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Understanding surface limiting processes occurring during the relaxation of steps on vicinal surfaces

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Abstract

In our recently constructed Fokker–Planck formalism for describing the equilibration of the terrace-width distribution of a vicinal surface from an arbitrary initial configuration, the meaning of the relaxation time, related to the strength of the random noise in the underlying Langevin equation, was rather unclear. Using kinetic Monte Carlo simulations we show that the time constant exhibits activated behavior with a barrier that has a physically plausible dependence on the energies of the governing atomistic model. Thus, the Fokker–Planck time has some physical meaning.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Good understanding of equilibrium properties of vicinal surfaces—especially the form of the terrace-width distribution (TWD)—has been achieved [1]. Accordingly, attention is now focusing on non-equilibrium aspects, which have long been of interest. Some of us previously [2] derived the following Fokker–Planck (FP) equation (equation (1)) to describe the distribution of spacings between steps on a vicinal surface during relaxation to equilibrium. The goal was to describe how this spacing distribution relaxed rather than the evolution of the positions of individual steps as in a previous investigation [3–6]. Starting with the Dyson Coulomb gas/Brownian motion model [7, 8], we made the mean-field-like assumption, when computing interactions, that all but adjacent steps are separated by the appropriate integer multiple of the mean spacing; and set the width of the confining (parabolic) potential in the model to produce a self-consistent solution. We found the following:

$$\frac{\partial P(s, \tilde{t})}{\partial \tilde{t}} = \frac{\partial}{\partial s} \left[\left(2b_\rho s - \frac{\rho}{s} \right) P(s, \tilde{t}) \right] + \frac{\partial^2 P(s, \tilde{t})}{\partial s^2}, \quad (1)$$

where s is the distance w between adjacent steps divided by its average spacing $\langle w \rangle$, determined by the slope of the vicinal surface. The steady-state solution of equation (1) is the

generalized Wigner surmise, thus

$$P(s) = a_\rho s^\rho \exp(-b_\rho s^2) \quad (2)$$

where the constants a_ρ and b_ρ assure unit mean and normalization, respectively:

$$b_\rho = \left[\Gamma \left(\frac{\rho+2}{2} \right) / \Gamma \left(\frac{\rho+1}{2} \right) \right]^2, \\ a_\rho = 2b_\rho^{(\rho+1)/2} / \Gamma \left(\frac{\rho+1}{2} \right).$$

The dimensionless variable ρ gauges the strength A of the A/w^2 energetic repulsion between steps: $(\rho - 1)^2 = 1 + 4A\tilde{\beta}/(k_B T)^2$, where $\tilde{\beta}$ is the step stiffness. The dimensionless FP time \tilde{t} can be written as t/τ ; here the relaxation time τ is $\langle w \rangle^2 / \Gamma$, where $\sqrt{\Gamma}$ is the strength of the white noise in the Langevin equation (for the step position) underlying the FP equation [2].

To make contact with data, both experimental and simulational, one typically investigates the variance σ^2 of this distribution. If the initial configuration of the vicinal surface is ‘perfect’ (i.e. has uniformly spaced straight steps), the standard deviation can be described exactly³ or well approximated by

³ For equation (3) to be exact, the first moment of $P_\rho(s)$ must be precisely one, 2 as for Dyson’s Coulomb gas [7].

the expression [2]:

$$\sigma(t) = \sigma_{\text{sat}} \sqrt{1 - e^{-t/\tau}} \quad (3)$$

where the variance σ_{sat}^2 for an infinite system at long time (saturation) takes the equilibrium value $[(\rho+1)/2b_\rho]-1$. Time in this formulation is not the natural fermionic time associated with the direction along the steps (\hat{y} in ‘Maryland notation’), the mapping between two spatial dimensions and a spatial and a time-like dimension. Instead it measures the evolution of the system toward equilibrium and the thermal fluctuations underlying dynamics. Since the time constant τ enters rather obliquely through the noise force of the Langevin equation, a key investigational objective in the previous letter [2] and in this paper is whether τ corresponds to a physically significant rate. Monte Carlo simulations allow the examination of a well-controlled numerical experiment. In the former we used our well-tested Metropolis algorithm [9] to study a terrace-step-kink (TSK) model of the surface. We found a satisfactory fit to the form of equation (3), from which we obtained $\tau = 714$ MCS (Monte Carlo steps per site) for $\rho = 2$ (or $A = 0$, only entropic repulsions) while $\tau \approx 222$ MCS for $\tau = 4.47$. This result is in qualitative agreement with the understanding that Γ should increase (and, so, τ should decrease) with increasing ρ , as discussed in [2].

Here we confront more systematically and thoroughly the above-noted crucial issue, showing that the time constant associated with the FP transcription can be related to the atomistic processes underlying the relaxation to equilibrium and that the FP time tracks the literal physical time of the relaxing system. We report more extensive simulations, using kinetic Monte Carlo (kMC) [10] rather than the Metropolis algorithm, for a solid-on-solid (SOS) rather than a TSK model, so that we have real mass transport. We find that the time constant, extracted from the numerical data by fitting to the time correlation function in the form predicted by the FP analysis, has an activated form that can be related to an atomistic rate-limiting process in the simulations.

2. Computational details

In our SOS model, which has been described elsewhere [12], we use barriers determined by standard bond-counting: the barrier energy E_b is a diffusion barrier E_d plus a bond energy E_a times the number of lateral nearest neighbors in the initial state.

This number is 1 for an edge atom leaving a straight segment of step edge for the terrace, 3 for a detaching atom that originally was part of this edge (leaving a notch or kink–antikink pair in the step), or 2 for a kink atom detaching, either to the step edge or the terrace. Sublimation is forbidden, as are vacancies. No Ehrlich–Schwoebel barrier hinders atoms from crossing steps. In all simulations reported here, the number of lattice sites in the \hat{y} direction $L_y = 10^4$, with periodic boundary conditions; 5 steps in the \hat{x} direction are created by screw-periodic boundary conditions. We chose values $0.9 \text{ eV} \leq E_d \leq 1.1 \text{ eV}$ and $0.3 \text{ eV} \leq E_a \leq 0.4 \text{ eV}$, using temperatures $520 \text{ K} \leq T \leq 580 \text{ K}$. At these temperatures we

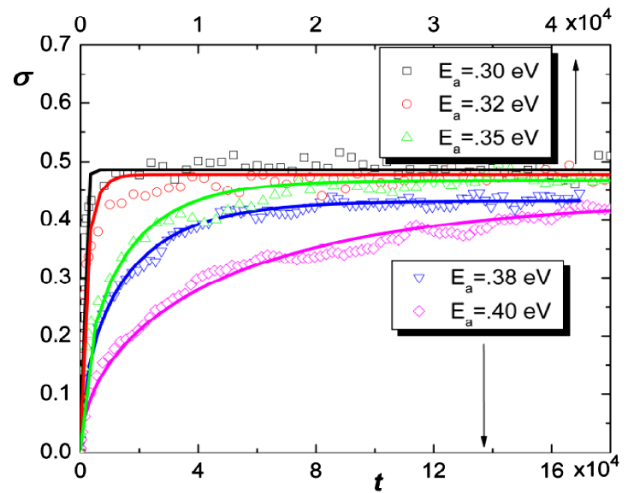


Figure 1. Five examples of fits (solid lines) using equation (3), used to extract τ . Note that the data (symbols) are well fit in all cases. The mean step spacing L is in lattice constants, and E_d and E_a are the energy barriers for diffusion and for breaking a bond, respectively. Time t is in seconds (see text). For all plots, $L = 6$, $T = 580 \text{ K}$, $E_d = 1.0 \text{ eV}$, $0.3 \leq E_a \leq 0.4 \text{ eV}$.

expect no significant finite-size effects in the \hat{y} direction for the values of the mean terrace width L (in lattice spacings) that we use: $4 \leq L \leq 15$. We saved essentially every hundredth update; that interval corresponds to our unit of time, which is about 1 s for the selected temperature and energies⁴. This update interval is long enough so that the sum of the kMC update times varies insignificantly ($\pm 0.01\%$) but short enough to capture the behavior during the steep initial rise.

3. Results and discussion

As illustrated in figure 1, we extract a time constant (or inverse rate) τ from numerical data fitting the dimensionless width using equation (3). The fit is notably better than that found in the Metropolis/TSK study in [2]. This rate is expected to have an Arrhenius form, so that $\tau \propto \exp(E_b/k_B T)$. We investigate E_b closely in the two traces of figure 2. We show typical runs at $T = 580 \text{ K}$, corresponding to $k_B T \approx 1/20 \text{ eV}$. First, we ramped E_d , holding E_a fixed at 0.35 eV (open squares). In the semilog plot we find a *reduced* slope (slope times $k_B T$) corresponding to 0.99 ± 0.02 , indicating that in the effective barrier, the multiplier of E_d goes like unity, as expected. In a second set of runs, we ramped E_a , holding E_d fixed at 1.0 eV (open circles). The observed reduced slope is 2.95 ± 0.10 , indicating that the effective energy barrier E_b is $E_d + 3E_a$. To confirm this idea, we ramped the temperature from 520 to 580 K, fixing $E_a = 0.3 \text{ eV}$ and $E_d = 1.0 \text{ eV}$. We find that the fitted activation energy is 1.067 ± 0.01 times $E_d + 3E_a$. Evidently the rate-determining process is the removal of a 3-bonded atom from a straight step, creating a pair of kinks (i.e., a kink and an antikink [13]) rather than the presumably more

⁴ The mean of the Poisson-distributed update intervals [11] was about 0.01 s. We saved when the counter reached 100 times this mean. The mean overshoot was also about 0.01 s.

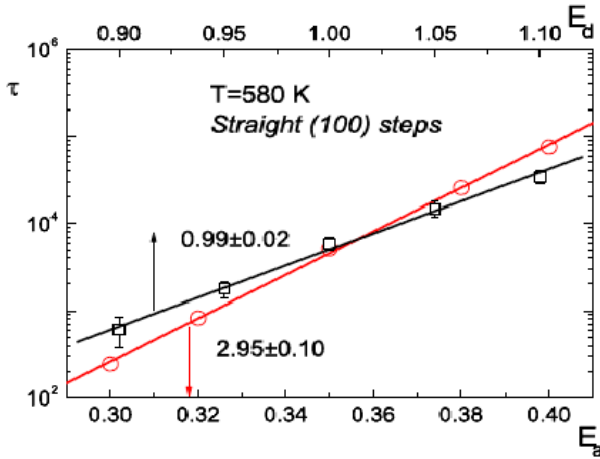


Figure 2. Semilog plots of the relaxation time τ (in seconds) versus the diffusion barrier E_d (squares) or the bond energy E_a (circles, red), with the other held fixed, both in eV. The numbers indicate the reduced slopes (the slopes divided by $k_B T = 0.05$ eV). Note that the slope of E_a —ramped relaxation times is about thrice that of the E_d —ramped times.

frequent process, with energy $E_d + 2E_a$, in which an atom leaves a kink position of a step [13, 14].

As a consistency check we compare the intercepts of the linear fits in the two semilog plots, i.e., the prefactors of the exponential term in which the appropriate energy is ramped. In addition to the activation components there is the leading factor $\tau_0 \equiv \langle w \rangle^2 / 4\nu_0$, where we fix $\nu_0 = 10^{13}$ Hz. Since $\langle w \rangle = 6$ in our simulations, τ_0 is 9×10^{-13} s. In the ramp of E_d , the prefactor is $\tau_0 \exp(3E_a/k_B T)$, predicted to be 1.19×10^{-3} s. The value we find from the simulations is $(1.2 \pm 0.1) \times 10^{-3}$ s, in excellent agreement. Similarly in the ramp of E_a , the prefactor $\tau_0 \exp(E_d/k_B T)$ is predicted to be 4.366×10^{-4} s and measured from the fit as $(4.36 \pm 0.15) \times 10^{-4}$ s.

We also varied the system size in the \hat{x} direction, holding the number of steps fixed, and thereby ramping $\langle w \rangle$. From the random-walk analogy, the prediction is that $\tau \propto \langle w \rangle^2$. We find tolerable agreement, with a slope 18% below the expected value.

An independent argument corroborates that the kink creation rate has an activation energy of $E_d + 3E_a$: since at equilibrium the creation and the annihilation rates are equal, we compute the latter. Annihilation of kinks requires that an adatom diffuses to a notch in the step edge—a kink–antikink pair, whose density is $n_{k-ak} \approx \exp(-2E_k/k_B T)$. Here, E_k is the formation energy of a kink, equal to $E_a/2$. Since the equilibrium adatom density is $c_{eq} = \exp(-2E_a/k_B T)$, the annihilation rate of kinks at a step edge is proportional to $Dc_{eq}n_{k-ak} \sim \exp[-(E_d + 2E_a + 2E_a/2)/k_B T]$ (cf [15]). This in turn implies that the activation energy for the kink creation rate is $E_d + 3E_a$.

It is remarkable that the key energy in the relaxation time is that for detaching 3-bonded atoms rather than kink atoms: neither equilibrium nor growth processes involve 3-bonded atoms. At equilibrium, step fluctuations are controlled by the so-called step mobility, which is proportional to the emission rate of adatoms from kinks [16]. The latter process only

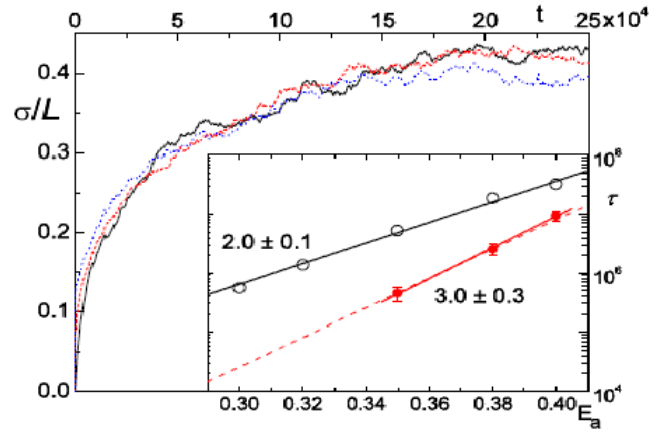


Figure 3. Checks of dependencies on initial conditions and update moves. Standard deviation σ of the TWD versus time for five steps starting from three initial configurations: straight steps (solid, black), ‘decimated’ edge (dash-dotted, red), and crenelated (dotted, blue) edge. For equilibrated non-interacting (free-fermion-like, $\rho = 2$) steps, $\sigma \approx 0.42$. $L = 6$, $T = 580$ K, $E_d = 1$ eV, and $E_a = 0.4$ eV. Inset: surface azimuthally misoriented by 0.0005 rad, forcing 5 kinks along the 10^4 -site steps. The three filled (red) circles represent runs with an initial ‘perfect’ configuration of 5 straight 2000-site segments; the reduced slope, indicated by the solid line, is 3.0 ± 0.3 , in excellent agreement with the steeper line in figure 2, indicated here with a dashed line, having reduced slope of 2.9 ± 0.1 . Thus, processes in which 3 bonds are broken govern the scaling of the relaxation time τ (given in seconds as in figure 1). The open circles are from runs with 3-bonded atoms immobile; the corresponding reduced slope is 2.0 ± 0.1 , so that now 2-bonded atoms control the (much larger) τ .

involves 2-bonded atoms. Thus, one would expect that the relaxation towards equilibrium is also controlled by the step mobility. However, our results clearly show that this is not the case.

One explanation for the present finding is that kinks have to be formed first, requiring the extraction of atoms from straight ledges. In that case, our initial configuration, in which steps are perfectly parallel and straight may be introducing a bias in the results. To investigate this possibility, we considered two other initial states with equal numbers of kinks and antikinks, i.e. in which one produces kinks by adding atoms to (or removing atoms from) a straight edge⁵. In one case every tenth atom along a straight step is removed; in the other case every other atom is removed to create a ‘fully kinked’ step, so that the edge resembles dentil molding or castle crenelations. In figure 3 we plot the resulting evolution of the standard deviation σ of the TWD for the three cases. During the early-time rapid spreading of the initial sharp TWD, the slope increases with the number of initial kinks, but after about 4×10^4 MCS the curves are essentially indistinguishable within the noise level, so fits of the displayed curves with equation (3) give comparable values of τ .

⁵ For initial states with small polar misorientations and so with small densities of kinks with one orientation, equilibration of the step shape still involves creation of new kinks, and this in turn implies detachment of 3-bonded atoms, since detachment of an atom from a kink does not change the number of kinks. For larger misorientations and kink densities, more subtle effects—with profound implications—come into play. We defer discussion to a separate paper [17].

To check that kink creation is indeed the rate-limiting process, we computed the relaxation rate of a surface with steps azimuthally misoriented so as to create kinks via screw boundary conditions in the \hat{y} direction. Specifically, in the initial state the in-plane misorientation slope was set at 0.0005, so that geometry forces the existence of 5 kinks for $L_y = 10\,000$. Keeping the diffusion barrier fixed at 1 eV, we varied E_a . The results are shown in the inset of figure 3 as filled circles. We computed just three points, but clearly, essentially no difference is found with respect to the relaxation rate of straight [100] steps (the red steeper line in figure 2). The latter is drawn as a dashed line in the inset. The fitted slope to the data (times $k_B T$) is 3.0 ± 0.3 , fully consistent with 3-bonded ledge atoms being responsible for the rate-limiting process. We also checked that the relaxation rate is enormously slowed if 3-bonded atoms are kept immobile: fitting the distribution width with equation (3), we ramped E_a while holding fixed $E_d = 1$ eV. The extracted relaxation times are shown in the inset of figure 3 as open circles. The reduced slope is 2.0 ± 0.1 , consistent with 2-bonded kink atoms providing the rate-limiting process for the step motion in this case. The characteristic time is at least an order of magnitude larger than the previous case, which can be interpreted as due to the inability to create new kink sites, so that the number of sources for 2-bond escape of atoms to the straight segments of the step is limited to the initial 5 kinks. Furthermore, the eventual width of the distribution, σ_{sat} , is only about half the size of the 3-bond case. Thus, at least over the course of our long runs, the surface is never able to equilibrate.

4. Conclusion

The equilibration of a (100) step and the fluctuations of the same step at equilibrium are apparently qualitatively different phenomena. The latter can take place with a constant number of kinks, while the former requires creation of new kinks. Thus, this system is a remarkable example of a situation in which the assumptions of the fluctuation-dissipation theorem [18] are not satisfied, rendering it inapplicable; the arbitrary initial configurations are far from equilibrium. In other words, fluctuations from the equilibrium distribution, having the form of equation (2), will not lead to arbitrary initial configurations such as a perfect cleaved crystal with straight, uniformly spaced steps.

In summary, we have shown that the relaxation time of Fokker–Planck formalism is related to microscopic processes, confirming that this approach provides useful physical insight into the evolution of complex surface structures toward equilibrium. Furthermore, the FP time tracks actual time in the evolving physical system.

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