Capture numbers in rate equations and scaling laws for epitaxial growth

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In this paper, we present a detailed exposition of the functional form of capture numbers that we found using an extended-island model. Our results suggest that the assumption $\sigma_s=\sigma_1$ for all s is only valid up to a time that scales like $O(R^{-1/2})$. After this time, a better approximation is $\sigma_s=as+b+$small correction and we show that in the limit $R\to\infty$, $\sigma_s\to as+b$. We link the functional form to the amount of nucleation of new islands on the surface and explain the differences between what is obtained with our extended-island model to what is obtained with a point-island model. Finally, we use our results to derive scaling laws for the adatom and total number densities. We found that the scaling in R remains unchanged, but that the time evolution is influenced by the functional form of the capture numbers.

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Molecular-beam epitaxy allows the possibility for controlling the growth of thin films with very high precision. Modern surface sensor techniques, such as scanning-tunneling microscopy, have led to a renewed effort in modeling epitaxial growth. One goal is to use predictive models in real time control algorithms to regulate the morphology of a growing film. Simple mean-field rate equations that are based on a set of coupled ordinary differential equations offer some hope to serve as a basis for such control algorithms, since they may be computationally fast enough to provide real time feedback.

Mean-field rate equations were introduced more than three decades ago[1–4] and offer a completely deterministic description of epitaxial growth. Such equations for the submonolayer regime (without detachment, evaporation, or direct deposition) typically read

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

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

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 σ_s are the so-called capture numbers. In principle, rate equations can be extended to include coalescence, and thus can be valid beyond the submonolayer regime.[5] However, there is a large number of additional parameters required, and their microscopic origin is anything but obvious. We want to point out, however, that the submonolayer regime is an important growth regime by itself, since many features such as typical island sizes and island-island correlations are determined by their properties in the submonolayer regime.

The capture numbers σ_s associated with islands of size s represent the propensity for such islands to compete for the available adatoms. Implicit in this definition is that these coefficients must take into account all the spatial components relevant to epitaxial growth. So far, rate equations have failed to reproduce quantities such as the cluster size distribution by using an analytical functional form for the capture numbers. This is because the proper spatial fluctuations of islands, notably those in the nucleation phase, determine the distribution of islands sizes at later times,[6] and are difficult to take into account using a single parameter.

An analytic formula for the capture numbers based on the uniform depletion approximation has been given by Venables.[4] It assumes that the local density of islands takes on its average values, so that the distribution of surrounding islands is independent of its size. It has been shown by Bales and Chrzan[7] that the integration of rate equations using this analytical formula for the capture numbers reproduces average quantities such as the adatom density and the total number density, but fails to reproduce the correct cluster size distribution. The reason is that the mean-field assumption prevents the spatial fluctuations of islands arising at the seeding phase and the subsequent fluctuations due to correlation between islands during the growth.

Bartelt and Evans addressed the first issue and numerically computed capture numbers by monitoring the aggregation of diffusive adatoms to the islands using Kinetic Monte Carlo (KMC) simulations with a point-island model.[8] The dependence of the capture numbers on the island size exhibits a plateau for islands smaller than the average size and approximately an affined part for islands bigger than the average size. This approach correctly takes into account the fluctuations in the nucleation phase since islands are seeded stochastically. However, the growth and subsequent correlations of islands are omitted in this approach, since a point-island model explicitly excludes this feature. As a consequence, the presence of too many nucleations rearranges artificially the capture zones. More recent studies[9,10] 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 a recent work Amar *et al.*[11,12] presented a model that explicitly takes into account the existence of a denuded zone around every island. In their approach, the rate equations for the island sizes are complemented by a set of rate equations for the capture zone distributions. For intermediate values of

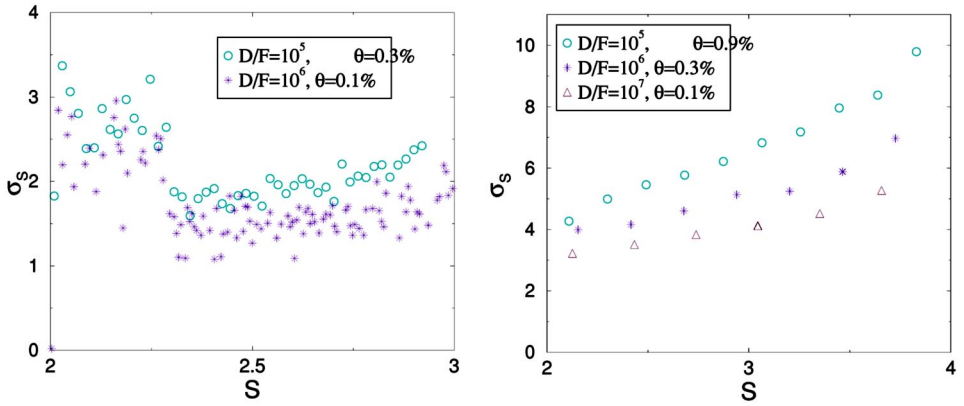

FIG. 1. Left: σ_s for the nucleation phase for two different values of $R=D/F$. Right: σ_s for three different values of R and a corresponding coverage θ chosen so that $\theta \propto R^{-1/2}$.

$R=D/F$ (10^7 to 10^8) the scaled island size distribution agrees much better with the one obtained from atomistic KMC simulation than with those obtained from any previous rate equation approach, but the obtained cluster size distribution at one fixed coverage and for a large array of values of R has not yet, to our best knowledge [D. Vvedensky, C. Ratsch, F. Gibou, R. Vardavas, Phys. Rev. Lett. (to be published)], been presented for this approach.

The form of the capture numbers needs to account properly for the cross correlations between the island sizes and the capture areas.[13,14] In this paper, we discuss the functional form of the capture numbers that have explicitly been measured from simulations. In Refs. 15 and 16, we followed the work of Bartelt and Evans[8] and computed numerically the capture numbers using the island-dynamics model.[17] Within this model, 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 $\partial\phi/\partial t + v_n|\nabla\phi| = 0$, where v_n is the local normal velocity of the island boundary. The velocity is computed from solving the diffusion equation for the adatom concentration.[18,19] The capture number for an island of size $\tilde{s}$ is given by

$$\sigma_{\tilde{s}} = \frac{\int_{\Gamma_{\tilde{s}}} v_n d\Gamma_{\tilde{s}}}{D n_1}. \tag{1}$$

Since in the level-set approach the island sizes are continuous in the lateral direction, we define the capture numbers for islands of size s to be the average of those for islands of size $\tilde{s} \in [s, s+1)$. This approach takes into account all spatial fluctuations during the nucleation phase as well as the growth phase. The interested reader is referred to Ref. 15 for more details in the computation of the capture numbers via this approach.

The results for the σ_s are presented in Figs. 1 and 2. We separate the nucleation phase from the rest of the process since nucleation of new islands rearranges the capture zones and therefore impacts the shape of the σ_s. In the nucleation phase, islands on the surface are of size two and start to grow. Figure 1 (left) depicts the capture numbers associated with the nucleation phase versus the islands sizes. Since the island dynamics is a continuous model, the islands sizes are between two and three. Typical island densities are defined as averages, as discussed in the previous section, and binning this data would give an average capture number $\sigma_1 \approx 2$, which is consistent with mean-field prediction. Past the nucleation phase, we find that a good approximation for the capture numbers is $\sigma_s \approx as + b$, with $a = O(R^{-1/3})$ and b affinely dependent on the coverage and weakly R dependent as depicted in Figs. 1 and 2. Our results suggest that the time at which the affined dependence is a fair approximation behaves asymptotically like $O(R^{-1/2})$ as illustrated in Fig. 1 (right) and we shall use this when deriving scaling laws for the adatom density and total number density. We note that the affined dependence is only an approximation and that it should be supplemented by a weak nonlinear dependence.

We now discuss why this functional form is consistent with irreversible aggregation and explain the differences between the capture numbers obtained with our extended-

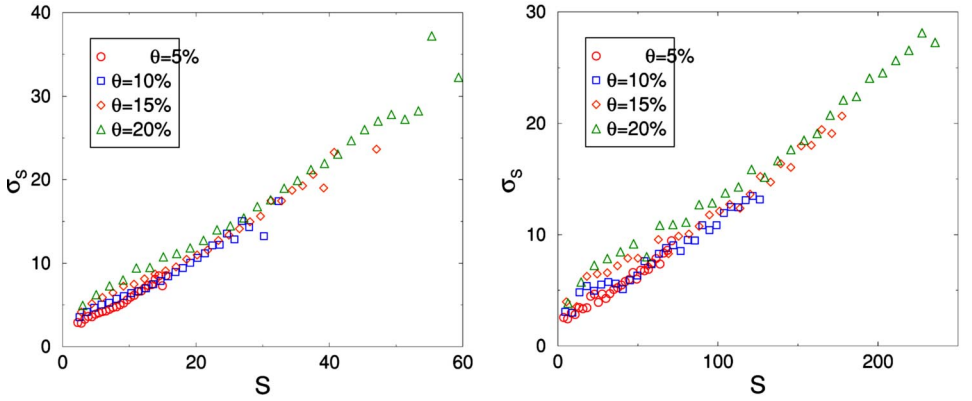

FIG. 2. Capture numbers σ_s versus the islands sizes s for $R=10^5$ (left), 10^7 (right), and four different values of the coverage.

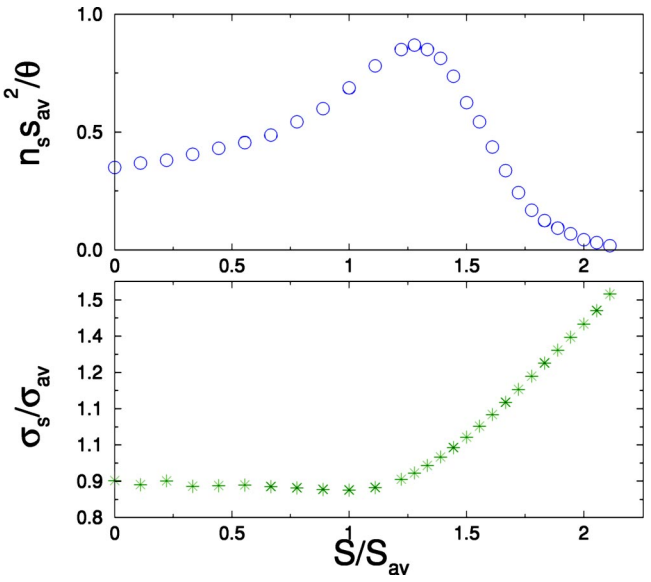

FIG. 3. Top: Data approximating the scaled cluster size distribution obtained by Bartelt and Evans (Ref. 8) using a point-island model. Bottom: Capture numbers obtained using formula (3) with $\beta=\frac{2}{3}$ exhibiting the plateau found in Ref. 8.

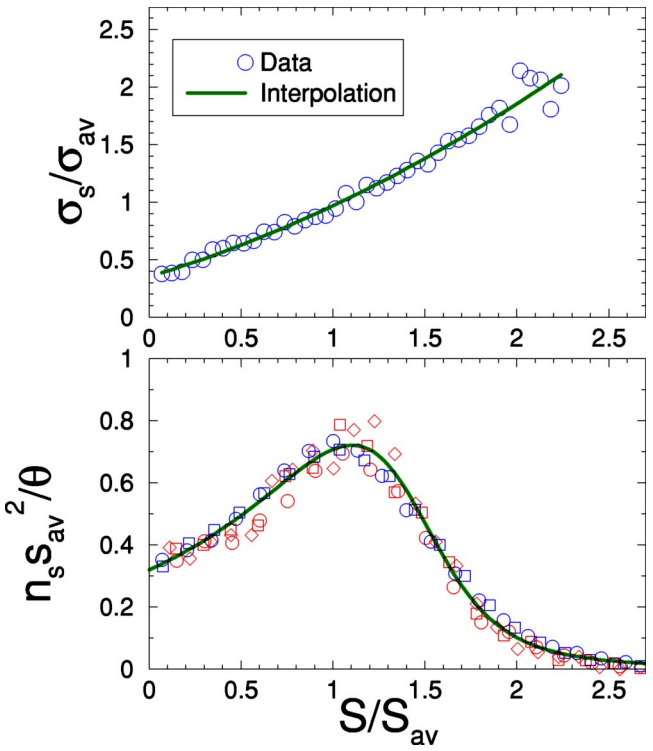

FIG. 4. Top: Quadratic interpolation $\sigma_s/\sigma_{av}=0.134x^2+0.484x+0.353$ with $x=s/s_{av}$ (solid line) of level-set data (circles). Bottom: The result of formula (2) with the quadratic interpolation is plotted as the green solid line on top of level set and KMC simulations (symbols).

island model and those obtained with a point-island model by relating the shape of the σ_s to the amount of nucleation of new islands on the surface. We also show that, as $R\to\infty$, the nonlinear dependence is negligible (i.e., $\sigma_s\to as+b$) and use this functional form to derive scaling laws for the adatom density and the total number density in the asymptotic regime of high R.

It was shown by Bartelt and Evans[8] that in the steady-state regime, the functional form of the scaled capture numbers $\sigma_s/\sigma_{av}=C(s/s_{av})=C(x)$, where σ_{av} and s_{av} are, respectively, the average capture number and island size, is related to the scaled cluster size distribution $m(x)=n_s s_{av}^2/\theta$ by

$$m(x)=m(0)\exp\int_0^x\frac{2\beta-1-C'(\xi)}{C(\xi)-\xi\beta}d\xi, \tag{2}$$

where $\beta=ts_{av}^{-1}d(s_{av})/dt$. Taking the natural logarithm on both sides (since all terms are positive) one can deduce a formula for $C(x)$ as a function of $m(x)$:

$$C(x)=\beta x+\frac{(\beta-1)\int_0^x m(\xi)d\xi+C(0)m(0)}{m(x)}. \tag{3}$$

The functional form of the capture numbers is then affined [with slope β and intercept $C(0)$] but with a correction term [from the last term on the right-hand side of Eq. (3)]. Equation (3) shows that given the cluster size distribution and a value for β, there exists a unique functional form for the capture numbers [given $C(0)$]. However, one can also see that for a given cluster size distribution, there exists an infinite family (β,C_β) that can reproduce it via Eq. (3). That is, given the cluster size distribution m, the value for β determines the functional form of the capture numbers. From our computations of s_{av}, we obtained $\beta\in[0.89,0.93]$ for $R\in[10^5,10^7]$ and found that β is slightly smaller for smaller values of R, whereas in the point-island model of Ref. 8, $\beta\approx\frac{2}{3}$.

One can explain this difference as follows. The rate of change of the average island size is

$$\frac{d}{dt}(s_{av})=\frac{F}{N(t)}\left\{1-t\frac{\frac{d}{dt}[N(t)]}{N(t)}\right\},$$

and therefore, $\beta\to1$ as $dN(t)/dt\to0$, which is related to the amount of nucleation of new islands. It is well known that the nucleation rate never reaches a steady state in a point-island model[20] and that explains the low value for β in Ref. 8. Our value for β (≈0.9), shows that there is still some nucleation in our model at 20% coverage, but this amount is small enough to properly model the decay in the nucleation rate observed in irreversible aggregation. Moreover, the slightly lower values of β for lower values of R is consistent with the fact that the amount of nucleation at the surface is larger for lower values of R. One can also use formula (3) with $\beta=\frac{2}{3}$ to reproduce the functional form of the capture numbers of Ref. 8, as shown in Fig. 3. We can therefore explain the existence of a plateau for the capture numbers obtained with the point-island model by the artificial presence of too many nucleation events. We note that the capture numbers presented by Popescu *et al.*[12] are consistent with our results. In their paper, the authors present capture num-

bers that exhibit a plateau for point islands, and capture numbers that are (almost) affined for extended islands. For both cases, the scaled size distributions are very similar.

Our results suggest that β asymptotically approaches one as R increases. For intermediate values of R, there is always some nucleation occurring and the functional form for the capture numbers is $\sigma_s = as + b +$ small correction. We found in Ref. 19 that a correction terms of the form cs^2 (with c small) is enough to reproduce the cluster size distribution using Eq. (2) as illustrated in Fig. 4, i.e., nucleation events tend to bend the curve of C.

The case where $\beta = 1$ is interesting. It corresponds to *no new nucleations*, and therefore implies $C(0) \to 0$ in Eq. (3), which in turn gives $C(x) \to x$. Thus, in the case $\beta = 1$, the capture numbers are simply linearly dependent on the island size. It was proven by Vvedensky[21] that taking this functional form for $R \to \infty$ does not determine a unique solution for the cluster size distribution and that one must specify the distribution at some initial coverage. Indeed, in this case the nucleation phase is reduced to an infinitesimal interval near $\theta = 0$, and $\beta = 1$ prevents any new nucleation. The burst of nucleation at $\theta = 0$ should thus define the initial condition, and only the initial condition taking into account the correct distribution in island densities would reproduce the scaled cluster size distribution at a later time.

Finally, we would like to comment on the effect of the two distinct regimes for the capture numbers on the scaling laws for island densities and adatom densities. Nucleation theory predicts scaling of island densities as a function of temperature and deposition flux. A well-known result[22] that can be obtained under the assumption that $\sigma_s = \sigma_1$ for all s predicts that $N \sim R^{-1/3}$ for irreversible aggregation, and more generally $N \sim R^{-i/(i+2)}$ for reversible aggregation, where i is the so-called critical island size. This result has successfully been employed to interpret experimentally measured island densities, and in fact to obtain microscopic parameters such as diffusion barriers and prefactors from the measured island densities.[23,24] For scaling with respect to time earlier work[20] predicted that asymptotically $N \sim (\ln t)^{1/2}$.

Our results on the capture numbers above suggest that the assumption $\sigma_s = \sigma_1$ holds for a coverage that scales like $\theta_0 = R^{-1/2}$. In this case, the resulting scaling laws are

$$n_1 = R^{-1/2}\tilde{\theta} = \theta,$$

$$N = (\sigma_1/3) R^{-1/2} \tilde{\theta}^3 = (\sigma_1/3) R \theta^3.$$

At later time, we found that, in the asymptotic limit of $R \to \infty$, $\sigma_s \to as + b$ with $a = \tilde{a} R^{-1/3}$ and $b = \tilde{b}\theta$. In this case, the scaling laws are found to be

$$n_1 = \theta^{-1} \left[3\tilde{b}^2 \ln\left(\frac{\theta}{\theta_0}\right) + c_0 \right]^{-1/3} R^{-2/3},$$

$$N = \tilde{b}^{-1} \left\{ \left[3\tilde{b}^2 \ln\left(\frac{\theta}{\theta_0}\right) + c_0 \right]^{1/3} - \tilde{a} \right\} R^{-1/3},$$

with $c_0 = -3\tilde{b}^2 \ln(\theta_0) + (\tilde{a} + R^{1/3}\tilde{b} N_0)^3$.

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