Deposition, diffusion, and nucleation on an interval

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Joint work with
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Thin films and nanostructures

Ultra-thin films are of interest in physics, chemistry, and materials science.

Examples of applications include:

- lasers, optical detectors, nanoscale photonics;
- semiconductor nanostructures, quantum confined systems, nanoscale electronics;
- recording heads, nanoscale magnetic devices.

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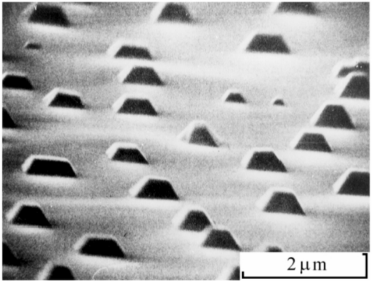
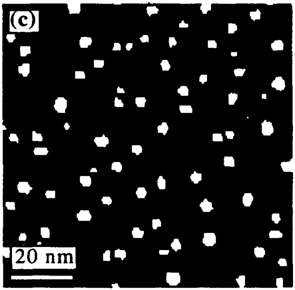
Thin films are often constructed via deposition of particles (adatoms) on a substrate, either using vapour or cathodic sputtering, and surface binding may be chemical (chemisorption) or physical (physisorption). Under certain conditions (Volmer–Weber dynamics), surface adatoms can diffuse until local binding conditions are such that nucleation occurs.

Thin films and nanostructures

At early stages of deposition, structures may look like:





'Islands' after deposition, seen under an electron microscope:
silver (left) and iron (right)
HARTIG *et al.* (1978); STROSCIO & PIERCE *et al.* (1994)

Mathematical modelling of deposition and nucleation is important for understanding and design of nanomaterials.

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Particles are deposited onto a substrate and undergo diffusion until sufficiently many particles come close together, when they nucleate to form a static island. Islands act as absorbing barriers for subsequent particles.

In the early stages, it is reasonable to ignore the spatial extent of islands. As time goes on, more islands form by nucleation, and islands grow by the accumulation of captured particles. Eventually, growing islands will coalesce into larger structures.

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Here we discuss a one-dimensional model for the early-stage dynamics, with binary nucleation and point islands.

Thin film growth dynamics

Formulating microscopic stochastic models for submonalyer deposition and growth processes goes back several decades in the applied literature, see especially:

- A. Michaels, G. Pound & F. Abraham (1974),
- M. Bartelt & J. Evans (1992),
- J. Blackman & P. Mulheran (1996).

Various approaches for analysis of these models, including Monte Carlo, as well as several different theoretical approaches, e.g.

- M. Grinfeld, W. Lamb, K. O'Neill & P. Mulheran (2012),
- J. Blackman, M. Grinfeld & P. Mulheran (2015),

but no previous work in the probability literature, as far as we are aware.

Acknowledgement
We learned about these interesting processes from Michael Grinfeld and Paul Mulheran.

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Diffusion and nucleation. Each active particle performs independent Brownian motion until either (i) it is captured by an existing island, or (ii) it meets another active particle, in which case the two colliding particles nucleate to create a new island. In either case, the particle is no longer active.

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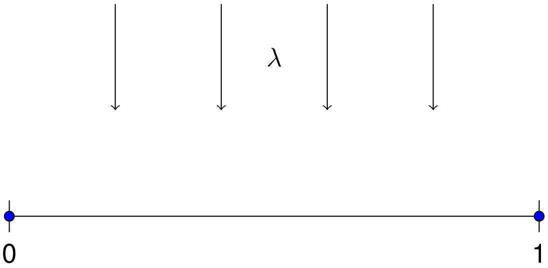

Initially: Islands at 0 and 1, no active particles.

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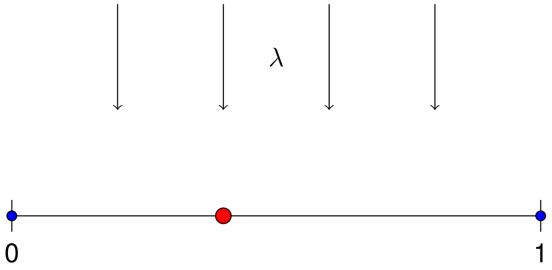

After an Exp(λ) random time, first active particle arrives at a uniform random location.

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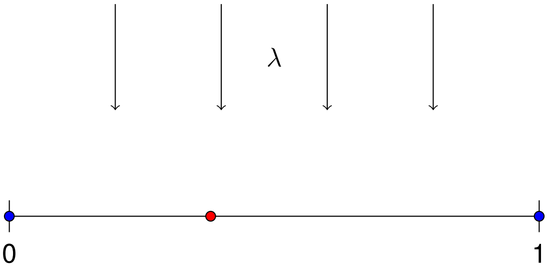

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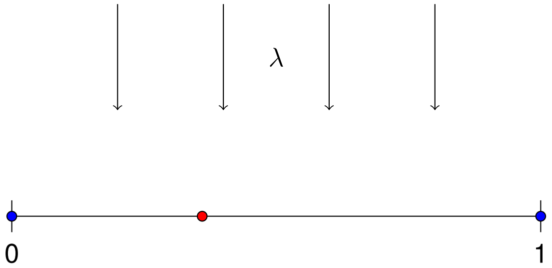

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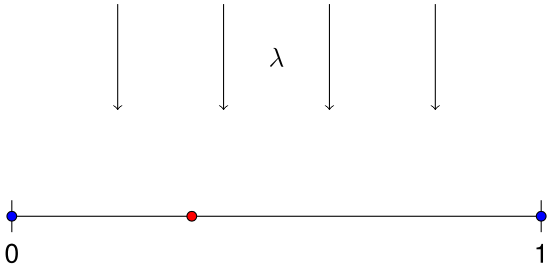

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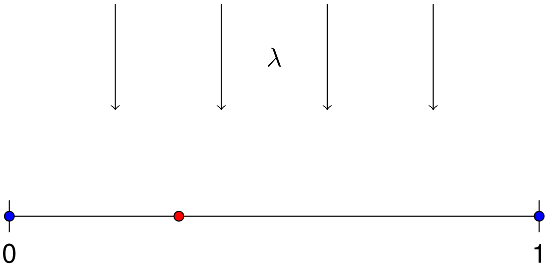

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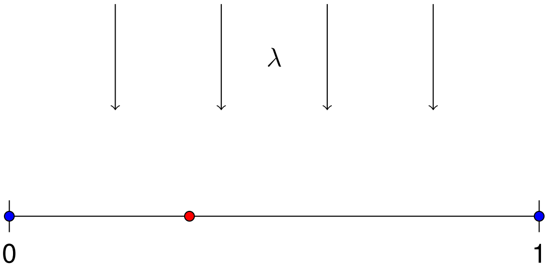

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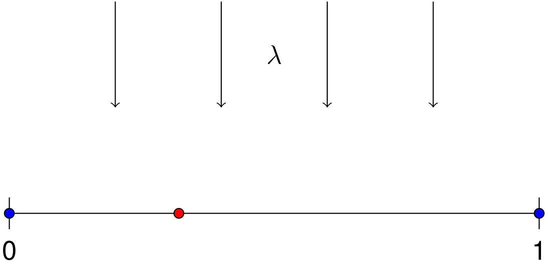

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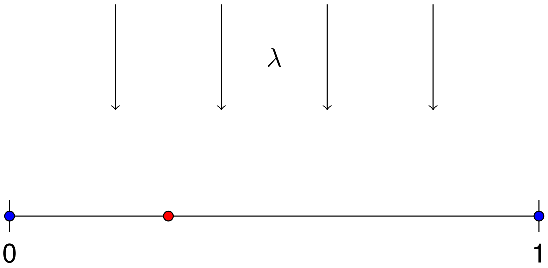

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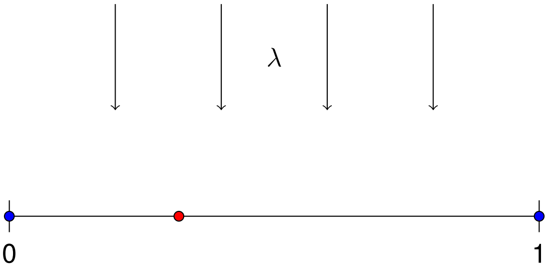

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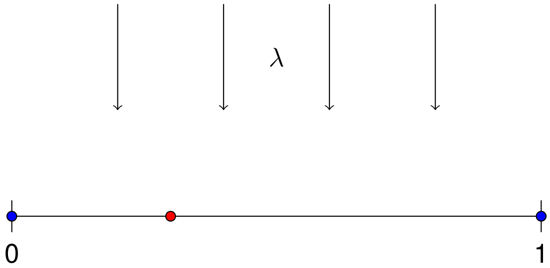

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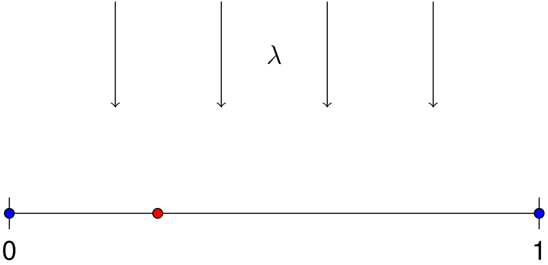

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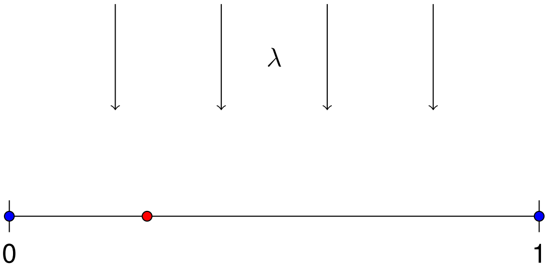

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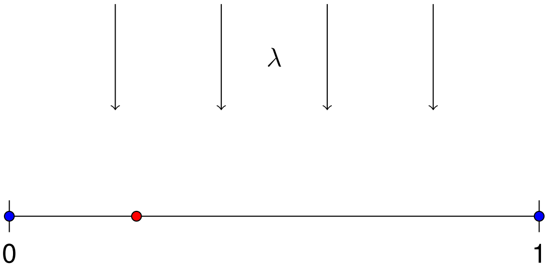

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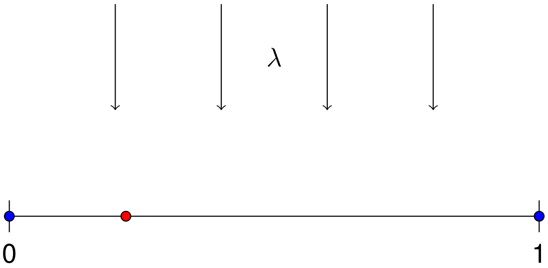

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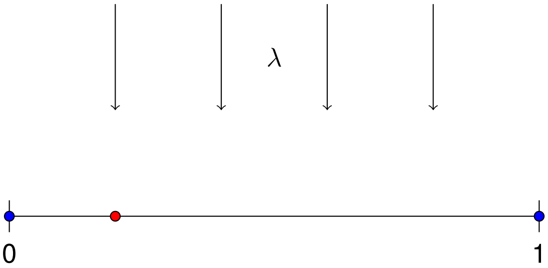

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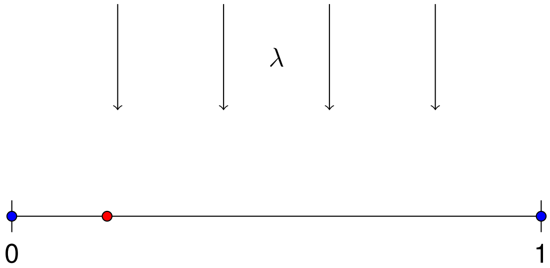

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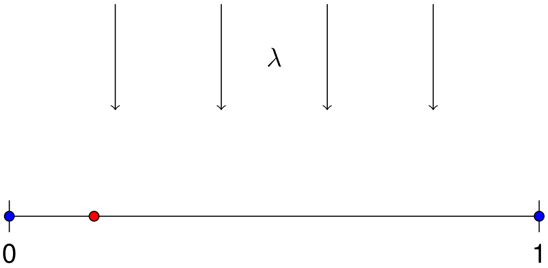

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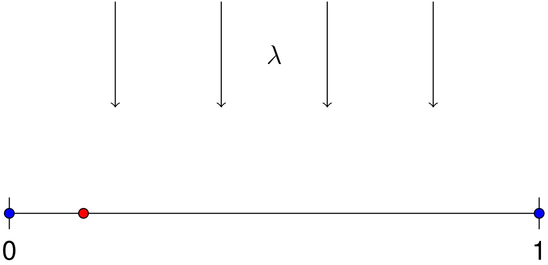

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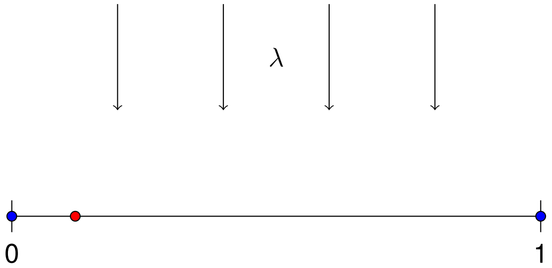

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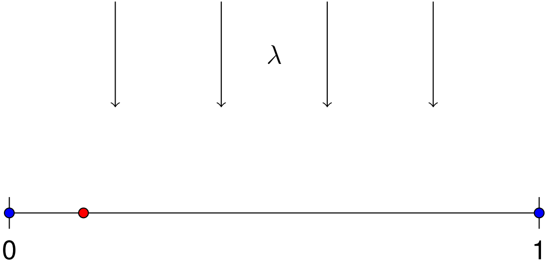

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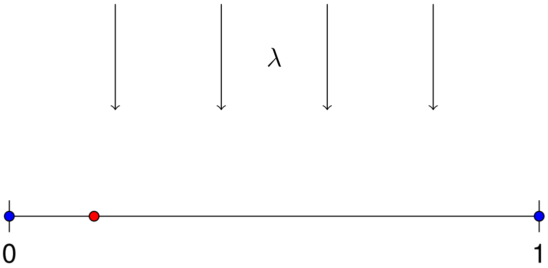

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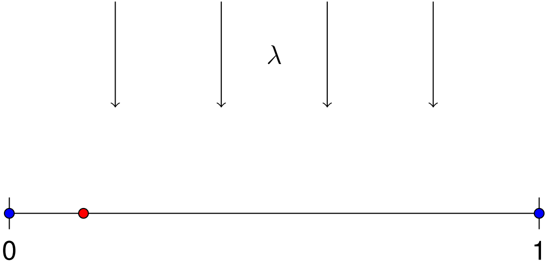

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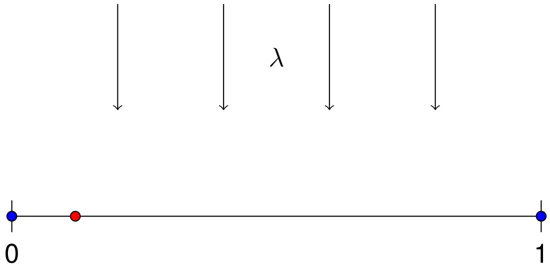

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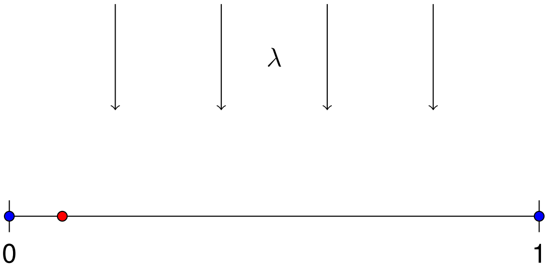

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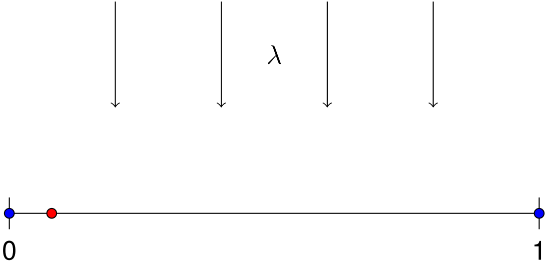

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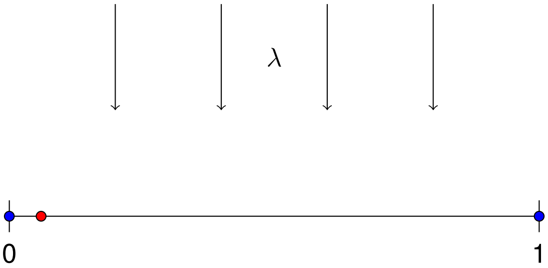

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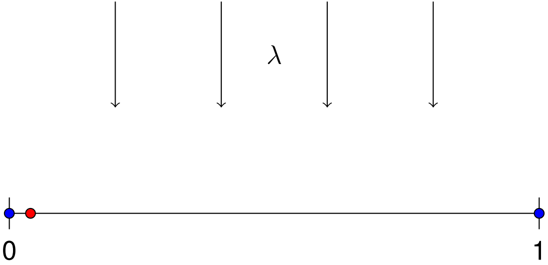

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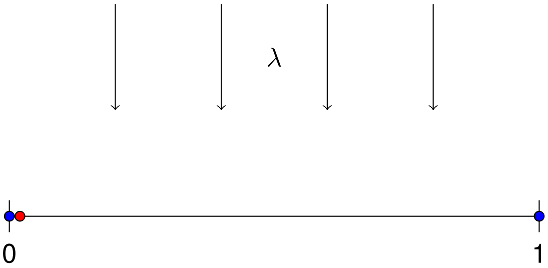

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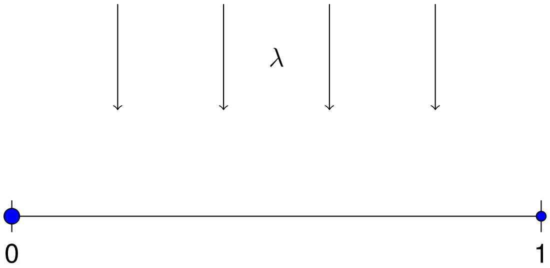

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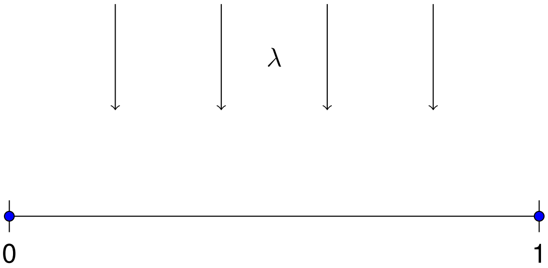

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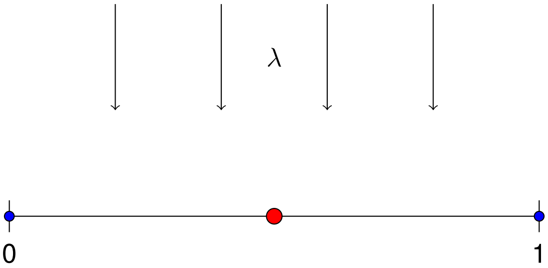

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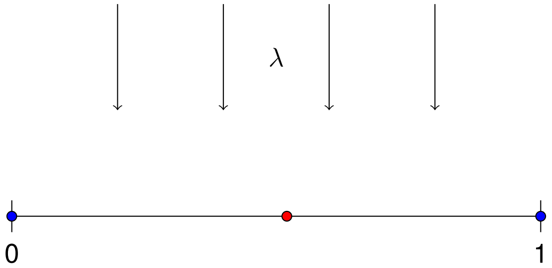

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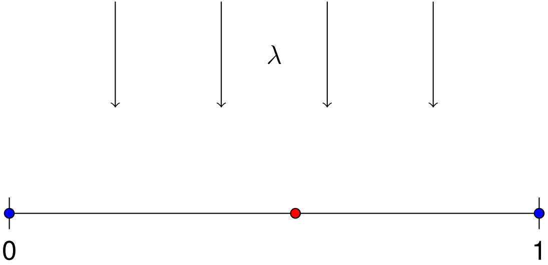

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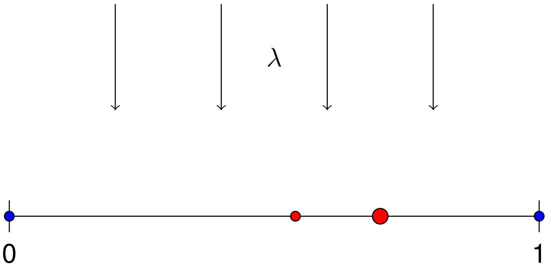

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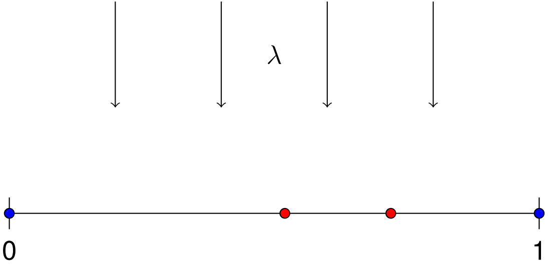

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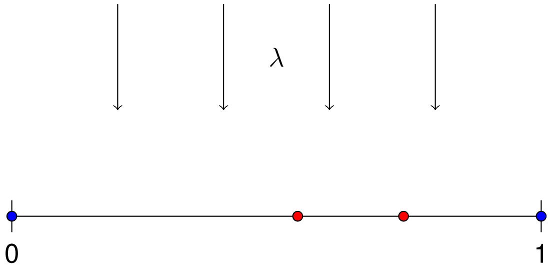

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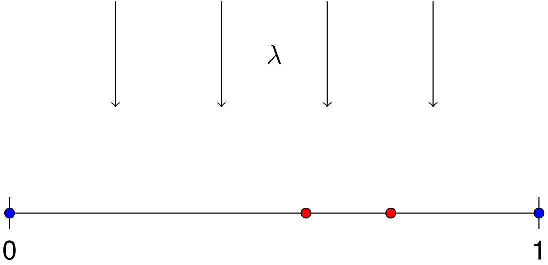

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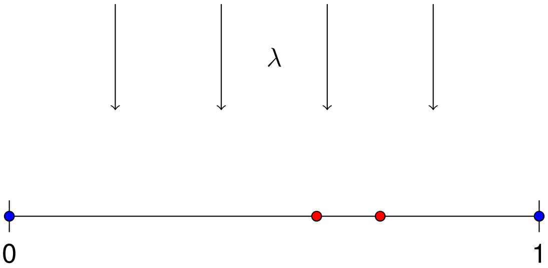

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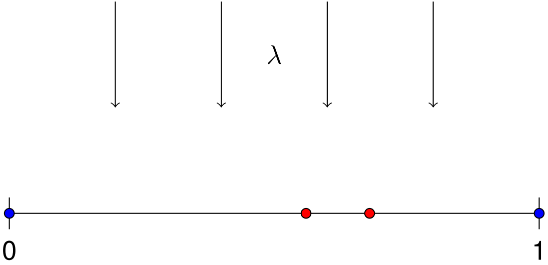

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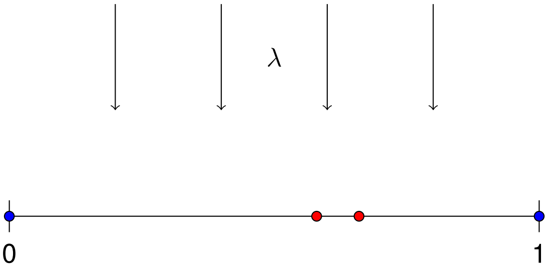

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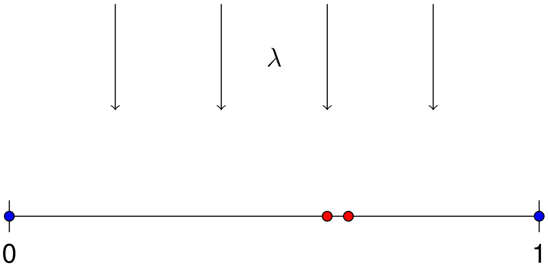

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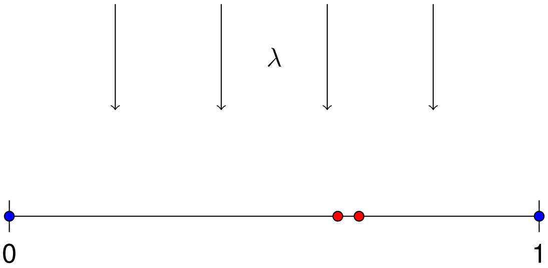

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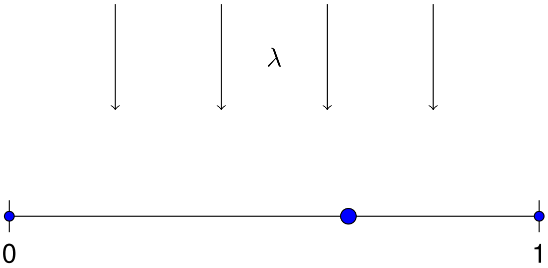

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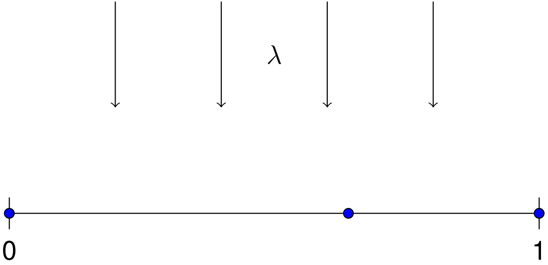

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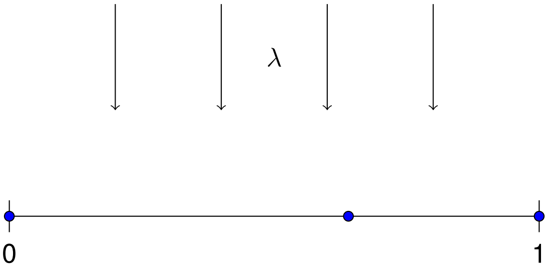

Question: How does the partition of the interval evolve?

This is a continuum analogue of a model considered in the applied literature by BARTELT & EVANS (1992) and BLACKMAN & MULHERAN (1996).

Overview of results

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2 Fixed λ. For fixed λ but large times ($t \to \infty$) the gap statistics are governed by the $\lambda \to 0$ limit process from 1.

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Let ν_n denote the time of the nth nucleation. Let $\mathcal{Z}_n$ denote the vector of island locations, listed left to right, at time ν_n.

Note that $\mathcal{Z}_n$ is not Markov, because there may still be active particles in the system at time ν_n that are not described by $\mathcal{Z}_n$.

We have two main results:

1. Sparse deposition. In the $\lambda \to 0$ limit, the process $\mathcal{Z}_n$ converges to a certain Markovian interval-splitting process.

   Why asymptotically Markov? When $\lambda \to 0$, most of the time there are very few active particles in the system.

2. Fixed λ. For fixed λ but large times ($t \to \infty$) the gap statistics are governed by the $\lambda \to 0$ limit process from 1.

   Why? For large times, there are many islands and so gaps are small. This increases the relative rate of capture by existing islands, and has a similar effect as driving $\lambda \to 0$.

Outline

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Interval-splitting process

Two parameters:
splitting exponent α and splitting distribution Φ on $[0, 1]$.

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- Choose randomly one of the current intervals, with an interval of length ℓ chosen with probability proportional to ℓ^α.

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At each step:

- Choose randomly one of the current intervals, with an interval of length ℓ chosen with probability proportional to ℓ^{α}.
- Split the chosen interval into two new intervals by inserting a point at a relative location drawn from distribution Φ.

Interval-splitting process

Two parameters:
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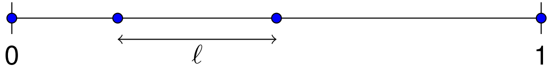

A configuration of intervals.

Interval-splitting process

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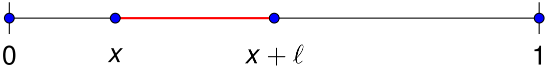

Select the next interval to split
with probability proportional to ℓ^{α} ($\ell =$ length).

Interval-splitting process

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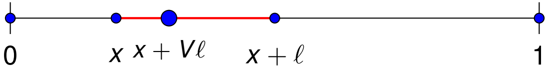

Choose the point to split at relative location $V \sim \Phi$
in the chosen interval.

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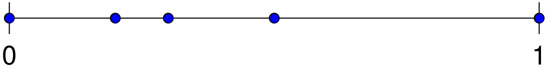

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Models of this type were studied by BRENNAN & DURRETT (1986–7).

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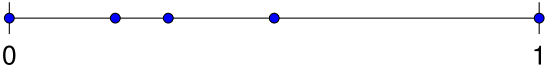

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Models of this type were studied by BRENNAN & DURRETT (1986–7).
The case where Φ is uniform is uniform splitting, which if $\alpha = 1$ gives a Dirichlet process and $\alpha \to \infty$ gives the Kakutani process.

Interval-splitting process

Two parameters:
splitting exponent α and splitting distribution Φ on $[0, 1]$.

The process that's going to be relevant for our nucleation process has $\alpha = 4$ and $\Phi = \Phi_0$ where

$$\Phi_0(B) = \frac{1}{\mu}\int_B \psi(z)\mathrm{d}z,$$

with

$$\psi(z) := \frac{24}{\pi^4}\sum_{n \text{ odd}}\left(\frac{4}{n^4}\tanh\left(\frac{n\pi}{2}\right) - \frac{\pi}{n^3}\right)\sin(n\pi z),$$

and

$$\mu := \int_0^1 \psi(z)\mathrm{d}z = \frac{48}{\pi^5}\sum_{n \text{ odd}}\frac{\operatorname{sech}^2(\frac{n\pi}{2})}{n^4} \approx 0.07826895.$$

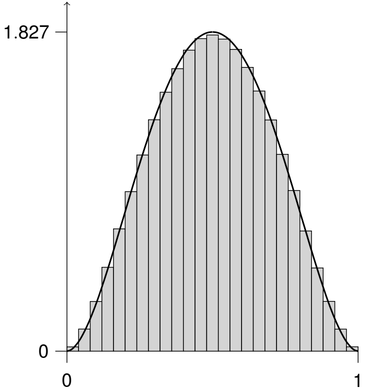
Result: Sparse deposition

Recall that $\mathcal{Z}_n$ is the vector of island locations, listed left to right, at the time ν_n of the n nucleation.

Theorem

As $\lambda \to 0$, the process $\mathcal{Z}_n$ converges, in the sense of total-variation convergence of finite-dimensional distributions, to an interval-splitting process with parameters $\alpha = 4$ and $\Phi = \Phi_0$.

Result: Sparse deposition



Plot of Φ_0 with simulation

Remarks: It turns out that ψ is twice continuously differentiable, and $\psi(z) \sim 3z^2$ as $z \to 0$.

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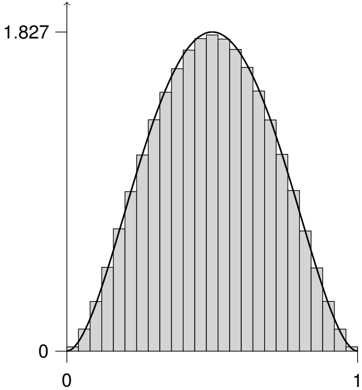

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The Fourier series for ψ converges slowly; a different representation related to the Clausen function yields better numerical approximation.

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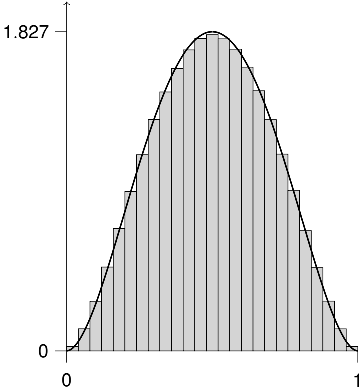

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Earlier work argued for a Beta$(3, 3)$ splitting distribution.

Result: Fixed deposition

Heuristic: For fixed λ, consider large time. Then gaps are small, which is, effectively, the same as sending $\lambda \to 0$. Smaller gaps $=$ faster capture by existing islands $=$ lower density of active particles. (A precise version of this statement is given via a scaling relation later on.)

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One can make a formal coupling statement. Roughly, for any $\varepsilon > 0$ we can find n_0 sufficiently large so that one can successfully couple, with probability at least $1 - \varepsilon$, the fixed-λ process run from $n \geq n_0$ with the Φ_0 Markovian interval-splitting process, started from the same initial configuration.

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One implication of this result is that certain long-time statistics of the fixed-λ process can be described purely via the Φ_0 Markovian interval-splitting process.

Result: Fixed deposition

Let $(L_{n,1}, \dots, L_{n,n+1})$ be the gap lengths at the time ν_n of the nth nucleation. For U_n uniform on $\{1, 2, \dots, n+1\}$, set

$$\tilde{L}_n = \frac{L_{n,U_n}}{\mathbb{E}\, L_{n,U_n}} = (n+1)L_{n,U_n},$$

the length of a randomly-chosen gap, normalized to mean 1.

Theorem

Let $\lambda > 0$. There exists a continuous density g_0 on $\mathbb{R}_+$ such that

$$\lim_{n\to\infty} \mathbb{P}\,(\tilde{L}_n \le x) = \int_0^x g_0(y)dy, \quad x \in \mathbb{R}_+.$$

Moreover, for constants $c_0, c_\infty, \theta \in (0, \infty)$,

$$g_0(x) \sim c_0 x^2 \;\; (x \to 0), \quad g_0(x) \sim \frac{c_\infty}{x^2} \exp(-\theta x^4) \;\; (x \to \infty).$$

Outline

Sparse deposition: proof outline

Key idea: regeneration.

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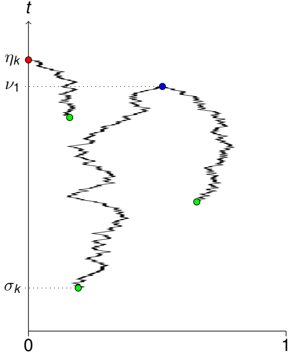
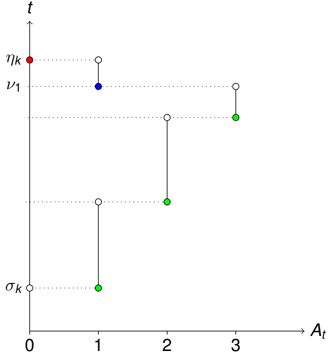
$$\sigma_k := \inf\{t > \eta_{k-1} : A_t = 1\}, \quad \eta_k := \inf\{t > \sigma_k : A_t = 0\}.$$





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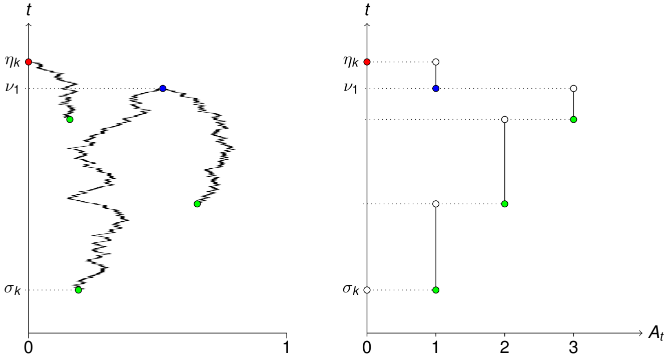

Call time interval $[\sigma_k, \eta_k]$ the kth cycle.

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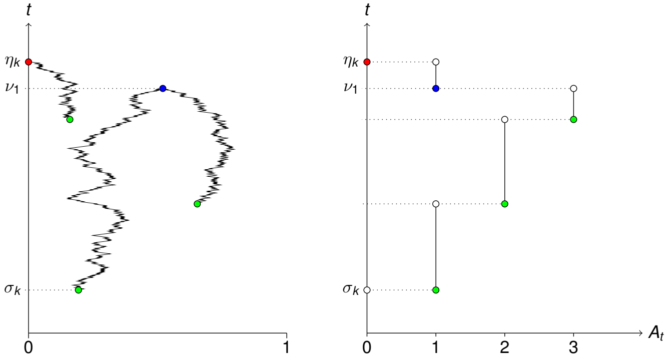

Call time interval $[\sigma_k, \eta_k]$ the kth cycle.

Up until the first nucleation, cycles are i.i.d.

Sparse deposition: proof outline

Generalize the model to an interval $[0, \ell]$. For $B \subseteq [0, 1]$, let

$$\nu(\ell, \lambda; B) = \mathbb{P}\left(\begin{array}{c} \text{nucleation occurs on first cycle} \\ \text{and at a point in set } \ell B \end{array} \right).$$

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- Scaling: $\nu(\ell, \lambda; B) = \nu(1, \ell^3\lambda; B)$.

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- Single-interval asymptotics:

$$\nu(1, \lambda; B) \sim \lambda\mu\Phi_0(B), \text{ as } \lambda \to 0.$$

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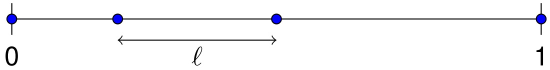
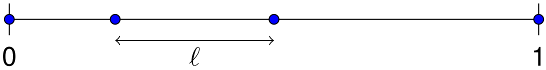
These two combine to give the many-interval asymptotics.

Consider a configuration like this, with some islands (blue) but no active particles.



Sparse deposition: proof outline

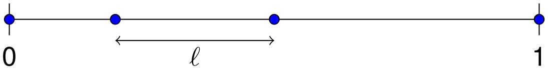


Probability of nucleation occurring in the indicated interval during the first cycle at relative location in *B* is

$$\ell \cdot \nu(\ell, \lambda; B) + \text{error term},$$

where the main term comes from the first arrival being in the desired interval, and the error term from nucleation occurring in an interval other than that containing the first arrival.

Sparse deposition: proof outline



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By scaling and single-interval asymptotics, this is about

$$\ell \cdot \nu(1, \ell^3\lambda; B) \sim \ell^4 \lambda \mu \Phi_0(B), \text{ as } \lambda \to 0.$$

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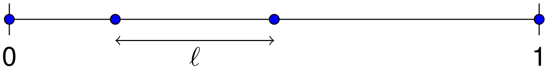

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Regeneration implies that the probability of the next nucleation occurring here is proportional to the first-cycle probability.

Scaling

Recall that for the model started from empty interval $[0, \ell]$,

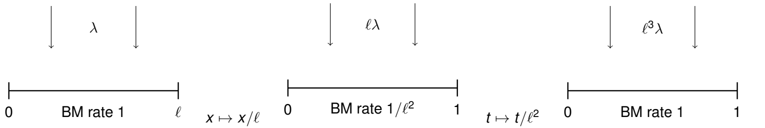
$$\nu(\ell, \lambda; B) = \mathbb{P}\left(\begin{array}{c} \text{nucleation occurs on first cycle} \\ \text{and at a point in set } \ell B \end{array} \right).$$

Lemma

We have $\nu(\ell, \lambda; B) = \nu(1, \ell^3\lambda; B)$.

Proof.

Follows from the scaling/mapping properties of the Poisson process and Brownian motion.



$\square$

Single-interval asymptotics

On interval $[0,1]$,

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Lemma

$$\nu(1,\lambda;B) \sim \lambda\mu\Phi_0(B),\ \textit{as}\ \lambda \to 0.$$

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Lemma

$$\nu(1, \lambda; B) \sim \lambda\mu\Phi_0(B), \ \textit{as}\ \lambda \to 0.$$

Proof.

Claim that the following mechanism has probability of order λ:

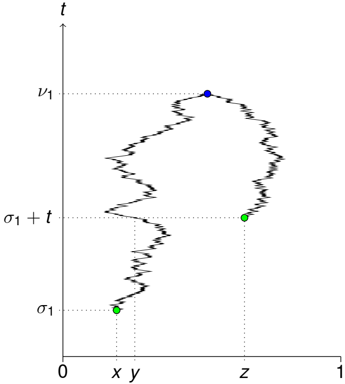
- The first particle arrives at a uniform random location x.
- The second particle arrives at an exponential random time t at a uniform random location z.
- The first particle has not been captured by time t, and at time t is at location y.
- The two particles started from y and z collide in B before either hits the boundary.

Single-interval asymptotics

Proof (cont.)

The following mechanism has probability of order λ:

- first particle arrives at x;
- second particle arrives time t later at location z;
- first particle survives and at time t is at location y;
- particles started from y and z collide in B before capture.



Single-interval asymptotics

Proof (cont.)

For b_t BM on $[0,1]$ set

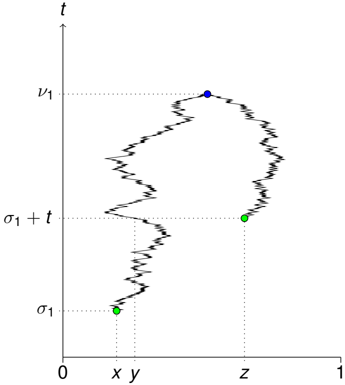
$$\tau = \inf\{t \in \mathbb{R}_+ : b_t \in \{0,1\}\},$$

and for $x, y \in [0,1]$ and $t \in \mathbb{R}_+$ the defective density $q_t(x,y) =$

$$\frac{\mathbb{P}_x(\tau > t, b_t \in [y, y + \mathrm{d}y])}{\mathrm{d}y}.$$

For $y, z \in [0,1]$ set $H(y,z;B) =$

$$\mathbb{P}\left(\begin{array}{c}\text{BMs started at } y, z \text{ meet} \\ \text{in } B \text{ before either hits } \{0,1\}\end{array}\right).$$



Then, the probability of nucleation happening as described is

$$\int_0^1 \mathrm{d}x \int_0^1 \mathrm{d}z \int_0^\infty \mathrm{d}t \int_0^1 \lambda e^{-\lambda t} q_t(x,y) H(y,z;B) \mathrm{d}y.$$

Single-interval asymptotics

Proof (cont.)

The probability of nucleation happening as described is

$$\begin{aligned}
&\int_0^1 \mathrm{d}x \int_0^1 \mathrm{d}z \int_0^\infty \mathrm{d}t \int_0^1 \lambda e^{-\lambda t} q_t(x,y) H(y,z;B)\mathrm{d}y \\
&\sim \lambda \int_0^1 \mathrm{d}x \int_0^1 \mathrm{d}z \int_0^\infty \mathrm{d}t \int_0^1 q_t(x,y) H(y,z;B)\mathrm{d}y \\
&=: \lambda \Phi_1(B).
\end{aligned}$$

All other mechanisms require two arrivals after the first, giving $o(\lambda)$ contributions.

Final step: must show $\Phi_1(B) = \mu \Phi_0(B)$. $\square$

Outline

Exit from a triangle

Recall we want to compute

$$\Phi_1(B) = \int_0^1 \mathrm{d}x \int_0^1 \mathrm{d}z \int_0^\infty \mathrm{d}t \int_0^1 q_t(x, y) H(y, z; B) \mathrm{d}y,$$

where (e.g. BORODIN & SALMINEN, 2002)

$$q_t(x, y) = 2 \sum_{m \in \mathbb{N}} \exp\left(-\frac{m^2 \pi^2 t}{2}\right) \sin(m\pi x) \sin(m\pi y),$$

and

$$\begin{aligned} &H(y, z; B) \\ = &\ \mathbb{P}(\text{BMs started at } y, z \text{ meet in } B \text{ before either hits } \{0, 1\}) \\ = &\ \mathbb{P}(\text{Planar BM exits right-angle triangle via diagonal in } B \times B). \end{aligned}$$

Exit from a triangle

$$
\begin{aligned}
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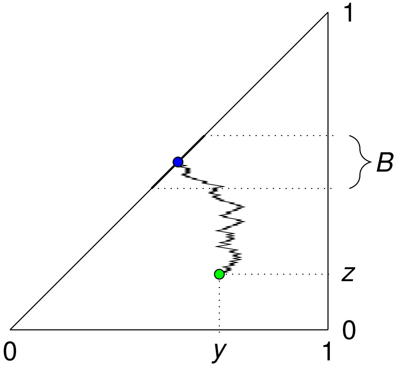

Exit from a triangle

Theorem

WLOG suppose $u > v$. Then

$$H(u, v; B) = \int_B h\left(\frac{u+v}{2}, \frac{u-v}{2}, w\right) dw,$$

where

$$h(x, y, z) = \sum_{n \in \mathbb{N}} \frac{2\sin(n\pi(1-z))}{\sinh n\pi} \big(s_n(x, y) + s_n(1-x, 1-y) - s_n(y, x) - s_n(1-y, 1-x)\big),$$

and $s_n(x, y) = \sin(n\pi x)\sinh(n\pi y)$.

Extends Smith & Watson (1967).

Proof.

Method of images for the Dirichlet problem. $\square$

Sparse deposition: proof conclusion

We have

$$\Phi_1(B) = \int_0^1 \mathrm{d}x \int_0^1 \mathrm{d}z \int_0^\infty \mathrm{d}t \int_0^1 q_t(x, y) H(y, z; B) \mathrm{d}y,$$

where we know the explicit infinite-series formulae for $q_t(x, y)$ and $H(y, z; B)$.

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where we know the explicit infinite-series formulae for $q_t(x,y)$ and $H(y,z;B)$.

After some work...we get $\Phi_1(B) = \mu\Phi_0(B)$, where, as claimed earlier,

$$\Phi_0(B) = \frac{1}{\mu}\int_B \psi(z)\mathrm{d}z,$$

with ψ the defective density

$$\psi(z) := \frac{24}{\pi^4}\sum_{n \text{ odd}} \left(\frac{4}{n^4}\tanh\left(\frac{n\pi}{2}\right) - \frac{\pi}{n^3}\right)\sin(n\pi z)$$

having total mass μ.

Outline

Fixed deposition: proof comments

We've presented the outline of the proof as $\lambda \to 0$.

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For fixed λ, note that for large times, gaps are small.

The scaling relation shows that small gaps has the same effect as small λ.

Idea: For large times, the fixed-λ process should be well-approximated by the $\lambda \to 0$ interval-splitting process. So large-time statistics of the nucleation process should be described by the large-time statistics of the interval-splitting process.

Fixed deposition: proof comments

We've presented the outline of the proof as $\lambda \to 0$.

For fixed λ, note that for large times, gaps are small.

The scaling relation shows that small gaps has the same effect as small λ.

Idea: For large times, the fixed-λ process should be well-approximated by the $\lambda \to 0$ interval-splitting process. So large-time statistics of the nucleation process should be described by the large-time statistics of the interval-splitting process.

To follow through this idea needs (i) more work on the preceding estimates, to get more quantitative bounds; and (ii) extension of work of BRENNAN & DURRETT on interval-splitting processes to get good asymptotics for the limiting normalized gap distribution.

Fixed deposition: proof comments

One element in the proof is to extend work of BRENNAN & DURRETT on limiting gap statistics for interval-splitting processes.

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Consider a general interval-splitting process with splitting exponent $\alpha > 0$ and splitting distribution Φ with a symmetric density ϕ on $[0, 1]$ satisfying $\phi(x) \sim bx^{\beta}$ as $x \to 0$, for $\beta \geq 0$.

BRENNAN & DURRETT obtained a characterization of the limiting distribution of a randomly selected gap via a distributional fixed-point equation. Building on this analysis, we obtain asymptotics for the limiting gap distribution.

Fixed deposition: proof comments

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Theorem

The distribution of a randomly selected gap, normalized to have unit mean, in the interval-splitting process converges to a distribution on $\mathbb{R}_+$ with density g.

There exist $c_0, c_\infty, \theta > 0$ such that $g(x) \sim c_0 x^{\beta}$, $(x \to 0)$, and, as $x \to \infty$,

$$g(x) \sim \begin{cases} c_\infty x^{2b-2} \exp(-\theta x^{\alpha}) & \text{if } \beta = 0; \\ c_\infty x^{-2} \exp(-\theta x^{\alpha}) & \text{if } \beta > 0. \end{cases}$$

For the interval-splitting processes associated with our nucleation process, $\alpha = 4$ and $\beta = 2$.

Outline

A few remarks on the splitting density

A key character in our results is $\Phi_0(B) = \frac{1}{\mu}\int_B \psi(z)\mathrm{d}z$, where

$$\psi(z) := \frac{24}{\pi^4}\sum_{n \text{ odd}}\left(\frac{4}{n^4}\tanh\left(\frac{n\pi}{2}\right) - \frac{\pi}{n^3}\right)\sin(n\pi z);$$

$$\mu := \int_0^1 \psi(z)\mathrm{d}z = \frac{48}{\pi^5}\sum_{n \text{ odd}}\frac{\operatorname{sech}^2(\frac{n\pi}{2})}{n^4} \approx 0.07826895.$$

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The second equality here is a consequence of the identity

$$4\sum_{n \text{ odd}}\frac{\tanh(n\pi/2)}{n^5} = \frac{\pi^5}{96} + \pi\sum_{n \text{ odd}}\frac{\mathrm{sech}^2(n\pi/2)}{n^4}.$$

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The first few moments of Φ_0 are $m_1 = 1/2$, $m_2 = \frac{1}{2} - \frac{1}{60\mu}$,

$$m_3 = \frac{1}{2} - \frac{1}{40\mu}, \text{ and } m_4 = \frac{1}{2} - \frac{11}{280\mu} + \frac{576}{\mu\pi^8}\sum_{n \text{ odd}}\frac{\operatorname{sech}^2(n\pi/2)}{n^8}.$$

A few remarks on the splitting density

An alternative series representation for ψ, better for numerical calculation, is

$$\psi(x) = \frac{84}{\pi^3} x\zeta(3) + \frac{8}{\pi} x^3 \log(\pi x) - \frac{8}{\pi}\left(\frac{11}{6} + \log 2\right) x^3 - 3x(1-x)$$
$$+ 48\pi x^5 \sum_{n=0}^{\infty} \frac{|B(2n+2)|\left(2^{2n+1}-1\right)}{(n+1)(2n+5)!} \pi^{2n} x^{2n}$$
$$- \frac{96}{\pi^4} \sum_{n \text{ odd}} \frac{d_n}{n^4} \sin n\pi x, \quad (0 \le x < 1),$$

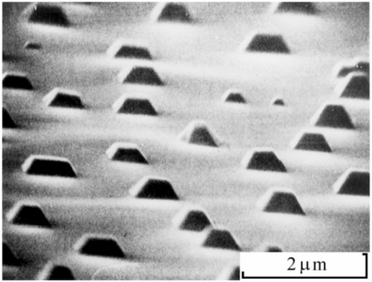
where $d_n = 1 - \tanh \frac{n\pi}{2}$ has $0 < d_n < 2e^{-n\pi}$, and $B(2\ell)$ are the Bernoulli numbers.

This comes from classical series expansions for the Clausen function and its relatives, such as

$$\sum_{n\in\mathbb{N}} \frac{\sin nx}{n^k}, \text{ and } \sum_{n\in\mathbb{N}} \frac{\cos nx}{n^k}.$$

Outline

Further challenges



- Nucleation threshold $3, 4, \ldots ?$

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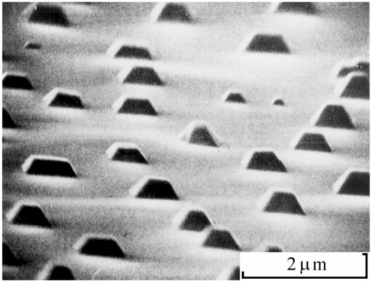

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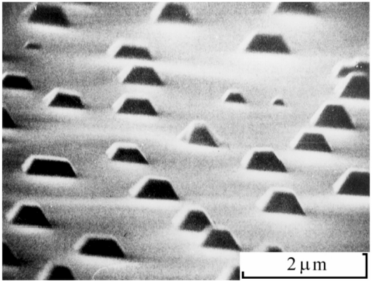

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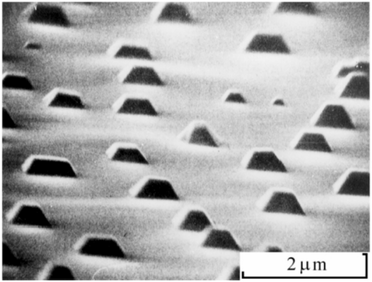

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Thank you!

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