Modeling Moving Contact Lines in Multiphase Flow

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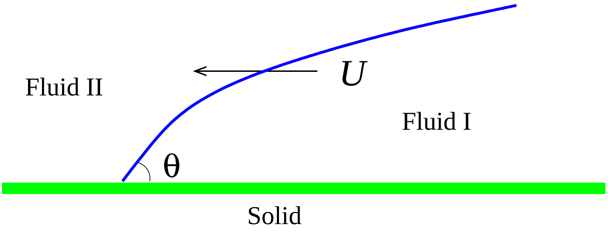
Outline of the talk

- Derive boundary conditions for the moving contact line (MCL) problem based on thermodynamics principles and molecular dynamics
- Numerical methods and some applications
- Wetting transition on textured surfaces

Contact Lines

Two immiscible fluids or two phases of one fluid in contact with a solid surface:



θ: the contact angle

The static case ($U = 0$):

- Young-Laplace equation for the fluid interface: $\gamma\kappa + [p] = 0$
- Young's relation for the contact angle: $\gamma_2 - \gamma_1 = \gamma \cos\theta_Y$

The Contact Line Singularity

Huh/Scriven 1971, Dussan/Davis 1974

$$\begin{cases} -\eta_i \Delta u + \nabla p = f \quad \text{in} \;\; \Omega_i \\ \nabla \cdot u = 0 \\ \text{No-slip boundary condition} \\ \text{interface condition} \end{cases}$$

$$\psi = r\left((C\phi + D)\cos\phi + (E\phi + F)\sin\phi\right)$$

$$\nabla u \sim \frac{1}{r}, \qquad \int |\nabla u|^2 dV = +\infty$$

“corner singularity”

The Slip Region

Physically, the no-slip boundary condition does not hold near the contact line — this has been confirmed by molecular dynamics simulation (Koplik, Qian/Wang/Sheng, Ren/E, ...):

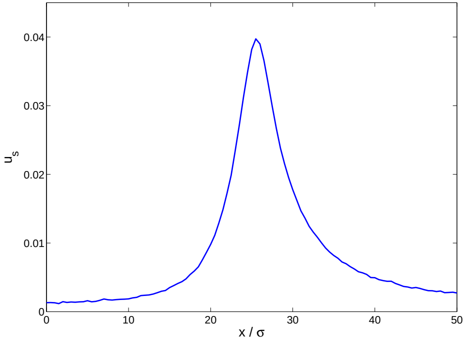


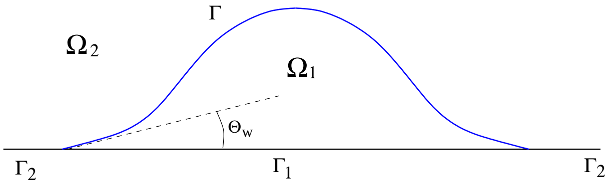
Figure: The slip velocity along the wall. The peak is at the CL.

Derivation of BCs based on “first principles”

- Derive the *form* of the BCs based on thermodynamic principles.

  What is the simplest form of the boundary conditions that is consistent with the 2nd law of thermodynamics?

- Use molecular dynamics to compute the details of the constitutive relations needed in the BCs.



Total energy (assume the substrate is at rest):

$$E = \sum_{i=1,2} \int_{\Omega_i} \frac{1}{2} \rho_i \, |\mathbf{u}|^2 \, d\mathbf{x} + (\gamma_1 - \gamma_2)|\Gamma_1| + \gamma|\Gamma|$$

Dynamic Equations

- Conservation of mass and momentum for incompressible fluids in $\Omega_i, \; i = 1, 2$:

$$\rho_i \left(\partial_t \mathbf{u} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \nabla \cdot \tau_d$$
$$\nabla \cdot \mathbf{u} = 0$$

- linear constitutive relation for the viscous stress:

$$\tau_d = \eta_i \left(\nabla \mathbf{u} + (\nabla \mathbf{u})^T \right)$$

- the interface conditions:

$$-[p] + \mathbf{n} \cdot [\tau_d] \cdot \mathbf{n} = \gamma \kappa$$
$$\mathbf{t} \cdot [\tau_d] \cdot \mathbf{n} = 0$$

where **n** and **t** are the normal and tangent to the fluid interface; κ is the curvature.

The Rate of Energy Dissipation

$$
\begin{aligned}
\frac{dE}{dt} = & -\sum_{i=1,2}\int_{\Omega_i}\eta_i\,|\nabla \mathbf{u}|^2\,d\mathbf{x} \\
& +\sum_{i=1,2}\int_{\Gamma_i}(\mathbf{t}\cdot\tau_d\cdot\mathbf{n})\,u_s\,d\sigma \\
& +\gamma\,(\cos\theta_w-\cos\theta_Y)\,u_\ell \le 0
\end{aligned}
$$

for any flow configuration, where

$$|\nabla \mathbf{u}|^2 = (\nabla\mathbf{u} + (\nabla\mathbf{u})^T) : (\nabla\mathbf{u} + (\nabla\mathbf{u})^T)$$

$u_s = \mathbf{u}\cdot\mathbf{t} =$ the slip velocity (the wall is at rest)

$u_\ell =$ the normal velocity of the contact line

This implies that each term has to be non-positive!

The Form of the Boundary Conditions

Relate the “generalized fluxes” (u_s and u_ℓ) to the “generalized forces”:

$$\mathbf{t} \cdot \tau_d \cdot \mathbf{n} = f(u_s)$$

$$\gamma\,(\cos\theta_w - \cos\theta_Y) = f_\ell(u_\ell)$$

where $uf(u) \leq 0, \quad uf_\ell(u) \leq 0.$

f and f_ℓ have to be obtained from other means.

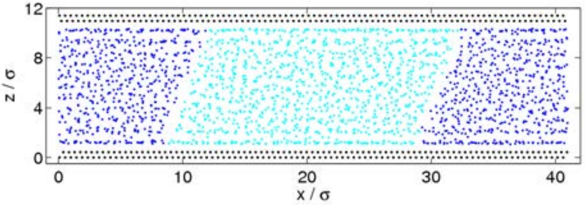
Computing the Constitutive Relations from MD:

Setup of molecular dynamics:

- Interaction: Lennard-Jones

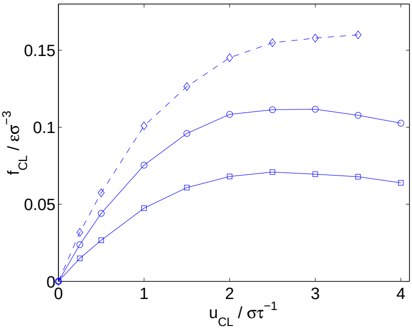
$$V(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \xi\left(\frac{\sigma}{r}\right)^{6}\right), \quad \xi = \pm 1$$

- Solid boundary modeled by FCC lattices
- Couette flow geometry
- Periodic boundary condition in z and y directions



Typical Profile of the Constitutive Relation $f_\ell(u)$

$f_\ell(u)$ computed from MD:



For simple fluids, the nonlinearity sets in at extremely large contact line speed ($1\sigma/\tau \approx 158 m/s$).

Linear Constitutive Relations

- Boundary condition for the slip velocity:

$$\mathbf{t} \cdot \tau_d \cdot \mathbf{n} = -\beta u_s \quad \text{(Navier BC)}$$

- Condition for the dynamic contact angle θ_w:

$$\gamma(\cos\theta_w - \cos\theta_Y) = -\beta^* u_\ell$$

where β^* is the three-phase friction coefficient.

dimension of $\beta = \eta/l_s$, where the slip length l_s is of molecular scale; β^* has dimension of viscosity.

Mesoscopic Continuum Model for the MCL

- Dynamic equations for the two fluids ($i = 1, 2$):

$$\rho_i \left(\partial_t \mathbf{u} + \mathbf{u} \cdot \nabla \mathbf{u}\right) = -\nabla p + \eta_i \Delta \mathbf{u}$$
$$\nabla \cdot \mathbf{u} = 0$$

- The fluid interface: $\dot{x}_\Gamma = \mathbf{u}$
- The interface conditions:

$$-[p] + \mathbf{n} \cdot [\tau_d] \cdot \mathbf{n} = \gamma \kappa$$
$$\mathbf{t} \cdot [\tau_d] \cdot \mathbf{n} = 0$$

- At the solid wall:

$$\mathbf{u} \cdot \mathbf{n} = 0, \quad \mathbf{t} \cdot \tau_d \cdot \mathbf{n} = -\beta_i u_s$$

- At the contact line:

$$\gamma \left(\cos \theta_w - \cos \theta_Y\right) = -\beta^* u_\ell$$

Energy Dissipation and Different Spreading Regimes

$$\frac{dE}{dt} = -\sum_{i=1,2} \int_{\Omega_i} \eta_i \left|\nabla \mathbf{u}\right|^2 d\mathbf{x} - \sum_{i=1,2} \int_{\Gamma_i} \beta_i u_s^2 d\sigma - \beta^* u_\ell^2$$
$$= \dot{E}_b + \dot{E}_s + \dot{E}_\ell$$

For a spreading drop:

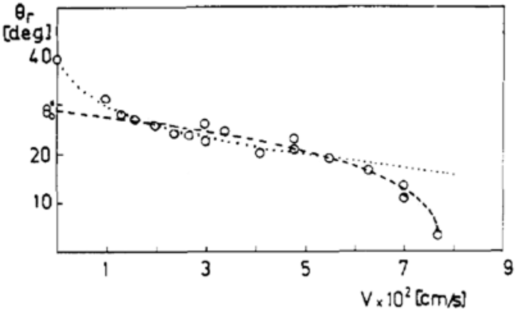
$$\dot{E}_s/\dot{E}_b \sim \ l_s/h_0 \ll 1, \qquad \dot{E}_\ell/\dot{E}_b \sim \ \theta_a \beta^*/\eta$$

θ_a = the apparent contact angle

- When $\theta_a < \eta/\beta^*$: viscous force dominates (hydrodynamic regime); $R(t) \sim t^{1/10}$
- When $\theta_a > \eta/\beta^*$: friction dominates; $R(t) \sim t^{1/7}$

Different spreading regimes observed in experiments

Petrov et al. Langmuir 1992



Circles: experimental data (PET/glycerol-water/air)
Dashed curve: fitting by the hydrodynamic theory
Dotted curve: fitting by the molecular kinetic theory (friction regime)

The CL model can describe the different spreading regimes.

Thin Film Model in the Lubrication Approximation

$h(x,t)$: the fluid interface at time t

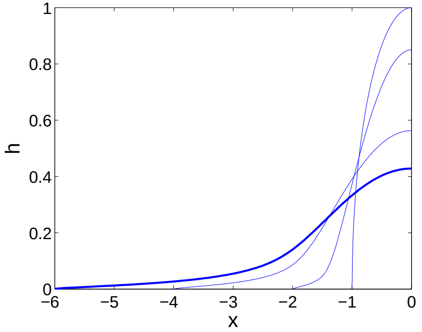
$$\partial_t h + \partial_x \left(\left(\frac{1}{3} h^3 + \lambda h^2 \right) \partial_x \left(\partial_x^2 h + \Pi(h) \right) \right) = 0$$

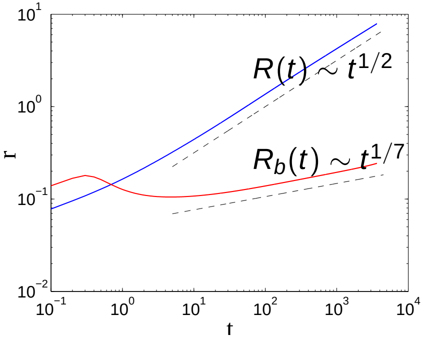
$$h = 0, \quad \beta^* \dot{a} = \frac{1}{2} \left((\partial_x h)^2 - \theta_Y^2 \right), \quad \text{at the CL}$$

$\Pi(h) = V'(h)$: disjoining pressure

Formation of Precursor Films

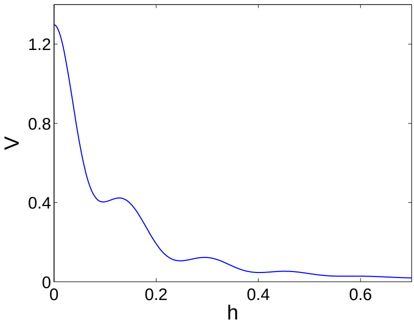
Numerical solution of the thin film model with $V(h) = \dfrac{A}{(h+h_0)^2}$:

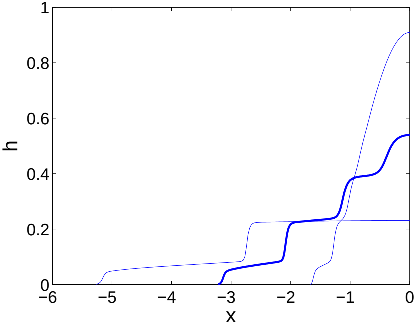




Layered Spreading

Numerical solution with an oscillatory $V(h)$ (the oscillation is due to surface treatment e.g. coating):





Numerical method for the CL model

- The interface is tracked using the level set method; the interface is represented by the zero level set of ϕ; ϕ is advected by the fluid velocity:

$$\partial_t \phi + \mathbf{u} \cdot \nabla \phi = 0. \tag{1}$$

- Write the dynamical equations into a unified form:

$$\rho(\phi)\left(\partial_t \mathbf{u} + (\mathbf{u} \cdot \nabla)\mathbf{u}\right) = -\nabla p + \nabla \cdot \tau_d + F, \tag{2}$$

$$\nabla \cdot \mathbf{u} = 0, \tag{3}$$

where

$$\tau_d = \eta(\phi)\left(\nabla \mathbf{u} + (\nabla \mathbf{u})^T\right),$$

$$F = -\gamma \kappa \delta(\phi) \nabla \phi, \quad \kappa = \nabla \cdot \left(\frac{\nabla \phi}{|\nabla \phi|}\right).$$

Numerical method for the CL model

- The boundary condition along the wall:

$$-\beta(\phi)u_s = \mathbf{t} \cdot \tau_d \cdot \mathbf{n} + \tau_Y, \tag{4}$$

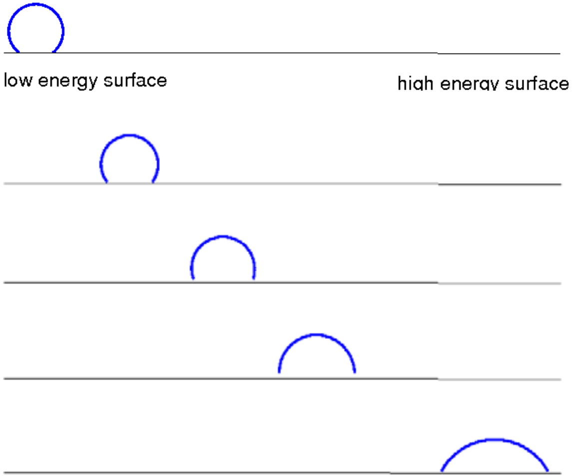
where

$$\tau_Y = \gamma \left(\mathbf{n} \cdot \frac{\nabla\phi}{|\nabla\phi|} - \cos\theta_Y \right) \mathbf{t} \cdot \nabla H(\phi),$$
$$\beta(\phi) = \beta_1(1 - H(\phi)) + \beta_2 H(\phi) + \beta^* |\mathbf{t} \cdot \nabla H|.$$

and $H(\phi)$ is the Heaviside function.

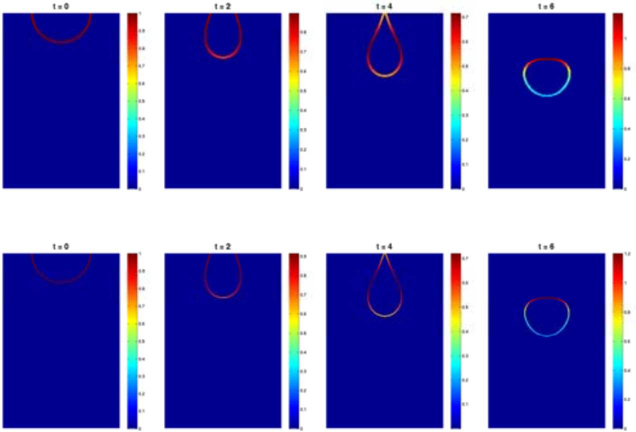
Equations (1)-(4) are solved using a semi-implicit scheme and the finite difference method.

MCL driven by surface tension gradient



Detachment of a Pendant Drop under Gravity

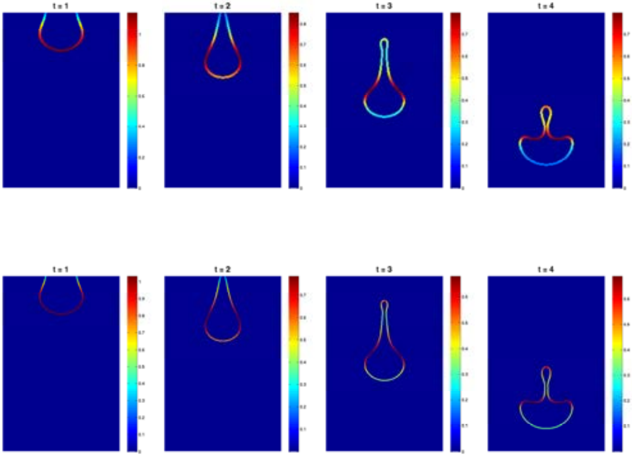
Density ratio $\rho_1/\rho_2 = 3$, viscosity ratio $\eta_1/\eta_2 = 2$.



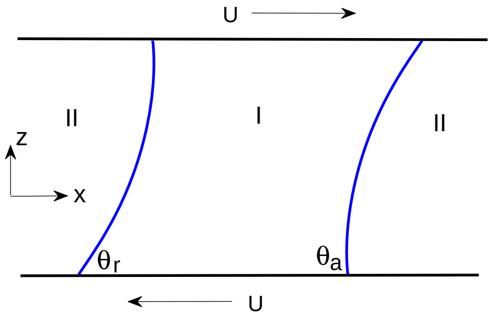
Dynamics of (insoluble) surfactant: $\dot{c} + (\nabla_s \cdot u)c = D_s \nabla_s^2 c$
Langmuir equation of state: $\gamma(c) = \gamma_0 + RTc_\infty \log(1 - c/c_\infty)$

Detachment of a Pendant Drop under Gravity

Density ratio $\rho_1/\rho_2 = 15$, viscosity ratio $\eta_1/\eta_2 = 2$.



MCL on a Chemically Patterned Surface



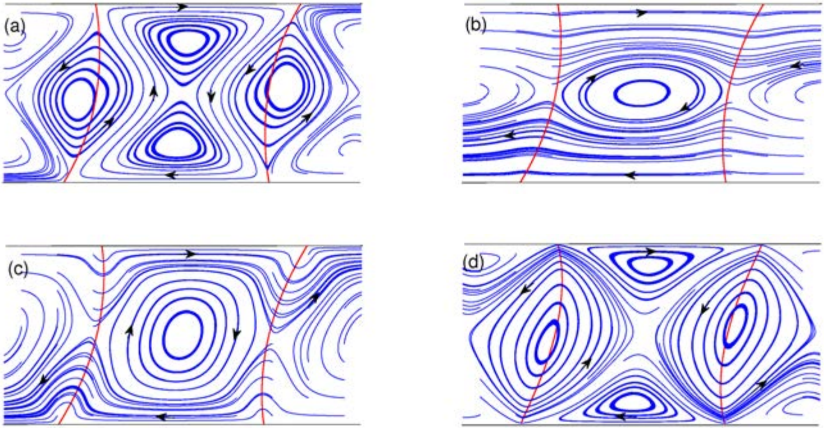
- Two immiscible fluids confined in a channel
- Imposed shear speed *U*
- Chemically patterned solid surface

$$\gamma \cos \theta_Y(x) = \Delta\gamma_0 + F_\varepsilon(x)$$

where $F_\varepsilon(x)$ is the force due to the periodic pattern.

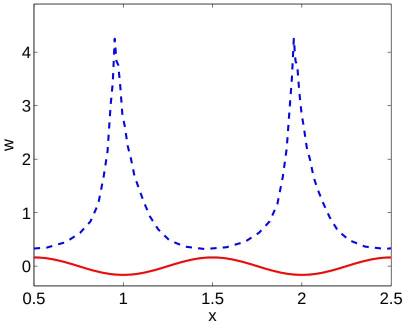
Instantaneous Flow Fields

Period motion of the fluid interface and the contact lines:

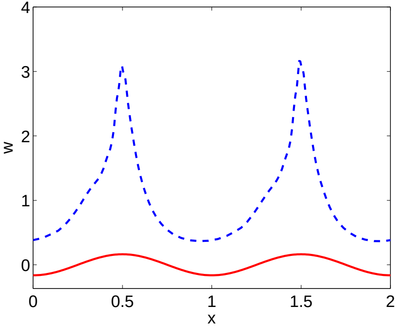


The Dynamics of the Advancing and Receding CLs

At small U, the advancing and receding CLs are pinned in different regions:



advancing CL

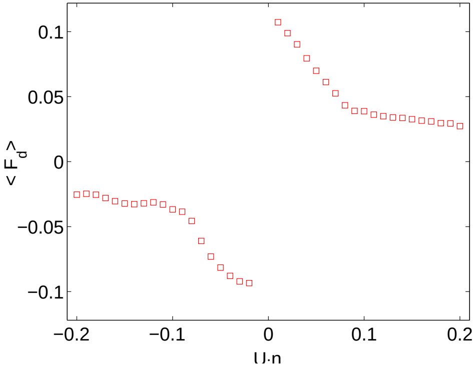


receding CL

Red curve: the defect force $F_\varepsilon(x)$
Blue curves: the inverse (normal) CL speed.

Contact Angle Hysteresis

- Time average of the defect force: $\langle F_\varepsilon \rangle = \frac{1}{T}\int_0^T F_\varepsilon(x)dt$



- Effect contact angle: time average of the contact angle condition $\gamma\cos\theta_d - (\Delta\gamma_0 + F_\varepsilon(x)) = -\beta^* u_l \quad \Rightarrow$

$$\gamma\cos\theta_{eff} = \Delta\gamma_0 + \langle F_\varepsilon \rangle + \beta^* U.$$

Wetting Transition

Superhydrophobic (water repelling) surfaces

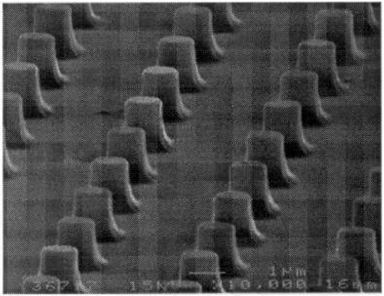


Figure: A textured surface

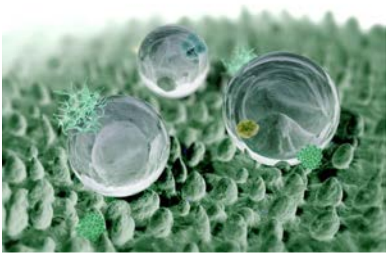


Figure: Micro structure of lotus leaf

Cassie-Baxter and Wenzel States

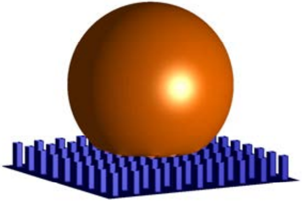


Figure: Cassie-Baxter state

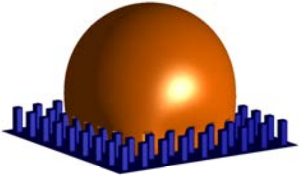
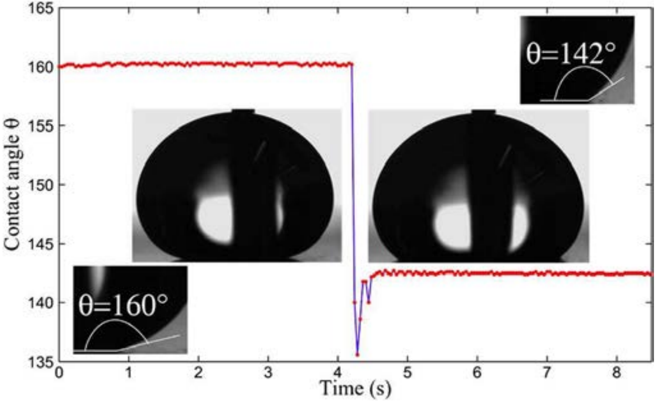


Figure: Wenzel state

Wetting Transition



Sbragaglia et al. Phys. Rev. Lett. 2007

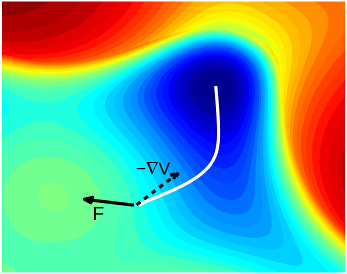
The Climbing String Method

Evolve a string (a curve parameterized by its normalized arclength) in the configuration space:

$$\partial_t \varphi(\alpha, t) = -\nabla V(\varphi) + \lambda \hat{\tau}, \quad 0 < \alpha < 1$$
$$\varphi(0, t) = a, \quad \partial_t \varphi(1, t) = -\nabla V + 2(\nabla V, \hat{\tau})\hat{\tau}$$

At the steady state,

- The final point $\varphi(1, t)$ converges to a saddle point;
- The string converges to the *minimum energy path* connecting the minima and the saddle point.



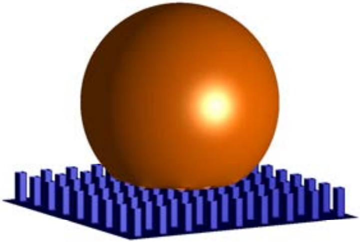
The Energy of the System

$$V(\phi) = \int_\Omega \left(\frac{1}{2}\kappa|\nabla\phi|^2 + f(\phi) \right) dx$$

$$f(\phi) = \frac{1}{2}\phi^2(\phi - 1)^2,$$

$\phi = \phi_s$ along the wall,

$$\int_\Omega \phi dx = \text{Const.}$$



Summary

- Derived a mesoscopic sharp-interface model for MCLs based on “first principle” thermodynamics and molecular dynamics; extended the contact line model to systems with surfactants.
- Developed a level set method for the CL model.
- As an interesting application, we studied moving contact lines on rough/heterogeneous surfaces.
  - Studied the contact angle hysteresis using numerical homogenization.
  - Studied the wetting transition using the string method.

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