PIRE Project Annual Review Meeting

Capillary Forces and Wetting Phenomena in the Diffuse Interface Theory

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Research Thrust 2: Formation and Control of Gas Hydrate Slurries

June 19th, 2018

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The Benjamin Levich Institute for Physico-Chemical Hydrodynamics

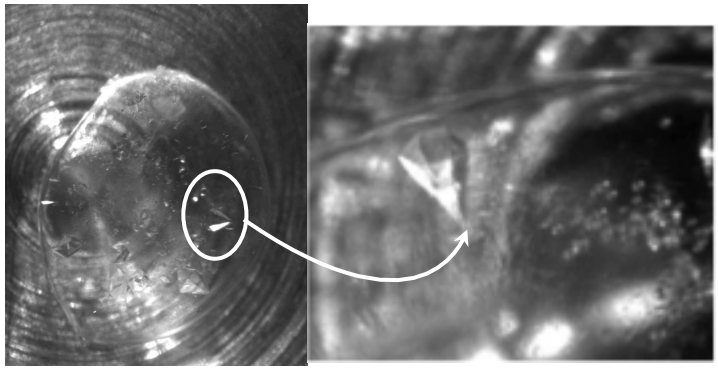
NSF PIRE Partnerships for International Research and Education

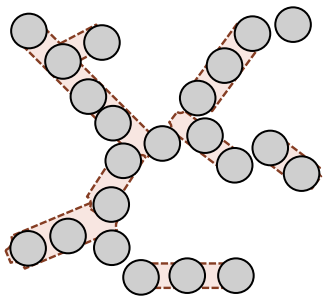
the City College of New York

Motivation

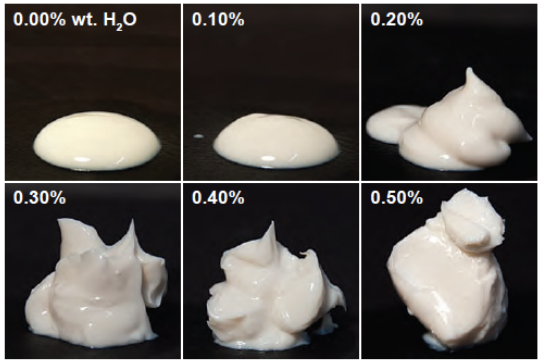
Three-phase contact lines are everywhere in nature and industry.

Wetting phenomena play a major role in the dynamics of complex systems.

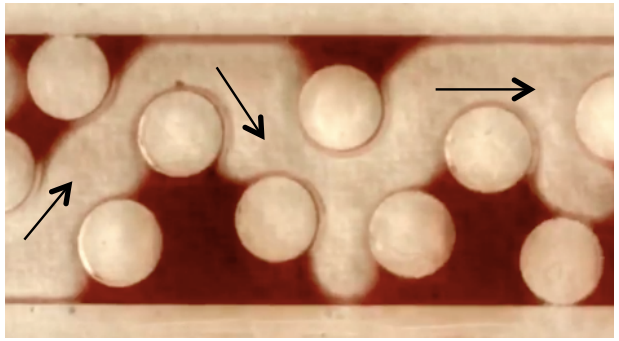




Hydrate formation. Water drop in cyclopentane, 0.1% Span 80



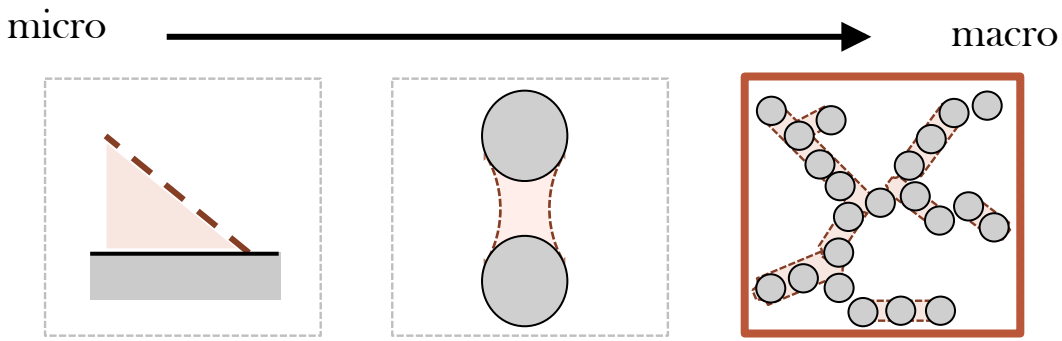
Particles in oil suspension
Koos et. al, *Science*, 2014



Two-phase flow through porous media

The crucial role of wetting

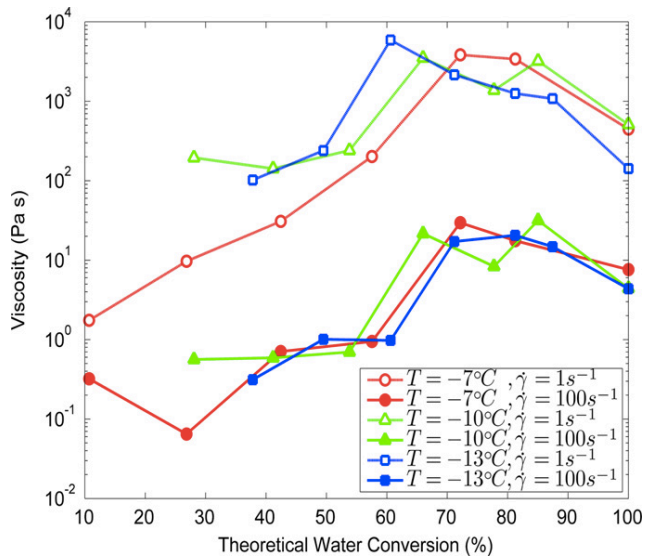
Understanding the dynamics on multiple scales



Contact line motion

Pair problem

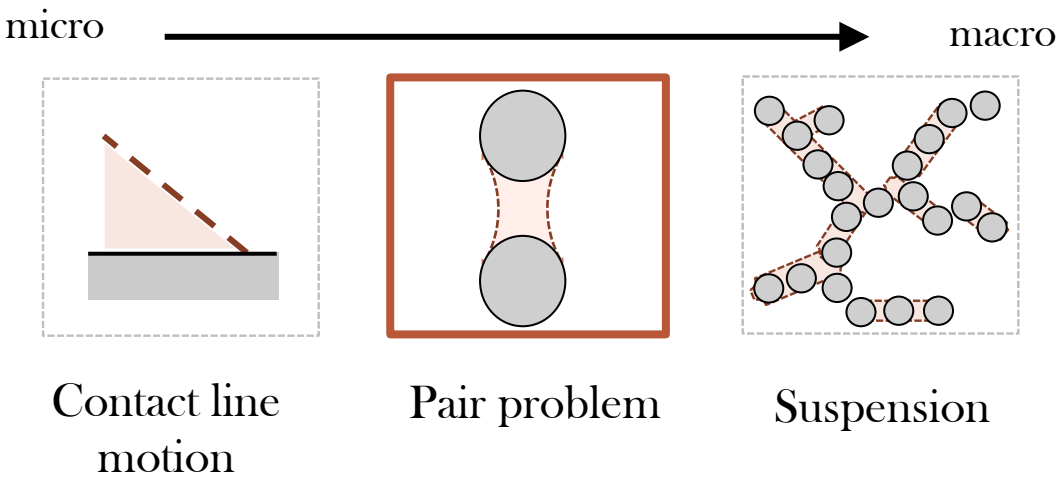
Suspension



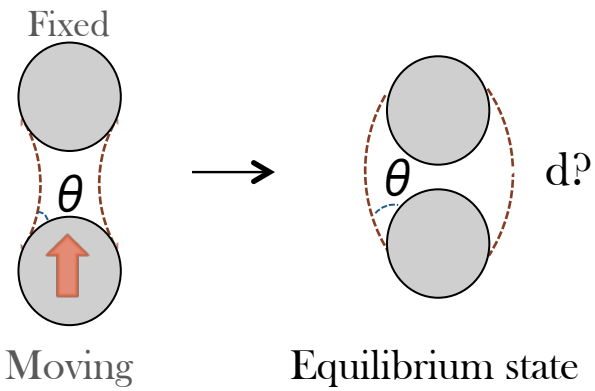
Zylyftari *et al. Chem. Eng Sci.* 2013

The crucial role of wetting

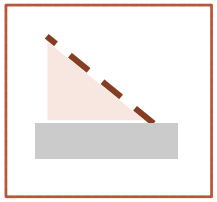
Understanding the dynamics on multiple scales



Interplay between the **capillary forces** of the system



The paradox of the moving contact line

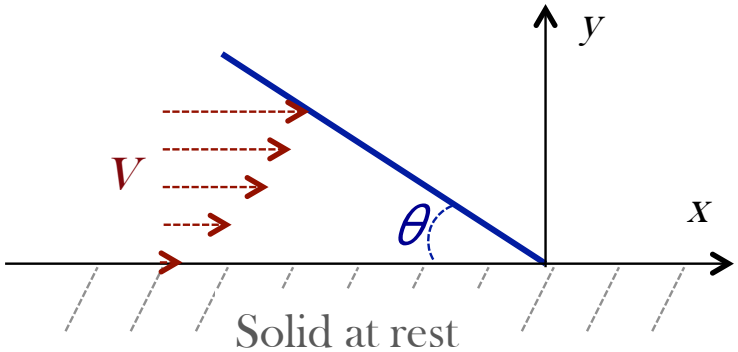


Huh and Scriven (1971) : classical hydrodynamic description breaks down at the contact line

No-slip condition $\longrightarrow$ Stress singularity

$$v(x=0, y=0) = ?$$

$$\frac{dv}{dy} \sim \frac{V}{\theta x} \to \infty$$



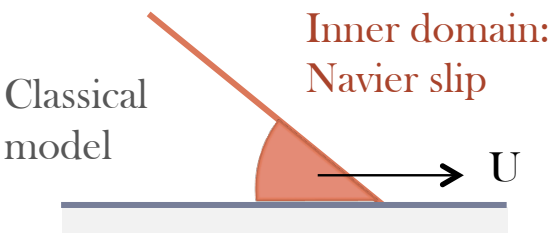
Microscopic effects have to be included! Multiscale problem

Overcoming the stress singularity

Main models in the literature

- Hydrodynamic theory

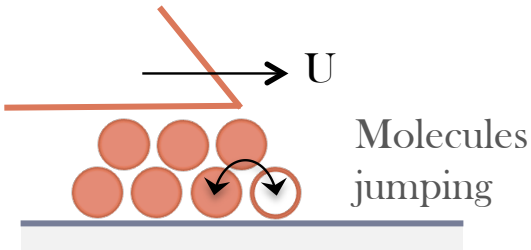
Slip condition near the contact line



(Huh and Scriven, 1971, Dussan, 1976)

- Molecular kinetic theory

Attachment / Detachment process



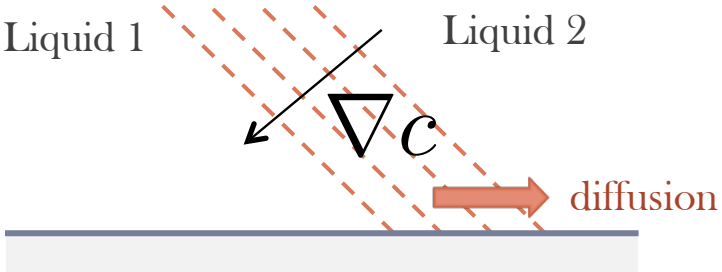
(Blake, 1969)

- Diffuse interface modeling

Interface of <u>finite thickness</u>

Order parameter (e.g. composition c)

Energy based approach



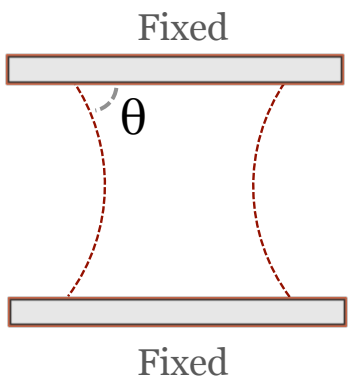
(Rowlinson, 1979, Jacqmin, 2000)

How does the DI model handle the stress singularity?

How to describe the capillary forces within the DI framework?

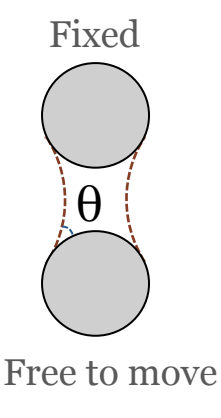
Approach

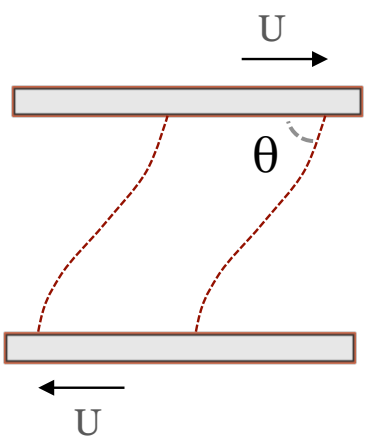
1. Implementation and validation on a simple system

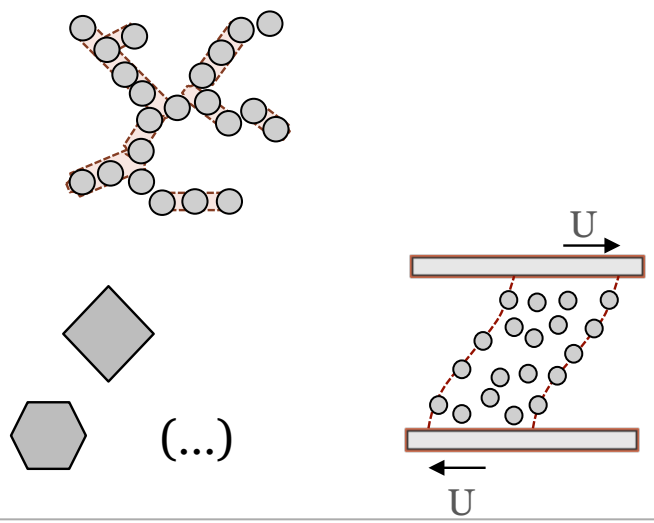


Numerical and analytical approaches

2. Extension to more complex systems







Diffuse interface theory

Formulation

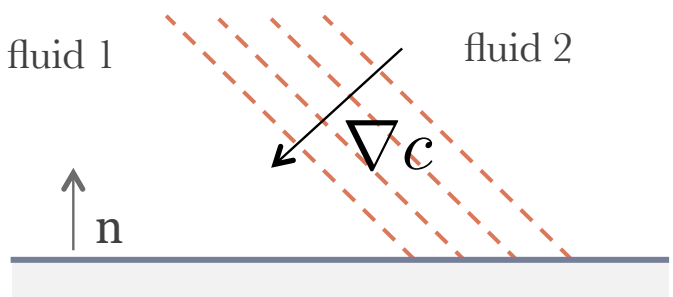
- Cahn Hilliard model for binary fluids

Helmholtz free energy (Cahn and Hilliard, 1958)

$$F(c, \nabla c) = F^0(c) + \frac{\kappa}{2}(\nabla c)^2$$

Thermodynamic equilibrium

$$\mu^0(c) - \kappa \nabla^2 c = \text{cste}$$



- Three-phase contact line

Additional wall free energy $\Psi_s(c_s)$ =>

$$\kappa\, \mathbf{n} \cdot \nabla c_s = -\frac{d\Psi_s}{dc_s} \quad \text{(contact angle)}$$

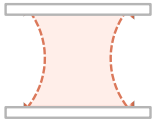
- Dynamics

$$\frac{\partial c}{\partial t} + \nabla \cdot (\mathbf{v} c) = M \nabla^2 \left(\mu_0 - \kappa \nabla^2 c\right)$$

Cahn-Hilliard equation

Lattice Boltzmann simulations

Test Case



- Discrete Boltzmann equation for Cahn Hilliard fluid (He *et al.*,1998)

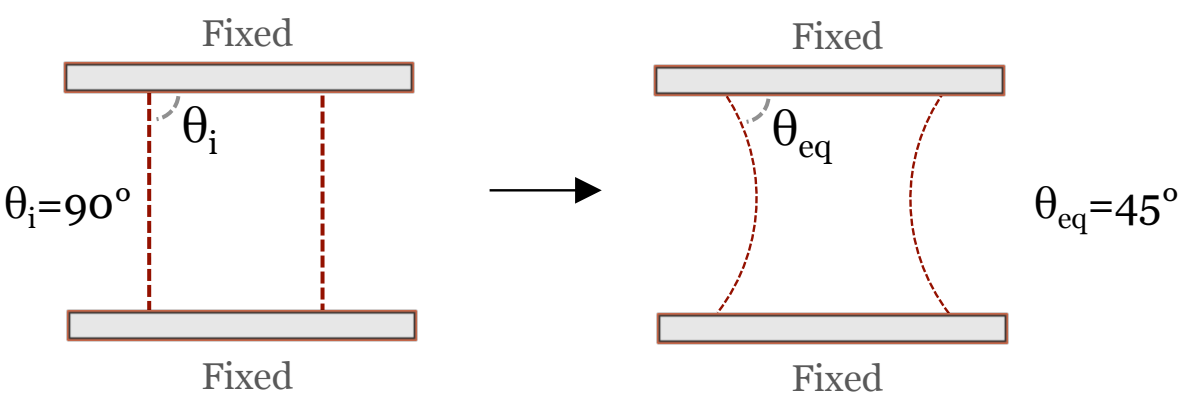
$$\frac{\partial f_\alpha}{\partial t} + \mathbf{e}_\alpha \cdot \nabla f_\alpha = -\frac{f_\alpha - f_\alpha^{eq}}{\lambda} + \frac{(\mathbf{e}_\alpha - \mathbf{u}) \cdot \boxed{\mathbf{F}}}{\rho c_s^2} f_{eq}$$

Intermolecular force: $\mathbf{F} = \nabla \rho c_s^2 - (\nabla p - C \nabla \mu)$

Dynamic pressure

Generalized chemical potential

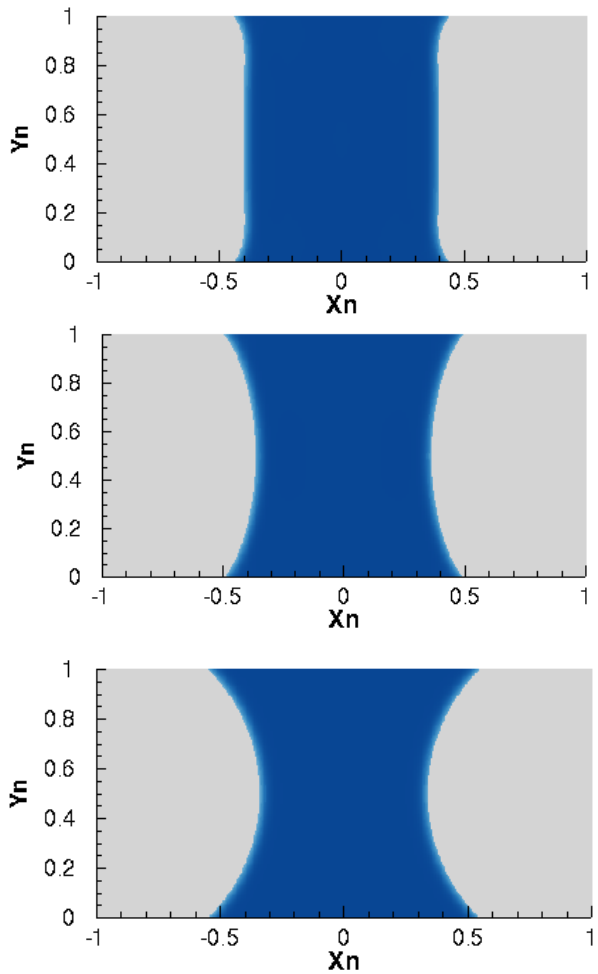
- Relaxation towards equilibrium



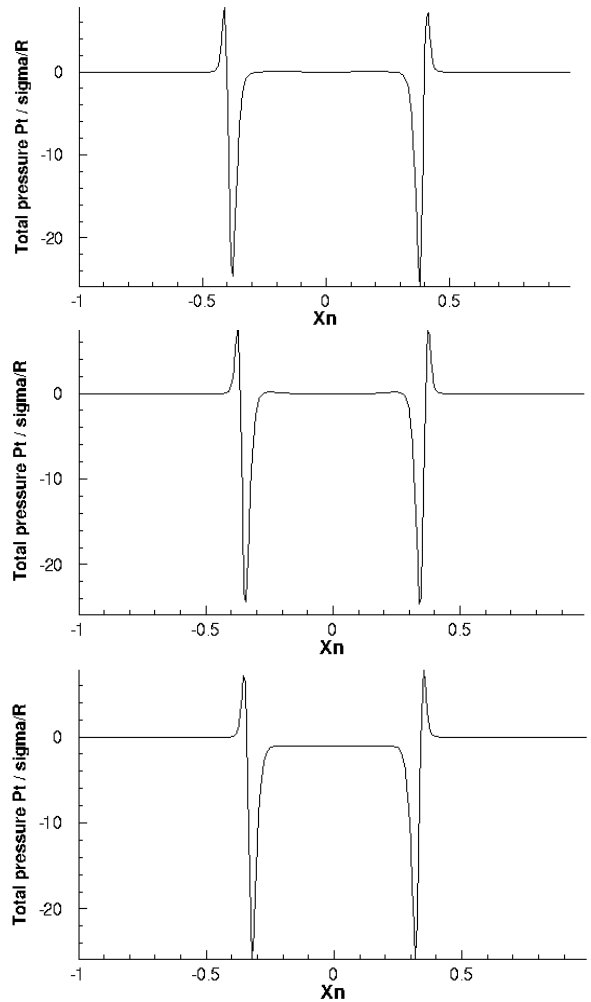
Liquid / liquid interface
2D system
Symmetry
No hysteresis
No gravity

Lattice Boltzmann simulations

Results



Pressure at the centerline



Mechanisms

$\theta \rightarrow \theta_e$

Boundary Condition

$\nabla \mu \rightarrow 0$

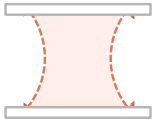
Relaxation to equilibrium shape

Moving contact line ✓

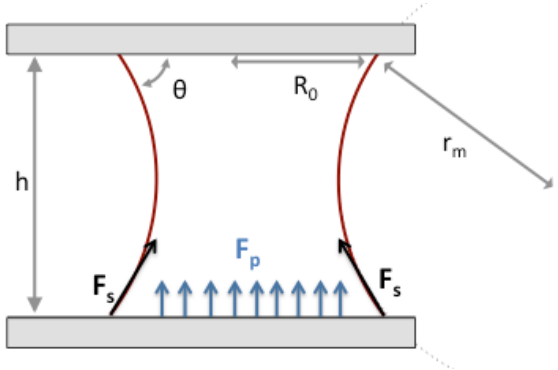
Expected equilibrium ✓

Capillary forces within the DI framework

Analytical Approach

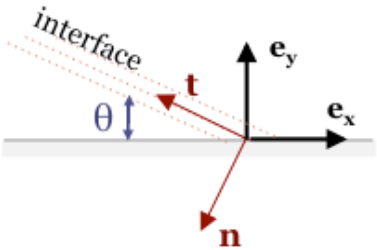


Macroscopic description



Diffuse interface modeling (Anderson, 1997)

$$\mathbf{T} = \left[-p_0 + \frac{1}{2}\kappa|\nabla c|^2\right]\mathbf{I} - \kappa\,\nabla\mathbf{c}\otimes\nabla\mathbf{c}$$



$$T = \begin{pmatrix} -p_t & 0 \\ 0 & -p_t + \kappa|\nabla c|^2 \end{pmatrix}$$

Capillary forces

$$\mathbf{F_c} = \mathbf{F_s} + \mathbf{F_p}$$

Normal component (*y*-direction):

$$F_{c,y} = 2\gamma\sin\theta - 2R_0\Delta P$$

$$\Delta P = \frac{\gamma}{r_m} \quad \text{(Laplace)}$$

$$\mathbf{F_c} = \int_{x=0}^{\infty} \mathbf{T}|_s \cdot \mathbf{e_y}\, dx$$

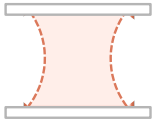
Macroscopic force is recovered with:

$$\gamma = \int \kappa|\nabla c_s|^2 dr$$

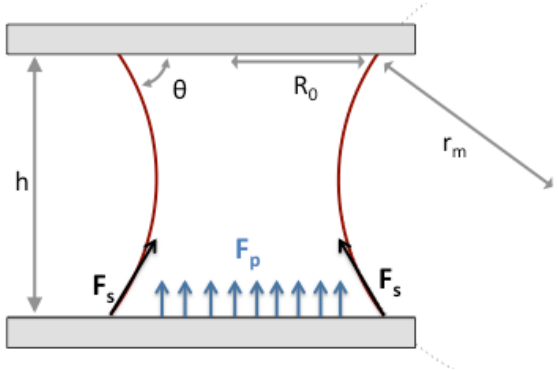
Surface tension

Capillary forces within the DI framework

Analytical Approach

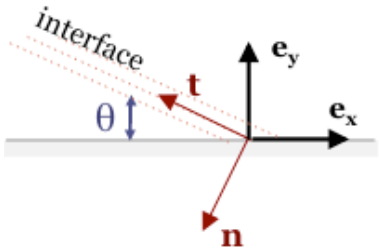


Macroscopic description



Diffuse interface modeling (Anderson, 1997)

$$\mathbf{T} = \left[-p_0 + \frac{1}{2}\kappa|\nabla c|^2\right]\mathbf{I} - \kappa\,\nabla\mathbf{c}\otimes\nabla\mathbf{c}$$



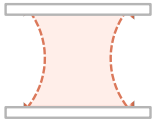
$$T = \begin{pmatrix} -p_t & 0 \\ 0 & -p_t + \kappa|\nabla c|^2 \end{pmatrix}$$

Capillary forces

Macroscopic		Diffuse interface		Molecular theory
$\mathbf{F_c}$	⟷	$\mathbf{T}$	⟷	$\gamma = \int \kappa\|\nabla c_s\|^2 dr$
Laplace equation		Capillary stress tensor		Surface tension = normal stress difference

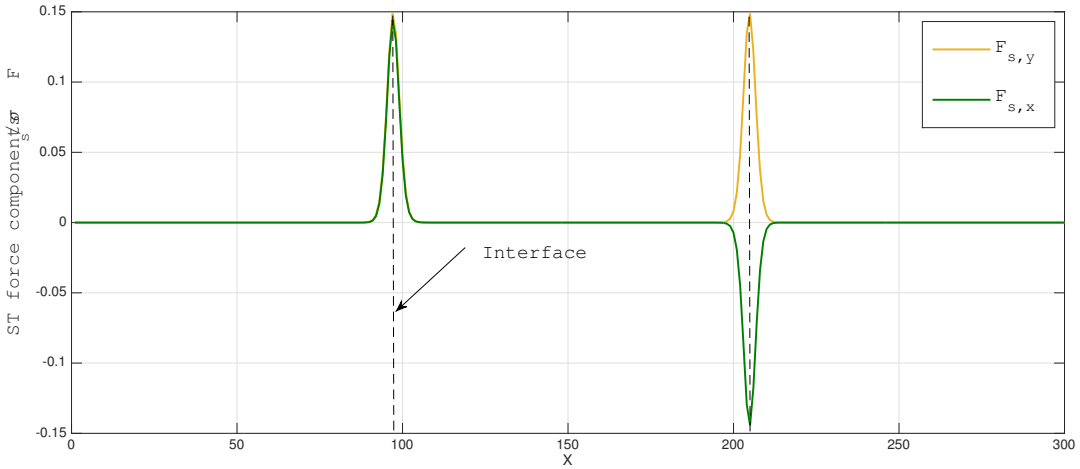
Capillary forces within the DI framework

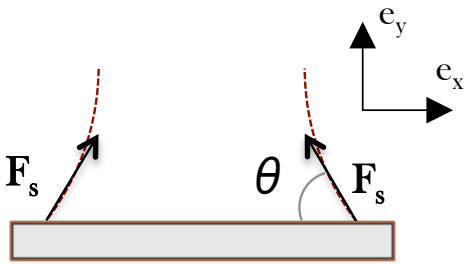
Numerical Approach



1. Pressure force: Laplace equation is recovered $\Delta P = \dfrac{\gamma}{r_m}$

2. Surface tension force (on the bottom plate):



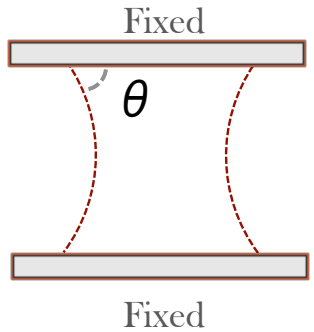


$$\tan\theta_{eq} = |F_N/F_T|$$

Local distribution of the tension force directly incorporated in the code

Test case

Discussion



Moving contact line

- Implementation of the LB model
- Validation
- Mechanisms

Description of the capillary forces

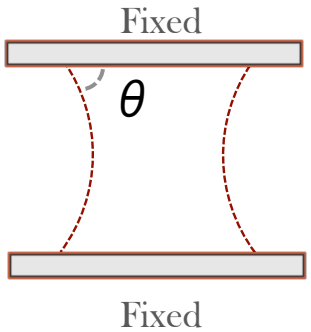
- Surface tension = excess energy in the interface
- Volumetric force directly in the code

→ Role of wetting phenomena in the dynamics?

Towards more complex systems

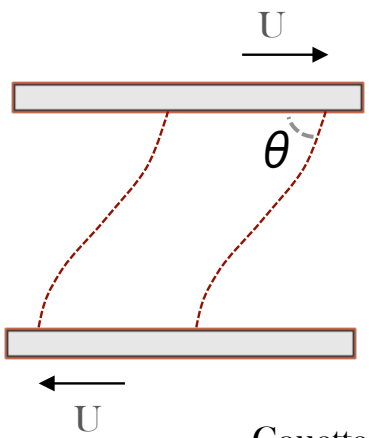
Motivation

Test Case

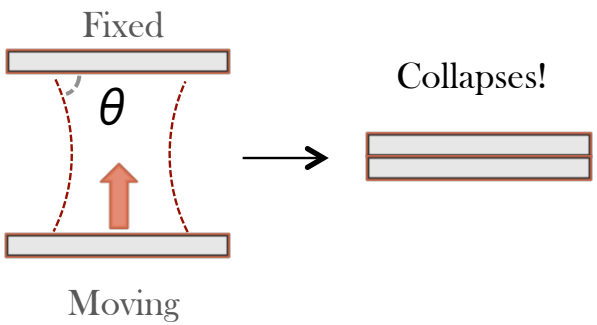


Moving contact line

Description of the capillary forces

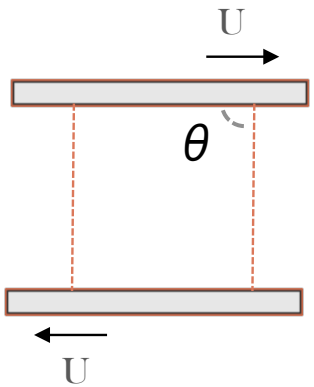


Couette geometry



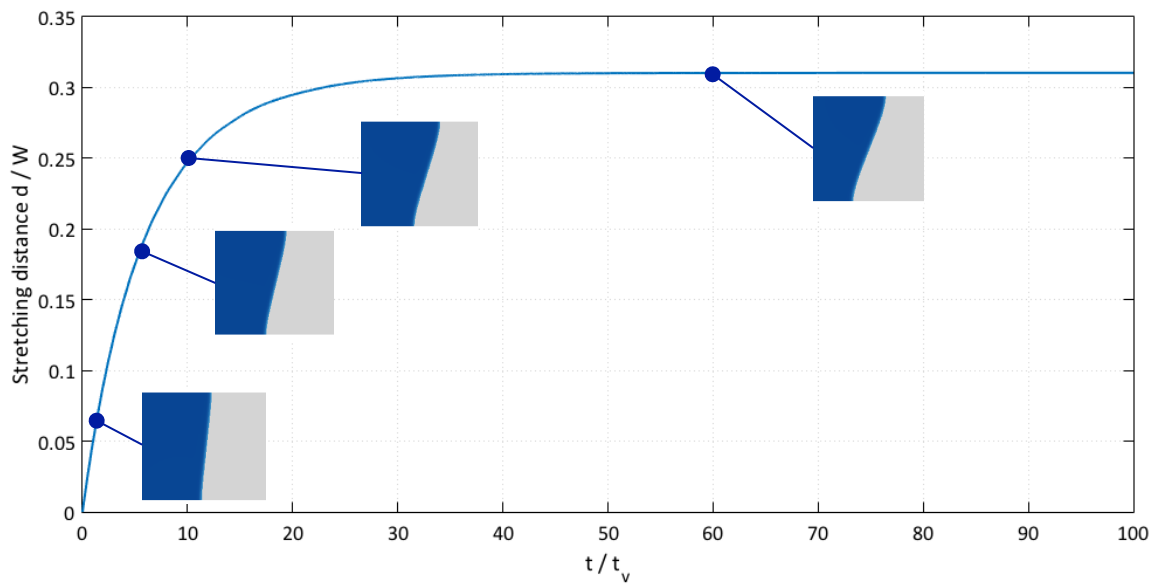
Couette flow with a liquid bridge

Pure fluid case

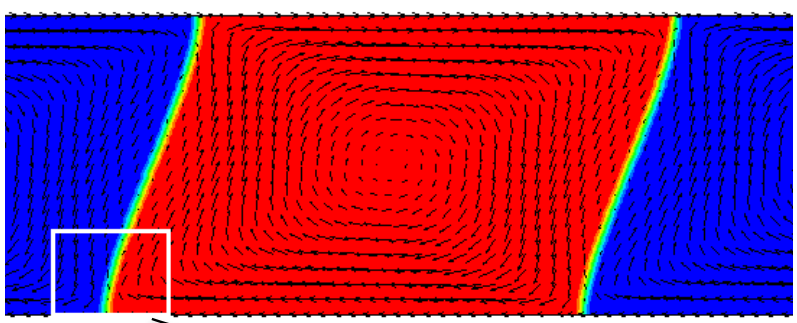


$Re \ll 1, Bo = 0$

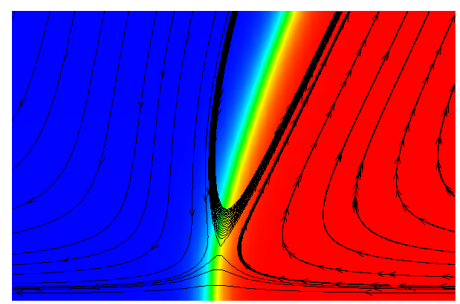
$Ca = 0.03, \mu_1/\mu_2 = 1, Cn = 0.04, \theta_S = 90$



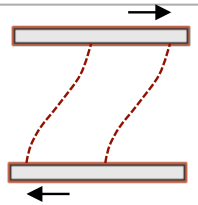
Flow field at steady state



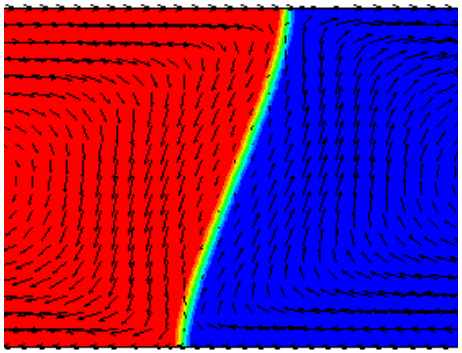
Stagnation point near the contact line



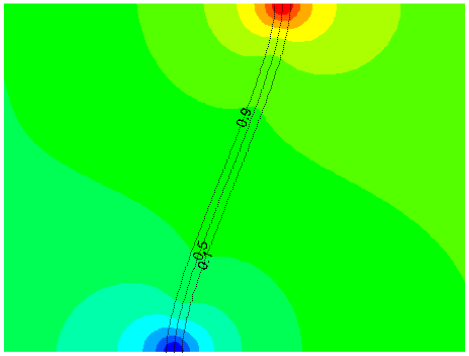
Couette flow with a liquid bridge



1. Realistic interface thickness – not computationally feasible



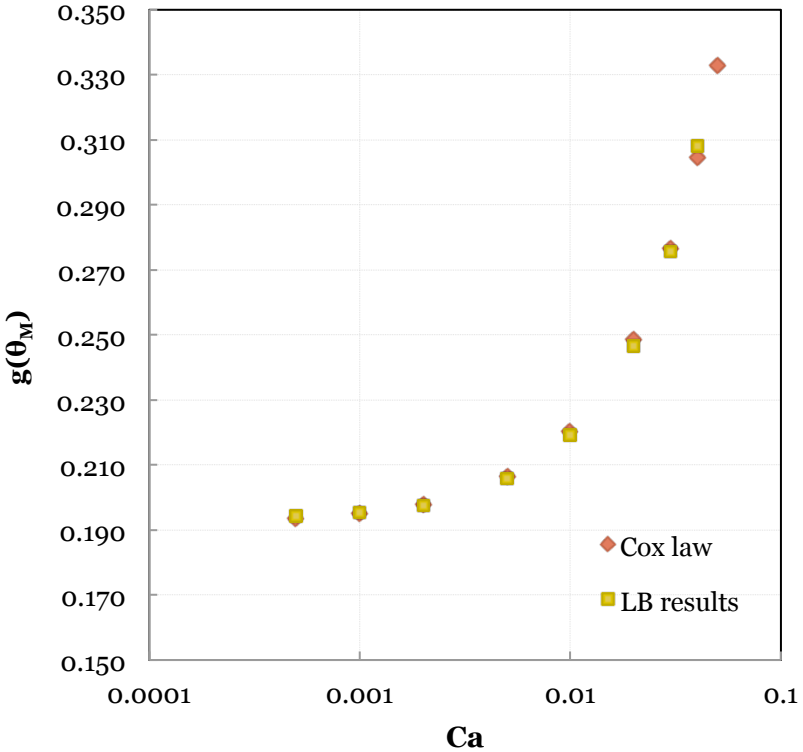
Composition



Chemical potential

Cox-Voinov law:

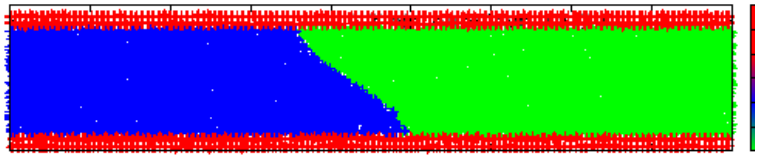
$$g(\theta_{app}) = g(\theta_E) + Ca \ln(x/L_s)$$



2. Role of mobility parameter

$$\frac{\partial c}{\partial t} + \nabla \cdot (\mathbf{v}c) = \boxed{M} \nabla^2 \left(\mu_0 - \kappa \nabla^2 c\right)$$

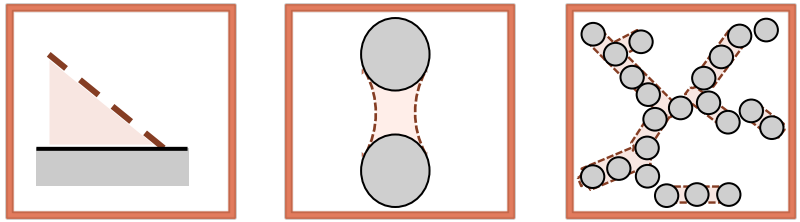
=> Mapping from molecular dynamics simulations



Koplik, J., Banavar, J. R., & Willemsen, J. F, *Physical Review Letter, 1988*
Qian, T., Wang, X. P., & Sheng, P., *Physical Review E, 2003*

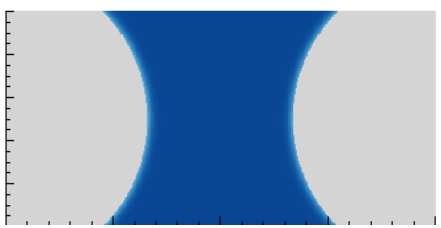
Conclusion

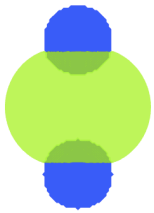
A computational tool to understand the role of wetting in the multiscale dynamics of three-phase systems



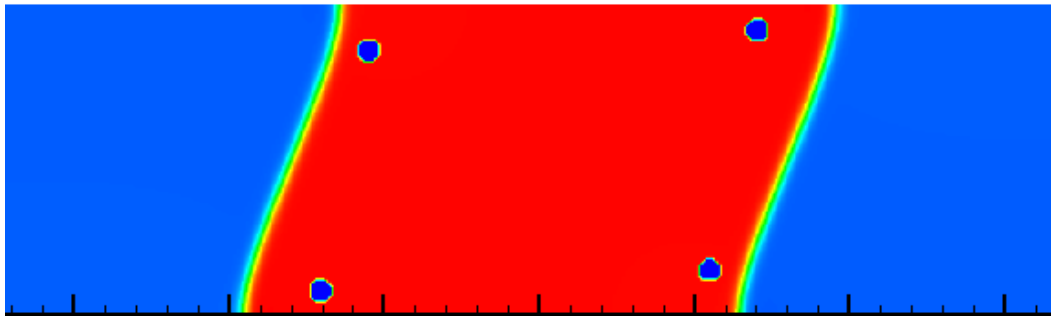
Macroscopic		Diffuse interface		Molecular theory
$\mathbf{F_c}$	⟷	$\mathbf{T}$	⟷	$\gamma = \int \kappa \lvert\nabla c_s\rvert^2 dr$

Moving contact lines and capillary forces





Ongoing work – Towards multi body systems



Thank you

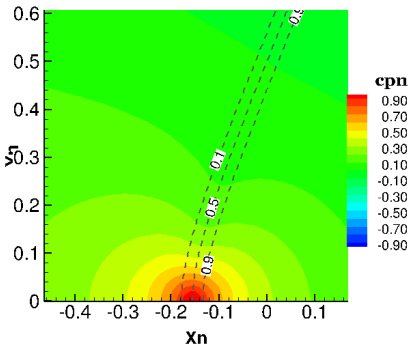
The Benjamin Lavich Institute for
Physico-Chemical Hydrodynamics

Couette flow with a liquid bridge

What is driving the contact line?

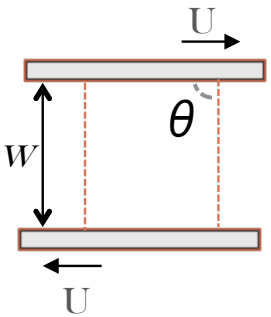
Role of mobility parameter? $$\frac{\partial c}{\partial t} + \nabla \cdot (\mathbf{v}c) = \boxed{M}\nabla^2 \left(\mu_0 - \kappa \nabla^2 c\right)$$

Contour lines of the generalized chemical potential



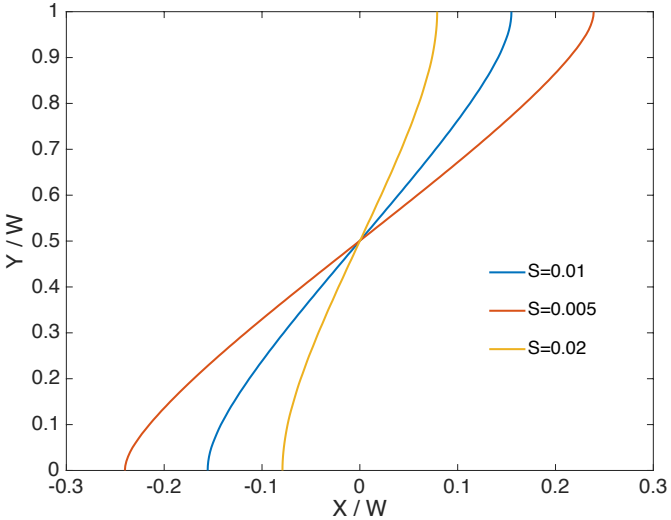
The "diffusion region" scales as:

$$S = \frac{\sqrt{\mu_l M}}{W}$$



$S \to \infty$ Perfect "slip" of the CL

$S \to 0$ No "slip" of the CL

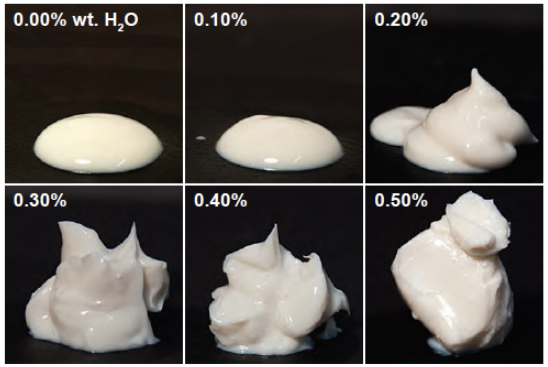


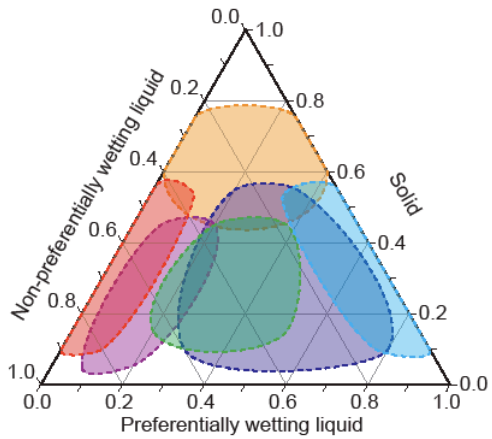
S is a dimensionless diffusion length. It is governing the contact line motion!
How to choose M ?

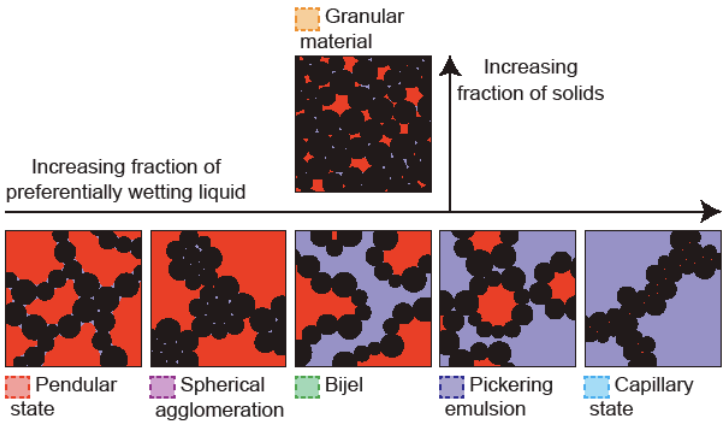
Extension to more complex systems

Multi body systems

- Networks of particles formed because of capillary forces







E Koos. Capillary suspensions: Particle networks formed through the capillary force. *Current opinion in colloid & interface science*, 19(6):575–584, 2014

- Connecting the bulk stress with the capillary forces

Impact on the rheological properties?

$$\sigma_y = f(\phi)\frac{F_c}{r^2}$$

σ_y Yield stress

ϕ Particle vol. frac.

r Particle radius

Dimensionless numbers & parameters

Relevant dimensionless numbers

$$Re = \frac{UL\rho}{\mu}, \qquad Ca = \frac{\mu U}{\gamma}, \qquad Bo = \frac{g\delta\rho L^2}{\gamma}.$$

inertia/viscous viscous / interfacial buoyancy / interfacial

Surface tension $\gamma \sim 25$ to 500 mN m^{-1} (water/air: $\sim 70 \text{ mN m}^{-1}$) M/T^2

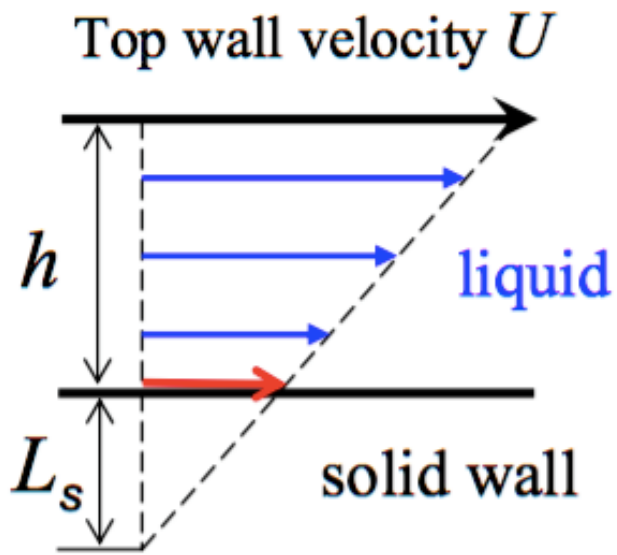
Viscosity $\mu \sim 10^{-3} \rightarrow 10^3 \text{ Pa s}$ $M/(LT)$

Re simulations << 1

Time scales $t_v = \rho L^2/\mu$ $t_s = \rho U L^2/\gamma$

Numerical limitations: density ratio / Viscosity ratio => Mach number

Navier slip condition



Navier slip condition $V_{slip} = L_s \dot{\gamma}$

Slip length vs. diffusion length

Connection with molecular theory

Cahn Hilliard vs. van der Waals

- Cahn and Hilliard extended the van der Waals theory to binary mixtures (1958)

	Van der Waals	Cahn-Hilliard
Order parameter	density ρ	composition c
Helmholtz free energy	$F(\rho, \nabla\rho) = F^0(\rho) + \frac{\kappa}{2}(\nabla\rho)^2$	$F(c, \nabla c) = F^0(c) + \frac{\kappa}{2}(\nabla c)^2$
Equilibrium condition	$\mu^0(\rho) - \kappa\nabla^2\rho = \text{cste}$	$\mu^0(c) - \kappa\nabla^2 c = \text{cste}$
Out of equilibrium	Mass conservation Capillary Stress tensor	Cahn-Hilliard equation (mass diffusion) $\frac{dc}{dt} = D\nabla^2\left(\mu_0 - \kappa\nabla^2 c\right)$ + Capill. Stress tensor

More details on the LB method

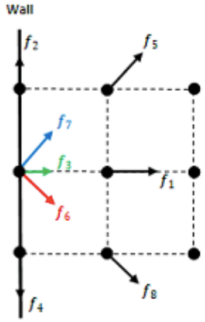
- **Intermolecular force: pressure form vs. potential form**

$$\mathbf{F} = \nabla(\rho c_s^2 - p_0) + \rho\kappa\nabla\nabla^2\rho \qquad \mathbf{F} = \nabla\rho c_s^2 - \rho\nabla\left(\mu_0 - \kappa\nabla^2\rho\right)$$

T Lee and PF Fischer. Eliminating parasitic currents in the lattice boltzmann equation method for nonideal gases. Physical Review E, 74(4):046709, 2006.

- **Boundary conditions**: have to reflect the macroscopic BCs

On grid bounce-back (no slip)



$$\kappa\mathbf{n}\cdot\nabla\rho_s = -\frac{d\Psi_s}{d\rho_s}$$

Normal gradient free on ρ and μ
(no unphysical mass transfer)

→ Applied on $\nabla^2\rho$

T Lee and L Liu. Wall boundary conditions in the lattice Boltzmann equation method for nonideal gases. Physical Review E, 78(1):017702, 2008