Exact island-size distributions for submonolayer deposition: Influence of correlations between island size and separation

M. C. Bartelt
Institute of Physical Research and Technology, Iowa State University, Ames, Iowa 50011

J. W. Evans
Department of Mathematics and Ames Laboratory, Iowa State University, Ames, Iowa 50011

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We determine the exact scaling form of the size distribution of islands created via homogeneous nucleation and growth during submonolayer deposition. This scaling form is shown to be controlled by the dependence on size of the propensity for islands to capture diffusing adatoms. This size dependence is determined directly from simulations. It is distinct from mean-field predictions, reflecting strong correlations between island size and separation. [S0163-1829(96)52648-2]

Homogeneous nucleation and growth of islands during the initial submonolayer stage of film growth has been studied intensively for decades.[1] The field has broad technological importance since these submonolayer structures can influence the morphology and properties of the resultant multilayer film. Quantities of primary interest are the mean island density, and the shape of the island size distribution. The latter has been the focus of several recent theoretical[2–6] and experimental[7,8] studies. Appropriate interpretation of their behavior for various deposition conditions can provide insight into the nature of the nucleation process, and allow extraction of key system parameters.

The traditional theoretical analysis is provided by mean-field (MF) rate equations.[1] This approach derives from work of Smoluchowski,[9] and has been applied extensively to analyze not just nucleation and growth, but various other diffusion-mediated processes including coagulation and chemical reactions.[10] Generally, the MF approach ignores certain spatial correlations, or equivalently particle number fluctuations, in the system. In the classic MF treatments of nucleation and growth,[1] as well as recent refinements,[11] the crucial MF assumption is that the *local environment* of each island is *independent* of its size (and shape). The MF rate equations for the density N_1 of diffusing adatoms, and the densities N_s of islands of various sizes $s>1$ (or for the average island density $N_{\rm av}=\Sigma_{s>1}N_s$) quantify their variation with control parameters (deposition flux F and substrate temperature T), and are traditionally used to analyze experimental data.

These MF predictions can be tested by ''exact'' Monte Carlo simulations for appropriate lattice-gas models of nucleation and growth. A large number of such recent studies[2–6] have demonstrated that the MF predictions apply for the scaling of $N_{\rm av}$ and N_1, although refinement of the simplest theory may be needed in the regime where island formation is reversible.[12] However, there appears to be a *fundamental discrepancy*[13] between the exact island size distribution and MF predictions, which has *not* been resolved previously. This impacts upon the intepretation of recent STM studies [7,8] which provide precise island size distributions.

In this paper, we present the first exact analysis of the shape of the island size distribution for irreversible nucleation and growth, in the scaling regime of low F or high T. Our result differs qualitatively from MF predictions,[1,2] as well as from other speculated forms based on simulation studies.[6] We show that this shape is determined by an unexpected dependence on size s of the propensity σ_s for islands to ''capture'' diffusing adatoms. This size dependence is obtained directly from simulations. It is quite distinct from the commonly accepted behavior based on self-consistent MF calculations,[11] and has not been previously characterized or elucidated. We show that it reflects a strong correlation between island size and separation which automatically develops during deposition. This size dependence is further elucidated using ideas from stochastic geometry to characterize the nucleation and aggregation processes. Finally, our results for the island size distribution are related to experimental findings.

First, we describe explicitly the basic steps in *irreversible* homogeneous nucleation and growth, and present a rate equation formalism which goes beyond the traditional MF analysis. In this process, atoms are deposited randomly on a periodic array of adsorption sites at rate F per site, and thereafter hop to adjacent sites at rate h. Subsequently, adatoms either meet other adatoms, irreversibly nucleating islands, or aggregate irreversibly with existing islands. The rate at which diffusing adatoms aggregate with islands of size s is written as $R_{\rm agg}(s)=h\sigma_s N_1 N_s$, *defining* σ_s as the ''capture number'' for islands of size s. Then the evolution of N_s with time t is described by the rate equations (cf. Ref. 1)

$$dN_1/dt \approx F - 2R_{\rm agg}(1) - \sum_{s>1} R_{\rm agg}(s),$$

and

$$dN_s/dt \approx R_{\rm agg}(s-1) - R_{\rm agg}(s) \quad \text{for } s>1. \tag{1}$$

Note that $\theta=\Sigma_{s\geq 1} sN_s = Ft$ gives the coverage, and $s_{\rm av}=(\theta-N_1)/N_{\rm av}\approx\theta/N_{\rm av}$ gives the average island size. One anticipates solutions of Eq. (1) of the form[2,3] $N_s \sim \theta s_{\rm av}^{-2} f(s/s_{\rm av})$, where

$$\int_0^\infty dx f(x) = \int_0^\infty dx\, x f(x) = 1.$$

It is instructive to reduce Eq. (1) to the approximate pair

$$dN_1/dt \approx F - h\sigma_{\rm av}N_1N_{\rm av}$$

and

$$dN_{\rm av}/dt \approx R_{\rm agg}(1) = h\sigma_1(N_1)^2, \qquad (2)$$

where $\sigma_{\rm av}=\Sigma_{s>1}\sigma_s N_s/N_{\rm av}$. From the N_1 equation, one anticipates an initial transient regime of increasing $N_1 \approx Ft$, followed by a *steady state regime* where $dN_1/dt \approx 0$, so $F \approx h\sigma_{\rm av}N_1N_{\rm av}$. The latter steady-state relation, when substituted into the $N_{\rm av}$ equation, yields $(\sigma_{\rm av})^2(N_{\rm av})^2 dN_{\rm av} \approx (h/F)^{-1}\sigma_1 d\theta$, which can be integrated to determine the behavior of $N_{\rm av}$, given the form of $\sigma_{\rm av}$ (and σ_1).

With the simplest assumption that $\sigma_s=\sigma_{\rm av}$ is constant, one obtains $N_{\rm av}\sim\theta^{\omega}(h/F)^{-\chi}$, with $\omega=\chi=\frac{1}{3}$. A more sophisticated approach by Bales and Chrzan[11] (BC) is to determine the σ_s self-consistently from diffusion equations for adatom capture at a specific island of size s. This approach is viable only with the simplifying MF assumption that the environment of each island (i.e., the distribution of surrounding islands) is *independent* of its size (and shape). BC show that the resulting σ_s depend primarily on the ratio of the linear island size to the mean island separation, and increases weakly with s. For *compact islands*, one has $\sigma_s = \mathcal{D}(\theta s/s_{\rm av})$, where $\mathcal{D}(y)\sim y^{1/2}$ for $y>1$, reflecting perimeter-mediated capture, so $\sigma_{\rm av}\approx\int_0^\infty dx\ \mathcal{D}(\theta x)f(x) = \sigma_{\rm av}(\theta)$. This modifies the above θ dependence of $N_{\rm av}$ to incorporate the observed saturation, but does not change the scaling with h/F. However, as noted above, predictions of both the simplest and the BC MF treatments for the island size distribution do *not* agree with exact behavior.[13]

I. POINT-ISLAND MODEL

We now show that the origin of this discrepancy is due to a dominant contribution to the s dependence of σ_s from correlations between island size and separation. To cleanly isolate this contribution from the above mentioned MF s dependence in the BC treatment, we consider a simplified model for irreversible nucleation and growth.[2] Here islands occupy a single site, but carry a label which indicates their size, and which is updated after each aggregation event (see Ref. 2). We emphasize that this model not only captures the essence of nucleation and growth, but it is especially useful here as MF capture numbers for point islands are clearly *independent* of s ($\sigma_s=\sigma_{\rm av}$, for all s)!

Figure 1 shows typical simulation results for distributions of islands, together with the associated Voronoi tessellations (see below). Previous analyses[1,2] have shown that the mean island density scales as $N_{\rm av}\sim\theta^{\omega}(h/F)^{-\chi}$, where $\omega\approx\frac{1}{3}$. The effective χ ($\approx$0.3 when $h/F=10^8$) increases slowly to $\frac{1}{3}$, as $h/F\to\infty$. The scaled island size distribution, shown in Fig. 2(b), should be contrasted with MF predictions in Fig. 2(a). We also emphasize that the shape of the size distribution is almost completely time invariant.[2] The increase of $N_{\rm av}$ with θ for point islands differs from the saturation behavior observed for compact islands.[3,13] but the island size distributions are very similar for $\theta\leqslant$0.2 ML where island coalescence is insignificant.[2,3]

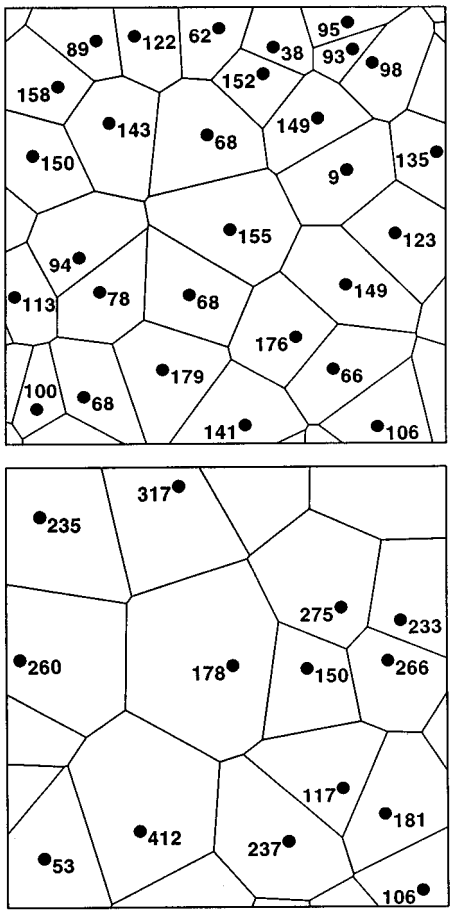

FIG. 1. Island distributions, with size labels, and associated Voronoi tessellations, from simulations with $h/F=10^8$ (top) and 10^{10} (bottom), at θ=0.2 ML. Panels are 120×120 sties.

II. CAPTURE NUMBER BEHAVIOR

In our simulations, we also directly obtain the σ_s (and related quantities) for the first time. This can be done by introducing a counter M_s which is incremented by 1 each time a diffusing adatom is captured by an island of size s on an $L\times L$ site lattice. One has $R_{\rm agg}(s)\approx\Delta t^{-1}L^{-2}[M_s(t+\Delta t)-M_s(t)]$, for sufficiently small $F\Delta t$, and thus obtains $\sigma_s=R_{\rm agg}(s)/(hN_1N_s)$. However, due to slow convergence as $\Delta t\to 0$, it is more efficient to use an approach in which

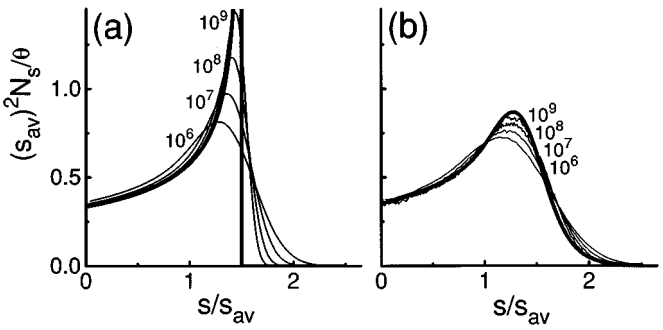

FIG. 2. Scaled island size distributions for $h/F=10^6-10^9$, at 0.2 ML: (a) MF results (σ_s=constant) with asymptotic form (thick line); (b) ''exact'' simulation results; the asymptotic form (thick line) is obtained from Eq. (4) using the fit of $C()$ shown in Fig. 3(a).

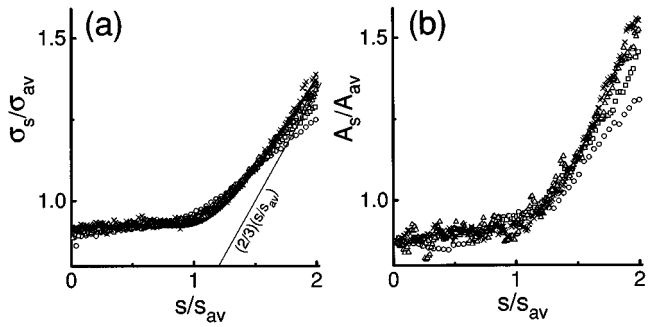

FIG. 3. Simulation results for: (a) σ_s/σ_{av}; (b) A_s/A_{av} versus s/s_{av}, at $\theta=0.2$ Ml, for $h/F=10^6(\bigcirc)$, $10^7(\square)$, $10^8(\triangle)$, $10^9(\times)$, where $\sigma_{av}\approx 0.93$, 0.78, 0.64, 0.43, and $s_{av}\approx 25$, 49, 98, 200, respectively. The thick solid line in (a) is a simple fit of $C(x)$. The decrease of σ_{av} with h/F (and a weak increase with θ) is explained from a 2D random walk analysis of aggregation[2] showing that $\sigma_{av}\sim\pi/\ln(\pi^{-1}N_{av}^{-1})$.

one switches off the island nucleation and growth (i.e., one stops incrementing the island size counters) at the desired θ, and monitors aggregation rates under continued deposition.[14] Figure 3(a) shows such results for σ_s/σ_{av} versus s/s_{av}, at 0.2 ML, for $h/F=10^6-10^9$. These reveal a MF-type plateau for $s<s_{av}$, but a dramatic deviation from s-independent MF behavior for $s>s_{av}$. The form $\sigma_s/\sigma_{av}\approx C(s/s_{av})$ is almost completely time invariant for fixed h/F (results not shown), and converges to a nontrivial scaling limit, as $h/F\to\infty$. Since $\int_0^\infty dx\, f(x)C(x)=1$, and $C(x)$ is nondecreasing, the plateau value of $C(x<1)\approx 0.92$ is below unity.

This behavior can be elucidated if one characterizes the stochastic distribution of islands via the associated Voronoi tessellation of the surface.[15] Each cell of such a tessellation corresponds to the region of the surface closer to an island than to any other island; see Fig. 1. If one assumes, as suggested in previous work,[1,15,16] that most atoms deposited within a cell will aggregate with the associated island, then there should be a strong correlation between cell areas and aggregation rates. For the ''simple'' process of *heterogeneous* nucleation about randomly distributed seeds, this results in an obvious direct relationship between the cell area distribution (which is known *a priori*) and the resulting island size distribution.[15,16] The same has been suggested for *homogeneous* nucleation,[16] but in fact here these distributions are qualitatively different, the nontrivial relationship between them being determined below.

It is, however, valuable to *quantify* the correlation between cell areas and aggregation rates, and to exploit the results to elucidate the crucial non-MF s dependence of the capture numbers in our model. We let A_s denote the mean area of cells associated with islands of size s. Then, since this tessellation covers the plane, the average cell area satisfies $A_{av}=\Sigma_{s>1}A_sN_s/N_{av}=1/N_{av}$. In Fig. 3(b), we show results for A_s/A_{av} versus s/s_{av}, obtained from tessellating the simulated island distributions at 0.2 ML for $h/F=10^6-10^9$. The form $A_s/A_{av}=B(s/s_{av})$ looks similar to the results for σ_s in Fig. 3(a). This s dependence of A_s can also be described as a correlation between island size and separation.[17] For a more precise comparison of σ_s and A_s, we first note that, from the steady-state relation, the aggregation rate can be rewritten as $R_{agg}(s)\approx FA_{av}(\sigma_s/\sigma_{av})N_s$. Now, if *all* atoms depositing within a cell aggregate with the associated island, then $R_{agg}(s)\approx FA_sN_s$, so it follows that $\sigma_s/\sigma_{av}\approx A_s/A_{av}$. Instead, analysis of our data reveals a quasilinear form, $\sigma_s/\sigma_{av}\approx(1-\alpha)(A_s/A_{av})+\alpha$, for all h/F, where $\alpha=0.30\pm0.03$. It then follows that $C(x)\approx(1-\alpha)B(x)+\alpha$, and consequently that $B(0)\approx 0.88$ is below unity, as is $C(0)$.

The above results provide a geometric interpretation of the relation $\sigma_s/\sigma_{av}\approx C(s/s_{av})$, but do not fully explain its form. To this end, we note that, in the absence of nucleation of new islands, time invariance of σ_s/σ_{av} demands[18] either MF-type s-independent σ_s, or that $\sigma_s/\sigma_{av}=s/s_{av}$. Thus, continuous nucleation throughout the process must play a key role in selecting the observed distinct form of $C(x)$. Since nucleation of new dimers must ''fit'' between existing islands, this process creates areas for new dimers which are smaller than A_{av} [as is demonstrated by the inequality $B(0)<1$]. This tends to produce A_s increasing with s at the onset of deposition, but as the process continues, islands grow due to aggregation, and areas for smaller islands are ''transferred'' to bigger islands. This equalizes areas for smaller islands to $A_2=B(0)A_{av}$, producing the plateau in $C(x)$. Selection of the quasilinear portion of $C(x)$, with $C'(x)<1$, is more subtle, but it is strongly influenced by preferred nucleation in the larger cells associated with the larger islands.

One can also characterize the invariance of $\sigma_s/\sigma_{av}=C(s/s_{av})$ and $A_s/A_{av}=B(s/s_{av})$ with increasing h/F (at fixed θ) from a different perspective. As h/F increases, both the average island separation, $l_{av}=N_{av}^{-1/2}$, and size s_{av} increase. However, if one rescales island sizes by $1/s_{av}$, and all linear dimensions by $1/l_{av}$, a ''similarity ansatz'' implies that the resulting island distributions are indistinguishable. This ansatz produces not only the well-known scaling[2–6] of N_s with s/s_{av}, but also that of the σ_s and A_s.

III. ISLAND SIZE DISTRIBUTION ANALYSIS

To analyze the asymptotic island size distribution for large s_{av}, it is most convenient to adopt a ''quasihydrodynamic approach'' (cf. Ref. 1). Here one treats $x=s/s_{av}$ as a continuous parameter in analyzing the equations $dN_s/dt\approx R_{agg}(s-1)-R_{agg}(s)$, for $s>1$. Then, using $N_s\sim\theta s_{av}^{-2}f(x)$, the right-hand side of this equation becomes

$$dN_s/dt\approx F(s_{av})^{-2}[(1-2\varpi)f(x)-\varpi x f'(x)], \quad (3a)$$

where $\varpi=d(\ln s_{av})/d(\ln t)=1-d(\ln N_{av})/d(\ln t)\approx 1-\bar{\omega}\approx\frac{2}{3}$, and $'=d/dx$. Converting discrete differences to derivatives, invoking the scaling forms for both N_s and σ_s, and using the steady-state condition, $F\approx h\sigma_{av}N_1N_{av}$, the left-hand side becomes

$$-hN_1d(\sigma_sN_s)/ds\approx -F(s_{av})^{-2}[C(x)f'(x)+C'(x)f(x)]. \quad (3b)$$

Above, we have used the independence of $C()$ and $f()$ on θ. Equating Eqs. (3a) and (3b), and integrating for $f(x)$ yields our main result,

$$f(x)=f(0)\exp\left\{\int_0^x dy[(2\varpi-1)-C'(y)]/[C(y)-\varpi y]\right\}. \quad (4)$$

The key determinant of the behavior of $f(x)$ is whether $C(x)$ decreases below $\varpi x \approx 2x/3$, while $C'(x)$ is below $2\varpi - 1$. If so, then $f(x)$ displays a singularity at $x = x_\infty$, where $C(x_\infty) = \varpi x_\infty$. This is the case in the MF treatment ($C = 1$) where $f \propto [1 - \varpi x]^{-(2\varpi - 1)/\varpi}$, for $x < \varpi^{-1}$, and $f = 0$ for $x > \varpi^{-1}$. In contrast, it is clear from Fig. 2(a) that the exact behavior is distinct:[19] $f(x)$ does not diverge, but achieves a finite maximum at $x = x_m (> 1)$, where $C'(x_m) = 2\varpi - 1$. Figure 2(b) shows the $f(x)$ obtained from Eq. (4) using the form for $C(x)$ shown in Fig. 3(a). Note that Eq. (4) implies that $f(0) > 0$, in contrast to recent suggestions,[6] its value of ≈ 0.35 being determined by the normalization of $f(x)$.

IV. COMPACT ISLANDS

As noted above, the same discrepancy between MF and exact behavior of $f(x)$ exists for irreversible nucleation and growth of compact islands[11,13] (even with the BC σ_s). This is not surprising, given Eq. (4). The slowly increasing BC form, $C(x) \sim x^{1/2}$, for large x, and an effective ϖ closer to unity due to saturation of $N_{\rm av}$, still leads to an artificial singularity[13] in $f(x)$. This discrepancy prompted us to obtain ''exact'' simulation results for σ_s for a model of irreversible nucleation and growth of square islands.[3] We found that the form of $C(x)$ is again controlled by island size-separation correlations, and is in fact remarkably similar to point-island behavior (even for $\theta \approx 0.2$ ML where the mean linear island dimension is 45% of $l_{\rm av}$). Its form is in marked contrast to the BC prediction. However, the BC approach does accurately predict $N_{\rm av}$, which is determined by σ_1 and $\sigma_{\rm av}$.

Next, we discuss the relevance of these asymptotic results to the analysis of real systems. Certainly, as temperature (and thus h/F) increases, the assumption of irreversible island formation will eventually break down. However, from Fig. 2 (or Ref. 13), it is clear that for finite h/F above 10^7, the MF prediction and exact island size distribution already differ significantly, reflecting the distinct asymptotic forms. For typical $F \approx 1$ ML/min, island formation is irreversible for Fe/Fe(100) homoepitaxy[7] at least up to 450 K where $h/F \approx 10^8$, and for Ag/Ag(100) homoepitaxy[8] up to 310 K where $h/F \approx 10^9$. Experimental size distributions for such h/F are fit reasonably by ''exact'' point- or square-island simulation results,[2,3] but not by the much more sharply peaked MF results.[13]

V. SUMMARY

We have provided, through Eq. (4) together with simulation results for $C(x)$, a precise characterization of the exact scaling form of the island size distribution for irreversible nucleation and growth during deposition. Our analysis naturally extends to *reversible* island formation with prescribed critical size $i > 1$ (where only islands of size $s > i$ are stable),[1] or to models with significant diffusion of small clusters.[20] In particular, Eq. (4) holds, but with $\overline{\omega}$ the form of $C(x)$ and thus $f(x)$ dependent on i, and on certain details of cluster mobility. A MF divergence in f is avoided due to a significant increase of $C(x)$ with x, and one retains $f(0) > 0$ contrasting previous claims.[6] Recently, we became aware of work[21] on homogeneous nucleation that relates island growth rates to Voronoi cell areas, as suggested previously.[1,15,16] However, Ref. 21 did not identify the key size dependence of the capture numbers, or relate this to the island size distribution, and thus made incorrect predictions for the latter.

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[17] We also determined the average distance l_s from an island of size s to its nearest neighbor: $l_s \propto A_s^{1/2}$, as expected.

[18] In the absence of new nucleation, cell areas A^* and capture numbers σ^* for each island are t invariant, but the size, $s(t)$, increases as $s(t_2) \approx s(t_1) + (t_2 - t_1) F A_{\rm av} \sigma^* / \sigma_{\rm av}$ due to aggregation. Since $s_{\rm av}(t) \approx \theta A_{\rm av}$, one has $s(t_2)/s_{\rm av}(t_2) \approx (\theta_1/\theta_2) s(t_1)/s_{\rm av}(t_1) + (1 - \theta_1/\theta_2)\sigma^*/\sigma_{\rm av}$. If $\sigma_s/\sigma_{\rm av} = s/s_{\rm av}$ at t_1, then the above shows that this relation is t invariant, as is $s(t)/s_{\rm av}(t)$ and the scaling function f. If $\sigma_s = \sigma_{\rm av}$, then f evolves with increasing lower cutoff.

[19] $f(x) > 0$ is analytic if $C(x) > \varpi x$, for all x. If $C(x_m) = \varpi x_m$ when $C'(x_m) > 2\varpi - 1$, then $f(x) \to 0$ continuously as $x \to x_{m^-}$, and $f = 0$ for $x > x_m$.

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