# Capture Zone Distribution in Submonolayer Deposition

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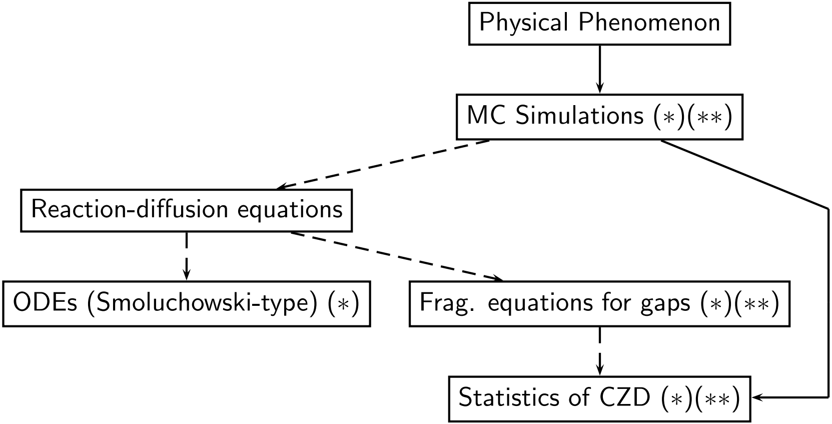
Joint work with M. Grinfeld, W. Lamb & P. A. Mulheran.

# Outline

# Overview

(∗) indicates where I work currently.

(∗∗) indicates where we'll focus on today.



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Thin films arise in variety of applications such as

- optical coatings
- semiconductor devices
- self-assembly of nanostructures.

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In recent years, there have been a number of theoretical investigations aimed at obtaining a better understanding of the scaling properties of the island size distribution in the initial submonolayer stage of film growth.

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A **stable** island is one from which monomers cannot disassociate. In this case, we are assuming that the aggregation is **irreversible**.

A **critical island size** $i$ is defined to be one less than the number of monomers needed for a stable island.

# Typical model

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Islands nucleate through at least $i + 1$ monomer coming together by chance. By the capture of single monomers islands can then grow.

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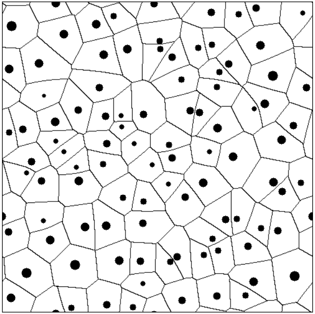
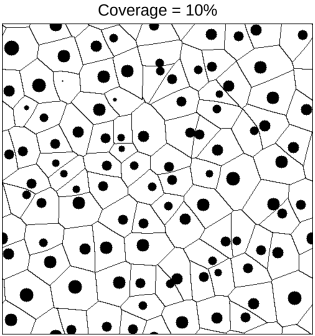
**Coverage**, $\theta = Ft$ (%), is the percentage of sites with monomers or islands on them.

# Coverage at 5%

Coverage = 5%

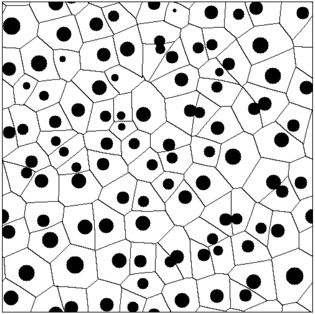


# Coverage at 10%

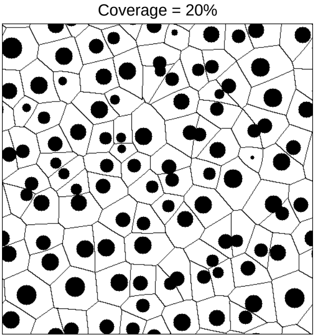


# Coverage at 15%

Coverage = 15%



# Coverage at 20%



# Rate equations

In the case of irreversible aggregation, rate equations that have been used to describe the case when the critical island size is $i = 1$, widely studied by authors such as Amar, Bales & Chrzan etc., are

## Rate Equations for $i = 1$

$$\frac{dc_1(t)}{dt} = F - 2D\sigma_1 c_1^2 - Dc_1 \sum_{j=2}^{\infty} \sigma_j c_j \quad (1)$$

$$\frac{dc_j(t)}{dt} = Dc_1(\sigma_{j-1}c_{j-1} - \sigma_j c_j), \quad j \geq 2. \quad (2)$$

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Consequently, when significant spatial fluctuations do exist, a rate-equation approach is likely to lead to predictions which differ substantially from results that are obtained experimentally or by MC simulations.

Hence, the mean-field rate equations alone cannot provide a complete description of film growth.

# Beyond the mean-field approach

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A way to generate numerical data that compare well with experiments is to do MC simulations. Furthermore, MC simulations allow us to obtain data on the **capture zone distribution**, a central concept due to Mulheran and Blackman which we describe next.

# The Mulheran and Blackman approach

The substrate is represented by a $d$-dimensional lattice. where $d = 1, 2, 3$.

- A decision must be made about shapes of islands. One may consider islands that have no spatial extent. This is known as **point islands**.

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- Randomly deposited monomers diffuse by nearest neighbour hops.
- The stable islands are assumed to be immobile.

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- Island's growth rate is taken to be proportional to the size (area, volume etc.) of its CZ. Monomers deposited into a CZ are more likely to be adsorbed by the occupant island than by any other.

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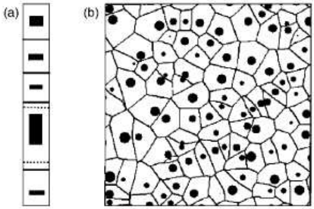
- Nucleation of new islands during deposition fragments the structure of capture zones.

# Figure of Capture Zone Distribution (CZD)




CZs for $1D$ (left) and $2D$ (right).

(a) Black rectangles correspond to $1D$ islands. Horizontal lines mark the midpoints between the edges of two islands, defining their CZs. (b) The islands appear approximately circular and the CZs are indicated by the cell boundaries.

# Generalised Wigner Surmise

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Pimpinelli & Einstein conjectured that

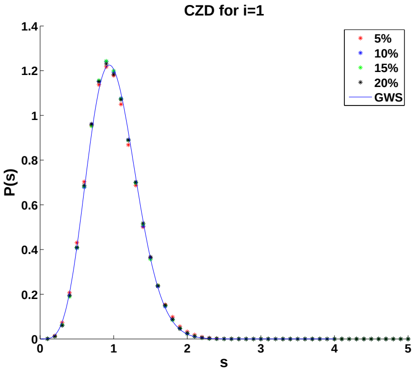
**Generalised Wigner Surmise (GWS)**

$$P_\beta(s) = a_\beta s^\beta \exp(-b_\beta s^2), \tag{3}$$

where $\beta = \frac{2}{d}(i + 1)$, $i \in \mathbb{Z}^+$, $d = 1, 2$. If $d > 2$ then $\beta = i + 1$.

$a_\beta$, $b_\beta$ - normalisation constants.

# CZD for $i = 1$, $d = 1$

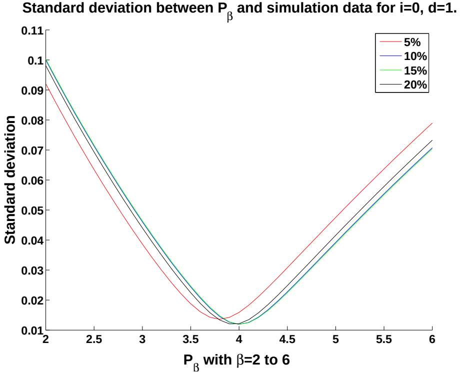



CZD for $i = 1$, $d = 1$.

Note that there are four different values of coverage, $\theta = 5\%,\ 10\%,\ 15\%$ and $20\%$. As $\theta$ increases the density of islands increases.

# Best fit $\beta$ for $i, d = 1$

Assuming GWS is true, we want to know whether the data does fit $\beta = \frac{2}{d}(i+1) = 4$ for $i = 1, d = 1$ better than any other integer values of $\beta$.

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# GWS for $d = 1$

Assuming GWS is true, for higher coverage $(15\% - 20\%)$ we find

| $i$ | GWS's $\beta$ | Approximate 95% confidence limit |
|---|---|---|
| 0 | 2 | $(2.8455, 2.9020)$ |
| 1 | 4 | $(3.9962, 4.0395)$ |
| 2 | 6 | $(5.8620, 5.9447)$ |
| 3 | 8 | $(6.4392, 6.5657)$ |

Table: Best fit $\beta$ for $d = 1$.

# GWS for $d = 2$

Assuming GWS is true, for higher coverage $(15\% - 20\%)$ we find

| $i$ | GWS's $\beta$ | Approximate 95% confidence limit |
|---|---|---|
| 0 | 1 | $(1.1194, 1.1419)$ |
| 1 | 2 | $(2.1009, 2.1228)$ |
| 2 | 3 | $(3.5515, 3.6221)$ |
| 3 | 4 | $(4.0669, 4.1444)$ |

Table: Best fit $\beta$ for $d = 2$.

# GWS for $d = 3$

For $d = 3$, $\beta$ is the same for $d = 2$ case.

Assuming GWS is true, for higher coverage ($15\% - 20\%$) we find

| $i$ | GWS's $\beta$ | Approximate 95% confidence limit |
|---|---|---|
| 0 | 1 | $(0, 0.0040)$ |
| 1 | 2 | $(0.6470, 0.6651)$ |
| 2 | 3 | $(2.0344, 2.0406)$ |
| 3 | 4 | $(1.8557, 1.8990)$ |

Table: Best fit $\beta$ for $d = 3$.

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Shi et al. compared their data for point islands to the GWS for $i = 1$ only and found better agreement with the GWS with $\beta = 4$ than the predicted value of $\beta = 2$ in $d = 2$.

However, they stated the GWS may be more applicable to realistic islands rather than point islands.

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If we follow the Blackman and Mulheran (B&M) approach in a one-dimensional **point-island** model in the case of $i = 1$ as a way to move beyond the mean-field approach then, as before,

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- monomers are initially deposited onto the $1D$ substrate with a rate $F$.
- These monomers then diffuse with a rate $D$.
- When one monomer joins together with another monomer, they form a stable island.
- Islands grow by capturing monomers that diffuse to their locations.
- Nucleation of new islands fragments the gaps between stable islands and its capture zone.

# Goal & diagram

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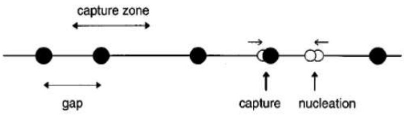
The following figure shows the graphical representation of the B&M model:




Summary of the features of the model. Solid circles represent an island; open circles are monomers. A capture zone is the separation of the bisectors of neighbouring gaps.

# Monomer density profile

In the B&M model, it is assumed that in the steady state, the monomer profile density, between islands at $x = 0$ and $x = y$ is

$$n_1(x) = \frac{1}{2R} x(y - x), \quad R = \frac{D}{F}.$$

Thus, the probability of a new nucleation at position $x$ is proportional to $n_1(x)^{i+1}$. ($n_1(x)^2$ if $i = 1$).

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Usually, a fragmentation process is modelled by an equation of the form

**Linear, continuous fragmentation equation**

$$\frac{\partial}{\partial t}u(x,t) = -a(x)u(x,t) + \int_x^\infty b(x|y)a(y)u(y,t)dy, \quad (4)$$

If we accept the B&M model along with its monomer density profile $n_1(x)$ and generalise this model for any $i \geq 0$, the evolution of gap sizes $u(x,t)$ during deposition is given by

## Gap evolution equation (GEE)

$$\frac{\partial}{\partial t}u(x,t) = -x^{2i+3}u(x,t) + \frac{\int_x^\infty x^{i+1}(y-x)^{i+1}u(y,t)}{B(i+3,i+2)}dy, \quad (5)$$

where $B(\cdot,\cdot)$ is the Beta function.

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The existence and stability of such similarity solutions is proved in Escobedo et al.

# Asymptotics of scaling solutions for the gap size distribution

Using the work of Cheng and Redner, we have

**Theorem (1)**

1. $\phi(x) \sim x^{i+1}$ *as* $x \longrightarrow 0$*;*
2. $\phi(x) \sim x^{-2} \exp(-cx^{2i+3})$ *as* $x \longrightarrow \infty$ *for some constant* $c$*.*

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We may use this information to understand the scaling function for the CZ distribution. If there is no correlation between the sizes of the two gaps the connection between gap size and CZ distributions is given by

$$P(s) = 2 \int_0^{2s} \phi(x)\phi(2s - x)dx.$$

# Asymptotics of scaling solutions for the capture zone distribution part I

Following Theorem 1 part 1, for small $s$ we have the following theorem

**Theorem (2)**

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The situation as $s \to \infty$ is more of a challenge, as it is not clear whether part 2 of Theorem 1 can be used directly.

## $s \longrightarrow \infty$

After some calculations, in the case of $i = 0$ only we derived an explicit form of Treat's $\phi(x)$ ('97, with setting Treat's notations $\eta \equiv x$, $\gamma = 1$, $k_1 = 6$ and $\omega = 3$)

$$\phi(x) = \frac{3x^2}{\mu^3 \Gamma(\frac{2}{3})} \int_{(x/\mu)^3}^{\infty} e^{-u} u^{-4/3} du, \tag{6}$$

where

$$\mu = \frac{4}{3} \Gamma\left(\frac{2}{3}\right).$$

# Asymptotics of the capture zone distribution part II

Using a modification of Laplace's method which involves computing a standard one-dimensional Laplace integral and then a two-dimensional one, we have CZ distribution for large $s$

**Theorem**

*If $i = 0$,*

$$P(s) \sim s^{-9/2} e^{-2s^3/\mu^3} \quad \text{as } s \to \infty.$$

# Asymptotics of the capture zone distribution part II

Using a modification of Laplace's method which involves computing a standard one-dimensional Laplace integral and then a two-dimensional one, we have CZ distribution for large $s$

**Theorem**

*If* $i = 0$,

$$P(s) \sim s^{-9/2} e^{-2s^3/\mu^3} \quad \textit{as } s \longrightarrow \infty.$$

Thus the GWS does not hold for $i = 0$ even asymptotically as $s \longrightarrow \infty$.

# Large asymptotics of GSD & CZD for $i = 1, d = 1$

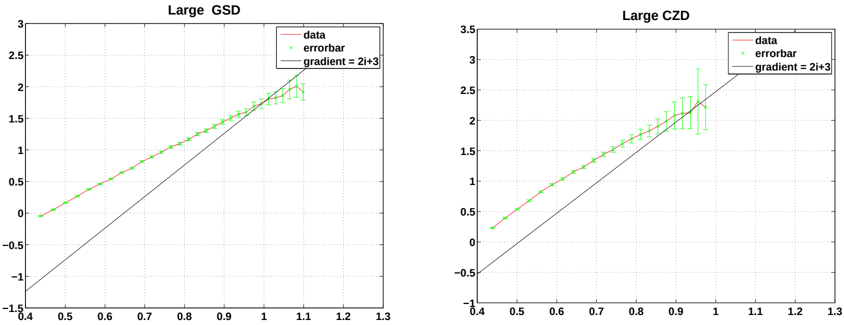


Figure: $\log(\log(GSD))$ & $\log(\log(CZD))$.

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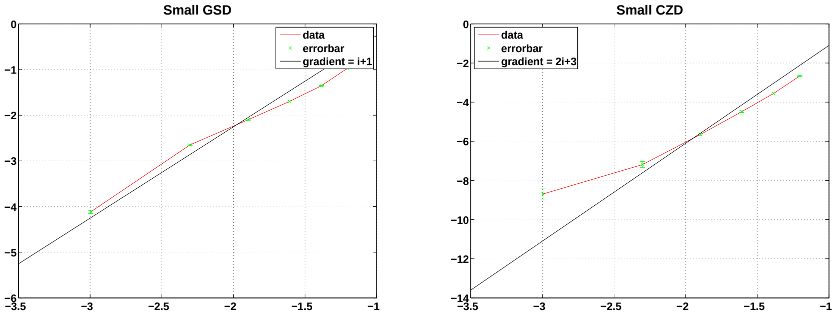


Figure: $\log(GSD)$ & $\log(CZD)$.

# Results for large asymptotics

In approximately 95% confidence interval,

| $i$ | Prediction | GSD | Prediction | CZD |
|---|---|---|---|---|
| 0 | 3 | $(2.2728, 2.3420)$ | 3 | $(2.9418, 3.0767)$ |
| 1 | 5 | $(2.9609, 3.0124)$ | - | $(3.6170, 3.7326)$ |
| 2 | 7 | $(4.1598, 4.3052)$ | - | $(4.3929, 4.6882)$ |
| 3 | 9 | $(4.7712, 5.0055))$ | - | $(4.6884, 5.2198)$ |

Table: Large $y$ and $s$ for GSD & CZD respectively.

# Results for small asymptotics

| $i$ | Prediction | GSD | Prediction | CZD |
|---|---|---|---|---|
| 0 | 1 | 1.0042 | 3 | 2.7084 |
| 1 | 2 | 1.8958 | 5 | 4.1574 |
| 2 | 3 | 2.8021 | 7 | 5.7334 |
| 3 | 4 | 2.8844 | 9 | 7.9404 |

Table: Small $y$ and $s$ for GSD & CZD respectively.

# Conclusions

We proved that the B&M model and the GWS cannot be simultaneously correct, even in the limits as $s \rightarrow 0$ and $s \rightarrow \infty$.

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So, a more accurate form of the fragmentation kernels seems to be called for.

Also, B&M's relation between GSD and CZD may not be correct either since this uses **mean-field** reasoning.

# Current/future works

The B&M model assumes that a nucleation event is rare in any gap size regardless of their size. After investigating the profile of each gap using MC data, it is found that the monomer density profile, $n_1(x)$, does not approach its saturated form for larger gaps.

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Thank you