Asymptotics of capture zone distributions in a fragmentation-based model of submonolayer deposition

J. A. Blackman[a], M. Grinfeld[b,*], P. A. Mulheran[c]

[a]*Department of Physics, University of Reading, Whiteknights, Reading RG6 6AF, UK*

[b]*Department of Mathematics and Statistics, University of Strathclyde, 26 Richmond Street, Glasgow G1 1XH, UK*

[c]*Chemical and Process Engineering, University of Strathclyde, 75 Montrose Street, Glasgow G1 1XJ, UK*

Abstract

We consider the asymptotics of the distribution of the capture zones associated with the islands nucleated during submonolayer deposition onto a one-dimensional substrate. We use a convolution of the distribution of inter-island gaps, the asymptotics of which is known for a class of nucleation models, to derive the asymptotics for the capture zones. The results are in broad agreement with published Monte Carlo simulation data [Phys. Rev. E **85**, 021601].

Keywords: sub-monolayer deposition, fragmentation, nucleation, capture zone distribution
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1. Introduction

The statistical properties of islands nucleated during submonolayer deposition have attracted much recent attention from experimentalists and theorists (see [1] for a recent review).

The nanoscale islands formed during the deposition are the building blocks for new technology, and pose interesting challenges for the understanding and control of the nucleation and growth processes. The capture zones of the islands, which dictate their growth rates, have been of particular interest to theorists due to their scaling properties. A number of theoretical approaches to this topic have been developed [2–12]. Here we extend the fragmentation theory approach [5] that describes the evolution of the inter-island gaps on a one-dimensional substrate, to obtain the large size asymptotics of the capture zones themselves.

The fragmentation theory approach considers the distribution of gaps between point islands on a one-dimensional substrate [5, 11]. The nucleation of a new island fragments an existing gap into two smaller ones. The probability of this event occurring, and the proportions into which the gap is fragmented, are determined by the steady state monomer density in the parent gap. This can be found from solving a diffusion equation for randomly deposited monomers that diffuse until they are absorbed by the islands at the two ends of the gap [5, 11].

*Corresponding author
Email addresses: j.a.blackman@reading.ac.uk (J. A. Blackman), m.grinfeld@strath.ac.uk (M. Grinfeld), paul.mulheran@strath.ac.uk (P. A. Mulheran)

The work in [5] considered only critical island size $i = 1$, where $i+1$ monomers must come together to nucleate an immobile point island that grows in size by capturing diffusing monomers. In [11], we extended the analysis to general values of i, $i = 0, 1, 2, 3, \ldots$. While it has not been possible for us to find closed-form, analytical solutions in this approach, using the work of Cheng and Redner [14], we were able to show in [11] that the gap size distribution (GSD) $\phi(y)$ has the following asymptotics:

$$\phi(y) \sim y^{i+1} \text{ as } y \to 0, \text{ and} \tag{1}$$

$$\phi(y) \sim y^{-2} \exp^{-cy^{2i+3}} \text{ as } y \to \infty. \tag{2}$$

Here y is the gap size scaled by the average gap size. Note that the arguments of [14] do not allow the determination of the constant c (which can depend on i) in (2). In these equations and everywhere below we use the notation $f(t) \sim g(t)$ as $t \to a$ to mean that

$$\lim_{t \to a} \frac{f(t)}{g(t)} = K,$$

for a positive constant K.

Given these results, we considered the asymptotics of the capture zone distribution (CZD) $P(s)$, defined as

$$P(s) = 2 \int_0^{2s} \phi(y)\phi(2s - y)\, dy, \tag{3}$$

where the convolution is justified by the mixing effect of subsequent nucleation events that remove the correlations between neighbouring gaps [5]. Here too the capture zone size s is scaled by the average. From (1) we were able to find the asymptotics of $P(s)$ as $s \to 0$, and subsequently showed good agreement with Monte-Carlo simulation data [13].

However, in [11] we were only able to find the large size ($s \to \infty$) asymptotics of $P(s)$ only in the case of spontaneous nucleation, $i = 0$:

$$P(s) \sim s^{-9/2} \exp\left(\frac{-2s^3}{\mu^3}\right) \quad \text{as } s \to \infty, \tag{4}$$

where $\mu = 4\Gamma(2/3)/3$.

It is the purpose of the present paper to derive the large-size asymptotics for $P(s)$ for general critical island size $i \geq 0$, using equations (2) and (3).

In Section 2 we present our new result and its proof. In Section 3, we compare this new result with data from our previously published Monte Carlo simulations [13], which is the only source we know of for large-size CZD asymptotics for a range of critical island sizes.

2. Large size asymptotics of CZD for general i

Equations (2) and (3), valid for the fragmentation theory of [5], are sufficient to prove the following result:

Theorem 1. *As $s \to \infty$, $P(s) \sim s^{-9/2-i} \exp(-2cs^{2i+3})$, where c is as in Eqn. (2).*

This is clearly consistent with Eqn. (4) for the case of $i = 0$.

Our proof is based on a very simple and striking property of convolutions, which we will illustrate by an example below. Thus our arguments are a particular case of a general theorem proved by Nagaev and Tsitsiashvili [15]. However, our reasoning is much more explicit and avoids reliance on deep probability theory constructions of that paper.

Let us first change variables in (3) by setting $y = 2sz$:

$$P(s) = 4s \int_0^1 \phi(2sz)\phi(2s(1-z))\, dz.$$

Now let us consider the integrand, $\psi(s,z) = \phi(2sz)\phi(2s(1-z))$. The crucial observation is that the structure of $\psi(s,z)$, $z \in [0,1]$, simplifies as s grows. For example, consider $\phi(y) = (y - 3.4y^2 + 3y^3)e^{-y^2}$ (here the coefficients have been chosen so that the function ϕ is positive for all $y \in [0,\infty)$). In Figure 1 we plot $\psi(0.5,z)$ and $\psi(5,z)$, scaled by their global maxima:

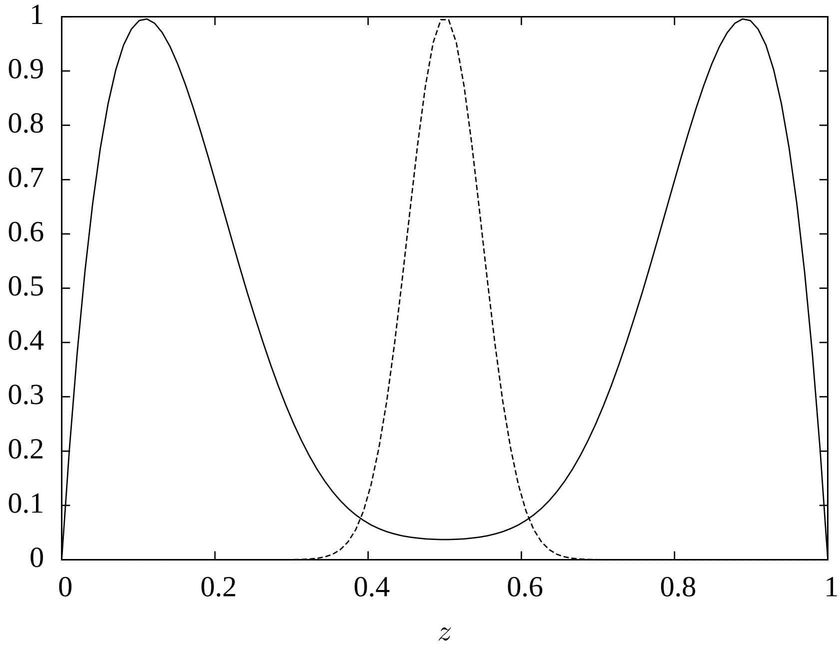

Figure 1: Scaled $\psi(0.5,z)$ (solid line) and $\psi(5,z)$ (dashed line) versus z

This is a general phenomenon: for the class of functions we are considering, as s increases, the function $\psi(\cdot,z)$ acquires a global maximum at $z = 1/2$. Incidentally, numerical evidence shows that this is the only critical point of $\psi(\cdot,z)$ for sufficiently large s, but that is not crucial for the application of Laplace's method [16].

Assume that $\phi(y) \sim y^\gamma \exp(-cy^\delta)$, where $\delta > 1$. To show that as $s \to \infty$, ψ acquires a global maximum at $z = 1/2$, consider the ratio $\psi(s,u)/\psi(s,1/2)$ for any fixed $u \in (0,1)$. Then we have

$$\lim_{s\to\infty} \frac{\psi(s,u)}{\psi(s,1/2)} = \lim_{s\to\infty} 2^{2\gamma}(u(1-u))^\gamma \exp(-cs^\delta(2^\delta u^\delta + 2^\delta(1-u)^\delta - 2)) = \begin{cases} 1 & \text{if } u = 1/2, \\ 0 & \text{if } u \neq 1/2. \end{cases}$$

Hence if $\phi(y) \sim y^\gamma \exp(-cy^\delta)$, I_ϵ is a small interval around $z = 1/2$, and EST stand for exponentially small terms,

$$P(s) \sim 2s \int_{I_\epsilon} \phi(2sz)\phi(2s(1-z)\,dz + EST,$$

Now putting in the asymptotic form of ϕ, we obtain

$$P(s) \sim 16s^{2\gamma+1} \int_{I_\epsilon} z^\gamma (1-z)^\gamma \exp(-c(2s)^\delta (z^\delta + (1-z)^\delta))\,dz,$$

and applying Laplace's method, we have that

$$P(s) \sim s^{2\gamma+1-\delta/2} \exp(-2cs^\delta).$$

Theorem 1 is recovered by putting $\gamma = -2$ and $\delta = 2i + 3$.

3. Discussion

Theorem 1 provides a new result for the large size asymptotics of the CZD in the fragmentation theory approach [5]. In [13] we presented results from Monte Carlo simulations for one-dimensional island nucleation and growth during submonolayer deposition, numerically analysing the asymptotics of the capture zone distributions. We found that in the spontaneous nucleation case $i = 0$, the measured exponent was 3.04 ± 0.04, very close to the value of 3 predicted by Eqn. (4). We also found higher exponents for higher critical island sizes [13], but had concrete theoretical results to compare them to at that time.

The values we reported for the exponents were, to 2 significant figures, 3.8, 5.5 and 6.5 respectively for $i = 1, 2, 3$ (see [13] for details including error estimates which are smaller than 0.1). Our predictions for this exponent depend on the mechanism that dominates nucleation. If it is driven solely by the diffusion of monomers on the substrate, as assumed in the original work of Blackman and Mulheran [5], we predict (from Theorem 1) exponents of 5, 7 and 9 respectively which are somewhat higher than the simulation results. However, in [13] we observed that in practice, the simulations do not reach a truly asymptotic regime. If nucleation is dominated by fluctuations caused by the stochastic deposition events, i in our formula is replaced by an effective i ($i_{eff} = i - 1$), yielding exponents 3, 5 and 7 respectively for $i = 1, 2, 3$. These are closer to the Monte Carlo results and support the proposition that, in practice, deposition events play a significant part in determining the capture zone distribution. In all the cases considered ($i = 0, 1, 2, 3$) it is clear that our fragmentation theory approach provides a good basis for understanding the observed behaviour.

Finally, in [6], Pimpinelli and Einstein have suggested, using the generalized Wigner surmise (GWS), that the large-size asymptotics of CZD should have Gaussian tails, leading to an exponent of 2. In later work [7, 8] these authors also considered the limitation of the GWS approach, while other research groups have cast doubt on the functional form they proposed in [6] for the CZD [9–11]. Nevertheless, in light of Theorem 1, it is instructive to consider that the GWS asymptotics will arise from a GSD of the form

$$\phi(y) \sim y^{i+1} \exp(-b_\beta y^2/2)$$

(see [6] for the definition of the constant b_β). It would be interesting to find a fragmentation mechanism consistent with the above form of GSD.

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[1] M. Einax, W. Dieterich, and P. Maass, Colloquium: Cluster growth on surfaces: Densities, size distributions, and morphologies, Rev. Mod. Phys, **85** (2013), 921–939.

[2] P. A. Mulheran and D. A. Robbie, Theory of the island and capture zone size distributions in thin film growth, Europhys. Lett. **49** (2000), 617–623.

[3] J. G. Amar, M. N. Popescu, and F. Family, Rate-equation approach to island capture zones and size distributions in epitaxial growth, Phys. Rev. Lett. **86** (2002), 3092–3095.

[4] J.W. Evans, P.A. Thiel, and M.C. Bartelt, Morphological evolution during epitaxial thin film growth: Formation of 2D islands and 3D mounds, Surf. Sci. Rep. **61** (2006), 1–128.

[5] J. A. Blackman and P. A. Mulheran, Scaling behavior in submonolayer film growth: a one-dimensional model, Phys. Rev B. **54** (1996), 11681.

[6] A. Pimpinelli and T. L. Einstein, Capture-zone scaling in island nucleation: universal fluctuation behavior, Phys. Rev. Lett. **99** (2007), 226102.

[7] D. L. Gonzalez, A. Pimpinelli, and T. L. Einstein, Spacing distribution functions for the one-dimensional point-island model with irreversible attachment, Phys. Rev. E **84** (2011), 011601.

[8] T. L. Einstein, A. Pimpinelli, and D. L. Gonzalez, Analyzing capture zone distributions in growth: Theory and applications, J. Cryst. Growth **401** (2014), 67–71.

[9] F. Shi, Y. Shim, and J. G. Amar, Capture-zone areas in submonolayer nucleation: Effects of dimensionality and short-range interactions, Phys. Rev, E. **79** (2009), 011602.

[10] M. Li, Y. Han, and J. W. Evans, Capture-zone scaling in island nucleation: Universal fluctuation behavior, Phys. Rev. Lett. **104** (2010), 149601.

[11] M. Grinfeld, W. Lamb, K. P. O'Neill and P. A. Mulheran, Capture-zone distribution in one-dimensional sub-monolayer film growth: a fragmentation theory approach, J. Phys. A: Math. Theor. **45** (2012), 015002.

[12] P. A. Mulheran, K. P. O'Neill, M. Grinfeld, and W. Lamb, Distributional fixed-point equations for island nucleation: A retrospective approach for capture-zone scaling, Phys. Rev E **86** (2012), 051606.

[13] K. P. O'Neill, M. Grinfeld, W. Lamb, and P. A. Mulheran, Gap size and capture zone distributions in one-dimensional point island nucleation and growth simulations: asymptotics and models, Phys. Rev. E**85** (2012), 021601.

[14] Z. Cheng and S. Redner, Scaling theory of fragmentation, Phys. Rev. Lett. **60** (1988), 2450.

[15] A. Nagaev and G. Tsitsiashvili, Tail asymptotics of the n-th convolution of super-exponential distributions, Stat. Prob. Lett. **76** (2006), 861–870.

[16] J. D. Murray, *Asymptotic Analysis*, Springer-Verlag, New York 1984.