Asymptotic capture number and island size distributions for one-dimensional irreversible submonolayer growth

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Using a set of approximate evolution equations [J. G. Amar *et al.*, Phys. Rev. Lett. **86**, 3092 (2001)] for the average gap size between islands, we calculate analytically the asymptotic scaled capture-number distribution (CND) for one-dimensional irreversible submonolayer growth of point islands. The predicted asymptotic CND is in reasonably good agreement with kinetic Monte Carlo (KMC) results, and leads to a *nondivergent* asymptotic scaled island size distribution (ISD). We then show that a slight modification of our analytic form leads to analytical expressions for the asymptotic CND and a resulting asymptotic ISD which are in excellent agreement with KMC simulations. We also show that in the asymptotic limit the scaled average gap distribution is identical to the scaled CND and thus demonstrate that in this limit, the self-averaging property of the capture zones holds exactly.

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Recently, considerable theoretical effort has been carried out towards a better understanding of the scaling properties of the island size distribution in submonolayer epitaxial growth.[1–9] For example, in the pre-coalescence regime the island size distribution $N_s(\theta)$ (where N_s is the number of islands of size s at coverage θ) satisfies the scaling form[1]

$$N_s(\theta)=\frac{\theta}{S^2}f\left(\frac{s}{S}\right), \tag{1}$$

where S is the average island size, and the scaling function $f(u)$ depends on the critical island size and on the island morphology.[1]

One of the standard tools used in these studies is the rate-equation (RE) approach which involves a set of deterministic coupled reaction-diffusion equations describing the coverage dependence of $N_s(\theta)$ through a set of rate coefficients usually called capture numbers.[10,11] For the irreversible growth of point islands, rate equations valid in the precoalescence regime may be written in the form

$$\frac{dN_1}{d\theta}=1-2R\sigma_1N_1^2-RN_1\sum_{s\geqslant 2}\sigma_sN_s, \tag{2a}$$

$$\frac{dN_s}{d\theta}=RN_1(\sigma_{s-1}N_{s-1}-\sigma_sN_s) \quad \text{for} \quad s\geqslant 2, \tag{2b}$$

where the capture numbers σ_s (σ_1) correspond to the *average* capture rate of diffusing monomers by islands of size s (monomers) and $R=D/F$ is the ratio of the monomer diffusion rate to the deposition rate. Accordingly, the central problem in using the RE approach is the determination of the average capture numbers $\sigma_s(\theta)$ and the corresponding capture number distribution (CND).

Recently, we have developed a self-consistent rate-equation approach to irreversible submonolayer growth in which correlations between the size of an island and the corresponding *average* capture zone are explicitly taken into account in order to accurately predict the scaled island size and capture number distributions.[7,8] Our method involves numerical integration of the island-density RE's Eq. (2), along with the analytical solution of a set of approximate evolution equations for the average Voronoi area surrounding an island of size s, and is based on the following two assumptions: the average capture area per freshly nucleated dimer is proportional (before rescaling) to the average area per island; the combined effects of the preferred nucleation of dimers in large capture zones and the preferred ''breakup'' of large capture zones due to nucleation may be approximated by a uniform rescaling of the average capture zone of each island.[7,8] Using this approach, we have obtained numerical results for the scaled capture number and island size distributions which agree well with kinetic Monte Carlo (KMC) simulations in both one and two dimensions over a wide range of experimentally relevant values of D/F ($D/F=10^5$–10^9).

Recently, it has been argued[13] that because our method does not explicitly take into account spatial fluctuations in the nucleation, it must lead to a diverging island size distribution (ISD) in the asymptotic limit corresponding to infinite D/F. However, as shown by Bartelt and Evans,[2] in the asymptotic limit the scaled ISD is related to the scaled CND as

$$f(u)=f(0)\exp\left[\int_0^u dx\,\frac{2z-1-C'(x)}{C(x)-zx}\right], \tag{3}$$

where $C(s/S)=\sigma_s/\sigma_{av}$ is the scaled CND, z is the dynamical exponent describing the dependence of the average island size on coverage ($S\sim\theta^z$), and $f(0)$ is determined by the normalization condition

$$\int_0^\infty du\,f(u)=1. \tag{4}$$

As pointed out in Ref. 2, Eq. (3) implies that if $C(u) > zu$ then no divergence will occur. However, if $C(u)$ crosses zu at some value u_c then the ISD will be cut off at u_c [i.e., $f(u)=0$ for $u \geqslant u_c$] if $C'(u_c) > 2z-1$ while a divergence in the ISD will occur if $C'(u_c) < 2z-1$. An example of a divergent asymptotic ISD is the usual mean-field theory with $C(u)=1$. Thus the question of whether or not our method leads to a divergence in the asymptotic limit is entirely determined by the asymptotic scaled CND.

Here we rigorously address the question of the asymptotic behavior obtained using our method by analytically deriving the asymptotic scaled CND along with the resulting asymptotic scaled ISD for the case of irreversible growth of point islands in one dimension. We find that our method leads to an asymptotic scaled CND which is close to that obtained in simulations and as a result, in contrast to the claims in Ref. 13, to a *nondivergent* asymptotic ISD. We also demonstrate that the asymptotic scaled gap distribution is identical to the scaled CND. As a result the self-averaging property of the capture zones holds exactly. Finally, we show that, by slightly modifying our original analytical form for $C(u)$, an analytical expression for the asymptotic scaled CND and a resulting ISD which are in excellent agreement with KMC simulations may be obtained.

We note that there are a number of physically interesting cases, such as nucleation and growth at steps,[12] or systems with high diffusion anisotropy,[4] which correspond to one-dimensional submonolayer growth. In addition, the point-island approximation is appropriate in the asymptotic limit for extended islands up to a finite coverage ($\theta \simeq 0.1$, see Ref. 9) as well as at higher coverage for islands which grow perpendicular to the substrate (e.g., quantum dots). Therefore the results presented here apply generally to such systems.

For clarity, we briefly review our method[7] and its application to the case of irreversible growth of point islands in one dimension.[8,14] In this case, we have shown that the *local* capture-number $\tilde{\sigma}(y)$ for an island with gap size y (corresponding to the distance to the nearest island) is

$$\tilde{\sigma}(y;\theta) = \frac{2\xi_1}{\xi^2} \tanh\left(\frac{y}{2\xi_1}\right), \tag{5}$$

where the monomer capture length ξ and the nucleation length ξ_1 are defined as

$$2\sigma_1 N_1 = 1/\xi_1^2, \quad 1/\xi_1^2 + \sum_{s \geqslant 2} \sigma_s N_s = 1/\xi^2. \tag{6}$$

From the evolution equations for the gap-length distribution, the average "gap length" $\tilde{y}_s$ (before rescaling) corresponding to an island of size s may be obtained as the solution of the equation

$$s-2 = \int_{\theta_y}^{\theta} R\, N_1(\phi) \tilde{\sigma}(\tilde{y}_s;\phi) d\phi. \tag{7}$$

The coverage θ_y is defined by $\tilde{y}_s = b\, Y(\theta_y)$ where b is the proportionality factor (before rescaling) between the average gap length of a freshly nucleated dimer and the average gap-length of all islands, $Y(\theta) = 1/N(\theta)$ is the average gap-length at coverage θ, and $N(\theta) = \Sigma_{s \geqslant 2} N_s(\theta)$ is the average island density. The integral in Eq. 7 may be interpreted as corresponding to the *average* number of particles added to a dimer since it was formed at coverage θ_y, neglecting any change in the capture zone due to nucleation and breakup. To include the effects of break-up and ensure length conservation, the gap lengths are rescaled by a rescaling factor $a = 1/\Sigma_{s \geqslant 2} N_s\, \tilde{y}_s$ so that the average gap length for an island of size s is given by $y_s = a\tilde{y}_s$ while the capture number is given by $\sigma_s = \tilde{\sigma}(y_s)$.

We now consider the asymptotic limit corresponding to infinite D/F. In this limit, and assuming that $\theta \gg \theta_x$ (where $\theta_x \sim R^{-1/3}$ corresponds to the coverage at which the island-density equals the monomer density), Eq. (5) may be rewritten as,

$$\tilde{\sigma}(y;\theta) \simeq y/\xi^2. \tag{8}$$

This implies that in the asymptotic limit the scaled gap distribution $B(s/S) = y_s/Y$ is *identical* to the corresponding scaled capture number distribution $C(s/S)$. This result also demonstrates the "self-averaging property" of the capture zones, i.e., in the asymptotic limit the average capture number σ_s is exactly equal to the *local* capture number evaluated at the average capture zone for an island of size s.

In the asymptotic limit that $\theta \gg \theta_x$ one also has $dN_1/d\theta = 1 - RN_1/\xi^2 \simeq 0$, which implies that $RN_1/\xi^2 = 1$. Using these results in Eq. (7) and assuming[15] that $\theta_y \gg \theta_x$, we obtain

$$s-2 = \tilde{y}_s(\theta - \theta_y). \tag{9}$$

Since in the asymptotic limit $S \gg 1$, this may be rewritten as

$$u = s/S = (\tilde{y}_s \theta/S)(1 - \theta_y/\theta). \tag{10}$$

In the asymptotic limit, one has $\theta/S = N = 1/Y$. Using $\tilde{y}_s = b/N(\theta_y)$ and $N(\theta_y) \sim \theta_y^{1/4}$, $N(\theta) \sim \theta^{1/4}$ (since $\theta_y, \theta \gg \theta_x$ and $z=3/4$ for irreversible growth of point islands in one dimension), one has $(\theta_y/\theta) = (bY/\tilde{y}_s)^4$. Thus, the asymptotic gap distribution before rescaling will satisfy

$$u = \tilde{B}(u) - b^4/\tilde{B}(u)^3, \tag{11}$$

where $\tilde{B}(u) = \tilde{y}_s/Y$.

Rescaling, we obtain for the asymptotic scaled gap distribution $B(u) = a\, \tilde{B}(u)$ the equation

$$u = B(u)/a - b^4[B(u)/a]^{-3}, \tag{12}$$

where the rescaling factor a and the proportionality factor b must satisfy the requirement that

$$\int_0^\infty B(u) f(u) du = 1. \tag{13}$$

It is easy to see that for any positive constants a and b, Eq. (12) has a unique positive solution for every positive u

while for $a \geqslant z$ one has $B(u) > zu$. Similarly, one may show that for $a < 2/3$ the ISD predicted by Eq. (3) will diverge while for $2/3 < a < z$ there will be a cut-off at u_c [i.e., $f(u > u_c) = 0$] corresponding to the value of u at which $B(u)$ crosses zu. We note that while the asymptotic CND and ISD depend on the three constants $f(0)$, a, and b, the two sum rules, Eqs. (4) and (13), determine two of the constants if the third one is known. Therefore, we consider separately two particular choices for the free constant.

We first consider the case $b = 1$, as was assumed in our numerical calculations for finite D/F.[7,8] This corresponds to the mean-field assumption that the average gap size for freshly nucleated dimers is exactly equal to the average island gap at that coverage. By solving Eq. (12) and numerically evaluating the integrals in Eqs. (3), (4), and (13), we find $f(0) \simeq 0.33$ and $a \simeq 0.70$. Since $a > 2/3$, we conclude that, in contrast to the claims in Ref. 13, our method leads to a *nondivergent* ISD in the asymptotic limit of infinite D/F. The resulting asymptotic scaled CND agrees very well with our previous numerical RE results[8] for $D/F = 10^7$, and as shown in Fig. 1, it is also in relatively good agreement with KMC results for higher D/F. However, in contrast to our previous numerical RE results for the ISD for finite D/F,[8] due to the extreme sensitivity of the ISD on the CND in the asymptotic limit, the asymptotic ISD is shifted to the right from the simulation result and cuts off to zero at $u_c \simeq 1.85$.

It is also interesting to consider the general case $b \neq 1$, i.e., the capture area of a freshly nucleated dimer is proportional to the average area per island with some unknown proportionality constant b. In this case, we assume that the value of the rescaling constant a is fixed to the value $a = z$ by the requirement that $B(u) \simeq zu$ for large u.[9] We then search for a value of b ($b \simeq 0.87$) such that the sum rule (13) is satisfied. As can be seen in Fig. 1, the resulting scaled gap-distribution $B(u)$ is now very close to the simulation results for all u except for small u ($u < 0.7$) where it is now significantly lower than for the case $b = 1$. Accordingly, the peak of the corresponding island-size distribution [Fig. 1(b)] is somewhat lower than the peak of the simulated distribution, and the distribution itself is somewhat wider.

We now present an accurate analytical expression for the asymptotic capture-number distribution which is based on our analytical result, Eq. (12), with $b = 1$. We note that Eq. 12 with $b = 1$ and $a = z$ implies that $B(0) = z$ and $B(u) \simeq zu$ for large u, although the normalization integral (13) is just slightly larger than 1. This suggests that the correct CND should have a similar form to Eq. (12) with $b = 1$ and $a = z$, but with additional higher-order powers of $[B(u)]^{-1}$, in order to satisfy the sum rule (13). As an example, we consider the expression

$$u = \hat{B}(u) - [b_2/\hat{B}(u)^3]\exp[b_1/\hat{B}(u)^n], \qquad (14)$$

where $\hat{B}(u) \equiv B(u)/z$, $b_2 = e^{-b_1}$ in order to satisfy $\hat{B}(0) = 1$, and n is a free parameter for which we will choose $n = 5$. We note that $b_1 = 0$ corresponds to Eq. (12) with $b = 1$ and $a = z$. As before, for any value of b_1, the corresponding ISD $f(u)$ is determined by Eqs. (3) and (4) while the correct value of b_1 ($b_1 \simeq 0.993$) is determined by the sum rule (13). The corresponding results for $B(u)$ and $f(u)$ are shown by the solid curves in Fig. 1. As can be seen, the agreement between the calculated scaled distributions $B(u)$ and $f(u)$ and the simulations is now excellent.

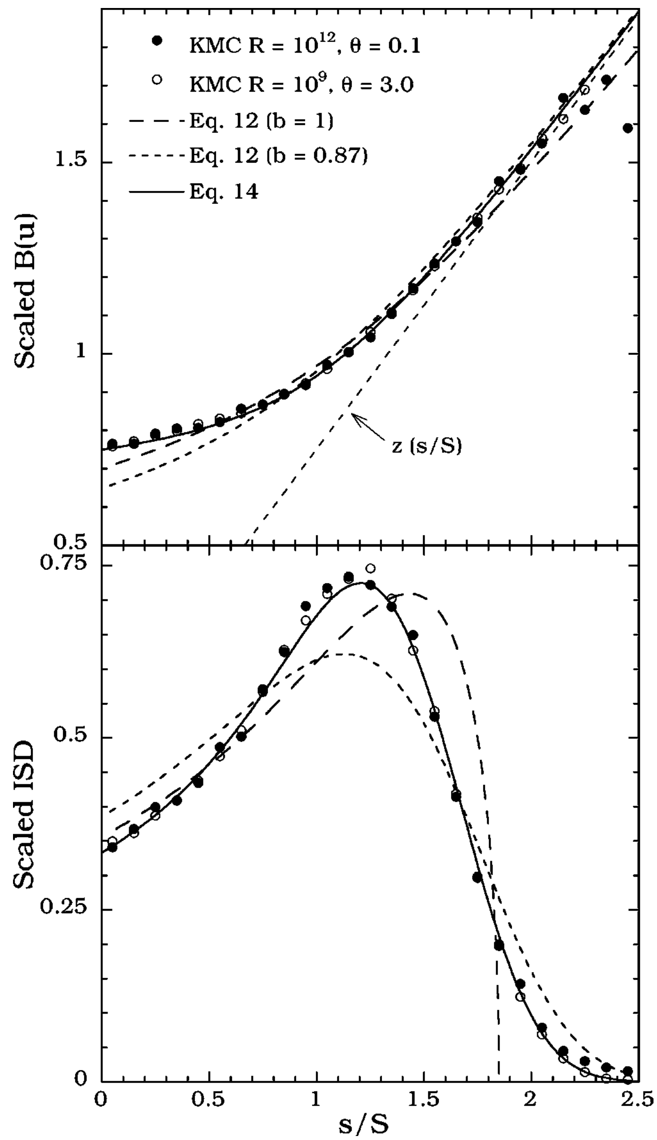

FIG. 1. Calculated asymptotic scaled (a) gap distribution $B(u)$ and (b) island size distribution $f(u)$, along with KMC results (symbols).

We have tried several other values of n ($n = 3,4,6$),[16] as well as polynomials in powers of $[\hat{B}(u)]^{-1}$ satisfying $\hat{B}(0) = 1$, and similarly good agreement with simulations has been found.[17] Thus, it would appear that almost any form similar to Eq. (12) with $b = 1$ and $a = z$ which satisfies the sum rule (13), leads to reasonably accurate results for the asymptotic scaled ISD and CND. The good agreement obtained suggests that simple refinements of our method may be possible which will allow the derivation of excellent approximations for the exact CND. However, a rigorous derivation of the functional form of the correction term(s) in Eq. (12) remains an open question.

In conclusion, using our self-consistent rate-equation approach,[7,8] we have derived analytical expressions for the asymptotic scaled capture-number, gap-, and island-size distributions for the case of one-dimensional irreversible growth of point islands. In particular, we have shown that our method leads to an asymptotic scaled CND which is close to that obtained in simulations and as a result to a *nondivergent* asymptotic ISD. While this leads to an ISD which is in excellent agreement with simulations for finite D/F,[7,8] due to the extreme sensitivity of the ISD on the CND in the asymptotic limit, the corresponding asymptotic ISD is shifted to the right, with a cutoff at finite scaled island-size. However, by slightly modifying our analytical expression (12) for the asymptotic scaled CND and solving self-consistently, we have obtained analytic expressions for the asymptotic CND and corresponding ISD which are in excellent agreement with simulations. These results also support our conjecture that $B(0)=z$ and that $B(u)\to zu$ for large u.

We have also shown rigorously that in the asymptotic limit the scaled gap distribution $B(u)$ is identical to the scaled capture-number distribution $C(u)$. This result also implies the "self-averaging property" of the capture zones, i.e., the average capture number σ_s is exactly equal to the local capture number evaluated at the average capture zone of islands of size s, which was assumed in our method.[7,8] If this "self-averaging property" holds more generally (as suggested by the good agreement obtained in our numerical results for finite D/F in both one and two dimensions[7,8]) then it may be possible in general to obtain accurate asymptotic ISD's without having to know the exact distribution of areas or the redistribution of areas due to nucleation events. This represents a significant simplification of the calculation of ISD's since the determination of the full distribution of capture zones is a very difficult problem for which no exact solution has so far been obtained even in the most simple cases.[5,9]

Finally, we consider the extension of these results to other cases of interest such as growth in two dimensions. The present analytical work was essentially dependent on the asymptotically valid relation $B(u)=C(u)$. It is not clear that such an explicit relation may be derived for the case of two-dimensional growth as serious mathematical difficulties occur due to complicated expressions for the local capture numbers. Consequently, further work is required to determine if a straightforward extension of the present work to this case is possible.

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[1] M.C. Bartelt and J.W. Evans, Phys. Rev. B **46**, 12 675 (1992); C. Ratsch, A. Zangwill, P. Smilauer, and D.D. Vvedensky, Phys. Rev. Lett. **72**, 3194 (1994); J.G. Amar, F. Family, and P.M. Lam, Phys. Rev. B **50**, 8781 (1994); M.C. Bartelt and J.W. Evans, J. Vac. Sci. Technol. A **12**, 1800 (1994); J.G. Amar and F. Family, Phys. Rev. Lett. **74**, 2066 (1995); P.A. Mulheran and J.A. Blackman, Philos. Mag. Lett. **72**, 55 (1995).
[2] M.C. Bartelt and J.W. Evans, Phys. Rev. B **54**, R17359 (1996).
[3] J.A. Blackman and P.A. Mulheran, Phys. Rev. B **54**, 11 681 (1996); P.A. Mulheran and J.A. Blackman, Surf. Sci. **376**, 403 (1997).
[4] Y.W. Mo, J. Kleiner, M.B. Webb, M.G. Lagally, and Phys. Rev. Lett. **66**, 1998 (1991); T.R. Linderoth, S. Horch, E. Lægsgaard, I. Stensgaard, and F. Besenbacher, *ibid.* **78**, 4978 (1997).
[5] P.A. Mulheran and D.A. Robbie, Europhys. Lett. **49**, 617 (2000); F.G. Gibou, C. Ratsch, M.F. Guyre, S. Chen, and R.E. Caflisch, Phys. Rev. B **63**, 115401 (2001).
[6] D.D. Vvedensky, Phys. Rev. B **62**, 15 435 (2001).
[7] J.G. Amar, M.N. Popescu, and F. Family, Phys. Rev. Lett. **86**, 3092 (2001); M.N. Popescu, J.G. Amar, and F. Family, Phys. Rev. B **64**, 205404 (2001).
[8] J.G. Amar, M.N. Popescu, and F. Family, Surf. Sci. **491**, 239 (2001).
[9] J.W. Evans and M.C. Bartelt, Phys. Rev. B **63**, 235408 (2001); **66**, 235410 (2002).
[10] M. von Smoluchowski, Phys. Z. **17**, 557 (1916); Z. Phys. Chem. Stoechiom. Verwandtschaftsl. **92**, 129 (1917).
[11] J.A. Venables, Philos. Mag. **27**, 697 (1973); J.A. Venables, G.D. Spiller, and M. Hanbucken, Rep. Prog. Phys. **47**, 399 (1984).
[12] A.D. Gates and J.L. Robins, Surf. Sci. **116**, 188 (1982); **191**, 492 (1987); **191**, 499 (1987).
[13] D.D. Vvedensky, C. Ratsch, F. Gibou, and R. Vardavas, Phys. Rev. Lett. **90**, 189601 (2003); J.G. Amar, M.N. Popescu, and F. Family, *ibid.* **90**, 189602 (2003).
[14] Our model of irreversible growth of point islands in one dimension may be defined as follows. Atoms are deposited randomly on an initially empty line of sites with a (per site) deposition rate F and diffuse with a diffusion constant D. When a monomer moves onto a site occupied by another monomer, a dimer island is nucleated at that site. Similarly, a monomer moving onto a site occupied by an island is absorbed and the island size s increases by one. All islands of size $s\geqslant 2$ are assumed to be stable and immobile.
[15] In the asymptotic limit a vanishingly small fraction of islands will have nucleated at a coverage θ_y which does not satisfy $\theta_y \gg \theta_x$ and therefore this assumption holds for essentially all islands.
[16] For example, Eq. (14) with $n=3$ leads to a distribution with a slightly higher peak which is just slightly shifted to the right and with a tail which is just slightly lower than in simulations.
[17] For example, the expression $u=\hat{B}(u)-\gamma\hat{B}(u)^{-3}-(1-\gamma)[\hat{B}(u)^{-9}+\hat{B}(u)^{-12}]/2$, with $\gamma\simeq 0.39$ in order to satisfy (13), leads to results which are essentially identical to those obtained using Eq. (14).