Mathematical modeling for assorted problems in crystal growth

A DISSERTATION
SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL
OF THE UNIVERSITY OF MINNESOTA
BY

Kerry Wang

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

Jeffrey J. Derby

December, 2019
Acknowledgements

There are a number of people and organizations that have supported me both as a person and as a researcher during my time as a graduate student here. First I’d like to thank my adviser, Jeff Derby, for supporting me and guiding me through this degree with its multiple projects. In these past few years working with Jeff, the biggest thing I’ll take away is learning how to think like a modeler — learning how to tease out important concepts from messy real-life problems and finding strategic ways to understand and approach complex systems. I have also been able to learn a lot from the various conferences attended and presented at with Jeff’s support. I’d like to also thank Andrew Yeckel who first instructed me on how to use Cats2D. I am deeply indebted to the CEMS staff, in particular the tireless efforts of Julie Prince and Teresa Bredahl. I have consulted them so many times for so many things throughout the years, and they have always been so helpful and patient. They are truly a treasure of this department.

In Jeff’s group I’ve been lucky to be in the company of brilliant cohorts that I also get to call friends. I’ve had so many insightful discussions and opportunities to go on informative but fun trips with Jeff Peterson and Mia Divecha. I love that I could have these engaging discussions about a deeply technical topic one moment, and something completely different the next. I’ve also learned so much from my current cohort, including Swanand Pawar, John Roerig, Chang Zhang, Linmin Wang, and Scott Dossa.

I’m grateful for the number of wonderful professors and teachers I’ve had the privilege of learning from. Thanks to my undergraduate research adviser Prof. Christy Landes at Rice University for her mentorship. Even as an undergraduate, I was taken seriously as a researcher and always felt my ideas and questions were valued in her research group. Thanks also to then-graduate students and now-Drs. Carmen Reznik, Charlisa Daniels,
and Lydia Kisley for their mentorship in Prof Landes’s research group. Thanks to Dr. Kristin Persson and Dr. Michael Kocher at Lawrence Berkeley National Laboratory, who I worked with during an undergraduate research internship in 2010. This was an extremely valuable experience as it was my first time doing simulation/theory research. Even though I didn’t end up doing ab-initio work as a grad student, I likely wouldn’t have ended up in a modeling group at all if I hadn’t worked with them that summer. I’d also like to thank my high school biology and research/design teacher, Karen ‘Mama Shep’ Shepherd for always keeping science fun, for her awful/awesome science puns, and for supporting me in independent research in science fairs from middle school through high school.

I’m thankful to my family — my sister Krystal, my cousins, and of course my parents, who have been waiting so anxiously for me to finish! And even though I have little or no memory of them, I’m thankful for my grandparents and ancestors, many of whom had backgrounds in science and engineering. I am separated by them in time, distance, and culture due to the political turmoil that led to my parents’ immigration from their homeland in China to the US. My mother would often remark, after seeing pages of equations scattered in my apartment, that grandpa (a professor of physical chemistry) would be proud. I unfortunately have no memory of him, but I hope I have made him proud.

I’m thankful for all of the amazing students and staff who supported me when I founded UMN Energy Club. I thank Professor Eray Aydil’s support and advisership for this group. I’m deeply grateful in particular to Beth Mercer-Taylor and Mary Oldham Hannemann from the Institute on the Environment’s Sustainability Education department. They have always supported me and pointed me to opportunities to develop myself and many other students as leaders in sustainability. Thanks also to Ben Koch from the College of Science and Engineering for supporting us as a CSE student organization. For the officers who I worked with — Burnell Lauer, Michelle Smeaton, Aaron Hanson, Andreas Hochrein, Waylon Macek, Brandon Noel, MK Anderson — thank you so much for making Energy Club happen. I can’t wait to see what we do in our lives and careers to make this world a better place.

Lastly, I’m deeply thankful for the amazing social network that supported me after moving to Minneapolis from Texas. Like many students, I’ve struggled a lot with my
mental health in graduate school, especially in my first few years here. My health and wellbeing I owe completely to the friends I’ve made here who have helped make Minneapolis my home. I’m grateful for my friendship with Nora Dahlberg, who was/is my first friend in Minnesota! Thanks my longtime and dear friend Kristie Lou, who has visited me many times in the cold, cold north! Thank you friends from the AcroYoga Mpls community for creating a safe place to connect and push physical limits. Thanks to the many wonderful friends I met through the Bengali Student Society of Minnesota including Maaz Ahmed, Adway De, Prerna Subramanian, Bhavtosh Rath, Sanhita Sengupta, and Diksha Srishyla. Thank you to everyone in the South Asian Arts and Theatre House (SAATH) for being such a warm and welcoming community. I can’t name all of you, or this acknowledgments section would be the length of an entire chapter! SAATH has been such an important place for me to learn new skills and keep my mind and body healthy through dance, which is something I had never done in my life until now. And of course, I am so deeply lucky and grateful to have met Shara Mafiz, who has been a pillar of support for me.

Land Acknowledgment

I would like to acknowledge that the place this work was conducted, the University of Minnesota Twin Cities, is located on traditional, ancestral, and contemporary lands of Indigenous people. *Minnesota* comes from the Dakota name for this region, Mni Sota Makoce — “the land where the waters reflect the skies.” The University resides on Dakota land ceded in the Treaties of 1837 and 1851. Many of us who pursue science and engineering do so hoping to make a positive impact to society. This land acknowledgment aims to do the same, by highlighting the important relationships we have with each other, the land, and the land’s original inhabitants. This acknowledgment is adapted from those prepared by the University’s Office for Equity and Diversity, Institute for Advanced Study, and Multicultural Center for Academic Excellence. I support my institution and all those who live, work, and study here, in recognizing, supporting, and advocating for American Indian Nations and peoples.
Dedication

This work is dedicated to all people struggling and working to make the world a happier, healthier, and more just place. Even though the work in this thesis is only distantly related to addressing some of the most pertinent social issues of our time like climate change and renewable energy, my training here has helped me tremendously in approaching complex problems. I hope to apply what I’ve learned more directly soon, and I hope the future researcher can find something useful in this thesis to benefit the planet.
Abstract

Crystal growth is a field that is ripe with opportunities for mathematical modeling to elucidate interesting phenomena. Important process parameters such as solute concentration, interface shape and location, and temperature field are uniquely difficult to observe \textit{in-situ} for many high temperature melt crystal growth systems. Additionally, the slow process of growing large, industrially-relevant single crystals can be prohibitive in time, material cost, and labor for tedious repeated experimental studies that are likely to be destructive. Modeling provides an efficient way for researchers to quickly gain an understanding of the physics underlying a crystal growth system.

In this thesis, we examine three different cases where mathematical modeling can be utilized to interrogate crystal growth systems. First, we investigate the transport of oxygen in Czochralski-grown silicon by posing a simple lumped-parameter model. The lumped-parameter model tracks transport of oxygen into and out of the melt without specifying its spatial distribution, relying only on estimated fluxes from various surfaces. The lumped-parameter model offers a near-instantaneous way to obtain a coarse estimate of oxygen given process parameters such as crystal/crucible rotation scheme, melt height, and melt overheating.

Second, we examine a past experiment involving Europium-doped BaBrCl monitored \textit{in-situ} via Energy-Resolved Neutron Imaging. Europium acts as a strong neutron attenuator, allowing visualization of its migration in both the solid and melt phases. A prior experiment was conducted to perform \textit{in-situ} imaging of a melt crystal growth system, and we realized this presented an opportunity to use modeling to extract additional data from this past experiment. A 1D model of europium migration in both phases was formulated and solve via Finite Fourier Transforms and Finite Difference Method. The Finite Difference Method, being more flexible, allowed us to deduce the apparent solid and liquid diffusion coefficients of Eu as well as its segregation coefficient. This coupling of \textit{in-situ} imaging and modeling presents an exciting new way to measure physical properties and extract additional value from past experiments.

Last, we analyze the curious phenomenon of Temperature Gradient Zone Melting (TGZM), whereby a solute-rich liquid particle migrates through a solid crystal under a
thermal gradient. While this phenomenon has been studied in the past, prior models failed to give practical predictions in the time-evolution behavior of such migrating particles. We pose analytical and numerical models of 1-dimensional TGZM, which agree well with each other. The numerical model, solved via Finite Element Method, shows reasonable agreement with experimental data on Te-rich second-phase particles migrating in CdTe. It additionally shows excellent agreement with another physical system, NaCl brine particles in water ice, providing a far more accurate description of the particle’s migration than previous theoretical models. Considerations are made for extending the model to higher dimensions in order to understand changes in particle morphology during migration.

Different types of modeling using various analytical and numerical techniques are employed for each of these case studies. These three example cases show different scenarios in which mathematical modeling can be utilized to help researchers gain insight in crystal growth systems.
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In subsequent chapters we will take the route on the right. We shrink the control volume down to an infinitesimally small size, and apply it to all points in a domain. In the same fashion, conservation equations can be applied on boundaries and interfaces between subdomains. What results is a partial differential equation, where conserved quantities can vary over space and time. Solving these equations typically require more in-depth numerical methods to approximate. While these models likely yield much higher-fidelity information concerning the system in question, they arguably require greater investment in time, labor, and computational resources to execute.

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LP models with multiple regions were proposed and investigated, but none provided any significant improvement in matching the 2D-3D models. The geometries explored include: a.) hemi-spherical region near the crystal, b.) parabaloid region near the crystal, c.) cylinder region under the crystal, d.) cone region under the crystal.

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Reproduced from [42].

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Chapter 1

Author’s foreward and outline

This thesis will likely read differently from most others from this department or those supervised by my adviser, Jeffrey Derby. Rather than one long-term project, this thesis explores how mathematical modeling can be used to better understand some complex phenomena observed in three separate applications in the field of crystal growth, each having a devoted chapter. The chapters are not ordered by the chronology of when the research was conducted. Rather, they are ordered in a way such that technical concepts in one chapter act as a foundation for subsequent chapters, facilitating comprehension. Additionally, the topics discussed illustrate how various levels of model complexity — from simple analytical models derived from the most basic conservation equations to complex numerical models solved with specialized software packages — can be used to gain useful insight from this variety of applications.

To maintain accessibility to science and research for all, I have attempted to write this thesis to be as understandable as possible without a background in crystal growth. Because of the breadth of topics included, each chapter will include a brief overview of the details pertinent to each application. The following outlines the structure of the thesis:

- Chapter 2 lays the general foundation for relevant topics in crystal growth that will be discussed later. It covers some common methods of industrial crystal growth and some of the applications of the materials discussed in this thesis.
• Chapter 3 discusses modelling of oxygen transport during growth of silicon using the Czochralski method. The analysis is relies on an analytical "lumped-parameter" approach, which tracks a quantity of interest (e.g. oxygen) in regions without regard for its spatial distribution.

• Chapter 4 discusses coupling modelling of europium transport through the solid phase in europium-doped barium bromochloride (BaBrCl:Eu) with data from energy-resolved neutron imaging (ERNI) experiments to determine Eu’s apparent solid state diffusion coefficient near the melting point temperature. Here, we construct a model and first solve it using Finite Fourier Transform and formalism of self-adjoint operators. We then opt use Finite Difference Method to back out diffusion coefficients of interest.

• Chapter 5 discusses modelling of the phenomenon of Temperature Gradient Zone Melting (TGZM). Applications are discussed for cadmium telluride (CdTe), a radiation detection material, and sodium chloride (NaCl) brine and water ice. This chapter utilizes a more complex numerical approach, Finite Element Method, to solve for multiple field equations (heat and concentration) over time and space, with moving boundaries. An analytical formulation is also derived which verifies the numerical model.

• Chapter 6 is a culminating conclusion
Chapter 2

Foundations

Crystal growth is a broad field that includes a wide range of interesting scientific phenomena. Relevant length scales can span from atoms to meters-long industrially-grown bulk crystals. Because this thesis is composed of investigations in several different applications in crystal growth, and may be useful to an audience of different backgrounds, from industrial/experimental crystal growers to modelers to geophysicists to nuclear security experts, this chapter serves as a general introduction to some of the relevant topics. A comprehensive understanding of the field is not necessary for the reader to grasp the research presented in this thesis. However, this chapter provides a surface-level discussion to give the reader context for the challenges and obstacles in the field of industrial crystal growth that subsequent chapters will refer to. The interested reader is referred to [1-6] for a more thorough overview of experimental and modelling practices as well as applications in crystal growth.

2.1 What is crystal growth?

Crystals are solids in which atoms or molecules are arranged in a highly-ordered repeating pattern. This regularity is exploited for many engineering applications - mechanical, optical, electronic, and more. In this thesis, we investigate growth and refining processes of three industrially-relevant inorganic crystals: silicon, europium-doped barium bromochloride, and cadmium telluride.

These inorganic crystals are typically grown from the melt. That is, the material
is first largely or completely melted down into a liquid state. The material is then cooled in a controlled way around the remaining solid or a seed crystal such that melt is resolidified as single crystal, with a continuous crystal lattice that persists through the entire structure. Here we briefly discuss two common methods of crystal growth: the Czochralski method, and the Bridgman method. For a more comprehensive overview of melt crystal growth, the interested reader is directed to [2,4,7,8].

2.1.1 Czochralski method

The Czochralski method is a popular crystal growth technique and is used extensively for growing the highest quality single crystalline silicon for semiconductor applications as well as photovoltaics for renewable energy. The crucible is first charged with highly purified raw material (polycrystalline silicon). After the crucible is heated and initial charge of silicon melted, a seed crystal is dipped into the melt. A combination of controlled heating and cooling, crystal rotation, and crystal pulling velocity allow a cylindrical boule of defect-free, single crystalline silicon to be “pulled” or grown from the melt. At high temperatures, many chemical species present in a crystal growth furnace have elevated volatility, miscibility, and reactivity. For silicon, contaminants like carbon (from the crucible) and oxygen (from a quartz crucible lining) can affect electronic performance of the final product. The flux and distribution of such chemical species must be controlled for to maintain crystal performance and homogeneity. Today, ingots of silicon grown industrially by Czochralski method are typically 200-300 mm in diameter and 1-2 m in length.

Figure 2.1: Crystal growth process in Czochralski method. Reproduced from [9].
2.1.2 Bridgman method

Another classic method of crystal growth is the Bridgman method (sometimes known as Bridgman-Stockbarger method). In Percy William Bridgman’s original design, a sealed ampoule of feedstock material is molten in a furnace; slowly, the ampoule is drawn directly out of the furnace into the atmosphere, where the lower temperature induces solidification. In modern Bridgman furnaces, an engineered temperature profile is maintained in the furnace which spans the material’s melting point as the ampoule is translated downward to cooler temperatures. A variant of the Bridgman method, known as Vertical Gradient Freeze, does not involve any ampoule movement. Instead, the heater profile is controlled such that the solidification interface moves upwards.

![Diagram of Classical Bridgman and Gradient Freeze](image)

Figure 2.2: Crystal growth process in a.) Classical Bridgman method and b.) Vertical Gradient Freeze method. Reproduced from [10].

2.2 Why modeling?

There are a number of reasons modeling is beneficial and often needed in the crystal growth industry. Growing industrially-relevant large single-crystals is typically an expensive process — in time, energy, and labor. Growth rates may be on the order of mm/hour or mm/day. The myriad of relevant process parameters — material properties, crystal pull rate, heater profile, dopant concentration, crucible/furnace geometry,
rotation schedule, and more — make it impractical to systematically examine these parameters experimentally. Additionally, environmental conditions for growth of many single crystals can make them prohibitively difficult to observe in situ by experimental techniques. For example, the inorganic single crystals discussed in this thesis have melting point temperatures around or in excess of 1000 K making in-situ monitoring practically impossible. A number of other material characteristics are also difficult or impossible to study in situ. Distribution of solute species, either those occurring natively in a material or doped intentionally, can be engineered to tailor certain material properties. Analysis of the solutal concentration fields can often only be done by destructive testing of grown crystal samples.

Modeling gives us a way to peer into systems we generally don’t have access to in reality. Additionally, it gives us structure to understand the dominant phenomena governing these complex systems. Rutherford Aris, one of the distinguished faculty of this department, wrote in Ut Simulacrum, Poesis (as is modeling, so is poetry\(^1\)): “If the purpose of the model is to imitate a natural situation with great fidelity, perhaps to predict its future behavior, then it will be judged by the accuracy of its correspondence; but a model can also serve the purpose of defining, clarifying, and enriching a concept”. In this thesis, we primarily build mathematical models from conservation equations involving heat or chemical species, which are then solved either analytically or by numerical means. Because these methods vary case-to-case, they are introduced and discussed in the chapters they are used.

2.3 Radiation detection

One major industrial application for growing large single-crystals is in radiation detection. In this context we are referring to high-energy ionizing radiation typically resulting from radioactive decay of nuclei (e.g., x-rays, gamma-rays). Radiation detectors are typically used to detect these high-energy particles for the purposes of monitoring of nuclear

\(^{1}\)Aris is referencing Horace, a first-century BC Roman poet, who used the phrase, Ut pictura poesis in Ars Poetica, literally meaning as is painting so is poetry. While Aris was better known as an engineer, he was also a scholar in the humanities and held a professorship in the Classical Studies department at the University of Minnesota. *Simulacrum* is a Latin word for likeness or similarity. Today, it refers to something that is used to represent or mimic something else (like how statue may be a simulacrum of a god or a photograph a simulacrum of scene or event in real life).
material and medical/scientific imaging. They do so by converting the energy from these particles directly into electrical signals or visible light. Two types of solid-state radiation detectors are discussed in this thesis: semiconductors and scintillators. The interested reader is referred to [11–14] for a more in-depth overview on these types of detectors.

2.3.1 Semiconductor radiation detectors

Semiconductors are materials whose valence and conduction bands are separated by a small bandgap (on order of 0.1-1 eV). The basic mechanism of radiation detection is to use incident radiation to excite electrons across the bandgap into the conduction band, where charges can be collected under an electric field. High-purity germanium (HPGe), an established and reliable radiation detector material, has a bandgap of only 0.7 eV and thus must be cooled with liquid nitrogen or other means to around 77 K in order to reduce thermionic noise and function properly as a detector. Room-temperature semiconductor detector materials have a wide bandgap, being greater than 1.5 eV at room temperature, high enough to prevent ambient thermal energy from exciting electrons into the conduction band. Radiation detection materials cadmium telluride and cadmium zinc telluride (discussed in Chapter 5) have bandgaps in the range of 1.4-2.2 eV.

Semiconductors are doped such that they contain an excess of electrons (n-type) or excess of vacant sites or holes (p-type). When these two types are put in contact, forming what is known as a p-n junction, excess electrons from the n-side diffuse into “holes” on the p-side, forming a depletion region. The diffusion depth of these charge carriers into the opposing side (i.e. the width of the depletion layer) is limited by the electric field generated by the separation of charges from their original material but can be expanded when the material is put under reverse-bias.

Several processes can occur when a high-energy photon impacts the semiconductor material, but the greatest contributor of charge is photoelectric absorption, whereby the all photon’s energy is transferred to an electron in the depletion region and excited to the conduction band. In the presence of an electric field, electrons are collected and the electric signal is processed.
Figure 2.3: a.) A depletion region is formed when p- and n-type semiconductor are in contact. b.) The depletion region grows wider when under reverse bias. c.) After a gamma photon strikes the depletion region, an electron-hole pair is formed. Charges are collected under an electric field, and the electronic signal is processed. This is the basic working mechanism of the common p-n junction radiation detector. Still more types of semiconductor radiation detectors can be constructed using different semiconductor structures.

2.3.2 Inorganic scintillator radiation detectors

While semiconductor detectors directly convert radiation into an electrical signal, scintillators work by converting energy from radiation into visible light first. Here, we specifically discuss a basic mechanism of scintillation for inorganic scintillators. After a high-energy photon strikes the scintillator crystal, a core electron is excited, causing a cascade of other electron-hole pairs to form (absorption and multiplication). These electrons-hole pairs migrate towards the conduction and valence band edges, dissipating energy by various processes along the way (migration). Scintillator crystals often include
dopants known as “activators”. For example, in Chapter 4 we discuss barium bromochloride doped or activated with europium. Activators serve to create energy states in between the conduction and valence bands that wouldn’t otherwise exist. Electron-hole pairs thus can eventually occupy these activator/dopant excited and ground states. When electron-hole pairs recombine from these states, the energy is dissipated in the form of an emitted photon with a longer wavelength, typically in the UV or visible range (Figure 2.4). These photons are then converted into an amplified electric signal by a photodetector, such as a photomultiplier tube or photodiode.

Figure 2.4: The basic mechanism of scintillation in an inorganic crystal consists of three main steps: absorption and multiplication, migration, and relaxation and emission of a UV or visible light photon. The emitted photon is then counted using a photodetector.
Chapter 3

Lumped parameter model of Oxygen transport in Czochralski silicon

3.1 Introduction

We begin our investigation with the Czochralski (Cz) method for growing silicon (Si). Numerical modeling has been an indispensable tool for optimizing this process, with modeling dating back to the 1980s [15–21]. This is particularly true for large-diameter growth processes, as such growth experiments can be cost-prohibitive. The high-fidelity modeling approach for the growing the cylindrical crystal body is typically achieved by combining a global, quasi-stationary, axisymmetric model of the Cz furnace assembly with a local three-dimensional, time-dependent model of the melt-crystal-crucible region. The Large Eddy Simulation (LES) is a well-established turbulence model used to simulate 3D melt flow [22–26].

However, such numerical calculations, giving precise, high-fidelity spatiotemporal profiles of important process parameters such as solute distribution, temperature distribution, and flow profiles, can take days to weeks to compute on high-performance computing clusters. To get a rapid estimation on the influence of process parameters on the crystal properties with reasonable quantitative accuracy, a lumped-parameter (LP)
model is desired where the results can be obtained in real time. Lumped-parameter models represent a simpler way of formulating transport problems by neglecting the variation of a quantity with respect to certain variables by "lumping" them all in fewer variables. Figure 3.1 illustrates the difference between the lumped-parameter route and the more complex route for solving for spatial variation of conserved quantities (such as heat and mass). In this chapter, we neglect the spatial variation of oxygen in the melt, "lumping" together all the spatial variables into one control volume. Such a model allows easier, straightforward understanding of the complex phenomena occurring in the melt, as long as the dominant physical processes and mechanisms are considered. In chapters 4 and 5, we will consider the more complex route, formulating and solving systems of PDEs with various analytical and numerical techniques.

Such LP models were more common in the 1970s and 1980s when numerical simulation of the Cz process was relatively new. One example is the boundary layer model for the oxygen transport published by Carlberg et al. [27] and later on by Hoshikawa et al. [28]. With increasing accuracy of numerical simulations, these reduced-order models have since fallen by the wayside. However, we desire to revisit these simple models in predicting the influence of various process parameters (e.g. oxygen transport), especially since they have not been extensively compared to their complex numerical counterparts.

Here, we used a further-developed version of the boundary layer model of [27,28] to calculate the influence of crystal and crucible rotation on the oxygen transport during Cz growth of large-diameter silicon crystals. The results from the LP model are compared to those obtained by coupled 2D-3D simulations from collaborators.

3.2 Coupled 2D-3D numerical simulations

Our collaborators provided 2D-3D simulations of heat and oxygen transport during growth of silicon crystals with 210mm diameter and a weight of 100kg in a 24-inch diameter crucible. The details of model formulation are found in reference [26]. In the 2D-3D model, the convective heat and oxygen transfer are computed by a time-dependent 3D-LES model [25]. Temperature, velocities and oxygen are averaged azimuthally and in time, and a turbulent heat flux is calculated from the observed fluctuations of temperature and velocity. These average values along with the turbulent heat fluxes are
Figure 3.1: Starting from the same conservation equations defined in a control volume, two common paths of modeling macro-scale transport phenomena are shown. On the left is the route we take in this chapter, the lumped-parameter approach. Here, we neglect spatial variation and apply our conservation equations to an entire control volume or reservoir (e.g., the melt in a Cz system). We specify the fluxes of a conserved quantity into or out of one reservoir and may even connect multiple reservoirs together (specifying the influx from to source equal to the outflux from another). In subsequent chapters we will take the route on the right. We shrink the control volume down to an infinitesimally small size, and apply it to all points in a domain. In the same fashion, conservation equations can be applied on boundaries and interfaces between subdomains. What results is a partial differential equation, where conserved quantities can vary over space and time. Solving these equations typically require more in-depth numerical methods to approximate. While these models likely yield much higher-fidelity information concerning the system in question, they arguably require greater investment in time, labor, and computational resources to execute.
then imported into a Reynolds-averaged form of the temperature equation inside the 2D-model, in which the temperature field as well as the SiO evaporated from the melt surface in the whole Cz puller geometry is calculated. The details of this method can be found in [25, 29]. The software packages CrysMAS [30] and OpenFOAM [31] were used to solve the combined model, the former for the global model and the latter for the local 3D model. These models were already validated by comparison to data from Direct Numerical Simulation (an extremely high-resolution model that doesn’t use turbulence modeling) as well as by comparison to experimental data with respect to the shape of the solid-liquid interface and oxygen distribution in large diameter Si Cz crystals [25].
3.3 The lumped-parameter model

Our approach in developing an LP model begins with the assumption of a single well-mixed melt region, thus eliminating spatial variation of dissolved oxygen from the crucible. Due to strong flows from the combination of Rayleigh-Bernard convection with azimuthal crystal and/or crucible rotation, nearly-complete mixing from turbulence is assumed. Fluxes of oxygen in and out are estimated as simple linear Fickian diffusion across boundary layers of defined width as originally proposed by [27, 28] (see Figure 3.3).

![Figure 3.3: An axisymmetric cartoon profile of basic mass flows utilized in the lumped-parameter model. Concentrations and fluxes pertain to oxygen.](image)

The basic variables of interest are defined in Table 3.1. Further variables will be defined as needed. In general, subscripts of c, cw, cb, s, m, and x will refer to crucible, crucible wall, crucible bottom, free melt surface, melt volume, and crystal, respectively. The material properties of silicon used in the present work can be found in [26].
<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_c)</td>
<td>Equilibrium concentration at crucible wall</td>
</tr>
<tr>
<td>(C_m)</td>
<td>Concentration in the melt volume</td>
</tr>
<tr>
<td>(C_s)</td>
<td>Concentration at the free melt surface</td>
</tr>
<tr>
<td>(C_x)</td>
<td>Concentration at the solid-melt interface</td>
</tr>
<tr>
<td>(A_{cw})</td>
<td>Contact area between melt and crucible wall</td>
</tr>
<tr>
<td>(A_{cb})</td>
<td>Contact area between melt and crucible bottom</td>
</tr>
<tr>
<td>(A_s)</td>
<td>Area of free melt surface</td>
</tr>
<tr>
<td>(A_x)</td>
<td>Area of solid-melt interface</td>
</tr>
<tr>
<td>(r_c)</td>
<td>Crucible radius</td>
</tr>
<tr>
<td>(r_x)</td>
<td>Crystal radius</td>
</tr>
<tr>
<td>(\delta_i)</td>
<td>Solutal boundary layer thickness</td>
</tr>
<tr>
<td>(\dot{n}_i)</td>
<td>Molar flow rate</td>
</tr>
<tr>
<td>(J_i)</td>
<td>Molar flux</td>
</tr>
<tr>
<td>(\omega_i)</td>
<td>Angular velocity</td>
</tr>
</tbody>
</table>

Table 3.1: Basic variables of the boundary layer model. In general, subscripts of \(c\), \(cw\), \(cb\), \(s\), \(m\), and \(x\) will refer to crucible, crucible wall, crucible bottom, free melt surface, melt volume, and crystal, respectively. All concentrations, fluxes, and flows refer to oxygen.

### 3.3.1 Molar fluxes \(J_i\) at crucible wall, free surface, and solid/liquid interface

We define the molar oxygen flows from the crucible into the melt, out of the free melt surface, and into the crystal as \(\dot{n}_c\), \(\dot{n}_s\), \(\dot{n}_x\), and \(\dot{n}_x\), respectively. Note that we have distinguished flux and surface area from the sidewalls of the crucible and the bottom, the reasoning of which we will discuss further in Section 3.3.3. Thus, the total flow of oxygen into the melt from the crucible wall is given by

\[
\dot{n}_c = J_{cw} A_{cw} + J_{cb} A_{cb} \quad (3.1)
\]

\[
J_{cw} = \frac{D}{\delta_{cw}} (C_c - C_m) \quad (3.2)
\]

\[
J_{cb} = \frac{D}{\delta_{cb}} (C_c - C_m) \quad (3.3)
\]

\(C_c\) is the equilibrium concentration of oxygen in the silicon melt at the crucible wall. We discuss and justify the choice to treat it as a constant in Section 3.3.2. At the melt
surface the flow of oxygen from the melt into the gas ambient is defined as

\[ \dot{n}_s = J_s A_s \]  

\[ J_s = \frac{D}{\delta_s} (C_m - C_s) \]  

We assume that we have an unhindered transport of SiO from the melt surface into the ambient gas. Therefore, all SiO formed at the surface is immediately removed and the oxygen concentration at the melt surface \( C_s \) approaches zero. This assumption is also used in our collaborators’ 2D-3D model, because it has been proven that the interaction of the gas flow with the melt flow can be neglected for the given puller geometry and process parameters \[26\]. At the solid-liquid interface the flow of oxygen out of the melt is given by

\[ \dot{n}_x = J_x A_x \]  

\[ J_x = k_{\text{eff}} V C_m \]  

Here we use the Burton-Prim-Schlichter (BPS) model \[32\] to derive an effective segregation coefficient \( k_{\text{eff}} = k / (k + (1 - k) \exp(-V \delta_x / D)) \) where \( V \) is the pull rate. \( \delta_x \) is the solute boundary layer at the solid-liquid interface. Accordingly, it can be approximated by the model for a rotating disk, which gives \[33\]:

\[ \delta_x = 1.6 D^{1/3} \nu^{1/6} \omega_x^{-1/2} \]  

### 3.3.2 Molar balance

Because of slow growth rates, we assume a pseudosteady concentration inside the melt volume. The pseudosteady state molar balance then becomes:

\[ \frac{d n_m}{dt} = 0 = J_{cw} A_{cw} + J_{cb} A_{cb} - J_s A_s - J_x A_x \]  

And solving for \( C_m \) gives
\[ C_m = \frac{C_c F}{F + \frac{A_x}{\delta_x} + \frac{k_{eff} V A_x}{D}} \]  
(3.10)

Where

\[ F = \frac{A_{cw}}{\delta_{cw}} + \frac{A_{cb}}{\delta_{cb}} \]  
(3.11)

If we neglect the deformation of the solid-liquid interface, then the areas \( A_i \) are all known from the crystal and crucible geometry and the initial melt mass. The equilibrium oxygen concentration at the crucible wall \( C_c \) is also known. Figure 3.4 shows the temperature dependence of oxygen equilibrium concentration in undoped silicon melt in contact with SiO\(_2\) as measured experimentally by Huang et al. 1993 [34] using secondary ion mass spectroscopy. While our collaborators have used the weak dependence on temperature in their coupled 2D-3D models derived from this study, [26], we chose in this LP model to neglect the temperature dependence completely and assume a constant value of \( C_c = 2 \times 10^{18} \text{ cm}^{-3} \).

Figure 3.4: Equilibrium oxygen concentration in undoped silicon melt in contact with SiO\(_2\) versus temperature as measured by Huang et al. 1993 [34].

The solute boundary layer thickness at the crucible and at the melt surface are unknown \textit{a priori} but can be estimated from transport scaling relationships and process parameters for the momentum boundary layers. Thereby, the Schmidt number \( Sc = \nu/D \)
is used to approximate the thickness of the solutal boundary layer $\delta_i$ from the momentum boundary layer $\delta'_i$ [35] which is marked by a prime henceforth.

$$\delta_i = 2.4 \ast \text{Sc}^{-1/3} \delta'_i$$ \hspace{1cm} (3.12)

### 3.3.3 Estimating momentum boundary layer thickness $\delta'_i$ at the crucible wall

To estimate $\delta'_i$, we turn to an analysis of King et al. [36], who investigated the different flow regimes in rotating Rayleigh-Benard configurations in dependence on the Ekman number $Ek$ and Rayleigh number $Ra$ which are defined here as follows:

$$Ek = \frac{\nu}{2\alpha c r_c^2}$$

$$Ra = \frac{\beta g \Delta T r_c^3 \left( \frac{h}{r_c} \right)}{\kappa \nu} = Gr \ast Pr$$

with volumetric expansion coefficient $\beta$, melt height $h$, crucible radius $r_c$, maximum melt overheating $\Delta T$, kinematic viscosity $\nu$, thermal diffusivity $\kappa$, Grashof number $Gr$, and Prandtl number $Pr = \kappa/\nu$.

King et al. [17] found that for geostrophic conditions, for $RaEk^{\frac{3}{2}} < 10$, the momentum boundary layer thickness follows a scaling relationship with the Ekman number $Ek$ of the system:

$$\delta'_{c,Ek} = 3Ek^{1/2}r_c$$ \hspace{1cm} (3.13)

The criterion for geostrophic flow is fulfilled for the present Czochralski set-up ($RaEk^{3/2} \sim 10^{-8}$), therefore (3.13) should be valid. To check this assumption we also used an alternate estimation of the viscous boundary layer thickness along the crucible wall for non-rotating Rayleigh-Bernard convection [36] using the Grashof number, $Gr$.

$$\delta'_{c,Gr} = Gr^{-1/4}r_c$$ \hspace{1cm} (3.14)
3.3.4 Estimation of the momentum boundary layer thickness $\delta_i'$ at the free melt surface

For the free surface, we utilize the analysis of Okana et al. 1989 [37]. The thickness of momentum boundary layer associated with Marangoni flow over the free surface is found to follow the following scaling relationship with the Marangoni number $\text{Ma}$ of the system. The relevant length scale here is the distance between the crucible wall and the crystal, or $r_c - r_x$. The Marangoni number is defined as

$$\text{Ma} = \frac{-\left(\frac{\partial \sigma}{\partial T}\right) \Delta T (r_c - r_x)}{\rho \nu^2}$$

with density $\rho$, and temperature dependence of surface tension $\frac{\partial \sigma}{\partial T}$.

Accordingly, the momentum boundary layer thickness at the free melt surface becomes:

$$\delta_i' = \text{Ma}^{-1/3} (r_c - r_x) \quad (3.15)$$

3.3.5 Assembling the LP model: two limiting cases

Recall in Section 3.3.1 that we differentiated fluxes and surfaces areas attributed to the crucible wall and bottom. Actual flow patterns in Czochralski systems are complex. Four major driving forces contribute to flow in the melt: the crystal rotation rate, the crucible rotation rate, buoyancy, and thermocapillarity. While the first affects flow locally around the crystal, the latter three largely determine the flow throughout the bulk of the melt: Ekman pumping from the crucible rotation draws melt downward along the axis and hurls it out radially along the crucible bottom. The flow must necessarily turn upward due to the presence of the crucible wall and is aided by buoyancy (Rayleigh-Bernard convection), since melt is heated from outside the crucible. At the free-melt surface, Marangoni flow directs fluid radially towards the center, where lower temperatures causes denser fluid to sink. While flow patterns in Czochralski-like geometries have been studied both numerically and experimentally, none thus far determine the scaling of crucible boundary layers to the aforementioned driving forces. Because of this, and to stay in the spirit of developing a straightforward and simple model, we present two limiting, idealized cases in assembling the LP model.
Figure 3.5: The basic driving forces of flow in the Czochralski system are depicted. 1.) Crystal rotation affects flows locally around the crystal. Since the crystal sits below the melting point, cooler more dense fluid here begins to sink. 2.) As the crucible rotates, the centrifugal forces draw fluid radially outwards along the bottom. The fluid is replaced by fluid drawn from above. This drawing of fluid down the central axis in a rotating container is known as *Ekman pumping*. 3.) Fluid that moves radially outward along the bottom of the crucible must turn upward as it meets the crucible wall. Heaters line the side and bottom of the crucible, so the heated fluid becomes slightly less dense and rises due to buoyancy. This is known as *Rayleigh-Bernard convection*. 4.) The free melt surface shows a strong temperature gradient, as the recently heated fluid from the outer edge, while crystal at the center is below the melting point. This temperature gradient at the free surface also creates a gradient in surface energy, which draws fluid from the warmer outer edge to the cooler center. Surface flows due to gradients in surface tension are known as *Maragoni flows*, or more specifically *thermo-capillary flows* when a temperature difference drives the gradient in surface tension.
The first, we assume that all boundary layers along the crucible bottom and wall are determined by the Ekman number. This implies that Ekman flow along the bottom continues upward along the wall uninterrupted and that buoyancy is neglected as a driving force for determining the momentum boundary layer on the crucible wall. In this case, the momentum boundary layer thickness in (3.13) is converted to a solutal boundary layer thickness by (3.12) and is used to substitute both $\delta_{cw}$ and $\delta_{cb}$ in (3.2) and (3.3). We will refer to this formulation as the Ekman LP model.

The second, we assume that the boundary layer along the crucible bottom is determined by the Ekman number, while the boundary layer along the crucible wall is determined by the Grashof number. This implies that the boundary layer due to vertical flow along the crucible wall is determined completely by buoyancy with no contribution from the Ekman-pumped melt along the bottom turning upward as it runs into the crucible wall. In this case, $\delta'_{c,Ek}$ from (3.13) will be used to determine $\delta_{cb}$ in (3.3) and $\delta'_{c,Gr}$ from (3.14) will be used to determine $\delta_{cw}$ in (3.2). (3.12) is again used to convert these momentum boundary layer thicknesses into solutal boundary layer thickness before substitution. We will refer to this formulation as the Ekman + Grashof LP model. Figure 3.6 illustrates the difference between these limiting cases.

After these substitutions, all the necessary parameters are set to determine $C_m$ in (3.10).

### 3.4 Comparison of the lumped-parameter model with coupled 2D-3D simulations

#### 3.4.1 Influence of crucible rotation for constant crystal rotation

Figure 3.7 shows melt oxygen concentration $C_m$ as computed by the LP models compared to the time-averaged average melt oxygen concentration from the 2D-3D simulations. The results of the LP model are in qualitative agreement to the 2D-3D simulations; increase of oxygen concentration with increasing crucible rotation is well-represented. The decrease of the oxygen concentration with increasing body length is also represented and is a result of the decrease of the crucible area in contact with the liquid silicon with decreasing melt volume. The increase in oxygen concentration for increasing crystal
Figure 3.6: a.) Visualization of the Ekman boundary layer. The Ekman boundary layer thickness is calculated from assuming an infinite disc spinning submerged in a fluid. b.) Visualization of the boundary layer determined by the Grashof number. As heaters heat the fluid near the crucible wall, heated fluid becomes slightly less dense and therefore buoyant, driving an upward flow. A boundary layer is formed near the crucible wall. c.) In the Ekman LP model, the boundary layers along the entire crucible (red dashed line) are determined by the Ekman number. In this limiting case, it would be as if fluid flung out along the crucible bottom turns upward with no loss in momentum. d.) In the Ekman + Grashof LP model, the boundary layer thickness along the crucible bottom (red dashed line) is determined by the Ekman number, while the boundary layer thickness on the wall (green dashed line) is determined by the Grashof number. In this limiting case, it would be as if none of the momentum from fluid flung out along the crucible bottom gets directed upwards at the crucible wall. Instead the upward flow is due to Rayleigh-Bernard convection only. In reality, the crucible obviously has finite radius. Thus fluid flung out radially needs to turn upwards as it meets the crucible wall, where heating will also aid in upward flow due to buoyancy of hotter fluid.
rotation, however, is severely underrepresented in both LP models.

The Ekman + Grashof LP model shows good quantitative agreement with the mean oxygen concentration from simulation data across multiple body lengths for all crucible rotation rates. The Ekman LP model has less accurate agreement but better describes the increase in melt concentration with increasing body length and decreasing melt height. These qualitative trends agree with the assumptions behind the two idealized cases. The Ekman LP model exaggerates the strength of the upward melt flow driven by Ekman pumping, especially as melt levels drop. On the other hand, the Ekman + Grashof model completely neglects the effect of Ekman pumping in providing upward flow along the crucible wall. Buoyancy-driven flow is comparatively weaker; this can be verified by the fact that $\operatorname{Ek}^2 \ast \operatorname{Gr} \ll 1$. Because of this nearly all the oxygen in this model comes from the crucible bottom, thus there is very weak dependence on changing body length and melt depth. In reality, especially with a rounded crucible bottom, some but not all radial momentum of fluid moved via Ekman pumping is converted upward in the axial direction as it meets the crucible wall, with additional upward driving force of buoyancy. Figure 3.8 shows the breakdown of oxygen flowrates for various crystal rotation speeds and body lengths for constant crucible rotation of -10 rpm. It is seen...
also here than the Ek + Gr LP model shows very weak dependence on body length and that predictions from both LP models converge when body length is increased (and thus contact surface area of crucible wall is decreased as melt levels decrease).

It is also notable that the oxygen flux through the solid-liquid interface is almost negligible in the LP model. This is also justified, as 99% of the oxygen entering the melt from the crucible will evaporate as SiO from the melt surface [38].

Figure 3.8: Atomic oxygen flowrates into and out of the melt using the Ekman and Ekman + Grashof LP models for varying crystal rotation and body length at -10 rpm crucible rotation. Horizontal axis labels denoted as crucible rotation/body length [mm]/crystal rotation, e.g. 10/20/12 refers to -10 rpm crucible rotation, 20 mm body length, 12 rpm crystal rotation. Each rotation/body length configuration has four columns: Inflows from Ek LP model, Outflows from Ek LP model, Inflows from Ek + Gr model, and Outflows from Ek + Gr model. The Ek LP model overexaggerates the inflow of oxygen from the crucible wall, while the Ek + Gr LP model underexaggerates it. Very little oxygen flows in from the walls under the Ek + Gr LP model, while the Ek LP model has significant contribution from the walls when body length is low (and melt height is high). In both models, the vast majority of oxygen leaves the system from the free surface.
Figure 3.9: LP models with multiple regions were proposed and investigated, but none provided any significant improvement in matching the 2D-3D models. The geometries explored include: a.) hemi-spherical region near the crystal, b.) paraboloid region near the crystal, c.) cylinder region under the crystal, d.) cone region under the crystal.

3.5 Limits of the lumped parameter model

While the actual oxygen concentration field exhibits little variation in the bulk of the melt, there is some degree of inhomogeneity that cannot be captured by the LP model. As exhibited above, the LP model fails to capture trends with changing crystal rotation. The suspected reason is that complex flow patterns arise due to these changing parameters, along with changing geometry as the solidified fraction increases and melt level decreases. These flow patterns likely make boundary layers along surfaces inhomogeneous in unpredictable ways.

Efforts were made to capture some inhomogeneity in the melt by further dividing the melt volume into regions separated by shear layers (largely inspired by the non-mixing cells observed in Czochralski systems in [39] and [40]). As seen in Figure 3.1, multiple regions can be created fluxes between regions defined. Some geometries investigated are pictured in Figure 3.9. However, none of these multi-reservoir models showed any significant improvement in matching the 2D-3D models. Later, image processing was used on the actual concentration fields from the 2D-3D model in order to suggest geometries to divide the melt region. The number of colors allowed to represent the concentration fields was reduced, hence lumping together regions of similar color (and hence similar concentration). Figure 3.10 shows two simulations at 20 mm body length, -8 rpm crystal rotation, and 5 or 15 rpm crucible rotation before and after image processing. Not only are the geometries of lumped concentrations in each case incredibly complex, they change completely with the increase in crucible rotation. This suggests that flow patterns in
the melt produce complex distributions of concentration in the melt that vary greatly in space and are also highly dependent on process parameters such as crystal/crucible rotation schemes. This makes this problem unamenable to be modeled in a lumped parameter approach beyond a single melt reservoir.

Figure 3.10: Dividing melt regions into multiple reservoirs by using image processing on 2D-3D model concentration fields. By reducing the number of colors in the concentration field, regions of similar color (hence concentration) are lumped together. Left images are original concentration fields, while right images are processed. The important feature in the processed images are not the actual colors, but the shape of the boundaries between colored regions. Both rows of images depict a configuration with 20 mm body length and -8 rpm crystal rotation. The upper row’s crucible rotation is 5 rpm, and the bottom row’s crucible rotation is 15 rpm. The complex geometries suggest that flow patterns make this problem unamenable and impractical to be modeled by lumped parameter means beyond a single melt reservoir.

To verify the inhomogeneity of the oxygen concentration in the melt and thickness of boundary layers, concentration profiles from the 2D-3D model normal to the crucible were plotted along various sections of the crucible (see Figure 3.11). With changing crystal and crucible rotation rates, it is observed that the fluxes of oxygen from the
Figure 3.11: Oxygen concentration profiles are plotted along lines normal to various positions of the crucible from 2D-3D simulations. Concentration profiles (and hence oxygen flux) can change markedly depending on position along the crucible.

crucible can change noticeably with position along the crucible wall in complex ways, though a comprehensive analysis of oxygen flux over time and as functions of these various process parameters is outside the scope of this study. General observations from the 2D-3D simulations show that oxygen flux primarily comes from the crucible bottom. Only at high melt levels and lower rotation rates do we observe significant flux from the crucible walls, but even then, oxygen flux from crucible bottom still dominates. Again, the complex ways these fluxes change with crystal and crucible rotation and melt level make the system less amenable to be modeled by lumped-parameter means.

3.6 Conclusion

The LP model allows instantaneous calculation of the oxygen concentration on any computer, whereas the coupled 2D-3D simulations would take days to weeks on a computing cluster. The comparison to the 2D-3D simulations shows that the accuracy of the LP model is sufficient for certain coarse case studies. It allows to one to quickly estimate the influence of various process quantities. Therefore, it can contribute to a improved understanding about the oxygen transport during silicon Czochralski crystal growth.
Extensions of the model to take into account magnetic field effects or the influence of the interaction of melt and gas flow can be incorporated given an understanding of how these additional processes affect flow structures \cite{25}.

However, the LP model fails when a precise analysis of the oxygen transport is required due to its inability to capture complex flow structures that form and how they affect oxygen transport. While numerical, analytical, and experimental studies exist examining flow in Czochralski-like geometry \cite{22,25,40}, these analyses do not extend to examination of boundary layers or consequences on oxygen transport. Thus, we anticipate this modeling approach could be significantly expanded by better understanding of a.) oxygen transport as affected by flow patterns through the entire growth process and b.) fundamental relations between process parameters as dimension of flow structures (e.g. shear layers, flow cells, etc) in Czochralski geometry. Presently, the LP model only gives rough estimations of oxygen transport; for more accurate treatments, coupled 2D-3D simulations are still indispensable.

3.7 Acknowledgments

Our collaborators’ contributions were part of the Korona project. Korona was funded partly by the German Federal Ministry for Economic Affairs and Energy (BMWI) under contract number 0324099B.
Chapter 4

Analysis and *in-situ* Observation of Migration of Europium in Eu-doped Barium Bromochloride

4.1 Introduction

Our next investigation is with solid-state diffusion, an extremely important phenomenon in the manufacturing of industrially-relevant crystals. A well-known example is the need for controlling precise dopant concentration during manufacturing for engineering electronic properties in semiconductor materials. However, determination of a material’s solid-state diffusion coefficient is notoriously difficult. Such experiments, usually measuring concentration profiles over time, are not only often long and tedious, they typically involve repeated destructive testing of the subject, incurring high costs in time, labor, and material (Figure 4.1).

In this chapter, we back out a liquid and solid-state combined diffusion coefficient of a dopant, elemental europium, in a sample of barium bromochloride, by analyzing data from energy-resolved neutron imaging (ERNI), a novel imaging technique that allows direct, *in-situ* observation of high-temperature melt crystal growth systems. 2D ERNI data is consolidated into 1D, and a transient 1D two-phase diffusion model is constructed and solved using Finite Fourier Transforms (FFT) and Finite Difference
Experimental methods to determine solid state diffusion coefficients are typically costly in time and material. Left: Micrographs of AISI 403 stainless steel after 1, 3, and 5 hrs of low-temperature plasma carburization. Carburization is the diffusion of carbon into steel, changing its mechanical properties. Depending on the application, it can be an engineered or unwanted phenomena. Carburization experiments involve diffusion of multiple samples of steel and cutting them open to measure penetration depth. Reproduced from [41]. Right: Plots of boron diffusion profiles into silicon. Boron is typically used as a p-type dopant in semiconductor-grade silicon. In a classic method of measuring its diffusion coefficient in silicon, a boron-rich layer is deposited onto silicon and allowed to diffuse in high temperature. Surface resistivity (and thus concentration) is measured via four-point probe method. Concentration profiles through the depth of the silicon material are done by repeatedly performing wet chemical etching (reaction with KOH and subsequent dissolution of etched layers with HF). Reproduced from [42].

Method (FDM). This model requires three input parameters - liquid diffusion coefficient, solid-state combined diffusion coefficient, and partition coefficient - which are adjusted manually to match the experimental 1D data. The combination of in-situ imaging techniques and modelling provides a largely unexplored avenue for deriving physical parameters from past experiments.

4.1.1 ERNI and the BaBrCl:Eu growth system

The materials system examined here is europium-doped barium bromo-chloride (BaBrCl:Eu), a promising inorganic scintillator radiation detection material. An overview on radiation detection materials and operating principles of scintillators was covered in the Introduction (Chapter 2).
Melt crystal growth systems are notoriously difficult to study *in-situ* due to high temperatures and accompanying thermal insulation material. Because of this, many such growth processes and experiments are done blind - experimentalists only get opportunities to examine materials before and after growth. Neutron imaging can be particularly advantageous in such situations, as neutrons are able to penetrate through most furnace and insulation materials easily. Unlike x-rays, which interact with the electron cloud of materials, neutrons interact primarily with atomic nuclei, resulting in a wide range of attenuation coefficients for elements and their isotopes whereas x-ray attenuation correlates heavily with atomic number. Using energy-resolved neutron imaging, it is possible to deduce the spatial distribution of specific elements *in-situ* provided they have sufficiently high attenuation coefficients (Figure 4.2). In this case, europium is both a common scintillation activator and an ideal imaging agent, having high neutron attenuation.

![Figure 4.2](image)

**Figure 4.2:** Because different elements have unique signatures of neutron attenuation, ERNI can be used to image the spatial elemental composition of materials. Europium has high neutron attenuation and thus acts as a good imaging agent. Reproduced from [43].
4.1.2 Old experiment, new insights

In 2016 a collaborative project between Lawrence Berkeley National Laboratory, Los Alamos National Laboratory, Japan Atomic Energy Agency, and the University of Minnesota has resulted in a first-ever examination of in-situ crystal growth of BaBrCl:Eu in a custom Bridgman furnace made to accommodate a neutron beamline [44].

While the original motivation of this project was to image Eu distribution during a Bridgman growth run, the neutron imaging data collection began during a pre-growth period, where movement of Eu was observed in the solid phase. It was this movement that prompted investigation into the dynamics of Eu migration in the solid phase.

4.1.3 Experimental set-up

Here we will briefly outline the experimental set-up of the ERNI and BaBrCl:Eu system during the pre-growth period. More details of the ERNI apparatus, specifications, and procedures related to imaging and post-processing can be found in references [44] and [43].

A BrBrCl:5%Eu sample ∼5 cm in length and 1.2 cm in diameter grown by vertical gradient freeze is placed in a modified clamshell furnace in the path of a pulsed neutron source at the Materials and Life Science Experimental Facility at the Japan Proton Accelerator Research Complex (J-PARC). 10 cm Behind the furnace is a fast neutron counting detector with a detection area of 28x28 mm². Neutron energies are calculated by Time of Flight (TOF) technique, and each dataset consists of neutron transmission data across 3100 spectral bins. With the neutron spectral response of europium known, spatial elemental composition can be deduced. Because europium also segregates readily across the solid-liquid interface in BaBrCl:Eu, ERNI data is able to reveal the location of the solid-liquid interface in-situ.

Prior to the a BaBrcl:Eu crystal growth experiment, the sample and furnace undergo a procedure a time when the furnace is powered and materials are near melting point temperature but no growth is taking place in order to let the furnace stabilize. During this time ERNI data collection began, which captured the solid-state migration of Eu (Figure 4.4). Figure 4.5 along with the list below describe this pre-growth procedure.

1. A pre-synthesized charge of BaBrCl:Eu is mounted in a clam-shell furnace at room
temperature.

2. Furnace is energized and gradually heated over approximately two hours. Set point of thermocouple is set to 950 °C. The sample is nearly entirely melted except for
material at the very bottom of the ampoule.

3. Thermocouple setpoint is set to 900 °C. Over the next hour, the material grows back such that the solid-liquid interface is approximately at the center of the neutron detection area.

4. Data collection begins. Furnace power and setpoint is maintained for the next four hours.

![Figure 4.5: Cartoon of stages of the BaBrCl:Eu pre-growth period. Black dot denotes position of the thermocouple (used to set setpoint temperature). Dashed lines show the approximate field of view for the neutron detector.](image)

### 4.2 Expected transport phenomena

Before delving into the model formulation, it is worth reviewing some of the transport phenomena we expect to observe in this experiment. Consider an ideal imaginary experiment where a solid with Eu distributed uniformly is instantly melted in half (4.6a) at \( t = 0 \). What would we expect to see? Immediately, we would expect some segregation to occur at the interface, as Eu would preferentially segregate into the liquid phase (4.6b). Of course, we should expect to track the amount of Eu leaving the solid and entering
the liquid. This segregation produces a negative concentration gradient in both phases, which allows for diffusion down the gradient towards the positive end of the domain. As seen in the ERNI data (Figure 4.4), the interface is observed to move slightly in time. This movement, coupled with the aforementioned interfacial segregation and mass balance, is expected to change the Eu concentration profile in the solid phase in ways that a stationary interface could never produce, namely a concave-up region near the interface (Figure 4.6). Lastly, if we were to imagine this sample to be held indefinitely, we would expect that diffusion would eventually flatten out the solid and liquid phase concentration profiles completely. The pre-growth process, however, was not long enough to observe this.

4.3 Model formulation

Since there are numerous uncertainties in this experiment, especially given that it was not originally designed to measure diffusion, a simple mathematical approach was chosen to capture only the dominant physical phenomena. Thus, our approach is to construct our model as a transient, 2-phase, 1-dimensional diffusion model, which can be solved quickly and reduces unnecessary complexity for which we do not have the experimental data or parameters to verify.

4.3.1 1D data extraction

ERNI produces datasets that show the projection of the true 3D Eu concentration field onto a 2D plane (Figure 4.4). That is, the resulting signal is the integrated concentration across the width of the sample. It is possible to deduce the 3D concentration profile if the sample is rotated while being imaged, using the mathematics of computed tomography (Figure 4.7). However, the Bridgman furnace used in this experiment, a small clamshell furnace made to fit in the path of a neutron source, was unable to rotate the sample during growth.

Our goal is to consolidate the 2D ERNI projection data into a reasonable 1D representation. To do this, we utilize Radon and inverse-Radon transforms, the foundation of computed tomographic reconstruction. The projection of a density field (e.g. concentration) onto a lower dimension is known as the Radon transform. To reconstruct the
original density field from projection data, one would use the inverse-Radon transform. An everyday example of these transforms is a CAT (computerized axial tomography) scan - as a patient lies in the scanner, an x-ray source and detector revolve about and translate down the patient’s longitudinal axis, recording projection data from multiple angles. These projection data then undergo an inverse-Radon transform to reconstruct 3D radiographic density of the patient’s anatomy. The mathematical details of these
transforms will not be discussed here as they are well-documented in many popular software packages for scientific computing such as MATLAB and Mathematica.

Because we only have one projection angle of in-situ ERNI data, it is possible to assume that the cylindrical sample is axisymmetric and perform an inverse-Radon transform, yielding a pseudo-axisymmetric concentration field. Using this method, we arrive at a 1D signal that represents the average concentration of a $\sim 6.7$ mm diameter cylindrical region down the sample length (Figure 4.8a). Details of this process, including additional efforts made to reduce noise, are found in Appendix D.

From this 1D profile, an interface location can be deduced. Because the actual interface appears to be concave (with respect to the solid phase), we take the interface location to be the local minimal in the 1D profile. Figure 4.8b shows the interface location plotted over time over the course of the experiment.

### 4.3.2 Governing equations

Presently, it is not known why the initial concentration Eu profiles exhibit such a pronounced downward trend or why the interface moves in the way it does. Relevant factors

---

**Figure 4.7:** 3D Eu concentration profile of a room-temperature sample of BaBrCl:0.1%Eu (from a separate experiment) derived via computed tomography of ERNI data. a.) Bulk Eu composition and Eu-deficient region shown b.) Only Eu-deficient region shown. Figure reproduced from [44].
such as the sample microstructure, original Eu distribution, or detailed furnace temperature profile are unknown and may play a role. We take these intriguing features as-is in our model. As seen in Figure 4.8, the interface location appears to hover around 13 mm for approximately 110 minutes and then begins to advance. To simplify our model, we assume that the interface location, which we will denote as $\gamma$, is stationary for those first 110 minutes. Afterwards, we reformulate the problem with a moving reference frame which begins to move at a constant velocity $v_{\text{int}} = 0.00652$ mm/min at 110 minutes.

The domain has a total length $L = 50$ mm. In each of the phases, the following field equations are applied during the stationary period for $0 < t < 110$ minutes:
\[
\frac{\partial C}{\partial t} = D(x) \frac{\partial^2 C}{\partial x^2}
\]  
\hspace{1cm} (4.1)

Where

\[
D(x) = \begin{cases} 
D_s, & 0 < x \leq \gamma \\
D_l, & \gamma < x < 1 
\end{cases}
\]  
\hspace{1cm} (4.2)

These equations are modified for \( t \geq 110 \) minutes, and the origin is taken to be the location of the interface:

\[
\frac{\partial C}{\partial t} + v_{\text{int}} \frac{\partial C}{\partial x} = D(x) \frac{\partial^2 C}{\partial x^2}
\]  
\hspace{1cm} (4.3)

Where

\[
D(x) = \begin{cases} 
D_s, & x \leq 0 \\
D_l, & x > 0 
\end{cases}
\]  
\hspace{1cm} (4.4)

At the interface, the concentration on the solid and liquid side are related by means of a partition coefficient \( K \). This is imposed on both stationary and moving formulations:

\[
C|_s = KC|_l
\]  
\hspace{1cm} (4.5)

Additionally, we account for mass balance across the interface for \( t < 110 \) minutes:

\[
D_s \left. \frac{\partial C}{\partial x} \right|_s = D_l \left. \frac{\partial C}{\partial x} \right|_l
\]  
\hspace{1cm} (4.6)

And for \( t \geq 110 \) minutes:

\[
D_s \left. \frac{\partial C}{\partial x} \right|_s = D_l \left. \frac{\partial C}{\partial x} \right|_l - C|_l v_{\text{int}}
\]  
\hspace{1cm} (4.7)

At the ends of the stationary formulation for \( t < 110 \), we impose no-flux conditions:

\[
\begin{align*}
\frac{\partial C}{\partial x}(x = 0, t) &= 0 \\
\frac{\partial C}{\partial x}(x = L, t) &= 0
\end{align*}
\]  
\hspace{1cm} (4.8)

At the ends of the moving reference formulation, we use Dirichlet conditions to match...
smoothed, interpolated concentration values derived from the experimental data.

For a starting initial condition, we use the first experimental 1D concentration profile, linearly extrapolating to the ends of the domains such that the total concentration remains 5% Eu (since data is only available for the 28 mm neutron sensor area).

Two simplified/idealized forms of this problem can be solved analytically. The first is solved via Finite Fourier Transforms in the method of Neal Amundson and D. Ramkrishna [45]. Due to limitations of this method, it was not used for the final calculation of diffusion coefficients. However, because this problem presents an opportunity to apply this unique mathematical technique, the solution method and results are described in Appendix B. The second is solved via similarity transforms. This requires an idealized homogeneous distribution of solute through the entire sample, which was not observed in this experiment. The method, however, is described in Appendix C.

The equations are fully solved using centered-time, centered-space Finite Difference Method. The details of the method are given in Appendix A.

4.4 Results

Three parameters are required to be inputted for the above numerical model: $D_s$ the apparent diffusion coefficient, $D_l$ the apparent liquid diffusion coefficient, and $K$ the partition coefficient. Maintaining the simplistic approach, these values were varied manually until the model results agreed with experimental data in a qualitatively satisfactory way, resulting in $D_s = 1.9 \times 10^{-10} \text{ m}^2/\text{s}$, $D_l = 2.5 \times 10^{-10} \text{ m}^2/\text{s}$, and $K = 0.45$. Model results are plotted over the experimental data are shown in Figure 4.9. While model results align well with experimental data for later times, significant deviation is observed for early timesteps. We hypothesize that this is largely due to the curvature of the interface in the actual sample. When the interface is curved, the path of neutrons will pass through both phases before contacting the detector, causing a “smearing” of the projected contrast signal, despite the segregation of europium across the interface. Thus, it takes some time for the sharp discontinuity in europium across the interface to appear in the ERNI data, whereas it is immediately apparent in the model data.

As stated before, we denote these parameters “apparent” diffusion coefficients because they lump together multiple modes of transport. In the liquid phase, a model reduction
to 1D prohibits convection, so weak flows that may exist can contribute to the overall apparent diffusion. In the solid, multiple modes of diffusion can occur. The slowest mode is diffusion through the bulk crystal, relying on Eu atoms moving through the crystal lattice. Additionally, high diffusivity paths exist along grain boundaries and through dislocations. All three modes are lumped together in the solid apparent diffusion coefficient. While it may seem odd to see apparent solid and liquid diffusion coefficients on the same order of magnitude. It is worth noting here that diffusion coefficients share an Arrhenius (i.e. exponential) relationship with temperature. Thus, it is not uncommon for solutes in materials with high melting points to have apparent solid diffusion coefficients that are of the same order of magnitude as their liquid phases', especially when summing up multiple modes of diffusion (Figure 4.10).

4.5 Conclusions

Solid state diffusion is a vital aspect of understanding and controlling crystal growth processes. Traditional means of experimentally determining solid state diffusion coefficients involve long, repetitive experiments of that are costly in time, labor, money, and energy. In this chapter, a transient, 1-dimensional model describing Eu migration was constructed based on an experimental “pre-growth” period of Eu-doped BaBrCl in a modified Bridgman furnace. Energy-resolved neutron imaging provided an in-situ view of Eu distribution during the process, and strong segregation of Eu over the solid-liquid interface provided a driving force for diffusion in both phases. While many experimental unknowns and non-idealities existed, coupling a simple 1-dimensional transport model with experimental energy-resolve neutron imaging data allowed us to back out the apparent solid diffusivity, apparent liquid diffusivity, and partition coefficient of the BaBrCl:5%Eu system near its melting point temperature.

A number of experimental modifications can be made to optimize this technique for determining diffusion coefficients. For example, a narrower ampoule would constrain the system to more resemble an ideal 1-dimensional experiment. This would reduce radial variation in the imaged solute and minimize the total interface deflection, creating a sharper contrast of the segregation of solute across the solid-liquid interface. Next,
having greater temperature control and measurements would do much to reduce experimental uncertainties. In the present study, there was only one temperature sensor, which was used to control the furnace’s single heater. Recording temperature data over time, and having more sensors (to record over space) would give us a better idea of conditions inside the furnace.

A significant point to emphasize is that the original experiment was not designed to measure diffusion coefficient, but simply to image Eu migration in-situ using the novel ERNI technique. Thus, coupling modeling with in-situ imaging presents a promising method of extracting additional value from already-existing experimental data with minimal additional effort. If this type of in-situ characterization of materials is pursued on a general scale, it would be advised that traditional characterization techniques (which may involve destructive testing) are used to verify both ERNI and model elemental composition data. In this case, after the pre-growth period, the BaBrCl:Eu in the charge went through the full Bridgman growth process, so the original sample is forever changed. Nonetheless, coupling in-situ measurements with modeling at a larger scale could generate a swath of valuable data about how such materials and dopants behave in difficult crystal growth environments.
Figure 4.9: Solutions of the numerical model plotted over experimental data from Eu migration ERNI experiment.
Figure 4.10: Diffusion coefficients of various modes of solid diffusion compared to liquid diffusion near melting point temperatures. Data is consolidated from multiple FCC metals and normalized with a reduced temperature. Superscripts are as follows: $S$: free surface; $B$: grain boundary; $D$: dislocation; $XL$: bulk crystal free of line or planar defects; $L$: liquid. Reproduced from [46].
Chapter 5

Temperature Gradient Zone
Melting of Second-Phase Particles

5.1 Introduction

In this last investigation of this thesis, we discuss the migration of liquid particles through solid crystals under thermal gradients. By action of thermal and molecular diffusion, melting or sublimation at the hotter side and freezing at the cooler side of an embedded second-phase (SP) particle produces the net effect of the particle migrating in the direction of higher temperature. A number of scientific and engineering disciplines would benefit from a greater quantitative understanding of this migration process. For example, particle migration plays an important role in the safe nuclear energy production - bubbles that cause swelling in nuclear fuel elements [47–49] and brine particles in salt mines used for nuclear waste storage are observed to migrate over time [50]. Current understanding of paleoclimate is derived from chemical analysis of entrained particles in ice core samples, but migration of brine particles may shift paleoclimate signals by thousands of years [51]. Finally, by manipulating thermal environments, migration of a liquid zone may be controlled and exploited in production of valuable semiconductor crystals [52,53].

In this chapter, we investigate the mechanism of particle migration by devising analytical and numerical 1D models. We then apply these methods to study tellurium-rich second-phase particles in cadmium telluride (CdTe), a promising room-temperature
semiconductor radiation detection material, as a material case study. Finally, we compare numerical model results against experimental data of sodium chloride (NaCl) brine and ice, a system whose physical parameters are well-known, showing excellent agreement.

5.1.1 Historical Development

In 1926, Whitman [54] first described a mechanism by which brine inclusions migrate in sea-ice under natural temperature gradients (often referred to as brine pocket migration in geophysics communities), informed from the correspondence of Canadian Arctic explorer Dr. Vilhjalmur Stefansson: “Pieces of sea-water ice, only a few days old, are too salty for cooking or drinking purposes...On the other hand, the saltiness of ice that has floated in the ocean during a warm season has decreased to such an extent that it is potable” [55]. With their lower melting point, second-phase brine particles remain liquid while the surrounding crystal of pure water ice remains solid. As Whitman’s hypothesis goes, a difference in temperature between the atmosphere and surrounding seawater sets up a necessary temperature gradient for migration, eventually causing the brine particle to expel itself from the sea ice.

In 1954, Pfann patented an industrial semiconductor doping process whereby a crystal containing second-phase zones of high concentration of solute/dopant is annealed under a temperature gradient [56]. Operating by the same physical mechanisms as brine expulsion in ice, the liquid zone migrates in the direction of the temperature gradient, leaving dopant behind in the regrown crystal (determined by the partition coefficient of the mixture). He coined the term temperature gradient zone melting (TGZM) to describe this process, which we continue using here.

A number of empirical studies have documented and characterized TGZM for a variety of systems. Pfann’s patent discussed operating principals and furnace design schematics that would perform this industrial process for extrinsic semiconductors such as germanium and silicon. Wernick’s empirical studies of molten aluminum and gold wire migration in silicon and germanium solids revealed that migration velocity was dependent on wire thickness and material orientation, implying that kinetics of melting/solidification on certain crystallographic faces were playing a role [57], though Mlavsky
and Weinstein found no such orientation-dependency in studies of gallium zones in gallium arsenide\cite{58}. Kingery and Goodnow and Hoekstra et al. performed experiments on NaCl and KCl brine particles undergoing TGZM in water ice and characterized migration velocities\cite{59}. Jones later performed experiments to measure kinetic coefficients for possible growth mechanisms\cite{60,62}. Prior theoretical analyses of TGZM are discussed in section 5.1.3.

5.1.2 General mechanism of migration

To keep generality in discussing TGZM, we will refer to “solute” as the impurity species that is dissolved in the liquid zone from a pure solid (e.g. salt is the solute of a brine particle embedded in ice). Consider a second-phase particle embedded in a crystal of a pure species (i.e., a mixture for which the solidus curve is very nearly vertical). At low temperatures, both phases are solid (Figure 5.1a). At an elevated temperature in an isothermal setting, the SP particle and some surrounding pure solid should melt and establish an equilibrium concentration $C_0$ (Figure 5.1b). Upon application of a temperature gradient (assume it is instant), the liquid particle is no longer in equilibrium with its surrounding solid (Figure 5.1c). The region at the cooler side of the particle is now undercooled and is too dilute to be in equilibrium with its thermal environment. Thus, the cooler interface attempts to equilibrate by growing, or forming new solid (Figure 5.1d). Conversely, the region at the warmer side of the particle is now superheated and is too concentrated to be in equilibrium with its thermal environment. The warmer interface attempts to equilibrate by melting (Figure 5.1e). The net effect of growth at the cooler interface and melting at the warmer interface is the migration of the liquid particle in the direction of the temperature gradient.

This growth and dissolution first described by Whitman occurs so that the solid-liquid interfaces can achieve a state more closely resembling equilibrium, but these very actions spur a cascade of processes that continually shift the equilibrium state further away. The formation of pure solid at the cooler interface rejects solute into the melt, and the melting of pure solid at the warmer interface dilutes solute in the melt. The accumulation and dilution of solute at the two ends of the particle produces a concentration gradient which the solute can diffuse down towards the warmer interface. The movement of solute also affects the concentration-dependent melting point temperature
Figure 5.1: Conceptual steps in 1D TGZM. a.) At low temperatures, both phases are solid. b.) At an elevated temperature in an isothermal setting, the SP particle and some surrounding pure solid melts and establishes an equilibrium concentration $C_0$. c.) Upon application of a temperature gradient the liquid particle is no longer in equilibrium with its surrounding solid. d.) The region at the cooler side of the particle is now undercooled and is too dilute to be in equilibrium with its thermal environment. The cooler interface attempts to equilibrate by growing, or forming new solid. e.) The region at the warmer side of the particle is now superheated and is too concentrated to be in equilibrium with its thermal environment. The warmer interface attempts to equilibrate by melting.
of both interfaces, as dictated by the liquidus curve of the mixture’s phase diagram. Further, as the particle migrates, both interfaces are moving into higher temperatures.

Several more conclusions can be drawn from this simple discussion. First, as the particle migrates into higher temperatures, the corresponding equilibrium concentrations decrease. For a solid that is always free (e.g. having a vertical solidus curve) of solute, the total amount of solute in the particle must remain constant. Conservation of mass thus implies that the particle must necessarily increase in size during migration. This means that particle migration via TGZM is a purely transient phenomenon, even for mixtures whose liquidus curves are very nearly linear.

5.1.3 Prior Models

The first attempt at a theoretical treatment of TGZM was made by Tiller \[63\] in 1963. In Tiller’s analysis, pseudo-steady thermal fields are determined by the Laplace heat diffusion equation, and interface velocities are determined by kinetic models of melting and freezing and incorporating the surrounding thermal profile and a kinetic coefficient. Thus, for a known particle size, particle shape, thermal profile, and kinetic model, the instantaneous migration velocity of the particle can be solved for.

After Tiller, many other researchers have proposed quantitative models to describe and predict TGZM behavior in a similar fashion, deriving expressions for particle velocity as a function of kinetic coefficients and other parameters such as thermal gradient, solutal diffusivities, thermal diffusivities, liquidus slope, undercooling, densities, and geometric parameters of fixed particle shapes \[60–62,64\]. Some researchers derived particle velocities using only continuum transport concepts, without kinetic coefficients describing atomic attachment/detachment \[65–67\].

Table 5.1 gives some examples of typical derivations for particle velocities from various prior models of the time. Here, \(D\) is the diffusivity of the solute, \(G\) is the temperature gradient, \(C\) is concentration, \(K\) is thermal conductivity, \(k_0\) is the partition coefficient, \(m\) is the liquidus slope, \(\mu\) is a kinetic coefficient, \(\rho\) is density, \(l\) is particle length, \(T\) is local temperature, \(T'\) is the y-intercept of the tangent line on the liquidus curve at the composition/temperature of interest, \(R\) is the gas constant. Subscripts \(l\) and \(s\) denote liquid and solid respectively, and subscripts \(ih\) and \(ic\) denote at the hotter and colder interface respectively.
Table 5.1: Equations describing particle velocity from various prior models of TGZM.

A few shortcomings are common to these types of models. Before delving into them in, let us propose a few practical questions that we might ask when presented with a material system known to exhibit TGZM. 1.) What is the time-evolution behavior of the particle? Can we predict where the particle will be after a certain time? 2.) Can we easily predict migration behavior given basic material and process parameters? 3.) What happens to the size or shape of the particle during migration? We will see these prior are unable address these questions.

First, describing particle motion by a single velocity that is a function of various constant inputs overlooks the inherent time-dependent nature of TGZM. One could conceivably integrate these expressions for velocity in these prior models to give particle position over time. However, these expressions still include parameters like shape factors (assuming constant particle shape), particle length, local temperature, and local particle concentration as constants. Second, many of these models rely on known kinetic coefficients and mechanisms. These values can be difficult to come by for many material systems. To be fair, several authors did note faceting and other kinetics that played important roles in the velocity of interface movement of their studied material systems [61, 63, 69]. In these cases, there may be not way to escape the need for kinetic coefficients in describing particle migration. However, there is no indication that crystallographic orientation or kinetics play a role in TGZM of Te-rich second-phase particles in CdTe. In the case of NaCl brine and ice, these factors do not appear affect migration in any way [66]. Third, many of these authors also conducted experiments with their theory development. In all these experiments, researchers noted changes in particle shape throughout migration. Peculiarly, particle shapes were always assumed to
remain constant in these models describing particle velocity. To summarize, these prior models all fail to provide a straightforward prediction of how particles migrate in space and how they change in shape or size over time.

Central to the study of TGZM is understanding how variables change in both time and space. Thus, it may make sense to approach modeling this phenomena with a system of partial differential equations.

5.1.4 Our approach

In the following section, we present an analytical and numerical model to describe migration of a 1-dimensional liquid zone through a solid under temperature gradient. While this idealization is geometrically simple, it readily captures the relevant physics - mass and heat transfer with phase equilibria - that govern migration behavior. Both models describe how particle position and size evolve over time. We apply our numerical model to an industrially-relevant crystal, cadmium telluride (CdTe). CdTe and related materials like CdZnTe are promising for use as x-ray and gamma-ray detectors, but their production is often stymied by the presence of tellurium (Te)-rich second phase particles [70]. Thus, TGZM has been proposed as a refining process to migrate second-phase particles to one region of the crystal and simply removed. Use of realistic physical parameters for the case of Te-rich second-phase particles in CdTe yields reasonable agreement with experimental results. Later we will find that the numerical model also yields excellent agreement with the NaCl brine and ice system.

5.2 Theory

5.2.1 Analytical model

The following analytical description of TGZM is based largely off the unpublished work of Yeckel [71]. Consider a particle migrating with velocity \( v \) under TGZM. Taking the moving reference frame of the particle, the convection-diffusion equation for 1D mass transport inside the liquid particle is:

\[
\frac{\partial C}{\partial \tau} + v \frac{\partial C}{\partial x} = D \frac{\partial^2 C}{\partial x^2} \tag{5.1}
\]
Where $C$ is solute concentration represented, $\tau$ is the dimensional time variable, and $v$ is the dimensional migration velocity of the particle, and $x$ is the dimensional spatial variable. By nondimensionalizing this equation to a characteristic length $L$ and a characteristic time of solute dilution, $\tau_d$.

$$\frac{L^2}{D} \frac{1}{\tau_d} \frac{\partial C}{\partial t} + Pe \frac{\partial C}{\partial X} = \frac{\partial^2 C}{\partial X^2}$$  \hspace{1cm} (5.2)

Where $Pe \equiv vL/D$ and can be thought of as a dimensionless migration velocity. Since $L^2/D$ is the characteristic timescale of solute diffusion, which we denote as $\tau_D$, the factor preceding the transient term in (5.2) is simply the ratio of timescales of solute diffusion to solute dilution.

The Stefan condition is derived from a heat balance over a moving melting/freezing interface, stating that the difference in flux is equal to the latent heat generated or consumed. In its non-dimensionalised form, it is given by:

$$G_l = \kappa G_s + \frac{Sf}{Le} Pe$$  \hspace{1cm} (5.3)

Where $Sf \equiv \Delta H/c_p T_{mp}$ and $Le \equiv \alpha/D$. $Sf/Le$ for CdTe and water ice is on the order $10^{-3}$, so we will neglect it here, meaning the temperature field is approximated simply by $G_l = \kappa G_s$ where $G$ is a constant temperature gradient, and $\kappa_s$ is the ratio of solid to liquid thermal conductivities. In the particle, the temperature is given by:

$$T = T_e + \kappa_s G_s X$$  \hspace{1cm} (5.4)

where $T$ is the nondimensional temperature and $T_e$ is a nondimensional reference temperature.

Additional constraints include those from the phase diagram, with a simple, linear liquidus curve represented by

$$T = 1 - mC$$  \hspace{1cm} (5.5)

where $m$ is the slope of the curve relating equilibrium melting point temperature and solute concentration. While a particle migrating under a temperature gradient is clearly not at thermodynamic equilibrium, we assume growth and dissolution is slow enough
such that its equilibrium phase diagram provides a good approximation of temperatures and concentrations at the particle interfaces.

In this study, we consider only systems such as tellurium and CdTe where the solidus curve is very nearly vertical, and virtually no solute is able to incorporate into the solid. Thus, solute mass conservation is imposed, specifying that total solute mass in the particle should never change in time. The time-derivative of the total solute mass is thus set to zero and expanded with use of the product rule:

$$\frac{dM}{dt} = 0 = \frac{d(C_{avg}H)}{dt} = C_{avg} \frac{dH}{dt} + H \frac{dC_{avg}}{dt}$$  \hspace{0.5cm} (5.6)

where $M$ is total mass of solute, $H$ is particle size, and $C_{avg}$ is the average concentration of solute in the liquid particle. If we take the derivative of (5.4) with respect to time we can find that

$$\frac{dC}{dt} = -\frac{1}{m} \frac{dT}{dX} \frac{dX}{dt} = -\frac{1}{m} G_l Pe$$  \hspace{0.5cm} (5.7)

Here, we can tell that the characteristic time for particle’s dilution $\tau_D \propto m/G_l$. Thus, so long as $m/G_s$ is large, $\tau_D/\tau_d \ll 1$. This is intuitive, as a steep temperature gradient and/or shallow liquidus curve would imply that equilibrium concentration can change significantly on the same timescale as solute diffusivity. A shallow temperature gradient and/or a steep liquidus curve, however, would imply that the concentrations do not change appreciably on the timescale of solute diffusion, meaning the transient term in (5.2) can be safely neglected. This gives:

$$Pe \frac{d^2C}{dX^2} = \frac{d^2C}{dX^2}$$  \hspace{0.5cm} (5.8)

In short, (5.6) describes the overall dilution of the particle as it migrates over long periods of time, while Equation (5.8) describes the solute transport within the liquid particle which occurs at such a fast timescale, that the concentration profile within the particle appears pseudosteady. Equation (5.8) can be solved by recognizing the following two constraints describing the average concentration of solute in the particle and species
flux at the interfaces:

\[ C_{\text{avg}} = \frac{1}{H} \int_{0}^{H} C \, dX \]  \hspace{1cm} (5.9)

\[ \frac{dC}{dX} \bigg|_{x=0,H} = -\text{Pe}C \]  \hspace{1cm} (5.10)

(5.8) is a second-order ODE which has general solution:

\[ C(X) = c_1 + c_2 \exp(-\text{Pe}X) \]

Employing constraints (5.9) and (5.10), the solution of this system of equations is:

\[ C(X) = C_{\text{avg}} \frac{\text{Pe}H \exp(-\text{Pe}X)}{1 - \exp(-\text{Pe}H)} \]  \hspace{1cm} (5.11)

For small growth rates or small \( \text{Pe}H \), the solution can be significantly simplified. In the limit of \( \text{Pe}H \rightarrow 0 \), (5.11) becomes \( C(X) \approx C_{\text{avg}} \exp(-\text{Pe}X) \). A first-order Taylor-series approximation of this results in:

\[ C(X) \approx C_{\text{avg}} (1 - \text{Pe}X) \]  \hspace{1cm} (5.12)

In other words, for slow growth rates seen in TGZM, the solute concentration profile across the particle is very nearly linear.

(5.12) can be inserted into Equation (5.5) and evaluated at \( X = 0 \) and \( X = H \):

\[ T(X = 0) = 1 - mC_{\text{avg}} \]
\[ T(X = H) = 1 - mC_{\text{avg}} (1 - \text{Pe}H) \]  \hspace{1cm} (5.13)

Subtracting one from the other and noting that \( (T(H) - T(0))/H = G_t = \kappa G_s \) and \( M = C_{\text{avg}}H \), we can find that:

\[ \text{Pe} = \frac{\kappa G_s}{mM} \]  \hspace{1cm} (5.14)

Rearranging (5.6), we can get:

\[ \frac{dH}{dt} = -\frac{H}{C_{\text{avg}}} \frac{dC_{\text{avg}}}{dt} \]  \hspace{1cm} (5.15)
Substituting (5.14) into (5.7)’s expression for $\frac{dC}{dt}$, and substituting that into the above equation, we get the following equation:

$$\frac{dH}{dt} = H^2 \frac{1}{C_{avg}} \frac{G_s^2 \kappa}{m \cdot m \cdot M}$$  \hspace{1cm} (5.16)

Recalling again that $M = C_{avg}H$, we have:

$$\frac{dH}{dt} = H^3 \kappa \left( \frac{G_s}{m \cdot M} \right)^2$$  \hspace{1cm} (5.17)

Rearranging and integrating, an expression can be derived for particle length $H$ as a function of time:

$$H(t) = H_0 \left[ 1 - 2\kappa H_0 \left( \frac{G_s}{m \cdot M} \right)^2 t \right]^{-\frac{1}{2}}$$  \hspace{1cm} (5.18)

where $H_0$ is an initial particle size. Additionally, since $Pe$ is a nondimensional particle migration velocity, integrating up to current time $t$ yields an analytical expression for nondimensional particle position $\chi(t)$ as a function of time:

$$\chi(t) = \int_0^t Pe(s)ds = \chi_0 - \frac{mM}{G_s H_0} \left( \sqrt{1 - 2\kappa H_0 \left( \frac{G_s}{m \cdot M} \right)^2 t} - 1 \right)$$  \hspace{1cm} (5.19)

5.2.2 Numerical model

While the analytical model is useful for conceptual understanding and provides an exact solution for a limiting case of linear, shallow liquidus curve, the numerical model will be able to solve the transient concentration and temperature profiles for more general cases and will serve as a foundation for future simulations that incorporate higher dimensionality and additional physics. Thus, the governing equations presented below for this idealized 1-dimensional numerical model are presented in vector-tensor notation to maintain generality. Figure 5.2 shows the 1-dimensional domain of interest with labeled regions and boundaries.

The transient numerical model is posed as a system of transient heat and mass
diffusion, this time taking the lab reference frame:

$$\frac{\partial T}{\partial t} = \alpha_i \nabla^2 T$$ \hspace{1cm} (5.20)$$

$$\frac{\partial C}{\partial t} = D \nabla^2 C$$ \hspace{1cm} (5.21)$$

where $i$ denotes the material region (solid or liquid) of the domain. (5.20) is active in all regions (R1, R2, and R3); this model neglects solid diffusion and thus (5.21) is only active in region R2. This system is subject to the following boundary conditions on the solid-liquid interfaces B2 and B3:

$$\mathbf{n} \cdot [k_s \nabla T_s - k_l \nabla T_l] = \rho \Delta H \mathbf{n} \cdot \mathbf{v}_{interface}$$ \hspace{1cm} (5.22)$$

$$\mathbf{n} \cdot D \nabla C = (1 - K) C \mathbf{n} \cdot \mathbf{v}_{interface}$$ \hspace{1cm} (5.23)$$

$$T_s = T_l = T_{liquidus}(C)$$ \hspace{1cm} (5.24)$$

Equations (5.22) and (5.23) represent interfacial heat and mass balances, respectively. Equation (5.24) states that the solid-liquid interface is determined to be at the location where solid and liquid temperatures are jointly equal to the equilibrium melting point temperature given by the mixture’s solute concentration-dependent liquidus curve. At the two ends of the domain (B1 and B4) are two Dirichlet boundary conditions that establish the temperature gradient across the domain:
\[ T(x = 0) = T_{\text{cold}} \]
\[ T(x = L_d) = T_{\text{hot}} \]  
(5.25)

where \( L_d \) is the total length of the domain.

The overall thermal gradient \( G \) is defined as \((T_{\text{hot}} - T_{\text{cold}})/L_d\). The domain length is selected to be at least one thousand times greater than the initial particle size and at least one hundred times the total expected migration distance for a particular simulation. The migration takes place near the center of the domain, far away from the boundaries to ensure that boundary conditions do not affect particle migration in an unnatural manner. Because heat flux is conserved through the solid and the liquid particle in this 1D simulation, a large domain relative to the size of the particle is used to ensure that the thermal gradients do not change significantly in either solid or liquid phases during migration.

An appropriate initial condition is constructed by finding the steady-state temperature field of the domain with a linear concentration profile inside the particle satisfying the equilibrium temperatures at the interfaces.

### 5.3 Solving model equations via Galerkin Finite Element Method

#### 5.3.1 Method overview

Equations (5.20) through (5.25) are nondimensionalized and solved with the Galerkin finite element method using the software Cats2D [72], which has been used successfully in a number of previous simulations of crystal growth processes [6, 73, 75].

Compared to the governing equations discussed in the previous chapter, the equations above represent a significant increase in complexity. Here, we are simultaneously solving for multiple field equations (heat and solutal concentration), invoking moving boundaries on a deforming grid, and applying boundary conditions on those moving boundaries. Similarly, the numerical methods utilized to solve these equations have increased in complexity. Compared to the Finite Difference Method discussed in Chapter 4, which is relatively intuitive and straightforward in its approach and derivation, the
Galerkin Finite Element Method used to solve these equations takes a completely different approach and requires a great deal more mathematical foundation to implement. Thus, only a brief overview of the method is discussed here; many texts have been written on this method alone, and the interested reader is referred to them for a more detailed discussion [72,76–78].

Like FDM, FEM involves discretizing the domain to express an approximation of the solution. While in FDM, the solution is in the form of nodal values, in FEM, the solution is formed as Lagrangian interpolations (a product of nodal values and basis functions \( \phi_k \), also sometimes known as shape functions or interpolation functions) over discretized regions known as finite elements. Thus, the solutions of field variables is described as:

\[
T \approx \hat{T} = \sum_{k=1}^{N_T} T^k(t) \phi_k(\xi, \eta) \\
C \approx \hat{C} = \sum_{k=1}^{N_C} C^k(t) \phi_k(\xi, \eta)
\]

(5.26)

Where \( \hat{T} \) and \( \hat{C} \) are the approximate solutions of the field variables, while \( T^k \) and \( C^k \) are the unknown coefficients or the nodal values at node \( k \). \( N \) is the number of basis functions that are defined on the element for the field variable. In our application of FDM in chapter 4, we created a simple mesh using uniformly spaced nodes so we could easily address the spacing with a simple \( \Delta x \). This means FDM is restricted mostly to quadrilateral-based domains. In TGZM, the interface location changes in time and will likely deform if we are considering modeling in 2D or 3D. Defining our basis functions \( \psi_k \) on a parent element, bi-unit square (which lies by definition between -1 and +1) which uses the natural coordinates \( \xi \) and \( \eta \), ensures that we can utilize the same basis functions over any quadrilateral element.

We can convert between the natural coordinates \( (\xi, \eta) \) to the physical coordinates \( (x, y) \) (or \( (r, z) \) for axisymmetric cylindrical domain) using the transformation:

\[
(x, y) = \sum_{k=1}^{N} \left( x^k, y^k \right) \phi_k(\xi, \eta)
\]

(5.27)

As mentioned earlier, the mesh is expected to change at each timestep in TGZM.
Thus the nodes and their spacing must be determined in a systematic way that their physical positions can change and deform. Additionally, mesh resolution can be finer where there is a need for greater accuracy, for example resolve boundary layers near interfaces. Cats2D does this by solving elliptic equations for nodal positions within mesh regions while subjecting the boundaries to boundary conditions (e.g. geometric constraints or conditions that specify location of a boundary like equation (5.24)) in the fashion of [79]:

\[
\nabla \cdot (D_\xi (\xi, \eta) \nabla \xi) = 0 \quad (5.28) \\
\nabla \cdot (D_\eta (\xi, \eta) \nabla \eta) = 0 \quad (5.29)
\]

When all the terms in equations (5.20) and (5.21) are moved to the RHS, the LHS is naturally zero. That is assuming the field variables \( T \) and \( C \) represent the true solutions of the system of equations.

\[
\frac{\partial T}{\partial t} - \alpha_i \nabla^2 T = 0 \quad (5.30) \\
\frac{\partial C}{\partial t} - D \nabla^2 C = 0 \quad (5.31)
\]

If we replace the true solutions with the approximate solutions \( \hat{T} \) and \( \hat{C} \), we arrive
at the residual equations:

\[
\begin{align*}
R_T &= \frac{\partial \hat{T}}{\partial t} - \alpha_i \nabla^2 \hat{T} \\
R_C &= \frac{\partial \hat{C}}{\partial t} - D \nabla^2 \hat{C} \\
R_\xi &= \nabla \cdot (D_\xi (\xi, \eta) \nabla \xi) \\
R_\eta &= \nabla \cdot (D_\eta (\xi, \eta) \nabla \eta)
\end{align*}
\]  

(5.32)

Our approximate solutions may conceivably not satisfy this constraint everywhere. But the idea behind finite element method is that the residual equations we get from our approximate solutions should be minimized. This is done by taking the inner product of a residual with a weighting function \( w \) over the entire domain and letting that equal zero.

\[
\int_\Omega w R d\Omega = 0
\]  

(5.33)

In the Galerkin formulation of FEM, the choice of weighting function \( w \) is the same as the basis function used to represent the approximate solution \( \phi \):

\[
\begin{align*}
\int_\Omega \phi^{k*}_T R_T d\Omega &= 0 \\
\int_\Omega \phi^{k*}_C R_C d\Omega &= 0 \\
\int_\Omega \phi^{k*}_\xi R_\xi d\Omega &= 0 \\
\int_\Omega \phi^{k*}_\eta R_\eta d\Omega &= 0
\end{align*}
\]  

(5.34)

The \( k* \) superscript indicates a global index over all elements as opposed to a local index on a particular element. Using the residual equations directly presents a problem. The \( \nabla^2 \) operator in the diffusion equations imply that the approximate solutions must be twice-differentiable; this form is known as the strong form. This is too stringent a requirement on the approximate solution, as it is difficult to construct the very smooth set of basis functions in more than 1D ( [77] presents a much more rigorous discussion of the necessities and sacrifices of transforming the strong form). Instead, we will use
the chain rule to first convert second-order derivative terms in to the following form:

\[ \phi \nabla^2 b = \nabla \phi \nabla b - \nabla \phi \cdot \nabla b \]  \hspace{1cm} (5.35)

Then, the first term on the RHS (in the integral) can be transformed using the divergence theorem:

\[ \int_{\Omega} \nabla \cdot \phi \nabla b d\Omega = \int_{\Gamma} \phi n \cdot \nabla b d\Gamma \]  \hspace{1cm} (5.36)

Applying these to the strong form residuals yields the weak forms:

\[ \int_{\Omega} \phi_T^k \frac{\partial \hat{T}}{\partial t} d\Omega + \int_{\Omega} \alpha_i \nabla \phi_T^k \cdot \nabla \hat{T} d\Omega + \int_{\Gamma} \alpha_i \phi_T^k n \cdot \nabla \hat{T} d\Gamma = 0 \]

\[ \int_{\Omega} \phi_C^k \frac{\partial \hat{C}}{\partial t} d\Omega + \int_{\Omega} D \nabla \phi_C^k \cdot \nabla \hat{C} d\Omega + \int_{\Gamma} D \phi_C^k n \cdot \nabla \hat{C} d\Gamma = 0 \]  \hspace{1cm} (5.37)

\[ \int_{\Omega} D_{\xi} \nabla \phi^k \cdot \nabla \xi d\Omega - \int_{\Gamma} \phi^k D_{\xi} n \cdot \nabla \xi d\Gamma = 0 \]

\[ \int_{\Omega} D_{\eta} \nabla \phi^k \cdot \nabla \eta d\Omega - \int_{\Gamma} \phi^k D_{\eta} n \cdot \nabla \eta d\Gamma = 0 \]

5.3.2 Arbitrary Lagrangian-Eulerian Formulation

When modeling physical systems in time and space, the choice of reference frames can play an important role in ease of computation. For example, when examining elastic deformation of a solid, it makes sense to use a Lagrangian reference frame, where mesh nodes move with the material. For a system with fixed boundaries and flow, it often makes sense to use an Eulerian reference frame, where material points flow past the mesh. For problems where there is a flow of material and a need to deform the mesh, we use an Arbitrary Lagrangian-Eulerian (ALE) formulation, where the mesh nodes move as a result of mesh deformation, but independently of material points (Figure 5.4). Thus when elements move in Eulerian frame, we must account for material flowing in and out of the element when we consider them in the parent element with the following
relationship:

\[
\frac{\partial \hat{T}}{\partial t} = \dot{T} - \hat{x} \cdot \nabla \hat{T}
\]

\[
\frac{\partial \hat{C}}{\partial t} = \dot{C} - \hat{x} \cdot \nabla \hat{C}
\]

(5.38)

Where the overdot indicates the time derivative from the parent frame and \( \hat{x} \) is the local mesh velocity. These equations are substituted into (5.37).

Figure 5.4: Illustration of Arbitrary Lagrangian-Eulerian formulation. Figure reproduced from [80].
Boundary Conditions

One of the strengths of FEM is that boundary conditions are implemented in a straightforward manner. Dirichlet conditions are implemented by completely replacing the residual equation pertaining to a node with an equation directly specifying that nodal value. Conditions that specify a flux (for example a heat flux like $k \mathbf{n} \cdot \nabla \hat{T}$ or species flux like $D \mathbf{n} \cdot \nabla \hat{C}$) can be implemented in the term involving the boundary $\Gamma$ in the weak forms (5.37). When the flux is zero, those boundary terms, too, go to zero.

5.3.3 Time-stepping and solution methods

Notice that in Section 5.3.1 we had only discretized the spatial dimensions. While it is possible to use the same finite element approach for the time dimension, we treated the transient problem of Section A.3 and continue in this section with a method of lines approach. By only discretizing the spatial dimensions, we have essentially created a system of ODEs, the unknowns being our time-dependent coefficients or nodal-values. We then use numerical methods for ODEs to discretize and solve the time-evolution of the system.

The weak form residual equations (5.37) can be expressed in a form of:

$$ [A] \dot{z} + [B] z + f = 0 $$

(5.39)

Where $z$ is the vector of unknowns and $\dot{z}$ is the vector of their time-derivatives. Now, we can discretize $\dot{z}$ however we like, for example with the finite difference approach while making appropriate substitutions:

$$ \dot{z} = \begin{cases} 
\frac{z_{n+1} - z_n}{\Delta t} & \text{(forward difference)} \\
\frac{z_n - z_{n-1}}{\Delta t} & \text{(backward difference)} \\
\frac{z_{n+1} - z_{n-1}}{2\Delta t} & \text{(centered difference)} 
\end{cases} $$

(5.40)

Here $z_n$ refers to $z(t_n)$. When the first option is used and unknown coefficients are evaluated at $z = \frac{z_n + z_{n+1}}{2}$ in the residual equations, the Crank-Nicolson (sometimes called trapezoidal rule) scheme is again implemented. Recall that Crank-Nicolson is an implicit method, having the advantage of unconditional stability. Here, a system of
nonlinear equations is produced and is solved with the Newton-Raphson method (to be discussed shortly). A good initial guess can be provided by an explicit method, though we can do better than the simple forward Euler. Given a differential equation:

$$\dot{z} = f(t, z(t))$$  \hspace{1cm} (5.41)

Using the First Fundamental Theorem of Calculus:

$$z_{n+1} - z_n = \int_{t_n}^{t_{n+1}} f(\tau, z(\tau)) d\tau$$  \hspace{1cm} (5.42)

We can replace $f$ with an approximating Lagrangian interpolating polynomial $p(\tau)$ of order $k$ which will give $k + 1$ order accuracy and require knowing the solution back to $n - k$ timesteps. If $k = 0$, we recover the first-order Euler method:

$$z_{n+1} - z_n = \Delta t f(t_n, z(t_n))$$  \hspace{1cm} (5.43)

This general approach is known as the **Adams-Bashforth method**. Using $k \geq 1$ is referred to as a **multistep method**, since it requires the solution at previous timepoints. Cats2D uses 3rd order explicit Adams-Bashforth method to predict a solution at a $t_{n+1}$ timepoint, then uses that as an initial guess for implicit 2nd order trapezoidal rule (Crank-Nicolson). The combination of using both explicit and implicit methods like this is known as a **predictor-corrector** method.

Newton-Raphson method used as the nonlinear solver:

$$z^{i+1} = z^i + f \Delta z$$  \hspace{1cm} (5.44)

Where $z^{i+1}$ is the updated solution at the $i + 1$ step, $f$ is a dampening factor, and $\Delta x$ is the solution update vector computed by solving:

$$[J] \Delta z = -r$$  \hspace{1cm} (5.45)

Where $r$ is the vector of residuals and $[J] \equiv r_x$ is its Jacobian. This system is solved via Gaussian-Elimination, and iterations continue until the L2 norms of the residual and
solution update vectors are less than a tolerance $\epsilon < 10^{-4}$. The L2 norm of a vector $x$ is given by:

$$\|x\|_{L^2} \equiv \sqrt{\sum_{k=1}^{N} |x_k|^2}$$  \hspace{1cm} (5.46)

This concludes the discussion of the numerical methods used to solve the TGZM problem using Galerkin Finite Element Method.

5.4 Results

5.4.1 Initial results with CdTe system

Annealing in temperature gradients is a process used for producing in industrially-relevant semiconductor crystals. CdTe and cadmium zinc telluride (CZT) are promising wide bandgap semiconductor x-ray and gamma-ray detector materials that are notorious for being extremely difficult to grow large, single crystals. One type of defect that has plagued researchers for years is the presence of Te-rich second-phase particles found in the crystals, typically on the order of 10-100 $\mu$m, which arise from inclusions (as a result of an unstable growth interface), precipitates (as a result of lower Te solubility in the solid as the crystal cools), or a combination of both [70,81]. To address these issues, TGZM has been proposed as a plausible refining technique to remove these SP particles after growth [52,53]. By annealing in a thermal gradient, second-phase particles can be induced to migrate to one region of the crystal, where they can be easily removed (illustrated in Figure 5.5).

Figure 5.5: Illustration of a concept to use TGZM to remove Te-rich second-phase particles in CdTe

By solving the system of partial differential equations in section 5.2.2 we obtain the following as a part of the time-dependent solution: a thermal profile across the entire domain, a concentration profile across the particle, and the location of the two solid-liquid interfaces. Figure 5.6 shows these three features plotted for various time-steps.
Figure 5.6: Results of the 1D numerical model for TGZM using CdTe properties.

of a typical solution to a problem. At each step in time, the thermal and concentration profiles in the solution are nearly linear. There is a clear negative concentration gradient, driving diffusion across the particle towards the hotter end, and the average concentration drops throughout migration as predicted in Section 5.1.2. Additionally, the particle size increases during migration, though this is difficult to perceive over this interval in time.

Using Yang 2020 as an experimental reference (Figure 5.7), the numerical model is solved using physical properties for CdTe with the same experimental thermal environment: 30 minutes under 10 °C/cm temperature gradient, and initial particle length and temperature of 35 µm and 700 °C., respectively. Phase equilibria data for CdTe
is adapted from Greenberg 1996 [82] with a polynomial fit of the form (temperature in degrees Kelvin, concentration in mole fraction):

$$T_{\text{liquidus}}(C) = p_1 C^3 + p_2 C^2 + p_3 C + p_4$$ (5.47)

Physical properties used are given in Table 5.2

In the experiment, these particles achieve an average migration velocity (total distance migrated divided by total elapsed time) of 38.1 $\mu$m/h. The numerical model produced an average migration velocity of 32.9 $\mu$m/h, showing agreement within 20%. Because no real-time or in-situ data exists of the annealing experiment, a number of experimental uncertainties are unaccounted for in this simple model. For example, though the documented annealing time is 30 minutes, it's unclear what other processes may have occurred between when the IR images were taken; varying heating and cooling rates and times would have allowed partial melting outside of the designated 30 minute annealing time.

There are several other important differences to note between the experiment in Yang 2010 and our simulation. First, the annealing experiment was conducted on CZT, whereas this simulation was conducted with physical properties of CdTe for simplicity of neglecting zinc segregation and use of a simpler temperature-composition phase diagram.
Figure 5.8: Phase diagram for CdTe. The Te-rich liquidus curve highlighted in green was fit with a cubic polynomial (fit parameters found in Table 5.2) Adapted from [82].
<table>
<thead>
<tr>
<th>Parameter</th>
<th>CdTe System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solute concentration tracked</td>
<td>Excess Te</td>
</tr>
<tr>
<td>Liquid thermal conductivity [W/(m·K)]</td>
<td>2.3630</td>
</tr>
<tr>
<td>Solid thermal conductivity [W/(m·K)]</td>
<td>1.5486</td>
</tr>
<tr>
<td>Liquid heat capacity [J/(kg·K)]</td>
<td>187 [83]</td>
</tr>
<tr>
<td>Solid heat capacity [J/(kg·K)]</td>
<td>159.5 [84]</td>
</tr>
<tr>
<td>Solute diffusivity [m²/s]</td>
<td>5.00e-9</td>
</tr>
<tr>
<td>Heat of fusion [J/kg]</td>
<td>2.092e5 [84]</td>
</tr>
<tr>
<td>Initial particle size [µm]</td>
<td>35</td>
</tr>
<tr>
<td>Average temperature gradient [°C/m]</td>
<td>10</td>
</tr>
<tr>
<td>Starting average temperature [°C]</td>
<td>700</td>
</tr>
<tr>
<td>Liquidus curve polynomial fit, p₁</td>
<td>-6221.0</td>
</tr>
<tr>
<td>Liquidus curve polynomial fit, p₂</td>
<td>3578.5</td>
</tr>
<tr>
<td>Liquidus curve polynomial fit, p₃</td>
<td>-1530.75</td>
</tr>
<tr>
<td>Liquidus curve polynomial fit, p₄</td>
<td>1369.375</td>
</tr>
</tbody>
</table>

Table 5.2: Physical parameters used for numerical models

Also, in addition to annealing in temperature gradient, the CZT crystal was subject to a cadmium vapor overpressure. Yang 2010 and previous annealing studies on CZT suggest that pressurized Cd vapor may encourage solid diffusion of Cd and recombination with excess Te to form stoichiometric CdTe [52,53], though solid diffusion was neglected in our simulation. Of course, the most obvious discrepancy is that our simulation only considers a single dimension. In 1D, all heat must flow through the particle in order to reach the other side of the domain, whereas in reality (3D), heat can flow around particles. In the case of a TGZM system in which the liquid phase thermal conductivity is greater than that of the solid’s, we expect the 1D simulation to underestimate the migration velocity compared to experiment, as heat would preferentially flow through the more conductive particle, even from the sides. Conversely, for TGZM systems for which the solid is more conductive, heat would preferentially be conducted through the crystal, around the particle; thus we’d expect a 1D simulation to overestimate the migration velocity compared to experiment.
Figure 5.9: Plots comparing 1D analytical model with 1D numerical model for a particle migrating under TGZM in 10°C/cm temperature gradient. Left: Particle position vs time. Center: Particle size vs time. Right: Starting and end points of the average particle temperature plotted on CdTe liquidus curve. The dashed green and red lines display the tangent lines (slope) on the liquidus curve at the start and end of the simulation. For short migration times/distances under mild temperature gradients, the slope of the liquidus curve changes negligibly during the simulation.

5.5 Model Verification

Both analytical and numerical methods show the transient nature of particle migration: the particle’s position, defined by the midpoint between the two interfaces, changes non-linearly with time (indicating time-dependent velocity), and the size increases over time. The latter feature was explained in the introduction, and the former is a direct result when considering a 1-dimensional geometry. When analytical and numerical models are compared, they show excellent agreement, as seen in Figure 5.9. For this comparison, the numerical model’s liquidus curve is idealized as a straight line.

Recall that in the development of the analytical model, $m/G_s$ is assumed to be large enough such that $\tau_D/\tau_d \ll 1$. To test the validity of this assumption, the analytical and numerical models were again compared with CdTe physical properties, but with a temperature gradient of 500 °C/cm, far beyond what is experimentally practical. Still, in these limits, Figure 5.10a shows there is excellent agreement between the analytical and numerical models, indicating the soundness of previous assumptions.

The major shortcoming of the analytical model is the idealization of the liquidus curve as a straight line. When the numerical model is allowed to incorporate the full liquidus curve of CdTe, the results of the analytical model begin to diverge from the
Figure 5.10: Comparing 1D analytical model with 1D numerical model for particle migrating under TGZM in 500°C/cm temperature gradient with a.) an idealized linear liquidus curve and b.) the realistic CdTe liquidus curve. The bottom right plot shows that the particle’s average temperature on the liquidus curve and liquidus slope has changed drastically during migration, as indicated by the different start/end points and tangent lines.

numerical model because as the SP particle migrates into higher temperatures in the domain, the interfaces are operating on parts of the phase diagram where the liquidus curve’s slope changes significantly (Figure 5.10b). Thus, the analytical model’s usefulness in predicting experimental migration behavior may be limited to cases for short migration times and distances or small temperature gradients – cases where the interfaces’ locations on the phase diagram change negligibly during migration.

5.6 Comparing with experimental data and previous theoretical models for the NaCl brine and ice system

Hoekstra et al. 1965 [66] (hereafter referred to as HOW) contains the most complete experimental data set concerning brine pocket migration, or TGZM of a liquid brine
particle in solid ice, so we have chosen it as a reference to compare our theory against. It and later Seidensticker 1966 [67] (hereafter referred to as RGS) both included theoretical descriptions of brine pocket migration, which showed excellent qualitative agreement with experimental data but had obvious quantitative discrepancies.

Figure 5.11 shows the results of our model overlayed onto experimental and theoretical results reproduced from HOW and RGS. Recall from Section 5.1.3 that both HOW and RGS treated brine pocket migration as steady-state processes. This view is reflected in the original portrayal of their data, where there is a unique steady-state velocity for a particle at a specific temperature. Another result of this view is that migration velocities are invariant to particle size. We are informed by our model that migration is actually time-dependent, and that two particles at the same location, with the same local temperature, can have different migration velocities depending on their size. Thus, in order to compare our model to HOW’s and RGS’s data, we ran several independent, transient simulations.

Each data point in our results represents such an independent transient simulation. Each simulation begins with an initial condition such that the particle is 35 µm in size, the maximum brine particle diameter observed in HOW’s experiments. The simulation domain included ice regions of more than fifty times the initial brine particle length on each side, providing ample room for migration and minimizing any unrealistic interactions between the particle and boundary conditions on either side. The temperature boundary conditions (5.25) are set such that the average temperature gradient over the entire domain is 1°C, as was in HOW’s experiments, and that the particle’s initial temperatures were -13, -12, -11, -10, -9, -8, and -7°C. Particles migrated for approximately three days in each simulation, allowing them to displace approximately one to two initial particle lengths. The velocities reported in Figure 5.11 represent the average velocity of the particle’s migration, or the total displacement over total elapsed time. The temperatures reported in Figure 5.11 represent the time-average temperature of the particle’s migration, or the mean of the particle’s temperatures at over all time-steps.

Most physical properties of ice and brine do not vary significantly over the small range of temperatures surveyed in these simulations, so only constant values are used. However, RGS noted that solutal diffusivity of NaCl can be significantly affected by temperature; thus, each simulation used a unique value for this parameter determined
Figure 5.11: Comparison of our model, HOW model and RGS model against HOW experimental data for NaCl brine in ice with 1 °C/cm temperature gradient. Data reproduced from [66,67].

Figure 5.11 shows clear quantitative agreement between our model and HOW’s experimental data. However, several factors exist that can affect migration behavior, whose effects are unknown. First, our model is 1D, while real experiments are obviously 3D. Higher dimensions allow curvature and perhaps faceting to affect migration behavior. These factors were not discussed by HOW but were considered by later researchers [60,61,68,69]. Equations (5.20) through (5.25) are generalizable to higher dimensions, which would allow for the model to incorporate additional physics accounting for surface energy and curvature in future simulations.

Additionally, many experimental details about HOW’s experiments were not discussed, particularly concerning how particle migration was measured. For example, how many particles were measured? How long were particles allowed to migrate? What was the time interval between measurements? What were the sizes of the particles that were being tracked? How did the particles change in shape over time? According to our model, all of these factors can affect migration behavior and/or final reporting of data.
5.7 Outlook

5.7.1 2D axisymmetric model

Now that the 1D TGZM system is fully understood, the next step in furthering model complexity is increasing dimensionality. Not only will this require greater computational demand of the model by increasing the sheer number of unknowns to solve for, a 2D axisymmetric (pseudo-3D) model allows implementation of physics that involve directionality and morphology that is impossible to account for in a 1D model.

A simplified representation of domains and boundaries of 2D TGZM is pictured in Figure 5.12, assuming a spherical initial particle shape. The basic heat equation (5.20) is active in R1 and R2 while the mass equation (5.21) is active only in R1. Instead of distinct growth and dissolution interfaces, the 2D axisymmetric model features a single, continuous solid-liquid interface with growth occurring at one end and dissolution at the other. Equations (5.22) and (5.23), which represent heat and mass balance across the interface is active along B1. B2 represents the axis of symmetry, and exhibit the symmetry (no-flux) boundary conditions. B3 and B5 represent the hot and cold ends, respectively, and are defined by the same temperature Dirichlet conditions as (5.25).

While it is possible to solve the Navier-Stokes equations in the 2D particle for flow fields, it is almost certain that convective effects play no significant role in TGZM given the small particle size [65]. While the critical Rayleigh number for Rayleigh-Bénard convection between two parallel plates is 1700, expected Rayleigh numbers in TGZM systems are on the order of $10^{-5}$. Thus, neglecting these equations drastically reduces the computational demand of this problem.

Initial 2D results using the same CdTe physical properties as the 1D model showing temperature and concentration contours as well as mesh are given in Figure 5.13. Two mesh-related features are immediately evident. First, internal nodes of the mesh collide/pinch against each other, which is the immediate cause of the simulation failure. Second, "scalloping" of the top and melting areas of the interface is shown enlarged in $t_2$. This may indicate an unstable interface due to constitutional supercooling from the solute inside the particle [85]. In the 1-dimensional problem, if the liquidus curve is concave down, and the temperature profile is linear through the particle, the entire particle is actually undercooled (Figure 5.14). In 1D, there is no interfacial surface, and
Figure 5.12: Domain regions and boundaries for a 2D axisymmetric model of TGZM. R1 represents the liquid particle while R2 represents the surrounding solid crystal. B1 is the solid-liquid interface. B2 is the axis of symmetry. B4 is the maximum radius of the sample domain. B5 is the cold end, and B3 is the hot end.

Thus no possibility of perturbations. In the 2D axisymmetric model, the undercooled particle leads to an interface that is easily destabilized by perturbations. This may require additional physics to address, discussed in the next section. Unfortunately, due to a change in computational resources in the group, we were unable to investigate this problem further after this simulation.

Interface curvature and kinetics

The current TGZM model utilizes phase equilibria data to determine concentration-dependent melting point and the interface(s). However, other factors such as surface energy can affect melting points. The Gibbs-Thomson effect describes the elevation in melting point for liquid particles with high curvature\(^1\) \cite{86}. The basic form of the Gibbs-Thomson equation is given below:

\[
T_{\text{melt}} = T_{eq} \left(1 + \frac{\sigma_{sl} \kappa}{\rho_s \Delta H_f}\right)
\]

(5.48)

where \(T_{eq}\) is the bulk equilibrium melting temperature, \(\sigma_{sl}\) is surface energy, and \(\kappa\) is the interface curvature. Sometimes this equation is simplified as \(T_{\text{melt}} = T_{eq}(1 + \gamma)\) where \(\gamma\) is known as the Gibbs-Thomson coefficient. For bulk crystal growth processes, usually the Gibbs-Thomson effect is neglected, as characteristic length scales may be tens of

\(^1\)The Gibbs-Thomson effect is usually described in relation to a solid particle. In this case, the effect would cause melting point depression, rather than elevation, for a solid particle of high curvature.
Figure 5.13: Initial 2D axisymmetric results for TGZM of Te SP in CdTe. Concentration, temperature, and mesh (top to bottom) of three timepoints $t_0 < t_1 < t_2$ are pictured. A vertical line marks the center of the particle at $t_0$ in each timepoint. The simulation fails at $t_2 \approx 13.6$ minutes in real time.

Figure 5.14: In the 1-dimensional problem, if the liquidus curve is concave down, and the temperature profile is linear through the particle, the entire particle is undercooled.
centimeters. However, for SP migrating under TGZM, surface energy may contribute significantly to interface morphology and may be a necessary component of the model to stabilize the particle interface during migration.

For a preliminary estimate of the stabilizing effect of Gibbs-Thomson, we can utilize Mullins and Sekerka’s seminal linear stability analysis on supercooled interfaces in unfavorable temperature gradients [85]. In this analysis, perturbation is applied to a planar interface. Perturbations below a critical wavelength will decay, and the interface will stabilize. Perturbations above the critical wavelength will amplify, and the interface will form unstable cellular structures. A stability parameter $a_0$ is derived, shown in (5.49), which is negative if the interface is stable and positive if unstable. Here $G$ is the nondimensional temperature gradient, $q$ is the ratio of solid to liquid thermal conductivities, $M$ is the nondimensional liquidus slope, $k$ is the partition coefficient, and $\omega$ is the wavenumber of the perturbation. $\gamma = \sigma T_m c_p v / \Delta H^2 D$ where $\sigma$ is surface energy, $T_m$ is the pure material melting point temperature, $c_p$ is heat capacity, $\Delta H$ is the heat of fusion, $v$ is the velocity of the interface, and $D$ is the solutal diffusivity. Figure 5.15 shows the stability parameter plotted against perturbation wavenumber when using physical and process parameters from the one-dimensional numerical model for CdTe, and surface energy data for CdTe [87], with and without the Gibbs-Thomson effect considered. The Mullins-Sekerka analysis predicts a critical perturbation wavelength of about half a millimeter, which is about an order of magnitude larger than typical particle lengths. This indicates that all perturbations to the migrating particle’s interface are likely to decay, and the interface should be stabilized for models that incorporate the Gibbs-Thomson effect.

$$\left(1 - \frac{2G}{M (1 + q) (1 + k)} - \frac{\gamma \omega^2}{M (k - 1)} \right) \left( k - 1/2 + \sqrt{1/4 + \omega^2 + a_0} \right) - k - a_0 = 0$$

(5.49)

Several previous studies show that interface kinetics may play an important role in determining TGZM migration velocity for certain materials [57, 58, 63, 88]. Additionally, it is known that crystal melt and dissolution kinetics can be asymmetrical, with melting being a rate-limiting step [88]. In the case of CdTe, the melting and crystallization kinetics at the solid-liquid interface are poorly understood. Melting of CdTe from purely ordered crystal to purely disordered liquid clearly does not occur at a well-defined melting
Using surface energy data for CdTe, the critical perturbation wavelength for an interface with velocity and local concentration gradients similar to those calculated from the 1D numerical model is about half a millimeter, a length scale an order of magnitude larger than the particle length. Thus, all perturbations to the migrating particle’s interface are likely to decay, and the interface should be stabilized for models that incorporate the Gibbs-Thomson effect.
Figure 5.16: Before and after IR micrographs of TGZM annealing experiment of CdTe under Cd vapor overpressure by Yang 2012 [53] (reproduced). Local particle temperature is approximately 670°C, with 30°C/cm temperature gradient. Initially round Te particles are shown to elongate after annealing.

point, and there is evidence from both experiment and modeling, *ab initio* and molecular dynamics, that there is significant short-range order present in liquid in the vicinity of the interface [89–97]. Thus, the following equation incorporating a kinetic coefficient may be more suitable to describe interface motion

$$
\mathbf{n} \cdot \mathbf{v}_{\text{interface}} = \beta_k (T_{eq} - T)^a = m\beta_k (C_{eq} - C)^a
$$

(5.50)

where $\beta_k$ is the atomic kinetic coefficient which may be orientation-dependent, and $a$ is an integer which equals to 1 for uniform interface motion or 2 for layer formation by screw dislocation [63].

Combining equations (5.48) and (5.50) and nondimensionalizing with characteristic length $L_{ch}$ and temperature $T_{ch}$, we arrive at a new equation for locating the solid-liquid interface, replacing equation (5.24) from the current model.

$$
\text{Pr} \mathbf{n} \cdot \mathbf{v}_{\text{interface}} = \frac{\beta_k L_{ch} T_{ch}^a}{k_l} \left[ \frac{T_{eq}}{T_{ch}} \left( 1 + \frac{\sigma_s \kappa}{\rho_s \Delta H_f} \right) - T \right]^a
$$

(5.51)

While several theoretical treatments of TGZM took a kinetic approach in describing
interface velocities, such studies did not construct their TGZM models as well-posed mathematical problems or allow for interface shape to deform during migration. A future study could be the first model of TGZM to address both of these while accounting for interfacial kinetics. While kinetic factors may not be an important role in Te SP particles in CdTe and NaCl brine in ice, early researchers encountered material systems that showed faceting and kinetics playing a significant role in particle shape and migration.

5.8 Conclusion

In this chapter, an analytical and numerical model of particle migration via TGZM is formulated. 1-dimensional models show excellent agreement with each other and reasonable agreement with experimental data. In particular, the TGZM theory and model outlined in this chapter agree very well with experimental data for the NaCl brine and water ice material system, though our analysis reveals insights about the system unknown to prior researchers, leaving a number of experimental uncertainties that we are unable to account for.

This model serves as a foundation for understanding the basic physics underlying TGZM and is a starting point for developing more complex models of TGZM. A 2-dimensional axisymmetric model solving the same governing equations has been started, but issues with mesh movement and perhaps instabilities of the interface likely require Gibbs-Thomson as a stabilizing condition. A more robust mechanism for mesh generation and deformation will also likely be required. The future researcher is recommended to investigate the open-source multi-physics software package, Goma, developed at Sandia National Laboratory, as a possible tool to solve a high-fidelity axisymmetric model.

Further, closer attention to interfacial phenomena in models may reveal mechanisms for particle splitting or collision. Subsequent models may include other effects such as solid diffusion and influence of defects on migration behavior.
References


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[71] Andrew Yeckel. 1d analysis of THM and particle migration, October 2013.


Appendix A

Solving Eu migration model equations via Finite Difference Method

A.1 Method overview

Finite difference method (FDM) is a numerical method that approximates a function’s derivatives by using the value of the function at discrete points. It’s derivation and implementation is relatively straightforward and fitting for the simple approach of this problem.

Recall the definition of a derivative:

\[ f'(x) = \lim_{\Delta x \to 0} \frac{f(x + \Delta x) - f(x)}{\Delta x} \]  \hspace{1cm} (A.1)

Recall also the Taylor series expansions for a function at \( \pm \Delta x \):

\[ f(x + \Delta x) = f(x) + \Delta x f'(x) + \frac{\Delta x^2}{2!} f''(x) + \frac{\Delta x^3}{3!} f^{(3)}(x) + \ldots \]  \hspace{1cm} (A.2)

\[ f(x - \Delta x) = f(x) - \Delta x f'(x) + \frac{\Delta x^2}{2!} f''(x) - \frac{\Delta x^3}{3!} f^{(3)}(x) + \ldots \]  \hspace{1cm} (A.3)
Equation [A.2] can be rearranged to yield a forward difference approximation:

\[
\frac{f(x + \Delta x) - f(x)}{\Delta x} = f'(x) + O(\Delta x) \tag{A.4}
\]

Similarly, equation [A.3] can be rearranged to yield a backwards difference approximation:

\[
\frac{f(x) - f(x - \Delta x)}{\Delta x} = f'(x) + O(\Delta x) \tag{A.5}
\]

A combination of equations [A.4] and [A.5] yields a centered difference approximation:

\[
\frac{f(x + \Delta x) - f(x - \Delta x)}{2\Delta x} = f'(x) + O(\Delta x^2) \tag{A.6}
\]

Adding (A.2) and (A.3) and rearranging yields a centered difference approximation for a second derivative:

\[
\frac{f(x + \Delta x) - 2f(x) + f(x - \Delta x)}{\Delta x^2} = f''(x) + O(\Delta x^2) \tag{A.7}
\]

---

Figure A.1: Discretization scheme of the domain for 1D FDM

The domain is discretized into \( n \) sections of \( \Delta x \) width, though we track \( n + 3 \) nodes. Because we will experience a concentration discontinuity at the solid-liquid interface, we have two nodes at the interface, one for each phase’s interfacial concentration. We have an additional two "fictitious nodes" in each phase to aid in implementing Neumann boundary conditions at the interface, to be discussed shortly.

The centered difference approximations replace the differential equations (4.1) and (4.3); taking the steady-state form of (4.3) and replacing \( f(x) \) with concentration \( C(x) \) for phase \( j \):
\[ D_j \frac{C(x + \Delta x) - 2C(x) + C(x - \Delta x)}{\Delta x^2} - v_{int} \frac{C(x + \Delta x) - C(x - \Delta x)}{2\Delta x} = 0 \] (A.8)

We can describe the above equation using array indices and then collect terms:

\[ D_j \frac{C_{i+1} - 2C_i + C_{i-1}}{\Delta x^2} - v_{int} \frac{C_{i+1} - C_{i-1}}{2\Delta x} = 0 \] (A.9)

\[ \left( \frac{D_j}{\Delta x^2} + \frac{v_{int}}{2\Delta x} \right) C_{i-1} + \frac{-2D_j}{\Delta x^2} C_i + \left( \frac{D_j}{\Delta x^2} - \frac{v_{int}}{2\Delta x} \right) C_{i+1} = 0 \] (A.10)

Equation (A.10) is then a linear equation describing the relationship between any three adjacent nodes. We can then construct a banded matrix describing the system of equations of all the nodes along the domain.

Another way of describing this process (and one more amenable to coding) is to express the difference approximations as a matrices operating on the vector of function unknowns (denoted as \([C]\)). Thus, the finite difference equations are written as:

\[
[D^2_x] [C] - v_{int} [D_x] [C] = [0] \] (A.11)

\[
\left( [D^2_x] - v_{int} [D_x] \right) [C] = [0] \] (A.12)

\[
[A] [C] = [0] \] (A.13)

**A.2 Boundary conditions**

Three types of boundary conditions are most common in solving partial differential equations. *Dirichlet conditions* specify the value of the field variable at a boundary:

\[ C(x_0, t) = f \] (A.14)

*Neumann conditions* specify the value of the derivative of a field variable at a boundary. This is often related to the flux of the field variable of interest (*e.g.* solutal flux or heat flux):
\[
\frac{\partial C}{\partial x}(x_0, t) = f
\] (A.15)

Mixed or Robin conditions specify a relationship between a field variable and its derivative at a boundary:

\[
\frac{\partial C}{\partial x}(x_0, t) = f(C)
\] (A.16)

In FDM, the Dirichlet conditions can be applied by directly setting the value of the field variable at a node. Derivatives in Neumann and Robin conditions can be expressed using the same finite difference approximations in the previous section and incorporated into the global matrix, though they may invoke the use of a "fictitious" or "ghost" node beyond the actual domain. All of these can be generalized to higher dimensions.

A.3 Time-stepping

The equations in section ?? are formulated for the steady-state solutions, but our problem is transient. This requires us to discretize the time variable to integrate forward in time. The easiest way to do this is a forward difference (sometimes known as explicit Euler) step, now denoting time step \( m \) in the superscript:

\[
\frac{\partial C}{\partial t} \approx \frac{C_{i}^{m+1} - C_{i}^{m}}{\Delta t} = \frac{C_{i}^{m+1} - C_{i}^{m}}{\Delta t}
\] (A.17)

So the transient form of (A.9) is now

\[
\frac{C_{i}^{m+1} - C_{i}^{m}}{\Delta t} = D_j \frac{C_{i+1}^{m} - 2C_{i}^{m} + C_{i-1}^{m}}{\Delta x^2} - v_{\text{int}} \frac{C_{i+1}^{m} - C_{i-1}^{m}}{2\Delta x}
\] (A.18)

\[
C_{i}^{m+1} = C_{i}^{m} + \Delta t \left( D_j \frac{C_{i+1}^{m} - 2C_{i}^{m} + C_{i-1}^{m}}{\Delta x^2} - v_{\text{int}} \frac{C_{i+1}^{m} - C_{i-1}^{m}}{2\Delta x} \right)
\] (A.19)

As long as an initial condition is present, (A.19) can be simply evaluated to calculate the next timestep’s concentration profile given the current timestep’s profile. However, while it will not be discussed here, it can be shown that forward Euler is unconditionally unstable for the advective problems. A better approach is to take the backwards difference (or implicit Euler) step:
\[
\frac{C_i^{m+1} - C_i^m}{\Delta t} = D_j \frac{C_{i+1}^{m+1} - 2C_i^{m+1} + C_{i-1}^{m+1}}{\Delta x^2} - v_{\text{int}} \frac{C_{i+1}^{m+1} - C_{i-1}^{m+1}}{2\Delta x} \quad (A.20)
\]

It is apparent now that the concentration profile in the future timestep is not so easily evaluated; it must now be solved for:

\[
(s_1 - s_2) C_i^{m+1} + (1 + 2s_2) C_i^{m+1} - (s_1 + s_2) C_{i+1}^{m+1} = C_i^m \quad (A.21)
\]

Where \( s_1 = \frac{v_{\text{int}} \Delta t}{2\Delta x} \) and \( s_2 = \frac{D_j \Delta t}{\Delta x^2} \). Here, we can see again that we can create a banded matrix which we can solve to calculate the next timestep concentration profile given the current timestep’s profile (note that the LHS of (A.21) is simply (A.10) with a factor of \( \Delta t \)). This backwards difference method exhibits first-order accuracy in time and is unconditionally stable.

If we wish to increase the accuracy a little more, we can average the forward and backward difference approximations to essentially create a centered difference approximation in time. The result is the \textit{Crank-Nicolson Method}, which is second-order accurate in both space and time and is what we use to solve our equations:

\[
\frac{C_i^{m+1} - C_i^m}{\Delta t} = \frac{1}{2} \left[ D_j \frac{C_{i+1}^{m+1} - 2C_i^{m+1} + C_{i-1}^{m+1}}{\Delta x^2} - v_{\text{int}} \frac{C_{i+1}^{m+1} - C_{i-1}^{m+1}}{2\Delta x} \right.
\]

\[
\left. + D_j \frac{C_{i+1}^m - 2C_i^m + C_{i-1}^m}{\Delta x^2} - v_{\text{int}} \frac{C_{i+1}^m - C_{i-1}^m}{2\Delta x} \right] \quad (A.22)
\]

\[
\frac{1}{2} (s_1 - s_2) C_{i-1}^{m+1} + (1 + s_2) C_i^{m+1} - \frac{1}{2} (s_1 + s_2) C_{i+1}^{m+1}
\]

\[
= \frac{1}{2} (s_1 - s_2) C_{i-1}^m + (1 + s_2) C_i^m - \frac{1}{2} (s_2 + s_1) C_{i+1}^m \quad (A.23)
\]
Appendix B

Solving Eu migration model equations via Finite Fourier Transforms

B.1 Method overview

This problem presents a unique opportunity to apply a technique used to solve linear transport problems in composite phases developed in this department by Neal Amundson and D. Ramkrishna by means of Finite Fourier Transforms [45]. Linear diffusion problems (second-order differential equations) with homogeneous boundary conditions can be framed as eigenvalue problems using the Sturm-Liouville operator, which is given by:

\[ \mathcal{L}_x = \frac{1}{w(x)} \left[ \frac{d}{dx} \left( p(x) \frac{d}{dx} \right) + q(x) \right] \]  

We will limit our discussion to the stationary case in this section. In this scenario, \(w(x) = 1, \ p(x) = D(x),\) and \(q(x) = 0\). Given a definition of an inner product of two functions \(f(x)\) and \(g(x)\) on the interval from \(a\) to \(b\), with weighting function \(w(x)\), for example:
An eigenvalue problem is considered self-adjoint if:

\( \langle L_x u, v \rangle = \langle u, L_x v \rangle \) (B.3)

Self-adjoint eigenvalue problems have the useful properties in that their eigenvalues

\( L_x \Phi = -\lambda^2 \Phi \) (B.4)

are real, and their eigenfunctions form an orthonormal basis:

\( \langle \Phi_n, \Phi_m \rangle = \delta_{nm} \) (B.5)

This allows us to represent any arbitrary function (in this case, our concentration profile) as a weighted sum of these eigenfunctions.

For FFT to work properly, our domain must be rescaled such that it ranges from 0 to 1. Thus, our governing equations are nondimensionalized using \( L \) as a characteristic length and \( L^2/D_s \) as a characteristic time. In this section, we will continue to use \( x, t, \gamma, \) and \( D_i \) as the spatial variable, time variable, interface location, and diffusivities, respectively, in order to avoid having to define another set of nondimensional variables. Thus, \( \gamma \) is now a fraction between 0 and 1, and the diffusivities are also scaled by the solid’s diffusivity.

Before proceeding, we must make a minor alteration to our Sturm-Liouville formulation. FFT is often used to represent arbitrary continuously differentiable functions with homogeneous boundary conditions. In our problem, we expect segregation at the interface to product a discontinuity in concentration, with each phase also having its own diffusivity (which we can think of as a discontinuous diffusivity that experiences a step change at the interface). To account for this, a new inner product is defined such that our Sturm-Liouville operator remains self-adjoint:
\[ \langle u, v \rangle \equiv \int_0^\gamma u(x) v(x) \, dx + K \int_\gamma^1 u(x) v(x) \, dx \]  
\[ (B.6) \]

### B.2 Implementation

We seek a solution in the form

\[ C(x, t) = \sum_{n=1}^\infty C_n(t) \Phi_n(x) \]  
\[ (B.7) \]

Where the basis function \( \Phi_n(x) \) is composed of:

\[ \Phi_n = \begin{cases} 
\Phi_n^{(1)} & 0 \leq x \leq \gamma \\
\Phi_n^{(2)} & \gamma \leq x \leq 1 
\end{cases} \]  
\[ (B.8) \]

The basis functions are required to obey the same homogeneous boundary conditions:

\[ \frac{d\Phi_n}{dx}(x = 0) = \frac{d\Phi_n}{dx}(x = 1) = 0 \]  
\[ (B.9) \]

Next, we define our transformed concentration \( C_n(x, t) \) as the inner product between \( C(t) \) and the basis function \( \Phi_n(x) \):

\[ C_n(t) = \langle C(x, t), \Phi_n(x) \rangle = \int_0^\gamma C\Phi_n^{(1)} \, dx + K \int_\gamma^1 C\Phi_n^{(2)} \, dx \]  
\[ (B.10) \]

We proceed to transform the differential equation, starting with the transient side:

\[ \left\langle \frac{\partial C}{\partial t}, \Phi_n \right\rangle = \frac{\partial C_n}{\partial t} \]  
\[ (B.11) \]

We then transform the spatial side, using the Sturm-Liouville operator \( \mathcal{L}_x \) and forming the eigenvalue problem:

\[ \langle \mathcal{L}_x C, \Phi_n \rangle = \langle C, \mathcal{L}_x \Phi_n \rangle = \langle C, -\lambda_n^2 \Phi_n \rangle = -\lambda_n^2 C_n \]  
\[ (B.12) \]

If we expand this out, employing integration by parts twice, and invoking boundary
conditions to zero out the boundary terms we get:

\[
\langle \mathcal{L}_x C, \Phi_n \rangle = D_s \int_0^\gamma \frac{d^2 C}{dx^2} \Phi_n dx + KD_l \int_\gamma^1 \frac{d^2 C}{dx^2} \Phi_n dx
\]

\[
= D_s \left( \frac{dC}{dx} \Phi_n - C \frac{d\Phi_n}{dx} \right) \bigg|_{\gamma^-}
- KD_l \left( \frac{dC}{dx} \Phi_n - C \frac{d\Phi_n}{dx} \right) \bigg|_{\gamma^+} + \langle C, \mathcal{L}_x \Phi_n \rangle
\]

For self-adjointness to be satisfied, the sum of the first two terms on the RHS above must equal to zero.

\[
D_s \left( \frac{dC}{dx} \Phi_n - C \frac{d\Phi_n}{dx} \right) \bigg|_{\gamma^-} - KD_l \left( \frac{dC}{dx} \Phi_n - C \frac{d\Phi_n}{dx} \right) \bigg|_{\gamma^+} = 0
\]

We will see that this is true when the basis functions are subject to two constraints at the interface:

\[
\Phi_n|_{\gamma^-} = K \Phi_n|_{\gamma^+}
\]

\[
D_s \frac{\partial \Phi_n}{\partial x} \bigg|_{\gamma^-} = D_l \frac{\partial \Phi_n}{\partial x} \bigg|_{\gamma^+}
\]

We then arrive at the fully transformed differential equation, which is now an ordinary differential equation:

\[
\frac{dC_n}{dt} = -\lambda_n^2 C_n
\]

This has the general solution:

\[
C_n (t) = C_n (0) \exp \left( -\lambda_n^2 t \right)
\]

The basis functions for this Sturm-Liouville problem are of the form:

\[
\Phi_n^{(1)} (x) = a_n \sin \left( \frac{\lambda_n x}{L_1} \right) + b_n \cos \left( \frac{\lambda_n x}{L_1} \right)
\]

\[
\Phi_n^{(2)} (x) = A_n \sin \left( \frac{\lambda_n x}{L_2} \right) + B_n \cos \left( \frac{\lambda_n x}{L_2} \right)
\]
Where $L_1^2 = D_s$ and $L_2^2 = D_l$. When we apply the boundary conditions (B.9), we find that $a_n = 0$ and $A_n = B_n \tan (\lambda_n/L_2)$. Here, we introduce two variables $f$ and $g$ for sake of abbreviation:

$$f \left( \frac{\lambda_n x}{L_1} \right) = \cos \left( \frac{\lambda_n x}{L_1} \right)$$

$$g \left( \frac{\lambda_n x}{L_2} \right) = \tan \left( \frac{\lambda_n}{L_2} \right) \sin \left( \frac{\lambda_n x}{L_2} \right) + \cos \left( \frac{\lambda_n x}{L_2} \right)$$

The basis functions, so far, are then:

$$\Phi_n^{(1)} = b_n f \left( \frac{\lambda_n x}{L_1} \right)$$

$$\Phi_n^{(2)} = B_n g \left( \frac{\lambda_n x}{L_2} \right)$$

Invoking the first of our constraints on the basis functions (B.14), we get:

$$b_n f \left( \frac{\lambda_n \gamma}{L_1} \right) = KB_n g \left( \frac{\lambda_n \gamma}{L_2} \right) \quad (B.18)$$

Invoking the second constraint (B.15), we get:

$$L_1 b_n \lambda_n f' \left( \frac{\lambda_n \gamma}{L_1} \right) = L_2 B_n \lambda_n g' \left( \frac{\lambda_n \gamma}{L_2} \right) \quad (B.19)$$

Where

$$f' \left( \frac{\lambda_n x}{L_1} \right) = -\sin \left( \frac{\lambda_n x}{L_1} \right)$$

$$g' \left( \frac{\lambda_n x}{L_2} \right) = \tan \left( \frac{\lambda_n}{L_2} \right) \cos \left( \frac{\lambda_n x}{L_2} \right) - \sin \left( \frac{\lambda_n x}{L_2} \right)$$

We assemble this system of equations as a matrix:

$$\begin{bmatrix}
  f \left( \frac{\lambda_n \gamma}{L_1} \right) & -K g \left( \frac{\lambda_n \gamma}{L_1} \right) \\
  L_1 \lambda_n f' \left( \frac{\lambda_n \gamma}{L_1} \right) & -L_2 \lambda_n g' \left( \frac{\lambda_n \gamma}{L_2} \right)
\end{bmatrix}
\begin{bmatrix}
  b_n \\
  B_n
\end{bmatrix}
= \begin{bmatrix}
  0 \\
  0
\end{bmatrix} \quad (B.20)$$

And we find the characteristic equation by letting the determinant equal 0:

$$-L_2 \lambda_n g' \left( \frac{\lambda_n \gamma}{L_2} \right) f \left( \frac{\lambda_n \gamma}{L_1} \right) + KL_1 \lambda_n g \left( \frac{\lambda_n \gamma}{L_2} \right) f' \left( \frac{\lambda_n \gamma}{L_1} \right) = 0 \quad (B.21)$$
The eigenvalues here need to be solved for numerically. We find that the first eigenvalue is $\lambda_0 = 0$, which we will handle separately.

We must now solve for the normalization constants $b_n$ and $B_n$. Thus, we evaluate the inner product of $\Phi_n$ with itself and ensure that it equals unity (B.5).

$$b_n^2 \int_0^\gamma f (\lambda_n \gamma / L_1)^2 \, dx + K B_n^2 \int_\gamma^1 g (\lambda_n \gamma / L_2)^2 \, dx = 1$$  \hspace{1cm} (B.22)

(B.18) can be used to express $b_n$ in terms of $B_n$. This can then be substituted into (B.22), where we can then solve for $B_n$.

$$B_n = \left( \frac{K^2 g (\lambda_n \gamma / L_2)^2}{f (\lambda_n \gamma / L_1)^2} \int_0^\gamma f (\lambda_n \gamma / L_1)^2 \, dx + K \int_\gamma^1 g (\lambda_n \gamma / L_2)^2 \, dx \right)^{-\frac{1}{2}}$$  \hspace{1cm} (B.23)

It is known that the 0th basis function for this system (corresponding with our $\lambda_0 = 0$) is constant on both sides of the interface, which we denote $\Phi_0$. Using the same normalization process for the 0th basis function, we get:

$$\int_0^\gamma \left[ \Phi_0^{(1)} \right]^2 \, dx + K \int_\gamma^1 \left[ \Phi_0^{(2)} \right]^2 \, dx = 1$$  \hspace{1cm} (B.24)

Again using (B.14), we express $\Phi_0^{(1)}$ in terms of $\Phi_0^{(2)}$. Substituting into (B.24) we find:

$$\Phi_0^{(2)} = \sqrt{\frac{1}{K^2 \gamma + K (1 - \gamma)}}$$  \hspace{1cm} (B.25)

$$\Phi_0^{(1)} = K \Phi_0^{(2)}$$

Now that our basis functions are fully specified, we have all the pieces to assemble our FFT solution:

$$C(x, t) = \langle C(x, t = 0), \Phi_0 \rangle \Phi_0(x) + \sum_{n=1}^{\infty} \langle C(x, t = 0), \Phi_n \rangle \exp\left(-\lambda_n^2 t\right) \Phi_n(x)$$ \hspace{1cm} (B.26)
We can note that the first term of the solution is time-independent and in fact is the steady-state solution for this problem, as solute segregates into constant equilibrium composition over the entire domain.

![Figure B.1: Characteristic equation](image)

**B.3 Results**

While the FFT method is indeed able to solve a two-phase diffusion problem, it is not the ideal for determining unknown diffusion coefficients. While the diffusion coefficients do appear as variables in the "semi-analytical" solution \(B.26\), in that they appear in \(\Phi_n\), they are also used in determining the eigenvalues. Changing values of \(D_s\) and \(D_l\) change the characteristic equation, thus changing the eigenvalues \(\lambda_n\) which need to be numerically solved for, itself a cumbersome process. Additionally, this analysis only covers the time period in which the interface is stationary, as FFT would not permit the types of boundary conditions for a moving reference frame problem. For this reason, we sought another method that would be more practical for determining diffusion coefficients. Nonetheless, FFT and the formalism of self-adjoint operators is
Figure B.2: Solutions of the FFT method using 100 eigenfunction terms plotted with non-dimensionalized position and over logarithmically-spaced time intervals. The interface is held at a constant position, and the domain is assumed to be only the width of the detection region. The initial condition is represented as a polynomial fit of the experimental data for easier analytical integration. The final time displayed is far beyond the length of the experiment and is intended to show that the systems tends toward the steady state of constant equilibrium composition in both phases. The diffusion coefficients and eigenvalues used to generate this solution are the ones derived from the following section. Though FFT solutions minimize error in a least-squares sense (compared to the true solution) [100], the plot shows that even with a large number of eigenfunction terms, oscillations are still noticeable in early times close to the discontinuity.

still a valuable technique in our mathematical toolbox for modeling and solving problems concerning diffusion.

In the next Appendix section, we discuss the use of Finite Difference Method to solve our governing equations. Compared to FFT, FDM is expected to be much more straightforward to implement, more flexible, and more accurate for the same amount of computational effort.
Appendix C

Solving Eu migration model equations via similarity solution

An idealized version of the diffusion problem in Chapter 4 can be solved analytically via similarity method. In fact, traditional diffusion couple experiments back out solid-state diffusion coefficients by matching experimental concentration profiles to those expected from a similarity solution. It can even be useful to think of the Eu-migration problem as a segregation-driven diffusion couple.

To utilize the similarity transform method, an ideal sample should be long enough so that its ends are “infinitely” far away from the diffusion zone. In practice, this would mean that the length of sample should be \((D t_f)^{1/2} \gg 1\), where \(D\) represents a characteristic diffusion coefficient and \(t_f\) is the time over which the experiment is performed.

The initial distribution of the species in the experiment is also important and will depend on the history of the sample, namely the original distribution of the species in the solid charge and how the charge is melted. While there is no segregation upon melting, any regrowth of solid will redistribute solutes and make the initial concentration profile non-constant. Ideally, the experiment would start with a solid of uniform composition that is melted back just once and held steady.

With a uniform concentration and the solid/liquid interface held stationary throughout the duration of the experiment, the following analytical expressions describe the evolution of species through both phases. If these conditions are not met, modifications
Figure C.1: Depiction of the idealized segregation-driven diffusion couple, showing (a) the initial species concentration profile as constant and (b) how segregation at the solid/liquid interface produces a discontinuity in concentration and drives diffusion of the species out of the solid and into the liquid.
to the mathematical model along with numerical solution techniques, such as discussed in Section 4, may be employed to predict the evolution of the concentration profiles.

A schematic depiction of the ideal experiment is presented in Figure C.1 along with definitions of the variables in the mathematical model. As noted previously, we presume a uniform concentration everywhere at \( t = 0 \), namely \( c_1(x, 0) = c_2(x, 0) = c_0 \). The field equations and boundary conditions are the same as presented in equations (4.1)–(4.8), except that the spatial domain for the ideal system is unbounded, with \(-\infty \leq x \leq \infty\), with \( x = 0 \) marking the location of the solid/liquid interface. In addition, the far-field boundary conditions, equations (4.8), are replaced by,

\[
\begin{align*}
    c_1(x \to -\infty, t) &= c_0, \\
    c_2(x \to \infty, t) &= c_0,
\end{align*}
\]

and the interface velocity is zero, so that \( v_{\text{int}} = 0 \) in equation (??).

We apply similarity transformations (see, e.g., [101]) over both domains, with similarity variables of \( \eta_1 = x/2(D_1 t)^{1/2} \) in the solid (for \( x \leq 0 \)) and \( \eta_2 = x/2(D_2 t)^{1/2} \) in the liquid (for \( x \geq 0 \)). Note that \( D_1 \) and \( D_2 \) denote the diffusivity in the solid and liquid, respectively.

By satisfying the matching conditions at the solid/liquid interface, we can show that,

\[
\begin{align*}
    c_1(\eta_1) &= \frac{k(1 + R) + (k - 1)\text{erf}(\eta_1)}{1 + kR}, \quad \text{for } \eta_1 = x/2(D_1 t)^{1/2} \leq 0, \\
    c_2(\eta_2) &= \frac{(1 + R) + R(k - 1)\text{erf}(\eta_2)}{1 + kR}, \quad \text{for } \eta_2 = x/2(D_2 t)^{1/2} \geq 0,
\end{align*}
\]

where \( k \) is the distribution coefficient, \( R = \left( \frac{D_1}{D_2} \right)^{1/2} \), and \( \text{erf}(\eta) \) denotes the error function,

\[
\text{erf}(\eta) = \frac{2}{\sqrt{\pi}} \int_0^\eta e^{-u^2} du.
\]

With knowledge of the equilibrium distribution coefficient, \( k \), this analytical solution may be used with relatively simple optimization techniques to yield best-fit estimates for the diffusion coefficients, \( D_1 \) and \( D_2 \), and the partition from the measured profiles.

Below, we plot the solution for multiple times using the same diffusivities derived
from the numerical model and initial homogeneous concentration of $c_0 = 0.05$.

Figure C.2: Evolution of Eu concentration profiles as solved by similarity transform, with an initial homogeneous concentration of $c_0 = 0.05$. The diffusion coefficients and partition coefficients used here are the same as those derived in Chapter 4.
Appendix D

Extracting centerline concentrations from neutron imaging data

The concentrations presented in Figure 4.4 were processed using the 2-dimensional contrast data, averaged through the local sample width, into images. While this approach is simple and relatively fast, it presumes uniform scattering of neutrons during their line of flight through the sample, which will only be strictly valid when the Eu concentration does not vary along the neutron transit path. In fact, there is some radial variation in composition in the sample, which will give rise to some error in the concentration field when processed in this manner.

The radial variation of europium needs to be accounted for to provide a more accurate determination of concentration. To do this, we utilize the mathematics of computed tomography, which has been widely applied in medical imaging, using an algorithm known as the inverse Radon transform. Here, it is useful here to think of the original scan, which depicts the integral of the real 3D density field onto the 2D projection surface, as the forward Radon transformed data.

The process in extracting 1D concentration data is illustrated in Figure D.1 To specifically isolate the axial concentration, we first start with average concentration data (a) and take an average of both sides of the centerline. This produces a pseudo-symmetric projection of our raw data (b). We then multiply each pixel’s concentration value by the sample width at that point, producing the sample-width-integrated concentration image.
Figure D.1: Top row: The process of deriving a cross-sectional axisymmetric concentration field from 2D ERNI averaged concentration data is illustrated. Bottom row: Using the derived axisymmetric concentration field, the Radon-transformed annular region is subtracted from the sample-width integrated concentration. The resulting data representing remaining Radon-transformed concentration field of the inner cylindrical area is averaged to give a one-dimensional concentration signal. The 3D shapes here are shown for reader comprehension only. Actual processing done was layer by layer of pixels down the direction of the axis.
The unit of each pixel’s value in the resulting image has \([\text{mole fraction} \times \text{length}]\). We then perform the inverse Radon transform to the sample-width-integrated concentration image, recovering a pseudo-axisymmetric meridional concentration field \((d)\). The quality of this data is quite poor, as directly using the inverse-transformed data from only a single projection angle when there are non-axisymmetric features results a large amount of noise. We conjecture that the ERNI data at the lateral ends would be less susceptible to noise because the neutron transmission travelled through less attenuating material (as the path length is shorter there in a cylindrical sample). Therefore, to rely more on our actual raw data, we isolated an annular region of our inverse-transformed data, excluding the \(\sim 6.7\) mm diameter cylindrical region down the axis. After constructing a 3D density field of the annular region, we then applied the forward transform and subtracted this from \((c)\). What results is the forward-transformed data in the \(\sim 6.7\) mm diameter cylindrical region down the sample axis. We integrate/sum each row of pixels, yielding a value with units \([\text{mole fraction} \times \text{area}]\); this is akin to integrating the concentration from the pseudo-axisymmetric concentration field in one layer of pixels. We then divide this value by the area of a circle of diameter \(\sim 6.7\) mm. The resulting value represents the average concentration in the cylindrical region at a given axial position.