

Rate equations and capture numbers with implicit islands correlations

F. G. Gibou,^{1,2,*} C. Ratsch,^{1,2} M. F. Gyure,² S. Chen,¹ and R. E. Caflisch¹

¹*Department of Mathematics, University of California, Los Angeles, California 90095-1555*

²*HRL Laboratories LLC, 3011 Malibu Canyon Road, Malibu, California 90265*

(Received 16 June 2000; revised manuscript received 23 October 2000; published 22 February 2001)

We introduce a numerical method based on the level-set technique to compute capture numbers used in mean-field rate equations that describe epitaxial growth. In our level-set approach, islands grow with a velocity that is computed from solving the diffusion equation for the adatom concentration. The capture number for each island is then calculated by integrating the growth velocity of an island around the island boundary. Thus, our method by construction includes all spatial correlations between islands. The functional form of the capture numbers σ_s is, to first approximation, affinely dependent on the island sizes. Integration of a completely deterministic set of mean-field rate equations for the first time properly reproduces the correct island densities and cluster size distribution.

DOI: 10.1103/PhysRevB.63.115401

PACS number(s): 81.15.Aa, 81.10.-h

Modeling early stages of epitaxial growth is of great practical interest for material scientists since the surface morphology in the submonolayer regime greatly influences the later stages of the growth process and therefore the properties of a thin-film device. Models to study epitaxial growth that have successfully reproduced such quantities as the cluster size distribution (CSD) of islands on the surface are kinetic Monte Carlo (KMC) methods¹⁻³ or, more recently, the island-dynamics model based on the level-set method.⁴ However, both of these methods include stochastic processes, so that many simulations need to be done (and averages need to be taken) in order to produce physical quantities of interest.

On the other hand, mean-field rate equations, introduced almost 30 years ago,^{5,6} offer a completely deterministic description of epitaxial growth. Such equations for the submonolayer regime (without detachment or evaporation) typically read as

$$\frac{dn_1}{dt} = F - 2D\sigma_1 n_1^2 - Dn_1 \sum_{s>1} \sigma_s n_s, \quad (1)$$

$$\frac{dn_s}{dt} = Dn_1(\sigma_{s-1}n_{s-1} - \sigma_s n_s) \text{ for all } s > 1, \quad (2)$$

where n_s is the density of islands of size s , n_1 is the density of adatoms, D is the diffusion constant, F is the deposition flux, and σ_s are the capture numbers. Clearly, deterministic equations that accurately reproduce the relevant physical quantities would be of great practical value; they usually are easier to understand and analyze, and can yield theoretical insights that cannot be reached within a stochastic framework. For example, nucleation theory predicts scaling of island densities as a function of temperature and deposition flux.⁶ This result has been confirmed in simulations and experiment, and is, in fact, used to extract microscopic parameters such as diffusion constants from experimental measurements.^{7,8} Thus far, however, there has been no success in finding deterministic equations that, when integrated, produce the correct results for quantities that include spatial

information. In particular, no deterministic approach has reproduced the CSD as observed in experiment and KMC simulations.⁹

The main problem with using rate equations in the submonolayer regime is that the functional form for σ_s is not known. Bales and Chrzan¹⁰ proposed an analytical formula in terms of modified Bessel's functions. Their work is based on the *mean-field* assumption which states that at every point outside of an island, the local densities take on their average values, so that the distribution of surrounding islands is independent of its size. The integration of rate equations using this analytical form for the capture numbers gives excellent agreement with KMC simulations for the adatom density and also for the total number density. However, it fails to reproduce the correct cluster size distribution, the reason being that the mean-field assumption excludes correlations between islands.

Bartelt and Evans addressed this issue and numerically computed capture numbers by monitoring the aggregation of diffusive adatoms to the islands using KMC simulations with a point-island model.¹¹ In the steady-state regime, the dependence of the capture numbers on the island size exhibits a plateau for islands smaller than the average size and an affine part for islands bigger than the average size. They then derived an asymptotic limit for the cluster size distribution using the resulting capture numbers and obtained excellent agreement with point-island KMC simulations results. However, the growth and subsequent correlations of islands are omitted in this approach, since a point-island model explicitly excludes this feature. More recent studies^{12,13} that include the spatial extent of islands still reveal a (less pronounced) plateau for the capture numbers. In these simulations, the capture numbers were measured for a fixed coverage and a geometry that was obtained from scanning tunneling microscopy images.

In this article we propose a new numerical method for computation of the capture numbers to remedy these issues. Our approach employs an island-dynamics model based on the level-set method,^{4,14-16} which is a general technique for simulating the motion of moving boundaries. We find that the dependence of the capture numbers on the island size is,

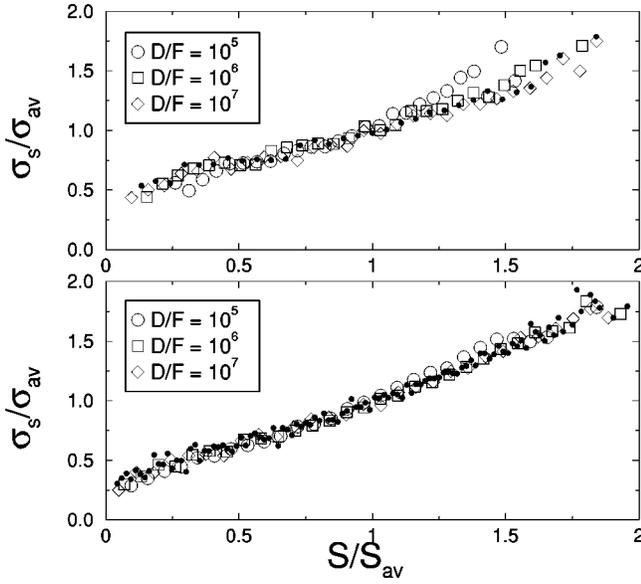


FIG. 1. Capture numbers σ_s as computed by Eq. (3) (open symbols) and by Eq. (4) (solid symbols) versus the islands size, scaled by their respective average. Results shown are at 5% coverage (top) and 20% coverage (bottom), for three different values of D/F .

to first approximation, affine. In particular, there is no plateau as found in previous works.^{11–13} We have confirmed this result by computing the capture numbers self-consistently and have obtained for the first time the correct result for the CSD after integrating the rate equations.

In the level-set method, the boundary of an island is represented as the zero level set of a smooth function ϕ . The evolution of the boundary is then dictated by the evolution of ϕ , which obeys the advection equation $d\phi/dt + v_n|\nabla\phi| = 0$, where v_n is the local normal velocity of the island boundary. In the case of irreversible aggregation $v_n = a^2[D\nabla n_1]$, where $[\cdot]$ refers to the jump across the boundary of the island, and a is the lattice constant. We note here that the seeding of new islands is performed in a probabilistic fashion in the island-dynamics model to ensure the correctness of the CSD as described in Ref. 4.

The capture number of each island is computed by monitoring the rate of aggregation of adatoms to that island. Consider an island of size \bar{s} with boundary $\Gamma_{\bar{s}}$. Growth of this island as described by velocity v_n is due to migration of adatoms toward this island (and subsequent capture), so the rate of aggregation of adatoms is equal to the rate of change in area. This is expressed easily in terms of the level-set function as $\int_{\Gamma_{\bar{s}}} v_n d\Gamma_{\bar{s}}$, so that the capture number of this island is given by

$$\sigma_{\bar{s}} = \frac{\int_{\Gamma_{\bar{s}}} v_n d\Gamma_{\bar{s}}}{Dn_1}. \quad (3)$$

We emphasize that the main originality in this approach is that we allow each island to grow in its own environment and do not use a simple model like the point-island model. So far, the size of any island can change continuously. In order to make comparisons with a discrete model, define a

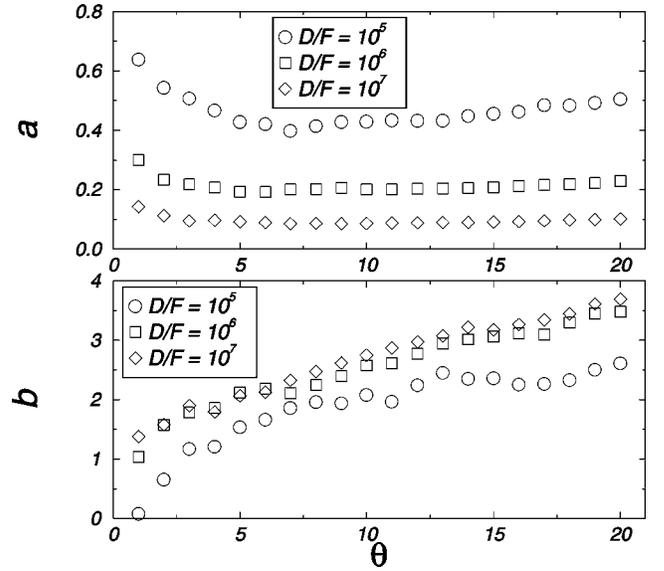


FIG. 2. Coefficients a (top) and b (bottom) in $\sigma_s = as + b$, as a function of coverage θ , for different values of D/F .

bin width $w=1$ so that islands of size s are those islands with sizes $\bar{s} \in [s, s+w)$. Then σ_s is the average of the $\sigma_{\bar{s}}$. For the results shown below, we chose $w > 1$ to reduce the noise in the data. All of our results represent averages over (at least) 50 simulations on a lattice with a lateral size of $L = 200$.

The results for the capture numbers are shown in Fig. 1. We observe scaling in coverage θ and in D/F for the capture numbers as a function of island size, scaled by their respective average. Our results suggest that the capture numbers have the functional form $\sigma_s = as + b$, that is, that they are affinely dependent on the island size. The slope $a(D/F, \theta)$ tends to a steady-state value $a(D/F)$ and attains this limit for a coverage $\theta \geq \theta_0(D/F)$, as shown in Fig. 2. The value of $\theta_0(D/F)$ is smaller for higher values of D/F , consistent with the scaling of the end of the nucleation phase and the beginning of the aggregation phase.¹⁷ The value of the steady-state value $a(D/F)$ is smaller for higher D/F and behaves asymptotically like $a(D/F) = O[(D/F)^{-1/3}]$. The intercept b is, to first approximation, affinely dependent on the coverage as shown in Fig. 2, and is weakly dependent on D/F .

The functional form $\sigma_s = as + b$ can be interpreted by considering the capture zones, whose boundaries are defined as the vertices of the diffusion field. On average, adatoms within a capture zone associated with an island will diffuse toward that island. Using this concept it was shown in Ref. 11 that at steady state

$$\sigma_s = \frac{F}{Dn_1} A_s, \quad (4)$$

where A_s is the average area of the capture zones of islands of size s . This implies that the capture number of an island is proportional to the area of its capture zone. Now, since the size of an island is itself proportional to the area of its capture zone, we would expect to have $\sigma_s = as + b$ (the intercept b corresponds to a point-island model). To check this, we

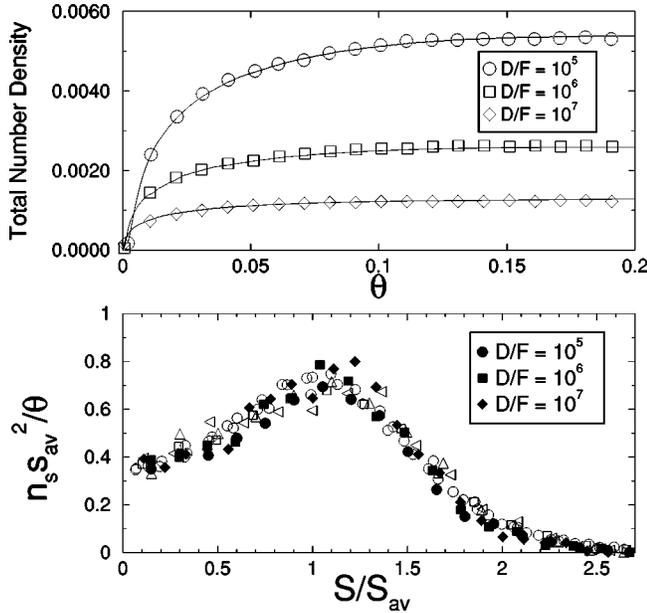


FIG. 3. Top: total number density as a function of coverage for different values of D/F . Bottom: cluster size distribution at 20% coverage for different values of D/F . The solid continuous line (top) and the solid symbols (bottom) are the results of rate equations using the σ_s^{eff} and the open symbols are the results of level-set simulations.

also computed the areas of the capture zones and found excellent agreement between the capture numbers obtained using Eq. (3) and those obtained using Eq. (4), as shown in Fig. 1. We note that the relation between the Voronoi polygonal and the island size has also been studied by Mulheran and Blackman.¹⁸

As an additional check to confirm our results, we also carried out a completely *self-consistent* approach to calculating the capture numbers. Since the number of islands $N_s = L^2 n_s$ is increased every time an island grows to the size s , and decreased every time an island of size s grows to a bigger size, we first rewrite the rate of change of n_s in the following conservative form:

$$\frac{dn_s}{dt} = J^{\text{IN}}(s) - J^{\text{OUT}}(s), \quad (5)$$

where $J^{\text{IN}}(s)$ is the flux of islands entering the size interval $[s, s+1)$ and $J^{\text{OUT}}(s)$ the flux of islands leaving that interval. By introducing a counter $\Delta t L^2 J(s)$ that is incremented by one every time an island grows to the size s or past that size, one can rewrite the rate equations as

$$\frac{dn_1}{dt} = F - 2J(2) - \sum_{s>2} J(s), \quad (6)$$

$$\frac{dn_s}{dt} = J(s) - J(s+1) \text{ for all } s > 1. \quad (7)$$

Comparison of Eqs. (2) and (7) gives the following expression for the *effective* capture numbers:

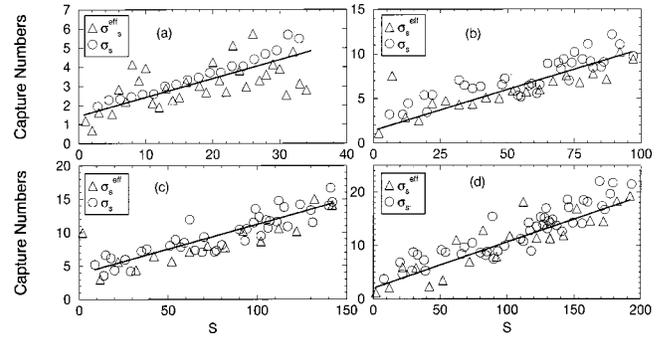


FIG. 4. Capture numbers for $D/F = 10^7$ and different coverage $\theta = 2\%$ (a), $\theta = 10\%$ (b), $\theta = 15\%$ (c), $\theta = 20\%$ (d). The solid line is a guide to the eye for the σ_s^{eff} .

$$\sigma_s^{\text{eff}} = \frac{\text{def} J(s+1)}{D n_1 n_s}. \quad (8)$$

We have also used our island-dynamics model with probabilistic seeding style to compute the $J(s)$. In the simulations we took a time step small enough to ensure that no island grows by more than one integer size. Using the measured values for $J(s)$ we have integrated the set of rate equations described in Eqs. (6) and (7), which by construction is equivalent to Eqs. (1), (2), and (8), using a third-order explicit Runge-Kutta scheme with initial condition $n_s = 0$ for all s . The results for the total number density and the CSD are shown in Fig. 3 in comparison with level-set and KMC simulations. The agreement is excellent. Thus, we conclude that a set of capture numbers exists that allows us to integrate mean-field rate equations to properly reproduce quantities such as the CSD that include spatial information.

Comparison of the extracted effective capture numbers σ_s^{eff} and the capture numbers σ_s previously described is shown in Fig. 4. The σ_s^{eff} are more noisy than the σ_s due to numerical difficulties [as defined, the N_s are discrete and lead to jumps in the computed fluxes $J(s)$, resulting in larger noise]. However, and more so for higher coverage ($\theta = 10\%$, $\theta = 15\%$, $\theta = 20\%$), the σ_s^{eff} exhibit the same functional form as the σ_s , that is, absence of a plateau for small islands.

We have not yet been able to find an *analytic* form for the capture numbers as a function of coverage [$\sigma_s = \sigma_s(\theta)$] that could be used in the integration of Eqs. (1) and (2). We speculate that the reason for this is that (i) small corrections to the affine dependence on s cannot be neglected; and (ii) the functional form for the capture numbers shown in Fig. 1 might not be valid at a very early time since the nucleation process rearranges the capture zones (and therefore the capture numbers) at each seeding of an island. Moreover, it is meaningless to refer to a functional form when only two or three distinct sizes are present.

The capture numbers presented here should be contrasted with the ones obtained in Refs. 11–13. The main difference is the absence of the plateau for small islands in our results. We believe that this difference comes from the fact that we allow islands to grow in their environment when computing

the capture numbers and therefore take into account all spatial correlations between islands. It is easy to see that a point-island model artificially increases the capture numbers for small islands, because it shifts the vertices of the capture zones in favor of small islands. We cannot clearly identify the reason for the existence of a plateau for simulations with spatially extended islands.^{12,13} However, we speculate that the reason might be any of the following. (i) Annealing of small islands might be the source. During this process, small islands close to bigger islands (thus with small capture numbers) are absorbed by the bigger islands, increasing the average capture number for small islands and leading to the plateau. (ii) Experimental uncertainties, including processes that are outside of irreversible aggregation in the submonolayer regime could also offer a plausible explanation; or (iii) the effect of the finite time interval required for the approach in Refs. 11–13 is not completely clear.

In conclusion, we have shown that capture numbers that include the effect of all spatial fluctuations are (to first approximation) affinely dependent on the island size, and that they are nearly time independent after the islands are seeded. Integration of the rate equations with these capture numbers for the first time reproduces the entire cluster size distribution. The question of existence of a scaling form for the CSD in the asymptotic limit of the ratio D/F can be answered by analyzing the rate equations at hand with the functional form extracted for the capture numbers here presented. Future work on this topic will explore the consequences of these results on the existence of a similarity solution for the CSD.

We gratefully acknowledge helpful discussions with D. D. Vvedensky. This work was supported by the NSF and DARPA through cooperative agreement DMS-9615854 as part of the Virtual Integrated Prototyping Initiative.

*Corresponding author. Electronic address: fgibou@math.ucla.edu

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