A continuum model of colloid-stabilized systems

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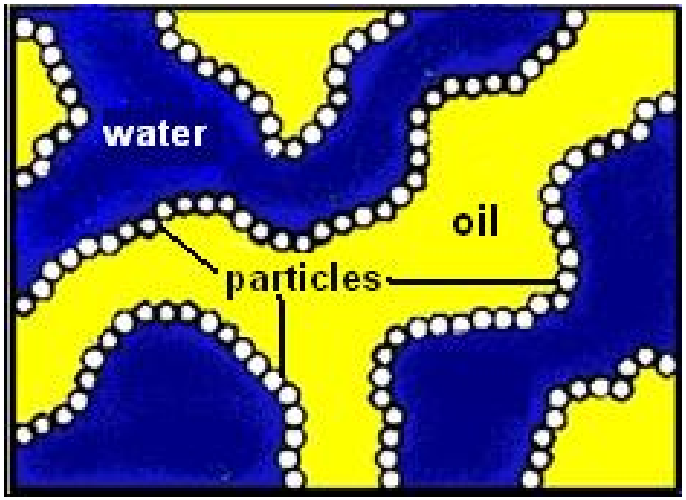
Bijels

Bicontinuous interfacially jammed emulsion gels

- Two immiscible fluids, separated by jammed colloidal particles
- Similar to Pickering emulsions
- Unusual material properties, interesting applications
- Challenging for simulations (and experiments)
- Our approach:
  Couple NS + CH + PFC



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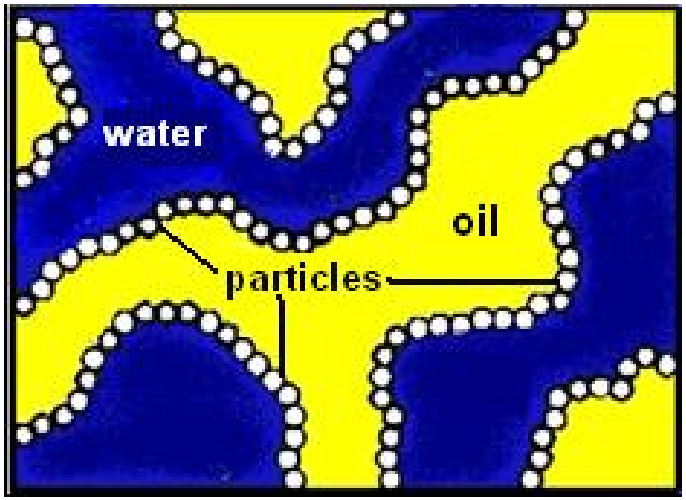

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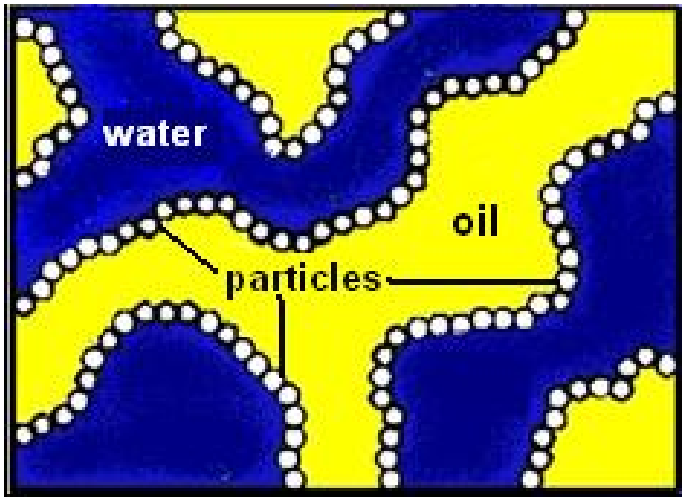

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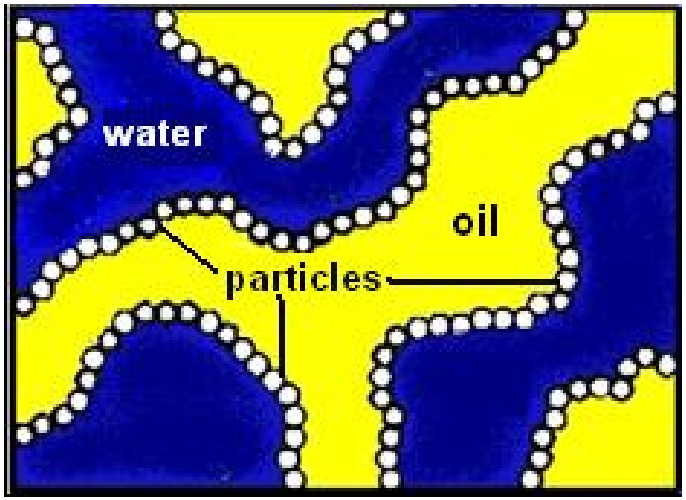

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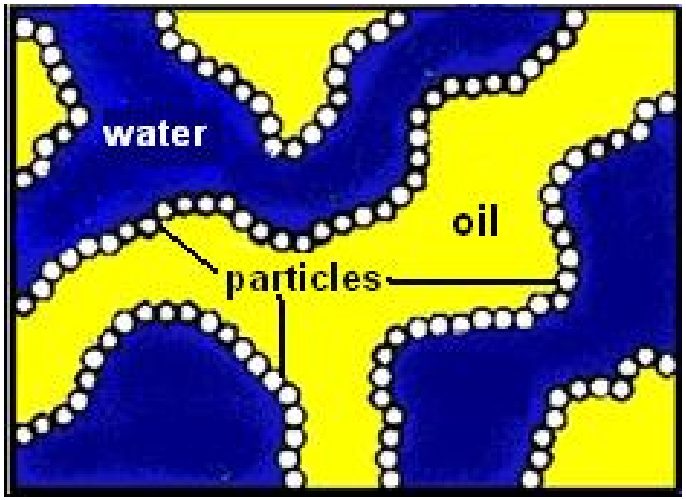
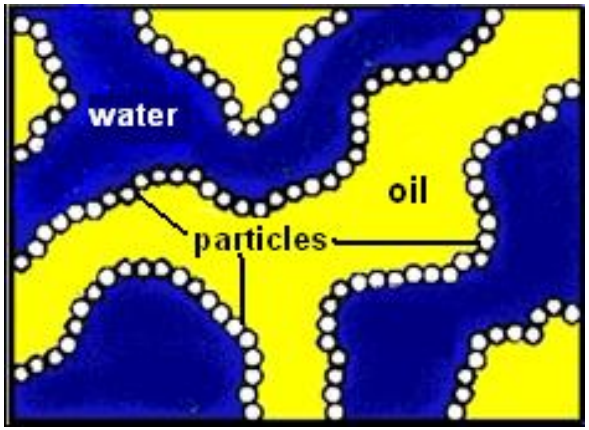


Outline

How to create a Bijel?

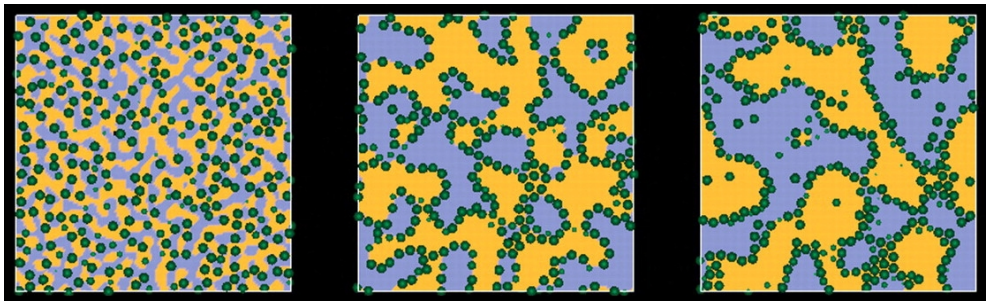


- Take two immiscible fluids initially in one phase
- Add colloidal particles
- Induce spinodal decomposition by deep quenching
- A huge interfacial area is created and coarsens fast due to surface tension
- Colloids attach to the interface
- Colloids jam and thus stabilize the structure
- Applications: new and better gels, fuel cells, microreactors, ...

Bijels - State of the art

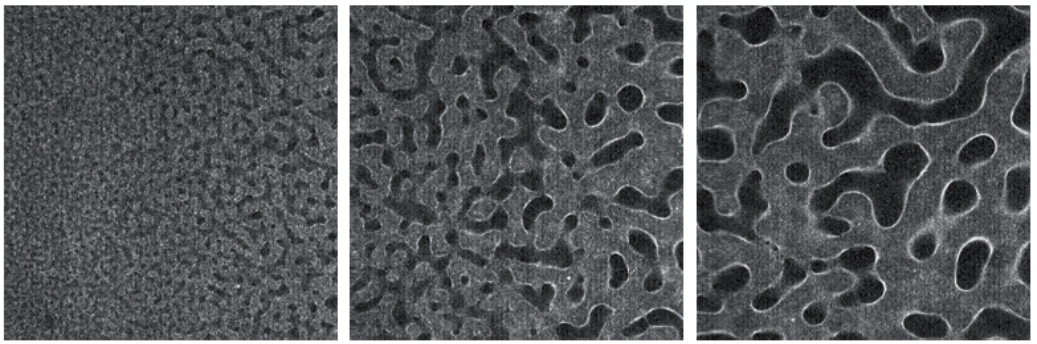
- Initially proposed by computer simulations (Lattice Boltzmann, Dissipative Particle Dynamics)

Stratford et al., Science, 2005



- Experimentally confirmed

Herzig et al., Nature Materials, 2007



- Systems stable for very long times (e.g., months).

Bijels - Challenges

Open questions

- Material properties
- Long-time stability

Challenges for Computer Simulations

- various spatial scales (domain size vs. intercolloidal forces)
- various time scales (arrest of the structure vs. colloidal motion)
- still a gap between experiments and simulations
- Lattice-Boltzmann/Diffusive Particle Dynamics simulations not suitable for long-time simulations

Our Approach

Couple Navier-Stokes Cahn-Hilliard equation with a Phase-Field-Crystal on the interface

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Multiphase fluid model I

Classical Model

$$\rho(\chi)\left(\frac{\partial \mathbf{u}}{\partial t}+(\mathbf{u}\cdot\boldsymbol{\nabla})\mathbf{u}\right) = -\nabla p+\boldsymbol{\nabla}\cdot\left(\eta(\chi)\left(\boldsymbol{\nabla}\boldsymbol{u}+\boldsymbol{\nabla}\boldsymbol{u}^T\right)\right)-\sigma\kappa\boldsymbol{n}\delta_\Gamma, \quad (1)$$

$$\boldsymbol{\nabla}\cdot\mathbf{u} = 0, \quad (2)$$

$$\frac{\partial\chi}{\partial t}+\boldsymbol{u}\cdot\boldsymbol{\nabla}\chi = 0, \quad (3)$$

where where χ identifies one of the domains, κ is the total curvature, $\boldsymbol{n}$ is the normal vector, δ_Γ is the surface delta function and σ is the surface tension. Can be derived variationally from

$$E = E_{kin}+E_s, \qquad E_{kin}=\int_\Omega |\boldsymbol{u}|^2/2\ dx, \qquad E_s=\int_\Gamma \sigma\ ds$$

$$\dot{E} = -2\int \eta\nabla\boldsymbol{u}:\nabla\boldsymbol{u}\ dx$$

Multiphase fluid model II: Navier-Stokes-Cahn-Hilliard

Introduce phase field ψ, interface thickness ϵ

Constant density. Model H (Hohenberg & Halperin, 1977)

$$\partial_t \mathbf{u} + (\mathbf{u}\cdot\nabla)\mathbf{u} = -\nabla p + \nabla\cdot\left(\eta(\psi)\left(\boldsymbol{\nabla}\boldsymbol{u} + \boldsymbol{\nabla}\boldsymbol{u}^T\right)\right) + \frac{\delta E_s}{\delta\psi}\nabla\psi, \tag{4}$$

$$\nabla\cdot\mathbf{u} = 0, \tag{5}$$

$$\partial_t\psi + \boldsymbol{u}\cdot\nabla\psi = \nabla\cdot(B(\psi)\nabla\mu), \tag{6}$$

$$\mu = \frac{\delta E_s}{\delta\psi} = \frac{\sigma}{\epsilon}B'(\psi) - \sigma\epsilon\Delta\psi, \tag{7}$$

where

$$E_s = \sigma\int_\Omega \frac{1}{\epsilon}B(\psi) + \frac{\epsilon}{2}|\boldsymbol{\nabla}\psi|^2\,dx, \quad B(\psi) = 18\psi^2(1-\psi)^2,$$

Can be derived variationally from $E = E_{kin} + E_s$.

Extensions for variable density: Lowengrub & Truskinovsky (1998), Boyer (2002), Ding et al. (2007), Abels et al. (2010)

Benchmarked in: Aland, Voigt; Int. J. Num. Meth. Fluids; (2011)

Bulk-Surface coupling in complex, evolving domains

Classical formulation

f concentration on surface, F concentration in bulk.

$$\frac{\partial f}{\partial t} + \boldsymbol{\nabla}_\Gamma \cdot (\boldsymbol{u} f) = \nabla_\Gamma \cdot \left(D_f \boldsymbol{\nabla}_\Gamma f \right) + j, \qquad \text{in } \Gamma(t)$$

$$\frac{\partial F}{\partial t} + \nabla \cdot (\boldsymbol{u} F) = D_F \boldsymbol{\nabla}^2 F \qquad \text{in } \Omega(t)$$

$$D_F \boldsymbol{\nabla} F \cdot \mathbf{n} = - j \qquad \text{on } \Gamma(t)$$

$j(F, f)$ accounts for adsorption/desorption, e.g.

$$j(F, f) = r_a F (f_\infty - f) - r_d f \qquad \text{on } \Gamma(t)$$

Diffuse domain approach

$$\frac{\partial}{\partial t}(\delta f) + \nabla \cdot (\delta f \boldsymbol{u}) = \nabla \cdot \left(D_f \delta \nabla f \right) + \delta j \qquad \text{in } \bar{\Omega}$$

$$\frac{\partial}{\partial t}(\chi F) + \nabla \cdot (\chi F \boldsymbol{u}) = \nabla \cdot (\chi \nabla F) - \delta j \qquad \text{in } \bar{\Omega}.$$

with surface delta function δ, e.g. $\delta \approx |\nabla \psi|$
and characteristic function of soluble bulk phase, e.g. $\chi \approx \psi$.

- standard tools can be used to solve the equations in domains and on surfaces
- convergence in ϵ

Rätz, Voigt; Comm. Math. Sci. (2006)
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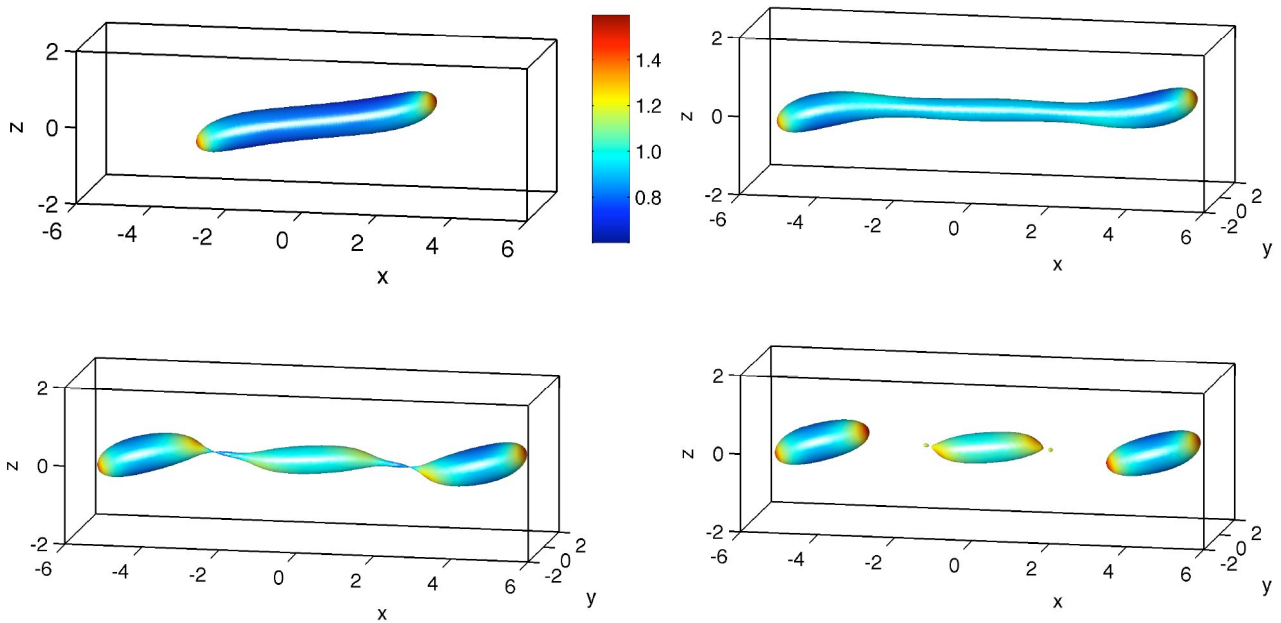
Application to soluble surfactant

Diffuse interface model for soluble surfactants (nondimensional)

Teigen et al., J. Comp. Phys. (2011)

$$\sigma(f) = \sigma_0 + RTf^\infty \ln\left(1 - \frac{f}{f^\infty}\right) \qquad \text{(surfactant dependent surface tension)} \tag{8}$$



Phase Field Crystal (PFC) model

Elder et al., Phys. Rev. Lett. (2002).

- Consider noise averaged particle density ρ
- Dynamics of ρ described by Dynamic Density Functional Theory (DDFT)
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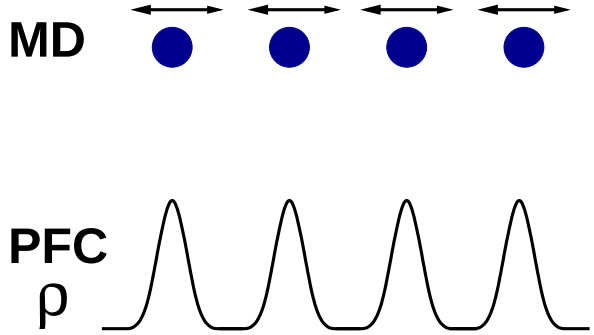
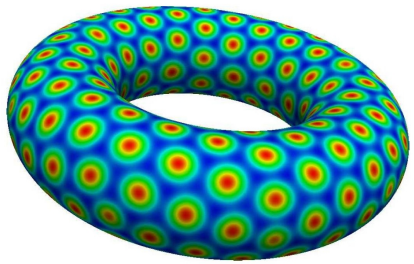


Nondimensional Free Energy (Swift-Hohenberg, 1977)

$$E_{pfc} = \int_\Omega \frac{1}{4}\rho^4 + \frac{1+r}{2}\rho^2 - |\nabla\rho|^2 + \frac{1}{2}\left(\nabla^2\rho\right)^2 \, d\mathbf{x} \tag{9}$$

- Models particles at atomic spatial scales but on diffusive time scales.
- Energy is minimized by periodic functions that describe the crystal lattice.



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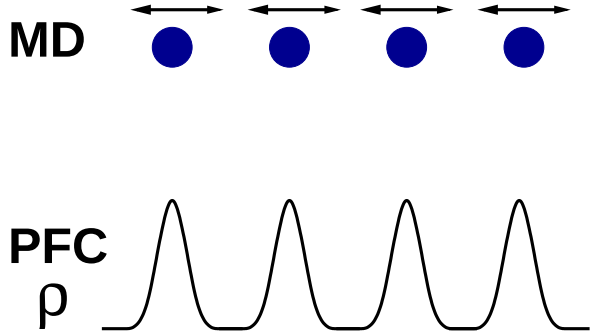

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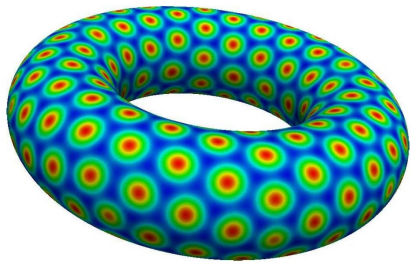

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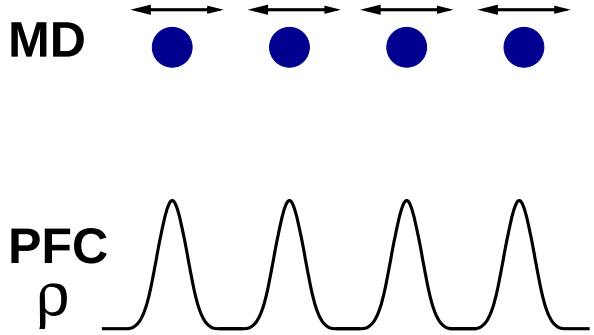

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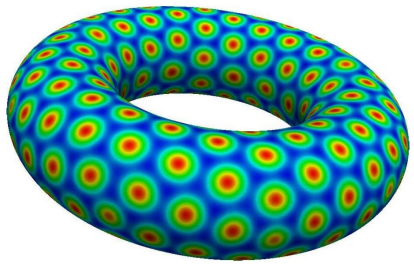

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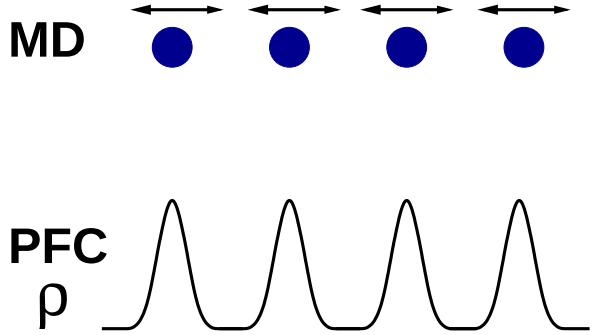

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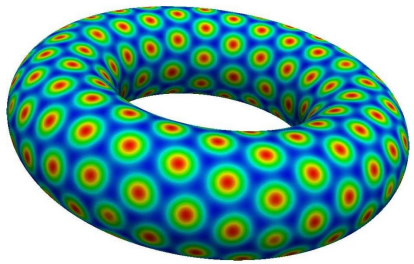

particle number density ρ on a torus

Phase Field Crystal II

Energy mimimized by periodic structure: $\rho = A\cos(\frac{2\pi}{a_{eq}}x) + B$.

Elasticity

Let a be the lattice spacing, then

$$E_{pfc}(a) = E(a_{eq}) + \frac{1}{2}\frac{\partial E}{\partial a}(a_{eq})(a - a_{eq})^2 + \dots \tag{10}$$

This gives Hooke's law. Costs energy to change the wavelength.
Model naturally captures elastic stress .

Dynamic model

Conserved Swift-Hohenberg equation.

$$\dot{\rho} = \nabla \cdot \left(M_\rho \nabla \frac{\delta E_{pfc}}{\delta \rho} \right), \tag{11}$$

M_ρ is a mobility.

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Free Energy Model (sharp)

Total free energy (nondimensional)

Nondimensionalized by domain size, Capillary relaxation time

$$
\begin{aligned}
E &= E_{pfc} + E_s + E_{kin}, \\
E_{pfc} &= El^{-1} \int_\Gamma \frac{1}{4}\rho^4 + \frac{1+r}{2}\rho^2 - |\nabla_\Gamma \rho|^2 + \frac{1}{2}\left(\Delta_\Gamma \rho\right)^2 dx, \\
E_s &= \int_\Gamma 1 \quad dx, \\
E_{kin} &= \int_\Omega \frac{1}{2}|\mathbf{u}|^2 dx \qquad \text{(constant density)}
\end{aligned}
$$

El^{-1} is the relative strength of the elastic to surface energy

Aland, Lowengrub, Voigt; Phys. Fluids (2011)

Variational derivation of surface colloid model

Energy variation (sharp)

Equivalent to varying Γ and ρ simultaneously.

$$\dot{E} = \int_\Omega \mathbf{u}\dot{\mathbf{u}} \; dx + \int_\Gamma \mathbf{u} \cdot \frac{\delta E}{\delta \Gamma} + \dot{\rho}\frac{\delta E}{\delta \rho} - \mathbf{u} \cdot \nabla_\Gamma \rho \frac{\delta E}{\delta \rho} dx \qquad \text{where}$$

$$\frac{\delta E}{\delta \rho} := E l^{-1} \left(\rho^3 + (1+r)\rho + 2\Delta_\Gamma \rho + \Delta_\Gamma^2 \rho \right)$$

$$\frac{\delta E}{\delta \Gamma} := -\kappa \mathbf{n} \left[1 + E l^{-1} \left(\frac{1}{4}\rho^4 + \frac{1+r}{2}\rho^2 - \frac{1}{2}(\Delta_\Gamma \rho)^2 - |\nabla_\Gamma \rho|^2 - \nabla_\Gamma \rho \cdot \nabla_\Gamma \Delta_\Gamma \rho \right) \right]$$
$$- 2El^{-1}(\nabla_\Gamma \rho, (Hess\Phi)\nabla_\Gamma \rho)_\Gamma - 2El^{-1}((Hess\Phi)\nabla_\Gamma \Delta_\Gamma \rho, \nabla_\Gamma \rho)_\Gamma$$

Aland, Rätz, Röger, Voigt; SIAM MMS, 2012

Balance laws

We assume the following equations hold

$$\dot{\mathbf{u}} = -\mathbf{u} \cdot \nabla \mathbf{u} - \nabla p + Re^{-1} \Delta \mathbf{u} + \delta \mathbf{F}_{el}, \quad \nabla \cdot \boldsymbol{u} = 0, \qquad \text{(NS)}$$

$$\dot{\rho} = -\nabla_\Gamma \cdot (\rho \mathbf{u}) - \nabla_\Gamma \cdot \boldsymbol{J}_\rho \qquad \text{(SPFC)}$$

where Re is a Reynolds number (defined in the usual way), and $\mathbf{F}_{el}$ and $\boldsymbol{J}_\rho$ are to be determined.

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Energy variation (sharp)

Using the balance laws in $\dot{E}$ gives

$$\dot{E} = \int_\Omega -\frac{1}{Re}\nabla\mathbf{u} : \nabla\mathbf{u} \;\; dx + \int_\Gamma \mathbf{u} \cdot \left(\mathbf{F}_{el} - \left(-\frac{\delta E}{\delta \Gamma} - \rho \frac{\delta E}{\delta \rho}\kappa\mathbf{n} - \rho \nabla_\Gamma \frac{\delta E}{\delta \rho} \right) \right) dx$$
$$+ \int_\Gamma J_\rho \cdot \nabla_\Gamma \frac{\delta E}{\delta \rho} dx.$$

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$$+ \int_\Gamma J_\rho \cdot \underbrace{\nabla_\Gamma \frac{\delta E}{\delta \rho}}_{\approx -J_\rho} dx.$$

Energy variation (sharp)

Using the balance laws in $\dot{E}$ gives

$$\dot{E} = \int_\Omega -\frac{1}{Re}\nabla\mathbf{u} : \nabla\mathbf{u} \; dx + \int_\Gamma \mathbf{u} \cdot \left(\mathbf{F}_{el} - \underbrace{\left(-\frac{\delta E}{\delta \Gamma} - \rho \frac{\delta E}{\delta \rho}\kappa\mathbf{n} - \rho\nabla_\Gamma \frac{\delta E}{\delta \rho} \right)}_{=:\mathbf{F}_{el}} \right) dx$$

$$+ \int_\Gamma J_\rho \cdot \underbrace{\nabla_\Gamma \frac{\delta E}{\delta \rho}}_{\approx -J_\rho} dx.$$

Indeed, taking $\mathbf{J}_\rho = -Pe_\rho^{-1}\nabla_\Gamma \frac{\delta E}{\delta \rho}$, $\Rightarrow$ decreasing energy for the system

$$\dot{\mathbf{u}} + \mathbf{u}\cdot\nabla\mathbf{u} + \nabla p + \frac{1}{Re}\Delta\mathbf{u} = -\delta\left(\frac{\delta E}{\delta \Gamma} + \rho\frac{\delta E}{\delta \rho}\kappa\mathbf{n} + \rho\nabla_\Gamma\frac{\delta E}{\delta \rho} \right) \qquad \text{(NS)}$$

$$\nabla\cdot\mathbf{u} = 0$$

$$\dot{\rho} + \nabla_\Gamma\cdot(\rho\mathbf{u}) = Pe_\rho^{-1}\Delta_\Gamma\frac{\delta E}{\delta \rho} \qquad \text{(PFC)}$$

Pe_ρ is a (surface) Peclet number.

Free Energy Model (diffuse)

Introduce the approximation to the surface delta function

$$e := \left(\frac{\epsilon}{2} |\nabla \psi|^2 + \frac{1}{\epsilon} B(\psi) \right) \approx \delta$$

with the double well potential $B(\psi) = 18\psi^2(1-\psi)^2$

Diffuse interface version of the energy

$$\begin{aligned} E_{pfc} &= El^{-1} \int_\Omega e \left(\frac{1}{4}\rho^4 + \frac{1+r}{2}\rho^2 - |\nabla \rho|^2 + \frac{1}{2}\nu^2 \right) dx, \\ E_s &= \int_\Omega e \quad dx, \\ E_{kin} &= \int_\Omega \frac{1}{2}|\mathbf{u}|^2 dx \qquad \text{(constant density)} \end{aligned}$$

where ν is the diffuse interface Laplace-Beltrami:

$$\nu := \frac{1}{e} \nabla \cdot (e \nabla \rho)$$

Aland, Lowengrub, Voigt; Phys. Fluids (2011)

Energy variation (diffuse)

Balance laws

Assuming conservation of mass and momentum:

$$\dot{\mathbf{u}} + \mathbf{u} \cdot \nabla \mathbf{u} + \nabla p + \frac{1}{Re} \Delta \mathbf{u} = \nabla \cdot \mathbf{T}_{el} \tag{NS}$$

$$\nabla \cdot \mathbf{u} = 0$$

$$\dot{\psi} + \mathbf{u} \cdot \nabla \psi = 0 \tag{Adv}$$

$$\dot{(e\rho)} + \nabla \cdot (e\rho \mathbf{u}) = \nabla \cdot \mathbf{J}_\rho \tag{PFC}$$

we get $\dot{E} \leq 0$ for

$$\mathbf{T}_{el} = El^{-1} e \left(2 \nabla\rho \otimes \nabla\rho + \nabla\nu \otimes \nabla\rho + \nabla\rho \otimes \nabla\nu\right) - \epsilon \nabla\psi \otimes \nabla\psi \frac{\delta E}{\delta e}$$

$$\mathbf{J}_\rho = Pe_\rho^{-1} e \nabla \frac{\delta E}{\delta \rho}$$

with

$$\frac{\delta E}{\delta \rho} := El^{-1} \left(\rho^3 + (1+r)\rho + 2\nu + \frac{1}{e} \nabla \cdot (e \nabla \nu)\right)$$

$$\frac{\delta E}{\delta e} := 1 + El^{-1} \left(\frac{1}{4}\rho^4 + \frac{1+r}{2}\rho^2 - \frac{1}{2}\nu^2 - |\nabla\rho|^2 - \nabla\nu \cdot \nabla\rho\right) - \frac{\delta E}{\delta \rho}\rho$$

Energy variation (diffuse)

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Governing Equations

Putting everything together yields the Navier-Stokes-Phase-Field-Crystal system:

1. PFC on diffuse interface

$$\begin{aligned} \partial_t(e\rho) + \nabla\cdot(e\mathbf{u}\rho) &= Pe_\rho^{-1}\nabla\cdot(e\nabla\omega) \\ e\omega &= e\rho(\rho^2+1+r) + 2e\nu + \nabla\cdot(e\nabla\nu) \\ e\nu &= \nabla\cdot(e\nabla\rho) \end{aligned}$$

2. Navier Stokes Equation with elastic force

$$\begin{aligned} \partial_t\mathbf{u} + (\mathbf{u}\cdot\nabla)\mathbf{u} + \nabla p - Re^{-1}\Delta\mathbf{u} &= \nabla\cdot\mathbf{T}_{el} \\ \nabla\cdot\mathbf{u} &= 0 \end{aligned}$$

3. Advection Equation

$$\partial_t\psi + \nabla\cdot(\mathbf{u}\psi) = 0$$

+ appropriate boundary conditions.

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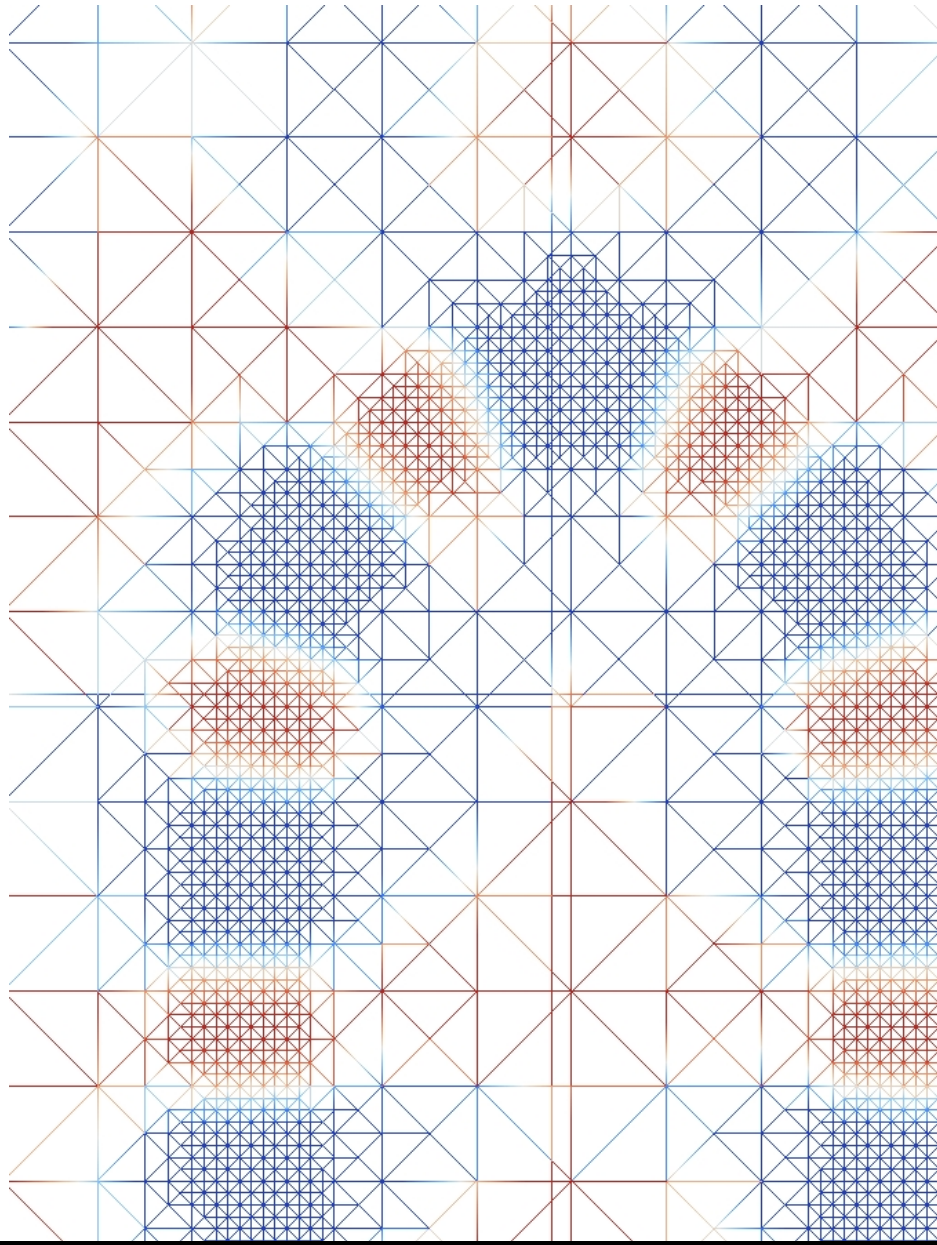
3. Cahn Hilliard Equation

$$\begin{aligned} \partial_t\psi + \nabla\cdot(\mathbf{u}\psi) &= Pe_\psi^{-1}\nabla\cdot(B\nabla\mu), \\ \mu &= \epsilon^{-1}B'(\psi) - \epsilon\Delta\psi, \end{aligned}$$

+ appropriate boundary conditions.

Numerical treatment

- C++ FEM library AMDiS
- adaptive mesh
- polynomial degree 1
- projection scheme for NS
- solver: UMFPACK / PETSc
- semi-implicit time discretization
- linearization by first order Taylor expansion



Stabilization of an Ellipse

- Without colloids, ellipse retracts to a circle due to surface tension.
- With colloids initially equilibrated on the interface, the ellipse is stabilized due to colloid interactions.

Stabilization of an ellipsoid

Left: No colloids, Right: Colloids

- Colloids prevent retraction. Jam the interface.
- Surface defects form and result in interfacial buckling. Not seen in 2D.
- Particles with 5 neighbors minimize energy by buckling.

Attachment of Colloids

- Assume one of the bulk phases contains colloidal particles in a disordered state (nearly uniform density).
- Introduce the bulk colloid density c.

The bulk density equation is given by:

$$\partial_t(\psi c) \quad = \quad Pe_c^{-1}\nabla\cdot(\psi\nabla c) - \nabla\cdot(\psi\mathbf{u}c) - h\ Bi|\nabla\psi|\left(c(\rho_\infty-\rho) - k^{-1}\rho\right)$$

with Pe_c, h, Bi, k, ρ_∞, the bulk Peclet number, penetration depth, Biot number (relative adsorption rate), relative desorption rate, and saturation density respectively.

The evolution of ρ now becomes:

$$\partial_t(e\rho) \quad = \quad Pe_\rho^{-1}\nabla\cdot(e\nabla\omega) - \nabla\cdot(e\mathbf{u}\rho) + Bi\ e\left(c(\rho_\infty-\rho) - k^{-1}\rho\right)$$

Stabilization of an Ellipse - with attaching colloids

Source of colloids at bottom of fluid domain.

- Colloids attach at bottom and move upwards
- Retraction stops first at bottom
- Asymmetric drop shape results since retraction occurs longer at top of drop

Spinodal Decomposition

Start the system without colloidal particles and allow spinodal decomposition to occur for a short time.

Stabilization of Bicontinuous Structure

Add colloids, allow equilibration on interface.
Left: Colloids, Right: No colloids

Stabilization of Bicontinuous Structure - jamming

Initially not enough colloids on the interface to crystallize. Interface contraction leads to jamming.

Stabilization of 3D bicontinuous structure

Figure: Left: No colloids, Right: Colloids

- Colloids prevent retraction. Jam the interface.
- Surface defects form and result in interfacial buckling.

Yield stress I

Solid ball moving through a multiphase fluid using diffuse domain approach.

$$\dot{\mathbf{u}}_{ball} = -\mathbf{G} + \int_{\partial\Omega_{ball}} \tau \cdot \mathbf{n} \; ds$$

with the total stress tensor

$$\tau = -pI + \frac{1}{Re}(\nabla\mathbf{u} + \nabla\mathbf{u}^T) + \mathbf{T}_{el}$$

and gravitational force $\mathbf{G}$.

Right: No colloids present.

Yield stress II

moderate colloid interaction ($El = 0.01$)

- ball penetrates the interface
- elastic forces hold the ball at the interface

strong colloid interaction ($El = 0.002$)

- interface behaves like a solid
- ball is "lying" on the interface

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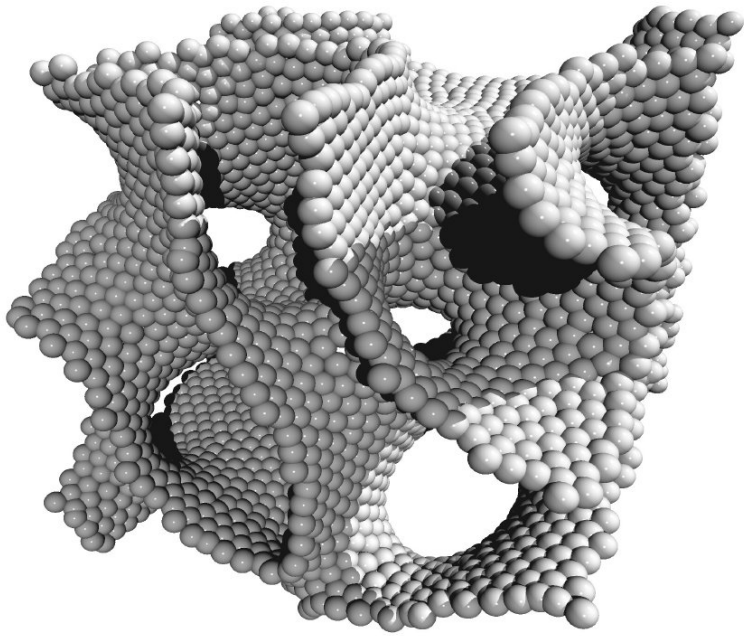
- model works phenomenologically
- elasticity from SPFC can be used to stabilize binary fluid mixture

To Do

- more colloids
- long time simulations
- microreactor
- material properties
- connect simulations to real world



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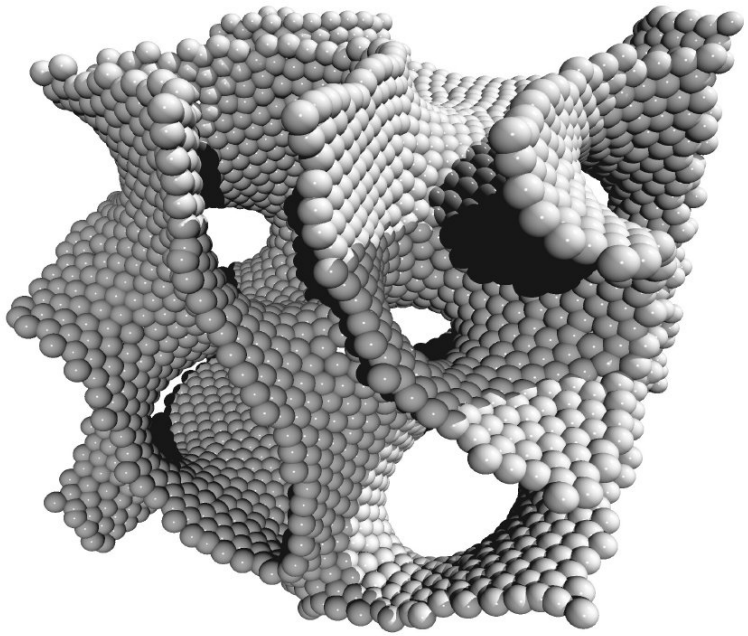

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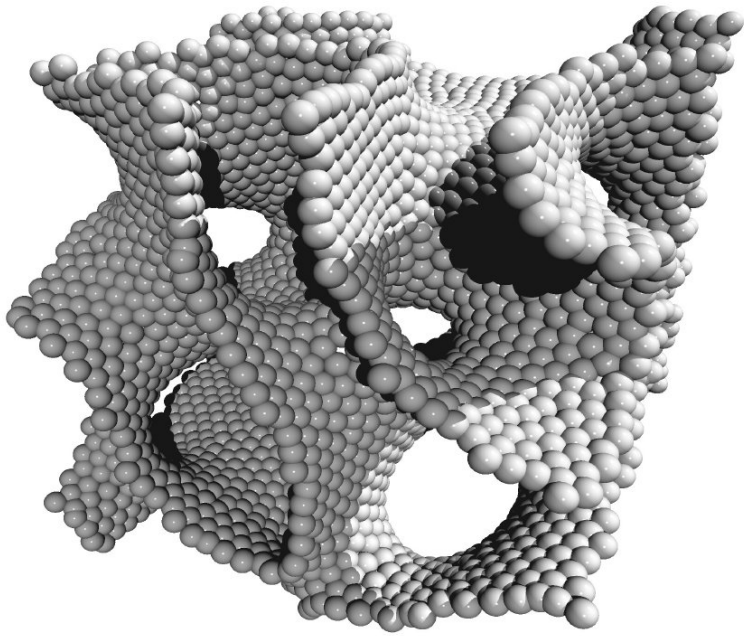

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