Self-consistent rate theory of submonolayer homoepitaxy with attachment/detachment kinetics

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The reversible nucleation and growth of two-dimensional islands during the submonolayer stage of epitaxial growth is studied with self-consistent rate equations and kinetic Monte Carlo simulations. In contrast to most previous work, we take account of the effects of both a finite energy barrier to the detachment of atoms from islands and a finite barrier to the incorporation of adatoms into islands. A correct boundary condition for the diffusion field at island edges is derived that takes account of these processes. For small detachment rates, quantitative agreement is obtained between the solutions to the rate theory and the simulations for the average monomer and island densities as a function of coverage. [S0163-1829(97)50404-8]

Scanning tunnelling microscopy studies[1] have generated renewed interest[2] in the rate equation description[3] of submonolayer homoepitaxial growth. The qualitative correctness of such rate theories was established long ago. But recently, Bales and Chrzan[4] were able to show that a self-consistent form of this theory[5] actually yields *quantitative* agreement for adatom and average island densities as a function of coverage when compared to kinetic Monte Carlo simulations that include deposition, single adatom diffusion, and irreversible aggregation to growing islands. Given this success, it is natural to inquire whether similar results can be obtained for the case of *reversible* aggregation, i.e., situations where the detachment of atoms from the perimeter of islands of any size is permitted. That is the purpose of the present work.

We begin with the rate equation analysis. The dynamical variables are the average areal densities of two-dimensional (2D) islands composed of s atoms $\langle n_s \rangle$. When detachment processes can occur,[6] the equation of motion for the adatom density is

$$\frac{d\langle n_1 \rangle}{dt} = F\left(1 - 2\kappa_1\langle n_1 \rangle - \sum_{s\geq 2}\kappa_s\langle n_s \rangle\right) - 2D\sigma_1\langle n_1 \rangle^2$$
$$- D\sum_{s\geq 2}\sigma_s\langle n_s \rangle\langle n_1 \rangle + 2\frac{\langle n_2 \rangle}{\tau_2} + \sum_{s\geq 3}\frac{\langle n_s \rangle}{\tau_s} \quad (1)$$

while those for the density of two-dimensional islands of size $s \geq 2$ are

$$\frac{d\langle n_s \rangle}{dt} = F(\kappa_{s-1}\langle n_{s-1} \rangle - \kappa_s\langle n_s \rangle) + D(\sigma_{s-1}\langle n_{s-1} \rangle$$
$$- \sigma_s\langle n_s \rangle)\langle n_1 \rangle - \frac{\langle n_s \rangle}{\tau_s} + \frac{\langle n_{s+1} \rangle}{\tau_{s+1}}. \quad (2)$$

In these formulas, F is the deposition rate, D is the adatom diffusion constant, κ_s is the rate at which an island of size s captures atoms deposited directly onto itself, τ_s^{-1} is the mean rate at which atoms escape from an island of size s

after detachment, and the capture number σ_s is a measure of the efficiency with which an island of size s captures atoms from the monomer population.

Since the ratio D/F emerges naturally as a control parameter in scaling analyses of Eq. (1) and Eq. (2) (Refs. 2,3,6) we focus here on the other rate coefficients defined there. The geometrical assignment

$$\kappa_s = s \quad (3)$$

for the direct impingement factors is expected to be valid when the transport of atoms to the perimeter of islands upon which they land is rapid compared to the rate at which the islands gather atoms deposited directly onto the substrate. In practice,[4] this is true for coverages up to the precoalescence regime of island density saturation in the absence of a large energetic barrier[7] to the downward motion of atoms over step edges.

The treatment of the capture numbers is more subtle. A self-consistent mean-field treatment[4] begins by writing a diffusion-reaction equation for the adatom density $n_1(\mathbf{r},t)$ outside of a typical (circular) island of radius R_s:

$$\frac{\partial n_1}{\partial t} = D\nabla^2 n_1 + \mathcal{J} - D\xi^{-2}n_1, \quad (4)$$

where by comparison with Eq. (1),

$$\mathcal{J} = F\left(1 - \sum_{s=1}\kappa_s\langle n_s \rangle\right) + 2\frac{\langle n_2 \rangle}{\tau_2} + \sum_{s\geq 3}\frac{\langle n_s \rangle}{\tau_s} \quad (5)$$

and

$$\xi^{-2} = (F/D)\kappa_1 + 2\sigma_1\langle n_1 \rangle + \sum_{s\geq 2}\sigma_s\langle n_s \rangle. \quad (6)$$

Now subtract Eq. (1) from Eq. (4) and assume that the quantity $n_1 - \langle n_1 \rangle$ is stationary to obtain

$$\nabla^2 n_1(\mathbf{r}) - \xi^{-2}[n_1(\mathbf{r}) - \langle n_1 \rangle] = 0. \quad (7)$$

The radially symmetric solution to the Helmholtz equation [Eq. (7)] that satisfies the boundary condition,

$$\lim_{r \to \infty} n_1(\mathbf{r}) = \langle n_1 \rangle, \tag{8}$$

is

$$n_1(r) = \langle n_1 \rangle - A K_0(r/\xi), \tag{9}$$

where K_0 is the modified Bessel function of order zero and A is a constant determined by the boundary condition to Eq. (7) at the island edge $r = R_s$.

The boundary condition at the island edge is obtained from a mass balance argument. A microscopic form for the flux at the edge of an average island of size s is set equal to the macroscopic flux proportional to the gradient of the adatom density from Eq. (9), i.e.,

$$2\pi R_s D \left. \frac{\partial n_1}{\partial r} \right|_{R_s} = m_s G_s n_1(R_s + a) - \frac{\omega_{s+1} \langle n_{s+1} \rangle}{\langle n_s \rangle}, \tag{10}$$

where ω_s is the rate at which atoms detach from an island of size s, $G_s = D e^{-\Delta_s/kT}$ is the rate at which atoms join an island of size s along any of the m_s paths that connect next-nearest-neighbor sites to nearest-neighbor sites adjacent to the island (for large islands $m_s \to 2\pi R_s/a$), and $n_1(R_s + a)$ is the density of adatoms at such sites. The quantity Δ_s accounts for the possibility that the energy barrier to adatom incorporation into an island may differ from the adatom diffusion barrier. Note that an adatom which contributes to the outgoing rate [last term in Eq. (10)] from an island of size s necessarily detached for an island of size $s+1$. The total outgoing rate per unit area is $w_{s+1} \langle n_{s+1} \rangle$. One then divides by $\langle n_s \rangle$ to obtain the average rate per island of size s.

Equation (10) takes the form of a true boundary condition whenever $n_1(R_s + a) = n_1(R_s) + a(\partial n_1/\partial r)|_{R_s}$ is an adequate approximation:

$$(2\pi R_s D - a m_s G_s) \left. \frac{\partial n_1}{\partial r} \right|_{R_s} = m_s G_s n_1(R_s) - \frac{\omega_{s+1} \langle n_{s+1} \rangle}{\langle n_s \rangle}. \tag{11}$$

The alternate form

$$\left. \frac{\partial n_1}{\partial r} \right|_{R_s} = \beta_s [n_1(R_s) - n_{eq}(R_s)] \tag{12}$$

follows from the observation that

$$n_{eq}(R_s) = \frac{\omega_{s+1} \langle n_{s+1} \rangle}{m_s G_s \langle n_s \rangle} \tag{13}$$

is the concentration of adatoms in equilibrium with an island of size s and the definition of

$$\beta_s^{-1} = (2\pi R_s/m_s) e^{\Delta_s/kT} - a \tag{14}$$

for the step kinetic coefficient. In contrast to Chernov's prescription,[8] Eq. (12) reduces to

$$n_1(R_s) = n_{eq}(R_s) \tag{15}$$

in the limit of no attachment barrier ($\Delta_s = 0$). Of course, the usual perfect sink condition $n_1(R_s) = 0$ is recovered when the detachment rate vanishes.

The constant A in Eq. (9) is found using Eq. (12) from which the net rate is computed to be

$$2\pi R_s D \left. \frac{\partial n_1}{\partial r} \right|_{R_s} = \frac{2\pi R_s D K_1(s)}{\beta_s^{-1} K_1(s) + \xi K_0(s)} [\langle n_1 \rangle - n_s(\text{eq})], \tag{16}$$

where the shorthand notation $K_0(s) \equiv K_0(R_s/\xi)$ and $K_1(s) \equiv K_1(R_s/\xi)$ has been introduced for the Bessel functions. One can also express Eq. (16) in terms of the capture number σ_s and escape rate τ_{s+1} directly from the rate equations. This gives a single equation

$$\frac{2\pi R_s D K_1(s)}{\beta_s^{-1} K_1(s) + \xi K_0(s)} [\langle n_1 \rangle - n_s(\text{eq})]$$

$$= D\sigma_s \langle n_1 \rangle - \frac{\langle n_{s+1} \rangle}{\tau_{s+1} \langle n_s \rangle} \tag{17}$$

from which to extract two coefficients. One can show that the choice of σ_s and τ_{s+1} is arbitrary as long as Eq. (17) is satisfied. It is conventional[5] and convenient to choose the capture number to be independent of the microscopic detachment rate by equating the first term on both sides of Eq. (17). Hence,

$$\sigma_s = \frac{2\pi R_s K_1(s)}{\beta_s^{-1} K_1(s) + \xi K_0(s)}. \tag{18}$$

With this choice for the capture number, τ_s^{-1} must satisfy

$$\frac{1}{\tau_s} = \frac{\omega_s \sigma_{s-1}}{m_{s-1} e^{-\Delta_{s-1}/kT}}. \tag{19}$$

Note that Eq. (18) reduces to the capture number expression for irreversible growth[4,5] when $\beta_s \to \infty$, i.e., large islands with no attachment barrier, while $\sigma_s \to \beta_s 2\pi R_s$ when $\Delta_s \to \infty$.

All effects of detachment are carried through τ_s^{-1} which in the above formulation becomes the rate at which detached atoms escape into the effective medium without returning. Equation (19) correctly reflects the fact that an atom that detaches from an island of size s either returns to the island or escapes to infinity in the diffusion field of an island of size $s-1$.

Equations (1), (2), (3), (18), and (19), together constitute our self-consistent rate theory for reversible island growth in the precoalescence regime. For a practical application, it remains only to specify the ratio D/F and the functions ω_s and R_s. We do this below for a simple model of homoepitaxy. However, for the purpose of testing our rate theory against kinetic Monte Carlo (KMC) simulation, the precise choice of detachment rates is not important so long as they are chosen the same in both.

Popular homoepitaxial growth models[9,10] employ atomic detachment rules that depend on local bonding geometry rather than island size. Such rules naturally generate dynamically evolving island morphologies for which the average detachment rates ω_s are difficult to estimate. However, for
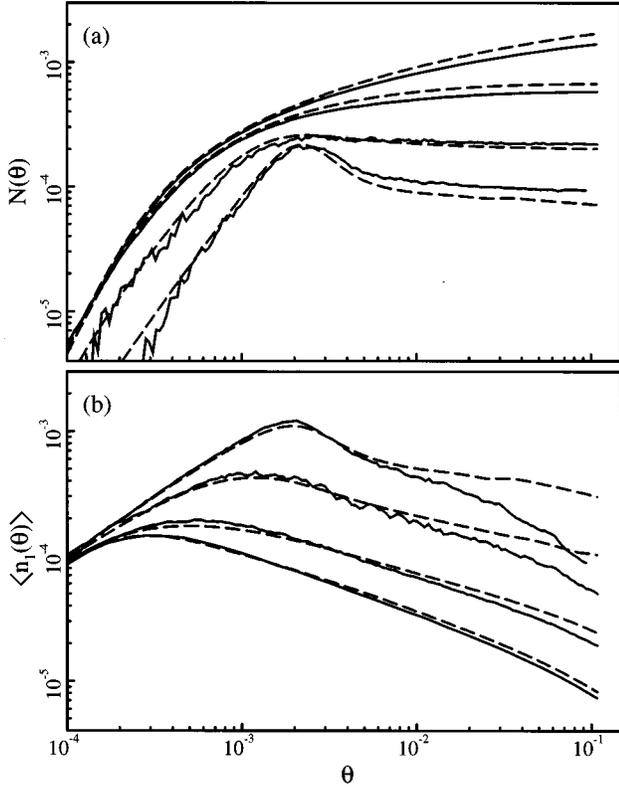
FIG. 1. Comparison of KMC (solid lines) with rate theory (dashed lines). For panel a (b), ω_0 varies from the top (bottom) curve to bottom (top) curve as 0.0, 3×10^{-6}, 3×10^{-5}, and 1.6×10^{-4}, respectively.

FIG. 2. Comparison of KMC (solid lines) with rate theory (dashed lines) for the total number density N (squares) and monomer density $\langle n_1 \rangle$ (circles) versus ω_0 at a fixed coverage of 0.1 ML.

large compact islands and slow growth rates the adatom density essentially satisfies the Gibbs-Thomson relation.[11] Since Eq. (13) is valid in this limit, it will be the case that

$$\omega_s = 2\pi R_s D n_\infty \exp(\Gamma/R_s), \tag{20}$$

where n_∞ is the density of adatoms in equilibrium with a straight step and Γ is a constant. Accordingly, we *legislate* that Eq. (20) shall be the detachment rate for islands of all sizes in both the KMC simulations and the rate equation analysis. Other choices may be more suitable to model other situations such as heteroepitaxy.[12]

The rules of the simulation are (i) atoms are deposited randomly onto the sites of a square lattice of size 500×500 at a rate F; (ii) adatoms on the bare substrate migrate to nearest-neighbor sites at a rate $4D/a^2$; (iii) a new island is created when two adatoms collide; (iv) adatoms that reach the perimeter of an island by diffusion from the substrate and atoms that are deposited on top of an island are instantly transported to the perimeter site that is closest to the island center; (iv) atoms on the perimeter that lay farthest from the island center detach at a rate ω_s and are placed onto a next-nearest-neighbor site of the substrate; (v) atoms cannot jump up onto the top of islands or desorb from the substrate.

Rule (iv) guarantees that the islands will be as circular as possible. This minimizes the uncertainty for the choice of island radii R_s in the rate equations. Nonetheless, the geometrical choice $R_s = \sqrt{s/\pi}$ turns out to be somewhat inaccurate for small island sizes. Hence, in the present work, we use the empirical form

$$R_s = \sqrt{s} + \sqrt{s/\pi} - \sqrt{1/\pi} \tag{21}$$

that well describes the radius of the nearly circular islands that result from the foregoing simulations rules.

Figure 1 illustrates the coverage $\theta = Ft$ dependence of the adatom density and total island density $N = \Sigma_{s>1} \langle n_s \rangle$ as obtained from the KMC simulations (solid curves) and by numerical integration of the rate equations (dashed curves) for $D/F = 10^7$, $\Delta_s = 0$, $\Gamma = 4$, and four values of $\omega_0 = Dn_\infty$. These parameters were chosen to produce agreement with atomistic simulations we performed similar to those reported in Ref. 10. Note the clear maximum in $N(\theta)$ that develops for large values of ω_0 when the dissociation rate for dimers finally exceeds their birth rate. This feature should be detectable in submonolayer growth experiments at elevated temperatures.

The results of Fig. 1 extend to the case of reversible aggregation the conclusion of Bales & Chrzan[4] that quantitative agreement can be achieved between KMC simulations and self-consistent rate equations for mean homoepitaxial island densities. However, when the detachment rates become large, we have discovered a discrepancy between the two that can be attributed only to an inadequacy of the rate equations. Figure 2 compares our KMC and rate equation results for the total island density at a fixed coverage as a function of the mean detachment rate ω_0. Clearly, the rate equations underestimate the saturated island density in a manner that worsens as the detachment rate increases.

We attribute this effect to the fact that Eqs. (6) and (7) presume that a monomer diffusing in the vicinity of an island of size s encounters a *uniform* density of other islands at all radial distances greater than R_s.[5] But, as is well known, there is actually a depletion zone around each island that is free of islands of any size.[13] Atoms that detach from a parent island cannot be captured immediately by other islands (and hence escape the parent) since they first must traverse the depletion zone. The result is an overestimate of the escape rate τ_s^{-1} that artificially depresses the saturated island density and increases the monomer density. Indeed, preliminary calculations that generalize the formalism presented here to

include this depletion zone effect largely eliminate the discrepancy seen in Fig. 2. These results will be reported in detail elsewhere.[14]

In summary, we have formulated and tested a self-consistent rate equation treatment of two-dimensional island densities during submonolayer homoepitaxy that takes account of atomic detachment from island edges. Correct boundary conditions were derived for a diffusion-reaction equation that describes the density of monomers outside of an island that both captures atoms (with a possible extra barrier to the incorporation process) and releases atoms by detachment. For small detachment rates, quantitative agreement for average densities was obtained between the rate equations and kinetic Monte Carlo simulations. Systematic deviations were observed for higher detachment rates and a probable origin and possible remedy noted.

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