Unravelling anomalous mass transport in antisolvent crystallisation

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Fick's law is not always appropriate to describe mixing in antisolvent crystallisation processes

1. Introduction

- **Mixing** greatly impacts the outcome of antisolvent crystallization processes, such as the CSD or the final crystal morphology [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 **diffusion model** for the microscale, illustrated in **Figure 2**.

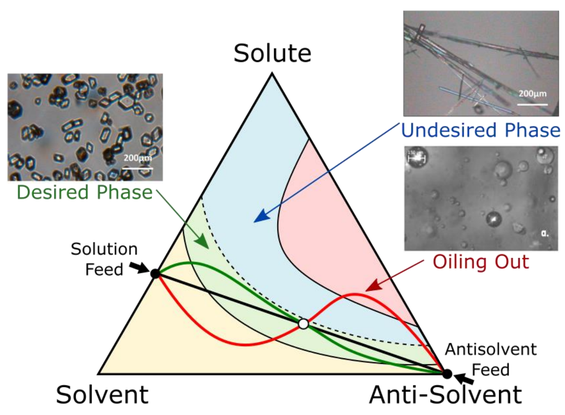


Figure 1. Ternary phase diagram illustrating that the crystallization path dictates which outputs are obtained.

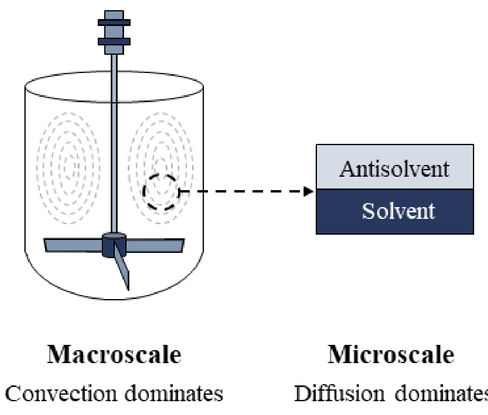


Figure 2. Diagram illustrating the different scales of mixing in a crystallizer, and their main transport mechanism.

- As an alternative, we propose a novel model based on the **Cahn-Hilliard**, **Maxwell-Stefan** and **Margules** equations.

Fick's diffusion law

$$J_A = -D_{AB} \cdot \nabla x_A$$

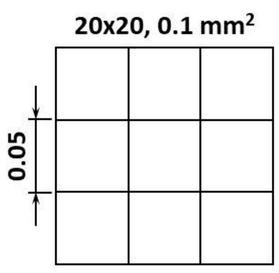
- **Concentration gradient** as the driving force
- Cannot be applied to phase-changing systems
- Assumes **ideal behavior**

Cahn-Hilliard-like phase-field model

$$\frac{\partial x_A}{\partial t} = \nabla[Đ_{AB} \cdot \nabla x_A] + \\ +\nabla\left[Đ_{AB} x_A \cdot \nabla[A(1-x_A)^2 - \varepsilon^2 \nabla^2 x_A]\right]$$

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

2. Methodology

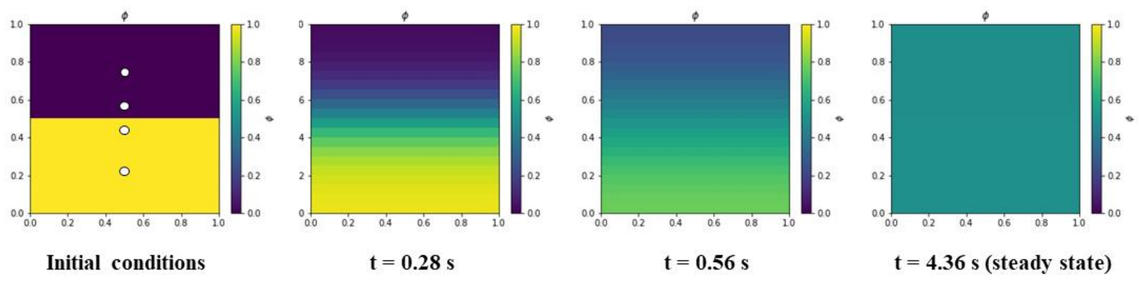


- **Equation discretisation:** finite volume method through FiPy library in Python
- **Boundary conditions:** zero gradient.
- **Initial conditions:** a layer of solvent over a layer of antisolvent, and a mixed phase.
- **System:** 2D, water and ethanol.

3. Preliminary results

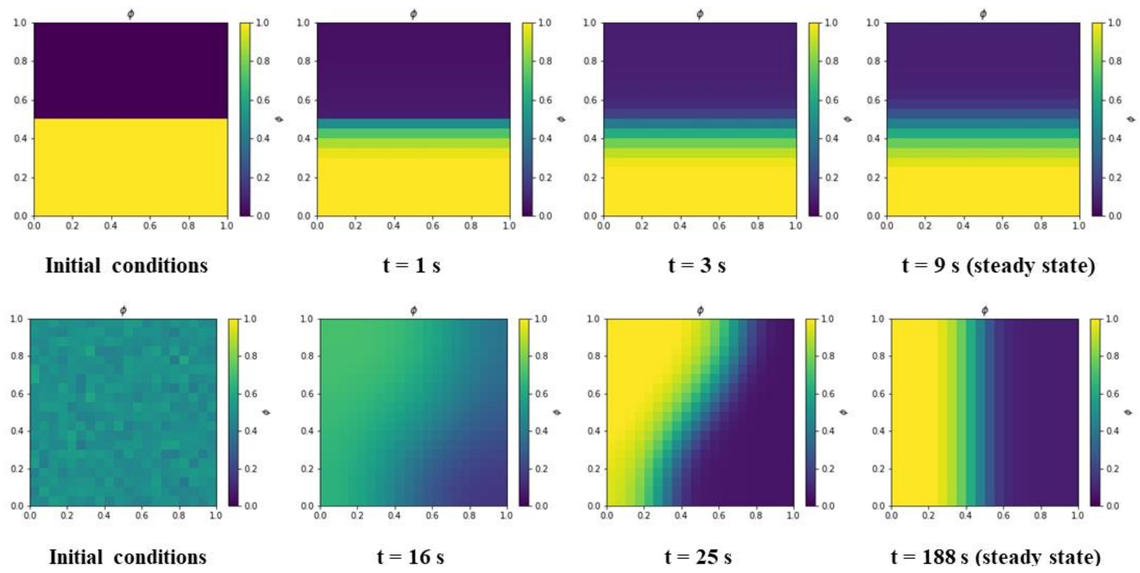
System evolution: Fick's law

The model outcome is always a homogeneous system, regardless of what the components of that system are.



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

The model accounts for the species forming the system through the value of A and yields a different outcome depending on that.



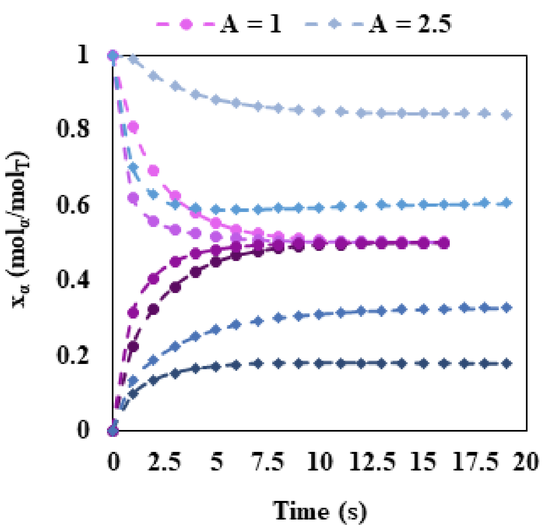


Figure 3. Time evolution of the white points shown above. Different values of A give a quicker/slower evolution towards a homogeneous/two-phase system.

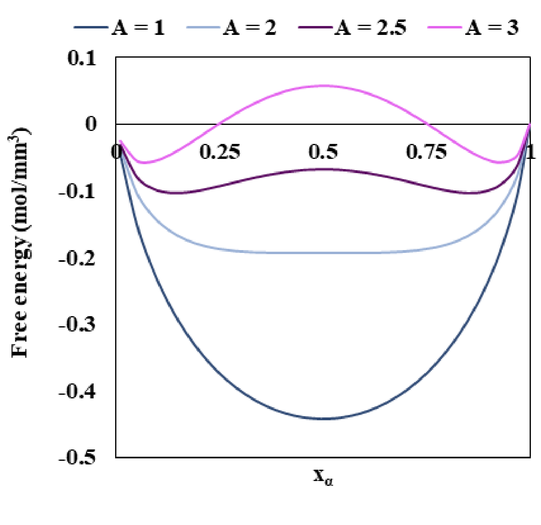


Figure 4. Margules free energy function for different A values. A > 2 yields a two-phase system, since the function has two minima instead of one.

4. Conclusions

- Fick's law is not an accurate representation of non-ideal systems.
- The model we have developed is promising for the simulation of these non-ideal systems.

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References: **[1]** A. Lewis, M. Seckler, H. Kramer, G. van Rosmalen, ISBN: 9781107052154. **[2]** R. Krishna, DOI: 10.1039/c4cs00440j