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A Theoretical and Experimental Study into the Kinetics of Solution Phase Thin Film Deposition

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A Theoretical and Experimental Study into the Kinetics of Solution Phase Thin Film Deposition

By

Cyrus Schaaf

Accepted in Partial Completion of the Requirements for the Degree of Master of Science

Kathleen L. Kitto, Dean of the Graduate School

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MASTER’S THESIS

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Cyrus Schaaf
5/18/2017
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A Thesis
Presented to
The Faculty of
Western Washington University

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Abstract

The performance of electronic and optoelectronic devices based on solution-processed organic semiconductor layers is strongly influenced by their mesoscale polycrystalline structure, including domain size and spatial distributions. In solution-processed films prepared by spin casting, solvent-based printing, and related methods, morphology is governed by a combination of interrelated thermodynamic and kinetic factors. Classical models of crystal formation in bulk solution or on bare surfaces in vacuum-deposited films fail to adequately capture these effects; the current theoretical understanding of crystallization in solution-deposited films is generally unable to provide much insight, let alone predictive design guidance for tailoring films with specific structural characteristics for a given set of experimental conditions and chemical properties. In this thesis solution-phase thin film formation has been studied for the purpose of developing and new experimental techniques new models for understanding and predicting mesoscale film structure and crystal morphology.

I will describe how nucleation can be modeled, and the predictions tested against experiment, by an approach that enables quantitative prediction of crystal coverage and intercrystalline spacing statistics as a function of processing conditions, using only a small number of experimentally-measureable parameters. To do this, a model is introduced that combines a mean-field rate equation treatment of monomer aggregation kinetics with classical nucleation theory and a supersaturation-dependent critical nucleus size to solve for the quasi-two-dimensional temporally- and spatially-varying monomer concentration and nucleation rate. Excellent agreement is observed with measured nucleation densities and inter-domain radial distribution functions in submonolayer tetracene films. The model leads
to the first universal set of predictive design rules for solution-phase thin film growth capable of guiding the selection of experimental conditions for truly engineered morphological control.

Accompanying this theoretical work a first of its kind experiment is also reported, in which monomer concentration has been spatially and temporally mapped in real time during the film formation process. Through the use of high resolution dark field fluorescence microscopy employing an internal fluorescent standard and multi-wavelength imaging optics the concentration dependence is visualized throughout all regimes of thin film formation. *In situ* measurements of local concentration contributes to the development of models which treat the role of variations in monomer concentration on mesoscale film morphology of polycrystalline thin films. This work opens the door to numerous studies enabling further development of models which allow for predictive control of polycrystalline thin films in solution-phase deposition techniques.

In addition to nucleation, growth of crystalline films is modeled through a set of numerical and computational methods which provide insight into the main factors influencing crystal growth habit. It is shown that crystal capture rate correlation with physical properties displays a distinct lack of agreement between the spacing and initial sizes of crystals with their relative growth rates. This lack of correlation points to the need for more sophisticated models. Through the use of a mean field numerical calculation of the volumetric growth rate changes in crystal morphology can be attributed to a variable sticking probability which depends on the crystal face. Kinetic Monte Carlo simulations are used to directly probe the physics which explain the deviation from the typical single sticking coefficient capture model. The change in shape at long deposition times further suggests that
crystal growth occurs in distinct regimes which dictate the final morphology of the crystals. This work provides an explanation to the change in shape of crystalline material at long deposition times which can be used to develop models to predict final crystal morphology.

This thesis is comprised of several parts. In the first chapter the broader context of the work is discussed. In chapter 2, I discuss the scientific background laying the foundation for theoretical models into solution-phase deposition. In the third chapter, I describe the experimental system as well as results from various measurements of fundamental chemical and physical properties needed later. The fourth chapter describes a set of models which I have developed to predict mesoscale film structure to create a set of universal design rules in order to engineer thin films grown in the solution-phase. In chapter 5, I describe a state of the art experimental set up allowing for monomer concentration to be mapped in real time. Finally in the last chapter I describe a set of exploratory models to describe change in crystal morphology during the course of thin film formation. This thesis creates new understanding, which will allow for an increase in production of thin films for applications where strict control over domain size, shape, spacing, and crystallographic orientation.
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Chapter 1: Introduction

Section 1.1: Semiconductors

Over the last 70 years inorganic semiconducting materials have become the material of choice for the electronics industry. A semiconductor is a crystalline or polymeric solid substance with conductivity between an insulator and a metal. The band theory model, Figure 1.1, is commonly used when talking about the electronic structure of a solid. It assigns the lowest unoccupied molecular orbitals to the conduction band, and highest occupied molecular orbitals to the valence band of the model providing a framework to discuss the electronic states of solid materials. The conductivity of a material can be portrayed by its relative band gap, the energy difference between the valence and conduction band allowing for classification into three main categories. The first being conductors, metals which have a miniscule band gap; the second, insulators, materials with a very large band gap; and third, semiconductors, materials with a medial band gap. In highly conductive metals, electrons can easily travel from relaxed electronic states to excited electronic states. This allows for easy transport of elections throughout the material. Insulators have a band gap above 3-4 eV, much larger than available thermal energy $kT$; as a result electrons cannot be transported through the material.

Figure 1.1: Band theory diagram. A comparison between conductors, insulators, and semiconductors.
Semiconductors, like silicon, have a medium-sized band gap below 4 eV and activation of conductivity requires an input of energy — such as photons, added thermal energy, or an applied electric field — to excite electrons into the conduction band. In the valence band, a hole is left behind and one of the two options either random diffusion causes recombination of the hole and electron or a net current flow is generated under an applied electric field. Figure 1.2 shows a diagram of the effect of an electric field on the movement of electron hole pairs. The electric field dependence on the performance of semiconducting devices allows for chemically and physically tunable materials and devices that make up most modern day electronics.¹² In order to classify a semiconductor’s ability to transfer charge, a common metric is the field effect carrier mobility (μ [cm²V⁻¹s⁻¹]) which is measured by the ratio of the velocity of the charge carrier to the magnitude of the electric field applied.

Figure 1.2: Diagram of a semiconductor after electron excitation under an applied electric field. The electron moves opposite of electric field generating a net current. If no electric field is applied random diffusion eventually causes recombination and a release of input energy.

The dominating semiconducting material in the last 70 years has been silicon due to its high abundance, easy manipulation, efficient solar response, and high conductivity.³ Silicon is mined in the form of silica (SiO₂) and has to be refined to create electronics grade silicon, Si. However, this reaction comes with a high energetic and environmental cost. The refinement of silica to silicon costs a minimum of 432 kJ g⁻¹ purified.⁴ Furthermore, the purification has a negative impact on the environment, through the release of chlorinated gas, or greenhouse
gasses like CO$_2$, into the atmosphere.$^4$ The environmental and energetic cost alone makes the investigation into new semiconducting materials necessary.

**Section 1.2: Organic Molecular Materials**

Even though the place of silicon has been well established, within the last thirty years the industry has gained an interest in organic semiconductors as a potential replacement for Si in some applications.$^5$ The strength of an organic based device is that methods of fabrication allow for low temperature deposition.$^6$-$^8$ This style of deposition has opened the door for their use as active layers for a wide range of electronic and optoelectronic applications such as flexible integrated circuits, displays, photovoltaics, actuators, and sensor arrays.$^9$-$^{17}$

Organic semiconductors come in two main classes: conductive polymers and organic molecular crystals (OMCs). Conductive polymers contain conjugated $\pi$ bonds that allow for the transport of electrons or holes along or in-between the polymer chains. Commonly used polymers are in the family of polythiophenes, and poly(triamine)s, which tend to have relatively high solubility in common organic liquids. This solubility allows for polymer based semiconductors to be easily fabricated with various solution based processing methods, but these semiconductors are currently not competitive in the area of device performance due to their low charge carrier mobility. OMCs, on the other hand, consist of molecular crystalline materials that have competitive charge carrying mobility but present problems in ease of fabrication.$^{18}$-$^{20}$ Due to the morphological impact on the performance of OMC thin films solution phase processing techniques tend to be less reliable, causing a lack of consistency when fabricating devices from OMCs. Although this makes the throughput of fabricating OMCs into thin film devices much lower than conjugated polymer devices, the OMCs high charge carrier mobility makes them potential replacements for high cost inorganic materials.$^{21}$
Much like inorganic materials, the performance of organic semiconductors is dependent on the purity and the crystallinity of the material.\textsuperscript{22-25} For organic semiconductors, such as tetracene, pentacene and rubrene, charge is passed by delocalized \( \pi \) orbitals when an electric field is applied to the material.

A key feature of OMCs are the weak Van der Waals forces which maintain its stability, morphology, and crystallographic orientation via \( \pi - \pi \) interactions.\textsuperscript{26-27} These noncovalent \( \pi - \pi \) interactions between molecules allow for charge to move more freely through the crystalline structure. More highly ordered materials tend to have higher charge carrier mobility.\textsuperscript{24-25} Amorphous organic materials show a decrease of up to 6 orders of magnitude in mobility when compared to highly crystalline materials, due to their irregular distance and orientation.\textsuperscript{28} Even when an OMC is highly crystalline its weak van der Waals forces can give rise to a loss in performance due to impurities and defects in the crystalline lattice. These impurities and defects hinder charge transfer by acting as charge traps which decrease the performance of the OMC devices.\textsuperscript{29}

The last important feature when measuring the performance of OMC based devices is the crystallographic orientation of the material. The degree of \( \pi - \pi \) overlap greatly impacts the material’s ability to generate current along the applied electric field.\textsuperscript{25,30} With this in mind, devices that are made from OMC materials must capitalize not only on purity but also on crystallinity and morphology. Therefore, fabrication and synthesis techniques for OMCs must create highly pure and crystalline materials in order to produce the highest efficiency devices. Fabrication techniques must also allow for control over general film morphology and structure while also allowing for a competitive cost and throughput to be considered viable techniques in the current semiconductor industry.
Section 1.3: Fabrication Techniques

OMC films are typically fabricated in two main environments: high vacuum and solution phase. High vacuum deposition environments allow for growth of pure and crystalline material, but with the drawback of low throughput and relatively high cost. Figure 1.3 diagrams two typical high vacuum physical vapor deposition (PVD) methods: sputter deposition and evaporation deposition.\textsuperscript{31-33}

\textbf{Figure 1.3:} Block diagrams of high vacuum deposition techniques (A) Molecular beam epitaxy and (B) sputter deposition.

Sputter deposition is a process in which positively charged ions are accelerated towards a sputtering target material, causing the target material to eject from the source and to diffuse towards the substrate. The deposition rate is controlled by a flux of sputtering ions onto the sputtering target or the amount of ionic gas in the deposition chamber.\textsuperscript{34} Techniques like molecular beam epitaxy (MBE) require evaporation of the material before deposition onto a substrate. Pure materials can be deposited with MBE performed at $10^{-8}$ to $10^{-12}$ Torr with a very low deposition rate of under 3 $\mu$m per hour.\textsuperscript{35} Typically solid material is heated in a quasi-Knudsen cell or electron beam evaporator until they begin to slowly evaporate. The vapor escapes the cell at a constant rate proportional to the partial pressure of the material in the cell. The material then diffuses onto the substrate to form thin films.\textsuperscript{35-36} This highly controlled form
of deposition allows for a relatively simple system for studies of crystal and thin film nucleation and growth kinetics. Most of our current understanding about nucleation comes from experiments performed by MBE, as summarized in chapter 2.\textsuperscript{37} Due to the highly-controlled environment, MBE is used in industry to deposit organic and inorganic conducting materials for electronic, magnetic, and optical applications.\textsuperscript{33} Thermal evaporation methods allow for slight control of crystal morphology size and unit cell structure; however they do not offer the same level of control of these features and furthermore, control of orientation or spatial separation as solvent deposition techniques do. High vacuum techniques allow for a high degree of control over the purity of materials but lack the mesoscale morphological control required to further the technological impact of organic semiconductors.

**Figure 1.4:** Diagram of solvent phase deposition techniques (A) drop casting and (B) spin casting.

Solution phase deposition techniques allow for control of overall film morphology as well as offer the high throughput in order to be viable for industrial device fabrication. However, it lacks the theoretical framework to predict crystal densities and spacing statistics, causing these methods to rely more on trial and error to fabricate crystals suitable for specific applications.\textsuperscript{38} The two main types of solution phase deposition techniques, shown in Figure
1.4, are drop casting and spin casting. Both use solvent evaporation as the driving mechanism for nucleation of new material.

Drop casting is a method that saturates a solution with an organic material, with strong self-assembling character, then drops the solution onto a substrate. The solvent is evaporated and the change in concentration of the organic material becomes the driving force for nucleation. As evaporation continues, crystals form in the liquid until they eventually settle onto the substrate. With evaporation as the driving force crystal density, purity, crystallinity, and morphology are primarily dependent on the rate of solvent evaporation. This means that methods for drop casting can be designed to give large single crystals for applications, not just in electronics but also in other areas, such as pharmaceutical research. However, deposition may take place over many days in order to grow crystals that are large enough for X-ray diffraction studies.

The other main technique is spin casting or spin coating, which is often used to make uniform thin films of OMC materials. A saturated solution is dropped onto the substrate which is then accelerated to a high angular velocity to spread the liquid and evaporate the solvent. Film thickness is dependent on the viscosity of the solution, the rate of spinning, and the amount of time that the solution is spun. These controllable parameters allow for spin coating to deposit a reproducible active layer thin film onto a substrate. Highly controlled and uniform films allow for high efficiency thin film transistors, optoelectronic devices, and other forms of small scale electronics that are increasing in popularity. As with drop casting there is little theoretical understanding of this form of solution phase processing. Most solution phase methods rely mainly on trial and error and not on a theoretical understanding of what causes nucleation or how the organic material grows as solvent evaporation continues.
These two methods cover only the basics of solution phase processing but illustrate the point that OMC processing methods are primarily formed not by an underlying fundamental understanding but by costly and time-consuming trial and error experimentation. If organic materials are going to be viable replacements for their inorganic counterparts, they need to not only increase in performance but deposition techniques must also rely on a theoretical framework and set of film design rules which increase the throughput and control of deposited films.
Chapter 2: Scientific Background

Section 2.1: Classical Nucleation Theory

Figure 2.1: A diagram of the phases of nucleation on a surface. Deposition begins with addition of individual growth units at a set flux. Growth units are allowed to randomly diffuse until they either aggregate to an existing crystal or they come in contact with a critical nucleus and form a new stable crystal.

Nucleation has been the subject of study for 90 years since the development of Classical Nucleation Theory (CNT) by Volmer and Weber. For nucleation occurring on a surface, the first step is deposition, with growth units arriving on the surface at a set flux rate. After a growth unit adsorbs it is may diffuse and collide with other growth units. According to CNT, when enough growth units come together in one place at the same time (ie. more than the critical nucleus size) a new phase of matter nucleates. Figure 2.1 shows an example of each of the steps in thin film deposition, diffusion, aggregation, and nucleation. The rate of nucleation by CNT is expressed as an Arrhenius reaction velocity:

\[
J = A \exp \left[ -\frac{\Delta G^*}{kT} \right]
\]

2.1
where $J$ is the nucleation rate, $\Delta G^*$ is the free energy barrier to nucleation, $A$ is a constant determined by kinetics, $k$ is the Boltzmann constant, and $T$ is the temperature.\textsuperscript{40-41} The free energy barrier in CNT can be calculated from the radius of a stable cluster, and is given by:

$$\Delta G^* = -\frac{4\pi r^3}{3a} kT \ln \left( \frac{P}{P_0} \right) + 4\pi r^2 \sigma$$

where the first term accounts for the entropic gain, decreasing the free energy, and $\frac{4\pi r^3}{3a}$ is the number of molecules in a cluster of radius $r$, with molecules having a volume $a$, and the supersaturation ratio of the vapor is $\frac{P}{P_0}$. The second term accounts for the free energy increase due to surface tension $\sigma$.\textsuperscript{40-41} Classical nucleation theory relies on three key assumptions: the first is that the nucleus can be described with the same density, structure, and composition as the stable crystalline phase. The second, the molecular shape is spherical which creates a spherical nucleus with a well-defined outer boundary. Finally the nucleus-source interface is flat regardless of critical cluster size.\textsuperscript{41} These assumptions allow for rough approximations of the nucleation rate but also cause the model to ultimately fall short in the prediction and modeling of real world systems, creating a need for further extensions and modifications.\textsuperscript{41} The search for the best adaptation of CNT has given way to a variety of new models which are used to describe specific systems or environments.

The combination of extended modified liquid drop (EMLD) and dynamic nucleation theory (DNT) models creates an extension of CNT that treats the energy of nucleation as being related to the number of monomers in a system. These models center around the idea that the volume of the vapor is greater than the volume of the nucleated droplet, causing nucleation to be driven by minimizing the pressure of vapor in a container.\textsuperscript{42} The EMLD-DNT combination
is able to approximate the nucleation rate of polar systems at changing temperature in orders of magnitude more effectively than CNT because intermolecular potentials are not required.\textsuperscript{42}

Density functional theory (DFT), or non-classical theory, is an extension to CNT that calculates the free energy of the system as a function of the number density of monomer units in the system.\textsuperscript{43-46} DFT is particularly useful for modeling the vapor-liquid or liquid-solid nucleation interactions, due to the operating assumption of a spherical fluid system. The nucleation rate in this modification is expressed by:

\[
J_{\text{DFT}} = A \exp \left( -\frac{\Delta G_{\text{DFT}}}{kT} \right)
\]

where $\Delta G_{\text{DFT}}$ is calculated using density functional energy calculation with a perturbation approximation to predict the intermolecular forces present in the system. From this energy calculation and approximation DFT predicts the nucleation rate of a material with several known constants such as equilibrium vapor pressure, liquid density, and surface tension more accurately than with CNT.

\textbf{Section 2.2: Submonolayer Film Growth by Vacuum Deposition}

Diffusion mediated growth of deposited films requires random diffusion in order to facilitate the creation of new nucleated material as well as growth of existing nuclei. In vacuum phase deposition, in particular where diffusion is purely random on the substrate surface, submonolayer nucleation and growth kinetics are adequately modeled by mean field rate equation (MFRE) and kinetic Monte Carlo (KMC) models. These types of numerical models make several important assumptions relating to the dynamics of diffusing monomers and subcritical clusters. The first defined variable is the critical cluster size $i^*$, which is one less than the number of monomers required for nucleating a stable crystal. Many calculations with these models assume small and constant $i^*$ values for nucleation in a vacuum environment.\textsuperscript{37}
The next assumption is that atoms diffuse across the crystal surface to form equilibrated compact crystals and that if an atom randomly arrives on a crystal it is instantaneously incorporated into that crystal.

MFREs initially were used to explore the average crystal density of isotropically diffusing monomers on a one dimensional surface. These types of calculations have since grown to explore much more complex systems by splitting submonolayer growth into multiple different regimes. The nucleation or transient regime encompasses the initial increase in monomer concentration that is built up as \( n = Ft \), which then leads to nucleation of new crystalline material. Here \( n \) is the monomer concentration, \( F \) is the flux rate of monomers, and \( t \) is time. As crystals nucleate, a depletion zone begins to form in the neighborhood of the new crystals, lowering local concentration and suppressing nucleation near already established crystals. Once the monomer concentration over the whole surface drops low enough, nucleation stops and the steady state regime begins. In the steady state regime, nucleation ceases and islands are assumed to grow based on the size of their capture zones, which can be modeled by a crystal’s Voronoi cell, edge cell, or diffusion cell area.

Separating deposition into multiple regimes allows MFREs to be used to predict the monomer concentration, crystal coverage \( \theta \), crystal density \( N \), and the size distribution of crystals throughout deposition. Furthermore, rate equations can be adapted to take monomer diffusion into account where the diffusion rate is found to be of the form \( D = \frac{za^2h}{4} \), where \( z \) is the number of coordination sites, \( a \) is the lattice constant, \( h = \nu \exp(-\frac{E_d}{kT}) \) is the hopping rate, \( \nu \) is the attempt frequency for hopping, and \( E_d \) is the energy required for diffusion, for a 2-dimensional system. Rate equations are built with three main kinetic terms:

\[
\frac{dN}{dt} \approx F(1 - \theta) - (i^* + 1)K_{\text{nuc}} - K_{\text{agg}}.
\]
The first term accounts for addition of monomers through a flux rate $F$ taking into account deposition on top of existing crystals by the factor $(1 - \theta)$. The second term considers the removal of monomers by nucleating new stable crystals. When $(i^* + 1)$ monomers are at the same location they are taken out of the diffusing system at a rate equal to $K_{\text{nuc}} = \sigma_l h n N_i$, where $\sigma_l$ is the capture number of an island that is the size of a critical cluster, $n$ is the monomer density, and $N_i$ is the number density of critical clusters. The final term accounts for the removal of monomers by existing crystals. The monomers are removed by some growth rate denoted by $K_{\text{agg}} = \sigma_{\text{avg}} h n N_i$. Here $\sigma_{\text{avg}}$ is the mean capture number of all of the crystals in the system. The density of stable crystals can be computed using the Walton relation:

$$N_i \approx c_i \exp \left[ -\frac{E_i}{kT} \right] (n)^i$$

where $c_i$ is the number of configurations of critical clusters that exceed the minimum energy $E_i$ which corresponds to the cluster size, $i$. From here the rate equation model can be combined with the Walton relation to give crystal densities for the transient regime, $N_i \sim \theta^{(i+2)} \exp \left[ -\frac{E_i}{kT} \right] \left(\frac{h}{F}\right)^i$, and the steady state regime, $N_i \sim \theta^{1/(i+2)} \exp \left[ -\frac{E_i}{kT(i+1)} \right] \left(\frac{h}{F}\right)^{-\chi}$, where $\chi$ is a scaling exponent which is defined by $\chi = i/(i + 2)$, during the steady state regime. Mean field theory has also been adapted to the calculation of the crystal size distribution, the capture numbers of crystals, and the nucleation rates of various systems.\textsuperscript{37,47,52}

Although this framework provides a simple and explicit to model nucleation, it tends to break down when trying to exactly calculate capture numbers and crystal densities, due to the correlation between a crystal’s size and its distance from its nearest neighboring.$^{37}$ To exactly calculate and explore this correlation, kinetic Monte Carlo models were developed as simulation based methods of taking isotropic diffusion into account. These models treat growth by employing randomly diffusing monomer units (walkers) placed on a diffusion surface.
Walkers are allowed to isotropically diffuse throughout the grid at a rate given by the hopping rate $h$. A nucleus forms when one more than $i^*$ land on the same spot at the same time.\(^{37}\) Monomer attachment is typically assumed to be irreversible. KMC simulations which employ far-from-equilibrium-attachment models can be modified to model particular systems. For example, in most KMC simulations for simplicity aggregates are assumed to be immobile. This assumption can be relaxed by allowing small clusters to move. This model is reported in reference 54 for the diffusion of both monomers and dimers. The movement of small clusters is shown to cause the prediction for the maximum island density ($N_i$) to deviate from the Walton relation, $N_i \sim \left(\frac{h}{F}\right)^{1/3}$ when $i^* = 1$, to become $N_i = \left(\frac{hh_2}{F^2}\right)^{1/5}$. Further expansion of this idea leads to the approximation that all clusters smaller than $i^*$ diffuse causing the $N_i = F^\chi$ where $\chi = \frac{i^*}{2i^*+1}$.\(^{35}\) KMC can also be used to explore different phenomena such as, anisotropic diffusion, cluster shape effects, extended versus point island crystals, and the effects of variable attachment probabilities and diffusion barriers.\(^{37}\) Where KMC type models break down is in systems where nucleation or aggregation is caused by microscopic or multiple atom concerted processes. These phenomena are not easily taken into account by most forms of the model and require a more semi-empirical approach. Development of new smart models which take free energy calculations into account allow for more accurate final crystal densities and size distributions at low $i^*$.\(^{37}\) CNT provides a strong framework for development of new nucleation models which have been centralized around simple vacuum phase nucleation systems. However, solution phase thin film deposition has received little attention in the way of extensions, while offering a rich environment for the development of new models for the purpose of controlling film nucleation and growth kinetics.
Section 2.3: Burst Nucleation

Figure 2.2: A qualitative description concentration driven solution phase burst nucleation. The induction regime is shown in the section I, the nucleation regime shown in the section N, and the growth regime is noted by a G, which are separated by dotted colored lines. The black curve represents the subcritical cluster concentration \( n \) while the orange curve represents the stable cluster concentration, \( N \). The metastable zone (MSZ) is the zone where growth of existing stable clusters, absent of nucleation, occurs. (Used with the permission of reference 52)

Systems which experience concentration dependent nucleation often nucleate new crystals via burst nucleation. The burst nucleation model splits thin film deposition into three distinct regimes—induction, nucleation, and growth—shown in Figure 2.2. The onset and the increase in monomer concentration before nucleation occurs is defined as the induction regime. During the induction regime monomer units are allowed to diffuse freely. As monomer concentration increases, the free energy barrier to nucleation responds inversely. When the critical supersaturation concentration is exceeded, the probability of nucleating a new crystal is high and transient nucleation occurs, marking the start of the nucleation regime. As new crystals continue to nucleate, the monomer concentration decreases below the critical
concentration, ending the nucleation of new crystals and beginning the growth regime where monomers are constantly added to nucleated crystals.

The first description of this three regime nucleation scheme comes from Victor LaMer and Robert Dinegar who studied nucleation monodisperse hydrosols. The reaction they investigated, $2 \text{HS}_2\text{O}_3^- = 2 \text{HSO}_3^- + \text{S}_2$, drives the concentration of dissolved sulfur upward at a rate that is dependent on the initial concentration of the reactants. The LaMer model of burst nucleation describes nucleation from the perspective of the concentration of molecular sulfur. Initially the reaction causes an increase in concentration, which eventually causes the dissolved sulfur to reach the critical concentration. At the critical concentration, monodispersed colloidal sulfur nucleates rapidly to cause the supersaturation ratio of dissolved sulfur to drop to nearly zero, stopping all further nucleation. When the nucleation halts, the reaction continues, causing the solution to remain slightly supersaturated and allowing for diffusion mediated growth of existing particles. To support this model, LaMer and Dinegar measured the optical density of crystalline sulfur dissolved in a mixture of water and ethanol. This revealed that the nucleation regime begins with few small nuclei, and as concentration increases the nucleation rate of new particles increases greatly until abruptly stopping when the supersaturation ratio drops to a stable regime. Growth continues controlled by monomer diffusion until the reaction is finished. LaMer type burst nucleation separates the nucleation and growth regimes which allow for easier development of solution-phase deposition models treating nucleation and growth kinetics.

In 2008 Robb and Privman proposed an extension to this model of burst nucleation by treating the free energy of formation of a nucleus of size $i$ at concentration $n$ as:

$$\Delta G_i(n) = -(i - 1)kT \ln \left( \frac{n}{n_0} \right) + 4\pi\sigma a^2 \left( \frac{2}{i^3} - 1 \right)$$

$$2.6$$
In equation 2.6 the free energy of formation is dependent not on the partial pressure but on the supersaturation ratio of monomers in the solvent, \( \frac{n}{n_o} \). This equation can be broken into two parts. The first term is negative and includes the free energy contribution of the removal of excess monomers from the saturated solution. This term favors larger nuclei and is derived from the entropy of a supersaturated solution. The supersaturation ratio causes this term to grow as concentration increases.\(^{57}\) The second term is positive, and accounts for the free energy cost of the surface interaction with the solvent. The model makes the assumption that clusters are spherical, ignoring geometric factors that would occur in real nuclei, and assumes a constant surface tension regardless of size.\(^{57}\) The critical cluster size given as a function of supersaturation is in the form:

\[
i^*(n) = \left[ \frac{8\pi a^2 \sigma}{3kT \ln(\frac{n}{n_o})} \right]^3 \tag{2.7}
\]

which is derived by finding the maximum change in free energy given from equation 2.6. As new nuclei form, the monomer concentration drops, and the supersaturation ratio decreases, causing an increase in the critical size and which ceases nucleation. Robb and Privman make the steady-state approximation that the concentration of nuclei in a range of cluster sizes \( i \) is given by a thermal distribution:\(^{57}\)

\[
P(i, n) = n \exp \left[ -\frac{\Delta G_i}{kT} \right] \tag{2.8}
\]

where \( n \) is the monomer concentration.

Two years ago, our group introduced an adaptation of the Robb and Privman burst nucleation model that takes into account monomer addition by an impinging gas flow. Burst nucleation and diffusion-mediated growth are modeled through a pair of coupled rate equations of the form:\(^{52}\)
\[
\frac{dn}{dt} = F - KP(i^*, n)n - KnN \tag{2.9a}
\]
\[
\frac{dN}{dt} = KP(i^*, n)n \tag{2.9b}
\]

where equation 2.9a is the change in monomer concentration over time and equation 2.9b is the nucleation rate. Monomer units are added to the system at a constant flux rate, \( F \). They are then taken out of solution by nucleation as well as through absorption by existing crystals. The rate of nucleation is modeled in a similar fashion to Robb and Privman where the distribution, \( P(i, n) \) becomes:

\[
P(i^*, n) = n \left( \frac{n}{n_o} \right)^{i-1} \exp \left[ -\frac{4\pi\sigma a^2 i^2}{kT} \right] \tag{2.10}
\]

upon substituting equation 2.6 for the Gibbs free energy term. Equations 2.9 and 2.10 were found to provide excellent agreement with experiment, as shown in Figure 2.3.\(^{52}\) These fits were obtained by treating the equations 2.9 and 2.10 with a modified form of the Smoluchowski collision kernel \( K \approx \gamma 4\pi a i^{1/3} D \), where \( \gamma \) is a parameter that accounts for

\[\text{Figure 2.3: Nucleation density generated through the use of a theoretical rate equation model compared with experimental data. The density of both monomer (left) and stable crystals (right) are plotted as a function of time since the start of deposition. Circles are measurements from experiment and the solid lines are model results. (Used with permission of Reference 52)}\]
microscopic processes, and $D$ is the monomer diffusion coefficient which is dependent on the viscosity $\eta$, via $D \sim \frac{kT}{6\pi\eta a}$. The kinetics associated with burst nucleation are useful in understanding many forms of particle development, from being able to synthesize uniform nanoparticles to controlling the size distribution of quantum dots.

**Section 2.4: Vapor Liquid Solid Deposition**

Vapor Liquid Solid Deposition was first introduced in 1964 as a new method to deposit crystalline silicon. This early study took Au-Si liquid alloy droplets on a heated Silicon substrate and fluxed a SiCl vapor into the liquid. With a small concentration of gold in the solution acting as a seeding agent, elongated Si whiskers grew in the $\{111\}$ direction under the liquid droplet until the gold in the alloy was used up leaving rounded ends to the whiskers. The unidirectional growth mechanism made it an ideal system to study preferential growth in nanowire type materials. In the original method of VLS growth a droplet of liquid sits on a substrate and material is fluxed onto the surface. The liquid acts as a solvent and collects the vaporized material. Then when nucleation of the nanowire occurs, the liquid provides for a constant flow of monomers that irreversibly stick to the growing wire due to the high concentration of monomer in the liquid. The nucleation rate under these conditions is given by:

$$J = \omega Z n \exp\left[\frac{-\Delta G}{kT}\right]$$

where $\omega$ is the attachment factor, $Z$ is known as the Zeldovich factor, and $n$ is the concentration within the liquid. The concentrated liquid provides a reservoir of monomers, which allows the face of the wire that is covered by liquid to grow much faster than it would otherwise, and
suppresses nucleation on areas of the substrate and crystal that are not covered in liquid, facilitating unidirectional growth.

The same concentration dependence of nucleation is the framework that Organic Vapor Liquid Solid (OVLS) Deposition is built on.\textsuperscript{62} Instead of using alloy mixtures and inorganic materials, OVLS relies on good solvents of organic solids such as organic liquids, ionic liquids or liquid crystalline solvents, combined with an organic precursor.\textsuperscript{52, 62-63} In OVLS, crystal formation occurs at the gas-liquid or liquid-solid interface. Crystals may also form freely floating in solution depending on the solvent/crystal system.\textsuperscript{62} This gives rise to an array of single crystals whose spacing and morphology depends on the interactions between the solid, liquid and substrate as well as the deposition conditions (i.e. flux rate and temperature). Rather than growing a whisker under a droplet of liquid, OVLS produces polycrystalline thin films and allow for control over both morphology and crystallite spacing.

Section 2.5: Thesis Summary

Solution-phase methods of thin film formation offer the potential to increase the throughput and decrease the cost of OMC thin films and applications based on them. However, the main barrier to solution phase methods is the lack of theoretical understanding. This lack of understanding creates methods of thin film formation which are primarily based on a cycle of costly guess and check. This thesis explores the kinetics of solution-phase deposition through \textit{in situ} optical microscopy measurements of highly controlled and reproducible thin film depositions. Various imaging methods allow for direct measurement of each regime of burst nucleation, creating well defined regions of interest for the development of theoretical models which provide a framework to predict both the mesoscale film structure and the individual crystal morphology.
Nucleation can be modeled by an approach enabling quantitative prediction of crystal coverage and inter-crystalline spacing statistics from only a small number of experimentally measurable parameters. The model combines a mean-field rate equation treatment of monomer aggregation kinetics with classical nucleation theory and a supersaturation-dependent critical nucleus size to solve for the temporally- and spatially-varying monomer concentration and nucleation rate. This work uses the designed models to lead to a set of predictive design rules useful for guiding selection of experimental conditions for predictive morphological control in any method of concentration dependent solution-phase molecular crystalline thin film formation.

The first experiment directly measuring the monomer concentration during thin film formation is also reported here. Through the use of high resolution dark field microscopy the spatially-resolved concentration can be visualized as a function of time. In situ measurements of local monomer concentration during nucleation contributes to the development of models which treat the role of monomer concentration on mesoscale film morphology of polycrystalline thin films. This work describes a cutting-edge technique for the measurement of monomer concentration which opens the door to numerous studies to further develop models that treat the control of thin film formation by solution-phase deposition techniques.

In the final part of this thesis growth of crystalline films are examined through a set of numerical and computational methods which provide unique insight into the change of morphology. The monomer capture rate shows a distinct lack of correlation with respect to various physical properties displaying a distinct lack of agreement between film morphology and the individual growth rates of crystals. The lack of correlation points to the need for more sophisticated models to determine which factors contribute to the change in crystal
morphology. Through the use of mean field numerical fitting and kinetic Monte Carlo simulations the change in crystal morphology can be contributed to various sticking probabilities on individual crystal faces. Variations in the shape of the crystals at long deposition times further suggests that crystal growth occurs in distinctly separated regimes which dictate the final crystal morphology of polycrystalline thin films. This work provides an explanation to the change in shape of crystalline material at long deposition times which can be used to develop models to predict final crystal morphology.

The findings presented here comprise a set of experimentally confirmed models which can be used to predict the domain size, shape, spacing, morphology, and crystallographic orientation of polycrystalline thin films, given a finite set of experimentally measured constants.
Chapter 3: Experimental Methods

Section 3.1: Organic Vapor Liquid Solid Deposition Overview

The Organic Vapor Liquid Solid (OVLS) Deposition chamber shown in Figure 3.1 allows for reproducible deposition of high purity organic molecular crystalline thin films. Organic material is loaded into a source crucible located in the interior of the chamber. A nichrome heating wire housed in ceramic heating blocks wraps around the crucible, heating it to well above the sublimation temperature of the organic solid. Sublimated vapor is carried up through a nozzle, which is designed to produce an axisymmetric laminar flow by ultra-high purity nitrogen gas. This flow impinges onto a 1 cm$^2$ area of the substrate which is attached to

Figure 3.1: Schematic of the OVLS deposition apparatus (left). The components are housed inside a sealed chamber (right). Film growth was monitored in situ via polarized optical microscopy through a viewport in the lid.
the lid of the chamber. A liquid layer on the substrate serves as the solvent in which crystals nucleate and grow.

The OVLS deposition is started by extensively cleaning a substrate in a series of 20 minute ultrasonic baths first in nanopure water, then wash grade acetone, and finally HPLC grade isopropanol. The substrate is then UV-Ozone treated for 20 minutes to prepare for spin casting. Gas chromatography grade squalane, 2,6,10,15,19,23-hexamethyltetrasosane, is used as a low vapor pressure solvent and is spun onto the substrate. The rate and time of spinning determines the liquid film thickness and has been calibrated to achieve reproducibly thick

\[
y = 10882x + 80
\]

\[
y = 4630x^{0.49}
\]

\[
(4.14 \times 10^6)x^{-1.02}
\]

**Figure 3.2:** Liquid layer thickness calibration plots. (A) The thickness of the liquid layer controlled by dilution with hexanes gives the ability to reach 100 nm thick films. The equation for the line is \( y = 10882x + 80 \). (B) Liquid thickness compared to spin time was fit the function \( y = 4630x^{0.49} \). (C) Thickness with respect to spin rate fits the equation \((4.14 \times 10^6)x^{-1.02}\)
liquid layers. Thickness calibration was done with UV-VIS interferometry as seen in Figure 3.2. Immediately after spin casting, the substrate is attached to the lid of the deposition chamber directly above the nozzle. A pump/purge cycle removes oxygen; solid tetracene (2,3-Benzoanthracene, TET) is then sublimed. The vaporized TET travels up the nozzle which is sealed by a metal shutter. After temperature stabilization the shutter is opened and the impinging nitrogen gas carries sublimed TET vapor to the substrate. The design of both the nozzle and crucible creates a system where there is constant flux of monomers independent of the mass of the organic solid in the crucible.

The design of the chamber allows for tight control over induction times and crystal densities. Through the control of the flux rate the chamber controls the supersaturation ratio with respect to time, which allows for control over the transient burst nucleation regime. As new crystals nucleate the flux remains constant. The concentration of dissolved monomer changes with respect to the removal of monomers by critical clusters and stable crystals. Nucleation stops after the monomer concentration drops below the critical supersaturation, and the growth of the crystalline material continues controlled only by the flux rate.

Section 3.2: Chamber Design and Properties

The OVLS deposition apparatus is in its fifth iteration of design. The current version was designed and assembled by Alex Baranov and Dane Stanfield, with further modifications and improvements added more recently by the author. The flux of monomers is controlled via the temperature of the stainless-steel crucible, which is heated by a coiled nichrome wire and ceramic heating blocks. Resistive heating causes the temperature of the crucible to rise and is controlled by a Digi-Sense temperature controller attached to a variac power supply. The temperature is monitored by a calibrated thermocouple placed directly below the vessel. By
heating the solid TET to a specified temperature, well above the sublimation temperature, the crucible is designed such that a constant flow of monomers escapes through a small opening in the lid of the holding cell. The opening, which is less than 1 mm in diameter, is inset by 18 mm into the crucible. TET vapor can only escape from the small hole in the top of the chamber, acting as a quasi-Knudsen cell. This means that the partial pressure of the vapor in the cell is constant as a small amount of vapor diffuses out of the holding cell. The sublimation rate is sufficiently high so that the organic vapor leaving the cell is independent of its remaining mass inside the crucible. Thus the flux reaching the substrate is controllable based on the temperature of the crucible and the flow rate of the carrier gas.

Ultra-high purity nitrogen gas carries TET through the 95.25 mm tall and 19.05 mm wide nozzle to the substrate. At the top of the nozzle there is a gradual contraction to 12.7 mm at the opening, creating a flat flow velocity profile impinging on the substrate. This results in a constant flux rate of TET vapor over a 1 cm² area. The gradual contraction of the nozzle causes the Reynolds number of the gas flow to be made very low, \( Re = \frac{Ud}{\nu} \approx 175 \), where the gas flow rate, \( U \), is about 1.0 m s⁻¹, the diameter of the nozzle is \( d \), and the gas velocity is \( \nu \), without disturbing the overall direction the vapor travels out of the nozzle. A low Reynolds number is indicative of a flat laminar flow profile. The flat profile of the gas flow allows for the impinging jet of carrier N₂ to be modeled as an axisymmetric point flow. This means that the flow of vapor is radially symmetric when it arrives on the substrate. This symmetry allows for the modeling of the gas flow dynamics as a two-dimensional system where there is a diffusive boundary layer and an outer flow region. The outer flow region can be modeled by the vertical and radial velocity components of the gas flow.

\[
\nu_r = \nu r \tag{3.1a}
\]
\[ \nu_z = -2 \nu z \]  

3.1b

The radial velocity depends only on the geometric and flow velocity constant, \( \nu \), and the radial distance from the center of the impinging jet, \( r \), whereas the vertical component of the velocity also depends on \( \nu \) but only on the distance from the nozzle to the substrate \( z \). Therefore, if particles were to aggregate in the gas phase there would be no effect on the radial distribution of particle sizes which enter the diffusive boundary layer. Transport through the diffusive boundary layer is dictated by gravitational, electrostatic, thermophoretic, and diffusive forces. In an experiment reported in reference 62, the only forces that had a large impact on the flux of monomers \( J \), which dissolve into the liquid layer, were the diffusive forces. The flux of monomer diffusing into the liquid layer is calculated via the following equation:

\[ J \approx \frac{c_o B S c^{1/3} R e^{1/2} D}{d} \]  

3.2

where \( c_o \) is the concentration of tetracene in the gas, \( B \) is a constant that depends on the experimental geometry of the flow of the gas, the Schmidt number is \( Sc = \nu / D \), and \( D \) is the diffusion constant. The diffusion constant can be calculated via Epstein’s equation:

\[ D_l = \frac{3}{8 \rho r_p^2 \delta} \sqrt{\frac{m k T_g}{2 \pi}} \]  

3.3

where \( \delta = 0.91 \) is the accommodation coefficient. From equation 3.2 an accurate value for the particle flux through the diffusive layer can be calculated to determine the diffusive efficiency of the system \( \epsilon \). The diffusive efficiency \( \epsilon = \frac{J}{J_{c}} \) is the fraction of monomers which are deposited onto the substrate and are carried through the diffusive layer by the carrier gas jet. For the OVLS method \( \epsilon = 10 \pm 5\% \) which is higher than both PVD and organic MBE film growth methods.
A Peltier thermoelectric temperature controller is used to control the temperature of the substrate before and during deposition. The temperature controller was built in house out of several high temperature Peltier thermoelectric devices. The temperature controller shown in Figure 3.3 is secured to the lid of the deposition chamber. Liquid cooling attached to the top of the chamber serves as heat sink for the whole device. Temperature is monitored and controlled by a thermocouple positioned behind the substrate and a Watlow temperature controller. The controller changes the direction of the current through the Peltier devices and is able to maintain a set substrate temperature.

Figure 3.3: Peltier thermoelectric temperature controller attached to lid of the deposition chamber.

Calibration measurements showed that the device holds substrate temperature constant with a precision of about ± 5 °C. To calibrate the temperature controller an OVLS deposition was run with a 100 nm thick liquid layer and a crucible temperature of 200 °C both with and without the controller. Substrate temperature without any form of temperature control or external cooling source raised 25 °C after the onset of flux, and over the course of a one-and-a-half-hour deposition the substrate raised another 50 °C. Within the first 10 minutes the temperature raised 15 °C, which impacted the solubility of the TET as well as the surface energy of the squalane-TET interface. This change in substrate temperature greatly impacts the relevant constants for application of physical models. When the same experiment was run
while using the temperature controller set to 50 °C, a similar initial spike was observed; yet the temperature ended up at a constant over longer times. Figure 3.4 shows that the temperature controller’s ability to reverse the current through the linked Peltier thermoelectric devices the system is able to maintain a constant substrate temperature of around 60 °C.

Figure 3.4: Substrate temperature measurements. The nozzle side of the substrate measured with a calibrated thermocouple started collection during the crucible ramping phase. At 10 minutes the shutter was opened and temperature measurements were continued by taking a reading every 5 minutes.

Section 3.3: In situ Video Microscopy

A camera secured above the microscope objective collects in situ video data of all burst nucleation regimes through the use of several different imaging techniques: epifluorescence, bright field, and dark field imaging, as shown in Figure 3.5. The nucleation of crystalline material is monitored by epifluorescence microscopy collected using a Black Fly PGE505HM-5M CCD camera. Crystals are excited by a 475 nm light emitting diode (LED) via a fiber optic wave guide. Excited crystalline tetracene emits light at 535 nm which is collected by the
camera through a band pass filter, centered at 535 nm with a full width half max of 35 nm, allowing for early detection of crystalline material.

**Figure 3.5**: Optical diagrams for various imaging methods. Bright field microscopy is used for growth measurements, epifluorescence is used for crystal nucleation imaging, and dark field fluorescence is used for solution phase monomer diffusion imaging.

Bright field microscopy, using a 475 nm LED point light source placed directly below the substrate, is used to determine the growth rate of crystalline material. Crystalline tetracene absorbs the 475 nm light and by using a 472 nm band pass optical filter all other wavelengths are filtered out. The only light which reaches the camera unabsorbed is 475 nm light from the LED. This causes the crystals to have a lower intensity than the background and are viewed as dark rod-like shapes, Figure 3.5. To calculate volume the cross-sectional area and the thickness must be determined from in situ bright field videomicroscopy. The cross-sectional area can be directly measured from the footprint of the crystal, but crystal thickness requires calibration from optical pixel brightness to thickness.
As the crystal grows in thickness more of the light from the LED is absorbed and the crystal becomes darker, affecting its gray scale pixel value from 0-255. To calibrate the absorbance of the crystal with its thickness, a model deposition was run with a 100 nm thick film, and a bright field microscopy video was taken over the course of two hours. Immediately

Figure 3.6: Crystal absorbance to thickness calibration. Crystals selected for AFM analysis are shown above. Left image is from the AFM whereas the right image is from bright field microscopy after crystal growth was finished. Below the crystals is a calibration curve made from the transmittance of optical pixels in several crystals compared to the pixels thickness.
afterward the substrate was removed from the chamber. Several representative crystals were selected for thickness measurement by atomic force microscopy. The absorbance $A$ of a crystal was calculated by:

$$A = \log\left(\frac{I_0}{I_a}\right)$$

where $I_0$ is the average pixel intensity of the background and $I_a$ is the average pixel intensity of the crystal. With these measurements a calibration curve from optical pixel value to thickness was found to have the function

$$Z_{AFM} = \log\left(\frac{I_0}{I_a}\right) 404.47 - 10.3$$

where $Z_{AFM}$ is the thickness of the crystal, in nm, measured by AFM, Figure 3.6.

Dissolved monomer concentration is visualized though the use of a fiber-optic ring light. Laser light at 405 nm is brought into the chamber through a window in the lid of the chamber. For these sensitive measurements the previously used camera was replaced with an ORCA Flash 4.0-LT camera. Each imaging band was selected for with an optical band pass filter. The dissolved monomer fluorescence filter was centered at 472 nm with a full width half max, FWHM, of 23 nm; the crystal fluorescence filter was centered at 535 nm with a FWHM of 25 nm; and the reference dye filter was centered at 700 nm with a FWHM of 50 nm. Refer to chapter 5 for a comprehensive explanation into the optical microscopy method.

**Section 3.4: Measurement of Certain Physical Properties of Tetracene and Squalane**

The flux rate was computed through calibration of the induction time. A substrate was prepared as previously described, then an aluminum foil mask was attached above the liquid layer allowing only 1 cm$^2$ of the liquid layer to be exposed to the impinging flux of TET monomer. A flux of vapor was applied to the exposed area of the substrate for precisely 15
minutes while monitoring the film with *in situ* epifluorescence microscopy. The substrate was removed from the chamber and the deposited TET was dissolved in 2 mL of toluene. Then a fluorescence emission spectrum of deposited TET in wash grade toluene was taken with an excitation wavelength of 443 nm and an emission range of 450 – 600 nm with a 1 nm step size and 1 second integration time using a Horiba Fluorolog FL-1039/40 fluorimeter. Calibration of the integrated counts allowed for determination of the concentration of TET on the substrate after 15 minutes of OVLS deposition, Figure 3.7. From the concentration the flux rate was determined by taking into account the area that was exposed, the time that flux was applied to the substrate, and the concentration of TET on the substrate. The critical supersaturation $n^*$ was computed from the flux rate and the induction time to be $1.57 \times 10^{24}$ monomers m$^{-3}$. The flux rate for every model deposition is calculated from $n^*$ and the induction time of the deposition.
The solubility of TET in squalane was determined by adding TET in excess to 4 mL of squalane. The solution vial was purged with nitrogen for 10 minutes then placed in an oven set to 22 °C. The solution was allowed to dissolve for two days, creating a saturated solution. After equilibrating to the oven temperature, 0.1 mL of toluene was taken into a warm gas-tight syringe. While the vial was still in the oven 0.1 mL of the squalane/TET solution was added to the syringe. This solution was added to 2.5 mL of toluene and a fluorescent emission spectra was taken in triplicate at 443 nm excitation and an emission range 500 – 530 nm with 1 nm step size and 1 second integration. The signal was converted into a concentration by a calibration curve and the process was repeated for each temperature listed in table 3.1.

**Figure 3.7:** Emission spectra of TET in toluene at various concentrations (g/L) the one titled OVLS was obtained by dissolving TET in toluene after 15 minutes of OVLS deposition. Inset: The calibration curve created from the integral of the emission spectra of various known concentrations of TET in toluene used to determine the concentration of TET squalane after 15 minutes of OVLS deposition at a crucible temperature of 210 C.
Table 3.1: Tetracene Solubility in Squalane.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Solubility (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>0.03</td>
</tr>
<tr>
<td>45</td>
<td>0.20</td>
</tr>
<tr>
<td>69</td>
<td>0.95</td>
</tr>
<tr>
<td>80</td>
<td>1.56</td>
</tr>
<tr>
<td>92</td>
<td>1.88</td>
</tr>
</tbody>
</table>

The temperature-dependent solubility data are fit in Figure 3.8 using the function:

\[
\ln(X) = \frac{-\Delta H_{fus}'(T_{fus}' - T)}{R T_{fus}' T} \tag{3.6}
\]

where \(X\) is the mole fraction of TET in a saturated squalane solution, \(\Delta H_{fus}'\) and \(T_{fus}'\) are treated as fitting parameters and \(R\) is the gas constant. This equation is based on the ideal solubility

Figure 3.8: Temperature-dependent solubility of TET in squalane. Error bars represent the 95% confidence intervals based on 3 replicate measurements. Solid line is a fit using the equation described in the text.
of crystalline solutes in a liquid solvent under the approximation that the difference between
the molar heat capacity of the crystalline form and the molar heat capacity of the hypothetical
supercooled liquid form is zero. The fitting parameters are found to be $\Delta H'_{fus} = 50.0 \text{ kJ mol}^{-1}$
and $T'_{fus} = 605 \text{ K}$, which gives a solubility $n_o = XN_A/V_m = 3.36 \times 10^{23} \text{ molecules m}^{-3}$ at $T = 333 \text{ K}$, where $N_A$ is Avagadro’s number and $V_m$ is the molar volume of squalane. The values
of the fitting parameters may be compared to the known heat of fusion and melting temperature
of TET, which are $35.9 \text{ kJ mol}^{-1}$ and $623 \text{ K}$, respectively. The measured solubility of TET in
squalane is about an order of magnitude smaller than that predicted for an ideal solution over
the temperature range in Figure 3.9.

The TET-squalane interfacial energy $\gamma_{SL}$ was computed using Young’s equation:\(^{68}\)

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\cos\theta$$  \hspace{1cm} 3.7

where the temperature dependence of the squalane-air interfacial energy $\gamma_{LG}$ is taken from
Reference 69:

$$\gamma_{LG} (\text{mN/m}) = 28.15 - 0.72(T - 293\text{K})$$  \hspace{1cm} 3.8

Contact angle measurements by surface tensiometery of squalane on bulk tetracene give $\theta \sim 9^\circ$. 

36
The Zisman plot gives TET-air interfacial energy $\gamma_{SG}$ by determining where the plot of the $\cos\theta$ against $\gamma_{LG}$ of various known surface energy liquids, water, diethylene glycol, Formamide, ethylene glycol, propylene glycol, and bis(2-ethylhexyl) sebacate, intercepts $\theta = 0^\circ$ giving $\gamma_{SG} = 30.09$ mN/m (Figure 3.9).\(^{70-72}\) Young’s equation gives $\gamma_{SL} = 5.13$ mN/m.

The temperature- and pressure-dependent viscosity of squalane is computed using:\(^{73}\)

$$\eta = \eta_o \left(\frac{P+E}{P_0+E}\right)^D \quad 3.8a$$

where

$$\eta_o = A \exp\left(\frac{B}{T+C}\right) \quad 3.8b$$

$$D = \sum_{i=0}^{2} d_i (1/T)^i \quad 3.8c$$

$$E = \sum_{i=0}^{2} e_i (1/T)^i \quad 3.8d$$

**Figure 3.9:** Zisman plot for the determination of the squalane-tetracene interfacial energy. The plot is constructed of water, diethylene glycol, Formamide, ethylene glycol, propylene glycol, and bis(2-ethylhexyl) sebacate.
Here $P = P_0 = 0.1$ MPa is the pressure, $T$ (K) is temperature, and the constants $A = 0.07610$ mPa s, $B = 752.8$ K, $C = -170.7$ K, $d_o = -4.488$, $d_1 = 3330$ K, $d_2 = 17,360$ K$^2$, $e_o = -468.4$ MPa, $e_1 = 5.072$ MPa K$^{-1}$, and $e_2 = -0.007421$ MPa K$^{-2}$. This gives $\eta = 7.87$ mPa s at $T = 333$ K.

The temperature- and pressure-dependent density of squalane is computed using: $^7$3

$$\rho = \rho_o \left[1 - J \log_{10} \left( \frac{P+G}{P_o+G_o} \right) \right]^{-1} \tag{3.9a}$$

where

$$G = \sum_{i=0}^{2} g_i(T)^i \tag{3.9b}$$

$$\rho_o = \sum_{i=0}^{2} h_i(T)^i \tag{3.9c}$$

Here $P = P_0 = 0.1$ MPa is the pressure, $T$ (K) is temperature, and the constants $g_0 = 0.2000$ MPa, $g_1 = 382.2$ MPa K$^{-1}$, $g_2 = -1.162$ MPa K$^{-2}$, $h_0 = 978.9$ Kg m$^{-3}$, $h_1 = -0.5355$ kg m$^{-3}$ K$^{-1}$, $h_2 = -1.571 \times 10^{-4}$ kg m$^{-3}$ K$^{-2}$, and $J = 9.305 \times 10^{-4}$. This gives $\rho = 7.832$ kg m$^{-3}$ at $T = 333$ K.
Crystalline TET has been found to have a single major polymorph with a crystallographic orientation of \{001\} and causes uniform extinction, Figure 3.10. In order to confirm crystallinity and morphology of TET thin film grown through OVLS, polarized optical microscopy and x-ray diffraction (XRD) are used to analyze substrates after deposition. From polarized optical microscopy, we see that single crystalline material will rotate polarized light to a singular direction causing uniform extinction of continuous crystals, Figure 3.10. Through the use of this property, crystals can be separated from each other and the morphology of the

**Figure 3.10:** Polarizing optical microscopy images. Crystals are viewed at three orientations of the sample stage and undergo uniform extinction.

**Figure 3.11:** X-ray diffractogram of a representative TET film after rinsing with hexanes to remove squalane. The peak at 32° is due to the Indium-Tin-Oxide substrate.

Crystalline TET has been found to have a single major polymorph with a crystallographic orientation of \{001\} and causes uniform extinction, Figure 3.10. In order to confirm crystallinity and morphology of TET thin film grown through OVLS, polarized optical microscopy and x-ray diffraction (XRD) are used to analyze substrates after deposition. From polarized optical microscopy, we see that single crystalline material will rotate polarized light to a singular direction causing uniform extinction of continuous crystals, Figure 3.10. Through the use of this property, crystals can be separated from each other and the morphology of the
film can be documented and studied. XRD allows for the determination of the crystallographic orientation and molecular scale crystal morphology. Crystalline TET generally forms in the \{001\} crystallographic orientation (Figure 3.11) making it a good model compound for the study of nucleation and growth kinetics.

Through the use of our custom apparatus and the measured experimental constants thin film depositions can be performed with high reproducibility. The controlled deposition environment allows for the development of accurate models in both nucleation and growth of OMC thin films. The following sections outline these models and their impact on the design of organic polycrystalline thin films.
**Chapter 4: Predictive Modeling of Polycrystalline Thin Film Nucleation**

**Section 4.1: Mean Field Rate Equation Model**

The model we have developed to treat the nucleation kinetics begins by considering the time evolution of the number of crystals formed per unit volume of solution (crystal density, $N$) as the monomer chemical potential $\mu_1(t)$ is driven toward and ultimately beyond a critical level inducing crystallization. $N(t)$ is a central quantity governing film structure; it determines the average domain size at high coverage (~1 ML), and is connected to the crystal size distribution and spacing statistics at all coverages. The method for driving $\mu_1(t)$ may vary depending on the experimental details, including solvent evaporation, a reduction in temperature of a saturated solvent, and introduction of an anti-solvent. The following analysis considers the situation where $\mu_1(t)$ is driven via the continual addition of new monomers to a quasi-2D liquid solvent layer having fixed volume, temperature and pressure. This is the situation represented by our experimental system, in which fresh monomers are continually and uniformly added to a thin liquid solvent layer coating a glass substrate at a constant flux rate $F$ (monomers $\mu$m$^{-3}$ s$^{-1}$). New monomers are carried by a gas flow impinging onto the surface of the solvent layer, which undergoes negligible evaporation due to its low vapor pressure. Once a monomer impinges and dissolves into the solvent it is assumed irreversibly trapped in the liquid. It is important to note that, within the context of the model, at an early stage of film formation this method of driving $\mu_1(t)$ is functionally equivalent to evaporating solvent from a saturated solution at a fixed rate; here monomers are added to a fixed initial solvent volume, rather than fixing the initial number of monomers and decreasing the volume. OVLS deposition method enables greater experimental control over the driving rate.
\[ \frac{d\mu_1(t)}{dt}, \] it produces large, high-quality crystallites suitable for device applications, and it enables growth of molecular films from compounds of even very low solubility.\(^7\)\(^5\)

Crystal formation and the addition and loss of monomers to/from solution can be treated using a set of coupled mean-field rate equations governing the concentrations of monomers \((n)\) and crystals \((N)\):\(^5\)\(^2\)

\[
\frac{dn}{dt} = F - KP(i^*, n)n - KnN \quad \text{4.1a}
\]

\[
\frac{dN}{dt} = KP(i^*, n)n \quad \text{4.1b}
\]

here \(K\) \((\text{m}^3\text{s}^{-1})\) is a collision/capture kernel for the rate of uptake of monomers by crystals, and \(P(i^*, n)\) is the concentration of aggregates of size \(i^*\) at concentration \(n\), where \(i^*\) is one monomer less than the critical nucleus size. The collision kernel was modeled with a Smoluchowski function for diffusion limited coalescence of spherical particles with diffusivity \(D\): \(K = \gamma 4\pi \left( a + ai^{*2/3} \right) \left( D + Di^{*-1/3} \right) \approx \gamma 4\pi ai^{1/3} D\), where \(\gamma\) is a parameter that is used to correct for microscopic processes that have been omitted from the full kernel, such as the effects of attractive or repulsive intermolecular forces on the aggregation rate.\(^7\)\(^6\) The function \(P(i^*, n)\) was derived from the free-energy change for the formation of aggregates of size \(i^*\) in the solvent, which is given by:\(^7\)\(^7\)\(^-\)\(^8\)

\[
\Delta G_i(n) = -(i - 1)kT \ln(n/n_0) + 4\pi \sigma a^2(i^{2/3} - 1). \quad \text{4.2}
\]

The concentration of critical clusters, \(P(i^*, n) = n \exp[-\frac{\Delta G_i}{kT}]\), is then

\[
P(i^*, n) = n \left( \frac{n}{n_0} \right)^{i^*-1} \exp \left[ -\frac{4\pi \sigma a^2(i^{2/3} - 1)}{kT} \right], \quad \text{4.3}
\]

where \(n_0\) is the equilibrium saturation value of monomers in the solvent, \(\sigma\) is the solid-liquid interfacial energy associated with the formation of the cluster, \(k\) is the Boltzmann constant,
and $T$ is the solvent temperature. Because temperature is held fixed in our experiment, the
temperature-dependence of $n_0$ and $D$ is omitted. In this treatment, only two cluster sizes,
monomers and stable crystals, are considered combining all other cluster sizes into these binary
categories. This approach is consistent with dividing the complete (infinite set of) rate
equations for clusters of all sizes into subcritical (assumed to be dominated by monomers) and
stable sizes, and summing over the stable crystals to create a net stable density.$^{47-48}$ The units
in Equations 4.1 are of volumetric flux, i.e. number per volume per time.

A key feature of this formulation, necessary for the accurate description of
crystallization in solution, is that $i^*$ is a function of the monomer concentration.$^{52}$ In classic
MFRE models treating submonolayer island nucleation in films prepared by PVD, $i^*$ is always
assumed constant, independent of the adatom coverage. This approximation is possible when
$i^*$ is small ($\leq \sim 5$), as is normally the case in vacuum nucleation. However for molecular
crystallization in a liquid solvent, where $i^*$ is much larger ($\gg 10$, see below), the assumption
$i^* = \text{constant}$ is no longer adequate. Treating the critical size $i^*(t)$ as a dynamical variable
thus distinguishes the present treatment from classic MFRE models of submonolayer island
formation in vacuum-deposited films, and turns out to be a necessary ingredient to describe
nucleation behavior in the liquid environment. $i^*(t)$ is derived assuming homogeneous
nucleation using classical nucleation theory (CNT) based on the free energy of formation of
spherical clusters of size $i^*$ at (supersaturated) concentration $n$, which gives$^{47,52}$

$$i^*(n) = \left( \frac{8\pi \sigma a^2}{3kT \ln\left( \frac{n}{n_0} \right)} \right)^{3/2}.$$  \hspace{1cm} 4.4

It is important to note that more sophisticated and potentially more accurate expressions for
$i^*(n)$ are available using contemporary theories of nucleation (see for example Reference 41),
but for the sake of simplicity and because the present approach already provides good agreement with experiment, here CNT is used to describe the critical nucleus size and its dependence on supersaturation $n/n_o$.

Section 4.2: Variable Flux Analysis

![Image](image.png)

**Figure 4.1:** An epifluorescence micrograph showing a representative TET film. The boxed area is an analysis region for nucleation modeling measurements. Scale bar is 100 µm.

A representative epifluorescence micrograph showing a typical film is presented in Figure 4.1. TET crystals are visible as bright, rod-shaped features, and grow with thin prismatic morphologies, reaching an eventual size of 10 - 100 µm in length and 100 - 150 nm in thickness as measured by atomic force microscopy, about equal to the thickness of the liquid solvent layer. The observed growth habit is much less compact than the predicted equilibrium barrel morphology, and more elongated than the predicted growth morphology, which is plate-like, based on shape simulations from molecular binding energies.\textsuperscript{79-81} Films prepared at significantly lower flux rates than those reported here included a higher proportion of crystals with plate-like morphologies, suggesting the elongated shape is kinetically influenced. The
{001} form dominates all others, comprising ~97% of total crystal surface area. Growth of this form is very slow, and limited to dislocations except at very high driving forces.\textsuperscript{79}

To gain further understanding about solvent nucleation, this work is interested in comparing the time evolution of the experimentally-measured nucleation rate $dN/dt$ and crystal density $N(t)$, to Equations 4.1. Each is readily determined simply by counting the number of crystals in each video frame. The results are shown in Figure 4.2 for films prepared using several different flux rates, where the origin on the time axis corresponds to the onset of monomer flux, initiated by opening a shutter. Three distinct regimes may be identified: \textsuperscript{52} (i) an induction regime between the onset of deposition and the first appearance of crystals. Its duration depended on $F$ (i.e. on both the areal flux rate and the solvent layer thickness), being shorter for higher rates. Since the smallest crystal which could be detected was $\sim 1 \, \mu m^2$ in area, and since during the nucleation regime crystals grew in size at a rate of $\sim 10 \, \mu m^2 \, min^{-1}$, the induction time coincided to within $\sim 6 \, s$ with the first appearance of crystals in the video images, which were acquired in $5 \, s$ intervals. (ii) The induction regime was followed by a nucleation regime during which all crystals formed in a narrow time interval lasting $30 \, - \, 60 \, s$. In terms of 2D coverage, the projected fractional surface area occupied by crystals was $\sim 1\%$ at the peak nucleation rate, increasing to $\sim 2\%$ by the time nucleation ceased. (iii) The
nucleation regime was followed by a growth regime during which crystals increased in size but no new crystals formed.

**Figure 4.2.** Time-dependent nucleation rate for TET films prepared using four different flux rates. The flux in units of $10^{21}$ monomers m$^{-3}$ s$^{-1}$ is indicated for each sample. Nucleation occurs in a brief burst, preceded by an induction regime and followed by a growth regime. Inset shows the time-evolution of the number of crystals per unit area. Solid lines result from fitting using Equations 4.1.

The solid-line fits in the inset of Figure 4.2 were obtained by numerical integration of Equations 4.1, using experimental values for all the relevant parameters ($n_0 = 3.36\times10^{23}$ m$^{-3}$, $a = 4.09\times10^{-10}$ m, $D = 7.58\times10^{-11}$ m$^2$ s$^{-1}$, and $T = 333$K). Fits were obtained by varying the Smoluchowski correction parameter $\gamma$ and the surface energy $\sigma$, which are challenging to independently measure experimentally. This gave (in order of increasing flux): $\sigma = 24$ mN m$^{-1}$, $\gamma = 13.6$; $\sigma = 24$ mN m$^{-1}$, $\gamma = 12.6$; $\sigma = 23$ mN m$^{-1}$, $\gamma = 11.9$; and $\sigma = 23$ mN m$^{-1}$, $\gamma = 14.4$, respectively. The independently fit Smoluchowski coefficients and surface energies are thus very consistent between independent experiments, and essentially independent of $F$, as expected. To compare the experimentally-measured critical concentration $c^*$ to the critical concentration $n^*$ implied by solving the MFREs, the latter being defined as the concentration
at which the nucleation rate becomes high enough to produce an average of one crystal per video frame (i.e. every 5 s) within a volume of solvent equal to that visible within the observation area (1.56×10^{-13} \text{ m}^3). Using this definition, the average critical concentration determined from the fits in Figure 4.2 is \( n^* = (2.1\pm0.3)\times10^{24} \text{ m}^{-3} = 3.5 \text{ mM} \) again essentially independent of \( F \), which compares to the experimental value \( c^* = (1.6\pm0.2)\times10^{24} \text{ m}^{-3} = 2.7 \text{ mM} \). Equations 4.1 are thus able to quantitatively capture all the major features of nucleation in these films, including the existence and duration of the induction, nucleation, and growth regimes, and the flux-dependence of the nucleation rate, onset time of nucleation, and limiting crystal density at high coverage.

Section 4.3: Determination of Critical Nucleus Size

Before proceeding to discuss application of the model to the treatment of crystal spacing statistics, it is instructive to examine the action of the concentration \( P(i^*, n) \) and \( i^* \) during the time integration of Equations 4.1. The integration is done numerically, updating the monomer and stable crystal concentrations, as well as the critical cluster concentration and the critical size, at each time step. The characteristic burst of nucleation seen in Figure 4.2 arises from the interplay of \( i^* \) and \( P(i^*, n) \); at low monomer density (but still maintaining supersaturation with \( n > n_0 \)) the critical size is large, and thus \( P(i^*, n) \approx 0 \), and the nucleation rate (given by \( KP(i^*, n)n \)) is suppressed. In this case, the monomer density increases linearly with flux. As the monomer density increases, \( i^* \) decreases, and eventually \( P(i^*, n) \) increases sharply, triggering a burst of nucleation. Following nucleation, the uptake of monomers by stable crystals (governed by the third term on the right in Equation 4.1a) becomes appreciable, and the critical size again increases, accompanied by a corresponding decrease in the concentration of clusters of size \( i^* \), and nucleation is once again arrested. The evolution of the
critical cluster size and concentration with time are shown in Figure 4.3, using the same parameters as Figure 4.2. The general behaviors described above are evident: the nucleation regime is demarked by a minimum in the critical size and a corresponding maximum of the critical concentration. Several other features are also apparent. Since the nucleation rate is proportional to $P$, we see that the origin of the flux dependence of the limiting crystal density $N_{max}$ stems from the increase in the maximum $P_{max}$ with flux. In addition, the width of the critical size concentration peak decreases markedly with increasing flux, and therefore the nucleation regime becomes shorter in duration, resulting in a more rapid increase in $N$ with increasing flux. The same behavior is also observed in the experimental results of Figure 4.2.

According to the results in Figure 4.3, the critical nucleus size at the onset of nucleation (i.e. at $n = n^*$) is $i^* \approx 59$ monomers for all four flux rates studied, close to the previously reported minimum critical size of TET in the organic solvent bis(2-ethylhexyl)sebecate ($i^* \approx$...
This may be compared to the critical nucleus size of TET in vacuum-deposited films, which was estimated to be $i^* \approx 3$ on bare SiO$_2$, and to that of structurally similar compounds such as pentacene ($i^* \approx 6$ on Si(001)) and sexithiophene ($i^* \approx 5$ on H-terminated Si(100)). $i^*$ is thus consistently about an order of magnitude larger in the liquid solvent environment than in vacuum.

**Section 4.4: Radial Probability Analysis**

Next it is shown how the model can be used to understand another important morphological property of solution-processed polycrystalline films, namely, the relative spatial separation of crystalline domains. A close examination of images such as the one in Figure 4.1 indicates the positions of crystals are not entirely random in these films, rather they tend to be more widely separated than would be expected for complete spatial randomness (CSR), i.e. a 2D Poisson distribution. This effect is shown more clearly in Figure 4.4, which shows the evolution of the mean nearest-neighbor spacing $\bar{d}_{nn}$ as a function of crystal density $\rho$ (crystals um$^{-2}$) during the nucleation regime for the same four flux rates examined above. Each symbol type in Figure 4.4 represents a different flux rate, all of which fall onto a single universal curve. Initially, when few crystals have formed and they are widely separated, their spacing statistics agree with a random distribution, $\bar{d}_{nn}^{CSR} = 1/(2\sqrt{\rho})$ (solid line in the main part of Figure 4.4). As the density increases however, $\bar{d}_{nn}$ begins to deviate from $\bar{d}_{nn}^{CSR}$, eventually exceeding it by about 20% when nucleation finally ceases at the highest flux. The inset compares the experimental and CSR mean nearest-neighbor spacing probability distributions at the end of the nucleation regime for one particular film ($F = 18.0 \times 10^{21}$ um$^{-3}$ s$^{-1}$). The CSR distribution is given by $P_{CSR}(r)dr = 2\pi r \rho e^{-\pi \rho r^2} dr$, where $r$ is the radial distance and $\rho_{av} = 8.1 \times 10^{-5}$ μm$^{-2}$ is the average areal density of crystallites. Compared to the
CSR model, the experimental distribution is skewed toward larger nearest-neighbor spacing, and no crystals are observed to form closer than about 25 μm from their nearest neighbor. The distributions produced by other flux rates are qualitatively similar.

The trends in Figure 4.4 indicate nucleation is suppressed near crystals that have already formed, a well-known consequence of diffusion-mediated competition for growth units. The effects are shown clearly in the radially-averaged crystal separation probability distribution, $\rho(r)$, equal to the probability of observing a crystal separated by distance $r$ from

**Figure 4.4:** Crystal spacing comparison during the nucleation regime. At the beginning of the nucleation regime, the first crystals to become visible are randomly positioned with nearest-neighbor (NN) spacing close to a CSR (2D Poisson) distribution (line). As the density increases, the mean NN spacing remains larger than that predicted by the 2D Poisson distribution, indicating suppressed nucleation in the vicinity of crystals that have already formed due to competition for monomers. Legend: squares, $F = 8.0 \times 10^{21} \text{ m}^{-3} \text{ s}^{-1}$; circles, $F = 11.0 \times 10^{21} \text{ m}^{-3} \text{ s}^{-1}$; upward triangles, $F = 12.8 \times 10^{21} \text{ m}^{-3} \text{ s}^{-1}$; downward triangles, $F = 18.0 \times 10^{21} \text{ m}^{-3} \text{ s}^{-1}$. (inset) Comparison of the experimental (bars) and Poisson (line) NN spacing probability distributions at the end of the nucleation regime for $F = 18.0 \times 10^{21} \text{ m}^{-3} \text{ s}^{-1}$. 
another crystal (Figure 4.5). In references 87 and 88 Evans and Bartelt postulated a radial probability distribution for 2D island nucleation in vacuum-deposited films of the form:

\[
\rho(r) = J[n(r)]/[n(r = \infty)],
\]

where the nucleation rate \( J \) is proportional to

\[
J \propto n(r)^{\nu+1},
\]

using the Walton relation. The main ideas of this approach are used here, but we modify the details to account for the concentration-dependent critical nucleus size and the kinetics of nucleation in a supersaturated solvent.

**Figure 4.5:** Comparison of the experimental crystal separation probability distribution to the predicted distribution given by the treatment described in the text (solid lines). Inset shows unscaled distribution. Legend: squares, \( F = 8.0 \times 10^{21} \text{ m}^{-3} \text{ s}^{-1} \); circles, \( F = 11.0 \times 10^{21} \text{ m}^{-3} \text{ s}^{-1} \); upward triangles, \( F = 12.8 \times 10^{21} \text{ m}^{-3} \text{ s}^{-1} \); downward triangles, \( F = 18.0 \times 10^{21} \text{ m}^{-3} \text{ s}^{-1} \). Line color is matched to symbol color.

Equation 4.5 equates the probability of observing a crystal at a distance \( r \) from a given crystal with the nucleation rate at \( r \), itself a function of the monomer concentration at that distance, \( n(r) \). Note that the function \( n(r) \) is the position-dependent monomer density, measured with respect to a crystal center—in contrast to the monomer and crystal densities
calculated via Equations 4.1a and 4.1b, which are average (mean-field) quantities. For the discussion here, the average monomer density is denoted by \( n(r = \infty) = \langle n \rangle \). The function \( n(r) \) may be constructed by solving the appropriate diffusion equation for monomers in the presence of a (constant) flux and an island sink. The problem is made tractable by careful consideration of the boundary condition on \( n(r) \) as \( r \to \infty \), where the solution for \( n(r = \infty) = \langle n \rangle \) is governed by equations 4.1a and 4.1b, which will be elucidated in detail below.

The appropriate diffusion equation is given by

\[
\frac{\partial n(r)}{\partial t} = D \nabla^2 n(r) + F - D \xi^{-2} n(r)
\]  
4.7

where \( D \) is the monomer diffusion constant, \( \xi \) is a characteristic diffusion length, and \( F \) is the flux rate (note that the regime was explicitly restricted to low-crystal-coverage, since the flux rate in Equation 4.7 refers to the flux of monomers into the free solvent, as opposed to impinging upon nucleated islands). In the limit of \( r \to \infty \), Equation 4.7 must recover Equation 4.1a; in this case, then, direct comparison yields, utilizing the definition of the collision kernel \( K \),

\[
\xi^{-2} = \left(4\pi a^* \right)^{\frac{1}{2}} (P(i, n) + \langle N \rangle).
\]  
4.8

To further simplify this result, note that Equation 4.7 will be solved in the physically relevant nucleation regime, when the local kinetics involve the processes of flux, nucleation, and growth, and therefore the local density variations are most significant. In the nucleation regime, \( P \approx P(i^*, n_{\text{max}}) \), where \( n_{\text{max}} \) is the peak in the monomer density (just after the onset of nucleation) from Equation 4.1a, and \( \langle N \rangle \approx \frac{1}{2} N_{\text{max}} \) where \( N_{\text{max}} \) is the final crystal density following cessation of nucleation. From the numerical solutions to 4.1a and 4.1b, we find that
under these conditions (see Figures 4.2 and 4.3) \( \langle N \rangle \gg P(n_{\text{max}}, i^*) \), and equation 4.8 simplifies to \( \xi^{-2} \approx (2\pi a i^{* \frac{1}{3}}) N_{\text{max}} \).

In order to proceed to a tractable (analytic) solution to Equation 4.7, Equation 4.8 is inserted into Equation 4.1a, and equation 4.1a is subtracted from 4.7, vis:

\[
\frac{a}{\partial t} (n(r) - \langle n \rangle) = D \nabla^2 (n(r) - \langle n \rangle) - D \xi^{-2} (n(r) - \langle n \rangle) \approx 0
\]

4.9

where, in the final step, the simplifying assumption is that time-varying deviations of the local density from the average value are negligible.\(^{89}\) In the present case, this is largely justified by the fact that in the nucleation regime, \( \langle n \rangle \) is near a peak, and its time derivative is therefore zero; since \( \langle n \rangle \) drives the time dependence of the overall concentration, the simplification is a reasonable approximation.

Solving Equation 4.9 requires a boundary condition on the monomer concentration at the crystal boundary, that is \( n(r = R) \), with \( R \) the radius of (an assumed) circular crystal. The value \( n(r = R) \) is given by a dynamic equilibrium at the crystal boundary. Since nucleation and growth are taking place in a supersaturated solution under a constant flux of fresh monomers, this boundary concentration must lie between the saturation concentration \( n_0 \) and the critical concentration \( n^* \). In particular, the value \( n(r = R) \) is set by the equilibrium between uptake of monomers by a crystal and addition of monomers at rate \( F \), which may be obtained from the rate Equations 4.1a and 4.1b. In the growth regime following the cessation of nucleation, the crystal density is constant, \( \langle N \rangle = N_{\text{max}} \), and the nucleation rate is zero, \( \frac{dN}{dt} = 0 \). Equation 4.1a then becomes \( \frac{d\langle n \rangle}{dt} = F - K_{eq} N_{\text{max}} \langle n \rangle \), where \( K_{eq} = 4\pi \gamma D (i^*)^{1/3} \) is the rate for the uptake of monomers at equilibrium. \( K_{eq} \) is computed using the value of \( i^* \) given by the critical monomer concentration \( n^* \) at the onset of nucleation, based on the experimentally-
observed nucleation time $t^*$ and flux rate. This equation has the solution $n_{eq} = \frac{F}{K_{eq}N_{max}} + c e^{-K_{eq}N_{max}t}$, so that at long times the equilibrium value for the monomer density is given by $n_{eq} = \frac{F}{K_{eq}N_{max}}$. During the nucleation regime, this concentration is used for the boundary condition $n(r = R)$. With this, the solution to Equation 4.9 is given (in plane polar coordinates) by

$$n(r) = \langle n \rangle + (n_{eq} - \langle n \rangle) \frac{K_0(\frac{r}{R})}{K_0(\frac{R}{R})}$$

4.10

where $K_0$ is the modified Bessel function of order 0, and the crystal radius $R$ is taken to equal the radius of a critical nucleus, found from Equation 4.4: $R = a(i^*(n = n^*))^{1/3}$. $\langle n \rangle$ is set equal to the average monomer concentration during the nucleation regime, found via the numerical integration of Equations 4.1. Equation 4.10 may then be used to produce the predicted function $\rho(r)$, from Equation 4.5, with the nucleation rate given explicitly by Equation 4.1b:

$$J = \frac{dN}{dt} = KP(i^*, n(r))n(r)$$

$$= \gamma 4\pi a (i^*)^{1/3} D n(r)^2 \left(\frac{n(r)}{n_0}\right)^{i^* - 1} \exp\left[-\frac{4\pi a^2 (i^*)^{2/3}}{kT}\right]$$

4.11

where $i^*$ is again concentration-dependent, and given by Equation 4.4.

Figure 4.5 shows that this treatment provides a remarkably accurate prediction of the crystal spacing statistics in these TET films over the full range of studied flux rates. The solid lines were computed for each flux rate using Equation 4.11, along with the experimentally-measured saturation and critical concentrations $n_0$ and $n^*$, and effective interfacial energy $\sigma$ determined from the MFRE treatment of the nucleation rate discussed above. Thus on the basis of the time-dependent nucleation rate alone, the radial distribution function can be
accurately predicted. Consistent with Equation 4.10, the distributions for different flux rates collapse to a single universal curve when scaled by $\xi$, which establishes a characteristic length scale for the mesoscale structure of these polycrystalline films. Nucleation is inhibited at distances $\leq \sim 3\xi$ from existing crystals, equal to about 1.4× the average nearest-neighbor spacing (for comparison, the prediction from the CSR model gives unity probability for all crystal spacings, in strong disagreement with the experimental observation). These results demonstrate that the spacing distribution follows a predictable, universal scaling caused by a local depletion of the monomer concentration around growing crystals, the effects of which are quantitatively captured by accounting for diffusion using boundary conditions consistent with the MFRE treatment of Equations 4.1.

**Section 4.5: Thin Film Design Rules**

Finally, to generalize these results to other systems, the behavior of Equations 4.1 and 4.11 are numerically evaluated for a range of different parameter values. This leads to a set of design rules useful for guiding the selection of experimental conditions in order to produce polycrystalline films having specific morphological properties. The effects of $F$, $D$, $\sigma$, and $\gamma$ on the final number of crystals $N_{\text{max}}$ formed per unit volume by the end of the nucleation regime are examined, as well as a measure of the crystal spacing distribution, which was characterized by the mean scaled distance $r_{1/2}$ at which $N(r) = N_{\text{max}}/2$. The quantity $r_{1/2}$ can be thought of as a “nucleation exclusion distance”, i.e. the length scale characterizing the tendency of crystals to avoid nucleating near one another. This leads to a set of relationships that turn out to be well-described by power law scalings (see Figures 4.6 and 4.7):

\[
N_{\text{max}} \sim F^v \quad 4.12a
\]

\[
N_{\text{max}} \sim D^w \quad 4.12b
\]
\[ N_{\text{max}} \sim \gamma^x \]  
\[ N_{\text{max}} \sim \left( \frac{D}{F} \right)^y \]  
\[ r_{1/2} \sim \xi \sigma^z \]

where \( v \approx 0.99 \), and \( w, x \) and \( y \approx -0.99 \). The exponents \( v, w, x \) and \( y \) are found to be essentially constant (within \( \pm 0.02 \)) for any combination of parameters within the range \( 7.0 \times 10^{21} \text{ m}^3 \text{ s}^{-1} \leq F \leq 3.0 \times 10^{22} \text{ m}^3 \text{ s}^{-1}, \ 1.6 \times 10^{-10} \leq D \leq 1 \times 10^{-11}, \ 11 \leq \gamma \leq 23, \) and \( 0.025 \text{ mN/m} \leq \sigma \leq 0.01 \text{ mN/m} \). The exponent \( z \), on the other hand, is not constant, but instead varies in a regular way between \(-0.4 \sim -0.6\), depending on \( F \) and \( \gamma \) (details are given in ESI). The range of conditions over which Equation 4.12 applies encompasses a large parameter space of chemical properties and experimental conditions, and therefore these relationships can be expected to apply to a wide range of organic crystalline materials, solvents, and growth conditions. Taken together, these relationships define a set of design rules that can be used to guide selection of experimental conditions resulting in film morphologies tailored to particular applications.
Figure 4.6. Scaling behavior of $N_{\text{max}}$ determined from numerical integration of Equations 4.1. Lines are a power-law fit to a representative series in each set, chosen to correspond to the average parameters found from experiment. For each figure part and symbol type the parameters are given as \{\sigma (\text{N m}^{-1}), \gamma ($\text{unitless}$), D ($\text{m}^2 \text{s}^{-1}$), F ($\text{m}^3 \text{s}^{-1}$)\} as follows: (A) squares \{0.017, 18.0, 7.58\times 10^{-11}, \text{variable}\}; upside-down triangles \{0.021, 13.0, 7.58\times 10^{-11}, \text{variable}\}; triangles \{0.0235, 13.0, 7.58\times 10^{-11}, \text{variable}\}; circles \{0.0205, 18.0, 7.58\times 10^{-11}, \text{variable}\}; diamonds \{0.021, 18.0, 7.58\times 10^{-11}, \text{variable}\}; solid hexagons are experimentally-measured values. (B) squares \{0.013, 13.0, \text{variable}, 1.05\times 10^{22}\}; upside-down triangles \{0.021, 10.0, \text{variable}, 1.05\times 10^{22}\}; triangles \{0.021, 13.0, \text{variable}, 1.05\times 10^{22}\}; circles \{0.021, 18.0, \text{variable}, 1.05\times 10^{22}\}; diamonds \{0.03, 13.0, \text{variable}, 1.05\times 10^{22}\}; circles \{0.021, 18.0, \text{variable}, 1.05\times 10^{22}\}; diamonds \{0.03, 13.0, \text{variable}, 1.05\times 10^{22}\}. (C) \{0.012, \text{variable}, 7.58\times 10^{-11}, 1.05\times 10^{22}\}; upside-down triangles \{0.021, \text{variable}, 7.58\times 10^{-11}, 1.45\times 10^{22}\}; triangles \{0.021, \text{variable}, 7.58\times 10^{-11}, 1.25\times 10^{22}\}; circles \{0.0205, \text{variable}, 7.58\times 10^{-11}, 8.5\times 10^{21}\}; diamonds \{0.03, \text{variable}, 7.58\times 10^{-11}, 1.05\times 10^{22}\}. (D) squares \{0.017, 18.0, \text{variable}, \text{variable}\}; upside-down triangles \{0.021, 16.0, \text{variable}, \text{variable}\}; circles \{0.0205, 18.0, \text{variable}, \text{variable}\}; diamonds \{0.021, 18.0, \text{variable}, \text{variable}\}. 

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Figure 4.7. Scaling behavior of $r_{1/2}$ at various flux rates. For each symbol parameters are given as follows \{ $\sigma$ (N m$^{-1}$), $\gamma$ (unitless), $D$ (m$^2$ s$^{-1}$), $F$ (m$^3$ s$^{-1}$), $z$ (unitless)\}: circles \{0.021, 18, 7.58\times10^{-11}, 8.0\times10^{21}, -0.42\}; squares \{0.021, 18, 7.58\times10^{-11}, 1.0\times10^{22}, -0.47\}; triangles \{0.021, 18, 7.58\times10^{-11}, 1.0\times10^{22}, -0.47\}; \{0.021, 18, 7.58\times10^{-11}, 1.2\times10^{22}, -0.49\}; upside-down triangles \{0.021, 18, 7.58\times10^{-11}, 1.4\times10^{22}, -0.50\}.
Chapter 5: Direct Qualitative Mapping of Time-Dependent Monomer Concentration

MFREs and KMC simulations have been used to predict the concentration gradient change during crystal nucleation. Simulations can easily display how the local concentration around these new crystals changes with respect to time. Aggregation of monomers on the crystal gives rise to local monomer depletion, which creates an exclusion zone where the local concentration is too low to form new critical nuclei. Efforts to model these depletion or exclusion zones oftentimes refer to various geometric forms of capture zones: Voronoi cells, edge cells, or diffusion cells.\textsuperscript{37, 50} Even though the existence of these zones has become commonly accepted in the field of thin film deposition, they have never before been visualized for solvent-phase thin film deposition.

\textbf{Figure 5.1:} Maximum normalized emission spectra of the dark field microscopy components. Each spectrum was taken with a 405 nm excitation wavelength. The blue accounts for dissolved TET in squalane, the green is solid TET, and the red is dissolved lumogen red in squalane. The dotted lines correspond to the filters used in dark field imaging.
Dissolved monomer concentration can be visualized using dark field microscopy. A fiber-optic ring waveguide feeds a 405 nm laser light through a window in the lid of the chamber. Figure 5.1 shows emission of both monomeric and crystalline material under 405 nm light which can be split using a Gemini W-View beam splitter. The splitter uses a dichroic mirror to redirect light at 535 nm while bandpass optical filters allow only specified wavelengths to reach the camera. The main issue with this form on microscopy is its dependence on the liquid thickness. Figure 5.2 shows how the liquid layers change during nucleation and growth of crystalline materials. The liquid thickness dependence on the monomer fluorescence signal is accounted for by saturating the liquid layer with an organic dye (F300 N,N-Bis(2,6-Diisopropylphenyl)-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetracarboxdiimide, also known as Lumogen Red). Lumogen Red emits high wavelength light which can be separated from the lower wavelength emission of dissolved monomers. This emission is only dependent on the thickness of the liquid and not the flux dissolving into the

![Figure 5.2: White light images of liquid layer during nucleation. Image A is taken right before nucleation starts showing a level liquid layer as crystals begin to nucleate. In images B-D a change in the thickness of the liquid can be seen. This interference fringing is caused by liquid being pushed by solid crystalline material.](image)
liquid layer. Pixel by pixel normalization creates a data set where the pixel brightness is only related to the concentration of monomers creating a concentration map independent of liquid thickness.

Using this microscopy technique and our newly developed models for the nucleation kinetics in the solution-phase — refer to Chapter 4 — we can investigate a variety of deposition types and film structures. The optical micrograph shown in Figure 5.3 gives the first ever micrograph of the time-dependent expansion of depletion zones independent of local liquid thickness. The deposition shown in Figure 5.3 was specifically designed to form a single crystal. This single crystal creates an exclusion zone expansion video which is not influenced by competition from surrounding crystals. When the crystal forms the flux is stopped by closing a shutter above the nozzle in the deposition chamber. This creates a system where the only monomers available for crystal growth are the monomers which are present at the time of nucleation. These collected videos can be further analyzed to determine the relative radial monomer concentration. By knowing the nucleation location we are able to calculate the concentration profile of monomers in solution, clearly showing, in Figure 5.4, the expansion of the exclusion zone with respect to time. This single crystal data can be used to inform models of monomer diffusion which are independent of flux rate and allows for further analysis of the rate of exclusion zone expansion, which causes a deviation from special randomness, refer to Section 4.4.
Figure 5.3: *In situ* optical micrograph of liquid thickness normalized monomer fluorescence for a single crystal deposition where the flux was stopped after nucleation and the exclusion zone was allowed to expand without competition with other crystals. (A) shows a time right before nucleation. (B-D) show the expansion of the exclusion zone. The each frame is 1 second apart and the frame number is denoted on the bottom right.

Figure 5.4: The time dependent radial concentration of a single crystal deposition. Concentration is calculated through averaging all of the monomer concentration in a range of $r - dr$ where $r$ is some radius from the center of a crystal and $dr = 2$ pixels.
Standard depositions measure the monomer concentration profile of the liquid layer, while allowing many crystals to nucleate and grow with a constant flux, shown in Figure 5.5. The first frame shown in Figure 5.5 shows a time before nucleation where the concentration is still below the critical supersaturation. The next frame shows the beginning of the nucleation regime; crystal nucleation creates areas of low concentration which hinders nucleation near the crystal. The local depletion creates an exclusion zone and dictates the non-random spacing statistics, discussed in Section 4.4. As the crystal depletes more monomer, the size of the exclusion zones increase and eventually monomer concentration drops below the critical supersaturation and nucleation stops. The exclusion zones will continue to spread until a steady state is reached. The steady state exclusion zone maps can later be used to check the radial probability distribution discussed in Section 4.4.

Figure 5.5: *In situ* optical micrograph of liquid thickness normalized monomer fluorescence during the nucleation regime of a standard deposition with many crystals nucleating in close proximity to each other.
Figure 5.6: The time dependent radial concentration of a standard deposition. Concentration is calculated through averaging all of the monomer concentration in a range of $r - dr$ where $r$ is some radius from the center of a crystal and $dr = 2$ pixels. As the monomer concentration rises nucleation occurs and there is a rapid decrease in local concentration.

Figure 5.6 shows the radially averaged concentration for a crystal which nucleates early in the deposition shown in Figure 5.5. To clearly display the radial expansion of the exclusion, zone the relative pixel brightness is interpreted as a local monomer concentration. Figure 5.6 shows that the monomer concentration continues to rise as time progresses, then after about 3 minutes of continuous flux the crystal nucleates at $r = 0$. A rapid drop in local concentration continues to expand outward even though new monomers are arriving via the flux rate. The addition of monomer can be seen at by the rising concentration at large radial distances from the center of the crystal. The time scale of the calculation in Figure 5.6 can be further expanded into a regime where there are many competing exclusion zones. However current analytical methods do not distinguish between which crystals are competing for monomer concentration.
These concentration profiles can be used to predict where a crystal will form. Current efforts have begun to numerically solve the time-dependent diffusion equation, where crystals are modeled as sinks on their centers of mass shown in Figure 5.7. This calculation gives an evolving concentration map which can be compared to experimental data shown in Figure 5.6. However, the current method requires the brightness of individual pixels to be calibrated to monomer concentration in order to fully apply the imaging method to model development.

This type of in situ monomer concentration imaging has never before been performed during a solution-phase thin film deposition. Imaging methods push the limits of the readily available technology but still require further optimization to reach the level of accuracy needed for quantitative concentration measurements. However, there is no limit to the predictive models which can be built from the time dependent monomer concentration data discussed here.

Figure 5.7: A concentration map relating to the numerical solution for the time-dependent 2D diffusion equation. The dark centers represent crystals as perfect point island sinks and the contours portray the monomer concentration and display the local depletion zones caused by these sinks.
Chapter 6: Exploration of Crystal Growth Kinetics

Section 6.1: Steady State Growth Regime

In polycrystalline thin films a crystal’s growth rate has long been postulated to be determined by its local environment, in the form of “capture zones” which can be approximated by a crystal’s Voronoi cell area.\textsuperscript{37, 50} Evans and Bartelt observed, through the use of MFREs and KMC simulations, that a crystal’s growth rate is related to the size of its capture zone as long as monomer attachment is subject to unity sticking, i.e. that every monomer striking to a crystals attached to that crystal.\textsuperscript{37} However in real systems, especially in solution-phase crystal growth, monomer attachment is subject to many intermolecular interactions which give rise to non-unity sticking probabilities and diffusion mediated growth. Here, \textit{in situ} crystal growth measurements, collected by bright field optical microscopy, are employed to evaluate and examine a set of exploratory growth models to determine the leading causes of morphological change of crystals grown in the solution-phase.

For growth kinetics measurements the solvent layer needs to be very thin, causing the timescale for monomer mixing throughout the thickness of the liquid, $\tau_{mix} = d_s D^{-1/2} \sim 10^{-2}$ s, to be essentially instantaneous within the scope of the experiment. Here $d_s = 100$ nm is the solvent thickness and $D = kT/6\pi\eta a$ is the diffusivity of TET in squalane ($k$ is Boltzmann’s constant, $T \sim 350$ K is temperature, $\eta \sim 5$ mPas is the viscosity,\textsuperscript{90} and $a = 4.11 \times 10^{-10}$ m is the molecular radius of TET\textsuperscript{91}). Note that since $d_s/a \gg 1$, the contribution of the solid substrate to the Stokes drag in these thin films is negligible, leading to bulk-like isotropic Brownian diffusion.\textsuperscript{92} The solvent layer thickness is also much less than the separation between crystals. In particular, at the highest saturation coverage, the average distance from a randomly chosen point within the analysis region $\mathcal{A}$ to the nearest portion of any crystal is $l_c \approx 25$ $\mu$m, giving a
ratio $l_c/d_s \sim 250$. We thus treat the concentration as being uniform throughout the thickness of the solvent, though spatially varying within the plane. The flux rate ($F = 1.6 \times 10^4 \text{TET monomers} \, \mu \text{m}^3 \, \text{of squalane} \, \text{s}^{-1}$) was determined from the induction time of $t_{\text{nucl}} \approx 140 \text{ s}$. In the nucleation regime where $T \approx 60 ^\circ \text{C}$, the saturation concentration, measured separately by UV-VIS absorption spectroscopy of equilibrated bulk solutions, was $n_o = 0.15 \text{ g L}^{-1}$. The supersaturation ratio required to initiate nucleation under the experimental conditions is $n^*/n_o \approx 5$, similar to that reported for VLS growth in some inorganic and related organic systems.$^{52,93}$

The ratio of the monomer diffusion rate (in sites s$^{-1}$) to the flux $F$ (site$^{-1}$ s$^{-1}$) $\Gamma \equiv D/F$ is known to govern many important aspects of submonolayer film formation, including island size distributions and nucleation density.$^{37}$ Here, the purpose of coating the substrate by a solvent layer is to increase the number of available ‘sites’ per unit area by a factor $3d_s/4\pi a^3$ as monomers disperse throughout the volume of the liquid. Consequently, the effective flux rate becomes very small compared to conditions typically employed in vacuum deposition, while diffusion in the liquid is relatively high. This high diffusion creates a system where every monomer that arrives on the substrate will be incorporated into a crystal at some steady state.
This allows for modeling of the change in crystal morphology to be dependent on monomer diffusion, alone.

For model development, a representative subregion containing $N = 343$ crystals was selected for growth analysis. The crystals nearest to the edge were excluded from further analysis. The position of the light source in this data set (see section 3.3) causes some crystals to be highly susceptible to lensing effects. By performing depositions in an ultra-thin liquid

Figure 6.1: In situ optical micrographs showing early and late stages of TET film development on squalane-coated ITO/glass. (A) Épifluorescence and (B-E) bright-field optical micrographs. (E) shows the full area analyzed in this chapter with Voronoi cell boundaries overlaid. Scale bar is 250 µm. Images (A-D) show crystal growth in a 400×400 µm subregion of (E).
layer most of these effects are minimized, allowing for accurate growth measurements of each crystal without perceivable lensing effects. Figure 6.1 shows a representative micrograph of several crystals which can be analyzed for growth kinetics as well as a few of which were subject to lensing effects. Final measurements of crystal growth statistics were performed on the remaining randomly distributed \( N = 189 \) crystals. Growth measurements were performed well into the steady state growth regime starting in the 58\(^{th}\) minute of deposition.

![Graph showing growth of crystals over time](image)

**Figure 6.2:** The mean crystal volume was fit to the equation \( \frac{\partial V}{\partial t} \propto \kappa(t - t_o)^\chi \). \( \chi = 1.05 \pm 0.02 \) consistent with a steady state growth. The insets show the growth rate of crystal’s area (lower right) and thickness (upper left).

Figure 6.2 shows the time-dependence of the average thickness, area, and volume of the crystals within the analysis region. To a first approximation the trends are well described by a growth model of the form:

\[
\frac{\partial M}{\partial t} = \kappa(t - t_o)^\chi, \tag{6.1}
\]

where \( \kappa \) is a constant, and \( \frac{\partial M}{\partial t} \) is the change of the analyzed measurement — thickness, area, and volume — with respect to time \( t \). Growth exponents for thickness, area, and volume, \( \chi = \)
(0.58 ± 0.02), (0.47 ± 0.01), and (1.05 ± 0.02), respectively, are determined by fitting all three measurements simultaneously. The fit induction time \( t_o = 14.6 \) minutes differs from the observed induction time due to the much higher initial growth rate of crystals within the nucleation regime. The volumetric growth exponent is close to 1, consistent with the quasi-steady-state growth conditions assumed in the following models (i.e. for every growth unit newly arrived from the vapor, one growth unit is incorporated into a crystal).

**Section 6.2: Experimental Correlations**

Crystal growth in all regimes has been thought to be determined largely by crystal separation distances because this affects the size of the local “territory” from which a crystal can gather monomer.\(^{37}\) We find this not to be the case in the present system. More accurately, the growth rate of a crystal is determined by several factors such as its initial size, shape, local monomer concentration gradient, as well as its proximity to its neighbors, and most of which are coverage- and time-dependent. Equation 6.1 is therefore only applicable for small relative changes in average crystal size. More generally growth is described by a set of size-dependent ‘capture numbers’ \( \sigma_s = \frac{\partial V_c}{\partial t} \). A variety of approaches have been proposed for computing these capture numbers\(^{47,49-50,53,94-100}\) (refer to reference 47 for a summary of methods), but in only a very few instances have they been experimentally measured, and never for crystals grown in a liquid solvent\(^{49-50}\).
Figure 6.3. Growth rate correlations to various physical properties of the measured crystals in the analysis region. A higher the correlation coefficient $R^2$, shows a greater dependence between the geometric calculation and the growth rate. (A) Compares the volumetric growth rate with the calculated Voronoi cell area. (B, C, D) Compare the growth rate for initial surface area, perimeter area (thickness multiplied by the perimeter of a crystal) and the perimeter, respectively. This gives $R^2$ values of, 0.28, 0.45, 0.45, and 0.60, respectively.

Figure 6.3 shows the relationship between $\sigma_s$ in the growth regime, measured by in situ videomicroscopy, to the Voronoi cell ($V_{cell}$) area. The Voronoi cell area is a geometric approximation of the capture zone of a crystal. $V_{cell}$ is found by determining the substrate area which is closer to a crystal’s center of mass than any other crystal, as shown in Figure 6.4. 49, 53, 87 These geometrically calculated capture zones provide a reasonably good prediction of the relative growth rate of crystals within thin films deposited in the vacuum-phase where monomers attach to a crystal with close to unity sticking probability. However, when looking
at how $V_{\text{cell}}$ area predicts the relative growth rate of crystals in the solution-phase by comparing the experimentally measured growth rate with the $V_{\text{cell}}$ area of each individual crystal, we find a correlation coefficient of only 0.28 (Figure 6.3a). This suggests that the $V_{\text{cell}}$ area does not adequately describe the physics associated with crystal growth.

We also examined how growth rate is related to the initial size of a crystal; this comparison is shown in Figure 6.3. The hypothesis that larger crystals grow faster than smaller crystals follows from the larger number of available sites, which allows the initial size of a crystal to be used as a metric to predict the relative growth rate of crystals in close proximity. However, both the initial surface area and the perimeter area, which is defined as the surface area excluding the top of the crystal, exhibits a correlation coefficient of around 0.45 (Figures 6.3b and 6.3c). This shows that crystal growth in solution is weakly dependent on the available surface area of the crystal but is a slightly better metric to predict the relative growth rate than $V_{\text{cell}}$ area. An interesting geometric correlation was found to exist between the initial perimeter of a crystal and its growth rate, giving $R^2 = 0.60$ (Figure 6.3d). This relatively high correlation implies that the primary sticking location of a monomer is on the perimeter of a crystal and
that the growth rate is relatively independent to the thickness of a crystal. However, it is important to note that the observed degrees of correlation are all significantly lower than those which have been found by simulation for films deposited in vacuum.\textsuperscript{50} Thus the direct correlation of any one geometric measurement to growth rate is not sufficient to describe the relative growth rates of crystals in a polycrystalline thin film.

\textbf{Section 6.3: Mean Field Numerical Model}

In order to determine which types of sticking sites have the highest sticking probability, TET crystals were analyzed to determine their crystallographic orientation. Crystalline tetracene is known to have one major polymorph with a triclinic unit cell that contains two tetracene molecules within that unit cell.\textsuperscript{74} From XRD data—refer to Figure 3.11—the \textit{ab} \{001\} face lies in the plane of the surface and comprises of \(\sim 95.22\%\) total crystal surface area.\textsuperscript{74} The \textit{ac} \{010\} and \textit{bc} \{100\} faces were determined by angle analysis from a representative set of crystals imaged by AFM.\textsuperscript{101-102} The angle analysis, shown in Figure 6.5, indicated that the long side of the rod-like crystal was the \{010\} (\textit{ac} unit cell face) and the short end was determined to be the \{100\} (\textit{bc} unit cell face) both of which account for about 4.15\% and 0.61\% of a crystal’s surface area, respectively.

In order to determine a mean field growth mechanism, the length, width, and thickness growth rates were measured for every crystal within the analysis region. Then the Voronoi cell volumes of all crystals were averaged over the whole analysis region, providing the mean field crystal with an approximation of its capture zone. Then the experimental growth rates were fit to:

\[
\frac{\partial N_{\text{face}}}{\partial t} = \frac{\beta_{\text{face}} F V_C A_{\text{face}}}{A_{\text{tot}}}
\]

6.2
where \( FV_{vc} \) is the flux which arrives in the average Voronoi cell volume, which represents the total number of monomer that will stick to the mean field crystal. The growth of each individual crystal face was considered with the use of its fractional surface area. This was calculated as the surface area of the face \( A_{\text{face}} \), divided by the entire exposed surface area \( A_{\text{tot}} \). \( \beta_{\text{face}} \) is a coefficient representing the relative impact of the surface area of each face on the overall crystal growth rate. From Equation 6.2 the number of monomers that attach to each face \( N_{\text{face}} \) in each time step \( dt = 180 \) sec can be converted into changes of length, width and thickness. This conversion required use of the dimensions of the triclinic unit cell of crystalline TET given by Trotter.\(^{74}\) Thus allowing for \( \beta_{\text{face}} \) to be the only fit variable in the mean field.

\( \theta = 57.5^\circ \) and \( \phi = 127.9^\circ \) which is consistent with the crystal face labeling diagram (bottom) where the top is the ab unit cell face, the long end is the ac unit cell face, and the short end is the bc crystal face.\(^{100-101}\) Two TET monomers sit in the unit cell as depicted allowing for accurate predictions of growth rate based on the number of monomers which stick to each face.

**Figure 6.5:** Tetracene crystal angle analysis and diagram of monomer position in a crystal. Angle analysis of and AFM image of a representative crystal (top) gives \( \theta = 57.5^\circ \) and \( \phi = 127.9^\circ \) which is consistent with the crystal face labeling diagram (bottom) where the top is the ab unit cell face, the long end is the ac unit cell face, and the short end is the bc crystal face.\(^{100-101}\) Two TET monomers sit in the unit cell as depicted allowing for accurate predictions of growth rate based on the number of monomers which stick to each face.
numerical growth model. The model provides excellent agreement (Figure 6.6) to the experimental growth rates with the $\beta_{\text{face}}$ values given in Table 6.1.

**Table 6.1: Numerical Model Fitting Results**

<table>
<thead>
<tr>
<th>Face</th>
<th>$\beta_{\text{face}}$</th>
<th>Percent Surface Area (%)</th>
<th>Percent Capture (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top ${001}$</td>
<td>0.61</td>
<td>95.22</td>
<td>59.64</td>
</tr>
<tr>
<td>Side ${010}$</td>
<td>6.41</td>
<td>4.15</td>
<td>27.40</td>
</tr>
<tr>
<td>End ${100}$</td>
<td>20.02</td>
<td>0.63</td>
<td>12.95</td>
</tr>
</tbody>
</table>

The determination of $\beta_{\text{face}}$ allows for a prediction of the effective surface area of each face. If the number of monomers which are captured on a face is directly related to the surface

**Figure 6.6:** Numerical model fits to experimental data collected from an average crystal. (A) shows the numerical model fit to the volumetric growth determined simultaneously fitting the length (B), width (C) and the thickness (D).
area of that face then the monomer capture percent of each face would be directly related to exposed facial surface area. For example, because the top of a crystal accounts for ~95.22% of the total exposed surface area it would also account for ~95.22% of the total number of monomers captured by the crystal. However, through the use of the mean field model we find that monomer captured by solely the top of a crystal accounts for 59.64% of total monomer capture. This means that the effective surface area of the top is 0.61 times less than the actual surface area. We find that the $A_{end} \{100\}$ accounts for 20.02 times more monomer growth than its proportional surface area of 0.63% suggests. As a result, the end of a crystal accounts for 12.95 % of the total monomer capture of the crystal. Table 6.1 shows that the sticking probability of attaching to the end or the side of a crystal is much greater than the probability of sticking on top of a crystal.

The variation in sticking probability increases the anisotropy of the crystals directly after nucleation. If we employ a cubic nucleus approximation to the initial shape of the crystal, then the rod-like shape can be attributed to a high sticking probability on the end of a crystal. This sticking probably changes as the supersaturation of the liquid layer changes causing a change in crystal shape. In nucleation regime, sticking is much more prevalent on the ends of a crystal due to the equal surface area ratios and the high density of monomers in a crystal’s local environment. The relatively low sticking coefficient of the top of a crystal causes the thickness to not change nearly as rapidly with respect to the length and width, which creates initially long and thin crystals. When the concentration begins to fall the sticking coefficients begin to change creating a shift in the growth pattern of TET crystals. When the concentration is lower the sticking coefficient changes causing the growth rate of each face to be more dependent on the exposed surface area due to a higher energetic barrier to sticking. When the
surface area of the ends with respect to the sides gets sufficiently small then the rate of monomer capture on the ends drops below that of the sides, creating a change in the growth character. The region of time in which the growth rate data was collected is well within this second growth regime. Figure 6.7 shows that as crystals grow, the aspect ratios between the length, width, and thickness changes over time. The $\frac{L}{W}$ aspect ratio trends downward indicating that over the course of the growth regime the width is catching up with the length of the crystals. When looking at the $\frac{T}{W}$ and the $\frac{T}{L}$ ratios, an upward trend suggests that the thickness of these crystals is also catching up with the cross-sectional area. Eventually, this model predicts that the shape of a crystal will go from rod-like to an energetically favorable cubic structure.

**Figure 6.7:** Maximum normalized aspect ratio analysis from the mean field numerical model versus time. Each line comes from the predicted change in $\frac{L}{W}$, $\frac{T}{L}$, and $\frac{T}{W}$ from the numerical fitting and the points come from the experimentally measured ratios. Due to the change in aspect ratios the crystal morphology at long times can be predicted from the relatively short analysis region.
Section 6.4: Kinetic Monte Carlo Simulations

In parallel with the analysis performed in section 6.3 a kinetic Monte Carlo approach was also used to examine various crystal growth models. Simulations were performed on a grid which placed existing crystals from the analysis region shown in Figure 6.1e. These crystals were placed based on their two-dimensional footprint and were not allowed to change in size or shape as monomers stuck to them. Monomers were fluxed randomly onto the grid and could diffuse randomly until stepping on top of a crystal. This step created an opportunity to stick to that crystal, where the probability of sticking was related to some sticking coefficient $\alpha$. Growth models were tested by varying $\alpha$ over several orders of magnitude and calculating the $R^2$ for the relationship between the simulation capture rate, with respect to the experimentally observed volumetric growth rate. The simulation boundaries were set as periodic to account for the constant concentration throughout the liquid. Therefore, creating a simulation was created with relatively low computational cost which allowed for examination of several sticking models.

We began by investigating a standard singular sticking model. This model sets the sticking coefficient of each site on a crystal to the same value, regardless of its position. Primarily used in vacuum-phase systems to predict how a crystal’s Voronoi cell area will impact its relative growth rate, this model was used as a baseline.\textsuperscript{37} It is important to note that with respect to solvent-phase depositions this simple singular sticking coefficient model does not encapsulate the three-dimensional nature of these thin films. A maximum correlation at $\alpha=0.01$ with a $R^2 = 0.49$ suggests that crystal growth is significantly more complex in a solution than in the vacuum phase, where much larger correlations are typically observed.\textsuperscript{37, 49, 53}
order to better understand the effect of the liquid solvent a series of exploratory growth models are discussed here.

Observation of the sizes of the crystals shows that at long deposition times the thickness of a crystal begins to approach on that of the 100 nm thick liquid solvent layer. Consequently the liquid thickness on top of crystals is either extremely small or non-existent. To take this into account, the simulation was modified to allow for variable sticking coefficients on different faces. Sticking was only allowed on the outer perimeter of each crystal, thus excluding the tops. From here two different models were tested to determine their impact on the correlation between the simulation and experiment growth rates. To examine the growth rates in the case of a very thin solvent layer, the model was set such that monomers could diffuse on top of the crystals but were only allowed to stick on the outer boundary. This edge-only sticking model provided a significant improvement over the previous model. The max $R^2$ value for the edge-only model was found at $\alpha=0.01$ to be 0.55.

The second case takes the potentially bare tops of a crystal into account by treating the crystals as infinitely tall objects. This simulation allowed for monomer diffusion on any space besides the inner area of the crystal. If a monomer walk onto the perimeter of a crystal it has some sticking probability $\alpha$. If sticking fails, the monomer is deflected off the crystal. After deflection, the monomer is then allowed to undergo Brownian diffusion until it eventually does stick. The max $R^2$ value for the obstacle model was found at $\alpha=0.01$ to be 0.54. Both edge-only sticking models performed better than the singular sticking model. This result shows the impact of the liquid layer thickness on the relative growth rate of crystals. However, these models do not consider the variable sticking coefficients suggested in section 6.3.
The next model tested was based on the variation in sticking probability found in section 6.3. From the numerical fit the relative surface area impact was represented by the \( \beta_{\text{face}} \) values. Condensation of Equation 6.2 gives:

\[
N_{\text{face}} = \frac{\beta_{\text{face}}N_{\text{tot}}S_{\text{face}}}{S_{\text{tot}}}
\]

where \( N_{\text{tot}} = FV_{\text{VC}}t \) and is the total number of monomer that will attach to the crystal in each time step. To get relative sticking multipliers for each face, \( \beta_{\text{face}} \) was isolated in Equation 6.3a to get the relationship:

\[
\beta_{\text{face}} = \frac{N_{\text{face}}S_{\text{tot}}}{N_{\text{tot}}S_{\text{face}}}
\]

which gives \( \beta_{\text{face}} \) values for the ends, sides, and top of the crystal. These coefficients were normalized to give 30, 10, and 1, respectively, and were implemented into the simulation. The variable sticking coefficient was multiplied by the \( \alpha \) value to determine the sticking probability. Direct translation of the surface area impact factors causes a decrease in correlation. These values, when entered into the simulation, give a max \( R^2 \) of 0.43 at an \( \alpha = 0.01 \). However, Figure 6.6 suggests that the sides of the crystal are growing more quickly than the ends of the crystal due to the decrease in the \( \frac{L}{W} \) aspect ratio. With this in mind, the end and side sticking coefficient multipliers were exchanged such that the sides had a greater probability of collecting monomer than the ends. This created an increase in the simulation the \( R^2 \) to 0.55 at an \( \alpha = 0.001 \). The increase in correlation is contrary to prediction from the numerical model but follows what is observed optically, suggesting a disconnect between the \( \beta_{\text{face}} \) values found in the numerical model with the actual sticking coefficient.

The final model which was tested was a hybrid between the variable sticking coefficient model and the edge-only model. This model uses the switched \( \beta_{\text{face}} \) values as relative sticking
coefficients on the outside edges of the crystal but does not allow monomer to stick on the top of a crystal, setting the \{010\} coefficient to 3, and the \{100\} coefficient to 1, while preventing sticking on the top altogether. This adaptation to the model gave a \( R^2 = 0.57 \) at an \( \alpha = 0.001 \) which was the best correlation seen in simulation. Figure 6.8 shows a comparison in \( R^2 \) for each of the five models explored from the KMC simulations described above.

**Figure 6.8:** Correlation coefficients comparing simulation growth rate and experimental growth rate for various KMC simulation models. Models are denoted as follows: Squares = Singular Alpha; Circles = Edge-only sticking single sticking coefficient; Triangles = Crystals as obstacles single sticking coefficient; Hexagons = Numerical model variable sticking coefficients; Diamonds = Numerical model variable coefficients with exchange edge and side sticking coefficients; Upside-down triangles = Edge-only variable sticking coefficient.

KMC simulations have allowed relatively rapid analysis of atomistic descriptions of crystal growth. However, the simplicity of the models fail to incorporate the exact physics of crystal growth. Models with constant sticking probabilities across the whole face of a crystal do not accurately predict the relative growth rates of crystals, whereas hindering sticking on the top of a crystal improves the correlation coefficient of the model.
This work has allowed us to show that crystal growth in solution is only partially determined by the initial size of a crystal and its $V_{\text{cell}}$ area, in contrast to what is often observed in vacuum. In a solution, low sticking coefficients and long diffusion distances are more important contributing factors. Further development of models which explore all aspects of crystal growth are needed to fully understand how the solvent impacts the final crystal size and shape. From the growth data, we can conclude here we can determine that crystal growth in a solvent occurs in at least two different regimes. These regimes greatly impact growth habit and are determined by variations in the sticking probabilities of crystal faces.


56. LaMer, V. K.; Dinegar, R. H., Theory, Production and Mechanism of Formation of Monodispersed Hydrosols. *Journal of the American Chemical Society* **1950**, *72* (11), 4847-4854.


Appendix

A: Computational Post-processing

ImageJ, a java based software package, can be used to edit and analyze videos with high amounts of flexibility and accuracy. After optical microscopy videos are collected the video files are loaded into ImageJ and analyzed through custom made tools and scripts to provide consistent analysis. A crystal counting program the location of every crystal in an analysis region is obtained and allows for easy determination of nucleation time. ImageJ provides video editing techniques to help remove non-crystal particulate from the analysis region.

Monte Carlo simulations simulate the Brownian motion of monomers on a substrate using a random number generator that dictates the direction that a monomer will move in solution. Growth of crystalline material is modeled by adding a single monomer to a grid, with already placed crystals from a model deposition. By allowing it to diffuse around the space until it hits a crystal a simulation growth rate can be calculated by the number of monomers that arrive at each crystal. Data collected after many monomers are allowed to diffuse around the substrate is used to test models of growth of our crystalline materials.

To model crystal nucleation of liquid based nucleation systems MFRE are used to predict nucleation statistics and critical nucleus size of crystalline material. The MFRE is a thermodynamically driven calculations which consists of mean field flux of monomer, $F$, adding to the system and the removal of monomer through aggregation into a new crystal or growth of an existing crystal. As concentration increases the entropic barrier of nucleating a stable crystal decreases thus causing the probably of starting nucleation to increase. When the simulation reaches the critical supersaturation, concentration burst nucleation occurs. The
nucleation rate of crystals by the MFRE can be compared to actual nucleation rates determined in experimentation. These comparisons are used to inform predictions about the mechanism of thin film formation by OVLS.

**B: Kinetic Monte Carlo Simulation Code**

Written in collaboration with Allison Stanfield

**Code begins:**

```java
import java.io.BufferedReader;
import java.io.BufferedWriter;
import java.io.File;
import java.io.FileReader;
import java.io.FileWriter;
import java.io.IOException;
import java.util.ArrayList;
import java.util.HashSet;
import java.util.List;
import java.util.Map;
import java.util.Random;
import java.util.Set;
import java.util.TreeMap;

public class MCSimulatorEdgeModel {
    /** A pixel map of the crystals. Every cell is a crystal id or 0 if empty space **/
    private short[][] crystalMap;

    /** Counts for each pixel of cycles during which a monomer has been on the pixel **/
    private short[][] contourDiagram;

    /** A tessellation of the crystal space. Each entry is the id of the crystal to * which the position is closest. */
    private short[][] tessellation;

    private short[][] edgeMap;

    /** A map from crystal id to crystal **/
    private Map<Short,Crystal> crystals;

    /** A list of monomers that have been used in this simulation **/
    private List<Monomer> monomers;
```
/** A sticking coefficient **/  
private double alpha;

/** Types of moves that a monomer can undergo, each with a designated probability **/  
public enum Move {
    WALK,          // move randomly in one of the 4 non-diagonal directions
    STICK_EDGE,    // stick to the edge of a crystal
    STICK_TOP,     // stick to the top of a crystal
    EDGE_BOUND,    // become edge-bound to a crystal
    UN_EDGE_BOUND; // become un-edge-bound from a crystal
}

/**
 * @return The probability of this move.
 */
double probability() {
    switch(this) {
        case WALK: return 1.0;
        case STICK_EDGE: return 0.1;
        case STICK_TOP: return 0.1;
        case EDGE_BOUND: return 0;
        case UN_EDGE_BOUND: return 0;
    }
    throw new AssertionError("Unknown move: "+ this);
}

// used to generate random numbers throughout the program
private static final Random random = new Random();

/**
 * Creates a new a new MC simulator with the given crystal image.
 * 
 * @param filename A csv file containing
 */
public MCSimulatorEdgeModel(String filename, double alpha) {
    crystalMap = arrayFromCSV(filename);
    tessellation = computeTessellation(crystalMap);
    //tessellation = arrayFromCSV("tessellation.csv"); // read in from file for efficiency
    contourDiagram = new short[crystalMap.length][crystalMap[0].length];
    crystals = initCrystals();
    monomers = new ArrayList<Monomer>();
    this.alpha = alpha;
}
public MCSimulatorEdgeModel(String imgFile, String tesselationFile, double alpha) {
    crystalMap = arrayFromCSV(imgFile);
    //tessellation = computeTesselation(crystalMap);
    tessellation = arrayFromCSV(tesselationFile);  // read in from file for efficiency
    contourDiagram = new short[crystalMap.length][crystalMap[0].length];
    crystals = initCrystals();
    monomers = new ArrayList<Monomer>();
    this.alpha = alpha;
}

public MCSimulatorEdgeModel(String imgFile, String tesselationFile, String edgeFile,
    double alpha) {
    crystalMap = arrayFromCSV(imgFile);
    //tessellation = computeTesselation(crystalMap);
    tessellation = arrayFromCSV(tesselationFile);  // read in from file for efficiency
    edgeMap = arrayFromCSV(edgeFile);
    contourDiagram = new short[crystalMap.length][crystalMap[0].length];
    crystals = initCrystals();
    monomers = new ArrayList<Monomer>();
    this.alpha = alpha;
}

/**
 * Creates one monomer, places it randomly, and has it walk randomly until
 * sticking to a crystal or falling off the edge of the image.
 */
public void doRandomWalk() {
    // create a new monomer and add it to the list of all monomers used in the
    // simulation
    Monomer m = new Monomer();
    monomers.add(m);

    // get the initial row and column for the monomer randomly
    int row = random.nextInt(crystalMap.length);
    int column = random.nextInt(crystalMap[0].length);

    // Figure out the crystal whose capture zone the monomer arrived in, and
    // increment this count for the crystal
    short captureZoneArrived = tessellation[row][column];
    crystals.get(captureZoneArrived).numArrived++;
    m.start = crystals.get(captureZoneArrived).id;

    boolean stuck = false;     // whether on not the monomer has become stuck to a crystal
    boolean edgeBound = false; // whether or not the monomer is edge bound to a crystal
    boolean onMap = true; // whether or not the monomer is on the map
boolean stuckOnEdge = false; // where something has stuck

// The set of crystals that this monomer has been next to or on top of.
// Used to keep track of sticking opportunities for crystals.
Set<Short> crystalsTouched = new HashSet<Short>();

// Walk until the monomer becomes stuck or walks off the edge
while (!stuck && onMap) {
    // increment the contour diagram for this position
    contourDiagram[row][column]++;

    // get the possible moves for this monomer based on its position
    List<Move> possibleMoves = possibleMoves(row, column, edgeBound);

    // Add to our set of crystals that have had sticking opps during this MC cycle
    if (possibleMoves.contains(Move.STICK_TOP)) {
        crystalsTouched.add(crystalMap[row][column]);
    } else if (possibleMoves.contains(Move.STICK_EDGE)) {
        crystalsTouched.add(adjacentCrystal(row, column));
    }

    Move nextMove = chooseMove(possibleMoves, m, numEdgeSites(row, column),
                                row, column);
    switch (nextMove) {
        case WALK:
            if (!edgeBound) {
                // choose randomly among the 4 directions to move or to not move
                int direction = random.nextInt(4);
                if (direction == 0) {
                    row++;
                } else if (direction == 1) {
                    column++;
                } else if (direction == 2) {
                    row--;
                } else if (direction == 3) {
                    column--;
                } else if (direction == 4) {
                    // no move selected cs
                }
            } else {
                // TODO: fill in the edge bound move
                // Calculate the two possible moves and decide randomly
                // between them
            }
            break;
    }
    // increment the distance traveled for the monomer
m.distT++;  
break;
case STICK_EDGE:
    stuck = true;
    stuckOnEdge = true;
    break;
case STICK_TOP:
    stuck = true;
    break;
case EDGE_BOUND:
    edgeBound = true;
    break;
case UN_EDGE_BOUND:
    edgeBound = false;
    break;
default:
    throw new RuntimeException("unknown move");
}

/*if (row < 0 || row >= crystalMap.length || column < 0 || column >= crystalMap[0].length)
    // We walked off the edge! End this random walk
    onMap = false;*/

// Defined Border Conditions: Periodic
if (row < 0)
    row = crystalMap.length - 1;
else if (row > crystalMap.length - 1)
    row = 0;
if (column < 0)
    column = crystalMap[0].length - 1;
else if (column > crystalMap[0].length - 1)
    column = 0;
}

if (onMap) {
    // The monomer has stuck! Update this position in the crystal map
    // to reflect that it is now part of a crystal

    if (stuckOnEdge){
        short adjacentCrystal = adjacentCrystal(row, column);

        // sanity check (since we're now stuck, we should be next to a crystal)
        assert adjacentCrystal != -1 : "no adjacent crystal found";

        // This spot now belongs to the adjacent crystal
//crystalMap[row][column] = adjacentCrystal;
crystals.get(adjacentCrystal).finalArea++;

if (adjacentCrystal == captureZoneArrived)
    // we stuck to the same crystal whose capture zone we arrived in,
    // update this count for the crystal
    crystals.get(adjacentCrystal).numStuck++;
} else{
    short topCrystal = topCrystal(row, column);

    // sanity check (since we're now stuck, we should be next to a crystal)
    assert topCrystal != -1 : "no adjacent crystal found";

    // This spot now belongs to the adjacent crystal
    //crystalMap[row][column] = adjacentCrystal;

    crystals.get(topCrystal).finalArea++;

    if (topCrystal == captureZoneArrived)
        // we stuck to the same crystal whose capture zone we arrived in,
        // update this count for the crystal
        crystals.get(topCrystal).numStuck++;
    m.end = crystals.get(topCrystal).id;
}

for (short cId: crystalsTouched) {
    // increment the # of sticking opps for any crystal this monomer touched
    crystals.get(cId).numStickingOps++;
}
}

/**
 * Returns a list of possible moves for the monomer based on its position and
 * whether or not it is edge bound.
 *
 * @param row The monomer's row
 * @param column The monomer's column
 * @param edgeBound True if the monomer is edge-bound
 * @return A list of possible moves
 */
private List<Move> possibleMoves(int row, int column, boolean edgeBound) {
    List<Move> moves = new ArrayList<Move>();
// It is always possible to walk so add this to the list
moves.add(move.WALK);

if (crystalMap[row][column] != 0) {
    // we are on a crystal so it is possible to stick to the top
    // added 2-16
    moves.add(move.STICK_TOP);
}

// Don't need to check if adjacent
else if (adjacentToCrystal(row, column)) {
    // we are next to a crystal; possible to stick to an edge
    moves.add(move.STICK_EDGE);
    // also possible to become edge-bound if we aren't already
    /*if (!edgeBound)
        moves.add(move.EDGE_BOUND);*/
    moves.add(move.EDGE_BOUND);
}

// can become un-edge-bound if we are currently bound
/*if (edgeBound)
    moves.add(move.UN_EDGE_BOUND);*/

return moves;
}

/**
 * Pick a move for the random walker based on weighted probabilities of
 * possible moves and update the monomer's time in existence.
 *
 * @param possibleMoves The list of possible moves to choose from
 * @param mmer The monomer to update the time for
 * @return The chosen move
 */
private move.chooseMove(List<move> possibleMoves, Monomer mmer, int numEdgeSites, int row, int column) {
    // cumulative functions for possible moves
    List<Double> R_i = new ArrayList<Double>;
    double cumProb = 0.0;
    for (int i = 0; i < possibleMoves.size(); i++) {
        Move m = possibleMoves.get(i);
        if (m == move.STICK_EDGE) {
            //cumProb += alpha; cannot stick edge (cs)
            // added to account for prob of sticking to top if non top of crystal
        } else if (m == move.STICK_TOP) {
            // cumProb += alpha; cannot stick edge (cs)
            // added to account for prob of sticking to top if non top of crystal
        } else if (m == move.EDGE_BOUND) {
            // alpha replaced with edge array and this is
            cumProb += ((double)edgeMap[row][column] * alpha);
else {
    cumProb += m.probability();
}
R_i.add(cumProb);
}

double unif0to1 = random.nextDouble();
double R_n = R_i.get(R_i.size() - 1);
double uR_n = unif0to1 * R_n;

// update the monomer's time based on the cumulative probability
mmer.updateTime(R_n);

/*bug check*/
// checks the prob of each move.
// if greater than random prob number then return that move.
for (int i = 0; i < possibleMoves.size(); i++) {
    double r_i = R_i.get(i);
    if (r_i >= uR_n)
        return possibleMoves.get(i);
}
return null;

/**
* Returns the id of the adjacent crystal if there is one. Returns -1 if the pixel
* at the given row/column does not have a face touching a crystal.
*/
private short adjacentCrystal(int row, int column) {
    // If we want to account for the possibility of multiple adjacent crystals,
    // this method may need to be changed later
    if (row != 0 && crystalMap[row-1][column] != 0)
        return crystalMap[row-1][column];
    if (row != crystalMap.length - 1 && crystalMap[row][column] != 0)
        return crystalMap[row+1][column];
    if (column != 0 && crystalMap[row][column] != 0)
        return crystalMap[row][column-1];
    if (column != crystalMap[0].length - 1 && crystalMap[row][column] != 0)
        return crystalMap[row][column+1];

    // no adjacent crystal found
    return -1;
}

private short topCrystal(int row, int column){
if (row != 0 && crystalMap[row][column] != 0)
    return crystalMap[row][column];
if (row != crystalMap.length - 1 && crystalMap[row][column] != 0)
    return crystalMap[row][column];
if (column != 0 && crystalMap[row][column] != 0)
    return crystalMap[row][column];
if (column != crystalMap[0].length - 1 && crystalMap[row][column] != 0)
    return crystalMap[row][column];

// not on crystal
return -1;

private int numEdgeSites(int row, int column) {
    int edges = 0;
    if (row != 0 && crystalMap[row - 1][column] != 0)
        edges++;
    if (row != crystalMap.length - 1 && crystalMap[row + 1][column] != 0)
        edges++;
    if (column != 0 && crystalMap[row][column - 1] != 0)
        edges++;
    if (column != crystalMap[0].length - 1 && crystalMap[row][column + 1] != 0)
        edges++;
    return edges;
}

/**
 * Returns true if the pixel at the given row/column is adjacent to a crystal
 * (has at least one face touching a crystal pixel), false otherwise.
 */

private boolean adjacentToCrystal(int row, int column) {
    return adjacentCrystal(row, column) != -1;
}

/**
 * Initializes the set of crystals in this image with their
 * initial area, perimeter, and whether or not an edge crystal (edge crystal
 * being defined as one whose capture zone touches the end of the image)
 * @return A map of crystal ids to crystals
 */

private Map<Short, Crystal> initCrystals() {
    Map<Short, Crystal> crystals = new TreeMap<Short, Crystal>();
    for (int i = 0; i < crystalMap.length; i++) {
        for (int j = 0; j < crystalMap[0].length; j++) {

short cId = crystalMap[i][j];
if (cId == 0)
    // no crystal here, advance to next pixel
    continue;
Crystal c;
if (crystals.containsKey(cId)) {
    // we've already seen this crystal
    c = crystals.get(cId);
    //System.out.println(c);
} else {
    // create a new crystal
    c = new Crystal(cId);
    crystals.put(cId, c);
}
c.initArea++;  // increment the crystal area for this pixel
c.finalArea++;
//c.initPerim += numPerimEdges(i, j, cId);
if (isEdgePixel(i, j, cId))
    // this pixel has a non-crystal pixel next to it; increment
    // the perimeter count
    c.initPerim++;
}

// Circle around the outer edge of the tessellation. Any crystal
// IDs found along these edges correspond to edge crystals,
// so mark them as such.
for (int i = 0; i < tessellation.length; i++) {
    if (!crystals.containsKey(tessellation[i][0])) {
        System.out.println(tessellation[i][0]);
        System.out.println(i);
    }
    if (!crystals.containsKey(tessellation[i][tessellation[0].length - 1])) {
        System.out.println(tessellation[i][tessellation[0].length - 1]);
        System.out.println(i);
    }
    crystals.get(tessellation[i][0]).edge = true;
    crystals.get(tessellation[i][tessellation[0].length - 1]).edge = true;
}
for (int i = 0; i < tessellation[0].length; i++) {
    crystals.get(tessellation[0][i]).edge = true;
    crystals.get(tessellation[tessellation.length - 1][i]).edge = true;
}
return crystals;
/**
 * Computes the final areas and perimeters for the crystals. To be called
 * at the end of the simulation before printing crystal stats.
 */
private void finalizeCrystals() {
  for (int i = 0; i < crystalMap.length; i++) {
    for (int j = 0; j < crystalMap[0].length; j++) {
      short cId = crystalMap[i][j];
      if (cId == 0)
        // no crystal here, advance to next pixel
        continue;
      Crystal c = crystals.get(cId);
      c.finalArea++;  // increment the crystal area for this pixel
      if (isEdgePixel(i, j, cId))
        // this pixel has a non-crystal pixel next to it; increment
        // the perimeter count
        c.finalPerim++;
    }
  }
}

/**
 * Returns true if this pixel has a face touching a pixel that is empty
 * space, has an id is different from the given id, empty space or the edge of the
 * diagram.
 *
 * @param row The row of the pixel
 * @param column The column of the pixel
 * @param cId The id of the crystal w
 * @return true if an edge pixel
 */
private boolean isEdgePixel(int row, int column, short cId) {
  if (row == 0 || column == 0 || column == crystalMap[0].length - 1 ||
    row == crystalMap.length - 1) {
    // we are on the edge of the map!
    return true;
  }
  return crystalMap[row][column - 1] != cId ||
         crystalMap[row][column + 1] != cId ||
         crystalMap[row - 1][column] != cId ||
         crystalMap[row - 1][column + 1] != cId ||
         crystalMap[row + 1][column] != cId ||
         crystalMap[row + 1][column - 1] != cId;
*/
* Prints a CSV file of the image of the current simulation state.
*
* @param filename The name of the file to write to.
*/
public void simulationStateToCSV(String filename) {
    arrayToCSV(filename, crystalMap);
}

/**
 * Prints stats for the crystals in the simulation in the form of a CSV file.
 *
 * @param filename The name of the file to write to.
 */
public void printCrystalStats(String filename) {
    try {
        File out = new File(filename);
        BufferedWriter output = new BufferedWriter(new FileWriter(out));
        //finalizeCrystals();
        output.write("id,edge,init_area,final_area,init_perim,final_perim,#sticking_ops,%stuck_arrived_in_zone\n");
        for (short cId : crystals.keySet()) {
            Crystal c = crystals.get(cId);
            output.write(c.id + "," + c.edge + "," + c.initArea + "," + c.finalArea + "," + c.initPerim + "," + c.finalPerim);
            output.write("\n" + (1.0 * c.numArrived)/(c.numArrived + c.numStuck) + "\n");
        }
        output.close();
    } catch (IOException e) {
        throw new RuntimeException(e.toString());
    }
}

/**
 * Writes stats for the monomers that have been used in the simulation to a file.
 */
* Prints the time in existence and distance traveled for every monomer.
* 
* @param filename The name of the file to write to.
*/
public void printMonomerStats(String filename) {
try {
    File out = new File(filename);
    BufferedWriter output = new BufferedWriter(new FileWriter(out));
    finalizeCrystals();

    output.write("time,dist,start_zone,end\n");
    for (Monomer m : monomers) {
        output.write(m.timeExist + "," + m.distT + "," + m.start + "," + m.end + 
"\n");
    }
    output.close();
} catch (IOException e) {
    throw new RuntimeException(e.toString());
}
}

/**
* Writes the contour map to a file in the form of a CSV file. Every entry is the
* number of MC cycles during which a monomer was on a particular pixel.
* 
* @param filename The name of the file to write to.
*/
public void printContourMap(String filename) {
    arrayToCSV(filename, contourDiagram);
}

// Represents a single crystal in the MC simulation
private static class Crystal {
    short id; // the crystal's unique id
    boolean edge; // true if this crystal's capture zone goes off the edge of the image
    int initArea; // the pre-simulation area of the crystal
    int finalArea; // the post-simulation area of the crystal
    int initPerim; // the pre-simulation perimeter of the crystal
    int finalPerim; // the post-simulation area of the crystal
    int numStickingOps; // the number of cycles a monomer has been adjacent to this crystal
    int numArrived; // the # of monomers that arrived in this crystal's capture zone
    int numStuck; // of those that arrived in this capture zone, the # that actually stuck
// Creates a new crystal with the given id
public Crystal(short id) {
    this.id = id;
    edge = false;
    initArea = 0;
    finalArea = 0;
    initPerim = 0;
    numStickingOps = 0;
    numArrived = 0;
    numStuck = 0;
}

//@Override
//@public int hashCode() {
//@  return Short.hashCode(id);
//@}

@override
public boolean equals(Object o) {
    if (!(o instanceof Crystal))
        return false;
    return ((Crystal)o).id == this.id;
}

/**
* Represents a single monomer (random walker).
*/
private static class Monomer {
    double timeExist;  // time in existence
    int distT;        // distance traveled
    short start;
    short end;

    // Creates a new monomer
    public Monomer() {
        timeExist = 0.0;
        distT = 0;
        start = 0;
        end = 0;
    }

    // Updates the time for the monomer at the end of a cycle
    // using the equation:
//
// t = t + ln(1/u') / R_n
//
// where R_n is the sum of the probabilities of all possible
// moves for the monomer at this cycle, and u' is a number
// chosen uniformly from 0 to 1
public void updateTime(double R_n) {
    timeExist += Math.log(1 / random.nextDouble()) / R_n;
}
}

////////////////////////////////////////////////////////////////////////////////////
///                       STATIC HELPER I/O METHODS                              ///
////////////////////////////////////////////////////////////////////////////////////

public static void arrayToCSV(String filename, short[][] pixels) {
    try {
        File out = new File(filename);
        BufferedWriter output = new BufferedWriter(new FileWriter(out));
        int rows = pixels.length;
        int columns = pixels[0].length;
        for (int j = 0; j < rows; j++) {
            for (int i = 0; i < columns; i++) {
                if (i == columns - 1) {
                    // last pixel on the row; print a newline instead of ','
                    output.write(pixels[j][i] + "n");
                } else {
                    output.write(pixels[j][i] + ",");
                }
            }
        }
        output.close();
    } catch (IOException e) {
        System.err.println("Caught IOException: " + e.getMessage());
        System.exit(1);
    }
}

public static short[][] arrayFromCSV(String filename) {
    short[][] crystalMap = null;
    try (BufferedReader r = new BufferedReader(new FileReader(filename))) {
        // Get the height in pixels of the image
        int rows = getLineCount(filename);
        String line;
        int lineNumber = 0;
        while ((line = r.readLine()) != null) {
            
        }
    }
}
String[] rowVals = line.split(",");
if (crystalMap == null) {
    // this is the first line we're reading; get the width and
    // initialize the crystal map
    int columns = rowVals.length;
    crystalMap = new short[rows][columns];
}

for (int i = 0; i < crystalMap[0].length; i++) {
    crystalMap[lineNumber][i] = Short.parseShort(rowVals[i]);
}

for (int i = 0; i < crystalMap[0].length; i++) {
    crystalMap[lineNumber][i] = Short.parseShort(rowVals[i]);
}

for (int i = 0; i < crystalMap[0].length; i++) {
    System.out.println(i + "/" + crystalMap.length);
}

return crystalMap;
}

public static short[][] computeTesselation(short[][] crystalMap) {
    short[][] tesselation = new short[crystalMap.length][crystalMap[0].length];
    for (int i = 0; i < crystalMap.length; i++) {
        for (int j = 0; j < crystalMap[0].length; j++) {
            short closestCrystal = computeClosestCrystal(crystalMap, i, j);
            tesselation[i][j] = closestCrystal;
        }
    }
    System.out.println(i + "/" + crystalMap.length);
    return tesselation;
}

private static short computeClosestCrystal(short[][] crystalMap, int row, int column) {
    if (crystalMap[row][column] != 0)
        // we are on a crystal (so closest crystal is this one)
        return crystalMap[row][column];
    short closestCrystal = -1;
    double minDist = Double.MAX_VALUE;
    for (int i = 0; i < crystalMap.length; i++) {
        for (int j = 0; j < crystalMap[0].length; j++) {
            if (crystalMap[i][j] == 0)
                continue;  // this point is not a crystal
            double xDist = row - i;
            double yDist = column - j;
            // we can skip the sqrt sine we're just interested in relative dists
            // we can get the closest crystal by finding the crystal with the smallest distance
            if (Math.abs(xDist) + Math.abs(yDist) < minDist) {
                minDist = Math.abs(xDist) + Math.abs(yDist);
                closestCrystal = crystalMap[i][j];
            }
        }
    }
double dist = xDist * xDist + yDist * yDist;
if (dist < minDist) {
    minDist = dist;
    closestCrystal = crystalMap[i][j];
}
}
assert (closestCrystal != -1) : "Closest crystal not found";
return closestCrystal;

/**
 * Returns the line count for the given file.
 */
public static int getLineCount(String filename) throws IOException {
    LineNumberReader l = new LineNumberReader(new FileReader(new File(filename)));
    l.skip(Long.MAX_VALUE);
    int numLines = l.getLineNumber();
    l.close();
    return numLines + 1;
}

public static void main(String[] args) {
    double[] alphas = {0.0001, 0.00001, 0.000001, 0.0000001};
    if (args.length != 5) {
        System.out.println("Invalid arguments. Usage: java MCSimulatorEdgeModel [input
file] [tesselation file] [edge file] [number of monomers] [ID].");
        System.exit(1);
    }
    String inputFile = args[0];
    String tesselationFile = args[1];
    String edgeFile = args[2];
    int numWalks = Integer.parseInt(args[3]);
    String id = args[4];

    for (int j = 0; j < alphas.length; j++) {
        System.out.println("Starting simulation = " + alphas[j]);
        MCSimulatorEdgeModel walker = new MCSimulatorEdgeModel(inputFile,
tesselationFile, edgeFile, alphas[j]);
        //arrayToCSV("tessellation.csv", walker.tessellation);
    }
}
//walker.simulationStateToCSV("initialState.csv");

for (int i = 0; i < numWalks; i++) {
    if ((i + 1) % 100 == 0) {
        System.out.println("walk " + (i + 1));
    }
    walker.doRandomWalk();
}

walker.simulationStateToCSV("finalState_alpha" + alphas[j] + "ID_" + id + ".csv");
walker.printCrystalStats("crystalStats_alpha" + alphas[j] + "ID_" + id + ".csv");
walker.printMonomerStats("monomerStats_alpha" + alphas[j] + "ID_" + id + ".csv");
walker.printContourMap("contourMap_alpha" + alphas[j] + "ID_" + id + ".csv");
}

C: Analysis Videos

Analysis videos can be viewed in the digital version of this work as supplementary materials. A represented video of epifluorescence microscopy, dark field microscopy, and bright field microscopy can be found titled as such.