# Irreversible island growth in the presence of anisotropic surface diffusion with long jumps

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Kinetic Monte Carlo (KMC) simulations are used to investigate the dynamics of island growth during submonolayer epitaxy in the presence of anisotropic surface diffusion, and the influence of a recently hypothesized crowdion diffusion mechanism. An existing rate equation mean-field analysis of island growth is extended to include anisotropic diffusion. The mean-field analysis is found to be at odds with results from KMC simulations indicating that the details of the surface diffusion mechanism influence the nucleation rate. It is found that anisotropy in adatom hopping reduces the density of stable islands. It is also found that although the shape of the island size distribution is sensitive to island relaxation processes, it is not discernibly affected by hopping anisotropy with ratios  $D_{xx}/D_{yy}$  up to 16.

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## I. INTRODUCTION

In the last few decades the understanding of nucleation and growth of islands during the early stages of thin film deposition processes has improved dramatically. While the technological importance of film growth is manifest, this process is only one example of a whole set of aggregation phenomena that includes the formation of snow flakes, setting of custard, and swelling of nuclear reactors. A general description of aggregation processes using a system of coupled rate equations was formulated by von Smoluchowski in 1916.<sup>1</sup> The particular problem of irreversible nucleation and growth of thin films (i.e., where dimers are the smallest stable clusters) has attracted particular interest in recent years because the process can be represented by the simplest nontrivial form of von Smoluchowski's rate equations, and more importantly, because theoretical and numerical descriptions of film nucleation can be tested directly by detailed scanning tunneling microscopy (STM) experiments. Thus the relatively simple problem of film growth provides a good model system for understanding more general aggregation phenomena.

When a metal on metal epitaxial film is grown by physical vapor deposition (PVD) atoms arrive at the substrate surface individually and move around on it randomly. Initially the concentration of lone atoms rises. The free energy of this sea of adatoms is reduced by the aggregation of monomers to form an archipelago of adatom clusters or "islands." Once these clusters have been nucleated, additional atoms arriving at the surface are more likely to encounter an island than another diffusing monomer. Thus, existing islands grow with little further nucleation of new islands. Eventually these islands coalesce and a contiguous film is formed. The kinetics of this process are limited by the time taken for diffusing monomers to collide with other monomers or stable and relatively immobile islands.

In the precoalescent regime of two-dimensional film growth the mean number density of stable islands,  $\langle n_{\chi} \rangle$ , and the distribution of island sizes are observed to exhibit scaling behavior over a wide range of materials systems and growth conditions.<sup>2–5</sup> The probability,  $P(s, \theta)$ , that at a surface coverage of  $\theta$  any atom chosen at random resides in an island of *s* atoms is defined to be

$$P(s,\theta) = \frac{s\langle n_s \rangle}{\sum_{s \ge 1} s\langle n_s \rangle},\tag{1}$$

where  $\langle n_s \rangle$  is the mean density of islands containing *s* atoms. It is found that  $P(s, \theta)$  obeys the scaling relation

$$P(s,\theta) = \overline{s}^{-1}(\theta)g\left(\frac{s}{\overline{s}(\theta)}\right),\tag{2}$$

where g(z) is a universal function that depends on the critical cluster size *i* (clusters of *i*+1 atoms do not dissociate).<sup>6</sup> The scaling arises from the correlated way in which Voronoi cells around growing islands are subdivided by further nucleation events.<sup>7</sup> The distribution, g(z), is narrower for larger critical island sizes, because the nucleation probability of a new island becomes more sensitive to the local monomer density.<sup>8</sup>

Villain *et al.*<sup>3</sup> proposed that the mean density of stable islands scales with the ratio of flux to the diffusion coefficient, that is

$$\langle n_{\chi} \rangle \sim \left(\frac{D}{F}\right)^{-\chi},$$
 (3)

where *D* is the diffusion coefficient and *F* is the deposition flux. The scaling exponent,  $\chi$ , is found to vary from  $\frac{1}{4}$  to  $\frac{1}{2}$ . For the case where the critical cluster size, *i*=1, Evans and Bartelt<sup>9</sup> find that  $\chi = \frac{1}{3}$  and  $\frac{1}{4}$  for isotropic and infinitely anisotropic (one-dimensional) diffusion, respectively. While when *i*=2 they find  $\chi = \frac{1}{2}$  and  $\frac{1}{3}$ . Implicit in these calculations is the idea that the density of stable islands depends on the rate of nucleation of islands alone (islands cannot move). Further it implies that for a given class of growth (*i*=1, *i* =2, etc.) the nucleation rate evolves with the total surface coverage in some universal way. This scaling form is significant: the island density is a property that can be easily measured and the scaling relation offers a straightforward way of measuring surface diffusion coefficients.<sup>10</sup>

The existence of scaling behavior in a wide range of epitaxial systems suggests that the nucleation and growth of films is to some extent insensitive to the details of how adatoms diffuse on a surface, and as a result much of the analysis to date assumes a continuum diffusion coefficient. This work examines the extent to which this assumption is valid. In particular the motivation for this work is to determine whether the evidence for the operation of a surface crowdion mediated self-diffusion mechanism can be found in the nucleation and growth behavior of homoepitactic films. The surface crowdion diffusion mechanism recently predicted by Xiao et al.<sup>11</sup> for diffusion of Cu on strained Cu (001) would provide highly anisotropic diffusion, in which transport along one direction occurs by long range concerted displacements of substrate atoms. Many seemingly isotropic substrates exhibit anisotropic surface diffusion, where symmetry is broken either by a surface reconstruction or by strain. The mobility of an adatom is a tensor property that depends exponentially on the whole surface strain tensor, thus even small deviatoric strains can yield anisotropic diffusion. As the surface crowdion only becomes metastable in the presence of strain the following question arises: does the crowdion lead to a different pattern of nucleation and growth of islands than would accrue if the macroscopic diffusion tensor was the same but transport was by anisotropic nearest neighbor hopping alone?

There is some evidence that the details of transport are important. Linderoth *et al.*<sup>12</sup> have conducted meticulous STM studies, and kinetic Monte Carlo (KMC) simulations of nucleation and growth of Pt on quasihexagonally reconstructed Pt (001) surfaces, on which diffusion is observed to be highly anisotropic. These researchers find that the scaling exponent,  $\chi$ , varies both with the degree of anisotropy, and the island shape. Amar, Family, and Hughes<sup>13</sup> perform KMC simulations for growth of islands in the presence of Lévy diffusion.<sup>29</sup> These researchers find that for both one- and two-dimensional diffusion  $\chi$  rises as the exponent of the power-law distribution of jump lengths decreases.

In this work it is demonstrated that the density of stable two-dimensional islands is sensitive to the mechanism of adatom diffusion from both the length of adatom jumps and anisotropic hopping. The remainder of the paper is arranged as follows: in Sec. II the impact of crowdion mediated selfdiffusion on the diffusion tensor is discussed and a KMC simulation of island growth with anisotropic diffusion is described. A mean-field rate equation treatment of film growth developed by Venables,<sup>14</sup> and then Bales and Chrzan<sup>4</sup> is extended to treat anisotropic diffusion in Sec. III. The results of the KMC and rate equation models are compared and discussed in Sec. IV, and the conclusions drawn are summarized in Sec. V.

## **II. KMC SIMULATIONS WITH LONG JUMPS**

The surface crowdion<sup>11</sup> is a metastable surface defect (shown in Fig. 1) in which an adatom is absorbed into a close packed atomic row in the substrate. The extra atom is accommodated in the surface by 8 or 10 atoms in a single atomic row all shuffling along that row. The row along which the



FIG. 1. Perspective picture of a crowdion on the (001) surface of Cu. Atom positions were calculated by Xiao *et al.* (Ref. 11). Arrows indicate the direction of compressive strain.

displacements are extended lies in the  $\langle 110 \rangle$  direction with the least compressive strain, hence in a homogeneously strained material all crowdions will be extended in the same direction.

Xiao *et al.* predicted the structure of the surface crowdion on strained Cu (001) by using the nudged elastic band method to find a minimum energy trajectory between the initial and final configurations of the exchange surface diffusion mechanism, and have also seen a similar structure on unreconstructed Pt (001).<sup>15</sup>

In a single component system, once a crowdion is formed, it is not possible to distinguish the original adatom from the other atoms at the center of the crowdion. Only by looking at the distribution of atomic displacement along the close packed row does the crowdion make itself apparent, thus the crowdion may be considered a quasiparticle that carries one quantum of "atomic displacement" parallel to the close packed row. As the displacements associated with the crowdion are distributed over approximately 10 atoms moving the center of the crowdion one atom spacing along its extended direction involves only small changes in the individual atom displacements, thus the energy barrier for moving the crowdion along its row is very small [O(0.001) eV, less than thermal energy at room temperature]. The energy required to move the crowdion from one row to an adjacent row, however, is larger than the decay energy of the crowdion. The effective mass of the crowdion in Cu has been estimated from the atomic displacements to be 0.07 times that of a Cu atom. Hence it is thought that the crowdion may be born with some kinetic energy, and once created will move freely in one direction until it is scattered by phonons, or surface adatoms, and it decays ejecting an atom to the surface. For (nontracer) self-diffusion this is equivalent to a diffusing adatom making a large surface jump in which the adatom "visits" all the surface sites on either side of the jump path.<sup>16</sup>

The macroscopic diffusion tensor, **D**, of a diffusing species is related to the microscopic transport processes that species can perform by<sup>17</sup>

$$\mathbf{D} = \frac{1}{2} \sum_{i} (\mathbf{r}_{i} \otimes \mathbf{r}_{i}) R_{i}, \qquad (4)$$

where  $\mathbf{r}_i$  is the displacement vector, and  $R_i$  is the rate of the *i*th jump process. The sum is performed over all possible displacement processes that the itinerant species can under-

take. The squared dependence on the jump length means that even if the occurrence of long jumps is rare they can make a significant contribution to the diffusion tensor. Furthermore, as the direction in which crowdions form is dictated by the surface strain state their contribution will be anisotropic. However, as the strain state that permits the formation of crowdions breaks the fourfold symmetry of the surface it will also cause transport of adatoms due to nearest neighbor hopping to become anisotropic.

A KMC model has been developed to simulate twodimensional irreversible island growth (where the critical island size i=1) on a square lattice. The purpose of this code is to investigate the consequences of a hypothesized diffusion mechanism involving the surface crowdion predicted by Xiao *et al.* on strained Cu (001),<sup>11</sup> and to see if it exhibits behavior that can be distinguished from diffusion by anisotropic nearest neighbor hopping in a real growth experiment. To this end the model is devised to be as simple as possible while including anisotropic surface diffusion, and the crowdion diffusion mechanism.

The dynamics of the KMC simulation are limited to include only six possible hopping processes. Three processes are accessible to isolated monomers. Two processes enable islands' shapes to relax and the final ingredient in the KMC code is adatom deposition.

#### A. Monomer diffusion

Isolated monomers (atoms with no first nearest neighbors) are permitted to make nearest neighbor hops in the [110] and [110] directions (defined to be the x and y directions, respectively, with rates  $R_x$  and  $R_y$ ), and to make a crowdion mediated jump (with rate  $R_c$ ). The movement of a crowdion is assumed to be more rapid than the total rate at which any event occurs on the substrate. Thus the rate of crowdion transport is limited by the rate of crowdion formation alone and the jump (as with all the other permitted processes) is assumed to be instantaneous. Hence there are no crowdioncrowdion interactions. A crowdion is restricted to traveling in the  $\pm x$  direction and only along one of the two adjacent atomic rows in the surface. The crowdion is assumed to jump  $d_c$  lattice spacings before ejecting the atom at its center to one of the two rows of empty surface sites to either side of it. Should the crowdion encounter any atoms in either of these two rows before traveling  $d_c$  the crowdion decomposes, and the ejected atom binds to the surface atom. The jump integer  $d_c$  represents the root mean squared displacement of the distribution of crowdion jumps. As calculating the phonon drag of a crowdion is nontrivial  $d_c$  is left as a controllable parameter.

For the surface diffusion processes outlined above the diffusion tensors for monomers is

$$\mathbf{D}_{1} = \frac{b^{2}}{2} \begin{vmatrix} (R_{x} + d_{c}^{2}R_{c}) & 0\\ 0 & \left(R_{y} + \frac{R_{c}}{2}\right) \end{vmatrix}.$$
 (5)

ī.

Here b is lattice parameter of the primitive square surface lattice (i.e.,  $b=a/\sqrt{2}$  where a is the lattice parameter of the FCC lattice).

There is theoretical evidence to suggest that vacancies in the Cu (001) surface are as mobile as adatoms.<sup>18,19</sup> As monomers are continually deposited on the surface during growth it is assumed that the population of monomers is larger than the population of vacancies, and diffusion by vacancies is ignored.

There are an infinite number of combinations of  $R_x$ ,  $R_y$ ,  $R_c$ , and  $d_c$  that will give the same monomer diffusion coefficient in Eq. (5). For simplicity only two extreme cases are considered in the simulations presented here, diffusion by anisotropic nearest neighbor hopping alone, and diffusion by isotropic nearest neighbor hopping with anisotropic crowdion jumps. In the former case the diffusion tensors for monomers is

$$\mathbf{D}_1 = \frac{b^2 R_h}{2} \begin{vmatrix} \lambda^2 & 0\\ 0 & \lambda^{-2} \end{vmatrix}, \tag{6}$$

where  $R_h = \sqrt{R_x R_y}$  is the geometric mean of the nearest neighbor hopping rate, and  $\lambda = (D_{xx}/D_{yy})^{1/4}$  parametrizes the anisotropy. In the latter case

$$\mathbf{D}_{1} = \frac{b^{2} \widetilde{R}_{h}}{2} \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} + \frac{b^{2} R_{c}}{4} \begin{vmatrix} 2d_{c}^{2} & 0 \\ 0 & 1 \end{vmatrix},$$
(7)

with  $R_h$  the reduced nearest neighbor hopping rate. Forcing the diffusion tensors to be the same gives the relations

$$\frac{\widetilde{R}_h}{R_h} = \frac{2d_c^2 - \lambda^4}{(2d_c^2 - 1)\lambda^2}$$

$$\frac{R_c}{R_h} = \frac{2(\lambda^4 - 1)}{(2d_c^2 - 1)\lambda^2}.$$

#### **B.** Island shape relaxation

Two further adatom diffusion processes are included in the code that allow islands to move and their shapes to relax. These are hopping along the edge of an island (with rate  $R_{e}$ ) and hopping away from a reentrant corner in the island perimeter (with rate  $R_s$ ). These are shown schematically in Fig. 2. Both of these are independent of the orientation of the island edge, and both include hopping around convex corners in the island edge. In general, atoms with one nearest neighbor can hop clockwise or anticlockwise around an island with rate  $R_{e}$ , atoms with two adjacent nearest neighbors and a next nearest neighbor between them can hop clockwise or anticlockwise with rate  $R_s$ , and all other atoms in islands are immobile. The requirement that a step hopping atom have a next nearest neighbor is necessary to obey detailed balance.  $R_s$  is set to be smaller than  $R_e$ , as the hopping atom is initially more highly coordinated for step hopping than edge hopping.

Mobility of atoms at island edges permits islands to move. The surface diffusion tensors for dimers, and trimers are, respectively,

$$\mathbf{D}_{2} = \frac{b^{2} R_{e}}{4} \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix}, \tag{8}$$

and



FIG. 2. Examples of atom motion at an island edge. The circles represent adatoms on the (001) surface (the substrate atoms are not shown). The mobility of the unhatched atom is considered. Panels (a), (b), and (c) are examples of hopping along an island edge that occurs with rate  $R_e$ . Panels (d) and (e) are examples of hopping away from a reentrant step and happen at rate  $R_s$ . Panels (f) and (g) show configurations in which the unhatched atom is immobile. In (f) the atom must be made immobile in order to not violate detailed balance.

$$\mathbf{D}_3 = \frac{55 \ R_e}{27} \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix}. \tag{9}$$

The result in Eq. (9) averages over the possible trimer configurations weighted by their relative abundance.<sup>30</sup>

#### C. Adatom deposition

To simulate the continued deposition of adatoms from the growth process adatoms are placed on the substrate with a rate  $FL^2$  (where F is the flux of monomers and L is the dimensions of the substrate). The new atom is placed in a site picked at random. Should that site lie under an existing island a new site is picked at random from the set of empty sites closest to the original site. This is justified in conditions of two-dimensional growth where adatoms that are deposited on top of existing islands diffuse to the island perimeter and are incorporated into the growing island edge.

### **D.** Testing

The KMC code was tested by comparing the evolution of  $\langle n_1 \rangle$  and  $\langle n_{\chi} \rangle$  with  $\theta$  for isotropic diffusion with the predictions from numerically integrated rate equations.<sup>4</sup> The agreement can be seen in Fig. 3 (circles and solid lines). Plot (a)



All simulations presented here were performed on a 500 atom by 500 atom substrate with periodic boundary conditions. All statistical data from KMC simulations is obtained from an average over 80 simulations.

### **III. MEAN-FIELD RATE EQUATION ANALYSIS**

Using a Smoluchowski-type system of coupled rate equations is an attractive method for modeling the early stages of nucleation and growth of epitaxial films. Such models of low temperature island growth generally assume that adatoms do not desorb from the substrate surface, and that there exists a critical cluster size, *i*, such that clusters of i+1 atoms do not dissociate. This implies that the islands cannot coarsen, and thus is only useful in the regime when island growth from a deposition flux is much faster than the rate of island coars-



FIG. 3. Scaled plots of  $\langle n_1 \rangle$  and  $\langle n_{\chi} \rangle$  versus  $\theta$  for fractal (a) and compact (b) islands. In both cases  $\sqrt{D_{xx}D_{yy}}/F=10^7b^4$ , solid lines are calculated from the self-consistent rate equation analysis, and symbols are the results of KMC simulations with anisotropy ratios,  $\lambda=1$  ( $\bigcirc$ ),  $\lambda=\sqrt{2}$  ( $\diamond$ ),  $\lambda=2$  ( $\square$ ), and in plot (b)  $\lambda=4$  ( $\triangleright$ ).

ening. In such a model for layer by layer growth with i=1 the rate of change in the mean population density of islands of size *s* (for s > 2) is given by

$$\frac{d\langle n_s \rangle}{d\theta} = (p_{s-1}\langle n_{s-1} \rangle - p_s \langle n_s \rangle) + (\langle n_{s-1} \rangle H_{s-1} - \langle n_s \rangle H_s) \frac{\langle n_1 \rangle}{F}.$$
(10)

Here time is parametrized in terms of the area of the substrate covered,  $\theta$ , by  $d\theta/dt=F$ , and the atomic area is set to unity. The first term in parentheses is the change in the population due to direct impingement of depositing monomers from the vapor, and  $p_s$  is the flux capture cross section of an island of *s* atoms and depends on the islands geometry, area, and sticking coefficient. The second term is the change in population due to the capture of monomers diffusing on the surface, where  $H_s$  is the diffusing monomer capture cross section. The change in the mean population of monomers is

$$\frac{d\langle n_1 \rangle}{d\theta} = \left(1 - \sum_{s \ge 1} p_s \langle n_s \rangle\right) - \left(p_1 + 2\langle n_1 \rangle \frac{H_1}{F} + \sum_{s \ge 2} \langle n_s \rangle \frac{H_s}{F}\right) \langle n_1 \rangle,$$
(11)

where the terms have been grouped into source terms in the first set of parentheses, and sink terms in the second set of parentheses. The detailed physics of a particular island growth problem lie in the innocuous looking capture cross sections  $H_s$ .

Venables,<sup>14</sup> and then Bales and Chrzan<sup>4</sup> developed a selfconsistent method for calculating the capture numbers for the case of layer by layer growth when the kinetics are limited by diffusion. These researchers found the flux of monomers at an island edge by solving, self-consistently, the diffusion equation for the local density of monomers in a mean field of monomer sinks (islands) and sources (the depositing vapor). This mean-field approach while successful at capturing the evolution of  $\langle n_{\chi} \rangle$  and  $\langle n_1 \rangle$ , it does not predict the observed distribution of island sizes,  $g[s/\overline{s}(\theta)]$ . More recently, Popescu, Amar, and Family<sup>21–23</sup> have developed a method for calculating the capture cross sections that does account for island-island correlations and predicts the observed island size distribution, however, the discussion here is limited to the mean-field treatment.

Following Bales and Chrzan<sup>4</sup> it is assumed that the kinetics of adatom attachment is limited by the flux of monomers to island edges. The distribution of monomers around an island is estimated by solving the diffusion equation,

$$\frac{\partial n_1(\mathbf{u},\theta)}{\partial \theta} = \nabla \frac{\mathbf{D}}{F} \nabla n_1(\mathbf{u},\theta) + \mathcal{J} - \mathcal{S}, \qquad (12)$$

where  $n_1(\mathbf{u}, \theta)$  is the mean local concentration of monomers at position  $\mathbf{u}$  from the island center. Here the first term is the diffusive change in the local monomer density, and the second term is a distributed source accounting for the continued deposition of monomers from the vapor,

$$\mathcal{J} = 1 - \sum_{s \ge 1} p_s \langle n_s \rangle. \tag{13}$$

The final term in the diffusion equation is a sink term to account for the continuous loss of monomers to islands (and other monomers and impinging vapor atoms). This is approximated by calculating the mean effective sink strength of all the islands and distributing it uniformly over the entire substrate (the mean-field approximation),

$$S = p_1 \langle n_1 \rangle + 2 \frac{H_1}{F} \langle n_1 \rangle + \sum_{s \ge 2} \langle n_s \rangle \frac{H_s}{F} = n_1(\mathbf{u}, \theta) \xi^{-1/2}.$$
(14)

This is equivalent to calculating a mean density of sinks of unit strength, which is related to a characteristic sink separation  $\xi$ .

If the diffusion tensor, **D**, only contains diagonal terms (which can certainly be accomplished by rotating the coordinate system providing the deformed lattice remains orthorhombic), the diffusive term on the right-hand side of Eq. (12) is

$$\nabla \frac{\mathbf{D}}{F} \nabla n_1 = \frac{D_{xx}}{F} \frac{\partial^2 n_1}{\partial x^2} + \frac{D_{yy}}{F} \frac{\partial^2 n_1}{\partial y^2}.$$
 (15)

where  $D_{xx}$  and  $D_{yy}$  are the diagonal elements of the diffusion tensor. This expression is rewritten in a coordinate system parametrized by r and  $\phi$  which are related to the Cartesian coordinated by  $x = \sqrt{(D_{xx}/D_0)r} \cos(\phi)$ , and  $y = \sqrt{(D_{yy}/D_0)r} \sin(\phi)$ , to give the Laplacian in cylindrical coordinates,

$$\nabla \frac{\mathbf{D}}{F} \nabla n_1(\mathbf{u}, \theta) = \frac{D_0}{F} \left( \frac{\partial^2 n_1}{\partial r^2} + \frac{1}{r} \frac{\partial n_1}{\partial r} + \frac{1}{r^2} \frac{\partial^2 n_1}{\partial \phi^2} \right).$$
(16)

Here  $D_0$  has the dimensions of a diffusion coefficient but is as yet undefined. The coordinate system stretches the *x* and *y* directions relative to the speed of diffusion in those directions. If  $D_0$  is chosen to be  $\sqrt{D_{xx}D_{yy}}$  the area of the substrate remains the same in the coordinate system and the dispersed sink density remains unchanged. This is equivalent to stretching the *x* axis by a factor  $\lambda$  and the *y* direction by a factor  $1/\lambda$ , where  $\lambda = (D_{xx}/D_{yy})^{1/4}$ .

The partial differential equation in Eq. (12) can be reduced to an ordinary differential equation by comparing the rate of change of the local density of monomers with the mean density of monomers,

$$\frac{F}{D_0} \left( \frac{d\langle n_1 \rangle}{d\theta} - \frac{\partial n_1}{\partial \theta} \right) = \left( \frac{n_1 - \langle n_1 \rangle}{D_0 \xi^2} \right) - \left( \frac{\partial^2 n_1}{\partial r^2} + \frac{1}{r} \frac{\partial n_1}{\partial r} + \frac{1}{r^2} \frac{\partial^2 n_1}{\partial \phi^2} \right) \approx 0.$$
(17)

The approximation to zero is justified when  $D_0/F$  is sufficiently large (compared to the square of the atomic area) so the term on the left-hand side can be neglected (the adiabatic approximation). This assumes that the shape of the monomer distribution changes very slowly and only the amplitude of the distribution changes significantly with the mean concentration. This approximation removes the time dependence from the problem and yields the Helmholtz equation,

$$\left(\frac{\partial^2 n_1}{\partial r^2} + \frac{1}{r}\frac{\partial n_1}{\partial r} + \frac{1}{r^2}\frac{\partial^2 n_1}{\partial \phi^2}\right) = \left(\frac{n_1 - \langle n_1 \rangle}{D_0 \xi^2}\right),\tag{18}$$

in which the variables r and  $\phi$  can be separated. The Helmholtz equation can be solved for the boundary conditions that the monomer density reaches the mean-field value infinitely far from the island and the monomer density is zero at the island edge. The simplest solution occurs when the perimeter of an island of size *s* (or its containment area if it is fractal) lies on a constant value of  $r=r_s$  in the diffusion weighted cylindrical coordinate system. This implies the islands are elliptical with an aspect ratio of  $\lambda^2$ . This will be the case if perturbations at the island edge can relax with sufficient speed to prevent a growth instability in the island shape but without relaxing so fast that the island becomes circular. A stronger argument can be made in which the detailed shape of the island is unimportant provided that the monomer depletion field around the growing island is roughly elliptical with an aspect ratio  $\lambda^2$ . This will be the case if the island does not exhibit a growth instability (i.e., growing in a needle shape in the direction of slowest diffusion). When the deviation of the island from circular matches the stretching of the coordinate system the angular dependence of the concentration disappears, and the Helmholtz equation reduces to that of Bales and Chrzan. Thus solving for  $n_1(r, \theta)$  subject to the conditions that  $n_1(r_s, \theta) = 0$  and  $n_1(r \to \infty, \theta) = \langle n_1(\theta) \rangle$ yields

$$n_1(r,\theta) = \langle n_1(\theta) \rangle \left( 1 - \frac{K_0(r/\xi)}{K_0(r_s/\xi)} \right), \tag{19}$$

Where  $K_j(x)$  is a modified Bessel function of order *j*. The capture coefficients can now be found by equating the rate of monomer capture with the flux perpendicular to the island perimeter,

$$\langle n_1(\theta) \rangle H_s = \oint_{\Gamma} (\mathbf{D} \, \nabla \, n_1(\Gamma, \theta)) \hat{\mathbf{p}}(\Gamma) dl(\Gamma),$$
 (20)

where  $\Gamma$  is the tracking vector of the perimeter of the island, and  $\hat{\mathbf{p}}(\Gamma)$ , and  $dl(\Gamma)$  are the outward unit vector perpendicular to the island edge, and the elemental perimeter length at  $\Gamma$ , respectively. Parametrizing the edge of the island with the angle  $\phi$  in the stretched cylindrical coordinates gives

$$\langle n_1(\theta) \rangle H_s = \sqrt{D_{xx}D_{yy}} \int_{\phi=0}^{2\pi} r_s \left. \frac{\partial n_1}{\partial r} \right|_{r=r_s} d\phi.$$
 (21)

This gives the capture strength as a function of the characteristic length  $\xi$ ,

$$H_s = 2\pi \sqrt{D_{xx}} \frac{r_s}{\xi} \left( \frac{K_1(r_s/\xi)}{K_0(r_s/\xi)} \right).$$
(22)

In turn,  $\xi$  depends on the sum of capture strengths of all island sizes weighted by their abundance [Eq. (14)]. As under/over estimating  $\xi$  over/under estimates  $H_s$  which increases/decreases the estimate of  $\xi$  the capture numbers can be found self-consistently in an iterative manner.

The coefficient  $H_s$  is proportional to the geometric mean of the diagonal elements of the diffusion tensor. This, at first

sight, is not surprising as an island on a substrate with anisotropic diffusion depletes the monomers from the same area of substrate in a given time as an island on an isotropic surface with diffusion coefficient  $\sqrt{D_{xx}D_{yy}}$ . Equation (22) implies that the geometric mean of the diffusion tensor is the only important parameter in the evolution of the density of stable islands,  $\langle n_{\chi} \rangle$ , with  $\theta$ . It must be noted that the meanfield approximation fails to capture the island size distribution, and thus the treatment outlined above gives no information about whether the universal function  $g[s/\overline{s}(\theta)]$  in Eq. (2) is lost with anisotropy.

In fact, as is demonstrated in the next section, the result found above is only accurate for relatively small diffusion anisotropies. Moreover, the erroneous predictions of this model at large anisotropies hints at a more general failing of macroscopic diffusion descriptions of island growth.

# **IV. RESULTS AND DISCUSSION**

The discussion of results is broken down in the following way. First the mean-field rate equation calculation for the number density of stable islands is compared to KMC simulation results and the usefulness of the rate equation approach is discussed. Next the distributions of island sizes yielded by KMC simulations are discussed. Finally the influence of crowdion mediated diffusion on the growth of islands is discussed and compared to island growth with nearest neighbor hopping alone.

### A. Rate equation analysis

The density of stable islands  $\langle n_{\chi} \rangle$  as a function of the coverage  $\theta$  computed using rate equations and the KMC simulations are shown in Fig. 3. Monomer diffusion in the KMC simulations was by nearest neighbor hopping alone with varying degrees of anisotropy (parametrized by  $\lambda$ ), but with the same magnitude of the diffusion coefficient,  $D_0 = \sqrt{D_{xx}D_{yy}}$ . From these plots two things are apparent. First increasing anisotropy in the KMC simulations reduces the density of stable islands (in disagreement with the rate equation analysis), and second, islands begin to coalesce at lower coverages.

It can be seen from Fig. 3 that the values of  $\langle n_{\chi} \rangle$  and  $\langle n_1 \rangle$ measured from the simulations diverge from the rate equation predictions more rapidly with increasing anisotropy for the case of fractal islands than compact islands. The cause is evident in the snapshot of the island archipelago for each case (Fig. 4). The fractal islands show a growth instability that has been described by Heyn.<sup>24</sup> These islands are elongated in the direction of slow diffusion. As there is no mobility of atoms at the island edge a perturbation in the island shape can only heal if the perturbation reduces the outward velocity of the growing island's perimeter. An asperity at the island periphery protruding in the slow direction of diffusion can grow rapidly by depleting the monomers from the regions of substrate laterally (in the fast direction) on either side of it. Thus the islands in map (a) of Fig. 4 extend in the slow direction creating depleted regions along the long edges but with very little depletion ahead of their fast growing tips.



FIG. 4. "Micrographs" of islands at  $\theta = 0.1$  grown with  $D_0/F = 10^7 b^4$  with  $\lambda = 2$  and no edge mobility (a), and  $\lambda = 4$  with island shapes able to relax (b). Image dimensions are  $500b \times 500b$ . Diffusion is fastest in the horizontal direction. Considerable coalescence can be seen in image (b). Image (c) shows compact islands grown with isotropic diffusion. Image (c) is included for comparison with (b) to show that the lower number density of islands grown with large anisotropy arises from a lower nucleation rate, rather than just early coalescence of islands.

(c)

Clearly this violates the assumption made in the rate equations analysis in Sec. III that the islands (or at least their depleted regions) have an aspect ratio of  $\lambda^2$ , and so one should not expect fractal islands simulations to agree with the mean-field theory.

From chart (b) of Fig. 4 it can be seen that the islands for the shape relaxing calculation retain an aspect ratio of approximately unity, even with a diffusion anisotropy of  $D_{xx}/D_{yy}=256$ , as required by the rate equation analysis. Figure 3 shows, however, that even compact islands do not adhere to the mean-field predictions (particularly evident in the monomer density for  $\lambda=4$ ). This indicates that the prediction from Sec. III that the geometric mean of the diffusion tensor is the only relevant parameter in the number density of stable islands is flawed.

The systematic deviation in  $\langle n_1 \rangle$ , and  $\langle n_{\chi} \rangle$  from the isotropic case with increasing  $\lambda$  in Fig. 3(a) can be understood by considering the number of unique sites visited by a random walker on a square lattice. If the walker steps north, south, east or west with equal probability then the expected number of unique lattice sites that the walker visits, defined to be  $\langle N_u \rangle$ , after taking N steps asymptotes to<sup>25</sup>

$$\langle N_u \rangle \sim \frac{\pi N}{\ln(N)},$$
 (23)

and for a one-dimensional walk this is



$$\langle N_u \rangle \sim \left(\frac{8N}{\pi}\right)^{1/2}.$$
 (24)

These two cases are the extreme lines in plot (a) of Fig. 5. The random walk on a two-dimensional lattice is completely space filling—that is, given an infinite number of steps a walker is certain to return to its starting point.<sup>31</sup> As the walk becomes anisotropic, however, the efficiency with which the random walker searches space is reduced, and the fraction of unique sites visited,  $\langle N_u \rangle / N$  diminishes until the extreme case gives one-dimensional diffusion.

For diffusion with a constant  $D_0$  however, the number of hops performed in a given time increases with  $\lambda$  [in fact N  $\sim D_{xx} + D_{yy} = D_0(\lambda^2 + 1/\lambda^2)$ ]. The result, as shown in plot (b) of Fig. 5, is that diffusing monomers sample more of the surface lattice in a given time when the diffusion is anisotropic. Clearly this must be important for the early time nucleation of islands when there is only a gas of monomers on the surface. At these times the notion of depleted regions is not applicable and nucleation depends on the time it takes monomers to search an area for other monomers, rather than the time it takes a monomer to travel a given distance (across a depleted region) to an existing island. The nucleation search area,  $1/\langle n_1 \rangle$ , decreases as more monomers are deposited on the surface. Thus a slow searching species will nucleate later, and with a higher density of islands, than a fast searching species. This behavior can clearly be seen in Fig. 3. Once islands have been established and act as sinks for monomers then the distance an adatom must travel to an island becomes important.



FIG. 5. Plot of the number of unique sites visited by a twodimensional isolated random walker with  $D_0 = \frac{1}{4}$  and  $\lambda = 1$  ( $\bigcirc$ ),  $\lambda = \sqrt{2}$  ( $\square$ ),  $\lambda = 2$  ( $\diamond$ ),  $\lambda = 2\sqrt{2}$  (\*). The plot marked by ( $\triangleleft$ ) is for a one-dimensional walker with D $= \frac{1}{4}$ . Panel (a) shows sites visited after *N* hops, panel (b) shows the site visitation as a function of time.

It must be noted that the diffusion coefficient only gives information on the distances that atoms move in a given time, not the area they search. Hence, rate equation formulations that rely only on macroscopic diffusion (such as that in Sec. III along with that of Bales and Chrzan<sup>4</sup>) overlook some of the physics of the problem (and hence the good agreement between these theories and numerical experiments must be, at least to some extent, fortuitous).

### B. Island size distribution

The mean-field rate equation analysis accounts for neither island coalescence nor spatial island-island correlations and so does not capture the correct island size distribution; hence, the discussion here is limited to the KMC simulations.

### 1. Size distribution scaling

The shape and scaling behavior of the island size distribution with hopping anisotropy is examined in Fig. 6. Panel (a) shows scaled plots of  $P(s, \theta)$  for fractal islands at a coverage of  $\theta=5\%$  (the low coverage was chosen to minimize effects of coalescence). Panel (b) shows the same plots for compact islands. The distributions in plot (a) are slightly different in shape to those in plot (b); however, remarkably with in each plot there are no gross (discernible from the noise) differences in the shape of the distribution arising from anisotropy.

The origin of the change in size distribution from fractal to compact islands is the mobility of dimers and trimers.<sup>26</sup> This is illustrated by Fig. 7 that shows unscaled (a) and scaled (b) size distributions of islands grown isotropically

FIG. 6. Plots of scaled island size distributions at  $\theta$ =0.05 grown with  $D_0/F=10^7b^4$  for fractal (a), and compact (b) islands. Diffusion anisotropies,  $\lambda$ =1 (O),  $\lambda$ = $\sqrt{2}$  ( $\Diamond$ ),  $\lambda$ =2 ( $\Box$ ),  $\lambda$ =4 ( $\triangleright$ ) [in (b) only].



with simple hopping and different degrees of edge mobility. Allowing dimers and trimers to move, albeit slowly, vastly increases the probability that these islands can coalesce with other islands, and so adds an additional sink term to the rate of population change of these small island. Furthermore, mobile trimers are most likely to capture a fourth monomer (and be rendered immobile) in regions with the largest average monomer concentration, that is, regions furthest away from other islands. The result is a narrowing of the distribution of capture areas (or Voronoi cell areas). So, although dimers and trimers are unable to dissociate, allowing them to move can be thought to increase the effective critical island size.

The robustness of the island size distribution scaling to diffusional anisotropy and the mechanism of transport is all the more remarkable given that the size distribution for islands grown with purely one-dimensional diffusion exhibit a different size distribution.<sup>27</sup>

#### 2. Coalescence

The KMC simulations exhibit more coalescence of islands as diffusion becomes more anisotropic. On isotropically diffusing substrates coalescence of islands is inhibited.



FIG. 7. Plots of unscaled (a) and scaled (b) island size distribution under diffusion by isotropic simple hopping. Islands were grown to  $\theta = 0.2$  under conditions  $D/F = 10^7 b^4$  with edge relaxation rates,  $R_e = 0$  and  $R_s = 0$  ( $\bigcirc$ ),  $R_e = D/400b^2$ , and  $R_s = D/4000b^2$  ( $\square$ ),  $R_e = D/400b^2$ , and  $R_s = 0$  ( $\diamond$ ),  $R_e = D/400b^2$ , and  $R_s = 0$  ( $\diamond$ ),  $R_e = D/40b^2$ , and  $R_s = 0$  ( $\diamond$ ). In plot (b) splines have been fit through the points for the fastest edge relaxation, and no edge relaxation to make the change in shape of the scaling function easier to discern.

As two neighboring islands approach each other the depletion regions around them overlap and the accretion of monomers in the overlap region is reduced, which slows the growth velocity of the sections of island perimeter that are heading toward collision. The islands screen each other from the sea of monomers as they approach each other. In the case of anisotropic diffusion the depleted regions are highly anisotropic. Thus, the screening in the slow diffusing direction is greatly reduced and coalescence can occur earlier in this direction. It can be clearly seen that in both "micrographs" (a) and (b) in Fig. 4 that the separation between islands is greater in the direction of fast diffusion (the *x* direction) than in the slow direction.

### C. Crowdion diffusion

There are two regimes of  $\overline{R}_h$  and  $R_c$  in the diffusion tensor in Eq. (7) that lead to qualitatively different trajectories of a diffusing adatom (Fig. 8). The first of these has  $R_h = O(R_c)$ [trajectory (a) in Fig. 8]. In this case crowdions are as likely to occur as simple hops. The trajectory looks like that of an isotropically hopping random walker; there are large regions of the surface that have a high density of site visitation. In



FIG. 8. Panels (a), (b), and (c) show trajectories of diffusing adatoms moving by crowdion jumping and simple hopping. In all cases the diffusion tensors are identical with  $\sqrt{D_{xx}D_{yy}}$  $=\frac{1}{2}b^2s^{-1}$  and  $\lambda = (D_{xx}/D_{yy})^{1/4} = 2\sqrt{2}$  and hopping is isotropic. In panel (a) the diffusion jump length,  $d_c$ , is 10 atomic spacings, while in (b) and (c) it is 100. The trajectories in (a) and (b) are 4000 time units long, while (c) is 80 000. It can be seen that the diffusion trajectories in (a) and (b) are qualitatively different, while increasing the diffusion time of the (b) to (c) yields a trajectory that resembles (a). It must be noted that the scales of the x and y axes are different in plots (a), (b), and (c) and in all cases the numbers given are atomic spacings. Plot (d) shows the number of unique sites visited with time for the two sets of diffusion parameters. The squares are for diffusion with  $d_c = 10$ , and the circles are for  $d_c = 100.$ 



the other extreme the rate of crowdion formation can be very small in comparison to the hop rate  $(R_h \ll R_c)$ , this is shown by trajectory (b) of Fig. 8. Trajectory (a) is qualitatively different than path (b), which has relatively few crowdion jumps but the jumps are large enough to carry the walker well away from the area it has already searched. Between these big jumps are local areas which are heavily explored by isotropic hopping.

The path of the adatom diffusing with large crowdion jumps looks similar to the trajectory of a Lévy walk (in one dimension).<sup>32</sup> Lévy walks are a class of random walks in which the second moment of the jump length probability distribution is infinite, i.e., the jump length probability distribution decays algebraically. This implies that species diffusing by a Lévy walk will have an infinite diffusion coefficient as infrequent long jumps cannot be neglected in the sum in Eq. (4). These walks have no intrinsic length scale, and the trajectory is self-similar. This is not the case for the crowdion walk where the jump length probability distribution is Gaussian; increase the diffusion time and the perambulation resembles ordinary hopping again. This can be seen from trajectory (c) in Fig. 8. The implication of this is that if the qualitatively different trajectory impacts island growth then the time scale over which atoms diffuse is also important, and hence there may be a window of growth parameters where island growth behaves differently to those grown by nearest neighbor hopping.

Anomalous diffusion at surfaces is not unique. Bychuk and O'Shaughnessy<sup>28</sup> observe anomalous diffusion of adatoms on a solid liquid interface where Lévy-type diffusion arises (over a limited time scale) because adatoms can appear to make large jumps by desorbing from the surface and diffusing through the liquid before reabsorbing to the surface. The consequence of anomalous diffusion on island growth has been considered by Amar, Family, and Hughes.<sup>13</sup> These researchers perform KMC simulations of growth of fractal islands in the presence of true Lévy diffusion where the probability of a jump of length  $\Delta x$  is given by  $P(\Delta x)$  $\sim \Delta x^{-d_s - \beta_L}$ , where  $d_s$  is the dimensionality of the substrate, and  $\beta_I$  is the Lévy exponent that determines the length of the tails of the probability distribution. Normal diffusive  $(\sqrt{Dt})$ behavior occurs for  $\beta_L \ge 2$ , while  $2 > \beta_L \ge 1$  is referred to as "enhanced diffusion," and  $\beta_L \le 1$  is "ballistic" diffusion. These researchers find that the island density scaling exponent,  $\chi$ , for both one- and two-dimensional diffusion rises with decreasing Lévy exponent.

FIG. 9. Plots of  $\langle n_{\chi} \rangle$  and  $\langle n_1 \rangle$  vs  $\theta$  for islands grown with crowdion diffusion and mobility to flux ratio  $D_0/F = 10^7 b^4$ . Plot (a) is calculated for fractal islands and plot (b) for compact islands. In both plots solid lines are the result of mean-field calculations and symbols (and dashed lines) are the results of KMC simulations for  $\lambda = 1$  and hopping only ( $\bigcirc$ ),  $\lambda = 2$  and hopping only ( $\square$ ),  $\lambda = 2$ and crowdions with  $d_c = 10$  ( $\diamond$ ), and  $\lambda = 2$  and crowdions with  $d_c = 50$  ( $\triangleright$ ).

#### 1. Stable island density

Understanding how the makeup of the diffusion tensor impacts adatom diffusion paths gives insight to the density of stable islands grown in the presence of crowdions. Two sets of KMC simulations including crowdion hopping were performed, both with anisotropy ratios of  $\lambda = 2$ . In one case the root mean squared crowdion jump length  $d_c=10$  atom spacings, and in the other  $d_c=50$  atom spacings (this gives a ratio of the rates of crowdion hopping to nearest neighbor hopping of  $R_c/\tilde{R}_h=0.16$ , and  $R_c/\tilde{R}_h=6\times10^{-3}$ , respectively). Figure 9 shows the evolution of  $\langle n_{\chi} \rangle$  and  $\langle n_1 \rangle$  with coverage for anisotropic diffusion with different extents of crowdion jumping. There are two features in these plots worthy of comment. First, the number density of islands and monomers rises sharply with increasing  $d_c$ . This is consistent with the reduction in the area searched by the crowdion flight as the jump length is increased.<sup>33</sup>

A second observation of interest when comparing panel (a) in Figs. 3 and 9 is the delayed coalescence of fractal islands as the crowdion jump length is increased. The origin of this behavior lies in the shape of the island, the embedding area of fractal islands grown with larger values of  $d_c$  becomes more circular (Fig. 10), and thus coalescence in the slow diffusing direction is delayed.

#### 2. Island shape and island-island correlations

Figures 10 and 11 show typical archipelago maps for growth of fractal and compact islands, respectively. These figures also show the average island-island correlation functions from 80 simulations, of which each map is an example. The island-island correlation function gives the probability distribution of finding the center of an island at a position **r** from the center of any other island. It is calculated by taking the autocorrelation function of the islands' centers of mass. It can be seen clearly that islands grown with anisotropic hopping exhibit a shape instability, while those grown with isotropic short hopping and anisotropic large jumps do not. So crowdions suppress the shape instability. More striking is the denuded (dark) regions in the island-island correlation plots. It can be seen that anisotropic arms of the denuded regions are reduced in width but not in length when the crowdion jump length increases. This means that the screening by islands becomes more isotropic with increasing  $d_c$ . Both of these observations can be explained by more closely examining the diffusion in the neighborhood of the island edge.



FIG. 10. "Micrographs" of islands and corresponding island-island correlations plots (averaged over 80 maps) at coverage  $\theta$ =0.05, grown under fractal growth conditions with  $D_0/F$ =10<sup>7</sup> $b^4$  and  $\lambda$ =2. Plots (a) and (b) have isotropic hopping and crowdion jump length  $d_c$ =10, (c) and (d) have isotropic hopping and crowdion jump length  $d_c$ =50, and (e) and (f) have anisotropic hopping with no crowdions. The islands in (a) and (c) have been shaded uniformly white, as the majority of the atoms in the islands are atoms that were originally in the substrate. Maps are 500 $b \times 500b$ , while island-island correlations are 200 $b \times 200b$ . Dark regions in the island-island correlations are anticorrelated, while light regions are correlated.



FIG. 11. "Micrographs" of islands and corresponding island-island correlations plots (averaged over 80 maps) at coverage  $\theta$ =0.05, for compact islands grown with  $D_0/F=10^7b^4$  and  $\lambda$ =2. Plots (a) and (b) have isotropic hopping and crowdion jump length  $d_c$ =10, (c) and (d) have isotropic hopping and crowdion jump length  $d_c$ =50, and (e) and (f) have anisotropic hopping with no crowdions. The islands in (a) and (c) have been shaded uniformly white, as the majority of the atoms in the islands are atoms that were originally in the substrate. Maps are  $500b \times 500b$ , while island-island correlations are  $200b \times 200b$ . Dark regions in the island-island correlations are anticorrelated, while light regions are correlated.



FIG. 12. Concentration profiles near an island edge calculated numerically after  $10^5$  s. The thin solid line is calculated for nearest neighbor hopping with a  $R_h=1$  s<sup>-1</sup>, the dashed line is for hopping and crowdion diffusion with the same diffusion coefficient as before and  $R_h=0.2$  s<sup>-1</sup>,  $R_c=8 \times 10^{-5}$  s<sup>-1</sup>, and jump length  $d_c=100$ , and the thick solid line is calculated for simple hopping only with hopping rate  $R_h=0.2$  s<sup>-1</sup>.

Fick's first law, and the definition of the diffusion coefficient, are appropriate only in regions with a slowly varying concentration gradient relative to the jump length—the simple derivation of Fick's first law for diffusion with atomic jumps of l lattice spacings assumes the gradient in concentration is uniform over 2l lattice spacings. At the island edge the concentration gradient changes abruptly, so within  $d_c$  lattice spacings of the island the simple diffusive model is no longer appropriate.

The transport of monomers to an island edge can be broken into two regions, an outer region greater than  $d_c$  from the island edge where diffusion is fast and crowdions can be included in Fick's first law, and an inner region in which one-half of the crowdion formation events instantly remove monomers to the island edge (the other one-half move atoms to the outer region). The inner region can be modeled by slow isotropic diffusion with a distributed sink strength given by the crowdion formation rate. This can be seen in Fig. 12 that shows the numerically computed concentration profiles for one-dimensional diffusion to a sink edge from an initially uniform solute reservoir. In this picture of growth the island edge sees an isotropic slow diffusion field. So, providing that perturbations in island shape do not "poke through" the inner isotropic region the asperities gain no extra growth velocity and the island shape is stable.

### 3. Island size distribution

The mode of diffusion seems to have little impact on the shape if the island size distribution,<sup>16</sup> which arises from the correlated break up of Voronoi cells.<sup>7,21</sup>

# 4. Scaling exponent $\chi$

The scaling exponent  $\chi$  in Eq. (3) is estimated by finding the gradient of a least-squares straight-line fit to the plot of  $\log_{10}(\langle n_{\nu} \rangle)$  versus  $\log_{10}(D_0/F)$  (shown in Fig. 13). The exponent is found to increase for both compact and fractal islands from  $\chi = 0.33 \pm 0.005$  for isotropic hopping to  $\chi$  $=0.34\pm0.005$ ,  $\chi=0.35\pm0.004$ , and  $\chi=0.36\pm0.008$  for anisotropic diffusion (with  $\lambda = 2$ ) for; no crowdions, and crowdions with jump lengths  $d_c = 10$ , and  $d_c = 50$ , respectively. This could indicate that over the length and time scales associated with an adatom moving to an island the transport appears to exhibit "enhanced" diffusion. Amar *et al.*<sup>13</sup> see  $\chi$  rise from 0.24 to 0.29 for one-dimensional diffusion, and go from 0.34 to 0.38 for two-dimensional diffusion as  $\beta_L$  is diminished from 4.0 to 1.33 (and the tails of the jump probability distribution become wider). The situation for crowdion diffusion is somewhat more complicated as here one-dimensional "enhanced" diffusion is embedded in a two-dimensional diffusion field.

Ratsch *et al.*<sup>26</sup> see an increase in the scaling exponent from 0.33 to 0.38 with increasing edge mobility from  $R_e/R_h=0.001$  to  $R_e/R_h=0.1$  as the effective critical island size rises above unity. As the site searching ability of the crowdion is reduced with increasing  $d_c$ , small clusters have more time to diffuse between collisions with monomers, which increases their relative mobility. It is possible that this accounts for the increasing  $\chi$  for compact islands but does not account for the change in  $\chi$  for fractal islands where there is no edge running.

## **V. CONCLUSIONS**

One aim of this work is to determine if evidence for crowdions can be found in the growth pattern of islands. It is demonstrated above that there are potentially experimentally observable differences between island growth in the presence of the postulated crowdion diffusing mechanism, and the islands grown by anisotropic simple hopping with the same diffusion tensor. The scaling exponent,  $\chi$ , is one experimental observable that is impacted by crowdions, however, other



FIG. 13. Plot of  $\langle n_{\chi} \rangle$  vs  $D_0/F$  at  $\theta$ =0.05 for fractal (a) and compact (b) islands grown with isotropic hopping ( $\bigcirc$  and solid line),  $\lambda$ =2 with anisotropic hopping only ( $\square$ ),  $\lambda$ =2 with isotropic hopping and a crowdion jump distance  $d_c$ =10 ( $\square$ ),  $\lambda$ =2 with isotropic hopping and a crowdion jump distance  $d_c$ =50 ( $\triangleright$ ).

factors that influence  $\chi$  must be ruled out (such as diffusion at island edges), and experiments must be able to measure  $\chi$ accurately. Similarly, the shape of fractal islands is another observable by which crowdions might reveal themselves. Again, one must observe islands with effectively circular embedding areas in the presence of strongly anisotropic diffusion. This requires long denuded arms in the island-island correlations, and presumably temperatures low enough to freeze out edge diffusion (so that the islands are fractal) but not so low that crowdions are also frozen out.

A more general conclusion from this work is that the nucleation and growth of islands is sensitive to how atoms

search the surface. Thus, the diffusion tensor by itself is not sufficient to describe island growth, it is necessary also to know how the diffusion tensor is composed.

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- <sup>1</sup>M. von Smoluchowski, Phys. Z. **17**, 557 (1916).
- <sup>2</sup>M. C. Bartelt and J. W. Evans, Phys. Rev. B 46, 12675 (1992).
- <sup>3</sup>J. Villain, A. Pimpinelli, and D. E. Wolf, Comments Condens. Matter Phys. **16**, 1 (1992).
- <sup>4</sup>G. S. Bales and D. C. Chrzan, Phys. Rev. B 50, 6057 (1994).
- <sup>5</sup>J. A. Stroscio and D. T. Pierce, Phys. Rev. B 49, R8522 (1994).
- <sup>6</sup>J. G. Amar and F. Family, Phys. Rev. Lett. **74**, 2066 (1995).
- <sup>7</sup>P. A. Mulheran and J. A. Blackman, Phys. Rev. B **53**, 10261 (1996).
- <sup>8</sup>C. Ratsch, M. F. Gyure, S. Chen, M. Kang, and D. D. Vvedensky, Phys. Rev. B **61**, R10598 (2000).
- <sup>9</sup>J. W. Evans and M. C. Bartelt, J. Vac. Sci. Technol. B **12**, 1800 (1994).
- <sup>10</sup>Y. W. Mo, J. Kleiner, M. B. Webb, and M. G. Lagally, Phys. Rev. Lett. **66**, 1998 (1991).
- <sup>11</sup>W. Xiao, P. A. Greaney, and D. C. Chrzan, Phys. Rev. Lett. **90**, 156102 (2003).
- <sup>12</sup>T. R. Linderoth, J. J. Mortensen, K. W. Jacobsen, E. Laegsgaard, I. Stensgaard, and F. Besenbacher, Phys. Rev. Lett. **77**, 87 (1996).
- <sup>13</sup>J. G. Amar, F. Family, and D. C. Hughes, Phys. Rev. E 58, 7130 (1998).
- <sup>14</sup>J. A. Venables, Rep. Prog. Phys. 47, 399 (1984).
- <sup>15</sup>W. Xiao, P. A. Greaney, and D. C. Chrzan, Phys. Rev. B 70, 033402 (2004).
- <sup>16</sup>P. A. Greaney, Ph.D. thesis, University of California at Berkeley, 2003.
- <sup>17</sup>P. H. Dederichs and K. Schroeder, Phys. Rev. B 17, 2524 (1978).
- <sup>18</sup>M. Karimi, T. Tomkowski, G. Vidali, and O. Biham, Phys. Rev. B 52, 5364 (1995).

- <sup>19</sup>U. Kürpick and T. S. Rahman, Phys. Rev. B **59**, 11014 (1999).
- <sup>20</sup>T. Vicsek, *Fractal Growth Phenomena* (World Scientific, Singapore, 1989).
- <sup>21</sup>M. N. Popescu, J. G. Amar, and F. Family, Phys. Rev. B **64**, 205404 (2002).
- <sup>22</sup>J. G. Amar, M. N. Popescu, and F. Family, Surf. Sci. **491**, 239 (2001).
- <sup>23</sup>F. Family, M. N. Popescu, and J. G. Amar, Physica A **306**, 129 (2002).
- <sup>24</sup>C. Heyn, Phys. Rev. B **63**, 033403 (2001).
- <sup>25</sup>B. D. Hughes, *Random Walks and Random Environments* (Oxford University Press, New York, 1995), Vol. 1.
- <sup>26</sup>C. Ratsch, M. C. Wheeler, and M. F. Gyure, Phys. Rev. B 62, 12636 (2000).
- <sup>27</sup>P. A. Greaney and D. C. Chrzan (unpublished).
- <sup>28</sup>O. V. Bychuk and B. O'Shaughnessy, Phys. Rev. Lett. **74**, 1795 (1995).
- <sup>29</sup>This is diffusion with long jumps in which the second moment of the probability distribution,  $P(\Delta x)$ , of a jump of length  $\Delta x$  is not finite.
- <sup>30</sup>The straight and "L" shaped trimer configurations are degenerate; their relative abundance is calculated from the transition rates between forms.
- <sup>31</sup>This is not the case for random walks on homogeneous lattices with dimensions larger than two (Ref. 25).
- <sup>32</sup>Strictly speaking this is a Lévy flight as each jump is assumed to happen instantaneously.
- <sup>33</sup>As  $d_c \rightarrow \infty$  the isotropic hopping diffusion tensor  $D_h \rightarrow D_0/\lambda^2$ , and the increased area searched with each crowdion jump only scales linearly with  $d_c$ .