Rate-Equation Approach to Island Capture Zones and Size Distributions in Epitaxial Growth

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Understanding and predicting the effects of correlations between island size and the rate of monomer capture has been shown to be the central problem in predicting the island-size distribution in submonolayer growth. Here we summarize a method which involves a self-consistent coupling of evolution equations for the capture-zone distributions with rate equations for the island-size distribution. The method has been successfully applied to irreversible submonolayer growth in both one and two dimensions to predict the size-dependent capture numbers and island-size distributions.

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Cluster nucleation and growth by aggregation is the central feature of many physical processes, from polymerization and gelation in polymer science, flocculation and coagulation in aerosol and colloidal chemistry, percolation and coarsening in phase transitions and critical phenomena, agglutination and cell adhesion in biology, to island nucleation and thin-film growth in materials science [1]. Detailed information about the kinetics of aggregation is provided by the time-dependent cluster-size distribution, a quantity which can be measured experimentally [2]. Based on the von Smoluchowski rate equations [3], considerable theoretical effort has been made toward a better understanding of the mechanisms determining the scaling properties of aggregation phenomena [4].

While the standard rate-equation (RE) approach has been successful in predicting the scaling behavior of average quantities such as the total cluster density, when there are significant spatial fluctuations it gives predictions which are in significant disagreement with both experiments and kinetic Monte Carlo (KMC) simulations [5–8]. This failure can be traced to the fact that the usual mean-field approach does not include correlations between the size of an island and its local environment [6–8]. Such correlations are especially important in lower dimensions, such as in cluster growth on surfaces.

In this Letter, we outline a new method for calculating the cluster-size distribution which solves the long lasting problem [9,10] of determining the correlations between the size of an island and that of its capture zone. Applying this method to submonolayer epitaxial growth, we show that by coupling a set of evolution equations for the capture-zone distributions with a set of rate equations for the island densities one may obtain accurate predictions for the time- and size-dependent rates of monomer capture. In particular, we show that by using this method one can obtain excellent results for the capture numbers and island-size distributions in irreversible growth on both one- and two-dimensional substrates.

The rate-equation approach to submonolayer nucleation and growth involves a set of coupled diffusion-aggregation equations [3,11] describing the time (coverage) dependence of the average densities of monomers, N_1, and of islands of size $s \geq 2$, N_s (s being the number of atoms in the island). For the case of irreversible growth with immobile clusters, a general form of these equations may be written

$$\frac{dN_1}{d\theta} = \gamma - 2N_1 - 2R\sigma_1 N_1^2 - RN_1 \sum_{s\geq 2} \sigma_s N_s , \quad (1)$$

$$\frac{dN_s}{d\theta} = RN_1(\sigma_{s-1}N_{s-1} - \sigma_s N_s) + k_{s-1}N_{s-1} - k_s N_s \quad \text{for } s \geq 2 . \quad (2)$$

Here, θ is the coverage, $R = D/F$ corresponds to the ratio of the monomer diffusion rate D to the deposition flux F, and the factor γ represents the fraction of the substrate not covered by islands. The terms with σ_s describe the rate of monomer capture by other monomers or by existing islands, while the terms with k_s (where $k_s = s^{d/d_f}$, d is the substrate dimension, and d_f is the fractal dimension of the islands) correspond to the deposition of adatoms directly on islands of size s.

In order to use (1) and (2) to predict the island-size distribution $N_s(\theta)$ during submonolayer growth, the coverage and size-dependent capture numbers $\sigma_s(\theta)$ must be determined. As shown in Fig. 1, for the case of a two-dimensional substrate we assume that each island of size s is surrounded by a local capture area or "exclusion" zone, A_{ex}, in which only monomers may be found. For simplicity, the island is replaced by a circle of radius R_s, while the exclusion zone is assumed to be a circle of radius $R_{\text{ex}} = \sqrt{A_{\text{ex}}/\pi}$ as shown in Fig. 1(b). Inside the exclusion zone, monomer diffusion is characterized by the average monomer nucleation length ξ_1, while outside the exclusion zone, the collection of islands and monomers is represented by a "smeared" distribution corresponding to an average monomer "decay" length ξ. We assume that the exclusion zone area is directly proportional to the Voronoi-cell area A_V, i.e., $A_{\text{ex}} = \eta A_V$, where η is a

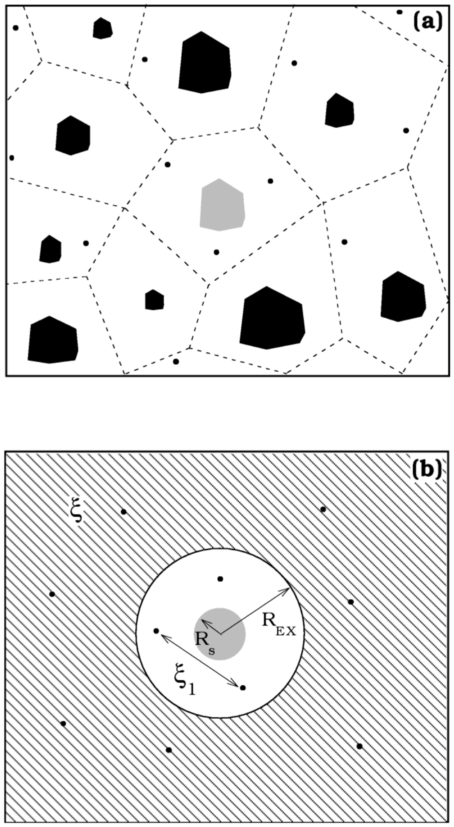

FIG. 1. Schematic diagram showing (a) two-dimensional islands with Voronoi cells (b) corresponding exclusion zone geometry.

coverage-dependent geometrical factor (typically larger than 1) which is the same for all islands.

Taking into account the effects of nucleation and growth of islands on the distribution, and ignoring the breakup (fragmentation) of Voronoi cells when new islands are nucleated, we can write down a set of evolution equations for the Voronoi-cell distribution in the form,

$$\frac{dG_2(A;\theta)}{d\theta} = (dN/d\theta)\delta(A - A_{\rm av}) - RN_1\tilde{\sigma}_2(A)G_2(A;\theta)\,, \qquad (3)$$

$$\frac{dG_s(A;\theta)}{d\theta} = RN_1[\tilde{\sigma}_{s-1}(A)G_{s-1}(A;\theta) - \tilde{\sigma}_s(A)G_s(A;\theta)]\ (s \geq 3)\,, \qquad (4)$$

where $G_s(A;\theta)$ is the number density of islands of size s surrounded by a Voronoi cell of size A, and $\tilde{\sigma}_s(A)$ is the corresponding "local" capture number. The first term on the right side of Eq. (3) corresponds to island nucleation, while the remaining terms in (3) and (4) correspond to the growth of islands via aggregation. In these equations we have assumed that at coverage θ the nucleation events produce, on average, new cells whose average Voronoi area is just the average area per island $A_{\rm av} = 1/N$ (where $N = \sum_{s\geq 2} N_s$ is the average island density at that coverage) and for simplicity the "source" term in Eq. (3) has been assumed to take the form of a delta function. For the description to be consistent, the local capture numbers $\tilde{\sigma}_s$ in (3) and (4) must be related to the capture numbers σ_s in the rate equations (1) and (2) by $\sigma_s = \langle \tilde{\sigma}_s(A)\rangle_{G_s(A)}$. As a result, the problem has been reduced to determining the Voronoi-cell distribution $G_s(A;\theta)$ and the local capture numbers $\tilde{\sigma}_s$.

In principle, Eqs. (3) and (4) can be numerically integrated once explicit expressions for the local capture numbers $\tilde{\sigma}_s(A)$ are known. However, if the local capture number $\tilde{\sigma}_s(A)$ has no explicit dependence on the island size s, then an analytic solution can be obtained. We therefore consider the mean-field approximation $\tilde{\sigma}_s(A) \simeq \tilde{\sigma}_S(A)$ [where $S = (\theta - N_1)/N$ is the average island size]. For the case of point islands (i.e., islands with no spatial extent) this approximation is exact, since in this case there is no explicit size dependence of the local capture numbers.

Changing the coverage variable to $x_A = \int_{\theta_A}^{\theta} RN_1(\phi)\tilde{\sigma}_S(A)\,d\phi$ [where $1/N(\theta_A) = A$ defines θ_A] and using the generating function $g(x_A,u) = \sum_{s=2}^{\infty} G_s(x_A;A)u^{s-2}$ one obtains the general solution [12],

$$G_s(A;x_A) = A^{-2}x_A^{s-2}e^{-x_A}/(s-2)!\ (s \geq 2)\,. \qquad (5)$$

Beyond the nucleation regime, the average Voronoi area $A_{\rm av}$, as well as x_A and the average island size S, is typically large. Thus, in the aggregation regime the Voronoi-area distribution $G_s(A;\theta)$ corresponds to a sharply peaked distribution as a function of A whose peak position $\hat{A}_s$ satisfies $x_{\hat{A}_s} = s - 2$. Because the effects of breakup of Voronoi cells due to nucleation have been neglected in (3) and (4), these values must be rescaled so that the average Voronoi area is equal to $A_{\rm av} = 1/N$ (in the case of extended islands additional geometrical corrections are included) as described in detail in [12,13]. Accordingly, the capture numbers are approximated by $\sigma_s = \tilde{\sigma}_s(A_s')$, where A_s' is the rescaled and corrected $\hat{A}_s$.

The calculation of the local capture numbers $\tilde{\sigma}_s$ is similar to the self-consistent scheme developed by Bales and Chrzan [14] and basically consists of comparing the microscopic capture rate of monomers by an island of size s with the rate-equation-like "capture" term $DN_1\tilde{\sigma}_s(A)$. To determine the microscopic capture rate, one has to self-consistently solve a quasistationary diffusion equation whose form and solution depend on the dimensionality and geometry of the system [12–14]. As an example, we will outline the calculation in the two-dimensional case.

Defining the monomer "nucleation" length $\xi_1^{-2} = 2\sigma_1 N_1$ and the monomer decay length $\xi^{-2} = \xi_1^{-2} + \sum_{s\geq 2}\sigma_s N_s$, the diffusion equation satisfied by the local monomer density surrounding an island of size s on a two-dimensional substrate is

$$\nabla^2 n_1 = \begin{cases} \xi_1^{-2}[n_1 - \alpha^2(N_1/\gamma)], & R_s < r < R_{\rm ex}\,, \\ \xi^{-2}(n_1 - N_1/\gamma), & R_{\rm ex} < r < \infty\,, \end{cases} \qquad (6)$$

where $n_1(r)$ is the local monomer density a distance r from the center of the island, $R_s = \rho s^{1/d_f}$, $R_{\rm ex} = \sqrt{\eta A_V/\pi}$, and $\alpha^2 = (\xi_1/\xi)^2$. Here ρ is a "geometrical" prefactor which accounts for the circular approximation of the island area, and the fractal dimension d_f depends on the morphology of the island. The explicit solution of Eq. (6), with appropriate boundary conditions for irreversible growth, is used to determine the local capture number $\tilde{\sigma}_s(A) = (2\pi R_s/N_1)(\partial n_1/\partial r)_{R_s}$ for $s \geq 2$. The monomer capture number σ_1 is also obtained by taking the limit of no exclusion zone, i.e., $R_{\rm ex} = R_1$. After choosing a reasonable value for ρ, the decay length ξ and the geometrical prefactor η are self-consistently obtained by requiring that the capture-number condition, $\xi^{-2} = \xi_1^{-2} + \sum_{s\geq 2} \sigma_s N_s$ and monomer-density condition that the average monomer density in all the Voronoi cells must equal N_1, are satisfied at all coverages [13].

We have numerically integrated the island-density rate equations (1) and (2), coupled with the solution of the Voronoi-area evolution equations (3) and (4) as described above, in order to calculate the scaled island-size distributions $f(s/S) = (S^2/\theta)N_s(\theta)$ and scaled capture-number and capture-zone distributions for the case of irreversible growth on both one- and two-dimensional substrates. Figure 2 shows typical results for the case of point islands in two dimensions. As can be seen, there is excellent agreement between the calculated scaled island-size distribution $f(s/S)$ (solid line) and kinetic Monte Carlo simulations (symbols), in contrast to the corresponding mean-field (MF) prediction (dashed line). The corresponding RE prediction for the scaled capture-number distribution $\sigma_s/\sigma_{\rm av}$ is also in good agreement with the KMC simulation results [7], as shown in Fig. 2(b). The small discrepancies which occur at large s/S have a negligible effect on the island-size distributions because the island density N_s is already small in that region.

Excellent agreement between the RE predictions and simulations has also been obtained for the case of compact islands ($d_f = 2$) as shown in Fig. 3. As for point islands, the reason for this is that the explicit inclusion of

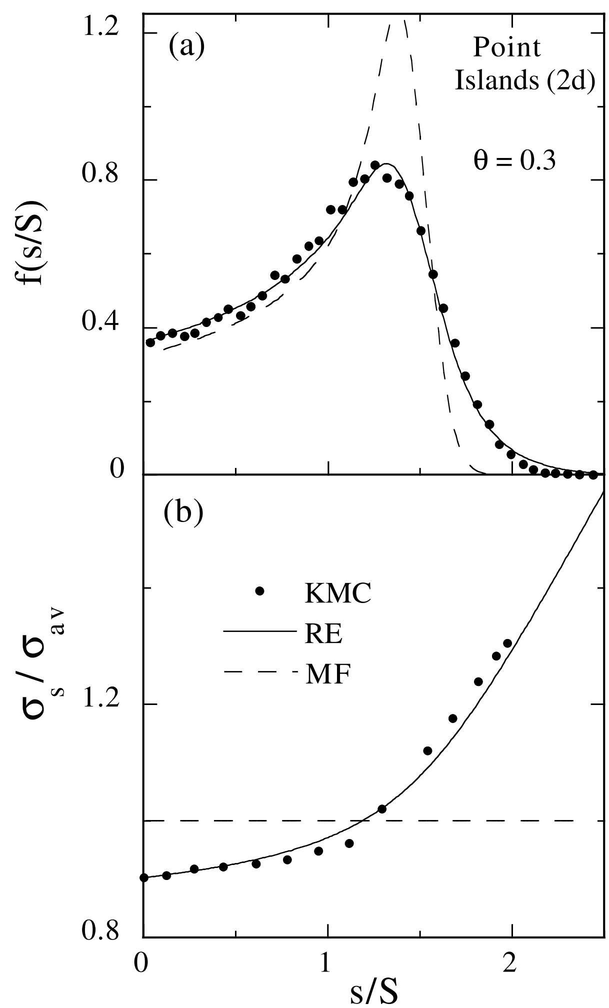

FIG. 2. Scaled island-size and capture-number distributions for point islands on a two-dimensional substrate ($R = 0.25 \times 10^8$). KMC results in (b) are from [7].

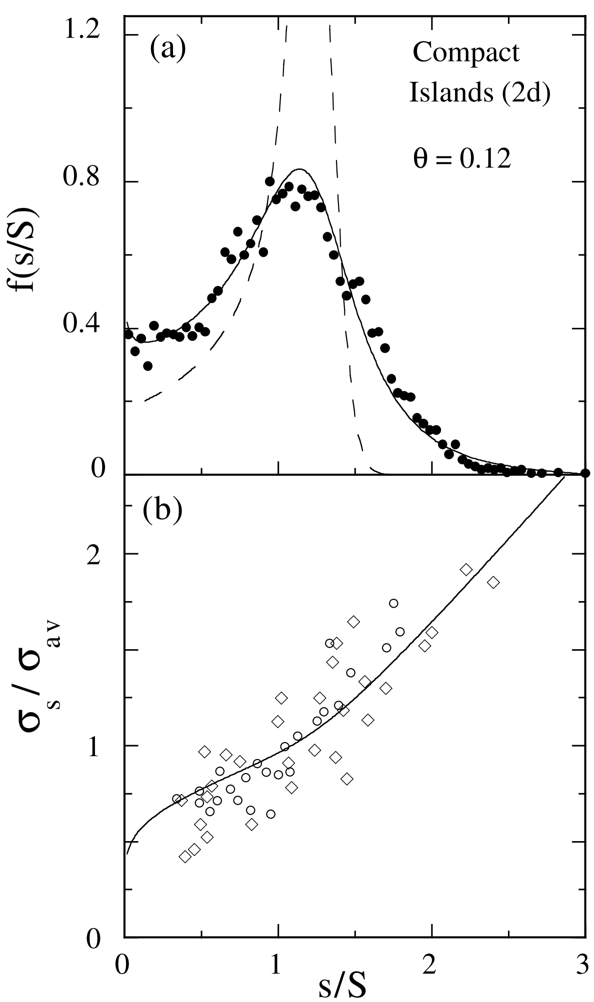

FIG. 3. Same as Fig. 2 but for compact islands ($d_f = 2$). Open symbols in (b) are experimental results from [8] for Cu/Co on Ru(0001) (diamonds) and for Ag/Ag(100) (circles).

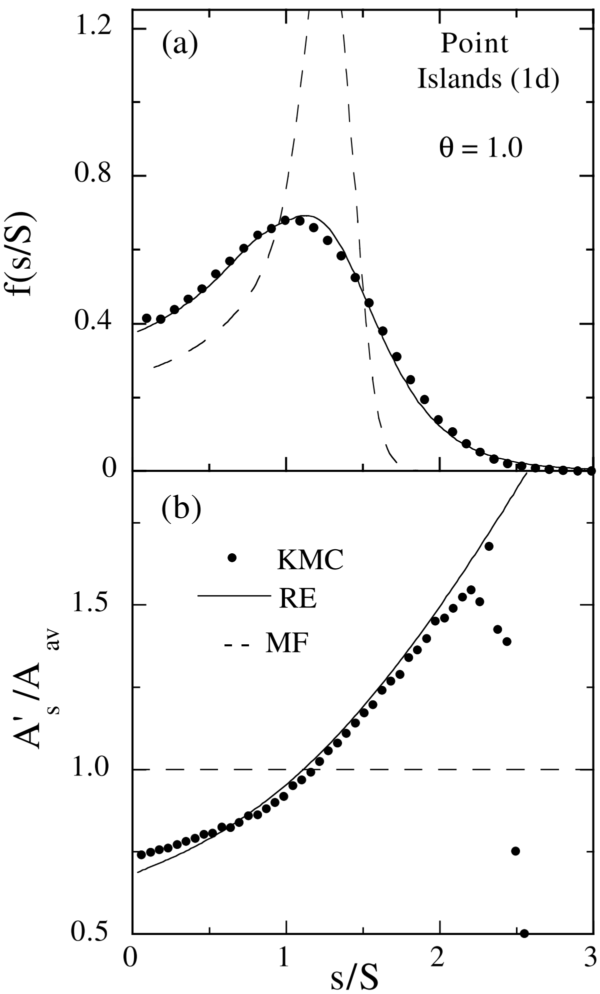

FIG. 4. Scaled island-size and capture-zone distributions for point islands on a one-dimensional substrate ($R = 0.5 \times 10^7$).

size correlations in the rate equations has led to correct expressions for the capture zones and capture numbers. As shown in Fig. 3(b), our RE predictions for the scaled capture-number distribution for compact islands are in very good agreement with experimental results for two different materials and growth conditions from [8].

Similar good agreement for both point and extended islands ($d_f = 1$) has also been obtained for irreversible growth in one dimension, although the details of the calculation of the capture zones and numbers are somewhat different due to the existence of strong spatial fluctuations [12]. Typical results for the cluster-size and capture-zone distributions for growth on a one-dimensional substrate are shown in Fig. 4 for the case of point islands.

In conclusion, we have developed a fully self-consistent rate-equation approach to irreversible submonolayer growth in the precoalescence regime. In our method, the existence of a denuded (capture) zone with a fluctuating area around every island and the correlations between the size of the island and the corresponding average capture zone are explicitly taken into account. This has led to RE results for the island-size distribution, capture zones, and capture numbers in very good agreement with experimental results and KMC simulations. The basic idea of coupled evolution of the capture zones and densities included in the present approach may be used in the rate-equation modeling of a wide variety of problems in which cluster nucleation and growth by aggregation involves strong correlations between the rate of aggregation and the size of the capture zone.

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