Liquid drops on soft elastic substrates

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Introduction

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.

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

- Rigid substrate: the equilibrium contact angle is determined by the Young’s relation
  \[ \gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta. \]

- 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 $\mathbf{u}(x, 0) = \mathbf{h}(x) = (h_1(x), h_2(x))$ $\mathbf{u}(x, -\infty) = (0, 0)$

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

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

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
  \[
  E_e = \int_V \sum_{i,j} \frac{1}{2} \sigma_{ij} \varepsilon_{ij} dV
  \]
  \[
  \sigma_{ij} = \sum_{k,l} C_{ijkl} \varepsilon_{kl}
  \]

For our two-dimensional semi-infinite solid,

\[
E_e = \int_{s} \sum_{i,j=1}^{2} \frac{1}{2} \sigma_{ij} \varepsilon_{ij} dx_1 dx_2 = \int_{s} \sum_{i,j=1}^{2} \frac{1}{2} \sigma_{ij} \frac{\partial u_i}{\partial x_j} dx_1 dx_2
\]

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

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

Stress components on the interface can be obtained by the constitutive relation (isotropic):

\[
\sigma_{ij} = 2\mu \varepsilon_{ij} + \lambda \delta_{ij} \sum_{k} \varepsilon_{kk}
\]

\[
\sigma_{12} = 2\mu \int_{-\infty}^{\infty} \frac{1}{2\pi} |k| \hat{h}_1 e^{ikx} dk = \frac{2\mu}{\pi} \int_{-\infty}^{\infty} \frac{h_1'(x_1)}{x - x_1} dx_1,
\]

\[
\sigma_{22} = 2\mu \int_{-\infty}^{\infty} \frac{1}{2\pi} |k| \hat{h}_2 e^{ikx} dk = \frac{2\mu}{\pi} \int_{-\infty}^{\infty} \frac{h_2'(x_1)}{x - x_1} dx_1.
\]
Free energy (bulk)

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

$$E_e = \frac{1}{2} \int_{-\infty}^{\infty} \sigma_{22}(x) dx, \quad \sigma_{22} = \frac{2\mu}{\pi} \int_{-\infty}^{\infty} \frac{h'(x_1)}{x-x_1} dx_1.$$
Free energy (interface)

- The liquid/vapor interface:
  
  the surface stress $\gamma = \text{surface energy } \gamma$, and unified named as surface tension.

- The solid/vapor, solid/liquid interfaces:
  
  Shuttleworth equation (Shuttleworth, 1950)
  
  $\gamma = \gamma + d\gamma/d\epsilon_\parallel$
  
  the tangential strain vanishes and $d\gamma/d\epsilon_\parallel = 0$, and hence the surface stress $\gamma = \text{surface energy } \gamma$. 

Free energy (interface and constraints)

2. Surface free energy

\[ E_c = \gamma_{lv} \int_{-R}^{R} \sqrt{1 + H'^2(x)} \, dx + \gamma_{sl} \int_{-R}^{R} \sqrt{1 + h_{sl}'^2(x)} \, dx \]

\[ + \gamma_{sv} \int_{-\infty}^{-R} \sqrt{1 + h_{sv}'^2(x)} \, dx + \gamma_{sv} \int_{R}^{\infty} \sqrt{1 + h_{sv}'^2(x)} \, dx \]

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

\[ E_V = P(V_L - \int_{-R}^{R} (H(x) - h(x)) \, dx) \quad E_S = \tilde{P} \int_{-\infty}^{+\infty} h(x) \, dx \]

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

\[
\gamma_{lv} \kappa_{lv} + P = 0, \quad \text{liquid-vapor interface}
\]

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

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

\(\kappa_{lv}, \kappa_{sl}, \kappa_{sv}\) 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

\[ H_t = -M_H(-\gamma_{lv} \kappa_{lv} - P), \]
\[ (h_{sl})_t = -M_h(\sigma_{n}(x) - \gamma_{sl} \kappa_{sl} + P + \tilde{P}), \]
\[ (h_{sv})_t = -M_h(\sigma_{n}(x) - \gamma_{sv} \kappa_{sv} + \tilde{P}), \]
\[ P_t = -M_P \left( V_L - \int_{-R}^{R} (H(x) - h(x)) \, dx \right), \]
\[ \tilde{P}_t = -M_P \left( \int_{-\infty}^{+\infty} h(x) \, dx \right). \]

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: $V \rightarrow V$
- $(1 - \varepsilon)V \rightarrow V$
- $(1 + \varepsilon)V \rightarrow V$
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!