Back to the basics:
Wettability, icing and ice adhesion

Lasse Makkonen

VTT Technical Research Centre of Finland, Espoo, Finland

IWAIS 2015

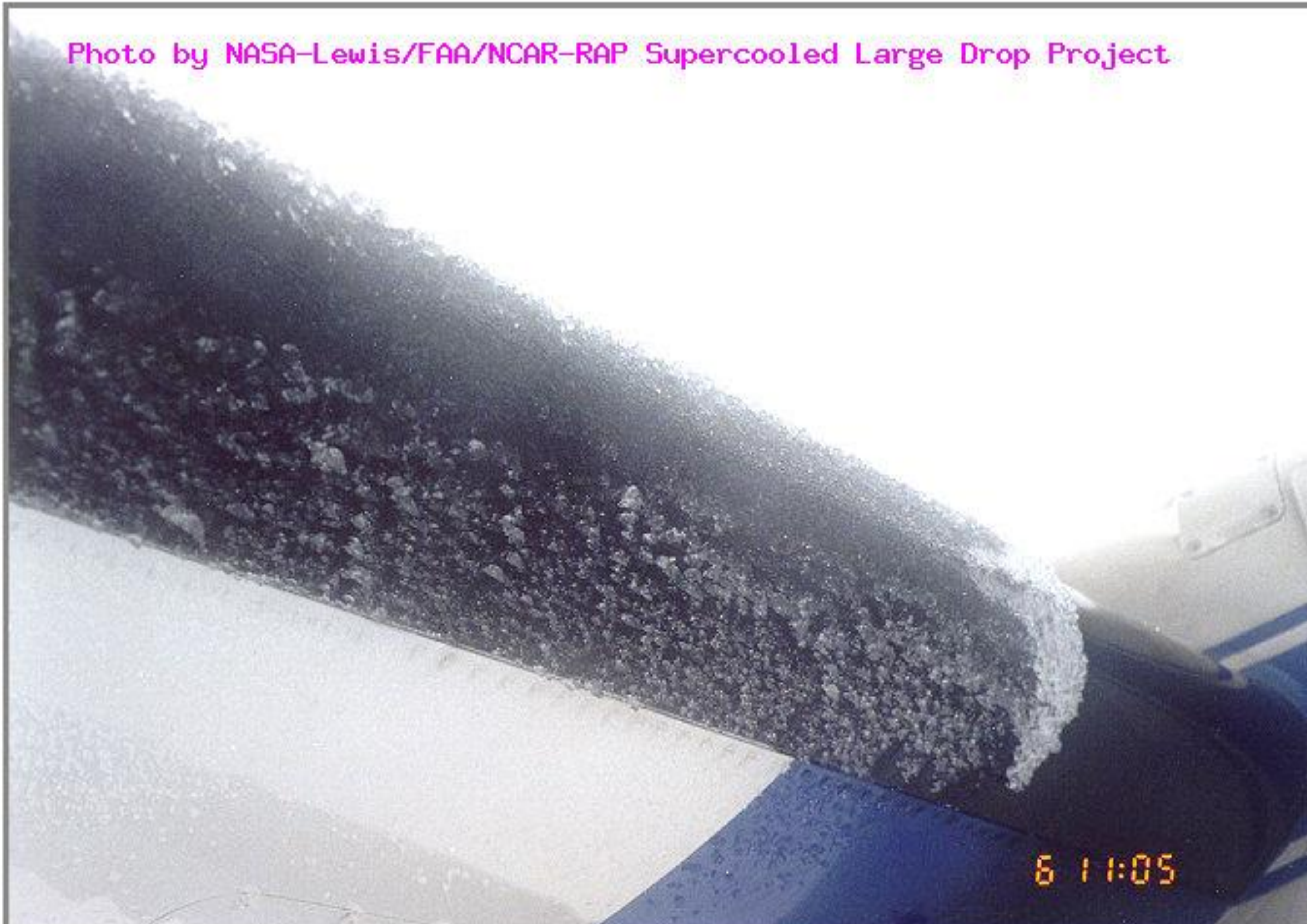
Photo by NASA-Lewis/FAA/NCAR-RAP Supercooled Large Drop Project
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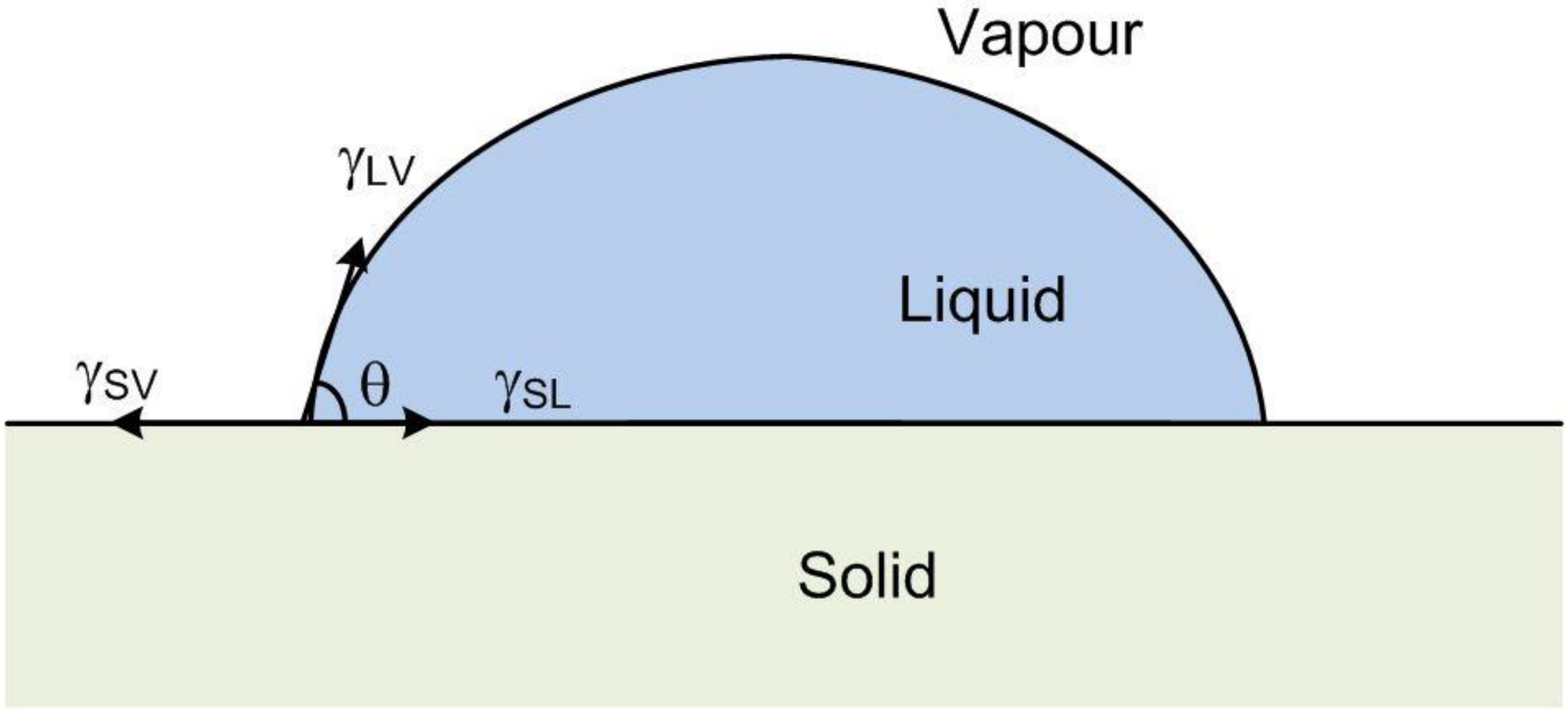
Young’s equation (1805)



$$\gamma_S = \gamma_{SL} + \gamma_{LV}\cos\theta$$

The origin of surface tension

- *The molecules in the bulk experience forces from neighboring molecules which are, on average, equal in all directions. For a molecule in or near the surface, these forces will not balance and the molecule will experience a pull towards the bulk. Many molecules will leave the surface, which is consequently more sparsely occupied than the internal layers so that the average spacing is slightly greater than the minimum, giving rise to the*

PROBLEM 1:

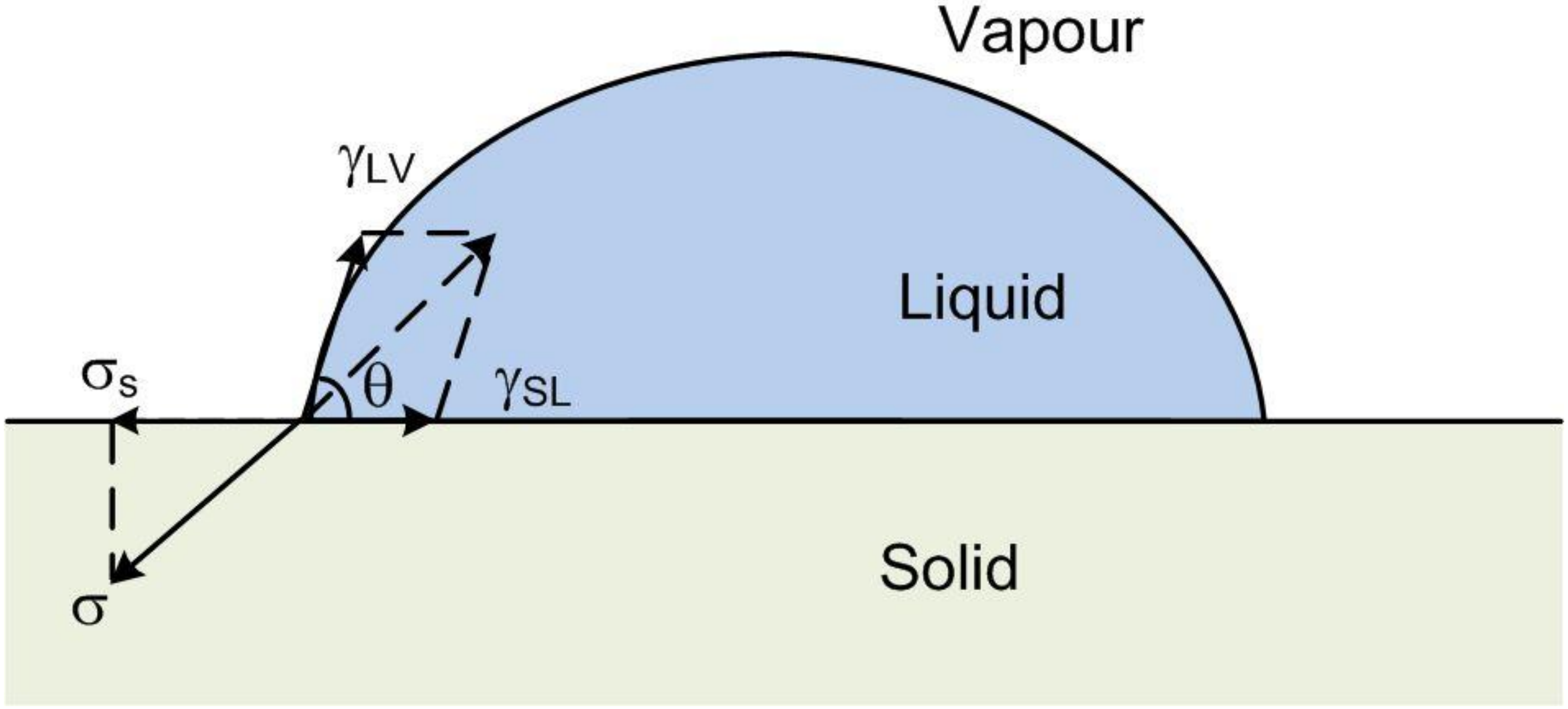
What is the origin of the mechanism by which the solid does lateral work?

Molecules cannot leave the surface =>

There is no such mechanism =>

There is no surface tension γ_S !

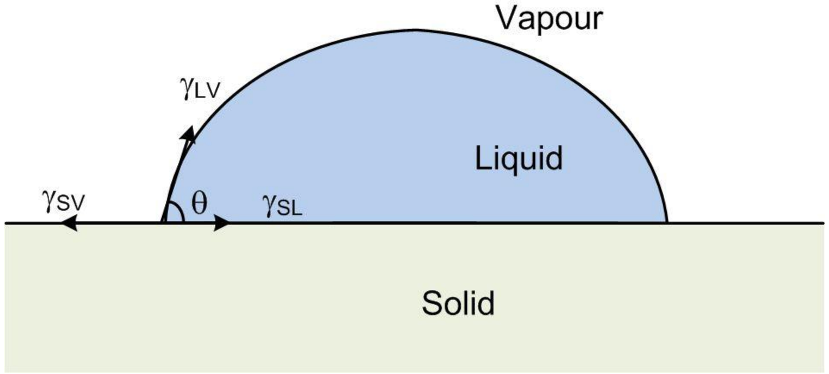
The mechanical balance



$$\sigma_S = \gamma_{SL} + \gamma_{LV} \cos\theta$$

PROBLEM 2:

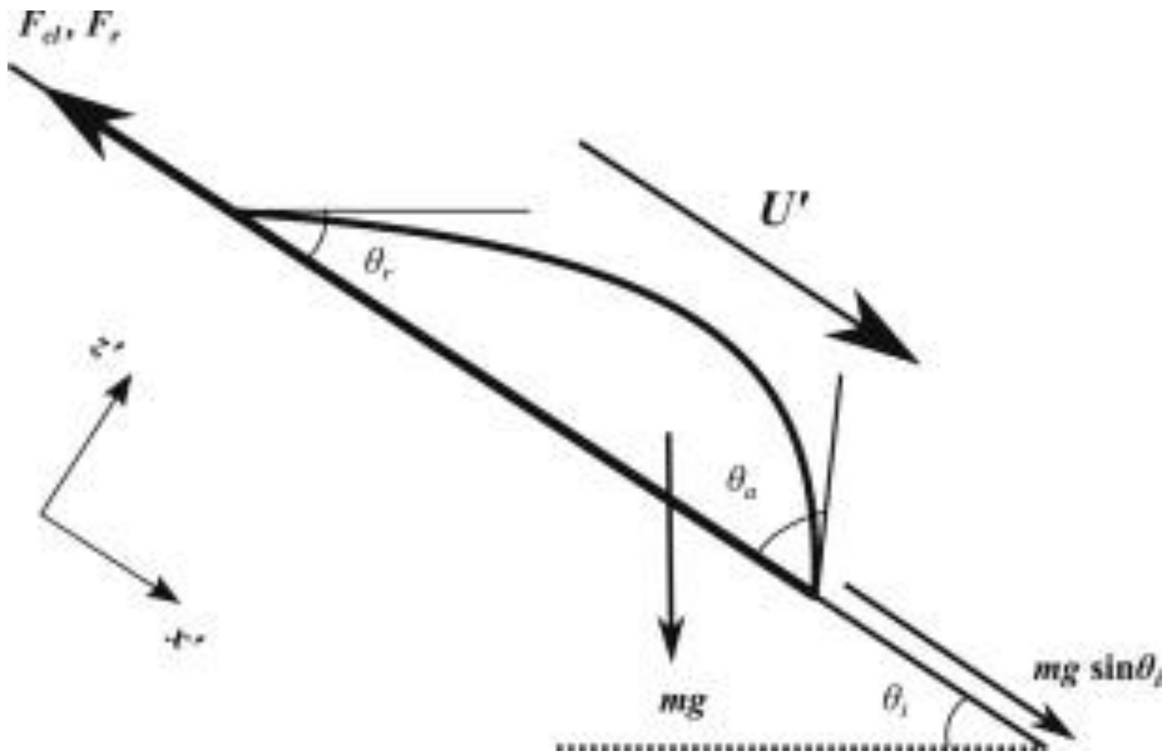
Young’s equation provides a stable mechanical equilibrium.

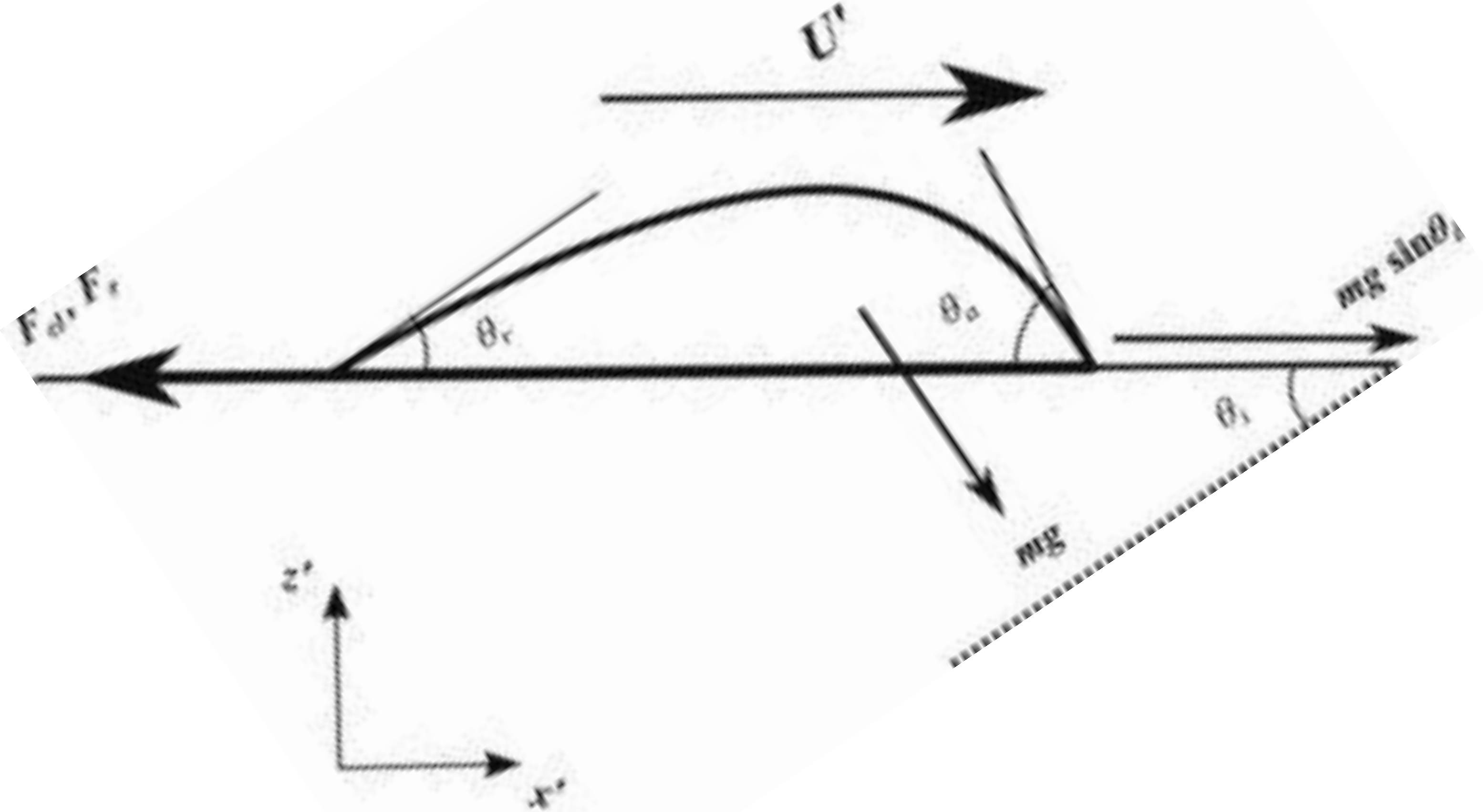


=>

There should be no obstacle to sliding !

Drop on a slope





U'
F_d, F_s
θ_r
θ_a
mg sinθ_t
mg
θ_t
z'
x'

Surface creation

When new surface with surface energy Γ is created by later motion, a resisting mechanical tension γ arises.

This is in analogy with the origin of friction.

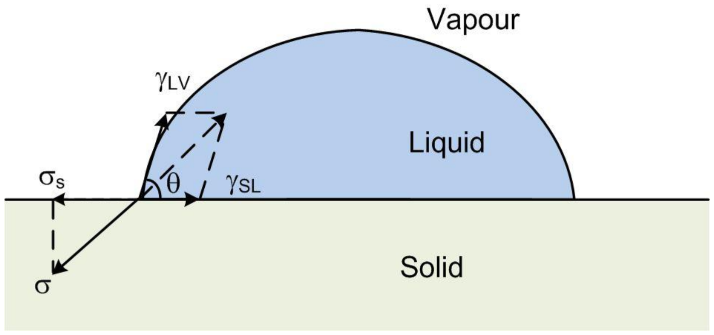
(Makkonen, L., 2012: A thermodynamic model of sliding friction. *AIP Advances* 2(1), 012179. doi:10.1063/1.3699027)

The minimum chemical potential

$$\Gamma_S = \Gamma_{SL} + \Gamma_{LV} \cos\theta$$

Γ_S, Γ_{SL} and Γ_{LV} are surface energies (scalar).

The contact line is pinned.



The system finds the equilibrium by the *adjustment of the free parameter θ*.

The tension caused by motion (creating new interface)

Advancing contact line: $\gamma_{SL} = \gamma_L \cos\theta - \gamma_L \cos\theta_a$

$$\Gamma_{SL} = \Gamma_L \cos\theta - \Gamma_L \cos\theta_a$$

Receding contact line: $\gamma_S = \gamma_L \cos\theta_r - \gamma_L \cos\theta$

$$\Gamma_S = \Gamma_L \cos\theta_r - \Gamma_L \cos\theta$$

Berthelot's rule (1898)

Geometric mean combining rule of intermolecular forces =>

$$\Gamma_S / \Gamma_L = [(1 + \cos\theta) / 2]^2$$

Dynamic contact angles

Advancing contact angle θ_a

$$\cos \theta_a = [-(\cos \theta)^2 + 6 \cos \theta - 1] / 4$$

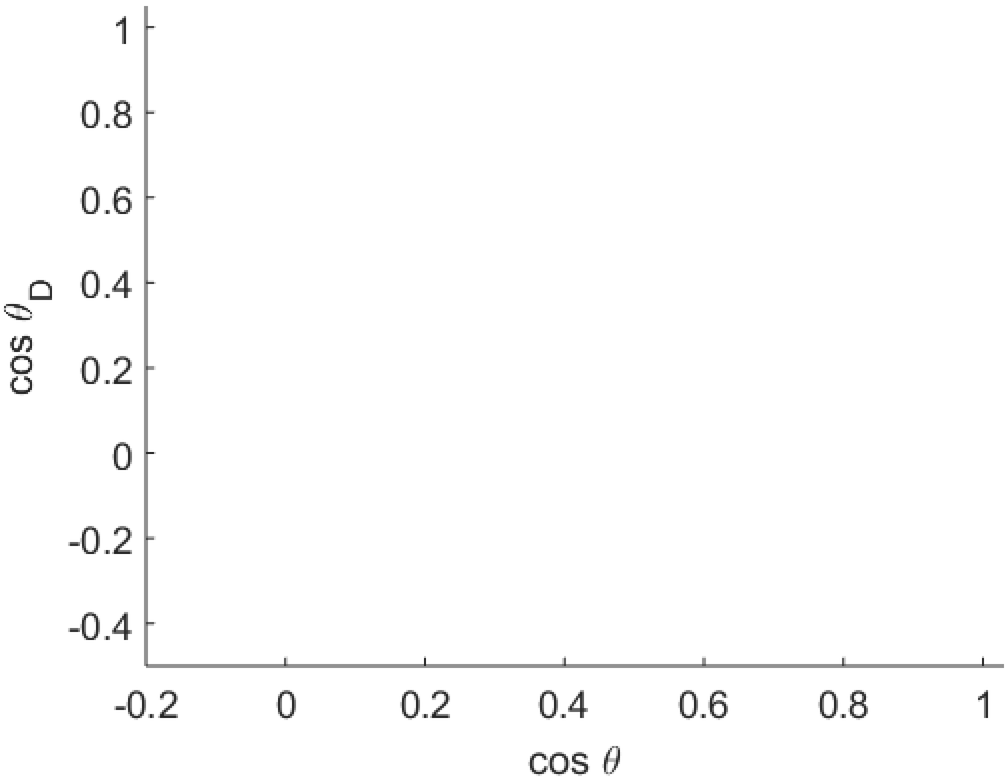
(when $\theta > 117.7^o$, $\theta_a = 180^o$)

Receding contact angle θ_r

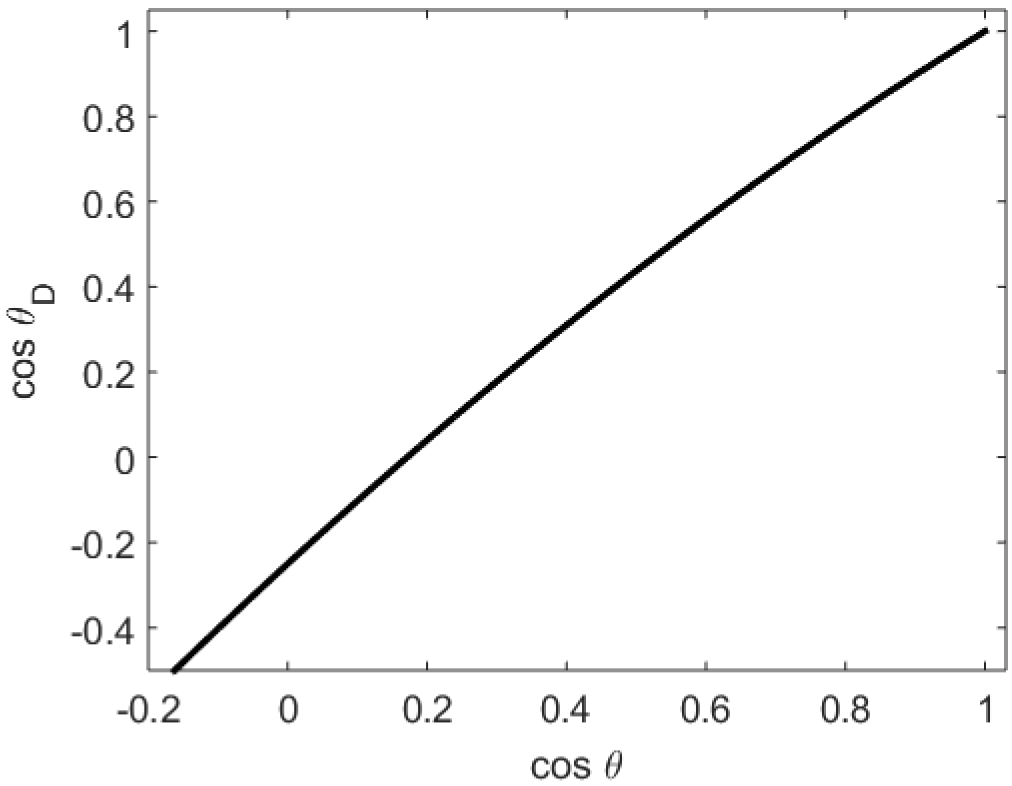
$$\cos \theta_r = [(\cos \theta)^2 + 6 \cos \theta + 1] / 4$$

(when $\theta < 62.3^o$, $\theta_r = 0^o$)

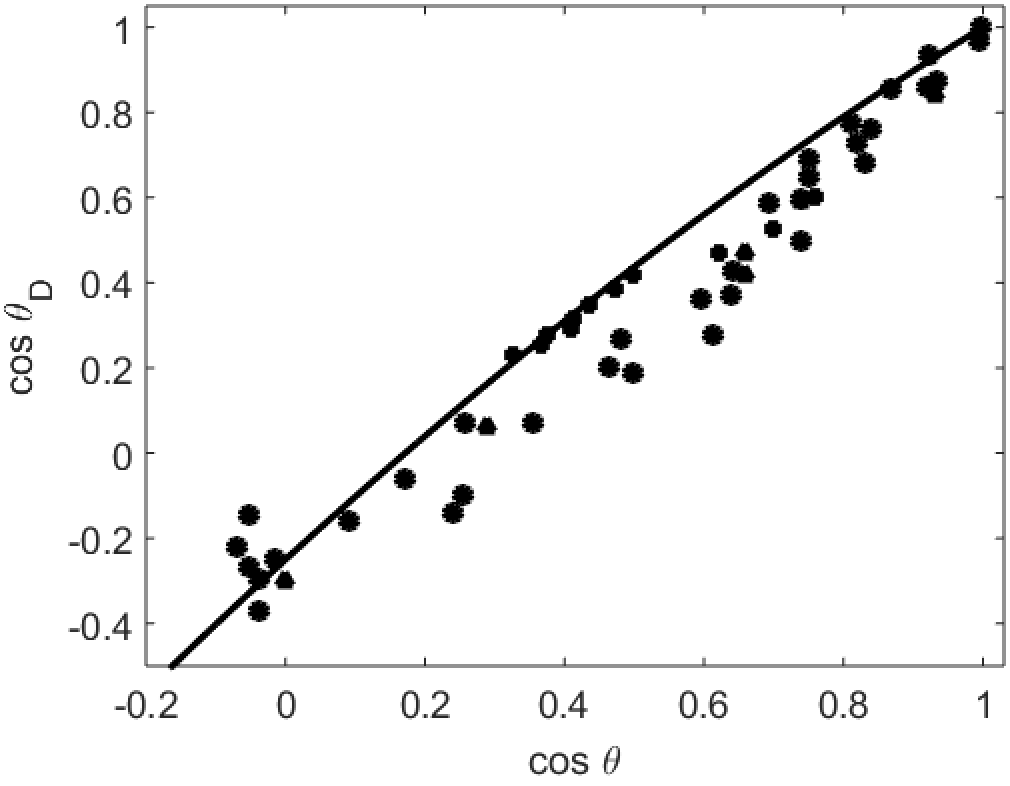
Dynamic contact angles



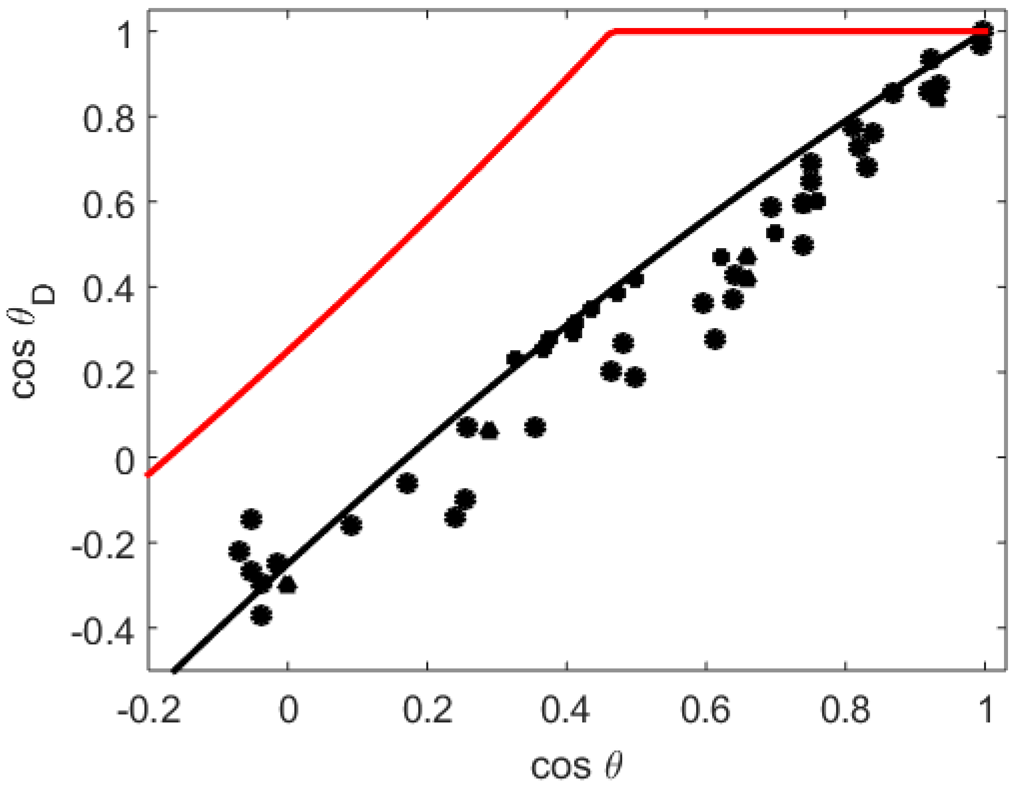
Advancing θ_a



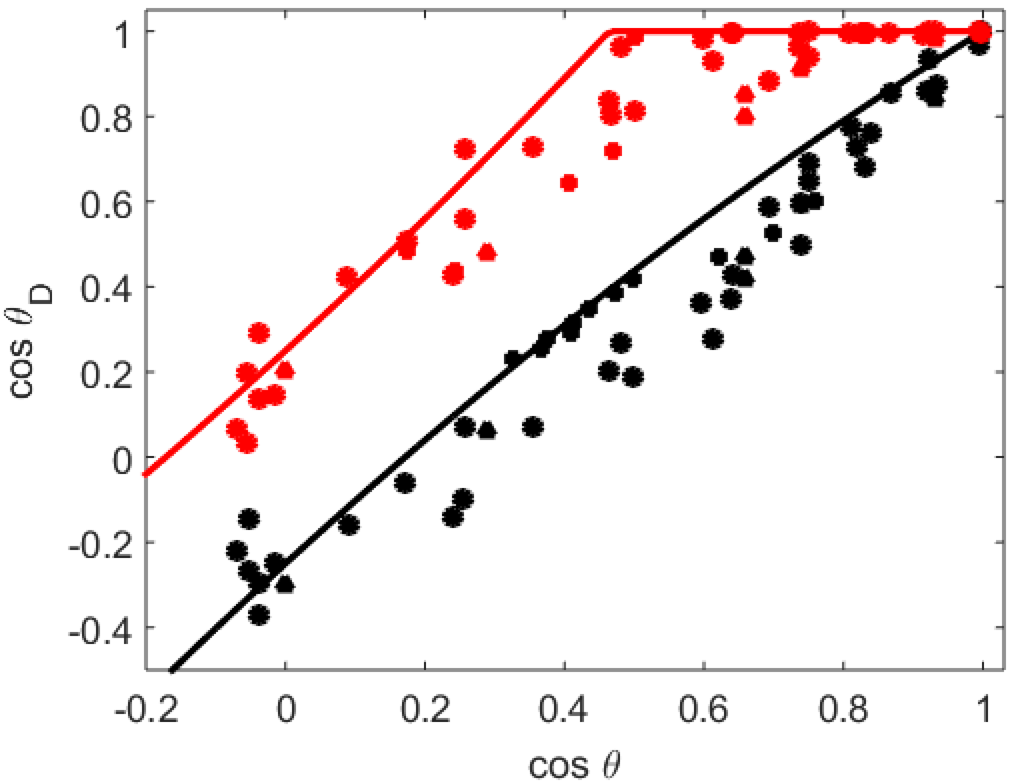
Advancing θ_a



Receding θ_r



Receding θ_r



Miyama et al. 1997. *Langmuir* 13, 5494-5503.

Lam et al. 2002. *Adv. Colloid Interface Sci.* 96, 169-191.

Rough surface

On a hydrophilic solid (Wenzel state) $H^R = r\,H$, where r is the ratio of the total surface area of the solid to its apparent area ($r > 1$). =>

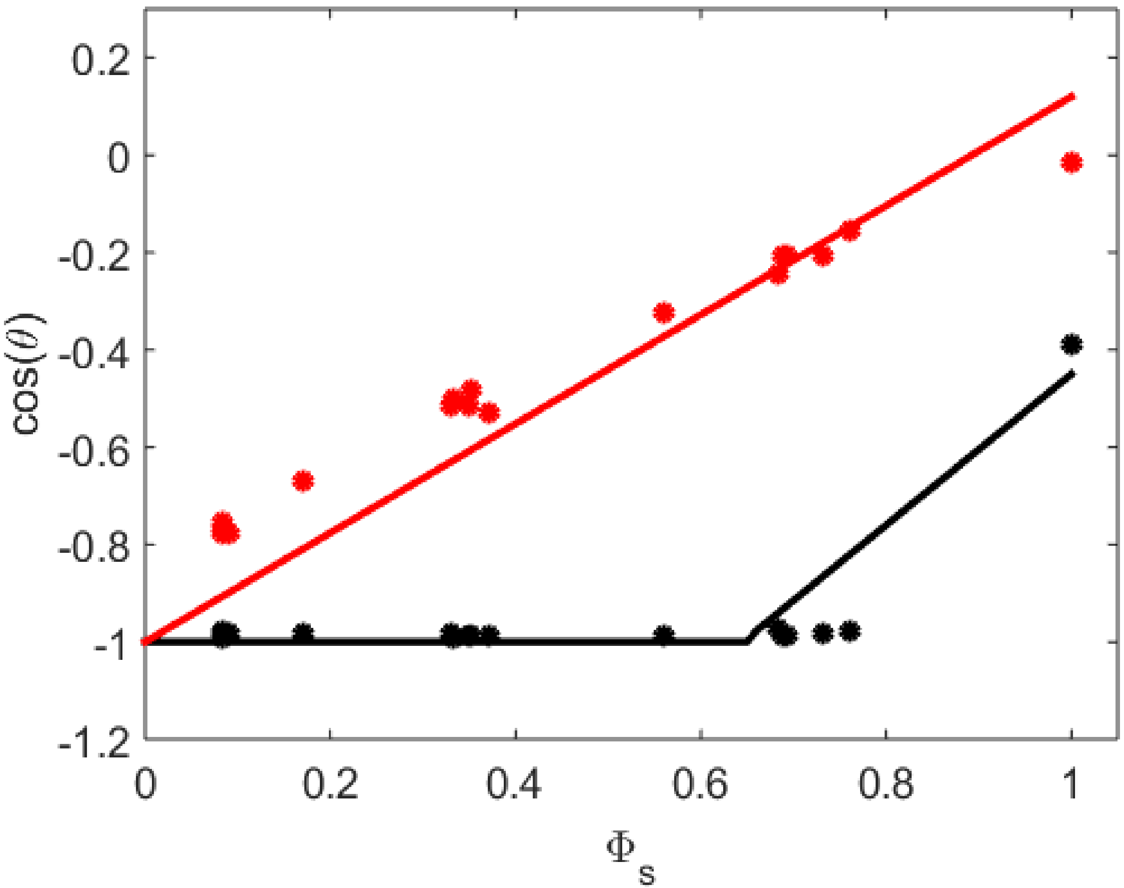
Increasing roughness *increases* the hysteresis.

On a hydrophobic solid (Cassie state)

$H^R = \Phi_s\,[((\cos\theta)^2 + 6\cos\theta + 5) / 4]$, where Φ_s is the fraction of the apparent interface where a solid-liquid contact exists ($\Phi_s < 1$). =>

Increasing roughness *decreases* the hysteresis.

Validation on a rough surface



Cassie factor

RECEDING

ADVANCING

Experimental data from: Koch, A. et al. 2014. *J. Phys. Chem.* C 118, 18554-18563.

Ice adhesion

The thermodynamic work of adhesion W_a is

$$W_a = \Gamma_S + \Gamma_L - \Gamma_{SL}$$

The contact angle hysteresis is

$$H = \Gamma_S + \Gamma_{SL} \quad \Rightarrow \quad W_a = H + \Gamma_L - 2\Gamma_{SL}$$

The relation between the work of adhesion and the adhesion hysteresis is not straightforward. However, it is *solvable by the theory*.

Simpler to use $W_a = (1 + \cos\theta)\,\Gamma_L$

Ice adhesion on a rough surface

The thermodynamic work of adhesion W_a is energy per true surface area, so that the actual work of adhesion depends, not only on the surface energies, but also on

- Morphology of the surface texture
- Size and impact speed of the drops
- Freezing time of the drops
- Contact angle hysteresis!

Thank you!