May 18th, 12:00 AM - May 22nd, 12:00 AM

Submonolayer Nucleation in Ultrathin Liquid Films: Scaling Properties and the Effects of the Critical Nucleus Size

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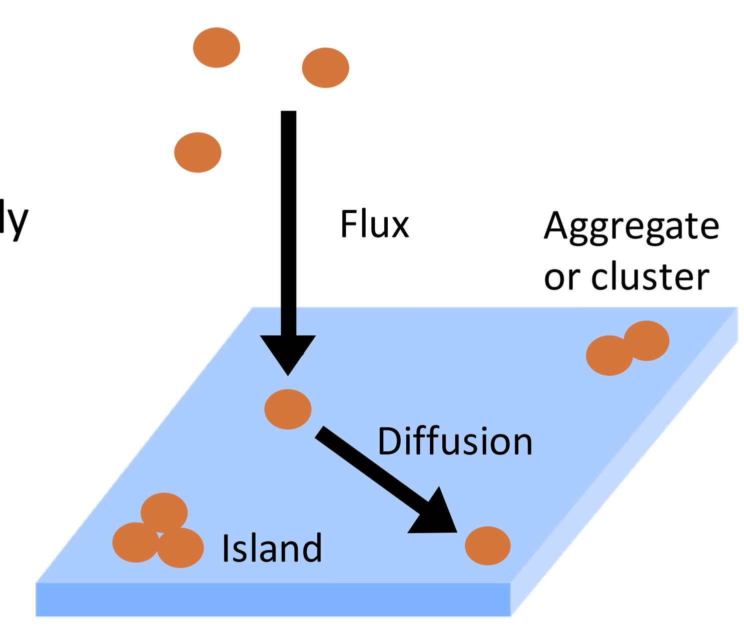
Background

- The system modeled by all approaches discussed here consists of a substrate that monomers (molecules or atoms) are fluxed onto at a constant rate F
- Monomers may move around and aggregate with other monomers, forming a cluster or stable island, but may not leave the substrate
- A stable island is formed when a cluster has one more monomer than the critical cluster size, i*
- A predominant approach to modeling these systems is via kinetic Monte Carlo (KMC) simulation; however, they are computationally expensive for large i* systems
- Mean free rate equation (MFRE) models consist of simple rate laws and are computationally inexpensive, but average over microscopic details that may be important
- Our novel multiscale model (MM) can achieve large i* systems without losing this detail



Example substrate, i*=2

Our Goal

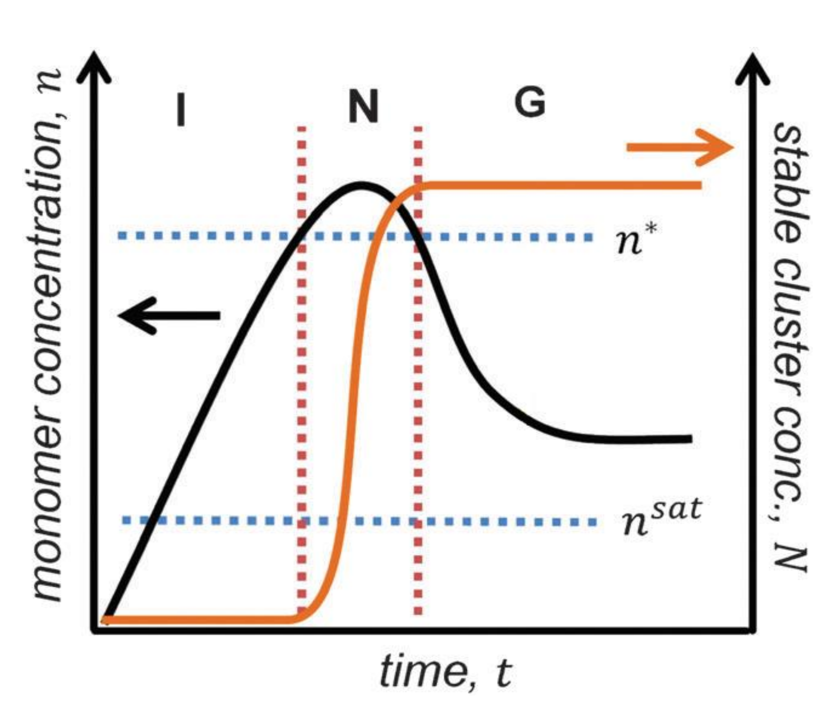
Submonolayer nucleation and growth in vacuum-deposited films are well described by KMC models due to their small critical cluster sizes. However, systems with large i* values, such as those that occur during solution-phase nucleation, remain unexplored. Such systems are of particular interest for the fundamental understanding of the physics behind the growth of large, low-defect organic crystals via organic-vapor-liquid-solid deposition, which have novel semiconductor applications. Additionally, the MM is built on physical principals alone, while others have more empirical approaches; how will their behavior compare, and will these small i* intended models be able to scale large i* systems?

The Multiscale Model

- The MM simulates a burst nucleation regime under a classical nucleation theory approach
- The MM includes a self-consistent treatment of i* that is integrated into a mean field approach, stochastic treatment of nucleation, and analytically calculated monomer diffusion via the 2D diffusion equation
- BN consists of phases and can be represented by couples rate equations
  - **Induction:** constant flux of monomers with no nucleation
  - **Nucleation:** critical concentration n* is reached and nucleation begins
  - **Growth:** monomers are more likely to join an island than aggregate with monomers, there is no nucleation and only island growth

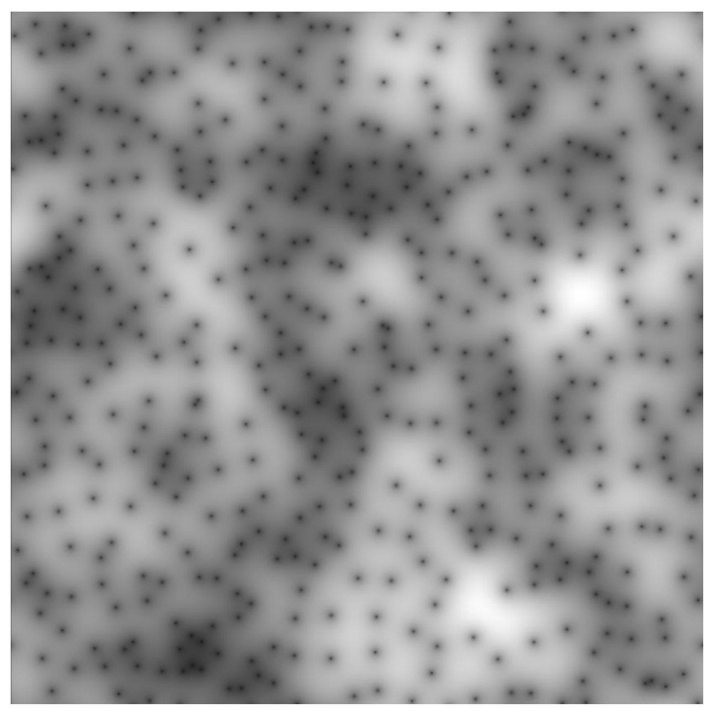
$$\frac{\partial N}{\partial t} = KP(i^*, n)n$$

$$\frac{\partial n}{\partial t} = F - KP(i^*, n)n - KnN$$



- Nucleation is periodically checked at every grid space by weighing the probability of nucleation, based on $P(i^*, n)$, against a random number generator
- The end result is a 2D landscape where each grid space represents the monomer concentration at that location
- Areas of lower monomer concentration are lighter and areas of greater concentration are darker
- Islands are likely to be found in the centers dark circles, due to their behavior as monomer sinks

N = supercritical stable cluster conce.
n = subcritical cluster conce.
K = collisions and capture kernel
$P(i^*, n)$ = conce. of aggregates with monomer conc. n and size i^*
F = flux



Scaling Models

Mulheran & Blackman's Semiempirical Model

$$F(s) = \left[\frac{\alpha^{\alpha}}{\Gamma(\alpha)}\right] s^{\alpha - 1}\exp(-\alpha s)$$

α is a normalizing constant

- Scales size distributions for Voronoi cell areas where s=cell size/average cell size
- Based on a model from a computational analytical experiment consisting of randomly dispersed particles, assigning Voronoi cells, and generating the above distribution from the outputs

Pimpinelli & Einstein's Wigner Surmise Application

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

a_{β} and b_{β} are normalizing constants

- An approximation that describes spacing statistics that is derived from random matrix theory

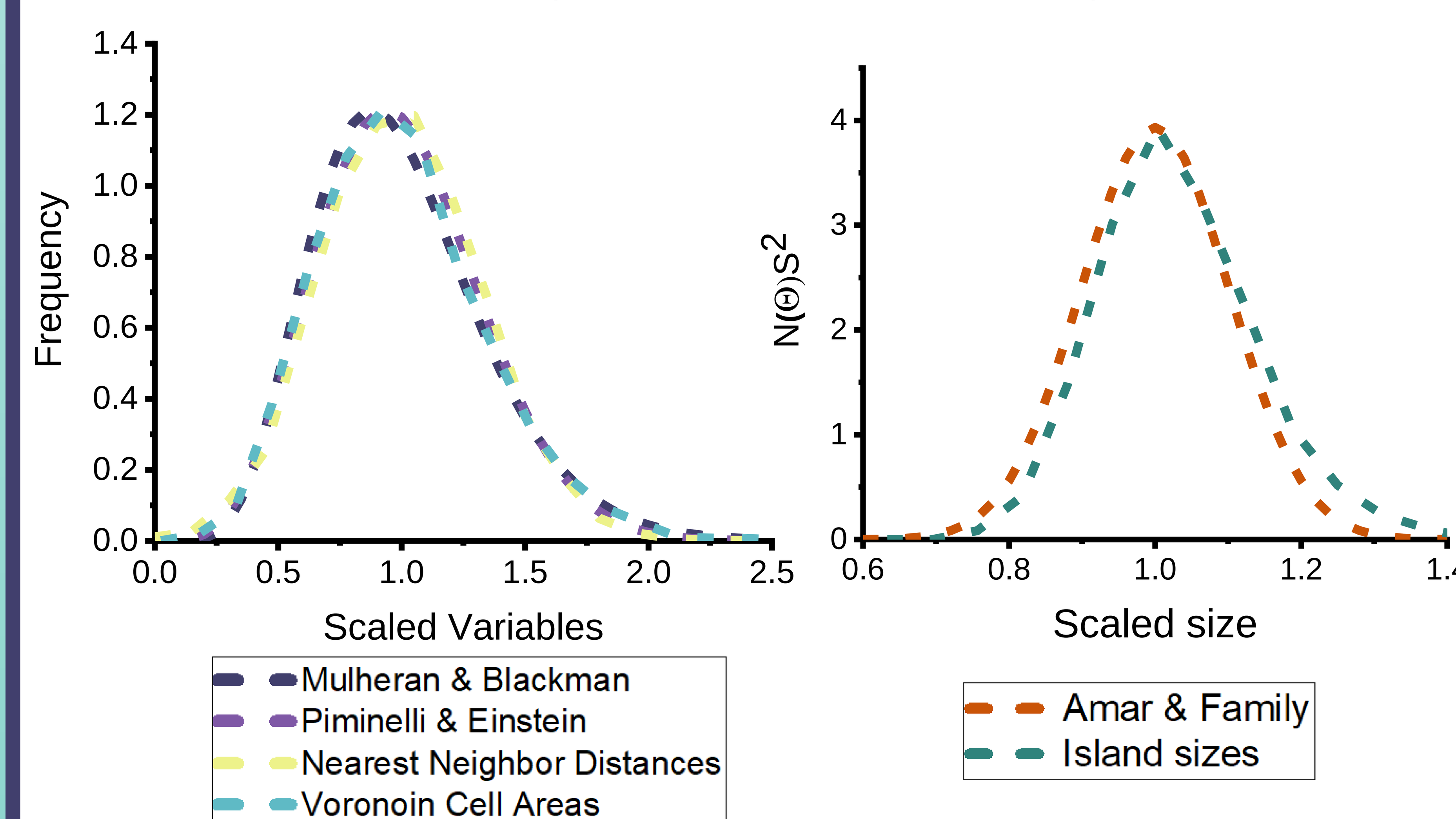
Amar & Family's General Scaling Form:

$$f(u) = C_i u^i \exp(-i a_i u^{\frac{1}{a_i}})$$

C_i and a_i are normalizing constants

- A general scaling form applied by Amar and Family to determine critical island sizes in physical experiments where iron is deposited onto iron and copper substrates
- Relates critical island size to island size scaling

Comparative Model Analysis



- Both Mulheran & Blackman and Pimpinelli & Einstein approaches agree very well with the multiscale model's nearest neighbor and Voronoi cell area distributions
- This suggests that these scaling forms hold true in large i* systems
- The Amar & Family fit predicts an i* of 38, where the multiscale model calculated an i* of 57 for the parameters run (Note θ is coverage and S is avg. island size)
- Although the parameters scaling these models to the multiscale models' behavior do not have direct meaning in the large i* regime, the fact that the curves themselves fit show that these fundamental models don't disagree with the multi-scale model
- The scaling agreements also prove that such a simple, computationally inexpensive model can provide accurate scaling behavior

References

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Acknowledgements

Special thanks to WWU department of chemistry, the Research Corporation for Science and Advancement, and the National Science Foundation