A Stochastic Approach to the Study of Atomistic Processes in the Early Stages of Thin-Film Growth

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Received: August 29, 1997; In Final Form: April 6, 1998

Much progress has been made in recent years in understanding the mechanistic details of atomistic processes in the early stages of thin-film growth. We present in this paper a "shorthand" theoretical method for assessing the statistical consequences of different assumptions on the mechanism of island growth, and we illustrate the generality of the method using several examples. The method is based on constructing transformations of the fundamental matrix of the theory of finite Markov processes.

I. Introduction

Recently, Zhang and Lagally[1] reviewed the progress made in understanding atomistic processes in the early stages of thin-film growth. Drawing on work reported in the extensive list of references cited in this review, progress in understanding the following phenomena was described: "adatom diffusion on terraces, along steps, and around island corners; nucleation and dynamics of the stable nucleus; atom attachment to and detachment from terraces and islands; and interlayer mass transport." This seminal review documented that, although an extremely complex phenomenon, "only a limited number of kinetic mechanisms form the atomistic basis for the initial stages of film growth, no matter what the growth mode or the deposition techniques." Their identification of these mechanisms provided a motivation for the study presented in this paper.

In earlier work reported in this journal,[2] we introduced a general method for calculating (and predicting) the rate constant for a kinetic process in which a coreactant, migrating on the surface of a catalyst (or molecular organizate) having clusters of stationary reaction centers, undergoes an irreversible reaction upon first encounter. The method was based on the relationship between the first moment of the underlying probability distribution function governing the process (the mean walklength $\langle n \rangle$ of the diffusing coreactant), the (zero-mode) relaxation time of the system (the reciprocal of the smallest eigenvalue λ_1 of the stochastic master equation for the problem), and a statistical (also information theoretic) expression for the entropy.

The stochastic approach developed in ref 2 can be applied directly to the class of problems described by Zhang and Lagally. What is presented in this study, however, is not a detailed elaboration of any single atomistic process using the full Markovian theory, but rather a new "shorthand" method to assess quickly the statistical consequences of different assumptions on the nature of island growth, starting from a given initial configuration. We believe the method is sufficiently simple and general that it can be applied to a wide variety of situations of interest to the experimentalist.

The plan of the paper is as follows. First, in section II, we review very briefly the relevant Markovian notation for random walks on lattices, and we develop the main theoretical results which are the basis of our "shorthand" method. Then, in the three sections following, we consider explicitly three different atomistic processes, and give examples; the examples are purposefully chosen to give the simplest numerical illustration of the method, and each can easily be generalized. Finally, in the concluding section, we summarize the approach taken and then lay the groundwork for a much more detailed illustration of the utility of the method in exploring one aspect of island formation; this application is presented in the following, companion paper.

II. Main Theoretical Results

The atomistic processes which lead to the growth of thin films will be studied in this paper using the theory of random walks on lattices.[3] Specifically, the random walks will be modeled by stationary Markov processes on a finite state space. The point on the surface (or lattice) where the diffusing adatom becomes immobilized shall be referred to as a "trap".

The number of points in the state space can often be substantially reduced by taking account of lattice symmetries,[4,5] and so in general, a point in state space will correspond to an entire symmetry class of nodes, or sites, on the lattice. A random walk on a lattice with N states can be characterized by an $N \times N$ Markov transition matrix, which we may denote by $\mathbf{P}$. The (i,j)th element of this matrix, p_{ij} is the probability, conditional on being in state i at any time, such that the next step of the random walk takes the walker to state j.

A random walk on a lattice with no traps continues forever. This property is expressed mathematically by the equation

$$\mathbf{P}\iota = \iota \tag{1}$$

where ι is a vector (here $N \times 1$) each element of which is 1. The equation says that the probability is 1 that, starting from any lattice site, the next step leads somewhere else on the lattice; in particular, the step may not lead into a trap in which the walker would disappear. Equation 1 implies that ι is an eigenvector of $\mathbf{P}$ with eigenvalue 1, from which it follows that ι is an eigenvector of $\mathbf{I} - \mathbf{P}$ with eigenvalue 0, so that $\mathbf{I} - \mathbf{P}$ is a singular matrix.

S1089-5647(97)02822-8 CCC: $15.00
Published on Web 08/29/1998

The sites corresponding to state i on a lattice are traps if the sum of the elements p_{ij}, $j = 1, ..., N$, of row i of $\mathbf{P}$ is less than 1. There is then a nonzero probability that the walk will end if it reaches state i. The most usual case is that of a *deep* trap: all the elements p_{ij} are zero, so that the walk ends with certainty whenever it reaches state i. Provided that there is a positive probability of reaching such a trap from any starting point on the lattice, any random walk will end in finite time with probability 1. In that case, one may inquire as to the average overall length of a random walk, and the average number of visits to each of the lattice states in the course of the walk, conditional on having started from some specified site.

The answers to these questions are furnished by the matrix $(\mathbf{I} - \mathbf{P})^{-1}$, which we denote as $\mathbf{\Pi}$. $\mathbf{\Pi}$ exists if and only if the expected walk length from each possible starting point is finite. In fact, π_{ij}, the (i,j)th element of $\mathbf{\Pi}$, is the expected number of visits to state j for a walk starting from state i. Although there are some interesting questions not answered by knowledge of the matrices $\mathbf{P}$ and $\mathbf{\Pi}$ alone, such as the distributions of the numbers of visits to various sites, rather than just the expected values of these numbers, we limit our attention in this paper to the numerous properties of random walks that can be derived from knowledge of these two matrices.

Specifically, we are interested in how $\mathbf{\Pi}$ changes in response to certain changes in $\mathbf{P}$. Clearly, the $\mathbf{\Pi}$ that corresponds to any given $\mathbf{P}$ can always be calculated by the inversion of an $N \times N$ matrix. But if N is large, this may be a costly operation if it has to be performed many times. We will show that, if the changes to $\mathbf{P}$ can be expressed as a matrix of rank $\nu < N$, then the corresponding changes to $\mathbf{\Pi}$ can be computed by inverting a $\nu \times \nu$ matrix instead of an $N \times N$ one.

Suppose then that we start from a lattice with a random walk characterized by $N \times N$ matrices $\mathbf{P}$ and $\mathbf{\Pi} = (\mathbf{I} - \mathbf{P})^{-1}$. Let $\mathbf{P}$ be changed to $\mathbf{P}' \equiv \mathbf{P} + \Delta\mathbf{P}$. Let $\mathbf{\Pi}' = (\mathbf{I} - \mathbf{P}')^{-1}$, and $\Delta\mathbf{\Pi} = \mathbf{\Pi}' - \mathbf{\Pi}$. Then

$$\begin{aligned}\Delta\mathbf{\Pi} &= (\mathbf{I} - \mathbf{P} - \Delta\mathbf{P})^{-1} - (\mathbf{I} - \mathbf{P})^{-1} \\ &= (\mathbf{I} - \mathbf{P})^{-1}(\mathbf{I} - \mathbf{P} - (\mathbf{I} - \mathbf{P} - \Delta\mathbf{P}))(\mathbf{I} - \mathbf{P} - \Delta\mathbf{P})^{-1} \\ &= (\mathbf{I} - \mathbf{P})^{-1}\Delta\mathbf{P}(\mathbf{I} - \mathbf{P} - \Delta\mathbf{P})^{-1}\end{aligned}$$

Now

$$\mathbf{I} - \mathbf{P} - \Delta\mathbf{P} = (\mathbf{I} - \Delta\mathbf{P}(\mathbf{I} - \mathbf{P})^{-1})(\mathbf{I} - \mathbf{P})$$

from which it follows that

$$\begin{aligned}\Delta\mathbf{\Pi} &= (\mathbf{I} - \mathbf{P})^{-1}\Delta\mathbf{P}(\mathbf{I} - \mathbf{P})^{-1}(\mathbf{I} - \Delta\mathbf{P}(\mathbf{I} - \mathbf{P})^{-1})^{-1} \\ &= \mathbf{\Pi}\Delta\mathbf{P}\mathbf{\Pi}(\mathbf{I} - \Delta\mathbf{P}\mathbf{\Pi})^{-1} \qquad (2)\end{aligned}$$

If $\Delta\mathbf{P}$ is of rank ν, say, then it is possible to find two matrices $\mathbf{A}$ and $\mathbf{B}$, of dimension $N \times \nu$, such that

$$\Delta\mathbf{P}\mathbf{\Pi} = \mathbf{A}\mathbf{B}^{\mathrm{T}} \qquad (3)$$

In the applications we consider in this paper, there are simple natural choices for A and B. Then, from eq 2,

$$\Delta\mathbf{\Pi} = \mathbf{\Pi}\mathbf{A}\mathbf{B}^{\mathrm{T}}(\mathbf{I} - \mathbf{A}\mathbf{B}^{\mathrm{T}})^{-1} \qquad (4)$$

Now

$$(\mathbf{I}_\nu - \mathbf{B}^{\mathrm{T}}\mathbf{A})\mathbf{B}^{\mathrm{T}} = \mathbf{B}^{\mathrm{T}} - \mathbf{B}^{\mathrm{T}}\mathbf{A}\mathbf{B}^{\mathrm{T}} = \mathbf{B}^{\mathrm{T}}(\mathbf{I}_N - \mathbf{A}\mathbf{B}^{\mathrm{T}})$$

whence

$$\mathbf{B}^{\mathrm{T}}(\mathbf{I}_N - \mathbf{A}\mathbf{B}^{\mathrm{T}})^{-1} = (\mathbf{I}_\nu - \mathbf{B}^{\mathrm{T}}\mathbf{A})^{-1}\mathbf{B}^{\mathrm{T}}$$

Thus from (4) we obtain

$$\Delta\mathbf{\Pi} = \mathbf{\Pi}\mathbf{A}(\mathbf{I}_\nu - \mathbf{B}^{\mathrm{T}}\mathbf{A})^{-1}\mathbf{B}^{\mathrm{T}} \qquad (5)$$

It is clear that computation of the right-hand side of eq 5 requires the inversion of a $\nu \times \nu$ matrix rather than of an $N \times N$ one.

III. Activation of a Neighboring Site

Our first application of eq 5 is very simple. We suppose that after a first diffusing adatom has been immobilized at a surface site, that that event activates the surrounding sites (i.e., the neighboring sites become possible "traps" for atoms subsequently deposited from the gas phase). In Markovian language, we suppose that some site (or state), which is not a trap for $\mathbf{P}$, is opened as a trap for $\mathbf{P}'$. Without loss of generality, let this site have index 1. Then the opening of the trap is effected by just setting the elements of the first row of $\mathbf{P}'$ equal to zero with no further changes to the matrix $\mathbf{P}$. Consequently,

$$\Delta\mathbf{P} = -\mathbf{e}_1\mathbf{P}_1 \qquad (6)$$

where $\mathbf{P}_1$ is the first row of $\mathbf{P}$, and $\mathbf{e}_1$ denotes the $N \times 1$ vector with all components zero except the first, which equals 1. In general, $\mathbf{e}_i$, $i = 1, ..., N$, will denote an $N \times 1$ vector with all components zero except the ith, which equals 1.

Now let us partition the matrix $\mathbf{\Pi}$ by columns, as follows:

$$\mathbf{\Pi} = [\boldsymbol{\pi}_1 \ldots \boldsymbol{\pi}_N]$$

so that $\boldsymbol{\pi}_i$ is the ith column of Π. Similarly, we may partition by rows:

$$\mathbf{\Pi} = \begin{bmatrix} \boldsymbol{\rho}_1 \\ \vdots \\ \boldsymbol{\rho}_N \end{bmatrix}$$

Then, given eq 6, we find that

$$\Delta\mathbf{P}\mathbf{\Pi} = -\mathbf{e}_1(p_{11}\boldsymbol{\rho}_1 + \sum_{i=1}^{N} p_{1i}\boldsymbol{\rho}_i) \qquad (7)$$

The sum which appears to run from 1 to N above will in fact have many fewer terms; this number being equal to what we may call the valency of site 1, which we denote by ν_1. We define the set $\mathbf{N}_1$ as the set of the indices of those sites which can communicate directly with site 1:

$$\mathbf{N}_1 = \{i \neq 1 \mid p_{1i} \neq 0 \text{ or } p_{i1} \neq 0\} \qquad (8)$$

$\mathbf{N}_1$ has just ν_1 members. We can rewrite eq 7 as

$$\Delta\mathbf{P}\mathbf{\Pi} = -\mathbf{e}_1(p_{11}\boldsymbol{\rho}_1 + \sum_{i\in\mathbf{N}_1} p_{1i}\boldsymbol{\rho}_i) \qquad (9)$$

Now, because $\mathbf{\Pi}$ and $\mathbf{I} - \mathbf{P}$ are inverse matrices, we have

$$(1 - p_{11})\boldsymbol{\rho}_1 - \sum_{i\in\mathbf{N}_1} p_{1i}\boldsymbol{\rho}_i = \mathbf{e}_1^{\mathrm{T}} \qquad (10)$$

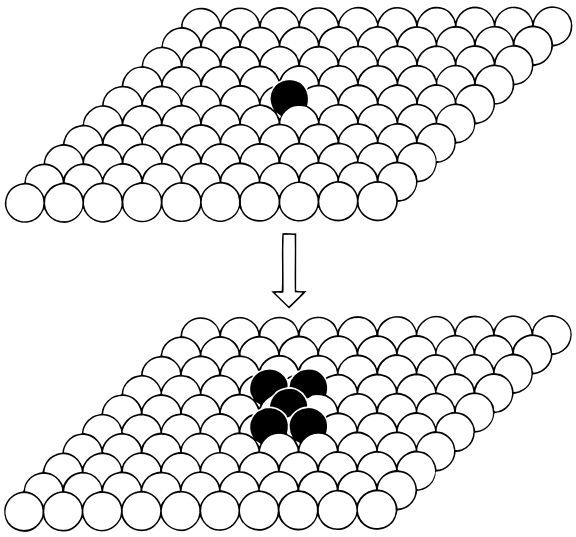

Figure 1. A sketch of the process explored in section III. The open circles designate an underlying substrate with square lattice geometry (e.g., a fcc (100) surface). Filled circles denote a site where a diffusing adatom can be immobilized (or trapped).

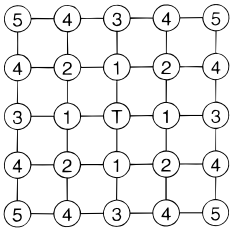

Figure 2. Site specification for a 5 × 5 square-planar lattice (see text).

Similarly, we note for later use that

$$\boldsymbol{\pi}_1(1 - p_{11}) - \sum_{i \in \mathbf{N}_1} p_{i1}\boldsymbol{\pi}_i = \mathbf{e}_1 \tag{11}$$

Using eq 10 in eq 9 yields

$$\Delta\mathbf{P}\boldsymbol{\Pi} = \mathbf{e}_1(\mathbf{e}_1{}^{\mathrm{T}} - \boldsymbol{\rho}_1) \tag{12}$$

Comparing eq 12 with eq 3, we see that we may take $\mathbf{A} = \mathbf{e}_1$ and $\mathbf{B}^{\mathrm{T}} = \mathbf{e}_1{}^{\mathrm{T}} - \boldsymbol{\rho}_1$, with both of these matrices being of rank just 1. It is immediate that $\mathbf{B}^{\mathrm{T}}\mathbf{A} = 1 - \pi_{11}$ and $(\mathbf{I} - \mathbf{B}^{\mathrm{T}}\mathbf{A})^{-1} = 1/\pi_{11}$. Further, $\boldsymbol{\Pi}\mathbf{A}$ is just the first column of $\boldsymbol{\Pi}$, namely, $\boldsymbol{\pi}_1$. Thus we have the very simple result that

$$\Delta\boldsymbol{\Pi} = \frac{1}{\pi_{11}}\boldsymbol{\pi}_1(\mathbf{e}_1{}^{\mathrm{T}} - \boldsymbol{\rho}_1) \tag{13}$$

We observe that these changes turn the first row of $\boldsymbol{\Pi}'$ into $\mathbf{e}_1{}^{\mathrm{T}}$, as we would expect for a trap at site 1: starting from that site, the walker is trapped and the walk ends in one step, so that the probability is zero of going anywhere else. In addition, because all the elements of $\boldsymbol{\Pi}$ are nonnegative, we see that, outside the first row, all the elements of $\Delta\boldsymbol{\Pi}$ are nonpositive. This simply means that opening a new trap cannot increase either the average walk length or the expected number of visits to any site.

To illustrate this case, consider the process illustrated in Figure 1 and the 5 × 5 square planar lattice depicted in Figure 2. The lattice has a centrosymmetric (deep) trap, is subject to periodic boundary conditions, and is annotated in such a way that sites bearing the same symmetry relation to the central trap are labeled the same. The matrices $\mathbf{P}$ and $\boldsymbol{\Pi}$ for the problem are

$$\mathbf{P} = \begin{bmatrix} 0 & 1/2 & 1/4 & 0 & 0 \\ 1/2 & 0 & 0 & 1/2 & 0 \\ 1/4 & 0 & 1/4 & 1/2 & 0 \\ 0 & 1/4 & 1/4 & 1/4 & 1/4 \\ 0 & 0 & 0 & 1/2 & 1/2 \end{bmatrix} \tag{14}$$

$$\boldsymbol{\Pi} = \begin{bmatrix} 4.0 & 4.0 & 4.0 & 8.0 & 4.0 \\ 4.0 & 5.6 & 4.8 & 10.4 & 5.2 \\ 4.0 & 4.8 & 6.4 & 11.2 & 5.6 \\ 4.0 & 5.2 & 5.6 & 12.8 & 6.4 \\ 4.0 & 5.2 & 5.6 & 12.8 & 8.4 \end{bmatrix} \tag{15}$$

Suppose now that we convert the four neutral sites labeled 1 in Figure 2 to deep traps. Then, from eq 13, we have

$$\Delta\boldsymbol{\Pi} = \frac{1}{\pi_{11}}\boldsymbol{\pi}_1(\mathbf{e}_1{}^{\mathrm{T}} - \boldsymbol{\rho}_1)$$

$$= 1/4 \begin{bmatrix} 4 \\ 4 \\ 4 \\ 4 \\ 4 \end{bmatrix} [-3 \ -4 \ -4 \ -8 \ -4] = -\begin{bmatrix} 3 & 4 & 4 & 8 & 4 \\ 3 & 4 & 4 & 8 & 4 \\ 3 & 4 & 4 & 8 & 4 \\ 3 & 4 & 4 & 8 & 4 \\ 3 & 4 & 4 & 8 & 4 \end{bmatrix} \tag{16}$$

Calculation shows that

$$\boldsymbol{\Pi}' = \begin{bmatrix} 1.0 & 0.0 & 0.0 & 0.0 & 0.0 \\ 1.0 & 1.6 & 0.8 & 2.4 & 1.2 \\ 1.0 & 0.8 & 2.4 & 3.2 & 1.6 \\ 1.0 & 1.2 & 1.6 & 4.8 & 2.4 \\ 1.0 & 1.2 & 1.6 & 4.8 & 2.4 \end{bmatrix}$$

For the configuration illustrated at the top of Figure 1, the average number of times that a diffusing adatom, deposited initially at site 1, will visit sites {2,3,4,5} before being immobilized irreversibly at the site *T*, is given by the sum of the elements of the first row of $\boldsymbol{\Pi}$, designated here by $\langle n \rangle_1 = 20$. The overall number of displacements of the adatom, deposited initially at any of the sites {1, .., 5}, before being immobilized at *T* is given by the sum of the $\langle n \rangle_j$, divided by the total number of nontrapping sites. Keeping in mind that there are 4 sites labeled 1, 2, 3, 5, and 8 sites labeled 4 (see Figure 2), for the above process, one calculates: $\langle n \rangle = 31.666...$.

For the configuration illustrated at the bottom of Figure 1, we use the matrix $\boldsymbol{\Pi}'$ to determine the overall number of displacements of a second diffusing adatom before immobilization; one calculates: $\langle n \rangle = 8.333...$. Thus, for the process diagrammed in Figure 1, the consequence of activating four nearest-neighbor sites following immobilization of the first adatom (at the site *T*) is a reduction by a factor of 20/8.333 in the number of displacements taken by a newly deposited adatom before the irreversible formation of an addimer.

The above example was designed to provide a concrete illustration of the theoretical method. More extensive results calculated using the full Markovian theory were reported in ref 2 for nonrandom distributions of trapping sites on hexagonal lattices. Many of the results reported in eq 2 can be recovered more easily using the approach developed here or, more

importantly, new results can be obtained on other configurations of trapping sites or on lattices of different symmetry.

IV. Deactivation of Sites

In this application, we suppose that the immobilization of a diffusing adatom at a specific site triggers the deactivation of nontrapping sites in the neighborhood of that site. In particular, all pathways, ingoing and outgoing, to the set of deactivated lattice sites are cut or "blocked", and we calculate the average distance a newly deposited adatom travels in this restricted diffusion space before encountering the initially immobilized adatom.

As in the previous section, let the site have index 1. Then we set $p_i = p_1 = 0$ for all $i = 1, ..., N$. If we stopped there, the sum of the probabilities of stepping somewhere from all sites i such that $p_{i1} \neq 0$ would now be less than 1—these sites would have become traps. To avoid this, for each i with $p_{i1} \neq 0$, we add p_{i1} to p_{ii}. This maneuver can be interpreted as stopping the walker for one step on a site i each time the walker would before blocking have stepped to site 1. Other ways of allocating the lost probability can be conceived, but this particular way is natural enough.

The matrix of changes $\Delta\mathbf{P}$ for this case of blocking can therefore by written as

$$\Delta\mathbf{P} = \sum_{i\in N_1} p_{11}(\mathbf{e}_i\mathbf{e}_1^{\mathrm{T}} - 1_i\mathbf{e}_1^{\mathrm{T}}) - \sum_{i\in N_1} p_{1i}\mathbf{e}_1\mathbf{e}_1^{\mathrm{T}} - p_{11}\mathbf{e}_1\mathbf{e}_1$$

Then we find that

$$\begin{aligned}\Delta\mathbf{P}\boldsymbol{\Pi} &= \sum_{i\in N_1} p_{i1}\mathbf{e}_i(\boldsymbol{\rho}_i - \boldsymbol{\rho}_1) - \sum_{i\in N_1} p_{1i}\mathbf{e}_1\boldsymbol{\rho}_i - p_{11}\mathbf{e}_1\boldsymbol{\rho}_1 \\ &= -\mathbf{e}_1(\mathbf{p}_{11}\boldsymbol{\rho}_1 + \sum_{i\in N_1} p_{1i}\boldsymbol{\rho}_i) + \sum_{i\in N_1}\mathbf{e}_i p_{i1}(\boldsymbol{\rho}_i - \boldsymbol{\rho}_1) \\ &= \mathbf{e}_1(\mathbf{e}_1^{\mathrm{T}} - \boldsymbol{\rho}_1) + \sum_{i\in N_1}\mathbf{e}_i p_{i1}(\boldsymbol{\rho}_i - \boldsymbol{\rho}_1) \qquad (17)\end{aligned}$$

where the last line follows from use of eq 10.

The matrices **A** and **B** of eq 3 can now be set up naturally for eq 17. In particular, we may choose for A a simple selection matrix, that is, a matrix each of whose columns is $\mathbf{e}_i$, for some $i = 1, ..., N$. We have

$$\mathbf{A} = [\mathbf{e}_1 \quad \mathbf{E}_1] \qquad (18)$$

and

$$\mathbf{B}^{\mathrm{T}} = \begin{bmatrix}\mathbf{e}_1^{\mathrm{T}} & - & \boldsymbol{\rho}_1 \\ & \mathbf{K}\mathbf{R}_1 & \end{bmatrix} \qquad (19)$$

The notation here is as follows: $\mathbf{E}_1$ is an $N \times \nu_1$ matrix of which the ν_1 columns are the $\mathbf{e}_i$, $i \in N_1$; $\mathbf{R}_1$ is a $\nu_1 \times N$ matrix of which the ith row is $\boldsymbol{\rho}_i - \boldsymbol{\rho}_1$, $i \in \mathbf{N}_1$, and $\mathbf{K}$ is a $\nu_1 \times \nu_1$ diagonal matrix with typical diagonal element p_{i1}. In order to implement eq 5, we must form the matrix

$$\mathbf{B}^{\mathrm{T}}\mathbf{A} = \begin{bmatrix}\mathbf{e}_1^{\mathrm{T}} & - & \boldsymbol{\rho}_1 \\ & \mathbf{K}\mathbf{R}_1 & \end{bmatrix}[\mathbf{e}_1 \quad \mathbf{E}_1] \qquad (20)$$

Since **A** is a selection matrix, the above matrix product is just a selection of $\nu_1 + 1$ columns of the first factor, the first, and those indexed by $\mathbf{N}_1$. For the rest of our development, it will be convenient to write out explicitly not only the first row but also the first column of this matrix, that is, the row and column corresponding to the blocked site. We may write eq 20 as

$$\mathbf{B}^{\mathrm{T}}\mathbf{A} = \begin{bmatrix}1 & - & \pi_{i1} & - & \hat{\boldsymbol{\rho}}_1 \\ & -\mathbf{c} & & & \mathbf{K}\hat{\mathbf{R}}_1\end{bmatrix}$$

where the hats on $\hat{\boldsymbol{\rho}}_1$ and $\hat{\mathbf{R}}_1$ mean that only the ν_1 columns corresponding to the indices in $\mathbf{I}_1$ are retained. In addition, **c** is a $\nu_1 \times 1$ vector with typical element $p_{i1}(\pi_{11} - \pi_{i1})$, $i \in \boldsymbol{N}_1$.

We now need to consider the inverse of the $(\nu_1 + 1) \times (\nu_1 + 1)$ matrix $\mathbf{I} - \mathbf{B}^{\mathrm{T}}\mathbf{A}$, that is, the inverse of

$$\begin{bmatrix}\pi_{11} & \hat{\boldsymbol{\rho}}_1 \\ \mathbf{c} & \mathbf{I}\nu_1 \quad -\mathbf{K}\hat{\mathbf{R}}_1\end{bmatrix} \qquad (21)$$

Although this inverse can simply be calculated directly, it is illuminating to express it in terms of the inverse of the bottom right block, which we write as

$$\mathbf{J} \equiv \mathbf{I}_{\nu_1} - \mathbf{K}\hat{\mathbf{R}}_1 \qquad (22)$$

By standard results on the inversion of partitioned matrices, the inverse of eq 21 can be expressed as

$$\begin{bmatrix} a & -a\hat{\boldsymbol{\rho}}_1\mathbf{J}^{-1} \\ -a\mathbf{J}^{-1}\mathbf{c} & \mathbf{J}^{-1} + \mathbf{a}\mathbf{J}^{-1}\mathbf{c}\hat{\boldsymbol{\rho}}_1\mathbf{J}^{-1}\end{bmatrix} \qquad (23)$$

where the scalar quantity a is given by

$$a = (\pi_{11} - \hat{\boldsymbol{\rho}}_1\mathbf{J}^{-1}\mathbf{c})^{-1} \qquad (24)$$

It turns out that $\mathbf{J}^{-1}\mathbf{c}$ can be expressed in terms of known quantities. Define the $\nu_1 \times 1$ vector $\hat{\mathbf{p}}_1$ as the vector with typical element p_{i1}, $i \in \mathbf{N}_1$. The hat once more signifies that we have selected from the first column of the matrix **P** only those elements that correspond to indices in $\mathbf{N}_1$. Then $\mathbf{J}\hat{\mathbf{p}}_1 = (1 - p_{11})\mathbf{c}$, as can be seen by straightforward calculation, making use of eq 11.

It then follows that

$$\mathbf{J}^{-1}\mathbf{c} = (1 - p_{11})^{-1}\hat{\mathbf{p}}_1 \qquad (25)$$

and, from eq 24, that

$$a = (\pi_{11} - (1 - p_{11})^{-1}\hat{\boldsymbol{\rho}}_1\hat{\mathbf{p}}_1)^{-1}$$

However, note that

$$\hat{\boldsymbol{\rho}}_1\hat{\mathbf{p}}_1 = \sum_{i\in\mathbf{N}_1}\pi_{1i}p_{i1} = (1 - p_{11})\pi_{11} - 1$$

where the second equality is given by the first row of the matrix identity eq 11. Thus

$$a = 1 - p_{11} \qquad (26)$$

substituting eqs 25 and 26 into 23 now allows us to conclude that

$$(\mathbf{I} - \mathbf{B}^{\mathrm{T}}\mathbf{A})^{-1} = \begin{bmatrix}1 - p_{11} & -(1 - p_{11})\hat{\boldsymbol{\rho}}_1\mathbf{J}^{-1} \\ -\hat{\boldsymbol{\rho}}_1 & \mathbf{J}^{-1} + \hat{\mathbf{p}}_1\hat{\boldsymbol{\rho}}_1\mathbf{J}^{-1}\end{bmatrix} \qquad (27)$$

The other two elements in eq 5 are $\mathbf{\Pi}\,\mathbf{A}$ and $\mathbf{B}^{\mathrm{T}}$. The former of these is just a selection of the columns of $\mathbf{\Pi}$, the first, $\boldsymbol{\pi}_1$, and the ν_1 columns $\boldsymbol{\pi}_i$, $i \in \mathbf{N}_1$. In particular, the first row of $\mathbf{\Pi}\,\mathbf{A}$ is just $[\pi_{11}\ \hat{\boldsymbol{\rho}}_1]$. From eq 27, we then obtain

$$\mathbf{\Pi A}(\mathbf{I} - \mathbf{B}^{\mathrm{T}}\mathbf{A})^{-1} = \begin{bmatrix} 1 & 0_{(1,\nu_1)} \\ 0_{(N-1,1)} & \tilde{\mathbf{\Pi}}\mathbf{J}^{-1} \end{bmatrix} \tag{28}$$

In deriving eq 28, we have made extensive use of eq 11. The $(\mathrm{N} - 1) \times \nu_1$ matrix $\tilde{\mathbf{\Pi}}$ is made up from the columns of $\mathbf{\Pi}$ indexed by $\mathbf{N}_1$ without the elements from the first row.

Finally, then

$$\begin{aligned} \Delta\mathbf{\Pi} &= \mathbf{\Pi A}(\mathbf{I} - \mathbf{B}^{\mathrm{T}}\mathbf{A})^{-1}\mathbf{B}^{\mathrm{T}} \\ &= \begin{bmatrix} 1 & 0_{(1,\nu_1)} \\ 0_{(N-1,1)} & \tilde{\mathbf{\Pi}}\mathbf{J}^{-1} \end{bmatrix} \begin{bmatrix} 1 - \boldsymbol{\pi}_1 & -\tilde{\boldsymbol{\rho}}_1 \\ -\mathbf{c} & \mathbf{K}\tilde{\mathbf{R}}_1 \end{bmatrix} \end{aligned} \tag{29}$$

where $\tilde{\boldsymbol{\rho}}_1$ and $\tilde{\mathbf{R}}_1$ are just $\boldsymbol{\rho}_1$ and $\mathbf{R}_1$, respectively, without their first columns. Similarly, we write $\tilde{\boldsymbol{\pi}}_1$ for $\boldsymbol{\pi}_1$ without its first element, and then performing the partitioned matrix multiplication in eq 29 gives

$$\Delta\mathbf{\Pi} = \begin{bmatrix} 1 - \boldsymbol{\pi}_1 & -\tilde{\boldsymbol{\rho}}_1 \\ -\tilde{\boldsymbol{\pi}}_1 & \tilde{\mathbf{\Pi}}\mathbf{J}^{-1}\mathbf{K}\tilde{\mathbf{R}}_1 \end{bmatrix} \tag{30}$$

because $\tilde{\mathbf{\Pi}}\mathbf{J}^{-1}\mathbf{c} = (1 - p_{11})^{-1}\,\tilde{\mathbf{\Pi}}\tilde{\mathbf{p}}_1 = \tilde{\boldsymbol{\pi}}_1$, the second equality following from eq 11.

Everything in eq 30, except the lower right block, merely serves to replace the first row and column of $\mathbf{\Pi}$ by zeros in $\mathbf{\Pi}'$, except for π'_{11}, which is 1. In order to pass from $\mathbf{\Pi}$ to $\mathbf{\Pi}'$, all that need be calculated is $\tilde{\mathbf{\Pi}}\mathbf{J}^{-1}\ \mathbf{K}\tilde{\mathbf{R}}_1$, and the only matrix inversion that this requires is of the $\nu_1 \times \nu_1$ matrix $\mathbf{J}$.

As an illustration, we consider the process illustrated in Figure 3, and again the 5×5 lattice of Figure 2, for which $\mathbf{P}$ and $\mathbf{\Pi}$ are given by eqs 14 and 15. Suppose now that the four neutral sites labeled 3 are blocked. Clearly the index 1 of the algebraic theory above becomes 3 for the numerical example, and the indices in $\mathbf{N}_3$ are 1 and 4. Thus we obtain

$$\mathbf{\Pi}' = \begin{bmatrix} 4.0 & 8.0 \\ 4.0 & 10.4 \\ 4.0 & 12.8 \\ 4.0 & 12.8 \end{bmatrix}, \quad \tilde{\mathbf{R}}_1 = \begin{bmatrix} 0.0 & -0.8 & -3.2 & -1.6 \\ 0.0 & 0.4 & 1.6 & 0.8 \end{bmatrix},$$

$$\mathbf{K} = \begin{bmatrix} {}^1\!/_4 & 0 \\ 0 & {}^1\!/_4 \end{bmatrix}$$

Similarly,

$$\begin{aligned} \mathbf{J} &= \mathbf{I} - \mathbf{K}\hat{\mathbf{R}}_1 \\ &= \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} - \begin{bmatrix} {}^1\!/_4 & 0 \\ 0 & {}^1\!/_4 \end{bmatrix} \begin{bmatrix} 0.0 & -3.2 \\ 0.0 & 1.6 \end{bmatrix} \\ &= \begin{bmatrix} 1.0 & 0.8 \\ 0.0 & 0.6 \end{bmatrix} \end{aligned}$$

from which we get

$$\mathbf{J}^{-1} = \begin{bmatrix} 1 & -{}^4\!/_3 \\ 0 & -{}^5\!/_3 \end{bmatrix}$$

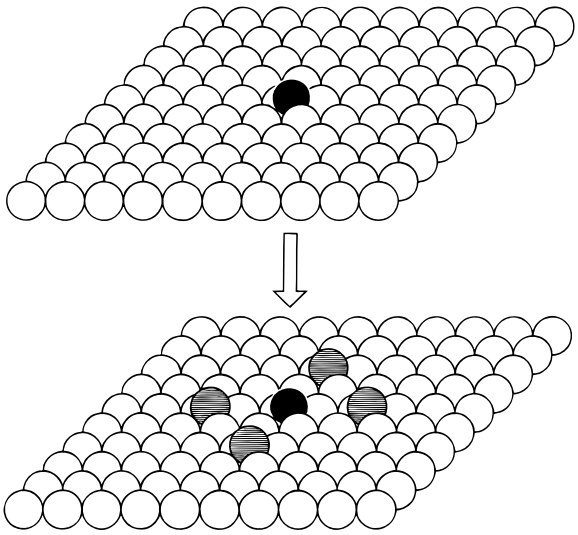

Figure 3. A sketch of the process explored in section IV. The same convention as described in Figure 1, except that the hatched circles denote sites on the substrate inaccessible to the diffusing adatom.

Thus, from eq 30, the changes to the rows and columns of $\mathbf{\Pi}$, except the third, are given by

$$\tilde{\mathbf{\Pi}}\mathbf{J}^{-1}\mathbf{K}\tilde{\mathbf{R}}_1 = \begin{bmatrix} 4.0 & 8.0 \\ 4.0 & 10.4 \\ 4.0 & 12.8 \\ 4.0 & 12.8 \end{bmatrix} \begin{bmatrix} 1 & -{}^4\!/_3 \\ 0 & -{}^5\!/_3 \end{bmatrix} \begin{bmatrix} {}^1\!/_4 & 0 \\ 0 & {}^1\!/_4 \end{bmatrix} \begin{bmatrix} 0.0 & -0.8 & -3.2 & -1.6 \\ 0.0 & 0.4 & 1.6 & 0.8 \end{bmatrix}$$

$$= \begin{bmatrix} 0.0 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.4 & 1.6 & 0.8 \\ 0.0 & 0.8 & 3.2 & 1.6 \\ 0.0 & 0.8 & 3.2 & 1.6 \end{bmatrix}$$

Using this result to construct the matrix $\mathbf{\Pi}'$, and then reorganizing the rows and columns to coincide with the convention in eq 15, we find

$$\mathbf{\Pi}' = \begin{bmatrix} 4 & 4 & 0 & 8 & 4 \\ 4 & 6 & 0 & 12 & 6 \\ 0 & 0 & 1 & 0 & 0 \\ 4 & 6 & 0 & 16 & 8 \\ 4 & 6 & 0 & 16 & 10 \end{bmatrix}$$

By calculating the overall mean walklength of the diffusing adatom for the two processes illustrated in Figure 3, one concludes that the consequence of blocking sites, and hence restricting the diffusion space accessible to a diffusing adatom, is a enhancement by a factor of 1.24 in the efficiency of the diffusion-immobilization process.

V. Nucleation of a New Island

We now consider a process in which a newly deposited adatom, rather than joining an existing island, nucleates a new island. This event can be studied by considering the consequences of blocking previously active, nucleation sites on the lattice and then calculating the average distance an adatom will have to travel before being immobilized at an alternative nucleation site. Although this differs in detail from blocking a

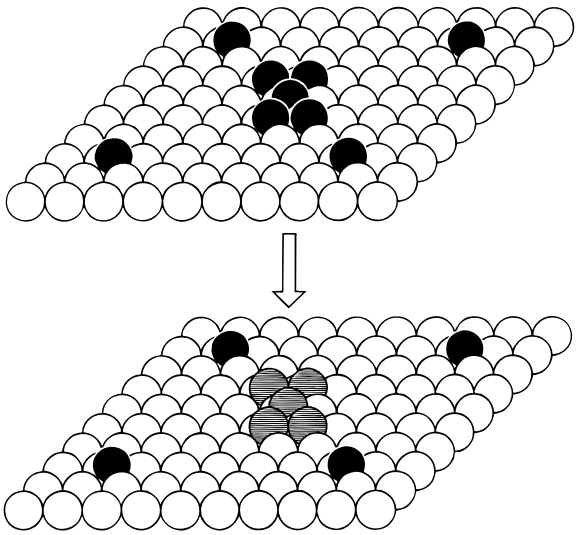

Figure 4. A sketch of the process described in section V. The same convention as in Figure 3.

nontrapping site, the nontrivial part of $\Delta\mathbf{\Pi}$ is identical to what we computed in the previous section. In order for blocking a trap not to lead to a lattice without traps, for which $\mathbf{\Pi}'$ would not exist, we must assume the existence of at least one other trap on the lattice. With that proviso, we may index the trap to be blocked by 1, and then before blocking $p_{1i} = 0$, $i = 1, ..., N$, $\pi_{11} = 1$, and $\tilde{\boldsymbol{\rho}}_1 = 0_{(1,N-1)}$, $\tilde{\boldsymbol{\rho}}_1 = 0_{(1,\nu_1)}$. The notation is as in the previous section: $\boldsymbol{\rho}_1$ is the first row of $\mathbf{\Pi}$; $\tilde{\boldsymbol{\rho}}_1$ is $\boldsymbol{\rho}_1$ without its first element; and $\tilde{\boldsymbol{\rho}}_1$ is $\boldsymbol{\rho}_1$ restricted to the elements indexed by $\mathbf{N}_1$, as defined in eq 8.

Blocking site 1 then, as in the previous section, means setting all nonzero elements p_{i1} to zero, and adding p_{i1} to p_{ii}. Thus the matrix of changes to $\mathbf{P}$ is

$$\Delta\mathbf{P} = \sum_{i\in\mathbf{N}_1} p_{i1}(\mathbf{e}_i\mathbf{e}_1^{\mathrm{T}} - \mathbf{e}_i\mathbf{e}_1^{\mathrm{T}})$$

By the same reasoning as that which led to eqs 18 and 19, and with the same notation, we obtain

$$\Delta\mathbf{P}\,\mathbf{\Pi} = \mathbf{E}_1\mathbf{K}\mathbf{R}_1$$

so that we may choose $\mathbf{A} = \mathbf{E}_1$, again just a selection matrix, and $\mathbf{B}^{\mathrm{T}} = \mathbf{K}\mathbf{R}_1$. As before, $\mathbf{B}^{\mathrm{T}}\mathbf{A}$ is a selection of the columns of $\mathbf{B}^{\mathrm{T}}$, those indexed by $\mathbf{N}_1$: $\mathbf{B}^{\mathrm{T}}\mathbf{A} = \mathbf{K}\hat{\mathbf{R}}_1$. Thus

$$\mathbf{I} - \mathbf{B}^{\mathrm{T}}\mathbf{A} = \mathbf{I} - \mathbf{K}\hat{\mathbf{R}}_1 \equiv \mathbf{J}$$

the same $\mathbf{J}$ as in (22).

It is once more convenient to write out the first row and column of $\Delta\mathbf{\Pi}$ explicitly. Because $\hat{\boldsymbol{\rho}}_1 = 0$, we obtain

$$\Delta\mathbf{\Pi}\mathbf{A}\mathbf{J}^{-1}\mathbf{B}^{\mathrm{T}} = \begin{bmatrix} 0_{(1,\nu_1)} \\ \tilde{\mathbf{\Pi}} \end{bmatrix}\mathbf{J}^{-1}[-\mathbf{c}\mathbf{K}\tilde{\mathbf{R}}_1]$$

$$= \begin{bmatrix} 0 & 0_{(1,N-1)} \\ \boldsymbol{\pi}_1 & \tilde{\mathbf{\Pi}}\mathbf{J}^{-1}\mathbf{K}\tilde{\mathbf{R}}_1 \end{bmatrix}$$

(Notation throughout as in previous section.) Thus the first row of $\mathbf{\Pi}'$ is annihilated, as needed so as to block site 1, π_{11} is unchanged at 1, and the first row of $\mathbf{\Pi}'$ is zero, as it was before the blocking. As when the blocked site was not a trap, all that needs to be calculated is $\tilde{\mathbf{\Pi}}\mathbf{J}^{-1}\,\mathbf{K}\tilde{\mathbf{R}}_1$, precisely as before.

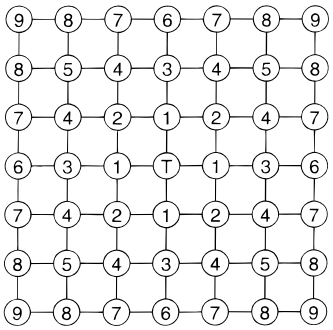

Figure 5. Site specification for a 7 × 7 square-planar lattice (see text).

To illustrate this case, we take a slightly more complex example than that treated in the last two sections. Consider the process described in Figure 4 and the 7 × 7 square planar matrix depicted in Figure 5; the four sites labeled 1 and the four sites labeled 9 are deep traps. In writing down the matrices $\mathbf{P}$ and $\mathbf{\Pi}$ for this case, we simplify by specifying site 1, but not site 9, explicitly. Then,

$$\mathbf{P} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1/2 & 0 & 0 & 1/2 & 0 & 0 & 0 & 0 \\ 1/4 & 0 & 0 & 1/2 & 0 & 1/4 & 0 & 0 \\ 0 & 1/4 & 1/4 & 0 & 1/4 & 0 & 1/4 & 0 \\ 0 & 0 & 0 & 1/2 & 0 & 0 & 0 & 1/2 \\ 0 & 0 & 1/4 & 0 & 0 & 1/4 & 1/2 & 0 \\ 0 & 0 & 0 & 1/4 & 0 & 1/4 & 1/4 & 1/4 \\ 0 & 0 & 0 & 0 & 1/4 & 0 & 1/4 & 1/4 \end{bmatrix} \quad \text{and } \mathbf{\Pi} =$$

$$\begin{bmatrix} 1.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 \\ 0.815 & 1.375 & 0.509 & 1.498 & 0.560 & 0.538 & 1.105 & 0.742 \\ 0.709 & 0.509 & 1.818 & 2.036 & 0.800 & 1.236 & 1.891 & 1.164 \\ 0.629 & 0.749 & 1.018 & 2.996 & 1.120 & 1.076 & 2.211 & 1.484 \\ 0.480 & 0.560 & 0.800 & 2.240 & 2.080 & 0.960 & 2.080 & 2.080 \\ 0.578 & 0.538 & 1.236 & 2.153 & 0.960 & 2.793 & 3.142 & 1.687 \\ 0.513 & 0.553 & 0.945 & 2.211 & 1.040 & 1.571 & 3.767 & 1.949 \\ 0.331 & 0.371 & 0.582 & 1.484 & 1.040 & 0.844 & 1.949 & 2.676 \end{bmatrix}$$

Because site 1 is a trap, the first row of $\mathbf{\Pi}$ is zero, except for the diagonal element. The elements of the first column are the expected number of visits to site 1. Normally these elements would all be 1, because, with only one trapping state, all walks visit that state just once, and are then trapped. Here there are two trapping states, and so the elements of the first column of $\mathbf{\Pi}$ are the probabilities of being trapped in state 1 rather than in state 9.

Suppose now that the four traps labeled 1 are converted to blocked sites. Apart from the diagonal element, the first row and column of $\mathbf{\Pi}'$ will be zero. We need only calculate the changes to the other rows and columns, as given by $\mathbf{\Pi}\mathbf{J}^{-1}\,\mathbf{K}\tilde{\mathbf{R}}_1$. Only states 2 and 3 have direct access to state 1, and so $\tilde{\mathbf{\Pi}}$ and

$\tilde{\mathbf{R}}_1$ have just two columns and rows respectively. In fact,

$$\tilde{\mathbf{\Pi}} = \begin{bmatrix} 1.375 & 0.509 \\ 0.509 & 1.818 \\ 0.749 & 1.018 \\ 0.560 & 0.800 \\ 0.538 & 1.236 \\ 0.553 & 0.945 \\ 0.371 & 0.582 \end{bmatrix}, \quad \mathbf{K} = \begin{bmatrix} 1/2 & 0 \\ 0 & 1/4 \end{bmatrix},$$

$$\tilde{\mathbf{R}}_1 = \begin{bmatrix} 1.375 & 0.509 & 1.498 & 0.560 & 0.538 & 1.105 & 0.742 \\ 0.509 & 1.818 & 2.036 & 0.800 & 1.236 & 1.891 & 1.164 \end{bmatrix}$$

Next,

$$\mathbf{J} = \mathbf{I} - \mathbf{K}\hat{\mathbf{R}}_1 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} - \begin{bmatrix} 1/2 & 0 \\ 0 & 1/4 \end{bmatrix} \begin{bmatrix} 1.375 & 0.509 \\ 0.509 & 1.818 \end{bmatrix}$$

$$= \begin{bmatrix} 0.313 & -0.255 \\ -0.127 & 0.545 \end{bmatrix}, \text{ so that } \quad \mathbf{J}^{-1} = \begin{bmatrix} 3.947 & 1.842 \\ 0.921 & 2.263 \end{bmatrix}$$

Finally the changes to $\mathbf{\Pi}$, except for the first row and column, are given by

$$\tilde{\mathbf{\Pi}}\mathbf{J}^{-1}\mathbf{K}\tilde{\mathbf{R}}_1 =$$

$$\begin{bmatrix} 4.520 & 3.175 & 6.291 & 2.387 & 2.725 & 5.000 & 3.258 \\ 3.175 & 3.234 & 5.332 & 2.042 & 2.553 & 4.425 & 2.836 \\ 3.145 & 2.666 & 4.793 & 1.827 & 2.187 & 3.894 & 2.516 \\ 2.387 & 2.042 & 3.655 & 1.394 & 1.672 & 2.973 & 1.920 \\ 2.725 & 2.553 & 4.374 & 1.672 & 2.049 & 3.595 & 2.313 \\ 2.500 & 2.212 & 3.894 & 1.486 & 1.798 & 3.180 & 2.051 \\ 1.629 & 1.418 & 2.516 & 0.960 & 1.156 & 2.052 & 1.324 \end{bmatrix}$$

Using this result, one can immediately write down the matrix $\mathbf{\Pi}'$.

$$\mathbf{\Pi}' =$$

$$\begin{bmatrix} 1.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 \\ 0.000 & 5.895 & 3.684 & 7.789 & 2.947 & 3.263 & 6.105 & 4.000 \\ 0.000 & 3.684 & 5.053 & 7.368 & 2.842 & 3.789 & 6.316 & 4.000 \\ 0.000 & 3.895 & 3.684 & 7.789 & 2.947 & 3.263 & 6.105 & 4.000 \\ 0.000 & 2.947 & 2.842 & 5.895 & 3.473 & 2.632 & 5.053 & 4.000 \\ 0.000 & 3.263 & 3.789 & 6.526 & 2.632 & 4.842 & 6.737 & 4.000 \\ 0.000 & 3.053 & 3.158 & 6.105 & 2.526 & 3.368 & 6.947 & 4.000 \\ 0.000 & 2.000 & 2.000 & 4.000 & 2.000 & 2.000 & 4.000 & 4.000 \end{bmatrix}$$

For the processes illustrated at the top and bottom of Figure 4, the mean number of displacements of a diffusing adatom before becoming immobilized is given by $\langle n \rangle = 9.9$ and $\langle n \rangle = 26.2$, respectively. Thus, the consequence of blocking previously active sites on the substrate is a dilation in the overall time scale for adatom immobilization by a factor of 2.6. Contrasting the examples developed in sections IV and V, blocking of "neutral" sites on the substrate leads to an enhancement in the efficiency of the process, whereas blocking "active" sites on the substrate leads to a decrease in efficiency.

VI. Conclusions

In this paper we have developed a "shorthand" theoretical method for studying atomistic mechanisms thought to be important in the initial phases of thin-film growth. These mechanisms are translated into the Markovian problem of studying the effect on (here) unbiased, nearest-neighbor random walks on a $d = 2$ dimensional lattice in which trapping sites are opened up, or neutral sites or trapping sites are "blocked" as a consequence of the immobilization of a diffusing adatom.

Our method is based on the observation that, in this class of problems, on creating a trap or blocking a neutral site on a lattice of N sites, it is only the ν sites in the nearest-neighbor environment of the affected site that are sensitive to the trapping/blocking properties of that site. This suggests (and we proved) that changes in the fundamental matrix $\mathbf{\Pi} = (\mathbf{I} - \mathbf{P})^{-1}$ where $\mathbf{P}$ is the Markov transition matrix and $\mathbf{I}$ is the identity matrix, can be computed by inverting a $\nu \times \nu$ matrix instead of an $N \times N$ one.

The approach developed in section II is valid for d-dimensional lattices of arbitrary symmetry and connectivity; hence, the method can easily be applied to such $d > 2$ problems as atom attachment to and detachment from terraces, and interlayer mass transport. In the following paper, we take up an experimental problem described in detail in the review of Zhang and Lagally, diffusion along island edges and the formation of compact islands.

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