Rate equations and capture numbers with implicit islands correlations

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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 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.

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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

\[
\frac{dn_1}{dt} = F - 2D\sigma_1 n_1^2 - Dn_1 \sum_{n_i > 1} \sigma_i n_i,
\]

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

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 \(\sigma_s\) 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 \(\sigma_s\) 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 studies12,13 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,
where \( v \) is represented as the zero level set of a smooth function \( f \) result for the CSD after integrating the rate equations.

We observe scaling in coverage \( \theta \) 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 \( \sigma_s = a_s + b \), 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 \( \theta = \theta_b(D/F) \), as shown in Fig. 2. The value of \( \theta_b(D/F) \) 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. 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 \( \sigma_s = a_s + b \) 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

\[
\sigma_s = \frac{F}{Dn_1} A_s,
\]

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 \( \sigma_s = a_s + b \) (the intercept \( b \) corresponds to a point-island model). To check this, we
By introducing a counter \( t L \) every time an island grows to the size \( s \), increased every time an island grows to the size \( s \) and decreased every time an island of size \( s \) is increased every time an island grows to the size \( s \), we first rewrite the rate of change of \( n_s \) as:

\[
\frac{d n_s}{dt} = J(s) - J(s + 1)
\]

for all \( s > 1 \).

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

\[
\sigma_{s, \text{eff}} = J(s + 1)_{\text{eff}} = \frac{J(s + 1)}{D n_s n_s}.
\]

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 \( \sigma_{s, \text{eff}} \) and the capture numbers \( \sigma_i \) previously described is shown in Fig. 4. The \( \sigma_{s, \text{eff}} \) are more noisy than the \( \sigma_i \) 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 \( \sigma_{s, \text{eff}} \) exhibit the same functional form as the \( \sigma_i \), 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 \( [\sigma_i = \sigma_i(\theta)] \) 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. However, we speculate that the reason might be any of the following.

1. 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.

2. Experimental uncertainties, including processes that are outside of irreversible aggregation in the submonolayer regime could also offer a plausible explanation; or

3. 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.

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