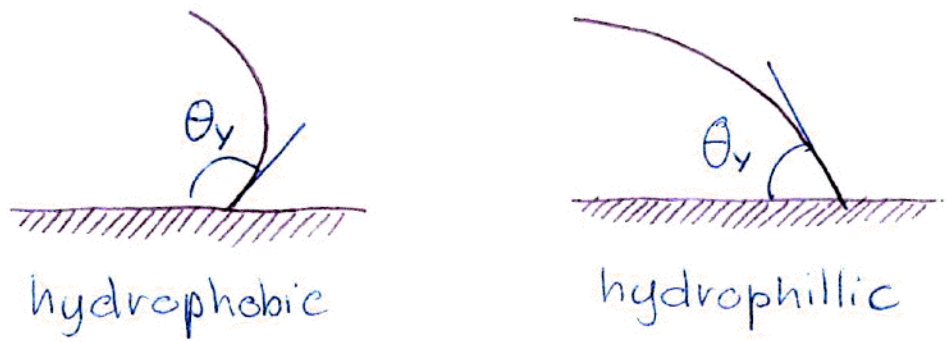
Lecture 3

Comments on the static model of capillarity

1. The surface on which the drop rests is called hydrophopic if $\theta_y > \pi/2$ (i.e. $\cos\theta_y < 0$), hydrophilic otherwise.

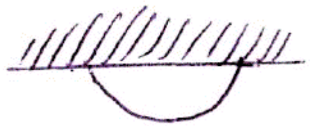


2. For large volumes the gravitational force dominate surface tension (puddles) while for small volumes is the contrary (drops).

Note that if you remove gravity, equilibrium conditions become purely geometric, and equilibrium configuration are invariant by scaling (there is no intrinsic length in the model, at least as long as nothing moves...)

3. What makes a drop stick to a surface?

Not gravity but surface tension!

remember the drop on the ceiling... 

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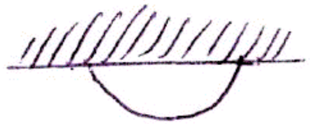
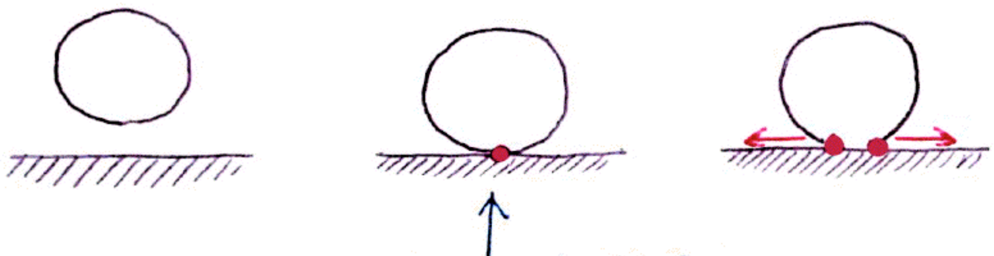


Indeed a spherical drop becomes unstable in the very moment it touches the surface:

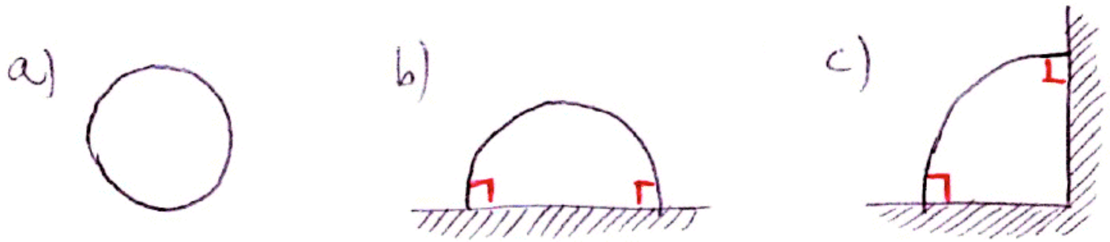


does not satisfy Young's law $\Rightarrow$ unstable!

4. Some equilibrium shapes in 2d, no gravity.

By Laplace equation the free surface (line) has constant curvature, i.e., is an arc of circle.

Examples ($\cos\theta_Y = 0$, that is, $\theta_Y = \frac{\pi}{2}$)



At equal area,

$$\text{energy}(a) > \text{energy}(b) > \text{energy}(c)$$

5. Equilibrium shapes in 3d, no gravity

Pieces of spherical surfaces have constant mean curvature.
But keep in mind that there are many more surfaces with constant mean curvature.

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But keep in mind that there are many more surfaces with constant mean curvature.

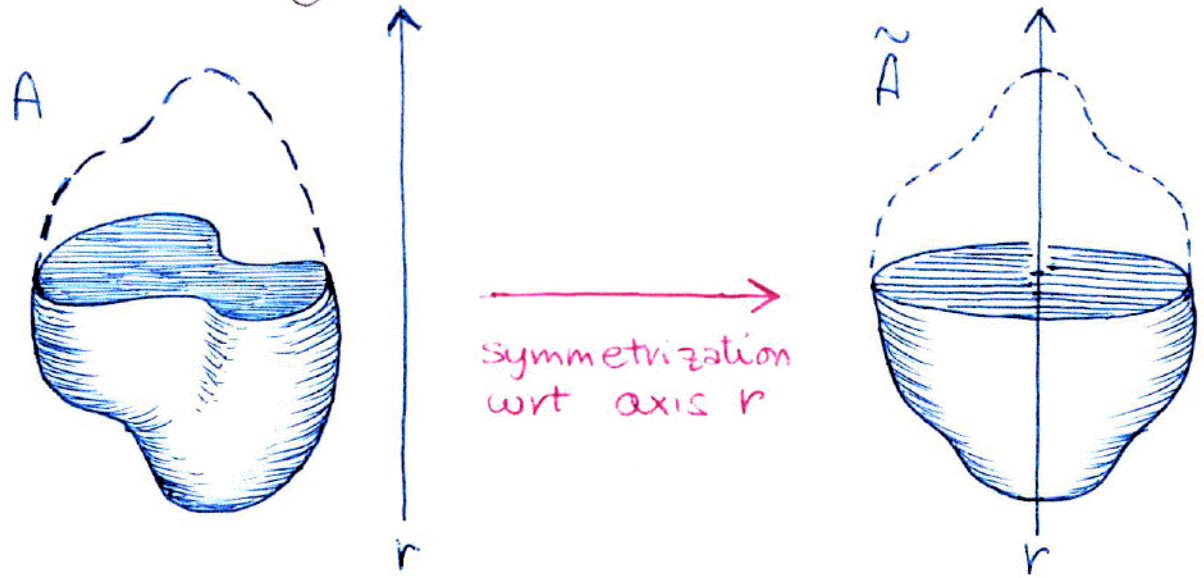
However:

If the solid surface is a plane then every minimizer of $\mathcal{E}$ (with given volume) is axially symmetric.

And the only axially symmetric surfaces with constant mean curvature are spherical caps.

The second part of the statement is an easy one-dimensional computation. Note that axial symmetry holds even if there is a volume energy with ρ depending only on the "vertical" coordinate.

Axial symmetry is proved by Steiner symmetrization:



$\tilde{A}$ is obtained from A by replacing every section orthogonal to the axis r by a disk with same area centered on the axis.

The key point is that Steiner symmetrization preserves volume and reduces the area of boundary.

6. Non-constant contact surface tension.

We can imagine that the value of σ_{SL} (and σ_{SV}) is not constant through the solid surface, that is, $\theta_y = \theta_y(x)$ depends on the position x.

In this case

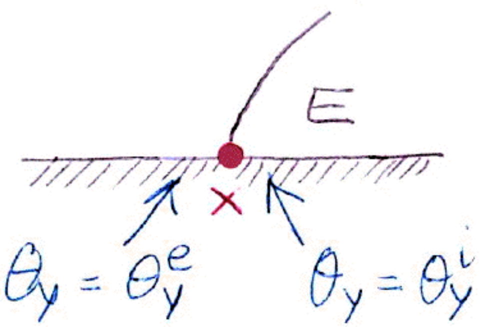
$$\mathcal{E} = \sigma_{LV}\left(|\Sigma^f| - \int_{\Sigma^c} \cos\theta_y(x)\, dx\right) + V,$$

Laplace equation remains the same, while Young's equation becomes $\theta(x) = \theta_y(x)$ for every $x \in \gamma$ (at least if θ_y is continuous).

Something interesting happens at a discontinuity point x of θ_y.

Assume 2d for simplicity.

Denote by θ_y^i and θ_y^e the values of θ_y at the two sides of x (interior and exterior w.r.t. the drop)



Then Young's law becomes:

a) if $\theta_y^e \geq \theta_y^i$ then $\theta_y^e \geq \theta(x) \geq \theta_y^i$;

b) if $\theta_y^e < \theta_y^i$ then E is unstable.

The proof is a modification of the previous one.
The key difference is that

$$\frac{d}{dh}\left[\int_{\Sigma^c(h)} \cos\theta_\gamma\right]\Bigg|_{h=0} = \int_\gamma \cos\theta^e_\gamma\,(v^c)^+ - \cos\theta^i_\gamma\,(v^c)^-$$

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positive part of v^c $= \begin{cases} v^c & \text{if } v^c \geq 0 \\ 0 & \text{if } v^c < 0 \end{cases}$

negative part of v^c $= \begin{cases} 0 & \text{if } v^c \geq 0 \\ -v^c & \text{if } v^c < 0 \end{cases}$

Since we compute only a right derivative, stability becomes

$$\frac{d}{dh^+} \mathcal{E}(E(h))\Big|_{h=0} - \lambda \frac{d}{dh} \mathrm{Vol}(E(h))\Big|_{h=0} \geq 0.$$

Using Laplace law (that can be obtained as before) this stability condition reduces to

$$0 \leq \int_{\gamma} \cos\theta\, v^c - \cos\theta_y^e (v^c)^+ + \cos\theta_y^i (v^c)^-$$

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In particular

$$0 \leq \int_\gamma (\cos\theta - \cos\theta_y^e)(v^c)^+$$

for all positive v^c, that is $\cos\theta - \cos\theta_y^e \geq 0$, that is $\theta \leq \theta_y^e$.

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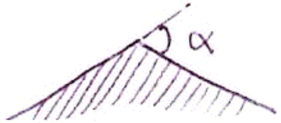
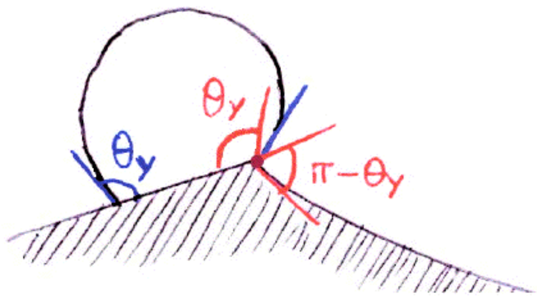
By considering all negative v^c we get $\theta_y^i \leq \theta$.

(In particular we get a contradiction if $\theta_y^e < \theta_y^i$.)

7. Non-smooth surface.

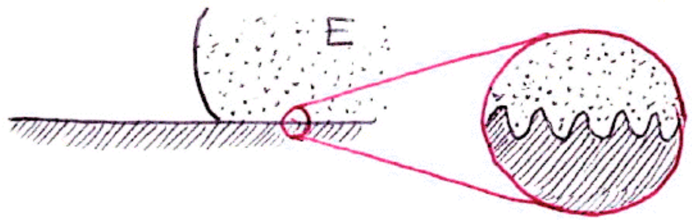
A similar situation occurs at points where the solid surface presents an angle.

If the angle si convex  then Young's law becomes $\theta_Y \leq \theta \leq \theta_Y + \alpha$



If the angle is concave, then this cannot be the contact point of a stable drop.

8. Consider a solid surface which is "wiggly" at some small (microscopic) scale.



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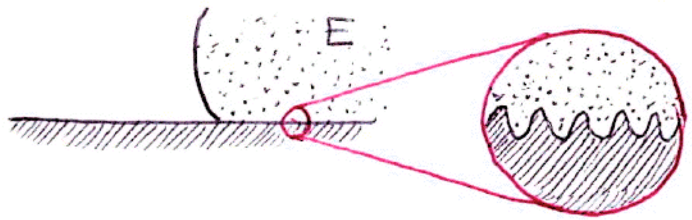

Then the apparent value of $|\Sigma^c|$ is not the real one. So $\mathcal{E}$ should be corrected as follows

$$\mathcal{E} = \sigma_{LV}\left(|\Sigma^f| - \lambda \cos\theta_y \, |\Sigma^c|\right) + V$$

where $\lambda := \dfrac{\text{effetive area}}{\text{apparent area}}$.

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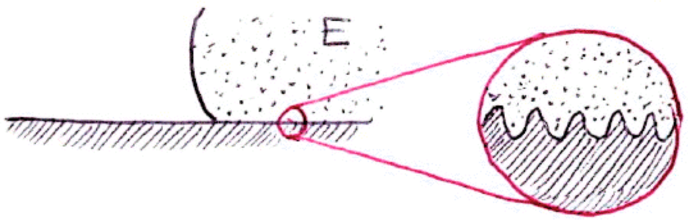

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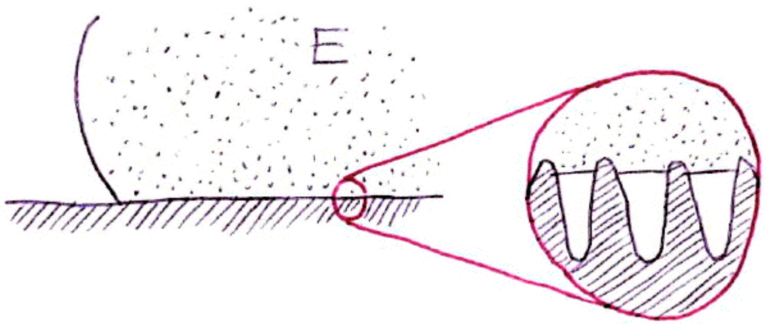

In principle it could be energetically more convenient to interpose some air between the drop and the solid surface...

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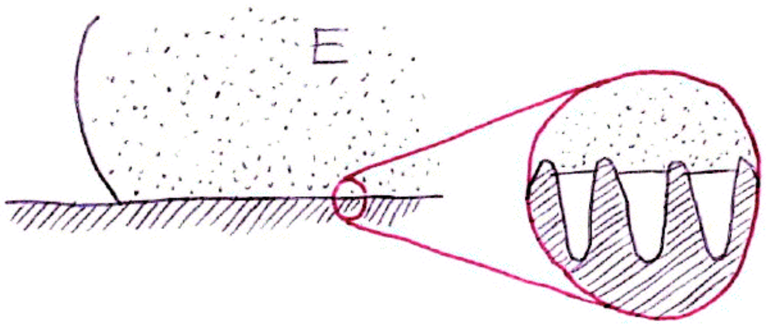

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Note that the effective Young's angle θ_Y^{eff} (the one observed macroscopically) satisfies:

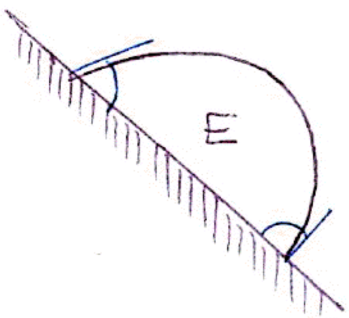
$\theta_Y^{eff} > \theta_Y$ if $\theta_Y > \frac{\pi}{2}$ (enhanced hydrophobicity)

$\theta_Y^{eff} < \theta_Y$ if $\theta_Y < \frac{\pi}{2}$ (enhanced hydrophilicity)

3. Contact angle hysteresis

The classical model for capillarity does not account for some (easily observed) facts

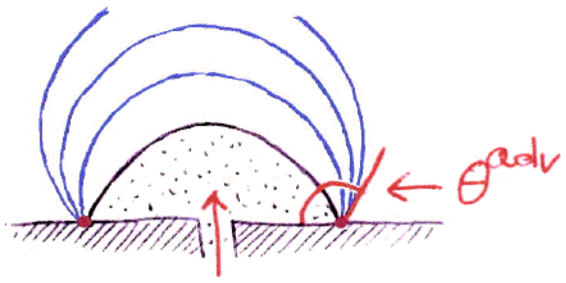
3.1. Drop sticking to an inclined plane



Why it doesn't slide down?

And why the angles are not the same?

3.2. Contact angle hysteresis



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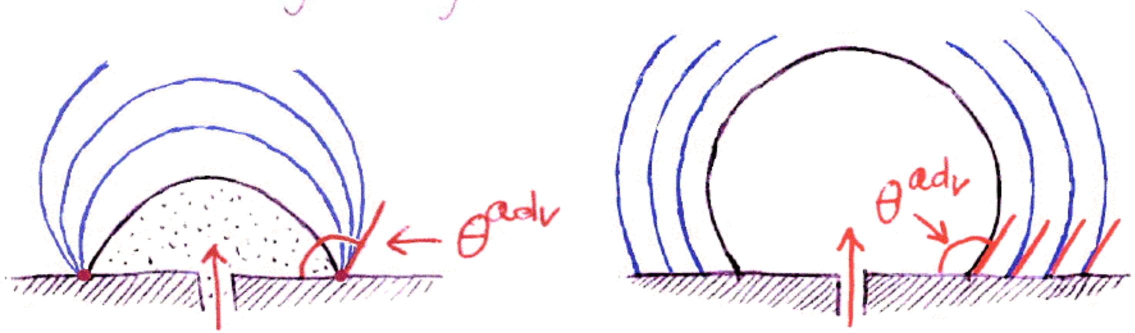

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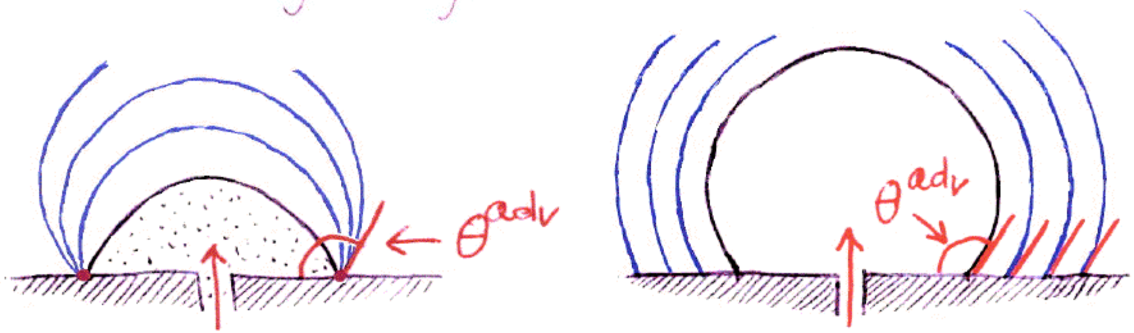

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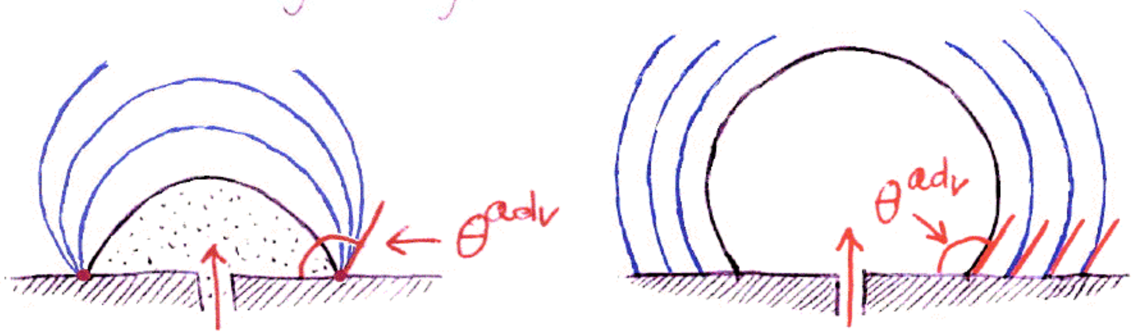

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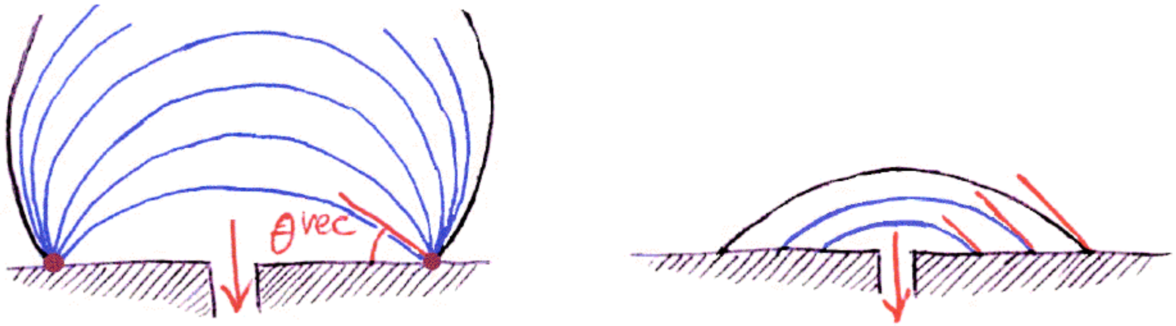
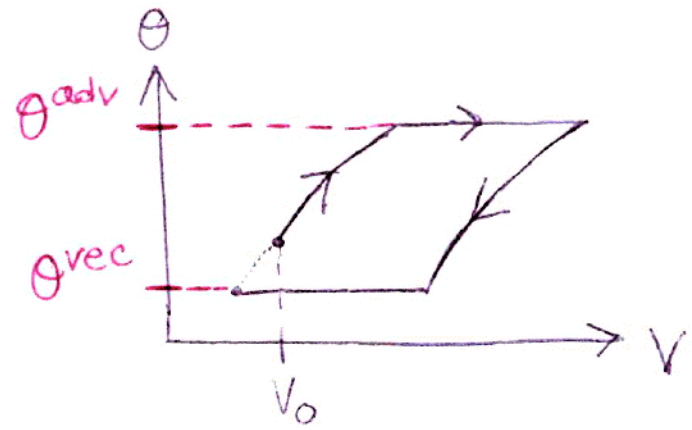


Plotting the contact angle against volume



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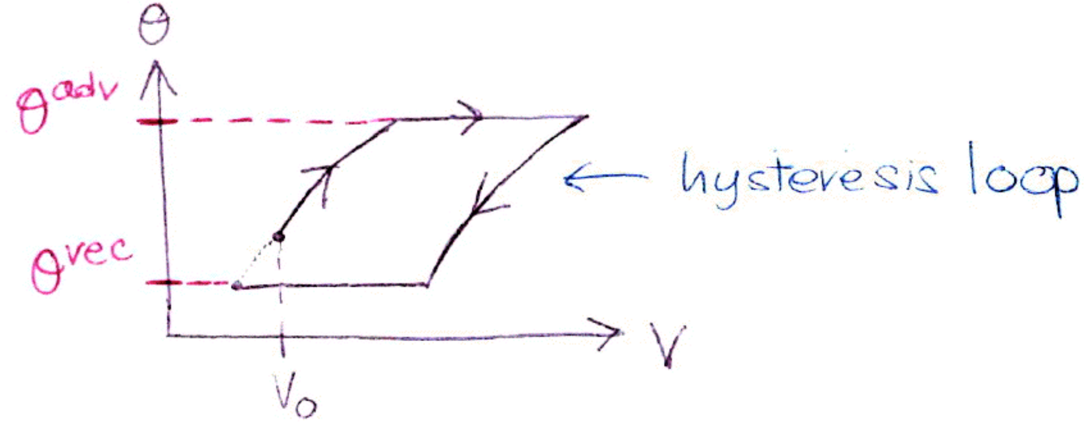

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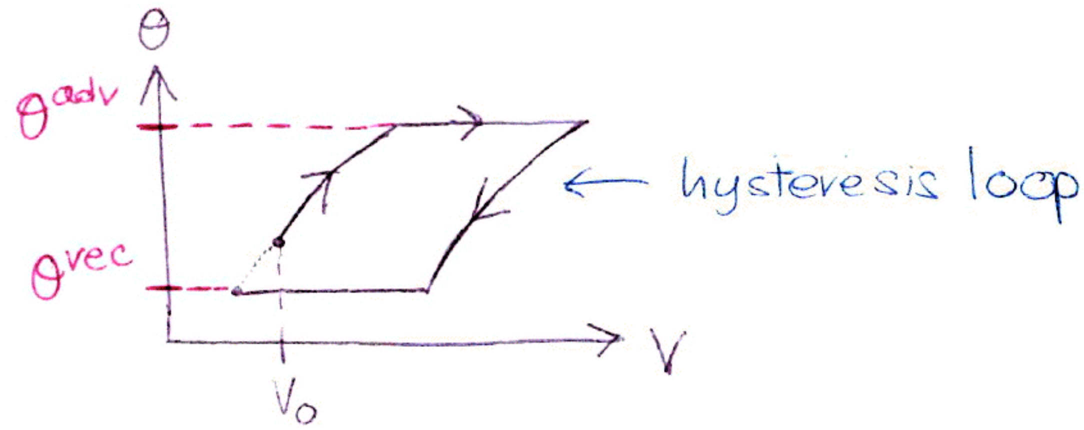

The real experiment is done differently (squeezing a drop between two plates...)

The difference $\theta^{adv} - \theta^{rec}$ is not so large...

The non straight curves in the hysteresis are not accurate.....

3.3. Adding a dissipation

I want to show that these phenomena can be explained by adding a simple dissipation mechanism, related to the movement of the contact line.

Dissipation potential: $\mathcal{D}(E,E') := \mu \left| \Sigma^c \Delta \Sigma^{c'} \right|$

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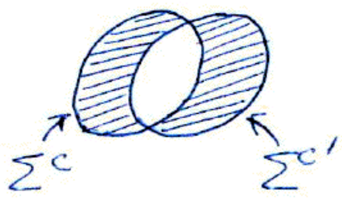
Symmetric difference of contact surfaces

i.e. $(\Sigma^c \setminus \Sigma^{c'}) \cup (\Sigma^{c'} \setminus \Sigma^c)$



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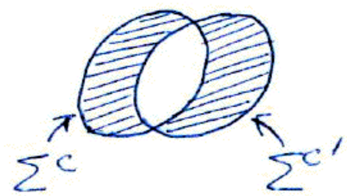

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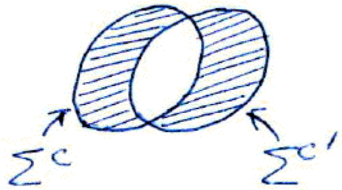

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contact surface of E

(outer) normal velocity of the contact line

Deviation of R from $\mathcal{D}$

$$R = \lim_{t \to 0} \frac{\mathcal{D}(E = E(0), E(t))}{t}$$

$$= \frac{d}{dt} \mathcal{D}(E(0), E(t)) \Big|_{t=0}$$

$$= \mu \frac{d}{dt} \Big[|\Sigma^c(t) \setminus \Sigma^c(0)| + |\Sigma^c(0) \setminus \Sigma^c(t)| \Big] \Big|_{t=0}$$

$$= \mu \Big[\int_\gamma (v^c)^+ + \int_\gamma (v^c)^- \Big] = \mu \int_\gamma |v^c|$$

Deviation of R from $\mathcal{D}$

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\begin{aligned}
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&= \mu \frac{d}{dt}\Big[|\Sigma^c(t)\setminus\Sigma^c(0)| + |\Sigma^c(0)\setminus\Sigma^c(t)| \Big]\Big|_{t=0} \\
&= \mu\Big[\int_\gamma (v^c)^+ + \int_\gamma (v^c)^-\Big] = \mu\int_\gamma |v^c|
\end{aligned}
$$

This form of R means that the contact line γ is subject to a frictional force (per unit length) normal, opposite to velocity, and with modulus μ.

3.4. Quasistatic evolution

We say that $t \mapsto E(t)$ is an energetic solution of the q.-s. evolution associated to $\mathcal{D}$ and $\mathcal{E}$ (with prescribed volume v) if $Var(E(t),[0,T]) < +\infty$ and

Global Stability: $\forall t$, $E(t)$ minimizes $\mathcal{E}(t,E)+\mathcal{D}(E,E(t))$ among all E with $vol(E)=v$.

Energy-Dissipation balance: $\forall t_0 < t_1$

$$\mathcal{E}(t_1, E(t_1)) - \mathcal{E}(t_0, E(t_0)) =$$
$$= \int_{t_0}^{t_1} \left[\int_{E(t)} \frac{\partial \rho}{\partial t}\, dx \right] dt - Diss(E(t), [t_0,t_1])$$

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As already mentioned, (EDb) could be replaced by

$$\mathcal{E}(T, E(T)) - \mathcal{E}(0, E(0)) = \int_0^T \left(\int_E \frac{\partial \rho}{\partial t}\, dx \right) dt - \mathrm{Diss}(E(t), [0,T])$$

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If the volume constraint is not constant in time, that is, $\mathrm{vol}(E(t)) = v(t)$ then one should add to the work of external forces

$$\int_{t_0}^{t_1} p(t)\, \dot{v}(t)\, dt$$

pressure in $E(t)$

Physical meaning of this integral....

3.5. Advancing and receding angles

Define θ^{adv} and θ^{rec} in $[0, \pi]$ by

$$\cos\theta^{adv} = \cos\theta_Y - \frac{\mu}{\sigma_{LV}} = \frac{\sigma_{SV} - \sigma_{LS} - \mu}{\sigma_{LV}}$$

$$\cos\theta^{rec} = \cos\theta_Y + \frac{\mu}{\sigma_{LV}} = \frac{\sigma_{SV} - \sigma_{LS} + \mu}{\sigma_{LV}}$$

These definitions make sense if the following modified wetting condition holds:

$$|\sigma_{SV} - \sigma_{LS}| \leq \sigma_{LV} - \mu$$

3.6. Differential formulation of q.s. evolution (flow rules)

Let $E(t)$ be an energetic solution. Then

(i) $\forall t$, $-2G_{LV} H + p = \text{const.}$ on Σ^{ℓ} [Laplace]

(ii) $\forall t$, $\theta^{rec} \le \theta \le \theta^{adv}$ on γ; moreover

$$\theta = \theta^{adv} \text{ where } v_c > 0,$$

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This explains contact angle hysteresis!

Note: (ii) is the natural equivalent of the condition on f_a for our simple mechanical model...

Deviation of flow rules.

The fact that $E(t)$ is stable at time t means that it minimizes

$$\mathcal{E}(t,E) + \mathcal{D}(E, E(t))$$

$$= \sigma_{LV}\left[|\Sigma^f| - \int_{\Sigma^c} \varphi\right] + V + \text{constant}$$

with

$$\varphi(x) := \begin{cases} \theta^{adv} & \text{if } x \notin \Sigma^c(t) \\ \theta^{rec} & \text{if } x \in \Sigma^c(t) \end{cases}$$

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From this we obtain (i) and $\theta^{rec} \leq \theta \leq \theta^{adv}$.

(We have already seen how!)

The rest of (ii) is obtained by taking the E-D balance with $t_1 = t$ and deriving it w.r.t. t:

$$\frac{d}{dt}\mathcal{E}(t, E(t)) = \int_{E(t)} \frac{\partial \varphi}{\partial t}\,dx - \mathcal{R}(\Sigma(t), v^{\varepsilon}(t))$$

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On the other hand

$$\frac{d}{dt}\mathcal{E}(t, E(t)) = \int_{E(t)} \frac{\partial \rho}{\partial t}\,dx + \sigma_{LV} \int_{\gamma(t)} (\cos\theta - \cos\theta_Y)\, v^c$$

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and we conclude.

Concluding Remarks

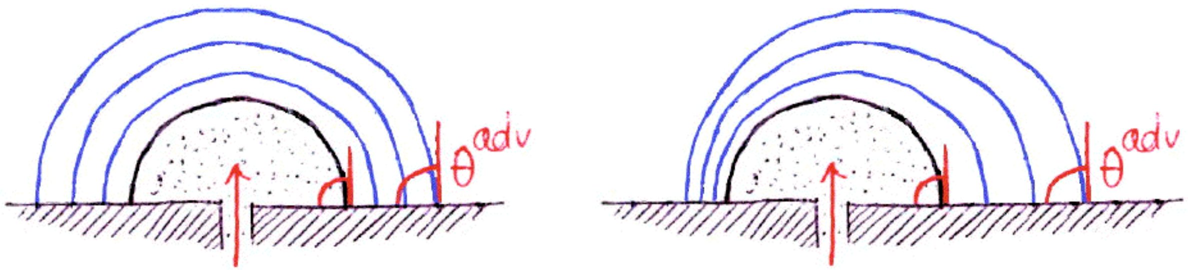
1. Un-physical jumps

as volume grows, the drop may suddenly jump far away (as in the picture) even if it is in a locally stable state.

The problem is twofold:

- as already discussed, that of energetic solution (globally stable at every time) is the wrong notion.
- Our specific choice of $\mathcal{D}$ is particularly bad, in that $\mathcal{D}$ is NOT the geodetic distance associated to the metric $\mathcal{R}$....

2. Solutions are not unique



Two (among many) energetic solutions for the quasistatic evolution of the initial drop (one axially symmetric the other not)

This type of non-uniqueness is related to the flatness (lack of strict convexity) of the L^1-norm, which is behind the definition of the dissipation potential $\mathcal{D}$).

3. On the possible geometric nature of friction

Assume the drop moves on a flat but microscopically wiggly surface.
Assume $\theta_Y = \pi/2$.

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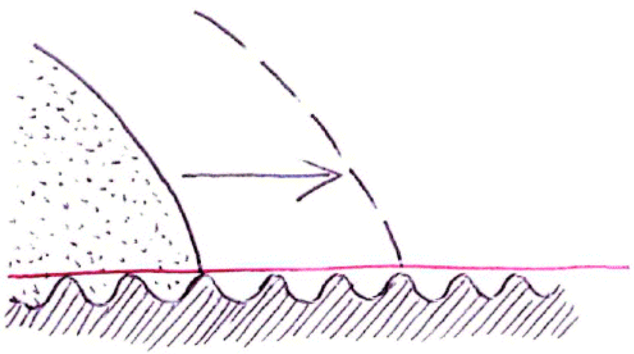

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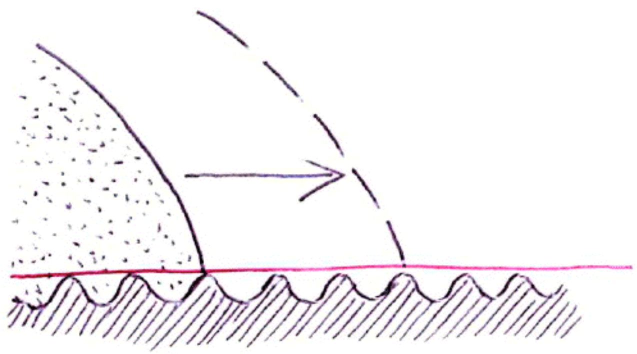

to move to the new position (with same energy) there is a small energy barrier to pass.

This means that energy is accumulated and then dissipated by internal friction in order to move. And the amount is proportional to the area swept by the contact line.