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# Step-edge versus interior barriers to atom incorporation at lattice steps

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Observations of the spatial distribution of individual atoms over close-packed (111) clusters of the fcc metals platinum as well as iridium reveal that atoms preferentially populate the inner region. The inner region is separated by an energy barrier from the step edge, leaving empty of adatoms a ring approximately three nearest-neighbor distances wide. The effect of such an interior energy barrier upon the lifetime to atom incorporation into steps is explored for one- as well as two-dimensional clusters. Interior barriers are found to increase the lifetime to incorporation much more than the conventional step-edge barrier, and may significantly affect the morphology of growing surfaces.

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## I. INTRODUCTION

For some time now it has been recognized that a potential barrier at the edge of a growing cluster will have important effects on the kinetics at which atoms deposited on the cluster incorporate into the step, and therefore also on the morphology of the surface that develops.[1] What so far has generally not been appreciated is that there may be significant energy barriers inhibiting the motion of atoms between different regions of a surface cluster, and that these interior barriers have important effects on the kinetics of adatom incorporation. Here we first sketch the evidence for interior barriers on clusters, and then examine how they affect the kinetics of atom motion into the cluster step.

## II. INTERIOR BARRIERS ON CLUSTERS

The presence of energetically distinct regions on a cluster was first discovered on the close-packed (111) plane of platinum, an fcc metal.[2] When a platinum atom is deposited close to the center of a one-atom high cluster on the Pt(111) plane, and is then observed in a field ion microscope after diffusing over the cluster, the atom is found to generally stay in the inner region. As is apparent in Fig. 1, the inner region is separated from the step edge by an empty zone, a ring, roughly three nearest-neighbor distances $l$ wide, in which atoms are not found. Mapping the locations at which a Pt atom is observed in the field-ion microscope has clearly revealed the presence of such an empty zone for clusters with a diameter as small as $8l$, but also on medium-sized clusters,[2,3] with a diameter five times as big. The physical effects responsible for this distribution are not clearly understood, although it has been speculated that strains at the cluster edge may be involved.[2] The energy landscape facing a Pt atom on a (111) cluster has, however, been explored in a variety of atomic observations,[4] and has been approximated by the potential diagram in Fig. 2. Most important is the fact that the inner cluster region is separated from the empty zone around it by a barrier of height $E_{B_1} \sim 0.33$ eV, significantly higher than the barrier to surface motion of Pt atoms on Pt(111), $E_D = 0.26$ eV.[5,6] The presence of an interior barrier, limiting transfer of atoms from the center to the outer cluster regions on Pt(111), is not unique to individual Pt atoms. Clusters of platinum, made up of two to seven atoms, have also been observed localized in the central region of the Pt(111) plane by an interior energy barrier appreciably higher than that for single Pt atoms, and also higher than the barrier to cluster diffusion.[7]

Similar behavior is observed for Ir atoms diffusing on Ir clusters on the Ir(111) plane. As is clear from Fig. 3(a), showing the locations of an Ir atom on a medium-sized cluster $19l$ across, atoms are concentrated in the central region, surrounded by an empty zone $\sim 3l$ wide. This is separated from the inner region by a barrier $>0.3$ eV high;[8] for comparison, atomic diffusion occurs over an energy barrier $E_D = 0.289$ eV.[5,9] The same sort of distribution is found on (111) planes half again as large.[10] When the diameter of the cluster is reduced to $7l$, as in Fig. 3(b), the width of the empty zone stays roughly constant, so that the atom is confined to a smaller patch in the center. We expect that as the cluster size is further reduced to twice the width of the empty zone or less, the cluster surface should become more uniform. That is in fact what happens: in Fig. 3(c), the Ir atoms are found at almost all sites on an $Ir_{37}$ cluster, and not only in the center; there are no interior barriers.

Not all metal clusters have an empty zone. The atom distribution has also been examined on a densely packed surface of a bcc metal—W(110). As is clear from the map in Fig. 4 of sites occupied by a tungsten atom diffusing on W(110) at a temperature $T = 340$ K, the entire cluster surface out to the edge of the plane is accessible to the atoms. There is *no* evidence for an empty zone around the interior region, or of any additional energy barriers to the movement of atoms from one part of the cluster surface to another.

Interior barriers to atom transfer between different cluster regions have been definitely identified for two fcc(111) surfaces, for the platinum family metals platinum and iridium, but they may occur with other fcc metals as well. In the next paragraphs, we show that when such interior barriers are present on a cluster, they can have significant effects on the kinetics at which atoms incorporate into lattice steps.

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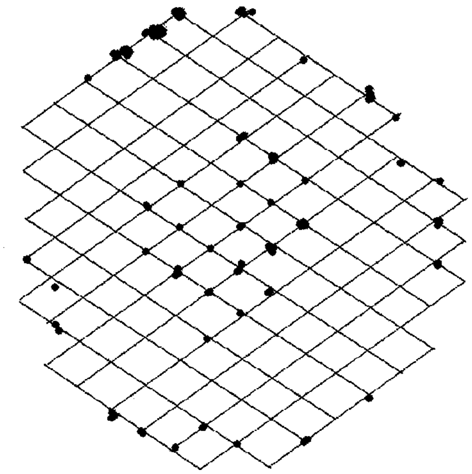

FIG. 1. Distribution of Pt atoms over a Pt(111) cluster, plotted on a grid of fcc sites. Cluster diameter: 11 nearest-neighbor distances *l*. Atom locations were determined after equilibration at 97 K. On heating to ~130 K, atoms escape from the interior and populate step-edge sites, leaving free an empty zone $3-4l$ wide.

## III. LIFETIMES TO ATOM INCORPORATION

In exploring the role of interior barriers to atom incorporation, we focus on model potentials that reveal the effectiveness of different structural features in affecting the lifetime of atoms on a cluster of fixed size. We first concentrate on one-dimensional (1D) clusters, for which it is simple to arrive at quantitative relationships that afford immediate insights into the kinetics of atom incorporation.

### A. One-dimensional models

Consider an atom jumping along a line of binding sites forming a 1D cluster. For an atom located at site *i*, jumps to the nearest-neighbor position to the right occur at the rate $\lambda_i$ and to the left at the rate $\mu_i$. Once an atom reaches either of the step sites, at $x=-b_2-1$ and $b_2+1$, its lifetime is zero. The lifetime $\tau_i$ of an atom starting at an interior site *i* before its incorporation into the step is given by the expression usual for a birth-death process[11]

$$\tau_i = 1/(\lambda_i+\mu_i) + \lambda_i/(\lambda_i+\mu_i)\,\tau_{i+1} + \mu_i/(\lambda_i+\mu_i)\,\tau_{i-1}. \tag{1}$$

Here the first term on the right is just the time spent at site *i*, the second term gives the likelihood of a jump to the right, to $i+1$, times the lifetime from that site, and the third the likelihood of a jump to the left, times the lifetime from site $i-1$. In the potential used in Fig. 2 to represent motion on the cluster, diffusion in the cluster interior occurs over an energy barrier $E_D$; a barrier $E_{B_1}$ beyond $x=\pm b_1$ opposes escape of atoms into the empty zone.[12] At the cluster edge, at $x=\pm b_2$, an atom has to overcome a barrier $E_{B_2}$ to escape and incorporate into the step. An atom returning from the edge to the center confronts a barrier $E_R$. The jump rates corresponding to the transitions in Fig. 2 are given by the usual Arrhenius relation $j_i=\nu\exp[-E_i/kT]$; the prefactor $\nu$ for all processes is assumed equal to that in atomic diffusion. Starting at the center of the cluster, at $x=0$, we take advantage of the symmetry of the cluster to write $\tau_1=\tau_{-1}$, so that Eq. (1) gives us

$$\tau_0 = 1/(2j_D) + \tau_1. \tag{2}$$

For $\tau_1$ we have

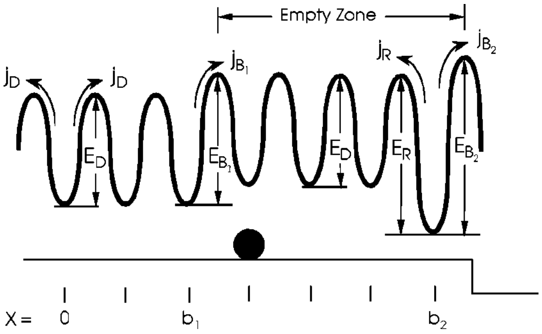

FIG. 2. Potential diagram (on top) approximating behavior of a Pt atom near the edge of a Pt(111) cluster (sketched below). For Pt, barrier heights are roughly $E_D=0.26$, $E_{B_1}\sim 0.33$, $E_{B_2}=0.36$, and $E_R=\sim 0.35$ eV (Refs. 4 and 5). The prefactor $\nu$ for all atom jumps is taken as $5.0\times10^{12}\ \mathrm{s}^{-1}$. In the empty zone, actual diffusion barriers are not well established.

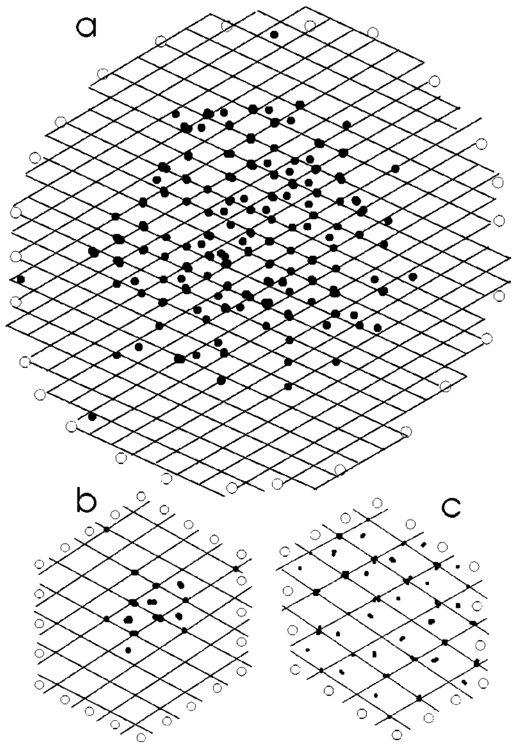

FIG. 3. Distribution of Ir atoms (in black) over Ir(111) clusters; edge atoms of (111) are shown as open circles. (a) Ir on grid for hcp sites on a cluster ~19 atoms across after equilibration at 120 K. (b) Ir distribution on $\mathrm{Ir}_{61}$, after equilibration at 120 K. (c) On $\mathrm{Ir}_{37}$, Ir atoms are distributed over the entire cluster after equilibration at 115 K.

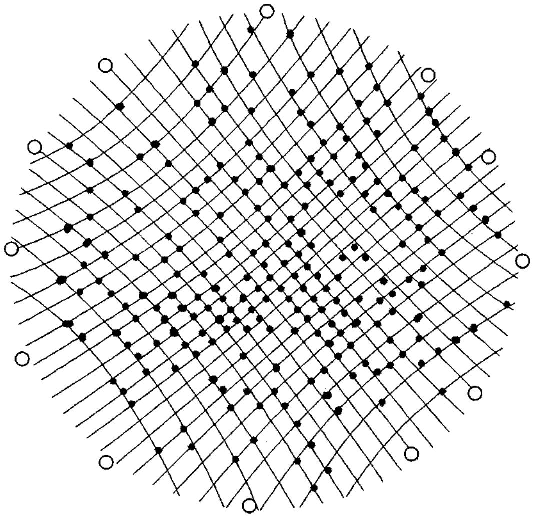

FIG. 4. Location of W atoms (in black) on W(110) plane, 25$l$ in diameter, after 15 sec equilibration at 340 K with $\langle \Delta x^2 \rangle = 4l^2$; edge atoms are indicated by open circles. W atoms spread out over the entire (110) plane, up to the step edge.

$$\tau_1 = 1/(2j_D) + \tau_2/2 + \tau_0/2. \tag{3}$$

Substituting for $\tau_0$ from Eq. (1),

$$\tau_1 = 3/(2j_D) + \tau_2. \tag{4}$$

We continue in this way to find lifetimes for all the other positions until we come to $\tau_{b_{2+1}} = 0$. After some tidying up, the lifetime to incorporation is found as

$$\tau_x = (b_1 - x)(b_1 + x)/(2j_D) + \tau_{b_1} \quad |x| < b_1, \tag{5}$$

$$\tau_x = (b_2 - |x|)[(b_2 - 2b_1 + |x| - 1)/(2j_D) + (b_1 + \tfrac{1}{2})/j_{B_1}] + \tau_{b_2} \quad b_1 \leqslant |x| < b_2, \tag{6}$$

$$\tau_{b_2} = \{1 + j_R[(b_2 - b_1 - 1)/j_D + (b_1 + \tfrac{1}{2})/j_{B_1}]\}/j_{B_2}. \tag{7}$$

We can now explore how atom lifetime depends upon different features of the energy landscape. To this end we examine the movement of atoms over the Pt potential in Fig. 2 and its variants in Fig. 5. Barrier heights are patterned on those found for Pt atoms on Pt(111), given under Fig. 2, and the prefactor for the various jump processes is taken as $5.0 \times 10^{12}$ s$^{-1}$, the value for the diffusion of Pt atoms.[5] All estimates are made at $T = 140$ K, a temperature at which jumps over step-edge barriers of the height assumed here occur on a time scale on the order of seconds.

For an atom starting at the origin on a cluster of radius $b_2$ without additional barriers or traps, the lifetime $\tau_0$ given by Eqs. (5)–(7) reduces to[13]

$$\tau_0 = (b_2 + 1)^2/(2j_D). \tag{8}$$

Given that in diffusion at 140 K the jump rate $j_D$ amounts to $2.15 \times 10^3$ s$^{-1}$, incorporation should occur rapidly; that is indeed the case as is evident in the plot of lifetime versus cluster size $b_2$ in Fig. 6. On a cluster with a total of 41 sites, that is, with $b_2 = 20$, the lifetime for an atom starting at the center is only 103 ms.

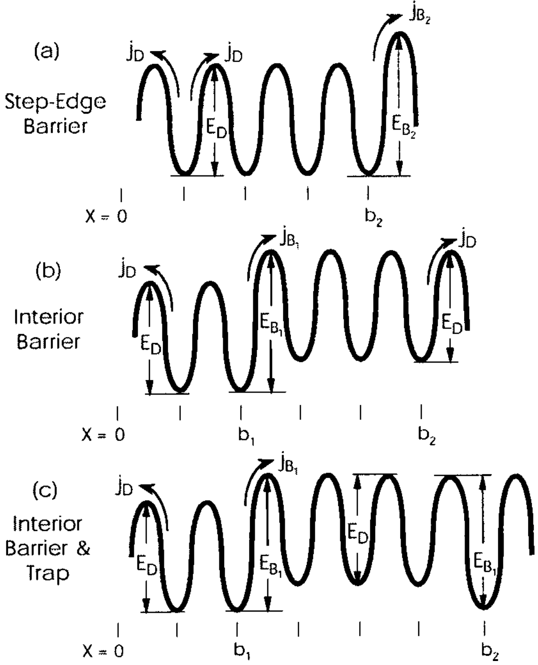

FIG. 5. Potentials for modeling atom motion on clusters. (a) Incorporation opposed by a repulsive step-edge barrier beyond $|x| = b_2$. (b) Cluster with interior barrier beyond $|x| = b_1$, normal diffusion beyond $|x| = b_1 + 1$. (c) Cluster with interior barrier beyond $|x| = b_1$, and a trap at $|x| = b_2$. Only the right half of the cluster potentials is shown.

All that is changed by the presence of a traditional step-edge barrier $E_{B_2}$, shown in Fig. 5(a). The lifetime for starts at the center is now given by

$$\tau_0 = b_2^2/(2j_D) + (b_2 + \tfrac{1}{2})/j_{b_2}. \tag{9}$$

The first term gives the time to an edge site, the second the lifetime to incorporation starting from that site. Inasmuch as the rate $j_{b_2}$ at which atoms jump over a step-edge barrier $E_{B_2} = 0.33$ eV is only 6.6 s$^{-1}$, orders-of-magnitude smaller than the rate of atom diffusion, the second term is limiting. The lifetime to incorporation on a cluster with $b_2 \leqslant 20$, in Fig. 6, has increased by more than a factor of 30 due to the presence of the barrier at the step edge.

Barriers placed not at the step edge but rather in the interior, between $|x| = b_1$ and $b_1 + 1$ as in Fig. 5(b), have an even more dramatic effect. That is clear in Fig. 7, where the lifetime to incorporation starting from the center is plotted for different interior barrier locations $b_1$, always on a cluster with radius $b_2 = 20$. Given an internal barrier at $b_1 = 16$, for example, comparable to what has been found in experiments, the lifetime is $\sim$4 times longer than for the same height barrier at the step edge of a cluster with $b_2 = 20$; this ratio is maintained roughly constant at temperatures from 120 to 180 K.

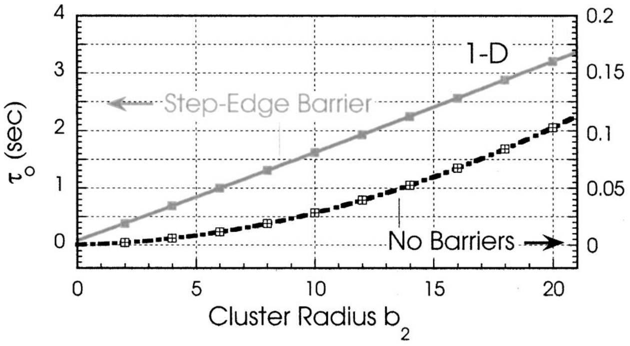

FIG. 6. Lifetime $\tau_0$ to incorporation into either step of a 1D cluster of radius $b_2$ for atoms starting at the center. Temperature $=140$ K, $E_D=0.26$ eV, and height of step-edge barrier $E_{B_2}=0.33$ eV. Results are for "no barriers" according to Eq. (8), and for "step-edge barrier" from Eq. (9).

What happens here is fairly obvious. Once an atom has overcome a step-edge barrier, it is gone from the cluster. That is not the case for an interior barrier. An atom that has escaped from the inner region of the cluster may, during its subsequent random movements, return again to the center and start all over again. This is also apparent from Eqs. (5)–(7) for the lifetime, which, for an interior barrier such as in Fig. 5(b), can be written as

$$\tau_0=b_1^2/(2j_D)+(b_1+\tfrac{1}{2})/j_{B_1}+\tau_{b_1+1}. \tag{10}$$

It is the term $\tau_{b_1+1}$ for the lifetime starting just beyond the interior barrier which, compared with Eq. (8), is new and accounts for behavior rather different from that for step-edge barriers. In the absence of any additional step-edge barrier, the lifetime $\tau_{b_1+1}$ is given by

$$\tau_{b_1+1}=(b_2-b_1)[(b_2-b_1+1)/(2j_D)+(b_1+\tfrac{1}{2})/j_{B_1}]. \tag{11}$$

The magnitude of $\tau_{b_1+1}$ is indicated in Fig. 7 by open circles, and is seen to be almost as large as the overall value of the lifetime $\tau_0$ to incorporation starting from the center. The effectiveness of interior barriers close to $x=0$ is not particularly pronounced, but increases rapidly as the barriers are moved midway between the center and step edge. There, the lifetime to incorporation is more than 5 times greater than for a barrier of the same height at the step edge. Closer to the edge, the lifetime decreases again, but even when only two spacings from the step the lifetime is more than 2.5 times that for a step-edge barrier. These trends are easy to understand. With a barrier close to the center, the atom will spend little time confined there. Most of the time the atom moves over the rest of the surface. For a barrier midway to the edge, the atom will be more uniformly distributed over the regions behind and outside the barrier.

If a potential trap is present at the outermost cluster site, as in Fig. 5(c), the lifetime of an atom on the cluster increases hardly at all: it overlaps the curve for a system with a single interior barrier in Fig. 7. An additional barrier at the step edge, however, even if small, has a significant effect. This is the situation for the Pt model potential, in which the potential at the step edge is ~0.01-eV higher than elsewhere. The lifetimes, plotted in Fig. 7 by solid diamonds, are now at least 20% higher than in the absence of a step-edge barrier. Again the time $\tau_{b_1+1}$ to incorporation starting just beyond the interior barrier (shown by open diamonds) makes the largest contribution.

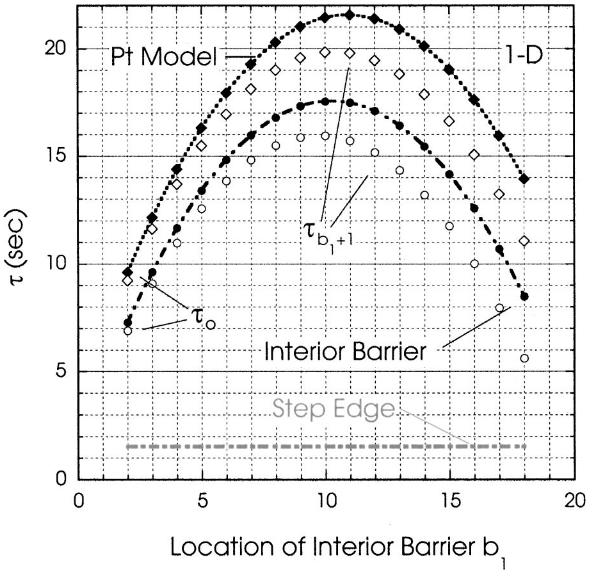

FIG. 7. Effect of interior barriers at $b_1$ on lifetime for incorporation $\tau$ into a step of a 1D cluster, radius$=20l$. Solid points indicate lifetime for atoms starting in the center, at $x=0$, according to Eqs. (10) and (11). Open circles and diamonds show lifetime $\tau_{b_1+1}$ starting at $|x|=b_1+1$, according to Eq. (11). Dashed horizontal line gives lifetime $\tau_0$ with only a step-edge barrier at $b_2=20$. All values are for $T=140$ K, and barriers are as for Pt in Fig. 2.

These estimates, for atoms starting at the cluster center, provide a good indication of how significant interior boundaries are in affecting the lifetime to incorporation. For some problems, however, such as the rate of nucleation on top of a cluster, what is of interest is the lifetime of atoms that have arrived from the vapor at random positions on the surface. Atoms landing on a cluster close to the edge are obviously going to have a shorter lifetime than atoms starting at the center; the mean lifetime of atoms randomly distributed over a cluster is therefore expected to be smaller than the estimates in Figs. 6 and 7.

This is clearly shown in Fig. 8, obtained by averaging Eqs. (5)–(7) over all starting positions. In the absence of barriers other than to diffusion, the mean lifetime may be as much as 30% lower than for an atom starting at the center. This has essentially no effect on the lifetime to incorporation over a step-edge barrier, however, which is limited by the rate of surmounting this barrier. In Fig. 9, we compare $\langle\tau\rangle$, the lifetimes for other potential models averaged over all starting positions, with lifetimes starting at the center. For interior barriers between $b_1=12$ and 2, random starts can lower lifetimes by one-fifth or more. This effect is largest for interior barriers midway between the center and the edges; when the interior barrier is near the edge, averaging has little effect, since most of the atoms start inside the barrier at $b_1$. Much the same holds true for lifetimes on the Pt model. The

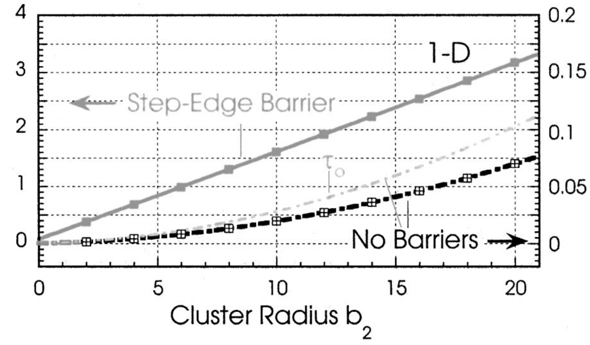

FIG. 8. Lifetimes $\langle\tau\rangle$ for atoms starting at random positions on a 1D cluster with radius $b_2$. Otherwise, conditions are as for Fig. 6. Gray curve depicts behavior of atoms starting in the center.

net result is that the curves in Fig. 9 for random starting positions are more asymmetrical, biased toward higher values of the barrier position $b_1$. Nevertheless, it is clear that for random starts also, interior barriers can significantly increase the lifetime to incorporation.

### B. Two-dimensional clusters

For more realistic estimates we have to consider two-dimensional clusters. On a circular cluster with a radius $b_2$, on which incorporation is hindered by a step-edge barrier, the lifetime $\langle\tau\rangle$ of an atom averaged over all starting points has been given as[14]

$$\langle\tau\rangle=(b_2+j_D/j_{B_2})b_2/(2j_D). \tag{12}$$

There is, however, no general relation for lifetimes on a cluster with a more realistic energy landscape. In considering more varied situations, we therefore resort to kinetic Monte Carlo simulations[15] on a roughly circular fcc(111) cluster, on which atoms are preferentially bound at fcc sites. Barriers to jumps from fcc sites are as listed above for 1D clusters. Jumps from hcp to fcc sites are assumed to occur over barriers ~85-meV lower, but with the same frequency factor $\nu=5.0\times10^{12}$.

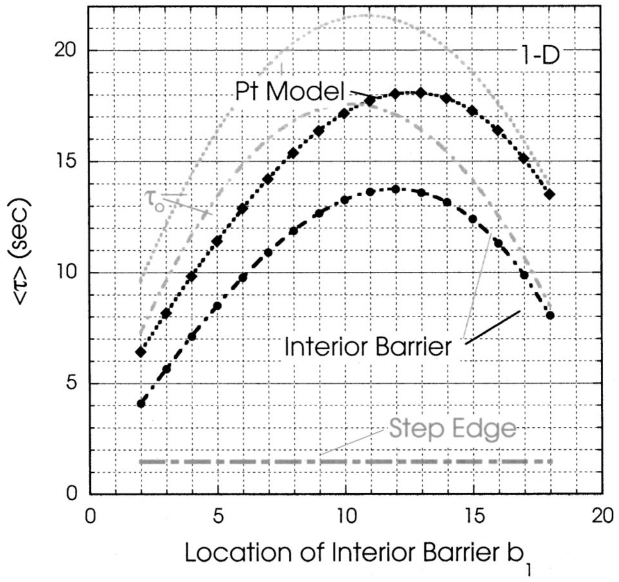

FIG. 9. Comparison of lifetimes $\langle\tau\rangle$ for atoms starting at random on a 1D cluster with radius of $20l$ (in black) with lifetimes starting in the center (in gray) from Fig. 7. Horizontal indicates $\langle\tau\rangle$ with a barrier at the step edge.

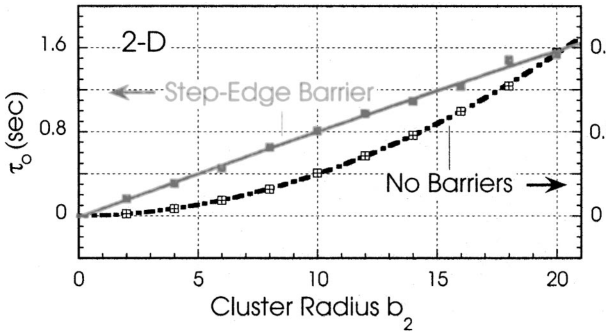

FIG. 10. Comparison of $\tau_0$ on a 2D circular cluster in the presence of a step-edge barrier and in its absence, as a function of cluster radius $b_2$. $E_{B_2}=0.33$ and $E_D=0.26$ eV; $T=140$ K. Points are from Monte Carlo simulations for atom starting at the center.

Inasmuch as the ratio of edge to interior sites is a factor of ~2 larger for roughly circular compared to 1D clusters of the same radius, we can expect shorter lifetimes. This trend is evident on comparing $\tau_0$ on a 2D cluster without any additional barriers to atom transfer, in Fig. 10, with that on a 1D cluster in Fig. 6. On a 2D cluster with a radius $b_2=20$, the lifetime for an atom starting at the center at $T=140$ K is 78 msec, compared to 103 msec on a 1D cluster of the same size. The same tendency is apparent for the lifetime to incorporation over a step-edge barrier—on the circular cluster the lifetime is roughly half that on the 1D cluster, independent of radius. In any event it is again obvious that the lifetime is dictated by the step-edge barrier and the cluster radius; the transit time generally amounts to less than 5% of the total.

That the presence of an interior barrier greatly increases the lifetime $\tau_0$ starting at the center of a 2D cluster is evident in Fig. 11. This effectiveness increases as the interior barrier is moved out from the center until a maximum is reached at $b_1\sim12$; thereafter the ratio of lifetimes for an interior as compared to a step-edge barrier diminishes again. An interior barrier located at $b_1=16$, which corresponds roughly to the width of the empty zone for Ir and Pt clusters, is still ~5 times as effective as the same barrier at a step edge, on a cluster with $b_2=20$. The introduction of an additional trap at the step edge, as in Fig. 5(c), changes the lifetime to incorporation very little. A slightly repulsive barrier at the step edge, however, has a big effect when added to an interior barrier. For locations of the interior barrier from $b_1=4-18$, the lifetime on the Pt model (shown by solid diamonds) is everywhere at least 3 times as large as with the barrier at the step edge; between $b_1=8$ and 16, this ratio is ~6 or larger.

So far we have been concentrating on atoms starting at the center of a two-dimensional cluster. When starting points are randomly distributed over the cluster, lifetimes are reduced, just as they were for 1D entities. The lifetime of an atom diffusing over a cluster without additional barriers, averaged

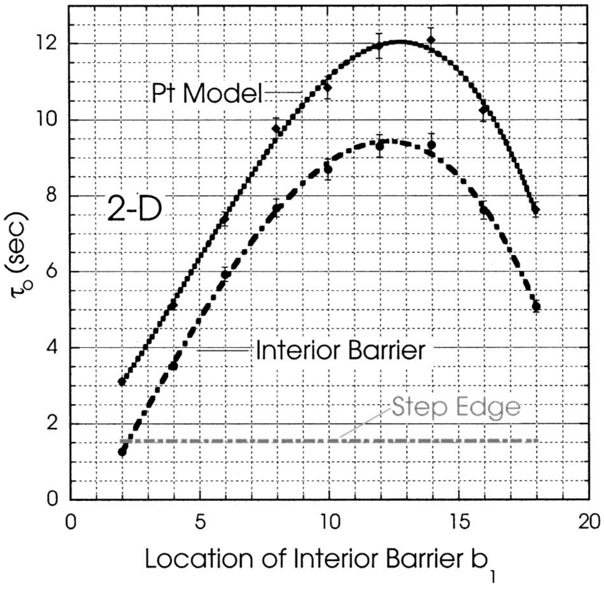

FIG. 11. Effect of interior barrier on lifetime $\tau_0$ to incorporation of atom starting from the center on a 2D cluster with radius of $20l$. $E_D = 0.26$ eV throughout. For step-edge barrier at $b_2$, $E_{B_2} = 0.33$ eV; this is also the height of the barrier $E_{B_1}$ at $b_1$ in the plot "interior barrier." Solid circles give results for interior barrier; dashed horizontal line indicates $\tau_0$ in the presence of a barrier at the step edge. Parameters for "Pt model" are as in Fig. 2. Curves are shown for guidance only. All points are from Monte Carlo simulations.

over all starting points as in Fig. 12, is lowered by 20% and more. However, the lifetime over a step-edge barrier again is hardly affected, since it is limited by the rate of jumping over the barrier at the edge, and not by the time for diffusion. For interior barriers, as well as barriers in the Pt model, the lifetime for random starts shown in Fig. 13 is cut by more than 25% compared to starts in the center for values of $b_1 < 14$, and the curves again become more asymmetric than for center starts. Nevertheless, interior barriers located between $b_1 = 5$ and 18 still increase the lifetime significantly compared to a step-edge barrier; for an interior boundary with $b_1 > 8$, this ratio is $\geqslant 2.5$.

The lifetimes to incorporation here are all uniformly smaller than on 1D clusters. However, the qualitative trends have all been presaged by the previously shown results for 1D structures, and confirm the important role of interior barriers.

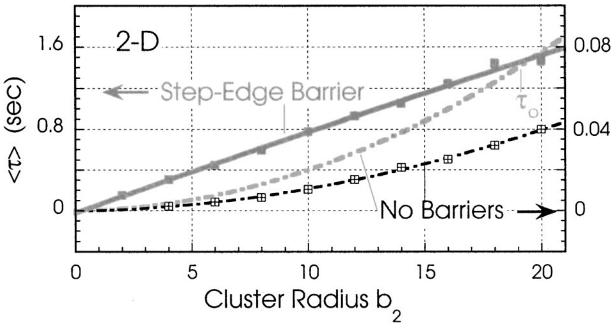

FIG. 12. Effect of starting an atom at random positions upon lifetime of the atom (in black) on a 2D cluster of radius $b_2$. Gray curve gives $\tau_0$ for atoms starting at the center, from Fig. 10.

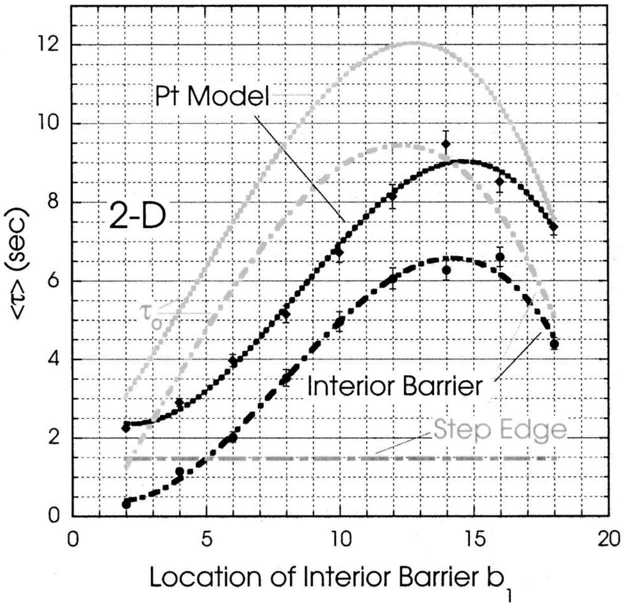

FIG. 13. Lifetimes of an atom starting at random positions on a 2D cluster of radius $b_2$ (in black). Curves in gray show $\tau_0$ for the atom starting at center, taken from Fig. 11. Horizontal gives $\langle\tau\rangle$ for step-edge barrier at $b_2 = 20$.

## IV. CONCLUSION

On clusters on the close-packed (111) plane of platinum family metals, the central region is separated from the cluster edges by a significant barrier to atom motion. Such interior barriers on a cluster are considerably more effective in inhibiting incorporation of atoms into a cluster step than barriers at the step edge: even atoms that have passed over the interior barrier may return to the center to start all over again. Located midway between the center and the edge, a barrier may increase the lifetime to incorporation of an atom starting at the center by as much as a factor of 5 or more compared to the lifetime over a step-edge barrier of the same height on a circular island. Adding a trap site at the edge has only little effect on the lifetime. However, an additional barrier at the step edge further enhances the potency of the interior potential; for an interior barrier roughly halfway between the center and the edge this may increase the lifetime more than 7 times that of a simple step-edge barrier. For atoms starting at random locations on the surface, as they would in deposition from the vapor, interior barriers are not quite as effective. Nevertheless, for a barrier four spacings from the edge, the lifetime is still more than 4 times that over a barrier at the step edge. This increase in the lifetime to atom incorporation will tend to have the effect of increasing the probability of nucleating 3D structures on a cluster. However, on small clusters (with a diameter $\leqslant 6l$) there does not appear to be any interior barrier. For small clusters, incorporation should therefore proceed more easily, just over a step-edge barrier.

Two important questions still need to be addressed. How widespread are barriers in the interior regions of clusters? So far, they have been found on two fcc surfaces only. It would be important to establish if such barriers are a general phenomenon on other fcc crystals as well. Above and beyond that, it is not obvious how the presence of an empty zone will affect nucleation of small clusters. The potential energy of an atom in the empty zone is higher than in the central region; atoms will therefore favor the central region, increasing the concentration and therefore also the rate of nucleation there. The extent to which trap sites are at the edge enter is not obvious, however. More detailed exploration of atomic behavior on clusters will clearly be desirable.

## ACKNOWLEDGMENTS

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