Unravelling anomalous mass transport in antisolvent crystallisation

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Phase-field models are more realistic than Fick's law for diffusion modelling.

I. Introduction

- **Mixing** greatly impacts the outcome of antisolvent crystallization processes, such as the Particle Size Distribution (PSD) of the product obtained [1].
- Poor understanding of this process leads to unwanted phenomena such as **oiling out** and **uphill diffusion** [2], as depicted in **Figure 1**.
- This project focuses on developing a **mass transfer model** for the microscale, illustrated in **Figure 2**.
- For this, we are coupling the **Cahn-Hilliard** and **Maxwell-Stefan** equations with an **activity model** – Margules is used in these results, but others such as NRTL can be applied too.

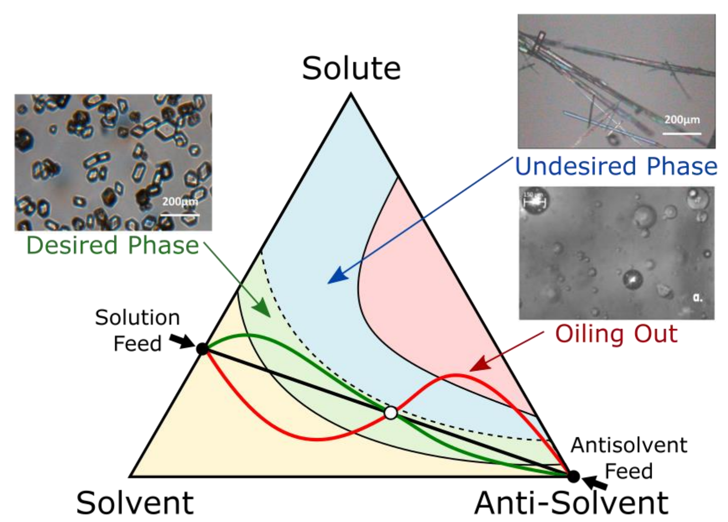


Figure 1. Ternary phase diagram illustrating that the crystallization path dictates the outputs.

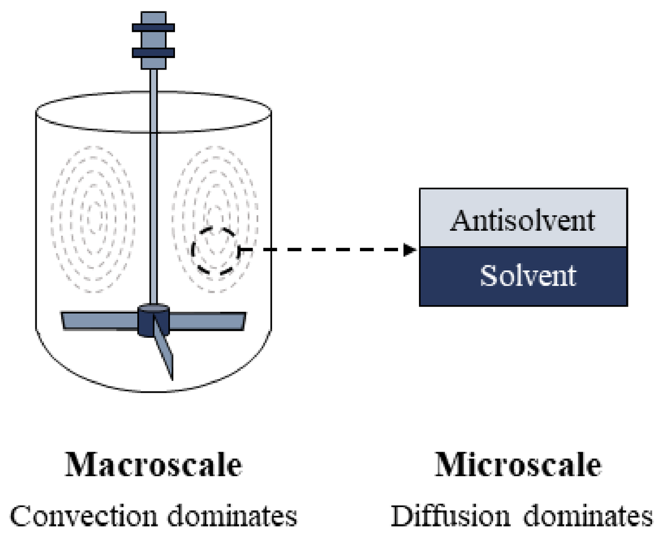


Figure 2. Diagram of the different mixing scales in a crystallizer.

II. Methodology

Fick's diffusion law

$$\frac{\partial x_A}{\partial t} = D_{AB} \cdot \nabla^2 x_A$$

- **Concentration gradient** as the driving force
- Assumes **ideal behavior**
- Cannot be applied to phase-changing systems

Cahn-Hilliard-like phase-field model

$$\frac{\partial x_A}{\partial t} = \nabla[\text{Đ}_{AB} \cdot \nabla x_A] + \nabla[\text{Đ}_{AB} x_A \cdot \nabla[A(1-x_A)^2 - \varepsilon^2 \nabla^2 x_A]]$$

- **Chemical potential gradient** as the driving force (Maxwell-Stefan)
- **Margules activity model**
- Considers interphase free energy due to surface tension $(\boldsymbol{\epsilon^2 \nabla^2 x_A})$

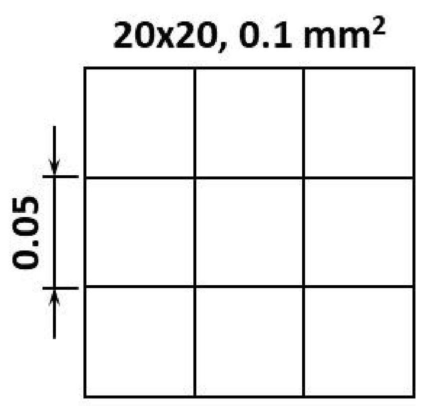


Figure 3. Space discretization.

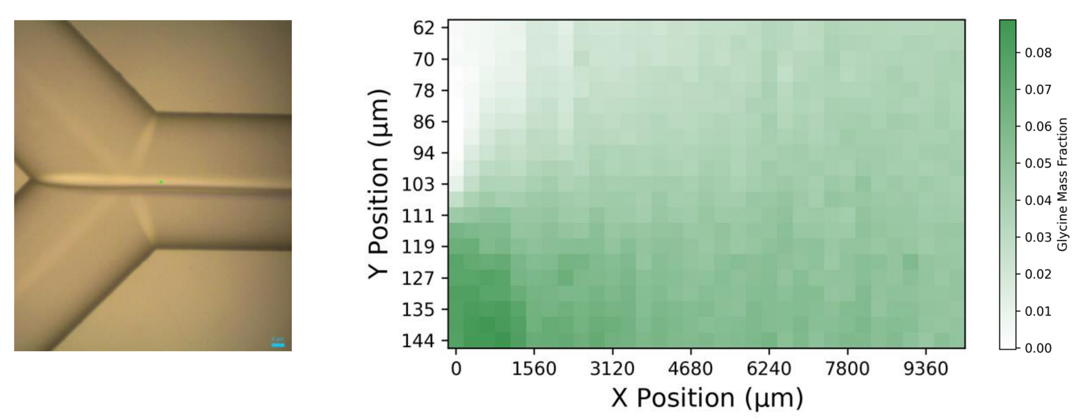


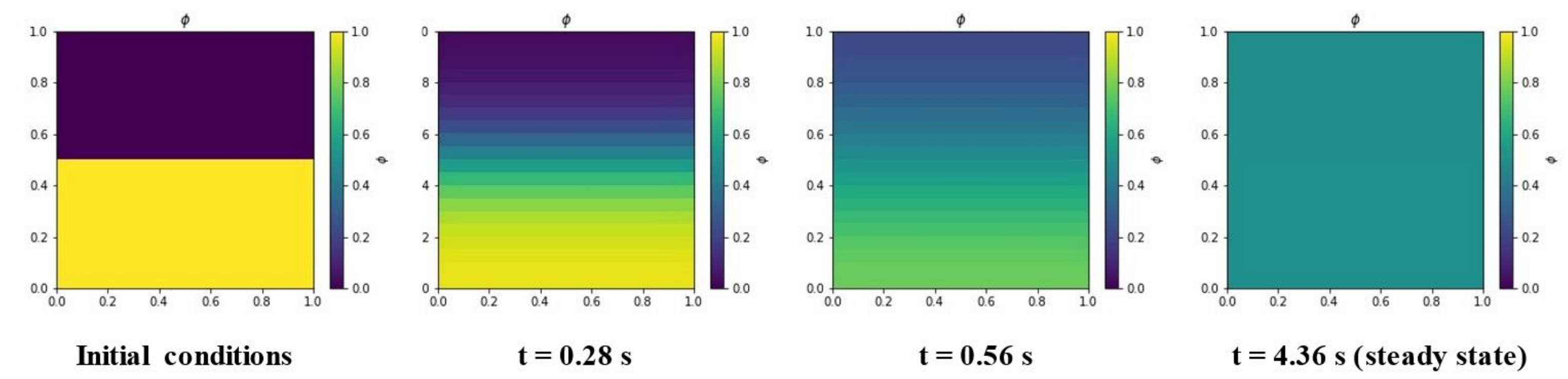
Figure 4. Left: water-glycine interphase. **Right:** experimental mass fraction map of glycine.

- **Eq. discretisation:** finite volume method - FiPy library in Python
- This model will be validated through microfluidic studies of EtOH, water and glycine systems, using **Raman microscopy (Figure 4)**.

III. Results

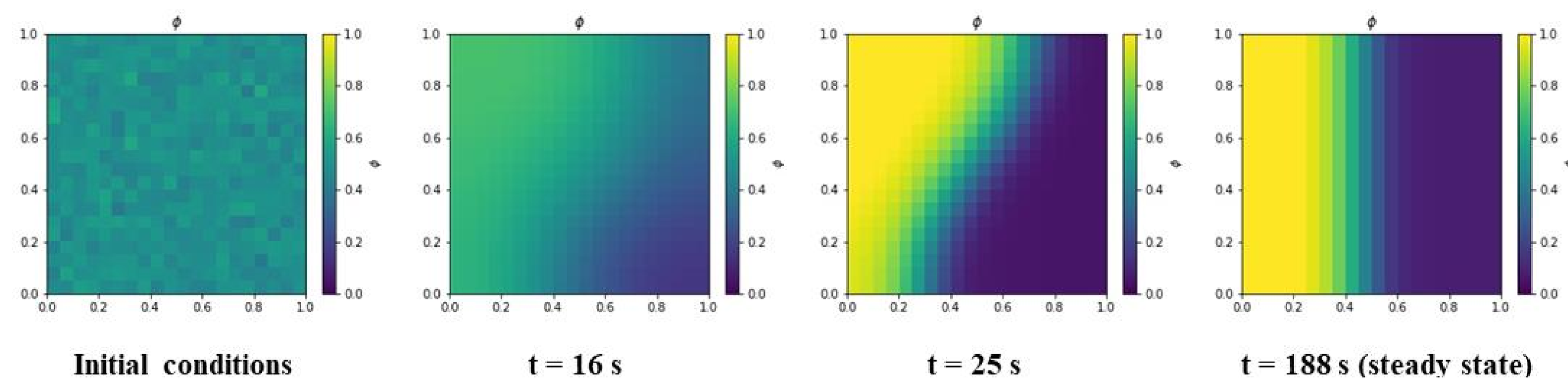
System evolution: Fick's law

The model outcome is always a homogeneous system.



System evolution: Cahn-Hilliard-like phase-field model (A = 3)

The model accounts for the non-ideality of the system through the value of A and yields a different outcome depending on that.



Conclusions

Although Fick's law is not adequate for diffusive mixing simulation in non-ideal systems, phase field models can potentially describe anomalous mass transport phenomena in antisolvent crystallisation.

Future work: Obtention of experimental composition maps and optimization of the model parameters to them. Currently introducing a convection term in the equations and preparing the optimization of Fick's law to a binary system, to check its accuracy.

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References: **[1]** A. Lewis *et al.*, ISBN: 9781107052154. **[2]** R. Krishna, DOI: 10.1039/c4cs00440j