Simulation of surfactant in diffuse interface flow

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Joint work

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Outline

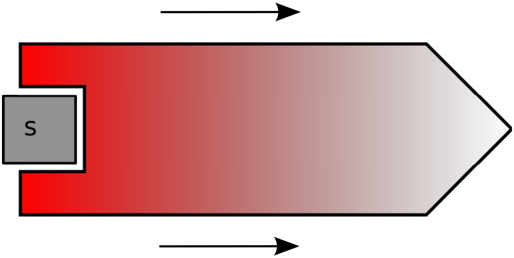
- Motivation: surfactants in fluid mixtures
- Diffuse interface modeling; the Ginzburg-Landau energy
- Diffuse interface modeling of surfactant two-phase flow
- Numerical illustrations and surprises

Motivation

Surface active agents:

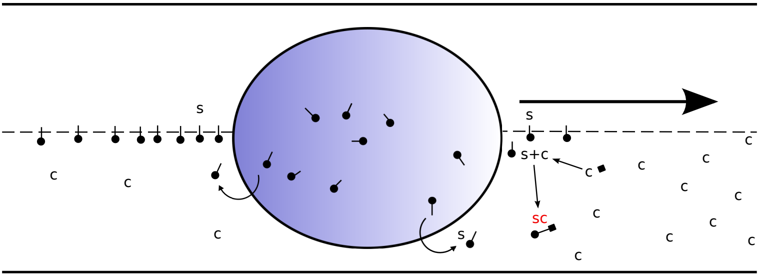
- Surfactants main usage comes from the fact that they lower the surface tension of liquid interfaces.
- Surfactants may therefore act as: detergents, wetting agents, emulsifiers (in food!), foaming agents, and dispersants (preventing settling or clumping in suspensions).

The soapraft



Realized very recently *in vivo* (Lagzi *et. al*, *J. Am. Chem. Soc.* (2010)) [maze.avi]

The maze solving droplet



Phase-field modeling

- Case: two immiscible fluids (eg. oil/water).
- Introduce the phase-field variable ϕ which is ± 1 in the two liquids, *diffuse* interface understood at $\phi = 0$.
- Goal: formulate a PDE in ϕ given thermodynamic potentials of the system (guess/ansatz/heuristics).

Phase-field modeling (cont.)

Non-dimensional Ginzburg-Landau free energy:

$$F_\phi = \int_V f(\phi) + \frac{\mathrm{Cn}^2}{4}(\nabla\phi)^2 \, dV,$$

with the standard choice $f(\phi) = (1-\phi)^2(1+\phi)^2$, a "double well" potential with two equilibrium states at $\phi = \pm 1$. *But this is clearly not unique!*

-Have also introduced the single parameter Cn, the *Cahn* number (i.e. the non-dimensional thickness of the interface).

Phase-field modeling (cont.)

Take the variation (functional derivative) of F_ϕ wrt. ϕ,

$$\frac{\delta F_\phi}{\delta \phi} = f'(\phi) - \frac{\mathrm{Cn}}{2}\Delta\phi =: \mu_\phi \quad \text{(chemical potential)}.$$

A suitable PDE for ϕ is now

$$\frac{\partial \phi}{\partial t} = \nabla \cdot M_\phi \nabla \mu_\phi \quad \text{(Cahn-Hilliard equation)},$$

plus appropriate BCs. *Note:* the mobility M_ϕ need not be constant!
-In practice: couple this to a flow field $\mathbf{u}$ driven eg. by the Navier-Stokes equations.

Phase-field modeling: pros and cons

- \+ Takes care of arbitrary topological changes at the cost of an implicit and diffuse interface.
- +/- *Phenomenological*: "A theory which expresses mathematically the results of observed phenomena without paying detailed attention to their fundamental significance" (*Concise Dictionary of Physics* (1973)). Some philosophers of science (Cartwright (1984)) argue that all laws of Nature are phenomenological generalizations...
- +/- "Straightforward" to generate new equations to account for new situations.
- \- The numerical resolution near the interface where $\phi \approx 0$ may have to be *very* thin in order to capture the correct dynamics.

Phase field modeling of surfactants

- Two immiscible fluids (eg. oil/water) plus a surfactant (eg. a detergent).
- Phase-field variable ϕ as before, new variable $\psi \in [0, 1]$ is the concentration of surfactant.

Suggested Ginzburg-Landau free energy

$$F = F_\phi + \int_V F_\psi + F_1 + F_{\text{ex}}\, dV,$$

$$F_\psi = \mathrm{Pi}\left[\psi \log \psi + (1-\psi)\log(1-\psi)\right], \quad \text{(a.k.a. diffusion!)}$$

$$F_1 = -\frac{\mathrm{Cn}^2}{4}\psi(\nabla\phi)^2,$$

$$F_{\text{ex}} = \frac{1}{4\,\mathrm{Ex}}\psi\phi^2.$$

(van der Sman *et. al*, *Rheol. Acta* (2006))

Phase field+surfactants (cont.)

The variation of F wrt. ϕ and ψ (chemical potentials),

$$\frac{\delta F}{\delta \phi} = ... =: \mu_\phi, \quad \frac{\delta F}{\delta \psi} = ... =: \mu_\psi.$$

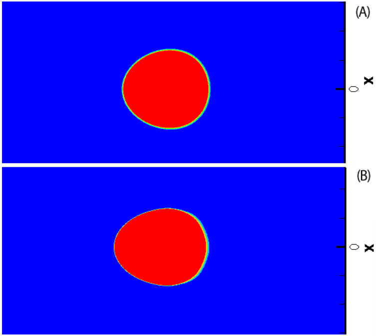
A suitable system of PDEs is now

$$\begin{aligned} \phi_t + \nabla \cdot (\phi \mathbf{u}) &= \nabla \cdot M_\phi \nabla \mu_\phi, \\ \psi_t + \nabla \cdot (\psi \mathbf{u}) &= \nabla \cdot M_\psi \nabla \mu_\psi, \\ \rho_t + \nabla \cdot (\rho \mathbf{u}) &= 0, \\ \rho \left(\mathbf{u}_t + \mathbf{u} \cdot \nabla \mathbf{u} \right) &= -\nabla P(\phi, \psi) + \frac{1}{\mathrm{Re}} \nabla \cdot \left(\rho \nu [\nabla \mathbf{u} + \nabla \mathbf{u}^T] \right). \end{aligned}$$

(van der Sman *et. al*, *Rheol. Acta* (2006))

Illustrations 1

- Multiple time-scales [phases.gif]
- Merging/bouncing bubbles [withoutsurf_phi.mov, withsurf_phi.mov, withsurf_psi.mov] (simulations by Minh Do-Quang)



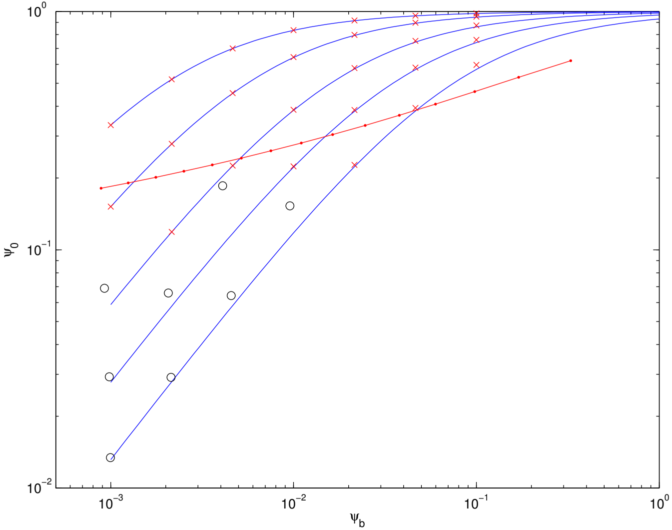
The Langmuir isotherm

At equilibrium we must have $\mu_{\psi_0} = \mu_{\psi_b}$, i.e. the chemical potential is the same in the interface ψ_0 and in the bulk ψ_b. Surprisingly, this relation can be solved up to order $O(\psi_b)$,

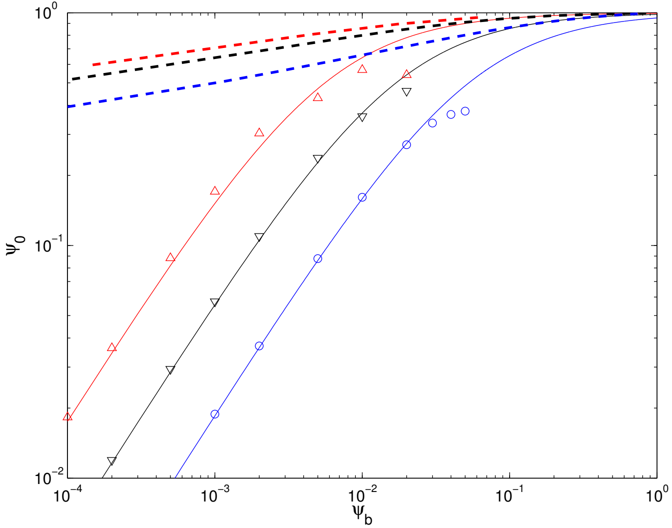
$$\psi_0 = \frac{\psi_b}{\psi_b + \psi_c},$$

the *Langmuir isotherm*, with ψ_c the *Langmuir constant*. Possessing an isotherm is a strength as ψ_c can be measured. (van der Sman *et. al*, *Rheol. Acta* (2006))

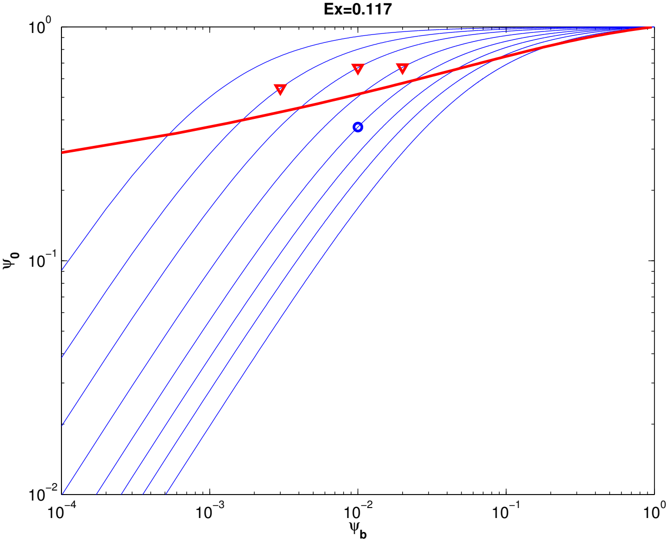
The Langmuir isotherm (1D, spectral)



The Langmuir isotherm (1D, FEM)



The Langmuir isotherm (2D, FEM)



Ill-posedness

Free-space problem in 1D with $\mathbf{u} = 0$. Make the perturbed equilibrium ansatz $\phi = \phi_\infty + \delta u$ and $\psi = \psi_\infty + \delta v$. The principal part is

$$\begin{bmatrix} u_t \\ v_t \end{bmatrix} = \begin{bmatrix} -\frac{\mathrm{Cn}^2}{2}\frac{1-\psi_\infty}{\mathrm{Pe}_\phi} D^4 & \frac{\mathrm{Cn}^2}{2}\frac{D(\phi_\infty)}{\mathrm{Pe}_\phi} D^3 \\ -\frac{\mathrm{Cn}^2}{2}\frac{\psi_\infty(1-\psi_\infty)D(\phi_\infty)}{\mathrm{Pe}_\psi} D^3 & \frac{\mathrm{Pi}}{\mathrm{Pe}_\psi} D^2 \end{bmatrix} \begin{bmatrix} u \\ v \end{bmatrix}.$$

"Frozen coefficient" Fourier transform ($D = d/dx \to -i\omega$),

$$\begin{bmatrix} \hat{u}_t \\ \hat{v}_t \end{bmatrix} = \begin{bmatrix} -\frac{\mathrm{Cn}^2}{2}\frac{1-\psi_\infty}{\mathrm{Pe}_\phi} \omega^4 & \frac{\mathrm{Cn}^2}{2}\frac{D(\phi_\infty)}{\mathrm{Pe}_\phi} i\omega^3 \\ -\frac{\mathrm{Cn}^2}{2}\frac{\psi_\infty(1-\psi_\infty)D(\phi_\infty)}{\mathrm{Pe}_\psi} i\omega^3 & -\frac{\mathrm{Pi}}{\mathrm{Pe}_\psi} \omega^2 \end{bmatrix} \begin{bmatrix} \hat{u} \\ \hat{v} \end{bmatrix}.$$

Calculations show that there is an eigenvalue

$$\lambda_2 = \frac{1}{\mathrm{Pe}_\psi}\left[\frac{\mathrm{Cn}^2}{2}\psi_\infty(D(\phi_\infty))^2 - \mathrm{Pi}\right]\omega^2 + O(1).$$

Unphysical instability whenever $\lambda_2 > 0$!

Illustrations 2

An *approximate* sufficient condition for instability is

$$\mathrm{Pi} < \frac{\psi_0}{2} \approx \frac{1}{2}\frac{\psi_b}{\psi_c + \psi_b}.$$

[explosion_refined0.gif]

Well-posedness

The PDE for ϕ is 4th order, for ψ 2nd order... Coupling through the two energy terms

$$F_1 = -\frac{\mathrm{Cn}^2}{4}\psi(\nabla\phi)^2,$$
$$F_{\mathrm{ex}} = \frac{1}{4\,\mathrm{Ex}}\psi\phi^2,$$

where the former is in fact a diffuse version of a *sharp* term,

$$F_1 \approx -\frac{\psi}{4}\cdot\delta_{\mathrm{interface}}.$$

A simple solution is to prefer $F_1 = -\psi/4\cdot(1-\phi^2)$. One can show that this does not change the isotherm.

Conclusions

- Surfactants and modeling of them through diffuse interfaces.
- Numerical simulations show qualitatively the correct behavior (bouncing bubbles, Langmuir isotherm).
- Result: conditional unphysical instability.
- Simple fix to this. [explosion_refined.gif]

The Langmuir isotherm revisited (new model)