Understanding nucleation and oiling out through phase-field modelling
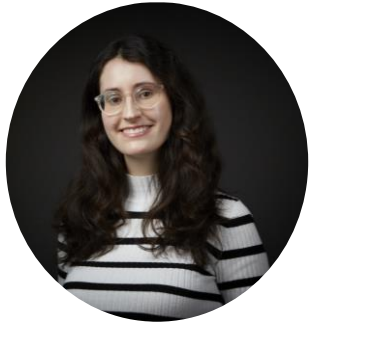
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Can we model composition pathways through phase diagrams more accurately during crystallization processes?
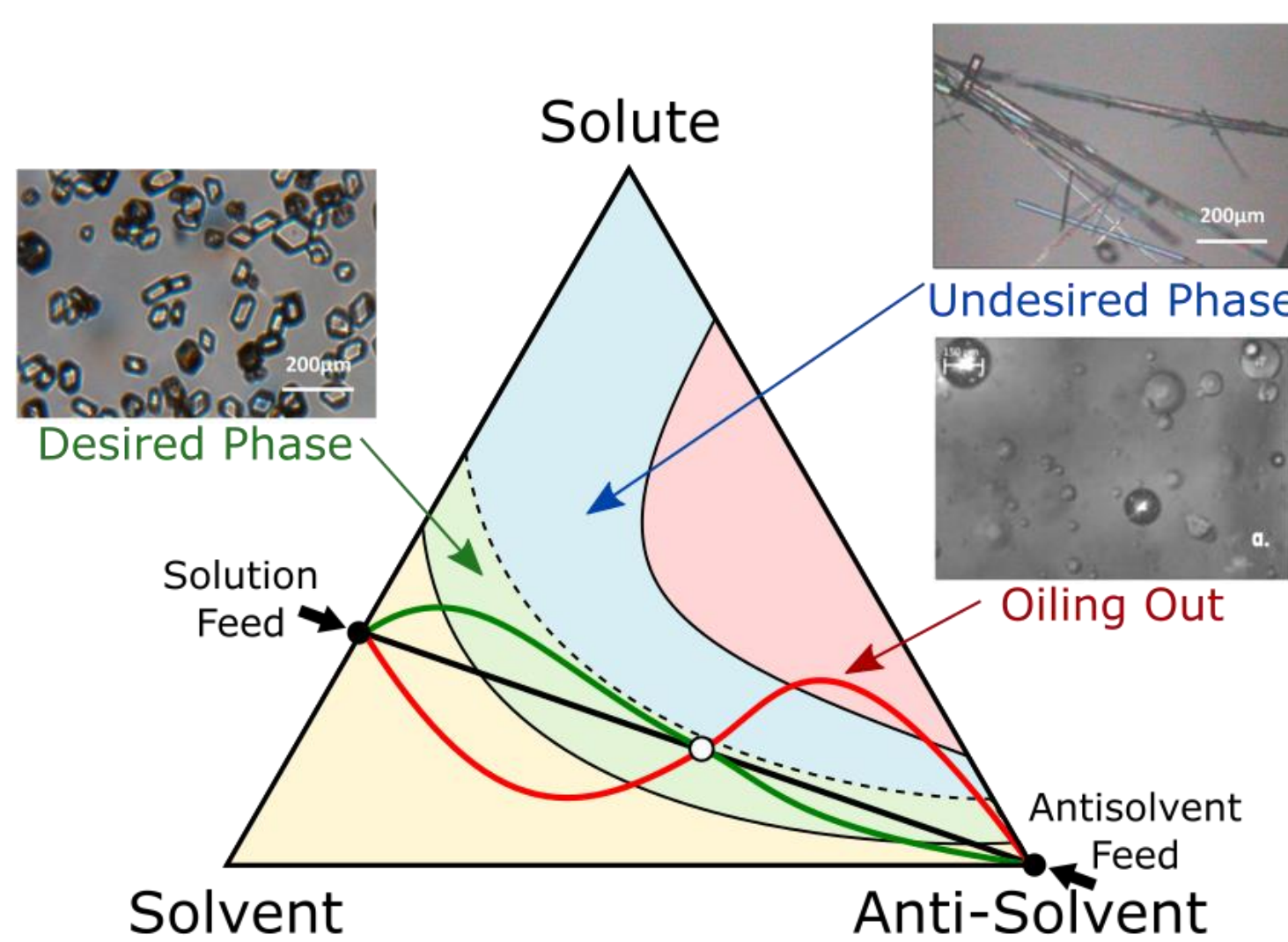

Figure 1. Ternary phase diagram illustrating that the mixing path dictates the outputs.

Poor understanding of **mixing** in crystallization (**Fick's law** as the standard)

↓

Oiling out, unexpected polymorphs (Figure 1)

Need for a better-suited **mass transfer model**

Scope

Combine the nucleation **KKS** [1] phase-field model (PFM) with a **Cahn-Hilliard-like** model (CaHiMaS) in a **2D binary system**.

Expand to **2D ternary systems** (working towards antisolvent crystallization systems).

Include **temperature** dependency (working towards cooling crystallization systems).

Description of the phase-field models

CaHiMaS PFM

$$\frac{\partial x_A}{\partial t} + \nabla(\mathbf{v}x_A) = \nabla[D_{AB} \cdot \nabla x_A] + $$
$$+\nabla[D_{AB}x_A \cdot \nabla[A(1 - x_A)^2 - \varepsilon^2\nabla^2 x_A]]$$

- Margules parameter
- Interface free E coef.

- **Chemical potential gradient** + Maxwell-Stefan
- **Margules activity model** (Figure 2)
- Interface free energy ($\varepsilon^2\nabla^2 x_A$)
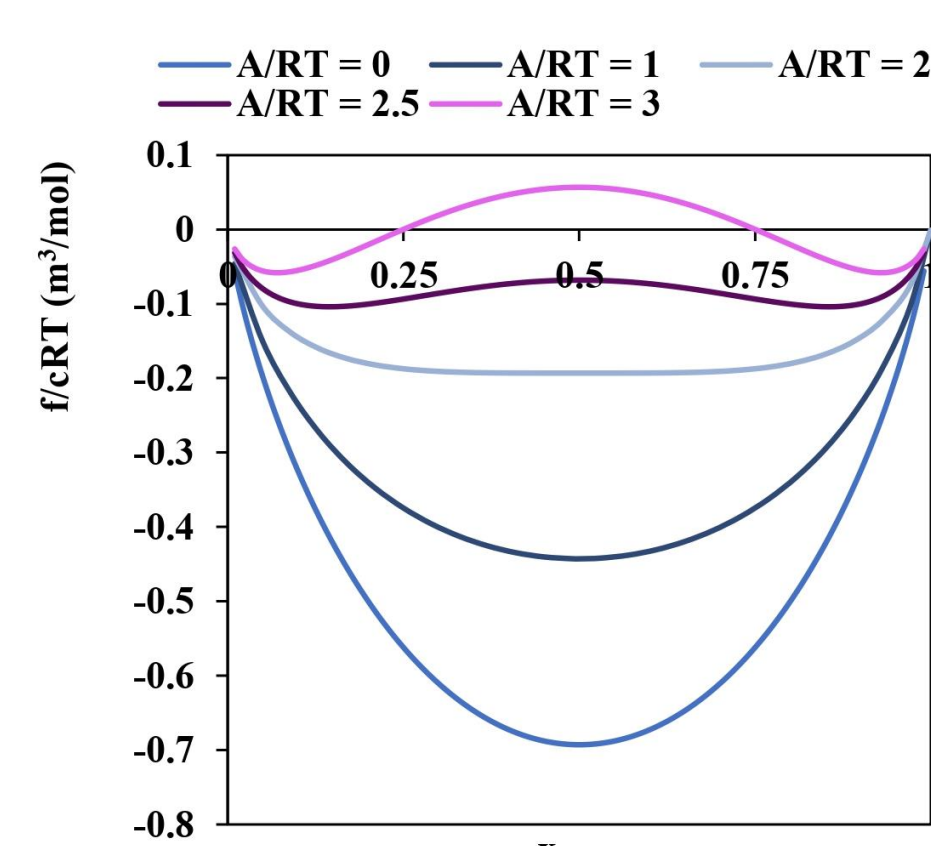- Implemented with FiPy [2]

Figure 2. Behaviour of the Margules model for different values of A/RT [3].
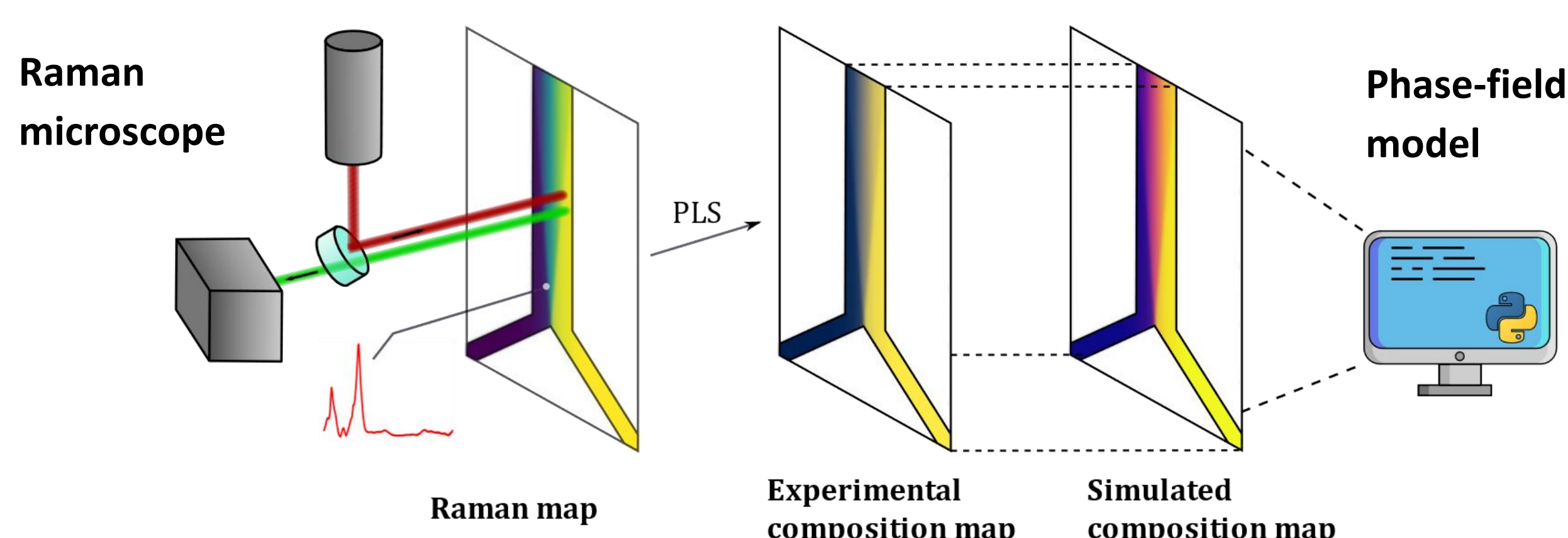
Kim-Kim-Suzuki PFM

$$\partial c/\partial t = \nabla(M/f, cc \cdot \nabla\mu_c); \quad \mu_c = f_{\alpha,c}(1 - H) + f_{\beta,c}H$$

$$\partial \eta/\partial t = -L\mu_\eta; \quad \mu_\eta = \left[f_\beta - f_\alpha - (c_\beta - c_\alpha)f_{\beta,c_\beta}\right]H + Wf_{Land} - \kappa\eta$$

- Mobility (CH and KKS)
- Interpolation function (H(η))
- Barrier height for η double well
- Penalty coefficient for the α-β interface

- **c** corresponds with composition, and **η** with the phase variable
- **Chemical potential gradient** as the driving force
- **Double-well** potential for η
- Probability of **nucleation** depends on **local supersaturation** [4, 5]
- Implemented with PRISMS-PF [6]

How would these models be validated?

Raman microscope — PLS — Experimental composition map — Simulated composition map — Phase-field model

Raman map

Case study: Fick vs CaHiMaS (LLPS)
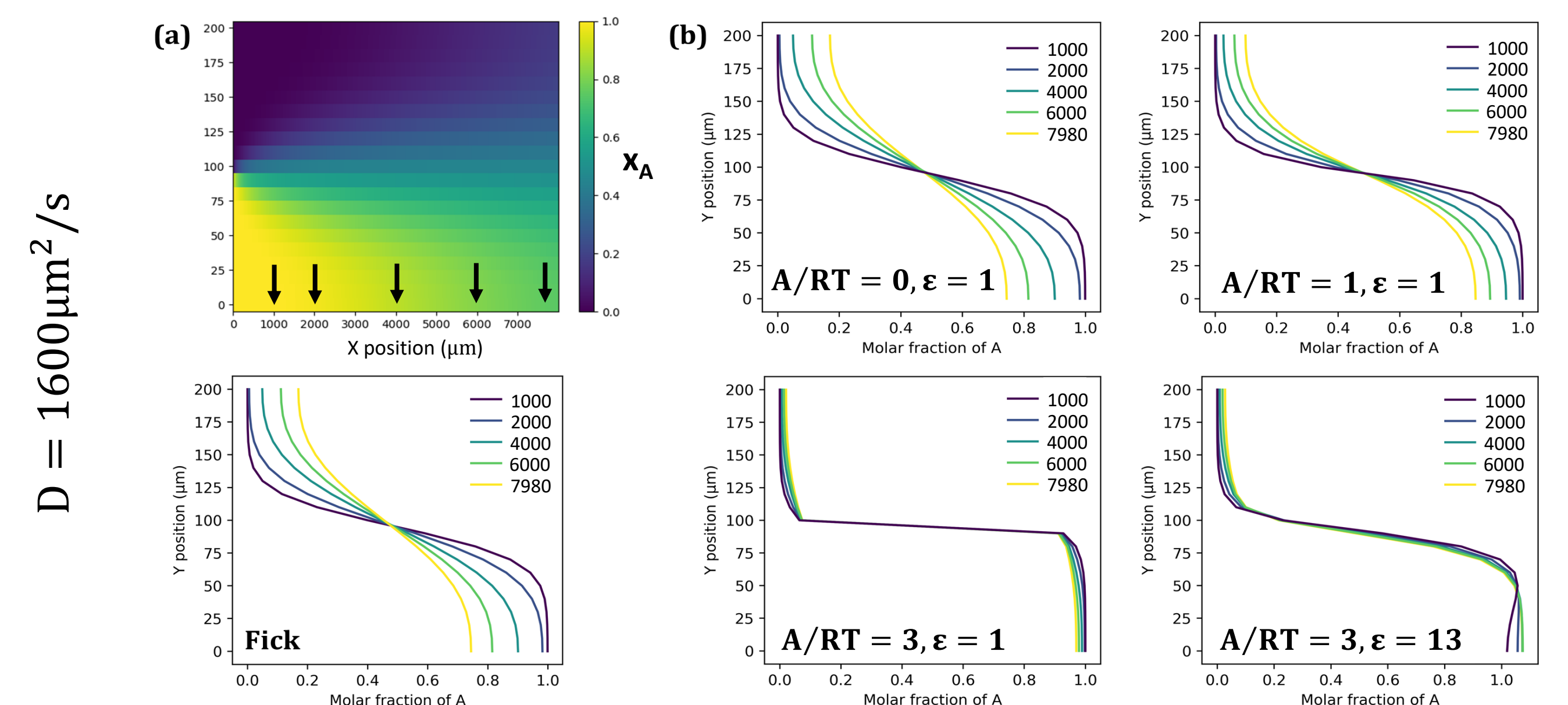

D = 1600μm²/s

Figure 3(a) Fick's law – top: example of steady state mixing map, obtained with Fick's law; **bottom** and **(b):** composition profiles at the marked mixing map points for Fick and CaHiMaS, respectively.

If **A/RT<2** the final system will be homogeneous (Figure 2), and if **A/RT>2**, it will phase split. For **higher ε**, the interface will be more diffuse.

Case study: KKS nucleation model

- Composition evolution.
- Light zone around the nuclei: supersaturation depletion in the area.

t = 0   t = 165   t = 357.5   t = 550

(a)

- Phase variable evolution.
- Diffuse interphase within all nuclei.
- No depletion zone – it is part of the liquid phase.

(b)

$M_\eta = M_c = 0.01$

A mobility reduction in both variables increases the nucleation time

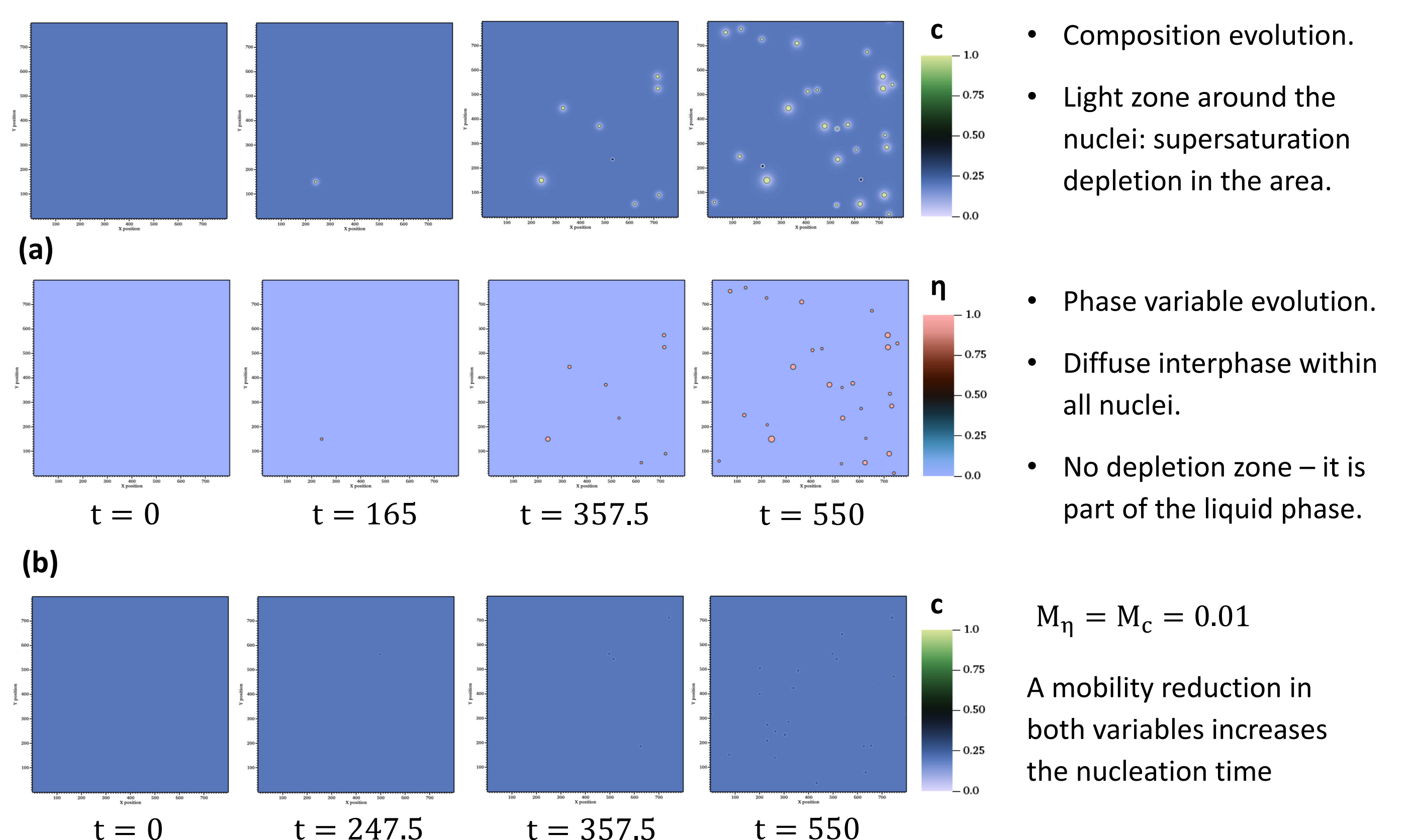t = 0   t = 247.5   t = 357.5   t = 550

Figure 4(a) top and bottom: composition and phase variable evolution (X vs Y 2D map), respectively, of a default system with $M_\eta = M_c = 1$. **(b)** Composition evolution of a system with reduced mobility.

Phase-field models hold a clear potential for the modelling of crystallization processes.