Asymptotic Capture-Number and Island-Size Distributions for One-Dimensional Irreversible Submonolayer Growth

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Using a set of evolution equations [J. G. Amar et al, Phys. Rev. Lett. 86, 3002 (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 non-divergent asymptotic scaled island-size distribution (ISD). We then show that a slight modification of our analytical form leads to an analytic expression 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 self-averaging property of the capture zones holds exactly while the asymptotic scaled gap distribution is equal to the scaled CND.

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. 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 $\theta$) satisfies the scaling form:

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

(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.

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. For the irreversible growth of point islands, rate-equations valid in the pre-coalescence regime may be written in the form:

$$\frac{dN_1}{d\theta} = 1 - 2R\sigma_1 N_1^2 - RN_1 \sum_{s \geq 2} \sigma_s N_s$$

(2a)

$$\frac{dN_s}{d\theta} = RN_1 (\sigma_{s-1} N_{s-1} - \sigma_s N_s), \quad \text{for} \quad s \geq 2 \quad (2b)$$

where the capture numbers $\sigma_s$ ($\sigma_1$) 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 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.

Our method involves numerical integration of the island-density RE’s (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: (1) the average capture area per freshly nucleated dimer is proportional (before rescaling) to the average area per island and (2) the combined effects of the preferred nucleation of dimers in large capture zones and the preferred “break-up” of large capture zones due to nucleation may be approximated by a uniform rescaling of the average capture zone of each island. This approach, which is based on the following two assumptions: (1) the average capture area per freshly nucleated dimer is proportional (before rescaling) to the average area per island and (2) the combined effects of the preferred nucleation of dimers in large capture zones and the preferred “break-up” of large capture zones due to nucleation may be approximated by a uniform rescaling of the average capture zone of each island, has been obtained numerically 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 that because our method does not explicitly take into account spatial fluctuations in the nucleation, then it must lead to a diverging ISD in the asymptotic limit corresponding to infinite $D/F$. However, as shown by Bartelt and Evans in the asymptotic limit the scaled ISD is related to the scaled CND as,

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

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 deter-
minded by the normalization condition,
\[ \int_0^\infty du \, f(u) = 1. \] (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 \( u \geq u_c \)) 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.

In this Rapid Communication we rigorously address the question of the asymptotic behavior obtained using our method by analytically deriving the asymptotic scaled CND along with the corresponding asymptotic scaled ISD for the case of irreversible growth of point islands in one-dimension. We find that, contrary to the claims in Ref. 11 our method leads to a non-divergent, asymptotic ISD as well as to an asymptotic scaled CND which is close to that obtained in simulations. We then show that by slightly modifying our original analytical form for \( C(u) \), an improved analytical expression for the asymptotic scaled CND may be obtained which is in excellent agreement with KMC simulations. The resulting analytic expression leads to a scaled ISD which is also in excellent agreement with KMC simulations. We also demonstrate that the asymptotic scaled gap distribution is identical to the scaled CND and as a result the self-averaging property of the capture zones holds exactly.

For clarity, we briefly review our method and its application to the case of irreversible growth of point islands in one-dimension. 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
\[ \tilde{\sigma}(y; \theta) = \frac{2\xi_1}{\xi^2} \tanh \left( \frac{y}{2\xi_1} \right), \] (5)
where the monomer capture length \( \xi \) and the nucleation length \( \xi_1 \) are defined as
\[ 2\xi_1 N_1 = 1/\xi_1^2, \quad 1/\xi_1^2 + \sum_{s \geq 2} \sigma_s N_s = 1/\xi^2. \] (6)

From the evolution equations for the distributions of gap lengths, the average “gap-length” \( \bar{y}_s \) (before rescaling) corresponding to an island of size \( s \) may be obtained as the solution of the equation,
\[ s - 2 = \int_{\theta_y}^\theta R N_1(\phi) \tilde{\sigma}(\bar{y}_s; \phi) d\phi. \] (7)
The coverage \( \theta_y \) is defined by \( \bar{y}_s = b \, Y(\theta_y) \) 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 \( \theta \), and \( N(\theta) = \sum_{s \geq 2} N_s(\theta) \) is the average island density. Physically, the integral in Eq. 7 may be interpreted as corresponding to the average number of particles added to the dimer since it was formed at coverage \( \theta_y \), neglecting any change in the capture zone due to nucleation and break-up. To include the effects of break-up, the gap lengths are rescaled by a rescaling factor \( a = 1/\sum_{s \geq 2} N_s \bar{y}_s \) so that the average gap length for an island of size \( s \) is given by \( \bar{y}_s = a \, \bar{y}_s \) while the capture number is given by \( \sigma_s = \tilde{\sigma}(\bar{y}_s) \).

We now consider the asymptotic limit corresponding to infinite \( D/F \). In this limit, and assuming that \( \theta >> \theta_x \) (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,
\[ \tilde{\sigma}(y; \theta) \simeq y/\xi^2. \] (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 \( \langle \sigma_s \rangle \) 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 \( \theta >> \theta_x \) one also has \( dN_1/d\theta = 1 - RN_1/\xi^2 \simeq 0 \), which implies that \( R N_1/\xi^2 = 1 \). Using these results in Eq. 7 and assuming that also \( \theta_y >> \theta_x \), we obtain
\[ s - 2 = \bar{y}_s (\theta - \theta_y). \] (9)

Since in the asymptotic limit \( S \gg 1 \), this may be rewritten as
\[ u = s/S = (\bar{y}_s \theta/S)(1 - \theta_y/\theta). \] (10)

In the asymptotic limit, one has \( \theta/S = N = 1/Y \). Using \( \bar{y}_s = b/N(\theta_y) \) and \( N(\theta_y) \sim \theta_y^{1/4} \), \( N(\theta) \sim \theta^{3/4} \) (since \( \theta_y \gg \theta_x \) and \( z = 3/4 \) for irreversible growth of point islands in one-dimension), one has \( \theta_y/\theta = (bY/\bar{y}_s)^4 \). Thus, the asymptotic gap distribution before rescaling will satisfy,
\[ u = \hat{B}(u) - b^4/\hat{B}(u)^3, \] (11)
where \( \hat{B}(u) = \bar{y}_s/Y \). Rescaling, we obtain for the asymptotic scaled gap distribution \( B(u) = a \, \hat{B}(u) \) the equation
\[ u = B(u)/a - b^4 [B(u)/a]^{-3}, \] (12)
where the rescaling factor \( a \) and the proportionality factor \( b \) must satisfy the requirement that
\[ \int_0^\infty B(u) f(u) \, du = 1 \] (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 $a \geq z$ 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 $u_e$, i.e. $f(u > u_e) = 0$.

We now consider the case $b = 1$ as was assumed in our numerical calculations for finite $D/F$ along with the requirement that $f(u) \to 0$ rapidly for large $u$, indicates that the asymptotic $B(u)$ should satisfy $B(u) \simeq zu$ for large $u$. Applied to Eq. 12 this implies that $a = z$ and thus $C(0) = B(0) = 3/4$, in very good agreement with our KMC simulation results. This leads to the following expression,

$$u = \hat{B}(u) - 1/\hat{B}(u)^3$$

(14)

where $\hat{B}(u) \equiv B(u)/z$ and $\hat{B}(0) = 1$. Unfortunately, integrating Eq. 3 numerically using Eq. 14 to determine $f(u)$, we find that the resulting “cross-integral” $\int_0^\infty B(u) f(u) du \simeq 1.15$ is somewhat larger than 1. This implies that a smaller value of the rescaling factor $a$ must be used. By carrying out the appropriate numerical integrals we find that $a \simeq 0.70$ satisfies the “cross-integral” normalization condition (13). The corresponding scaled CND and ISD with $b = 1$ are shown in Fig. 1. As can be seen, the calculated asymptotic ISD is shifted to the right from the simulation result and is cut off to zero at $u_e \simeq 1.85$ where $C(u)$ crosses $zu$. Thus we find that, contrary to the claims in Ref. 11, our method leads to a non-divergent ISD in the asymptotic limit of infinite $D/F$.

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 the asymptotic behavior of $B(u)$ is given by $B(u) \simeq zu$ for large $u$. 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 $\hat{B}(u)$ 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 analytical form for the capture-number distribution $C(u) \equiv B(u)$ which provides excellent agreement with simulations and thus strongly supports our conjecture that $B(0) = z$ and that $B(u) \to zu$ for large $u$. Since Eq. 12 with $b = 1$ and $a = z$ leads to an expression for $B(u)$ (14) which satisfies $\hat{B}(0) = 1$ and $\hat{B}(u) \to zu$ for large $u$, but a cross-integral (13) which is just slightly larger than 1, we propose that the correct analytic expression for $B(u)$ has the same form as (14) but with additional terms corresponding to higher order powers of $[\hat{B}(u)]^{-1}$. As an example, we chose the following form,

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

(15)

where $b_2 = e^{-b_1}$ in order to satisfy $\hat{B}(0) = 1$, and $n$ is a free parameter for which we will choose $n = 5$. We then use Eq. 3 to calculate $f(u)$ and search for a value of $b_1$ ($b_1 \simeq 0.993$) such that the sum-rule (13) is satisfied. Our results for the corresponding $B(u)$ and $f(u)$ obtained in this manner are shown by the solid curves in Fig. 1. As can be seen, the agreement between the calculated scaled gap-distribution $B(u)$ and simulations is now excellent. Accordingly, the agreement between the corresponding calculated ISD and simulations is also very good. This result also confirms that $C(u) = B(u)$ in the asymptotic limit.

We have also tried several other values of $n$ ($n = 3, 4, 6$) and obtained similarly good agreement with simulations. Finite expansions in powers of $[\hat{B}(u)]^{-1}$ satisfying $\hat{B}(0) = 1$ also lead to reasonably good agree-
ment. In particular, the expression

\[ u = \hat{B}(u) - \gamma \hat{B}(u)^{-3} - \frac{1 - \gamma}{2} [\hat{B}(u)^{-9} + \hat{B}(u)^{-12}], \]  

(16)

(with \( \gamma \approx 0.39 \) to satisfy \( 13 \)) leads to results which are essentially identical to those obtained using Eq. 15. Thus, it would appear that almost any form similar to Eq. 15, but with higher order corrections, which satisfies the condition \( \hat{B}(0) = 1 \) as well as the sum-rule \( 13 \), leads to reasonably accurate results for the asymptotic scaled ISD and CND.

In conclusion, 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 non-divergent asymptotic ISD. Our analytical results also indicate that in the asymptotic limit the scaled gap-distribution \( \hat{B}(u) \) is identical to the scaled capture-number distribution \( C(u) \). Finally, by slightly modifying our analytical expression \( 14 \) for the scaled CND and solving self-consistently, we have obtained analytic expressions for the scaled CND and corresponding ISD which are in excellent agreement with simulations.

We note that our analytical results also demonstrated that the “self-averaging property” of the capture zones (i.e. the average capture number \( \sigma_s \) is exactly equal to the local capture number evaluated at the average capture zone of islands of size \( s \)) is exact in the asymptotic limit for the case of irreversible growth of point-islands in one-dimension. If this “self-averaging property” holds generally (as suggested by the good agreement obtained in our numerical results for finite \( D/F \) in both one- and two-dimensions\(^6,7,8,9\)) then it may be possible in general to obtain accurate asymptotic ISDs 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 ISDs since the determination of the full distribution of capture zones is a very difficult problem for which no exact solution seems to be possible even in the most simple cases\(^10,11,12\).

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 \( \hat{B}(u) = C(u) \). It is not clear that such an explicit relation may be derived for the case of two-dimensional growth, and additional mathematical difficulties occur due to complicated expressions for the local capture numbers. As a result, it is not clear if a straightforward extension of the present work to this case is possible, and further work is required to answer this question.

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1 M.C. Bartelt and J.W. Evans, Phys. Rev. B 46, 12675 (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. Tech. 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, 11681 (1996); P.A. Mulheran and J.A. Blackman, Surf. Sci. 376, 403 (1997).
4 P.A. Mulheran and D.A. Robbie, Europhys. Lett. 49, 617 (2000); F.G. Gibou, C. Ratsch, M.F. Guyre, S. Chen, R.E. Caflisch, Phys. Rev. B 63, 115401 (2001).
5 D.D. Vvedensky, Phys. Rev. B 62, 15435 (2001).
6 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).
7 J.G. Amar, M.N. Popescu, and F. Family, Surf. Sci. 491, 239 (2001).
8 J.W. Evans and M.C. Bartelt, Phys. Rev. B 63, 235408 (2001); ibid. 66, 235410 (2002).
9 M. von Smoluchowski, Z. Phys. Chem. 17, 557 (1916); ibid. 92, 129 (1917).
10 J.A. Venables, Philos. Mag. 27, 697 (1973); J.A. Venables, G.D. Spiller, and M. Hanbucken, Rep. Prog. Phys. 47, 399 (1984).
11 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, Phys. Rev. Lett. 90, 189602 (2003).
12 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 \( s \geq 2 \) are assumed to be stable and immobile.
13 In the asymptotic limit a vanishingly small fraction of islands will have nucleated at a coverage \( \theta_0 \) which does not satisfy \( \theta_0 >> \theta_s \) and therefore this assumption holds for essentially all islands.
14 For example, Eq. 15 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.