

STEP FLUCTUATIONS: FROM EQUILIBRIUM ANALYSIS TO STEP UNBUNCHING AND CLUSTER DIFFUSION IN A UNIFIED PICTURE

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INTRODUCTION

In addition to providing information about the energy of kinks, thermal fluctuations of steps on a vicinal surface provide a rich source of insight into the microscopic atomic processes which underlie the fluctuations. In recent years it has become possible to make quantitative measurements of these fluctuations using STM (scanning tunneling microscopy), LEEM (low-energy electron microscopy), and REM (reflection electron microscopy). The fluctuations of the steps can be viewed as a form of Brownian motion (viz. random motion of a heavy entity due to thermal fluctuations of light particles) and can be analyzed using a capillary-wave approach and Langevin formalism. From this analysis one can deduce the key macroscopic parameters of step stiffness, step-step interaction strength, and mobility which govern the macroscopic behavior of the steps. These parameters can then be applied to situations far from equilibrium or in which the steps are driven by some external force. Furthermore, the analysis of nearly-straight steps can be adapted to treat nearly-circular steps and thereby describe the Brownian motion of monolayer clusters of atoms or vacancies on surfaces, for which quantitative experimental data has also been obtained recently. In this short review we gather together, integrate, and in some cases amplify results from several previous papers. We also summarize and catalog the relevant experimental results.

EQUILIBRIUM FLUCTUATIONS OF ISOLATED STRAIGHT STEPS

For a theorist it is easy to model the equilibrium fluctuations of steps by performing Monte Carlo simulations within the SOS (solid-on-solid) model. In this model, one assigns to each site i on a square net (2D lattice) an integer h_i , which denotes the height (in units of the lattice constant) at that site. The Hamiltonian is then a characteristic energy ϵ times the sum over all nearest neighbor pairs i, j of the height difference $|h_i - h_j|$. Thus, both the energy of a single-height step per lattice constant along a principal direction and the energy of a simple kink in such a step is ϵ , while the energy of an isolated adatom or vacancy is 4ϵ . For specificity, we shall assume that the step runs along the y direction, so that dislocations perpendicular to it are in the x direction (sometimes called "Maryland" notation), as depicted in Fig. 1. To create such a step, one can simply apply screw periodic boundary conditions in the x direction: $h_{i+L_x} = h_i + 1$, where L_x is the upstairs-pointing vector spanning the lattice, projected in the terrace plane.

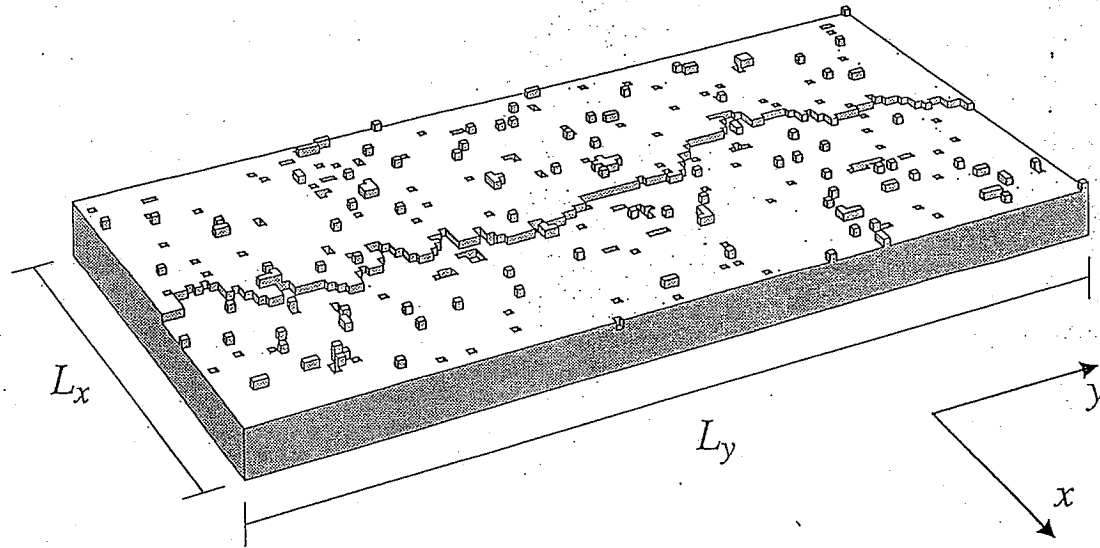


Fig. 1. A step in the SOS model at temperature $k_B T/\epsilon = 0.9$. The concentration of adatoms and of vacancies is about $0.02/\Omega$, where Ω is the area of the surface unit cell. From Bartelt *et al.* (1994a), with permission.

In Monte Carlo propagation of this lattice system, one can graphically watch how the step configuration changes as adatoms or vacancies attach to or detach from the step edge. In LEEM, REM, or STM experiments, one either lacks the resolution to observe atomic events or these events happen so rapidly that they cannot be observed individually. The challenge, then, is to deduce as much as possible about these atomic processes from observations of the step configurations alone. To do so, we apply capillary wave analysis. As the "wavelengths" (characteristic size in the y direction) of the equilibrium fluctuations increase, so do their amplitudes (in x) and their duration, as shown below.

There are three well-characterized limiting cases, denoted hereafter EC, TD, and PD (Bartelt *et al.*, 1992, 1994a). In EC [2D] evaporation/condensation, or attachment/detachment, of atoms and/or vacancies at the step edge limit the production and decay of fluctuations. Once the adatom or vacancy is free of the step, it is assumed to be instantly equilibrated into a 2D "gas" of "carriers" on the terraces. In TD, diffusion across the terrace is the limiting process, leading to slower behavior and a non-uniform distribution of carriers on the terrace that decays exponentially toward the thermal value for a flat surface. The slowest process is PD: periphery (or edge) diffusion. Here motion along the step edge limits the rate of the healing of fluctuations.

To make quantitative progress, we use a Langevin formulation. This amounts to an overdamped harmonic oscillator driven by a noise term (Kardar, 1994). The generic form is

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$$\partial x(y,t) / \partial t = -\text{restoring "force"} + \eta(y,t) \quad (1)$$

While one might hope that the restoring force [divided by "mass"] is linear in $x(y,t)$ with a prefactor τ^{-1} from dimensional arguments, in general the behavior is more complicated, involving a convolution over y . However, by performing a capillary-wave analysis, i.e. writing $x(y,t)$ as $\sum_q \exp(iqy)x_q(t)$, we find

$$\partial x_q / \partial t = -\tau_q^{-1} x_q(t) + \eta_q(t), \quad \langle \eta_q(t) \eta_{q'}(t') \rangle = L_y^{-1} f(q) \delta_{q,q'} \delta(t-t'), \quad (2)$$

where $f(q)$ is given below. We seek the behavior of the [measurable! (Bartelt *et al.*, 1993; Bartelt and Tromp, 1996; Pai *et al.*, 1996)] autocorrelation function $G_q(t-t')$ of the capillary modes:

$$G_q(t-t') \equiv \langle [x_q(t) - x_q(t')]^2 \rangle = 2 \langle [x_q(t)]^2 \rangle - 2 \langle x_q(t) x_q(t') \rangle = A (1 - e^{-|t-t'|/\tau_q}) \quad (3)$$

From equipartition arguments, one finds that the prefactor $A = 2k_B T / \tilde{\beta} q^2 L_y$ depends simply on known quantities, except perhaps the step stiffness $\tilde{\beta}$, which can thus be determined from this relation or checked with previous independent determinations. [The stiffness is the coefficient of the integral of $(1/2)(\partial x / \partial y)^2$ in the Hamiltonian of the step; $\tilde{\beta}(\theta) = \beta(\theta) + \beta''(\theta)$, where $\beta(\theta)$ is the free energy per length of a step.] The q^2 dependence does not depend on the limiting case. On the other hand, by integrating eqn. (2) and computing $\langle x_q(t) x_q(t') \rangle$, we find

$$\tau_q^{-1} = \tilde{\beta} q^2 f(q) / 2k_B T; \quad f(q) = 2\Gamma_a, \quad 4D_{su} c_{su} \Omega^2 |q|, \quad 2\Gamma_{st} q^2 \quad (4)$$

for the cases EC, TD, and PD, respectively. The subscripts *su* and *st* are abbreviations for surface and step, respectively. The lattice spacings a_\perp and a_\parallel are in the unit spacings in the \hat{x} and the \hat{y} directions, respectively, and $\Omega = a_\perp a_\parallel$ is the area per atom (i.e. of the surface unit cell). The mobility or friction coefficients can be related to microscopic times:

$$\Gamma_a = a_\perp^2 a_\parallel / \tau_a \quad \text{and} \quad \Gamma_{st} = a_\perp^3 a_\parallel^2 / \tau_{st}, \quad (5)$$

where τ_a is the mean time between successive attachment (or successive detachment) events, and τ_{st} is the mean time between successive hops in the same direction along the step edge. Similarly, on a square lattice of sites $D_{su} = a^2 / 4t_h$, where t_h is the time between hops, and c_{su} is the sum of the adatom and vacancy concentrations far from the fluctuating step. [Bartelt *et al.* (1994a) also show how in Monte Carlo simulations one can change TD behavior to EC—except at very small q —by including a [very small] sticking coefficient in the attachment/detachment of carriers to step edges, thereby making that the rate-limiting process. We can now characterize this crossover analytically (Khare and Einstein, 1996, 1997).]

In terms of the models of dynamical critical phenomena (Hohenberg and Halperin 1977), EC and PD are examples of cases A (no conservation law) and B (conserved order parameter), respectively. The behavior $\tau_q^{-1} \propto q^2$ in EC is due to the fact that the relaxation is proportional to the gradient of the local surface free energy, which in this case is just the local curvature of the step edge. The extra factor of q^2 in PD ($\tau_q^{-1} \propto q^4$) arises from the additional $-\partial^2 / \partial y^2$ coming from the conservation condition. In spite of some similarities, TD is not (Siggia, 1996) an example of case C (coupling to an auxiliary conserved density). The extra factor of $|q|$ ($\tau_q^{-1} \propto |q|^3$) comes from the exponential decay of the concentration toward the

terrace value as one moves away from the step edge. In contrast, the terrace concentration is uniform in EC and effectively zero in PD. From the perspective of the long-studied problem of the decay of sinusoidal gratings in 3D, reviewed/studied from different perspectives by H. Bonzel, W.W. Mullins, L.-H. Tang, W. Selke, J. Erlebacher, and M.V. Ramana Murty in this volume, EC, TD, and PD are called [3D] evaporation/condensation, volume diffusion, and surface diffusion, respectively. Notice from eqn. (3) that in all three cases the early-time behavior of $G_q(t)$ is linear in t , characteristic of diffusive, exponential relaxation. In contrast, the real space analogue, the mean-square width $w^2(t-t') = \langle [x(t) - x(t')]^2 \rangle$ is not linear in any of the simple cases; instead, $w^2(t) \propto t^{1/2}$, $t^{1/3}$, $t^{1/4}$, for EC, TD, PD, respectively. (Cf. Note 1.) Fluctuations of positions along the step edge—in contrast to those of the q -modes—are interdependent. This problem of coupled Brownian oscillators has a rich history (Wax, 1954).

There are other ways to obtain many of these results. Decades ago Mullins (1957, 1959, 1963) showed the fruitfulness of formulating the problem in terms of a step chemical potential. Bales and Zangwill (1990) used the linear kinetic approximation that the step velocity is proportional to the difference between the adatom concentration near the step edge and its equilibrium value. Pimpinelli *et al.* (1993) trisect each system into a fluctuating step, a reservoir of atoms enabling the fluctuations, and a pipe connecting the two, through which the exchange of atoms occurs. From this incisive perspective, they can quickly account for a large number of limiting cases, including multi-step situations, but sacrifice the factors of π and the like appearing in more precise derivations. Elsewhere in this volume, B. Blagojević and P.M. Duxbury formulate the problem in terms of the probability $P(y)$ that atoms leaving the step at one point return to this step a distance y away. Not only do they retrieve the early-time growth of the mean-square width in the three limiting cases EC, TD, and PD, but they can achieve intermediate values $t^{1/(\alpha+1)}$ if $P(y) \propto y^{-\alpha}$. It is not immediately clear how the form of $P(y)$ relates to the physical nature in our formulation. We (Khare and Einstein, 1996, 1997) have also been able to produce cross-over behavior between limiting cases by considering a unified formulation that considers all three mechanisms simultaneously, as well as reproducing and extending the multistep behavior of Pimpinelli *et al.*

As an illustration of the application to actual data of the analysis procedure developed at Maryland, we consider the case of an isolated step on Ag(110) directed 30° from the close-packed $[1\bar{1}0]$ direction, measured by STM at room temperature by Reutt-Robey's group at Maryland (Ozcomert *et al.*, 1994; Pai *et al.*, 1996; Reutt-Robey and Pai, 1997). A best fit of the early-time measurements of the autocorrelation function is $w^2(t) = 33.7 \text{ \AA}^2 \cdot t^{0.49}$, consistent with EC. In the capillary wave analysis, the lowest value of q was $2.1 \times 10^{-3} \text{ \AA}^{-1}$, corresponding to a wavelength 3000 \AA . Some half-dozen values of q up to eight times that lowest value were analyzed for up to 1000 sec. From the fits of $G_q(t)$, A (and thence $\tilde{\beta} \approx 18 \text{ meV/\AA}$) and τ_q were obtained. In the plot of τ_q^{-1} vs. q , the fit to q^2 was much better than the alternatives, supporting the view that the fluctuations are EC limited. From the prefactor of this fit and the deduced $\tilde{\beta}$, we find a mobility $\Gamma_a = 1.8 \times 10^2 \text{ \AA}^3 \text{ s}^{-1}$, leading to $\tau_a \approx 350 \text{ msec}$. For an isolated step along the $[1\bar{1}0]$ direction, the stiffness is over 8 times as large, but $\tau_a \approx 400 \text{ msec}$, indicating that the ability of steps to supply Ag atoms to the terrace ($\tau_a^{-1} \approx 3$ [events] per second [per step site]) has little dependence on step orientation (and so kink density) (Pai *et al.*, 1996). For Si surfaces at much higher temperatures, also examples of $\tau_q^{-1} \propto q^2$, the mobilities are much higher: for Si (111) at 900°C , $\tau_a^{-1} \approx 10^6 \text{ atoms/sec}$ (Alfonso *et al.*, 1992; Bartelt *et al.*, 1993); for Si (100) at $700\text{--}1200^\circ\text{C}$, $\tau_a^{-1} = 10^3 - 10^6 \text{ dimers/sec}$ (Bartelt *et al.*, 1994b; Bartelt and Tromp, 1996). Kuipers *et al.* (1993, 1995) had found similar fluctuations on vicinal Au(110) and Pb(111). Cases of vicinals on which fluctuations with $\tau_q^{-1} \propto q^4$ have been observed are: Ag(111) (Poensgen *et al.*, 1992), Cu(100) (Giesen, 1992; Poensgen *et al.*, 1992; Giesen-Seibert *et al.*, 1993, 1995; Masson *et al.*, 1994; Barbier *et al.*, 1996) and Ag(100) (Hoogeman *et al.*, 1996; Wang *et al.*, 1996). To date there have

been no observations of $\tau_q^{-1} \propto |q|^3$; as discussed in the penultimate section, there may be reasons for this related to the isolated-step approximation.

APPLICATIONS TO SYSTEMS AWAY FROM EQUILIBRIUM

Our hope in finding mobilities from well-defined experiments in equilibrium is to be able to use them in situations away from equilibrium. As an example, we consider the problem of step unbunching. When vicinal Ag(110) is oxidized, it is energetically favorable for the oxygen to form chains on the terraces in the [001] (next-nearest neighbor) direction. Since it is energetically favorable to have a few long chains rather than several short ones, the surface phase separates into wide flat terraces covered with (1×n) chains and closely-spaced bunches of steps with temperature-dependent average misorientation. The oxygen can be rapidly removed by dosing with CO. The surface is left in an unstable configuration, and the steps relax back to the original uniform vicinality. Using formalism developed by Rettori and Villain (1988), we seek to account quantitatively for this behavior in an essentially 1D picture (viz. average position of each step as a function of time or CO exposure).

To start this discussion we need an expression for the free energy as a function of the local misorientation from the terrace [or facet] plane, or more precisely, the free energy per projected area, namely

$$f(\phi, T) = f_0(T) + \beta / \ell + g / \ell^3, \quad (6)$$

where $f_0(T)$ is the free energy per area of the terrace, and $\ell = (\text{step height } h) / \tan(\phi)$ is the distance between steps. Thus, β was defined after eqn. (3), and g/ℓ^2 is the repulsion between steps. Such an interaction always exists because of entropic repulsion due to the non-crossing of steps and is usually enhanced considerably by an elastic repulsion. The formula for g is given in Note 2; when the repulsion is purely entropic, g reduces to $(\pi k_B T)^2 / 6\beta$ (Williams *et al.* 1994). The repulsion produces what amounts to a 2D pressure defined as the negative derivative of the surface free energy with respect to surface area, with the number of steps held fixed (Ozcomert *et al.*, 1993). Since the width can be taken as constant,

$$p(\ell) = -\partial(f(\ell)) / \partial \ell_{\# \text{ steps}} = -f_0 + 2g / \ell^3. \quad (7)$$

Thus, the pressure difference on the two sides of the step is proportional to the difference of the inverse cubes of the terrace widths (neglecting possible interactions with more distant steps). Again in the overdamped limit, the step velocity $\partial x / \partial t$ is proportional to the pressure from the terrace behind the step minus the pressure from the terrace ahead of the step. Since the motion is again step diffusion, the prefactor ought to contain the same transport coefficient as that for equilibrium fluctuations, Γ_a for EC or $D_{\text{su}}c_{\text{su}}$ for TD, in either case divided by $k_B T$. Alternatively, this can be described as a current produced by the gradient of a chemical potential associated with each step (Rettori and Villain, 1988).

As a theoretical check of these ideas, Bartelt *et al.* (1994a) created in an SOS model a step bunch of 5 steps by initially confining them to half the lattice [in the \hat{x} direction], then watching them evolve to nearly uniform spacing. There was no energetic interaction between steps, just entropic. In Fig. 2 we show the average positions $\langle x_i(y, t) \rangle_y$ of the steps ($i = 1, \dots, 5$) as functions of time. Coplotted with these wiggly curves are smooth curves obtained by integrating the first-order equations of motion of each of the steps. The value of $D_{\text{su}}c_{\text{su}}$ in these curves is similar to that obtained from an analysis of the fluctuations of an isolated single step as well as from an explicit calculation of both D_{su} and c_{su} for a flat surface.

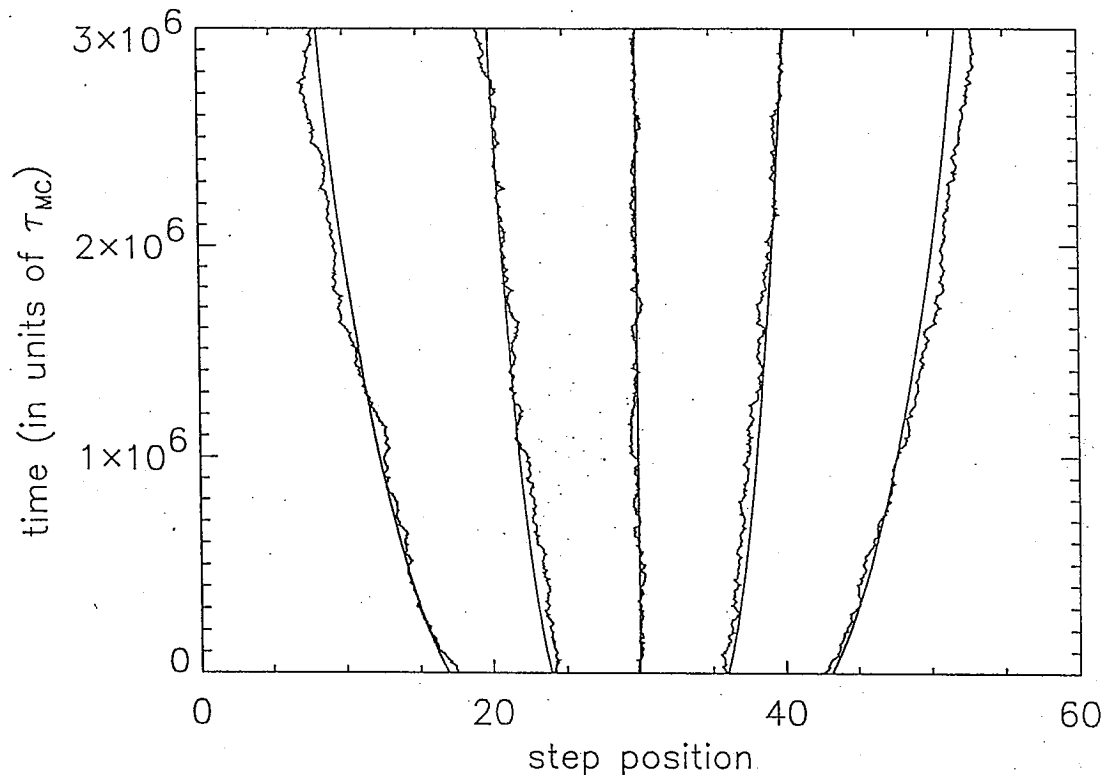


Fig. 2. Time evolution of the average position of steps in a step bunch relaxing back to their equilibrium distribution. The fluctuating lines are generated by Monte Carlo simulation, while the smooth curves come from the theory of Rettori and Villain (1988). From Bartelt *et al.* (1994a), with permission.

The experimental evidence for this scenario, mentioned at the outset of this section, is less compelling since it is harder to control this sort of dosage-sensitive STM experiment than a Monte Carlo simulation. (Specifically, it is problematic to convert from CO dosage to the evolution time from initial instability; the analysis would be better if the surface could be instantaneously de-oxidized.) From an earlier examination of the terrace-width distribution for Ag(110)2° → [001], Ozcomert *et al.* (1993) concluded that to a good approximation the step-step interactions were purely entropic repulsions (by finding a good fit to a free-fermion form (Joós *et al.*, 1991)). (But see also Pai *et al.* (1994) for remarkable behavior under different conditions.) From the relationship (Bartelt *et al.*, 1992)

$$\tilde{\beta} = k_B T (y - y') / \langle (x(y) - x(y'))^2 \rangle \quad (8)$$

(rather than capillary-wave theory), they also determined the stiffness to be $\tilde{\beta} = k_B T / (5\text{\AA}) = 5 \text{ meV/\AA}$ for steps in low-symmetry directions. In Fig. 3 we show a fit of the experimentally measured average (over y) of each step position as a function of time (or CO exposure),

along with smooth curves indicating a best fit to integrated Rettori-Villain equations for EC (Ozcomert *et al.*, 1995; Reutt-Robey and Pai, 1997). The best fit is obtained with $\tau_a = 200$ msec, similar to (about half) the value deduced from capillary-wave analysis of equilibrium fluctuations.

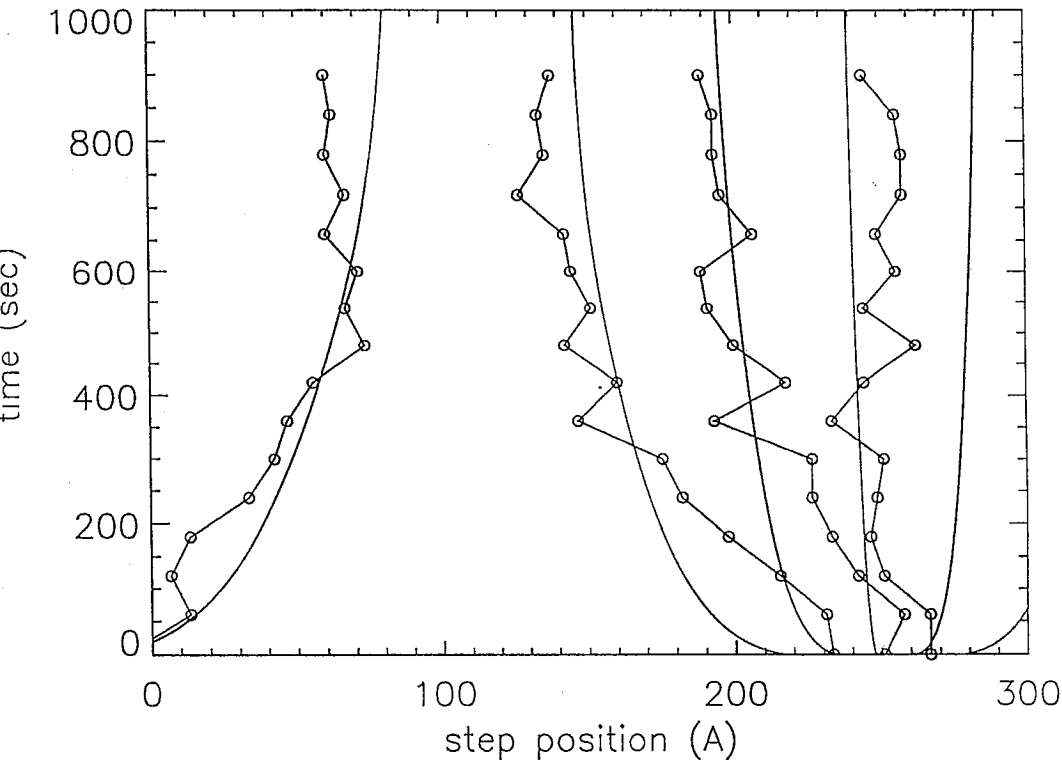


Fig. 3. Time evolution of the positions of the steps on vicinal Ag(110) after removal of the surface oxygen by reaction with CO. As in Fig. 2, the smooth curves are from the theory of Rettori and Villain (1988). Replotted from Reutt-Robey and Pai (1997), with permission.

APPLICATIONS TO DIFFUSION OF LARGE SINGLE-LAYER CLUSTERS

It is by now well established (Kellogg, 1994; Wang and Ehrlich, 1990) that field ion microscopy (FIM) can be used to monitor the diffusion of small clusters of atoms or vacancies on metallic surfaces. In recent years (room-temperature) STM has allowed for quantitative measurements of the Brownian-like motion of large single-layer clusters of 100's of atoms or vacancies on surfaces. As the cluster engages in this diffusive process, its center of mass can be tracked in a succession of images. One then expects the mean-square

displacement of this center of mass to be proportional to elapsed time, the proportionality constant being four times the cluster diffusion constant D_c . Such behavior was indeed observed by Trevor and Cidsey (1990) for Au(111), by de la Figuera *et al.* (1994) for vacancies on Cu(111) dosed with Co, by Wen *et al.* (1994, 1996, 1997) for Ag islands on Ag(100), by Wendelken *et al.* (1997) for Cu islands on Cu(100), and by Morgenstern *et al.* (1995) for vacancies on Ag(111). In each case, again as expected, D_c decreases as the number N of atoms or vacancies in the cluster (or, equivalently, its average mean-square radius R^2) increases. Long ago, Binder and Kalos (1980) argued that D_c should decrease by some integer power of R : $D_c = D_{co}R^{-\alpha}$, where the integer α depends on the atomistic process governing the diffusion. Morgenstern *et al.* (1995) found that $\alpha = 1.97 \pm 0.39$ for R between 20 and 150 atomic spacings (viz. 2.9\AA), while Wen *et al.* (1994) reported $1/2 \leq \alpha \leq 1$. Issues of interest include: what these values of α indicate about the atomistic processes underlying the diffusion, and what the prefactor D_{co} reveals about activation energies.

While there have been several other different direct approaches (Morgenstern *et al.*, 1995; Van Siclen, 1995; Sholl and Skodje, 1995; Soler, 1994, 1996) to this problem, we here pursue the perspective that the fluctuations of the cluster can be viewed as fluctuations of its boundary, which is a closed single-height step (Khare *et al.*, 1995; Khare and Einstein, 1996). Our approach is to adapt the formalism for open nearly straight steps to closed nearly circular steps. Denoting by $r(\theta, t)$ the radial distance of the edge from the center of mass, we define a normalized deviation $g(\theta, t)$ from a perfect circle and do the equivalent of capillary-wave decomposition:

$$g(\theta, t) \equiv (r(\theta, t) - R) / R = \sum_n g_n(t) e^{in\theta}. \quad (9)$$

The Langevin equation for $g_n(t)$ is essentially the same as eqn. (2) for $x_q(t)$, with τ_n^{-1} replacing τ_q^{-1} and $R^{-1}\eta_n$ replacing η_q . Our previous calculations for straight steps can be carried over to circular steps by making the replacement $q \rightarrow n/R$. Since the displacement of the center of mass at time t is given by $r_{CM}^2 = x_{CM}^2 + y_{CM}^2$, we find

$$D_c \equiv \langle r_{CM}^2 \rangle / 4t = R^2 \langle |g_1|^2 \rangle / t = R^2 f_n \tau_n (1 - e^{-2t/\tau_n}) / 2t \sim k_B T R \tau_1^{-1}(R) / \pi \bar{\beta} = D_{co} R^{-\alpha} \quad (10)$$

where we have again used the result that in equilibrium $\langle |g_n(t)|^2 \rangle = k_B T / 2\pi R \bar{\beta} n^2$ (Nozières 1992). [See also Note 3.] Thus, again the relation between the microscopic and macroscopic perspectives occurs through the characteristic time. For the cases EC, TD, and PD, since $\tau_q^{-1} \propto q^2, q^3, q^4$, we now have $\tau_1^{-1} \propto R^{-2}, R^{-3}, R^{-4}$, and so $\alpha = 1, 2, 3$, respectively, or equivalently, $D_c \propto N^{-1/2}, N^{-1}, N^{-3/2}$. (In late-stage coarsening by cluster coalescence—in contrast to the near-constant size regime treated here—Sholl and Skodje (1996) show that the average cluster radius increases like t^β , where $\beta = 1/(\alpha+2) = 1/3, 1/4, 1/5$, respectively, rather than the $t^{1/3}$ behavior for all 3 cases in the limit of Ostwald ripening. Furthermore, they find the dynamic scaling law for n_s , the density of islands of area s : $n_s(t) \sim t^{-2\beta} f(s/t^{2\beta})$.)

To check whether this behavior, based on a continuum viewpoint, is applicable to vacancy clusters on the scale of the experiments, we performed Monte Carlo simulations using the standard Metropolis algorithm. Since the goal was not to replicate any experiment, we invoked several simplifications and “tricks” to bring out the central physics with minimal complications. We used a square lattice with just an (attractive) nearest-neighbor (NN) energy $-e$. We worked at $k_B T/e = 0.6$ (0.5 for TD), well below the roughening temperature of the corresponding SOS model but high enough so that the equilibrium shape was nearly circular. For EC, we used straightforward Glauber (atom hops to/from “reservoir”) dynamics, adjusting the chemical potential to keep the number of vacancies about constant. Alternatively, after removing an atom at some random value of θ , we could simply

immediately reattach it at some other random position along the periphery, avoiding the nuisance of adjusting a chemical potential for the reservoir. (In this approach it is important when scaling the Monte Carlo data to include the fact that the chance of such a move per unit increases proportional to the circumference, contributing a factor of R to $D_c(R)$.) For TD, we used Kawasaki (atom hops to [NN] vacancy) dynamics. To prevent the vacancy cluster from dissolving, we forbade vacancy diffusion from the cluster boundary into the surrounding atomic lattice. To enhance motion across the terrace, we reduced the energy of an isolated atom in the interior of the monolayer pit to ϵ [from 4ϵ]; this had the added benefit of suppressing atom-cluster formation in the pit. For PD we again used Kawasaki dynamics, but with the modification that only NNN (next nearest neighbor), not NN hops were allowed. This "trick" enhanced the probability of creation, along a straight edge, of atom-vacancy (notch) pairs and prevents diffusing atoms from being trapped in corners. We considered clusters of size 100, 400, 1600, and 6400 vacancies [embedded in a much bigger lattice] and found from log-log plots of D vs. R the best-fit exponents $\alpha = 0.97, 2.03, \text{ and } 3.1$, respectively, in excellent agreement with the predictions of the continuum theory.

In this framework, the Morgenstern *et al.* (1995) experiment for Ag(111) pits is an example of TD, as they themselves concluded from an argument following the approach of Pimpinelli *et al.* (1993). Microscopically, the picture is that Ag atoms cannot surmount the barrier, so that they are trapped inside the pit. Thus, there are not the particle fluctuations associated with EC. On the other hand, Wen *et al.* (1994, 1996, 1997) find behavior more similar to EC. There are considerable particle fluctuations: Wen *et al.* (1994) remark that they exclude islands which decrease in area by more than 20% during the course of the observations. Moreover, the islands are more nearly square than circular (Wen *et al.*, 1996, 1997); much of the evaporation may occur by an edge-peeling mechanism (Van Siclen, 1995; Evans *et al.*, 1997) which is rate-limited by the detachment of a corner atom and so virtually independent of island size. In that case, the experimental exponent α could be more like 1/2 than 1. On the other hand, Wendelken *et al.* (1997) have just reported PD behavior for Cu islands on Cu(100). They also considered Ag islands on Ag(100), and there are preliminary indications that α is much greater than 1 and close to 3 (Pai 1997), consistent with measurements of vicinal Ag(100) (Wang *et al.*, 1996).

Our Langevin analysis also produces exact expressions for the prefactors D_{c0} for the three cases: $\Gamma_{2/TD}$, $D_{su}c_{su}\Omega^2/\pi$, and $D_{st}c_{st}\Omega^2/\pi$. [See Note 4.] The last of these is the 2D analogue of the 3D expression derived by Gruber (1967). To check the numerical values of D_{c0} obtained from the y -intercepts of the log-log plots, we also computed the diffusion constant directly by applying a weak potential gradient F to straight steps (or to adatoms on a flat terrace for TD) and seeking the resulting average velocity \bar{v} . Thence, the carrier diffusion constant can be calculated from the Einstein-Nernst relation $D = k_B T \bar{v} / |F|$. The resulting values agree to within 25% with those from the log-log plots. It is tempting to extract activation energies from the prefactors, an activity in which we have participated (Khare and Einstein, 1996). While the numbers obtained are semiquantitatively sensible, the level of correspondence to the real physical numbers depends on the accuracy of the presumptions made by the investigator about the microscopic Hamiltonian and how the macroscopic parameters depend on these energies.

UNIFIED FORMALISM, CROSSOVER, AND STEP REPULSIONS

Most of the preceding has been couched in terms of three separate, distinct cases. For the cluster problem we have presented a unified formalism encompassing all 3 limits and permitting the examination of crossover between them. We sketch the derivation, referring the interested reader desiring more details to Khare and Einstein (1996). The starting point is

to define a chemical potential for the cluster edge analogous to that for a step (Mullins, 1957, 1959, 1963; Bonzel and Mullins, 1996), having the form $\mu_s = -\Omega R^{-1} \beta \partial^2 g / \partial \theta^2$. We next apply the radiation boundary condition in the adiabatic or quasistatic approximation (Bales and Zangwill, 1990; Cahn and Taylor, 1994). With the assumption of a steady-state concentration of carriers on both the interior and the exterior terraces, the diffusion equation for the concentration reduces to a Laplace's equation. At any point along the edge, the net flux is determined by the normal component of the flux from the interior and exterior terraces—assumed to be *linear* in the difference between the concentrations on the two terraces—and by the motion along the island periphery. On the outside (inside) of the nearly-circular step this flux is equated to the mobility $\Gamma_{+(-)}$ times the difference of the carrier concentration just outside (inside) the step minus $(1 + (\mu_s/k_B T))$ times the concentration far from the edge. This provides the boundary condition needed to solve Laplace's equation for the concentration. Furthermore, the sum of the net attachments on the two sides determines the motion of the step (and hence of the island as a whole) $R \partial g / \partial t$. Decomposing into circular modes as in eqn. (9) and inserting into the equivalent of eqn. (2), we find a complicated expression for the characteristic times τ_n of the modes. For simplicity we assume an atom island, with all the atomic motion on the exterior. We define two characteristic lengths: 1) $R_{su} = \Omega D_{su} / \Gamma$ is essentially the ratio of the tracer (atomic) diffusion constant of the terrace D_{su} to the mobility. When it is large, diffusion over the terrace is much greater than attachment or detachment, so the motion is limited by the latter and so more likely to be EC than TD. 2) $R_{st} = (a_1 \Omega D_{st} / \Gamma)^{1/2}$ is a similar ratio of the tracer diffusion constant along the step to the mobility. To determine the cluster diffusion constant D_c , we again need only τ_1^{-1} . We find

$$D_c = \frac{c_{su} \Omega \Gamma}{\pi R} \left[1 + \frac{(R/R_{st})^2}{1 + (R/R_{st})(R_{su}/R_{st})} \right]^{-1} \quad (11)$$

From eqn. (11) it is straightforward to compute the exponent $\alpha_{eff} = -\partial \log D_c / \partial \log R$ that one extracts from log-log plots of data. Fig. 4 gives a contour plot of this effective exponent in terms of two dimensionless ratios of the three lengths. For very small clusters, EC eventually dominates (although the continuum approximation may well fail before this limit is reached). For very large clusters (perhaps unphysically large, depending on the size of R_{su} and R_{st} , TD eventually is reached. The most important feature is that the crossover regimes are relatively narrow, little over a decade in R . This suggests that α_{eff} should attain a constant value if the data contains a large range of sizes and that one should not find values of α_{eff} other than 1, 2, or 3 for this constant. Contrary findings indicate either problems with the experiment or significant physics missing from the theoretical analysis (e.g. the edge-peeling of Ag(100) islands).

Some clarification of the names of the three regimes should be made. In the extreme case $D_{su} = 0$, so $R_{su} = 0$, eqn. (11) reduces to $D_c^{-1} \propto R[1 + (R/R_{st})^2]$, and we find smooth crossover directly from $\alpha = 3$ to $\alpha = 1$, as suggested by the bottom of Fig. 4. In this limit, atoms cannot escape from the step to the terrace, even if they can detach. Physically, when the atomic motion along the periphery is very long range, the local mass flow is effectively driven by the curvature rather than its second derivative, and we find EC-like behavior. Thus, EC denotes only that attachment/detachment limits the rate, and not that there is a finite carrier concentration on the terrace. What we label TD was called "correlated EC" by Soler (1996) and by Van Siclen (1995). The essential physical mechanism characterizing this regime is evolution by single-atom jumps from one site on the island edge to another, mediated by a concentration field on the nearby terrace region.

Bonzel and Mullins (1996) have carried out a similar analysis for an isolated straight step, and we (Khare, 1996; Khare and Einstein, 1997) have extended our formalism to treat

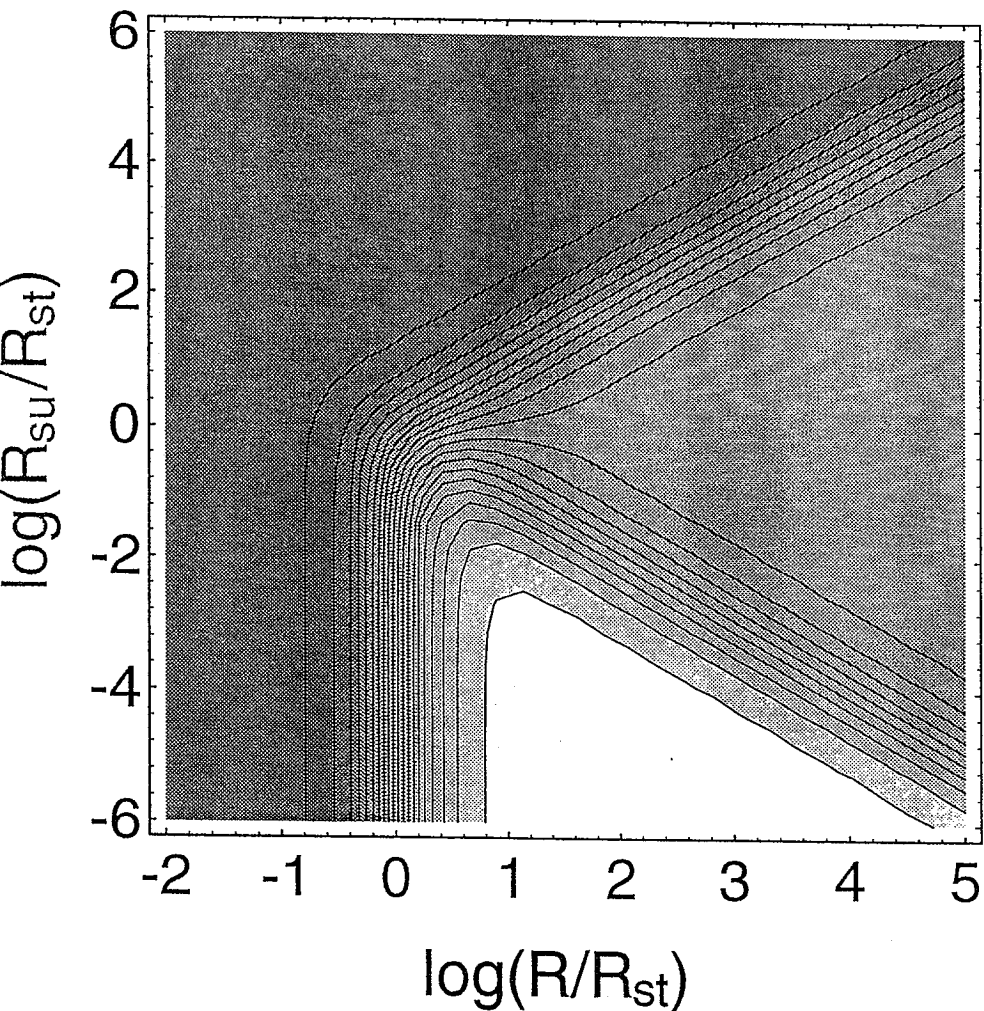


Fig. 4. Countour plot, with gray-scale shading of the effective exponent α_{eff} as a function of the common logarithms of the dimensionless ratios R/R_{st} and $R_{\text{su}}/R_{\text{st}}$. The large regions of gray, light gray, and white represent $\alpha = 1, 2,$ and $3,$ indicative of EC, TD, and PD, respectively. The crossover regions are relatively narrow. From Khare and Einstein (1996), with permission.

both such steps and a vicinal surface, i.e. an infinite array of steps. As for islands, one can examine the crossover between the three limiting regimes for isolated steps. The main result, again, is that the crossover regions comprise a rather narrow portion of phase space. We

also recover the important cases of transport between steps when the q -dependence of τ_q^{-1} and the early-time dependence of the mean-square width do not correspond to the corresponding behavior of an isolated step, cases D and E in Pimpinelli *et al.* (1993). In case D, there is no diffusion along the step edge ($D_{\text{st}} = 0$). Since $D_{\text{su}}q/\Gamma \ll 1$, the transport is terrace-diffusion limited, but now $|q|\ell \ll 1$. As a result, $w^2 \sim t^{1/2}$ and $\tau_q^{-1} \propto \ell^{-1}q^2$: the latter inequality leads to a factor of q being replaced by ℓ^{-1} . For case E, atomic motion along the step edge is again forbidden, $D_{\text{su}}q/\Gamma \ll 1$, and $|q|\ell \ll 1$, but now there is also the condition of a perfect (infinite) Schwoebel barrier: atoms approaching a step from the upper side are reflected back rather than crossing over the step and possibly attaching to it. Following through the algebraic reductions from taking the appropriate formal limits, we find that $\tau_q^{-1} \propto \ell q^4$ rather than q^3 , and $w^2 \sim t^{1/4}$. Thus, it is important to measure step fluctuations for different vicinalities to be certain of the correct assignment of transport mode. On the other hand, if one does find q^3 or $t^{1/3}$ behavior, it most likely is due to the TD mechanism. We are in the process of characterizing the crossover between TD and case D or case E behavior.

Other crossover behavior can arise when one moves to a regime where the continuum picture is not valid. For examples, Giesen-Seibert *et al.* (1995) show that for PD, at very early times w^2 behaves like $t^{1/2}$ rather than $t^{1/4}$ because the dynamics are dominated by random walks of kinks. In their simulations the effective exponent decreases smoothly with increasing temperature, with no evident crossover in any of the fixed- T log-log plots of w^2 vs. t . They also show how to take into account "fast events," viz. rapid, inconsequential back-and-forth motion of atoms ("blinkers"). This work builds on an earlier analysis (Giesen-Seibert and Ibach, 1994) in which they examine the structure of the probability distribution of the time between jumps as a function of the number of scans and the time of each scan, showing that the result does not depend simply on the product of these two arguments and that this sort of analysis can be used to filter out blinker events. Masson *et al.* (1994) propose a way to scale the step-step correlation function in terms of the STM scanning speed to allow the separation of diffusive behavior at fast scanning speeds from rapid temporal fluctuations at slow speeds.

A final issue of importance is the role of energetic repulsions between the steps. From eqn. (6), expanding about the average position of the step, we find the leading correction to the step free energy discussed while treating eqn. (1) is cx^2 , where $c = 6g\ell^{-4}$. Then in the EC case, $\beta\partial^2x/\partial y^2$ (implicitly in eqn. (1) is replaced by $\beta\partial^2x/\partial y^2 - 2cx$, leading ultimately to the replacement of βq^2 in A and $\tau(q)$ by $\beta q^2 + 2c$. This effect should only be noticeable for $q \leq 2\ell^{-2}\sqrt{(3g\beta)}$. Nonetheless, it can mask crossover behavior expected in the long-wavelength limit. For the PD case, Masson *et al.* (1994) provide an expression for $\langle |x(y,t) - x(0,0)|^2 \rangle$ in terms of a generalization of the equation in Note 1.

CONCLUSIONS

We have shown how capillary-wave analysis in a Langevin framework is a conceptually enlightening and computationally fruitful way to explore the quantitative data on step fluctuations that is now becoming available. The same perspective that is used for conventional steps near equilibrium can be applied to the closed, nearly circular steps defining a monolayer island and can assist the study of step bunches far from equilibrium. Most of phase space is dominated by one of three distinct physical mechanisms of atomic motion (EC, TD, and PD), the entire problem can be treated in a unified way within a single Langevin equation. It is consequently possible to examine the crossover between these limiting cases.

As a continuum approximation, this approach should break down by the atomistic level. For islands it is presumably inappropriate for the small clusters imaged with FIM. More importantly, in many cases the stiffness may not be nearly anisotropic, as we have assumed it to be in our analysis. Then, as perhaps for Ag(100) islands, new mechanisms may play a role. For vacancy clusters, there can be trapping in corners in systems that might seem to be cases of PD from consideration of vicinal surfaces.

In future work we plan to extend this approach to consider the effect of external fields due to applied potentials or adsorbed species, as well as the modifications when surface islands can change their mean size (ripening or decaying). Correspondingly, there is noteworthy current work on the effect of sublimation or deposition on the step fluctuations of a vicinal surface (E.g. Pierre-Louis and Misbah, 1996). It would also be interesting to consider the effects of weak pinning potentials.

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NOTES

1. To obtain the early-time behavior of the mean-square width, we take the continuum limit of the sum over q , note that the integrand is even, convert to dimensionless variables, and integrate by parts (Khare, 1996):

$$w^2(t) = \frac{k_B T}{2\pi\beta} \int_{-\infty}^{\infty} [1 - \exp(-2tA_n |q|^n)] q^{-2} dq = \frac{k_B T}{\pi\beta} (2tA_n)^{1/n} \Gamma\left(1 - \frac{1}{n}\right),$$

where A_j is the prefactor defined by $\tau_q^{-1} \equiv A_n |q|^n$, and $\Gamma(z)$ here is the gamma function. Here $n = 2, 3, 4$, for EC, TD, and PD, respectively, and $\Gamma(1/2) = \sqrt{\pi} = 1.77245\dots$, $\Gamma(2/3) = 1.3541\dots$, and $\Gamma(3/4) = 1.2254\dots$. In this expression one of the time indices in eqn. (3) is taken as 0, implying the step is initially straight. If both time variables are taken as large, but with a fixed difference t , then step fluctuates initially. Then in the intermediate expression above, the prefactor doubles and the exponent halves, so that $2^{1/n}$ is replaced by 2 in the final expression, as noted for the PD case by Masson *et al.* (1994). See also Appendix A of the chapter by Blagojević and Duxbury. (In our later section on island diffusion, α corresponds to $n-1$.)

2. The full, correct formula for the amplitude $g(\theta, T)$ in the expansion of the free energy per projected area, eqn. (6), is (Williams *et al.* 1993, 1994):

$$g(\theta, T) = \frac{\pi^2 k_B T b^2(\theta, T)}{24 a_n h^3} \left\{ 1 + \left[1 + \frac{4 A_n a_n}{k_B T b^2(\theta, T)} \right]^{1/2} \right\}^2,$$

where h is the step height, A_{el} is the amplitude of the energetic l^{-2} decay, due typically to elastic repulsions, and $b^2(\theta, T)$ is the diffusivity of the step, i.e. $\langle |x(y) - x(y')|^2 \rangle = b^2(y-y')/a_n$ for small $|y-y'|$; in terms of the stiffness, $b^2(\theta, T) = k_B T a_n / \beta(\theta, T) \cos^3 \theta$.

3. In the middle of eqn. (10) we have made an early time approximation which requires some justification since the observation time is much longer than τ_1 . However, τ_1 in turn is much greater than the time for macroscopic events: e.g. in the EC case, $\tau_1 = (k_B T / \beta a) (R/a)^2 \tau_a$, where the first term is somewhat smaller than unity and the second factor considerably greater. Next we can consider the position of the center of mass after each of M atomic events:

$$\mathbf{r}_{CM}(t) \equiv \mathbf{r}_{CM}(t_M) = \sum_{i=1}^M [\mathbf{r}_{CM}(t_i) - \mathbf{r}_{CM}(t_{i-1})].$$

In then computing $\langle \mathbf{r}_{CM}^2(t) \rangle$ to find the cluster diffusion constant, we note that these differences are all in the early-time regime. The diagonal terms each contribute $4D_C(t_i - t_{i-1})$ while the off-diagonal terms have random sign; hence the diagonal term is of order M while the off-diagonal sum is of order unity. If we were to compute shape fluctuations, as discussed in Khare and Einstein (1996), the diagonal term is also limited in size rather than increasing linearly with total time, confounding application of the method to experimental data.

4. From eqn. (4) we can identify $\Gamma_{st} \equiv D_{st} c_{st} \Omega^2$, i.e. only the combination $D_{st} c_{st}$ enters the transport coefficient. From this perspective the separation of D_{st} and c_{st} is somewhat arbitrary, leading to a subtle difference in notation between Khare *et al.* (1995) and Khare and Einstein (1996). In the former, c_{st} is the actual carrier density along the step, and D_{st} is then the actual diffusion constant along the edge. In the latter reference, $c_{st}^{[eff]}$ is defined as c_{suA_1} in conjunction with eqn. (23), leading to an effective D_{st} [e.g. in eqns. (9) and (23)] equalling $D_{st}^{[actual]} c_{st} / (c_{suA_1})$.

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