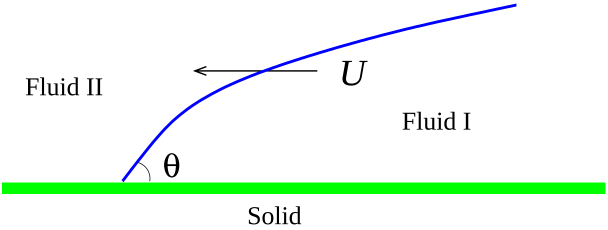
Modeling and Simulation of Moving Contact Lines

Weiqing Ren

National University of Singapore and
Institute of High Performance Computing, A*STAR

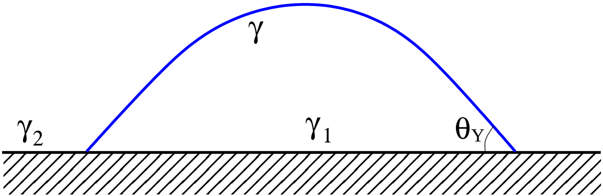
Contact Lines

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



θ: the contact angle

Static case



- Free energy of the droplet:

$$E = \gamma|\Gamma| + (\gamma_1 - \gamma_2)|\Gamma_1|$$

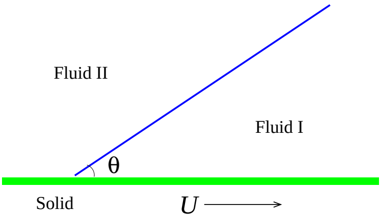
  where γ, γ_1 and γ_2 are the interfacial tensions; $|\cdot|$ denotes the length of the curve.

- Minimizing the free energy with the volume constraint:

$$\gamma\kappa + [p] = 0, \quad \text{(Young-Laplace equation)}$$
$$\gamma_2 - \gamma_1 = \gamma \cos\theta_Y, \quad \text{(Young's relation)}$$

Huh/Scriven 1971

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



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

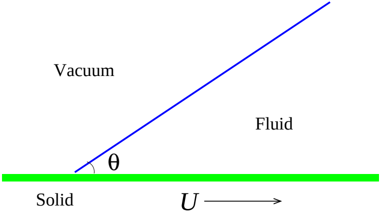
$$\nabla u \sim \frac{1}{r}, \qquad \int |\nabla u|^2 dV = +\infty$$

Dussan/Davis 1974

With the no-slip boundary condition, the velocity field must be multi-valued at the moving contact line.

Dynamics

$$\begin{cases} -\eta_i \Delta u + \nabla p = 0 \quad \text{in } \Omega_i \\ \nabla \cdot u = 0 \\ \text{No-slip bc, } u_n = 0 \\ \text{Plannar interface, stress condition} \end{cases}$$



Theorem (Cui/Ren '18)

The problem above admits no solution
$u \in C^2(\Omega) \cap C^1(\Omega \cup \Gamma_{ff}) \cap C(\Omega \cup \Gamma_{fw})$, $p \in C^1(\Omega) \cap C(\Omega \cup \Gamma_{ff} \cup \Gamma_{fw})$.

Ω: interior of fluid region; Γ_{ff} and Γ_{fw}: fluid-vacuum and fluid-wall interfaces with the CL excluded.

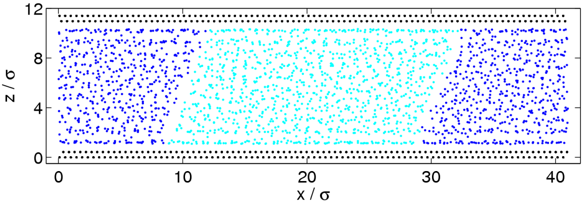
Empirical models

The introduction of different mechanisms to relieve the contact line singularity:

- Slip models
- Thin film models with long-range interaction
- Diffuse interface models
- Interface break-up/formation models

Molecular dynamics simulation

Setup of molecular dynamics in Couette flow geometry:



- N particles with pairwise interaction: Lennard-Jones

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

  where r_{ij} is the distance between particles i and j.
- Solid boundary modeled by FCC lattices

Molecular dynamics

- Solve the equations of motion (Newton's second law):

$$m_i \ddot{\mathbf{x}}_i = -\sum_j \nabla V(r_{ij}) + \text{thermostat}$$

- Compute the statistic (e.g. slip velocity, forces, etc) near the moving contact line.

The slip velocity

Physically, the no-slip boundary condition does not hold near the moving contact line (Koplik, Qian/Wang/Sheng, Ren/E, ...):

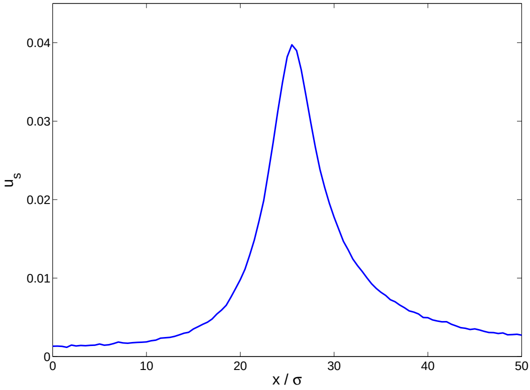


Figure: The slip velocity along the wall. The peak is at the CL.

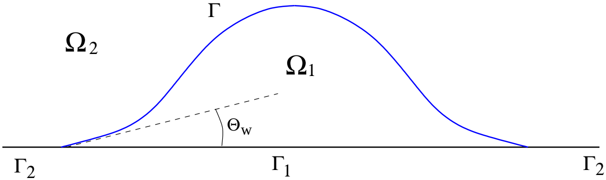
Derivation of BCs based on “first principles”

- 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.

A liquid droplet on a solid Substrate



Total energy (assume the substrate is at rest):

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

Dynamic equations

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

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

with the linear constitutive relation for the viscous stress:

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

where $\eta_i (i = 1, 2)$ are the viscosity of the fluids.

The rate of energy dissipation

$$\frac{dE}{dt} = -\sum_{i=1,2}\int_{\Omega_i}\eta_i|\nabla\mathbf{u}|^2\,d\mathbf{x} + \sum_{i=1,2}\int_{\Gamma_i}\mathcal{P}(\tau_d\cdot\mathbf{n})\cdot\mathbf{u}_s\,d\sigma$$
$$+\int_{\Gamma}\Big([\tau_d - p\mathbf{I}]\cdot\mathbf{n} + \gamma\kappa\mathbf{n}\Big)\cdot\mathbf{u}d\sigma$$
$$+\int_{\Lambda}\gamma\Big(\cos\theta_d - \cos\theta_Y\Big)u_l\,dl \le 0$$

for any flow configuration, where

$$|\nabla\mathbf{u}|^2 = (\nabla\mathbf{u} + (\nabla\mathbf{u})^T) : (\nabla\mathbf{u} + (\nabla\mathbf{u})^T)$$
$$u_s = \text{the slip velocity at the wall}$$
$$u_l = \text{the normal velocity of the contact line}$$

Interface and boundary conditions

- The interface condition:

$$[\tau_d - p\mathbf{I}] \cdot \mathbf{n} = -\gamma\kappa\mathbf{n}$$

- Boundary conditions: relate the "generalized fluxes" (u_s and u_l) to the "generalized forces"

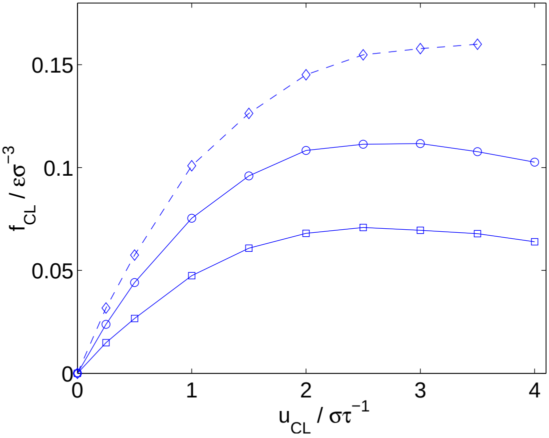
$$\mathcal{P}\left(\tau_d \cdot \mathbf{n}\right) = f(\mathbf{u}_s)$$

$$\gamma\left(\cos\theta_d - \cos\theta_Y\right) = f_\ell(u_l)$$

where $\mathbf{u} \cdot f(\mathbf{u}) \leq 0, \quad u f_\ell(u) \leq 0.$

f and f_ℓ have to be obtained from other means.

Typical profile of the friction force



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

Linear constitutive relations

- Boundary condition for the slip velocity:

$$\mathcal{P}\left(\tau_d \cdot \mathbf{n}\right) = -\beta \mathbf{u}_s \quad \text{(Navier BC)}$$

- Condition for the dynamic contact angle θ_d:

$$\gamma(\cos\theta_d - \cos\theta_Y) = -\beta^* u_l$$

  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.

Continuum model for the MCL (Ren/E 2007; Ren/Hu/E 2010)

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

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

- Kinematic condition for the fluid interface: $\dot{x}_\Gamma = \mathbf{u}$
- The interface condition:

$$[\tau_d - p\mathbf{I}] \cdot \mathbf{n} = -\gamma \kappa \mathbf{n}$$

- Boundary condition at the solid wall:

$$\mathbf{u} \cdot \mathbf{n} = 0, \quad \mathcal{P} \left(\tau_d \cdot \mathbf{n} \right) = -\beta_i \mathbf{u}_s$$

- Condition for the dynamic contact angle:

$$\gamma \left(\cos \theta_d - \cos \theta_Y \right) = -\beta^* u_l$$

Different spreading regimes

$$\frac{dE}{dt} = -\sum_{i=1,2} \int_{\Omega_i} \eta_i |\nabla \mathbf{u}|^2 \, d\mathbf{x} - \sum_{i=1,2} \int_{\Gamma_i} \beta_i |u_s|^2 d\sigma - \int_{\Lambda} \beta^* u_l^2 dl$$

$$= \dot{E}_b + \dot{E}_s + \dot{E}_\ell$$

For a spreading drop:

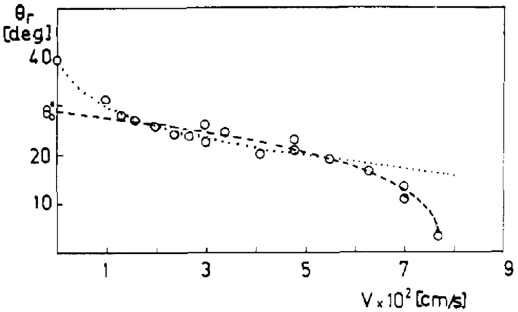
$$\dot{E}_s/\dot{E}_b \sim \; l_s/h_0 \ll 1, \qquad \dot{E}_\ell/\dot{E}_b \sim \; \theta_a \beta^*/\eta$$

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; $R(t) \sim t^{1/7}$

Comparison with 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)

MCLs with insoluble surfactants (Zhang/Xu/Ren 2014

- Dynamics of the fluids:

$$\begin{cases} \rho_i \left(\partial_t \mathbf{u} + \mathbf{u} \cdot \nabla \mathbf{u}\right) & = -\nabla p + \eta_i \Delta \mathbf{u} \\ \nabla \cdot \mathbf{u} & = 0, \quad \text{in} \quad \Omega_i \end{cases}$$

$$\dot{x}_\Gamma = \mathbf{u} \quad \text{(kinematic condition)}$$

$$\begin{aligned} [\tau_d - p\mathbf{I}] \cdot \mathbf{n} = -\gamma(c)\kappa\mathbf{n} + \nabla_s \gamma(c) \quad & \text{on} \quad \Gamma \\ \mathbf{u} \cdot \mathbf{n} = 0, \quad \eta_i \partial_n \mathbf{u}_s = -\beta_i u_s, \quad & \text{on} \quad \Gamma_i \\ \gamma(c) \cos\theta_d + (\gamma_1 - \gamma_2) = -\beta^* u_l, \quad & \text{at} \quad \Lambda \end{aligned}$$

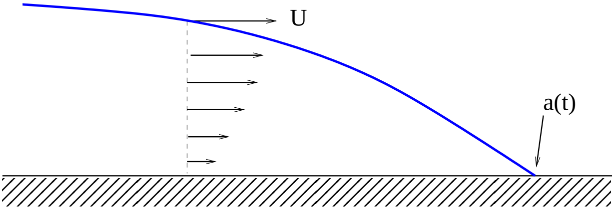
- Dynamics of surfactants:

$$\frac{Dc}{Dt} + (\nabla_s \cdot \mathbf{u})c = D_s \nabla_s^2 c, \quad \text{on} \quad \Gamma$$

with the no-flux condition at the contact line: $\nabla_s c \cdot \mathbf{n}_s = 0$.

Thin films and lubrication approximation

$h(x, t)$: height of the thin film;
$a(t)$: the moving contact line.



Thin film equation

For the thin film, the contact line model reduces to

$$\frac{\partial h}{\partial t} + \frac{\partial}{\partial x}\left(h^2 (h+\lambda) \frac{\partial^3 h}{\partial x^3}\right) = 0, \quad 0 < x < a(t)$$

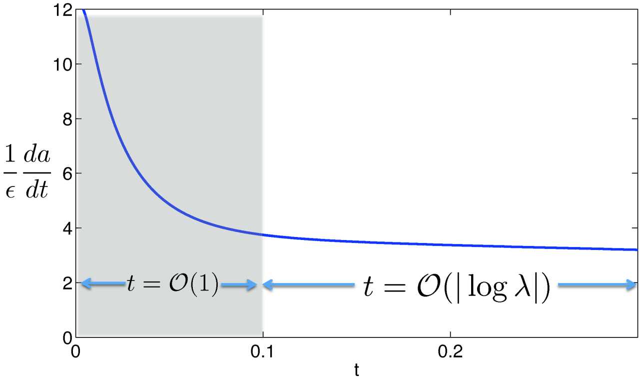
$$h = 0, \quad \beta \frac{da}{dt} = \left(\frac{\partial h}{\partial x}\right)^2 - \theta_Y^2, \quad \text{at } x = a(t)$$

$$\text{conditions (e.g. symmetry) at } x = 0$$

What is the limiting behavior as the slip length $\lambda \to 0$?

Two time scales

The dynamics has two time scales: (1) fast relaxation, and (2) slow contact line motion.



Distinguished limits

According to the two time scales, in the perturbation analysis we distinguish the two regimes:

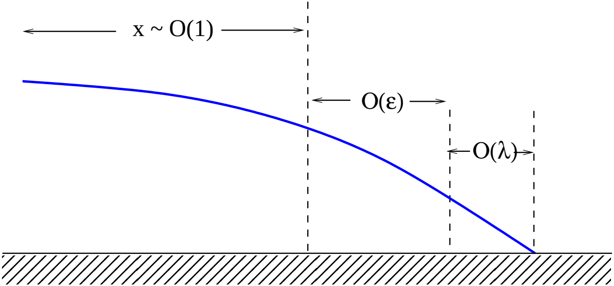
(1) $\lambda \to 0$, and $t = t^*$ fixed;

(2) $\lambda \to 0$ and $t \to \infty$.

Earlier works (Voinov, Hocking, Cox, etc) considered the second case.

Matched asymptotics

Scale of the intermediate region: $\varepsilon = \dfrac{1}{|\log \lambda|}$



Main results (Ren/Thinh/E 2017)

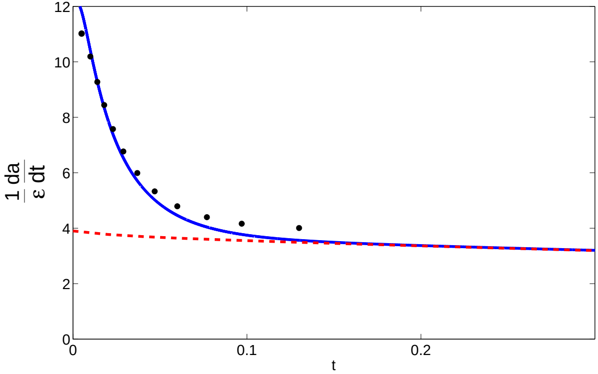
(1) $\lambda \to 0, \quad t = t^* : \quad \theta_{app}^3(t) - \theta_Y^3 = \frac{3}{\varepsilon}\frac{da}{dt}$

- θ_{app} is the angle of the outer solution to the leading order problem;
- The leading order outer problem is the equation with $\lambda = 0$ (no slip, fixed contact line);
- The contact line slippage is a “regular” perturbative effect.

(2) $\lambda \to 0, \quad t = |\log \lambda|\tau : \quad \theta_{app}^3[a(\tau)] - \theta_Y^3 = 3\frac{da}{d\tau}$

- The leading order outer problem is quasi-static; the solution (a parabola) depends on the contact line position.
- The contact line position $a(\tau)$ can be found by solving the angle-speed relation (an ODE).

Verification by numerics



dots: asymptotic results;
curve: solution of the thin film equation.

Numerical methods (Ren/E 2011, Xu/Ren 2014))

- 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 methods

- The boundary condition at the wall (in 2d):

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

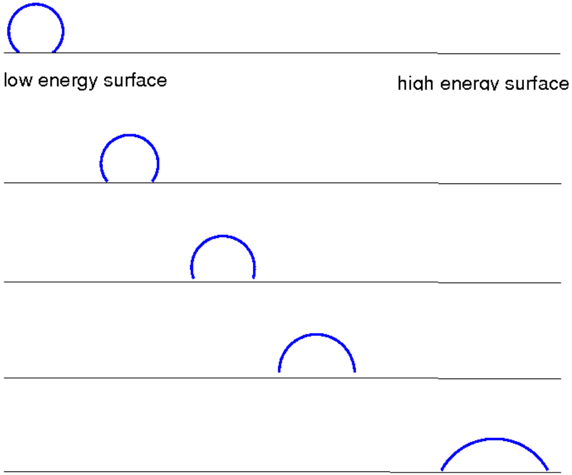
where

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

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

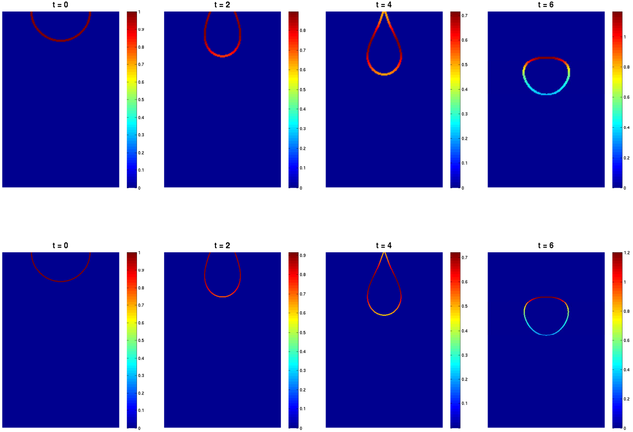
Equations (1)-(4) are solved using a semi-implicit scheme and the finite difference method.

MCL driven by surface tension gradient



Detachment of a pendant drop under gravity

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

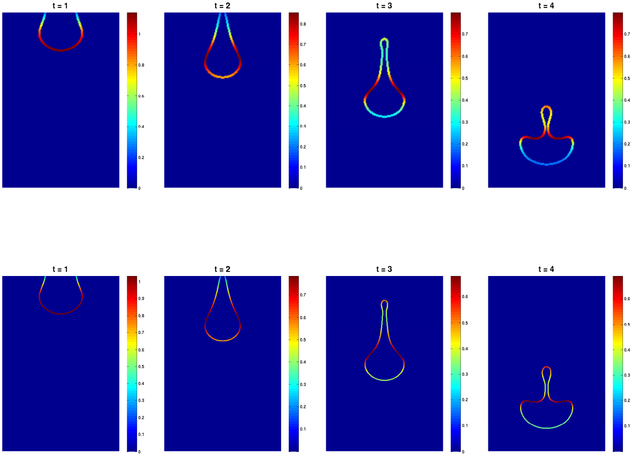


Dynamics of (insoluble) surfactant: $\dot{c} + (\nabla_s \cdot u)c = D_s \nabla_s^2 c$

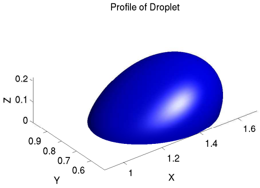
Langmuir equation of state: $\gamma(c) = \gamma_0 + RTc_\infty \log(1 - c/c_\infty)$

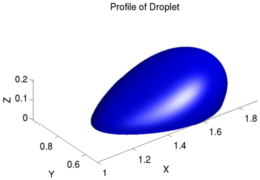
Detachment of a pendant drop under gravity

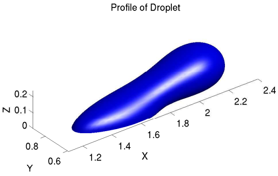
Density ratio $\rho_1/\rho_2 = 15$, viscosity ratio $\eta_1/\eta_2 = 2$.



Sliding drop on an inclined plane under gravity



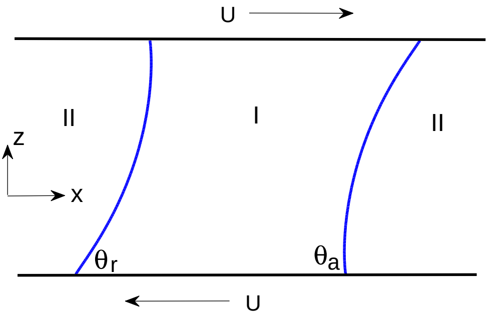




Contact angle hysteresis

Motion of the rain drops down a window: advancing angle in the front $\neq$ receding angle in the rear.

MCL on a chemically patterned surface



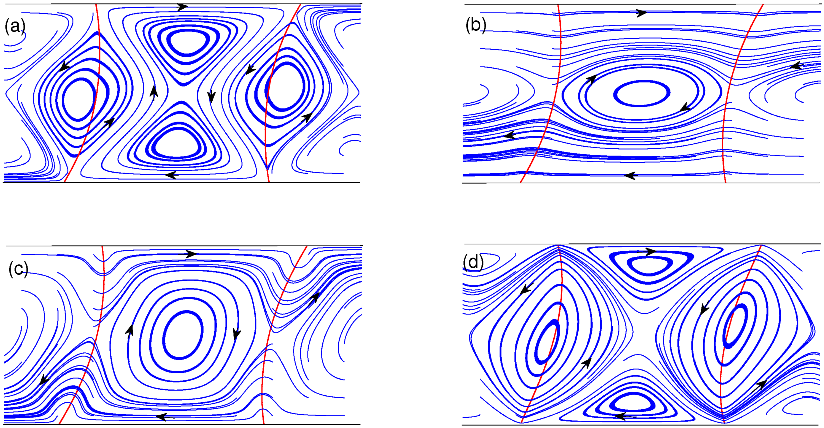
- Two immiscible fluids confined in a channel
- Imposed shear speed U
- Chemically patterned solid surface

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

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

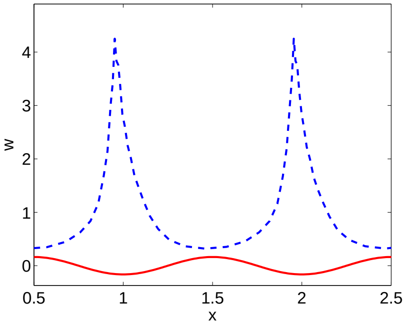
Instantaneous flow fields

Period motion of the fluid interface and the contact lines:

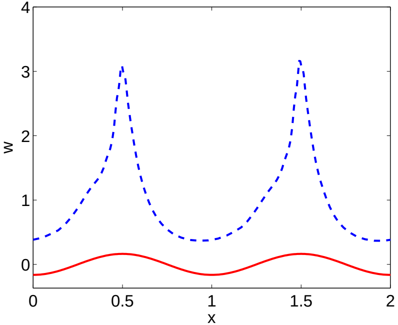


The dynamics of advancing and receding CLs

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



advancing CL



receding CL

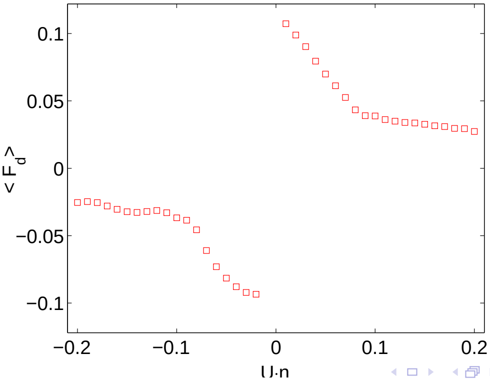
Red curve: the defect force $F_\varepsilon(x)$
Blue curves: the inverse (normal) CL speed.

Contact angle hysteresis (Ren/E 2011)

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

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

where $\langle F_\varepsilon \rangle = \dfrac{1}{T}\displaystyle\int_0^T F_\varepsilon(x)dt.$



Summary

- **Modeling:** Derived a mesoscopic sharp-interface model for MCLs based on “first principle” thermodynamics and molecular dynamics;
- **Analysis:** Analyzed the distinguished limits of the contact line dynamics as the slip length $\to 0$.
- **Simulation:** Developed level set methods for the CL model, and studied interesting applications.

Collaborators and References

- W. Ren and **W. E**, Boundary conditions for the moving contact line problem, Phys. Fluids, **19**, 022101 (2007)
- W. Ren, **D. Hu** and **W. E**, Continuum models for the contact line problem, Phys. Fluids, **22**, 102103 (2010)
- **Z. Zhang, S. Xu** and W. Ren, Derivation of a continuum model and the energy law for moving contact lines with insoluble surfactants, Phys. Fluids, **26**, 062103 (2014)
- W. Ren, **P. H. Trinh** and **W. E**, On the distinguished limits of the Navier slip model of the moving contact line problem, J. Fluid Mech. **772**, 107-126 (2015)
- **J.-J. Xu** and W. Ren, A level-set method for two-phase flows with movig contact line and insoluble surfactant, J. Comput. Phys. **263**, 71-90 (2014)
- **S. Xu** and W. Ren, Reinitialization of the level-set function in 3d simulation of moving contact lines, Commun. Comput. Phys. **20**, 1163 (2016)
- W. Ren and **W. E**, Contact line dynamics on heterogeneous surfaces, Phys. Fluids **23**, 072103 (2011)