A phase field approach to wetting and contact angle hysteresis

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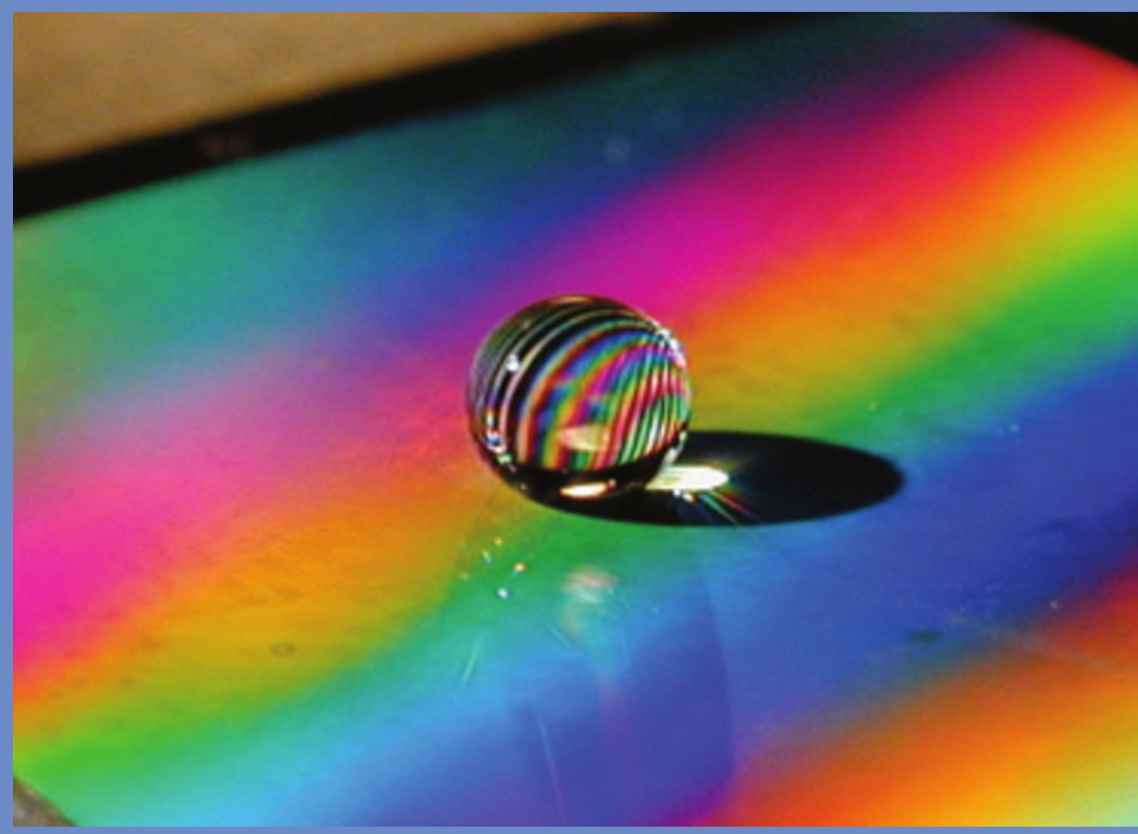
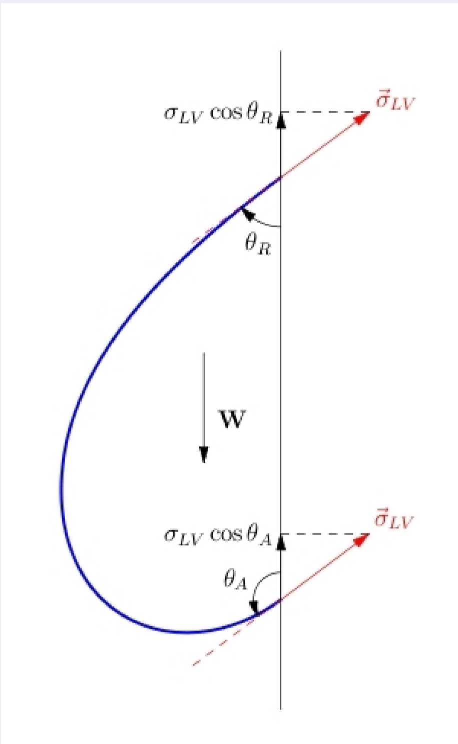


1. Physical review

Liquid drops can adhere to vertical or inclined plates by exploiting surface tension and frictional forces that can pin the contact line. These forces give rise to a phenomenon , called contact angle hysteresis, that allows the drop to adapt its contact angles and resist to gravity. In a two dimensional geometry the drop is in equilibrium if:



$$\rho g A + \sigma_{LV}\cos\theta_A - \sigma_{LV}\cos\theta_R \le 0 \qquad (1)$$

where σ_{LV} is the surface tension, ρ is the liquid density, g is the usual gravity acceleration, A is the area of the drop and θ_A and θ_R are the *advancing contact angle* and the *receding contact angle*. The maximum value A_{crit} of A compatible with (1) is:

$$A_{crit} = \frac{\sigma_{LV}}{\rho g}(\cos\theta_R - \cos\theta_A) \qquad (2)$$

Formula (2) prompts two remarks:

- necessary condition for adhesion is that $\cos\theta_A \neq \cos\theta_R$ (i.e. Young's law is violated).
- A_{crit} is proportional to $(\cos\theta_R - \cos\theta_A)$.

2. Mathematical approach

The energy of an homogeneus liquid drop ω in contact with an homogeneus solid S and surrounded by a fluid is

$$E(\omega) = (\sigma_{SL} - \sigma_{SV})|\Sigma_{SL}| + \sigma_{LV}|\Sigma_{LV}| + \int_\omega G(x)d\mathcal{V}_x + k$$

where $|\Sigma_{SL}|$ is the measure of the solid-liquid interface, $|\Sigma_{LV}|$ is the measure of the liquid-vapor interface, σ_{AB} is the surface tension on the *AB* interface, $G(x)$ stands for a generic potential related to an external force field (gravity). Given a volume $\mathcal{V} > 0$, the geometric capillarity problem is to find the surface such that:

$$\omega^* = \underset{|\omega|=\mathcal{V}}{\text{argmin}}\{E(\omega)\}.$$

3. The phase field approach

We are looking for ϕ (the *phase function*), which equals one on the region occupied by the liquid. Given $\Omega \subset \mathbb{R}^3$, whose boundary $\partial_S\Omega$ is the solid S, a potential $W(s) = a^2 s^2 (1-s)^2$ (with $a > 0$ to be specified later) and a continuous function $\sigma : [0, +\infty) \to \mathbb{R}$ we define

$$E_\epsilon(\phi) = \int_\Omega \left(\epsilon|\nabla\phi|^2 + \frac{1}{\epsilon}W(\phi) + \phi G(x)\right)dx + \int_{\partial\Omega}\sigma(\widetilde{\phi})d\mathcal{H}_{n-1}(x)$$

We can extend E_ϵ in L^1 in the following way:

$$E_\epsilon(\phi) = \begin{cases} E_\epsilon(\phi) & \text{if } \phi \in H^1(\Omega, \mathbb{R}) \\ +\infty & \text{otherwise in } L^1 \end{cases} \qquad (3)$$

Now, following Modica [2], if we consider

$$\hat{\sigma}(t) = \inf_{s\ge 0}\left\{\sigma(s) + 2\left|\int_t^s \sqrt{W(y)}dy\right|\right\}, \qquad c_0 = \int_0^1 \sqrt{W(y)}dy$$

then E_ϵ Γ-converges to

$$\widetilde{E_0}(\phi) = \begin{cases} 2c_0|\Sigma_{LV}| + \hat{\sigma}(1)|\Sigma_{SL}| + \hat{\sigma}(0)|\Sigma_{SV}| + \\ + \int_\Omega \phi(x)G(x)dx & \text{if } \phi \in BV(\Omega, \{0,1\}) \\ +\infty & \text{otherwise in } L^1 \end{cases}$$

and if ϕ_ϵ^* is a family of minimizers of E_ϵ, and if ϕ^* is its limit in L^1, then ϕ^* is a minimizer for $\widetilde{E_0}$.
If we choose $\sigma(x) := Nx$ (with this choice $-2\epsilon\frac{\partial\phi}{\partial n} = N$ on $\partial_S\Omega$) and set:

$$2c_0 = \frac{a}{3} = \sigma_{LV}, \qquad \hat{\sigma}(0) = 0,$$

$$\hat{\sigma}(1) = \inf_{s\ge 0}\left\{Ns + 2a\left(\frac{s^3}{3} - \frac{s^2}{2} + \frac{1}{6}\right)\right\} = \sigma_{SL} - \sigma_{SV}.$$

we can conclude that E_ϵ Γ-converges to the capillarity energy.

4. The solution scheme

The Euler-Lagrange equation for the phase field model is (for sake of simplicity we set $G = 0$ and $a = 1$):

$$\begin{cases} -\epsilon\triangle\phi + \frac{1}{\epsilon}\phi(1-\phi)(1-2\phi) + \lambda = 0 & \text{in } \Omega \\ \frac{\partial\phi}{\partial n} = -\frac{N}{2\epsilon} & \text{on } \partial_S\Omega \end{cases} \qquad (4)$$

where λ is a lagrangian multiplier for the constraint $\int_\Omega \phi = \mathcal{V}(t + \delta t)$.
We transform (4) into a parabolic PDE generated by a gradient flow:

$$\phi_\tau = \epsilon\triangle\phi - \frac{1}{\epsilon}\phi(1-\phi)(1-2\phi) - \lambda. \qquad (5)$$

The solution will be $\lim_{\tau\to+\infty}\phi(\tau,\cdot)$.

5. The quasi-static evolutionary model for hysteresis

The capillary energy can't describe the hysteresis effect: a necessary condition for stationarity is that Young's law is valid. So it's necessary to introduce a dissipative term able to capture the frictional effects.
For a quasi-static evolutionary drop a new functional can be written:

$$\omega^*(t+\delta t) = \underset{|\omega|=\mathcal{V}(t+\delta t)}{\text{argmin}}\{E(\omega, t+\delta t) + D(\omega, \omega^*(t))\}$$

where $\omega^*(t)$ is the configuration at time t
$D(\omega_1, \omega_2) = \mu|\partial_S\omega_1 \triangle \partial_S\omega_2|$ is the dissipation
$(A \triangle B) = (A \setminus B) \cup (B \setminus A)$
$\mu > 0$ is a parameter giving the dissipated energy per unit area.
From a mathematical point of view this description is equivalent to consider a bi-component solid surface; so we are going to solve:

$$\phi_\epsilon^*(t+\delta t) = \arg\min\left\{E_\epsilon(\phi, t+\delta t), \ \text{subject to} \int_\Omega \phi = \mathcal{V}(t+\delta t)\right\}$$

$$\phi_\epsilon^* = \begin{cases} N_A & \text{on } \partial_S\Omega_A^\epsilon \\ N_R & \text{on } \partial_S\Omega_R^\epsilon \end{cases}$$

where $\partial_S\Omega_R^\epsilon$ and $\partial_S\Omega_A^\epsilon$ are ϵ-approximations of the wet and the dry part of the solid, and N_A (N_R) are the Neumann boundary condition associated with the advancing (receding) angle.

6. Numerical results

We checked the validity of the proposed model by determing the critical volume (that is the maximum value over which a drop is no longer in equilibirum) of water drops placed on differently treated vertical glasses, comparing and checking them against experiments by Shanahan [3]. The graph below shows the good agreement.

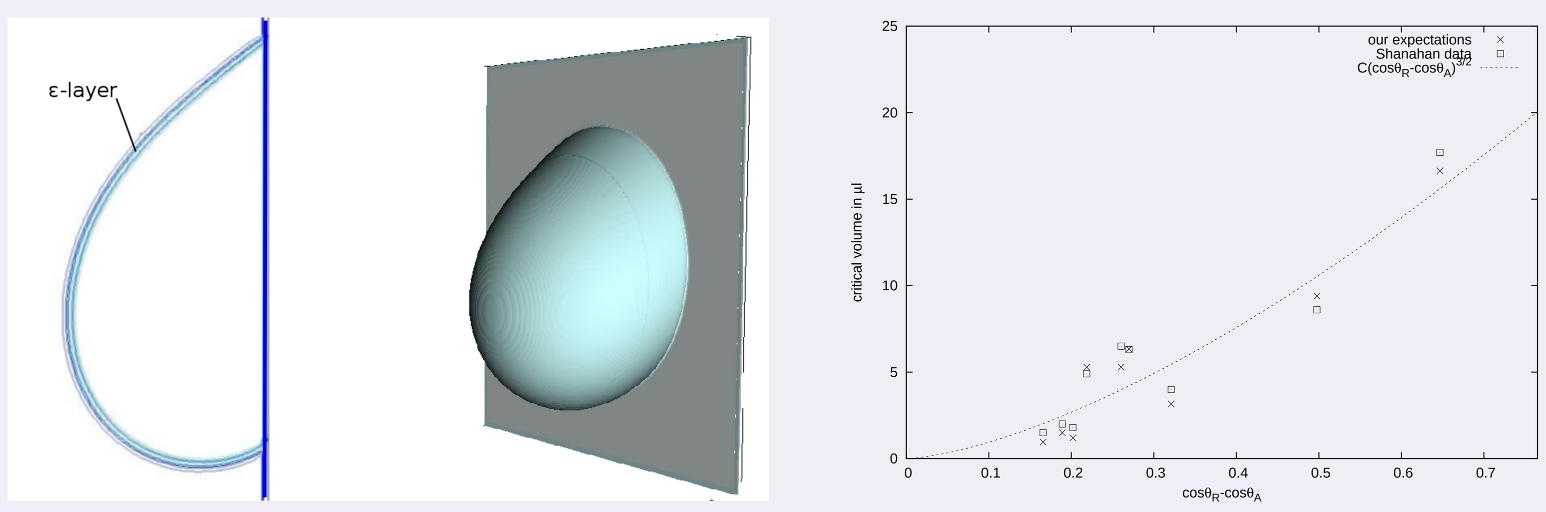


Figure: On the left a vertical slice and a 3-D picture of a phase field drop on a tilted plate; on the right the plot of the obtained results.

References

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The third image is taken from the review *Wetting and Roughness*, David Quéré, Laboratoire de Physique et Mécanique des Milieux Hétérogènes, ESPCI, 75005, Paris

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