ETH zürich

COMPUTATIONAL MECHANICS GROUP

Phase-field modeling of elastic microphase separation

Laura De Lorenzis, ETH Zürich

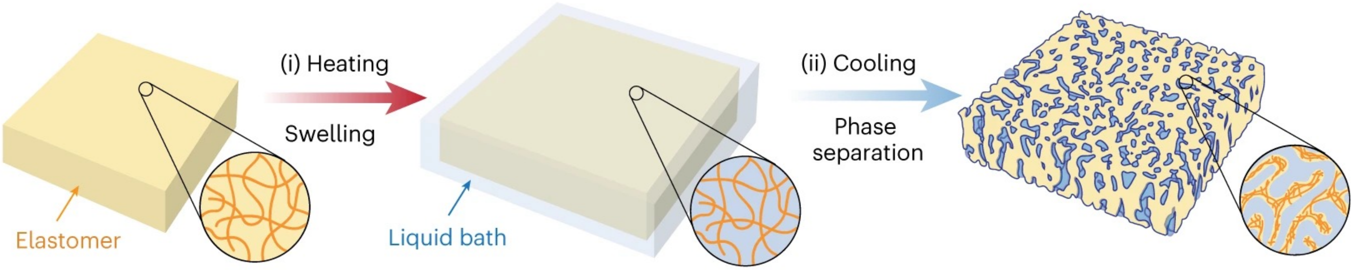
Joint work with **Hamza Oudich**, **Pietro Carrara**

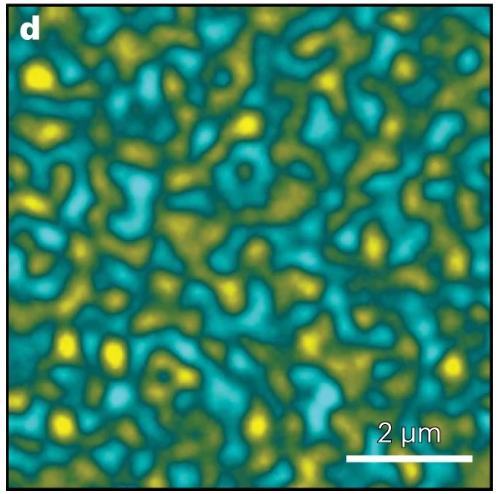
MPDE 2024, Prague, *27.09.2024*

Motivation: experiments

Elastic microphase separation

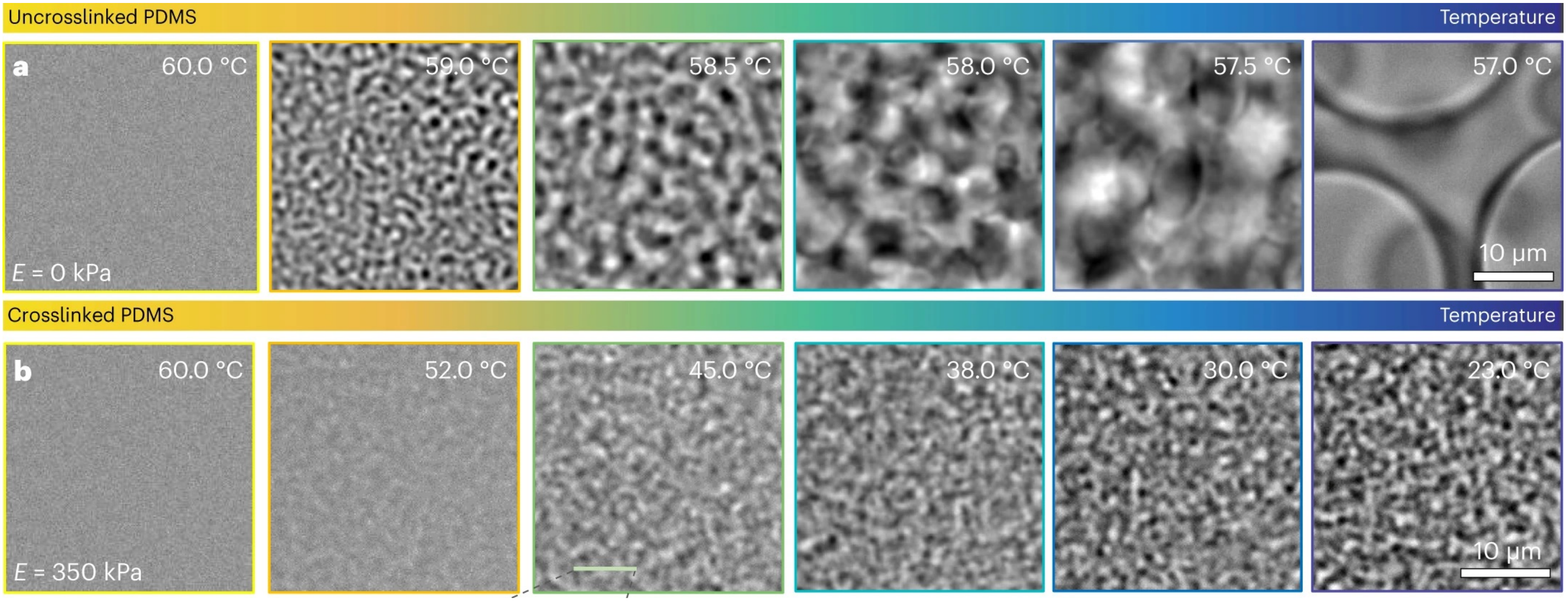
- Recent experiments [Fernández-Rico et al., Nat. Mater. 2023]





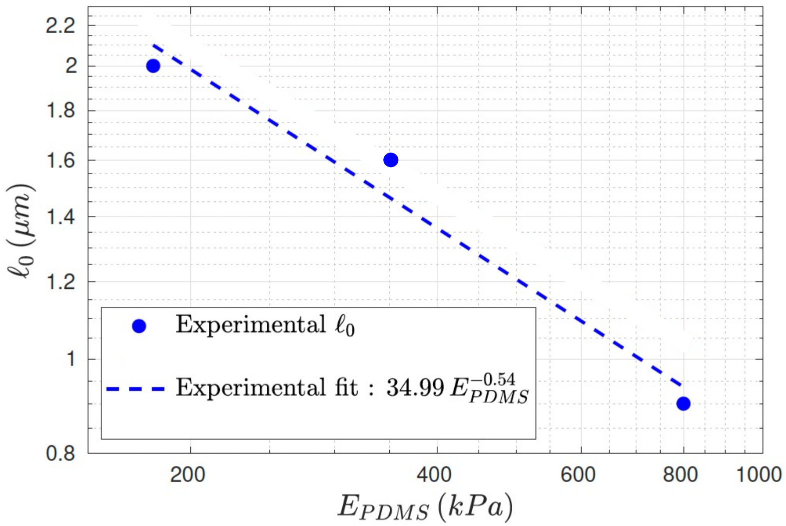
Elastic microphase separation

- Recent experiments [Fernández-Rico et al., Nat. Mater. 2023]



Elastic microphase separation

- Recent experiments [Fernández-Rico et al., Nat. Mater. 2023]



- But not clear whether what is observed is l_0 (initial characteristic length) or l_D (characteristic length at arrest)!

Modeling in 1D

Preliminaries

- Variable definition
  - Local volume fraction of oil φ, $0 \leq \varphi \leq 1$ (initial value φ_0)
  - Rescaled local volume fraction $\tilde{\phi} = 2\varphi - 1$, $-1 \leq \tilde{\phi} \leq 1$ (initial value $\tilde{\phi}_0 = 2\varphi_0 - 1$)
  - Phase-field variable $\phi = \tilde{\phi} - \tilde{\phi}_0 = 2\varphi - 1 - (2\varphi_0 - 1) = 2(\varphi - \varphi_0)$ (initial value $\phi_0 = 0$)

A model in 1D

- Free energy density

  - **Cahn-Hilliard**

$$\psi_{CH}(\phi, \phi_{,x}) = \overbrace{\frac{1}{2}\xi\phi^2 + \beta\phi^4}^{\psi_b(\phi)} + \overbrace{\frac{1}{2}\kappa\left|\phi_{,x}\right|^2}^{\psi_{int}(\phi_{,x})}$$

$$\xi = \frac{T_r - T_{inc}}{T_{inc}} < 0$$

  - **Cahn-Hilliard + elasticity**

$$\psi_{CH+E}(\phi, \phi_{,x}, \varepsilon) = \overbrace{\gamma\left(\frac{1}{2}\xi\phi^2 + \beta\phi^4\right)}^{\psi_b(\phi)} + \overbrace{\frac{1}{2}\gamma\kappa\left|\phi_{,x}\right|^2}^{\psi_{int}(\phi_{,x})} + \overbrace{\frac{1}{2}E(\phi)\varepsilon^2 - E_0\varepsilon_0(\varepsilon - \varepsilon_0)}^{\psi_{el}(\phi, \varepsilon)}$$

$$E(\phi) = E_0 + 2m_1\phi + 2m_2\phi^2$$

  - **Cahn-Oono + elasticity**

$$\psi_{CO+E}(\phi, \phi_{,x}, \varepsilon) = \overbrace{\gamma\left(\frac{1}{2}\xi\phi^2 + \beta\phi^4\right)}^{\psi_b(\phi)} + \overbrace{\frac{1}{2}\gamma\kappa\left|\phi_{,x}\right|^2}^{\psi_{int}(\phi_{,x})} + \overbrace{\frac{1}{2}E(\phi)\varepsilon^2 - E_0\varepsilon_0(\varepsilon - \varepsilon_0)}^{\psi_{el}(\phi, \varepsilon)} \overbrace{- \frac{\alpha}{4}\phi(x,t)\int_0^L \phi(s,t)\, g(x,s)\, ds}^{\psi_{conv}(\phi)}$$

$$g(x,s) = |x - s|$$

A model in 1D

- Chemical potential

$$\mu_{CH} = \frac{\partial \psi_b}{\partial \phi} - \frac{\partial}{\partial x}\left(\frac{\partial \psi_{int}}{\partial \phi_{,x}}\right) = \xi\phi + 4\beta\phi^3 - \kappa\phi_{,xx}$$

$$\mu_{CH+E} = \frac{\partial \psi_b}{\partial \phi} - \frac{\partial}{\partial x}\left(\frac{\partial \psi_{int}}{\partial \phi_{,x}}\right) + \frac{\partial \psi_{el}}{\partial \phi} = \gamma\left(\xi\phi + 4\beta\phi^3\right) - \gamma\kappa\phi_{,xx} + \left(m_1 + 2m_2\phi\right)\varepsilon^2$$

$$\mu_{CO+E} = \frac{\partial \psi_b}{\partial \phi} - \frac{\partial}{\partial x}\left(\frac{\partial \psi_{int}}{\partial \phi_{,x}}\right) + \frac{\partial \psi_{el}}{\partial \phi} + \frac{\partial \psi_{conv}}{\partial \phi} = \gamma\left(\xi\phi + 4\beta\phi^3\right) - \gamma\kappa\phi_{,xx} + \left(m_1 + 2m_2\phi\right)\varepsilon^2 - \frac{\alpha}{2}\int_0^L \phi\left(s,t\right)|x-s|$$

- Stress

$$\sigma = \frac{\partial \psi_{el}}{\partial \varepsilon} = E\left(\phi\right)\varepsilon - E_0\varepsilon_0$$

A model in 1D

- Governing equations in $\Omega = (0, L)$

$$\frac{\partial \phi}{\partial t} = -\frac{\partial J}{\partial x}$$

$$J = -M \frac{\partial \mu}{\partial x}$$

$$\Longrightarrow \begin{cases} \dfrac{\partial \phi}{\partial t} = M \left\{ \dfrac{\partial^2}{\partial x^2} \left[\gamma \left(\xi \phi + 4 \beta \phi^3 \right) - \gamma \kappa \phi_{,xx} + \left(m_1 + 2 m_2 \phi \right) \varepsilon^2 \right] - \alpha \phi \right\} \\ \dfrac{\partial \sigma}{\partial x} = 0 \end{cases}$$

$$\Longrightarrow \sigma(x,t) = E(\phi)\, \varepsilon - E_0 \varepsilon_0 \overset{!}{=} 0 \quad \forall x \in \Omega, t \in [0, T]$$

$$\Longrightarrow \boxed{\varepsilon = \frac{E_0}{E(\phi)} \varepsilon_0}$$

- Boundary and initial conditions

$$J(0,t) = J(L,t) = 0 \qquad u(0,t) = 0 \qquad \forall t \in [0, T]$$

$$\phi_{,x}(0,t) = \phi_{,x}(L,t) = 0 \qquad \sigma(L,t) = 0 \qquad \forall t \in [0, T]$$

$$\phi(x, 0) = \phi_0 = 0 \qquad \forall x \in \Omega$$

«Standard» Cahn-Hilliard + elasticity

- Free energy density, chemical potential, stress [Onuki et al. 1990, Zhu et al. 2001, Garcke et al. 2005]

$$\psi^{st}_{CH+E}\left(\phi,\phi_{,x},\varepsilon\right)=\frac{1}{2}\xi\phi^2+\beta\phi^4+\frac{1}{2}\kappa\left|\phi_{,x}\right|^2+\frac{1}{2}E\left(\phi\right)\left(\varepsilon-\varepsilon_0-\frac{\Omega}{2}\phi\right)^2$$

$$\mu^{st}_{CH+E}=\frac{\partial\psi_b}{\partial\phi}-\frac{\partial}{\partial x}\left(\frac{\partial\psi_{int}}{\partial\phi_{,x}}\right)+\frac{\partial\psi^{st}_{el}}{\partial\phi}=\xi\phi+4\beta\phi^3-\kappa\phi_{,xx}+\frac{1}{2}E'\left(\phi\right)\left(\varepsilon-\varepsilon_0-\frac{\Omega}{2}\phi\right)^2-E\left(\phi\right)\frac{\Omega}{2}\left(\varepsilon-\varepsilon_0-\frac{\Omega}{2}\phi\right)$$

$$\sigma^{st}=\frac{\partial\psi^{st}_{el}}{\partial\varepsilon}=E\left(\phi\right)\left(\varepsilon-\varepsilon_0-\frac{\Omega}{2}\phi\right)$$

no coupling in 1D

- Governing equations (+ same initial and boundary conditions)

$$\frac{\partial\phi}{\partial t}=M\frac{\partial^2}{\partial x^2}\left[\xi\phi+4\beta\phi^3-\kappa\phi_{,xx}+\frac{1}{2}E'\left(\phi\right)\left(\varepsilon-\varepsilon_0-\frac{\Omega}{2}\phi\right)^2-E\left(\phi\right)\frac{\Omega}{2}\left(\varepsilon-\varepsilon_0-\frac{\Omega}{2}\phi\right)\right]$$

$$\frac{\partial\sigma}{\partial x}=0\qquad\Longrightarrow\qquad\sigma^{st}\left(x,t\right)=E\left(\phi\right)\left(\varepsilon-\varepsilon_0-\frac{\Omega}{2}\phi\right)\overset{!}{=}0\quad\forall x\in\Omega,t\in[0,T]\qquad\Longrightarrow\qquad\varepsilon=\varepsilon_0+\frac{\Omega}{2}\phi$$

Linear stability analysis

- Linearized mass balance equation ($\phi_0 + \delta\phi = \delta\phi$)

$$\frac{\partial \delta\phi}{\partial t} = M\left[h_0 \frac{\partial^2 \delta\phi}{\partial x^2} - \gamma\kappa \frac{\partial^4 \delta\phi}{\partial x^4} - \alpha\delta\phi\right] \qquad h_0 = \gamma\xi + \left(2m_2 - 4\frac{m_1^2}{E_0}\right)\varepsilon_0^2$$

- Take $\delta\phi = e^{\omega t + ikx} \implies \omega = -M\left(h_0 k^2 + \gamma\kappa k^4 + \alpha\right)$ wave dispersion equation

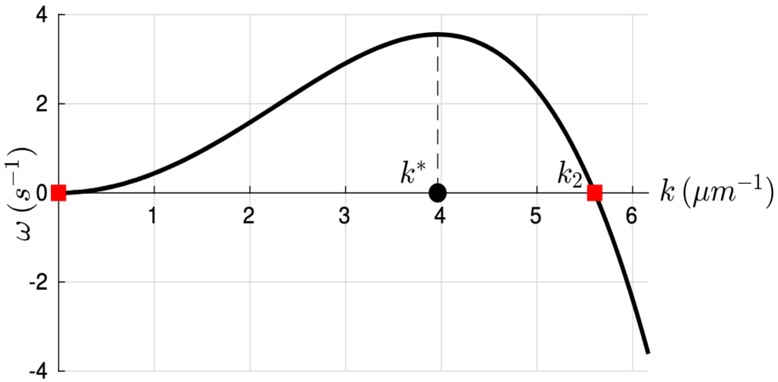
Cahn-Hilliard + elasticity ($\alpha = 0$)

$h_0 > 0 \implies \omega < 0 \implies$ no spinodal decomposition

$h_0 < 0 \implies \omega > 0$ for $k \in (0, k_2)$, $k_2 = -\frac{\xi}{\kappa} - \left(2m_2 - 4\frac{m_1^2}{E_0}\right)\frac{\varepsilon_0^2}{\gamma\kappa}$

$$l_0 \sim \frac{2\pi}{k^*} = 2\pi\sqrt{-\frac{2\gamma\kappa}{h_0}} = 2\pi\sqrt{-\frac{2\kappa}{\xi + \left(2\frac{m_2}{\gamma} - 4\frac{m_1^2}{\gamma E_0}\right)\varepsilon_0^2}}$$

$$\tau \sim \frac{2\pi}{\omega\left(k^*\right)} = \frac{8\pi\gamma\kappa}{M h_0^2} = \frac{8\pi\kappa}{M\gamma\left[\xi + \left(2\frac{m_2}{\gamma} - 4\frac{m_1^2}{\gamma E_0}\right)\varepsilon_0^2\right]^2}$$



Linear stability analysis

- Linearized mass balance equation ($\phi_0 + \delta\phi = \delta\phi$)

$$\frac{\partial \delta\phi}{\partial t} = M\left[h_0 \frac{\partial^2 \delta\phi}{\partial x^2} - \gamma\kappa \frac{\partial^4 \delta\phi}{\partial x^4} - \alpha\delta\phi\right] \qquad h_0 = \gamma\xi + \left(2m_2 - 4\frac{m_1^2}{E_0}\right)\varepsilon_0^2$$

- Take $\delta\phi = e^{\omega t + ikx} \implies \omega = -M\left(h_0 k^2 + \gamma\kappa k^4 + \alpha\right)$ wave dispersion equation

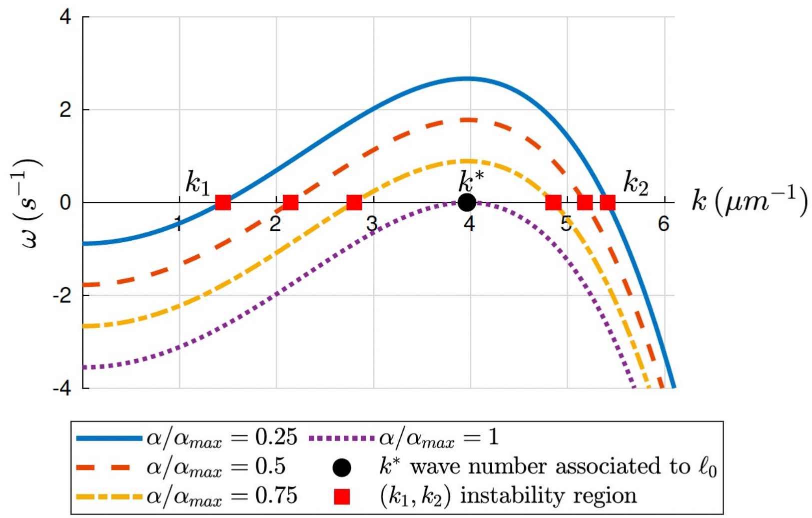
Cahn-Oono + elasticity ($\alpha > 0$)

$\omega > 0$ for $k \in (k_1, k_2)$, $k_{1/2} = \sqrt{\frac{-h_0 \mp \sqrt{h_0^2 - 4\alpha\gamma\kappa}}{2\gamma\kappa}}$

with $\alpha < \alpha_{max} = \frac{1}{4\gamma\kappa}\left\{\gamma\xi + \left[2m_2 - 4\frac{m_1^2}{E_0}\right]\varepsilon_0^2\right\}^2$

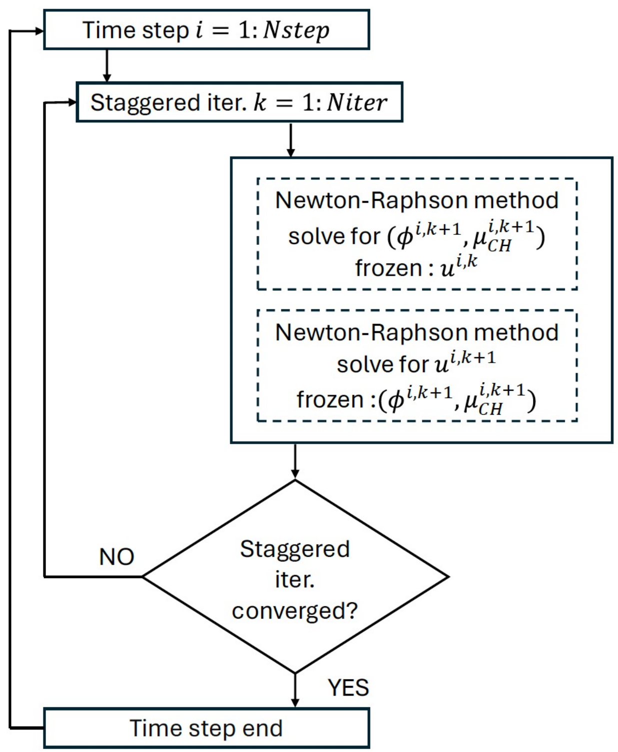
$$l_0 \sim \frac{2\pi}{k^*} = 2\pi\sqrt{-\frac{2\gamma\kappa}{h_0}} = 2\pi\sqrt{-\frac{2\kappa}{\xi + \left(2\frac{m_2}{\gamma} - 4\frac{m_1^2}{\gamma E_0}\right)\varepsilon_0^2}}$$ same as before!

$$\tau \sim \frac{2\pi}{\omega(k^*)} = \frac{8\pi\gamma\kappa}{M\left(h_0^2 - 4\alpha\gamma\kappa\right)}$$



Numerical implementation

- Mixed formulation (unknowns u, μ, ϕ)
- Finite element discretization in space
- Backward Euler in time
- Staggered solution algorithm
- Adaptive time stepping

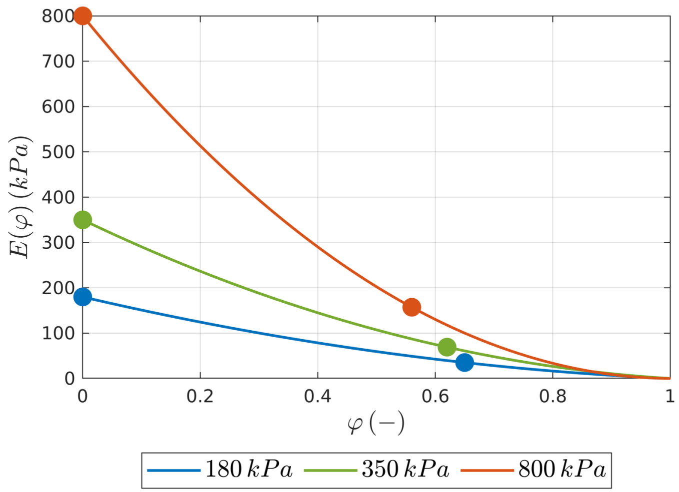


Parameter calibration

$$\psi_{CO+E}(\phi,\phi_{,x},\varepsilon)=\gamma\left(\frac{1}{2}\xi\phi^2+\beta\phi^4\right)+\frac{1}{2}\gamma\kappa\left|\phi_{,x}\right|^2+\frac{1}{2}E(\phi)\,\varepsilon^2-E_0\varepsilon_0(\varepsilon-\varepsilon_0)-\frac{\alpha}{4}\phi(x,t)\int_0^L\phi(s,t)\,g(x,s)\,ds$$

$$E(\phi)=E_0+2m_1\phi+2m_2\phi^2$$

- $\xi=\dfrac{T_r-T_{inc}}{T_{inc}}$, ε_0, E_0 from experiments
- m_1, m_2, from experiments through interpolation

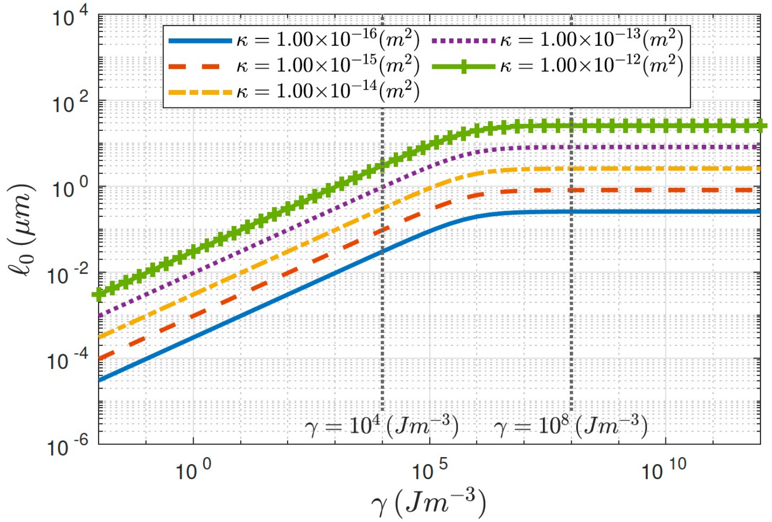


Parameter calibration

$$\psi_{CO+E}\left(\phi,\phi_{,x},\varepsilon\right)=\gamma\left(\frac{1}{2}\xi\phi^2+\beta\phi^4\right)+\frac{1}{2}\gamma\kappa\left|\phi_{,x}\right|^2+\frac{1}{2}E\left(\phi\right)\varepsilon^2-E_0\varepsilon_0\left(\varepsilon-\varepsilon_0\right)-\frac{\alpha}{4}\phi\left(x,t\right)\int_0^L\phi\left(s,t\right)g\left(x,s\right)ds$$

$$E\left(\phi\right)=E_0+2m_1\phi+2m_2\phi^2$$

- $\xi=\dfrac{T_r-T_{inc}}{T_{inc}}$, ε_0, E_0 from experiments
- m_1, m_2, from experiments through interpolation
- γ chosen in the range where results are influenced by elasticity
- κ chosen to match experimental and numerical l_0 for $E_{PDMS}=350kPa$

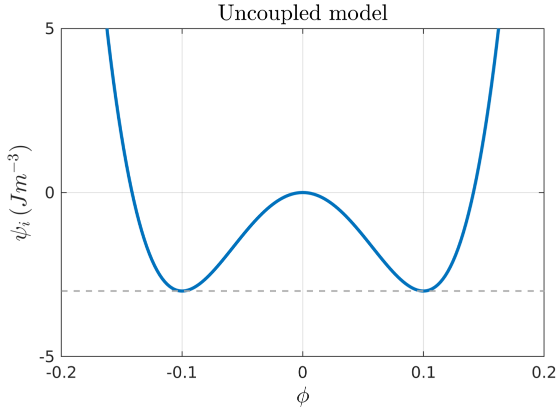


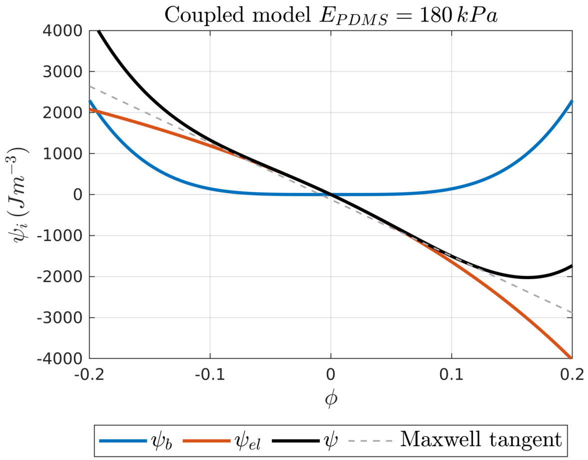
Parameter calibration

$$\psi_{CO+E}(\phi,\phi_{,x},\varepsilon)=\gamma\left(\frac{1}{2}\xi\phi^2+\beta\phi^4\right)+\frac{1}{2}\gamma\kappa\left|\phi_{,x}\right|^2+\frac{1}{2}E(\phi)\,\varepsilon^2-E_0\varepsilon_0(\varepsilon-\varepsilon_0)-\frac{\alpha}{4}\phi(x,t)\int_0^L\phi(s,t)\,g(x,s)\,ds$$

$$E(\phi)=E_0+2m_1\phi+2m_2\phi^2$$

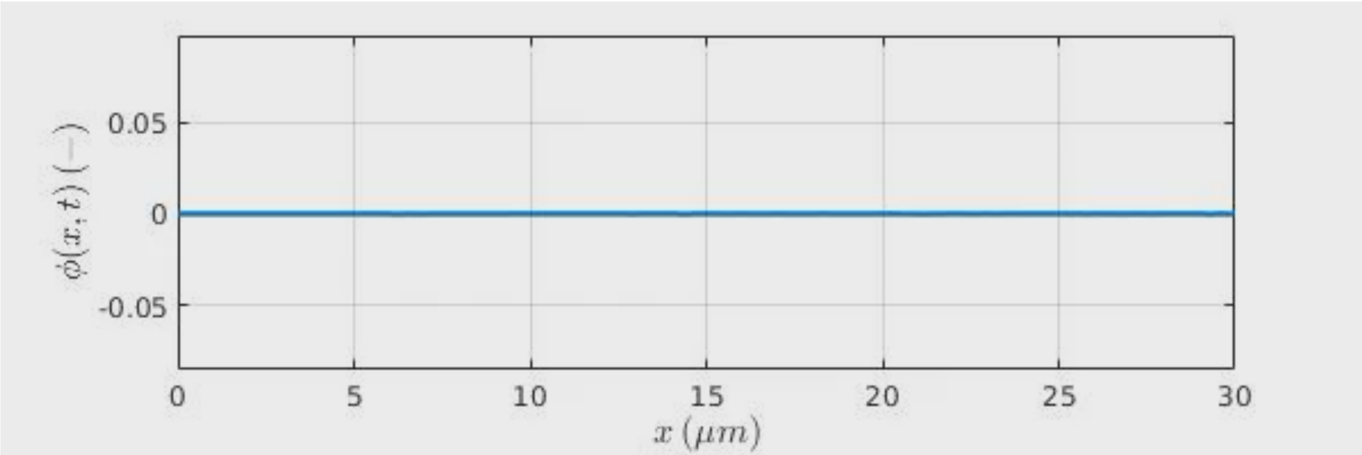
- $\xi=\dfrac{T_r-T_{inc}}{T_{inc}}$, ε_0, E_0 from experiments
- m_1, m_2, from experiments through interpolation
- γ chosen in the range where results are influenced by elasticity
- κ chosen to match experimental and numerical l_0 for $E_{PDMS}=350kPa$
- β chosen to match experimental binodal points $\phi=\pm0.1$
- α used for parametric study





Numerical results

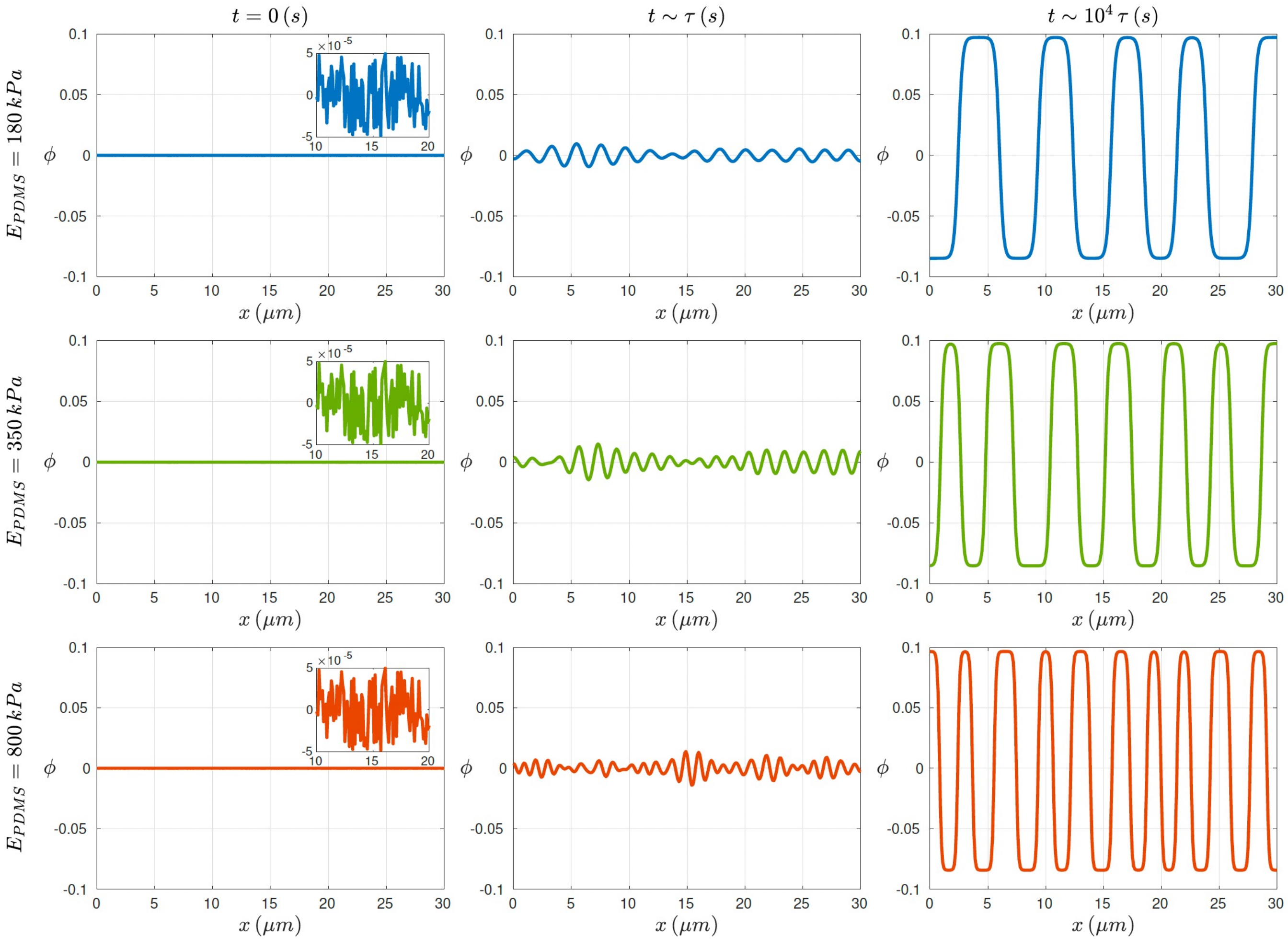
- Cahn-Hilliard + elasticity ($\alpha = 0$)



$E_{PDMS} = 180kPa$

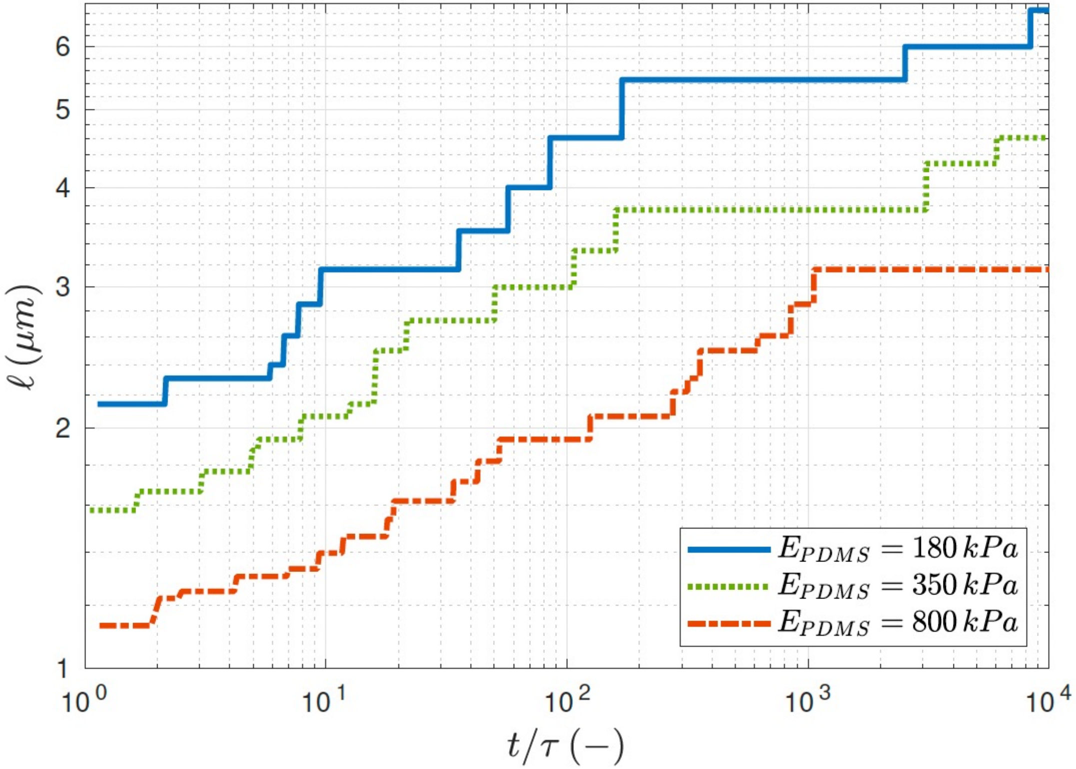
Numerical results

- Cahn-Hilliard + elasticity ($\alpha = 0$)



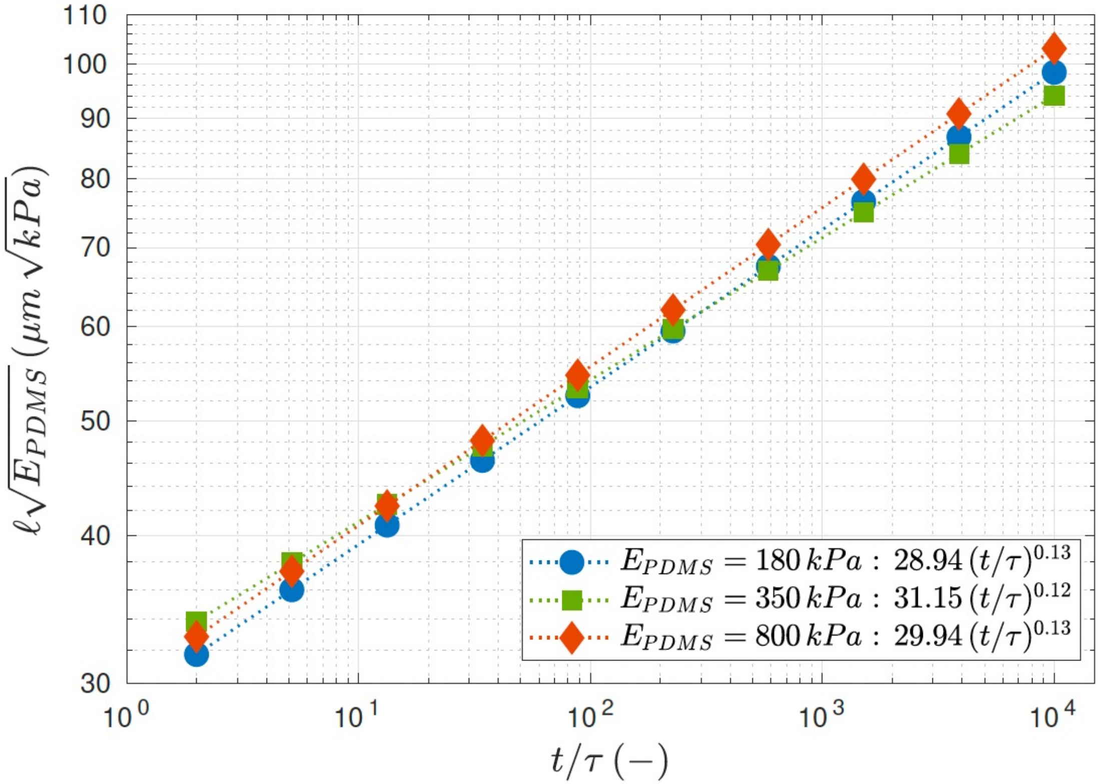
Numerical results

- Cahn-Hilliard + elasticity ($\alpha = 0$)



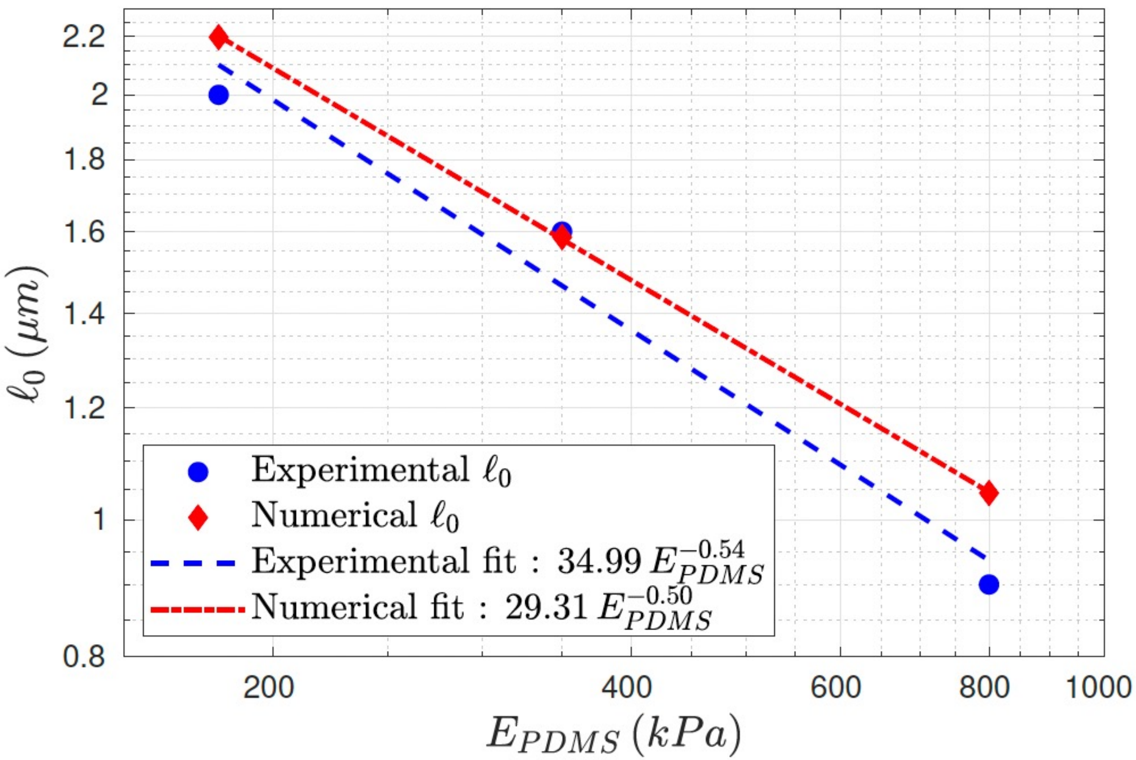
Numerical results

- Cahn-Hilliard + elasticity ($\alpha = 0$)



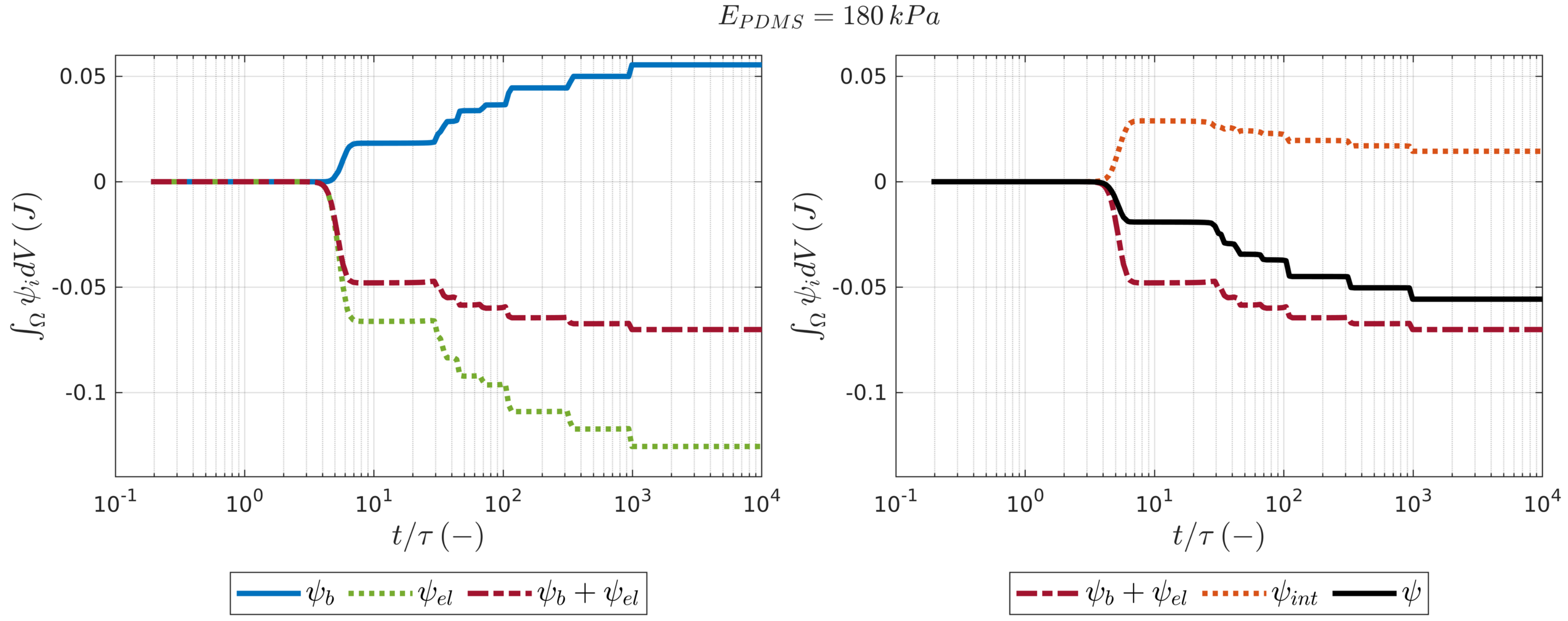
Numerical results

- Cahn-Hilliard + elasticity ($\alpha = 0$)



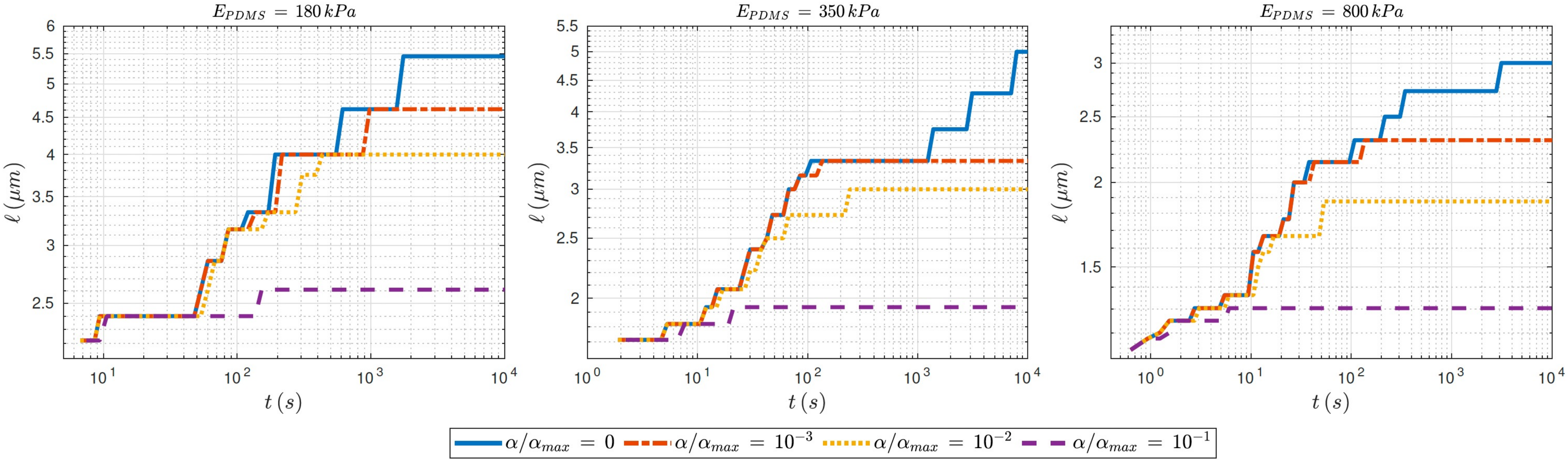
Numerical results

- Cahn-Hilliard + elasticity ($\alpha = 0$)



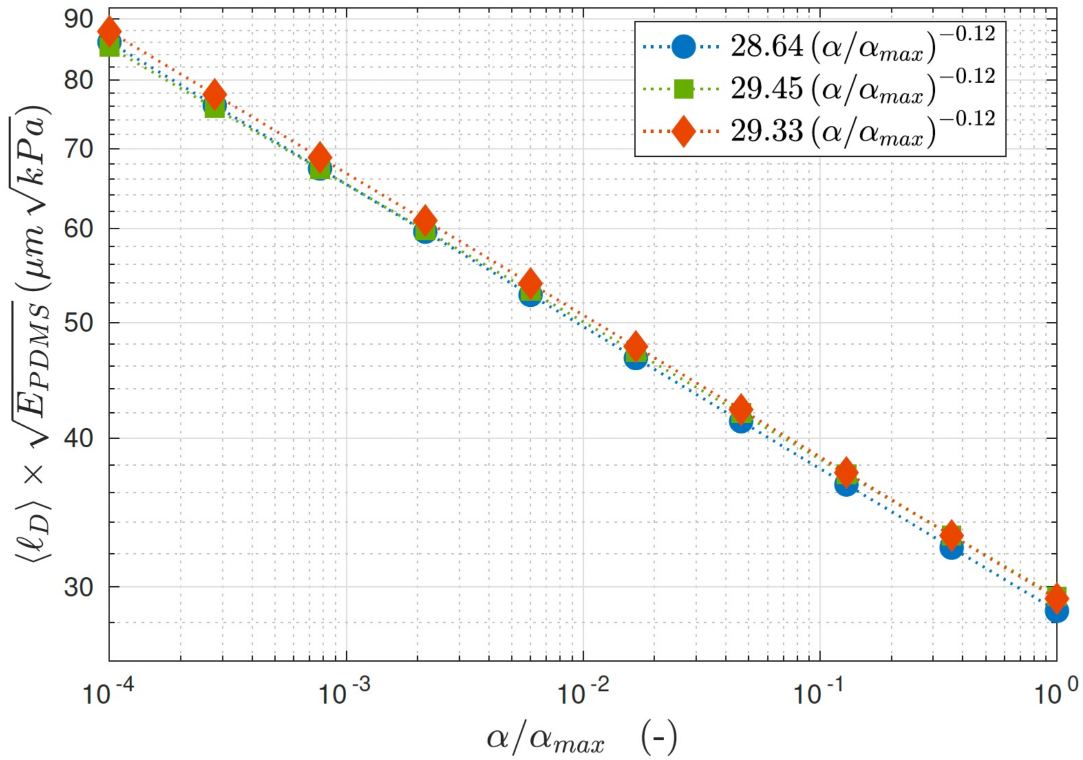
Numerical results

- Cahn-Oono + elasticity ($\alpha > 0$)



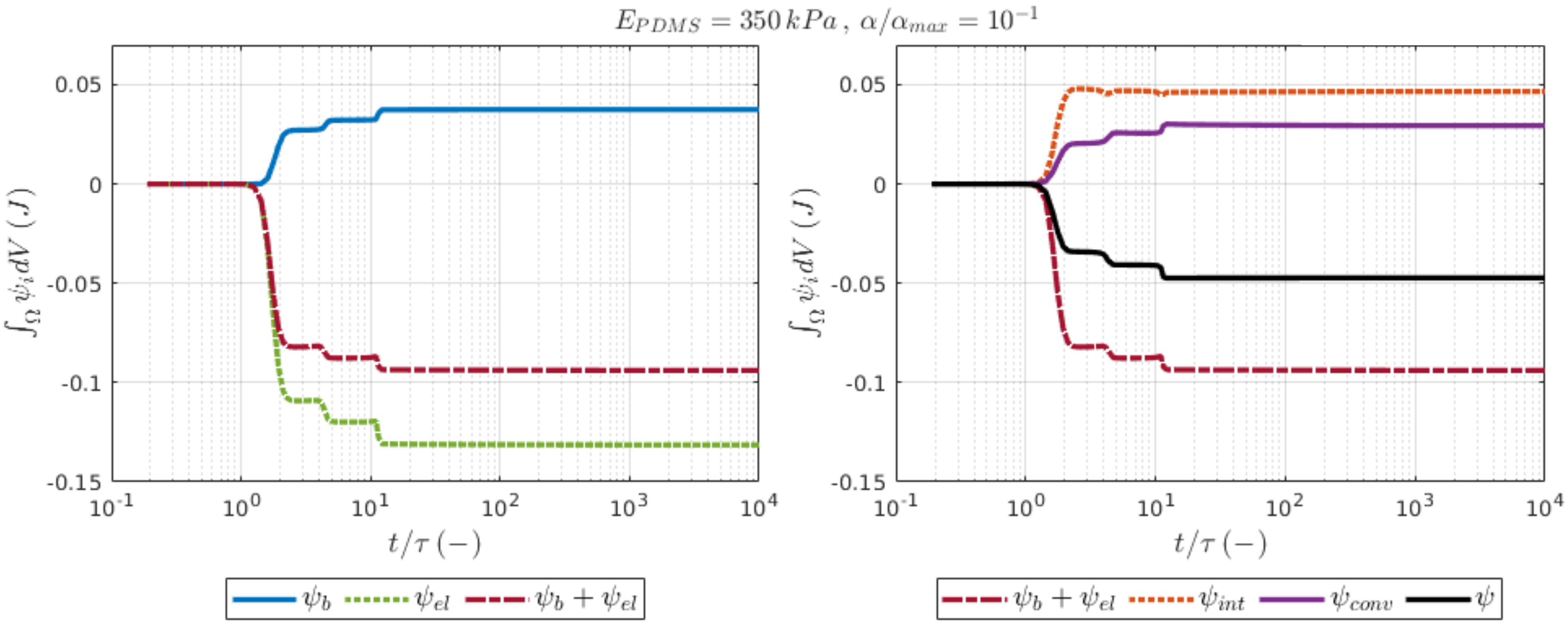
Numerical results

- Cahn-Oono + elasticity ($\alpha > 0$)



Numerical results

- Cahn-Oono + elasticity ($\alpha > 0$)



ETH zürich

Modeling in 2D

Extension to 2D

- Free energy density
  - **Cahn-Hilliard**

$$\psi_{CH}(\phi,\nabla\phi) = \underbrace{\frac{1}{2}\xi\phi^2 + \beta\phi^4}_{\psi_b(\phi)} + \underbrace{\frac{1}{2}\kappa\left|\nabla\phi\right|^2}_{\psi_{int}(\nabla\phi)}$$

$$\xi = \frac{T_r - T_{inc}}{T_{inc}} < 0$$

  - **Cahn-Hilliard + elasticity**

$$\psi_{CH+E}(\phi,\nabla\phi,\boldsymbol{\varepsilon}) = \underbrace{\gamma\left(\frac{1}{2}\xi\phi^2 + \beta\phi^4\right)}_{\psi_b(\phi)} + \underbrace{\frac{1}{2}\gamma\kappa\left|\nabla\phi\right|^2}_{\psi_{int}(\nabla\phi)} + \underbrace{\frac{1}{2}\lambda(\phi)\,\mathrm{tr}^2(\boldsymbol{\varepsilon}) + G(\phi)\,\boldsymbol{\varepsilon}\cdot\boldsymbol{\varepsilon} - \lambda_0\mathrm{tr}(\boldsymbol{\varepsilon}_0)\,\mathrm{tr}(\boldsymbol{\varepsilon}) - 2G_0\boldsymbol{\varepsilon}_0\cdot\boldsymbol{\varepsilon}}_{\psi_{el}(\phi,\boldsymbol{\varepsilon})}$$

  - **Cahn-Oono + elasticity**

$$\psi_{CO+E}(\phi,\nabla\phi,\boldsymbol{\varepsilon}) = \underbrace{\gamma\left(\frac{1}{2}\xi\phi^2 + \beta\phi^4\right)}_{\psi_b(\phi)} + \underbrace{\frac{1}{2}\gamma\kappa\left|\nabla\phi\right|^2}_{\psi_{int}(\nabla\phi)} + \underbrace{\frac{1}{2}\lambda(\phi)\,\mathrm{tr}^2(\boldsymbol{\varepsilon}) + G(\phi)\,\boldsymbol{\varepsilon}\cdot\boldsymbol{\varepsilon} - \lambda_0\mathrm{tr}(\boldsymbol{\varepsilon}_0)\,\mathrm{tr}(\boldsymbol{\varepsilon}) - 2G_0\boldsymbol{\varepsilon}_0\cdot\boldsymbol{\varepsilon}}_{\psi_{el}(\phi,\boldsymbol{\varepsilon})} \underbrace{- \frac{\alpha}{4}\phi(\mathbf{x},t)\int_\Omega \phi(\mathbf{s},t)\,g(\mathbf{x},\mathbf{s})\,d\mathbf{s}}_{\psi_{conv}(\phi)}$$

Extension to 2D

- Chemical potential

$$\mu_{CH} = \frac{\partial \psi_b}{\partial \phi} - \nabla \cdot \left(\frac{\partial \psi_{int}}{\partial \nabla \phi} \right) = \xi \phi + 4\beta \phi^3 - \kappa \Delta \phi$$

$$\mu_{CH+E} = \frac{\partial \psi_b}{\partial \phi} - \nabla \cdot \left(\frac{\partial \psi_{int}}{\partial \nabla \phi} \right) + \frac{\partial \psi_{el}}{\partial \phi} = \gamma \left[\xi \phi + 4\beta \phi^3 \right] - \gamma \kappa \Delta \phi + \left[b_1 + 2b_2 \phi \right] \mathrm{tr}^2 \left(\boldsymbol{\varepsilon} \right) + \left[g_1 + 2g_2 \phi \right] \boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}$$

$$\mu_{CO+E} = \frac{\partial \psi_b}{\partial \phi} - \nabla \cdot \left(\frac{\partial \psi_{int}}{\partial \nabla \phi} \right) + \frac{\partial \psi_{el}}{\partial \phi} + \frac{\partial \psi_{conv}}{\partial \phi} = \gamma \left[\xi \phi + 4\beta \phi^3 \right] - \gamma \kappa \Delta \phi + \left[b_1 + 2b_2 \phi \right] \mathrm{tr}^2 \left(\boldsymbol{\varepsilon} \right) + \left[g_1 + 2g_2 \phi \right] \boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon} - \frac{\alpha}{2} \int_\Omega \phi \left(\mathbf{s}, t \right) g \left(\mathbf{x}, \mathbf{s} \right) d\mathbf{s}$$

- Stress

$$\boldsymbol{\sigma} = \frac{\partial \psi_{el}}{\partial \boldsymbol{\varepsilon}} = \lambda \left(\phi \right) \mathrm{tr} \left(\boldsymbol{\varepsilon} \right) \mathbf{I} + 2G \left(\phi \right) \boldsymbol{\varepsilon} - \lambda_0 \mathrm{tr} \left(\boldsymbol{\varepsilon}_0 \right) \mathbf{I} - 2G_0 \boldsymbol{\varepsilon}_0$$

$$\nu = 0.45 \qquad \lambda \left(\phi \right) = \lambda_0 + 2b_1 \phi + 2b_2 \phi^2 \qquad G \left(\phi \right) = G_0 + g_1 \phi + g_2 \phi^2 \quad \Longrightarrow \quad b_i = \frac{\nu m_i}{\left(1 + \nu \right) \left(1 - 2\nu \right)} \qquad g_i = \frac{m_i}{\left(1 + \nu \right)}$$

Extension to 2D

- Governing equations in Ω

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot \mathbf{J} \qquad \Longrightarrow \qquad \frac{\partial \phi}{\partial t} = \nabla \cdot (\mathbf{M} \nabla \mu)$$

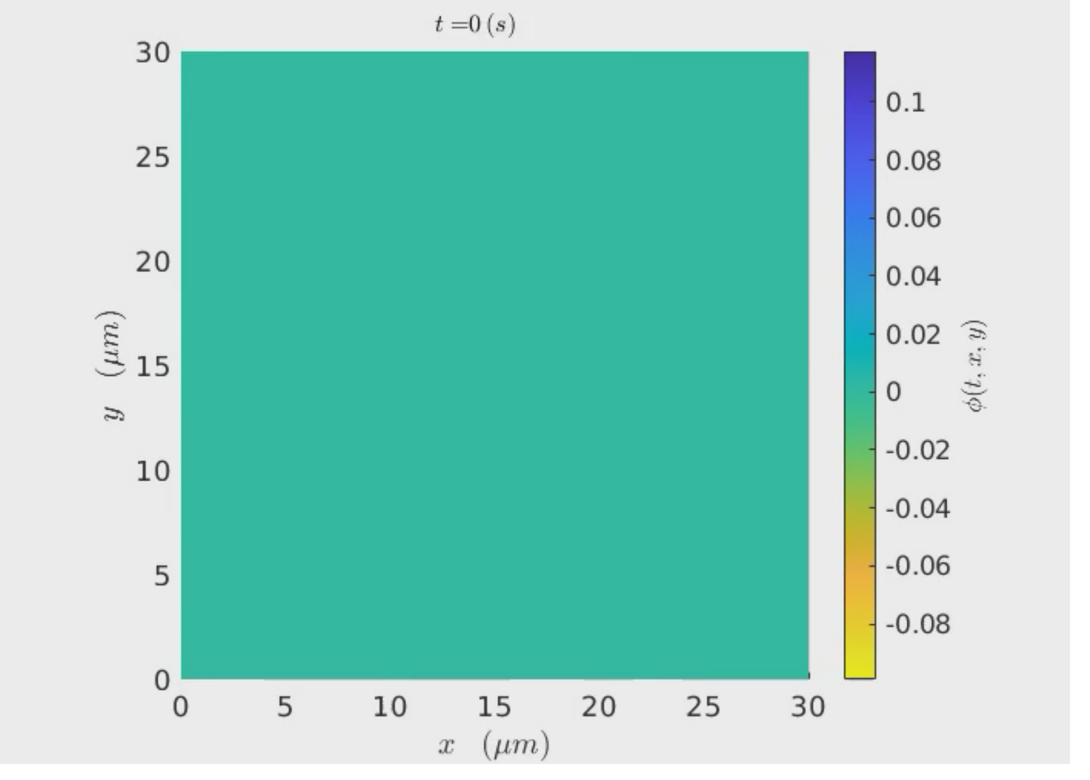
$$\mathbf{J} = -\mathbf{M} \nabla \mu \qquad\qquad \nabla \cdot \boldsymbol{\sigma} = \mathbf{0}$$

$$\mathbf{M} = M \mathbf{I} \qquad \Longrightarrow \qquad \frac{\partial \phi}{\partial t} = M \Delta \mu$$

- Boundary and initial conditions
  - Periodic on ϕ
  - Zero average stress

Numerical results

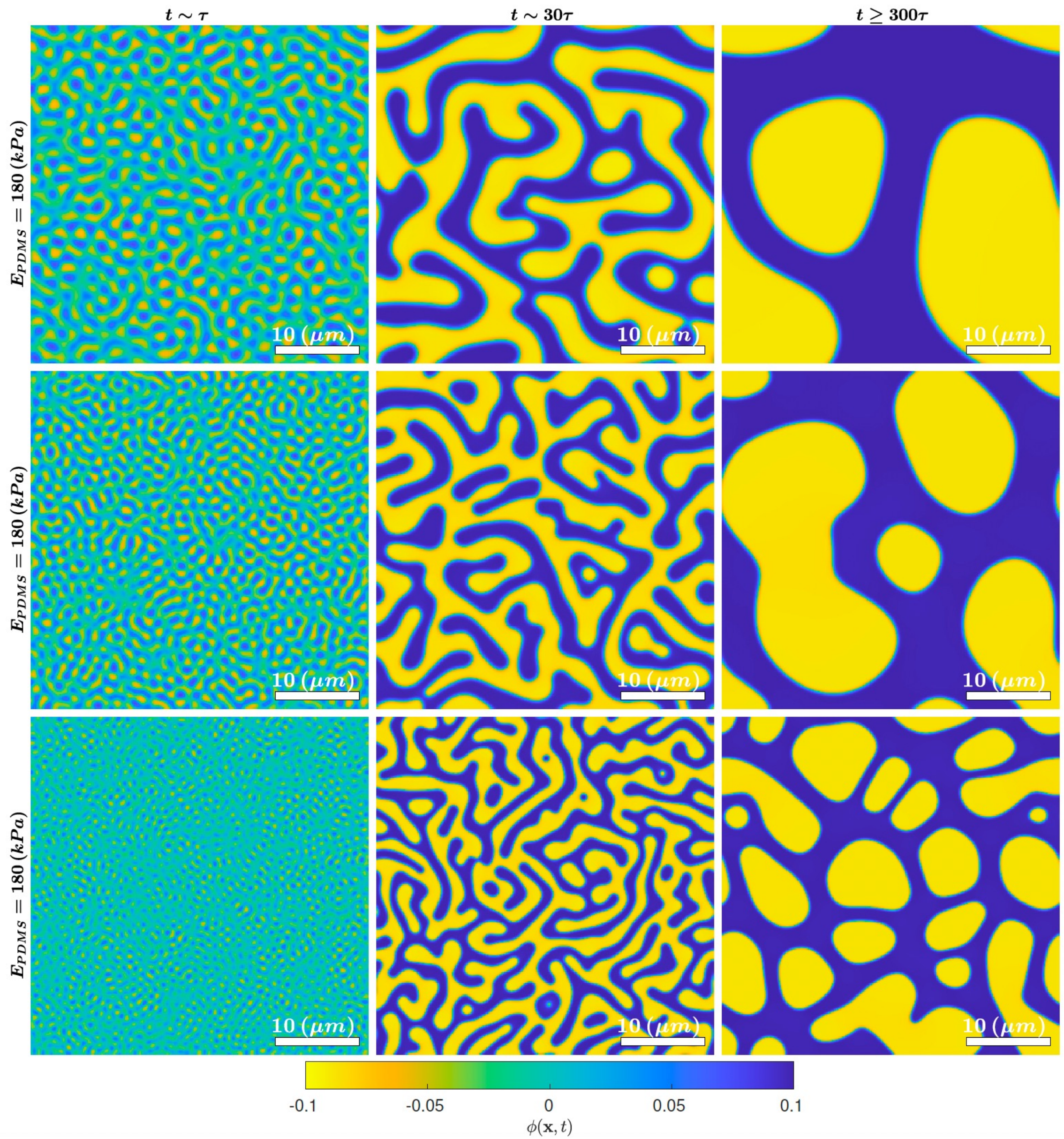
- Cahn-Hilliard + elasticity ($\alpha = 0$)



$E_{PDMS} = 180kPa$

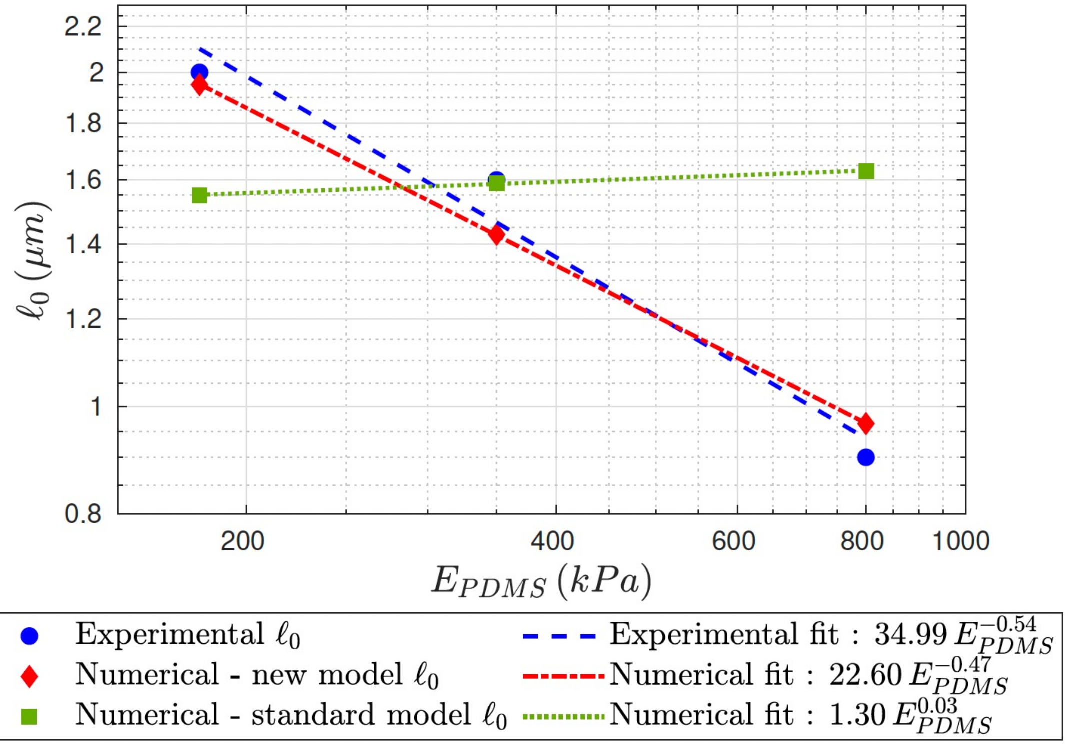
Numerical results

- Cahn-Hilliard + elasticity ($\alpha = 0$)



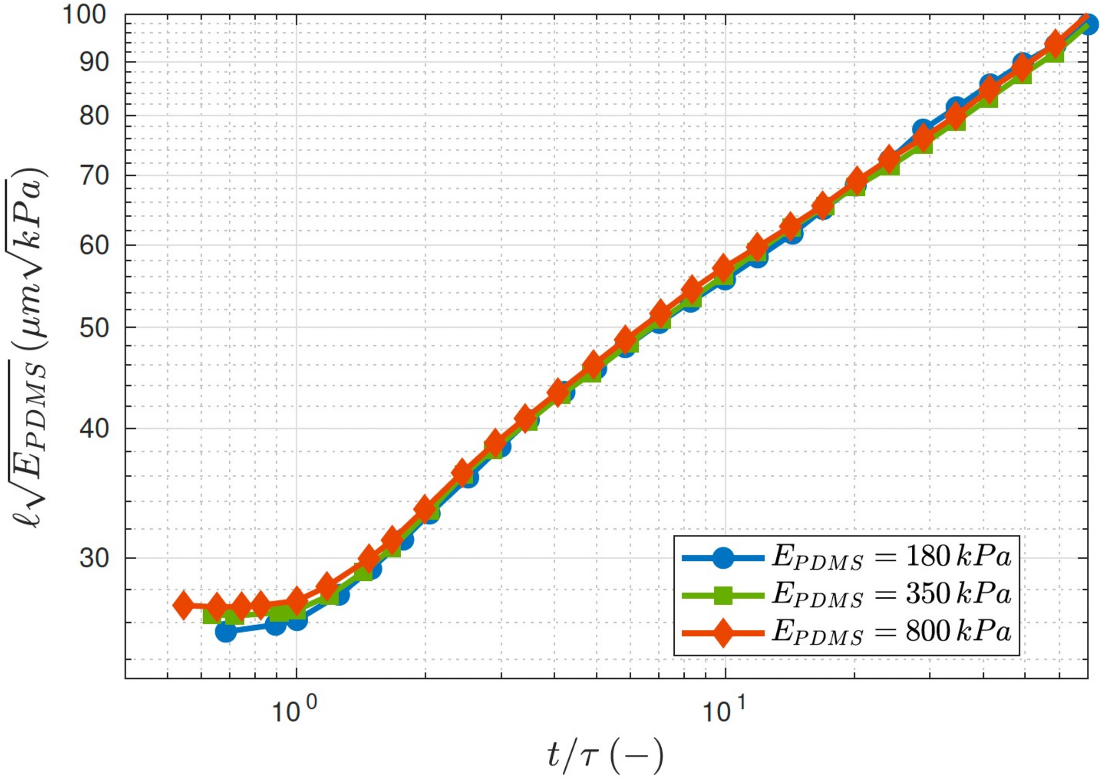
Numerical results

- Cahn-Hilliard + elasticity ($\alpha = 0$)



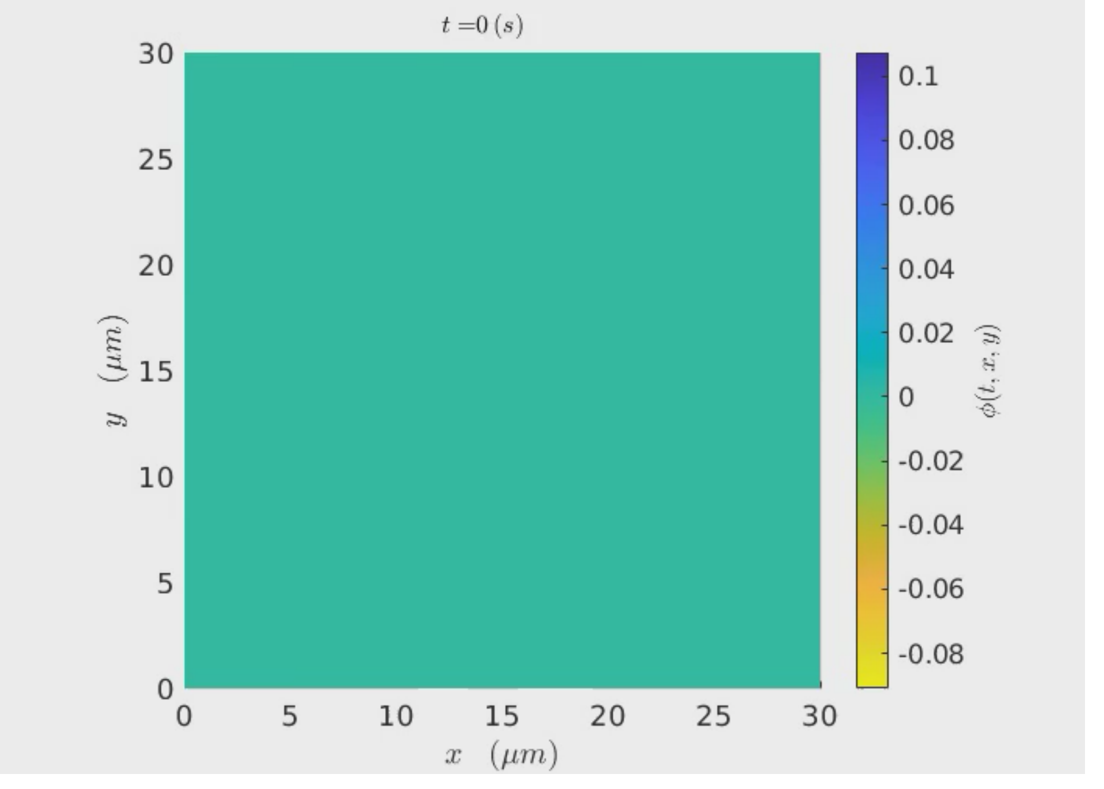
Numerical results

- Cahn-Hilliard + elasticity ($\alpha = 0$)



Numerical results

- Cahn-Oono + elasticity ($\alpha > 0$)

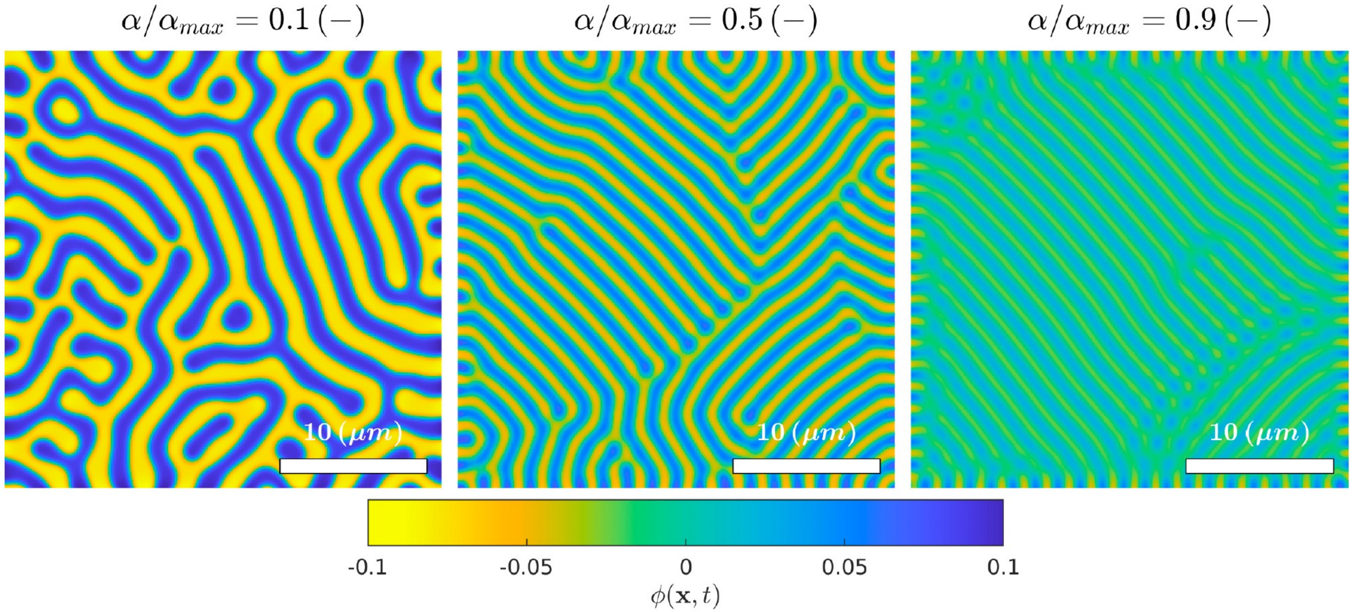


ETH zürich

$E_{PDMS} = 180kPa,\ \alpha/\alpha_{max} = 0.1$

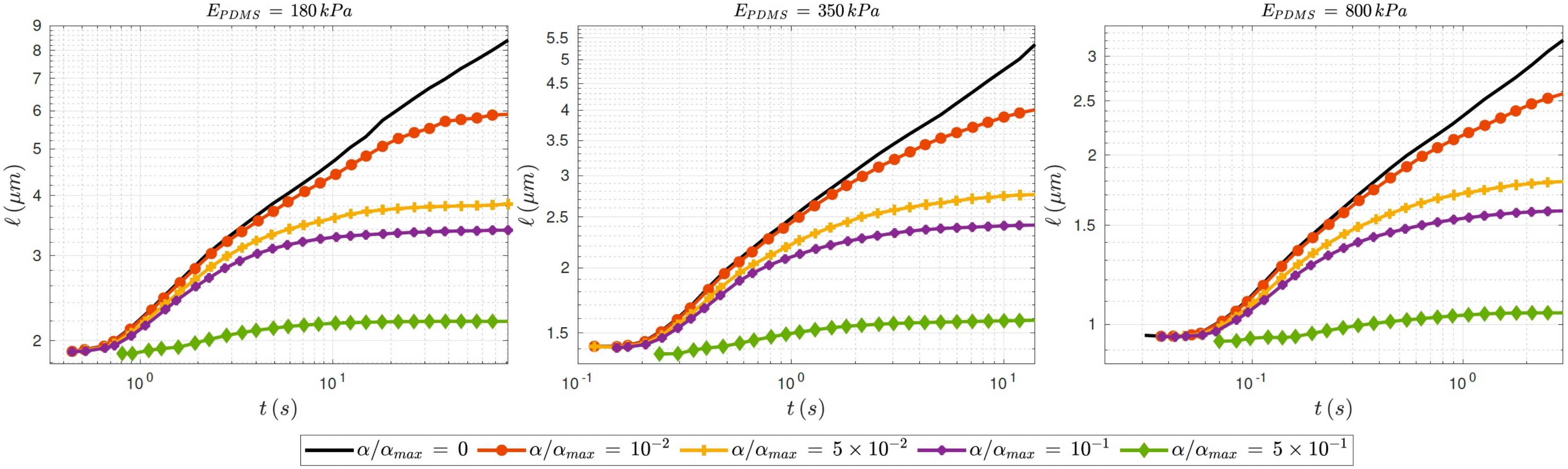
Numerical results

- Cahn-Oono + elasticity ($\alpha > 0$)



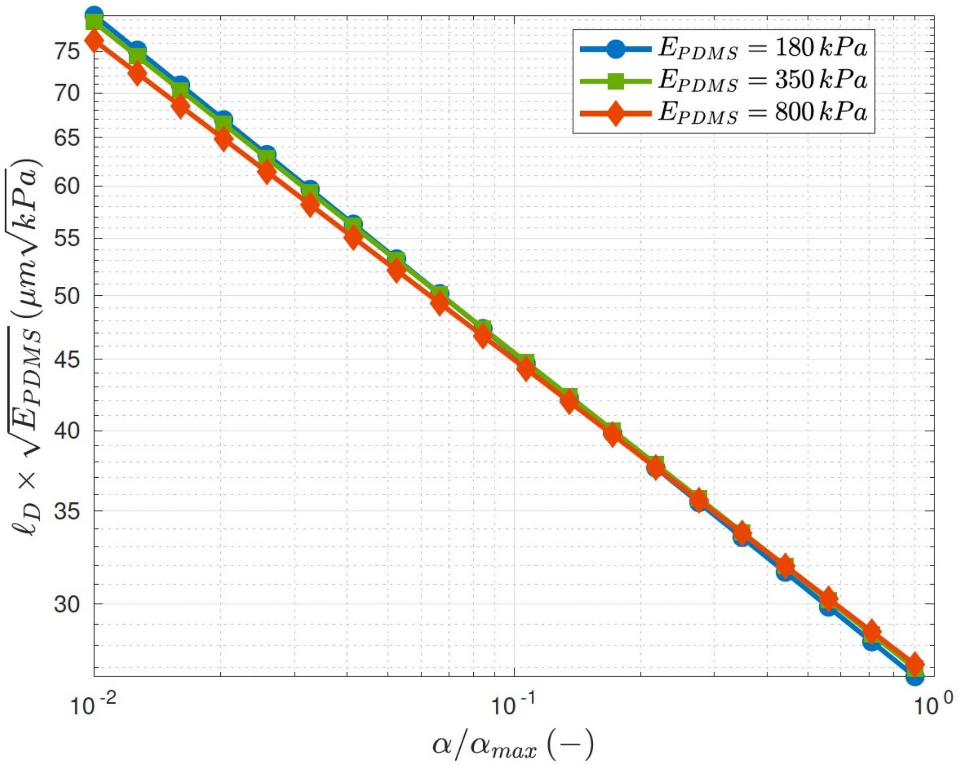
Numerical results

- Cahn-Oono + elasticity ($\alpha > 0$)



Numerical results

- Cahn-Oono + elasticity ($\alpha > 0$)



Conclusions

Conclusions

- Elasticity seems to play an important role on spinodal decomposition in some polymers
- We proposed a new model which combines the Cahn-Hilliard equation with
  - a non-standard elasticity coupling term, which reproduces the **scaling of the initial characteristic length** with the elastic modulus of the matrix
  - a long-range (Cahn-Oono) interaction term, which reproduces the **arrest** of the spinodal decomposition and the **scaling of the characteristic length at arrest** with the elastic modulus of the matrix
- Further analyses needed to better understand the model
- Further experiments needed to better understand the physics of the phenomenon