

Diffusion in Potential Fields: Time-Dependent Capture on Radial and Rectangular Substrates

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ABSTRACT

In rate equation models of nucleation and growth on surfaces, and it has often been assumed that the energy surface of the substrate is flat, that diffusion is isotropic, and that capture numbers can be calculated in the diffusion-controlled limit. We lift these restrictions analytically, and illustrate the results using a hybrid discrete FFT method of solving for the 2D time-dependent diffusion field of ad-particles, which has been implemented in Matlab[®] 6.5. A general substrate energy surface is included by transformation of the field. The method can work with any boundary conditions, but is particularly clear for periodic boundary conditions, such as might be appropriate following nucleation on a regular (rectangular) array of defects. The method is instructive for visualizing potential and diffusion fields, and for demonstrating the time-dependence of capture numbers in the initial stages of deposition and annealing.

INTRODUCTION

Diffusion and capture processes involved in nucleation and growth on surfaces have received widespread attention over the last thirty-five years [1, 2]. Scanning tunneling microscopy (STM) and field ion microscopy (FIM) experiments are able to follow atomic-level events, and to measure energies for individual activated processes. Over the last few years, it has become clear that capture of adatoms cannot always be treated in the diffusion-controlled limit. Analyses have been presented of low-temperature STM data on close-packed metal surfaces [3-5], in which repulsive interactions, between diffusing adatoms and other adatoms and clusters, causes capture rates to be reduced, sometimes substantially [6,7]. Progress in this area has been reviewed [7, 8], where more background information and references can be found.

In this paper, we have two aims. The first is to treat diffusion and capture on a substrate that has a non-uniform potential for diffusing ad-particles, analytically. This potential is defined with respect to an origin in the 2-dimensional (2D) space of the substrate, and so is written $V(\mathbf{r})$. The object at the origin can be a cluster, a defect site, or another (diffusing) ad-particle. The second aim is to illustrate numerical time-dependent solutions for the diffusion field in both radial and rectangular geometry, the latter case with anisotropic diffusion coefficients [9]. We adapt a new algorithm [10] to this rectangular case, and show how the processes taking place at the cluster edges influence the simulated growth of 2D quasi-rectangular clusters arranged on a lattice.

DIFFUSION IN 2D POTENTIAL FIELDS: ANALYTIC FORMULATION

We are interested in solutions of a 2D diffusion equation for the ad-particle concentration $c(\mathbf{r}, t)$, when there may be sources and sinks at various positions. The simplest case to think about is when we have a loss term governed by a characteristic mean lifetime τ . The governing partial differential equation (PDE) is then

$$\partial c(\mathbf{r})/\partial t = G - c(\mathbf{r})/\tau - \nabla \cdot \mathbf{j}(\mathbf{r}), \quad (1)$$

where $\mathbf{j}(\mathbf{r})$ is the diffusive flux at position \mathbf{r} . In the epitaxial growth literature [1,2,7,8], the source term G is equal to the deposition flux F during deposition and is typically zero during annealing, and the ad-particle concentration may be variously described as c , n , or n_1 .

In the absence of a potential field, the flux term $\mathbf{j}(\mathbf{r})$ is defined as $-D\nabla c(\mathbf{r})$, where D is the *chemical* diffusion constant. Thus the last term in (1) is equal to $D\nabla^2 c(\mathbf{r})$ if D is indeed constant; but on an anisotropic substrate, the general form of D is a second rank tensor [9], and there is no absolute reason for D to be independent of position or of time. Equation (1) has been solved for constant D in various approximations to determine the growth rate of clusters by capture of ad-particles on surfaces. The case when τ is finite (i.e. $\tau^{-1} > 0$) is a general way of introducing competing loss processes, such as re-evaporation, or capture by other clusters, in the *uniform depletion*, or mean-field approximation [1,7,11,12]. The other limiting possibility is to omit this term (i.e. $\tau^{-1} = 0$), but to arrange the clusters on a lattice and use appropriate boundary conditions. This *lattice* approximation to capture numbers was developed for radial symmetry by Halpern, Lewis, Stowell and others [1,13]. The search for realistic intermediate expressions, taking into account cluster sizes and positions during deposition or annealing, is an ongoing research problem that has been reviewed recently [8] but is not pursued further here.

Diffusion in a potential field obeys the Nernst-Einstein equation [14], and the resulting advection-diffusion equations for the ad-particle concentration show, in general, both diffusion and drift [10]. We show that previous results in the 2D nucleation and growth literature [6, 7] correspond to this type of equation and solutions. With non-zero $V(\mathbf{r})$ we need to evaluate the response to concentration ($\nabla c(\mathbf{r})$) and potential ($\nabla V(\mathbf{r})$) gradients, via consideration of phenomenological transport coefficients, which leads to a more general definition of $\mathbf{j}(\mathbf{r})$ in terms of the gradient of the chemical potential, $\nabla\mu(\mathbf{r})$. This definition can be written in terms of either D , the *chemical* or D^* , the *tracer* diffusion coefficient. Under certain reasonable conditions [7, 14], $(D/D^*) = \beta(\delta\mu/\delta(\ln(c)))$. The simplest expression for $\mathbf{j}(\mathbf{r})$, using this ratio, is

$$\mathbf{j}(\mathbf{r}) = -(D^*c)\beta\nabla\mu. \quad (2)$$

We now need the expression for $\mu(\mathbf{r})$ for a non-ideal adsorbed gas of ad-particles, which is $\mu(\mathbf{r}) = \mu_0 + V(\mathbf{r}) + \beta^{-1}\ln(\gamma c)$, where γ is the activity. For this form of $\mu(\mathbf{r})$, the original definition of $\mathbf{j}(\mathbf{r})$ can be written as [7]

$$\mathbf{j}(\mathbf{r}) = -(Dc)(1+\delta\ln(\gamma)/\delta(\ln(c)))^{-1}\beta\nabla\mu; \quad (3)$$

the term $(1+\delta\ln(\gamma)/\delta(\ln(c)))$ is known as the thermodynamic factor.

Pooling the above expressions, we find that

$$\mathbf{j}(\mathbf{r}) = -D\nabla c(\mathbf{r}) - (c(\mathbf{r})D^*)\beta\nabla V(\mathbf{r}). \quad (4)$$

The derivative of $\gamma(\mathbf{r})$ is needed to obtain D in the first term in equation (4), but D^* remains in the second term. Moreover, if we assumed $\gamma(\mathbf{r}) = \gamma$ in the model, the thermodynamic factor would be unity, so that D and D^* would be the same; thus solutions for low concentrations are undoubtedly simpler. In particular, we are concerned here with solving the capture problem for reasonable forms of the dimensionless potential $\beta V(\mathbf{r})$, for example due to adatom-adatom, or adatom-cluster repulsion. Using equation (4), equation (1) becomes

$$\partial c(\mathbf{r})/\partial t = G - c(\mathbf{r})/\tau + \nabla \cdot (D\nabla c(\mathbf{r})) + \nabla \cdot ((c(\mathbf{r})D^*)\beta\nabla V(\mathbf{r})). \quad (5)$$

Note that although the \mathbf{r} -dependence is written out explicitly for c and V and there is an implied time-dependence, the ‘constants’ G , τ , D and D^* may also be functions of position (e.g. via concentration or a diffusion energy), or in the cases of G , τ , of time (e.g. during deposition or annealing), without changing equation (5).

The remainder of this paper is concerned with solving equation (5) in various approximations, to illustrate relevant physical situations in radial and rectangular geometries. There are no analytic solutions for the general form of equation (5), even in radial geometry. But we can expand the last two terms to obtain

$$\partial c(\mathbf{r})/\partial t = G - c(\mathbf{r})/\tau + D\nabla^2 c(\mathbf{r}) + \mathbf{A}\cdot\nabla c(\mathbf{r}) + \mathbf{B}\cdot\nabla(\beta V(\mathbf{r})). \quad (6)$$

The first four terms of equation (6) are the same as those derived from equation (1) in the absence of a potential field. The last two terms depend on the gradient of the concentration $c(\mathbf{r})$ and of the potential, where $\beta = (kT)^{-1}$ makes the variable $\beta V(\mathbf{r})$ dimensionless. The magnitude of these two terms are controlled by gradient vector operators \mathbf{A} and \mathbf{B} , in the scalar product form

$$\mathbf{A}\cdot = (\nabla D + D^*\nabla(\beta V(\mathbf{r})))\cdot; \quad \mathbf{B}\cdot = (c(\mathbf{r})\nabla D^* + c(\mathbf{r})D^*\nabla)\cdot. \quad (7)$$

The combination of equations (6) and (7) represent the most general equation we wish to consider. The extra terms given by (7) mean that equation (6) is a type of advection-diffusion equation, in which diffusion coexists with drift along concentration and potential gradients. Depending on the model details, we may wish to consider fixed or moving boundary conditions.

DISCRETIZATION OF ADVECTION-DIFFUSION EQUATIONS

There are several simplifications to equation (6) that may be appropriate. Perhaps the most obvious is to separate out the effects of concentration on diffusion coefficients, by writing $(D/D^*) = f_i(c)$, where $f_i(c)$ is the thermodynamic factor. For low concentration, $f_i(c) = 1$, and hence there is only one diffusion coefficient, notionally the tracer diffusion coefficient, which we write as $D^* = D_1$ to avoid confusion. However, D_1 can still be a function of position.

In the more restrictive limit that D_1 is constant, the terms ∇D and ∇D^* in equations (7) will disappear, leaving the extra terms in equation (6) of the form

$$\mathbf{A}\cdot\nabla c(\mathbf{r}) + \mathbf{B}\cdot\nabla(\beta V(\mathbf{r})) = D^*\nabla(\beta V(\mathbf{r}))\cdot\nabla c(\mathbf{r}) + (c(\mathbf{r})D^*\nabla^2(\beta V(\mathbf{r}))); \quad (8a)$$

this equation can be rearranged as

$$\mathbf{A}\cdot\nabla c(\mathbf{r}) + \mathbf{B}\cdot\nabla(\beta V(\mathbf{r})) = D_1\nabla[c(\mathbf{r})\cdot\nabla(\beta V(\mathbf{r}))]. \quad (8b)$$

If $D^* \neq D$ the remaining terms, the difference between the last two terms of equation (6) and those in equation (8) are cross-terms involving the gradients of the diffusion coefficients, namely

$$C = \nabla D\cdot\nabla c(\mathbf{r}) + c(\mathbf{r})\nabla D^*\cdot\nabla(\beta V(\mathbf{r})). \quad (9)$$

We can see that C may well be small, based on the following argument. If the potential effects are large, then $c(\mathbf{r})$ will be dominated by equilibrium effects, such that $c(\mathbf{r}) \cong c_0 \exp(-\beta V(\mathbf{r}))$, where c_0 is a constant. Thus $\nabla c(\mathbf{r}) \cong -c(\mathbf{r})\nabla(\beta V(\mathbf{r}))$, and equation (9) can be written

$$C \cong -c(\mathbf{r})(\nabla D - \nabla D^*)\cdot\nabla(\beta V(\mathbf{r})). \quad (10)$$

Thus C vanishes at low concentration, where $D^* = D$, and corresponds approximately to an extra contribution to the loss term $-c(\mathbf{r})/\tau$ in equation (6) in the general case. This means that we do not need to consider equation (9) separately, and we will neglect it for the moment.

The numerical solution of advection-diffusion equations (ADEs) has a long history, but recently a new algorithm has been developed that is very efficient in solving equations of this type. Grima and Newman [10] considered ADEs of the general form

$$\partial c(\mathbf{r})/\partial t = \nabla\cdot(D\nabla c(\mathbf{r})) - \nabla\cdot(c(\mathbf{r})\mathbf{v}(\mathbf{r})), \quad (11)$$

where the velocity field $\mathbf{v}(\mathbf{r})$ can depend on the concentration $c(\mathbf{r})$. The velocity field can be specialized to be proportional to a potential gradient as $\mathbf{v}(\mathbf{r}) = -\alpha\nabla V(\mathbf{r})$ [15]. With this constraint, the last term of equation (11) corresponds exactly to equation (8b), with $D_1 = \alpha/\beta$.

The main algorithm proposed in [10] was called Master Equation Discretization (MED). It is based on an exponential variable transformation that turns equation equation (11), via two

Laplacians, into the form of a master equation. A general solution was given for 1D ADEs of the form (11) and this was generalized to all dimensions for the case considered here. Equation (11) was then shown to be equivalent to

$$\partial c(\mathbf{r})/\partial t = D_1[(E^{-1})\nabla^2(c(\mathbf{r})E) - (c(\mathbf{r})E)\nabla^2(E^{-1})], \quad (12)$$

in our notation, where $E = \exp(\gamma V(\mathbf{r}))$ and $\gamma = \alpha/2D_1$. Since, for our application, we have shown that $D_1 = \alpha/\beta$, the exponential involved in the transformation is $E = \exp(\beta V(\mathbf{r})/2)$.

The discretization of equation (12) is especially simple because the Laplacians can be expressed as sums of the relevant quantities over neighboring lattice points on a grid. As shown in [10], this results in the MED for the grid point concentration c_i in the form

$$\partial c_i / \partial t = \sum_j [W_{j \rightarrow i} c_j - W_{i \rightarrow j} c_i], \quad (13)$$

where in the special case we are considering, the transition probabilities, or hopping rates $W_{i \rightarrow j}$ are given on a lattice of size a , for nearest neighbors (i and j) only, by

$$W_{i \rightarrow j} = (D_1 / a^2) \exp\left[\beta(V_i - V_j) / 2\right]. \quad (14)$$

The results presented here are based on this MED algorithm. However, in detail, we used a hybrid FFT method, in which the local average diffusion terms were solved by the FFT method in reciprocal space, while the local difference diffusion terms were applied in real space at each time step. This method satisfies the particle conservation sum rule for zero potential [9]; for finite $V(\mathbf{r})$ this rule is not quite satisfied, but the method is very stable and fast for all reasonable time steps.

CAPTURE NUMBERS IN RADIAL AND RECTANGULAR GEOMETRY

Two modeling papers have been published on the effect of repulsive potential fields on capture numbers in the context of nucleation and growth on surfaces [6, 7]. In the first, Ovesson [6] used a 2D square lattice and argued on physical grounds that the energy of each diffusive jump, the transition state energy, would be augmented by half the potential energy difference between the final and the initial sites. In our notation, the diffusion constant for transitions between sites i and j was modified from D_1 to $D_1(\exp(-\beta(V(\mathbf{r}_i) - V(\mathbf{r}_j))/2))$. The continuum limit was taken, and then this model was applied with radial symmetry. He showed that the effect was the same as replacing the term $\nabla^2(c(\mathbf{r}))$ in the usual diffusion equation by $\nabla^2(c(\mathbf{r})) + \nabla(\beta V(\mathbf{r})) \cdot \nabla c(\mathbf{r}) + c(\mathbf{r})\nabla^2(\beta V(\mathbf{r}))$. These two terms are the same as those appearing in equations (8) and can therefore be lumped together as $\nabla[c(\mathbf{r}) \cdot \nabla(\beta V(\mathbf{r}))]$, corresponding to equation (8b). Ovesson [6] used his procedure to calculate mean field nucleation densities with a specific form of $V(r)$, constructed to mirror recent low-temperature STM data on close-packed metal surfaces [3-5]. Venables and Brune [7] developed a continuum approach based on equations (4) and (5), again in radial geometry, and obtained mean field capture numbers, which can be exponentially reduced. Here, we show that time-dependent capture numbers can be calculated for rectangular geometry with general repulsive potentials $V(\mathbf{r})$.

Figure 1(a) shows the concentration profile which is initially in equilibrium under a 2D anisotropic Gaussian repulsive potential, with maximum value of $\beta V(\mathbf{r})$, $\beta V_m = 2.5$. At the center of the field is the 5×11 island that acts as a sink. The capture numbers shown in figure 1(b) have strongly reduced values relative to the case of zero potential. The absence of the spikes in the

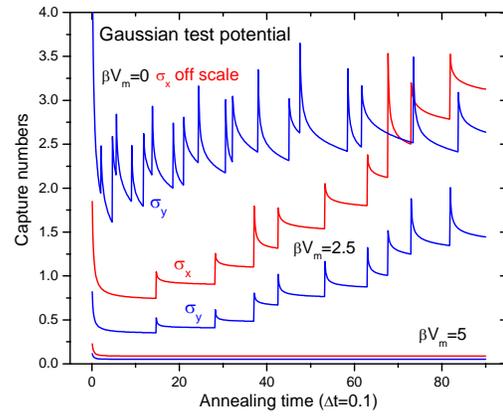
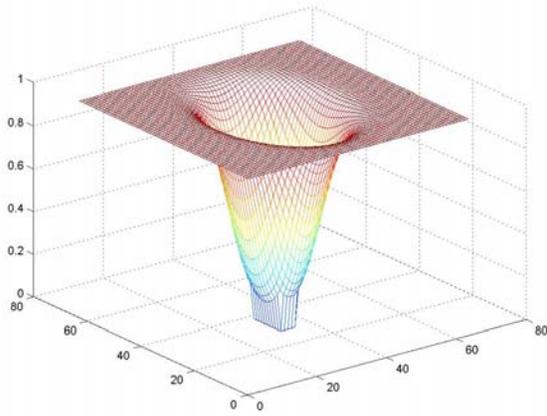


Figure 1: a) Concentration profile, initially in equilibrium under a Gaussian test potential; b) Capture numbers σ_x (red lines) and σ_y (blue lines) for an initial 5×11 rectangular island (height $h = 5$), and $\beta V(\mathbf{r}) = 0, 2.5$ and 5 , to compare with ref [9], figure 4(b) for $V(\mathbf{r}) = 0$.

curves for $\beta V_m = 5$ means that essentially no growth occurred during the whole annealing period to $t = 90$. This can be directly compared with ref [9], figure 4(b) for $V(\mathbf{r}) = 0$.

Figure 2(a) shows a rectangular potential approximating to the strain distribution around a 5×11 rectangular island. Here the potential is much “rougher” and more anisotropic, leading to a more challenging test of the numerical method. For the hybrid FFT method, the sum rules are not quite as well satisfied as in figure 1, indicating a larger ratio of drift to diffusion terms at the edge of the island. Physically, though, we notice that the capture number stays low, because as the island size is updated, the potential field gets stronger, in contrast to figure 1, where it effectively weakens. This situation is more realistic for strained epitaxial islands, e.g. for Ge/Si(001).

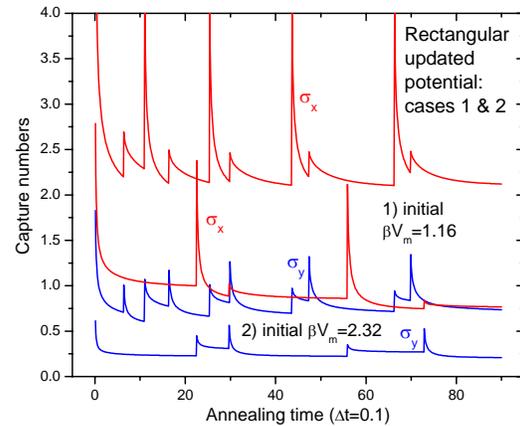
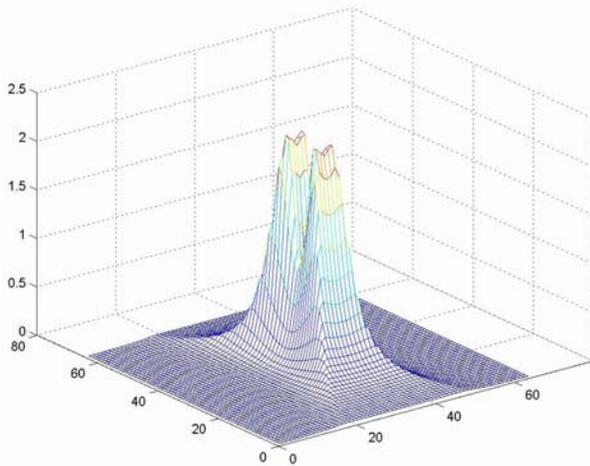


Figure 2: a) Initial rectangular potential for case 2, with initial maximum $\beta V_m = 2.32$ at the edge of the 5×11 island; b) capture numbers σ_x (red lines) and σ_y (blue lines) with no corner crossing, for this potential, as a function of annealing time, starting from the equilibrium distribution. Note that the potential is recalculated every time the island size changes.

An intriguing point is that Ovesson [6] and Grima and Newman [10] have studied the same problem from opposite ends. Grima and Newman started from the general continuum equation (11), and arrived at their MED as a very efficient numerical method of solving this whole class of problems. The present discussion shows that, for constant diffusion constants, the two approaches are completely equivalent, and can be represented concisely by equation (12). But their general approach [10] will work in any geometry, and thus we can proceed with confidence into new areas of application.

In conclusion, we have set out the differential equations needed to solve for capture numbers in the presence of general potential fields. A new algorithm has been introduced to the epitaxial growth community [10]. The numerical solution of these equations has been demonstrated using a hybrid FFT method in rectangular geometry. Further work is in progress to compare these numerical methods in some detail, and to establish realistic potentials for systems such as hut clusters on Ge/Si(001) and the growth of nanowires [9, 16].

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15. In ref. [10], the same case is considered, but the velocity $\mathbf{v}(\mathbf{r}) = +\alpha\nabla\Phi(\mathbf{r})$, where $\Phi(\mathbf{r})$ is a general scalar field. Here $\mathbf{v}(\mathbf{r})$ is directed down the potential gradient $\nabla V(\mathbf{r})$.
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