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A diffuse-interface method for two-phase flows with soluble surfactants

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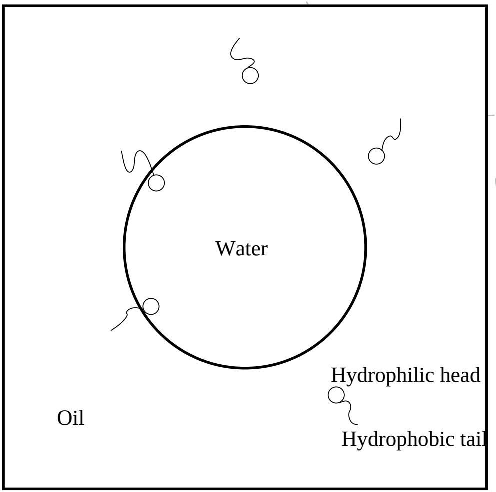
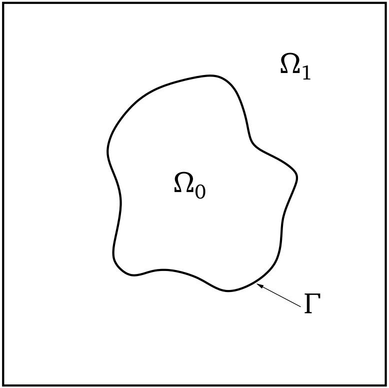
Surfactant flow

- Surfactants occur in many systems of industrial interest
- Surfactants reduce the surface tension by adsorbing at the liquid-liquid interface



Mathematical formulation

Consider a domain with an interface, Γ, which can deform, stretch and change topology.

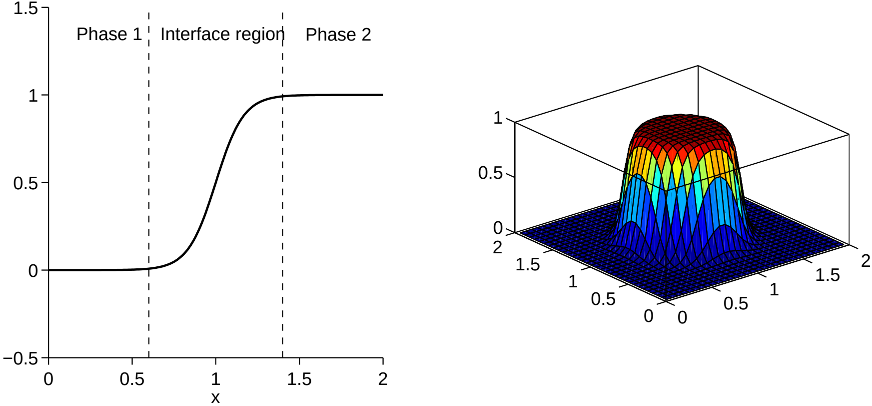


- Want to model a substance only soluble in Ω_1
- Also want to track a quantity moving on Γ
- There is adsorption/desorption between Ω_1 and Γ

This work is based on

- Ratz and Voigt, *PDEs on surfaces – a diffuse interface approach*, CMS (2006)
- Li, Lowengrub, Ratz, Voigt, *Solving PDEs in complex geometries: A diffuse domain approach* , CMS (2009)
- Teigen, Li, Lowengrub, Wang, Voigt, *A diffuse-interface approach for modelling transport, diffusion and adsorption/desorption of material quantities on a deformable interface*, CMS (to appear)

The phase-field method



- Treat the interface as a smooth transition
- Widely used method for treating interfacial dynamics

The Cahn–Hilliard equation

If a velocity field is present, the following system must be solved to advect the phase-field function

$$
\begin{aligned}
\frac{\partial c}{\partial t} + \boldsymbol{\nabla}\cdot(c\boldsymbol{u}) &= \boldsymbol{\nabla}\cdot(M(c)\boldsymbol{\nabla}\mu_c), \\
\mu_c &= g'(c) - \epsilon^2 \boldsymbol{\nabla}^2 c \\
M(c) &= \sqrt{c^2(1-c)^2} \\
g &= \frac{1}{4}c^2(1-c)^2
\end{aligned}
$$

Note that the first equation contains a 4th order term

The surface equation

- The interface dynamics are governed by

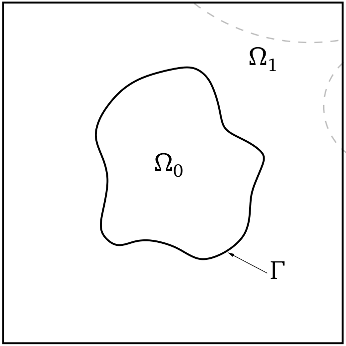
$$\frac{\partial f}{\partial t} + \nabla_\Gamma \cdot (\boldsymbol{u} f) = \nabla_\Gamma \cdot (D_f \nabla_\Gamma f) + j,$$
$$j = r_a F(f_\infty - f) - r_d f,$$

- The phase-field method makes this easy, by instead solving

$$\frac{\partial}{\partial t}(f\,\delta_\Gamma) + \nabla\cdot(f\,\delta_\Gamma\,\boldsymbol{u}) = \nabla\cdot(\delta_\Gamma D_f \nabla f) + \delta_\Gamma j$$

in Ω.

- Can prove convergence to the sharp interface model using asymptotic analysis



The bulk equation

- Dynamics of the bulk surfactant,

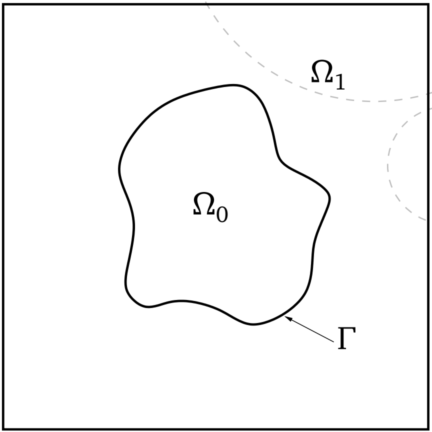
$$\frac{\partial F}{\partial t} + \nabla\cdot(F\boldsymbol{u}) = D_F \nabla^2 F \text{ in } \Omega_1,$$
$$D_F \nabla F \cdot \boldsymbol{n} = -j \text{ on } \Gamma$$

- With the phase-field method,

$$\frac{\partial (HF)}{\partial t} + \nabla\cdot(HF\boldsymbol{u}) = D_F\, \nabla\cdot\,(H\nabla F) - \delta_\Gamma j$$

in Ω.

- Again, can prove convergence using asymptotic analysis



The delta and Heaviside functions

The delta function is

$$\int_\Gamma f \, \mathrm{d}\Gamma = \int_\Omega f \delta_\Gamma \, \mathrm{d}\Omega$$

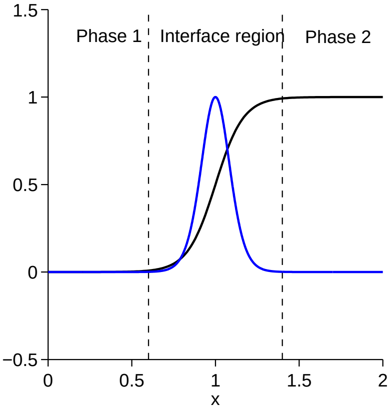
One example of a delta function is

$$\delta_\Gamma \approx \frac{3\sqrt{2}}{\epsilon} c^2 (1-c)^2$$

The Heaviside function is

$$H = \begin{cases} 1 & \text{in} \quad \Omega_1, \\ 0 & \text{in} \quad \Omega_0. \end{cases}$$

One example is $H = 1 - c$.



Coupling to the Navier–Stokes equations

$$\rho\left(\frac{\partial \boldsymbol{u}}{\partial t}+(\boldsymbol{u}\cdot\nabla)\boldsymbol{u}\right)=-\nabla p+\nabla\cdot[\mu(\nabla\boldsymbol{u}+\nabla\boldsymbol{u}^T)]+\nabla\cdot\boldsymbol{F_c},$$
$$\nabla\cdot\boldsymbol{u}=0$$

This is “standard” Navier–Stokes, except for the capillary pressure tensor,

$$\boldsymbol{F}_c=\sigma\delta(\boldsymbol{I}-\boldsymbol{n}\otimes\boldsymbol{n})$$
$$\nabla\cdot\boldsymbol{F}_c=\sigma\kappa\delta\boldsymbol{n}-(\nabla_\Gamma\sigma)\delta$$

The relationship between surface tension and surfactant concentration is

$$\sigma(f)=\sigma_0\left[1-\beta\ln\left(1-\frac{f}{f_\infty}\right)\right]$$

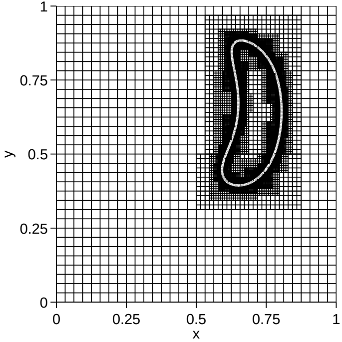
Numerical methods

- Finite differences in space
- Semi-implicit Crank-Nicolson in time
  - Solve the equation systems using adaptive FAS multigrid
- Solve f and F together as a system
- Projection method for the Navier–Stokes equations

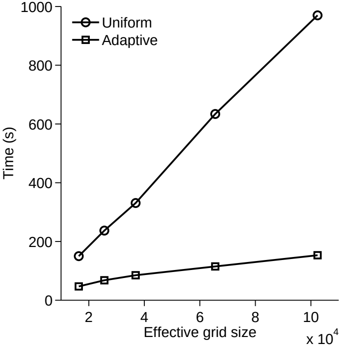
Adaptive mesh refinement

The equations are solved on block-structured, adaptive grids, giving high resolution around the interface in an efficient manner.

Accurate tracking of the interface

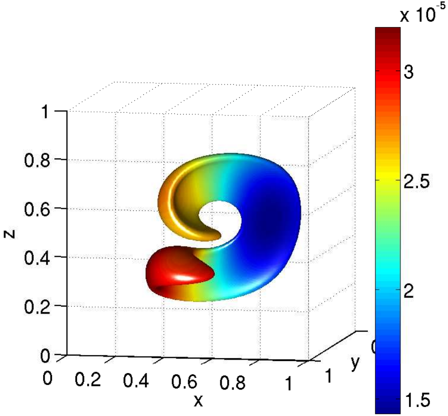


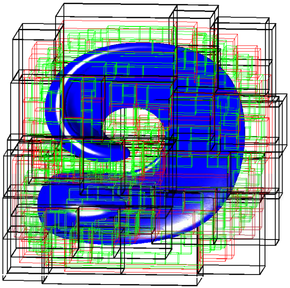
High speedup



Also note the linear run-time complexity, which is a result of the multigrid algorithm used to solve the equations

Adaptive mesh refinement in 3D





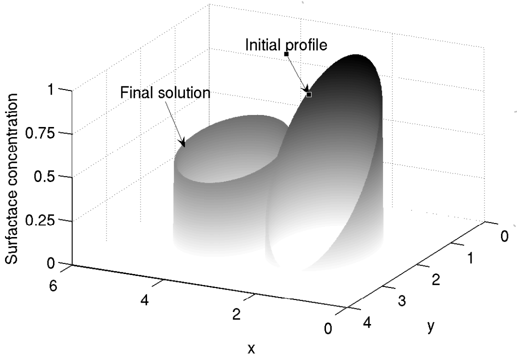
Interfacial diffusion on an advected circle

The initial surfactant profile is given by

$$f_0(\theta) = \frac{1}{2}(1 - \cos\theta)$$

This evolution has an analytical solution

$$f(\theta, t) = \frac{1}{2}\left(1 - e^{-D_f t}\cos\theta\right)$$



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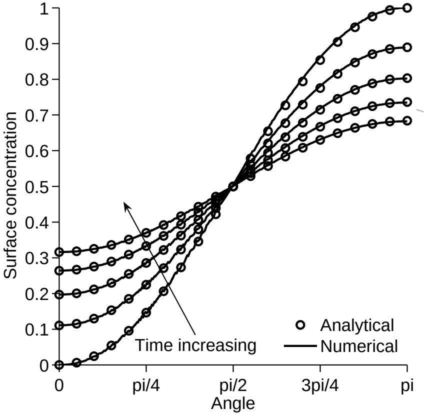

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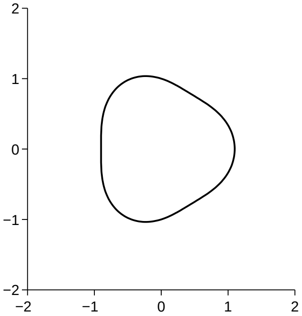
Grid spacing	Error ($\times 10^{-2}$)	Order
1/8	4.60	-
1/16	2.47	0.90
1/32	1.23	1.01
1/64	0.62	0.99
1/128	0.31	1.01

Bulk-surface coupling on a perturbed circle

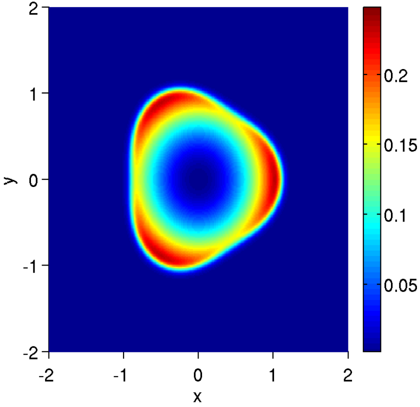
$$\frac{\partial f}{\partial t} = \nabla_\Gamma^2 f - f + F + \zeta_1 \text{ on } \Gamma$$
$$\frac{\partial F}{\partial t} = \nabla^2 F - F + \zeta_2 \text{ in } \Omega_0$$
$$\nabla F \cdot \boldsymbol{n} = f - F \text{ on } \Gamma.$$

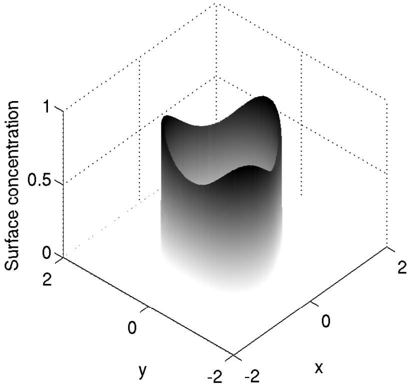
Choose ζ_1 and ζ_2 so that

$$F = \frac{1}{4}(x^2 + y^2)e^{-3t},$$
$$f = \left(\frac{1}{2}\frac{r(\theta)}{\sqrt{r(\theta)^2 + r'(\theta))^2}} + \frac{1}{4}r(\theta)^2 \right) e^{-3t}.$$

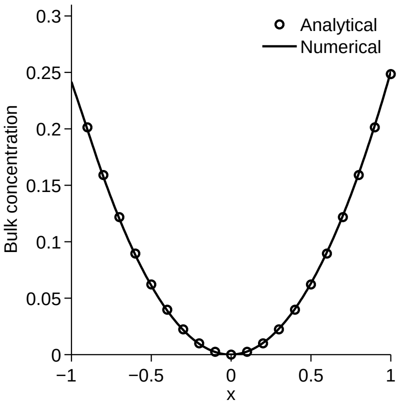


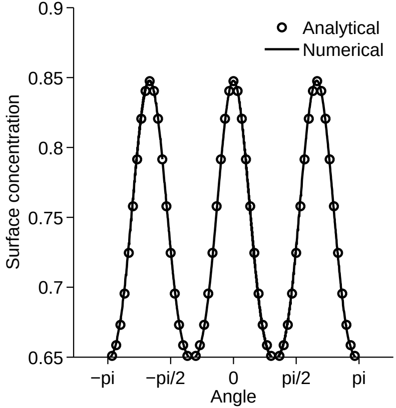
Solution


2
1
0
-1
-2
y
-2
-1
0
1
2
x
0.2
0.15
0.1
0.05


Surface concentration
1
0.5
0
2
0
y
-2
-2
0
x
2

Comparison to analytical solution

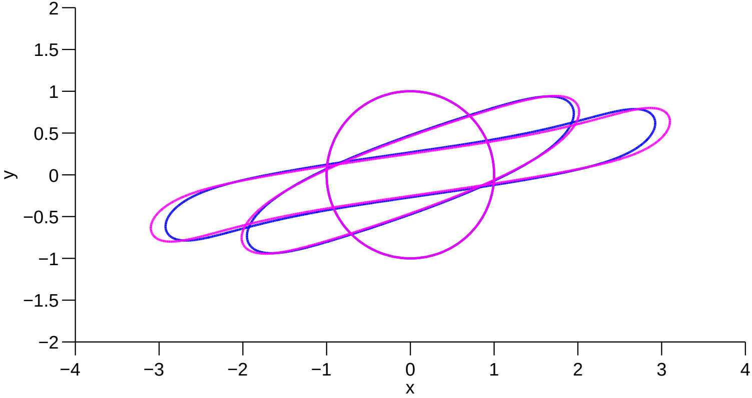




Convergence

Grid spacing	Bulk concentration Error ($\times 10^{-3}$)	Bulk concentration Order	Surface concentration Error ($\times 10^{-2}$)	Surface concentration Order
1/16	17.0	-	11.0	-
1/32	9.5	0.84	4.4	1.32
1/64	5.1	0.90	1.5	1.55
1/128	2.6	0.97	0.74	1.02

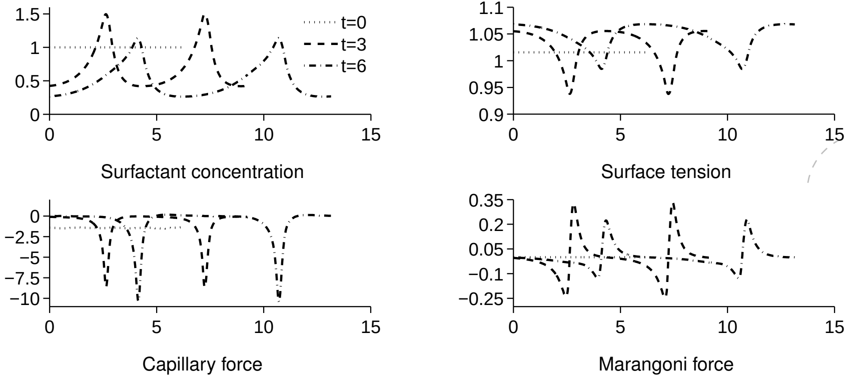
Drop in shear flow - insoluble surfactant



Blue: clean, magenta: surfactant-covered

The non-uniform surfactant distribution leads to greater deformation.

Drop in shear flow - insoluble surfactant



Compare very well to Xu, Li, Lowengrub, Zhao, *A level-set method for interfacial flows with surfactant* , JCP (2006)

Soluble surfactant

We will look at the influence of two non-dimensional quantities:

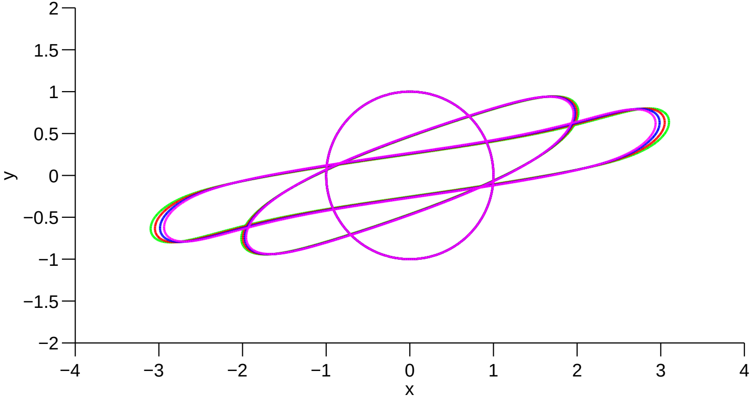
- The Biot number

$$Bi = \frac{\text{bulk/interface transport}}{\text{interfacial convection}} = \frac{r_d}{\dot{\gamma}}$$

- The bulk Peclet number

$$Pe_F = \frac{\text{convection}}{\text{diffusion}} = \frac{\dot{\gamma} r^2}{D_F}$$

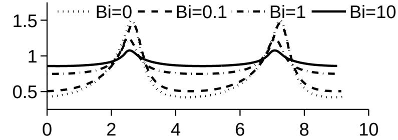
Soluble surfactant - Biot number



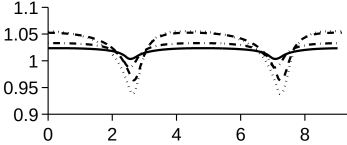
Green: $Bi = 0$, red: $Bi = 0.1$, blue: $Bi = 1$, magenta: $Bi = 10$.

Lower deformation for higher Biot numbers. More adsorption gives a more uniform surfactant distribution.

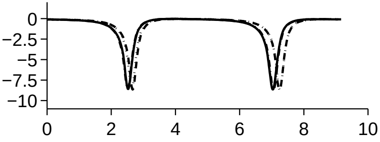
Soluble surfactant - Biot number



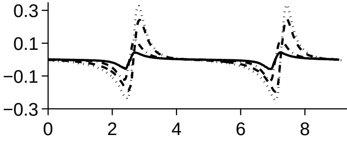
Surfactant concentration



Surface tension



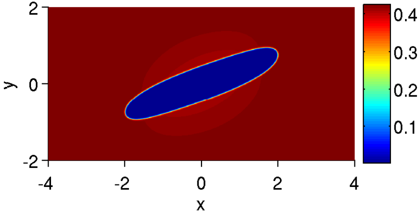
Capillary force



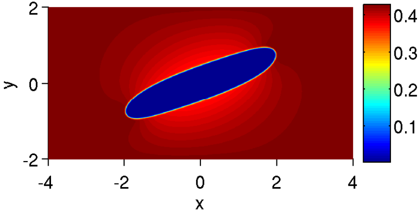
Marangoni force

At $Bi = 10$, the process is *diffusion-limited*.

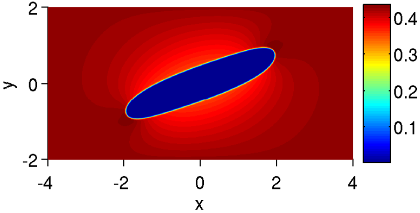
Soluble surfactant - Biot number



$Bi = 0.1$

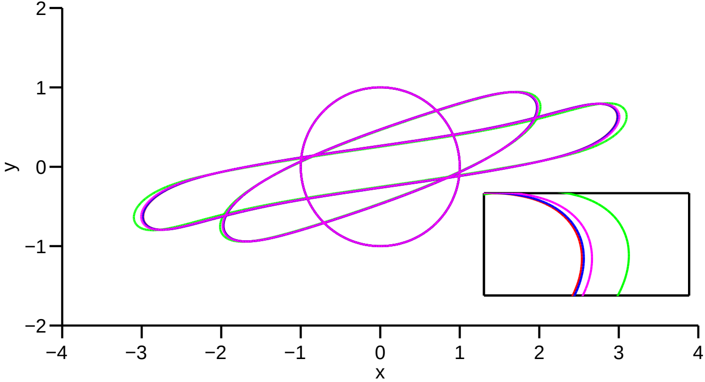


$Bi = 1$



$Bi = 10$

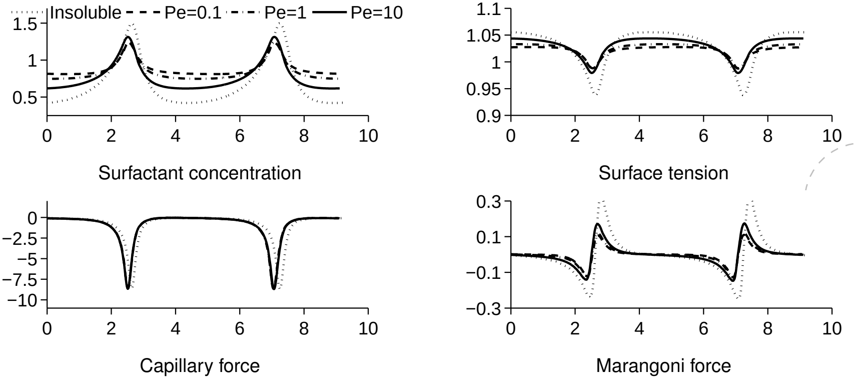
Soluble surfactant - bulk Peclet number



Green: insoluble, red: $Pe_F = 0.1$, blue: $Pe_F = 1$, magenta: $Pe_F = 10$.

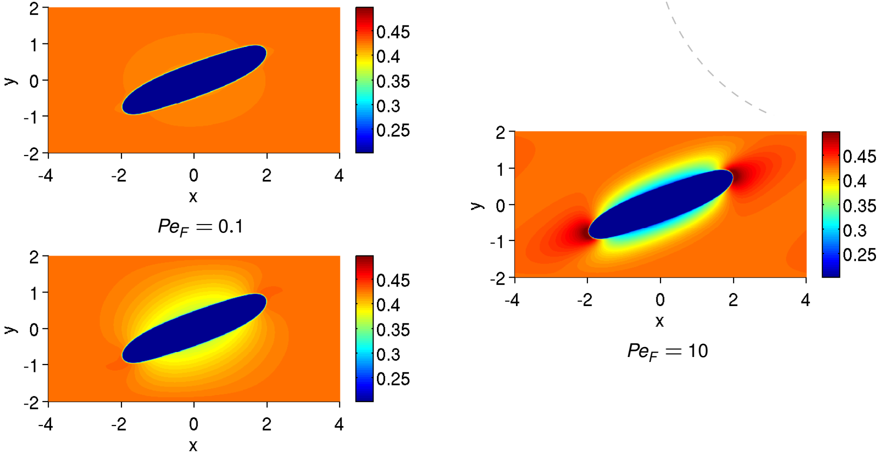
Lower deformation for lower Peclet numbers, higher diffusion in the bulk leads to higher adsorption and more uniform surfactant distribution.

Soluble surfactant - bulk Peclet number



At $Pe_F = 0.1$, the process is *adsorption-limited*.

Soluble surfactant - bulk Peclet number

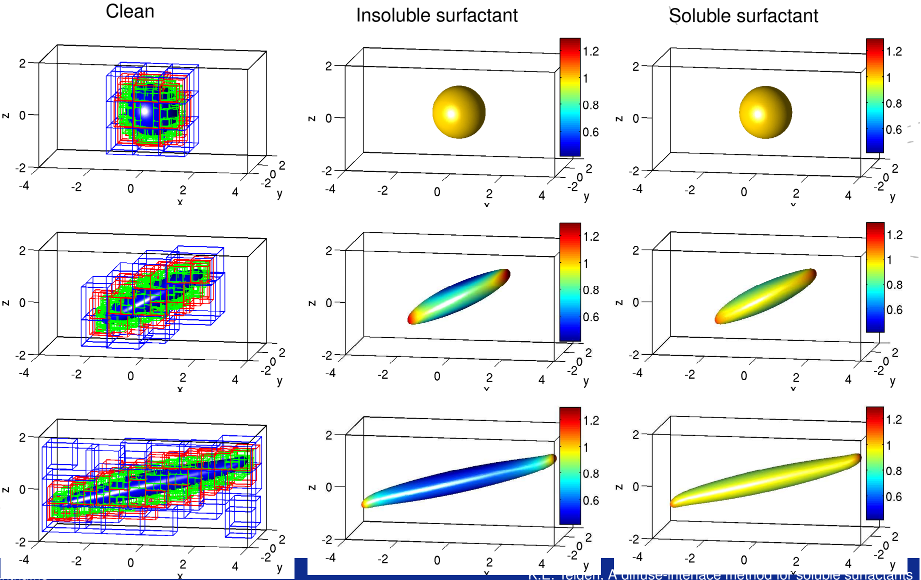


$Pe_F = 0.1$

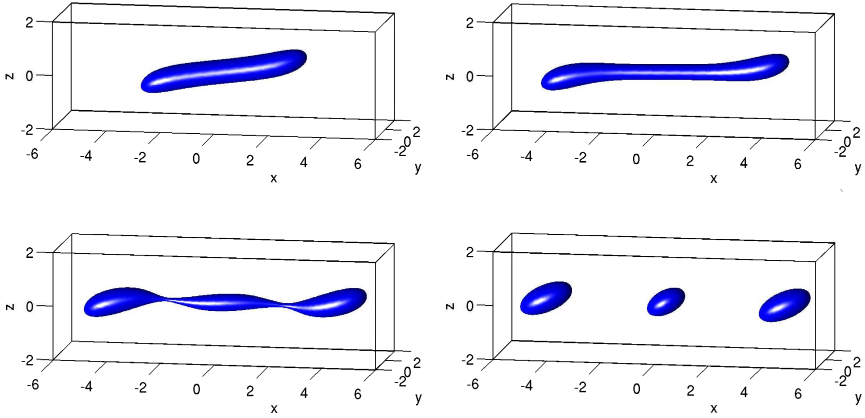
$Pe_F = 1$

$Pe_F = 10$

Drop in shear flow - 3D



Drop breakup - 3D



Summary

- The presence of a surfactant will increase drop deformation
- Surfactant solubility gives rise to several interesting physical phenomena
- The phase-field method is a very flexible tool
  - Can handle a wide range of complex physics
  - Easy to implement using standard numerical techniques
  - Amenable to mathematical analysis

Summary

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  - Easy to implement using standard numerical techniques
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This is a work in progress, so any feedback is highly appreciated!