

Crystallization Simulation Report

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Abstract

The study of crystal nucleation generally focuses on the properties of a cluster, and we see the evolution of the concentration of crystal through the distribution of monomers to form clusters of varying degrees of size and order. To investigate the evolution of these crystals, we developed a simple program that when given the rate coefficients of the crystal's growth, decay, order, and disorder. We represent these as a series of differential equations, which we use to determine the nucleation based on the cluster size and degree of order. The results of these equations enable us to perform numerical analysis based on the results, by examining the steady state and the nucleation of the system. We can then determine the effectiveness of a specific crystal from these conditions would look for the specific surface we set in our coefficients. [1]

I. INTRODUCTION

THE motivation for the model simulation is that we want to visualize the properties and distribution of the crystals, given the conditions in which a crystalline structure is present. These crystals are defined as having two properties. Each crystal has an overall 'size'; n . They also have an 'order of crystallization' denoted as ϕ . We can examine the values of n and ϕ up to a predefined maximum value called N , in which $1 \leq n \leq N$. The transitions between values of n and ϕ are defined through a set of four rate coefficients for each size and order of crystal.

We denote these four coefficients: Growth: K_n^+ , Decay: K_n^- , Order: ω_ϕ^+ , and Disorder: ω_ϕ^- . These coefficients contain the relevant details such as temperatures, pressures and surface conditions for our current crystal with values n and ϕ , transforming it into one of $n \pm 1$ and $\phi \pm 1$.

To calculate the concentration of a specific size of crystal, we can model it as a differential equation. The first equation defined is the transformation from a crystal of characteristics $N_{(n,\phi)}$ to a crystal of neighboring characteristics.

tics.

$$\begin{aligned} N_{(n,\phi)} = & - (K_n^+ \cdot N_{n,\phi}) - (\omega_\phi^+ \cdot N_{n,\phi}) \\ & - (K_n^- \cdot N_{n,\phi}) - (\omega_\phi^- \cdot N_{n,\phi}) \end{aligned} \quad (1)$$

We can define a second equation from our first: Since we can move from size $N_{(n,\phi)}$, we must also be able to move from a different sized crystal to our predefined size $N_{(n,\phi)}$.

$$\begin{aligned} N_{(n,\phi)} = & (K_{n+1}^- \cdot N_{n+1,\phi}) + (\omega_{\phi-1}^+ \cdot N_{n,\phi-1}) \\ & + (K_{n-1}^+ \cdot N_{n-1,\phi}) + (\omega_{\phi+1}^- \cdot N_{n,\phi+1}) \end{aligned} \quad (2)$$

We can then combine these equations together to form the resulting overall differential equation for every size of crystal we define for our system:

$$\begin{aligned} \frac{dN_{(n,\phi)}}{dt} = & (K_{n+1}^- \cdot N_{n+1,\phi}) + (\omega_{\phi-1}^+ \cdot N_{n,\phi-1}) \\ & + (K_{n-1}^+ \cdot N_{n-1,\phi}) + (\omega_{\phi+1}^- \cdot N_{n,\phi+1}) \\ & - (K_n^+ \cdot N_{n,\phi}) - (\omega_\phi^+ \cdot N_{n,\phi}) \\ & - (K_n^- \cdot N_{n,\phi}) - (\omega_\phi^- \cdot N_{n,\phi}) \end{aligned} \quad (3)$$

The goal of the model is that we gain an understanding of the concentration of sub-crystals amounts for the values of n and ϕ we

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assign the system can take on. From this, we can characterize the conditions of the system to what effects it would have on the formation of specific crystals. The model will enable an understanding of the most ideal crystal given the specific external characteristics that the coefficients of the system represent.

II. MODEL SCOPE

The main exogenous variables we have for the model were the conditions in which it is being simulated. While not directly included, the underlying conditions are built into the coefficients that we assign the model to perform over, enabling us to include the impact they display on the crystals whilst not actually defining them outright. There is also a predefined upper limit the general size of crystal we want to examine, this is implemented through the number of coefficients we defined, which is further explained below. The reason why not to explicitly define this is due to the fact a crystal could theoretically grow to include all of Avogadro's Number (6.022×10^{23}) of monomers. This would pose significant computational power and memory, and thus had to be limited to just the amount of groups of coefficients.

The model primarily assumes that the crystallization can be represented two-dimensionally, with an x-axis as time and the y-axis as the concentration of monomers, with slope representing the concentration of a given type of crystal as a function of time. In reality, crystallization would have several more dimensions, such as the transfer of charges between monomers to stabilize. As well, the model assumes that once a crystal reaches our predefined cap of N that we defined based on the coefficients, we subdivide the size N crystal into N size one crystals. This enables us to ensure conservation of the overall number of monomers we see in the system, while enabling us to reach a 'steady state' for the system. This means we basically exclude examining crystals of a size larger than N . We are also assuming that once the model reaches

the 'steady state', or as such all the sum of the differential equations converges to 0, then we assume the model no longer changes, and can extract the information about our crystal from that.

III. MODEL DESIGN

We can envision each of the crystal types of n and ϕ as being a value on the graph as we defined in our scope. We primarily need to consider the area under the graph due to the constraint we cannot possibly be more ordered than n : ($\phi \leq n$). This area is highlighted in gray in Figure 1.

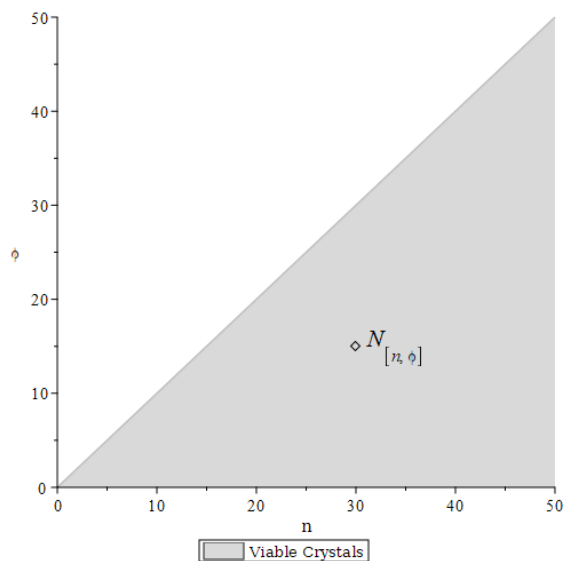


Figure 1: The area highlighted on the slope is the possible valid crystals we can see within the system.

This depiction, while covering the entire surface area, is inaccurate due to how a crystals are composed of an number of monomers. Since we cannot really have half of a monomer making up a crystal of a fractional size or order, we can simplify this to only consider the nodes on whole number indices, as seen in figure 2.

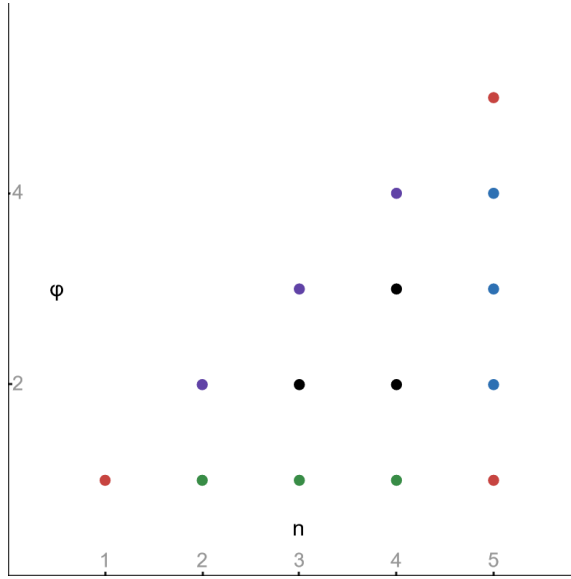


Figure 2: The points in this plot correspond to what we consider valid crystals. Notice that certain nodes have different colors to others.

We can see there exists five different types of nodes defined with the different colors. These nodes are defined as having existent or non-existent neighbors. It is important to note that when describing the usage of coefficients, we do so in terms of the ones as described in Equation 3.

Central Nodes are defined as the black nodes. They use all eight coefficients, meaning it uses the entire differential equation to find value for the time step, and thus has flows in/out of a node in all directions.

End-Boundary Nodes are defined as the blue nodes. These nodes have seven coefficients. Since they exist on the rightmost boundary, they are at the maximum value of N we defined. Thus, there cannot exist flow from $N + 1$ to N , but they can flow, since the amount is transferred from the $N - th$ node back to the stockpile.

Lower-Boundary Nodes are defined as the green nodes. These nodes only have six coefficients. It is impossible for $n > 1$, since

otherwise they would just be loose monomers without being crystals. So, such nodes cannot have coefficients from a below node, or more significantly, cannot have flows from a node below.

Diagonal Nodes are defined as the purple nodes. These nodes only have four coefficients. Since they exist where the value of $n = \phi$, they can only gain/lose a monomer from a crystal with $n + 1$ size, or gain/lose order from a crystal of order $\phi - 1$.

Finally, the Corner Nodes are defined as the red nodes. These three nodes are unique in that each of the three we examine have unique properties compared to each other, which we can see in Figure 3.

1. The left corner node has four coefficients; two inflows and two outflows. One inflow is from the stockpile and one is from the neighbor, and the outflows are one to the stockpile and one to the neighbor.
2. The bottom-right corner node has five coefficients. Two flowing in/out of the crystal of size $n - 1$, two flowing in/out of the crystal of $\phi + 1$, and finally one flowing into the boundary.
3. The top-right corner node has three coefficients. Two flowing in/out of the crystal of order $\phi - 1$, and one following into the boundary.

With the explanation of the general structure, we can explain the implementation of the model. The model was coded in Julia. This language was chosen due to its strong mathematical background, as well as having a powerful differential equation solver, enabling the solution to be calculated easily. We can store the coefficients for a specific node as a struct. We only consider the coefficients flowing out of the node for this struct. This decision was made since we can examine the neighbouring nodes for a given index in order to determine the coefficients that flow into said index node.

```
struct nodeStructure
    Growth::Float64
```

```

Decay :: Float64
Order :: Float64
Disorder :: Float64
end

```

We then need to store these structures within an array. We define this array to be of size $M \times (M + 1)$. The reason we have an additional column, is that we wish to store the stockpile as an array index so that it can be used for the stockpile of monomers not included within the crystal. Otherwise, the rows and columns are filled with these structures in the triangular shape as defined in Figure 3.

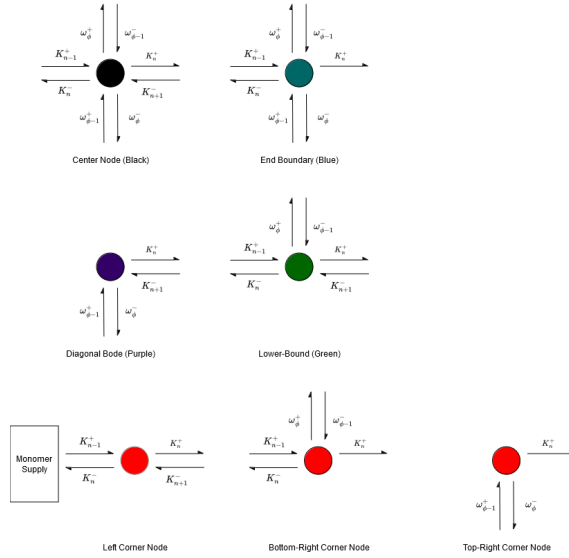


Figure 3: All five colors of nodes, and the corresponding coefficients we see from the inflows and outflows related to them.

We also need to create a separate array of the same size of $N \times (N + 1)$. This is because we need to modify the total concentration of each type of crystal, in which for both arrays, the indices match (ie: $\text{CoefArray}[i, j] = \text{NodeArray}[i, j]$).

From there, we can use the current position of our current node, and find the coefficients for the inflows into the current node using several functions to find the coefficients, the values for the node, then finally numerically integrate the differential equation with these values. From there, we can plot the results of

this differential equation and extract the meaning from this. We would want to run this over a specific time horizon.

IV. MODEL CALIBRATIONS

The primary calibrations performed on the model were comparisons to preexisting empirical findings from previous research. We would expect the model to have an initial spike to a peak due to going from 0 monomers present before this time step to a high due to the lack of outflows, then slowly decrease into an equilibrium state, where the interaction between the crystal of parameters (n, ϕ) and all the other crystals in the system reaches the steady state. This is shown in Figure 4.

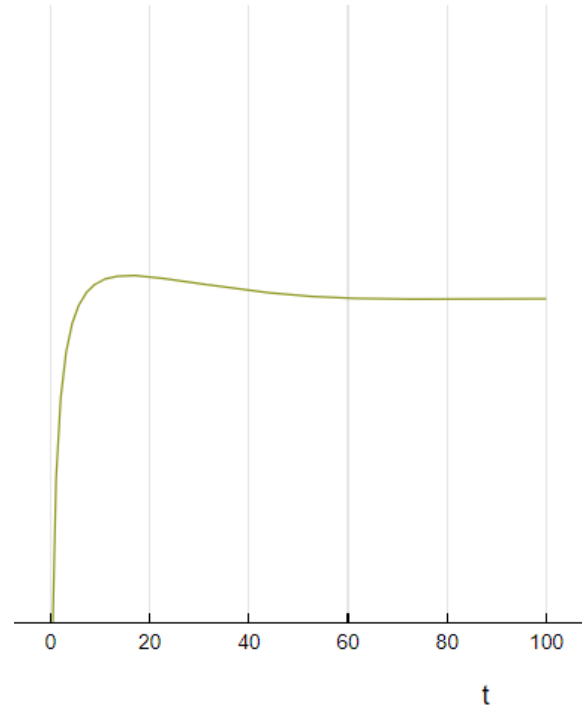


Figure 4: The curve we would expect to see on the crystal nodes. Notice the sharp rise to a peak, then the slow flattening of the curve to equilibrium.

The alternative variant we would see is from the monomer stockpile. We would see the stockpile decrease significantly lower than at the steady state, then slowly climb back up

until it reaches the steady state.

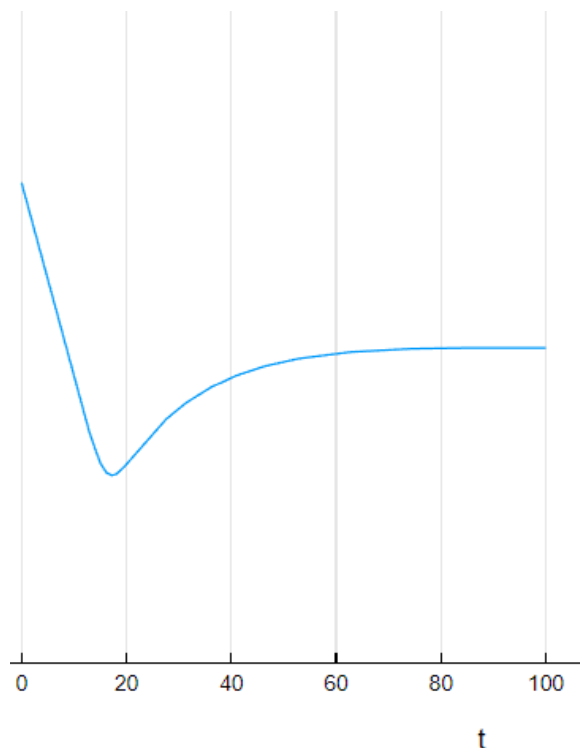


Figure 5: The curve we would expect to see on the stockpile node. Notice the sharp decrease below the equilibrium value, then the slow climb to equilibrium.

The comparisons to empirically calculated data from [1] and Figure 4 matches the general trend we would expect to see in our data. There is a documented similar pattern with it reaching a similarly shaped peak then slowly decreasing until the system reaches the steady state.

V. SENSITIVITY ANALYSES

The analyses performed on the model are able to be performed by altering the various coefficients. We can use the coefficients for a parameter analysis. This also has the added benefit of enabling the structural analysis of the model by setting specific coefficients to specific values, representing the conditions of the system we wish to analyze. For example, we

disable the ability for specific crystals to be formed, by limiting the coefficients to them, or to enable the occurrence of certain phenomena. An interesting example analysis would be setting all the order coefficients to 0. This would mean we would only ever see crystals of order $\phi = 1$, but at $(1 \leq n \leq N)$ crystal size, which could prove size of monomer clusters would be most abundant for the material in which it prohibits crystal formation. The graph for this run through is shown in Figure 6. It is noted that the greyed out labels on legend are irrelevant to the plot.

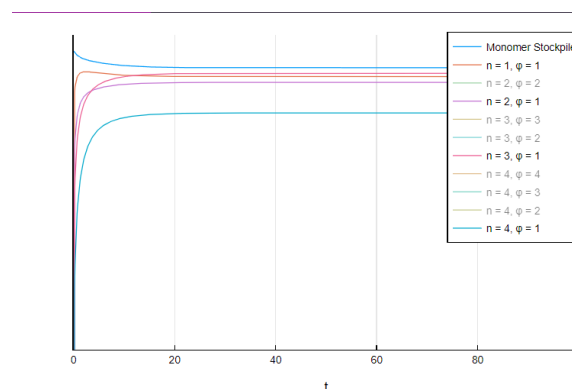


Figure 6: The plot in which we disable the ability for order to increase. Notice that eventually the system reaches an equilibrium faster than something like Figure 4 since it only needs to worry about the distribution of monomers across time, rather than the formation of crystals.

Another good analysis that can be performed would be to modify the growth coefficient for specific sizes. We can use this in order to define a limit on how a specific crystal grows or perform a drip-feed of monomers into the system, and viewing what phenomena would occur with the slow introduction of more material. We can also set each of the other three coefficients individually to zero after as well to see how that would affect the system. For extreme value analyses, we can primarily use values ≈ 0 or 1.

VI. SCENARIOS

In terms of a baseline scenario, we want a scenario in which all the coefficients are randomly selected to be numbers $0 \leq \text{coeff} \leq 1$. This is because we want to view all phenomena that can occur from the crystal of size (n, ϕ) interacting with of the neighbors. While which overall size of N does not really matter since the phenomena should occur regardless of size, a good value to use for it would be a value of $N \geq 4$. This way, we would see all five types of nodes defined in the Model Design section. However, the baseline can work with as few as one node. The results of these scenarios often provide interesting insights into the dynamics in play. For example, when have $N = 4$ (Figure 7) or $N = 10$ (Figure 8), we see this as a system.

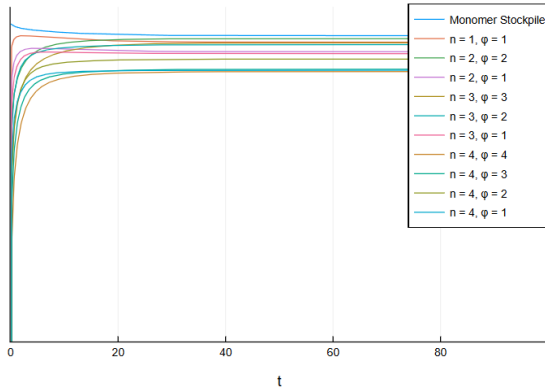


Figure 7: The solution plot we see for $N = 4$.

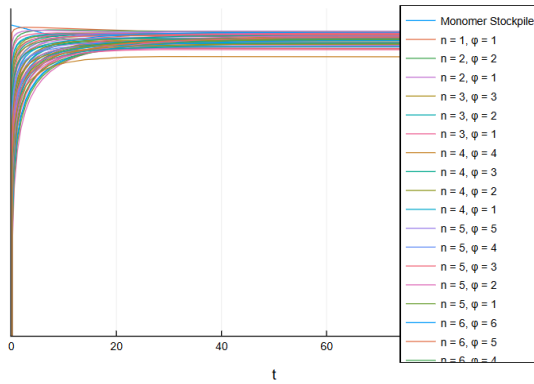


Figure 8: The solution plot we see for $N = 10$.

We can create various alternative scenarios from this by limiting or increasing the total amount of monomers present within the system, by modifying the total count 6.022×10^{23} to different numbers if we wish to see the dynamics on a smaller or larger scale, such as decreasing the system to be a specifically defined concentration of monomers.

VII. INSIGHTS

If I were to undertake this project again, I feel that I set the model up as best as I could for what was asked. The general process I performed for this model I felt makes sense, as I defined each node to have the four coefficients flowing out of it, then can easily find the neighboring coefficients by viewing the relevant indices of the array. However, the only change to the architecture I would possibly make is to use more performance enhancing data structures. This would primarily involve changing the structure of the coefficients from an array to a tuple. However, the difference in performance isn't significant enough to pose that much of an increased cost.

When it comes to the technical challenges of the model, I would say it was rather difficult. The primary issue with the model came with structuring the differential equations in a way such that there is no leaks of monomers. This was a significant issue for a time, but after a rework of the way the inflows and outflows are calculated, the leakage stopped.

In terms of trade offs in the model architecture, I figured the readability and ease of access of having a 2D array instead of a 1D array is a fair trade for the loss in performance of a 1D array, since otherwise it would require mathematical formulas to find the appropriate information due to the linearity that the data would possess.

VIII. FUTURE WORK

Ideally, this model would enable further study of specific materials based on the properties

defined by the coefficients. This would enable potential research on the crystalline forming ability of a material. We have can also use this information to determine the most abundant type of crystal that would be expected, given the coefficients of our material.

IX. CONCLUSION

In conclusion. We created a simulation in Julia to demonstrate and calculate the evolution of a given set of crystal clusters with various size and order by solving a series of differential

equations. We have four transitions of the crystal. We can use the associated coefficients to evolve our system over a function of time. Each of these coefficients contain the parameters of the model such as temperature and pressure. Here, we viewed the crystals in terms of two-dimensions: concentration and time. From this, we can then gather useful information by examining this plot in order to find the steady state where all phases of the crystal exist in equilibrium. With this information, the model enables us to gain an analysis of the size and order kinetics that influence the crystal.

REFERENCES

- [1] Richard K. Bowles and Peter Harrowell. Influence on crystal nucleation of an order-disorder transition among the subcritical clusters. *Phys. Rev. E*, 105:L062602, Jun 2022.