Island-size scaling in surface deposition processes

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Abstract
Diffusion-mediated nucleation and growth of islands during deposition occurs essentially irreversibly in a variety of systems. We provide a scaling theory for the full island-size distribution, both with the ratio of surface diffusion to deposition rates and with time. Scaling functions and exponents are determined by simulation and explained analytically by an unconventional rate-equation analysis. Experimental tests for theoretical predictions are discussed, including the scaling of superlattice beam profiles for diffraction studies of heteroepitaxial systems.

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Island-size scaling in surface deposition processes

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(Received 24 July 1992)

Diffusion-mediated nucleation and growth of islands during deposition occurs essentially irreversibly in a variety of systems. We provide a scaling theory for the full island-size distribution, both with the ratio of surface diffusion to deposition rates and with time. Scaling functions and exponents are determined by simulation and explained analytically by an unconventional rate-equation analysis. Experimental tests for theoretical predictions are discussed, including the scaling of superlattice beam profiles for diffraction studies of heteroepitaxial systems.

Competition between birth, growth, and coalescence of islands during deposition is fundamental to a variety of diffusion-mediated surface adsorption processes. Although traditional nucleation theory provides a rate-equation description of nucleation and growth, the focus is on the dynamics of the formation of stable islands of critical size \( i \geq 1 \), within a quasiequilibrium framework. In a number of adsorption processes, the critical size is effectively one atom or molecule, so aggregation is irreversible. The basic issues then become the determination of the far-from-equilibrium scaling of the island size and separation with system parameters, and characterization of possible nonequilibrium island structure. We provide for such models a precise analysis of the scaling of the full island-size distribution both with the ratio of diffusion to deposition rates and with time. We note that knowledge of this scaling provides a powerful tool for determination of activation energies for surface diffusion (see Ref. 2).

Many experimental studies of such processes can be found in the literature. Mo et al. analyzed scaling associated with irreversible island formation in their scanning tunneling microscopy (STM) study of Si on Si(001) deposition. In studies of metal-on-metal epitaxy, it is often assumed (but not proved) that the critical size is one. In deposition of \( \text{H}_2\text{O} \) on (111) transition-metal surfaces, the surface mobility of \( \text{H}_2\text{O} \) is high, but strong H bonding provides an effective mechanism for irreversible island formation. At the end of the paper, we discuss the use of surface sensitive diffraction as an effective and alternative experimental probe to test the predictions of our theoretical analysis.

Scaling of the island-size distribution, for large surface diffusion rate(s), at low (precoalescence) coverages, should not depend on the details of island shapes or restructuring processes. These "scaling-irrelevant" processes are strongly system dependent, and need to be modeled accordingly. Since our focus is on island-size scaling, we can circumvent these complications by considering a model where island structure is "suppressed." Specifically, we consider particles depositing at random on a square lattice, at constant rate \( r \). Deposited particles hop between neighboring empty sites, until they meet other such particles or immobile islands. In the simplest case, this will be an isotropic walk with hop rate \( h \), but we shall also consider anisotropic walks. In the simulation, islands are chosen to occupy a single site, but with variable size. When a particle undergoing a random walk hops to a site adjacent to another such particle, it aggregates with that particle (irreversibly) nucleating an island of size two. When a particle undergoing a random walk arrives at a site adjacent to an isolated island of size \( s \geq 2 \), it aggregates with that island converting it to size \( s + 1 \). In the rare event (in the regime of large \( h \)) that a particle reaches a site with more than one neighbor occupied by an island or another particle, it aggregates with one of these chosen randomly but weighing by size. In all cases, aggregation is irreversible and trapping occurs instantaneously.

Clearly (at fixed dose \( \theta \) or time \( t \)) the island distribution in this model is determined solely by the ratio \( h/r \) (as confirmed by inspection of the exact master equations). As \( h/r \) increases, particles can on average travel further between deposition events resulting in a lower island density and correspondingly larger average size. Let \( N_s \) denote the density of islands of size \( s \), so the total island density is given by \( N = \sum_{s \geq 1} N_s \) and the particle density by \( n = N_1 \). Then the total dose is \( \theta = \sum_{s \geq 1} s N_s \), and one measure of the average island size is

\[
sav = \frac{\sum_{s \geq 1} s N_s}{\sum_{s \geq 1} N_s} = \theta / (n + N) \sim \theta / N,
\]

when \( N >> n \). We postulate the (precoalescence) scaling relation

\[
N_{s \geq 1} \sim (rt)^{2s+1}(h/r)^{-2s}g[s(h/r)^{1-s}(rt)^w] \quad (1)
\]

for large \( h/r \), and all but short times [specifically for \( rt_{\min} \sim (h/r)^{-1}\), \( rt \ll rt < O(1) \)]. From (1), it follows that \( \theta \sim rt \) given \( \int_0^\infty dx xg(x) = 1 \).
\[ N \sim (r \tau)^{\alpha+1} (h/r)^{-\chi} \int_0^\infty dx \, g(x), \quad (2) \]

\[ n \sim (r \tau)^{-\omega} (h/r)^{-\varphi}, \]

where \( \alpha = -(2\omega + 1), \varphi = 2\chi \), given \( g(0) \neq 0 \); (2) also implies that \( s_n \sim (r \tau)^{-\omega} (h/r)^{\chi} \). Here we determine these scaling exponents and functions. We note that scaling analyses of cluster size distributions have been performed for many diverse models, e.g., percolation,\(^7\) droplet coalescence,\(^8\) Volmer-Weber film growth,\(^9\) and coagulation.\(^10\) Our analysis parallels also recent studies of diffusion-mediated reactions, especially those with input of reactants.\(^11\)

Our simulation results are summarized as follows (more details are presented elsewhere\(^12\)). The simulations involved more than 200 runs on lattices of at least 10\(^2\) sites, with periodic boundary conditions, and over a range of diffusion ratios. At these lattice sizes, and for \( h/r \leq O(10^3) \), finite-size corrections were negligible. The same code is used to analyze average nucleation and aggregation lifetimes, granting a direct check of the rate equations advanced in this work. To study strongly anisotropic diffusion, particles undergoing a random walk were allowed to hop horizontally but not vertically. This case of extreme anisotropy is not equivalent to, but scales like the purely one-dimensional process.\(^12\) Figure 1 shows the scaling with \( h/r \) of the particle and island densities. Estimates \((\pm 0.03)\) of the exponents \( \chi \) and \( \varphi \), in the range \( h/r = 10^4 - 10^6 \), are obtained from the average slopes: \( \chi \approx 0.24, \varphi \approx 0.52 \) for \( d_w = 1 \), and \( \chi \approx 0.30, \varphi \approx 0.62 \) for \( d_w = 2 \), to be compared with the asymptotic values given by the rate-equation theory below, respectively \( 1/4, 1/2, 1 \), and \( 1/3 \). The small but significant discrepancies between simulation and rate-equation exponents reflect the fact that the simulations have not reached the true asymptotic regime. We confirm this by noting that the rate equations for \( d_w = 2 \) (with certain logarithmic corrections) essentially exactly reproduce the simulation results over the finite range of \( h/r \leq 10^5 \). Figure 2 explores the scaling of the densities of islands and particles (undergoing random walks) with time, as suggested in (2), and indicates that \( \omega \approx -0.76, \alpha = 0.48 \) for \( d_w = 1 \), and \( \omega \approx -0.67, \alpha \approx 0.31 \) for \( d_w = 2 \). The scaling of the island-size distribution is demonstrated in Fig. 3, according to (1). Again data collapse improves with increasing \( h/r \). Clearly the scaling function \( g(x) \) approaches a nonzero constant as \( x \to 0 \). We have obtained similarly good collapse for the island-size scaling in time.\(^12\)

Two key observations underlie our analysis of this process via "unconventional" rate equations: (i) the lifetimes \( \tau \) for particles to undergo nucleation (meeting other particles) and aggregation (meeting islands) are comparable for large \( h/r \). We directly confirmed this in the simula-

![Figure 1](image1.png)

**FIG. 1.** Simulation results for the scaling of the average island \( N \) and particle \( n \) densities with the ratio \( h/r \), in the range \( h/r = 10^4 - 10^6 \), at fixed dose \( \theta \). Shown are the cases of isotropic \((N, \circ; n, \bullet; \theta = 5\% \rangle\), and strongly anisotropic \((N, \square; n, \blacksquare; \theta = 10\%)\) diffusion.

![Figure 2](image2.png)

**FIG. 2.** Simulation results for the scaling in time of the average island and particle densities, in the range \( h/r = 10^4 - 10^6 \), for (a) isotropic \((rt \leq 5\%)\) and (b) strongly anisotropic diffusion \((rt \leq 10\%)\). The axes were scaled using the asymptotic values of the scaling exponents (see text). The dashed lines show the asymptotic slopes (whose values are in parentheses) in the scaling regime, as well as the corresponding time dependence in the initial transient regime, in which, from (3), \( n \sim rt \) and \( N \sim (h/r)(rt)^{1/3} \).
tions (see Table II in Ref. 12); (iii) the probability that a deposited atom nucleates rather than aggregates scales like \( p \sim n/(n+N) \approx n/N \ll 1 \), if \( n \ll N \). One thus obtains the equations

\[
\frac{dN}{dt} \approx rN + \frac{n}{\tau} p, \quad \frac{dn}{dt} \approx -\frac{n}{\tau}.
\]

(3)

While (i) and (ii) apply for rather general dynamics of deposited atoms, we only elucidate their validity for random walks (RWs) of relevance here. The space-filling property of \((d_w \leq 2)\)-dimensional RW guarantees that particles undergoing a random walk meet near rather than distant neighboring islands or particles. Thus atoms must deposit in the “vicinity” of another particle for nucleation, which occurs with probability \( p \sim n/N \). Furthermore, after short times, for both nucleation and aggregation lifetimes, \( h \tau \) measures the number of steps for a RW to visit \( 1/(N+n) \sim 1/N \) sites associated with each island or particle. Thus one has\(^{13} \) \( h \tau \sim \pi /\sqrt{N}^2 \,(1/\pi N) \), for \( d_w = 1 \) \((2)\) (see also Table II in Ref. 12). This contrasts Mo et al.,\(^2\) who assume that a particle visits \( 1/n \) sites before nucleation.

The above rate-equation formulation for the particle and island densities can be extended to characterize the full island-size distribution \( N_s \) for sizes \( s \geq 1 \). We note that our \( N_s \) equations are presented in a form somewhat different from the usual Smoluchowski equations (cf. Refs. 9 and 10). Let \( p_i \) denote the probability of deposition in the “vicinity” of an island of size \( s \), so \( p_i \sim N_i/(n+N)-N_i/N \). \( p_i \) and \( \sum_s p_s \) are. Islands of size \( s \) can be created by deposition adjacent to or aggregation with an island of size \( s-1 \); likewise they can be removed by conversion to size \( s+1 \) islands through deposition or aggregation processes. Since the characteristic time for all aggregation processes is \( \tau \), specified above, we conclude that

\[
\frac{dN_s}{dt} \approx rN_{s-1} - rN_s + \frac{n}{\tau} p_{s-1} - \frac{n}{\tau} p_s.
\]

(4)

The equation for \( N_1 = n \) is as above, and applying \( \sum_{s \geq 2} \) to (4) recovers the \( dN/dt \) equation.

Integration of (3) demonstrates that a quasistationary regime exists, where \( dn/dt \sim 0 \) (giving \( n \sim r \tau \), for large \( h/r \) and \( n \ll N \ll 1 \)), in which the relations

\[
\left\{ \begin{array}{l}
n(1) = \frac{1}{(h/r)N}, \quad n(d_w = 1) = \frac{1}{(h/r)N^2} \end{array} \right.
\]

(5)

hold. Substitution of (5) into the \( dN/dt \) equation in (3) yields after integration \( \chi = \frac{1}{2}, \omega = -\frac{1}{2} \) for \( d_w = 1 \), and \( \chi = 2, \omega = -\frac{1}{2} \) for \( d_w = 2 \); \( \alpha \) and \( \varphi \) follow from (5) or the scaling relations described above. Note that the set of exponents corresponding to strongly anisotropic diffusion is different from the one postulated in Ref. 2. Logarithmic corrections to the lifetimes for isotropic diffusion\(^{12} \) introduce corresponding corrections to scaling, e.g., \( N \sim (r \tau)^{\alpha/(\alpha+1)} \), where \( \alpha = 0,1 \) for \( d_w = 1 \), \( 2 \) for \( d_w = 2 \), and \( \varphi \) follow from (5) or the scaling relations described above. Note that some of the quantitative differences between simulation and rate-equation results in Fig. 3 derive from the use of different effective exponents and from the approximate estimate of lifetimes.\(^{12} \) Neglect of fluctuations in the rate equations may produce more fundamental differences. Detailed analysis of (4) yields a non-analytic scaling function \( g(x) \) identically zero for \( x \) above some cutoff.\(^{12} \) Nonanalyticity of \( g(x) \) is not clear from the simulation data.

It is important to verify the predicted scaling theory in (1) and (2) as a function of all the parameters involved, i.e., time \( t \) and the ratio \( h/r \), and to obtain the scaling function \( g(x) \). Although STM studies provide directly the island density and size distribution (if the atomic resolution is not compromised in order to increase the scan over larger areas needed for good statistics), the time dependence is less accessible. The STM analysis is performed on a frozen-in configuration, at the end of the run after the crystal is cooled back to room temperature.

In contrast, surface-sensitive diffraction techniques often have sufficient time resolution to monitor the real-time deposition process. One also obtains excellent statis-
and Blakely\textsuperscript{14} and expected to be reasonable in the precoalescence regime\textsuperscript{15} that one can ignore the interference between scattering from different islands at the superlattice spot. Let \( \mathbf{q} \) denote the lateral momentum transfer (multiplied by the lattice constant), \( \delta \mathbf{q} = \mathbf{q} - \mathbf{q}^* \) denote the reciprocal-space distance from the center of the superlattice spot \( \mathbf{q}^* \), and \( I_s(\delta \mathbf{q}) \) denote the average scattered intensity for islands of size \( s \). Then one has for the superlattice spot profile \( I_s(\delta \mathbf{q}) = \sum_i N_i I_s(\delta \mathbf{q}) \). In the scaling regime of large \( s_{av} \), one has \( I_s \sim s^2 f(s^{1/2} \delta \mathbf{q}) \), for \( s^{1/2} \delta \mathbf{q} = O(1) \), and one can then invoke (1) to obtain

\[
S(\delta \mathbf{q}) \sim \langle \mathbf{q} \rangle^{1-\alpha} \left( \frac{\hbar}{m} \right) \delta \mathbf{q} \frac{g(\mathbf{q})}{\mathbf{q}^2} \left( \frac{h}{r} \right)^{\chi/2} \delta \mathbf{q}^{1/2}
\]

where \( g(\mathbf{q}) = \int_0^{\alpha} dx x^2 g(x) f(x) \). In particular, (6) predicts that the readily measured superlattice spot peak intensity should scale as \( S(0) \sim \langle \mathbf{q} \rangle^{1-\alpha} (\hbar/r)^{\chi/2} \). Figure 4 demonstrates the full scaling (6) for two sets of \( h/r \) and \( rt \) values. We used, somewhat arbitrarily, the scattered intensity profile for circular islands with \( p(m \times m) \) structure, for which \( f(x) = 4 \pi m^2 x^{-1} J_1^2(\pi n x \pi z) \), where \( z = |\mathbf{q}| \) and \( J_1 \) is the first-order Bessel function of the first kind.

Finally, it is appropriate to note here that additional information on the island distribution is contained in the specular diffracted spot, specifically from the shape of the profile near \( \mathbf{q} = 0 \). This might be expected to be related more directly to the average island separation \( l_{av} = N^{-1/2} \), so its analysis would provide an additional probe to scaling.\textsuperscript{16}

The work of M. C. B. and J. W. E. was supported by the National Science Foundation Grant No. CHE-9014214. M. C. T. was supported by Ames Laboratory. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82.

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\textsuperscript{1}J. A. Venables, Philos. Mag. 27, 697 (1973).
\textsuperscript{6}The often used measure is a weight average \( s_{av} = \sum s^n n_i / \sum n_i \), but with regard to the scaling with \( t \) and \( h/r \), the choice is irrelevant. However, the relation between \( s_{av} \) and \( \theta \) is not as simple.
\textsuperscript{13}A \( (d_u = 2) \) RW between nearest neighbor sites visits on average \( \pi H / \ln H \) distinct sites after \( H \) steps, for large enough \( H \), while for the \( (d_u = 1) \) RW this number is only \( (8H/\pi)^{1/2} \). Since a particle needs to visit an average of \( 1/N \) sites to be annihilated, \( H(d_u = 2) = 1/(\pi N) \ln(1/\pi N) \) and \( H(d_u = 1) = \pi/(8N^2) \).