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Wetting of Interfaces and Tribology

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Lecture: 4/7

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Outline

We will look mainly at the following concepts:

• Contact angles and how to measure them.

• Interfacial energies and how to measure them.

• Adhesion.

• Friction.

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Liquid-Gas Equilibrium

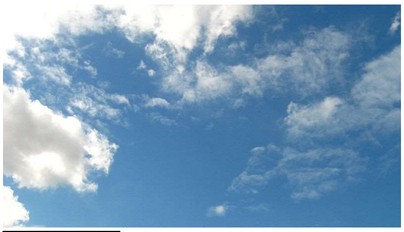
What makes surfaces wet? If we do not pour liquid on them…

Condensation occurs when partial pressure is above equilibrium pressure.

Langmuir equation (another one) determines flux J from partial pressure p at equilibrium.

$$J = [p^*(T) - p]\left[\frac{m}{2\pi k_\mathrm{B} T}\right]^{1/2}$$

Here p^* is the equilibrium pressure of vapor at the given temperature.



Wikipedia: *Sky*

Wikipedia: *Dew*

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Terminology

Interfacial energy (γ) is work (per area) required to increase the area of the boundary of two adjacent phases that do not mix. Relates to solids, liquids and gases.

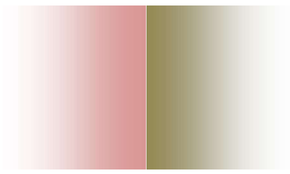
- Solid/gas: surface energy
- Liquid/gas: surface tension

"surfaces"

- Solid/liquid: interfacial tension/energy

"interfaces" also include liquid-liquid and solid-solid

Can also be viewed as a force per distance or "spring constant" ($J/m^2 = Nm/m^2 = N/m$).



phase 1 phase 2

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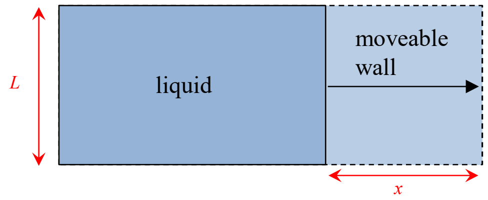
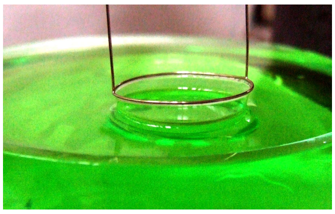
Measuring Surface Tension

Measurements of surface tension can be done directly.

Assume a liquid is placed in a frame with one moveable wall and pulled out. The force required to pull is γL if L is the width. Energy cost of pulling a distance x is simply γLx.

One common device type is the Du Noüy ring which measures the force required to pull up a ring.





Wikipedia: *Tensiometer*

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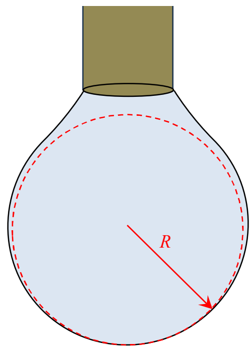
Pendant Droplet

The shape of a dangling droplet depends on the balance between surface tension and gravity.

Derivation of final expression for γ is quite complicated, but handled by the instrument.

Some advantages:

- Smaller volumes needed.
- No particular requirements on the solid material in contact with the liquid.
- Less susceptible to contaminations.



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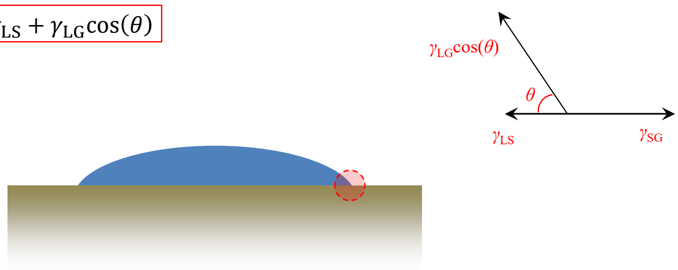
Young's Equation

The static contact angle is defined for a *sessile droplet* resting on the surface.

Assumes gravity can be ignored (small droplet) and no reactions occurring.

Force balance along the surface at the edge:

$$\gamma_{SG} = \gamma_{LS} + \gamma_{LG}\cos(\theta)$$



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Measuring Contact Angle

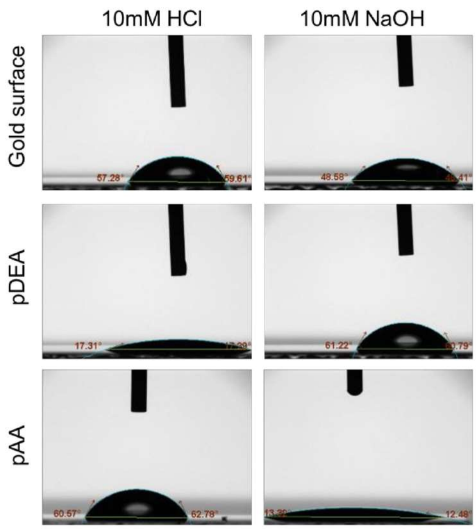
Simply measured optically by a camera.

Droplet volume: a few µL

Size on surface: a few mm

Note that the surface appears perfectly smooth compared with the droplet dimensions.

Still the droplet cannot be too large because we want to avoid gravity effects.



Ferrand-Drake et al.
Journal of Physical Chemistry C **2018**, 122 (48), 27516-27527.

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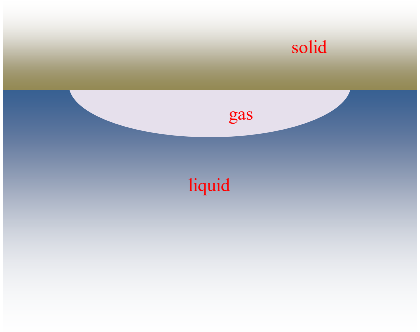
Bubble Method

Look at a bubble on the top surface in a solid container filled with the liquid.

Young's equation is the same!



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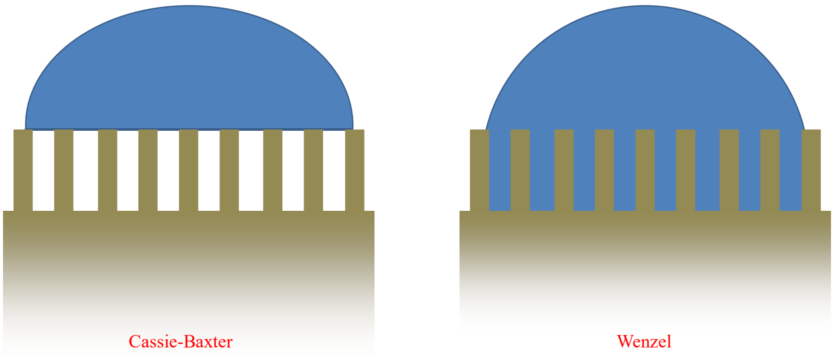
Structured Surfaces

The structure also contributes to wetting behavior!

Cassie-Baxter state: drop rests on top, gas trapped underneath.

Wenzel state: wetting the whole surface.



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Sliding Angle

The plane where the sessile drop is resting is tilted. When does the droplet start to move?

Relevant for some applications like keeping outdoor surfaces free from rain or keeping sprayed paint from running down.

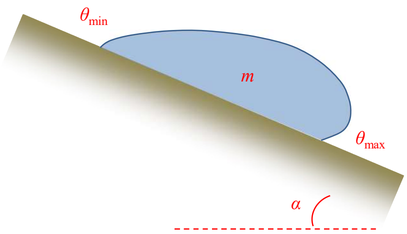
If α is the angle where the droplet starts to move, the gravity pull is equal to the force derived from the different contact angles:

$$mg\sin(\alpha) \propto L\gamma_{\mathrm{LG}}[\cos(\theta_{\mathrm{min}}) - \cos(\theta_{\mathrm{max}})]$$

Here L is the width of the drop.

The mass of the droplet is now important!

Need to know the angles to do something useful with this…



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Dynamic Contact Angles

The contact angle will also be different when the liquid is moving.

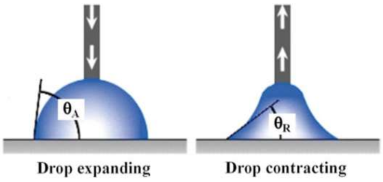
The *advancing* contact angle is "the highest contact angle that can be measured".

The *receding* contact angle is "the lowest contact angle that can be measured".

These angles are not strictly the same thing as θ_{min} and θ_{max} (when tilting), but similar…

Can be captured by videos of sessile droplet spreading.

The dynamic contact angles do not only depend on surface tension, but also viscosity!



Wilhelmy Plate

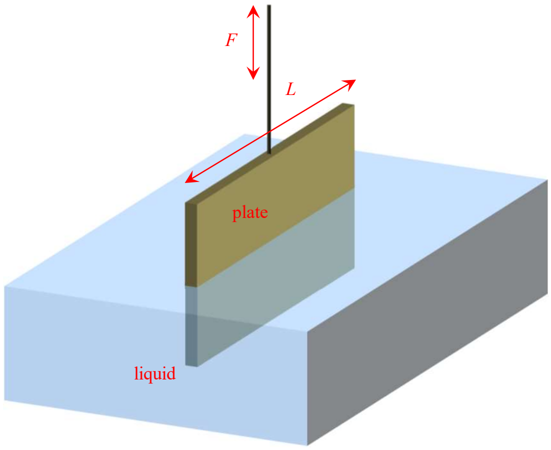
Measure advancing and receding contact angles from force when dipping and pulling out:

$$F_a = 2L\gamma_{LG}\cos(\theta_a)$$

$$F_r = 2L\gamma_{LG}\cos(\theta_r)$$

But this is indirect, you cannot see the angle!

Also requires γ_{LG} first!



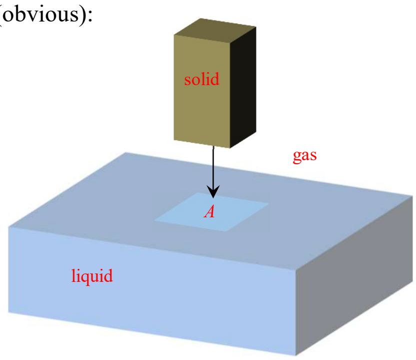
Work of Adhesion

The *work of adhesion* W_{ad} between a solid and a liquid is defined from the interfacial/surface tension/energy. According to Dupré (obvious):

$$\frac{W_{ad}}{A} = \gamma_{LS} - \gamma_{LG} - \gamma_{SG}$$

This can be combined with Young's equation:

$$\boxed{\frac{W_{ad}}{A} = -\gamma_{LG}[1 + \cos(\theta)]}$$



Exactly those quantities we can easily measure!

Interestingly, W_{ad} is always attractive.

For two solid surfaces, W_{ad} depends on distance between them (Lecture 1).

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Berthelot’s Assumption

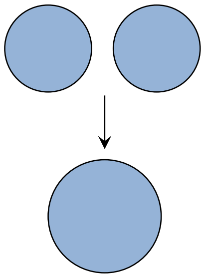
The *work of cohesion* W_{co} is the work of adhesion when bringing two identical materials into contact. For two liquid droplets:

$$\frac{W_{co\ LG}}{A} = -2\gamma_{LG}$$

Berthelot proposed that the work of adhesion can be written as the <u>geometric</u> mean of the works of cohesion for the solid and the liquid:

$$W_{ad} = -\sqrt{W_{co\ LG} \times W_{co\ SG}}$$

Why this is believable remains unclear…



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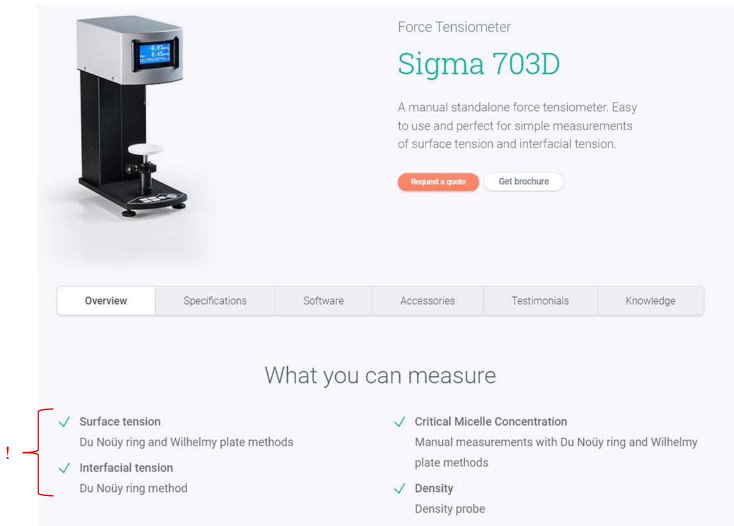
Liquid-Liquid Interfacial Tension

Can be measured?



Biolin scientific
https://www.biolinscientific.com/

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Surface Energy

The surface energy cannot be measured so easily! Using Young's equation does not help directly because the solid-liquid interfacial energy (γ_{SL}) is needed as well.

Combining Berthelot with Dupré we can get:

$$2\sqrt{\gamma_{LG}\gamma_{SG}} = -\gamma_{LG}[1 + \cos(\theta)]$$

Again, surface tension and contact angle are directly measurable, so γ_{SG} is possible to calculate, but it requires that one believes the assumption underlying this equation.

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The OWRK Method

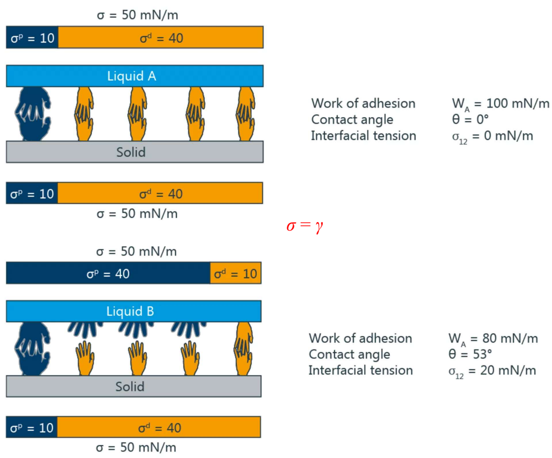
A more detailed measurement of the surface energy is the Owen-Wendt-Rabel-Kaelble (OWRK) method. Fundamental assumption: there are many <u>additive</u> contributions to the surface energy. We can split them into *polar* and *dispersive*:

$\gamma = \gamma_d + \gamma_p$

This applies to all the different γ.

The polar forces originate from permanent dipoles and charges, while the dispersive forces are temporary fluctuations (essentially van der Waals forces).

The OWRK method aims to determine both contributions to the surface energy: $\gamma_{d\,SG}$ & $\gamma_{p\,SG}$



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OWRK Theory

Let us go back to the definition of W_{ad} and Berthelot:

$$\gamma_{LS} = \gamma_{LG} + \gamma_{SG} + \frac{W_{ad}}{A} = \gamma_{LG} + \gamma_{SG} - \frac{\sqrt{W_{co\,LG} \times W_{co\,SG}}}{A} = \gamma_{LG} + \gamma_{SG} - \frac{\sqrt{-2A\gamma_{LG} \times -2A\gamma_{SG}}}{A} = \gamma_{LG} + \gamma_{SG} - 2\sqrt{\gamma_{LG}\gamma_{SG}}$$

Now we assume this relation holds "separately" for both dispersive and polar interactions:

$$\gamma_{d\,LS} = \gamma_{d\,LG} + \gamma_{d\,SG} - 2\sqrt{\gamma_{d\,SG} \times \gamma_{d\,LG}}$$

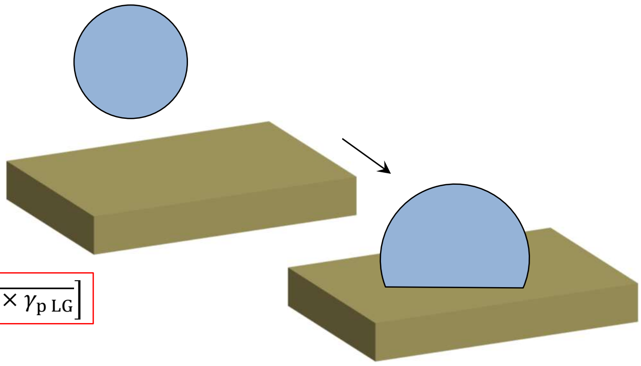
$$\gamma_{p\,LS} = \gamma_{p\,LG} + \gamma_{p\,SG} - 2\sqrt{\gamma_{p\,SG} \times \gamma_{p\,LG}}$$

Combining the contributions we can write:

$$\gamma_{LS} = \gamma_{LG} + \gamma_{SG} - 2\left[\sqrt{\gamma_{d\,SG} \times \gamma_{d\,LG}} + \sqrt{\gamma_{p\,SG} \times \gamma_{p\,LG}}\right]$$

We throw in Young's equation again:

$$\left[\gamma_{d\,LG} + \gamma_{p\,LG}\right]\left[1 + \cos(\theta)\right] = 2\left[\sqrt{\gamma_{d\,SG} \times \gamma_{d\,LG}} + \sqrt{\gamma_{p\,SG} \times \gamma_{p\,LG}}\right]$$



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OWRK Data

Use liquids with known values of $\gamma_{d\,LG}$ & $\gamma_{p\,LG}$ that are ideally very different to cover a broad range.

Br_2: $\gamma_{d\,LG}$ = 33 mN/m, $\gamma_{p\,LG}$ = 3 mN/m

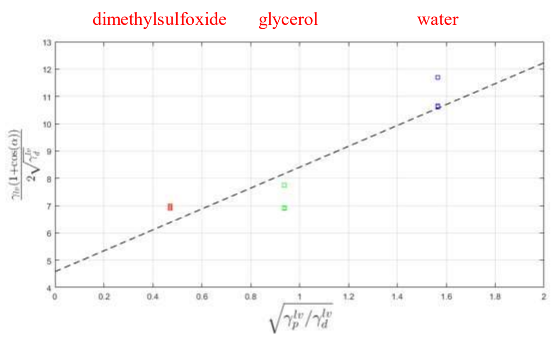
EtOH: $\gamma_{d\,LG}$ = 16 mN/m, $\gamma_{p\,LG}$ = 50 mN/m

Results are normally presented as a plot:

$$y = \frac{\left[\gamma_{d\,LG} + \gamma_{p\,LG}\right]\left[1 + \cos(\theta)\right]}{2\sqrt{\gamma_{d\,LG}}} \qquad x = \sqrt{\frac{\gamma_{p\,LG}}{\gamma_{d\,LG}}}$$

Fitting a straight line gives the surface energies from:

$$y(x = 0) = \sqrt{\gamma_{d\,SG}} \qquad \frac{\partial y}{\partial x} = \sqrt{\gamma_{p\,SG}}$$



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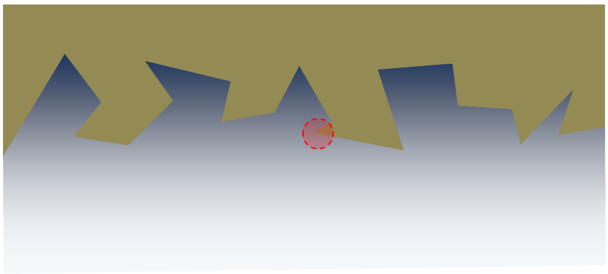
Adhesion

Mechanical adhesion: Attachment by cavities in the surface structure.

Can be achieved by a glue that solidifies, great on rough surfaces like wood.
(But not all glues work like this!)

We are more interested in adhesion due to chemical bonds or surface forces.



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Adhesion Tests

Adhesion is in the end a measure of energy per area. Important for glues and protective coatings.

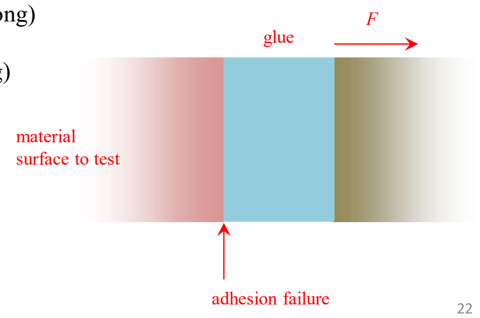
Measure by integrating force-distance curve when pulling things apart from each other.

Can also be measured with shear stress for coatings like paints etc.

Adhesive failure: the glue detaches (hopefully after much force is applied)

Cohesive failure: the glue breaks within (not great, but adhesion is strong)

Substrate failure: material breaks inside (adhesion and glues are strong)

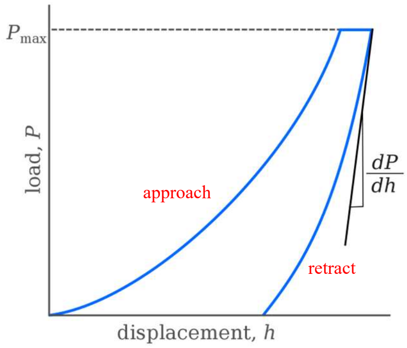


Indentation Measurements

An *nanoindentation* instrument can be used to measure mechanical properties (modulus and plasticity).

By looking at different positions, the uniformity of the sample can be investigated.

However, tip properties will influence the results!

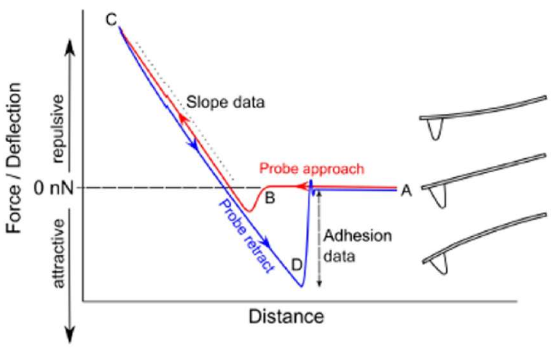


Wikipedia: *Nanoindentation*

AFM to Test Mechanical Properties

AFM operation by indentation mode measures interactions on an even smaller scale.

Here the tip itself will greatly influence the results and that is usually the whole point!



Tribology

Tribology is the study of friction and surface wear.

Extremely important for industry to increase lifetime of mechanical components.

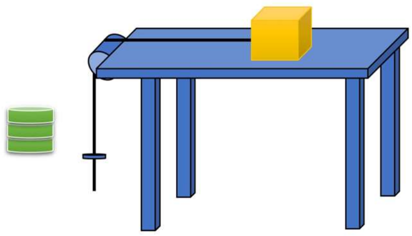
Lubrication is generally the way to reduce friction.

The *breakaway force* is when the object starts to move.

The friction coefficient μ is given by:

$$F_f = \mu F_n$$

Determined by surface properties, in particular *roughness*.



Roughness

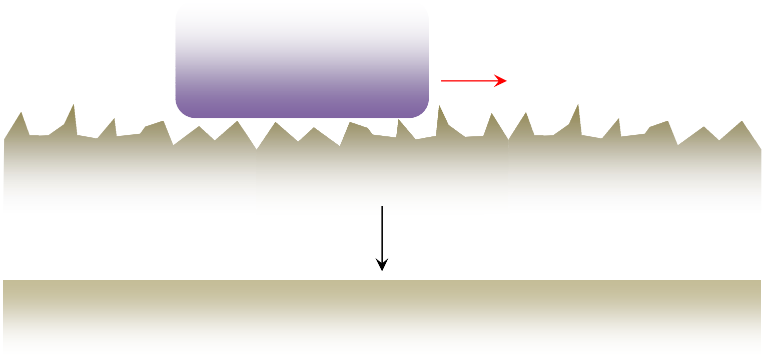
Surface roughness is characterized by two parameters: a spatial frequency and a magnitude.

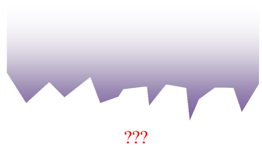
Sometimes only a magnitude is reported!

Measure by *profilometer* or AFM.

Polishing

You have to polish with a flat and hard tool to make sure you do not increase the roughness instead!

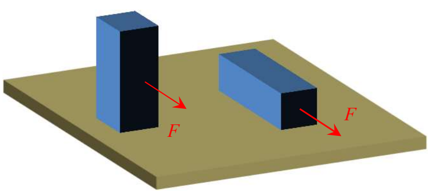


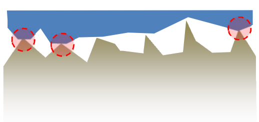


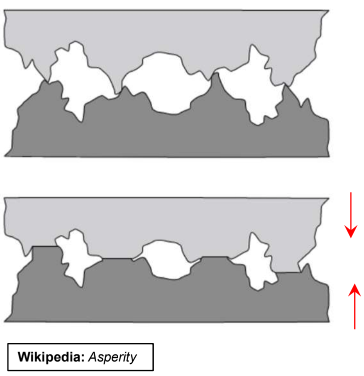
Why no Area Dependence?

The friction force is not influenced by the contact area, only the normal force (Amontons 1699). Why?

Actually the “real” contact area (atomic contact points) is the same for the same load.



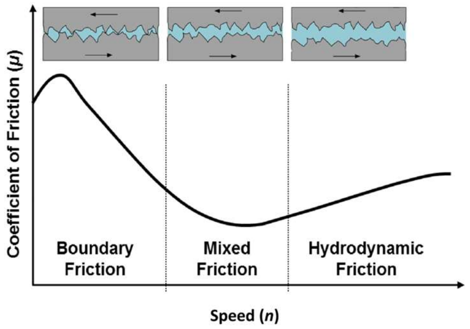




Stribeck Curves

Lubricated systems behave in a completely different manner. At sufficiently high speed there is no more surface contact.

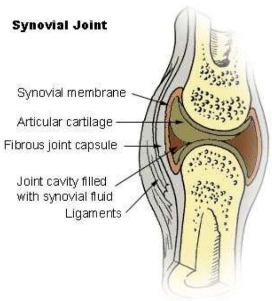
The friction as a function of speed can also depend on <u>acceleration</u>, so there is no generic curve even for a specific system.



Biological Friction

Joints are lubricated with *synovial fluid* to reduce wear on bones.

Problems lead to *arthritis*: swollen and stiff joints (many different types).



Wikipedia: *Synovial fluid*

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Checklist 4

- Measuring surface tension, surface energy and interfacial energy
- Measuring contact angles, static and dynamic
- Work of adhesion
- OWRK method
- Adhesion tests
- Surface roughness
- Stribeck curves

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Exercise 4.1

Derive Young's equation for the case of a bubble instead of a droplet!
The contact angle is inside the liquid phase.