Surface Energy

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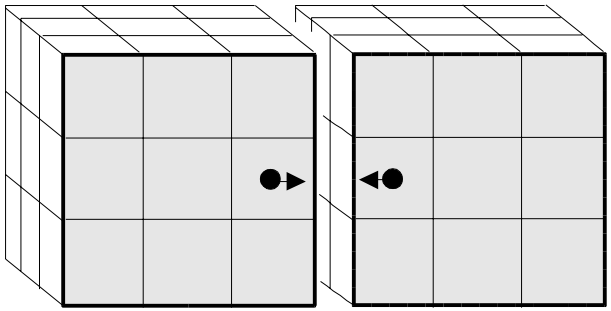
The **work** W_{11} to bring two **identical ideal surfaces** in vacuum together is related to the **surface energy** γ_1 of the material:

$$W_{11} = -2\,\gamma_1$$ (normalized to unit area!)

W_{11} corresponds to to the work of **cohesion** in an ideal case and is normalized to the area of the surfaces. This **work** should be identical to **separating** a body into two halves. In reality the separation process is irreversible (due to energy dissipation), thus the separation / cohesion work is larger than the surface energy.

$\Rightarrow$ high surface energy $\leftrightarrow$ strong cohesion $\rightarrow$ high boiling point...

$\Leftarrow W_{11} \Rightarrow$



about 1/6 new surface per structure element in the cleavage plane

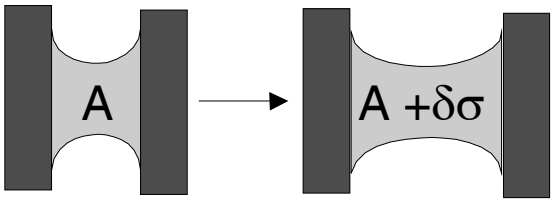
substrate material	*surface energy* γ *(mJ m^{-2})*
mica	4500
gold	~1000
PTFE	19
OTE (octadecane surface)	28

$\Rightarrow$ **high energy surfaces** tend to **reduce** energy by **adsorption** of **contaminants** from environment !

Surface Tension

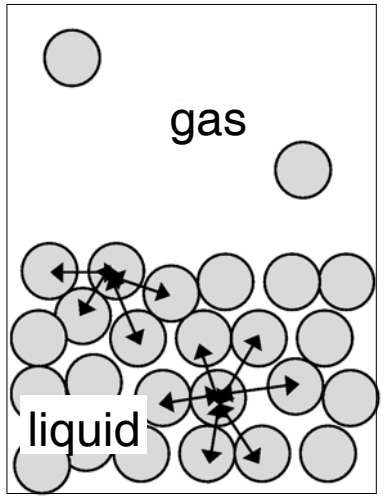
Surface tension γ is defined by the infinitesimal work dw required to increase the surface by an infinitesimal area $d\sigma$:

$$dw = \gamma \, \delta\sigma$$



→ work has to be applied to increase surface, since liquids tend to minimize their surface (spherical droplet)

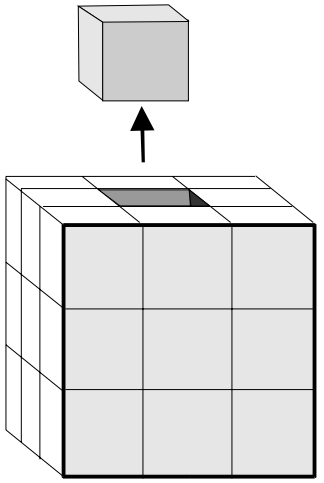
→ force balance



→ surface tension of liquids corresponds to surface energy of solids

→ surface tension / surface energy correlates to evaporation enthalpy ΔH_{vap} (approximation)

material	γ *(mN m^{-1})*	ΔH_{vap} *(kJ mol^{-1})*
C_6H_6	28.8	30.8
MeOH	26.6	35.3
H_2O	72.7	40.7
Hg	472	59.3



~ 5/6 new surface per structure element

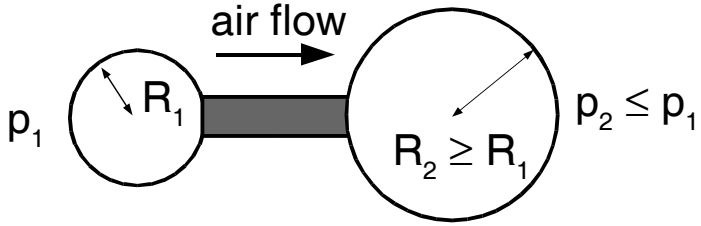
Measuring Surface Tension

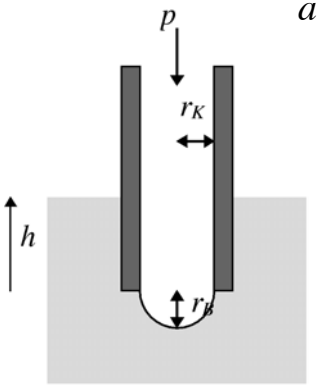
The **Young–Laplace equation** describes the **pressure difference** Δp between the inside and the outside of a **curved object** (bubble, droplet, cavity) with radius r_a and r_b ($r_a \perp r_b$, in symmetric geometry $r = r_a = r_b$) with respect to the **surface tension** γ :

$$\Delta p = \gamma \left(\frac{1}{r_a} + \frac{1}{r_b} \right)$$

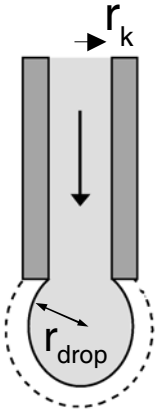
or in terms of internal pressure:

$p_{in} = p_{out} + 2\gamma / r$



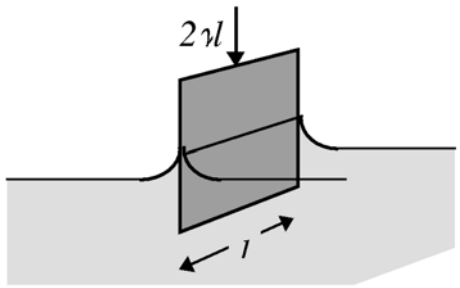


a) maximum bubble pressure method: a gas is pressed through a capillary with radius r_K till the cavity reaches $r_B = r_K \rightarrow \gamma = r_K \Delta p / 2$ with $\Delta p = p_{bubble} - h \rho g$ (hydrostatic pressure, ρ: densiy of liquid, g: gravitational constant)



b) drop weight method: maximum drop size before release $m_{drop}\, g = 2\pi\, r_k\, \gamma$ with weight of drop m_{drop}

$\Rightarrow$ $4/3\, \pi\, r_{drop}\, \rho_{liq}\, g = 2\pi\, r_k\, \gamma$

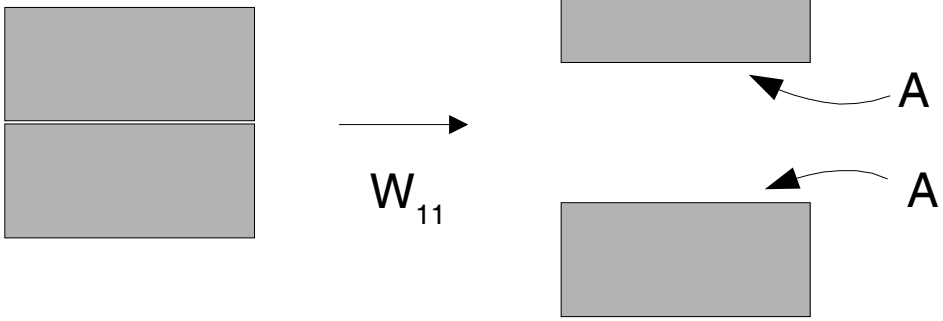


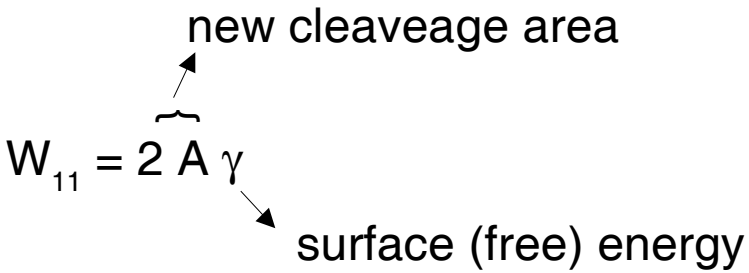
c) Wilhelmi plate method: force F (in addition to gravitational force) on a plate with width l partially immersed into a liquid $F = 2l\, \gamma$

Cohesion

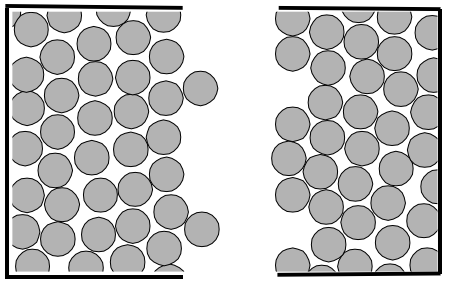
Cohesion forces act **within** a **condensed material** (liquid, solid) to keep it together.

work of cohesion W_{11}: free energy change, or reversible work done, to cleave / separate a material from contact to infinity in vacuum

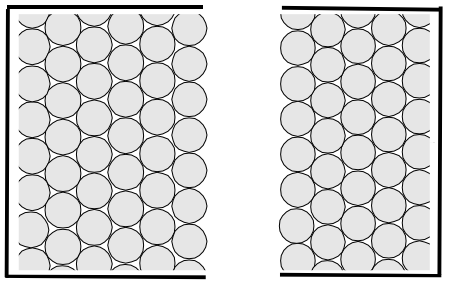




– cohesion in amorphous solids and liquids is isotropic:
→ random fracture plane (e.g. glass)

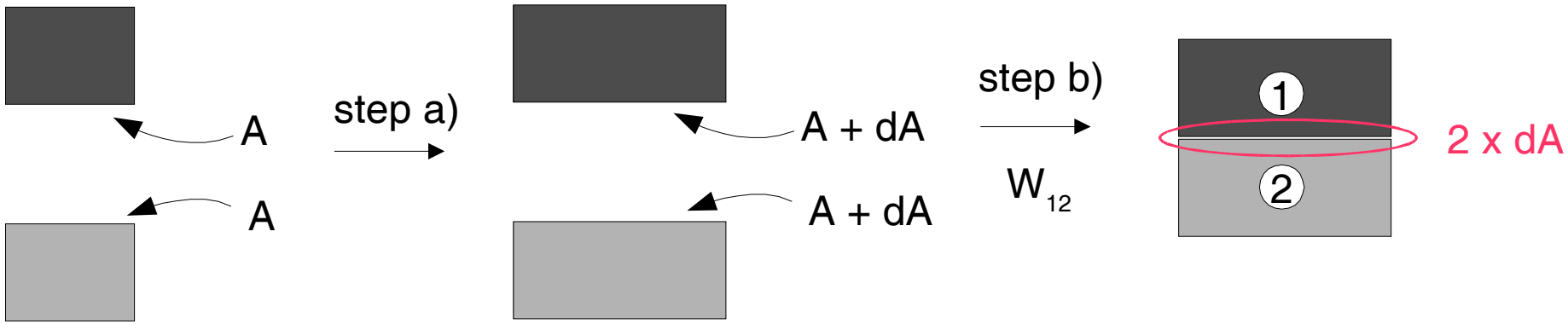


– cohesion in crystalline solids is anisotropic:
→ fracture along crystal planes (e.g. Si single crystal wafer)



Adhesion

The **adhesion** forces act **between** the **surfaces** of two **different** condensed bodies **in contact.**



Dupré equation: total free energy change corresponds to interfacial energy γ_{12}

surface energies 1 and 2

$$\gamma_{12} = \gamma_1 + \gamma_2 - W_{12}$$

work of adhesion

$\rightarrow$ this process can be split into two hypothetical steps:

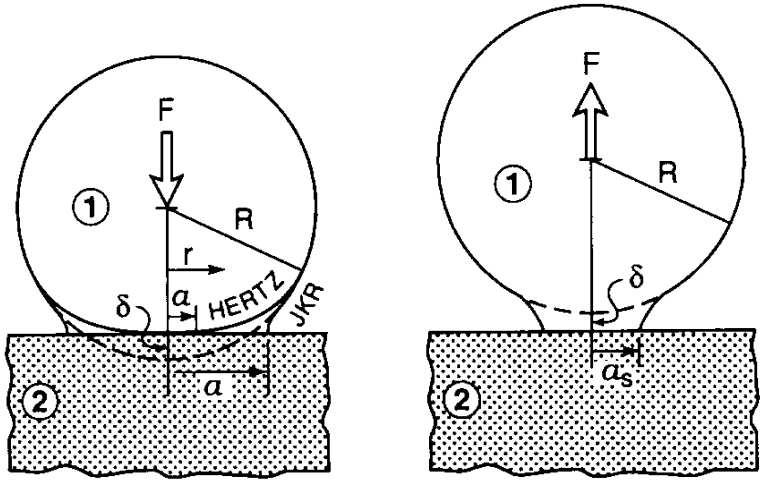
a) generate new surface for materials 1 and 2 in vacuum: $W = \gamma_1 + \gamma_2$ (normalized to unit area!)

b) bring two new surfaces into contact (work of adhesion): W_{12}

$\Rightarrow$ since all media attract each other (assuming neutral total charge) in vacuum: work of cohesion (W_{11}) and work of adhesion (W_{12}) are always positive (work is required to separate material)!

Measurement of Adhesion

– **microscopic:** the Hertz and JKR (Johnson, Kendal, Roberts) models



Hertz: sphere on surface in vacuum, no adhesion, only elastic deformation

→ contact radius (γ_{12} = 0 J m^{-2}):

$$a = \sqrt[3]{\frac{RF}{K}}$$

K : elastic modulus of sphere

⇒ can be measured in the surface force apparatus (SFA)

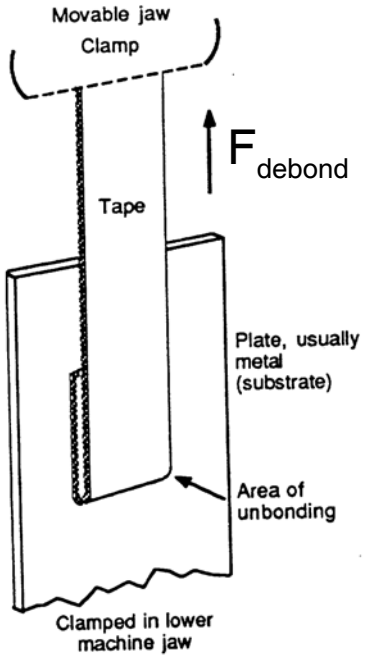
JKR: sphere on surface in vacuum, adhesive deformation contact radius

→ contact radius:

$$a_0(F = 0\,N) = \sqrt[3]{\frac{12\pi R^2 \gamma_{12}}{K}}$$

pull–off force:

$F_s = -3\pi R\,\gamma_{12}$

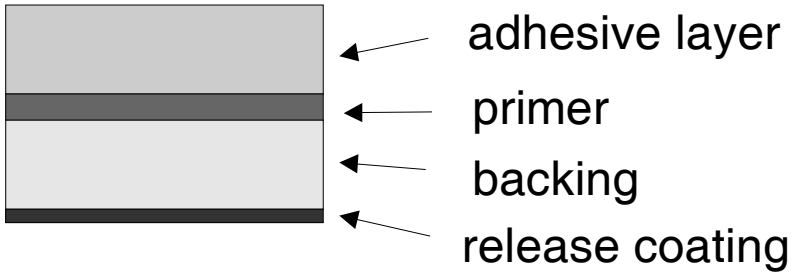


– **macroscopic:** peel–adhesion test → adhesive tape testing

adhesive tape is applied to hard surface under specific conditions and removed at specified rate and angle (180°)

→ force for debonding process is measured F_{debond}

Practical Example: Adhesive Tape



tack: in adhesives tack describes the property to bond at moderate applied pressure (tack involves both, 1. bonding and 2. debonding step)

adhesion layer: – base elastomer (rubber, polyacrylates, block copolymers), high M_w, low T_g (below RT)
– tackifiers (rosin, terpenes, hydrocarbon resins), low M_w (300–3000 g/mol), high T_g (> RT)

primer: increases adhesion ($\rightarrow$ covalent bonding) of adhesive layer to backing (phenolic elastomer resins, corona–treatment, chlorinated polyolefins)

backing: supports adhesive layer, mechanical strength (paper, polypropylene)

release coating: reduces adhesion of adhesive layer and allows release of rolled up tapes etc. (silicones, alkyds, stearyl derivatives of vinyl polymers)

physical parameters determining adhesion properties:
- **tack**: immediate "bond" formation upon contact with surface
- **adhesion**: force required to remove adhesive tape / "break bond" $\rightarrow$ depends on debonding process
- **cohesion**: internal mechanical strength that holds adhesive layer (and whole tape structure) together