Epitaxial thin film growth involves deposition of atoms onto a substrate and diffusion of these adatoms, leading to their aggregation into islands of ever-increasing size. The resulting island morphology and mass distribution depends intimately on the diffusion processes of the adatoms. While this connection has long been recognized, a complete understanding of this evolution is still lacking. For a variety of atomic transport mechanisms, there is a power-law dependence of the effective island diffusivity $D_k$ on its mass $k$, $D_k \propto k^{-\mu}$, with $\mu$ typically in the range $(1/2, 3/2)$. Starting with this observation, various approaches have suggested that the growth of islands due to their clustering is a power law in time.

In this Letter, we provide a comprehensive account for the evolution of the island size distribution in the submonolayer regime by solving the Smoluchowski rate equations. For mobility exponent $0 \leq \mu < 1$, a steady state arises in which the concentration of islands of mass $k$ is given by $c_k \propto k^{-\tau}$, with $\tau = (3 - \mu)/2$. For all $\mu > 1$, logarithmic island evolution occurs in which their total density grows as $(\ln t)^{\mu/2}$ while $c_k(t)$ varies as $(\ln t)^{-(2k-1)\mu/2}$. More generally, our approach applies to any epitaxial system in which the diffusivity of an island vanishes more rapidly than inversely with its mass.

In the diffusion-controlled limit, the aggregation rate $K_{ij}$ of an $i$-mer and a $j$-mer is given by the Smoluchowski formula $K_{ij} \sim (D_i + D_j)(R_i + R_j)^{d-2}$. Here $R_i$ is the linear size of an $i$-mer (island of mass $i$), which is assumed to be compact, and $d$ is the spatial dimensionality of the substrate. This Smoluchowski formula is applicable in $d > 2$, while in the physically relevant case of two dimensions the reaction rate depends logarithmically on the island size. For both simplicity and because little quantitative information is lost, we shall ignore these logarithmic factors. This is equivalent to treating the islands as point-like throughout their evolution.

With $D_k \propto k^{-\mu}$, an appropriate choice of time units, and the neglect of logarithmic corrections, the reaction rate in two dimensions becomes

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

We investigate submonolayer epitaxial growth with a fixed monomer flux and irreversible aggregation of adatom islands due to their effective diffusion. When the diffusivity $D_k$ of an island of mass $k$ is proportional to $k^{-\mu}$, a Smoluchowski rate equation approach predicts steady behavior for $0 \leq \mu < 1$, with the concentration $c_k$ of islands of mass $k$ varying as $k^{-(3-\mu)/2}$. For $\mu \geq 1$, continuous evolution occurs in which $c_k(t) \sim (\ln t)^{-(2k-1)\mu/2}$, while the total island density increases as $N(t) \sim (\ln t)^{\mu/2}$. Monte Carlo simulations support these predictions.

The leading constant factor in each line is finite and coincides with the definition given in Eq. (3) if the exponent

$$C(\tau) = N + C\Gamma(1 - \tau)(1 - z)^{-1} + \ldots, \quad C_\mu(z) = N_\mu + C\Gamma(1 - \tau - \mu)(1 - z)^{-\mu - 1} + \ldots$$

These rate equations represent a mean-field approximation in which spatial fluctuations are neglected, and also a low-coverage approximation, since only binary interactions are treated.

Let us first consider the behavior in the steady state regime. To solve the rate equations in this case, we introduce two generating functions

$$C(z) = \sum_{k=1}^{\infty} c_k z^k, \quad C_\mu(z) = \sum_{k=1}^{\infty} k^{-\mu} c_k z^k.$$
of the second term is positive. Otherwise, the constant factor vanishes and the generating function has a power-law divergence as \(z \to 1\). Substituting these expansions into Eq. (3) and matching the leading behavior in \((1 - z)\) leads to the decay exponent \(\tau = (3 - \mu)/2\). The condition for a steady state to occur, \(\tau > 1\), thus imposes an upper bound on the mobility exponent, \(\mu < 1\). From matching the leading behavior in \((1 - z)\), the constant \(C\) may also be determined, from which the island mass distribution in the steady-state regime \(0 \leq \mu < 1\)

\[
c_k \simeq \sqrt{\frac{F}{4\pi}} \left(1 - \mu^2\right) \cos(\pi\mu/2) \ k^{-(3-\mu)/2}. \tag{7}
\]

It is important to note that this mass distribution holds only up to a mass cutoff \(k_c(t) \sim t^\xi\) whose value is determined by requiring that the total mass in the system due to the steady input is proportional to \(t - \) islands of mass greater than \(k_c(t)\) have not yet formed. Therefore

\[
M(t) = \sum_{k=1}^{\infty} k c_k(t) \sim \sum_{k=1}^{k_c} k^{(\mu-1)/2} \sim k^{(\mu+1)/2} \sim t, \tag{8}
\]

which gives the mass cutoff exponent

\[
\zeta(\mu) = 2/(\mu + 1). \tag{9}
\]

We now investigate the asymptotic behavior of the island mass distribution for \(\mu \geq 1\). In the extreme case of \(\mu = \infty\), i.e., diffusing monomers and immobile islands, the island density grows as a power law in time, \(N(t) \sim (3Ft)^{1/3}\). \([12\ 14]\) We shall argue that continuously evolving behavior occurs for all \(\mu \geq 1\), but with anomalously slow logarithmic kinetics. When \(\mu\) is strictly greater than unity but still finite, we find

\[
N(t) \simeq \sqrt{F} \left[\frac{\sin(\pi/\mu)}{\pi} \ ln T\right]^{\mu/2}, \tag{10}
\]

with \(T \equiv t\sqrt{F}\), while the concentration of \(k\)-mers decays in time as

\[
c_k(t) \sim \sqrt{F} \left(k^!\right)^\mu \left(ln T\right)^{-(2k-1)/2}. \tag{11}
\]

It is remarkable that such logarithmic dependences, a feature which generally signals marginal behavior, occurs in the entire regime \(1 < \mu < \infty\). In the borderline case of \(\mu = 1\), even more unusual behavior arises with \(N(t) \sim \sqrt{\ln T/\ln(\ln T)}\).

Our argument leading to Eqs. (10) and (11) is based on a quasi-static approximation, in which the time derivative in Eq. (3) is neglected. Indeed, the logarithmic behavior in Eqs. (10) and (11) immediately implies that the temporal derivatives in the Smoluchowski rate equations are asymptotically negligible. Within this quasi-static framework, Eqs. (2) become

\[
0 = 1 - c_1 \left(N + N_\mu\right), \text{ and } 0 = \frac{1}{2} \sum_{i+j=k} \left(i^{-\mu} + j^{-\mu}\right) c_i c_j - c_k \left(k^{-\mu} N + N_\mu\right). \tag{12}
\]

Further, by summing Eqs. (12) over all \(k\), the total island density in the quasi-static limit obeys

\[
0 = 1 - NN_\mu \tag{13}
\]

In Eqs. (12) and (13) we have set \(F = 1\) by a rescaling of units. Eq. (13) immediately gives \(N_\mu = N^{-1}\), and then from the first of Eqs. (12), \(c_1 \simeq 1/N\). The remainder of Eqs. (12) may then be solved recursively. By writing the first few of these equations, it is evident that the dominant contribution to \(c_k\) is the term in the quadratic product which is proportional to \(c_1 c_{k-1}\). If we keep only this contribution, the resulting recursion may be solved straightforwardly to yield

\[
c_k \simeq \frac{1}{N} \prod_{j=2}^{k} \left(1 + N^2 j^{-\mu}\right)^{-1} \prod_{j=1}^{k-1} (1 + j^{-\mu}) \prod_{j=2}^{k} B_j \prod_{j=1}^{k-1} b_j. \tag{14}
\]

Since the factors \(B_j \ll 1\) for \(j^\mu \ll N^2\), while \(B_j \to 1\) for \(j^\mu \gg N^2\), this implies that \(c_k\) is a rapidly decreasing function of \(k\) for \(k \ll N^\mu\) and then becomes constant for larger \(k\).

To compute \(c_k\), first note that for \(\mu > 1\) the product \(\prod j b_j\) converges, so that it may treated as constant. We then write the second product as the exponential of a sum and take the continuum limit. This leads to

\[
c_k \sim \frac{1}{N} \exp \left[-\sum_{j=2}^{k} \ln(1 + N^2 j^{-\mu})\right] \sim \frac{1}{N} \exp \left[-N^{2/\mu} \int_0^x \ln(1 + w^{-\mu}) \, dw\right], \tag{15}
\]

where \(w = j/N^2\) and \(x = k/N^2\). This form has two slightly different asymptotic behaviors depending on whether \(\mu\) is strictly greater than or equals 1. For \(\mu > 1\), the monotonically increasing integral in Eq. (15) converges as \(x \to \infty\). Thus \(c_k\) decreases as a function of \(k\) until a threshold value \(k_{th} \simeq N^{2/\mu}\), beyond which \(c_k\) remains constant with a value determined by taking the upper limit of the integral as infinite. Hence

\[
c_{th} \sim \frac{1}{N} \exp \left[-A_{\mu} N^{2/\mu}\right], \tag{16}
\]

with \(A_{\mu} = \int_0^\infty \ln(1 + w^{-\mu}) \, dw = \pi/\sin(\pi/\mu)\). Physically, we expect this constancy in \(c_k\) to persist until \(k\) reaches the cutoff \(k_c \sim t^\xi\).

To check this result, we performed numerical simulations in the mean field limit of submonolayer epitaxial growth. In the simulation, an island of mass \(k\),
which remains point-like throughout the aggregation process, moves equiprobably to any site with a probability proportional to \( k^{-\mu} \), as mandated by the power-law mass-dependent island diffusivity. There is also a steady monomer flux entering the system. As shown in Fig. 1, \( c_k(t) \) is nearly constant in \( k \) over a substantial range as predicted by our theory. However, when \( k \approx k_c \), there is a peak in \( c_k \) which is not accounted for in our quasi-static description.

The time dependence of the total island concentration may now be determined by using the fact that the mass density in the system grows linearly with time, \( M(t) = \sum_{k \geq 1} c_k(t) = t \). The dominant contribution to this sum is from the plateau region \( k_{th} < k < k_c \), where \( c_k \) is approximately constant in \( k \), \( c_k \approx c_{th} \). Thus

\[
M(t) \sim c_{th} \sum_{k=k_{th}}^{k_c} k \sim c_{th} k_c^2 \sim t. \tag{17}
\]

Here we also use the fact that \( k_{th} \) grows only logarithmically in time (see below), so that the lower limit can be taken to be zero. Furthermore, \( k_c(t) \sim t^{\mu_2} \) grows more rapidly than \( t^{1/2} \). Indeed, since the cutoff exponent \( \zeta(\mu) = 2/(\mu + 1) \) for \( \mu < 1 \) (Eq. (1)) and \( \zeta(\mu = \infty) = 2/3 \) \([12][14]\), we anticipate that \( 2/3 \leq \zeta(\mu) \leq 1 \) when \( 1 \leq \mu < \infty \). In fact, \( \zeta = 1 \) in this range of mobility exponent, as we will show below. Using \( \zeta = 1 \), Eq. (17), together with \( c_{th} \sim \exp( -A_\mu N^{2/\mu} ) \) and \( k_c \sim t^{\mu_2} \), we immediately obtain Eq. (10). Our data for \( N(t) \) as a function of time (Fig. 2) is qualitatively consistent with \( N(t) \) growing as a power of \( \ln t \), but with a smaller exponent than \( \mu_2/2 \). Note finally that \( k_{th} \sim N^{2/\mu} \) which is proportional to \( \ln t \).

To determine \( c_k(t) \) for \( k^{th} \ll N^2 \), we now use the approximation \( B_j \sim j^{\mu_2}/N^2 \) in Eq. (14) to give

\[
c_k \sim \frac{(k!)^{\mu}}{N^{2k}}, \tag{18}
\]

which directly leads to Eq. (11). Finally, the time dependence of \( c_{th}(t) \) and \( k_c(t) \) may be determined from the sum rules \( \sum c_k \sim c_{th}, k_c \sim N \). These two relations give \( c_{th} \sim N^2/t \) and \( k_c \sim t/N \). Thus in the plateau region \( k_{th} < k < k_c \),

\[
c_k(t) \sim \frac{(\ln t)^\mu}{t}, \quad k_c(t) \sim \frac{t}{(\ln t)^{\mu/2}}. \tag{19}
\]

It is important to note that our approach applies to any mass-dependent island diffusivity which decays faster than its inverse mass. For this general situation, the analog of Eq. (13) is \( c_k \sim N^{-1} \prod_{j=1}^{k}(1 + D_j)(1 + N^2 D_j)^{-1} \). For example, for \( D_k \sim e^{-2a k} \), a case that was considered numerically in \([15]\), we obtain \( N(t) \sim \exp(\sqrt{a \ln t}) \). This unusual growth – faster than any power of logarithm but slower than any power law – would be difficult to observe numerically.

In the specific case \( \mu = 1 \), subtler nested logarithmic behavior arises, as reflected by the additional singularity in Eq. (10) as \( \mu \to 1 \). First, the product \( \prod_{j=1}^{k-1} b_j = \prod_{j=1}^{k-1} (1 + j^{-1}) \) in Eq. (13) now equals \( k \). Second, the term \( c_2 c_{k-2} \) also contributes to the asymptotic behavior. Third, and most importantly, the integral in Eq. (13) diverges at the upper limit. Due to the second attribute, the recursion relation for \( c_k \) becomes

\[
\frac{c_k}{k} \frac{1 + k/N^2}{k^{-N^2}} = \frac{c_{k-1}}{k-1} + \frac{c_{k-2}}{k-2} \frac{1}{N^2}. \tag{20}
\]

We seek a solution for \( c_k \) in the form of Eq. (14). Thus we write

![Fig. 1. \( c_k(t) \) versus \( k \) on a double logarithmic scale at \( t \approx 22000 \) for \( \mu = 1.5 \). The data is based on 5000 realizations of an initially empty system with \( F = 0.05 \).](image1)

![Fig. 2. \( N(t) \) versus \( \ln(t^{1/2}) \) for \( \mu = 1.2 \) (○), 1.4 (○), 1.5 (△), and 2.0 (▽). The data is based on 1000 realizations. Also shown are power law fits to the data in the range \( t > 3 \). This gives, for the exponent of \( \ln t \), 0.38, 0.55, 0.64 and 0.76, respectively, for \( \mu = 1.2, 1.4, 1.5 \), and 2.0.](image2)
\[ c_k \sim C_k \frac{k}{N} \prod_{j=2}^{k} \left(1 + N^2 j^{-1}\right)^{-1}, \tag{21} \]

where the factor \( C_k \) accounts for the additional term in Eq. (20). Substituting into Eq. (20) gives

\[ C_k = C_{k-1} + C_{k-2} \left( \frac{1}{k-1} + \frac{1}{N^2} \right). \tag{22} \]

These coefficients are slowly varying in \( k \) when \( k \gg 1 \) and we may treat \( k \) as continuous in this asymptotic regime. Eq. (22) then becomes a differential equation whose solution is \( C_k \sim k e^x \) (with \( x = k/N^2 \)). Consequently,

\[ c_k \sim \frac{k^2}{N} \exp \left[ x - N^2 \int_0^x \ln \left(1 + w^{-1}\right) \, dw \right]. \tag{23} \]

Thus for \( \mu = 1 \), \( c_k \) decreases rapidly in \( k \) for \( k \ll N^2 \) and then increases until \( k \) reaches \( k_c \). The island mass distribution attains a minimum at \( x_{th} = N^2 \) whose value is

\[ c_{th} \sim \exp \left[ -N^2 \ln N^2 \right]. \tag{24} \]

Paralleling the analysis of the case \( \mu > 1 \), the total island concentration is

\[ N(t) \sim \sqrt{\frac{\ln t}{\ln(\ln t)}}, \tag{25} \]

while Eq. (21), together with \( C_k \sim k \) implies that the concentration of islands for mass \( k \ll N^2 \) is

\[ c_k \sim \frac{(k+1)!}{N^{2k-1}} \sim (k+1)! \left[ \frac{\ln(\ln t)}{\ln t} \right]^{k-1/2}. \tag{26} \]

Finally from Eq. (23), the time dependence of \( c_k(t) \) and \( k_c(t) \) is given by

\[ c_k(t) \sim \frac{1}{t} \frac{\ln t}{\ln(\ln t)}, \quad k_c(t) \sim t \frac{\ln(\ln t)}{\ln t}. \tag{27} \]

Our results should be generally applicable to real epitaxial systems in the submonolayer regime. This regime requires \( Ft \ll 1 \), while the asymptotic predictions of our Smoluchowski theory apply for \( t \sqrt{F} \gg 1 \). Consequently, our results should be valid for \( F^{-1/2} \ll t \ll F^{-1} \). Since the dimensionless flux \( F \) is small in typical epitaxy experiments, the time range over which our theory will apply is correspondingly large. Notice that the maximum island density attained at the end of the submonolayer regime \( t_{max} \) scales with flux as \( N_{max} \sim F^{1/2} \ln(1/F)^{\mu/2} \). In fact, for all systems with the diffusivity of an island decaying more rapidly than its inverse mass, our approach leads to \( N_{max} \) universally being proportional to \( F^{1/2} \) times a subdominant model-dependent factor.

In conclusion, we determined the kinetics of islanding in submonolayer epitaxial growth, in which adatom hopping induces a power-law mass-dependent island diffusion, with \( D_k \propto k^{-\mu} \). This leads to the reaction rate \( K_{ij} \propto (i^{-\mu} + j^{-\mu}) \) between two islands of mass \( i \) and \( j \) in the Smoluchowski rate equation. A steady state arises for mobility exponent \( 0 \leq \mu < 1 \), in which the island concentration varies as \( c_k \sim k^{-(3-\mu)/2} \) for \( k < k_c \propto t^\zeta \), with \( \zeta(\mu) = 2/(1+\mu) \). Strikingly, logarithmic time dependence arises for all \( 1 < \mu < \infty \), a feature suggestive of marginal behavior over this entire range. In this regime, the total island density \( N(t) \) grows as \( (\ln t)^{\mu/2} \), while the density of islands of mass \( k \) is \( c_k(t) \propto (\ln t)^{-2(k-1)/\mu} \), for \( k \ll k_{th} \propto \ln t \), \( c_k(t) \) independent of \( k \), with \( c_k(t) \sim t^{-1}(\ln t)^{\mu} \), for \( k_{th} \leq k \leq k_c \), and \( c_k \) vanishingly small for \( k > k_c \). For \( \mu = 1 \), even more unusual nested logarithmic behavior occurs.

JFFM gratefully acknowledges support from Fundação Luso Americana para o Desenvolvimento (FLAD), and JNICT/PRAXIS XXI: grant /BDP/6084/95 and project PRAXIS/2/1/Fis/299/94. PLK and SR gratefully acknowledge support from NSF grant DMR9632059 and ARO grant DAAH04-96-1-0114.

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