Influence of island diffusion on submonolayer epitaxial growth

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We investigate the kinetics of submonolayer epitaxial growth which is driven by a fixed flux of monomers onto a substrate. Adatoms diffuse on the surface, leading to irreversible aggregation of islands. We also account for the effective diffusion of islands, which originates from hopping processes of their constituent adatoms, on the kinetics. When the diffusivity of an island of mass k scales as $k^{-\mu}$, the (mean-field) Smoluchowski rate equations predicts steady behavior for $0 \leqslant \mu < 1$, with the concentration c_k of islands of mass k varying as $k^{-(3-\mu)/2}$. For $\mu \geqslant 1$, a quasistatic approximation of the rate equations predicts a slow continuous evolution, in which the island density increases as $(\ln t)^{\mu/2}$. A more refined matched asymptotic expansion reveals unusual multiple-scale mass dependence for the island size distribution. Our theory also describes basic features of epitaxial growth in a more faithful model of growing circular islands. For epitaxial growth in an initial population of monomers and no external flux, a scaling approach predicts power-law island growth and a mass distribution with a behavior distinct from that of the nonzero flux system. Finally, we extend our results to one- and two-dimensional substrates. The physically relevant latter case exhibits only logarithmic corrections compared to the mean-field predictions. [S0163-1829(99)09223-1]

I. INTRODUCTION

Submonolayer epitaxial thin-film growth involves deposition of atoms onto a substrate, and diffusion of these adatoms (monomers) leading to aggregation of islands of ever-increasing size.[1,2] The resulting island morphology and mass distribution ultimately depend on these substrate diffusion processes. While it has long been recognized that these mass transport details are crucial to epitaxial growth,[1] its ramifications are still incompletely understood. Part of the reason for this slow progress is that a variety of microscopic details can and do influence the rate at which adsorbate islands move.[3–15]

One direction of previous investigation was based on a picture that only monomers can diffuse, while larger islands are immobile.[2–5] In this case, the island density N scales with time as $t^{1/3}$ before it reaches a maximum density which scales with flux F as $F^{1/3}$. Subsequent work revealed, however, that basic results are sensitive to minor alterations to the mass transport mechanism. For example, if both monomers and dimers diffuse while larger islands remain immobile, the exponents of the time and flux dependences change.[10] More generally, these exponents depend on the threshold size between mobile and immobile islands.

On the other hand, there has been increasing appreciation[11–14] that adatom hopping continues to occur even when adatoms are incorporated into islands of arbitrary size. This leads to a nonzero diffusivity of such islands. For appropriate systems and experimental conditions there is ample evidence that the effective island diffusivity D_k has a power-law dependence on mass k.[11–14] This adatom hopping also typically leads to islands maintaining compact shapes, an important simplifying feature for theoretical modeling.

The goal of this paper is to determine the aggregation kinetics of compact islands in the submonolayer regime with power-law and more general mass-dependent island diffusivities.[16] An essential, and at first sight surprising, feature about such compact islands is that their reactivity depends only logarithmically on island size in two dimensions. Accordingly, our theoretical treatment is based on a model of pointlike islands. Such a description should accurately describe island growth, up to these logarithmic corrections in the low-coverage limit.

Within the mean-field Smoluchowski rate equations, we will consider a system with (i) a fixed monomer flux, (ii) pointlike islands with diffusivity which decays faster than inversely with island mass, and (iii) irreversible mass-conserving coalescence of islands. We will show that the number of islands grows logarithmically in time, and that the island mass distribution exhibits a multiple-scale mass dependence. Our predictions are also found to apply to a more faithful model of epitaxial growth in which islands are growing circles, with the radius of a mass-k island proportional to $\sqrt{k}$. Thus the point-island model provides a useful framework to describe submonolayer epitaxial growth, and gives quantitative predictions which are robust to variations in model parameters.

In Sec. II, we introduce our model and discuss the applicability of the Smoluchowski approach to epitaxial growth. In Sec. III, we present our main results about the asymptotic growth of islands based on the rate equations. Different behaviors arise depending on whether the mobility exponent μ

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is smaller than, larger than, or equal to unity. We also discuss the flux dependence of the maximum island density and the time range where our theory should apply. In Sec. IV, we briefly discuss island growth kinetics in the absence of external flux. In Sec. V, we present numerical simulations, and compare results for the epitaxial growth of point islands and growing circular islands with radius proportional to $\sqrt{k}$. Section VI contains a summary and discussion. In Appendix A, we generalize our theory to one-dimensional substrates, and in Appendix B we outline a more accurate treatment for two-dimensional substrates which accounts for the logarithmic corrections in the reaction rate.

II. MICROSCOPIC MODEL

We consider submonolayer epitaxial growth which results from the irreversible deposition of atoms from a gas onto a substrate and subsequent irreversible aggregation. Adatoms (or monomers) diffuse on the substrate and aggregate upon colliding, creating dimers and larger islands. We consider the class of models for which adatoms which are already incorporated into islands can continue to diffuse—this often occurs along the periphery of islands (see, e.g., Ref. 14). Such adatom hopping induces an effective diffusion in which islands of mass k hop on the substrate with diffusion coefficient D_k. This microscopic mechanism also typically leads to compact island shapes. Whenever two islands meet and aggregate, we assume that adatom hopping quickly causes the resulting aggregate to become compact. We therefore treat islands as circular throughout our modeling.

Within this picture for islands, a classic way to calculate the island mass distribution is based on the Smoluchowski rate equations.[17] This approach requires knowledge of the rate K_{ij} at which an island of mass i and an island of mass j aggregate to form an island of mass $i+j$. If the aggregation process is diffusion-controlled and islands are spherical, this aggregation rate is given by the Smoluchowski formula $K_{ij} \sim (D_i+D_j)(R_i+R_j)^{d-2}$ in d dimensions.[17] Here R_i is the radius of an island of mass i. This formula applies for $d>2$, while in the physically relevant case of two-dimensional substrates there is only a slow logarithmic dependence on island radius.[17] Thus a reasonable starting point for theoretical investigation is to ignore the logarithmic term; this significantly simplifies the resulting analysis. In Appendix B we will return to the two-dimensional case and show that these logarithmic corrections do not alter our main findings but rather give rise to a logarithmic renormalization of the monomer flux.

As discussed in the Introduction, we consider the island diffusion coefficient to be a homogeneous function of island mass, $D_k \sim k^{-\mu}$ with μ non-negative on basic physical grounds. In appropriate time units the reaction rate is

$$K_{ij} = i^{-\mu} + j^{-\mu}. \tag{1}$$

However, our approach can equally well be applied to *any* functional dependence of D_k on k which decays faster than k^{-1} as $k \to \infty$.

For a self-contained discussion, we give a qualitative argument for the exponent value $\mu = \frac{3}{2}$ for the "periphery" adatom hopping mechanism; this was obtained previously by a Langevin approach.[14,18] In periphery diffusion, adatoms on the edge of an island can hop freely to neighboring sites on the periphery. Consider an island of linear size $R \gg 1$. In a time interval $\Delta t \sim R^2$ an adatom on the edge will typically explore the entire island boundary, so this adatom will typically be a distance R from its initial location. Hence the effective island center-of-mass displacement is $\delta x \sim R/R^2 = R^{-1}$. If each edge adatom diffuses independently, the total center-of-mass displacement Δx is the sum of R independent identically distributed random variables with variance $\delta x \sim R^{-1}$. This implies $\Delta x \sim \sqrt{R(\delta x)^2} \sim R^{-1/2}$. Thus the effective center-of-mass diffusion coefficient is $D_R \sim (\Delta x)^2/\Delta t \sim R^{-3}$, or $D_k \sim k^{-3/2}$. For a d-dimensional substrate, a straightforward generalization of this argument gives $\mu = 1 + 1/d$. Similarly, in the case of so-called "terrace" diffusion,[14] it is found that $D_k \sim k^{-1}$ independent of d.

Before presenting detailed results, we discuss some limitations of our rate-equation approach. As stated previously, we ignore the effect of a finite island radius on the form of the reaction rates, as this dependence is only logarithmic in two dimensions. Moreover, as the coverage increases a rate-equation description based on two-body aggregation eventually breaks down. Our approach is also inapplicable to fractal-shaped islands, a situation which can arise at low temperature.[19] Finally, the rate-equation description should fail below an upper critical dimension d_c (Ref. 20) which is given by $d_c = 2/(1-\mu-\lambda)$, with λ the homogeneity degree of the reaction kernel. For our point-island model with kernel given by Eq. (1), $\lambda = -\mu$, and hence $d_c = 2$. Thus the relevant two-dimensional case corresponds to the critical dimension, and logarithmic corrections to mean-field predictions, in addition to the previously discussed logarithmic corrections to the reaction rate, can be anticipated.

III. GROWTH WITH FLUX

Consider a point-island system with a steady monomer flux F onto the substrate. The mean-field rate equations for the concentrations c_k of islands of mass k in the presence of this flux are

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - c_k \sum_{k=1}^{\infty} K_{kj} c_j + F\,\delta_{k1}. \tag{2}$$

A. Steady-state regime

As derived in Ref. 16, the steady-state concentration approaches the power-law form

$$c_k \sim k^{-\tau} \tag{3}$$

as $k \to \infty$, with $\tau = (3-\mu)/2$. This steady state holds as long as $\tau > 1$, which thus imposes an upper bound $\mu < 1$ on the mobility exponent. In the special case of constant reaction rate, $\mu = 0$, one can find the time-dependent solution, which we quote for completeness. The rate equation for the density is

$$\frac{dN}{dt} = -N^2 + F, \tag{4}$$

and the rate equation for the generating function, $C(z,t) = \sum_{k=1}^{\infty} c_k(t) z^k$, is

$$\frac{d\mathcal{C}(z,t)}{dt}=\mathcal{C}(z,t)-2\mathcal{C}(z,t)N(t)+Fz. \tag{5}$$

The solutions to these equations for initially clean surface, $c_k(0)=0$, are

$$N(t)=\sqrt{F}\tanh(t\sqrt{F}),$$
$$\mathcal{C}(z,t)=N(t)-\sqrt{F(1-z)}\tanh[t\sqrt{F(1-z)}]. \tag{6}$$

Expanding the generating function $\mathcal{C}(z,t)$ in a series in z gives the concentrations $c_k(t)$. Relatively simple results are obtained in the long-time limit

$$c_k(t)=\sqrt{\frac{F}{4\pi}}\,\frac{\Gamma(k-\frac{1}{2})}{\Gamma(k+1)}. \tag{7}$$

Notice that islands of sizes comparable with $(1-z)^{-1}$, or smaller, give dominant contribution to the generating function, while larger islands provide an asymptotically negligible correction. The second of Eqs. (6) also shows that the crossover from a time-dependent to a saturated behavior takes place when $t\sqrt{1-z}\sim 1$. Using $k\sim(1-z)^{-1}$ this implies that the steady state is established for small islands in the size range, $k\ll t^2$. For a general mobility exponent, one physically expects a similar crossover to steady behavior when $k\sim t^{\zeta}$, with a mass cutoff exponent ζ dependent on μ. To determine ζ, we use the physical condition that the total mass on the substrate $\Sigma k c_k(t)$ equal Ft together with the steady-state asymptotics of Eq. (3). This gives

$$\sum_{k=1}^{\infty} kc_k(t)\sim\sum_{k=1}^{t^{\zeta}} k^{(\mu-1)/2}\sim t^{(\mu+1)\zeta/2}\sim t, \tag{8}$$

that is, $\zeta=2/(\mu+1)$.

B. Continuous island evolution

For a mobility exponent $\mu\geq 1$, continuous evolution can be anticipated. Indeed, in the extreme case of $\mu=\infty$ (that is, mobile monomers and *immobile* islands), power-law growth in the number of islands, $N(t)\simeq(3F^2t)^{1/3}$, occurs.[2–5] As discussed in Sec. II A, values of the mobility exponent $\mu\geq 1$ naturally appear for different microscopic mass-transport mechanisms. The marginal case of $\mu=1$ is also interesting since it corresponds to the experimentally relevant case of terrace diffusion.[14]

Our primary results are that when μ is strictly greater than unity but still finite,

$$N(t)\simeq\sqrt{F}\left[\frac{\sin(\pi/\mu)}{\pi}\ln(t\sqrt{F})\right]^{\mu/2}, \tag{9}$$

while the concentration of islands of mass k decays in time as

$$c_k(t)\sim\sqrt{F}\,(k!)^{\mu}\,[\ln(t\sqrt{F})]^{-\mu(2k-1)/2} \tag{10}$$

for $k\ll\ln(t\sqrt{F})$. Remarkably, these logarithmic dependences, a feature which generally signals marginal behavior, occur in the entire regime $1<\mu<\infty$.

Our approach is based on the physical picture that the slow growth of islands by aggregation is substantially counterbalanced by monomer input. This competition leads to nearly steady island concentrations within an "inner" size range, while time-dependent behavior occurs in an "outer" range. In the inner region, the near balance between aggregation and input motivates the quasistatic approximation, where the time derivative in Eq. (2) is initially neglected. The time dependence of the island concentrations is then determined by the condition that the total mass in the system is proportional to t. The validity of this approach is verified *a posteriori*—the logarithmic dependences in Eqs. (9) and (10) indeed imply that the temporal derivatives in the Smoluchowski rate equations are asymptotically negligible.

Solving the resulting quasistatic equations recursively gives[16]

$$c_k\simeq\frac{1}{N}\left[\prod_{j=2}^{k}\frac{j^{\mu}/N^2}{1+j^{\mu}/N^2}\right]\prod_{j=1}^{k-1}(1+j^{-\mu}). \tag{11}$$

This implies that c_k is a rapidly decreasing function of k for $k\ll N^{2/\mu}\equiv\kappa$, which then converges[16] to a finite value ρ, for $k>\kappa$, whose value is

$$c_k\to\rho\sim\frac{1}{N}\exp[-A_{\mu}N^{2/\mu}], \tag{12}$$

with $A_{\mu}=\int_0^{\infty}\ln(1+w^{-\mu})\,dw=\pi/\sin(\pi/\mu)$. This constancy in c_k should persist over the range, $\kappa\lesssim k\ll K(t)$. Here $K(t)$ defines the upper limit for the "inner" regime where the quasistatic approximation remains valid (see below). This value corresponds to the size where islands are only beginning to form, and is determined below.

Because the temporal decay of the densities is relevant in the outer size range, $k\gg\kappa$, an alternative to the quasistatic approximation is needed. Our approach is to account separately for these "raw" (evolving) islands, and then perform a matched asymptotic expansion,[21] to join the inner ($k\ll K$) quasistatic solution of "ripe" islands to the outer ($k\gg\kappa$) solution of raw islands in the overlap region $\kappa\ll k\ll K$. This approach gives[16]

$$c_k(T)\sim\frac{[\ln(T-k)]^{\mu/2-1}}{T-k}, \tag{13}$$

where $T=\int_0^t dt'\,c_1(t')$. Thus the density of raw islands reaches a peak value of the order of $t^{-1/2}$ when $k\approx K(t)=T$, and then rapidly decreases for larger k. Note also that the relation between the real and modified times, $T=\int_0^t dt'\,c_1(t')$, together with $c_1\cong 1/N$, gives $T\simeq t/N$ and thus the criterion $K(t)\simeq t/N\sim t/(\ln t)^{\mu/2}$. In real time the island density is

$$N(t)\simeq\left\{A_{\mu}^{-1}\ln\left[t\left(\frac{\ln t}{A_{\mu}}\right)^{1-3\mu/2}\right]\right\}^{\mu/2}, \tag{14}$$

where $A_{\mu}=\pi/\sin(\pi/\mu)$. Upon neglecting the logarithmic temporal factor inside the logarithm, our basic result quoted in Eq. (9) is recovered.

C. The case $\mu=1$

In the borderline case $\mu=1$, a subtler nested logarithmic behavior arises, as reflected by a singularity in Eq. (9) upon formal continuation to $\mu\to 1$. Here we outline the main features of our analysis for the inner size range, which closely parallels that for the case $\mu>1$.[16] The interesting features associated with $\mu=1$ are (i) the product $\Pi_{j=1}^{k-1}(1+j^{-1})$ in Eq. (11) now equals k, i.e., it diverges; and (ii) the term c_2c_{k-2}, in addition to c_1c_{k-1}, contributes to asymptotic behavior. Due to this latter attribute, the recursion relation for c_k becomes

$$\frac{c_k}{k}\,\frac{1+k/N^2}{k/N^2}=\frac{c_{k-1}}{k-1}+\frac{c_{k-2}}{k-2}\,\frac{1}{N^2}. \tag{15}$$

We seek a solution for c_k in the form of Eq. (11). Thus we write

$$c_k\sim\mathcal{C}_k\frac{k}{N}\left[\prod_{j=2}^{k}\frac{j/N^2}{1+j/N^2}\right], \tag{16}$$

where the factor $\mathcal{C}_k$ accounts for the additional term in Eq. (15). Substituting into Eq. (15) gives the recursion formula for this correction factor $\mathcal{C}_k$:

$$\mathcal{C}_k=\mathcal{C}_{k-1}+\mathcal{C}_{k-2}\left(\frac{1}{k-1}+\frac{1}{N^2}\right). \tag{17}$$

These coefficients are slowly varying in k when $k\gg 1$, and we may treat k as continuous in this asymptotic regime. Then the difference equation (17) becomes a differential equation whose solution is $\mathcal{C}_k\sim k\,e^x$ (with $x=k/N^2$). Consequently,

$$c_k\sim\frac{k^2}{N}\exp\left[x-N^2\int_0^x\ln(1+w^{-1})\,dw\right]. \tag{18}$$

Thus, for $\mu=1$, the concentration c_k decreases rapidly in k for $k\ll N^2$ and reaches a minimum at $k=N^4$ whose value is

$$\rho\sim\exp[-N^2\ln N^2]. \tag{19}$$

In the outer size range, the matched asymptotic expansion approach is still valid, and gives the total island concentration

$$N(t)\sim\sqrt{\frac{\ln t}{\ln(\ln t)}}. \tag{20}$$

Equation (16) together with $\mathcal{C}_k\sim k$ implies that the concentration of islands for mass $k\ll N^2$ is

$$c_k(t)\sim\frac{(k+1)!}{N^{2k-1}}\sim(k+1)!\left[\frac{\ln(\ln t)}{\ln t}\right]^{k-1/2}. \tag{21}$$

Then the island mass density is approximately constant,

$$c_k(t)\sim t^{-1}(\ln t)^{-1}[\ln(\ln t)]^{-1}. \tag{22}$$

This holds over the range $\kappa\lesssim k\ll K$ with $K(t)\sim t\sqrt{\ln(\ln t)/\ln t}$. Finally, the raw island density given by Eq. (22) holds up to a mass cutoff $K(t)$.

IV. GROWTH WITHOUT FLUX

We now consider epitaxial growth for point islands with a nonzero initial monomer density, reaction rate $K_{ij}=i^{-\mu}+j^{-\mu}$, and no subsequent monomer flux. Such a system has been extensively investigated within the framework of irreversible aggregation,[22–26] as well as in theoretical studies of point-island aggregation with immobile islands.[3,27] More realistic examples of the latter system have also been investigated numerically and experimentally in recent studies (see Refs. 13 and 28 and references therein).

We give here a simple argument for the asymptotic form of the island size distribution. This argument is based on first solving for the island and monomer densities, $N(t)$ and $c_1(t)$, respectively, and then using scaling[17] to infer the asymptotics of the distribution. According to the scaling ansatz, the asymptotic island-mass distribution should have the form

$$c_k(t)\simeq N^2G(x),\quad x=kN, \tag{23}$$

for finite x. The constraints $\int dx\,G(x)=1$ and $\int dx\,x\,G(x)=\theta$ automatically enforce the conditions $\Sigma c_k(t)=N(t)$ and mass conservation $\Sigma kc_k(t)=\theta$. Starting with the exact rate equation for $N(t)$,

$$\frac{dN}{dt}=-\frac{1}{2}\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}K_{ij}c_ic_j, \tag{24}$$

we substitute the scaling ansatz [Eq. (23)] to obtain $\dot N\sim -N^{2+\mu}$, whose solution is

$$N(t)\sim t^{-1/(1+\mu)}. \tag{25}$$

Now consider the rate equation for the monomer density, $\dot c_1=-Kc_1(N+N_\mu)$. As shown by the quasistatic approximation,[16] we may neglect the second term and integrate the resulting equation to yield $c_1(t)\sim\exp[-t^{\mu/(1+\mu)}]$. This result, together with Eqs. (23) and (25), predicts the small-x asymptotic behavior $\exp(-1/x^\mu)$ for the scaling function. Conversely, for the entire class of reaction kernels of the form $K_{ij}=i^{-\mu}+j^{-\mu}$, the scaling function $G(x)$ decays exponentially[17] in x for large x. Combining these results gives the asymptotic forms of the island size distribution in the absence of monomer flux:

$$G(x)\sim\begin{cases}e^{-1/x^\mu}, & x\downarrow 0,\\ e^{-x}, & x\uparrow\infty.\end{cases} \tag{26}$$

To determine the validity of these mean-field predictions, let us consider the kinetics of this process in general spatial dimension. To this end, we determine the reactivity of an arbitrary cluster by a dimensional argument. Consider an island of radius R which diffuses with the diffusion coefficient D in d-dimensional space. During a time interval t this particle traces out the so-called "Wiener sausage," whose volume is[29]

$$V_d(t)\sim\begin{cases}Dt[\ln(Dt/R^2)]^{-1}, & d=2\\ DtR^{d-2}, & d>2.\end{cases} \tag{27}$$

For epitaxial growth with no flux, R corresponds to a (growing) average island radius, and D to the diffusivity of a mass-

k island, $D\sim k^{-\mu}\sim R^{-d\mu}$. Clearly, all monomers initially within a Wiener sausage aggregate into a typical island by time t. Consequently, the initial coverage of the substrate θ is given by $R^d\sim\theta V_d(t)$. This, together with Eq. (27), gives $R^2\sim Dt$ for *all* $d\geq 2$. Finally, combining $R^2\sim Dt$ and $D\sim R^{-d\mu}$ leads to

$$R\sim t^{1/(2+d\mu)},\quad N\sim t^{-d/(2+d\mu)}. \tag{28}$$

In two dimensions, the rate-equation predictions [Eq. (25)] and the above heuristic argument agree. Thus in the absence of a monomer flux, and under the assumption of compact islands, the two sources of logarithmic corrections—a logarithmic dependence of the reaction rate on island radius and the fact that the system is at the critical dimension—evidently cancel each other. Therefore the Smoluchowski rate equations appear to be asymptotically correct in two dimensions.

V. NUMERICAL RESULTS

We performed Monte Carlo simulations for island growth for two models of epitaxial growth. We first consider point islands, in which single-site islands hop with equal probability to any lattice site (diffusion on a complete graph) and aggregate whenever two islands occupy the same site. This corresponds to the mean-field limit, and thus provides a direct test of some of the delicate approximations made in our theoretical analysis. The second model is a more faithful description in which circular island "droplets" with radius proportional to the square root of the island mass diffuse to nearest-neighbor sites on a two-dimensional lattice. Whenever there is overlap of two islands, they immediately coalesce to a single island which is centered at the initial position of the larger island. After each coalescence, a test is made to determine if additional overlaps have been created. All such higher-order coalescences are performed until all overlaps are resolved. Here we treat only the case with external flux, since growth without flux has already been investigated numerically (see, e.g., Ref. 26 and references therein).

The point-island model is relatively easy to implement. Additionally, this model has a technical advantage over growing droplets in that the submonolayer description applies over a longer time range. For point islands, the submonolayer regime is defined by the criterion $N\ll 1$, which is considerably less stringent than the criterion $Ft\ll 1$ appropriate for the droplet-island model. Therefore our theoretical results may be compared with the point-island simulations in the time range $F^{-1/2}\ll t\ll\exp(-F^{-1/\mu})$, and with droplet-island simulations in the time range $F^{-1/2}\ll t\ll F^{-1}$.

A. Point islands

Due to the pointlike nature of islands and the equiprobable hopping to any site of the system, the simulations correspond directly to the Smoluchowski rate equations. Simulations of point islands were performed on a graph of L sites with the following time evolution. At any stage, the total deposition rate is FL^2, while the aggregation rate is $L_{\rm occ}^2$. Here $L_{\rm occ}$ is the number of occupied sites in the system. In a microscopic event, deposition is chosen with probability $r_{\rm dep}=FL^2/(FL^2+L_{\rm occ}^2)$, and aggregation is chosen with probability $r_{\rm agg}=1-r_{\rm dep}$. In a deposition event, a monomer is deposited onto a randomly chosen vacant site. We checked that restricting the deposition onto unoccupied sites only does not alter our results. In an aggregation event, two sites were chosen randomly from the list of occupied sites. If these sites contain islands of mass i and j, aggregation occurs with probability $(i^{-\mu}+j^{-\mu})/2$. Time is then increased by $\Delta t=1/(FL^2+L_{\rm occ}^2)$, and the procedure is repeated.[30]

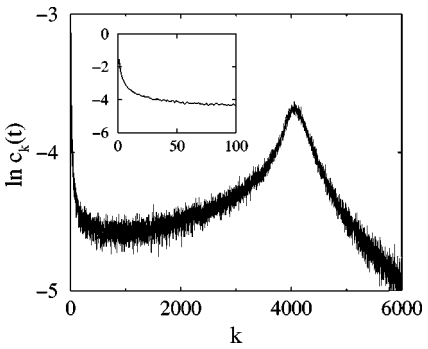

FIG. 1. Semilogarithmic plot of $\ln c_k(t)$ vs k at $t\approx 22\,000$ for $\mu=1.5$ based on simulations of point islands. The data are based on 5000 realizations of an initially empty system of 2000 sites with $F=0.05$. Notice the existence of an inner scale $k\lesssim\kappa\approx 50$ (inset), and an outer scale for $k\approx K\approx 4000$.

To test our algorithm, we considered first the extreme case of immobile islands, $\mu=0$, where a complete time-dependent analytical solution is available [Eq. (6)]. Simulations were performed for an initially empty system with L between 10^3 and 10^4. We found excellent agreement between numerical and theoretical predictions, both for the steady state and transient characteristics. More generally for $\mu<1$, our simulations showed that the system reaches a steady state with the observed steady-state characteristics, in good agreement with the theoretical prediction of Eq. (3).

For $\mu>1$, the total number of islands is found to increase indefinitely, and the island mass distribution substantively agrees with our theoretical predictions (see Fig. 1). Indeed, the island mass distribution $c_k(t)$ sharply decreases for small mass (ripe islands), and then increases in a mass range which corresponds to raw islands. In the proximity of $k\approx K$, there is a peak in c_k as predicted by our description based on matched asymptotic expansions. Our data for the time dependence of the total island density (Fig. 2) are consistent with $N(t)$ growing as a power of $\ln t$, as predicted by Eq. (9), but with somewhat smaller exponent than $\mu/2$. We consider our data sufficient to exclude a power-law time dependence of the island density. However, impractically long simulation would be needed to determine the exponent of the logarithmic factor in Eq. (9).

B. Circular island droplets

We now consider simulations of compact growing circular islands which we term as droplets. We additionally assume that islands are always centered on sites of the square lattice. In the simulations, we consider a system of size L^2 to which we add monomer droplets of radius $r_0=0.495$ to guarantee that adjacent monomers do not overlap. Monomers,

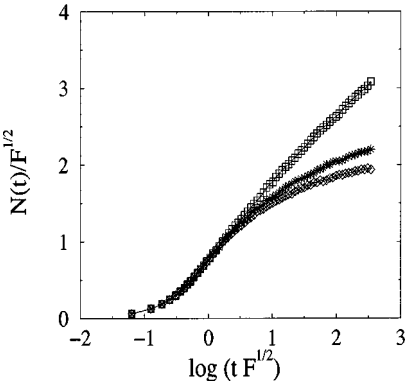

FIG. 2. Plot of $N(t)/\sqrt{F}$ vs $\log(t\sqrt{F})$ for $\mu=1.2$ ($\diamond$), $\mu=1.4$ ($\star$), and $\mu=2.0$ ($\square$), based on simulations of point islands. The simulation parameters are the same as in Fig. 1.

however, can overlap with larger droplets. When two droplets of radii r_1 and r_2 overlap they coalesce to form a droplet of radius $\sqrt{r_1^2+r_2^2}$ which is located at the center of the larger of the two initial coalescing droplets. As the coverage increases, multiple coalescences become increasingly probable and we therefore check for new island overlaps after each coalescence event and perform additional coalescences and continue to resolve all additional overlaps, if needed.

In the time evolution, a microscopic process, either deposition onto any system site or diffusion to a nearest-neighbor site, is chosen with respective probabilities $p_{\rm dep}=F/(F+N)$ and $p_{\rm dif}=1-p_{\rm dep}$. We then test for and perform all possible subsequent coalescences after each event. After completion of this microscopic event the time is incremented by $\Delta t=(FL^2+NL^2)^{-1}$ and the process is repeated.

Figure 3 compares the time evolution of point and growing circular islands. For $t<1/\sqrt{F}$, the plots of $N(t)$ versus t for the two processes coincide, thus indicating that the point-island model provides an excellent early-time description for the more realistic model of growing droplets. However, when $t>1/\sqrt{F}$, multibody aggregation starts to become important, and the density of droplets decreases with time while the density of point islands continues to grow. Thus the point-island model is a suitable starting point to interpret simulational and experimental data of epitaxial growth.[31]

A visualization of the aggregation of circular droplets at a relatively late stage is shown in Fig. 4. Here many-body

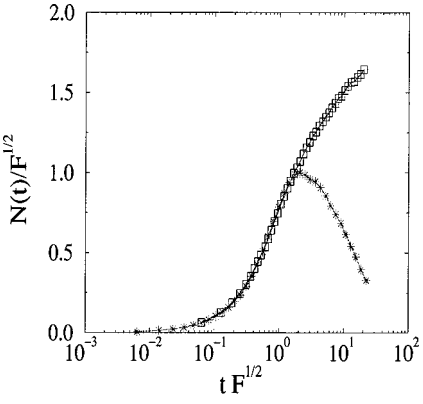

FIG. 3. Plot of $N(t)/\sqrt{F}$ vs $t\sqrt{F}$ for $\mu=1.2$ and $F=0.001$ for point ($\square$) and growing circular islands ($\star$).

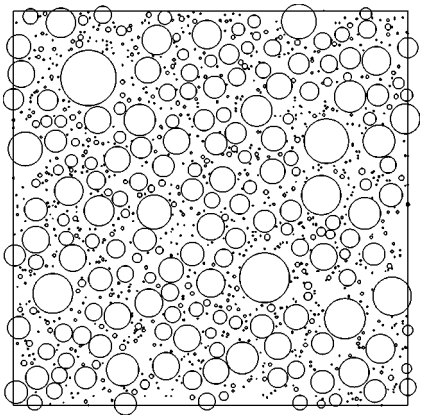

FIG. 4. Central portion of a typical droplet configuration for $\mu=1.2$ and $F=0.001$ for a system of size 500×500.

effects become significant, and a coalescence of two large droplets can lead to a large avalanche of coalescence events.

In Fig. 5 we plot the dependence of the maximum island density as a function of the flux. Using the power-law form $N_{\rm max}\sim F^{\chi}$ leads to a best-fit value $\chi\approx0.43$, while taking into account the logarithmic correction given by Eq. (29) gives $\chi\approx0.50$, in excellent agreement with our theory. However, using the additional flux renormalization from our more accurate treatment of the reaction rate (Appendix B) to fit the data leads to the somewhat different exponent estimate of $\chi\approx0.53$.

We have also performed simulations of two-dimensional fractal islands. Specifically, when two monomers occupy neighboring sites they stick irreversibly to form a dimer. This process continues and leads to the formation of fractal islands which hop as a rigid unit. Simulation of this process is simpler than in the growing droplet model because coalescences subsequent to the primary event cannot occur. This model has been studied earlier,[15] and our respective results agree. For example, for the case $\mu=1.2$ we obtain $\chi\approx0.43$ if we fit the data for $N_{\rm max}$ versus F to power-law behavior. Our interpretation for this exponent value differs, however, from that of Ref. 15. Indeed, they suggest that there might be a deep connection to a point-island model where both monomers and dimers diffuse and larger islands are immobile, since the exponent in that model, $\chi=\frac{2}{5}$,[32] is close to their simulation results. We believe that there is no connection

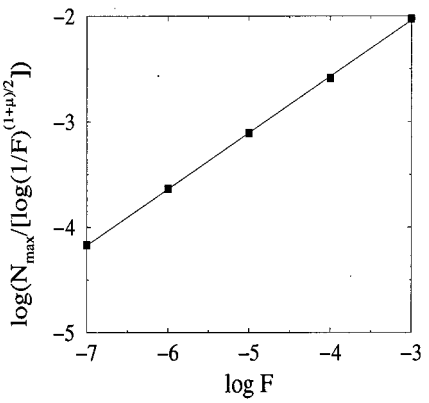

FIG. 5. Plot of $\log[N_{\rm max}/[\log(1/F)]^{(1+\mu)/2}]$ vs $\log(F)$ for $\mu=1.2$. The slope of the line is 0.53.

between these two models and the exponent observed by simulation is just an effective value whose asymptotic value is governed by the logarithmic correction in Eq. (B3). Our theory predicts universal flux exponent $\chi=1/2$, and the difference with observed *effective* flux exponent is due to the logarithmic correction. When this feature is taken into account, a value for χ very close to our prediction is found.

VI. SUMMARY AND DISCUSSION

We have investigated the kinetics of submonolayer epitaxial growth within a simple model which incorporates basic physical features of epitaxial growth—deposition, island diffusion, and aggregation. We have shown that our model displays universal kinetics—up to logarithms—as the governing exponents associated with the time and flux dependence of observables are detail independent. This is in contrast to the behavior exhibited by models where islands below a cutoff size are mobile while larger islands are immobile. In this case, characteristic exponents depend on this mass threshold.

We analyzed in detail the situation where the effective diffusivity D_k for islands of mass k is $D_k \propto k^{-\mu}$. Such a diffusivity arises, e.g., in periphery diffusion, where an adatom on the edge of an island detaches, hops to a neighboring site on the edge, and then reattaches to the island. This mechanism also causes islands to be compact. A Smoluchowski approach shows that the reaction rate between two islands of mass i and j is $K_{ij} \propto i^{-\mu}+j^{-\mu}$ multiplied by a factor which depends logarithmically on their radii in two dimensions. This weak dependence implies that a model with pointlike diffusing islands should be quantitatively accurate when applied to the submonolayer regime. The net effect of the logarithmic factor is the flux renormalization, $F \to F \ln(1/F)$, as demonstrated in Appendix B.

For mobility exponent $0 \leqslant \mu < 1$, there is a steady state, with the concentration of islands of mass k, $c_k \propto k^{-(3-\mu)/2}$. For $\mu \geqslant 1$, a logarithmic time dependence arises in which the total island density $N(t) \propto (\ln t)^{\mu/2}$. In this regime, the island distribution exhibits a rich mass dependence in which there is (i) a precipitous decay in a ''boundary layer'' $k \ll \kappa$ (with $\kappa \sim \ln t$), (ii) a gradual growth in the main part of the mass distribution $\kappa < k < K$ [with $K \sim t(\ln t)^{-\mu/2}$], and (iii) an internal layer $|k-K| \sim \sqrt{t}$ where the density of islands reaches a peak and then sharply vanishes. The entire regime $1 \leqslant \mu < \infty$ exhibits this same behavior up to logarithmic corrections, while the transition between the steady and evolving regimes at $\mu=1$ is characterized by nested logarithmic behavior.

Our results are valid in the time range $F^{-1/2} \ll t \ll F^{-1}$, where the former inequality is necessary for asymptotic behavior to apply, and the latter corresponds to the low-coverage regime. Since the (dimensionless) flux F is typically small in epitaxy experiments, the time range over which our theory should apply is correspondingly large. A commonly employed connection between theory and experimental results is to determine the maximum island density at the end of the submonolayer regime, $t_{\max} \sim F^{-1}$. Our analysis predicts that the maximum island density attains the value

$$N_{\max} \sim F^{1/2}[\ln(1/F)]^{\mu/2}, \tag{29}$$

so that $\chi=\frac{1}{2}$ is generic and applies to *any* model where island diffusion leads to continuous evolution.

Our theoretical approach can also be applied to epitaxial systems with an *arbitrary* mass-dependent diffusivity D_k which decays faster than the inverse mass. For example, for a diffusivity which decays exponentially in island mass, $D_k = e^{-a(k-1)}$, the case investigated numerically in Ref. 33, our theory predicts

$$N(t) \sim \sqrt{F} \exp\left[\sqrt{\frac{a}{2}\ln(t\sqrt{F})}\right] \tag{30}$$

and $K \sim t/N$, leading again to the same universal value of the mass cutoff exponent $\zeta(a) \equiv 1$. Equation (30) exhibits an unusual time dependence—faster than any power of logarithm and slower than any power law—and may be difficult to observe numerically. The maximum island density is

$$N_{\max} \sim \sqrt{F} \exp\left[\sqrt{\frac{a}{4}\ln(1/F)}\right], \tag{31}$$

so again $\chi=\frac{1}{2}$. Numerically, the exponent $\chi(a)$ appears to decrease as a increases.[33] Our analysis suggests that in the asymptotic regime $\chi(a) \equiv \frac{1}{2}$ for all $0<a<\infty$. However, fitting the functional form in Eq. (31) to a single power law in F gives $\chi_{\rm eff} = \frac{1}{2} - \sqrt{a/[4\ln(1/F)]}$. Therefore even for small flux the effective exponent may be considerably smaller than $\frac{1}{2}$. Also, $\chi_{\rm eff}(a)$ is a decreasing function of a, in agreement with the observations from the simulation.[33]

ACKNOWLEDGMENTS

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APPENDIX A: EPITAXIAL GROWTH ON 1D SUBSTRATES

We now extend our results to the case of a one-dimensional substrate. Since the upper critical dimension $d_c=2$,[20] the mean-field approximation does not apply in one dimension. In the absence of a theoretical framework to systematically treat the case $d<d_c$, we give a heuristic treatment. We will derive results for the specific cases of $d=1$ and 2; comparison between the latter result and the rate-equation result provides a check of our approach.

Consider first the simpler case of systems that approach a steady state. We present an argument based on the volume swept out by a Wiener sausage, as in the case of systems without flux (Sec. IV). To mimic the effect of the flux, we suppose that there is no flux but that all islands have initial mass which equals t. At time t, all islands within a reaction volume $(Dt)^{d/2}$ have coalesced into a single island. Ignoring logarithmic correction in two dimensions, this gives the following estimate for the average island mass M:

$$M(t) \sim t \times \begin{cases} Dt, & d=2 \\ \sqrt{Dt}, & d=1. \end{cases} \tag{A1}$$

Combining Eq. (A1) with $D \sim M^{-\mu}$, and using the fact that the average island mass M scales as the mass cutoff, we find

$$K(t) \sim \begin{cases} t^{2/(1+\mu)}, & d=2 \\ t^{3/(2+\mu)}, & d=1. \end{cases} \tag{A2}$$

In the steady-state regime, $c_k \sim k^{-\tau}$. Consequently the sum rule $t = \Sigma^K k c_k \sim K^{2-\tau} \sim t^{\zeta(2-\tau)}$ implies the relation $\tau = 2 - 1/\zeta$. This, together with Eq. (A2), gives

$$\tau = \begin{cases} (3-\mu)/2, & d=2 \\ (4-\mu)/3, & d=1. \end{cases} \tag{A3}$$

This argument reproduces the correct values of the cutoff and the decay exponents when $d=2$, and we anticipate that the one-dimensional results are also exact. Indeed, an exact solution[34] of one-dimensional aggregation with monomer input and mass-independent island diffusivities gives $\tau = \frac{4}{3}$. Finally, note that the exponents ζ and τ attain the critical value $\zeta = \tau = 1$ when the mobility exponent $\mu = 1$ in both one and two dimensions.

When $\mu \geqslant 1$, continuous evolution occurs. We now argue that the densities asymptotically evolve according to generalized rate equations. For monomers, we write

$$\frac{dc_1}{dt} = F - \frac{c_1}{\Delta t}. \tag{A4}$$

Here Δt is the collision time for a monomer to encounter an island. During this time interval, a monomer visits $\sqrt{\Delta t}$ different sites in one dimension, so that the collision time is determined by $N\sqrt{\Delta t} \approx 1$. Consequently, the rate equation for the monomer density becomes

$$\frac{dc_1}{dt} = F - N^2 c_1. \tag{A5}$$

Continuing this line of reasoning we obtain the rate equations for the densities $c_k(t)$, which differ from Eqs. (2) by a factor N in each reaction term.

We now analyze these equations by the same quasistatic framework as in Sec. II. Thus we need to solve

$$\begin{aligned} 0 &= F - N^2 c_1, \\ 0 &= \frac{1}{2} \sum_{i+j=k} (i^{-\mu} + j^{-\mu}) c_i c_j - c_k (k^{-\mu} N + N_\mu). \end{aligned} \tag{A6}$$

Repeating the steps of our previous derivations we obtain, e.g., for the density of islands,

$$N(t) \simeq F^{1/3} \left[\frac{\sin(\pi/\mu)}{\pi} \ln(tF^{2/3}) \right]^{\mu/2}, \tag{A7}$$

and for the behavior of the density of relatively small islands $c_k \sim F^{1/3} (k!)^\mu / N^{\mu k}$. Thus in the continuously evolving regime, the time dependence remains primarily unaffected by the dimensionality of the substrate. However, the flux dependence does change with d, and we find $N_{\max} \sim F^{1/3} [\ln(1/F)]^{\mu/2}$ [compared to the $F^{1/2}$ dependence in Eq. (29)]. Overall, universal behavior arises in continuous evolution which is only slightly affected by model details, substrate dimensionality, etc.

APPENDIX B: REACTION RATE IN TWO DIMENSIONS

We now account for the logarithmic corrections to the reaction rate [Eq. (1)] that appears in two dimensions. We first demonstrate that these logarithmic corrections can be accounted for within modified rate equations. Let us first consider a simpler model where point islands diffuse at the same mass-independent rate. Then the total island density $c(t)$ obeys $\dot{c} = -c/\Delta t$, where Δt is the time between successive collisions. A collision is expected when the island visits $1/c$ distinct sites. Since the number of distinct sites visited by a random walk in time t grows as $Dt/\ln(Dt)$ in two dimensions,[29] the collision time follows from the condition $D\Delta t/\ln(D\Delta t) \sim 1/c$. The resulting expression for Δt leads to the rate equation $\dot{c} = -Dc^2/\ln(1/c)$. Similarly, for an island of radius R, we obtain $\dot{c} = -Dc^2/\ln(1/cR^2)$.

For growing droplets with mass dependent diffusivity, these logarithmic factors imply that the reaction rate $K_{ij} = D_i + D_j$ should be replaced by

$$K_{ij} \sim \frac{D_i + D_j}{\ln[N^{-1}(R_i + R_j)^{-2}]}. \tag{B1}$$

In the low-coverage limit, the average separation between neighboring islands $N^{-1/2}$ is much larger than the average island size. Keeping only this dominant factor inside the logarithm gives the asymptotic form of the reaction rate $K_{ij} \sim (D_i + D_j)/\ln(1/N)$. Moreover, we can replace the total island density by $\sqrt{F}$ inside the logarithm. This is obvious when $\mu < 1$, since in this case the island density indeed approaches a steady-state value $N_\infty \sim \sqrt{F}$. For $\mu \geqslant 1$, the island density grows according to $N \sim \sqrt{F} (\ln t)^{\mu/2}$. However, the time-dependent factor is clearly subdominant as it is at most logarithmic in the flux, $(\ln t_{\max})^{\mu/2} = [\ln(1/F)]^{\mu/2}$. Hence for arbitrary mobility exponent μ, the form $K_{ij} \sim (D_i + D_j)/\ln(1/F)$ provide an asymptotically correct description for the reaction rate.

Therefore in two dimensions we can continue to use the mean-field Smoluchowski equations, with the modification of the reactive term by the factor $1/\ln(1/F)$. Upon rescaling the densities by $c_k \to c_k \sqrt{F \ln(1/F)}$, and the time variable by $t \to t\sqrt{F^{-1} \ln(1/F)}$, we formally map Smoluchowski equations for epitaxial growth in two dimensions onto the mean-field equations (2) with $F = 1$ and the reaction rates given by Eq. (1).

We therefore conclude that we can apply the mean-field results to two-dimensional substrates upon making the flux renormalization

$$F \to F \ln(1/F). \tag{B2}$$

This renormalization does not alter the basic predictions of the Smoluchowski approach; for example, all exponents remain the same. However, this renormalization does alter some logarithmic factors, e.g., Eq. (29) for the maximum island density is replaced by

$$N_{\max} \sim F^{1/2} [\ln(1/F)]^{(\mu+1)/2}. \tag{B3}$$

[1] J. J. Métois, K. Heinemann, and H. Poppa, Philos. Mag. **35**, 1413 (1977).
[2] J. A. Venables, G. D. T. Spiller, and M. Hanbücken, Rep. Prog. Phys. **47**, 399 (1984).
[3] N. V. Brilliantov and P. L. Krapivsky, Fiz. Tverd. Tela (Leningrad) **31**, 172 (1989) [Sov. Phys. Solid State **31**, 271 (1989)]; J. Phys. A **24**, 4787 (1991).
[4] J. A. Blackman and A. Wielding, Europhys. Lett. **16**, 115 (1991); J. A. Blackman, Physica A **220**, 85 (1995).
[5] M. C. Bartelt and J. W. Evans, Phys. Rev. B **46**, 12 675 (1992).
[6] J. G. Amar, F. Family, and P. M. Lam, Phys. Rev. B **50**, 8781 (1994).
[7] G. L. Kellogg, Phys. Rev. Lett. **73**, 1833 (1994); Surf. Sci. Rep. **21**, 1 (1994).
[8] A. F. Voter, Phys. Rev. B **34**, 6819 (1986).
[9] S. C. Wang and G. Ehrlich, Surf. Sci. **239**, 301 (1990); Phys. Rev. Lett. **79**, 4234 (1997).
[10] I. Furman and O. Biham, Phys. Rev. B **55**, 7917 (1997).
[11] K. Morgenstern, G. Rosenfeld, B. Poelsema, and G. Comsa, Phys. Rev. Lett. **74**, 2058 (1995).
[12] G. M. Wen, S.-L. Chang, J. W. Burnett, J. W. Evans, and P. A. Thiel, Phys. Rev. Lett. **73**, 2591 (1994); J. M. Wen, J. W. Evans, M. C. Bartelt, J. W. Burnett, and P. A. Thiel, *ibid.* **76**, 652 (1996).
[13] W. W. Pai, A. K. Swan, Z. Zhang, and J. F. Wendelken, Phys. Rev. Lett. **79**, 3210 (1997).
[14] S. V. Khare, N. C. Bartelt, and T. L. Einstein, Phys. Rev. Lett. **75**, 2148 (1995).
[15] P. Jensen, A.-L. Barabasi, H. Larralde, S. Havlin, and H. E. Stanley, Phys. Rev. B **50**, 15 316 (1994), and references therein.
[16] A preliminary account is given in P. L. Krapivsky, J. F. F. Mendes, and S. Redner, Eur. Phys. J. B **4**, 401 (1998).
[17] M. H. Ernst, in *Fractals in Physics*, edited by L. Pietronero and E. Tosatti (Elsevier, Amsterdam, 1986), p. 289.
[18] E. E. Gruber, J. Appl. Phys. **38**, 243 (1967).
[19] R. Q. Hwang, J. Schröder, C. Günter, and R. J. Behm, Phys. Rev. Lett. **73**, 553 (1994).
[20] P. G. J. van Dongen, Phys. Rev. Lett. **63**, 1281 (1989).
[21] A. H. Nayfeh, *Introduction to Perturbation Technique* (Wiley, New York, 1981).
[22] P. Meakin, Physica A **165**, 1 (1990).
[23] M. Moreau and G. Oshanin, J. Chem. Phys. **102**, 2977 (1995).
[24] D. S. Sholl and R. T. Skodje, Physica A **231**, 631 (1996).
[25] S. Cueille and C. Sire, Phys. Rev. E **55**, 5465 (1997).
[26] D. Kandel, Phys. Rev. Lett. **79**, 4238 (1997).
[27] J. Li, A. G. Rojo, and L. M. Sander, Phys. Rev. Lett. **78**, 1747 (1997).
[28] D. S. Sholl and R. T. Skodje, Phys. Rev. Lett. **75**, 3158 (1995).
[29] W. Feller, *An Introduction to Probability Theory and its Applications* (Wiley, New York, 1968).
[30] K. Kang, S. Redner, P. Meakin, and F. Leyvraz, Phys. Rev. A **33**, 1171 (1986).
[31] Note, however, that there are alternative approaches which are based on ''self-consistent'' rate equations. See, e.g., G. S. Bales and D. C. Chrzan, Phys. Rev. B **50**, 6057 (1994); G. S. Bales and A. Zangwill, *ibid.* **55**, 1973 (1997); M. N. Popescu, J. G. Amar, and F. Family, *ibid.* **58**, 1613 (1998).
[32] J. Villain, A. Pimpinelli, L.-H. Tang, and D. E. Wolf, J. Phys. I **2**, 2107 (1992); J. Villain, A. Pimpinelli, and D. E. Wolf, Comments Condens. Matter Phys. **16**, 1 (1992).
[33] L. Kuipers and R. E. Palmer, Phys. Rev. B **53**, 7649 (1996).
[34] H. Takayasu, I. Nishikawa, and H. Tasaki, Phys. Rev. A **37**, 3110 (1988); B. R. Thompson, J. Phys. A **22**, 879 (1989).