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

The maze solving droplet
Phase-field modeling

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

Non-dimensional Ginzburg-Landau free energy:

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

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 \( F_\phi \) wrt. \( \phi \),

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

A suitable PDE for \( \phi \) 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 \( M_\phi \) 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 $\phi$ as before, new variable $\psi \in [0, 1]$ is the concentration of surfactant.

Suggested Ginzburg-Landau free energy

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

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

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

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

Phase field + surfactants (cont.)

The variation of $F$ wrt. $\phi$ and $\psi$ (chemical potentials),

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

A suitable system of PDEs is now

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

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 $\mu_0 = \mu_b$, i.e. the chemical potential is the same in the interface $\psi_0$ and in the bulk $\psi_b$. Surprisingly, this relation can be solved up to order $O(\psi_b)$,

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

the \textit{Langmuir isotherm}, with $\psi_c$ the \textit{Langmuir constant}. Possessing an isotherm is a strength as $\psi_c$ can be measured. (van der Sman et. al, \textit{Rheol. Acta} (2006))
The Langmuir isotherm (1D, spectral)
The Langmuir isotherm (1D, FEM)

Surfactant in diffuse interface flow

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The Langmuir isotherm (2D, FEM)

Surfactant in diffuse interface flow

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Ill-posedness

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

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

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

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

Calculations show that there is an eigenvalue

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

Unphysical instability whenever \( \lambda_2 > 0! \)
An *approximate* sufficient condition for instability is

\[ \Pi_i < \frac{\psi_0}{2} \approx \frac{1}{2} \frac{\psi_b}{\psi_c + \psi_b}. \]

[explosion_reined0.gif]
Well-posedness

The PDE for $\phi$ is 4th order, for $\psi$ 2nd order... Coupling through the two energy terms

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

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

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

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

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)