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Studying Transient Mobility and Energy Loss Using Scanning Tunneling Microscopy

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STUDYING TRANSIENT MOBILITY AND ENERGY LOSS USING SCANNING TUNNELING MICROSCOPY

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Abstract

We show how scanning tunneling microscopy can be used to determine aspects of transient mobility in the adsorption process, in chemical reactions, and energy transfer processes at surfaces. For adsorption from the gas phase both the mean accommodation length and the promptness of energy loss can be elucidated using real space imaging.

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I. Introduction

The processes by which adsorbates move across surfaces are important in such diverse areas as catalysis, film growth, semiconductor device fabrication, surface processing, wetting, corrosion, and etching [1–4]. This importance is largely due to the special and often dominant chemical roles played by special surface sites such as steps and defects [1,2]. It is motion to and reaction at these sites which are thought to determine many surface reaction rates [1,2]. While many measurements have been made of surface diffusion [5–8], the motion due to adsorbate momentum parallel to the surface upon adsorption or due to exothermic surface processes has received much less attention [9–14]. Only a handful of measurements have been made, and the results of these are in apparent conflict. This is due in part to the difficulty in knowing the starting positions: the initial point of impact of an adsorbate, or the initial reactant positions in the case of exothermic surface reactions. The advent of scanning tunneling microscopy has enabled the study of this transient mobility on large terraces. Here we show how the adsorbate distributions can be used to determine the mean accommodation length and other aspects of the energy loss. This analysis is applicable to adsorption and reaction phenomena where there is a well defined initial energy.

In one of the few experimental measurements made, for adsorption of Xe on Pt{111} at 4K, we have depended upon terrace widths to set a lower limit of several hundred Ångstroms for the transient mobility [9]. At low coverage essentially all Xe atoms are found by scanning tunneling microscopy (STM) to be at step edges, with only a very small fraction on terraces [9]. The incident atoms had a well defined direction in the laboratory frame, impacting 60° from normal incidence, and at random sites on the Pt{111} terraces. By considering step edges as boundaries for the incident Xe atoms after impact, we inferred an average length of travel (accommodation length) of at least half the terrace width, consistent with finding all Xe atoms at step edges [15]. Tully and coworkers had predicted such long parallel motion for rare gases in the adsorption process [10].

Wang and Ehrlich have used field ion microscopy to show that refractory metal atoms impacting an Ir{111} field ion microscope (FIM) tip at incident atom temperatures up to 3000K, and angles of incidence of 45° relative to the FIM tip terrace normal, stuck at point of impact so long as the FIM tip temperature was lower than that required for thermally activated diffusion [11]. This determination was made on the basis of finding an essentially equal number of adatoms in the fcc versus the energetically favorable hcp sites so long as low FIM tip temperatures were maintained. At higher FIM tip temperatures, the energetically favorable sites were more highly populated. It would, in fact, be difficult in this experiment to distinguish between zero transient mobility and "prompt" energy loss in which the adatoms travel across the surface, but come to rest suddenly thus equally populating both fcc and hcp sites. Particularly if the terrace walls reflect atoms transiting the surface, the experimental results would be the same as described above. With a detailed knowledge of the behavior of these atoms at step edges, however, one is apparently able to eliminate this latter possibility [12]. Wang and Ehrlich's conclusions are supported by molecular dynamics calculations by Sanders and DePristo [13].

For homoepitaxy and heteroepitaxy of other metals, long accommodation lengths have been inferred from the persistence of reflection high energy electron diffraction (RHEED) oscillations in low temperature layer by layer growth [14]. Low temperature in this case refers to being lower than the temperature at which thermally activated diffusion is substantial enough to affect significantly the positions of the surface atoms. Persistent RHEED oscillations were found for Cu and Fe on Cu(100) and for Ag, Cu, Fe, and Mn on Ag(100) [14]. These oscillations were interpreted in terms of quasi–layer–by–layer growth in which the near completion of lower layers is accomplished by transient mobility of the adsorbing metal atoms. The interpretation of these diffraction oscillations as layer by layer growth is not straightforward, however. Evans has proposed an alternative explanation to the RHEED oscillations in which there is a very short range (1–2 atomic sites) transient mobility along three–dimensional surface structures built up in the early stages of growth [16]. The so–called funnelling mechanism and other similar short–range atomic rearrangements have been shown to have the effect of smoothing surface sufficiently to give oscillations in the RHEED intensities [16]. Damped oscillations have been observed in Spot Profile Analysis of Low Energy Electron Diffraction (SPA–LEED) measurements of the low temperature growth of Pt on

Pd(100) [17]. In more recent work, Egelhoff and coworkers have found that low temperature growth of Fe, Cu, and Co overlayers on Cu(100) give LEED spot profiles consistent with island separations of $\sim$10 atoms [18]. Such regions of bare terrace would require transient mobilities of *ca.* this separation distance. The discrepancies between these sets of experimental and theoretical results have not yet been resolved.

Transient mobility may also play an important role in the thermally activated diffusion of surface adsorbates. Once an adsorbate obtains sufficient energy to overcome the barrier to diffusion, only loss of kinetic energy will halt the lateral motion of the adsorbate. Indeed, Ganz *et al.* have observed that only half of the observed diffusional motions of Pb atoms in substitutional sites on Ge(111) are to nearest neighbor sites [19]. The remainder are so–called "long jumps" in which the Pb atoms hop further than one site. These long jumps have been known for some time from FIM measurements of metal atoms on metal surfaces [7,8]. Doren and coworkers have predicted substantial contributions to the overall diffusion rates of CO on Ni{111} due to long jumps [20].

In this paper we assess the possibility of measuring not only the mean accommodation lengths, but aspects of the energy loss as well, from the real space distributions of adsorbates found on surfaces after adsorption or other processes which lead to surface mobility. The interpretation of these "post–mortem" measurements of dynamics depend upon the adsorbate–surface combination fulfilling a number of requirements as described below. This technique is shown to be applicable to adsorption, reaction, and the purposeful mechanical rearrangement of adsorbates. The goal of this work is to show under what circumstances and how we can extract mean accommodation lengths and further elucidate the processes by which adsorbate kinetic energy is lost. This work is motivated by the paucity of experimental data in this area, the apparent conflict between the results of the existing data, and the ability of the STM to determine the locations of individual adsorbates for a wide variety of adsorbate/substrate combinations.

II. Calculations

We consider the case of atoms or molecules with intermediate accommodation lengths, greater than zero, but less than terrace widths obtainable by standard surface preparations (300–3000Å). Systems that appear to fit this description are CO adsorption on Pt{111} at low temperature [21], and Xe adsorption on Ni{110} at low temperature [9,22]. We have performed one–dimensional Monte Carlo simulations in order to assess the feasibility and the number of measurements required to determine energy losses and mean accommodation lengths. We have in each case assumed an energy loss probability distribution per sampled lattice site as the adsorbate transits the surface after trapping upon impact. The interesting limits are large sudden energy loss as opposed to gradual energy loss. We show that with a reasonable number of experimental measurements, we can differentiate between these limits. We also show a straightforward method for measuring the mean accommodation lengths that is independent of the energy loss mechanism.

In our calculations, we assume that atoms impact the surface from the gas phase at random sites on 100 atom wide terraces of a solid surface. Each adatom has an initial energy of E_i associated with its momentum *parallel* to the surface after impact. Each incident atom travels in one dimension towards the upward riser of the next step edge. The adatom continues to travel along the terrace until it loses all of its initial energy either due to interactions with the surface atoms or because it hits the step edge, which acts as a perfect sink for atoms and energy. We do these calculations in the dilute limit in which there are no adatom–adatom interactions, a situation easily and routinely obtainable in STM experiments [9].

The distribution of energy loss at each site has been varied in the simulations so as to assess how best to extract information as to the promptness of the energy loss and the mean accommodation length from the distributions of adatoms found in scanning tunneling microscopy "post–mortem analyses" of the adsorption process. For each energy loss model the distribution of adatoms across the terraces is tabulated so as to compare the distributions resulting from different energy loss mechanisms. We are thus able to assess our sensitivity to the mechanism of energy loss, to ascertain which parts of these distributions contain the most information regarding the accommodation process, and to determine how many adatoms need to be measured in order to obtain this information.

Assumptions implicit in these calculations are:

1) The adatoms are deposited in the dilute limit of low coverage so that we are able to neglect the effects of adsorbate–adsorbate interactions.

2) The step edges are perfect sinks, so that any adsorbates that hit step edges stick there.

3) There are no defects on the terraces, *i.e.* all lattice sites, except the step edge, have equal probability distributions for energy loss.

4) The temperature is low enough that surface diffusion rates are negligible on the time scale of the measurement.

5) The energy loss probability distribution is independent of kinetic energy.

We note that assumptions 1–4 were essentially met in our earlier STM measurements of Xe on Pt{111} [9]. The extent to which assumption 5 is correct would need to be tested experimentally by varying incident atom kinetic energies.

The energy loss distributions used in this study were chosen so as to compare small (gradual) energy losses at each terrace site to large (prompt) but less likely energy losses per terrace site which overall lead to approximately the same average accommodation lengths. In Fig. 1, we show schematically the arrangement for adsorption that we consider here. This was the orientation in our earlier work of Xe on Pt{111} [9]. The atoms arrive from an angle off normal incidence. The azimuthal angle is chosen so that the atoms impinge with the component of their momentum which is parallel to the surface pointing towards a step riser (a step "up" as shown in the right hand side in Fig. 1) [23]. In this way, the step edge can be used as a sink for adatoms transiting the surface and as the "earliest" adsorption site on each terrace. If an adatom lands just below the step riser and has sufficient mobility to transit the surface, it will be stopped and will stick to the step edge. If an adatom lands just above the step riser, it can transit some fraction of the terrace and come to rest somewhere further along on the terrace.

III. Results and Discussions

Fig. 2 shows the results of a calculation in which 10^9 adatoms impact at random sites for a fixed accommodation length of eight sites on a 100 atom wide terrace as described in section II. As indicated in the figure, the atoms arrive from the left side with the terrace beginning with the step riser. After a denuded region, the distribution rises sharply to a steady value, A. The step edge then has an increased density of adatoms, B, because it has captured all the atoms that would have continued past it. These simple distributions can be used to demonstrate how we determine the mean accommodation length.

The mean accommodation length on terraces is given by:

$$\text{Accommodation Length} = \frac{B - A}{A} \qquad (1)$$

where A and B are as shown in Fig. 2 and described above. For any distribution where the accommodation length is substantially shorter than the terrace width, the number of adatoms per site reaches a steady value on the terrace moving toward the step riser (as indicated by A in Fig. 2). The density at the step edge, B, is higher because the step traps all those atoms that would have gone past it if the step had not been there, (B – A), in addition to those that would have come to rest at this site if the step had been just another terrace site, A. The net excess is then (B – A) and measures the number of denuded sites above the riser, n, that would have been populated by the atoms which instead ran into the step. The density A gives the density that each of these n sites in Fig. 2 would have had, so that:

$$nA = B - A \tag{2}$$

where A, B, and n are defined above. Note that n, the number of denuded sites above the step riser in Fig. 2, is equal to the mean accommodation length on terraces. The excess density at the step edge (B – A) must exactly balance the integrated reduction in density (from the density A) of the sites in what will be called the transition region above the step riser. All the atoms that landed just below the step riser, at sites 92–99, moved to and stopped at the step edge. In the absence of the step edge, the atoms impacting at sites 93–100 would have continued on and populated terrace sites in the transition region (here 1–8 or 101–108).

Eqn. (1) gives a general method for determining the mean accommodation length [24]. While Fig. 2 is useful in showing how to extract accommodation lengths, the energy loss distribution leading to the adatom positions is unrealistic. Here we address two limiting cases of the promptness of energy loss in order to see how these can be differentiated from experimental data. We note that while the "promptness" will be determined by the energy loss mechanism, the models that we assume do not depend upon a particular energy loss mechanism, nor are we able to use experimental distributions to infer an energy loss mechanism.

For modeling gradual energy loss, we choose a Gaussian distribution for the energy loss per site, peaked at $\Delta E_t=0$. The specific terrace site energy loss distribution, $P(\Delta E_t)$, we use is:

$$P(\Delta E_t) = C \exp\left\{-\left(5\Delta E_t/E_i\right)^2\right\} \tag{3}$$

where ΔE_t is the energy loss at a terrace site, E_i is the initial energy associated with momentum parallel to the surface, and C is a normalization factor ($C = \frac{10}{\sqrt{\pi}\ \mathrm{erf}(5)} \approx 5.6$). The adatom continues moving until its energy ($E = E_i - \Delta E_1 - \Delta E_2 - \ldots$) drops to or below 0. The adatom distribution we find for this energy loss distribution with 10^9 incident adatoms with fixed E_i is shown in Fig. 3. Similar distributions are found for other energy loss distributions which give small energy losses at each site sampled. The derived mean accommodation length on terraces from the distribution shown in Fig. 3 and Eqn. (1) is 8.8 lattice sites. Note that the distribution shown in Fig. 2 results from the limiting case of the gradual energy loss mechanism in which the energy loss distribution $P(\Delta E_t)$ is so sharply peaked (at $E_i/8$) that all the incident atoms have the same mean accommodation length.

Fig. 4 shows the results of a prompt but relatively improbable energy loss. As a limiting case of a prompt distribution, we take the probability of coming to rest as 10% at each terrace site sampled. In the most probable (90%) case that the atom does not come to rest, then there is no energy loss. This distribution was chosen to give a mean accommodation length on terraces of 9 lattice sites so as to facilitate a comparison found for the limiting case shown in Fig. 3. The form of the distribution in the transition region just above the step riser is clearly different than that given by the gradual energy loss mechanism in Fig. 3 above. First, there is no region that is nearly totally denuded as there is a substantial possibility of being stopped at the first site sampled. Second, moving from left to right the distribution exponentially approaches the asymptotic value B. This gives a distribution which has a negative (or at least non–positive) second derivative.

In each of the cases described above, the mean accommodation length on terraces can be determined from Eqn. (1). The accuracies derived for A and B will depend not only on statistical considerations, but also on the width of the terraces measured. As can be seen in Figs. 3 and 4, the distribution rises to a steady value as the step riser is approached from below. Note that for these measurements the terraces used must be substantially larger than the mean accommodation length. Having a mean accommodation length comparable to the terrace width can result in truncating the distribution of adatoms such that an asymptotic value is not reached for determining A, and B is similarly reduced from its "ideal" value.

We have found two general features which can be used to differentiate between adatom distributions determined by prompt vs. gradual energy loss. Adatom distributions resulting from prompt energy loss have no region that is totally denuded, and have negative curvature in the transition region. Adatom distributions resulting from gradual energy loss have a denuded region, followed by a region of positive curvature, followed by a point of inflection, followed by a region of negative curvature. For a sufficiently sharply peaked (gradual) energy loss distribution, the adatom distribution can have a very narrow transition region. Any energy loss mechanism in which the incident atom can come to rest at the site of impact will have no denuded region. This is a direct result of the definition of a "prompt" energy loss — that at any site there is a nonzero (measurably large) probability of coming to rest. This criterion ignores the effects of the breadth of the incident energy distribution as discussed with regard to diffusion, below. Also, note that the limiting case for a prompt distribution chosen above was that all or no energy was lost at each site.

In Fig. 5, we show the results of a calculation using the same energy loss distribution as used for Fig. 3, but for a smaller number of incident atoms — 80,000. By measuring the distributions of atoms in the transition region above the step riser *to determine the energy promptness of the energy loss*, at a small number of sites below the step risers *to determine B*, and at the step edges *to determine A*, the mean accommodation length can be extracted using Eqn. (1) while counting a reasonable number of adatoms, $\leq 10^4$ [25]. Thus this technique can be applied directly to the distribution of adatoms deposited on a low temperature substrate by focusing the analysis on the adatoms in the vicinity of the step edges [26].

IV. Application to Transient Surface Mobility

Processes in which adsorbates acquire mobility parallel to the substrate surface are: adsorption, chemical reaction, two–dimensional collisions between adsorbates [27], mechanical rearrangement of surface species, and diffusion. We have recently demonstrated transient mobility upon adsorption for Xe on Pt{111} [9]. As discussed above, low temperature epitaxial growth of Cu on Cu(100) [14] and of Pt on Pd(100) [17] may be interpreted as due to substantial transient mobility upon adsorption.

Behm and coworkers have demonstrated that some of the energy due to the exothermicity of a reaction can be partitioned into motion parallel to the surface [28]. This was shown using STM for the reaction products for the exothermic O_2 dissociation on Al to form two chemisorbed O atoms [28]. Some of the $\sim$7 eV reaction exothermicity is deposited in kinetic energy associated with motion parallel to the surface, and the product O atoms are found separated by tens of Ångstroms. A similar situation was found by Hamers and coworkers for the dissociative chemisorption of Si_2H_6 on Si(100) [29]. If these systems were studied at dilute coverages, so that reaction fragment pairs could be identified, the transient mobilities could be tabulated by measuring the separation of the fragment pairs. The promptness of the energy loss could once again be determined by analyzing the rise of the distribution.

Surface atoms and molecules can be set in motion by collisions, but it may be difficult to analyze such data by the above arguments because of the higher coverages required and by the adsorbate–adsorbate interactions which we have up to now neglected in our work. Surface atoms and molecules can be set in motion using the STM tip [30,31]. If the STM tip can be kept sufficiently distant from the atoms that are made to collide, then the effects of the STM tip on the collision can be made negligible. This situation has been realized experimentally by Schweizer and Eigler by setting in motion one Xe atom which was made to collide with a line of six Xe atoms that had been constructed on Ni{110} [32]. They found that the Xe atom farthest from the point of (2D) impact left the end of the adatom line and moved several lattice sites away from the line of (once again) six atoms [32].

As described in the Section I, long jumps have been observed in the diffusion of surface adsorbates using FIM [7] and STM [19]. In the case of diffusion, the initial ("incident") energy, E_i, is low and consists of a distribution of energies. This energy originates from thermal activation, so that perhaps with a better understanding of the surface–adsorbate potential energy surfaces, this energy distribution could be determined by statistical means [20] in a manner similar to that used in treating gas phase unimolecular thermal or multiphoton–induced dissociation [33]. In particular, having part of the E_i distribution near 0 for thermally activated diffusion results in even very small ΔE being sufficient to halt the motion of the adsorbate. This prevents us from being able to distinguish between prompt and gradual energy loss, because folded into the distribution of accommodation lengths is the distribution of E_i, peaked at a low value. Indeed in ref. [20], Doren and coworkers found that a mechanism resulting in gradual energy loss leads to a functional form for the accommodation length identical to that used to obtain Fig. 4 (prompt energy loss). The difference is the incident energy distributions. We conclude that for long jumps in thermally activated diffusion analyzing the shape of the distributions of accommodation lengths is not useful (with this method) in studying the promptness of the energy loss because of the low initial energies of the diffusing species. Accommodation lengths have previously been inferred from distributions in FIM measurements of diffusion, and analyzed as to the probability of long jumps, but no information on energy loss was extracted from these data [8].

For the case of adsorption, we depend upon step edges to be both traps of adsorbates and to be the "earliest" point of impact in the laboratory frame. That is, the atoms with the longest distance to travel to get to the next step edge riser are those that impinge just above the riser of the previous step edge. The incident energy is determined from the thermal and geometric configuration of the crystal and instrument. For Xe on Pt{111} [9], and in our current instruments [34], the adsorbing gas impinges with a thermal energy distribution (characterized by a temperature between room temperature and its freezing point) at a well defined angle on a low temperature crystal. By properly orienting the steps on the crystal surface in the laboratory frame, the atoms transit the surface in the direction of the step edge riser. The energy and internal state distributions of the incident particles could be further narrowed using molecular beam techniques [35].

While the incident atoms will yield a range of kinetic energies for the adsorbed (trapped) bu mobile species, this distribution is likely to be determined largely by the incident kinetic energy and angle. For the case of surface reaction or mechanical impulse, the initial kinetic energy parallel to the surface is likely to much more poorly defined. For gas phase reactions, the product kinetic energies are known to vary widely, to be broad and typically to depend critically upon the placement of the barriers in the reaction potential energy surfaces [33]. Measuring the transient mobility of the surface reaction or collision product fragments may provide a means to measure the kinetic energies released in these surface processes by comparing with direct measurements in adsorption experiments.

V. Conclusions

We have shown how it is possible from scanning tunneling microscope images to determine mean accommodation lengths and the promptness of the energy loss after adsorption or surface chemical reaction. Experiments to utilize this method are currently underway in our laboratory.

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[23] Even if the crystal used is not miscut, steps can be found with the correct orientation with respect to the incoming beam of atoms.

[24] Similarly, Eqn. (2) can be generalized by integrating the reduced density above the step riser for an arbitrary energy loss mechanism to obtain a value for "nA".

[25] This is approximately the number of diffusion events measured by Ganz *et al.* using STM, and could easily be accomplished by a skilled undergraduate (MJA).

[26] Note that even if the steps reflect incident atoms as apparently found in some FIM experiments [12], the measurements of the accommodation process described here could still be made, but the procedure would require modification as follows. The atoms above the step riser would be unaffected by this phenomenon, so that the transition region could still be used to determine the promptness of the energy loss. The step edge would have either no excess (B – A) or a reduced excess from the central terrace value (A). The remaining excess would be found just beneath the step riser on the lower terrace. By counting the excess atoms at the step edge and below the step riser on the lower terrace (as for the transition region above the step riser), the mean accommodation length could be determined.

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FIGURE CAPTIONS

Fig. 1. Schematic of atoms impinging at a well defined incident angle upon terraces of a surface which are separated by monatomic step heights. In the model used, the steps are separated by 100 clean, perfect, and identical sites at which the incident atoms can lose all or part of their kinetic energy (transient mobility).

Fig. 2. Distribution of 10^9 adatoms for adsorption randomly distributed about a single terrace 100 sites wide for a fixed accommodation length of eight sites. The step edges are at the extrema of the plot, and the atoms start with momentum parallel to the surface directed to the right. It is assumed that each atom that hits the step edge sticks and that in the dilute limit adatom–adatom interactions can be neglected. The first eight sites above the step edge riser are thus denuded. "A" denotes the average occupation once the steady state value has been reached (from left to right). "B" denotes the occupation at the step edge.

Fig. 3. Distribution of 10^9 adatoms for adsorption randomly distributed about a single terrace 100 sites wide for a gradual (Gaussian) energy loss as the adatoms transit the surface as described in the text. The transition region above the step riser is as indicated.

Fig. 4. Distribution of 10^9 adatoms for adsorption randomly distributed about a single terrace 100 sites wide for prompt energy loss in which the adatoms have a 10% chance of coming to rest at each terrace site encountered. The transition region above the step riser is as indicated.

Fig. 5. The same gradual (Gaussian) energy loss distribution as for Fig. 3, but for only 8×10^4 incident atoms.

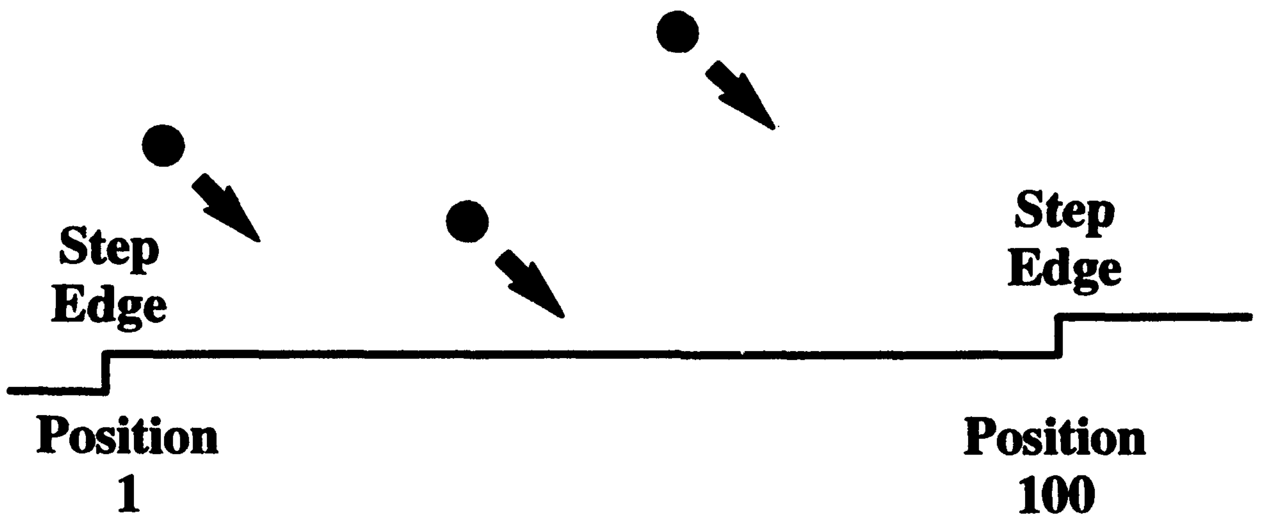

Figure 1

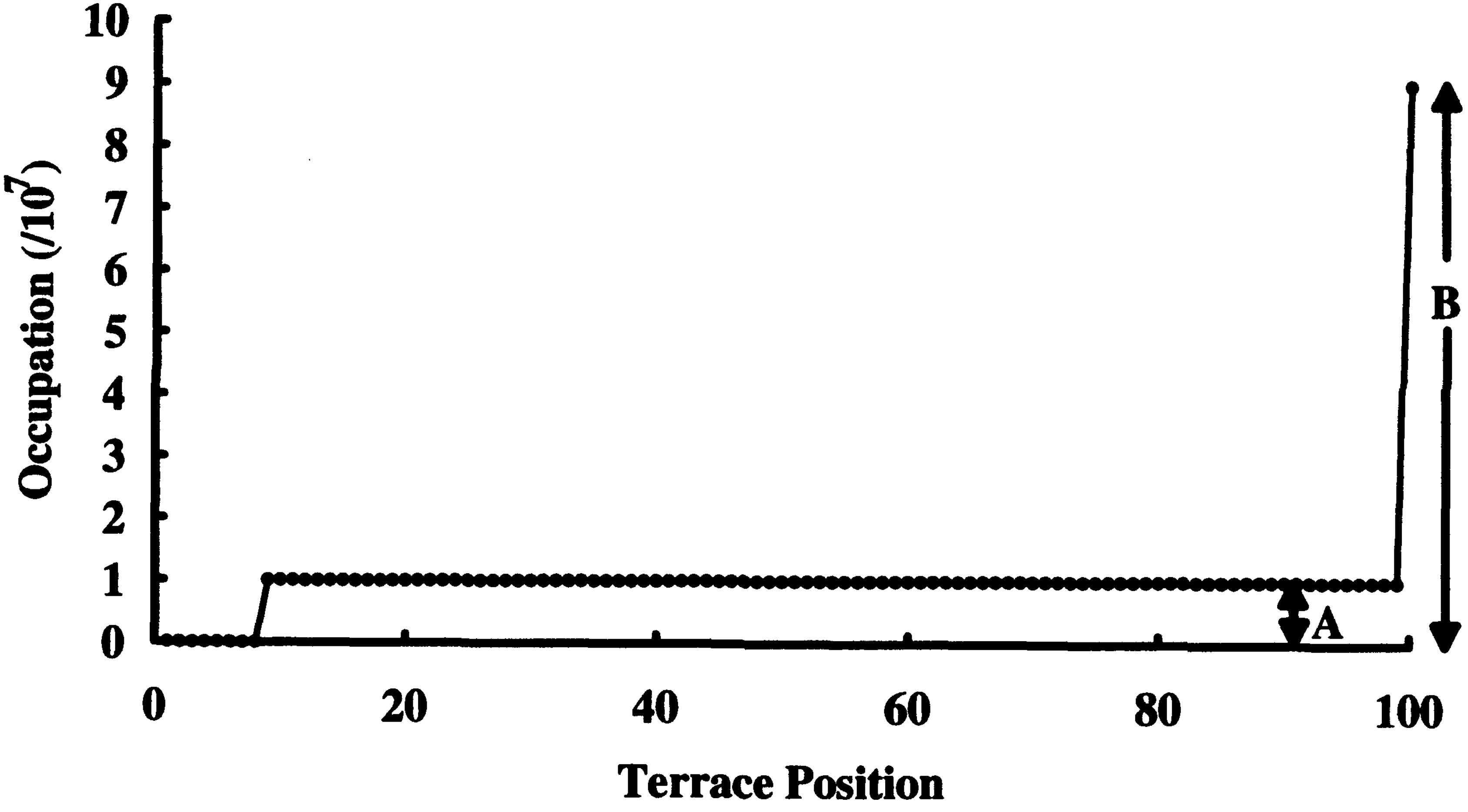

Figure 2

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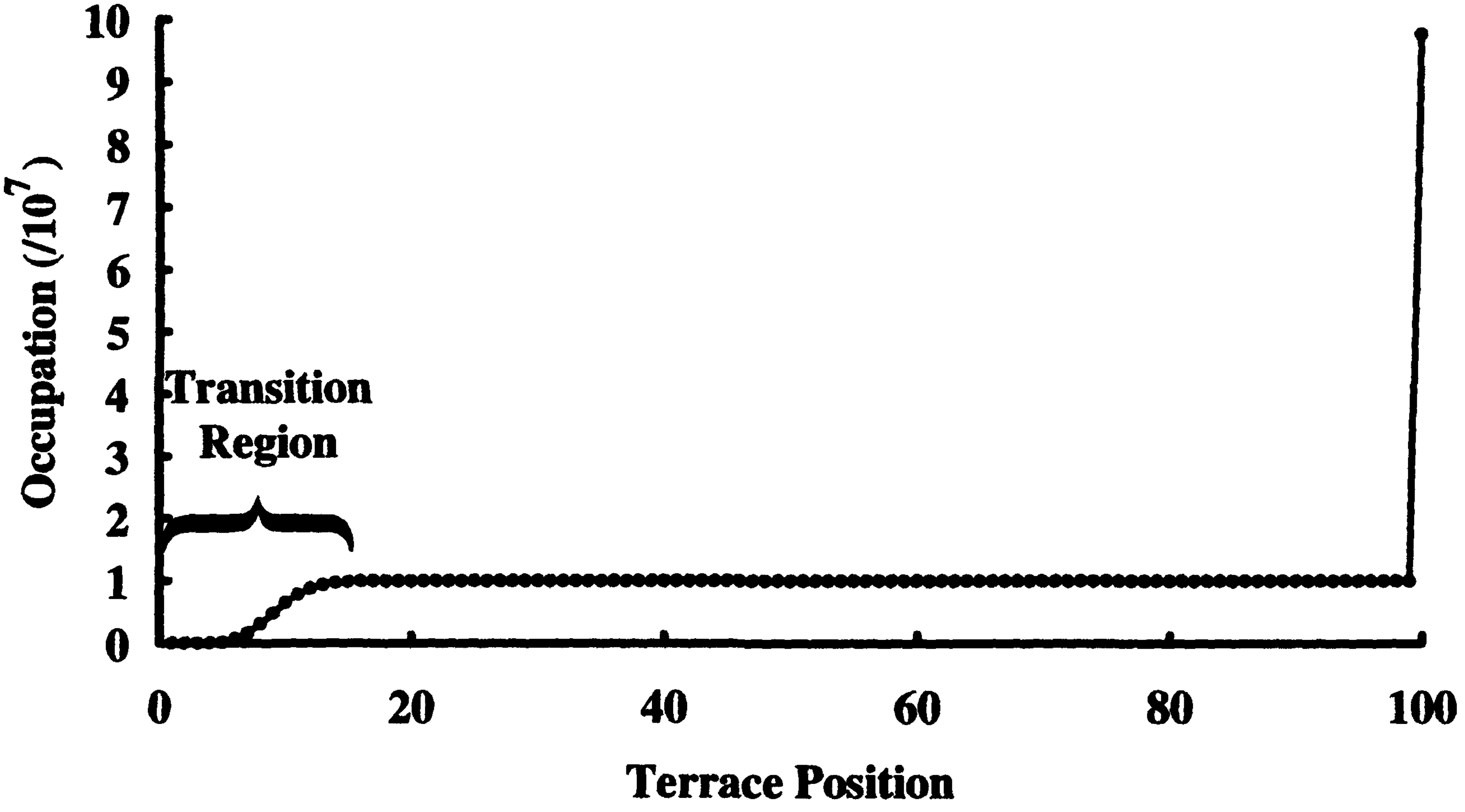
Occupation (/10^7)
10
9
8
7
6
5
4
3
2
1
0
Transition
Region
0
20
40
60
80
100
Terrace Position

Figure 3

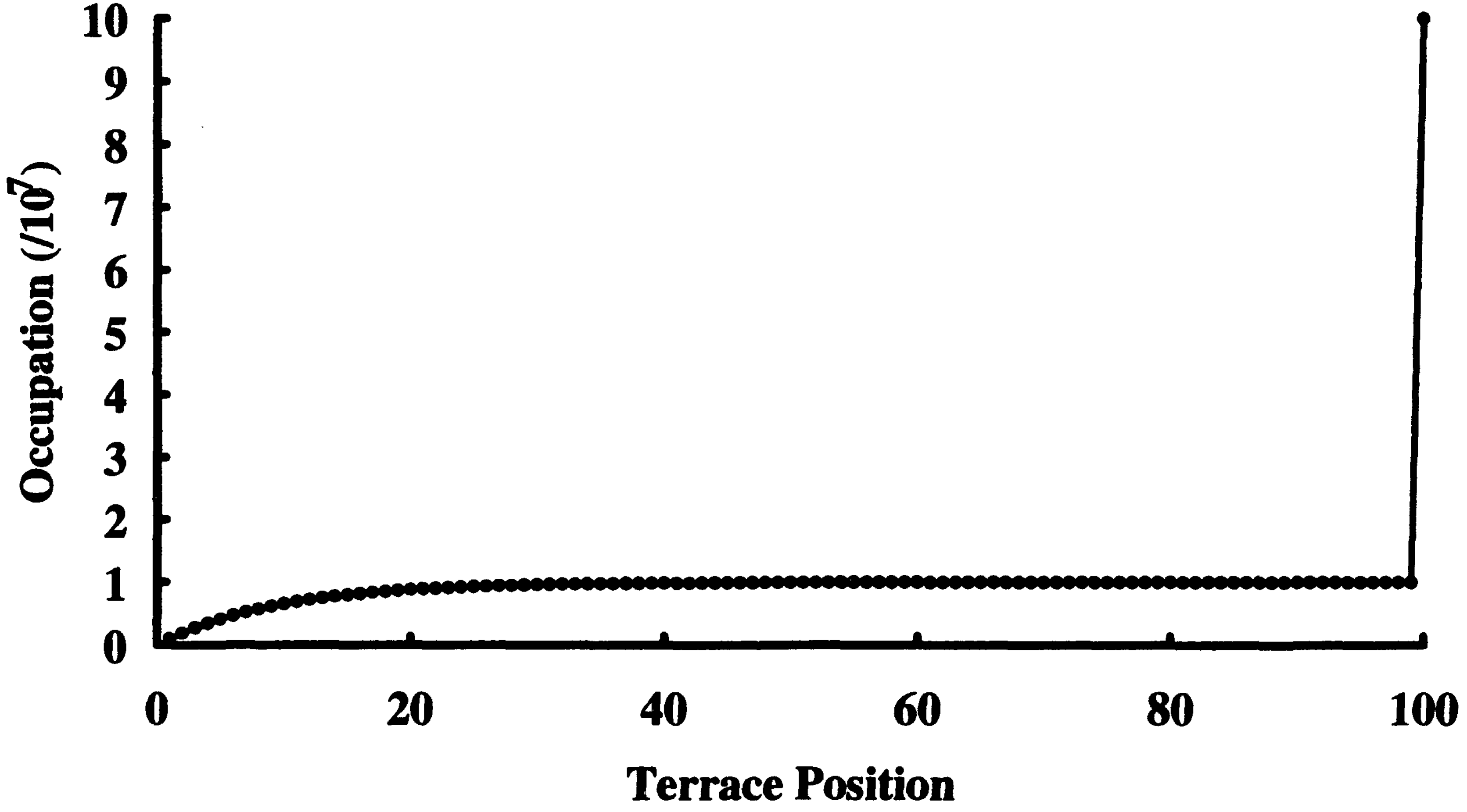
Occupation (/10^7)
10
9
8
7
6
5
4
3
2
1
0
0
20
40
60
80
100
Terrace Position

Figure 4

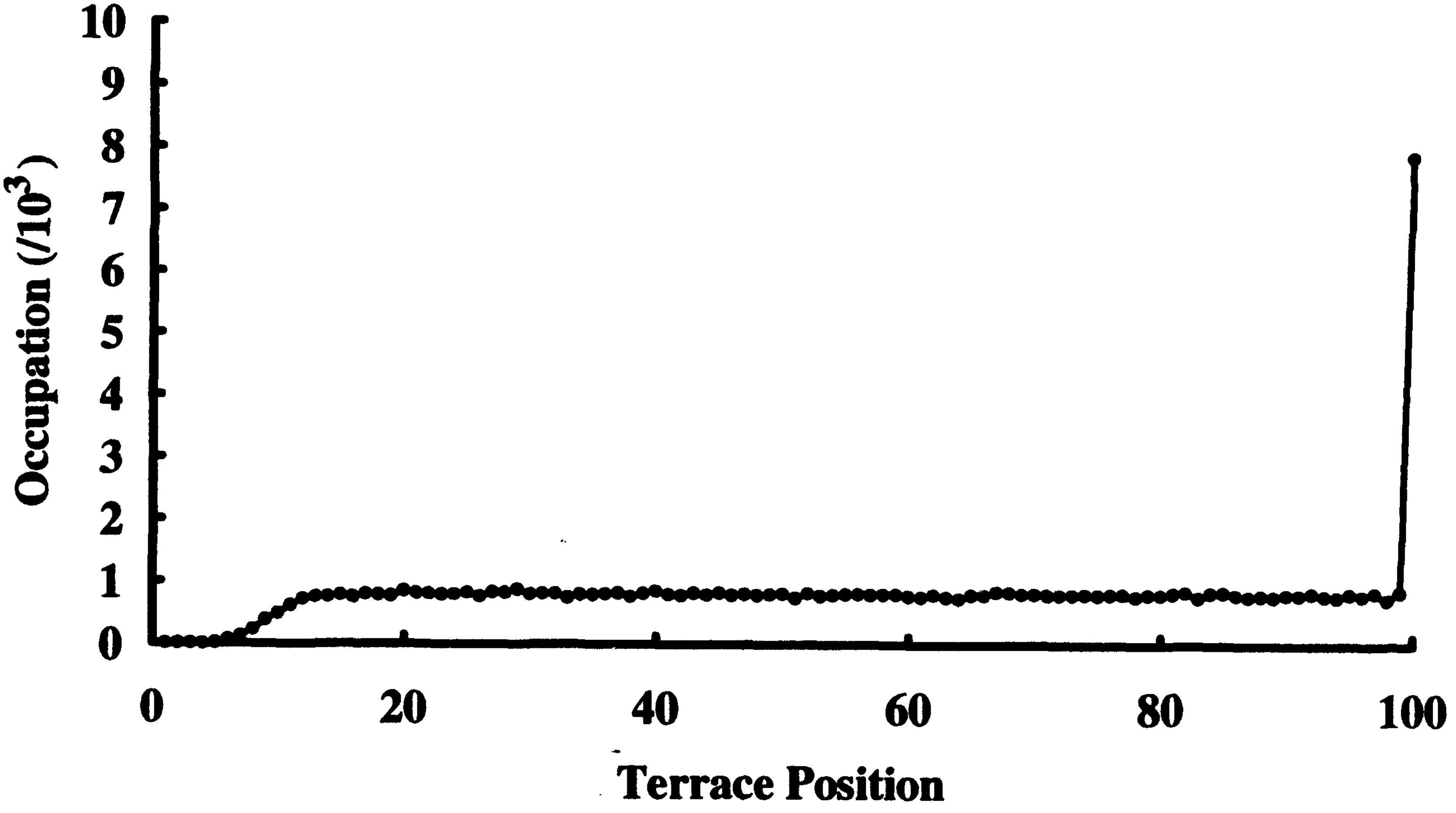

Figure 5

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