TPFA method for Cahn-Hilliard equations with surfactants

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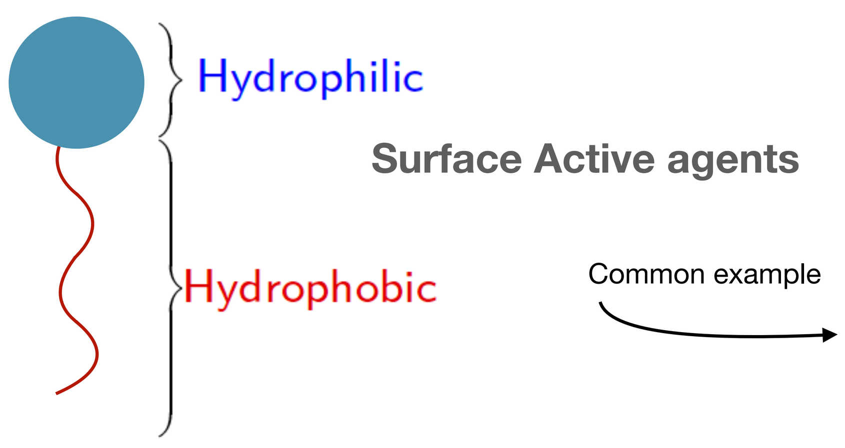
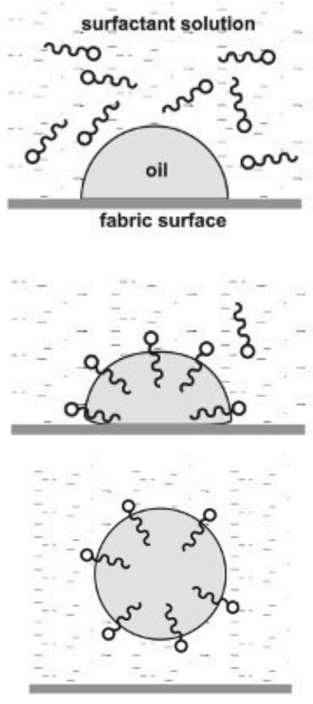
What are surfactants



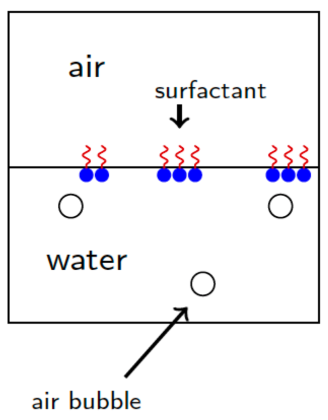


Industrial applications

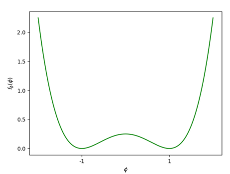
- Microfluidics applications
- Multiple emulsions for the controlled release or protection of some ingredients (probiotics)

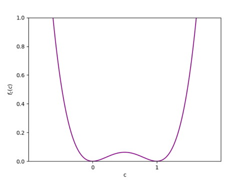
The model

Find $\phi : (0,T) \times \Omega \to \mathbb{R}$ and $c : (0,T) \times \Omega \to \mathbb{R}$ such that



$$\begin{cases} \partial_t \phi &= \Delta \mu \\ \mu &= -\epsilon_\phi \Delta \phi + \dfrac{1}{\epsilon_\phi} f'_\phi(\phi) + \partial_\phi F(\phi, c) \\ \partial_t c &= \Delta \eta \\ \eta &= -\epsilon_c \Delta c + \dfrac{1}{\epsilon_c} f'_c(c) + \partial_c F(\phi, c) \\ \nabla \phi \cdot \vec{\mathbf{n}} &= \nabla c \cdot \vec{\mathbf{n}} = \nabla \mu \cdot \vec{\mathbf{n}} = \nabla \eta \cdot \vec{\mathbf{n}} = 0 \end{cases}$$



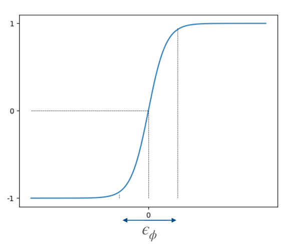


Coupling potential $F(\phi, c)$

$$F(\phi, c) = \underbrace{\beta \phi^2 c - \gamma \phi^3 c - \alpha |\nabla \phi|^2 c}_{F_i} + \underbrace{\delta |\nabla \phi|^4}_{F_s}.$$

$$\hookrightarrow \partial_\phi F(\phi, c) = 2\beta\phi c - 3\gamma\phi^2 c + 2\alpha \nabla \cdot (c \nabla \phi) - \delta \nabla \cdot (\nabla \phi)^3,$$

$$\hookrightarrow \partial_c F(\phi, c) = -\alpha |\nabla \phi|^2 + \beta \phi^2 - \gamma \phi^3.$$

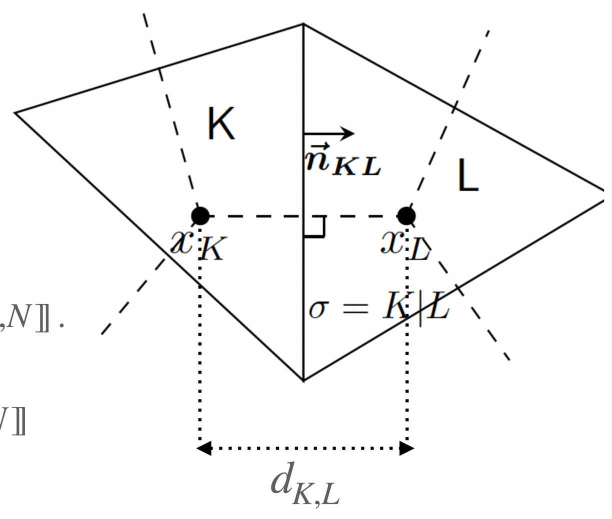


Finite volume framework [1]

- **Space discretization**

We consider a mesh $\mathscr{M}$ that verifies the orthogonality condition: $[x_K, x_L] \perp \sigma = K|L$.

N_v = number of control volumes.



- **Time discretization**

Let $N \in \mathbb{N}^*$ and $T \in]0, +\infty[$.

Time step: $\Delta t = \dfrac{T}{N} \Rightarrow t_n = n\Delta t, \quad \forall n \in [\![0,N]\!]$.

- **Discrete unknowns** For $n \in [\![0,N]\!]$

$\phi^n_{\mathscr{M}} = (\phi^n_K)_{K\in\mathscr{M}}, \quad \mu^n_{\mathscr{M}} = (\mu^n_K)_{K\in\mathscr{M}},$

$c^n_{\mathscr{M}} = (c^n_K)_{K\in\mathscr{M}}, \quad \eta^n_{\mathscr{M}} = (\eta^n_K)_{K\in\mathscr{M}}.$

- **Discrete H¹ seminorm** For $u_{\mathscr{M}} \in \mathbb{R}^{N_v}$, $\quad |u_{\mathscr{M}}|^2_{1,\mathscr{M}} := \displaystyle\sum_{\sigma \in \mathscr{E}^{int}} \frac{m_\sigma}{d_{K,L}} |u_K - u_L|^2.$

Finite volume scheme

Knowing $(\phi^n_{\mathscr{M}}, c^n_{\mathscr{M}}) \in \mathbb{R}^{N_v} \times \mathbb{R}^{N_v}$, find $(\phi^{n+1}_{\mathscr{M}}, \mu^{n+1}_{\mathscr{M}}, c^{n+1}_{\mathscr{M}}, \eta^{n+1}_{\mathscr{M}}) \in \mathbb{R}^{N_v} \times \mathbb{R}^{N_v} \times \mathbb{R}^{N_v} \times \mathbb{R}^{N_v}$ such that, for all $K \in \mathscr{M}$

$$\begin{cases} m_K \dfrac{(\phi^{n+1}_K - \phi^n_K)}{\Delta t} &= -\displaystyle\sum_{\sigma\in\mathscr{E}^{int}_K} \frac{m_\sigma}{d_{K,L}} (\mu^{n+1}_K - \mu^{n+1}_L), \\ m_K \mu^{n+1}_K &= \epsilon_\phi \displaystyle\sum_{\sigma\in\mathscr{E}^{int}_K} \frac{m_\sigma}{d_{K,L}} (\phi^{n+1}_K - \phi^{n+1}_L) + \frac{1}{\epsilon_\phi} m_K d^{f_\phi}_\phi(\phi^n_K, \phi^{n+1}_K) \\ & \quad + m_K d^F_\phi(\phi^n_K, \phi^{n+1}_K, c^n_K, c^{n+1}_K), \\ m_K \dfrac{(c^{n+1}_K - c^n_K)}{\Delta t} &= -\displaystyle\sum_{\sigma\in\mathscr{E}^{int}_K} \frac{m_\sigma}{d_{K,L}} (\eta^{n+1}_K - \eta^{n+1}_L) \\ m_K \eta^{n+1}_K &= \epsilon_c \displaystyle\sum_{\sigma\in\mathscr{E}^{int}_K} \frac{m_\sigma}{d_{K,L}} (c^{n+1}_K - c^{n+1}_L) + \frac{1}{\epsilon_c} m_K d^{f_c}_c(c^n_K, c^{n+1}_K) \\ & \quad + m_K d^F_c(\phi^n_K, \phi^{n+1}_K), \end{cases}$$

Theoretical results

The continuous case

Definition of the free energy of the system

$$\mathscr{E} : H^1(\Omega) \times H^1(\Omega) \longrightarrow \mathbb{R}$$
$$(\phi, c) \longmapsto \int_\Omega \left(\frac{\epsilon_\phi}{2} |\nabla \phi|^2 + \frac{\epsilon_c}{2} |\nabla c|^2 \right) + \int_\Omega \left(\frac{1}{\epsilon_\phi} f_\phi(\phi) + \frac{1}{\epsilon_c} f_c(c) \right) + \int_\Omega F(\phi, c).$$

Energy dissipation

$$\frac{d}{dt} \mathscr{E}(\phi, c) = -\int_\Omega |\nabla \mu|^2 - \int_\Omega |\nabla \eta|^2 \le 0.$$

$$f_c(c) \ge \tau_1 c^2 - \tau_2, \quad \tau_1 > 0, \tau_2 \ge 0$$

Bound from below? $\boxed{-\alpha |\nabla \phi|^2 c + \delta |\nabla \phi|^4 = \delta(|\nabla \phi|^2 - \frac{\alpha}{\delta} c)^2 - \frac{\alpha^2 c^2}{\delta}}$ [3]

The discrete setting

Definition of the discrete energy

$$\mathscr{E}_{\mathscr{M}}(\phi_{\mathscr{M}}, c_{\mathscr{M}}) := \frac{\epsilon_\phi}{2} |\phi_{\mathscr{M}}|^2_{1,\mathscr{M}} + \frac{\epsilon_c}{2} |c_{\mathscr{M}}|^2_{1,\mathscr{M}} + \sum_{K\in\mathscr{M}} m_K \Big(\frac{1}{\epsilon_\phi} f_\phi(\phi_K) + \frac{1}{\epsilon_c} f_c(c_K) + F(\phi_{\mathscr{M}}, c_{\mathscr{M}}) \Big).$$

$\to F(\phi_{\mathscr{M}}, c_{\mathscr{M}})$ is the discrete coupling potential

$$F(\phi_{\mathscr{M}}, c_{\mathscr{M}}) := -\frac{\alpha}{2m_K} \sum_{\sigma\in\mathscr{E}^{int}_K} \frac{m_\sigma}{d_{K,L}} c_\sigma |\phi_K - \phi_L|^2 + \beta \phi_K^2 c_K - \gamma \phi_K^3 c_K + \frac{\gamma}{8m_K} \sum_{\sigma\in\mathscr{E}^{int}_K} \frac{m_\sigma}{d^3_{K,L}} |\phi_L - \phi_K|^4.$$

Energy estimate and construction of the semi-implicit discretization.

$$\begin{aligned} \Delta t \quad & |\mu^{n+1}_{\mathscr{M}}|^2_{1,\mathscr{M}} + \Delta t |\eta^{n+1}_{\mathscr{M}}|^2_{1,\mathscr{M}} + \mathscr{F}(\phi^{n+1}_{\mathscr{M}}, c^{n+1}_{\mathscr{M}}) - \mathscr{F}(\phi^n_{\mathscr{M}}, c^n_{\mathscr{M}}) \\ & + \frac{\epsilon_\phi}{2} |\phi^{n+1}_{\mathscr{M}} - \phi^n_{\mathscr{M}}|^2_{1,\mathscr{M}} + \frac{\epsilon_c}{2} |c^{n+1}_{\mathscr{M}} - c^n_{\mathscr{M}}|_{1,\mathscr{M}^2} \\ & + \sum_{K\in\mathscr{M}} m_K \Bigg(\frac{1}{\epsilon_\phi} \Big[d^{f_\phi}_\phi(\phi^n_K, \phi^{n+1}_K)(\phi^{n+1}_K - \phi^n_K) - f_\phi(\phi^{n+1}_K) + f_\phi(\phi^n_K) \Big] \\ & \qquad + \frac{1}{\epsilon_c} \Big[d^{f_c}_c(c^n_K, c^{n+1}_K)(c^{n+1}_K - c^n_K) - f_c(c^{n+1}_K) + f_c(c^n_K) \Big] \\ & \qquad + d^F_\phi(\phi^n_K, \phi^{n+1}_K, c^n_K, c^{n+1}_K)(\phi^{n+1}_K - \phi^n_K) \\ & \qquad + d^F_c(\phi^n_K, \phi^{n+1}_K)(c^{n+1}_K - c^n_K) - F(\phi^{n+1}_K, c^{n+1}_K) + F(\phi^n_K, c^n_K) \Bigg) = 0. \end{aligned}$$

Semi-implicit discretization for the double-well potential and the interaction

$d^{f_*}_*(x,y)(y-x) - f_*(y) + f_*(x) = 0$, where $f_* = \{f_\phi, f_c, F_i\}$ and $* = \{\phi, c\}$.

Semi-implicit discretization for the stabilization

$$\begin{aligned} & d^{F_s}_\phi(\phi^{n+1}_K)(\phi^{n+1}_K - \phi^n_K) - F_s(\phi^{n+1}_K) + F_s(\phi^n_K) \\ &= \frac{\delta}{4} \sum_{\sigma\in\mathscr{E}^{int}} \frac{m_\sigma}{d^3_{K,L}} \left((\phi^{n+1}_K - \phi^{n+1}_L)^2 - (\phi^n_K - \phi^n_L)^2 \right)^2 \\ & \quad + \frac{\delta}{2} \sum_{\sigma\in\mathscr{E}^{int}} \frac{m_\sigma}{d^3_{K,L}} (\phi^{n+1}_K - \phi^{n+1}_L)^2 (\phi^{n+1}_K - \phi^{n+1}_L - \phi^n_K + \phi^n_L)^2. \end{aligned}$$

$\Rightarrow$ energy estimate unconditionally stable $\forall \Delta t$.

Existence of a discrete solution:

For all $\phi^0_{\mathscr{M}}, c^0_{\mathscr{M}} \in \mathbb{R}^{N_v}$, supposing that the double-well potentials f_ϕ and f_c satisfy a dissipativity hypothesis, and supposing that the following condition is satisfied,

$$\frac{\tau_1 \rho}{\epsilon_c} - \frac{\alpha^2 \rho}{\delta} \left(1 + \max_{\sigma\in\mathscr{E}^{int}} \left(\frac{d(x_L, \sigma)}{d(x_K, \sigma)}, \frac{d(x_K, \sigma)}{d(x_L, \sigma)} \right) \right) \ge 0,$$

there exists at least one solution $((\phi^n_{\mathscr{M}}, \mu^n_{\mathscr{M}}, c^n_{\mathscr{M}}, \eta^n_{\mathscr{M}}))_n$ to the discrete problem.

$\hookrightarrow$ Tools for the proof: topological degree theory (*a priori* estimates).

Convergence?

1. Existence of limits

There exists $\phi, \mu, c, \eta \in L^2(\Omega)$ such that (up to a subsequence) we have $\phi_{\mathscr{M}} \to \phi, \mu_{\mathscr{M}} \rightharpoonup \mu, c_{\mathscr{M}} \to c$ and $\eta_{\mathscr{M}} \rightharpoonup \eta$.

These fonctions are $H^1(\Omega)$ and the following weak convergence hold $\nabla \phi_{\mathscr{M}} \rightharpoonup \nabla \phi, \nabla \mu_{\mathscr{M}} \rightharpoonup \nabla \mu, \nabla c_{\mathscr{M}} \rightharpoonup \nabla c, \nabla \eta_{\mathscr{M}} \rightharpoonup \nabla \eta \rightharpoonup \eta$ in $(L^2(\Omega))^d$.

2. Passing to the limit

For $\psi \in \mathscr{C}^\infty_c(\Omega)$

✅ $\displaystyle\int_\Omega 2\alpha \nabla \cdot (c_{\mathscr{M}} \nabla \phi_{\mathscr{M}}) \psi = -\int_\Omega 2\alpha c_{\mathscr{M}} \nabla \phi_{\mathscr{M}} \cdot \nabla \psi.$

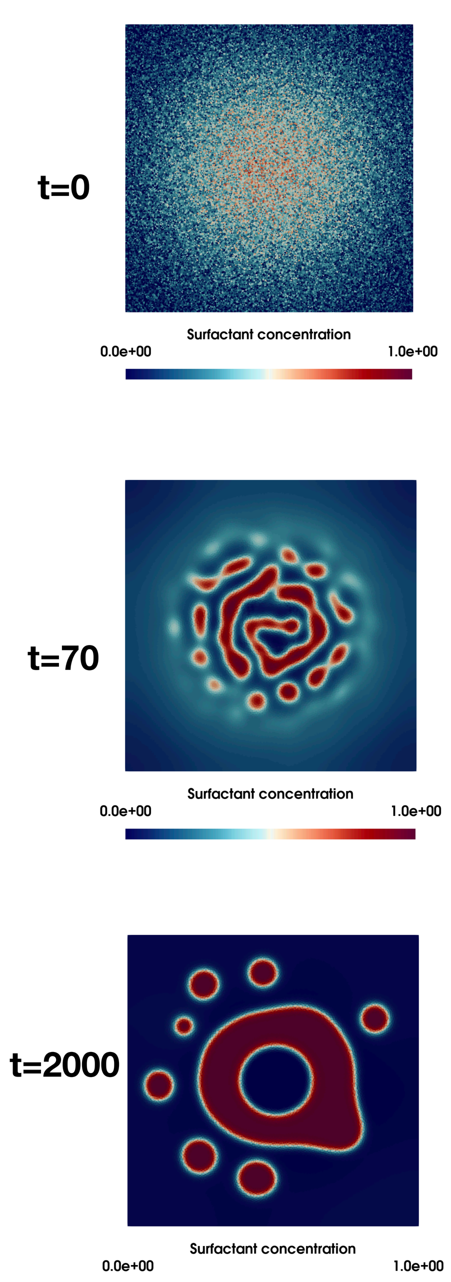
❌ $\displaystyle\int_\Omega -\alpha \nabla \phi_{\mathscr{M}} \cdot \nabla \phi_{\mathscr{M}} \psi = \int_\Omega 2\alpha \phi_{\mathscr{M}} \nabla \cdot (\nabla \phi_{\mathscr{M}} \psi).$

❌ $\displaystyle\int_\Omega -\delta \nabla \cdot (\nabla \phi_{\mathscr{M}} |\nabla \phi_{\mathscr{M}}|^2) \psi = \int_\Omega \delta |\nabla \phi_{\mathscr{M}}|^2 \nabla \phi_{\mathscr{M}} \cdot \nabla \psi.$

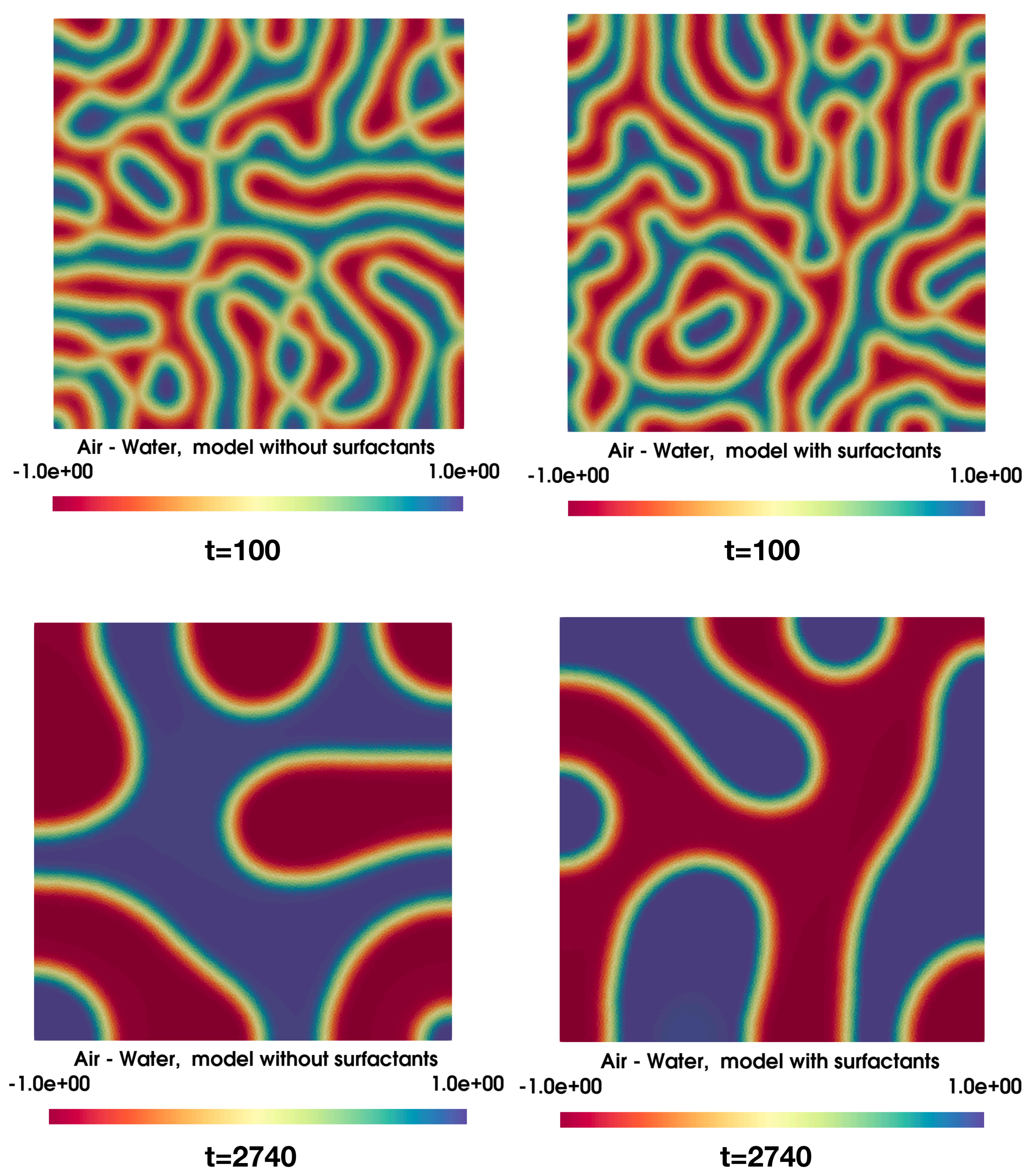
$\hookrightarrow$ Possible solutions: [2] or DDFV (Discrete Dual Finite Volume).

Numerical results

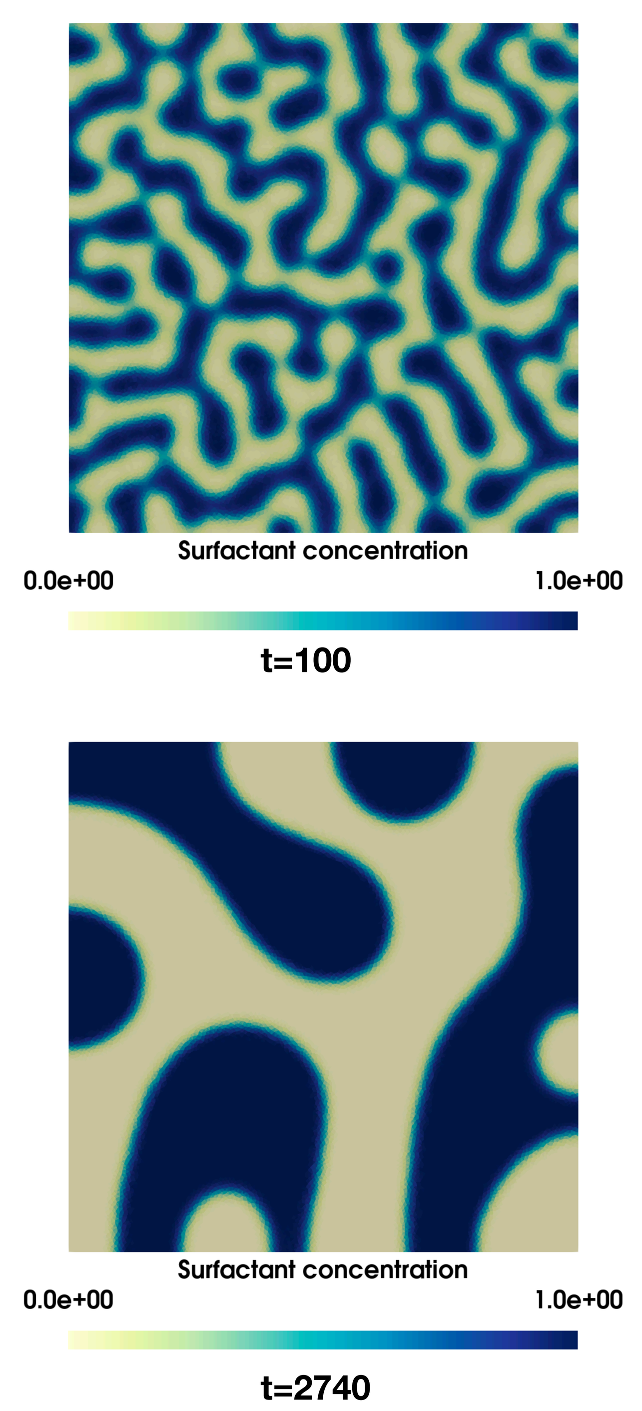
Surfactants distribution around one air bubble



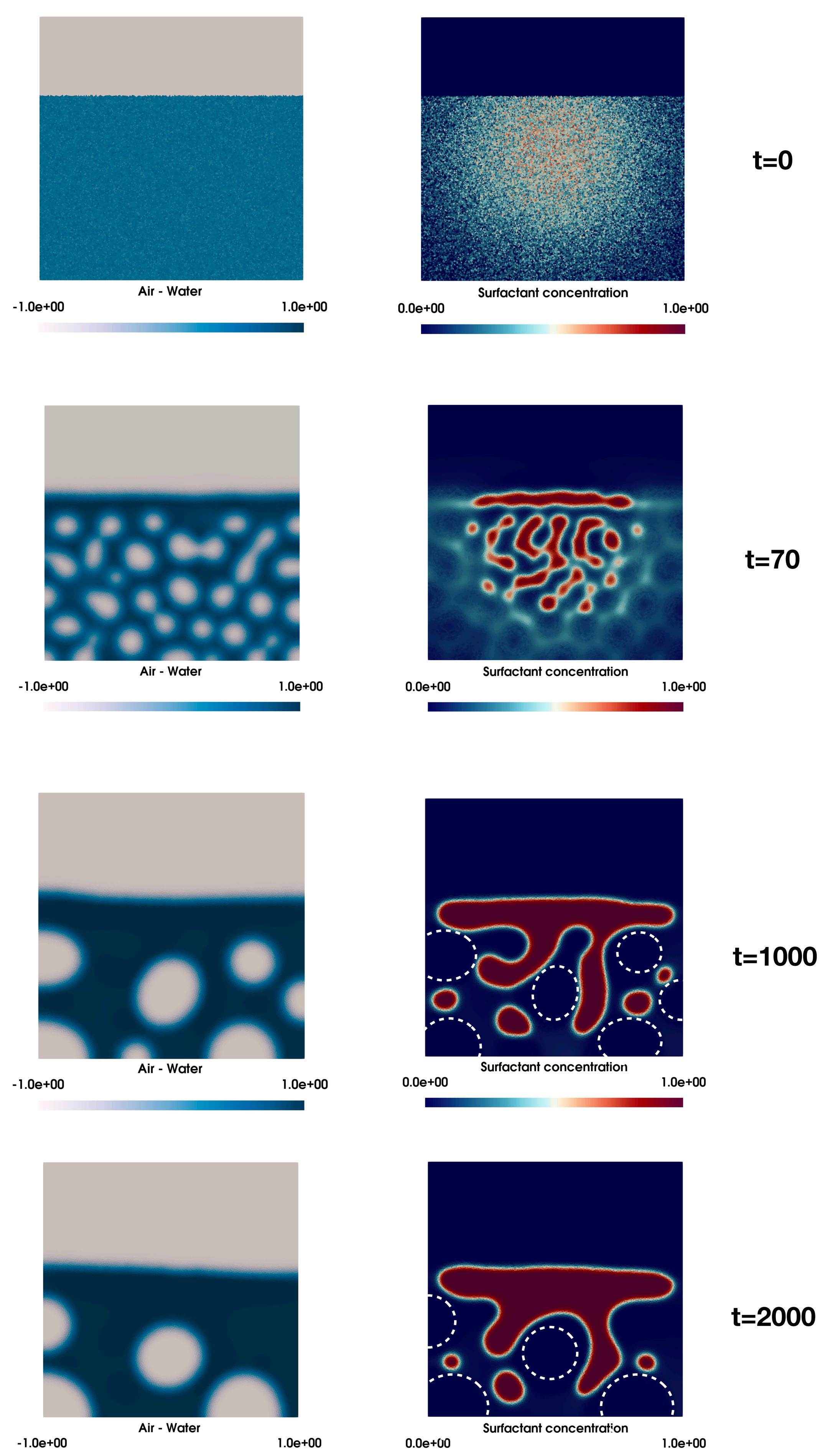
Comparison of Air-Water phase separation with vs without surfactants



Surfactant concentration for the model with surfactants



Surfactants distribution around multiple air bubbles



References

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[2] **Abdallah Bradji and Raphaèle Herbin.** "Discretization of coupled heat and electrical diffusion problems by finite-element and finite-volume methods". In: *IMA Journal of Numerical Analysis* 28.3 (2008), pp. 469–495.
[3] **Jun Zhang et al.** "Efficient, second oder accurate, and unconditionally energy stable numerical scheme for a new hydrodynamics coupled binary phase-field surfactant system". In: *Computer Physics Communications* 251 (2020).
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