicting even complex decay behavior.

Reliability and cumulative performance

Using measured fluctuations as the basis for modeling diffusion and decay rates is a natural extension of the methodology of traditional materials physics. However, as interest in nanostructures grows, so too does the possibility that the fluctuations themselves could be of practical interest. Two scenarios (among many) for this possibility come to mind. In both, nanoscale structures that can fluctuate between two configurations having different properties could be used to perform a crucial function, such as electronic switching.

In the first scenario, fluctuations are undesirable

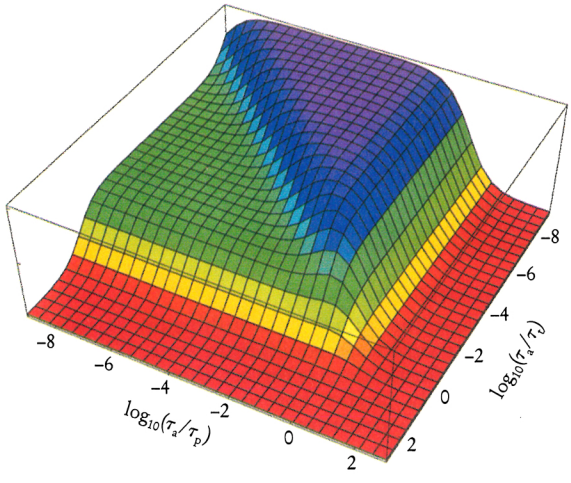

FIGURE 3. EXPONENT OF THE TEMPORAL CORRELATION FUNCTION in terms of the relative values of the time constants for the three limiting physical mechanisms—namely, periphery diffusion (τ_p, $z = 4$; shown in blue), terrace diffusion (τ_t, $z = 3$; shown in green), attachment–detachment (τ_a, $z = 2$; shown in red). The plot (for a fluctuation whose wavelength is 30 times the lattice spacing) demonstrates that the three diffusion mechanisms are sharply separated and intermediate behaviors rarely occur.

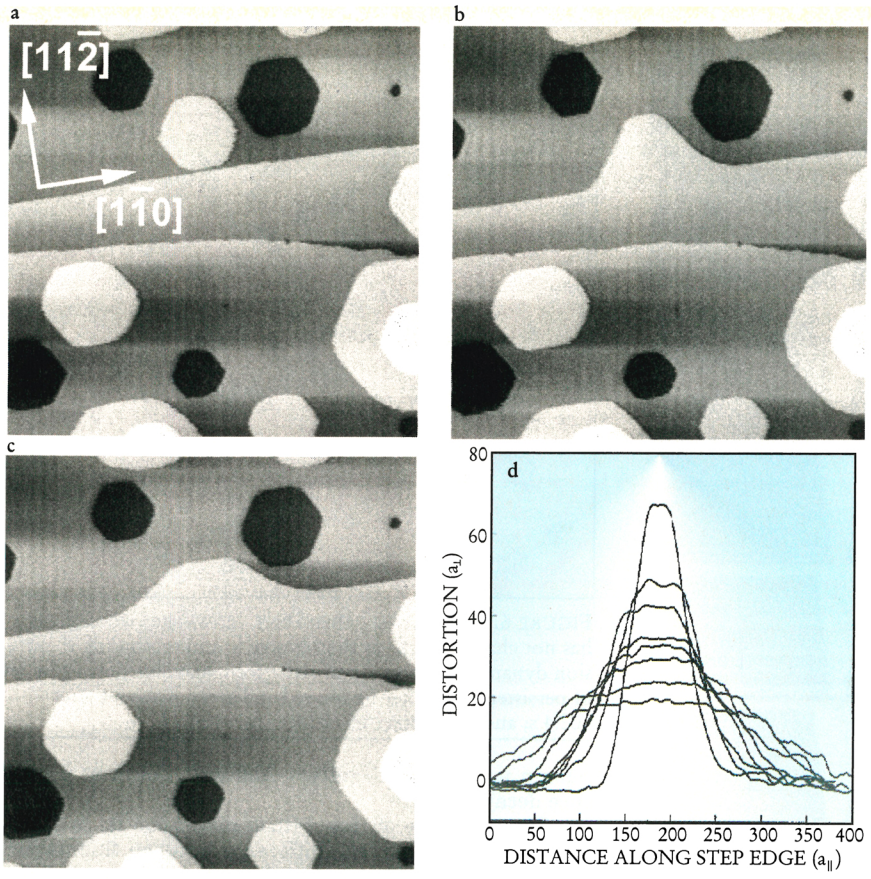

FIGURE 4. DECAY OF A MONATOMIC ISLAND on a 90 × 90 nm sample of copper (111) surface at a temperature of 303 K, as viewed with scanning tunneling microscropy. The island suddenly attaches to the step edge forming a bump (**a** and **b**) and then decays in time (**c**) due to edge diffusion, which is shown graphically in (**d**) with 100-second time steps. (Adapted from M. Giesen, G. S. Icking-Konert, *Surface Science*, volume 412/413, page 645, 1998.)

because only one of the system's fluctuation configurations gives the performance required. In this case, predicting the time it takes a single structure to change shape is crucial because it determines the redundancy needed to realize the desired reliability. Known as the persistence problem, this question is an active area of research.

In the second scenario, the inevitability of structural fluctuations provides the basis for the device's function. Here, a key quantity is the cumulative time that the structure spends in one of its fluctuation configurations. Predicting this fractional on-time or cumulative-state time is known as the sign-time or residence-time problem, and is closely related to the persistence problem.

To illustrate the richness of the physics of persistence, a simple numerical experiment can be performed on a model that incorporates the simplest and most commonplace process that can take place on a surface—atomic diffusion. At first, to make things even simpler, only the relaxational dynamics of diffusion contributes to the evolution of the initially rough surface. On a two-dimensional substrate, a rough surface is initially prepared by choosing h randomly from a Gaussian distribution with zero mean. Then the surface is allowed to evolve deterministically through the diffusion equation. As the surface fluctuates, the persistent sites are kept track of—that is, sites at which the deviation of the height from its mean of zero did not change sign up to a given time t. If a fluctuation changes the sign of the height (measured as the deviation from its mean) at a site before or at time t, that site is simply discarded from that moment on.

Figure 6 displays in the unit square the distribution of persistent sites at various times for which $h \geq 0$. Despite the simplicity of the dynamics, the generated sets have complex structures that appear—unexpectedly—to be fractal. (The Haussdorff dimension of the persistent set is 1.55, in contrast to the initial configuration, which, being area filling, has a geometrical dimension of 2.)

As the system evolves in time, fewer and fewer sites remain persistent, and the total number of persistent sites decays according to a power law $N(t) \sim t^{-\theta}$, where θ is the so-called persistence exponent. For the simple dynamics model described above the value of θ has been determined numerically with great precision[3] to be $\theta = 0.1875(10)$.

The apparent simplicity of the dynamics has spurred an extensive search to find a rigorous derivation of the exponent—but so far without success. Recently, however, a fruitful approach to the persistence problem has emerged in the form of the so-called distribution of sign times (DST),[4,5,6] which is also known as the residence time distribution.[7] Less restrictive in its definition than persistence time, the DST concept incorporates persistence as a particular case. With DST, when site i changes sign in h, we do not discard the site (as we did when constructing

Atomistic description of step bending

By relying on a thermodynamic evaluation of step properties, the step continuum approach outlined in the article spares us the complexities of the true atomic potentials near low-symmetry structures on surfaces. However, we can recover some insight into the underlying physics by using simple models of atomic interactions, such as lattice models. Using such a model, it is immediately apparent that the free energy cost for bending a step arises from the cost of creating kink sites at the step edges.

Analytical expressions for the free energy of the step as a function of temperature have been derived for a number of lattice models. For the simplest square lattice with near-neighbor interactions, the dependence is:

$$\tilde{\beta} = \frac{kT}{a} \sinh^2\left(\frac{\varepsilon}{2kT}\right),$$

where a is the interatomic spacing and ε is the attractive energy between two atoms. Given an estimate of the kink energy, the lattice model can be used to derive the expected value of the stiffness at different temperatures. However, regardless of any understanding of the underlying atomistic structure, thermodynamic values of the step stiffness can be determined from the steps' experimentally derived spatial correlation function.

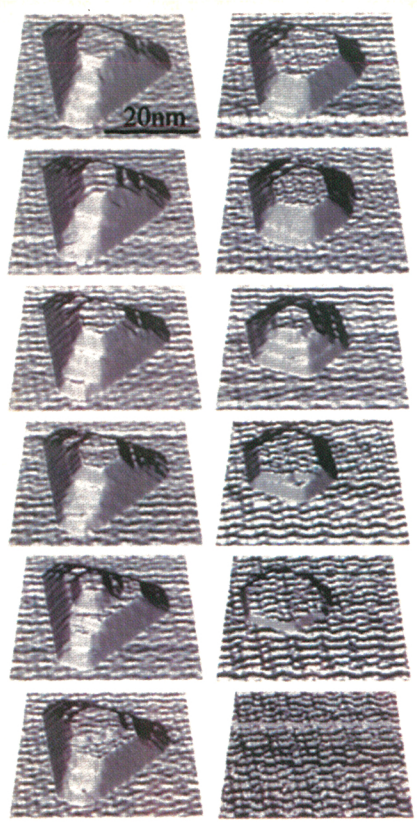

FIGURE 5. DECAY OF A SILICON PYRAMID. A pyramid is first formed by drawing atoms from the surface by means of the strong field at the tip of a scanning tunneling microscope. At moderate temperatures, few, if any, free Si atoms diffuse on the surrounding substrate, with the result that Si atoms from the bottom edges of the pyramid are not replaced when they leave and the pyramid decays. (Adapted from A. Ichimiya, Y. Tanaka, K. Hayashi, *Surface Review and Letters*, volume 5, page 821, 1998.)

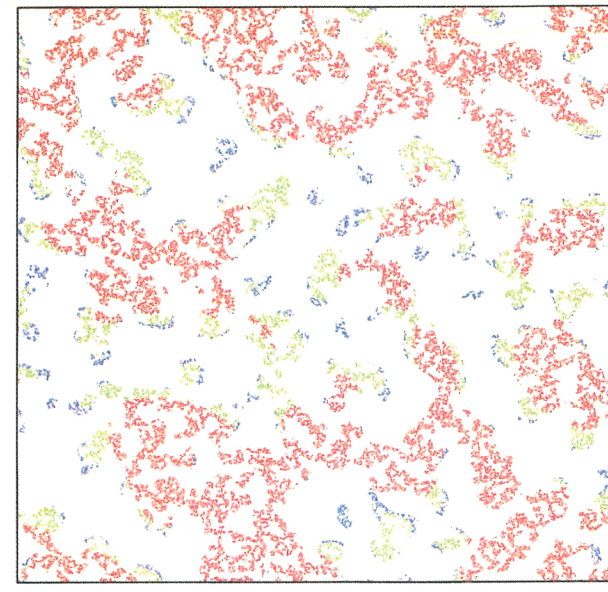

FIGURE 6. SIMULATED PERSISTENT SITES—sites whose height has not changed sign—as they evolve in time according to diffusion dynamics. The union of red, green, and blue dots is the set of persistent sites after 51.2 s; red and green is the set after 102.4 s; and red represents the set after 409.6 s.

the persistence probabilities). Rather, we keep the site, but record the time τ_i at the site only when its value of h is positive. It's as if each site has its own clock that ticks only when h (or, generally speaking, the fluctuation) at the site has a positive sign. Thus, at time t, each site has a clock value τ_i associated with it, and, since the interface fluctuates in a stochastic fashion, τ_i is a random variable. The probability $S(\tau, t)d\tau$ that one finds a site with a sign-time clock value between $\tau - d\tau$ and τ gives the sign-time density. Clearly, sites for which $\tau = t$ are those for which $h \geq 0$ up to time t—in other words, the persistent sites. Based on the sign-times approach, an analytic expression can be derived for the persistence exponent, $\theta=(4-\pi)/(4\pi-8)=0.1879\ldots$, which agrees remarkably with the experimentally derived value quoted above.

Although more general than the persistence probability, the DST is easier to measure because more sites remain in play for longer as the measurement proceeds. Moreover, it can be measured with the same experimental techniques used for directly measuring step fluctuations. The data are the same sort, too.

Theoretical analysis of the DST—even on simple growth models—has led to a few surprises. In particular, it turns out that for models described by the Langevin equation, the DST depends only on the substrate dimension and on the order of the relaxational term. That is, the DST for step fluctuations has only three different functional forms, and they correspond to the three classes of diffusion mechanism—just like the temporal correlation function, $G(t)$.

This class of Langevin process has provided another surprise: Ergodicity breaks down across a critical spatial dimension d^*. In general, an ergodic variable is one that, given enough time, will eventually adopt every one of its possible values. But here, when $d > d^*$, persistence is highly favored—that is, once positive (or negative), a site will remain positive (or negative). Above d^*, however, persistence decays rapidly.

The existence of this critical dimension is, in fact, a key manifestation of the difference between fluctuations mediated by attachment–detachment and those mediated by periphery diffusion. Furthermore, attachment–detachment tends to predominate in the tails of the DST—that is, for residence times that tend either to zero or to the elapsed time t.

Looking ahead

Historically, observations of thermal fluctuations have been interpreted in terms of Brownian motion or through the relationship between fluctuations or the macroscopic quantities, such as the diffusion coefficient and magnetic susceptibility. The advent of our ability to observe step fluctuations in real time at the nanoscale has changed our perspective profoundly. Nowadays, any theoretically interesting correlation function is experimentally accessible. On the theoretical front, it has been truly and pleasantly surprising that a relatively simple approach yields solutions that are also simple, belying Wolfgang Pauli's belief that the devil—not God—is responsible for the fiendishly complex nature of surfaces.

Some of the applications of this technological advance are clear and immediate. Quantitative predictions of structural stability, for example, are well under way. Other potential applications, such as those stemming from direct experimental connections to persistence problems, are in that pleasant state limited only by our imaginations.

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