Liquid drops on soft elastic substrates

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Joint work with Professor Ren Weiqing

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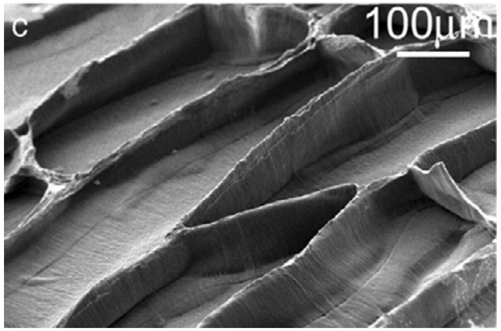
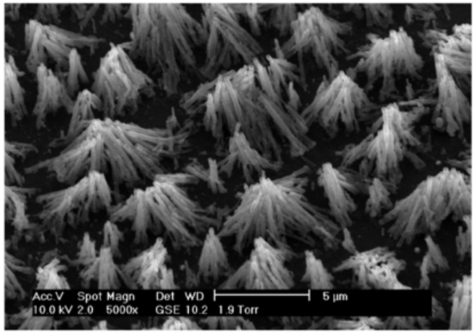
Introduction





N. Chakrapani et al, PNAS, 2004, 101 4009-12

K. Lau et al, Nano Lett., 2003, 3, 1701-5

Behaviors and properties depend on the liquid and substrates

- ubiquitous in nature;
- biological activities: self-organization of cell tissue, wound healing, controlling of the spreading of cancer cells;
- commercial manufacture: painting formulation, textile dyeing, mechanical lubrication;
- not well understood.

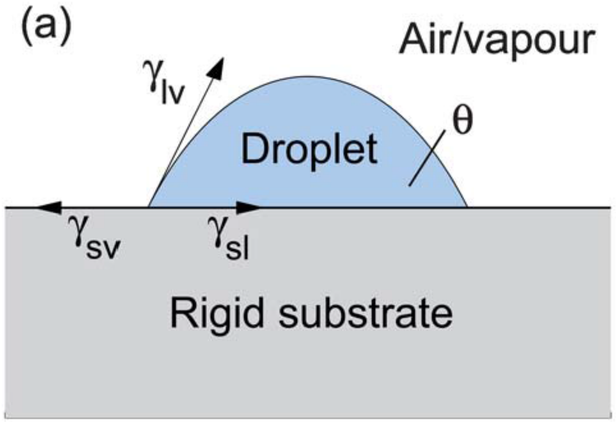
Introduction

• Rigid substrate: the equilibrium contact angle is determined by the Young's relation

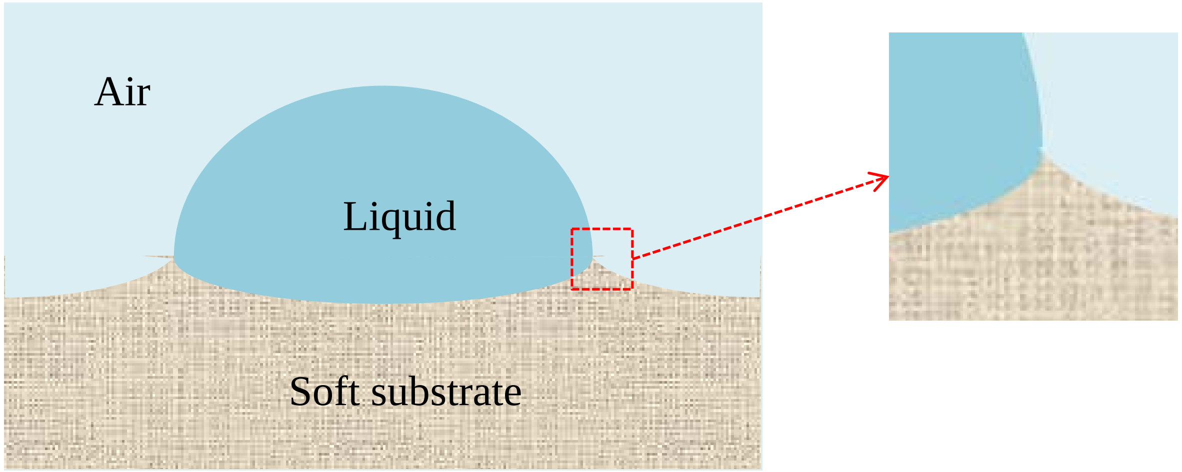
$$\gamma_{\mathrm{sv}} = \gamma_{\mathrm{sl}} + \gamma_{\mathrm{lv}} \cos\theta .$$

• The dynamics of spreading is determined by the balance of horizontal capillarity and viscous forces.

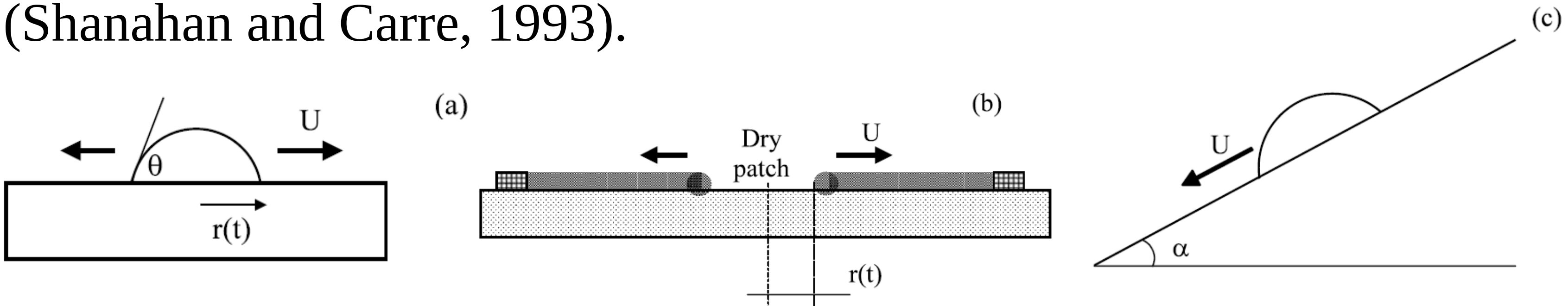
• The motion of the contact line is governed by the viscous dissipation in the liquid.



Drops on a soft substrate

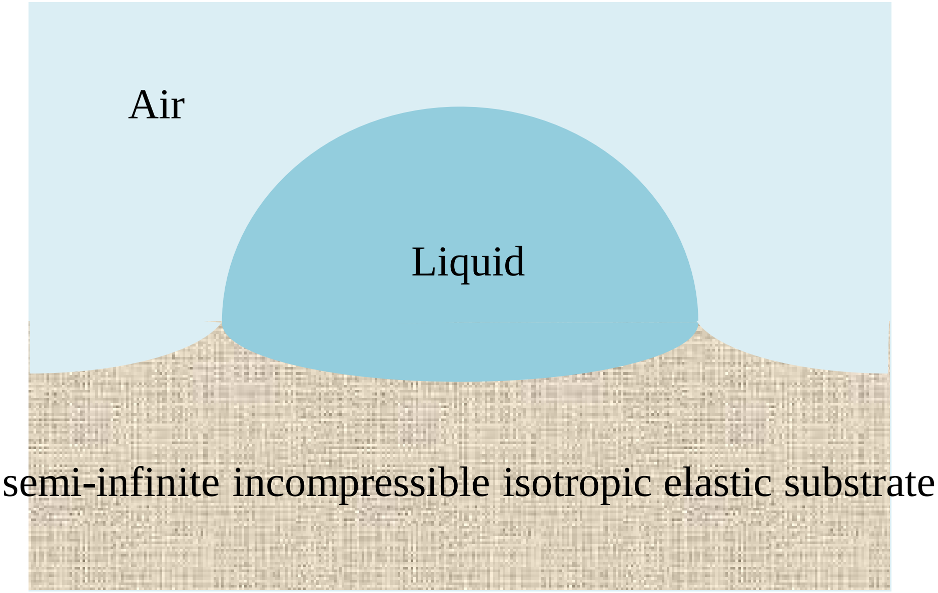


- Soft substrate:
  - The substrate is deformed;
  - A sharp ridge forms due to coupling between elasticity and surface energy;
  - Multi-scale and non-local due to the long range of elastic interactions;
  - Viscoelastic braking: spreading of the liquid is much slower, (Shanahan and Carre, 1993).

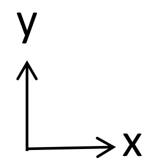


Drops on a soft substrate

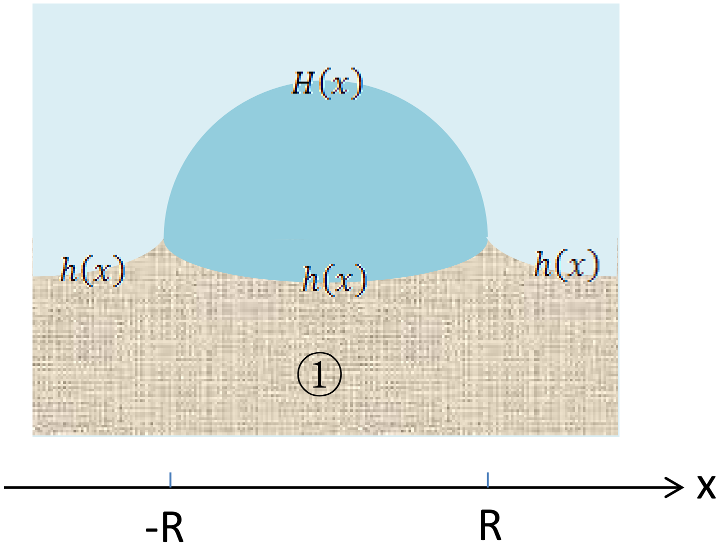
Two-dimensional system of a liquid droplet on a semi-infinite incompressible isotropic elastic substrate.



Free energy (bulk)



1. Elasticity in the isotropic solid



- Displacement $\mathbf{u}(x,y) = (u_1(x,y), u_2(x,y))$ in the bulk

$$\nabla(\nabla \cdot \mathbf{u}) + (1-2\nu)(\nabla^2 \mathbf{u}) = 0$$

BC: solid surface displacement $\mathbf{u}(x,0) = \mathbf{h}(x) = (h_1(x), h_2(x))$ $\mathbf{u}(x,-\infty) = (0,0)$

$$u_1 = \frac{1}{2\pi}\int_{-\infty}^{\infty}\left[\hat{h}_1 - \frac{1}{3-4\nu}k\left(i\hat{h}_2 - \hat{h}_1\frac{k}{|k|}\right)y\right]e^{|k|y}e^{ikx}dk,$$

$$u_2 = \frac{1}{2\pi}\int_{-\infty}^{\infty}\left[\hat{h}_2 - \frac{1}{3-4\nu}k\left(i\hat{h}_1 + \hat{h}_2\frac{k}{|k|}\right)y\right]e^{|k|y}e^{ikx}dk,$$

where $\hat{h}_1, \hat{h}_2$ are the Fourier transforms of h_1, h_2.

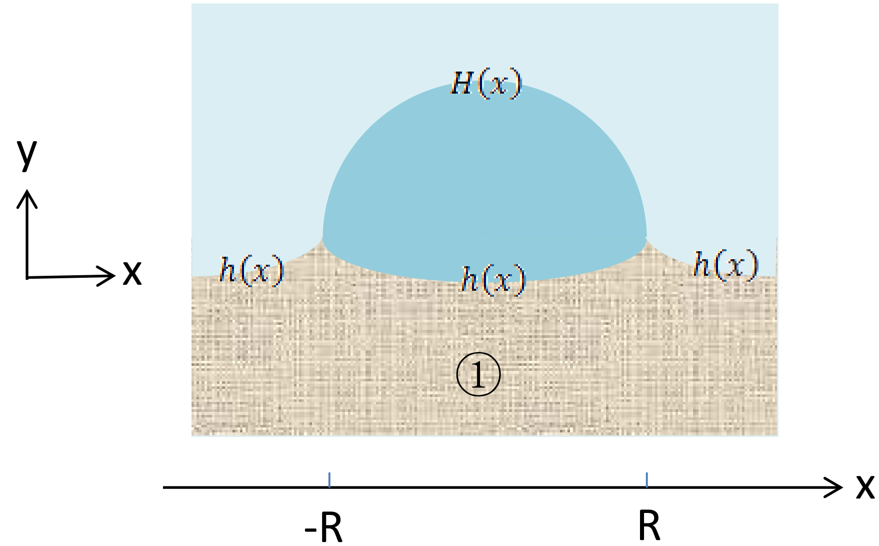
Free energy (bulk)

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

  ① Poisson's ratio $\nu = 1/2$

  ② Volume conservation of the solid

  $$\int_{-\infty}^{\infty} h(x) = C$$



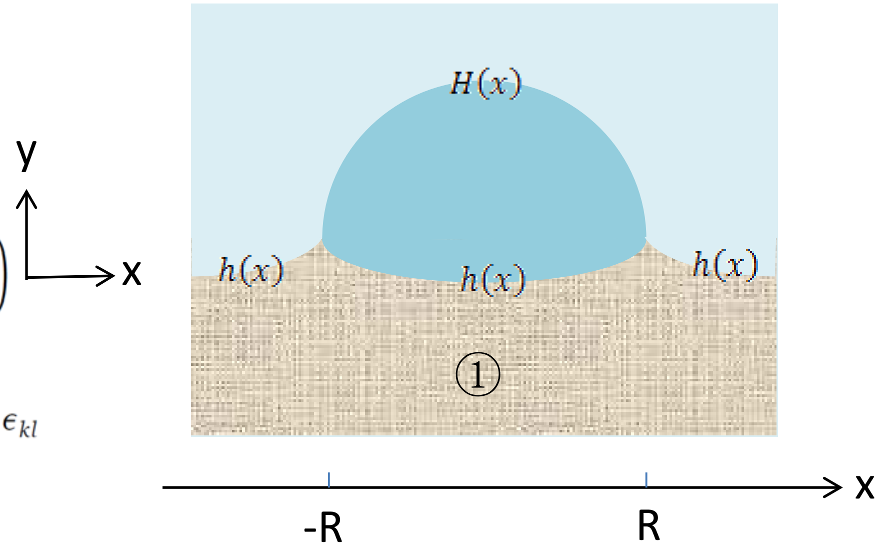
Free energy (bulk)

- Elasticity energy in the bulk

$$\epsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)$$

$$E_e = \int_V \sum_{i,j} \frac{1}{2}\sigma_{ij}\epsilon_{ij}\,dV$$

$$\sigma_{ij} = \sum_{k,l} C_{ijkl}\epsilon_{kl}$$



For our two-dimensional semi-infinite solid,

$$E_e = \int_S \sum_{i,j=1}^{2} \frac{1}{2}\sigma_{ij}\epsilon_{ij}\,dx_1 dx_2 = \int_S \sum_{i,j=1}^{2} \frac{1}{2}\sigma_{ij}\frac{\partial u_i}{\partial x_j}\,dx_1 dx_2$$

$$= -\frac{1}{2}\int_S \sum_{i,j=1}^{2} u_i \frac{\partial \sigma_{ij}}{\partial x_j}\,dx_1 dx_2 + \frac{1}{2}\int_{-\infty}^{\infty}\left(\sum_{i,j=1}^{2} u_i\sigma_{ij}\right)\cdot \mathbf{n}\,dx_1 \qquad \nabla\cdot\sigma = 0$$

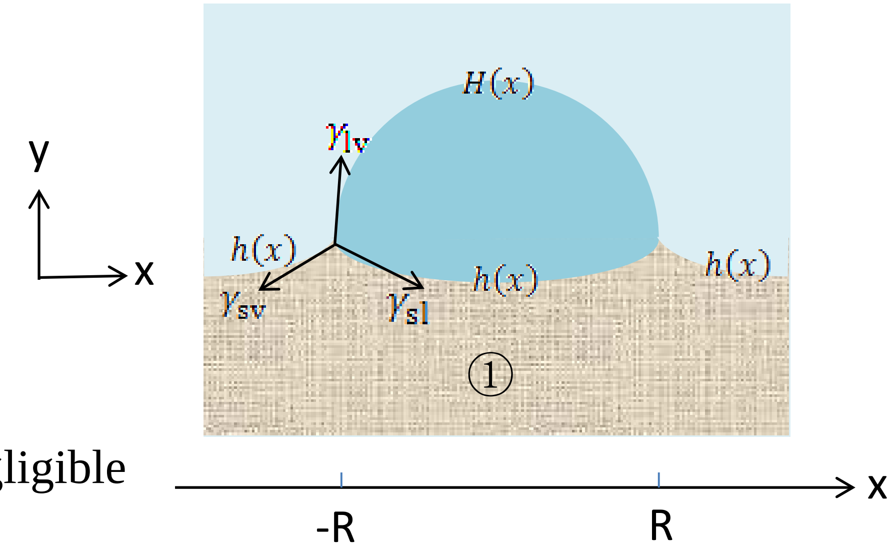
$$= \frac{1}{2}\int_{-\infty}^{\infty}(\sigma_{12}h_1 + \sigma_{22}h_2)\,dx$$

Stress components on the interface can be obtained by the constitutive relation (isotropic): $\sigma_{ij} = 2\mu\epsilon_{ij} + \lambda\delta_{ij}\sum_k \epsilon_{kk}$

$$\sigma_{12} = 2\mu\int_{-\infty}^{\infty}\frac{1}{2\pi}|k|\hat{h}_1 e^{ikx}\,dk = \frac{2\mu}{\pi}\int_{-\infty}^{\infty}\frac{h'_1(x_1)}{x - x_1}\,dx_1,$$

$$\sigma_{22} = 2\mu\int_{-\infty}^{\infty}\frac{1}{2\pi}|k|\hat{h}_2 e^{ikx}\,dk = \frac{2\mu}{\pi}\int_{-\infty}^{\infty}\frac{h'_2(x_1)}{x - x_1}\,dx_1.$$

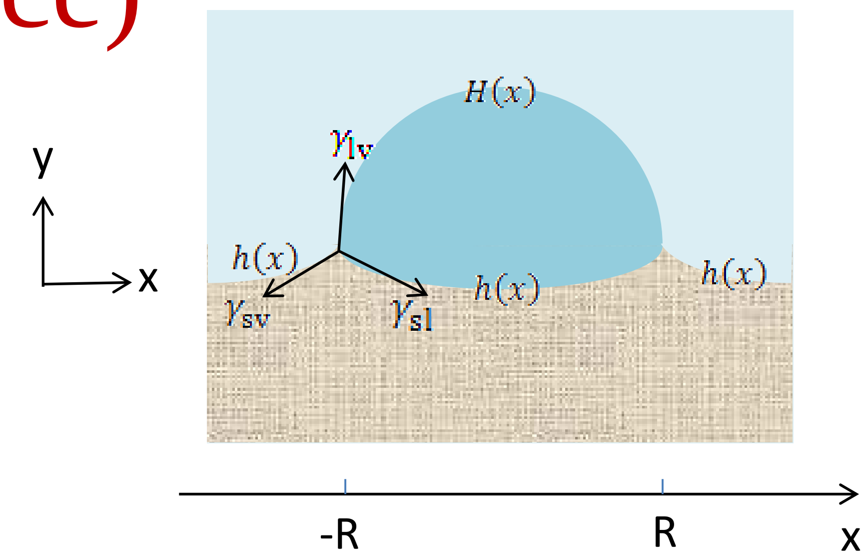
Free energy (bulk)



- The horizontal displacement $h_1(x)$ is negligible
  - $h_1(x) = 0$;
  - denote $h_2(x)$ as $h(x)$.

$$E_{\mathrm{e}} = \frac{1}{2}\int_{-\infty}^{\infty} \sigma_{22} h(x)dx, \quad \sigma_{22} = \frac{2\mu}{\pi}\int_{-\infty}^{\infty} \frac{h'(x_1)}{x - x_1}dx_1.$$

Free energy (interface)



- The liquid/vapor interface:

  the surface stress Υ = surface energy γ ,
  and unified named as surface tension.

- The solid/vapor, solid/liquid interfaces:

  Shuttleworth equation (Shuttleworth, 1950)

$$\Upsilon = \gamma + d\gamma/d\epsilon_{||}$$

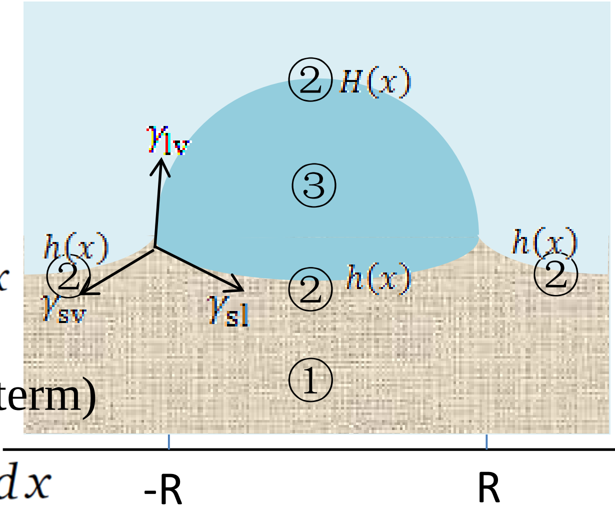
  the tangential strain vanishes and $d\gamma/d\epsilon_{||} = 0$,

  and hence the surface stress Υ = surface energy γ .

Free energy (interface and constraints)

2. Surface free energy

$$E_c = \gamma_{lv} \int_{-R}^{R} \sqrt{1+H'^2(x)}\,dx + \gamma_{sl} \int_{-R}^{R} \sqrt{1+h'^2_{sl}(x)}\,dx$$
$$+ \gamma_{sv} \int_{-\infty}^{-R} \sqrt{1+h'^2_{sv}(x)}\,dx + \gamma_{sv} \int_{R}^{+\infty} \sqrt{1+h'^2_{sv}(x)}\,dx$$



3. Constant droplet and solid volumes (Lagrange multiplier term)

$$E_V = P(V_L - \int_{-R}^{R} (H(x) - h(x))dx) \qquad E_S = \tilde{P} \int_{-\infty}^{+\infty} h(x)dx$$

4. Constraint: $H(x), h_{sl}(x), h_{sv}(x)$ have the same value at $x = \pm R$

Lagrange multiplier terms:

$$E_R = \lambda_{sl}^{+}(H(R) - h_{sl}(R)) + \lambda_{sl}^{-}(H(-R) - h_{sl}(-R)) + \lambda_{sv}^{+}(H(R) - h_{sv}(R)) + \lambda_{sv}^{-}(H(-R) - h_{sv}(-R)).$$

$$E_{\text{total}} = E_e + E_c + E_V + E_S + E_R.$$

Force balance

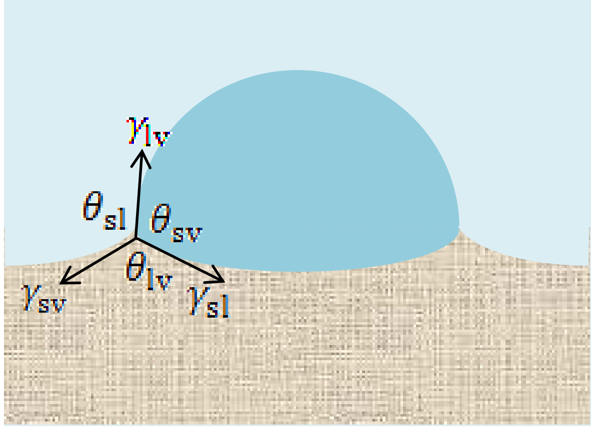
By taking the variation of the total energy, the force balance of the interfaces is

$$\gamma_{lv}\kappa_{lv} + P = 0,$$ liquid-vapor interface

$$\sigma_n(x) - \gamma_{sl}\kappa_{sl} + P + \tilde{P} = 0,$$ solid-liquid interface

$$\sigma_n(x) - \gamma_{sv}\kappa_{sv} + \tilde{P} = 0,$$ solid-vapor interface

$\kappa_{lv}, \kappa_{sl}, \kappa_{sv}$ are the corresponding curvatures.



Contact line constraints

$$\frac{\gamma_{lv}}{\sin\theta_{lv}} = \frac{\gamma_{sl}}{\sin\theta_{sl}} = \frac{\gamma_{sv}}{\sin\theta_{sv}},$$

where $\theta_{lv}, \theta_{sl}, \theta_{sv}$ are the angles at the contact line point against the liquid-vapour, solid-liquid and solid-vapour interfaces, respectively. These equations are called the Neumann's triangular law.

Numerical methods: find the equilibrium state

Evolution equations for the interface functions: gradient flow

$$
\begin{aligned}
H_t &= -M_H(-\gamma_{lv}\kappa_{lv} - P), \\
(h_{sl})_t &= -M_h(\sigma_n(x) - \gamma_{sl}\kappa_{sl} + P + \tilde{P}), \\
(h_{sv})_t &= -M_h(\sigma_n(x) - \gamma_{sv}\kappa_{sv} + \tilde{P}), \\
P_t &= -M_P\left(V_L - \int_{-R}^{R} (H(x) - h(x))dx\right), \\
\tilde{P}_t &= -M_P\left(\int_{-\infty}^{+\infty} h(x)dx\right).
\end{aligned}
$$

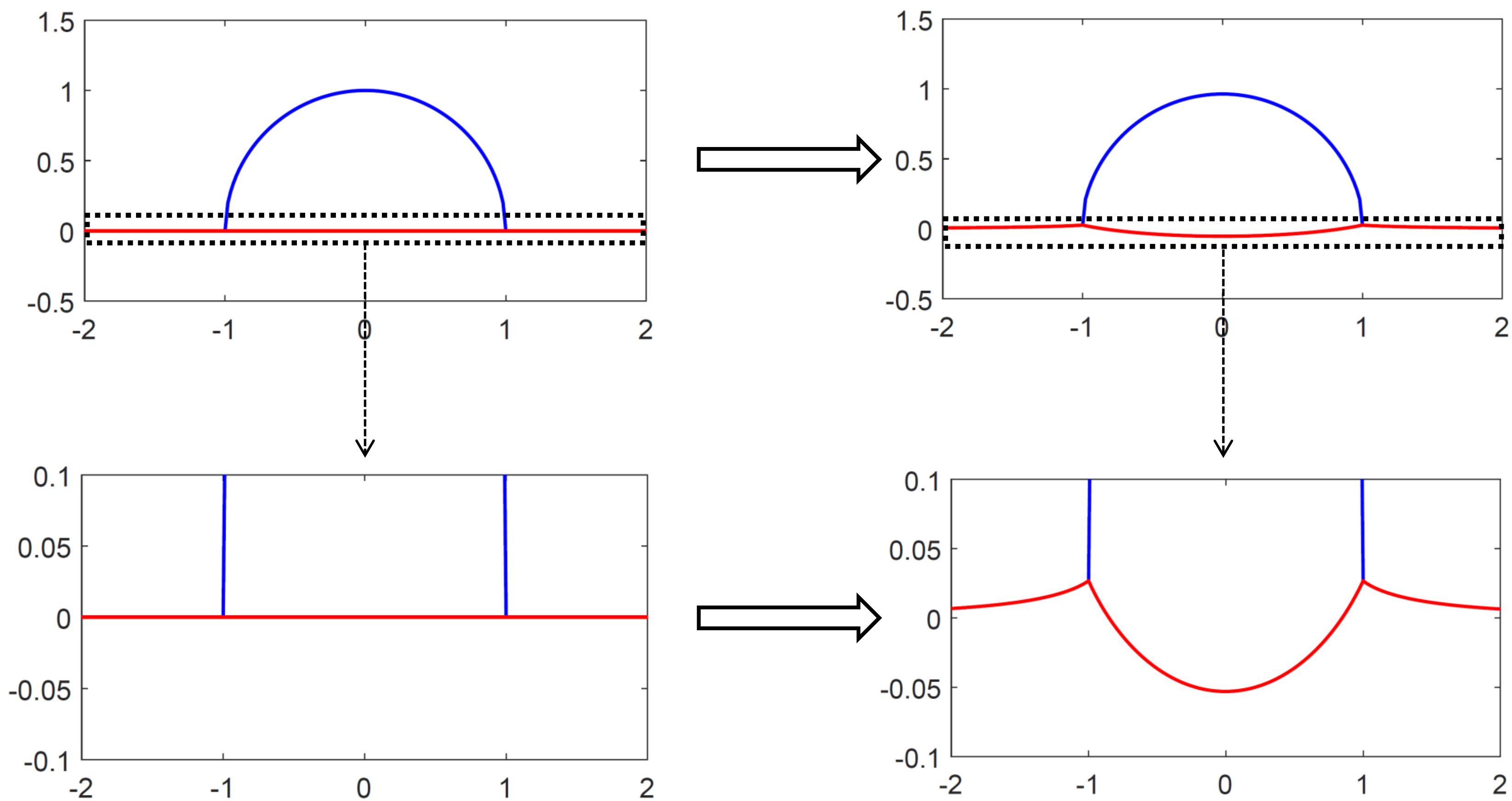
with the contact line boundary condition

$$
\frac{\gamma_{lv}}{\sin\theta_{lv}} = \frac{\gamma_{sl}}{\sin\theta_{sl}} = \frac{\gamma_{sv}}{\sin\theta_{sv}},
$$

Simulations: find the equilibrium state

Initial configuration:

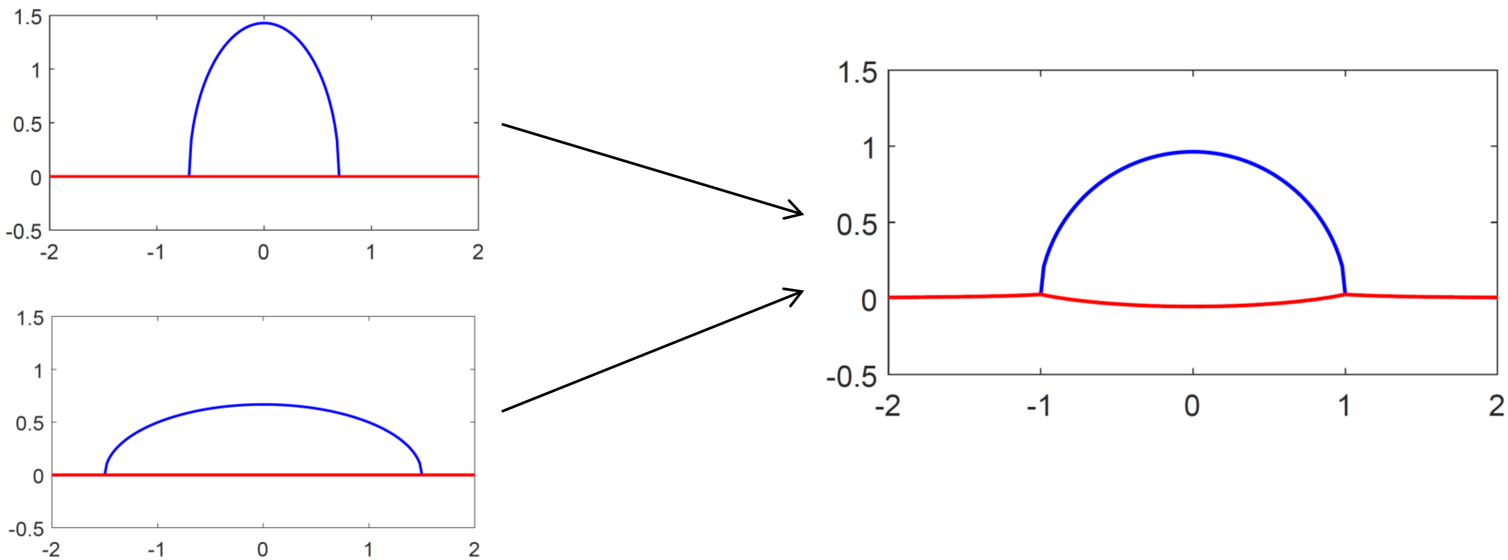
Equilibrium state:



Simulations: find the equilibrium state

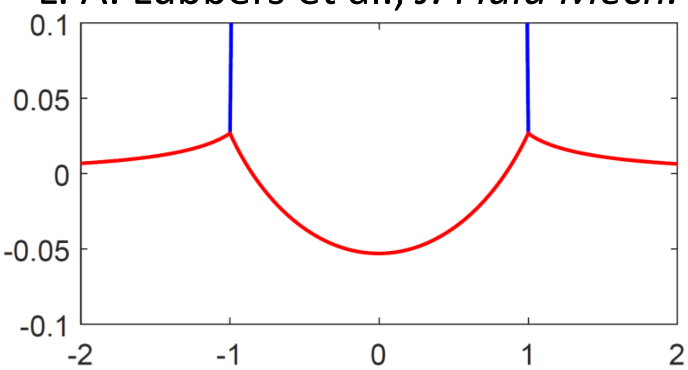
Other initial configurations:

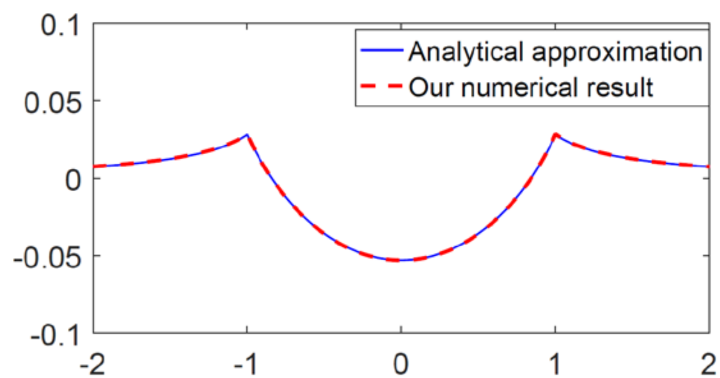
Equilibrium state:



Comparison of solid interface with analytical approximation:

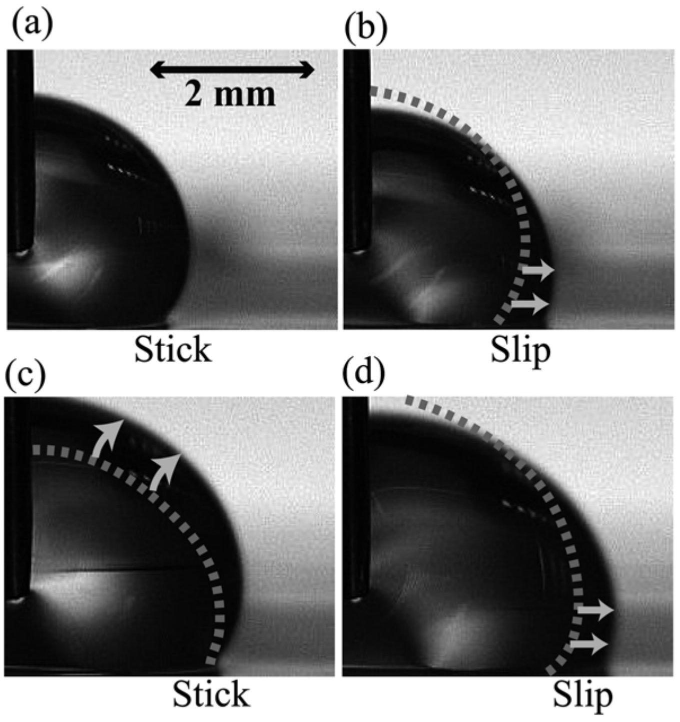
L. A. Lubbers et al., *J. Fluid Mech.* 747, R1

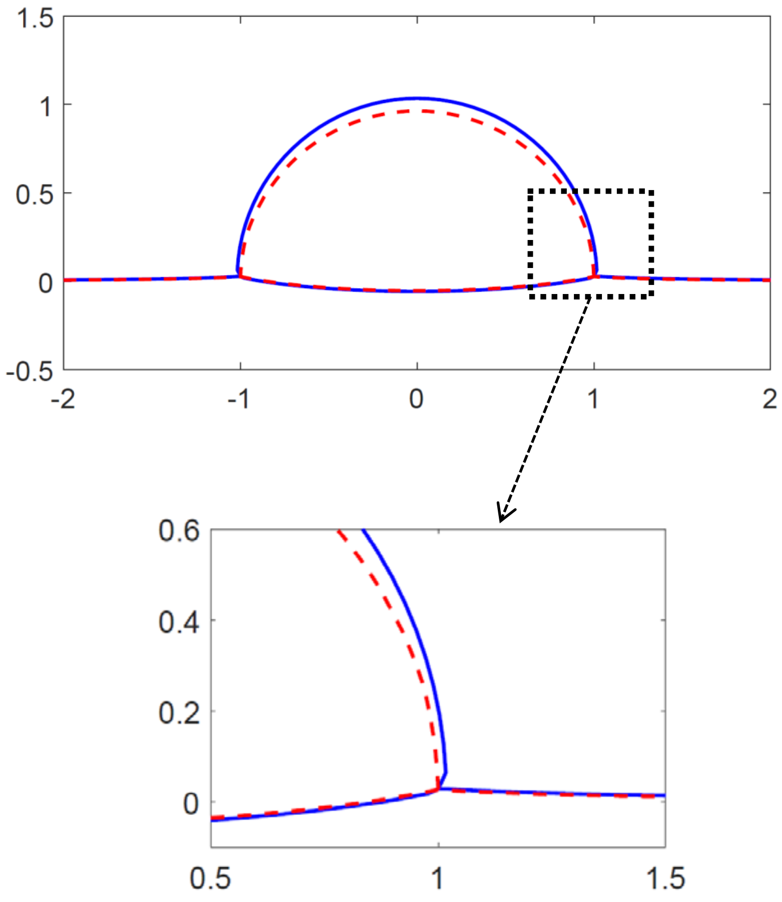




Simulations: stick-slip motion

T. Kajiya et al, Soft Matter, 2013, 9, 454

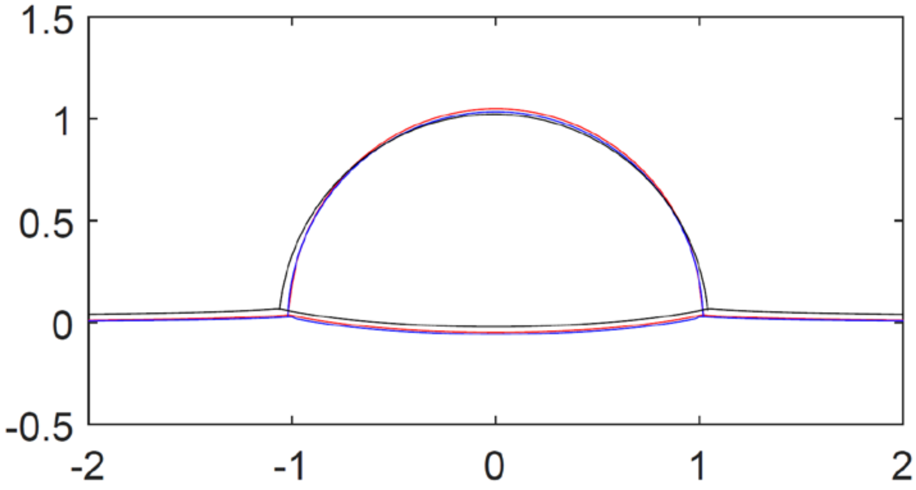




Simulations

Droplets with volume V have multiple equilibrium states:

- global energy minimization: V→V
- (1 - ε)V→V
- (1 + ε)V→V



Summary

- Two-dimensional system of a liquid droplet on a semi-infinite incompressible isotropic elastic substrate
- Numerical method: gradient flow from energy variation
- Simulations to find the equilibrium state, stick-slip phenomenon, multiple equilibrium states.

On-going & future work

- Simulations of stick-slip phenomenon, multiple equilibrium states
- Dynamics of the liquid spreading on soft substrates

Thank you!