

Simulation of common features and differences of surfactant-based and solid-stabilized emulsions

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ABSTRACT

A continuum model is used to study thermodynamical stability of surfactant-based and solid-stabilized emulsions. Both modeling approaches are based on a phase-field description. In the case of solid particles along the fluid–fluid interface a local approximation to a classical dynamic density functional theory is used to account for particle–particle interactions. This allows for attractive as well as repulsive interactions. Coarsening studies are performed, which demonstrate thermodynamic stability for both cases. For surfactant-based emulsions this is achieved by a drastic reduction of surface tension, whereas for solid-stabilized emulsions the same effect results from an elastic force. Both types of emulsions behave different if a macroscopic force is applied. This is demonstrated by a rigid body interacting with the emulsion. The surfactant-based emulsion behaves like a fluid, whereas the solid-stabilized emulsion shows properties of a solid with a finite elastic modulus and a yield stress.

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1. Introduction

Emulsions are widely used in many fields of our daily life such as the food, cosmetic, pharmaceutical, paint, and petroleum industries. In an emulsion, one kind of liquid is dispersed in another kind of liquid in the form of droplets. To maintain such a state and prevent coalescence or coarsening of droplets so called emulsifiers are required. Typically amphiphilic molecules such as surfactants are used for such purposes to reduce the interfacial tension significantly. But besides the commonly used surfactants, emulsifiers can be nanometer- and micrometer-sized solid particles that adsorb at the liquid–liquid interface. The resultant solid-stabilized emulsions have been termed Pickering emulsions [19]. In the last two decades, solid particles as emulsion stabilizers have attracted much attention because of their irreversible adsorption, low toxicity, and low cost. Unlike conventional surfactant-based emulsions, droplets in Pickering emulsions can exhibit frozen aspherical shapes. In these cases the particle layer has solidified, presumably imparting mechanical rigidity to each droplet. This solidification could be promoted by attractive particle interactions, but might also stem from the jamming of particles into repulsive contact

under the influence of interfacial tension alone. For a review on particle-stabilized emulsions we refer to [7].

Besides dispersed droplets also bicontinuous structures of interpenetrating, continuous domains of two liquids are of growing interest. Again such structures can be stabilized either using amphiphilic molecules such as surfactants or solid particles. The later case has been proposed as bicontinuous interfacially jammed emulsion gels (“bijels”), a new class of soft material with potential applications in catalysis. These materials have initially been proposed on the basis of computer simulations. However, a detailed understanding what causes the stability in these materials still remains open. For a review on bijels we refer to [8].

Here we will address this issue using mathematical modeling and computer simulations. We will therefore review currently used models for Pickering emulsions and bijels. Such models are mainly based on Lattice–Boltzmann models [21,12]. Only recently also continuum models have been proposed [13,1,2]. We will review these models in Section 2 and show simulation results in Section 3. Conclusions are drawn in Section 4.

2. Mathematical model

Using computer simulations to understand the dynamic properties of Pickering emulsions and bijels is a promising approach. However, there are various shortcomings of traditional approaches due to very different scales involved, spatially as well as temporally. On one hand fluid dynamics have to be considered on mesoscopic

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spatial scale resolving droplet size or domain structures. On the other hand the motion of particles and fluid–particle interactions have to be considered. The particle size thereby is in the nano- or micrometer range. Various Lattice Boltzmann methods have been applied for the description of the solvent. These method can be combined with molecular dynamic algorithms to simulate particles in a flow [15–17,21,14,12]. However this approach can only partly account for the different temporal scales since the simulation time is limited by the Brownian diffusion time making it difficult to perform long-time simulations.

Using a Navier–Stokes equation to describe the solvent allows to reach the large time scales of interest for investigations on stability. However an incorporation of particles into such an approach leads to limitations on the size of the system. A first attempt in this direction is given in [13]. Here a diffuse interface approach is used which sets limitations to the system size, as the particle scale has to be substantially larger than the interface width.

In [1] a different approach is considered, which models the particles using a classical dynamic density functional theory approach. This allows to average out the vibrational modes and to model particle–particle interactions on diffusive time scales. The approach implicitly assumes a contact angle of 90°. Combined with a multi-phase Navier–Stokes equation this gives a promising way to simulate Pickering emulsions and bijels over a long time frame, while resolving the particle interactions appropriately. In [2] this model has been further improved and will be the basis for our investigation.

2.1. Two-phase flow

We assume the fluid motion to be governed by the incompressible Navier–Stokes equation

$$\nabla \cdot u = 0 \quad t > 0, x \in \Omega^i(t) \quad (1)$$

$$\partial_t u + \nabla \cdot (u \otimes u - S) = 0 \quad t > 0, x \in \Omega^i(t) \quad (2)$$

$$S = -\pi I + 2\mu^i D \quad t > 0, x \in \Omega^i(t) \quad (3)$$

$$D = 0.5(\nabla u + \nabla u^T) \quad t > 0, x \in \Omega^i(t) \quad (4)$$

with $\Omega^i(t)$ the bulk fluid domain, u , π and μ_i the bulk velocity field, the bulk pressure and bulk viscosity, respectively. At the fluid–fluid interface $\Gamma(t)$ we specify:

$$[[u]] = 0, \quad V = u \cdot \nu \quad t > 0, x \in \Gamma(t) \quad (5)$$

$$S\nu = -F \quad t > 0, x \in \Gamma(t) \quad (6)$$

with ν the outer normal to the interface, $u = V\nu + T$ a decomposition of the interface velocity into a normal and tangential component, V and T respectively. $[[.]]$ is the jump across the interface, and F a force, to be obtained by energy minimization and thermodynamic consistency. In the simplest form without an emulsifier we consider the interface energy

$$\mathcal{F}^\Gamma = \int_\Gamma \sigma_\Gamma \, d\Gamma \quad (7)$$

with σ_Γ the interface tension. From this we obtain for the force F

$$F = -\frac{\delta \mathcal{F}^\Gamma}{\delta \Gamma} = -\sigma_\Gamma H\nu$$

with the mean curvature H . In [4] a diffuse interface approximation for this system is used. The resulting system is the classical “Model H” in [10], also known as the Navier–Stokes–Cahn–Hilliard (NSCH) equation.

So far we assume σ_Γ to be constant. Incorporating an emulsifier into the model will alter this assumption and modifications for the force F are needed.

2.2. Molecular surfactant

In case of a molecular surfactant we consider a density c and a local continuity equation for c on the interface $\Gamma(t)$

$$\partial_t c + \nabla_\Gamma \cdot (cT) + cVH = -\nabla_\Gamma \cdot q$$

with an interfacial flux q . We specify $q = -\nabla_\Gamma c$ to obtain diffusion along the interface. Furthermore we define

$$\mathcal{F}^\Gamma[c] = \int_\Gamma \sigma_\Gamma(c) \, d\Gamma \quad (8)$$

with an interface tension σ_Γ as a function of surfactant concentration c . Varying the interface independently from c leads to the generalized Laplace–Young condition $S\nu = -F$, now with

$$F = -\frac{\delta \mathcal{F}^\Gamma}{\delta \Gamma} = -\sigma_\Gamma(c)H\nu + \sigma'_\Gamma(c)\nabla_\Gamma c.$$

In [22] a diffuse interface approximation for this system is used based on the general approach in [20,18]. The resulting system is named Navier–Stokes–Cahn–Hilliard–Surface–Convection–Diffusion (NSCHSCD) equation. For $\sigma_\Gamma(c)$ a Langmuir law of the form $\sigma_\Gamma(c) = \sigma_0(1 - \beta \ln(1 - \frac{c}{c_\infty}))$ with a physical parameter β can be used.

2.3. Solid particle interaction

In order to consider interaction of solid particles on an interface we consider a particle density ρ as in classical dynamic density functional theories. As an energy on the interface $\Gamma(t)$ we define

$$\mathcal{F}^\Gamma[\rho] = \int_\Gamma \sigma_\Gamma - EI^{-1} \left[\delta^2 |\nabla_\Gamma \rho|^2 + \frac{\delta^4}{2} \|\Delta_\Gamma \rho\|_\Gamma^2 + f(\rho) \right] \, d\Gamma. \quad (9)$$

where δ is a parameter relating the characteristic size of the particles to the characteristic length scale of the fluid system, EI is an elasticity number which measures the strength of the elastic energy and $f(\rho) = 0.25\rho^4 + 0.3\rho^2$. The local continuity equation now reads

$$\partial_t \rho + \nabla_\Gamma \cdot (\rho T) + \rho V H = -\nabla_\Gamma \cdot q$$

with an interfacial flux q which has not yet been specified. This modeling approach allows to operate on diffusive time scales, while keeping a microscopic particle resolution. In [6] this phenomenological approach is validated for the classical Thomson problem of how the arrange particles interacting via a Coulomb potential on a sphere. Following the approach in [23,5] the energy can also be related to a pairwise potential $u(|\mathbf{r}_i - \mathbf{r}_j|) \approx 1/|\mathbf{r}_i - \mathbf{r}_j|^\alpha$ for particles $\mathbf{r}_i, i = 1, \dots, N$. Various ways have been proposed how to parametrize the energy in order to approximate the direct correlation function corresponding to such interactions [9,25,23,11]. We will not further discuss this issue here but concentrate on the structure of the equations. The energy (9) leads to a strong coupling of Γ and ρ . Therefore we vary Γ and ρ simultaneously, which gives decreasing energy with the choice of $q = -\nabla_\Gamma \frac{\delta \mathcal{F}^\Gamma[\rho]}{\delta \rho}$ and

$$F = -\frac{\delta \mathcal{F}^\Gamma}{\delta \Gamma} + \rho \frac{\delta \mathcal{F}^\Gamma}{\delta \rho} H\nu - \rho \nabla_\Gamma \frac{\delta \mathcal{F}^\Gamma}{\delta \rho}$$

Evaluating $\frac{\delta \mathcal{F}^\Gamma[\rho]}{\delta \rho}$ leads to the system of equations

$$\partial_t \rho + \nabla_\Gamma \cdot (\rho T) + \rho V H = EI^{-1} \Delta_\Gamma \mu \quad (10)$$

$$\mu = 2\delta^2 \omega + \delta^4 \Delta_\Gamma \omega + f'(\rho) \quad (11)$$

$$\omega = \Delta_\Gamma \rho \quad (12)$$

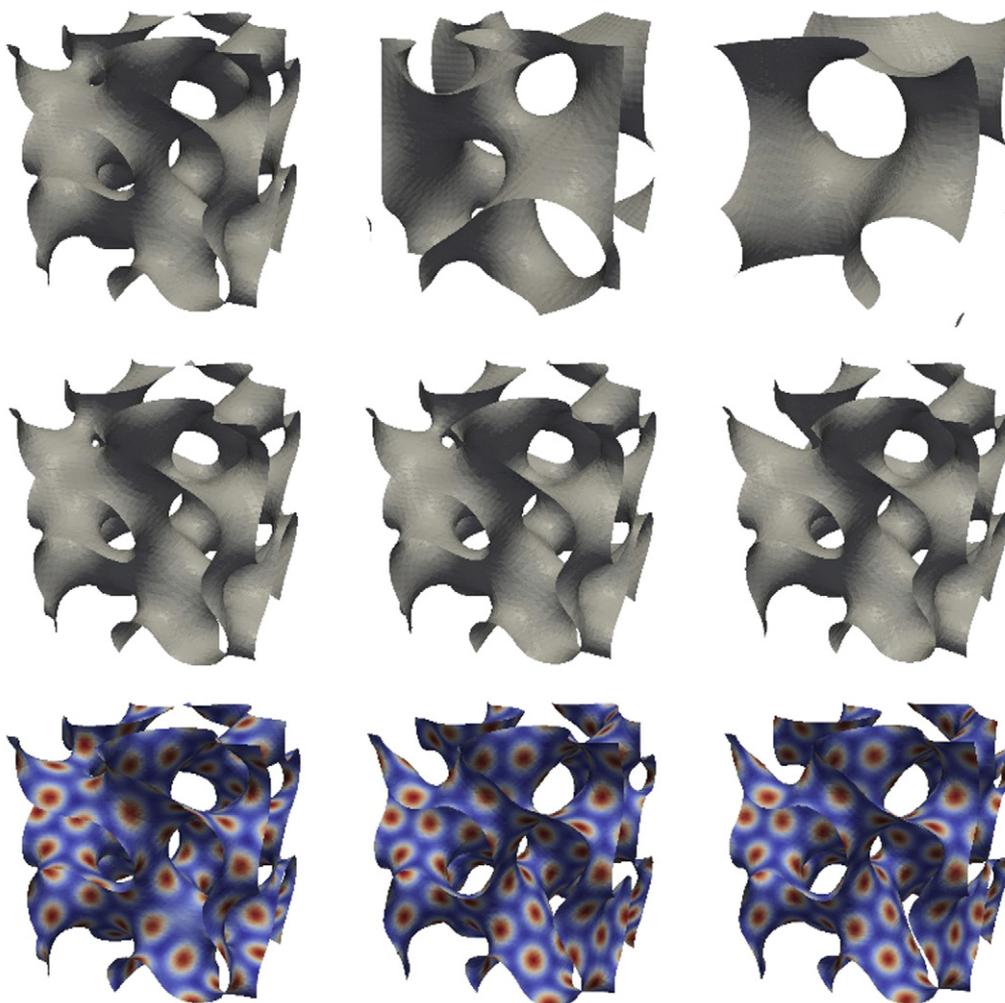


Fig. 1. Coarsening of a fluid structure after spinodal decomposition without an emulsifier (top), with a molecular surfactant (middle) and with solid particles (bottom) at times $t=0, 134, 267$. In the bottom row the color coding shows the particle density of the solid particles on the interface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

and the generalized Laplace–Young condition becomes

$$\begin{aligned}
 F = & -\sigma_{\Gamma}H\nu + El^{-1} \left[2\delta^2(\nabla_{\Gamma}\rho, (\text{Hess}\Phi)\nabla_{\Gamma}\rho)_{\Gamma} + \delta^2\|\nabla_{\Gamma}\rho\|_{\Gamma}^2 H\nu \right. \\
 & + \frac{\delta^4}{2}\omega^2 H\nu + \delta^4(\nabla_{\Gamma}\omega, \nabla_{\Gamma}\rho)_{\Gamma} H\nu + 2\delta^4((\text{Hess}\Phi)\nabla_{\Gamma}\omega, \nabla_{\Gamma}\rho)_{\Gamma} \\
 & \left. -f(\rho)H\nu + \rho\mu H\nu - \rho\nabla_{\Gamma}\mu \right]
 \end{aligned}$$

where Φ is the surface identity $\Gamma \rightarrow \mathbf{R}^{n+1} : \Phi(x) = x$. See [3,2] for a detailed derivation which is based on mass conservation and energy dissipation. For the overall system thermodynamic consistency can be shown. In [1,2] a diffuse interface approximation for this system is used based on the general approach in [20,18]. The resulting system is named Navier–Stokes–Cahn–Hilliard–Surface–Phase–Field–Crystal (NSCHSPFC) model.

3. Simulation results

All simulation results are based on the corresponding diffuse interface approximations. Adaptive finite elements are used to discretize the equations using the simulation toolbox AMDiS [24].

3.1. Stability of bicontinuous structures

We investigate the potential of molecular surfactants and solid particles to stabilize bicontinuous structures. The computational domain is $\Omega = [0, 8/3]^3$. As initial condition, we first generate fluid structures via spinodal decomposition by solving a Cahn–Hilliard equation in the absence of flow ($u=0$) for a few time steps, using the initial condition $\psi = 0.5 \pm 0.1$ for the order parameter ψ with a large interface thickness $\epsilon = 0.1$. To generate the initial condition for the full NSCH system, the Cahn–Hilliard equation is solved for several more time steps, again in the absence of flow, with $\epsilon = 0.03$ to refine the interface thickness. To generate the initial condition for the full NSCHSPFC system, the Cahn–Hilliard and Surface–Phase–Field–Crystal equations are solved together for several more time steps, again in the absence of flow, with $\epsilon = 0.03$ to create the solid particle structure on the complex interface. As initial data for the CHSPFC solver, the previously generated ψ is used together with the number density $\rho_0 = -0.3 \pm 0.05$. The resulting ψ and ρ are used as the initial condition for the full NSCHSPFC system. We set $\delta = \frac{1}{15}$ in all simulations.

Fig. 1 shows a comparison between the NSCH, the NSCHSCD and the NSCHSPFC models. In the former case the structure coarsens significantly. The interfacial tension is $\sigma_{\Gamma} = 0.24$, the elasticity number is $El = 0.042$. In the presence of surfactants the interfacial tension is significantly reduced, which prevents the coarsening process, or at

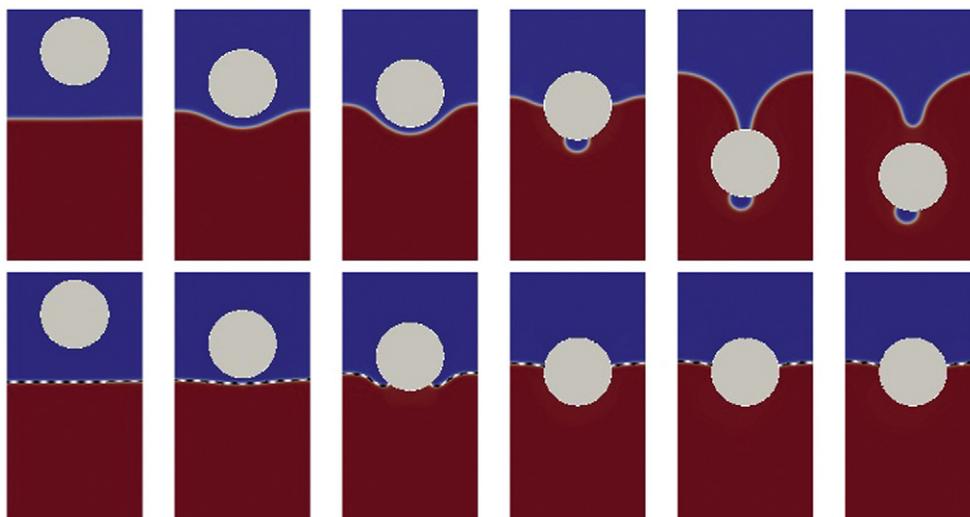


Fig. 2. Falling rigid body into two-phase system without solid particles (top), and with solid particles at the interface (bottom) at times $t = 0, 110, 148, 208, 465, 525$. The density of both fluids is the same. The contact angle is 90° .

least can slow it down significantly. For simplicity the simulations in this case are done with a constant interfacial tension reduced to $\sigma_\Gamma = 0.0024$. When solid particles are present, the elastic force induced by the particles is able to prevent the coarsening as the particles jam and the interface crystallizes. Again $\sigma_\Gamma = 0.24$ is used.

Within this scenario the effect of a molecular surfactant and solid particles are comparable. Both lead to a kinetically stabilized structure. The reason however is different: For a molecular surfactant the surface tension is reduced and with it the driving force for coarsening. In the case of solid particles an additional elastic force is present which kinetically stabilizes the structure and prevents the morphology from coarsening.

3.2. Responds to macroscopic forces

As a second test case we consider the influence of a macroscopic force. Therefore a rigid body is falling within a two-phase system. In order to simulate this scenario the diffuse domain approach [18] is used to approximate the rigid body. The influence of a molecular surfactant will be negligible for such a case. However, if the solid particles on the interface really solidify, the structure should become a solid gel with a finite elastic modulus and a yield stress and thus should have an impact on the rigid body.

The simulations are restricted to two dimensions. Fig. 2 shows a time sequence for the case without and with solid particles along the interface.

Within this configuration the yield stress of the structure is strong enough to stop the falling of the rigid body. This clearly shows a significant difference to emulsifiers of amphiphilic molecules such as surfactants and solid particles. Also phenomenological modeling approaches in which solid particles are used to reduce the interfacial tension, as considered in [12], will fail to account for this solid like behaviour of particle-stabilized emulsions.

4. Conclusions

A continuum modeling approach is used to demonstrate the common features and differences of emulsions with amphiphilic molecules and solid particles as an emulsifier. Within the first case the amphiphilic molecules, in our case surfactants, reduce the surface tension significantly and thereby prevent the structure from coarsening. However, the system remains fluid like, the emulsion

is not much more viscous than their component fluids. In the later case an elastic force is introduced which again prevents the structure from coarsening but also makes it solid like with a finite elastic modulus and a yield stress. Both models result from free energy minimization and mass conservation. In the case of solid particle laden interface a local approximation to a classical dynamic density functional theory for the particles interactions is used to account for diffuse time scales which are of interest to study the thermodynamically stable configurations. This also allows to account for different particle interactions, which include purely repulsive particles.

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