

Manipulating Dendritic Growth: An Undergraduate Laboratory Experience in the Interplay between Mass Transport, Supersaturated Solutions, and Dendrite Structure

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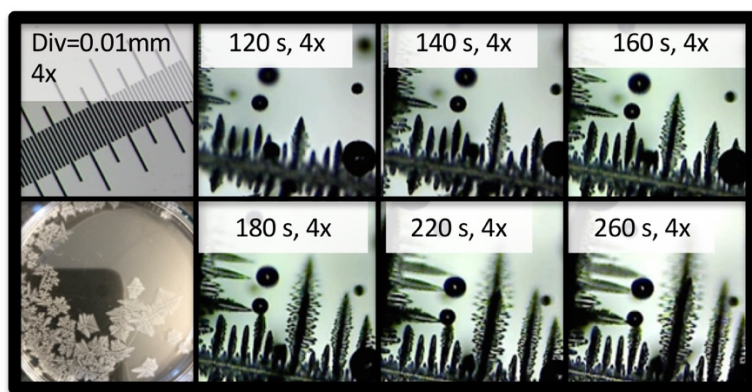
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Abstract (< 250 words)

Dendrite growth affects material systems across applications as diverse as lithium batteries, organic light emitting diodes, turbine blades and biological sensors. Their unique crystal structure and ability to physically see growth makes for a unique undergraduate laboratory experience. This experiment uses dendrite growth to explore the physical and chemical driving forces behind dendrite growth through a set of viscous, supersaturated solutions of varying ammonium chloride and gelatin concentrations. The degree of NH_4Cl supersaturation determines growth rate, which can be mediated by the gelatin limiting diffusional mass transfer. This exercise was designed for a Material Science course, though could easily be adapted to an Inorganic or General Chemistry course. Through this experiment, students are introduced to optical microscopy for quantitative analysis, a common, inexpensive analytical research tool but rarely seen in the undergraduate laboratory. When chemical driving forces are dominant (low gelatin, high salt concentrations), a more ordered dendrite structure forms, with primary branches at 90° angles. Conversely, as diffusion becomes more dominant, a more disordered, denser dendrite structure is observed and the growth rate is slower. Students use both qualitative and quantitative observations to make connections between a fundamental laboratory exercise and critical materials processing techniques that rely on physicochemical driving forces.

Graphical Abstract



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Introduction

Dendritic growth occurs across natural and engineered systems as diverse as snowflake formation to the tin whiskers that commonly plague electronics¹. Dendrites grow at the electrode-electrolyte interface in lithium batteries over multiple charge/discharge cycles, reducing battery performance and lifetime, and causing safety issues due to short circuiting²⁻⁴. Understanding dendrite growth and mitigating its effects is an active interdisciplinary research area to enable better prediction and control over material properties⁵. In this laboratory experience, dendrite growth is used as a platform to explore the physicochemical factors driving growth rate and morphology as a function of supersaturation, a chemical driving force, and viscosity, which physically limits growth by slowing diffusional mass transfer.

In this exercise students consider the growth rate and morphology of dendrites precipitating out of a warm supersaturated ammonium chloride (NH_4Cl) and gelatin solution as it cools to room temperature. The gelatin is used to manipulate the viscosity of the solution, thereby altering the diffusivity of ions in the solution, impacting both the growth rate and morphology of the dendrites. NH_4Cl dendrites are well studied in the literature; they exhibit cubic symmetry with four sets of side branches that grow perpendicular to the main dendrite stem⁵. Such a system was suggested in the *Journal of Chemical Education (JCE)* in 1969 to show 3-dimensional growth in gel rods⁶. However, by maintaining a “thin” layer of solution on a growth plate, it is possible to grow dendrites along an x-y plane, one layer thick, which allows students to quantitatively analyze growth rate and morphology using an optical microscope equipped with a USB camera. This gives students experience in working with an inexpensive instrument common in analytical research laboratory settings yet often not included in chemistry and engineering laboratory curricula^{7,8}.

Students are asked to discuss the morphology of the dendrites in relation to an experimental paper from literature⁹, and to calculate a growth rate for different viscosity and salt concentration solutions using imaging software. The overarching goal of the laboratory is for students to understand how local mass transport affects both the growth rate of dendrites and their morphology, and how solubility and degree of supersaturation impact this diffusion, a critical concept for chemists and engineers alike¹⁰. This exercise advances current experiments in *JCE* that study only morphology, lacking quantifiable measurements^{11,12}. This laboratory exercise is complemented with in-class discussion about dendrite growth in lithium batteries (outline included in Supplementary Information) and its connections to fundamental materials science.

The pedagogical goals of this laboratory experience include:

1. Students make connections between mass transport (diffusion) limitations and chemical driving forces (supersaturation) on the growth rate and structure of dendrites;
2. Students become familiar with the use of optical imaging for quantitative analysis;
3. Students practice oral communication skills by delivering a video laboratory report;
4. Students recognize the connection of a fundamental laboratory exercise to critical materials processing techniques that rely on physicochemical driving forces.

This exercise has been used in Introduction to Materials Science, a junior level required course in Mechanical Engineering at Boston University. Since the laboratory exercise is self-contained, it can easily be adapted to an Inorganic Chemistry course or General Chemistry Laboratory. In Materials Science, students are exposed to chemistry, physics, engineering, and design in a truly interdisciplinary class. This laboratory covers concepts from all the aforementioned disciplines and aligns with fundamental materials science and chemistry concepts, such as mass transport (diffusion), phase diagrams and transformations, supersaturated solutions, nucleation and materials processing. Our class sizes limit this to a 1.5-hour exercise with only four solutions, however this activity could be expanded to include a larger and/or a multi-

session iterative experimental matrix where students develop, and subsequently test their hypotheses based on initial data.

Experimental Section

Before the laboratory session, instructors prepare four batches of supersaturated salt (ammonium chloride, reagent grade) and gelatin (Knox unflavored gelatin) solutions, detailed in Table 1 (preparation details and experimental budget given in Supplemental Information). The solutions are thoroughly mixed and aliquots kept in 50 mL disposable centrifuge tubes in a water bath at approximately 60°C. At this temperature the salt and gelatin remain in solution. Working in groups of two or three, students record the growth of dendrites for each solution as they cool to room temperature. While the rate of undercooling may impact steady state tip-radius growth rate, it has been shown in the literature (and confirmed in our experiments) that the approach to the undercooling temperature required to initiate growth – and therefore the ambient temperature – will not impact the results of this laboratory exercise^{13,14}. Two NH₄Cl concentrations were used; one was slightly below the solubility limit of NH₄Cl in water at 25 °C (of 39.3 g/100 g_{water})⁹ and one above. However, the addition of gelatin lowers the solubility limit (aqueous solutions of this strength will not precipitate at 25 °C, while those with gelatin do). This is likely due to a Donnan equilibrium, whereby gelatin cations are confined within the framework of the gel, increasing osmotic pressure¹⁵. In the case of NH₄Cl, the salt and gelatin establish an osmotic equilibrium; in areas where the salt ions are in equilibrium with the gel, the concentration is lower than aqueous (non-gel) areas, in turn supersaturating the aqueous areas¹⁶. This opens the door to discussions in class about the dependence of supersaturation on solvent choice and equilibrium factors. This setup provides one of the slowest measurable dendrite growth rates, ensuring that students have adequate time to take measurements.

Table 1. Salt and Gelatin Concentrations Tested

Solution Number	Concentration (g/ 100 g H ₂ O)	
	NH ₄ Cl	Gelatin
1	35	3
2	35	10
3	45	3
4	45	10

Dendrite Formation

Using a clean disposable plastic pipette for each trial, students transfer approximately 1 mL of solution from the centrifuge tubes into a 6mm diameter disposable petri dish positioned on a digital compound microscope stage. The petri dish is gently swirled to achieve a thin layer of solution on the bottom of the dish. As the solution cools the salt begins to precipitate out and form dendrite structures. Using a USB camera attached to a compound digital microscope (AmScope M120C-2L-PB10-E), students record the growth of dendrites with time lapse video up to five minutes. Dendrites growing in the center region of the solution were imaged, while those growing from the edge were observed but not quantified. The students repeated the process three times for each of the four solutions.

Quantification of Dendrite Growth Rate

Using a calibrated length scale in the AmScope imaging software, students record the change in length of the dendrite over time by identifying a main trunk of the dendrite and then following its growth over the recorded time period. From the data they can calculate a growth rate for each of the four solutions.

Identification of Dendrite Morphology and Growth Directions

In addition to the quantitative growth rate, students use the dendrite images to discuss the main driving forces for dendrite growth. As discussed by Oaki and Imai⁹, dendrites traverse distinct morphology regimes based on the rate determining physics (kinetics vs. diffusion), illustrated in Figure 1. Based on the density of branches growing off of the main dendrite trunk, and the angle of the branches, students hypothesize what the rate limiting physics are for each of the salt solutions. Additionally, the angles of the branches can also be used to determine the crystal orientation of dendrite growth. In classroom discussions, we help students understand that as the degree of supersaturation increases, we expect chemical driving forces to dominate; dendrites nucleate on any heterogeneity and rapidly grow as growth is not limited by diffusion. However as viscosity increases, diffusion limits growth (both a chemical and physical consequence of the presence of gelatin). Students then explore these relationships quantitatively using Fick's 2nd law and Stokes-Einstein equation, as detailed in the SI.

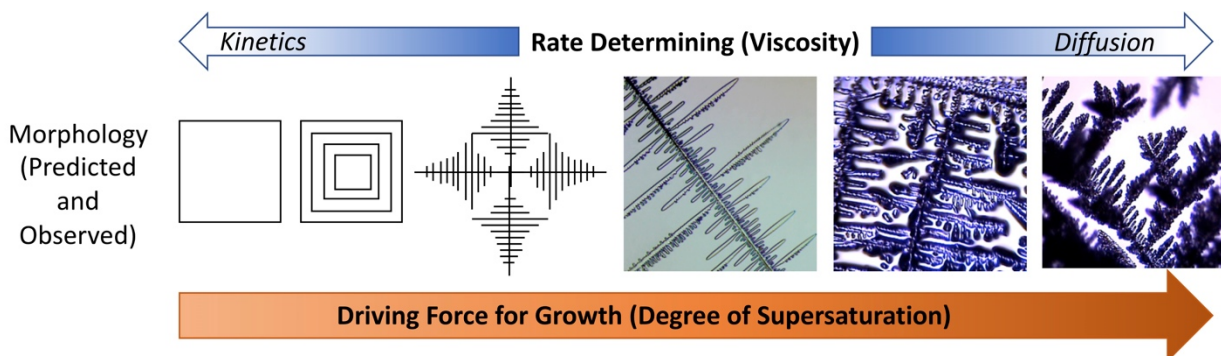


Figure 1: Schematic of dendrite morphology based on the rate determining physicochemical properties of the system. Adapted from Oaki and Imai⁹

Hazards

Protective clothing, gloves, and eyewear should be used at all times. Ammonia chloride (NH_4Cl) is a weak acid in solution and may cause irritation in contact with skin and eyes. Students should be advised to use safe lab practices and to thoroughly wash their hands after the laboratory.

Results and Discussion

This laboratory was run 18 times over the course of a semester for 135 undergraduate students in an Introduction to Materials Science Course at Boston University. In each laboratory section, groups of two to three students collected data on dendrite growth for the four solutions of Table 1. The representative results presented here were collected by the authors (two faculty and one undergraduate student).

For each solution, time lapse images of dendrite growth were used to calculate an average growth rate. As shown in Figure 2a, the dendrite growth was plotted over time for a minimum of three sets of experiments for each solution (12 datasets total) over the first 15 seconds of growth; (additional plots available in the

Supplemental Information, SI). A best fit line is plotted for each solution and the slope of that line is the average dendrite growth rate. As shown in Table 2, the growth rate increases with NH_4Cl salt concentration and decreases with increasing gelatin concentration. This leads to the solution with 45 g NH_4Cl and 3 g gelatin to have the highest growth rate and the solution with 35 g NH_4Cl and 10 g gelatin to have the lowest growth rate.

Overall, the four solutions have a roughly linear dendrite growth rate. However, the solution with 35 g NH_4Cl and 10 g gelatin deviates slightly from linear growth after approximately 15 s (Figure 2b). This could be attributed to the higher viscosity of the solution retarding the transport of ions to reaction sites; curvature of dendrites is known to occur in high surface tension solutions¹³. To relate this, the teaching assistants measured the viscosity of lab solutions to report with calculations (Table 2).

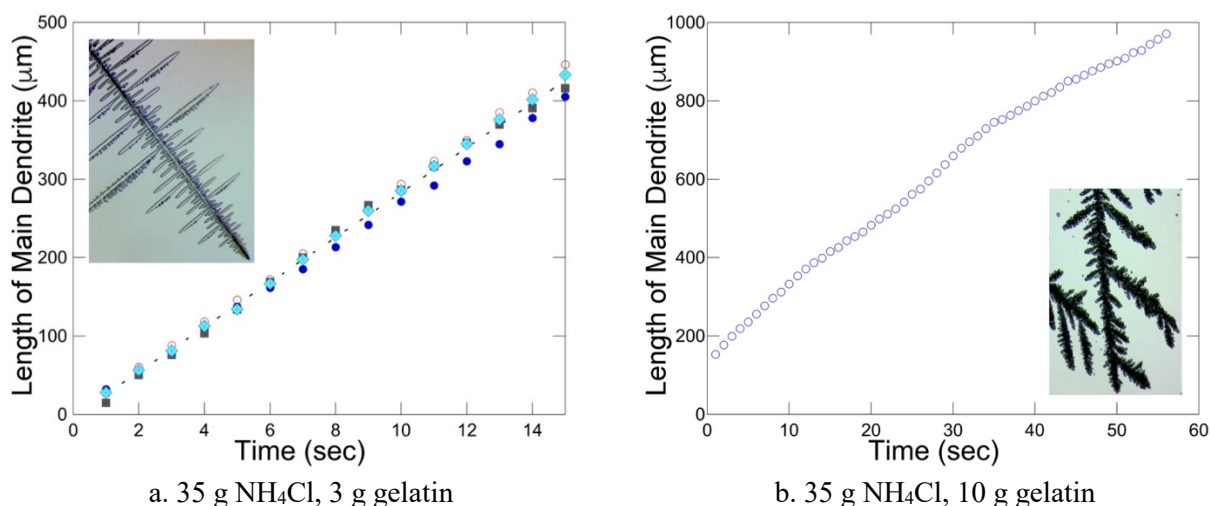


Figure 2: Dendrite growth as a function of time for solutions 1 and 2; additional plots and images available in SI

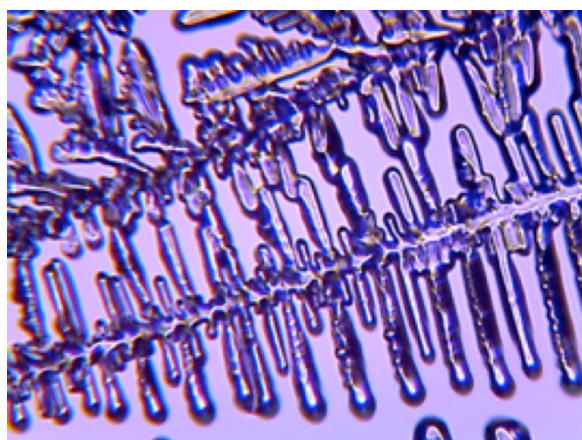
Table 2. Comparative Results for the Average Dendrite Growth Rate

Solution Number	Solution Concentration/ 100 g H_2O		Average Growth Rate for Main Branch ($\mu\text{m}/\text{s}$) ^a	R^2 of Linear Regression of Compiled Results ^b	Solution Viscosity at Room Temp. (cP) ^c
	NH_4Cl , g	Gelatin, g			
1	35	3	28.6 ± 0.3	0.994	1.886
2	35	10	19.7 ± 0.3	0.995	5.635
3	45	3	66.1 ± 1.2	0.988	1.673
4	45	10	60.6 ± 0.6	0.995	5.167

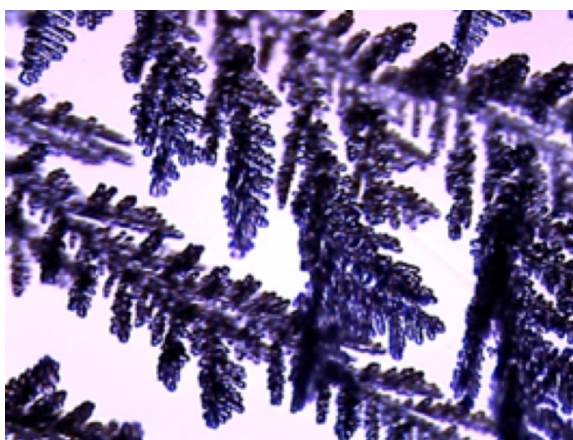
^aGrowth rate with 1 standard deviation for each solution. ^bDetermined by slope of data compiled for at least 3 runs for each solution over a minimum of 10 s per run. ^cViscosity data collected by teaching assistants.

The changes in dendrite morphology for the four solutions were also considered. Varying the degree of supersaturation and the gelatin density produces distinct differences in density of branches and orientation of the branches. These structures can be discussed in terms of the driving physics in the system. As Oaki and Imai⁹ show (Figure 1), in systems where the kinetics are dominant a more ordered dendrite structure forms. As diffusion becomes more dominant, a more disordered, denser dendrite structure is seen. From

the data collected in this laboratory, it is seen that a lower NH_4Cl and gelatin concentration solution produces a structure (Figure 3a) with a very ordered, uniform growth, consisting of a distinct main trunk and branches (initially) oriented at 90° to the trunk. This indicates that both the kinetics and the diffusion are significant in this solution. Increasing the gelatin in the 35 g NH_4Cl solution (Figure 3b) produces a very different dendrite structure, with denser branching and branches growing at approximately 45° from the main trunk. For this case the dendrite structure is dominated by diffusion. A similar structure emerges for the high gelatin case with 45 g NH_4Cl with slightly denser branching than the 35 g NH_4Cl (additional images available in SI). For the 45 g NH_4Cl and low gelatin solution, the branching is mostly at 90° from the trunk, but the branching is denser than for the 35 g, NH_4Cl / 3g gelatin solution. This higher degree of supersaturation causes some branches to emerge at 45° from the trunk, indicating that the physics is still mixed between the kinetics and diffusion but the diffusion is becoming dominant.



a. 35 g NH_4Cl , 3 g gelatin after 5 minutes, 40x



b. 35 g NH_4Cl , 10 g gelatin after 5 minutes, 40x



c. 35 g NH_4Cl , 3 g gelatin time lapse images at 1x



d. 35 g NH_4Cl , 10 g gelatin time lapse images at 1x

Figure 3: Morphology of dendrite growth for solution 1, 35 g NH_4Cl , 3 g gelatin, and for solution 2, 35 g NH_4Cl , 10 g gelatin as observed at “bench” scale (images in Fig c,d taken every 30-40 seconds with cell phone camera) and after 5 minutes at 40x (Fig a,b)

In addition to the microscopic growth of the dendrites, the overall macroscopic structure of the solutions during and after cooling is also considered; a sample time series for solution 1 is shown in Figure 3c. At the macroscopic level students can see clear grain boundaries between the very ordered dendrite structures of the 35 g NH_4Cl 3 g gelatin solution, while the less ordered structure of the higher gelation solution does not have clear grain boundaries between dendrites (see SI for additional images). For the more concentrated gelatin solution, areas of the image are void of dendrites, most likely due to restricted transport. For the 45 g NH_4Cl solution with low gelatin concentration, an ordered macroscopic structure similar to Figure 3a is seen, with all dendrites nucleating at the edges of the solution and growing into the center. The voids observed in Figure 3d are likely caused by lack of dissolved salt in these regions as the dendrite structure restricts the transport of dissolved salt. Finally, in the 45 g NH_4Cl high gelatin solution, a disordered macroscopic structure is seen with most dendrite growth starting at the edges of the solution and large voids with no dendrite growth.

For all solution types, the Berg effect is observed, whereby supersaturation is higher along the edges of a growing interface than at the center¹⁷. This is especially noticeable if the solution does not completely cover the base of the petri dish (Figure S1 in SI). This results in a thick, opaque crystallized lining around the edge of the solution areas in which individual dendrite growth is not readily seen at the macroscopic level. These areas were also typically the first to crystallize, consistent with heat transfer effects of the outer edge cooling before the bulk. Since the degree of undercooling drives the precipitation of the dendrites out of solution, the edges tend to be a nucleation point for dendrites. This can be minimized by using a layer of gelatin that coats the entire petri dish as shown in Figure 3, such that dendrites will nucleate in the bulk solution and around the sides at the same time. This phenomenon was previously explored in *JCE* by Davidson and Slabaugh in the context of “Magic Crystal Gardens” where dendrites are grown along the edge of porous media¹⁸.

Assessment, Implications and Limitations

Learning outcomes were assessed through a pre-lab quiz, laboratory report, in class discussion, and an exam question. The pre-lab quiz was administered at the beginning of the laboratory after students had been assigned the Oaki and Imai⁹ paper as pre-lab reading. The quiz tested the students’ understanding of what triggers dendrite growth, what determines the structure of the dendrites, and the main driving forces in a reactive system. Only 1/3 of the students were able to identify a drop in temperature as the trigger for dendrite growth; approximately half the class identified kinetics and diffusion as factors in determining dendrite structure, and only 1/3 of students knew that reactions and diffusion are driving forces in general reactive transport systems. In the pre-lab quiz the questions on triggering dendrite growth and the structure of dendrites were multiple choice, while the question on the driving forces in reactive systems was fill-in-the-blank (SI).

A video format was used for the laboratory report. Students were asked to produce a five minute video reporting their results and answering the discussion questions at the end of the laboratory handout. The video was supplemented with one page of annotated calculations. Based on course evaluations, students had mixed feelings on the video format of the laboratory. Some students felt it was a waste of time as they had to use a video editor and edit their laboratory report while others enjoyed the opportunity to utilize a more creative medium. The instructors felt that it was a unique way to encourage students to think about the data, and to help students cultivate oral communication skills. Developing the ability to communicate across different media and audiences is a critical ABET student outcome¹⁹. Since the dendrite structure aspects of the laboratory are qualitative, the video format allowed students to describe the structures without the need for a lengthy report. By verbally explaining their data, the students need a solid understanding of their results so that they can articulate them in a clear, concise manner. The video was supplemented with a page of annotated calculations, which showed how they calculated growth rate from the data collected in the laboratory. As discussed in the SI, quantitative calculations could be expanded to consider how changes to the viscosity of the solution effect local salt concentrations. Using Fick’s 2nd Law, students can calculate the local concentration and investigate how it changes over time, space and material properties. This can be done using an analytical solution or using computational fluid dynamics software, such as COMSOL or FLUENT. These expanded calculations can help students more clearly see how changes to viscosity effect the diffusion vs. reactions in the system as discussed in Oaki and Imai⁹

A final assessment was on the course’s final exam. One question was centered on the lab and re-asked the questions from the pre-lab quiz, but this time in a fill-in-the-blank form (removing random-guessing of multiple choice). Three sub-questions asked about the trigger for dendrite growth, the driving forces for

structural changes, and the main driving forces in reactive transport systems. Each of the sub-questions was a short answer format. 55% of students were able to identify temperature as the trigger for dendrite growth, and 64% knew that the structure was determined by the concentrations of gelatin and salt. For the question on general reactive transport driving forces, only 24% were able to answer correctly.

The results of the laboratory assessment show a significant increase in understanding of dendrite growth triggers and structural factors, while there was a slight regression in terms of overall reactive transport system understanding seen in the course's final exam. To address this, future course implementation included in-class discussion/practices and homework questions involving calculation of diffusive fluxes and crystallization rates in analogous systems.

Associated Content

Additional data and images, lecture and instructor notes, student hand-outs, and assessment material are available in online Supplemental Information (SI).

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