Phase separation dynamics in deformable droplets

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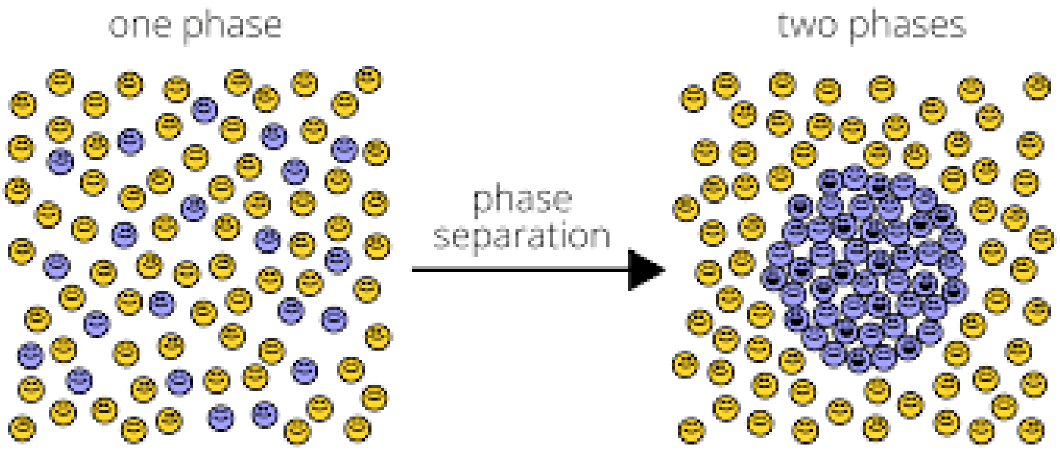
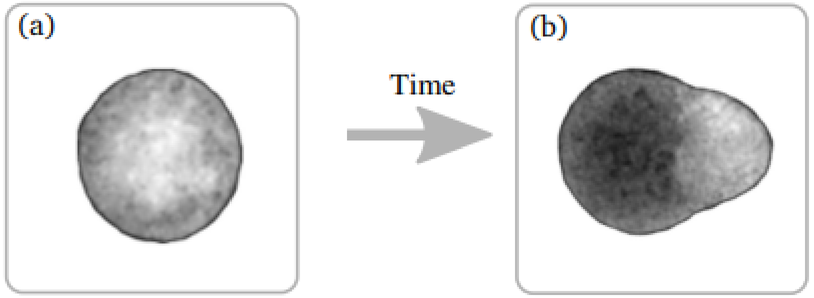
Phase Separation

- Phase Separation process
  - Ostwald ripening $\longrightarrow$ $\lambda \sim t^{\frac{1}{3}}$
  - Advection with hydrodynamic flows
    - speed up domain coarsening $\longrightarrow$ $\lambda \sim t$



- Phase separation has been used for industrial process and to study some biological systems.
  - The interior of biological cells is organized in part through fluid compartments that can emerge from phase separation.

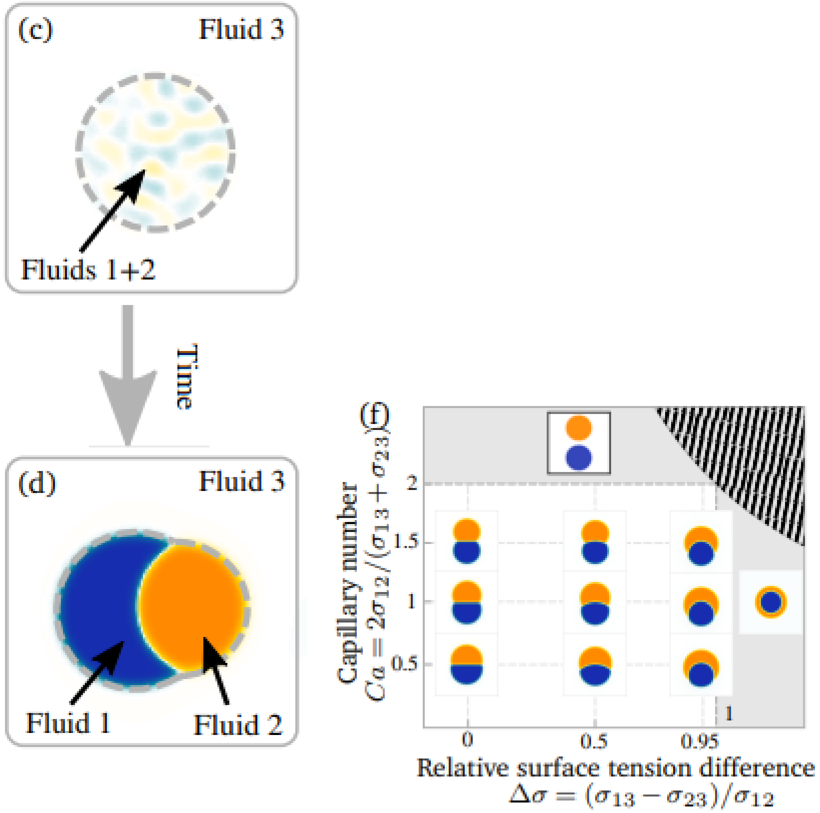
Phase Separation of Biological Tissues



(a,b) Microscopy images of cell aggregates mimicking early vertebrate development, taken 1 day apart from each other.

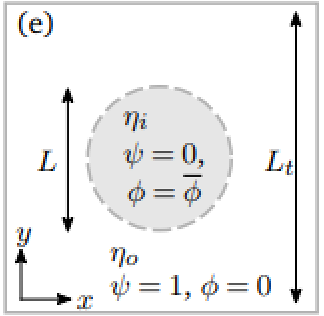
- Aggregates of stem cells
- Spherical aggregates
- Form polarized structures with different cell populations
- Mimic vertebrate development
- Study how this agregated system formation

Ternary phase separating system

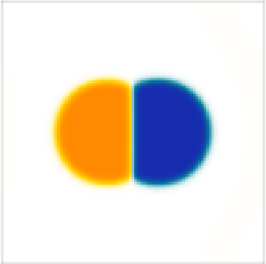


- Initial state where fluids 1 and 2 are almost homogeneously mixed inside of a spherical droplet
- Passive dynamic
- Droplet made out of two fluid phases is submerged in a third fluid phase
- Thermodynamic equilibrium is drive by the ratio of :
  - Interface tension σ_{12}
  - Surface tensions σ_{13} and σ_{23}
- Equilibrium at: $\sigma_{12} < \sigma_{13} + \sigma_{23}$ or $|\sigma_{13} - \sigma_{23}| < \sigma_{12}$

Numerically study



(e) Schematic representation of the physical configuration.



- 2D hybrid finite-volume Lattice-Boltzmann simulations
- Coupled Cahn-Hilliard and Stokes equations
- Peclet number P_e
  - Characterizes the magnitude of hydrodynamic advection comparing to diffusive effects
- Increasing P_e make the phase separation process faster
- Intermediate P_e make a long “croissant” state
  - Slowing the separated state
- The results are not changed by the surface tensions

σ_{13} and σ_{23}

Model: Free Energy

- 2D ternary system with area fractions C_j

$$C_1 + C_2 + C_3 = 1$$

- Free energy os the phase separation

$$\mathcal{F} = \int_{\Omega} \Big[\frac{\kappa_1}{2} C_1^2 (1 - C_1)^2 + \frac{\kappa_2}{2} C_2^2 (1 - C_2)^2 + \frac{\kappa_3}{2} C_3^2 (1 - C_3)^2 + \frac{\kappa_1'}{2} (\nabla C_1)^2 + \frac{\kappa_2'}{2} (\nabla C_2)^2 + \frac{\kappa_3'}{2} (\nabla C_3)^2 \Big] \mathrm{d}A.$$

Local minima at $C_j = 0$ and $C_j = 1$

κ_j is the energy density scale

- Third area fraction vanishes

$$\alpha_{jk} = \sqrt{\frac{\kappa_j' + \kappa_k'}{\kappa_j + \kappa_k}}$$

$\alpha = \alpha_{jk}$

(Interface width)

$$\sigma_{jk} = \frac{\alpha_{jk}}{6} (\kappa_j + \kappa_k)$$

(Surface tension)

Model: Dynamic Equations

Dynamics of the area fractions Cj $\longrightarrow$ $C_1 + C_2 + C_3 = 1$

Phase Fields ϕ and ψ

$\phi = C_1 - C_2$ and $\psi = C_3$

Expressing the Free energy in terms of the phase fields

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (\boldsymbol{u}\phi) = \nabla \cdot \left([1-\psi]\Gamma_\phi \nabla \mu_\phi \right) \quad (1.a)$$

$$\frac{\partial \psi}{\partial t} + \nabla \cdot (\boldsymbol{u}\psi) = \nabla \cdot \left(\Gamma_\psi \nabla \mu_\psi \right), \quad (1.b)$$

Where t is time, **u** is the local field velocity, Γ_ϕ and Γ_ψ mobility parameters and $\mu_\phi = {}^{\delta\mathcal{F}}/_{\delta\phi}$, $\mu_\psi = {}^{\delta\mathcal{F}}/_{\delta\psi}$ are the Chemical potentials.

Eq (1.a) ensures that fluids 1 and 2 do not diffuse to fluid 3

Hydrodynamic effect $\longrightarrow$ Incompressible Newtonian fluid $\longrightarrow$ incompressible Stokes' eq

$$0 = \nabla \cdot \boldsymbol{u}, \quad (2.a)$$

$$0 = -\nabla \Pi + \nabla \cdot (2\eta \boldsymbol{S}) - \phi \nabla \mu_\phi - \psi \nabla \mu_\psi. \quad (2.b)$$

Where Π fluid pressure, η fluid viscosity, $\boldsymbol{S}$ is the shear-rate tensor $\boldsymbol{S} = (\nabla u + (\nabla u)^T)/2$

Model: Initial and Boundary Condition

Initial the 2D system

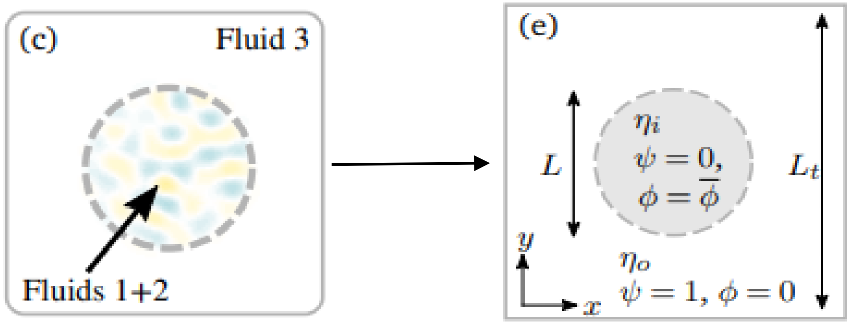


Table 1 Values of dimensionless parameters used in our simulations

parameter	$\bar{\phi}$	L/α	Ca	Pe_ψ	η_i/η_o	$\Delta\phi_{IC}$	L_t/L
value	0	64	1	15/32	20	0.01	2

parameter	$\Delta x/\alpha$	$\Delta t/(\Delta x \eta_i/\sigma_{12})$
value	1	1/640

- L = droplet diameter, L_t = chamber lenght
- Fluids 1 and 2 with $\psi = 0$ and fluid 3 with $\psi = 1$ and $\phi = 0$
- The inside of the droplet is initialize with $\phi = \bar{\phi} + \Delta\phi_{IC}\xi,$
- $\bar{\phi} = \int_\Omega (1-\psi)\phi \, \mathrm{d}A / \int_\Omega (1-\psi)\, \mathrm{d}A.$ is the conserved area average of ϕ
- ξ is the zero-mean, delta-correlated Gaussian white noise.

Model: Dimensionless Parameter

Equilibrium state:

parameter	$\bar{\phi}$	L/α	Ca
value	0	64	1

The equilibrium state depends on four dimensionless parameters:

- $\bar{\phi}$ is the area fractions between fluids 1 and 2. $\longrightarrow$ $\bar{\phi} = 0$
- Ratio between droplet size L and interface width $\longrightarrow$ $\frac{L}{\alpha} = 64$
- The equilibrium state also depends on the three tensions σ_{jk}

$$Ca = \frac{2\sigma_{12}}{\sigma_{13} + \sigma_{23}}, \qquad \Delta\sigma = \frac{\sigma_{13} - \sigma_{23}}{\sigma_{12}}.$$

C_a is the Capillary number = ratio between the inner and outer surface tensions controls the deformability of the droplet due to capillary effects.

$\Delta\sigma$ quantifies the surface tension difference between fluids 1 and 2 with respect to fluid 3.

- $0 \leq \Delta\sigma < 1$
- Equilibrium state is a dipole structure

Model: Dimensionless Parameter

Relaxation dynamic

The four phenomenological coefficients $\Gamma_\phi,\ \Gamma_\psi,\ \eta_i\ and\ \eta_0$ affect only the relaxation dynamics

- Peclet number that compares advective fluxes due to hydrodynamic flows to the diffusive fluxes

$$Pe = \frac{L\alpha}{\Gamma_\phi \eta_i}. \longleftrightarrow Pe = \tau_D/\tau_A$$

τ_D is the diffusive time and τ_A is the advective time

- Peclet number with respect to the ψ field $\quad Pe_\psi = \alpha^2/(\Gamma_\psi \eta_i).$

Have a small value to ensure that the outer droplet interface remains stable during the simulation

- Fix the viscosity ratio between droplet and the surrounding fluid
  - This ratio do not strongly affect the simulation if

$$\eta_i/\eta_0 \gtrsim 10$$

Pe_ψ	η_i/η_o
$15/32$	20

Results: Advection Speeds up the Polarization Process

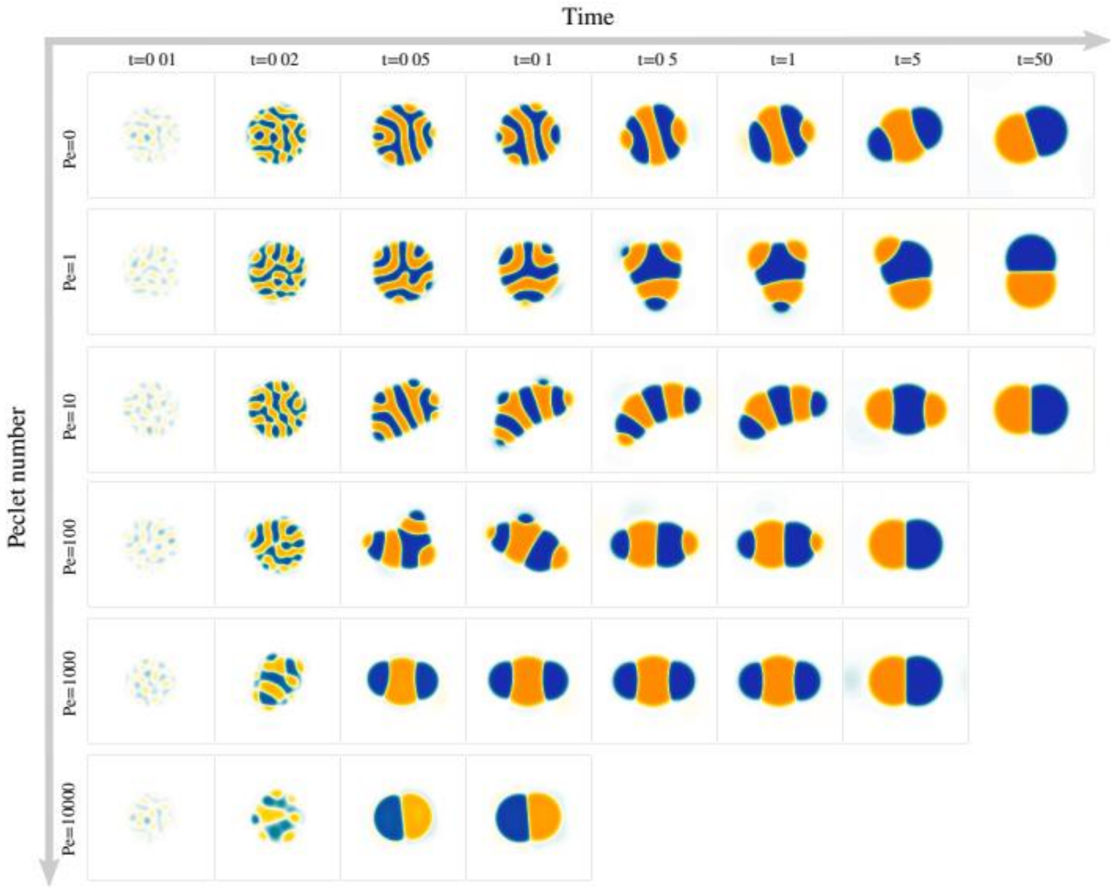


Fig. 2 Advection affects the coarsening dynamics and the time to reach the polarized equilibrium state. For each value of the Peclet number, a time series of snapshots is shown, representing the ϕ field from -1 (blue) to 1 (orange). Here we set $\Delta\sigma = 0$, i.e. the outer surface tension is independent of ϕ.

Results: Advection Speeds up the Polarization Process

Peclet number growth:

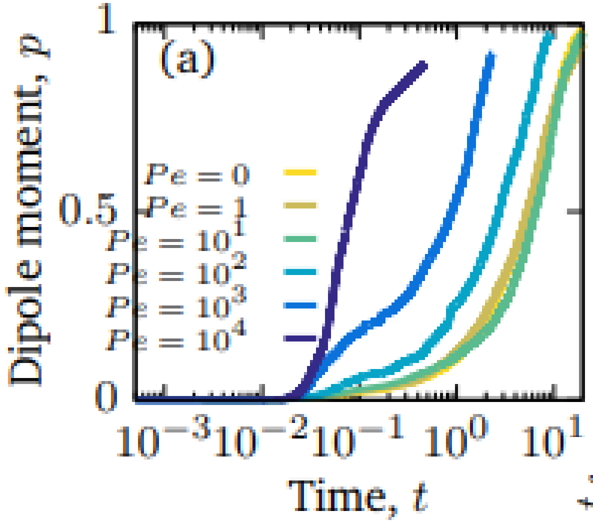
Measure the time evolution of a dipole moment

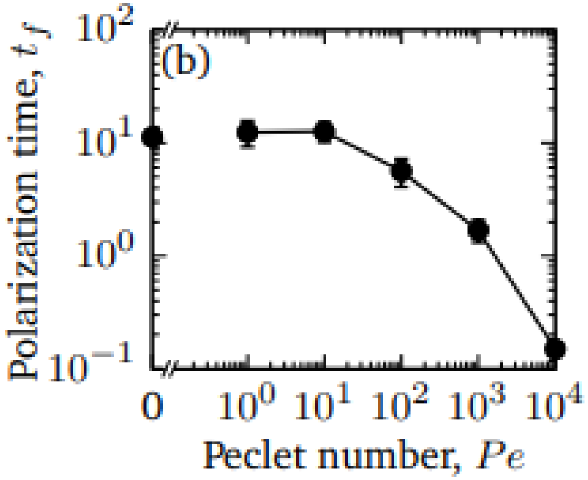
$$\boldsymbol{P}(t) = \int_{\Omega} (1-\psi)\phi\,(\boldsymbol{x}-\boldsymbol{c})\,\mathrm{d}A.$$

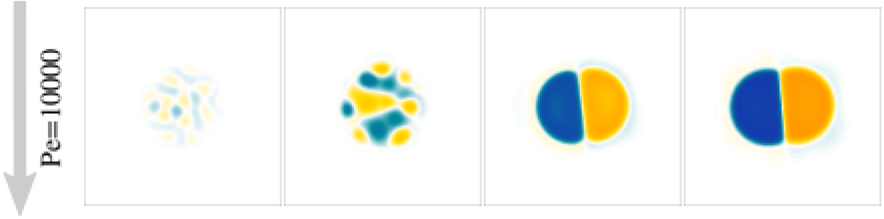
c is the barycenter of the droplet

- dipole moment p grows faster for higher Peclet number

t_p is the time when the polarization first reaches the equilibrium state







Results: Advection Speeds up the Polarization Process

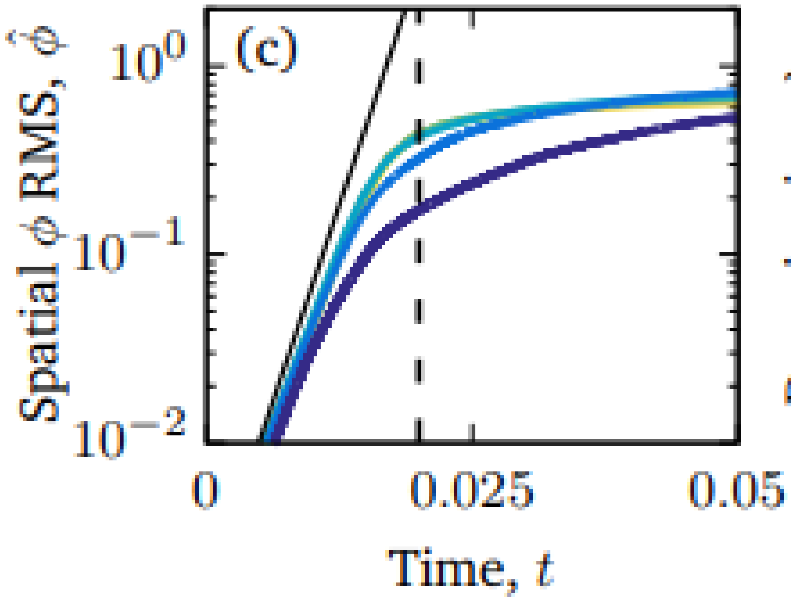
Initial decomposition

- Quantify the phase field amplitude |ϕ| during the initial decomposition phase
  - Spatial root mean square

$$\hat{\phi}^2 = \int_\Omega (1-\psi)\phi^2 \, dA / \int_\Omega (1-\psi) \, dA.$$

- $\hat{\phi}$ initially increases exponentially
- Reaches a saturation at approximately t_d
- Initial phase does not depend very strongly on the

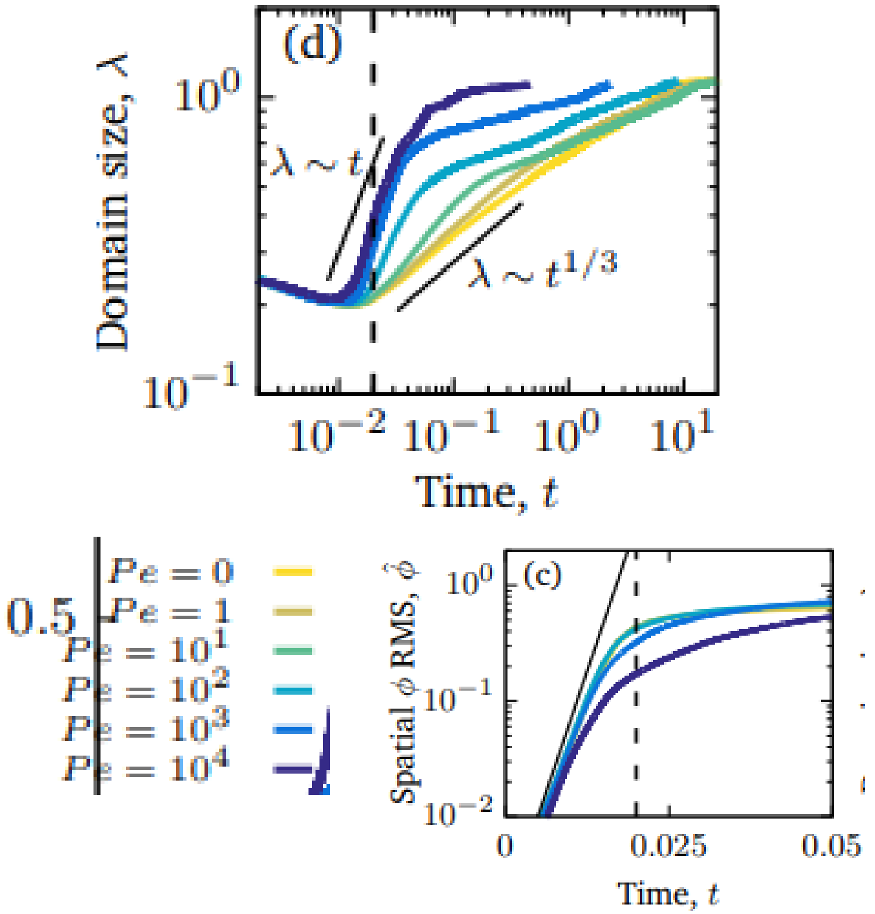
Peclet number



Results: Advection Speeds up the Polarization Process

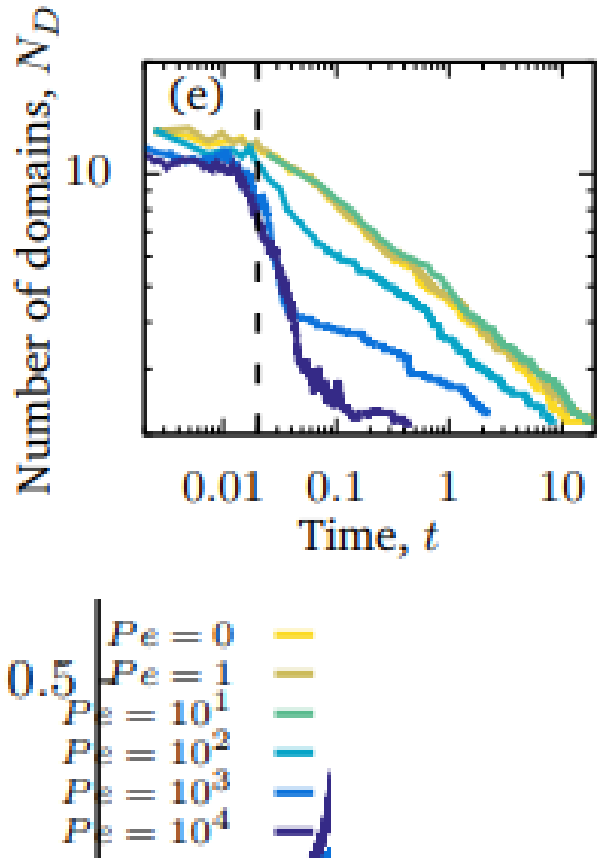
Coarsening

- Coarsening phase is strongly affected by the Peclet number
- For $P_e = 0$ λ coarsens approximately to $\sim t^{1/3}$
- For very large Peclet number, $P_e \gtrsim 10^3$, we observe a coarsening exponent close to 1
  - Corresponds to the expected result for advection-dominated coarsening
  - The early coarsening is also the likely reason for the slowing down of the initial decomposition for very large P_e



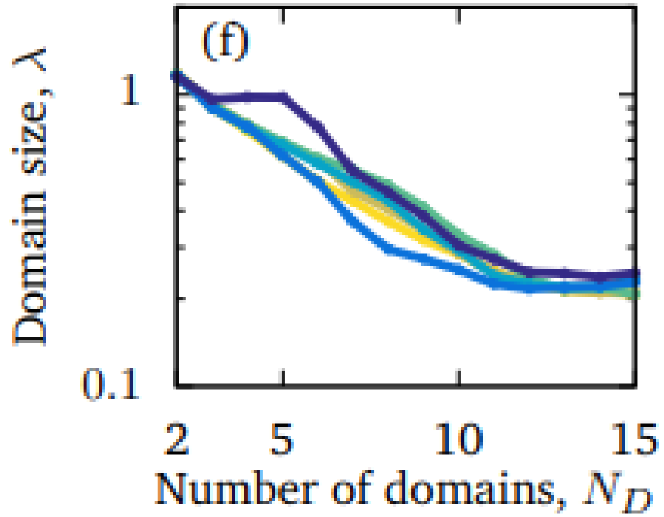
Results: Advection Speeds up the Polarization Process

- The difference in the coarsening behavior between small and large Peclet number is also apparent when studying the behavior of the number of phase domains N_D
- N_D decreases during the coarsening process until it reaches a minimum of two
- ND decreases more rapidly for larger Peclet number

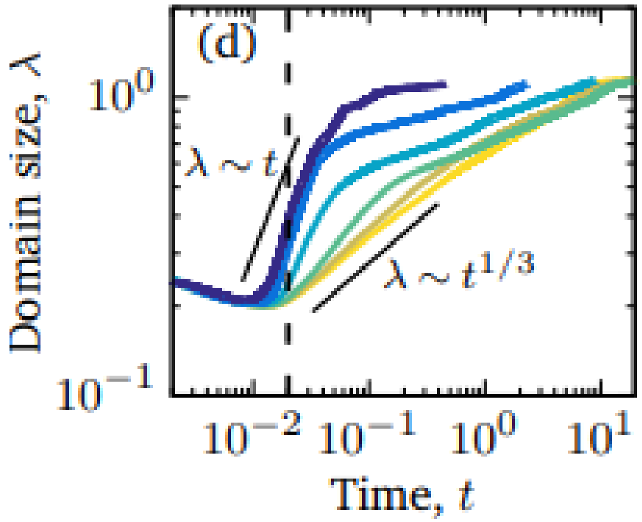


Results: Advection Speeds up the Polarization Process

The high correlation between N_D *and* λ Confirms that advection speeds up the coarsening process



Intermediate Peclet number, initially have a relatively fast coarsening. But it slowed subsequently.

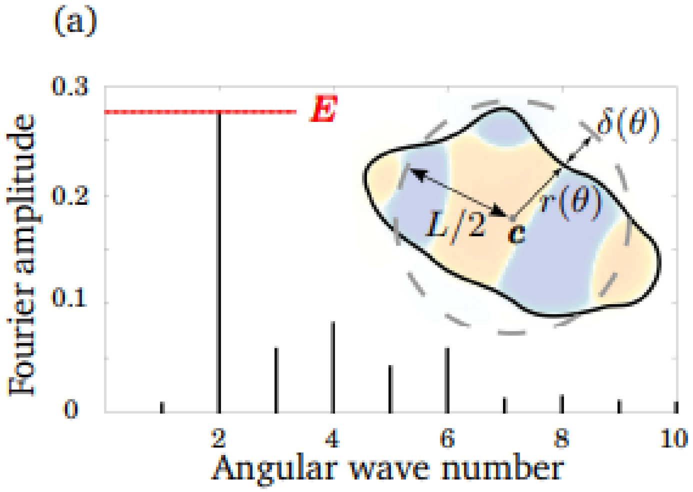


This is reason why the polarization time t_p decreases only for very large P_e

Elongated, striped droplets at intermediate P_e

Is the elongated, striped droplets that emerge for intermediate P_e be related to the slow down of the coarsening ?

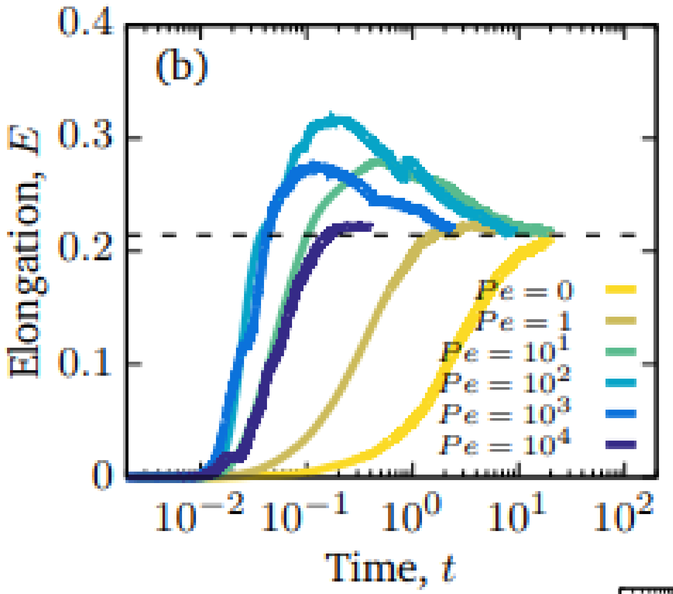
E is the quantified time Evolution of the droplet elongation



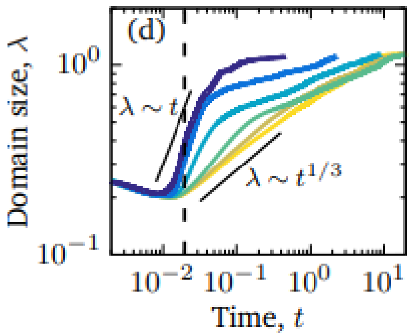
E corresponds to the maximal radius variation of the second Fourier mode relative to the initial droplet radius $r_0 = L/2$

(a) Illustrative example of droplet surface deformation, at P_e = 100 and t = 0.1, and resulting angular Fourier spectrum used to define the droplet elongation E.

Elongated, striped droplets at intermediate P_e

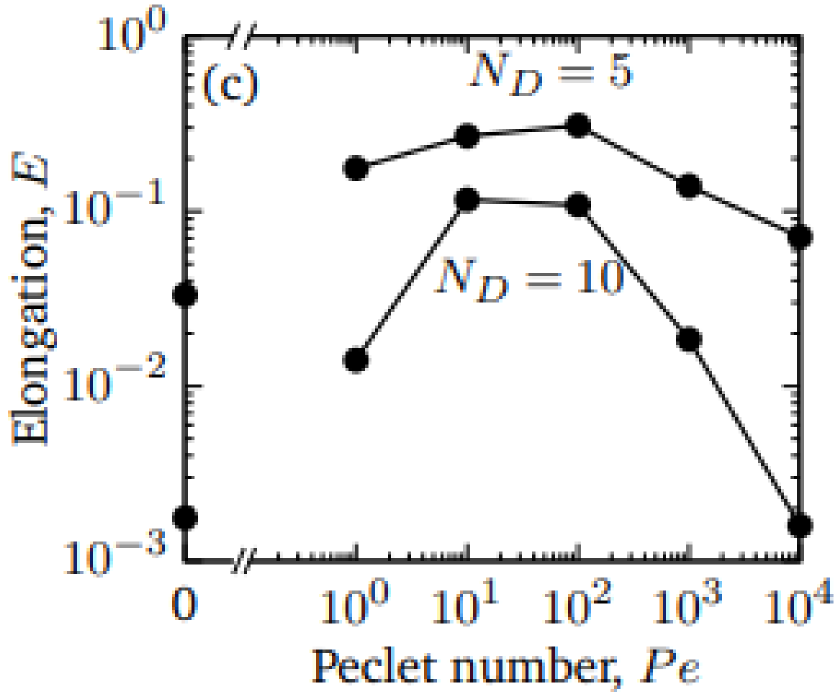


- ➢For P_e = 0 and very large P_e, the droplet elongation E monotonically increases with time until $E \approx 0.2$
- ➢for intermediate P_e, droplet elongation first increases to E $\approx$ 0.3 and decrease back to $E \approx 0.2$
- ➢The regime of transient elongation is correlated in time to the phase of slow coarsening
- ➢Elongated droplet structures could be related to the observed coarsening slow down for intermediate P_e



Elongated, striped droplets at intermediate P_e

Plotting the P_e over the droplet elongation with a fixed number of domains N_D



They find that at the same N_D, elongation can be up to two orders of magnitude larger for intermediate P e

Elongated, striped droplets at intermediate P_e

Stripped patterns could be used to to explain the observed coarsening slow down even for intermediate P_e

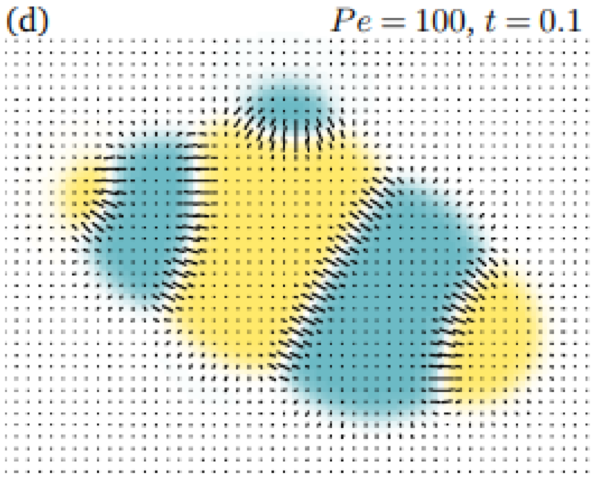
- Close to a mechanical equilibrium
- Coarsening would occur almost entirely through diffusion
- Increase Laplace pressure in small stripes
- Larger domain would slowly grow
  - Diffusive fluxes across the domains of opposite color

Elongated, striped droplets at intermediate P_e

Testing the ideia: quantify the nematic order of inner domain boundaries by an order parameter Q

Introduce a tensor field $A_{\alpha\beta}$ that characterizes the local orientation of ϕ interfaces

$$A_{\alpha\beta} = (1-\psi)\frac{\partial\tilde{\phi}}{\partial x_\alpha}\frac{\partial\tilde{\phi}}{\partial x_\beta} \xrightarrow[\text{field}]{\text{Normalized}} \tilde{\phi} = (C_1 - C_2)/(C_1 + C_2) = \phi/(1-\psi)$$



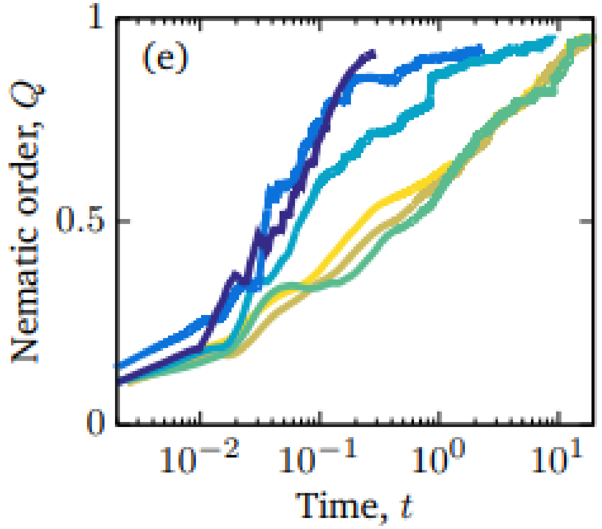
Tensor $Q_{\alpha\beta}$ as the spatially averaged, symmetric, traceless part of $A_{\alpha\beta}$

$$Q_{\alpha\beta} = \frac{1}{\langle A_{\gamma\gamma}\rangle}\left\langle A_{\alpha\beta} - \frac{1}{2}\delta_{\alpha\beta}A_{\gamma\gamma}\right\rangle$$

Magnitude of the nematic order parameter $Q = \sqrt{Q_{xx}^2 + Q_{xy}^2}$

$Q = 0$ for randomly oriented domain interfaces
$Q = 1$ for straight and perfectly aligned oriented domain interfaces

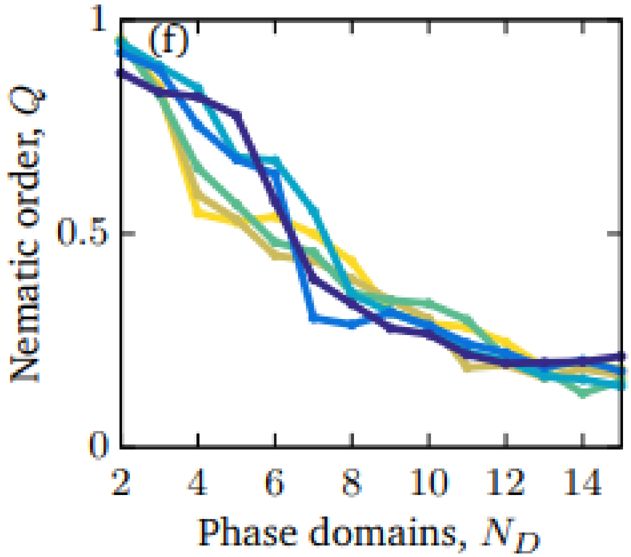
Elongated, striped droplets at intermediate P_e



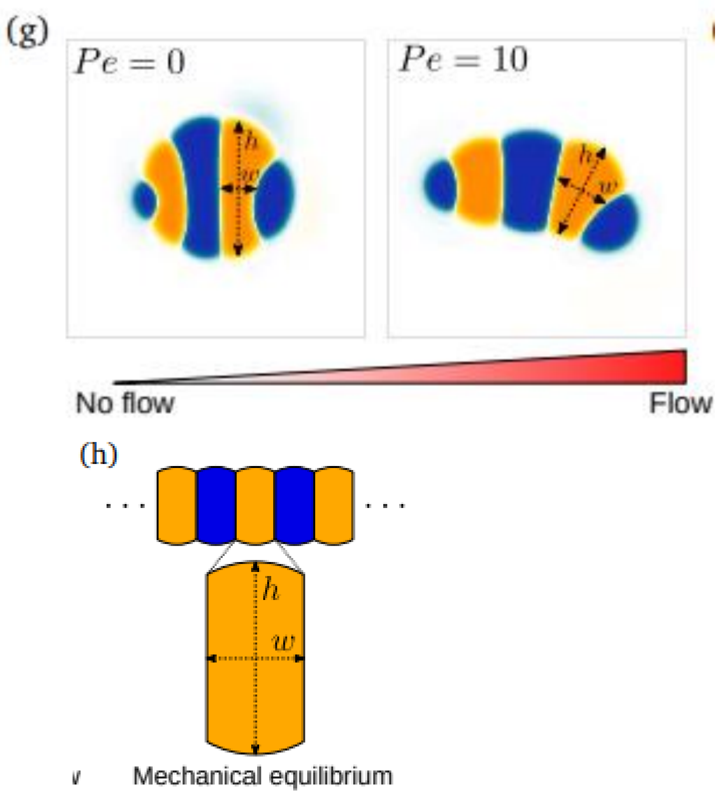
- Q increases over time
  - More quickly for large P_e
- Final equilibrium state at $Q \approx 1$

- Q over N_D (Inverse of (e))
- Striped domain patterns for $P_e = 0$
- why do we find elongated droplets only

for intermediate P_e?



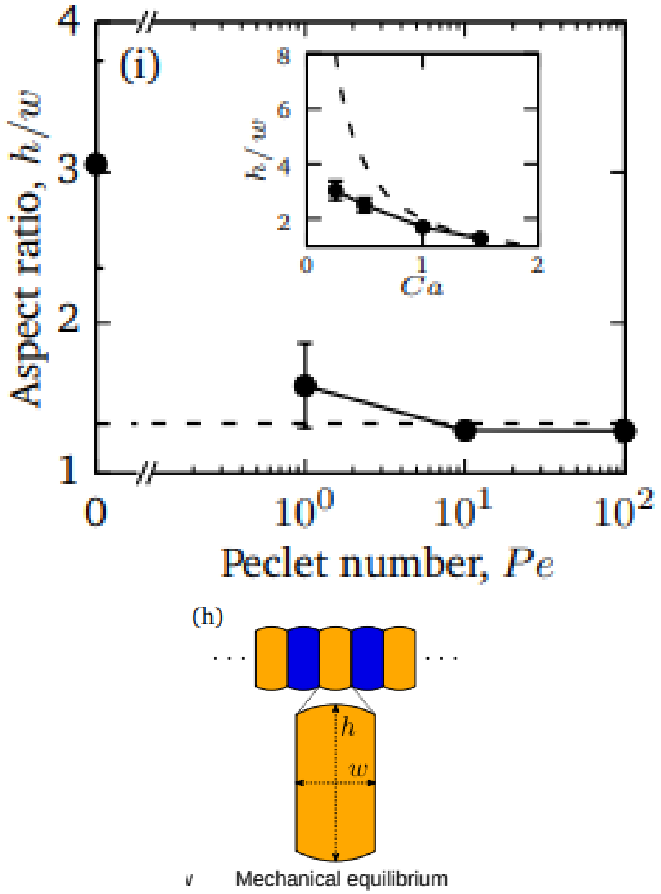
Elongated, striped droplets at intermediate P_e



- A possibility is that hydrodynamic flows would drive the system closer to mechanical equilibrium, where in mechanical equilibrium the droplets might be elongated
- first analytically compute the mechanical equilibrium state for a striped droplet for the case (h)
- Approximated result: A droplet with N_D domains in mechanical equilibrium would have aspect ratio ${}^{N_D w}/_{h} = {}^{N_D Ca}/_{2}$

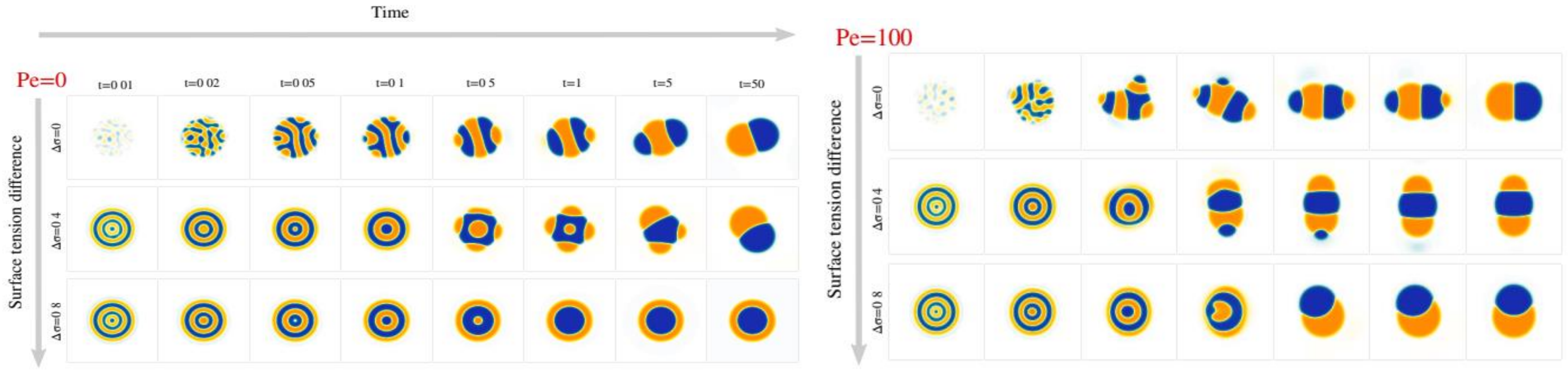
(h) Limiting case of infinite chain of equally-sized phase domains in mechanical equilibrium, where h/w = 2/Ca

Elongated, striped droplets at intermediate P_e



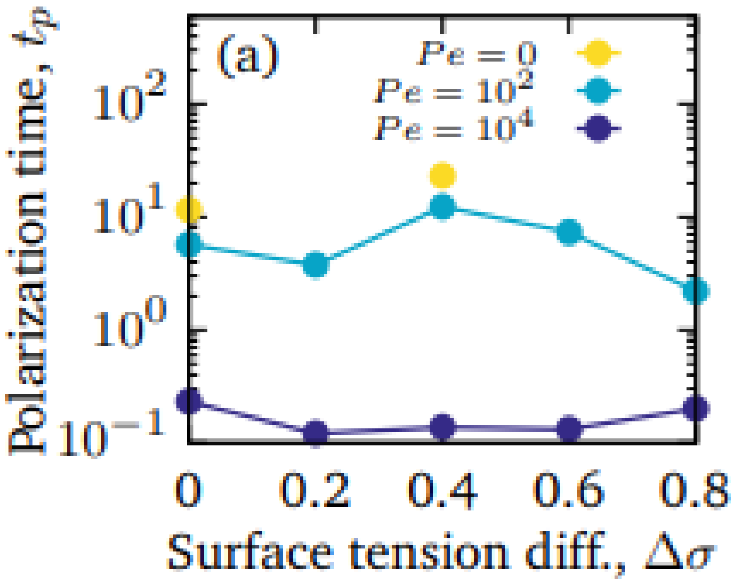
- Droplets P_e over h/w for $C_a = 1.5$
- Compare to the theoretical solution of the infinite chain
- Results suggest that the droplets do indeed approach mechanical equilibrium as P_e increases
- Comparing domain aspect ratios also across different values of C_a
- For smaller C_a, the measured aspect ratio started to become smaller than the theoretical prediction
  - Simulated droplets deviate more strongly from the theoretical picture of a chain of equally sized domains

Effect of a difference between the surface tensions of the two droplet phases



Effect of different surface tensions between the two droplet phases, $\Delta\sigma \neq 0$

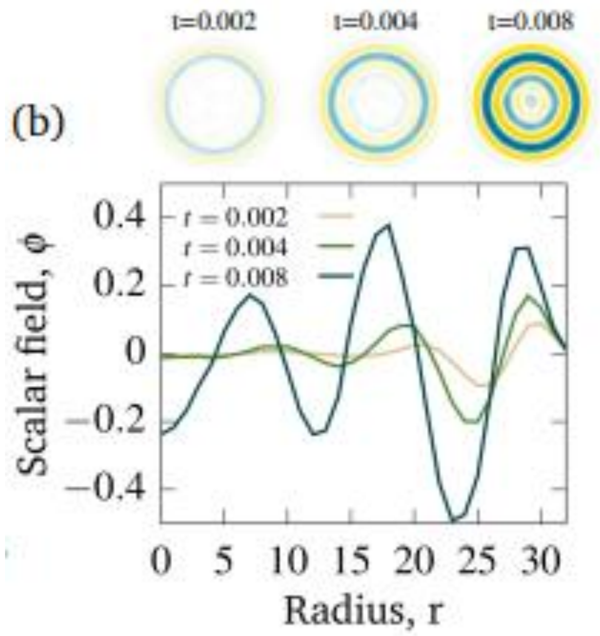
Effect of a difference between the surface tensions of the two droplet phases



- How $\Delta\sigma$ change the time t_p
- For $P_e = 0$, only simulations with $\Delta\sigma = 0$ and $\Delta\sigma = 0.4$ reached the polar equilibrium
- For the others equilibrium state has always been reached after a finite time t_p
- No clear dependency on $\Delta\sigma$ is apparent

Effect of a difference between the surface tensions of the two droplet phases

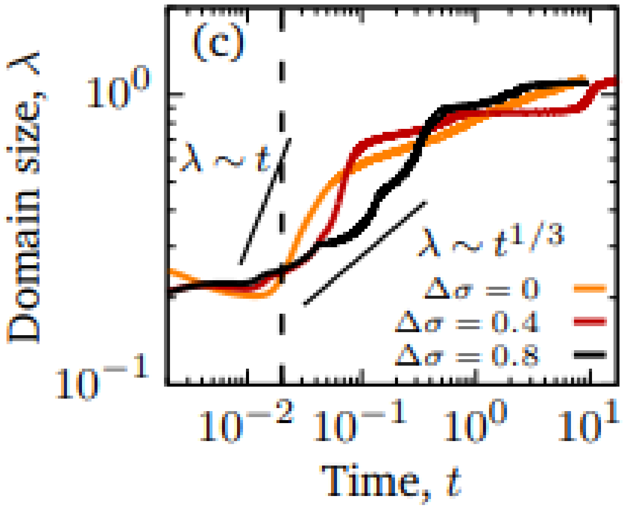
Initial decomposition: $(\boldsymbol{\Delta\sigma > 0})$



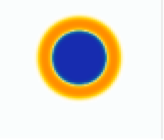
- ➢Droplet boundary inwards in concentric circles (composition wave)
- ➢Fluid 2 (orange) has a lower surface tension. Supplants fluid 1 (blue) in this region, pushing it further inwards
- ➢Abundance of fluid 1 next to fluid 2 attracts more of fluid 1, supplanting more of fluid 2, which is pushed further inwards
- ➢This continue until reach saturation $|\phi| \approx 1$

Effect of a difference between the surface tensions of the two droplet phases

Coarsening:

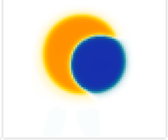


$P_e = 0$



$P_e = 100$

$P_e = 10000$

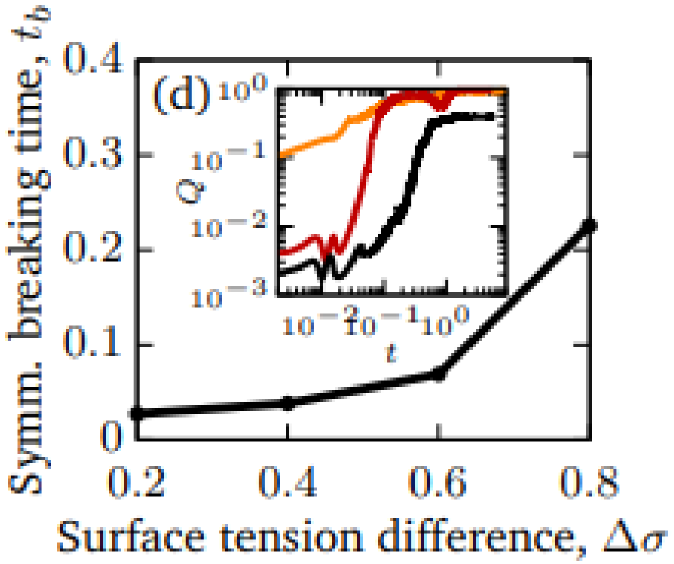


The rotationally symmetric pattern coarsens through progressive broadening of the stripes and occasional annihilation of the innermost phase domain

- For $P_e = 0$ the system remained in a state with two concentric phase domains
- For $P_e > 0$, the rotational symmetry got broken
- $P_e = 100$ during the coarsening phase, and for $P_e = 10000$ already during the initial decomposition phase.

Effect of a difference between the surface tensions of the two droplet phases

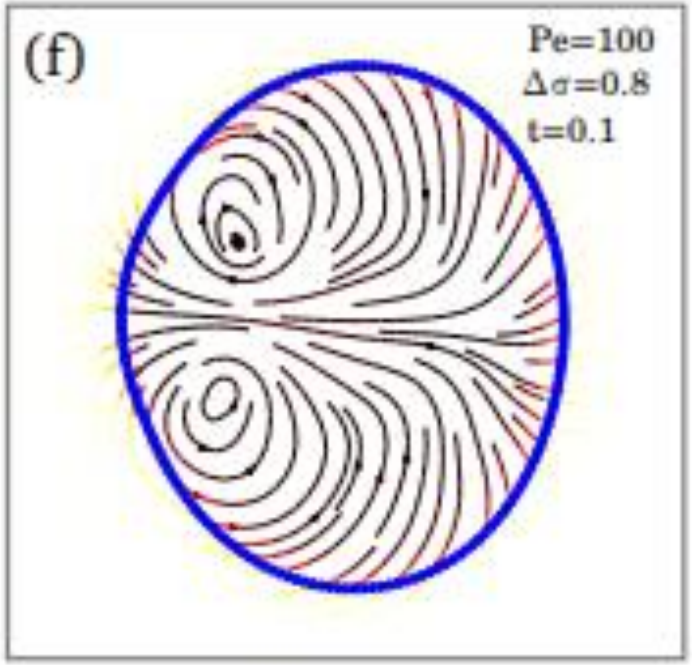
Symmetry breaking



- The time of symmetry breaking t_b is defined as the first time when the nematic order of the inner domain boundaries, Q, surpassed a value of 0.01
- For $P_e = 100$, they found that t_b increased monotonically with $\Delta\sigma$
- Showing that t_b has a dependence on $\Delta\sigma$

Effect of a difference between the surface tensions of the two droplet phases

Transient flows

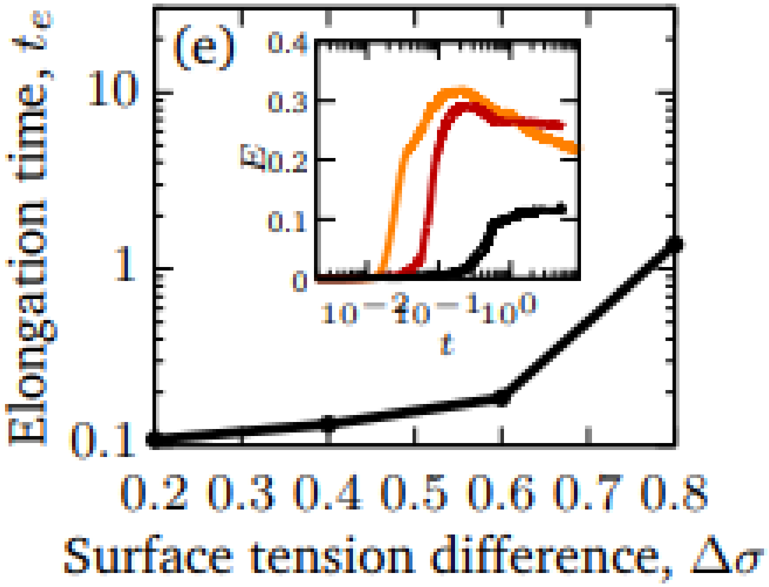


The symmetry breaking usually triggered complex transient hydrodynamic flows

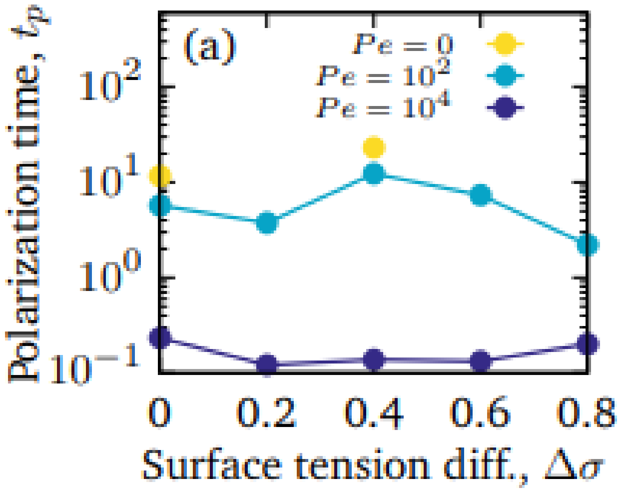
For $P_e = 100$, these flows typically resulted in a croissant state.

Effect of a difference between the surface tensions of the two droplet phases

Slowly relaxing “croissant” state



- t_e is the first time when the droplet elongation E reached 90% of its maximum value
- t_e increase monotonically with $\Delta\sigma$, that is t_e shows a dependence with $\Delta\sigma$
- While the time t_p, for the whole process varies non-monotonically with $\Delta\sigma$, the time t_e, when the croissant state appears, increases monotonically, and is generally much smaller than t_p



Conclusion

- For intermediate P_e, transient droplet states form, which are striped and elongated. They are close to mechanical equilibrium and coarsen only through diffusive fluxes, which makes them long-lived.
- Advection can speed up the coarsening process as reported earlier for big P_e, which leads to coalescence of the phase domains before a striped pattern can develop.
- The effect of an asymmetry between the surface tensions of the two droplet phases changes the beginning of the phase separation process. The emergence of composition waves initially creates a rotationally symmetric system, which then starts to coarsen diffusively. Breaking of this rotationally symmetric state triggers transient flows that are reminiscent of Marangoni flows in droplets.

Thank You!