RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 15 15 APRIL 1993-I

Linear decay of islands on metal surfaces

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(Received 21 December 1992)

Scanning-tunneling-microscope studies of mass flow on (111) Au have shown that the rate of decay of the area of monolayer islands is linear in time. We demonstrate by Monte Carlo simulation that a proper accounting of the detachment and reattachment rates of kink site atoms produces a linear decay. In our simulation, adatoms emitted from kink sites on mesa edges execute an unbiased random walk and may reattach to the home mesa or be absorbed by an outer ledge, possibly after several reflections from the step down at the outer ledge. The linear decay of mesa areas is found to be rather insensitive to variations in the probability of reflection from the outer ledge.

In a scanning-tunneling-microscope study of surface mass flow on (111) gold, Peale and Cooper have reported[1,2] that, at room temperature in air, the area of single-monolayer islands decays linearly with time. We have repeated their experiments and find the same results.[3] A linear decay of island areas is puzzling at first sight. If the rate of mass loss is proportional to the circumference of the island (a natural assumption if the number of kink sites per unit length along the perimeter is constant), then the number N of atoms decays as $dN/dt \sim -(N)^{1/2}$, and the decay is parabolic, not linear. In this Rapid Communication, we show, by Monte Carlo simulation, that a proper accounting of the kink atom detachment and reattachment rates leads to a linear decay.

We have developed two distinct computer models, which produce nearly identical results. Our models are based on the assumption that the potential near a monatomic step has the form shown in Fig. 1, with a deep well at the base of the step (site B), small activation barriers between shallow wells far from the step, and a somewhat higher shallow well at the site on the top terrace adjacent to the step (site A). Site A is somewhat higher because it lacks a second-nearest neighbor. As a consequence of the asymmetry in this potential, a kink site atom in the deep well B is more likely to activate out onto the lower terrace than up onto the higher terrace. Also, an adatom approaching the step from the left has some tendency to be reflected, while an adatom approaching the step from the right has no such tendency and will be captured in the deep well B. The qualitative form of this potential is supported by embedded-atom-method calculations.[4] Also, reflection of an adatom by a step down has been observed on metal surfaces by field ion microscopy.[5]

Because the terrace corrugation is small, the time for an adatom to random walk between ledges is very fast compared to the mean time for a kink site atom to detach.[6,7] For (111) Au at room temperature, the mean time for a kink atom to detach is 10^{-5}–10^{-2} s depending on the depth of the well B, while an adatom on a (111) surface wanders tens of nanometers in about 10^{-7} s. Consequently, at low temperatures ($T < 0.25 T_{\text{melting}}$), the rate-limiting step in mass flow is the detachment of kink atoms and there is rarely more than one adatom on a given terrace at any time.

The linear decay may be understood qualitatively as follows. An adatom emitted from a kink site on the edge of a mesa is quite likely to reattach somewhere along the mesa's perimeter after a brief random walk. Only occasionally do adatoms wander to the outer ledge of the terrace before encountering the perimeter of the home mesa. However, this high reattachment rate drops as the mesa shrinks, because the wandering adatoms are less likely to encounter the smaller mesa. The dropping reattachment rate counterbalances the dropping emission rate as the perimeter shrinks and nearly linear decay results.

In our first model, we assume that the number of kink sites on the perimeter of an island is proportional to the perimeter length. We also assume that all kink sites have the same constant probability per unit time to detach so that the mean time between detachment events is inversely proportional to the perimeter length. In this model, which is a hybrid lattice-continuum simulation, a mesa is represented by a circle I of radius R_i centered on the origin. R_i is determined by an integer N representing the number of atoms in the mesa: $R_i = (N/\pi)^{1/2}$. A larger

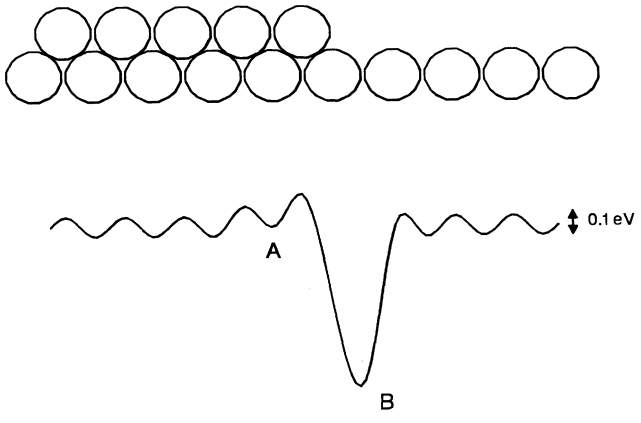

FIG. 1. Potential near a monatomic step.

circle O of fixed radius R_0, also centered on the origin, represents an outer ledge which can capture adatoms emitted by I. A walker, representing an atom detached from a kink on the perimeter of I, is released from the smallest positive integer position on the x axis outside I and begins an unbiased random walk on the xy lattice, jumping to one of its four nearest neighbors in each step. If the walker crosses the outer circle O before crossing I, then it may be absorbed with probability $(1-k)$ or it may reflect with probability k and continue its meandering trek. If it is absorbed by O, the time is advanced by $\Delta t = N^{-1/2}$ (the inverse of the mesa circumference), N is then reduced by 1, the radius of I is reduced accordingly, and a new walker is released from the smallest integer position on the x axis outside the now smaller circle I. The time increment Δt represents the mean time between detachment events, assumed inversely proportional to the circumference of I and the number of kink sites.

During its random walk, the adatom may undergo multiple reflections from O before being absorbed by O, or it may return to I after one or more reflections from O, or (most likely) it may return to I without reaching O. If the walker crosses the inner circle I, it is immediately absorbed, the time is advanced by $\Delta t = N^{-1/2}$, N is unchanged, and a new walker is released from the starting point just outside I. The process repeats until I completely evaporates, while N is recorded as a function of time.

Note that our model assumes that successive walkers do not interact, which is the case if the time between detachment events is long compared to the time of the random walk. Also note the length of the random walk does not affect the advancement of time in the simulation. The total time in the simulation is the sum of the times between successive detachment events. The random walk proceeds "in parallel" with the wait till the next detachment event.

Figure 2 displays the results of this simulation for an inner circle of starting radius near 20 ($N = 1257$), outer circles of radius 25, 50, 100, and 200, and a reflection coefficient $k = 0$ (walkers always absorbed upon contact with the outer circle). For outer circles large compared to the inner circle, we see that the mesa area decay is very nearly linear, but as R_0 approaches the inner circle's starting radius R_i, the mesa decay becomes more parabolic. A smaller outer circle captures adatoms more effectively, resulting in a lower reattachment rate and a net evaporation rate which is more dominated by the rate of emission, leading to more parabolic decay.

Figure 3 displays the results of the same simulations, but with a reflection coefficient $k = 0.95$. For larger outer circles, the decay is only slightly slower than the $k = 0$ case and is still nearly linear. This insensitivity of the linear decay to k is because, once the walker has wandered to the outer circle, it is very likely to undergo multiple reflections and be absorbed by O before finding the small inner island.

Next we describe a cubic lattice solid-on-solid model, similar in spirit but more realistic in detail than the model described above. The initial configuration is a stack of mesas, concentric circular terraces separated by monatomic steps. During the simulation, a list of "active" sites on the perimeters of the mesas is maintained. Active sites are those with fewer than three in-plane nearest neighbors and include kink and corner sites (see Fig. 4). At the start of the simulation, an atom is chosen at random from the list of active sites. The atom detaches from its mesa by jumping one step away from the perimeter and begins an unbiased random walk, stepping to any of its empty in-plane first- or second-nearest-neighbor sites. An atom is detached from a mesa if it has no nearest-neighbor in-plane, even though it may have a second-nearest-neighbor in-plane. As in the lattice-continuum model, a detached atom may reattach to its home mesa, or it may attach to the perimeter of an outer mesa by jumping down one level, possibly after several reflections from the step. Hops up onto higher terraces are not allowed; hops down to lower terraces are allowed with probability $(1-k)$.

When the meandering atom attaches to a mesa, it explores the perimeter for some time, searching for a highly coordinated site, and comes to rest when it finds a local maximum in bond number. This perimeter search procedure is required to keep the mesas compact as the simulation proceeds. If the wandering atom were to stick where it first hit a mesa, the mesas would develop a highly ramified, fractal shape, as in diffusion-limited aggregation. In computing the local coordination of a perimeter

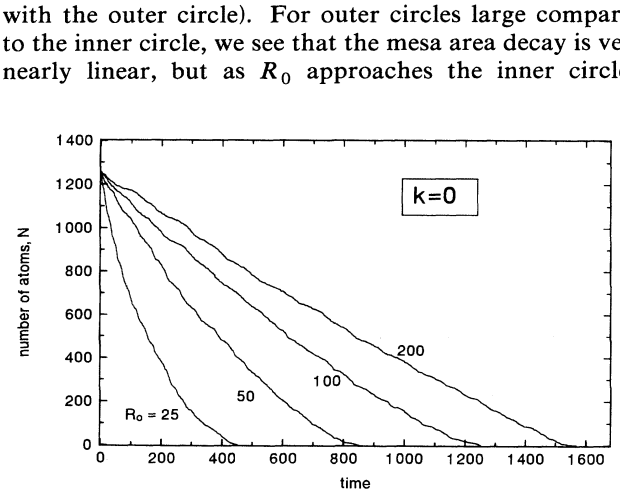

FIG. 2. Decay of an island of radius 20 with outer absorbing circles of reflection coefficient $k = 0$.

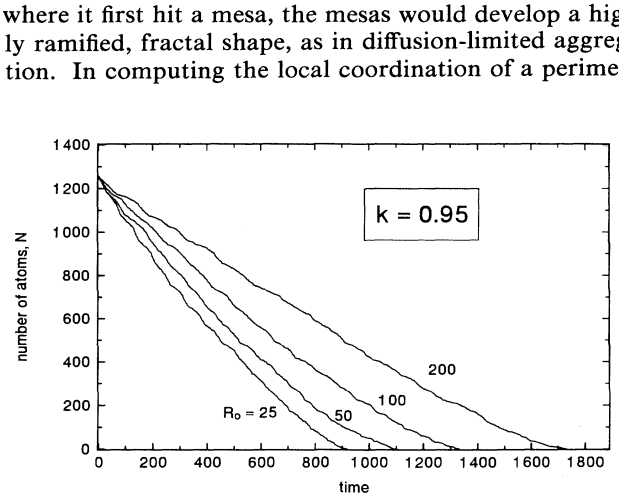

FIG. 3. Decay of an island with outer absorbing circles of reflection coefficient $k = 0.95$.

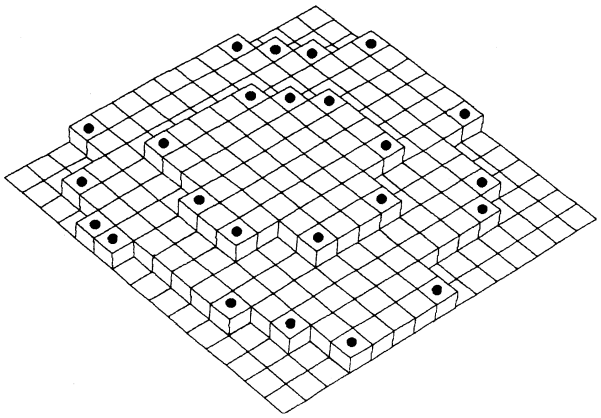

FIG. 4. Two stacked mesas in the cubic lattice solid-on-solid model. Active sites are marked with a dot.

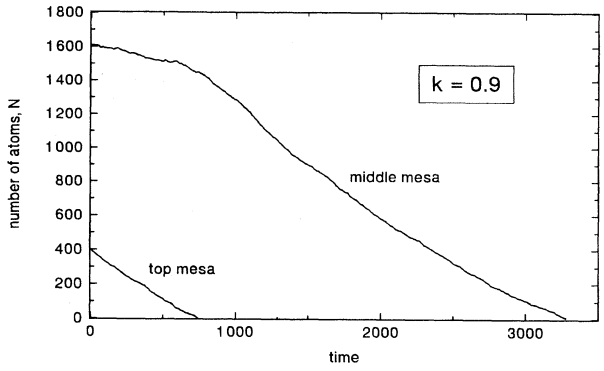

FIG. 5. Decay of the top and middle mesas in a three-mesa system of starting sizes 400, 1600, and 6400 atoms. The reflection coefficient $k=0.9$.

atom, we weight first- and second-nearest-neighbor bonds 3 to 1 (approximately the weight in a van der Waals solid). In searching for a final resting place along the perimeter, the atom random walks for up to 50 steps (an arbitrary number) and is allowed to temporarily reduce its second-nearest-neighbor count by one in order to move around corners. If the atom has not found a local bond number maximum after 50 steps, as in the case of a atom exploring the edge of square mesa, the atom stops.

When the walking atom finally comes to rest, the time is advanced by $\Delta t = 1/B$ where B is the total number of active sites in the system of mesas. The list of active sites is then updated, and a new walker is chosen at random from the updated list. Maintaining the list of active sites requires some ingenuity, since old active sites disappear (either evaporate or are covered by new atoms) and new ones appear as the simulation proceeds.

In this cubic lattice simulation, as in the simpler continuum-latice model above, we assume a constant probability per unit time that an active site will detach. Hence, the mean time between detachment events is inversely proportional to the number of active sites. Note that, in this lattice model, we do not need to assume that the number of kink sites is proportional to the mesa circumference.

One might argue that corner atoms should detach more often than kink atoms since corners have only one in-plane second-nearest neighbor, while kinks have two. However, for reasons of simplicity, we make no such distinction. We note that for the (111) face of an fcc lattice, corner and kink sites have very similar local coordinations, each with three nearest neighbors in-plane. Occasionally, an active site with a single in-plane nearest neighbor is produced. This occurs when one of two adjacent kink sites detaches, leaving behind a ledge adatom (see the lower left of the bottom mesa of Fig. 4). Our simulation makes no distinction between such ledge adatoms and other active sites, although it would be more realistic to allow ledge adatoms to explore the mesa perimeter, seeking a kink site. We believe that because such ledge active sites are rare, their occurrence does not significantly affect our results.

This cubic lattice model produces results which are nearly identical to the results of the simpler lattice-continuum model. The area of a single isolated mesa decays nearly linearly with time if it is on top of a larger mesa with a radius at least twice the starting radius of the smaller top mesa. As before, this result is rather insensitive to value of the reflection coefficient k, at least for $k<0.95$.

Our lattice model produces interesting behavior for a series of a stacked mesas. Figure 5 shows area versus time for the top two mesas of a three-mesa stack with beginning sizes of 400, 1600, and 6400 atoms. The bottom mesa (not shown in the figure) is surrounded by an absorbing circle of radius 1.5 times the radius of the bottom mesa. The reflection coefficient $k=0.90$. While the top mesa decays linearly, the middle mesa decays slowly at first and then more rapidly when the top one has disappeared. This is because the middle mesa is at first fed by the top one. This is precisely the behavior that has been observed experimentally for stacked mesas on (111) Au.[2,8]

In summary, we have shown, by Monte Carlo simulation, that the linear decay of monolayer islands on metal surfaces may arise from a competition among the rate of emission of adatoms by kink sites, the rate of absorption by an outer ledge, and the rate of reattachment to the home mesa. Linear decay is found when the distance to the outer absorbing ledge is more than 2 or 3 times the starting radius of the mesa, and it is rather insensitive to variations in the probability of reflection from the outer ledge.

The authors acknowledge useful conversations with R. B. Phillips, D. R. Peale, and B. H. Cooper. This work was supported in part by the National Science Foundation through Grant No. DMR-8857364 and through REU Site Grant No. PHY-9200029.

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