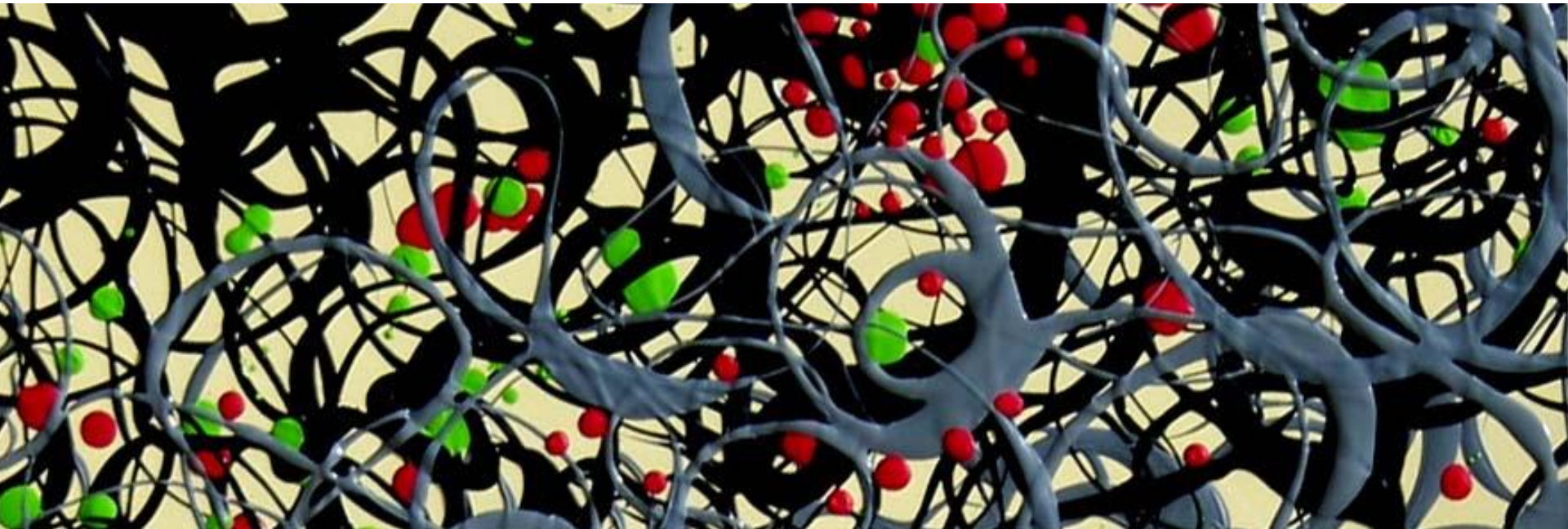


# Nanostructured Materials and Nanotechnology



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# ***SURFACES & INTERFACES AT THE NANOSCALE***

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# Interfaces at the nano-scale

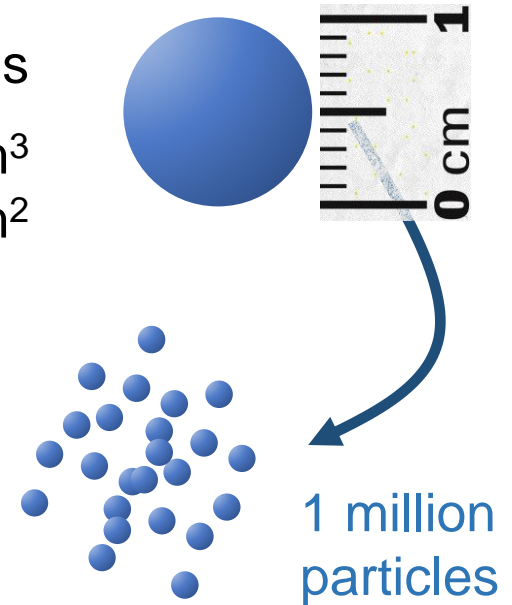
*The surface of an object becomes increasingly important as its size decreases*

Consider a spherical particle of 5 mm radius

volume  $\approx 0.5 \text{ cm}^3$

Area  $\approx 3.1 \text{ cm}^2$

Number of particles	Particle radius	Total area
1	5 mm	$3.1 \text{ cm}^2$
$10^6$	5 $\mu\text{m}$	$310 \text{ cm}^2$



# Surface Energy

Atoms at the surface have fewer bonds than atoms in the bulk

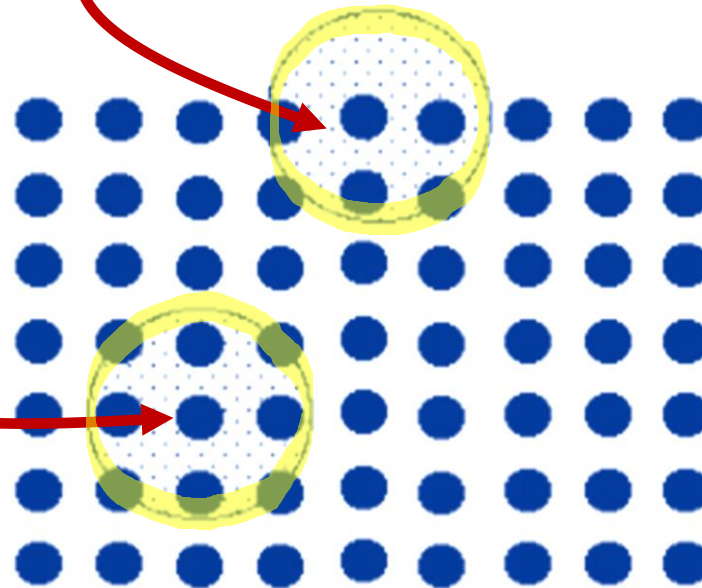
**In bulk, atoms are evenly surrounded by other atoms**

Cohesive forces between the atoms tend to balance

The energy of surface atoms is higher: this extra energy per unit area is the **Surface Energy**

**On the surface there are atoms on one side only**

There is a net inward force that tends to minimize the objects area



$$\gamma = \frac{1}{2} n_a n_b \varepsilon$$

$n_a$  – atoms/unit area

$n_b$  – bonds broken/atom

$\varepsilon$  – bond energy



# Surface Energy at the nano-scale

Surface energy & huge surface area

⇒ **Increased Reactivity**

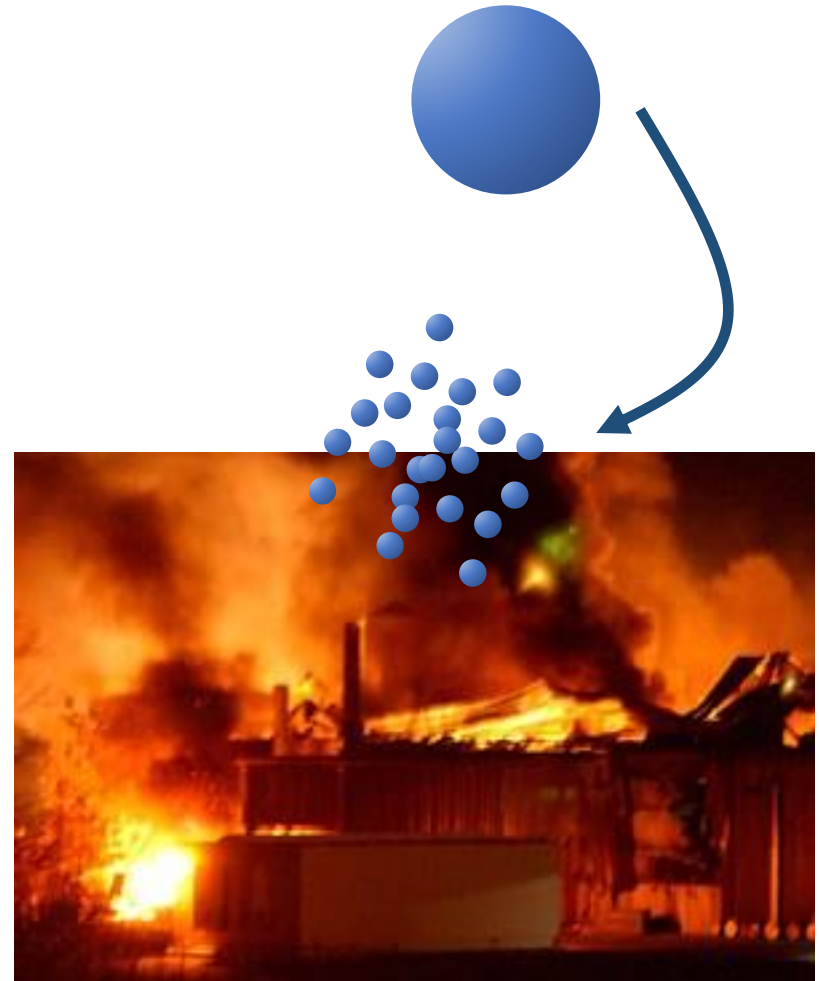
Examples:

***Catalysis with metal nanoparticles***

***Powder ignition*** - hazard in underground coal mines, grain elevators, and industrial environments processing powder material

*Oct 5, 2005*

*CSB determines fatal 2003 incident at Hayes Lemmerz plant in Indiana most likely caused by explosion in aluminum dust collection system*



# Surface Energy minimization

In **amorphous materials**, surface energy minimization is achieved by reducing the surface for a given volume

→ **spherical shape**

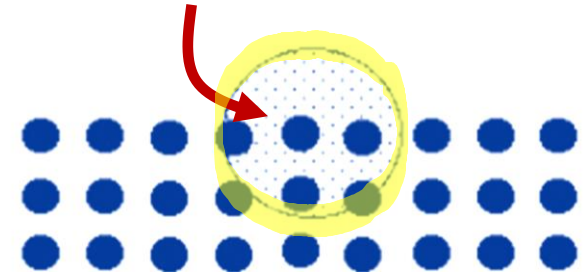
In **crystalline materials**, each crystal plane has a different value of surface energy

*For a crystal to assume a spherical shape, high energy planes would be exposed*

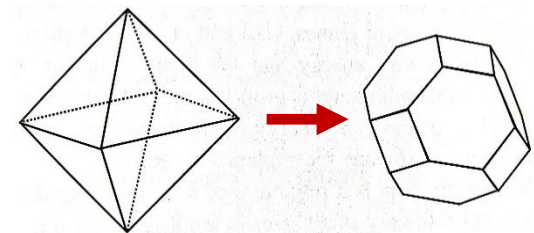
The equilibrium shape of the nanocrystal is obtained by minimizing both the exposure of higher energy planes and the total surface area

On the surface there are atoms on one side only

There is a **net inward force** that tends to minimize the surface area

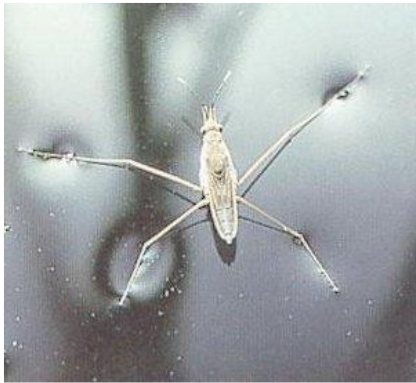


**Wulff construction approximation:** a set of vectors is drawn from a common point in directions which are normal to the different crystal planes, the length of which is proportional to the surface energy of the corresponding plane



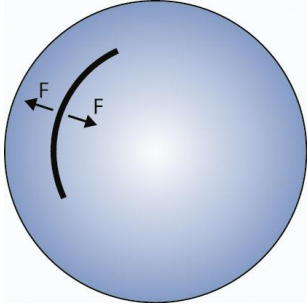
# Liquid-vapor interface

At the liquid–vapor interface the Surface Energy (energy per unit area) is called **Surface Tension**



Surface tension of liquids on air	
	$\gamma \times 10^3 \text{ (Nm}^{-1}\text{)}$
Liquid Helium (-269 °C)	0.12
Liquid Nitrogen (-183 °C)	6.6
Ethanol (20 °C)	22.8
Water(20 °C)	72.8
Water(100 °C)	59
Water with soap (20 °C)	~25
Blood (37 °C)	58
Mercury (20 °C)	440
Silver ( $T_f^0$ )	966
Iron ( $T_f^0$ )	1872

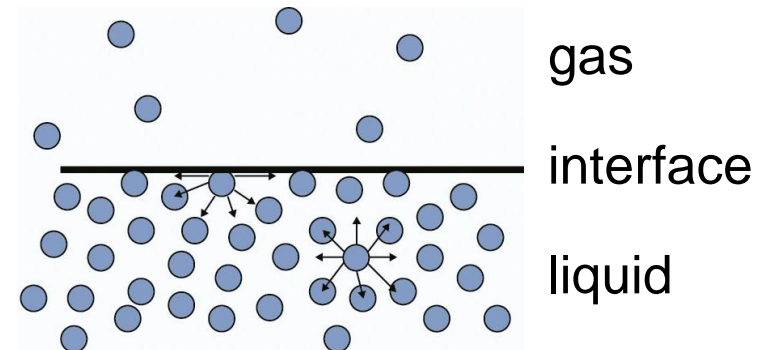
**Surface tension:** *force per unit length* acting tangentially to the surface, perpendicular to an element  $\delta x$  on the surface.



$$\gamma = \frac{F}{\delta x}$$

## Molecular origin of surface tension

- Intermolecular forces acting on the liquid phase are isotropic.
- Molecules at the surface are subject to a resulting force towards the liquid phase

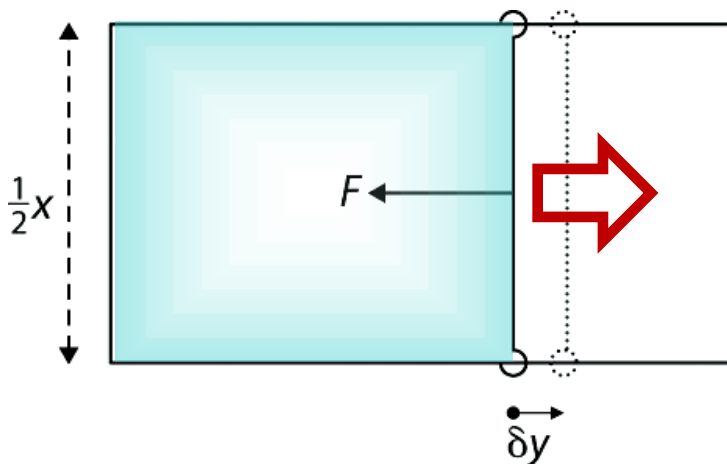


**The system tends to minimize the surface area**



**Surface tension:** *energy per unit area* to modify the surface area

Example: liquid film supported on wire frame



Contact between the film and the wires in the direction of deformation :  $2 (\frac{1}{2} x)$

Force due to surface tension opposing the increase in area:

$$F = \gamma x$$

Work for extension of the surface:  $w = F \delta y$

$$\delta A = x \delta y \quad (\text{change in area})$$

$$w = \gamma \delta A$$

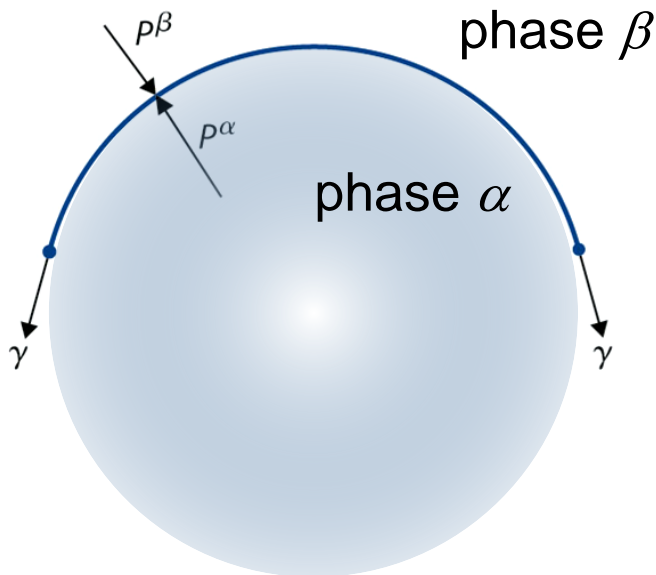
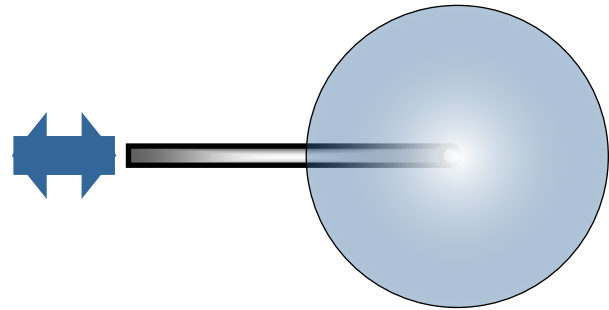
**Surface tension:** *work of extension per unit area* to deform the surface.

$$\gamma = \frac{w}{\delta A}$$

# Surface curvature

The curvature of a fluid interface is associated with a difference in pressure between the two sides of the interface

- It is necessary to increase the pressure to fill the soap bubble
- Opening the tube, the bubble flushes the air to form a planar film at the tube



In equilibrium, the difference in pressure due to the curvature of the interface is balanced by surface tension.

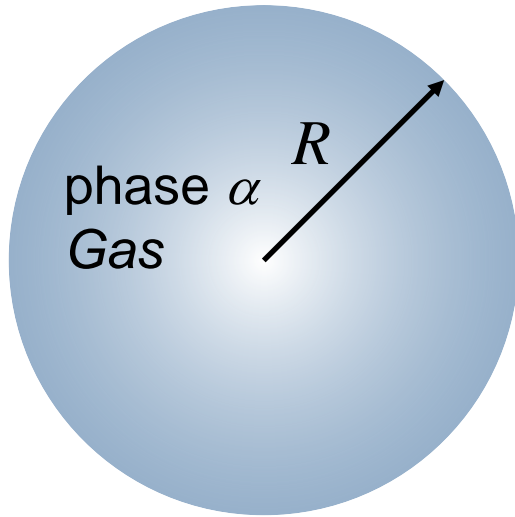
The **difference in pressure** exerted by the  $\alpha$  and  $\beta$  phases on the curved surface creates a force normal to the surface at each point.

The **surface tension** originates a force parallel to the perimeter of the bubble.

The internal pressure of the bubble is higher than its external pressure

phase  $\beta$   
Liquid

$$P^\alpha - P^\beta > 0$$



Work to increase the radius of the bubble by  $dR$

$$dw = (P^\alpha - P^\beta) dV$$

$$dV = 4\pi R^2 dR$$

To increase the surface area by  $dA$

$$dw = \gamma dA$$

$$dA = 8\pi R dR$$

Resulting:  $(P^\alpha - P^\beta) 4\pi R^2 dR = \gamma 8\pi R dR$

$$P^\alpha - P^\beta = \frac{2\gamma}{R}$$

**Laplace Equation** for spherical surfaces

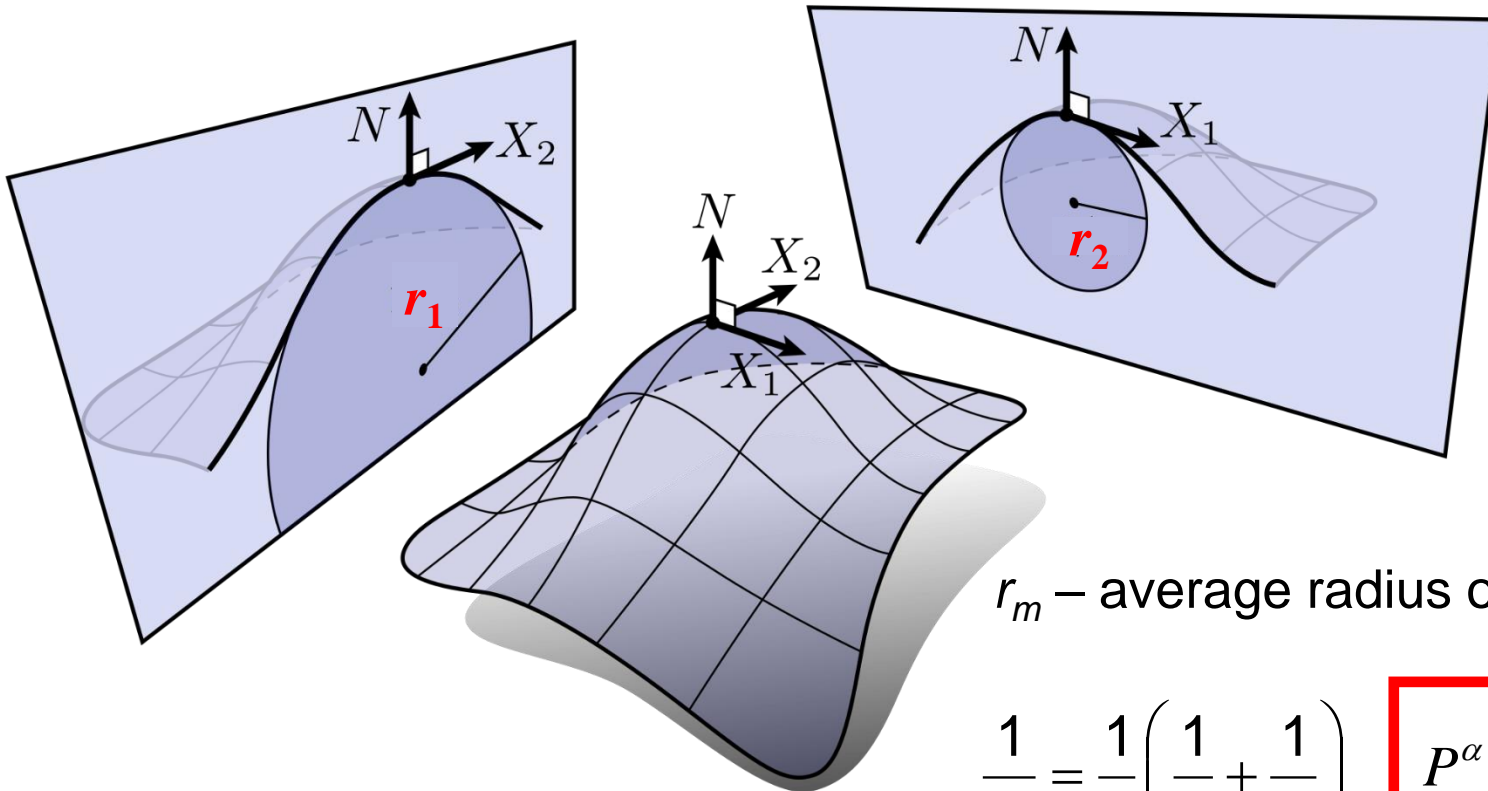
Pierre-Simon,  
Marquis de Laplace, 1749-1827



Non-spherical surfaces are defined by two radii of curvature

$$P^\alpha - P^\beta = \gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$$

**Laplace Equation** for  
non-spherical surfaces

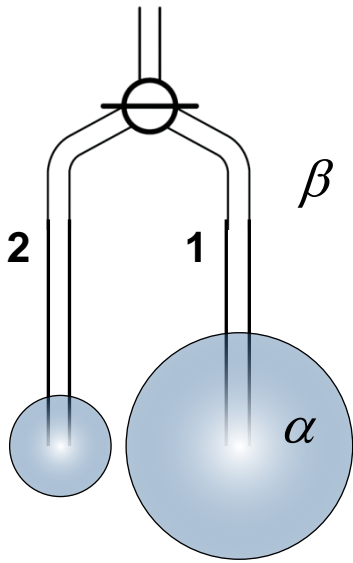


$r_m$  – average radius of curvature

$$\frac{1}{r_m} = \frac{1}{2} \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$$

$$P^\alpha - P^\beta = \frac{2\gamma}{r_m}$$

## Example: Interconnected bubbles of different sizes

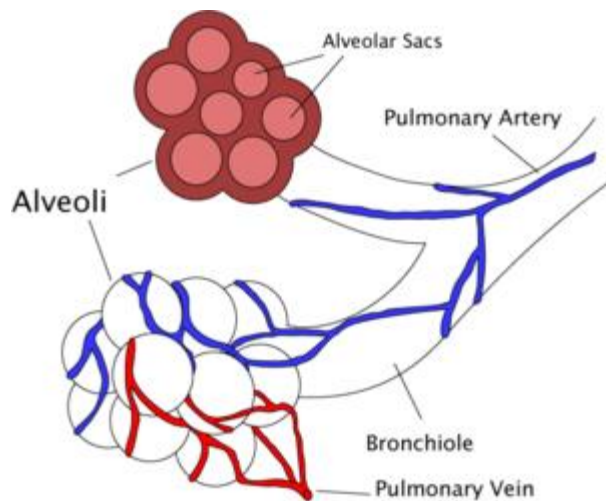


$$P^{\alpha} - P^{\beta} = \frac{2\gamma}{r}$$

$$r_1 > r_2 \Rightarrow P_1^{\alpha} - P^{\beta} < P_2^{\alpha} - P^{\beta} \Rightarrow P_1^{\alpha} < P_2^{\alpha}$$

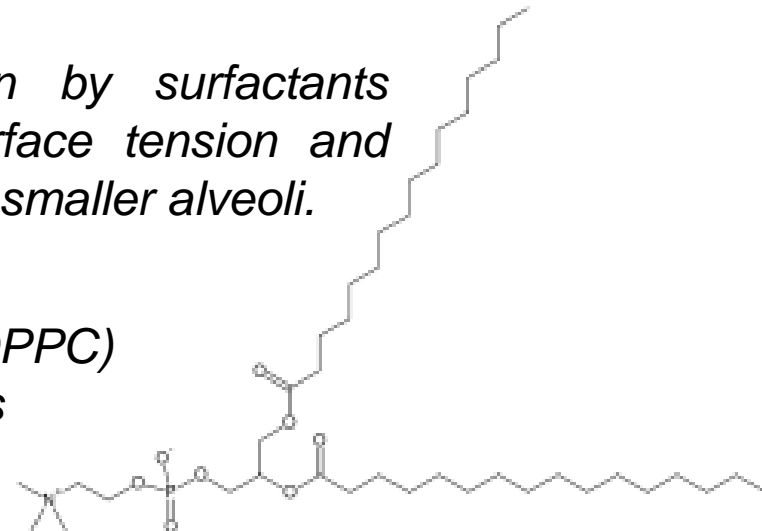
Internal pressure larger on smaller bubble.

The smaller bubble decreases in volume until it forms a film with curvature equal to the largest bubble.



*Alveolar stabilization by surfactants that reduce the surface tension and avoid collapse of the smaller alveoli.*

*Dipalmitoil-lecithin (DPPC) secreted by the lungs*

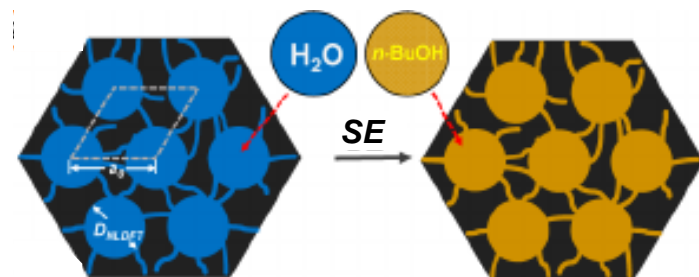




## Example: Capillary pressure in pores

Transformation pathways of SBA-15 mesophase with various template cleaning routes

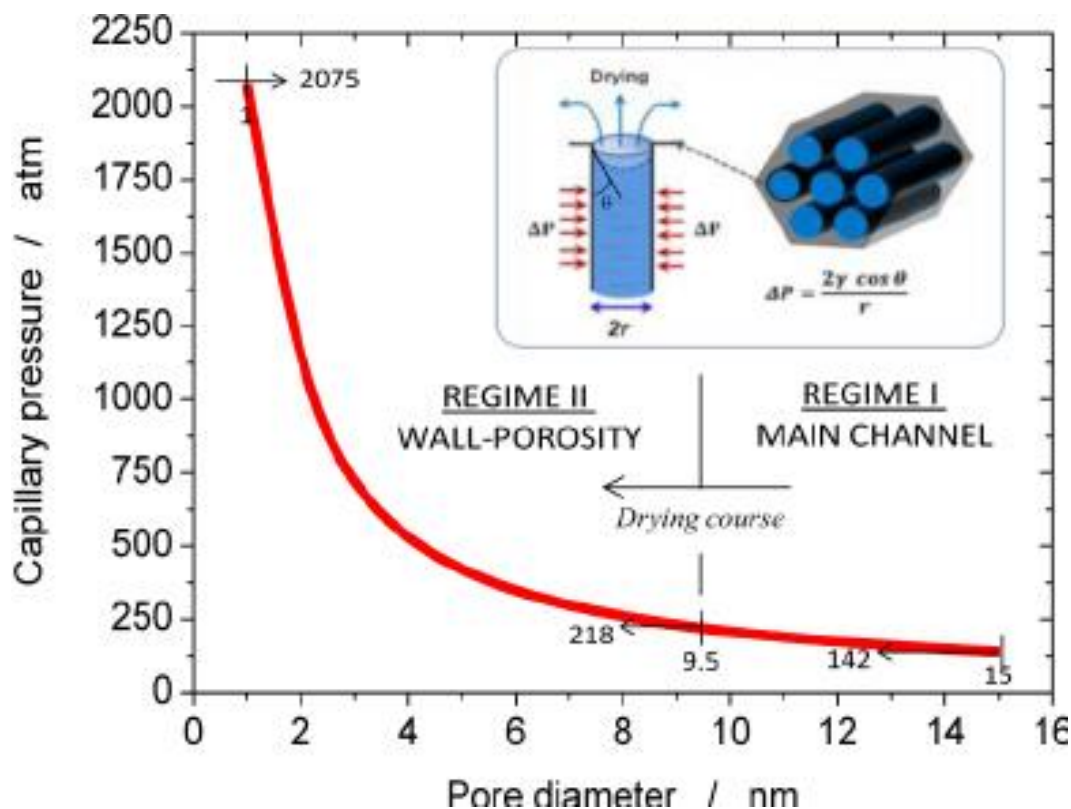
$$\Delta P = \frac{2\gamma}{r_s}$$



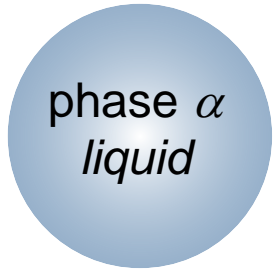
$T \sim 100^\circ\text{C}$



Capillary pressure as a function of pore diameter



# Vapor pressure dependence on surface curvature



phase  $\beta$   
vapor

Chemical potential:

$$\mu_i = \left( \frac{\partial G}{\partial N_i} \right)_{T, P, N_{j \neq i}}$$

$$\partial \mu = \bar{V} \partial P - \bar{S} \partial T$$

$\bar{V}$  – molar volume

constant  $T$

Laplace equation

$$\frac{2\gamma}{r_m} = P^\alpha - P^\beta$$

In equilibrium:  $\mu^\alpha = \mu^\beta$

$$\partial \mu = \bar{V} \partial P$$

$$\bar{V}^\alpha \partial P^\alpha = \bar{V}^\beta \partial P^\beta$$

If the system is disturbed

$$2\gamma \partial \left( \frac{1}{r_m} \right) = \partial P^\alpha - \partial P^\beta$$

$$2\gamma \partial \left( \frac{1}{r_m} \right) = \partial P^\beta \left( \frac{\bar{V}^\beta}{\bar{V}^\alpha} \right) - \partial P^\beta$$

$$2\gamma \partial \left( \frac{1}{r_m} \right) = \partial P^\beta \left( \frac{\bar{V}^\beta - \bar{V}^\alpha}{\bar{V}^\alpha} \right)$$

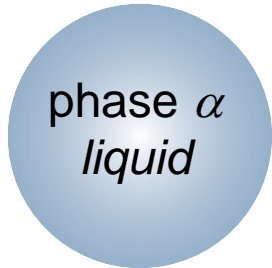
phase  $\beta$ , vapor

$$\bar{V}^\beta \gg \bar{V}^\alpha$$

$$2\gamma \partial \left( \frac{1}{r_m} \right) = \partial P^\beta \left( \frac{\bar{V}^\beta}{\bar{V}^\alpha} \right)$$

$$\partial \mu = \bar{V} \partial p$$

$$2\gamma \partial \left( \frac{1}{r_m} \right) = \frac{\partial \mu}{\bar{V}^\alpha}$$



phase  $\alpha$   
liquid

phase  $\beta$   
vapor



$$2\gamma \partial \left( \frac{1}{r_m} \right) = \frac{\partial \mu}{\bar{V}^\alpha}$$

Integrating from a flat surface ( $1/r = 0 ; \mu^\infty$ ) to a curved surface ( $r_m ; \mu^c$ )

$$2\gamma \int_0^{r_m} (1/r) \partial(1/r) = \frac{1}{\bar{V}^\alpha} \int_{\mu^\infty}^{\mu^c} \partial \mu$$

$$2\gamma \left( \frac{1}{r_m} \right) = \frac{1}{\bar{V}^\alpha} (\mu^c - \mu^\infty)$$

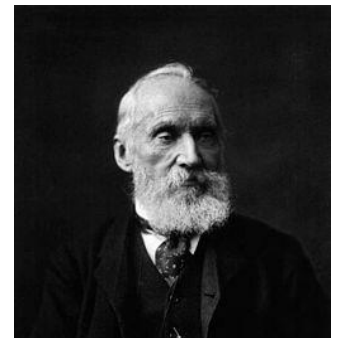
$$\Delta \mu = \gamma \bar{V}^\alpha \frac{2}{r_m}$$

$$\mu = \mu^0 + RT \ln \left( \frac{P}{P^0} \right)$$



$$\ln \left( \frac{P^c}{P^\infty} \right) = \frac{\bar{V}}{RT} \left( \frac{2\gamma}{r_m} \right)$$

**Kelvin equation**



William Thomson  
1<sup>o</sup> Baron Kelvin (1824-1907)

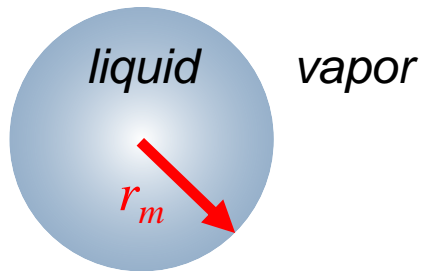
# Applications of the Kelvin equation

Explains various phenomena important for engineering applications:

- Growth of larger drops by depletion of the smallest (*Ostwald ripening*)
- Difficulty of self-nucleation of a new phase
- Condensation in pores and capillaries

$$P^c = P^\infty \exp \left[ \frac{\bar{V}}{RT} \left( \frac{2\gamma}{r_m} \right) \right]$$

## droplet

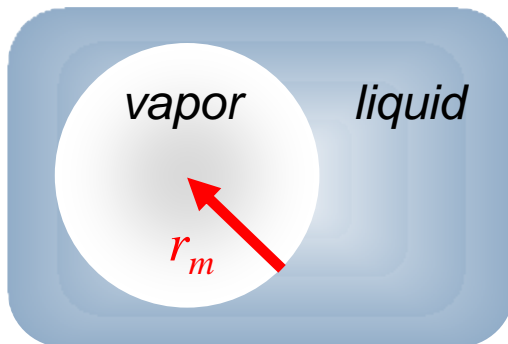


$$r_m > 0 \Rightarrow P^c > P^\infty$$

**Smaller droplets have higher vapor pressure**

- tend to *evaporate* and contribute to the growth of larger drops (rain, *Ostwald ripening*,...)

## bubble



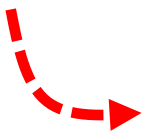
$$r_m < 0 \Rightarrow P^c < P^\infty$$

**Smaller bubbles have a lower vapor pressure**

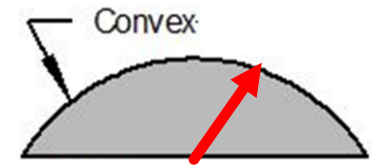
- tend to *condensate* (become unstable under a critical size: difficult nucleation of stable bubbles)

# Young-Laplace Equation for solid surfaces

Similar results as for liquid-vapor interfaces  
(chemical potential  $\mu$ , instead of pressure)


$$\Delta\mu = \bar{V} \left( \frac{2\gamma}{r_m} \right)$$

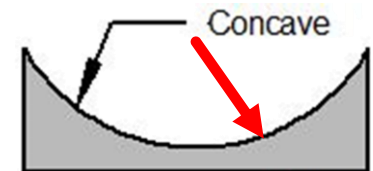
Convex surfaces  $r > 0$



Flat surfaces  $r = \infty$



Concave surfaces  $r < 0$



$$\mu_{\text{convex}} > \mu_{\text{flat}} > \mu_{\text{concave}}$$

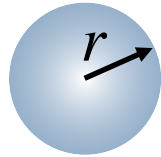
***Higher chemical reactivity of convex surfaces  
compared to flat and concave surfaces***



# Reactivity of nanoparticles

NPs have very high surface chemical potential, leading to very high reactivity (catalysis, surface modification, etc.)

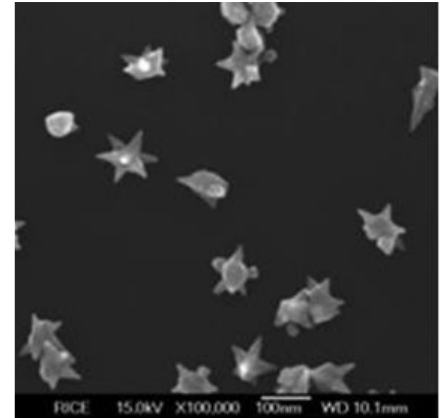
$$\Delta\mu = \gamma V_a \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$$



$r > 0$  (but very small)



Large  $\mu$   
Very high reactivity



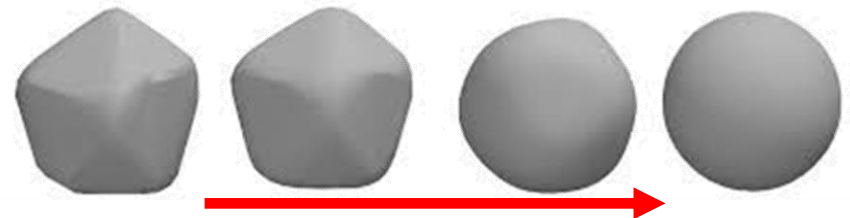
SEM of Au nanostars

## Solubility of solid NPs

Solubility of a curved surface

$$\mu = \mu^0 + KT \ln \left( \frac{C}{C^0} \right) \quad \ln \frac{C_c}{C_\infty} = \frac{V_a}{KT} \gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$$

Sharp edges and corners in NPs have high positive curvature ( $r > 0$  but small) and are more soluble than flat and concave regions



# Coarsening of nanoparticles – Ostwald ripening

## *NPs in a gas*

In a mixture of solid nanoparticles of different sizes, the vapor pressure is higher over smaller particles (smaller  $r$ )

$$P^c = P^\infty \exp\left[\frac{\bar{V}}{RT} \left(\frac{2\gamma}{r_m}\right)\right]$$

The vapor pressure gradient causes accumulation of atoms at the larger NP, which incorporate the atoms to reduce the pressure (larger  $r$ )

*Larger NPs grow and smaller NPs tend to disappear*

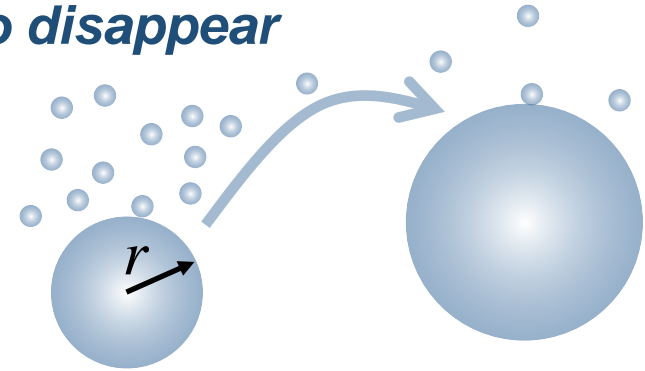
## *NPs in a liquid*

$$C_c = C_\infty \exp\left[\frac{V_a}{KT} \left(\frac{2\gamma}{r_m}\right)\right]$$

Smaller NPs (high positive curvature,  $r > 0$  but small) have larger saturation concentration than larger NPs

Small NPs will dissolve, and the solute is deposited in the larger NPs

*Larger NPs grow and smaller NPs tend to disappear*



# Melting point of NPs

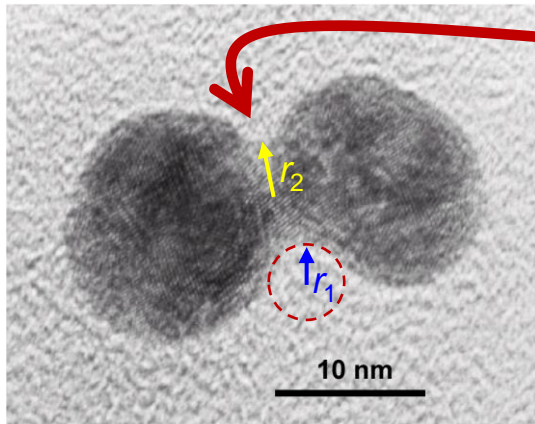
Excess pressure due to the surface curvature

$$P^\alpha - P^\beta = \frac{2\gamma}{r_m}$$

This adds to the chemical potential of the solid NPs to decrease the melting point of smaller NPs

## Sintering of NPs

Particle compacting and densification below their melting point

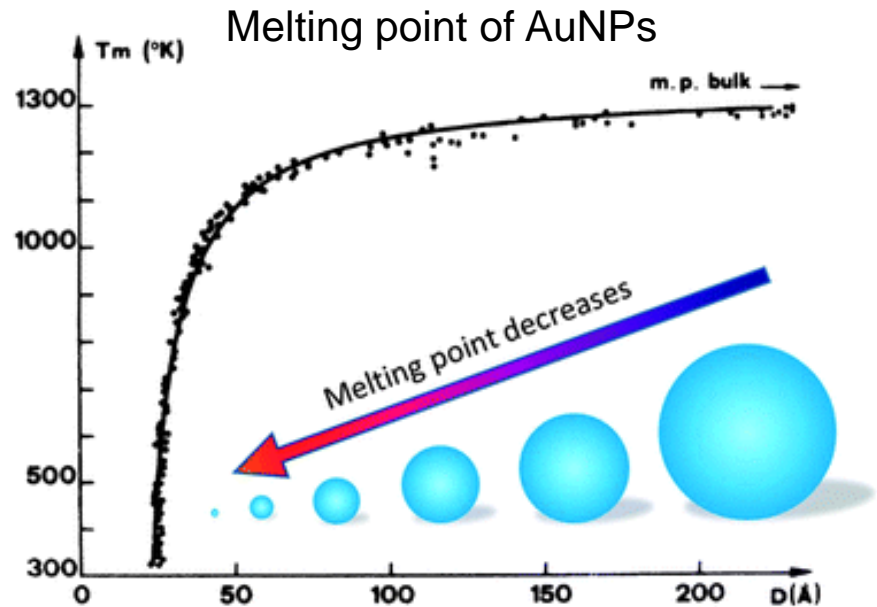


TEM AuNPs

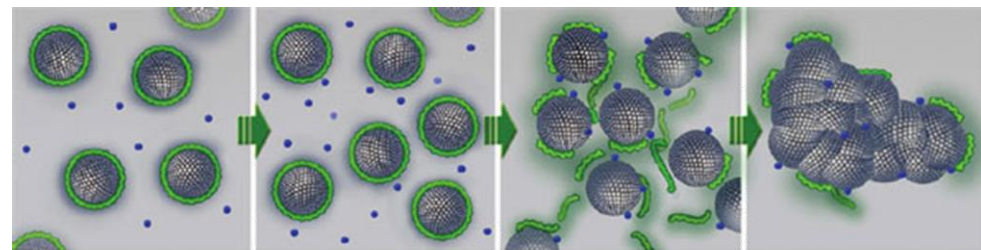
Neck formation

$$r_1 < r_2$$

$$r_1 < 0$$



Accumulation of material at the interface and densification



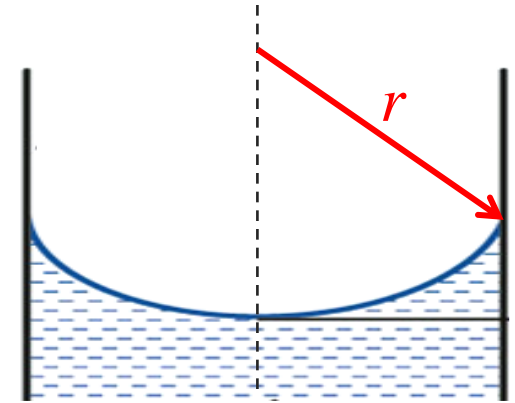
Example: Silver conducting ink

# NP agglomeration by vapor condensation

Condensation occurs when the vapor pressure reaches saturation pressure

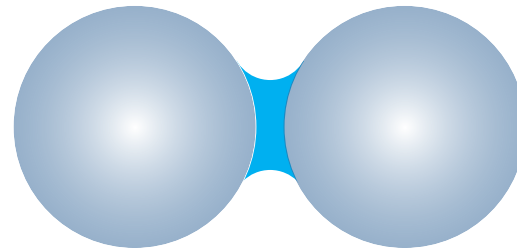
If the liquid forms a concave meniscus inside a capillary, the equilibrium vapor pressure is lower and vapor condenses inside the capillary

$$P^c = P^\infty \exp \left[ \frac{\bar{V}}{RT} \left( \frac{2\gamma}{r_m} \right) \right] \quad r < 0 \Rightarrow P^c < P^\infty$$

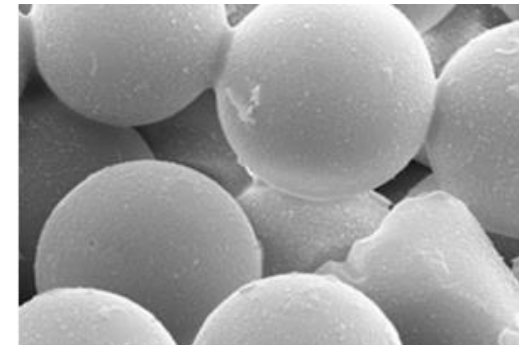


Moisture condenses in pores and between nanoparticles, even at temperatures above the dew point

The contact point between the NPs behaves like a capillary



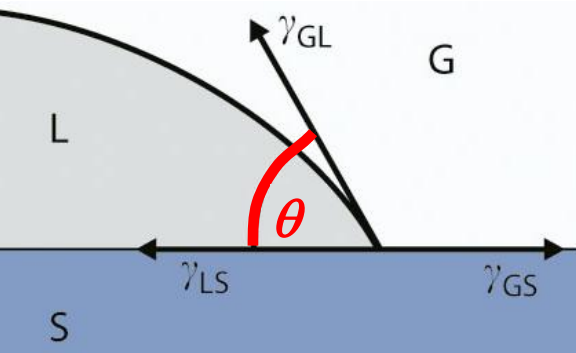
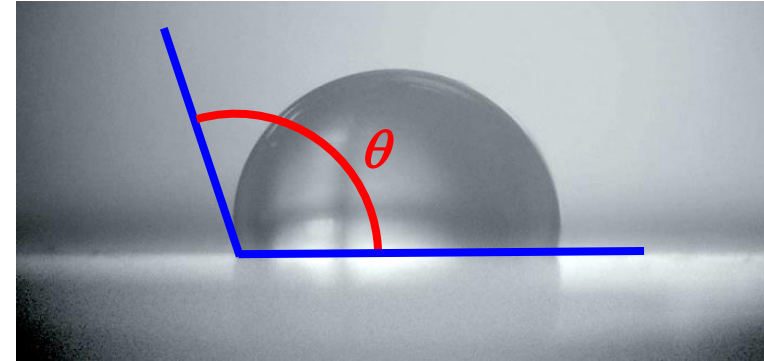
The condensed liquid forms a bridge between the particles, causing agglomeration



# Solid-Liquid Interface

## Contact angle $\theta$

angle between the solid surface and the tangent to the liquid at the contact line



The equilibrium position of the triple contact line determines the shape of the droplet and depends on the horizontal components of the surface tensions.

$$\gamma_{GS} = \gamma_{LS} + \gamma_{GL} \cos \theta$$

**Young equation**

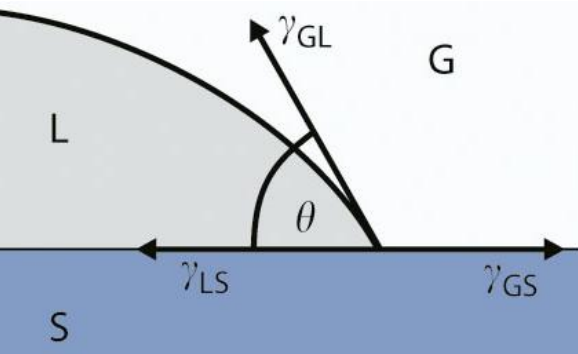
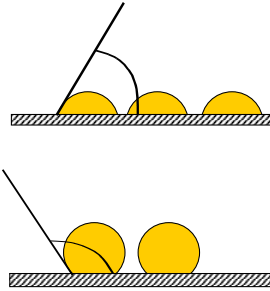
Thomas Young  
1773-1829





The contact angle is related to the interactions between molecules in the liquid (**cohesive forces**) and between these and the solid surface (**adhesive forces**)

- Hydrophilic surfaces (high affinity for water) have dominant adhesive forces and low contact angle with water
- Hydrophobic surfaces (low affinity with water) have dominant cohesive forces and large contact angle with water



$$\cos \theta = \frac{\gamma_{GS} - \gamma_{LS}}{\gamma_{GL}}$$

## Wettability

A liquid wets the surface when  $\theta < 90^\circ$  and does not wet if  $\theta > 90^\circ$

## Spreading

A liquid spreads on the surface when  $\theta = 0^\circ$  (non-equilibrium)

## Work of adhesion

Work per unit area of surface formed when separating 2 phases  $\alpha$  and  $\beta$  inside a phase  $\omega$

$$w_{\alpha\beta} = -\gamma_{\alpha\beta} + \gamma_{\alpha\omega} + \gamma_{\beta\omega}$$

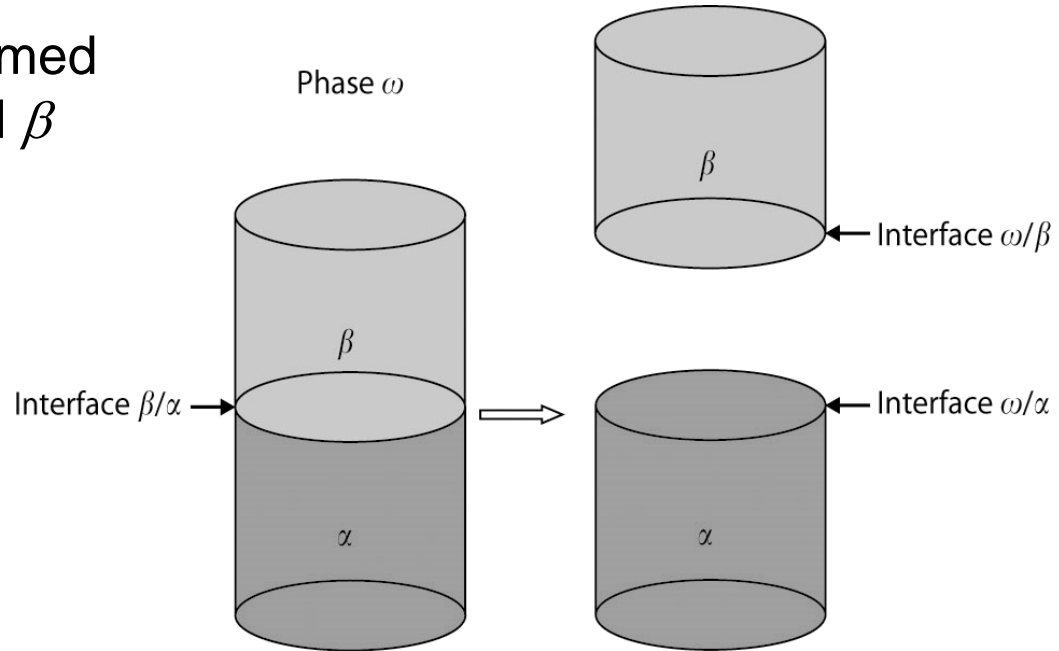
Liquid-solid adhesion:

$$w_{LS} = -\gamma_{LS} + \gamma_{LG} + \gamma_{SG}$$

$$\gamma_{SG} = \gamma_{LS} + \gamma_{GL} \cos \theta$$

$$w_{LS} = \gamma_{LG} (1 + \cos \theta)$$

**Young-Dupré equation**



## Work of cohesion

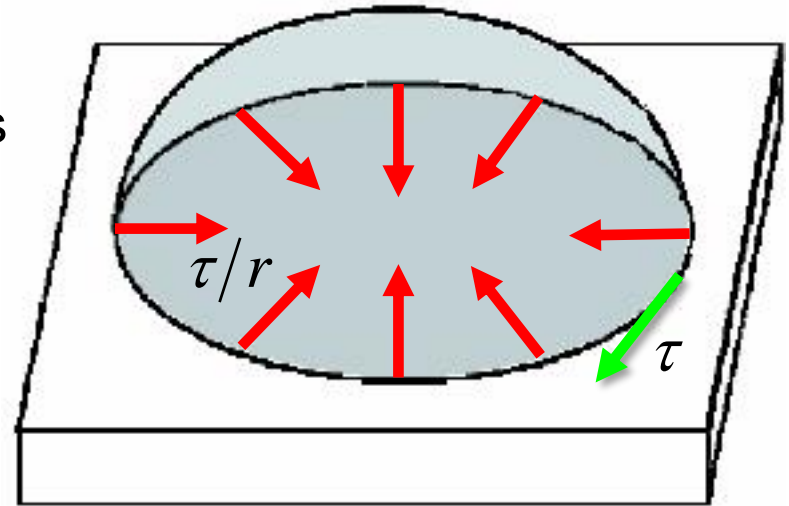
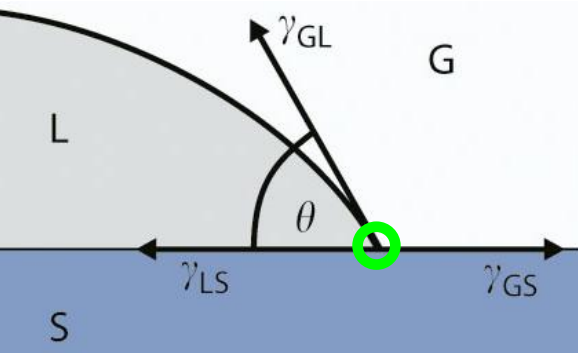
Work per unit area of surface formed when separating a single phase in two

$$w_{\alpha\alpha} = 2 \gamma_{\alpha\omega} \quad (\gamma_{\alpha\alpha} \equiv 0)$$

# Contact angle at the nanoscale

The **line tension**  $\tau$  of the liquid-solid-vapor contact becomes non-negligible for surfaces with  $r < 100\text{nm}$

The line tension force  $\tau/r$  acts inwards on the liquid-solid-vapor contact circle



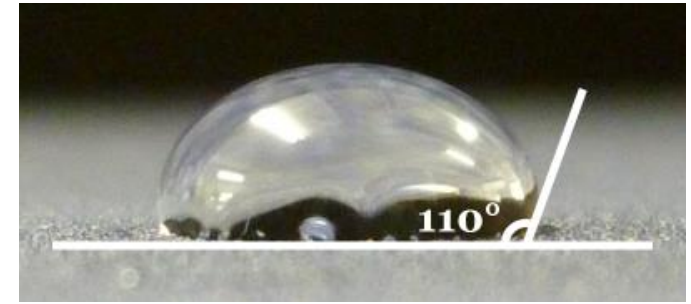
$$\gamma_{GS} = \gamma_{LS} + \gamma_{GL} \cos \theta + \frac{\tau}{r}$$

$$\cos \theta = \frac{\gamma_{GS} - \gamma_{LS} - \frac{\tau}{r}}{\gamma_{GL}}$$

# Superhydrophobic surfaces

Highest water contact angle in a flat highly hydrophobic surface is  $\theta \approx 120^\circ$

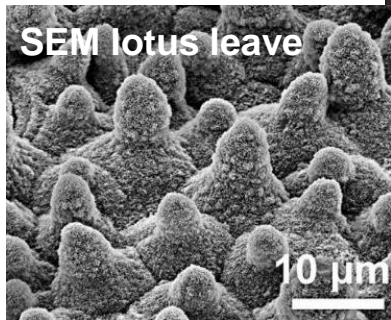
Superhydrophobic surfaces have  $\theta > 150^\circ$



Water in Teflon



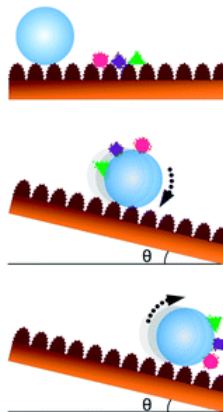
*Nelumbo nucifera* (Lotus)



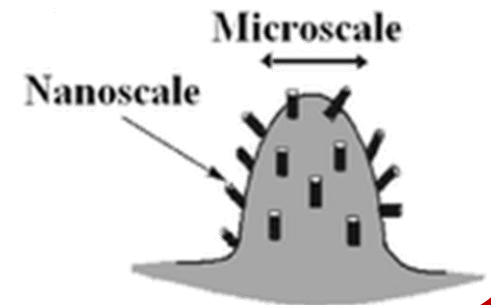
Water has a contact angle  $\theta > 150^\circ$  on the leaf surface. The surface is covered with a wax with water contact angle  $\theta \approx 90^\circ$

## Self-cleaning surface

Water does not wet the surface and rolls off taking the dirt on the surface



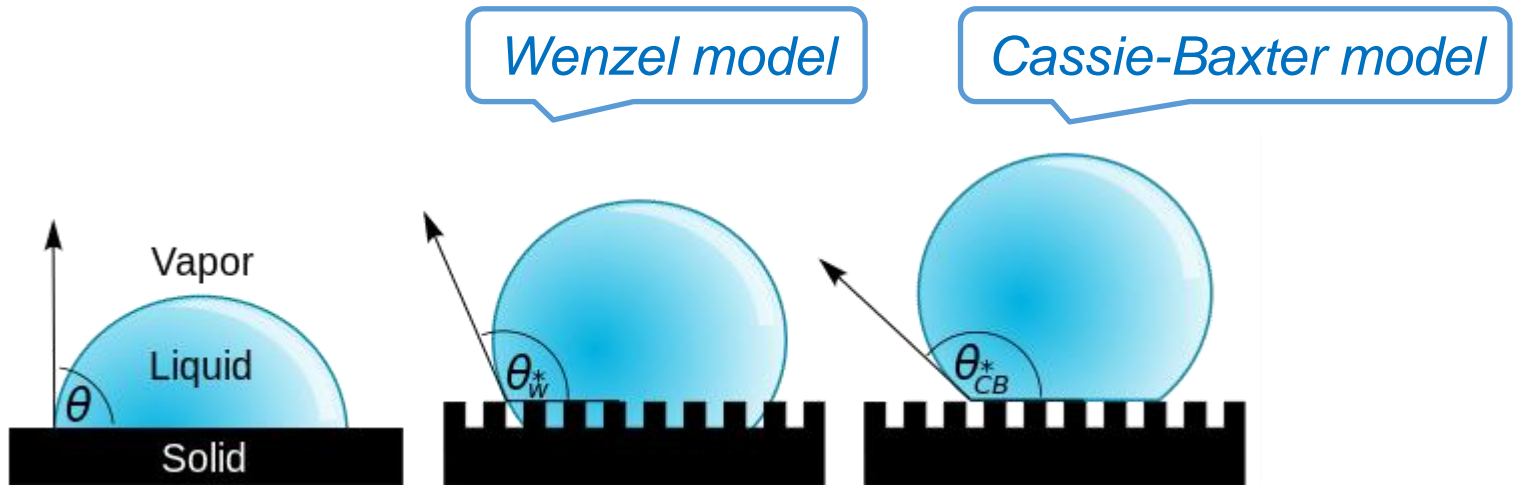
Hierarchical structure of 5-9  $\mu\text{m}$  pillars with 120 nm structures



## Surface roughness effect

Two situations can occur:

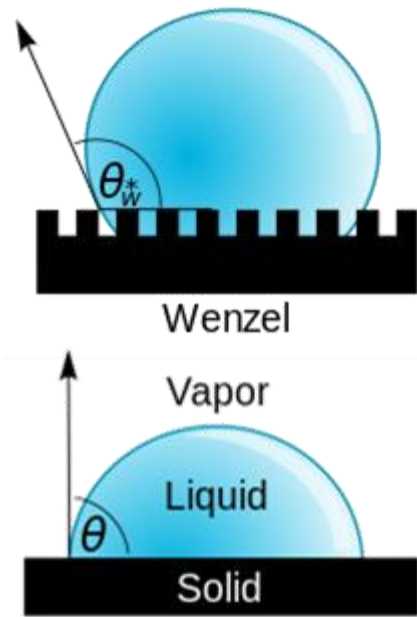
- The liquid drop follows the surface topography
- The liquid drop rests on the peaks enclosing air beneath



In both cases the observed contact angle  $\theta^*$  is larger than the contact angle for a flat surface of the same hydrophobic material ( $\theta > 90^\circ$ )



## Wenzel model



Solid-liquid contact area increased by a factor  $\alpha$

$$\cos \theta_w^* = \alpha \cos \theta \quad \alpha = \frac{\text{actual contact area}}{\text{projected area}}$$

$$\gamma_{GS} = \gamma_{LS} + \gamma_{GL} \cos \theta$$

$$\cos \theta_w^* = \alpha \left( \frac{\gamma_{GS} - \gamma_{LS}}{\gamma_{GL}} \right)$$

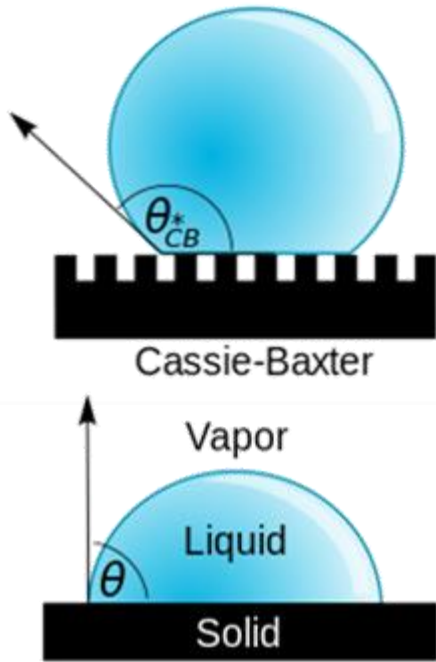
- If the flat surface is **hydrophobic**,  $\theta > 90^\circ$

$\alpha > 1 \Rightarrow \theta_w^* > \theta$  The rough surface can be **superhydrophobic**

- If the flat surface is **hydrophilic**,  $\theta < 90^\circ$

$\alpha > 1 \Rightarrow \theta_w^* < \theta$  The rough surface can be **superhydrophilic**

## Cassie-Baxter model



The liquid rests part in the solid, part in air

$$\cos \theta_{CB}^* = f_{LS} \cos \theta_{LS} + f_{LV} \cos \theta_{LV}$$

$$f_{LS} = \frac{\text{area in contact with solid}}{\text{projected area}}$$

$$f_{LV} + f_{LS} = 1$$

$$f_{LV} = \frac{\text{area in contact with trapped air}}{\text{projected area}}$$

$$\theta_{LV} = 180^\circ$$

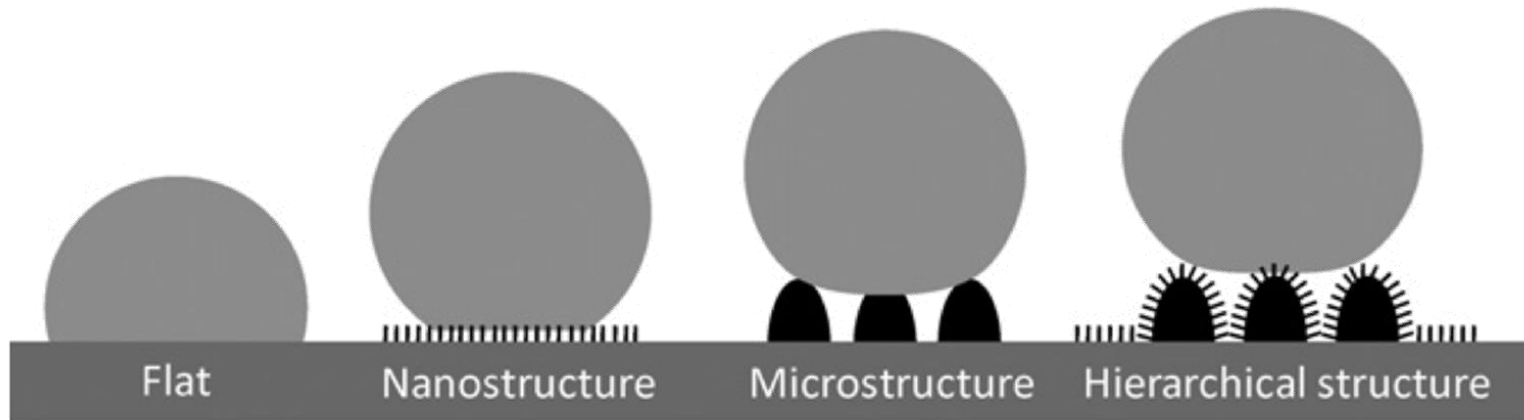
$$\cos \theta_{CB}^* = f_{LS} \cos \theta_{LS} - f_{LV} = f_{LS} (1 + \cos \theta_{LS}) - 1$$

- If the flat surface is **hydrophobic**,  $\theta_{LS} > 90^\circ$

$$f_{LS} < 1 \Rightarrow \theta_{CB}^* > \theta \quad \text{The rough surface can be } \textbf{superhydrophobic}$$

*If the flat surface is hydrophilic the model do not apply*

## What about hierarchical structures?



Hierarchical structures have better performance



*Nelumbo nucifera*  
(Lotus)



Gecko lizards



# Adhesion scaling in nature

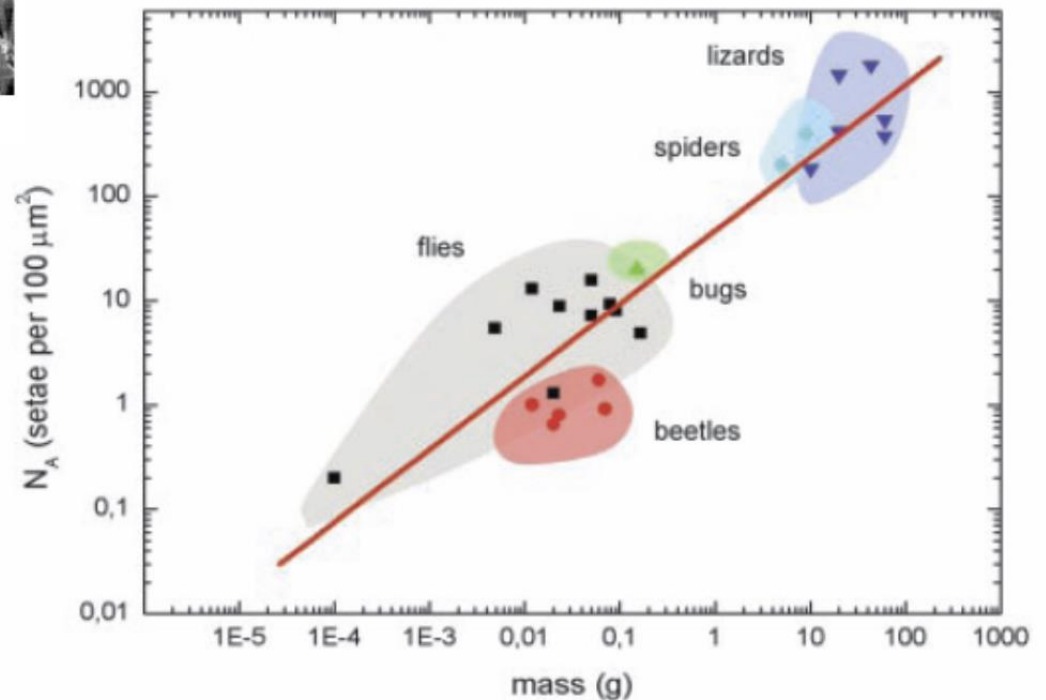
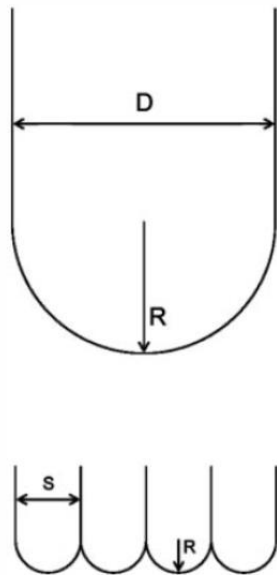
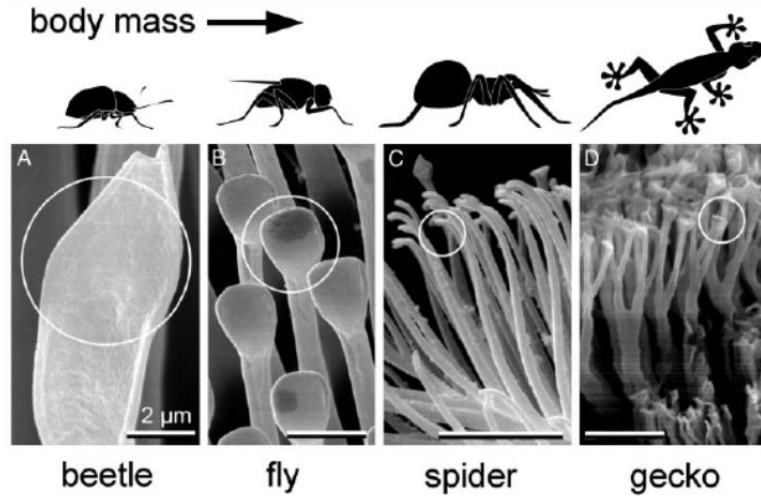
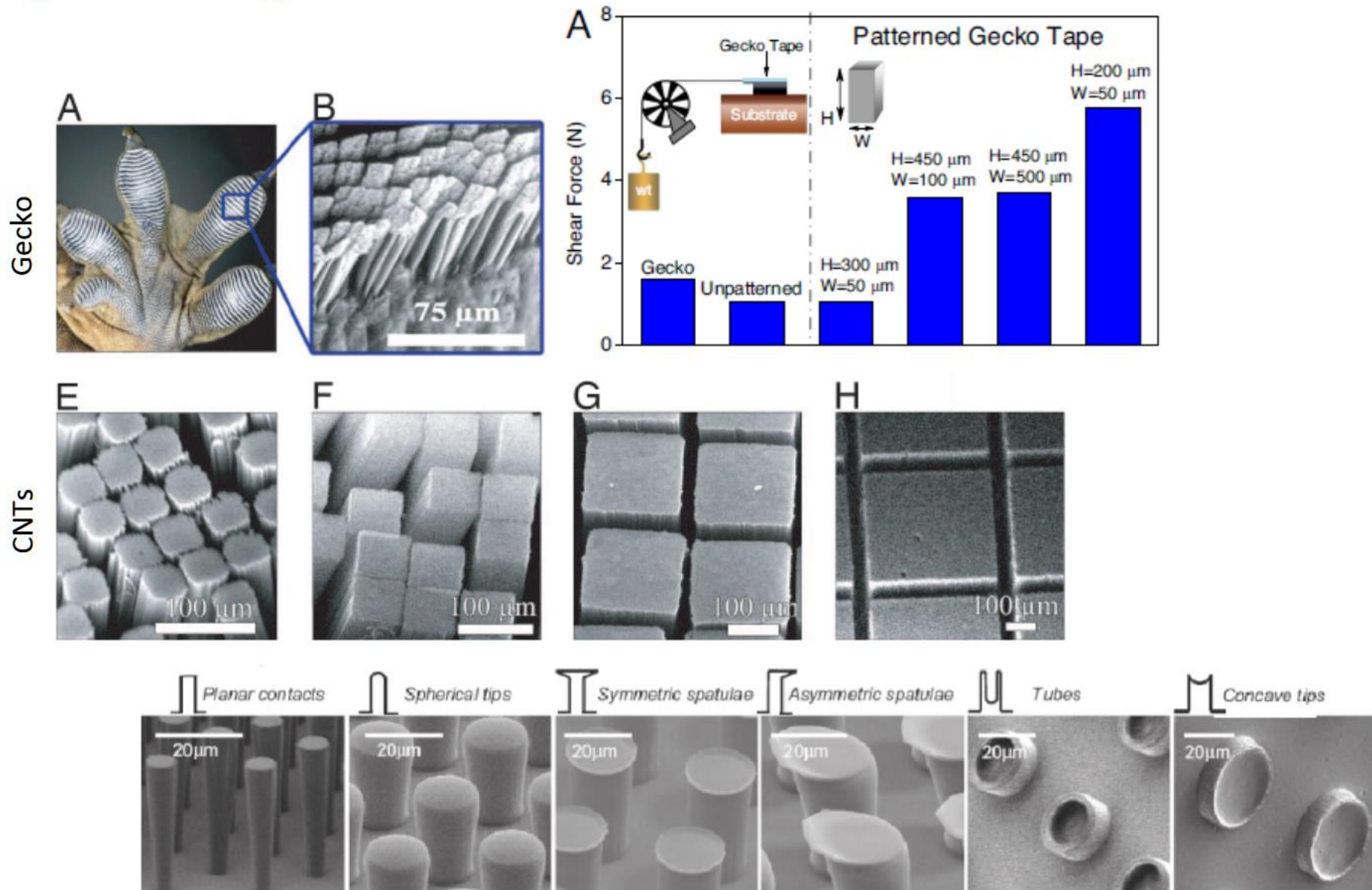


Fig. 2. Dependence of the terminal element density ( $N_A$ ) of the attachment pads on the body mass ( $m$ ) in hairy-pad systems of diverse animal groups ( $\log \cdot N_A(m^{-2}) = 13.8 + 0.699 \cdot \log \cdot m(\text{kg})$ ,  $R = 0.919$ ).



# Synthetic gecko adhesives



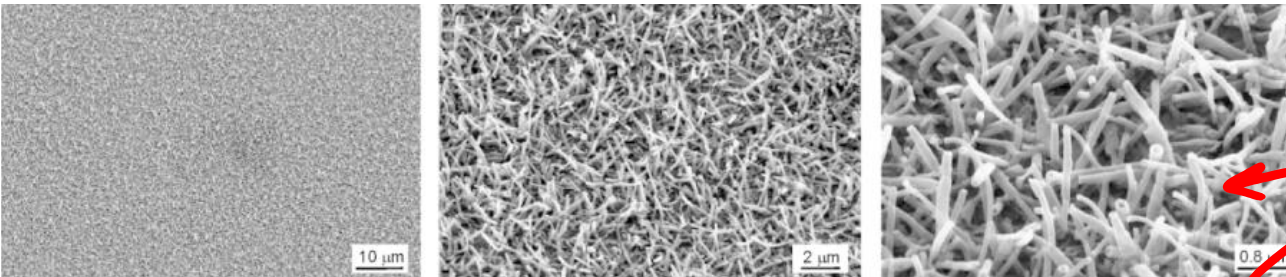
Ge et al., PNAS 104(26):10792-10795, 2007.

Zeng et al., Langmuir 25(13):7486-7495, 2009.

# Synthetic lotus type surface

SEM of polymer nanostructure on flat replica, microstructures, and hierarchical structure.  
 Nano and hierarchical structures coated with  $0.8 \mu\text{g}/\text{mm}^2$  of Lotus wax

Nanostructure on flat surface



Water contact angles:

Flat epoxy resin	$76 \pm 0.9$
Flat with thin wax layer	$119 \pm 2.4$
Nanostructure	$167 \pm 0.7$
Microstructure	$160 \pm 1.8$
Hierarchical structure	$173 \pm 0.8$

Micro-patterned surface with no nanostructure



Nanstructure on micro-patterned surface

