Models of incompressible binary flows with surfactant

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Mixtures: Modeling, analysis and computing

EMS TAG **MIXTURES**

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French vinaigrette: basic ingredients and instructions

- olive oil
- vinegar
- mustard
- salt and pepper

Place mustard, salt, pepper, and vinegar in a bowl.

Whisk to dissolve mustard and salt.

Slowly whisk in olive oil into an emulsion.

Ref. H. Benabdelhalim, D. Brutin: Phase separation and spreading dynamics of French vinaigrette, Phys. Fluids 2022 [Special Collection: Kitchen Flows]

If you don’t use mustard...

this is what happens after some time (room temperature)

If you use mustard...

Surfactant in fluid mixtures

- surfactants lower the surface tension
- examples: detergents make the water more “wet” and grease can be removed, emulsifying agent stabilizes an emulsion by preventing small droplets to coalesce (mustard in olive oil + vinegar mixture)
- surfactant molecules spontaneously aggregate in stable groups called micelles which have a strong preference to occupy sites at the fluid-fluid interfaces
- below the critical micelle concentration (CMC), surfactants adsorb efficiently to the interfaces where their physical effects become prominent
- above the CMC, additionally, spontaneous formation of micelles occurs in the bulk solution

Phase field approach: free energy

- Ω bdd domain with smooth boundary in $\mathbb{R}^d$, $d \in \{2, 3\}$
- $\phi : \Omega \times [0, T) \to [-1, 1]$ relative volume fraction difference between the two fluids
- $\psi : \Omega \times [0, T) \to [0, 1]$ volume fraction of the surfactant
- free energy

$$E_{\text{free}}(\phi, \psi) = E_\phi(\phi) + E_\psi(\psi) + \int_\Omega G(\phi, \psi)\, \mathrm{d}x$$

Ref. S. Engblom et al., On Diffuse Interface Modeling and Simulation of Surfactants in Two-Phase Fluid Flow, Commun. Comput. Phys. 2013 [and refs. therein]

Free energies E_ϕ and E_ψ

- we postulate

$$E_\phi(\phi) = \int_\Omega \left(\frac{|\nabla \phi|^2}{2} + F_\phi(\phi) \right) dx$$
$$E_\psi(\psi) = \int_\Omega \left(\frac{|\nabla \psi|^2}{2} + F_\psi(\psi) \right) dx$$

- where $\varepsilon, \beta > 0$ and

$$F_\phi(s) = \frac{\Theta}{2}[(1+s)\ln(1+s) + (1-s)\ln(1-s)] + \frac{\theta_1}{2}(1-s^2)$$
$$F_\psi(s) = \frac{\Theta}{2}[s\ln s + (1-s)\ln(1-s)] + \frac{\theta_2}{2}s(1-s)$$

with $\Theta, \theta_1, \theta_2 > 0$

Interaction energy density G: first choice

- we postulate

$$G(\phi, \psi) = \frac{\gamma_1}{2}\psi\phi^2 - \gamma_2\psi|\nabla\phi|^2$$

where $\gamma_1, \gamma_2 \geq 0$

- with this choice we need to add a regularizing higher-order term in E_ϕ, namely,

$$+\sigma|\Delta\phi|^2$$

with $\sigma > 0$

- also, we need to approximate F_ϕ using a smooth double well potential

$$F_\phi^a(s) = \frac{\alpha}{4}(1 - s^2)^2$$

with $\alpha > 0$

First hydrodynamic model

- matched densities ($\rho_1 = \rho_2 = 1$)
- **u** (volume averaged) fluid velocity
- constant mobilities ($= 1$)

$$\begin{cases} \partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla)\mathbf{u} - \nabla \cdot (\nu(\phi,\psi) D\mathbf{u}) + \nabla \pi = \mu_\phi \nabla \phi + \mu_\psi \nabla \psi \\ \mathrm{div}\ \mathbf{u} = 0 \\ \partial_t \phi + \mathbf{u} \cdot \nabla \phi = \Delta \mu_\phi \\ \mu_\phi = \Delta^2 \phi - \Delta \phi + (F_\phi^a)'(\phi) + \nabla \cdot (\psi \nabla \phi) \\ \partial_t \psi + \mathbf{u} \cdot \nabla \psi = \Delta \mu_\psi \\ \mu_\psi = -\Delta \psi + F_\psi'(\psi) - |\nabla \phi|^2 \end{cases}$$

in $\Omega \times (0,T)$, $T > 0$

Main results (Di Primio, G., Wu, M3AS 2023)

- i.c. + no-slip b.c. for **u** + no-flux b.c. for $\phi, \psi, \mu_\phi, -\Delta\phi, \mu_\psi$
- existence of a global weak solution if $d = 2, 3$
- existence of a local (global) strong solution if $d = 3$ ($d = 3$)
- continuous dependence estimate ($\Rightarrow$ uniqueness) if $d = 2$
- regularization properties of the weak solution and validity of the strict separation property for ψ ($d = 2$)

Total energy and energy identity

$$\mathcal{E}_{\rm tot}(\boldsymbol{u}(t),\phi(t),\psi(t)) + \int_0^t \|\sqrt{\nu(\phi(\tau),\psi(\tau))}D\boldsymbol{u}(\tau)\|^2 \mathrm{d}\tau$$
$$+ \int_0^t \left(\|\nabla\mu_\phi(\tau)\|^2 + \|\nabla\mu_\psi(\tau)\|^2\right) \mathrm{d}\tau = \mathcal{E}_{\rm tot}(\boldsymbol{u}_0,\phi_0,\psi_0)$$

for all $t \geq 0$, where

$$\mathcal{E}_{\rm tot}(\mathbf{u},\phi,\psi) = \int_\Omega \left(\frac{1}{2}|\mathbf{u}|^2 + \frac{\sigma}{2}|\Delta\phi|^2 + \frac{|\nabla\phi|^2}{2} + F_\phi^a(\phi)\right) \mathrm{d}x$$
$$+ \int_\Omega \left(\frac{|\nabla\psi|^2}{2} + F_\psi(\psi) + \underbrace{\frac{\gamma_1}{2}\psi\phi^2 - \gamma_2\psi|\nabla\phi|^2}_{G(\phi,\psi)}\right) \mathrm{d}x$$

Approximating the interaction energy density G

- Following G.-P. Zhu et al., Thermodynamically consistent modelling of two-phase flows with moving contact line and soluble surfactants, JFM 2019

$$-\gamma_2\psi|\nabla\phi|^2 \approx -\frac{\gamma_3}{4}\psi(1-\phi^2)^2$$

  where $\gamma_3 > 0$
- so that

$$G_a(\phi,\psi) = \frac{\gamma_1}{2}\psi\phi^2 - \frac{\gamma_3}{4}\psi(1-\phi^2)^2$$

- with this choice we no longer need the regularizing higher-order term in E_ϕ
- also, we no longer need to approximate F_ϕ with a smooth double well potential

Second hydrodynamic model

- unmatched densities (following Abels, Garcke, Grün, M3AS 2012)

$$\rho(\phi) = \frac{\rho_1 - \rho_2}{2}\phi + \frac{\rho_1 + \rho_2}{2}, \quad \mathbf{J} = -\frac{\rho_1 - \rho_2}{2} m_\phi(\phi)\nabla\mu_\phi$$

$$\begin{cases} \partial_t(\rho(\phi)\mathbf{u}) + \operatorname{div}(\mathbf{u}\otimes(\rho(\phi)\mathbf{u} + \mathbf{J})) - \operatorname{div}(\nu(\phi,\psi)D\mathbf{u}) + \nabla\pi \\ = \mu_\phi\nabla\phi + \mu_\psi\nabla\psi \\ \operatorname{div}\ \mathbf{u} = 0 \\ \partial_t\phi + \mathbf{u}\cdot\nabla\phi = \operatorname{div}(m_\phi(\phi)\nabla\mu_\phi) \\ \mu_\phi = -\Delta\phi + F'_\phi(\phi) + \partial_\phi G_a(\phi,\psi) \\ \partial_t\psi + \mathbf{u}\cdot\nabla\psi = \operatorname{div}(m_\psi(\psi)\nabla\mu_\psi) \\ \mu_\psi = -\Delta\psi + F'_\psi(\psi) + \partial_\psi G_a(\phi,\psi) \end{cases}$$

in $\Omega \times (0, T)$

Main results (G., Ouyang, Wu, in progress)

- i.c. + no-slip b.c. for **u** + no-flux b.c. for $\phi, \psi, \mu_\phi, \mu_\psi$
- non-degenerate or degenerate mobilities
- existence of a global weak solution if $d = 2, 3$ with a reaction term of Oono type in the CH eq. for ϕ

$$\sigma_1(\phi)\big(\overline{\phi} - c\big) + \sigma_2\big(\phi - \overline{\phi}\big)$$

  where $\sigma_1, \sigma_2 \geq 0$, $c \in (-1, 1)$, and $\overline{\phi}$ stands for the integral mean of ϕ
- non-degenerate m_ϕ: σ_1 can be a positive constant
- degenerate m_ϕ: σ_1 must properly vanish at ± 1

Total energy and energy identity

$$\mathcal{E}_{\text{tot}}(\boldsymbol{u}(t), \phi(t), \psi(t)) + \int_0^t \|\sqrt{\nu(\phi(\tau), \rho(\tau))} D\boldsymbol{u}(\tau)\|^2 \mathrm{d}\tau$$
$$+ \int_0^t \left(m_\phi(\phi(\tau)) \|\nabla \mu_\phi(\tau)\|^2 + m_\psi(\psi(\tau)) \|\nabla \mu_\psi(\tau)\|^2 \right) \mathrm{d}\tau$$
$$= \mathcal{E}_{\text{tot}}(\boldsymbol{u}_0, \phi_0, \psi_0)$$

for all $t \geq 0$, where

$$\mathcal{E}_{\text{tot}}(\mathbf{u}, \phi, \psi) = \int_\Omega \left(\frac{\rho(\phi)}{2} |\mathbf{u}|^2 + \frac{|\nabla \phi|^2}{2} + F_\phi(\phi) \right) \mathrm{d}x + \int_\Omega \left(\frac{|\nabla \psi|^2}{2} + F_\psi(\psi) + G_a(\phi, \psi) \right) \mathrm{d}x$$

Proofs: scheme

The proofs are based on suitable adaptations of the ones devised in Abels, Depner, Garcke (JMFM 2012 and AIHP 2013)

- implicit time discretization scheme for the nondegenerate mobilities
- approximating the degenerate mobilities
- approximating the mixing entropies in such a way that the approximations of ϕ and ψ still take their values in $[-1, 1]$ and $[0, 1]$, respectively
- use the previous result (non-degenerate mob.) to get the existence of an approximate solution
- pass to the limit w.r.t. the regularization parameters by extraction and compactness

Some open issues

- 1st model: convergence to equilibrium? F_ϕ singular?
- 2nd model (non-deg. mob.): additional results (e.g., well-posedness if $d = 2$, local strong sols. if $d = 3$)
- 2nd model (deg. mob.): more general source terms in the CH eq. for ϕ
- nonlocal models for the mixture and/or the surfactant (deg. mob.: more chances to go beyond the existence of a weak soln.)
- replacing Cahn-Hilliard eqs. with conserved Allen-Cahn eqs. (X. Jiang, CMAME 2021)
- dynamic boundary conditions (G. Zhu et al., JFM 2019, 2nd model)
- stochastic models (T. Tachim-Medjo, DCDS 2024, 1st model)

THANK YOU