

Crystallization is a unit operation that both separates and purifies components in a single process.¹ Demand for fundamental crystallization knowledge is high, as crystallization enables for food, pharmaceutical, and chemical production.¹ Employing crystallization as a separations alternative to less thermodynamically efficient processes, such as distillation, represents one way to reduce energy demands significantly across industry and society.²

The US Department of Energy, with the University [REDACTED], recently identified inadequate predictive capabilities for solution thermodynamics as a research gap limiting the widespread use of adsorption and crystallization technologies.² Currently, engineers model crystallization processes using empirical data.³ Though researchers can measure solubility, the meta-stable zone width (MSZW) is difficult to measure with strong repeatability and does not translate easily to crystallization models.⁴ Researchers have not determined whether MSZW represents a kinetic or thermodynamic limit of supersaturation where crystal nucleation will occur, as changes in crystallization conditions shift the apparent location of the MSZW curve.^{5,6}

I desire to enable predictive crystallization capabilities by developing thermodynamic models of MSZW based on input solubility data and pure component physical properties. I plan to complete this work in the [REDACTED] at the [REDACTED] as a graduate student. I will accomplish this goal by **(1) collecting fundamental solid-liquid equilibrium (SLE) data** through rapid screening of solubility and MSZW for selected systems; **(2) determining the relationship between MSZW and solubility**; **(3) developing a model** to estimate the thermodynamic limit of MSZW; **(4) testing the model** to predict SLE for systems of societal importance; and **(5) publishing the model** for academic and industrial use. I will also establish a standard methodology for collecting solubility data for MSZW prediction and create a public database of solubility data that I will augment throughout the project.

As an undergraduate, I improved methods for isolating cellulose nanocrystals by reducing acid usage during the nanocrystal production process.⁷ After graduation, I developed expertise in crystallization, filtration, and rapid solid-liquid equilibrium screening to enhance my separations knowledge. I designed an efficient method to collect multiple solubility and MSZW data points for a given solute-solvent pair. I screened over 130 proprietary solute-solvent systems and now have the capability to screen up to four systems per day.⁸ As a graduate student, I will continue using the same method and equipment, an Avantium Crystal16, that I currently use. Across all experiments, I standardized the heating and cooling rates of samples to ensure our results are comparable. I also selected a sufficiently small cooling rate and sample mass that will enable me to assume that a system is at thermodynamic equilibrium when the screening equipment measures MSZW. As we progress, I will measure solubility data multiple times for each system to ensure I am collecting repeatable, precise, and accurate data. Repeating the data collection process and using purified solutes/solvents are crucial, as the presence of dust particles or impurities can drastically affect the measurement of MSZW.

As I collect additional SLE data, I will establish a relationship between solubility curves and the thermodynamic limit of MSZW. For each system, I will determine the temperature at which each solute dissolves and recrystallizes for multiple concentrations that span the solubility space. Using temperature and concentration pairs that correspond to solute recrystallization and the MSZW, I will determine the solute concentration that corresponds to the same temperature on the solubility curve. This data analysis process is presented in Figure 1. If the MSZW is a truly thermodynamic phenomenon, then a clear pattern exists between the MSZW and solubility curves that transcends solute and solvent identities; this has not been demonstrated yet.⁶

Reiterating the relevance of the project **Figure makes the method much easier to understand. It would be even better on the same page as the description**

The specific training/ qualifications that will allow completion of the research goals

Establishes research area and why it's important

Identifies a specific problem to tackle

The specific solution is proposed, and a high-level overview of the plan presented

Broader impact (BI)

Shows reviewers that the whole process has been carefully thought through from start to end

I will standardize the model inputs to account for molar volume and concentration so I can compare solvents and solutes on a similar basis. I will analyze acids, aromatic compounds, and pharmaceutical compounds initially, as these materials were identified as system components that are appropriate for alternative distillation technologies.² Analyzing various classes of solutes and solvents will allow me to evaluate the effect of functional groups within molecules on the ability of solvents to induce crystallization or solutes to be crystallized.

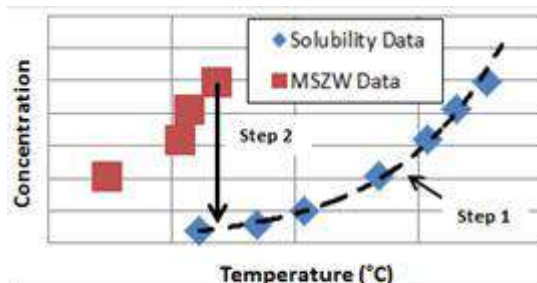


Figure 1. Experimental data used to determine the relationship between the MSZW and solubility curves.

Ultimately, our MSZW and crystallization models will account for functionality, molecular weight, and molecular volume of solvents and solutes as well as solubility – all variables that can be measured. If time allows, I will expand this model to estimate the conditions required for crystallization at various cooling rates, as increasing cooling rates increases the apparent MSZW.

Once the model is implemented and predicts MSZW accurately, I will present my findings to members of academia and industry. I desire to present my work at an annual International Conference on Crystal Growth and Epitaxy and publish my findings in the Journal of Crystal Growth. I would also like to publish the standard methods I use to collect solubility data so that researchers will be able to screen solubility data rapidly for using my model to its fullest capabilities. Finally, I will collaborate with other researchers to create a public database that includes experimental solubility and MSZW data for industrially important systems where the data collection methods are standardized. Ultimately, my MSZW model, coupled with experimental solubility data and physical property data, will enable researchers across the globe to predict cooling crystallization without requiring MSZW data at a variety of cooling rates.

BI clear again

Intellectual merit: Researchers have not determined whether MSZW is a kinetic or thermodynamic phenomenon, as the presence of impurities, cooling rates, and the identity of solutes and solvent affect the location of experimentally measured MSZWs.^{5,6} My previous experience in solid-liquid separations will enable me to use molecular modeling, experimental solid-liquid equilibrium data, physical property data, thermodynamics, and kinetics to develop a rigorous MSZW model. I will complete this project as a graduate student at [REDACTED] to illustrate that MSZW is a thermodynamic phenomenon. That MSZW model will enable academic and industrial researchers to predict and simulate crystallization processes while reducing the need for generating experimental data.

Makes it easy for reviewers to find the information they're looking for

Broader impacts: Through developing predictive crystallization modeling, we will enable the widespread use of crystallization as an energy-saving alternative to distillation. We will increase collaboration among industrial and academic researchers, as we will establish a public database of physical property and solubility data for industrially important solute-solvent systems. We will share our findings with the scientific community at conferences and through journal publications. In addition, we will continue to provide outreach opportunities and mentoring for K-12 students through creating and conducting mini-research solubility projects for [REDACTED] a mentoring program in which I currently participate.

References: [REDACTED]