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Crystallization Processes In 1-D

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Abstract. Consider a crystallization process in which nucleation sites expand radially outward at a constant rate until the crystal impinges upon an adjacent site. The Kolmogorov–Avrami model studies how the volume of the crystal varies as a function of time. This model has been used to describe crystallization kinetics, and also how solids undergo phase transformations at a constant temperature.

In this paper we study and generalize the Kolmogorov–Avrami model in 1-dimensional Euclidean space. Using the Beta distribution, we derive an analytic expression for the expected crystal volume at time t from a uniformly-random sample of N initial nucleation sites. Furthermore, we generalize this equation to a wider class of crystal growth models, including crystals whose growth ceases when they are within a fixed distance from another crystal, or crystals in which each nucleation site only expands up to a bounded diameter. We simulate these models computationally and display the resulting volume curves. These generalized models may allow us to describe more complex scenarios that occur in physics, chemistry, and biology, such as nucleation in gel substances or perhaps even the formation of tafoni.

1 Introduction

Consider some substance that crystallizes about crystallization nuclei. The crystallization process occurs for accumulation of micro crystals with nonzero radius that grow at a constant velocity v until they impinge on one another — at which time the growth of the nuclei stops. The model used to demonstrate this phenomena is known as the Kolmogorov or Johnson–Mehl–Avrami model. The Avrami equation for the expected fraction of material crystallized as a function of time was first discovered in 1937 by Andrey Kolmogorov, a Russian mathematician of the 20-th century [4]. The formula is given by

$$V(t) = 1 - e^{-kt^n}$$

where $V(t)$ represents the fraction of material crystallized after some time t, k is a fitted constant, and $n = 1, 2, 3, \ldots$ is the dimension of the space we are working in. From this equation, one can clearly see that when we take the limit as $t \to \infty$ the function value converges to one, *i.e.*

$$\lim_{t\to\infty} V(t) = \lim_{t\to\infty} 1 - e^{-kt^n} = 1.$$

This corresponds to the fact that in the limit as $t \to \infty$, all of the material will crystallize. This model is widely used to demonstrate phase transformation kinetics.

In this paper, we will work in 1-dimensional Euclidean space by means of thinking of the random distribution of nuclei on a circle or similarly the unit interval [0,1]. From this, we will discover the fraction of the substance that is crystallized by some time t. We also develop several modified models which include the nuclei ceasing to grow a distance Δ apart upon impingement, as well as fixing a defined maximum width such that nucleation stops once the value is achieved. We plot our results of the growth or volume with respect to time t. We construct a formula for the volume crystallized at a specified time t using a probability distribution of gap sizes with respect to the number of nucleation sites.

Throughout this paper, we will describe the underlying process of how we simulate the models. We create programs in MATLAB to provide visual results of our models.

In Section 2 we derive a formula for the expected fraction of volume crystallized at a given time t. We then generalize several models of crystal growth and provide a condensed formula of the fractional volume crystallized in Section 3. We then transition into Section 4 in which we provide a marginal PDF of the Beta distribution which provides us with the probability of a given gap size being present on the unit interval. Finally, we provide simulation results in Section 5.

1.1 Derivation of V(t)

In this subsection we define the Avrami model in the planar case. Let D^2 be the unit disk in the plane and let $P \subseteq D^2$ be the set of nucleation seeds that nucleate radially outward at a rate $r = vt$. Define the nucleation region

$$R = \{x \in D^2 \mid \exists\ p \in D^2 \mid \text{dist}(x, p) \leq vt\}.$$

Define $B_{vt}(c) \subseteq D^2$. We want to calculate the probability of any point $p \in P$ that is not in $B_{vt}(c)$ with $c \in D^2$ given by, $\Phi(t) = \left(\frac{A-\pi(vt)^2}{A}\right)^{|P|} = \left(1 - \frac{\pi(vt)^2}{A}\right)^{|P|}$ where A is the area of D^2 and the area of $B_{vt}(c) = \pi(vt)^2$. From this we have that,

$$\Phi(t) = \left(1 - \frac{\pi(vt)^2}{A}\right)^{|P|} = e^{|P|ln(1-\frac{\pi(vt)^2}{A})} \approx e^{-(\frac{|P|\pi(vt)^2}{A})} = e^{-(\frac{|P|\pi v^2}{A})t^2}.$$

Letting $\gamma = \frac{|P|\pi v^2}{A}$ yields $\Phi(t) = e^{-\gamma t^2}$. Taking the compliment of $\Phi(t)$ gives us the probability of c's being nucleated to be $\Psi(t) = 1 - e^{-\gamma t^2}$. This is analogous to the general Avrami equation $V(t) = 1 - e^{-kt^n}$ where $n = 1, 2 \ldots$ is the dimension one is working in.

2 First model of crystal growth

Consider a crystallization process on random nucleation sites on the unit interval or unit circle, where the crystal grows radially outward from each nucleation site at velocity v in both directions, until it impinges on its neighboring crystal.

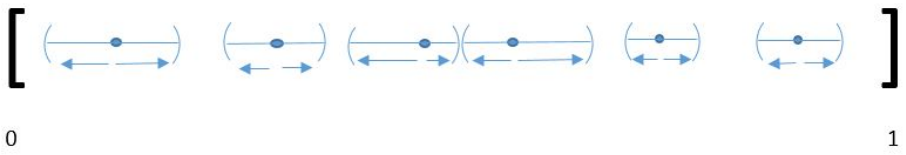

Figure 1: Visualization of seed placement and associated critical times on the unit interval

Let $v > 0$ be the velocity of the crystal growth, and let $f\colon [0,1] \to [0,\infty)$ be the probability density function of gap sizes between adjacent nuclei.

First let us consider the general Avrami Model and let $V(t)$ be the expected fraction of volume crystallized at time t. For $0 \leq 2vt \leq 1$ we have

$$V(t) = \int_0^{2vt} sf(s)\ ds + \int_{2vt}^1 2vtf(s)\ ds.$$

Here, the first integral represents the volume contributed from gaps of size $s < 2vt$ since s is the current gap size and $f(s)$ is the probability of a gap of size s being present in the interval. Similarly, the second integral represents the volume contributed from gaps of size $s > 2vt$. Indeed, we multiply $f(s)$ by $2vt$ which is the volume crystallized at time t for gaps of size $s > 2vt$. Summing these two integrals provides us with the expected fraction of volume that is crystallized at time t on the entire unit interval $[0,1]$, as mentioned above.

Note:

$$V'(t) = 2vtf(2vt) - 2vtf(2vt) + 2v\int_{2vt}^1 f(s)\ ds = 2v\int_{2vt}^1 f(s)\ ds,$$

which makes sense because the rate of change in $V(t)$ is determined by the fraction of the gaps which are not yet filled at time t.

Now consider the case when the nucleation stops growing a distance $\Delta > 0$ apart from adjacent sites, and let $V_\Delta(t)$ be the expected volume crystallized at time t. For $0 \leq 2vt + \Delta \leq 1$ we have

$$V_\Delta(t) = \int_0^{2vt+\Delta} (s-\Delta)f(s)\ ds + \int_{2vt+\Delta}^1 2vtf(s)\ ds.$$

Similarly to the general case, the first integral represents the contribution from gaps of size $s < 2vt + \Delta$ and $f(s)$ is the probability of a gap of size s being present in the interval. Likewise, the second integral corresponds to the volume contributed from gaps of size $s > 2vt + \Delta$. The bounds for this integral change to compensate for the remaining interval $[2vt + \Delta, 1]$. Indeed, we multiply $f(s)$ by $2vt$ which is the volume crystallized at time t for gaps of size $s > 2vt + \Delta$. Summing these two integrals together allows us to compute the expected fraction of volume crystallized at time t on the entire interval $[0,1]$ for any given velocity $v > 0$, as mentioned above.

3 Generalized models of crystal growth

We now generalize the previous section by letting $h\colon \mathbb{R}^2 \to \mathbb{R}$ such that $h(t,s)$ is the volume crystallized in a single gap of size s at time t. What follows are four example models that simulate different nucleation processes:

3.1 Model 1

For velocity v held constant we have that

$$h(t,s) = \begin{cases} 2vt & \text{if } 2vt < s \\ s & \text{otherwise.} \end{cases}$$

This is the classic Avrami model described in Section 2.

3.2 Model 2

For the case with $\Delta > 0$ we obtain

$$h(t,s) = \begin{cases} 0 & \text{if } s \leq \Delta \\ 2vt & \text{if } s > \Delta \text{ and } 2vt < s - \Delta \\ s - \Delta & \text{otherwise.} \end{cases}$$

The above is the second model considered in Section 2. What follows are two new models not yet considered in the paper.

3.3 Model 3

Our third model is as follows and simulates nucleation growth until the growth cycle hits a fixed width.

Let $w > 0$ be the width (to either side). Fixing velocity v to be held constant, we have that

$$h(t,s) = \begin{cases} 2vt & \text{if } 2vt < \min(2w, s) \\ \min(2w, s) & \text{otherwise.} \end{cases}$$

3.4 Model 4

We can combine models 2 and 3. For the case where $w > 0$ and $\Delta > 0$ and velocity v held constant as before, we have

$$h(t,s) = \begin{cases} 0 & \text{if } s \leq \Delta \\ 2vt & \text{if } s > \Delta \text{ and } 2vt < \min(2w, s - \Delta) \\ \min(2w, s - \Delta) & \text{otherwise.} \end{cases}$$

With any such model we can deduce the following result:

$$V(t) = \int_0^1 h(t,s) f(s)\, ds.$$

Here, $V(t)$ is the expected volume crystallized at time t, and $h(t,s)$ is defined to be the volume crystallized in a single gap of size s at time t, and $f(s)$ is the probability of a gap of size s being present. Multiplying $h(t,s)$ by $f(s)$ and integrating provides us with the expected volume over the entire unit interval. The above formula holds true since at time t, a gap of size s contributes $h(t,s)$ to the volume and $f(s)$ is the probability of a gap of size s being present in the interval $[0,1]$.

In the following section, we will determine what the function f is in terms of the Dirichlet and Beta distributions.

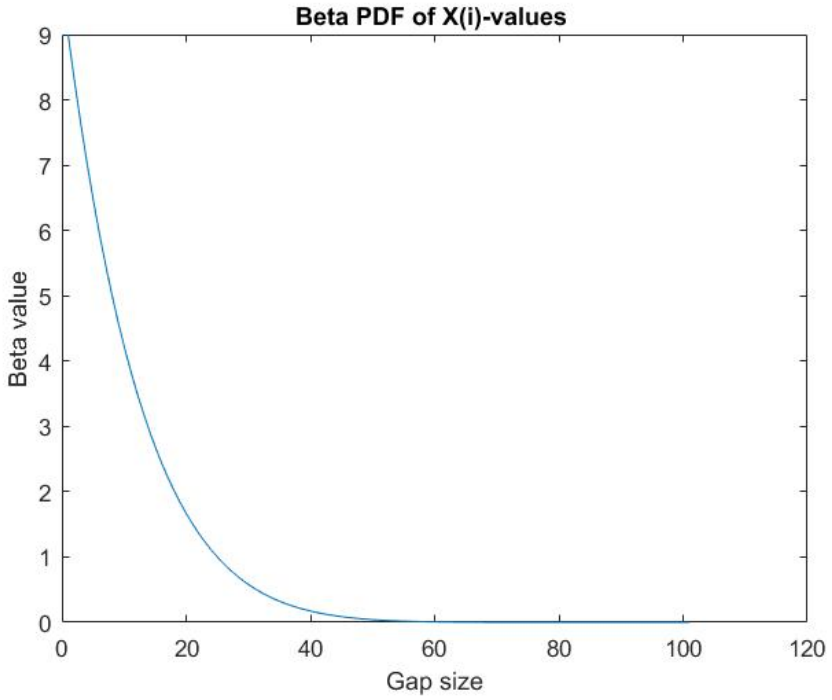

Figure 2: $k = 10$ gaps

4 Marginal PDF of Beta Distribution

Knowing that the formula derived in the previous section holds true, we can now determine the probability distribution function f using the Dirichlet and Beta distributions. First note that the flat Dirichlet distribution, which is the uniform distribution on the $(k-1)$-simplex, describes uniform random sampling of gaps $X_i \geq 0$ such that $\sum_{i=1}^{N} X_i = 1$, where N is the number of gaps. The Beta distribution is the marginal distribution of the Dirichlet, and hence describes the probability density function of a single gap.

For simplicity, let the number of gaps $k = 10$. We can estimate the size of each gap by calculating the Beta distribution $\text{Beta}(1, k-1)$ which is the distance between each adjacent nucleation site. The Beta distribution will give our probability density function $f\colon [0,1] \to [0,\infty)$ as defined in the previous section. The marginal distribution is defined as

$$X_i \sim \text{Beta}(\alpha_i, (\sum_{j=1}^{N} \alpha_j) - \alpha_i)$$

but since we are performing a flat distribution with $\alpha_i = 1$ for all $1 \leq i \leq N$ our marginal distribution transforms into

$$X_i \sim \text{Beta}(1, k-1).$$

Here, k is the number of gaps between N nucleation sites. Utilizing MATLAB's built-in betapdf function we obtain the graphical result shown in Figure 2 of the marginal flat Dirichlet distribution.

We can then find the mean gap size μ by the following formula:

$$\mu = \frac{\alpha}{\alpha + \beta}$$

where $\beta = (k-1)$ and all $\alpha = 1$. This gives

$$\mu = \frac{1}{1+\beta} = \frac{1}{1+(k-1)}.$$

We can see from Figure 2 above that the median value is half the area under the curve and we can calculate the mean gap size using the equations above. Hence, $\mu = \frac{1}{10}$ and we see that as we increase the value of k, the value of μ decreases and we can conclude that the average distance between each individual nucleation site is quite small, and the nuclei impinge on one another fairly quickly.

5 Simulation Process

The problem we face is simulating the standard Avrami model in 1-dimension, as well as altering our model to compensate for nuclei impinging on one another a distance Δ apart. These two models will allow us to determine the fractional decomposition of a substance that has crystallized by a specific time t. The models will also allow us to observe the growth of N randomly placed nucleation sites and compare our results. The growth is assumed to grow radially outward at a constant velocity v. After some time t, the growth ceases due to the impingement of nearby nuclei. Our goal throughout this section is to accurately explain and simulate the models in 1-dimension and hypothesize a solution to the altered models by providing plots of our results with respect to all the models.

We begin by defining nucleation growth by the following: Let

$$X = X_0 = \{x_1, \ldots, x_N\} \subseteq S^1$$

be our nucleation sites and let

$$X_t = \{y \in S^1 \mid d(y, x_i) \leq 2vt \text{ for some } i = 1, \ldots, N\}$$

be the crystallized region at time t. From this definition we will be studying the function

$$V(t) = V(X_t)$$

where the nucleation sites X are chosen uniformly at random on S^1. We start our simulation method by randomly placing N seeds or nuclei on a line in 1-dimension and transform the line into a circle as described in the definition above. By doing so, we are able to disregard boundaries on the line. We then sort the points or nuclei and define a constant velocity v. This allows us to simulate a constant growth of the nuclei over a given time t. We sort the nucleation sites so that they appear in a clockwise order $P_1, P_2, \ldots, P_i, \ldots, P_N \in S^1$. We denote the length of the i-th gap (between seeds i and $i+1$) as s_i:

$$s_i = \begin{cases} P_{i+1} - P_i & \text{if } i < N \\ (1 - P_N) + P_1 & \text{if } i = N. \end{cases}$$

Now that we have the distance between each of our N number of randomly distributed nuclei, we can analytically calculate the critical times t_i^* when the nuclei impinge on one another. This is given by

$$t_i^* = \frac{s_i}{2v},$$

where t_i^* is the time when the i-th gap fills, s_i is the length of the gap between the distributed nuclei i and $i+1$, and v is the assumed constant velocity. We multiply v by 2 in the denominator due to the growth of the nuclei expanding from both the left and right side at the constant rate as defined above. In the case where nuclei impinge upon each other a distance Δ apart, we have

$$t_i^* = \begin{cases} \frac{s_i - \Delta}{2v} & \text{if } s_i > \Delta \\ 0 & \text{otherwise.} \end{cases}$$

The next step in our simulation requires us to find all t_i^* for each associated s_i, *i.e.* each gap. For each gap, we have a growth curve that can be represented by the following diagram:

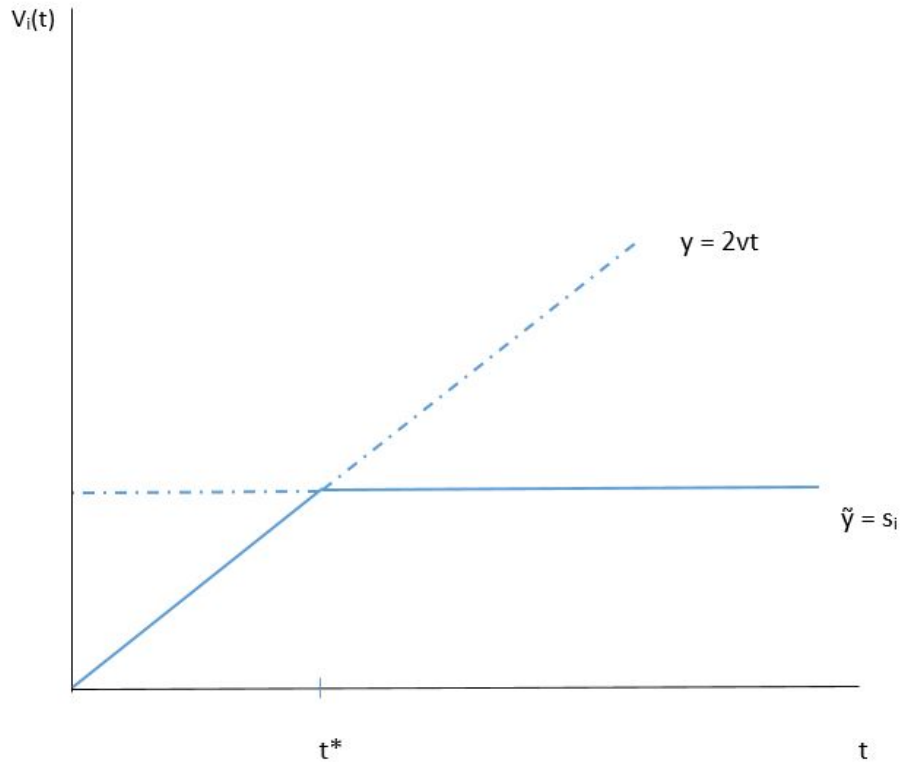

Figure 3: Here the t-axis represents time and the $V_i(t)$-axis represents the volume or growth of crystallization

This growth function for a single gap is defined by

$$V_i(t) = \begin{cases} 2vt & \text{if } t < t_i^* \\ s_i & \text{otherwise.} \end{cases}$$

We take the minimum of $y = 2vt$ and $\tilde{y} = s_i$ (as shown in Figure 1) *i.e.* where the two lines in the diagram above intersect for all i at time t_i^*. We then sum all of $V_i(t)$'s together to get the total growth or volume curve $V(t)$ where $i = 1, \ldots, N$ such that each curve $V_i(t)$ and $V_i^{\Delta}(t)$ are computed to allow us to obtain our final growth or volume curve $V(t)$ and $V^{\Delta}(t)$ which is represented by the

following:

$$V(t) = \sum_{i=1}^{N} V_i(t).$$

As mentioned above, this can be thought of as the length or volume the nuclei achieve in a 1-dimensional assumption. Similarly for our delta model, we take the minimum of $y = 2vt$ and $\hat{y} = s_i - \Delta$ which can be visualized by Figure 4 and is defined as

$$V_i^{\Delta}(t) = \begin{cases} 2vt & \text{if } t < t_i^* \\ s_i - \Delta & \text{otherwise.} \end{cases}$$

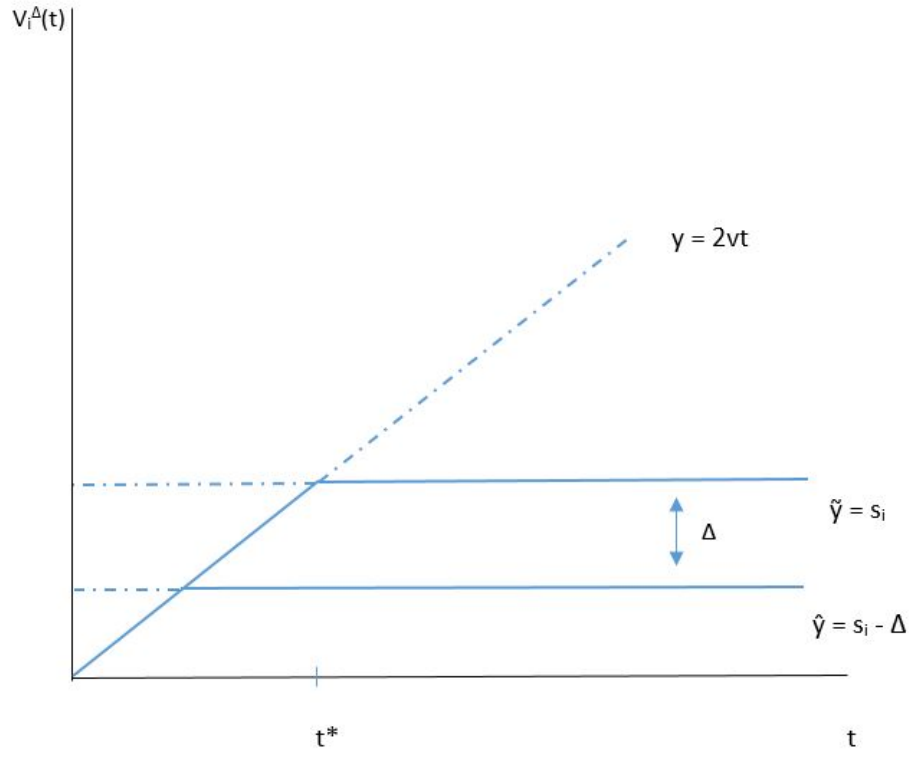

Figure 4: Here the t-axis represents time and the $V_i^{\Delta}(t)$-axis represents the volume or growth of crystallization

Similarly for our delta model, the summation is as follows:

$$V^{\Delta}(t) = \sum_{i=1}^{N} V_i^{\Delta}(t)$$

(For a visual representation of $V(t)$ and $V^{\Delta}(t)$ refer to the Results in Section 4). What follows are our results.

6 Results

Now that we have defined all necessary variables and explained our simulation process above, we are able to successfully simulate the Avrami model in 1-dimension assuming a circular model. To do this, we simply plot the results with time on the x-axis and growth or volume on the y-axis. This will allow us to visually analyze the fraction of material crystallized at a given time t. We will first provide the results of all four models defined in Section 3 with a fixed $N = 1000$. We define $\Delta = \frac{CL}{N}$ where we call C the delta coefficient, L is the length or domain of the nucleation restriction, and N is the number of randomly distributed nuclei. Here $L = 1$ since we are only considering the unit interval. So, Δ reduces to $\frac{C}{N}$. However, in general we have $\Delta = \frac{CL}{N}$. Note that for the models that incorporate delta, namely Models 2 and 4, we will declare the delta coefficient $C = 0.50$ and compare the result to that of a value of $C = 0.75$. Also note that in models 3 and 4 we define the fixed width $w = 0.001$. What follows are the results.

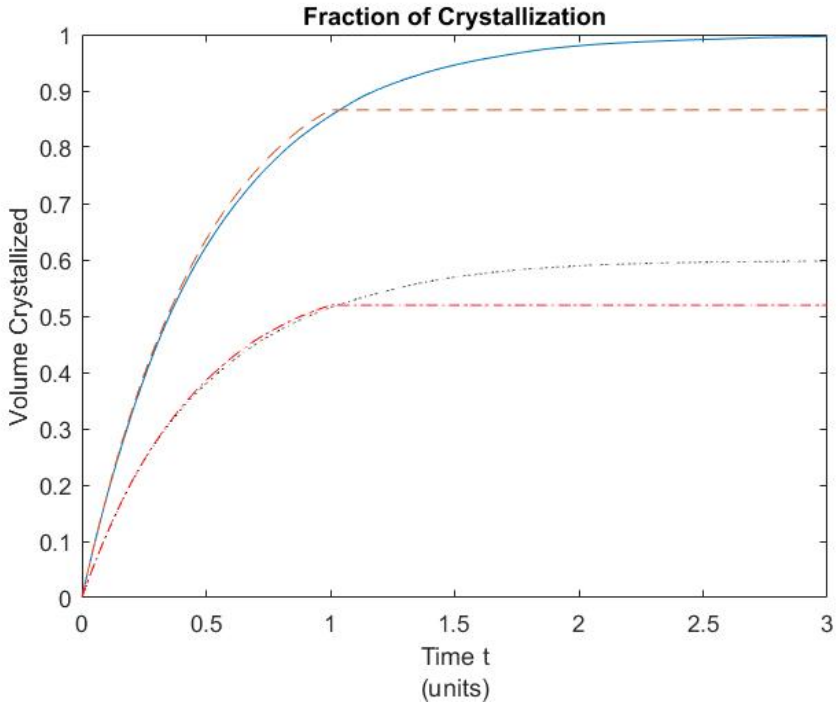

Figure 5: Model 1 (Solid line), Model 2 (Dotted line), Model 3 (Dashed line), Model 4 (Dash-dot line) with parameters $N = 1000$, delta coefficient $C = 0.50$.

Figure 5 shows us the plots of the fraction of material crystallized at time t with $N = 1000$ randomly distributed nuclei. We can see that the results seem to be modeling the crystallization process quite well. This can be seen because at time $t = 0$ the slopes of our curves are $2v$ and converge at $t = 0$. Note that the curves relate to the models described in Section 3. We notice that as $t \to \infty$ model 1 converges to one and model 3 converges to approximately 0.85, where model 2 tends to a value of 0.60 and model 4 tends to the value 0.50. The figure that follows will demonstrate the results when we adjust our C value.

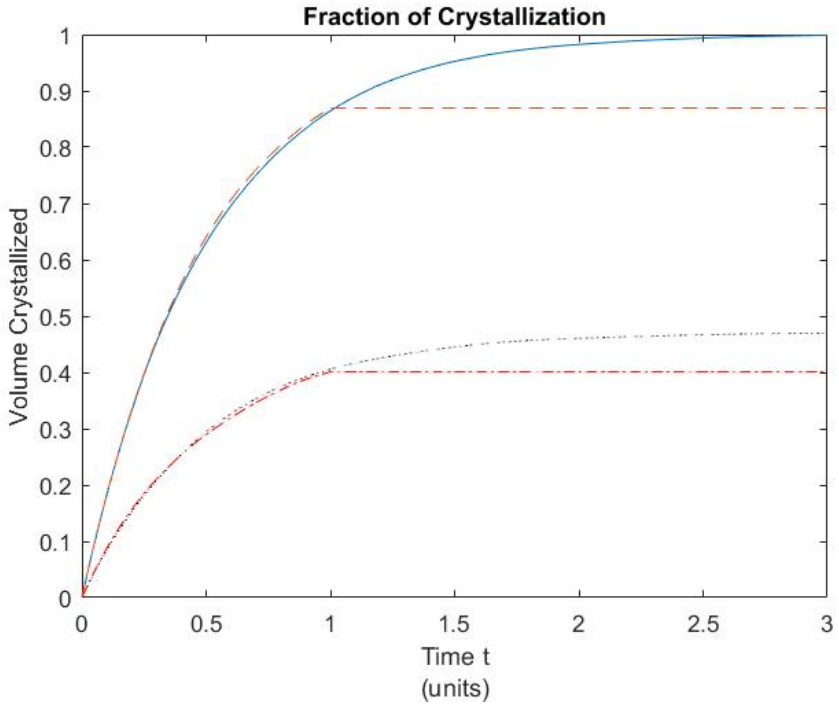

Figure 6: Model 1 (Solid line), Model 2 (Dotted line), Model 3 (Dashed line), Model 4 (Dash-dot line) with parameters $N = 1000$, delta coefficient $C = 0.75$.

Analyzing Figure 6 shown above, we see that when we increase our C value to $C = 0.75$ the impingement distance Δ increases. We can deduce that there is a direct relationship between the size of Δ and the delta coefficient C. This can be interpreted as the amount of "waste" that the crystal lattice produces [3].

Comparing Figure 5 to Figure 6 we notice that when we hold N constant and change our delta coefficient by a factor of 50%, *i.e.* 0.50 to 0.75, that the nucleation models 2 and 4, as defined in Section 3, impinge on one another sooner in Figure 6 than as shown in Figure 5. This can be seen since as $t \to \infty$ model 2 converges to 0.60 and model 4 converges asymptotically to a value of 0.50. One can interpret (for example) that the difference $1 - 0.60 = 0.40$ and $1 - 0.50 = 0.50$ are the distance Δ where the nuclei stop growing.

7 Conclusion

From our simulations, we were able to successfully analyze the fraction of crystallization that occurs at a given time t assuming a constant growth velocity v. We also see that given a value of N, the asymptotic behavior of our growth or volume curves associated with models 2 and 4 have a sensitive change when changing the delta coefficient C. The simulated models allow us to better understand the behavior of the nucleation growth by providing a visual representation of the seed placement at time $t = 0$. We were also able to analytically derive a general formula for predicting the volume crystallized at a given time t for any such model. We then conducted a marginal probability density function of the Dirichlet distribution to determine the probability density function of a single gap on the unit interval [0,1]. From our research we have a better idea of how the impingement of nuclei behave in higher dimensions. Our Avrami models allow us to manipulate the critical times

where the nuclei stop growing a distance Δ apart from one another. From this, we are able to better understand how nuclei grow and further understand crystallization dynamics and phase transformation kinetics.

8 Acknowledgments

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