Diffuse-interface simulations of interfacial dynamics in complex fluids

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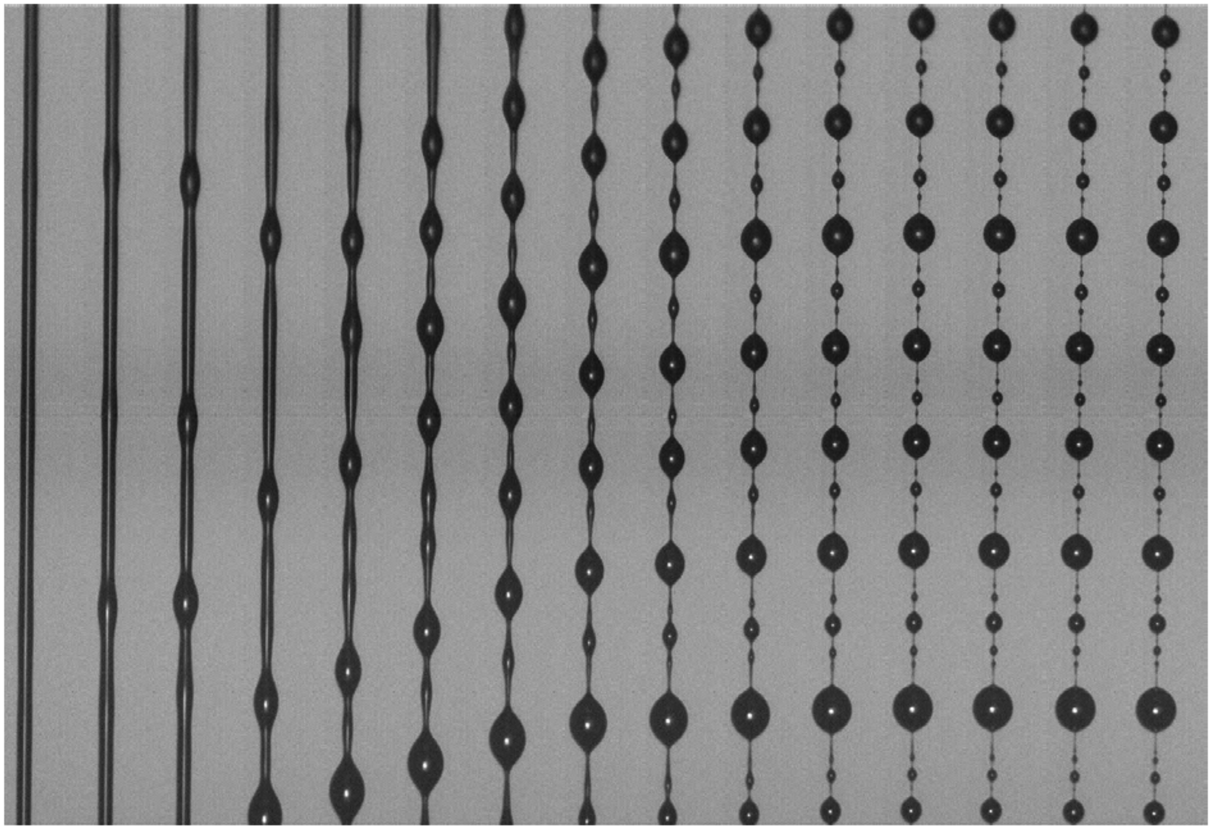
Outline

- Why interfacial dynamics in complex fluids?
- Partial coalescence: Newtonian and polymer solutions
  - Experimental observations
  - Diffuse-interface simulations
- Droplets self-assembly in nematic liquid crystal
  - Experimental observations
  - Diffuse-interface simulations

Motivation: interfacial anomalies

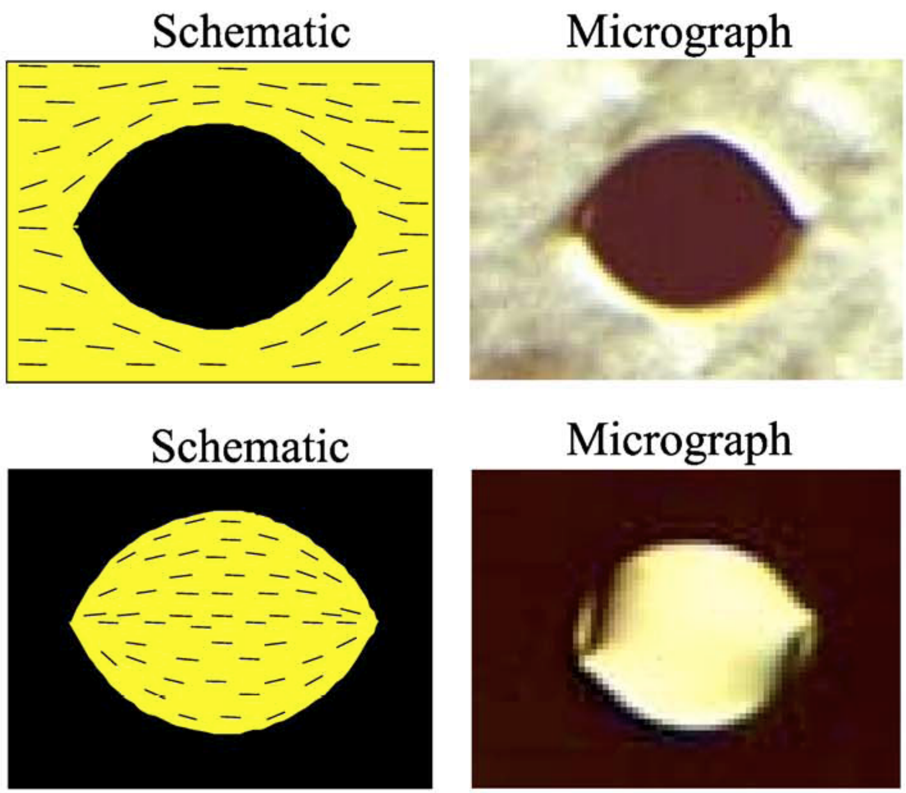
Beads-on-string morphology (0.2% PEO solution)



$t - t_B$ (ms)	0	25	50	75	100	125	150	175	200	225	250	275	300	325	350

Motivation: interfacial anomalies

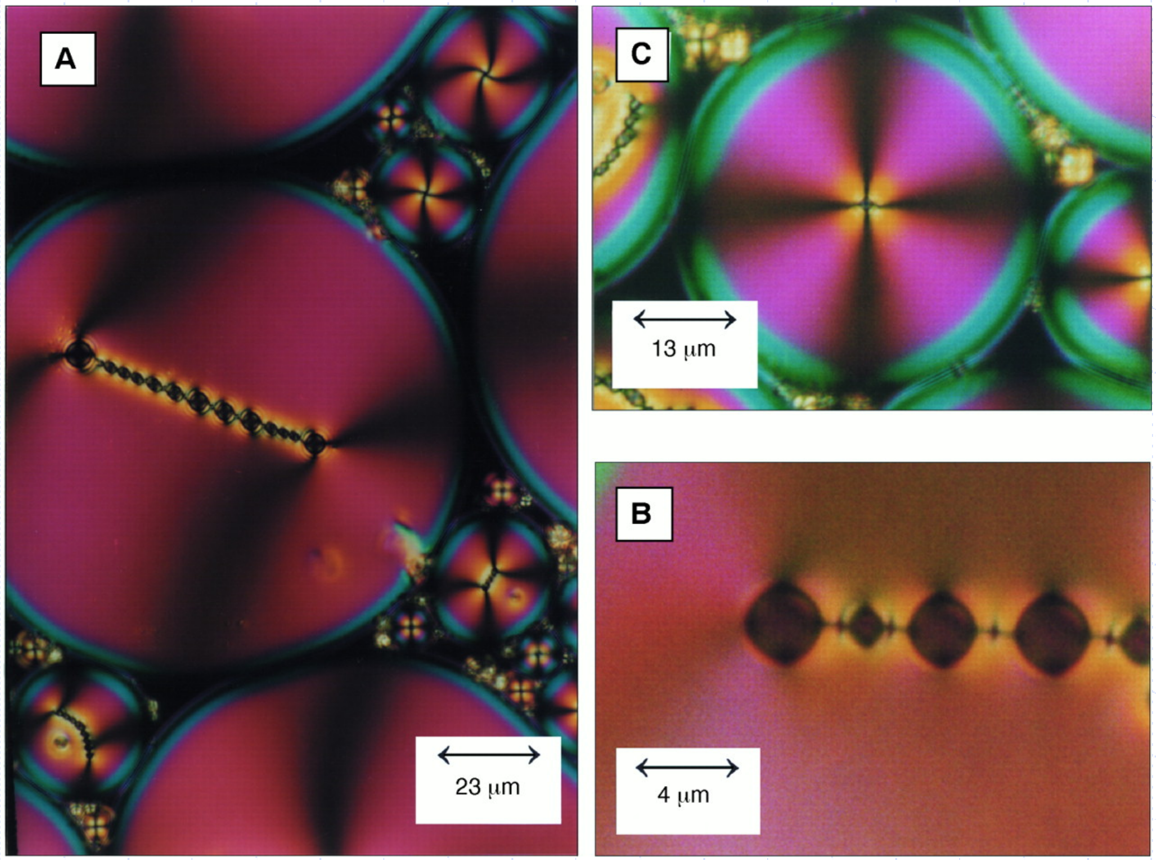
Interfacial shape in complex fluids



Liquid crystal

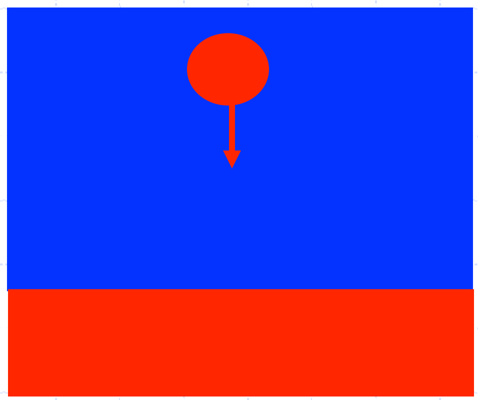
Self-assembly in nematic liquid crystal

(Observation of water droplets in large nematic drops)

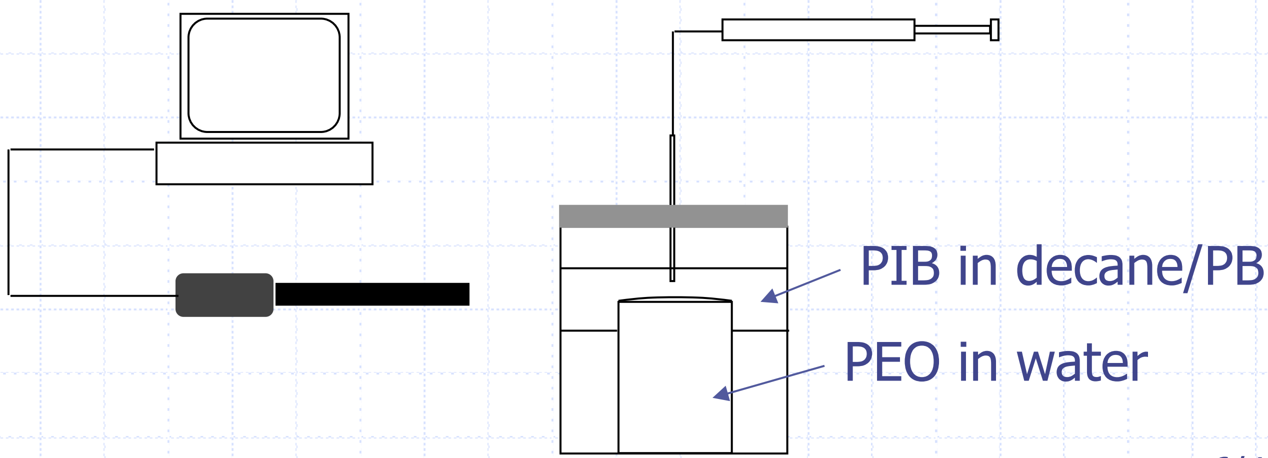


Poulin et al. *Science* **275** (1997) p. 1770

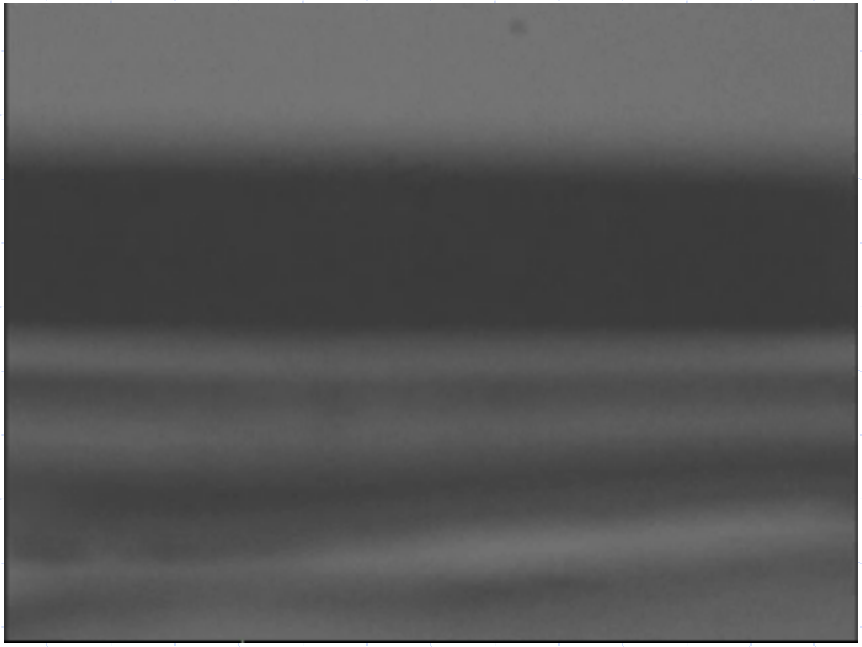
I.1. Partial coalescence: experiments



Red: water
Blue: oil

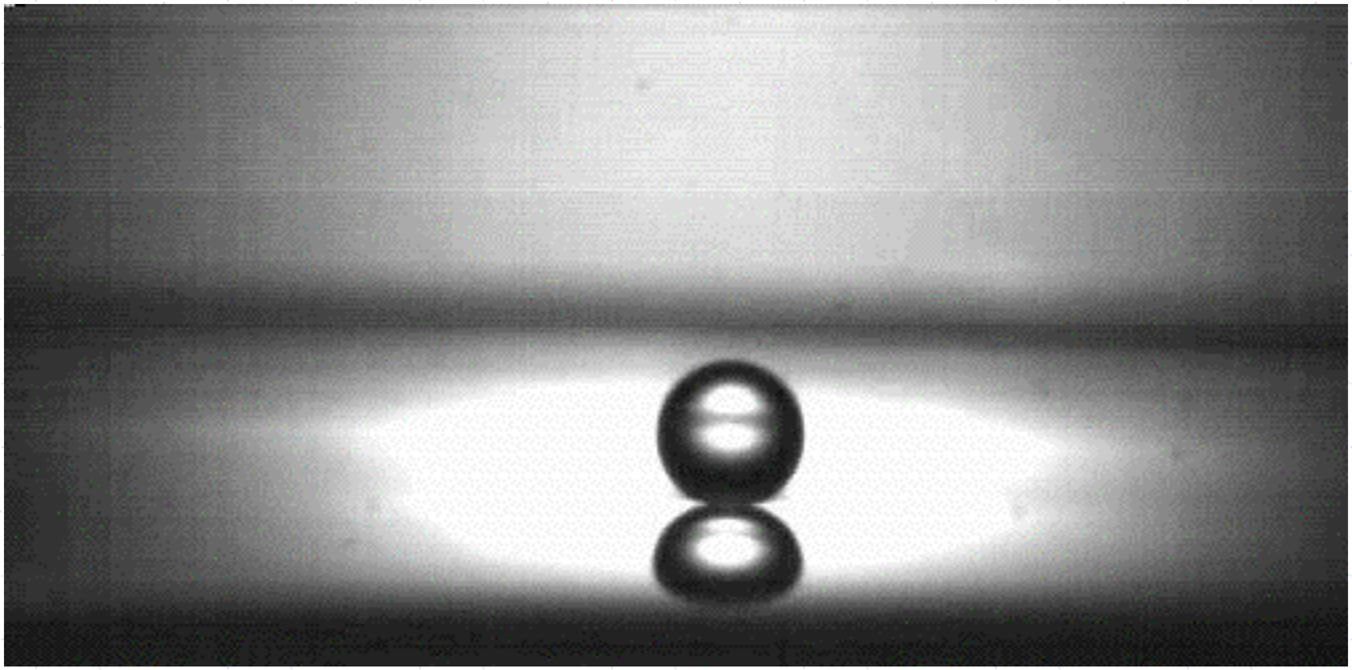


Partial coalescence in Newtonian liquids



Partial coalescence cascade

Partial coalescence in Newtonian liquids

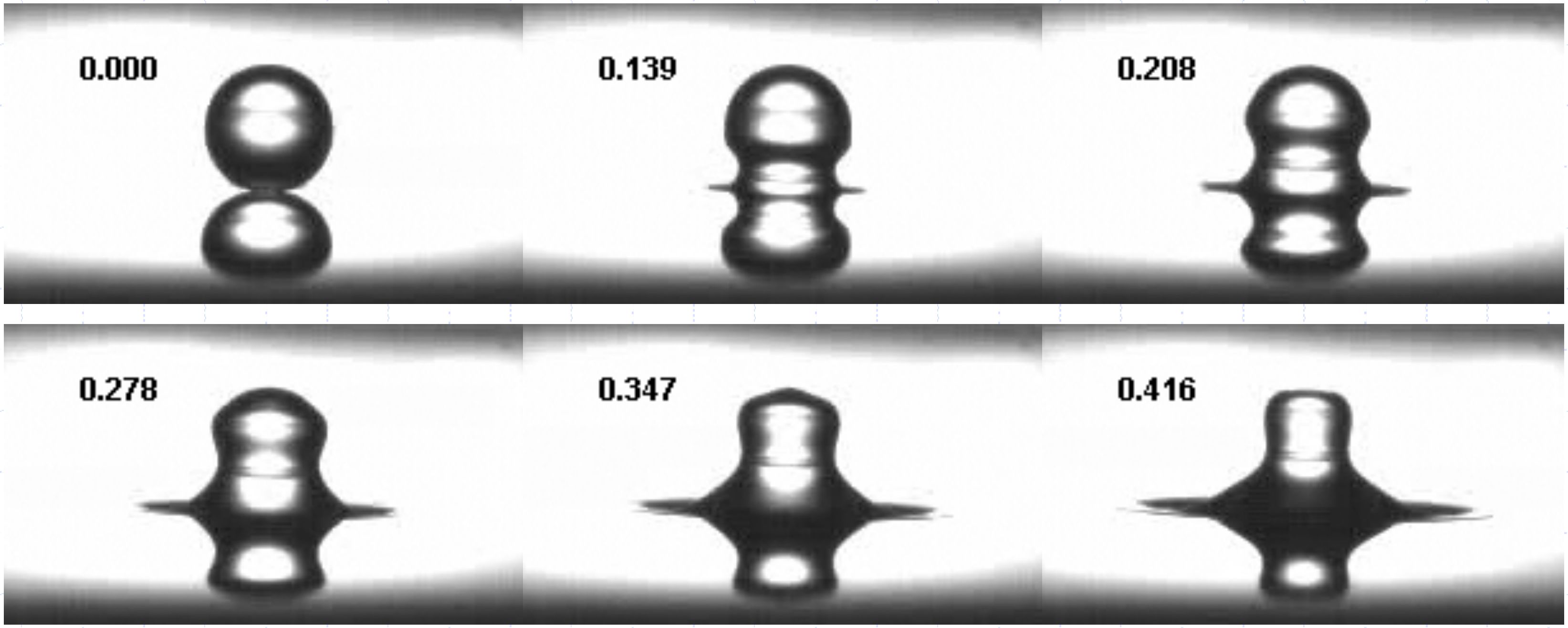


Captured by high speed camera

Drop size, 1.1mm, duration, 18 ms.

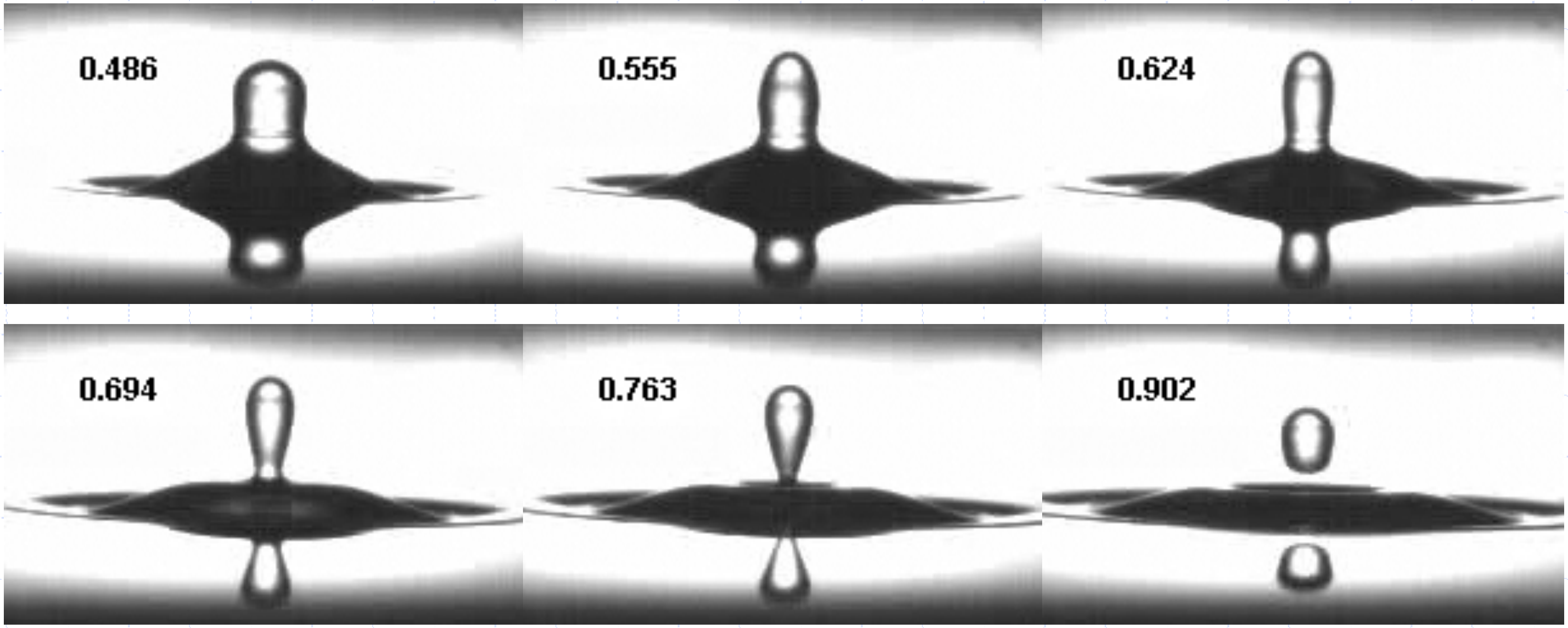
Stages of partial coalescence

- Capillary wave propagation



Stages of partial coalescence

- Drop pinch-off by capillary instability



What controls the process?

- Factors at play:
  - Interfacial tension σ
  - Gravity g
  - Inertia $m=\rho\pi D^3/6$
  - Viscosity μ
- Dimensionless numbers:

Ohnesorge Number

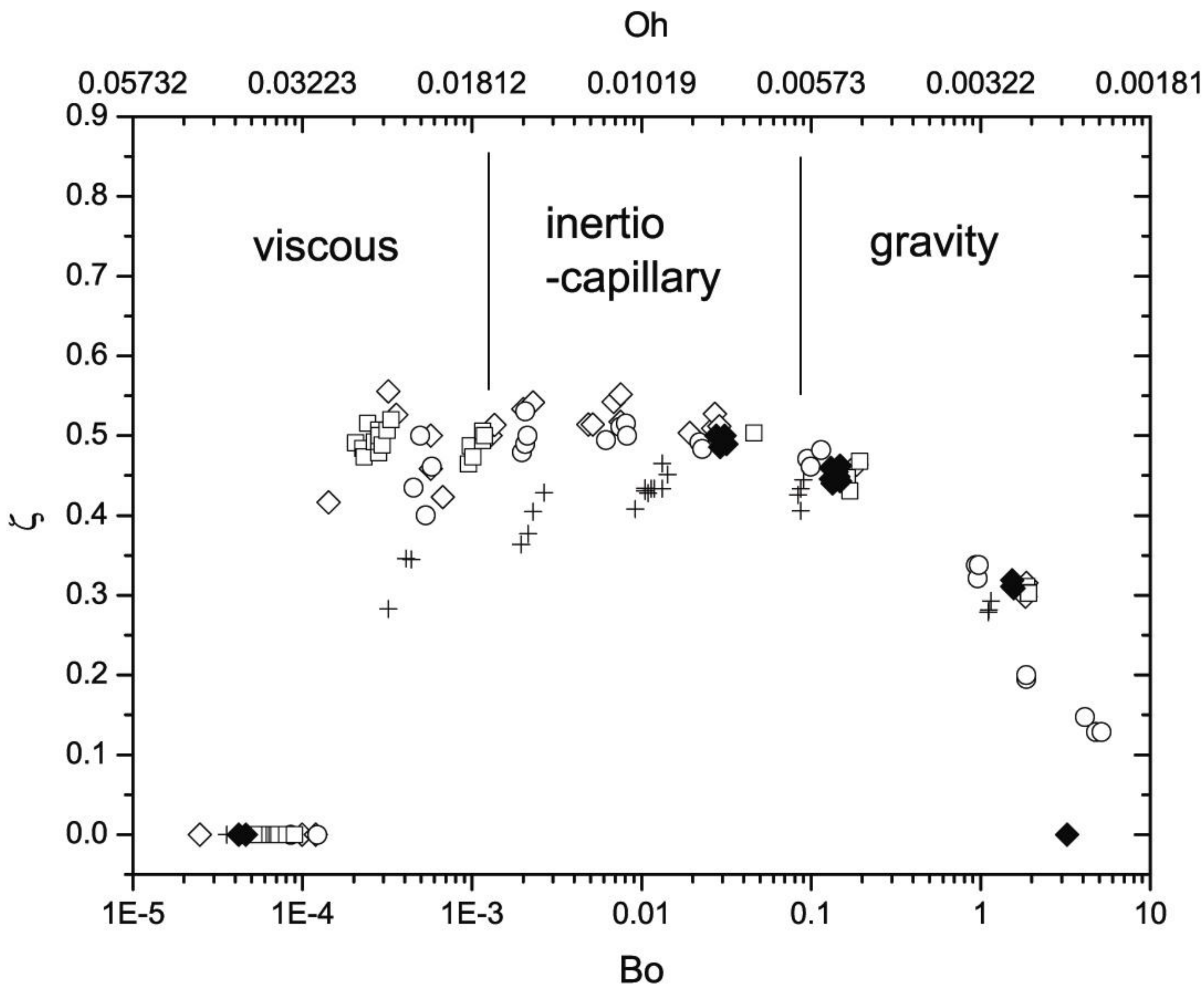
$$Oh = \frac{\mu}{\sqrt{\rho D \sigma}}$$

Bond number

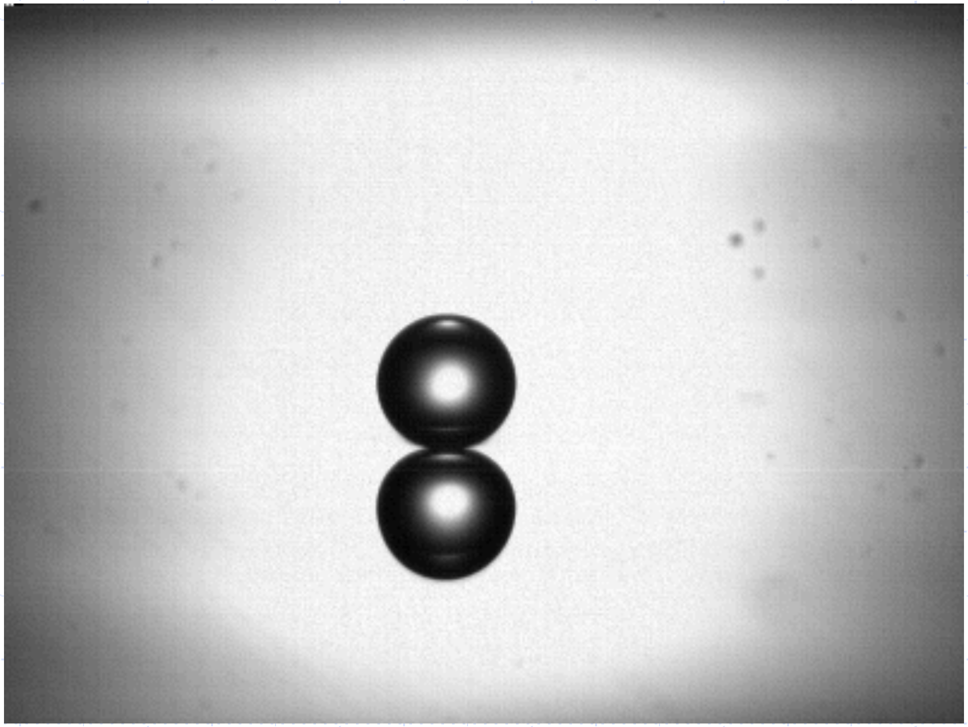
$$Bo = \frac{\rho g D^2}{\sigma}$$

- Competition of time scales

Size ratio between daughter/mother drop

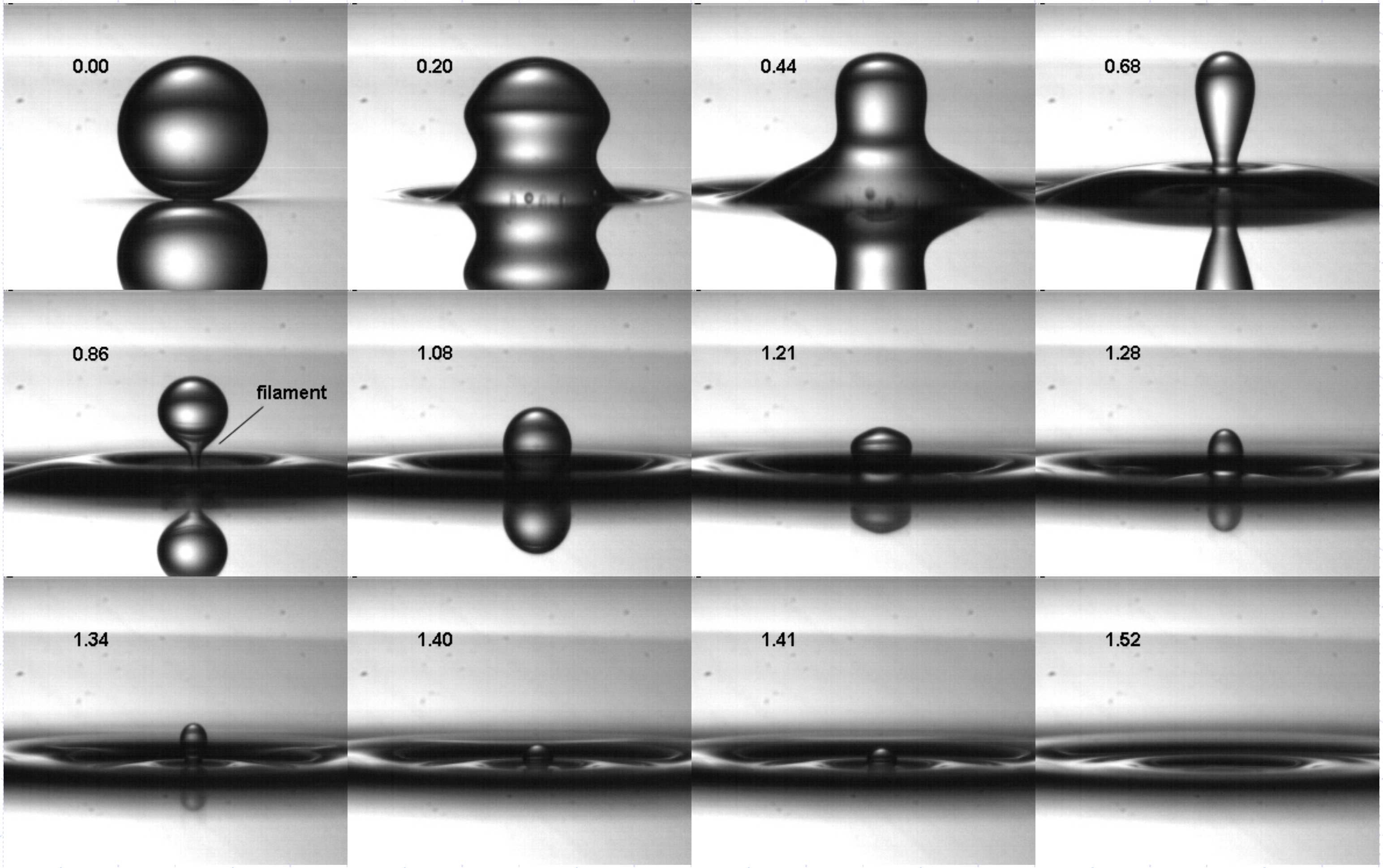


Partial coalescence in polymer solutions



- 0.18 *wt* % PEO (drop), in Decane matrix
  drop size ~ 1 mm

Polymer drop: filament fails to pinch off



I.2. Partial coalescence: numerical simulations

Governing equations for each component:

- Incompressibility: $\nabla \cdot \boldsymbol{u} = 0$
- Momentum balance: $\rho \dfrac{d\boldsymbol{u}}{dt} = -\nabla p + \nabla \cdot \boldsymbol{\tau}$
- Constitutive equation: how is the stress $\boldsymbol{\tau}$ related to the flow and deformation of the material?

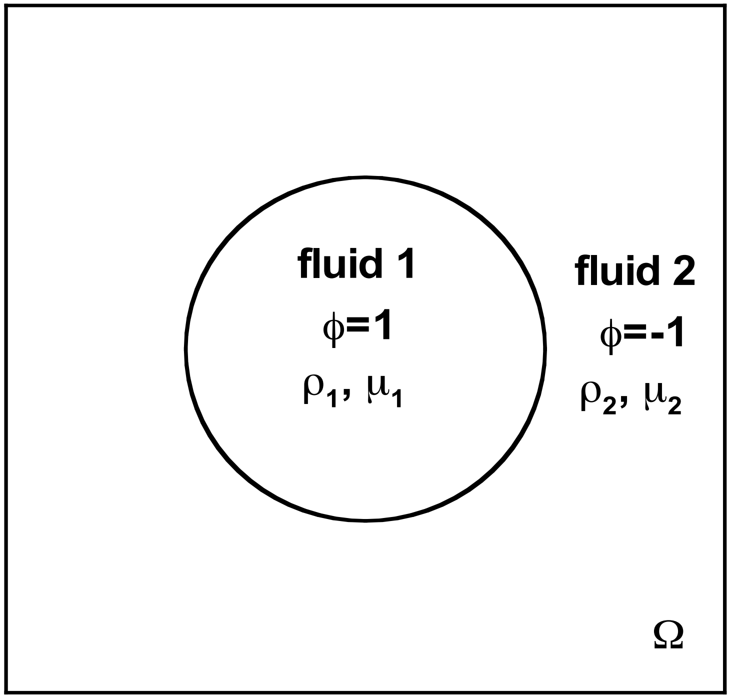
(a) Newtonian fluids: $\boldsymbol{\tau} = \mu(\nabla \boldsymbol{u} + \nabla \boldsymbol{u}^{\mathrm{T}})$

(b) Viscoelastic Maxwell fluids:

$$\boldsymbol{\tau} + \lambda\left(\frac{d\boldsymbol{\tau}}{dt} - \nabla \boldsymbol{u}^{\mathrm{T}} \cdot \boldsymbol{\tau} - \boldsymbol{\tau} \cdot \nabla \boldsymbol{u}\right) = \mu(\nabla \boldsymbol{u} + \nabla \boldsymbol{u}^{\mathrm{T}})$$

Diffuse interface (phase-field) method

- Interface: physically diffuse
- Phase field variable $\phi(r)=\pm 1$
- Governed by mixing energy:



$$F = \int_\Omega f_{mix}\, d\Omega = \int_\Omega \lambda \left[\frac{(\nabla\phi)^2}{2} + \frac{(\phi^2-1)^2}{4\epsilon^2} \right] d\Omega$$

Gradient energy　　Bulk energy

- Cahn-Hilliard equation:

$$\frac{\partial\phi}{\partial t} + u\cdot\nabla\phi = \nabla\cdot\left(\gamma\nabla\frac{\delta F}{\delta\phi}\right) = \gamma\lambda\nabla^2\left[-\nabla^2\phi + \frac{(\phi^2-1)\phi}{\varepsilon^2}\right]$$

Governing Equations

Momentum Equation

$$\rho\left(\frac{\partial \boldsymbol{u}}{\partial t}+\boldsymbol{u}\cdot\nabla\boldsymbol{u}\right)=-\nabla p+\mu\Delta\boldsymbol{u}+G\nabla\phi+\rho\boldsymbol{g}$$

Interfacial force

Continuity Equation

$$\nabla\cdot\boldsymbol{u}=0$$

Cahn-Hillard Equation

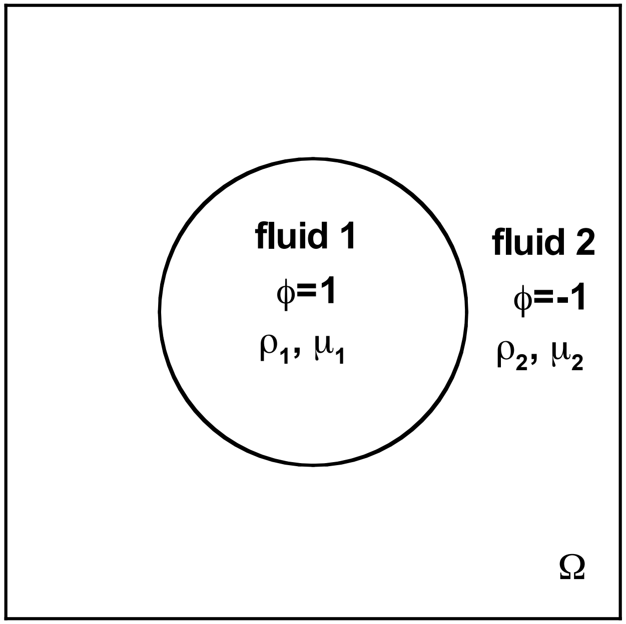
$$\frac{\partial\phi}{\partial t}+\boldsymbol{u}\cdot\nabla\phi=\gamma\Delta G$$

Density $\rho=\frac{1+\phi}{2}\rho_1+\frac{1-\phi}{2}\rho_2$

Viscosity $\mu=\frac{1+\phi}{2}\mu_1+\frac{1-\phi}{2}\mu_2$

Mixing energy $F=\int_\Omega f_{mix}\,d\Omega=\int_\Omega\lambda\left[\frac{(\nabla\phi)^2}{2}+\frac{(\phi^2-1)^2}{4\epsilon^2}\right]d\Omega$

Chemical potential $G=\frac{\delta F}{\delta\phi}=\lambda\left[-\Delta\phi+\frac{(\phi^2-1)\phi}{\epsilon^2}\right]$



Partial coalescence in decane/water system

$$\rho_{decane} = 0.74 g/cm^3$$

$$\rho_{water} = 1 g/cm^3$$

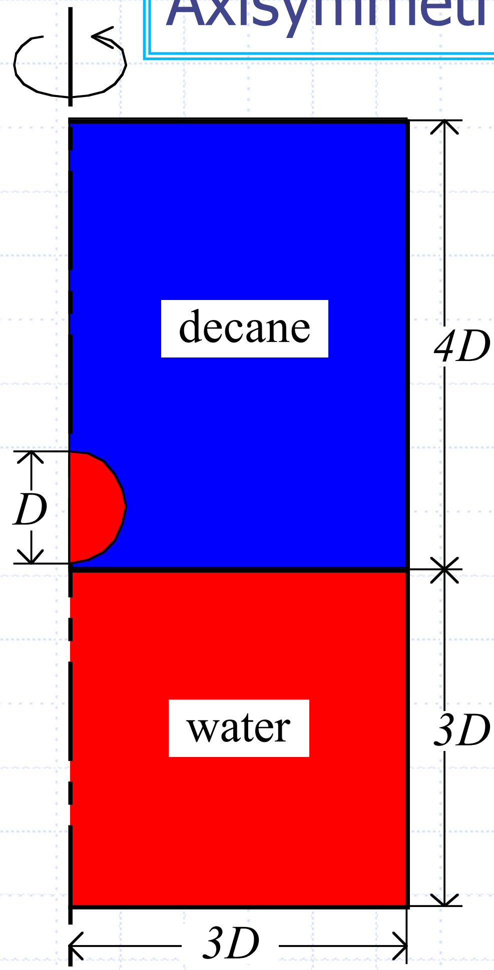
$$\mu_{decane} = \mu_{water} = 0.01 g/(cm \cdot s)$$

$$\sigma = 32 dyne/cm$$

$$Bo = \frac{\Delta \rho g D^2}{\sigma}$$

$$Oh = \frac{\mu_{drop}}{\sqrt{\rho_{drop} \sigma D}}$$

Axisymmetric

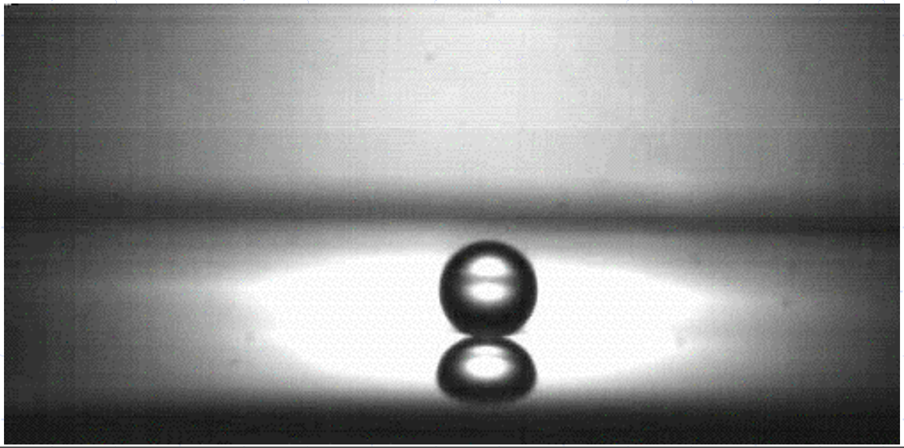


Newtonian systems

Water/oil (decane)

Experiment

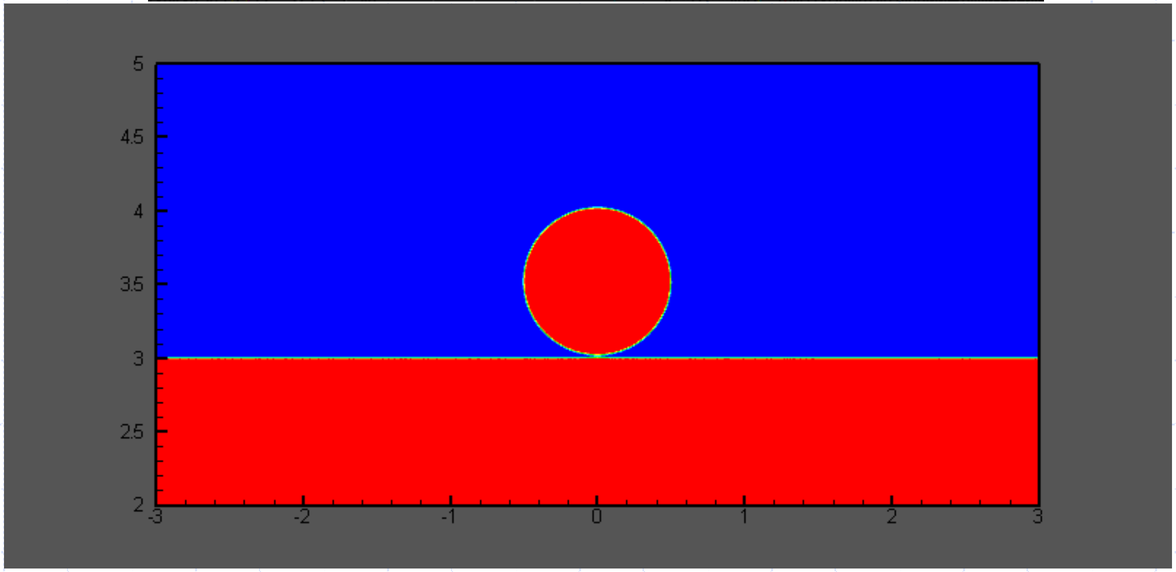
D=1.1mm



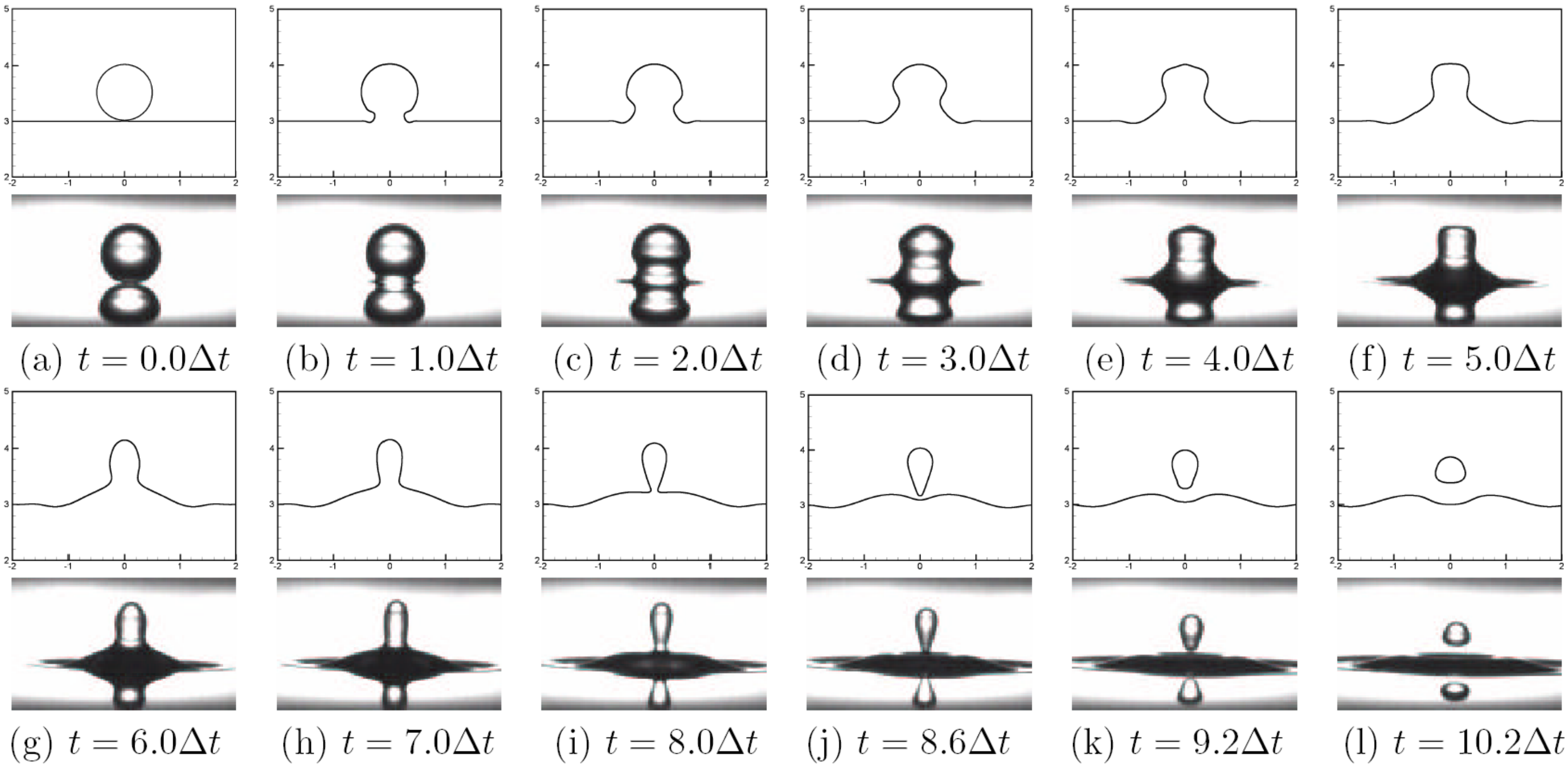
Phase-field simulation

Blue: oil

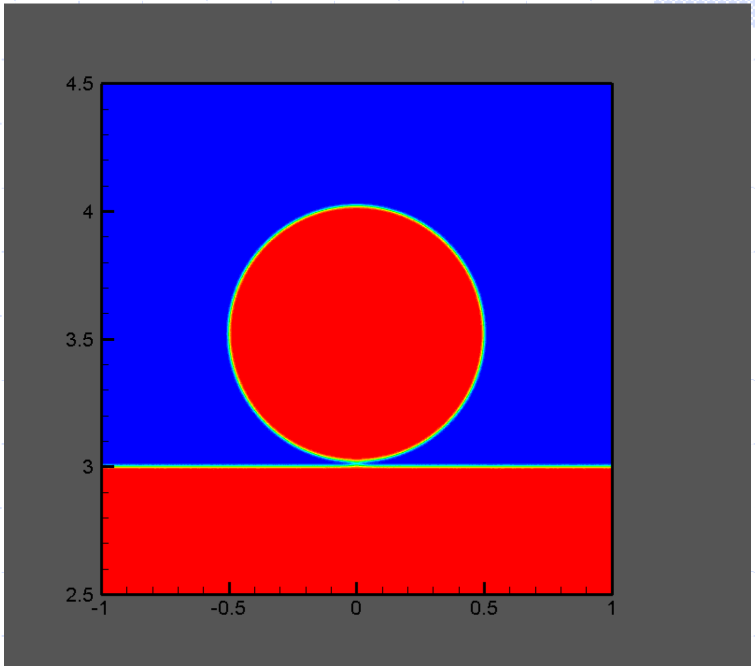
Red: water



A frame by frame comparison

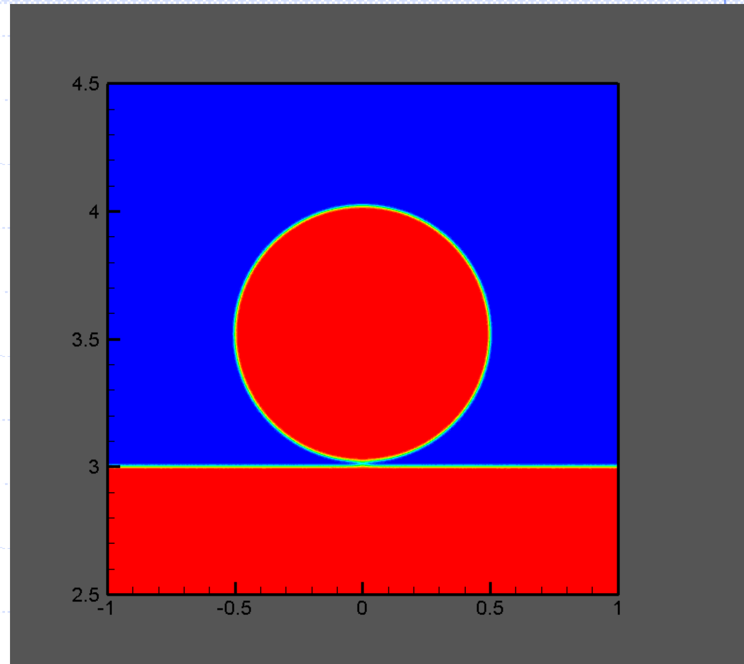


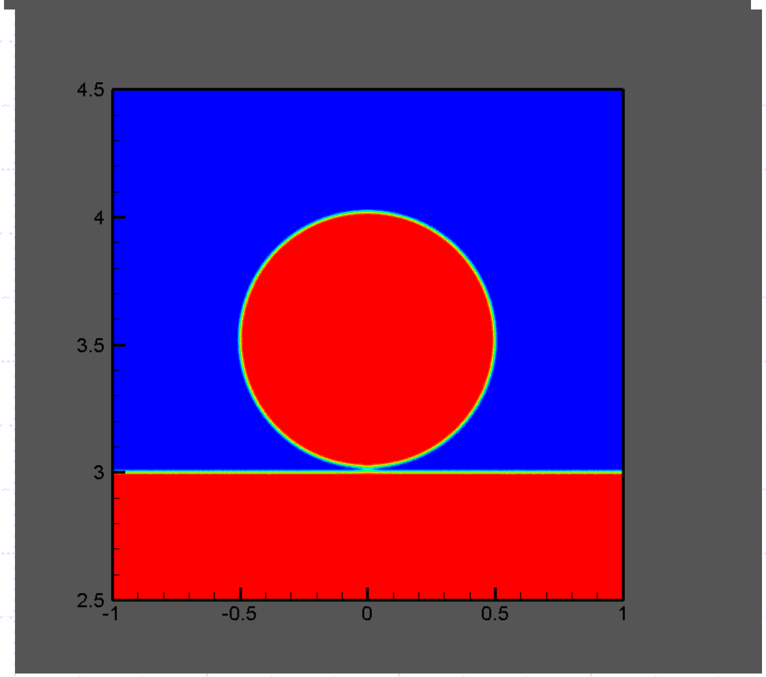
(Experimental: Δt=542 μs)



←D=2 cm
Oh=1.25E-3
Bo=31.9

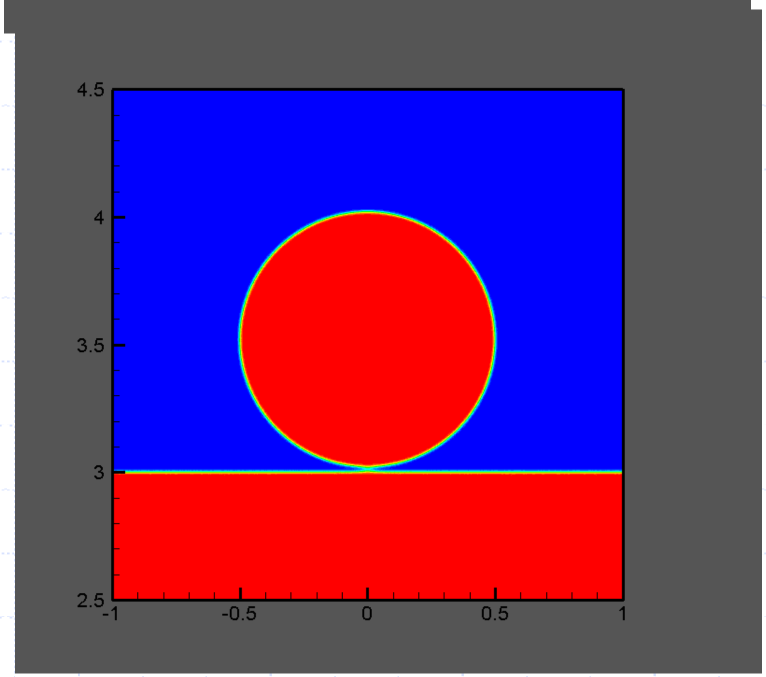
D=2.5 mm→
Oh=3.54E-3
Bo=4.98E-1





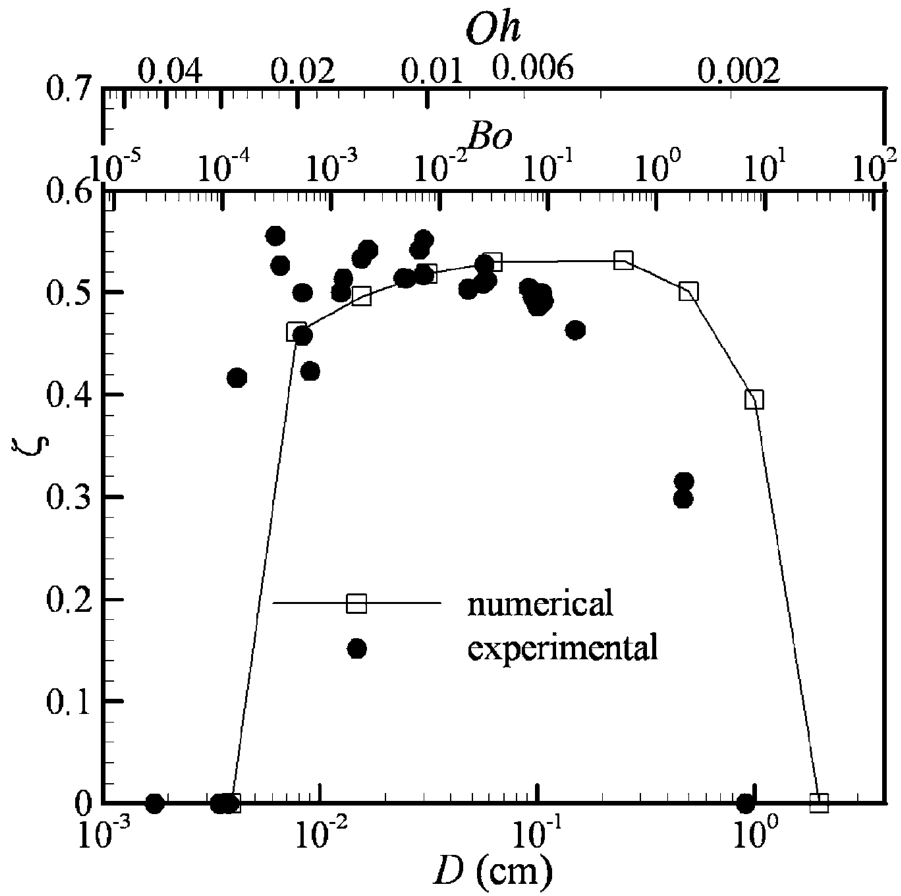
←D=78.1 [illegible]m
Oh=2.00E-2
Bo=4.86E-4

D=39.1
[illegible]m→
Oh=2.83E-2
Bo=1.22E-4



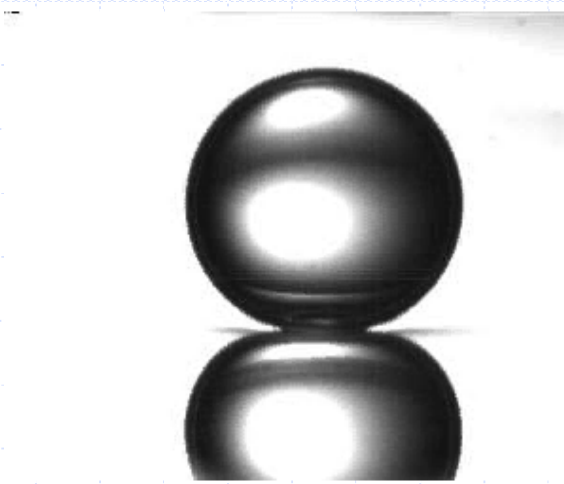
Condition for partial coalescence

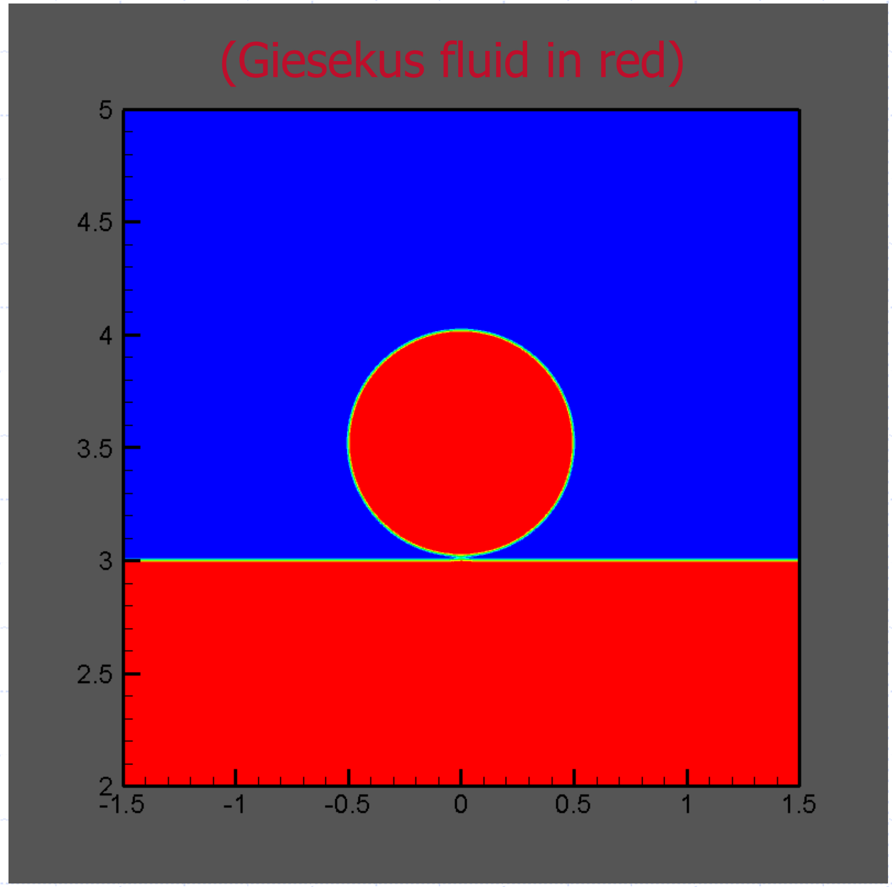
- Partial coalescence occurs for intermediate range of drop sizes
- Lower limit (viscosity):
  - 39-78 μm (exp. ~ 41 μm)
- Upper limit (gravity):
  - 1-2 cm (exp. ~ 1cm)
  - Relatively large error due to initial condition



Effect of viscoelasticity

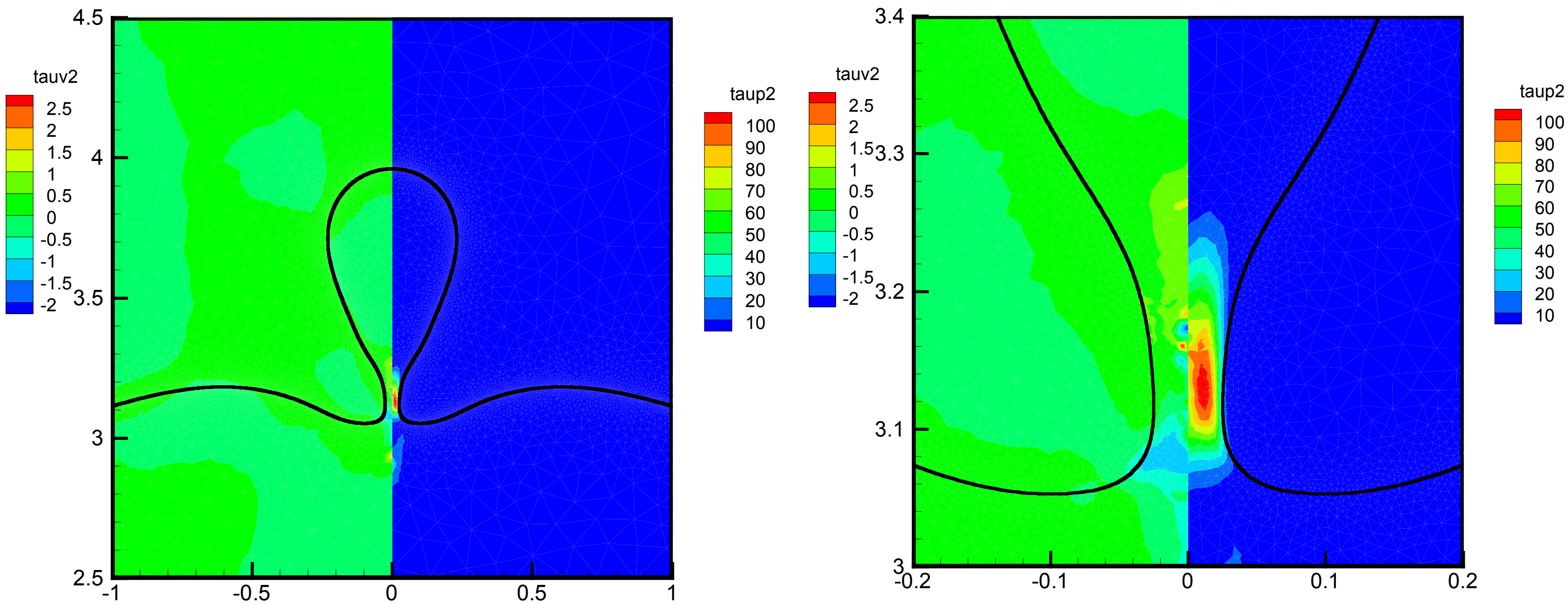
PEO droplet in decane





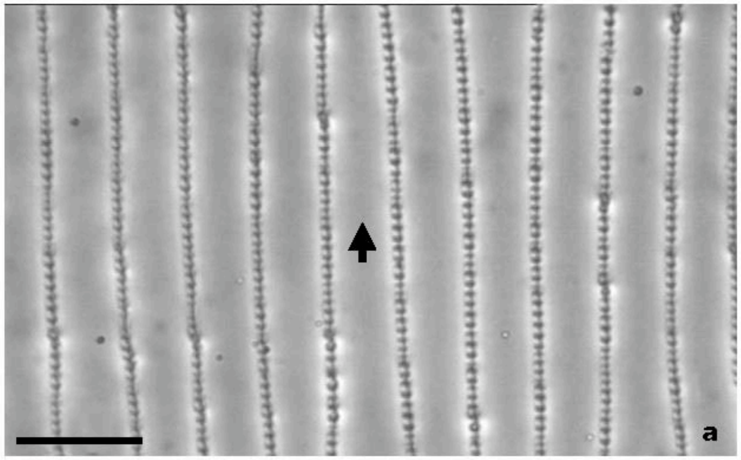
❖Partial coalescence is suppressed

Delayed breakup of polymer thread

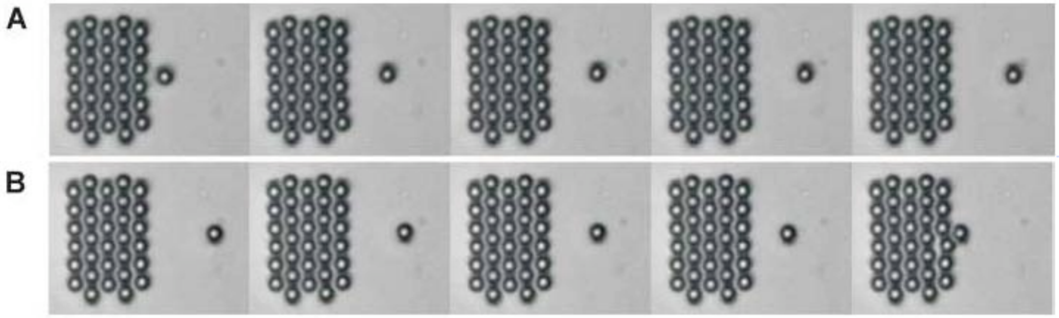


II. Self-assembly of droplets in liquid crystal

Parallel chains and 2D arrays

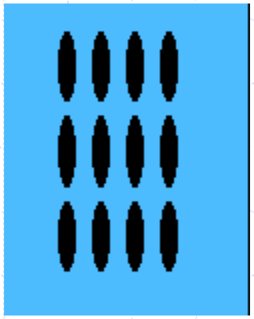


Loudet et al. *Nature* **407** (2000)



Zumer et al. *Science* **313** (2006)

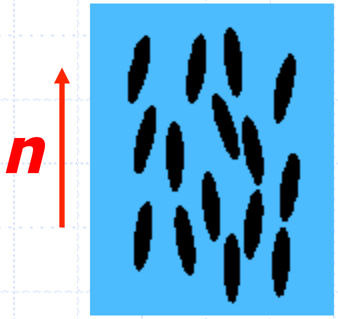
What are nematic liquid crystals?



Solid phase

Liquid phase

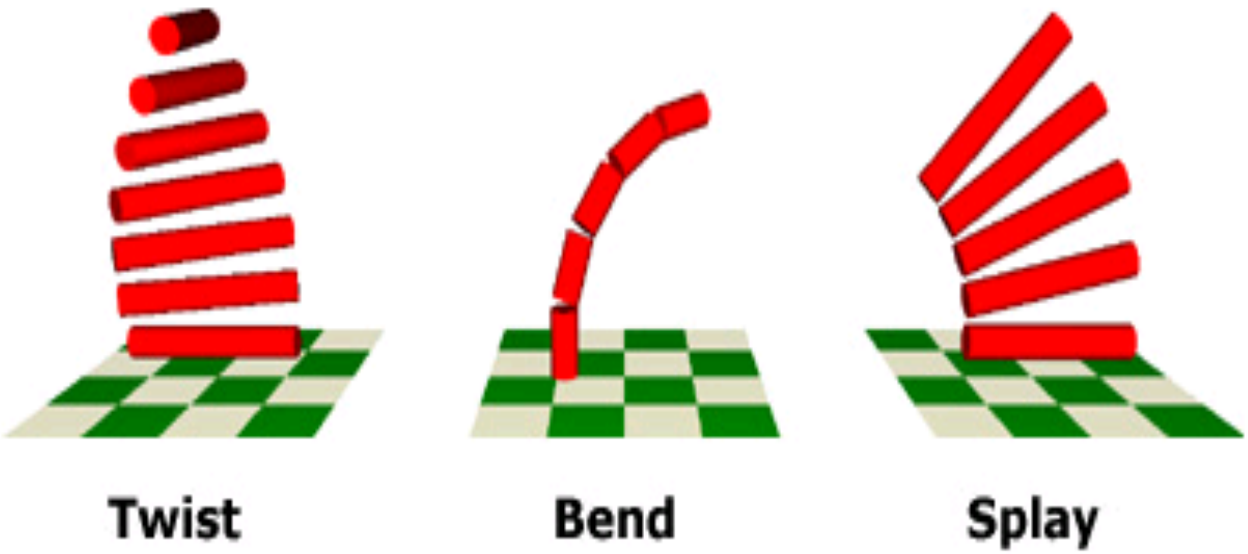
Gas phase



liquid crystalline
(nematic) phase

- Solid-liquid duality: flow like liquids but transmit torque

Nematic: bulk distortions

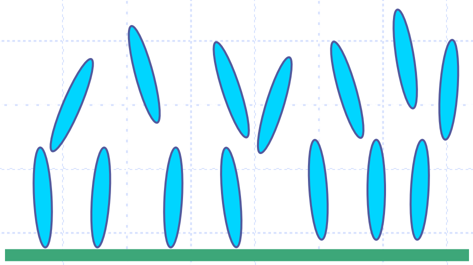


$$f_{bulk} = \frac{1}{2}K_1(\nabla \cdot \boldsymbol{n})^2 + \frac{1}{2}K_2(\boldsymbol{n} \cdot \nabla \times \boldsymbol{n})^2 + \frac{1}{2}K_3(\boldsymbol{n} \times \nabla \times \boldsymbol{n})^2, \ |\boldsymbol{n}|=1$$

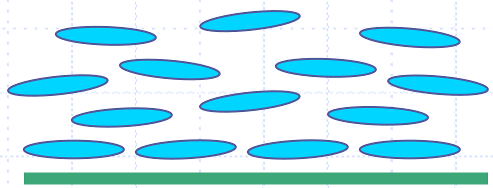
$$f_{bulk} = \frac{1}{2}K\nabla\boldsymbol{n} : (\nabla\boldsymbol{n})^{\mathrm{T}} \quad \text{if} \quad K = K_1 = K_2 = K_3$$

Nematic: surface anchoring

- Preferred orientation on interfaces/substrates



Homeotropic anchoring



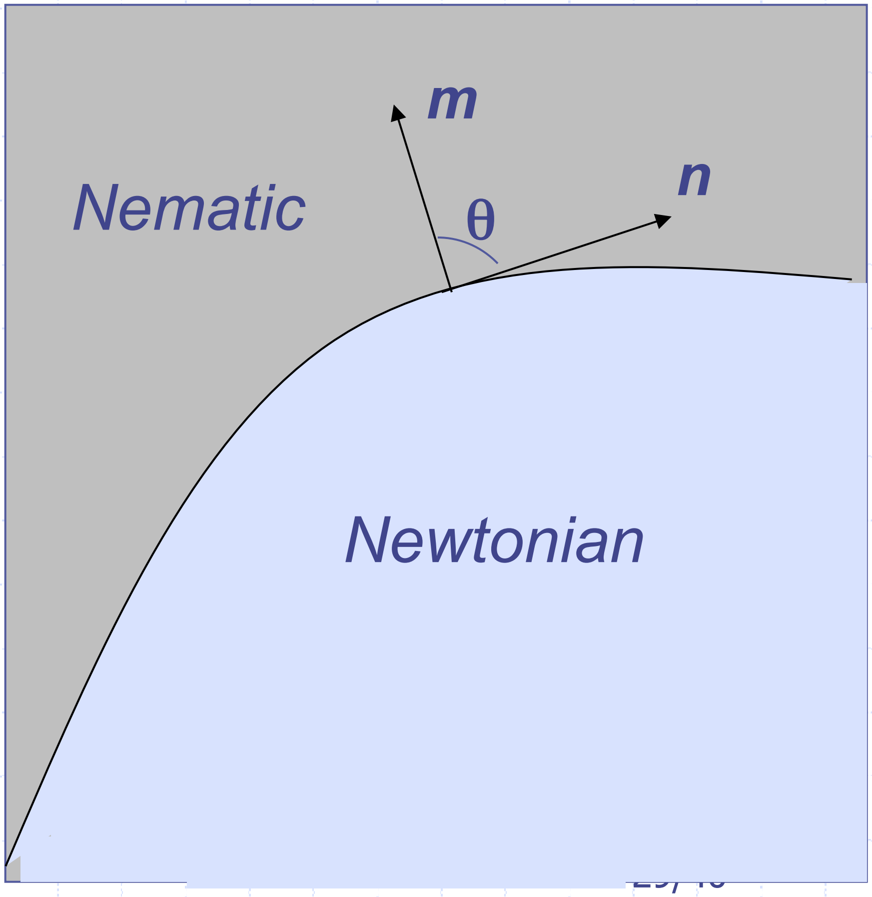
Planar anchoring

Interfacial anchoring energy

Energy penalty for *n* deviating from anchoring

$$f_{planar}(\vec{n},\vec{m}) = \frac{1}{2}W(\vec{n}\cdot\vec{m})^2$$

$$f_{homeotropic}(\vec{n},\vec{m}) = \frac{1}{2}W[1-(\vec{n}\cdot\vec{m})^2]$$



Competition between bulk orientation and anchoring: Wa/K

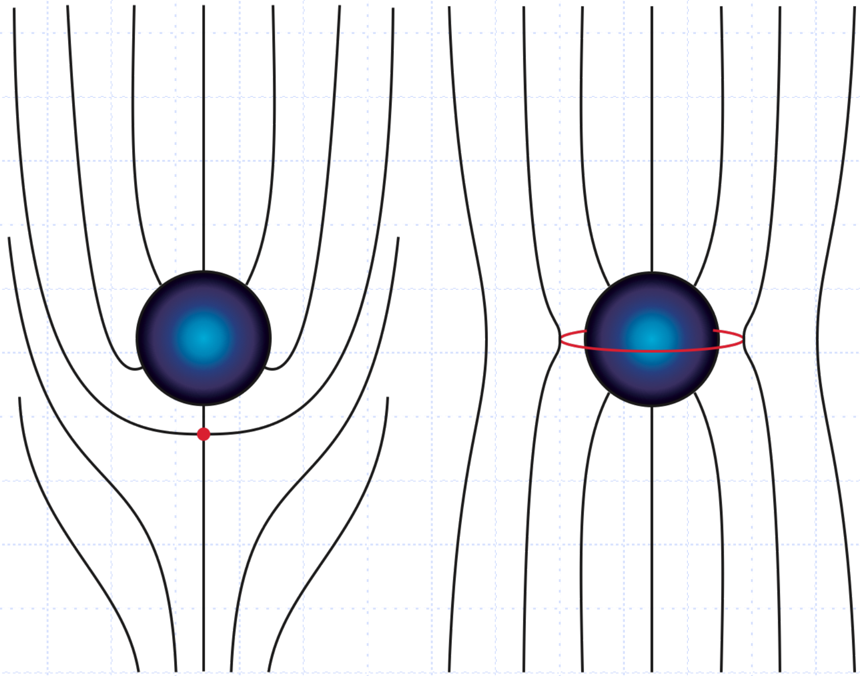
Defects for homeotropic anchoring

Satellite vs. Saturn ring: an artist's conception:

Satellite defect

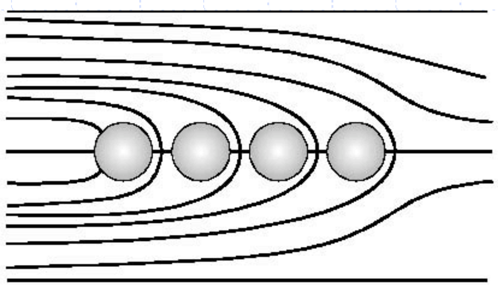
↓

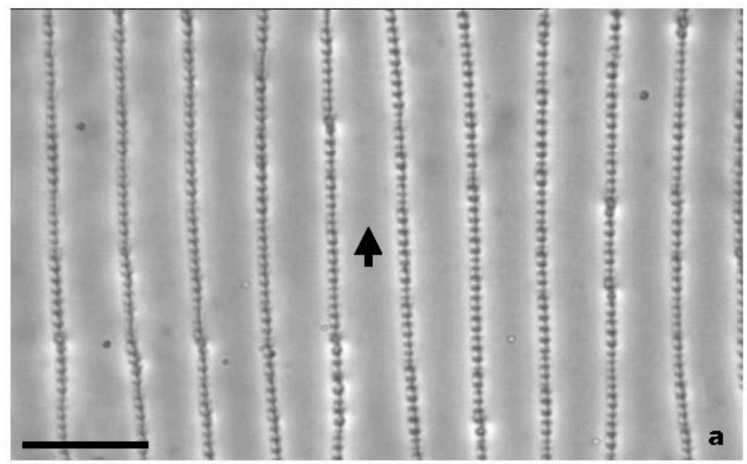
Dipole



Saturn ring defect

Defect-mediated self-assembly?





The need to study defect dynamics in self-assembly and flow

Diffuse-interface simulations:

$$\nabla \cdot \boldsymbol{v} = 0, \quad \rho\left(\frac{\partial \boldsymbol{v}}{\partial t} + \boldsymbol{v} \cdot \nabla \boldsymbol{v}\right) = -\nabla p + \nabla \cdot \boldsymbol{\sigma}$$

$$\frac{\partial \phi}{\partial t} + \boldsymbol{v} \cdot \nabla \phi = \gamma \, \lambda \nabla^2 \left[-\nabla^2 \phi + \frac{\phi(\phi^2 - 1)}{\varepsilon^2}\right]$$

$$\gamma_1 \left(\frac{\partial \boldsymbol{n}}{\partial t} + \boldsymbol{v} \cdot \nabla \boldsymbol{n} - \boldsymbol{\Omega} \cdot \boldsymbol{n}\right) + \gamma_2 \boldsymbol{D} \cdot \boldsymbol{n} = \boldsymbol{h}$$

Leslie-Ericksen theory

$$\boldsymbol{h} = K\left[\nabla \cdot \left(\frac{1+\phi}{2} \nabla \boldsymbol{n}\right) - \frac{1+\phi}{2} \frac{(\boldsymbol{n} \cdot \boldsymbol{n} - 1)\boldsymbol{n}}{\delta^2}\right] + \boldsymbol{g}$$

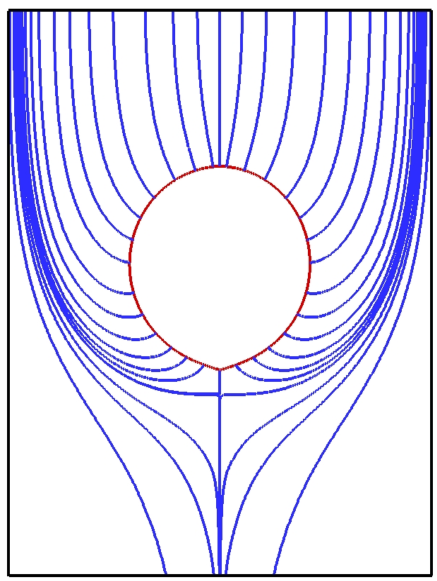
$$\boldsymbol{\sigma} = -\lambda \nabla \phi \nabla \phi - K \frac{1+\phi}{2} \nabla \boldsymbol{n} \cdot (\nabla \boldsymbol{n})^{\mathrm{T}} - \boldsymbol{G} + 2\mu \boldsymbol{D} + \boldsymbol{\sigma}_{\mathrm{visc}}$$

$$\boldsymbol{\sigma}_{\mathrm{visc}} = \alpha_1 \boldsymbol{D} : \boldsymbol{nnnn} + \alpha_2 \boldsymbol{nN} + \alpha_3 \boldsymbol{Nn} + \alpha_4 \boldsymbol{D} + \alpha_5 \boldsymbol{nn} \cdot \boldsymbol{D} + \alpha_6 \boldsymbol{D} \cdot \boldsymbol{nn}$$

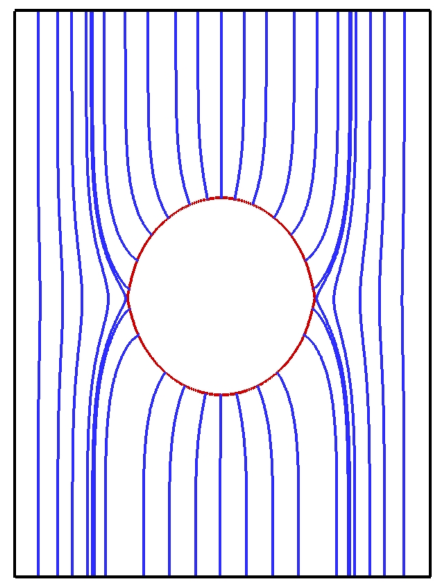
$$\boldsymbol{G} = \begin{cases} A(\boldsymbol{n} \cdot \nabla \phi)\boldsymbol{n} \nabla \phi & (Planar) \\ A[(\boldsymbol{n} \cdot \boldsymbol{n})\nabla \phi - (\boldsymbol{n} \cdot \nabla \phi)\boldsymbol{n}]\nabla \phi \end{cases} \qquad \boldsymbol{g} = \begin{cases} A(\boldsymbol{n} \cdot \nabla \phi)\nabla \phi & (Planar) \\ A[(\nabla \phi \cdot \nabla \phi)\boldsymbol{n} - (\boldsymbol{n} \cdot \nabla \phi)\nabla \phi] \end{cases}$$

Static Drop: homeotropic anchoring

Depending on the initial conditions: metastability



W/σ=1.0
Wa/K=30

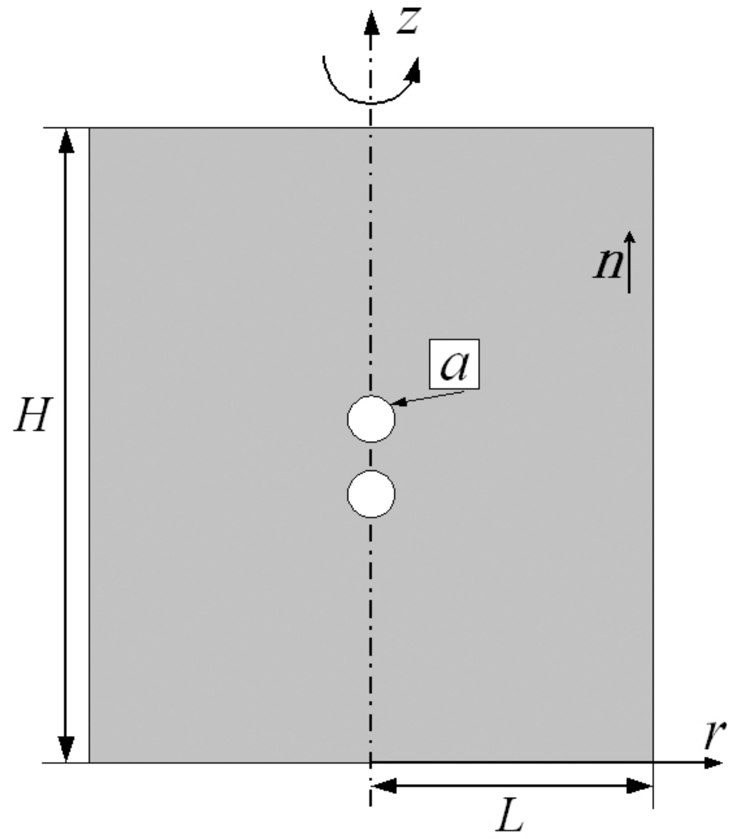


W/σ=1.0
Wa/K=30

Pairwise interaction: computation

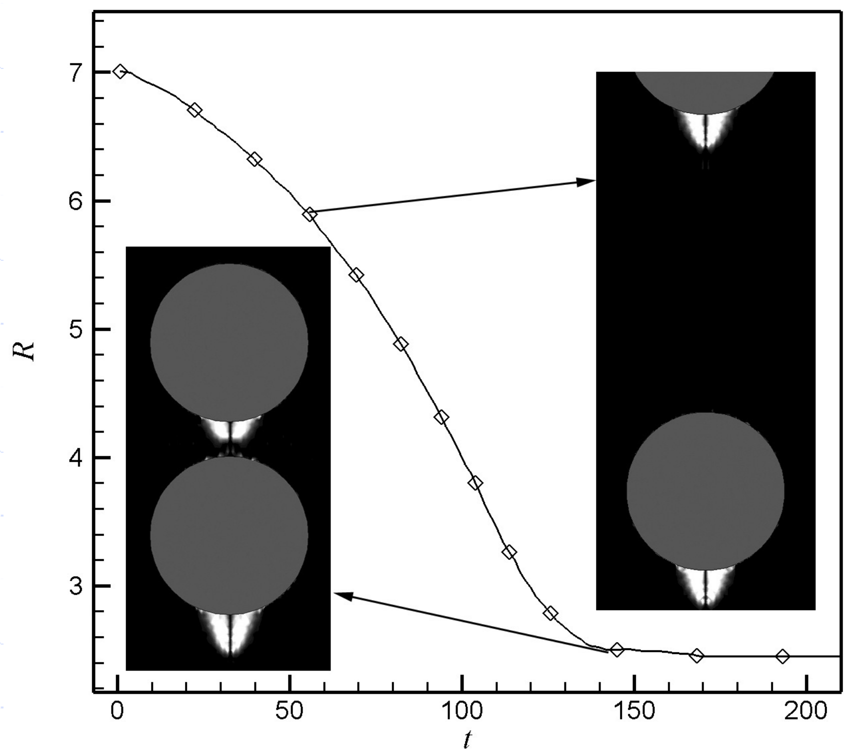
Axisymmetric,
L/a=15, H/a=24,
ε/a=0.01, h_1=0.006,
h_2=0.04, h_3=0.06.

Vertical alignment
in the far field.

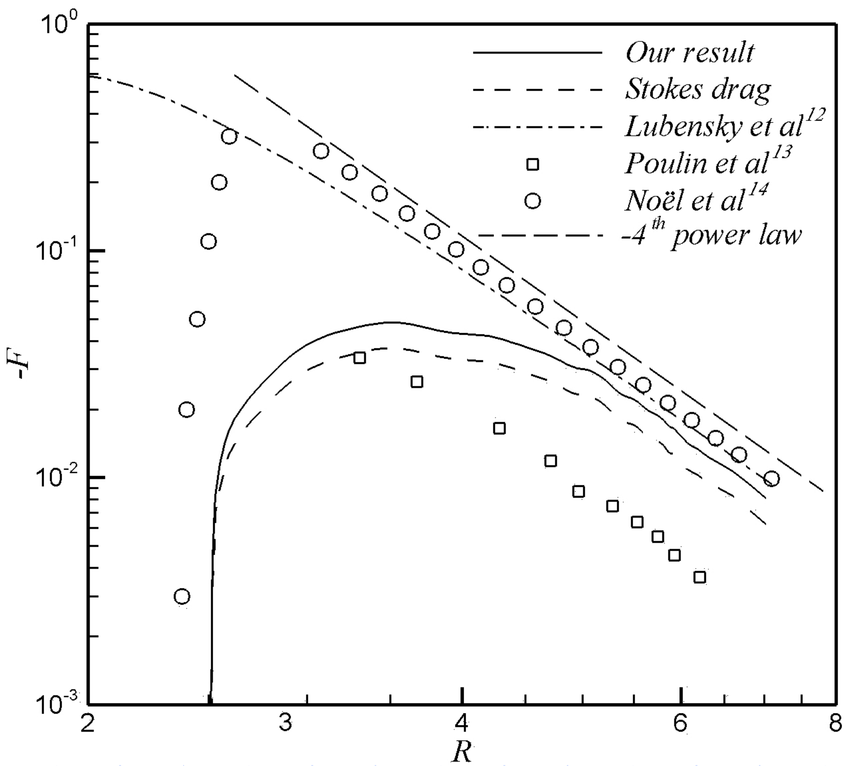


Attraction force

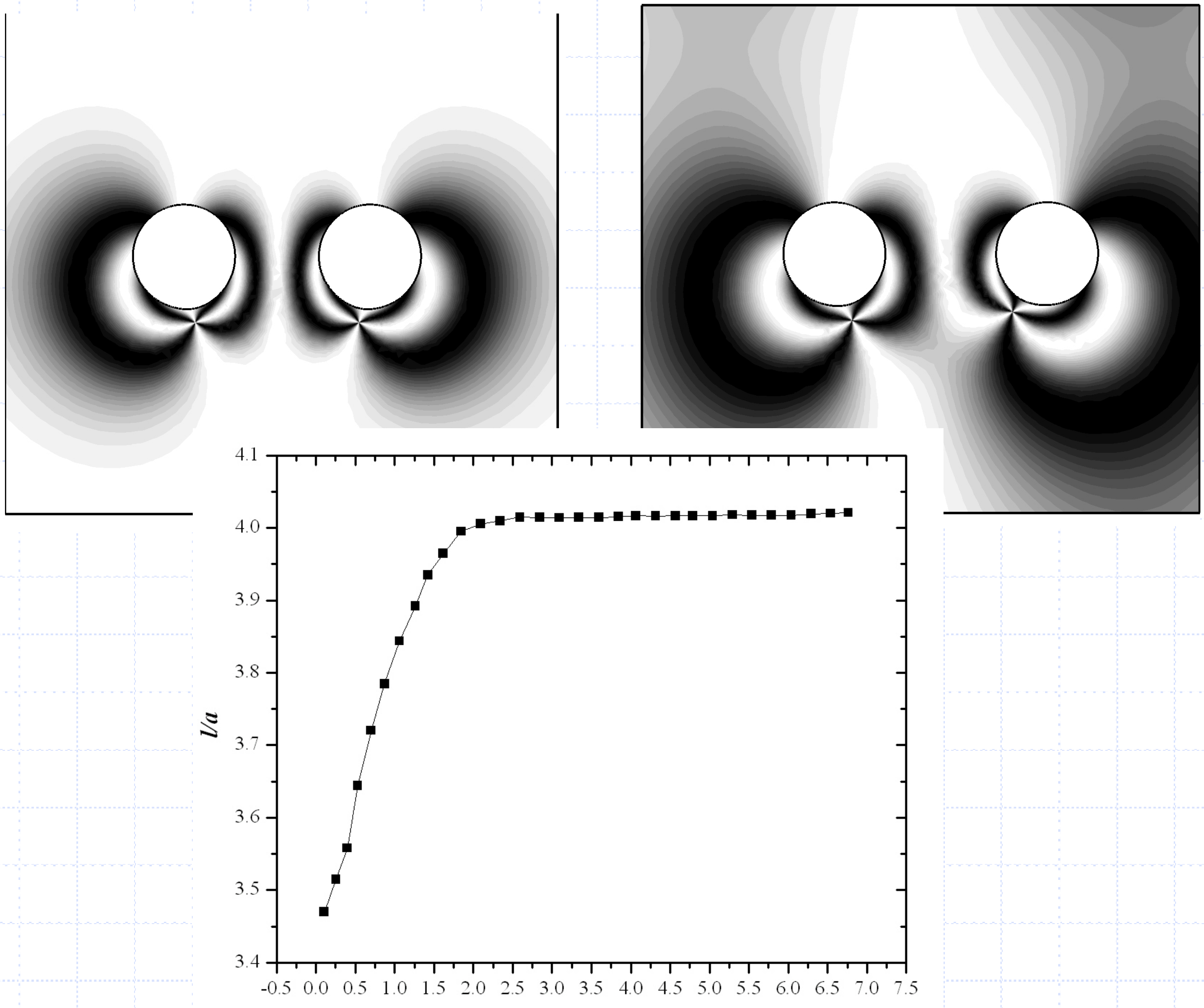
Distance



Attraction force



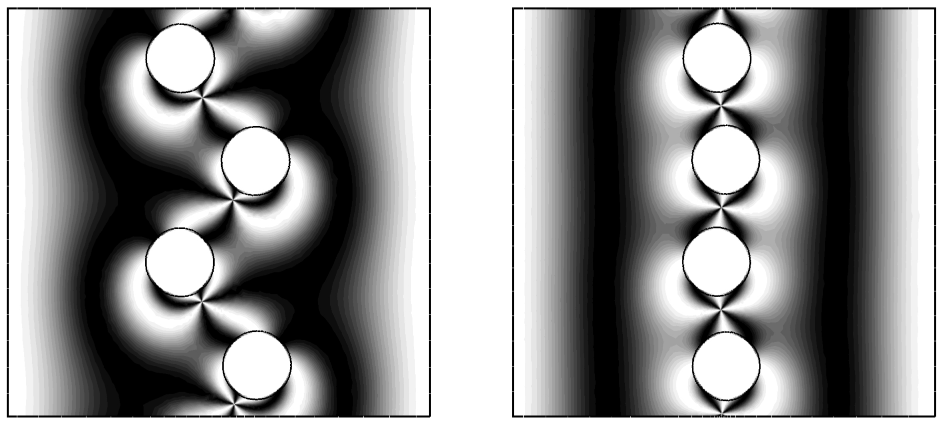
Lateral repulsion

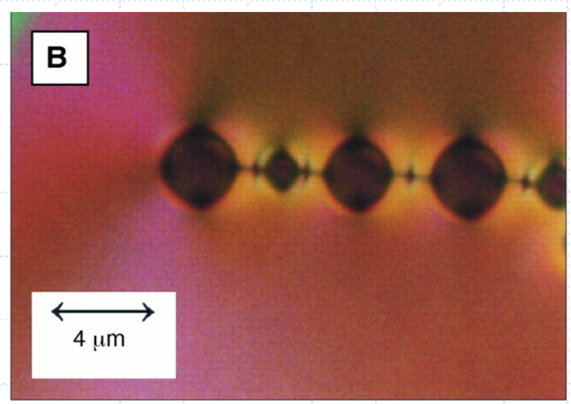


Self-assembly of droplets

(2D numerical simulations in doubly periodic cell)

4-particle assemblage

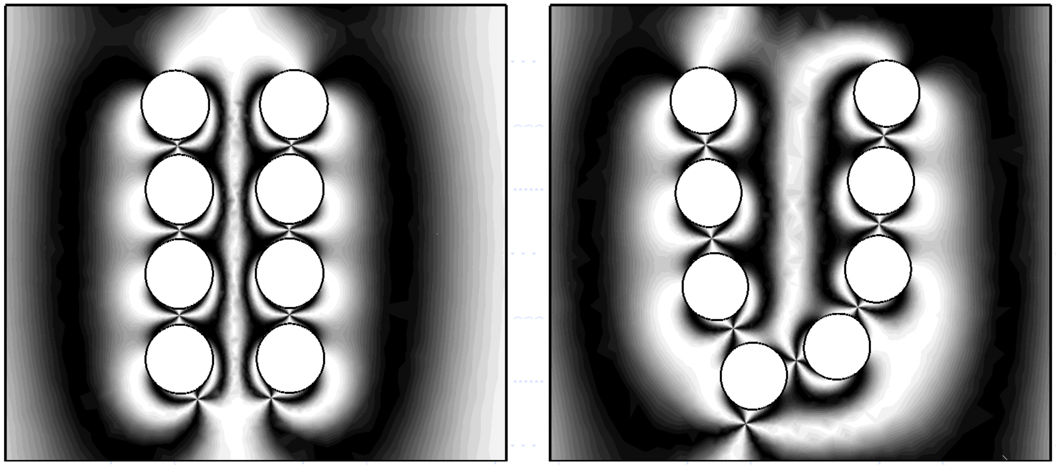




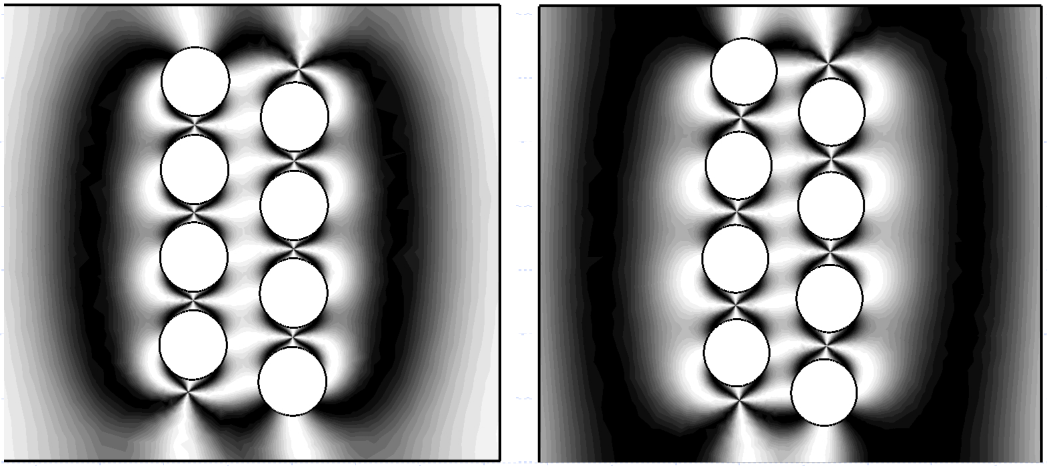
Self-assembly of droplets

Chain-chain interaction:

Repulsion

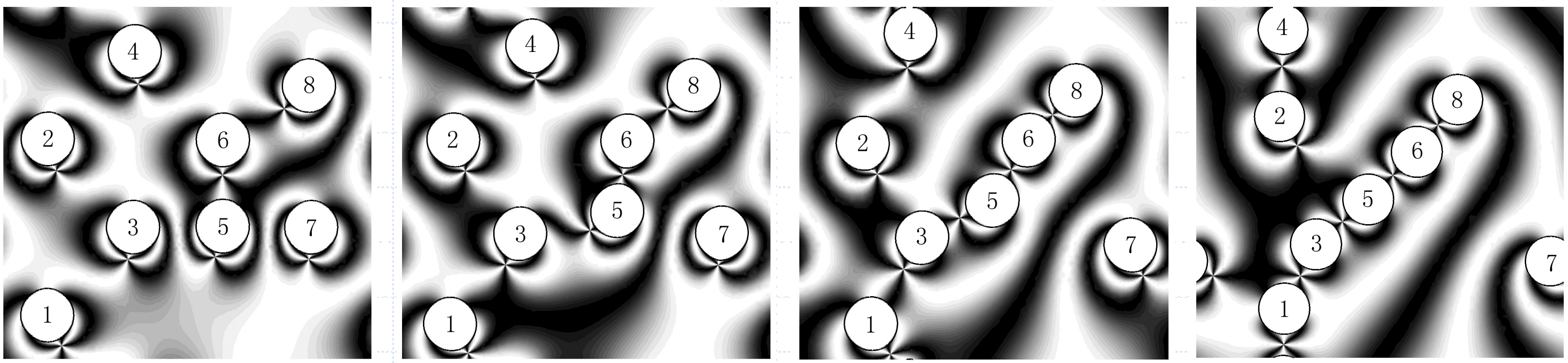


Attraction



Self-assembly of 8 droplets

(2D numerical simulations in doubly periodic cell)



(a) (b) (c) (d)

Conclusion

- Diffuse-interface method for drop/bubble dynamics: strengths and limitations
- Bulk viscoelasticity affects interfacial behavior: suppression of partial coalescence
- Drop/bubble motion in nematic liquid crystal: coupling among flow, defect configuration and drop shape; drop self-assembly

References

- Numerical methodology
  - Yue et al., *J. Comput. Phys*. **219**, 47 (2006); **223**, 1 (2007); **229**, 498 (2010).
- Partial coalescence
  - Experimental: Chen et al., *Phys. Fluids* **18**, 051705, 092103 (2006).
  - Simulation: Yue et al., *Phys. Fluids* **18**, 102102 (2006)
- Drop and bubble in nematic & self-assembly
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