# Submonolayer Island Nucleation and Growth for Subdiffusive Random Walkers
# The University of Toledo Physics REU 2015
# Final Report

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The breadth and variety of applications for thin film deposition, among them solar cell manufacturing and microprocessor fabrication, make the theoretical and computational study of surface growth important. While classical nucleation theory has long modeled these types of systems, it applies only to normally diffusing particles on the surface. Here, we employ kinetic Monte Carlo simulation to investigate submonolayer nucleation and growth for subdiffusive random walkers, and find that the classical theory does not hold.

## I. INTRODUCTION

Nucleation and growth drives many physical processes, both natural (as in crystallization) and human-made (as in deposition of all kinds – sputtering, atomic layer, vapor, etc.). Because of this, much effort has focused on studying the process.

Suppose we deposit some material on a two-dimensional (2D) surface. The individual constituents (particles) will undergo random walks, diffusing around the surface, until (due to whichever molecular or atomic forces dominate the process) they begin to stick together and no longer move. This is called nucleation, and the new structure is called a stable island; we let $i+1$ be the number of particles needed to form a stable island, and call $i$ the critical island size. Figure 1 shows an illustration of this on a one-dimensional (1D) surface.

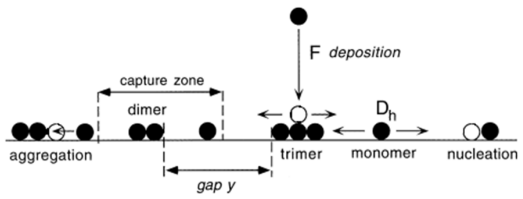


FIG. 1. Illustration of Nucleation and Growth

As in Figure 1, these stable islands aggregate, or grow, as more monomers (single particles – they could also be dimers, trimers, etc. depending on $i$) attach to the edges.

### A. Classical Nucleation Theory

Classically, nucleation is modeled by the set of rate equations in (1),

$$\frac{dN_1}{dt} = F\gamma - 2FN_1 - 2D\sigma_1 N_1^2 - DN_1 \sum_{s\geq 2} \sigma_s N_s$$
$$\frac{dN_s}{dt} = RD\left(\sigma_{s-1}N_{s-1} - \sigma_s N_s\right) + Fk_{s-1}N_{s-1} - Fk_s N_s \tag{1}$$

where $t$ is time, $F$ is the deposition rate per site on the substrate, $D$ is the diffusion rate per monomer, $N_1$ is the monomer density, $N_s$ is the density of islands of size $s$ (containing $s$ particles), $\sigma_1$ is the monomer capture number, $\sigma_s$ is the capture number for islands of size $s$, $\gamma$ is the fraction of the substrate not covered, and $k_s$ is the direct impingement term (not important at low coverage).

There are a number of important variables in characterizing nucleation and growth. In this report, the most important of these is the peak island density $N_{\text{peak}}$, which scales as

$$N_{\text{peak}} \sim \left(\frac{D}{F}\right)^{-\chi}, \tag{2}$$

with $\chi$ unknown. Classically, for normal diffusion on a 2D substrate, the theory gives

$$\chi = \frac{i}{i+2}. \tag{3}$$

### B. Super- and Sub-Diffusion

Diffusion is a phenomenon characterized by many individual particles each undergoing random walks: in normal diffusion, for each unit of time, the particle takes a

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unit step in a random direction; the mean squared displacement from the starting position $\langle R^2 \rangle \sim t$.

However, there are at least two other types of diffusion: superdiffusion and subdiffusion. For a superdiffusive particle, instead of each step being unit length, the step size $\xi$ follows a power-law distribution. Naturally, this gives rise to larger mean squared displacement, and it turns out that $\langle R^2 \rangle \sim t^\beta$ with $\beta > 1$.

For subdiffusion, the particle takes a unit-length step but waits a time $\tau$ – where $\tau$ follows a power law distribution – before taking its next step. Thus, the process gets "slowed down," and $\langle R^2 \rangle \sim t^\beta$ with $\beta < 1$.

Thus, generally, one can characterize the type of diffusion by the mean squared displacement as in (4).

$$\langle R^2 \rangle \sim t^\beta \begin{cases} \beta > 1 & \text{superdiffusion} \\ \beta = 1 & \text{normal diffusion} \\ \beta < 1 & \text{subdiffusion} \end{cases} \tag{4}$$

### C. Research Question

Previous work by J. Amar and others has investigated systems where the constituent particles were either normally diffusive or superdiffusive. In contrast, subdiffusive random walkers have not previously been studied in terms of nucleation and growth. Thus, for this project, we ask:

**What is the form of $\chi$ for subdiffusive walkers? Does it differ from the classical theory's prediction ($\chi \approx 0.35$ for normal diffusion and irreversible island growth with $i = 1$)? Does it depend on $\beta$?**

## II. SIMULATION

To tackle this question, we employ kinetic Monte Carlo (KMC) simulation, which has previously served to verify and or/check the analytical theory. KMC works by knowing the *rates* of all possible events – in this case, diffusion $D$ or deposition $F$ (either a monomer moves, or a new one is deposited) – and then at each "step" deciding which event to carry out. This is illustrated in Figure 2.

To make the decision process, we first define a "total rate" $R_{\text{total}} = DN_1 + Fn_{\text{o}} =$ diffusion rate + deposition rate (where $n_{\text{o}}$ is the total number of open sites), and then pick a random number between 0 and $R_{\text{total}}$. If the number falls below $Fn_{\text{o}}$, we diffuse; else, we deposit. This ensures that the likelihood of a deposition (or diffusion) is proportional to its rate compared with the total rate.

For this project, we model on a 2D substrate with $i = 1$ (only monomers are mobile) and irreversible island growth.

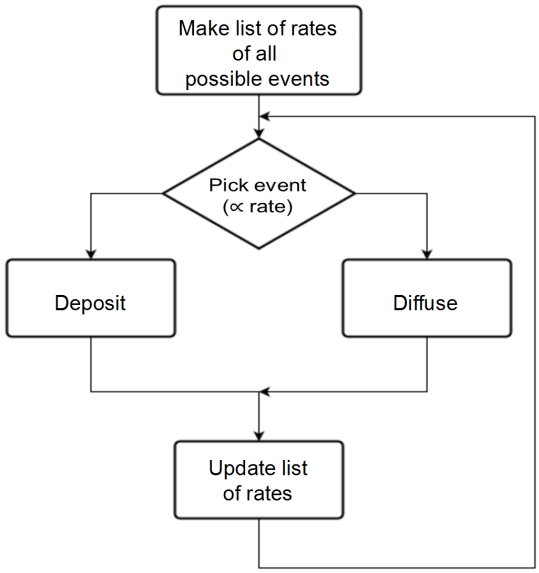


FIG. 2. Kinetic Monte Carlo Outline

### A. Time-Based KMC

The introduction of subdiffusion requires changing this process: the rate is harder to define when the particle waits a random time between each diffusive step. Since Rate $\equiv$ time$^{-1}$, we first redefine Figure 2 to replace "rates" with "waiting times." The deposition "time" $\tau_{\text{dep}} = -\log X/$ (deposition rate), where $X$ is a uniformly distributed random variable between 0 and 1. After every deposition, we assign the new monomer a waiting time $\tau$. For every monomer diffusion, we update that monomer with a new $\tau$. Then, we run through the list of $\tau$ values and carry out the event with the shortest waiting time.

Actually generating $\tau$ in the computer starts with its power law probability density function (PDF), given by (5).

$$\rho(\tau) \propto \tau^{-1-\beta} \tag{5}$$

Michael Shlesinger and others have shown that this PDF satisfies the subdiffusive criteria in (4). Letting $\tau \in [1, \infty)$[1] and $\beta > 0$[2] gives the explicit version of (5):

$$\rho(\tau) = \beta\tau^{-1-\beta} \text{ for all } \tau \geq 1. \tag{6}$$

The corresponding cumulative distribution function (CDF) $P(\tau)$[3] is

$$P(\tau) = 1 - \tau^{-\beta}. \tag{7}$$

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[1] The choice of the minimum $\tau = 1$ simply implies there is some finite minimum waiting time. If we could have $\tau = 0$, there would be no wait at all; we may as well normalize any $\tau = \epsilon > 0$ to 1.

[2] The domain of $\tau$ and normalization requirements on (5) force $\beta > 0$.

[3] $P(\tau) \equiv \int_{-\infty}^{\tau} \rho(\tau)\, d\tau$. In this case, the lower bound on $\tau$ is 1, so we integrate from $\tau = 1$ to $\infty$.

By setting (7) equal to the CDF of $X$ as previously defined,

$$P(X) = X, \tag{8}$$

we solve for $\tau$ in terms of $X$ and obtain

$$\tau(X) = (1 - X)^{-1/\beta}. \tag{9}$$

Now, $X$ (being a uniformly-distributed random number between 0 and 1) is very easy to generate in a computer. However, if $X$ is allowed to be exactly 1, this produces an infinity and cannot work; this problem is solved easily by either using a non-inclusive generator or by adding an extra subroutine in case of $X = 1$.

Finally, since $X$ is uniform, $1-X$ and $X$ are equivalent for the purpose of generating a random number. We make this change, and use

$$\tau(X) = X^{-1/\beta} \tag{10}$$

to generate a waiting time for every monomer's next step, realizing a time-based version of the KMC structure in Figure 2.

### B. Implementation

To implement the time-based KMC, we modified previous KMC code from J. Amar, written in the C programming language, which simulates up to a specified coverage (fraction of the surface covered). Our purpose was to simulate $\chi$, so we varied $D/F$ and simulated far enough to pass the peak number of islands (and therefore island density); we then plotted the calculated island density for each $D/F$. We repeated this entire process for different $\beta < 1$; then, for each $\beta$, the slope of $N_{\text{peak}}$ versus $D/F$ on a log-log plot gives the value of $-\chi$ for each $\beta$.

We simulated subdiffusion on a 2D square lattice of size 2048 by 2048, doing 10 runs for each $\beta$ and $D/F$ combination. The code was run at the Ohio Supercomputer Center.

## III. RESULTS

The plot of $N_{\text{peak}}$ versus $D/F$ is shown in Figure 3, which shows a clear difference in slope for different $\beta$, indicating a definite $\beta$-dependence in $\chi$. This exciting result indicates that the classical theory is inconsistent with results for subdiffusion.

Figure 4 shows the final result of $\chi$ vs $\beta$ – indeed, $\chi$ depends rather strongly on $\beta$. The dotted line shows the result of a new theory being developed by J. Amar.

## IV. CONCLUSIONS AND FUTURE WORK

Simulated results show that there is definitely a strong $\beta$-dependence in $\chi$, and therefore that the classical theory for normal diffusion does not work. An independently-formulated theory by J. Amar features a $\beta$-dependence which agrees very closely with simulated results, making it a promising candidate for describing this phenomenon.

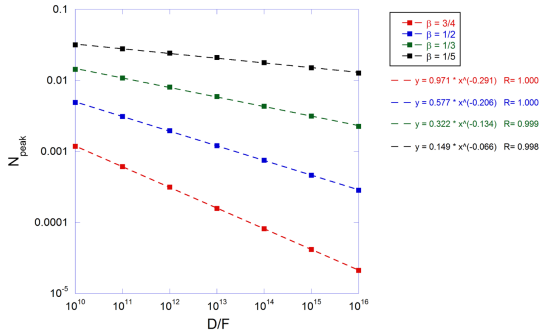


FIG. 3. $N_{\text{peak}}$ versus $D/F$

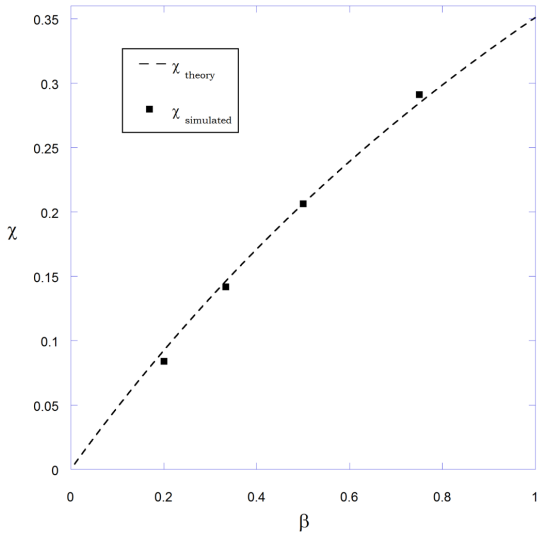


FIG. 4. $\chi$ versus $\beta$

Additional simulations for larger system sizes and different $D/F$ are currently being run to increase the statistical accuracy of the simulated data. We are also obtaining data for $\beta = 0.9$ and 1.0. It would be interesting to compare the results obtained here for "fractal islands" (with fractal dimension $d_f \approx 1.7$) with the corresponding results for "compact islands" ($d_f = 2$), as well as the effects of quenched randomness on scaling behavior.

## V. ACKNOWLEDGEMENTS

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