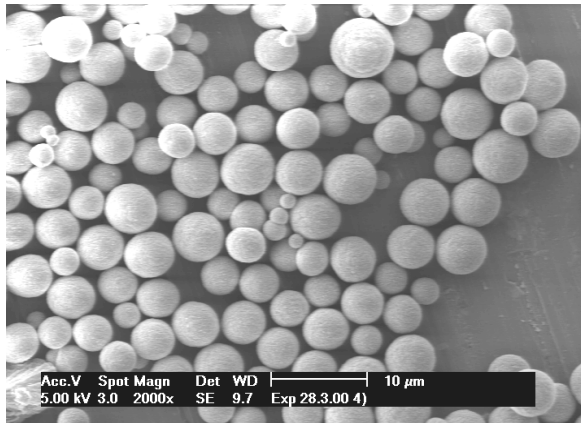


Week 7

7. Powder Treatment (2)

Dispersion-Wetting-Van-der-Waals Forces

A. Testino



The Colloidal Domain - DF Evans & H. Wennerström, Wiley, 1999. (Chp. 2 & 5)

Summary – week 7

Manufacture of ceramics (5-6)

Dispersion - Suspensions and Pastes (7)

Surface tension/interfacial energy (8-13)

Electrolyte Solutions – Water – (14-15)

Wetting – Dispersion of ceramics(16-22)

- Cohesion and adhesion (17-18)
- Work of Dispersion (19-20)
- Contact Angle (21-22)
- Surface roughness (23-24)
- Lotus leaf effect (24-27)
- Contact angle - surfactants(28)

Surface tension measurement (29-30)

- capillary rise (29)
- Wilhelmy balance (30)

Dispersion – Suspensions and Pastes (31)

- Colloidal Stability – Inter particle forces (32)
- Overall Interaction Energy (33)

Attractive Forces – Intermolecular Forces(34)

- Van der Waals Forces (34)

Dispersion interaction-Fundamentals (35)

- Instantaneous dipole- induced dipole (35)
- London dispersion forces (36)
- Hamaker approach (37)
- semi-infinite plates in a vacuum (38)
- ghecko (39)
- semi-infinite plates in a solvent (40)
- between curved surfaces (41-43)

Les Trait  des Mat riaux –Hamaker - (23-25)

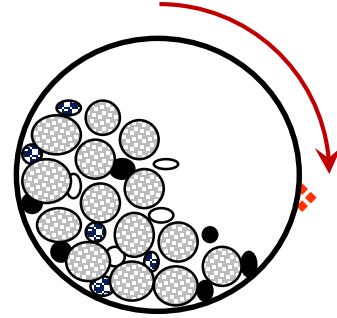
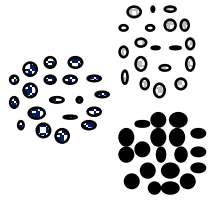
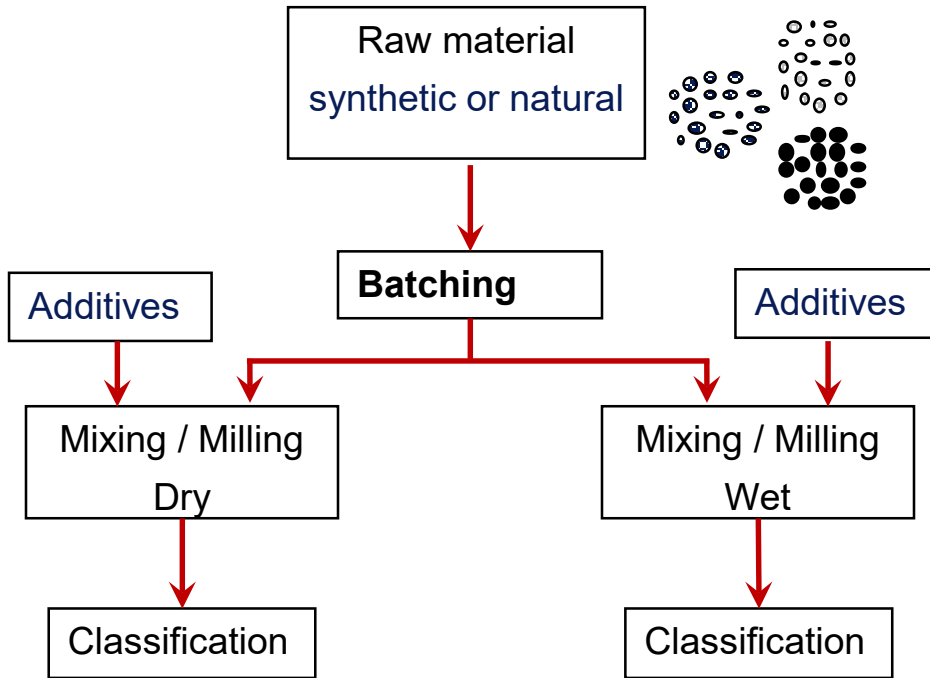
Summary – Van der Waals – Hamaker (45)

Attractive Magnetic forces (46)

Repulsive forces (47)

Course Outline – November-Decemeber (48)

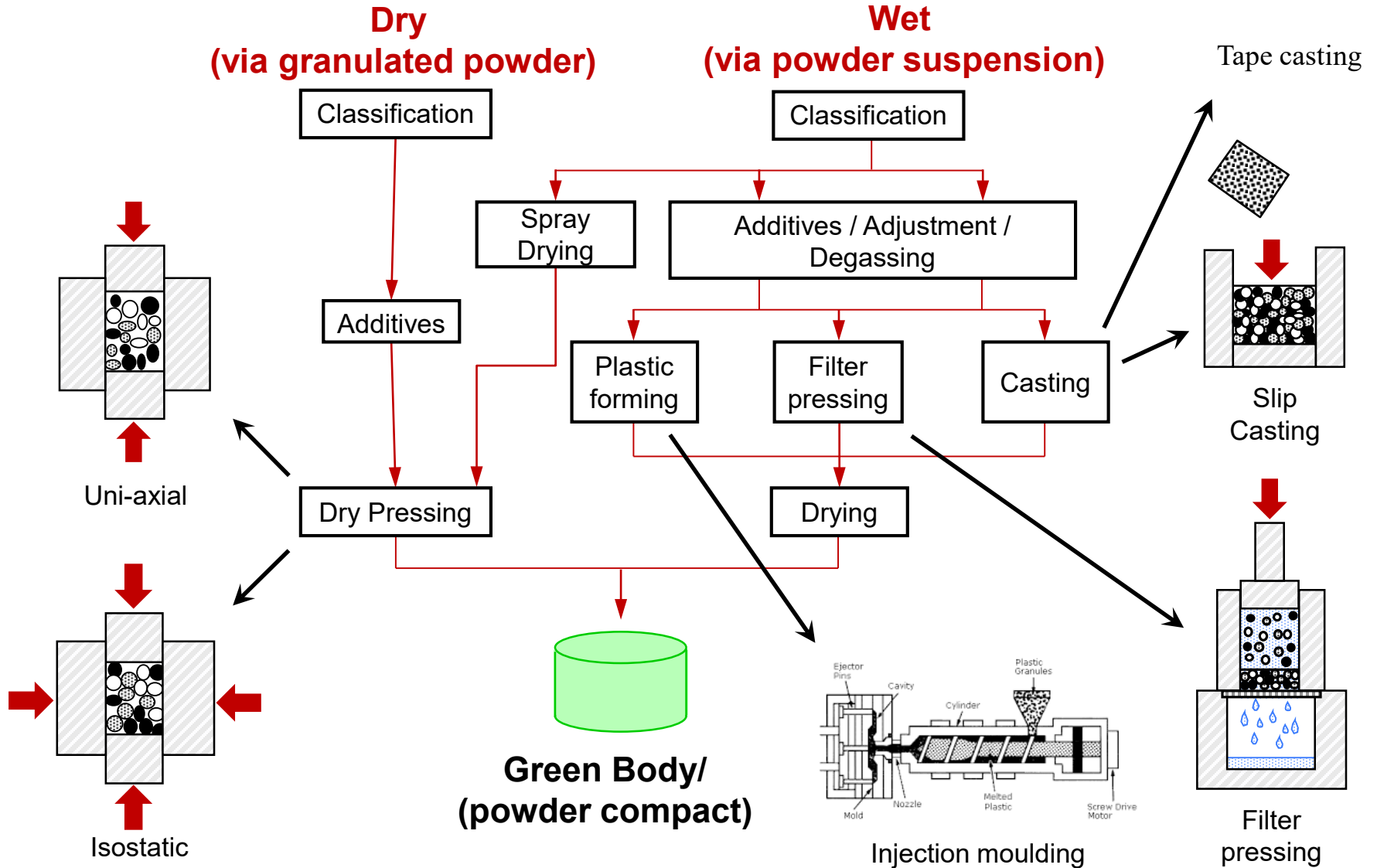
Ceramic Processing – 1 - Powders



- ❖ Commercial powders, often modified for application
- ❖ milling step in order to break up the agglomerates,
- ❖ Synthesized by solid route or by precipitation
- ❖ Different types of equipment - practical aspects and some scientific principles

- **known** chemical purity,
- good reactivity
(size ~1 μm and specific surface ~ 5-15 m²/ g) and
-good homogeneity - physical and chemical.

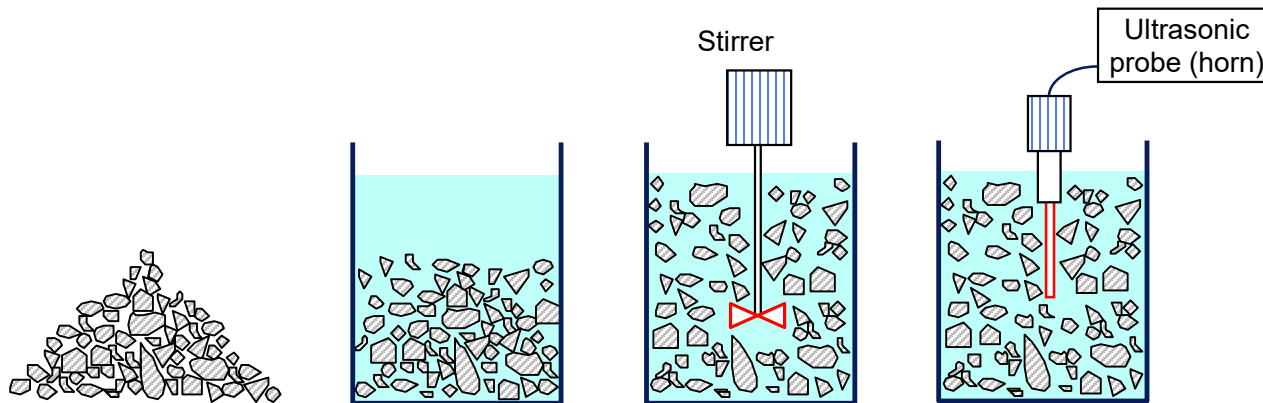
Manufacture of Ceramics - Ceramic Processing



Dispersion - Suspensions and Pastes

The key factors in producing a paste or dispersion are;

- ❖ wetting the surface of the powder with the liquid;
- ❖ the dispersion of the powder in the volume of this liquid by mixing or stirring;
- ❖ breaking up agglomerates (soft) or aggregates (hard) by ultrasonic treatment or by grinding;
- ❖ the ability to keep the powder well dispersed and to avoid agglomeration or phase separation by sedimentation.
- ❖ agglomerates (soft) - no chemical bond
- ❖ aggregates (hard) - chemical bond



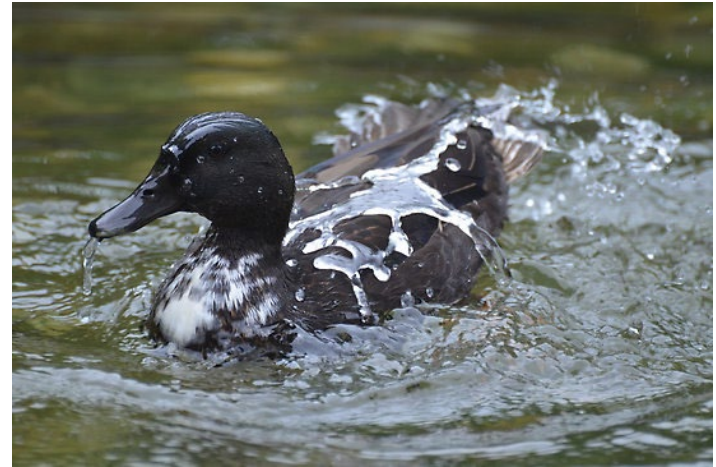
Surface Tension / Interfacial Energy

Metallic paper clip.

Density $\sim 8 \text{ g / cm}^3 \gg$ water but does not sink ...

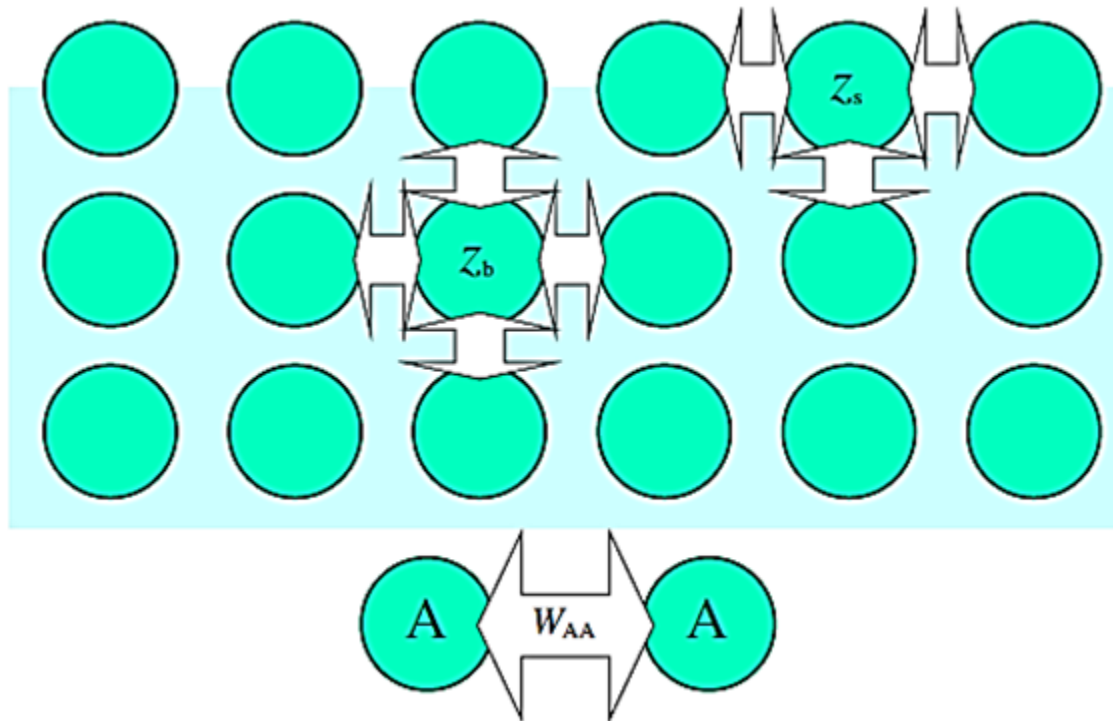


Water on a duck's back...



Surface Tension / Surface Energy

- ❖ Surface tension - Surface energy
 - Work of transferring a molecule to the surface



Surface Tension / Surface Energy *

❖ Surface tension - Surface energy

Work of transferring a molecule to the surface

Interaction energy between molecules A in the bulk :

$$E_{A,b} = (z_b/2)W_{AA} \quad (2.1.1)$$

Interaction energy between molecules A at the surface :

$$E_{A,s} = (z_s/2)W_{AA} \quad (2.1.2)$$

Z_b, number of nearest neighbours to a molecule A in the bulk,

Z_s: number of nearest neighbours to a molecule A at the surface.

W_{AA}: interaction energy between two molecules A *per unit area*, i.e. - surface energy or surface tension,

$$E_s/A = (E_{A,s} - E_{A,b})/a_0 = W_{AA} (z_s - z_b)/(2a_0) \quad (2.1.3)$$

A: surface area created.

a₀: area of occupancy of an A molecule at the surface.

*The Colloidal Domain - DF Evans & H. Wennerström, Wiley, 1999. (Chp. 2.1)

Surface Tension / Surface Energy

❖ Surface tension - Surface energy

- Work measurement ΔW_s creation of an additional surface ΔA

$$\Delta W_s = \gamma \Delta A \quad (2.1.6)$$

γ : surface energy (J /m²).

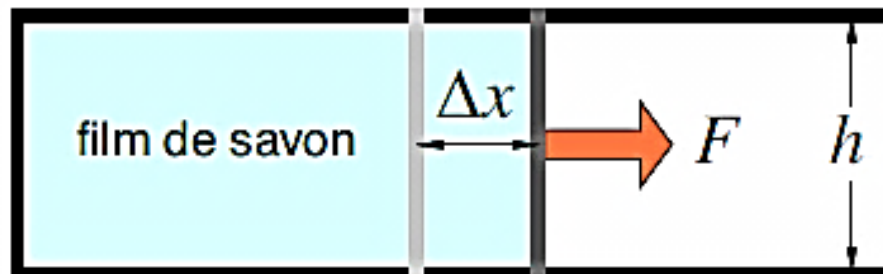
Surface equilibrium tension:

$$\Delta W_s = F \Delta x; \Delta A = 2h \Delta x \Rightarrow \gamma = F / 2 h \quad (2.1.7)$$

γ : surface tension [N / m].

At constant temperature T and pressure p :

$$\Delta G = \gamma \Delta A \Rightarrow \gamma = (\partial G / \partial A)_{p,T} \quad (2.1.10)$$

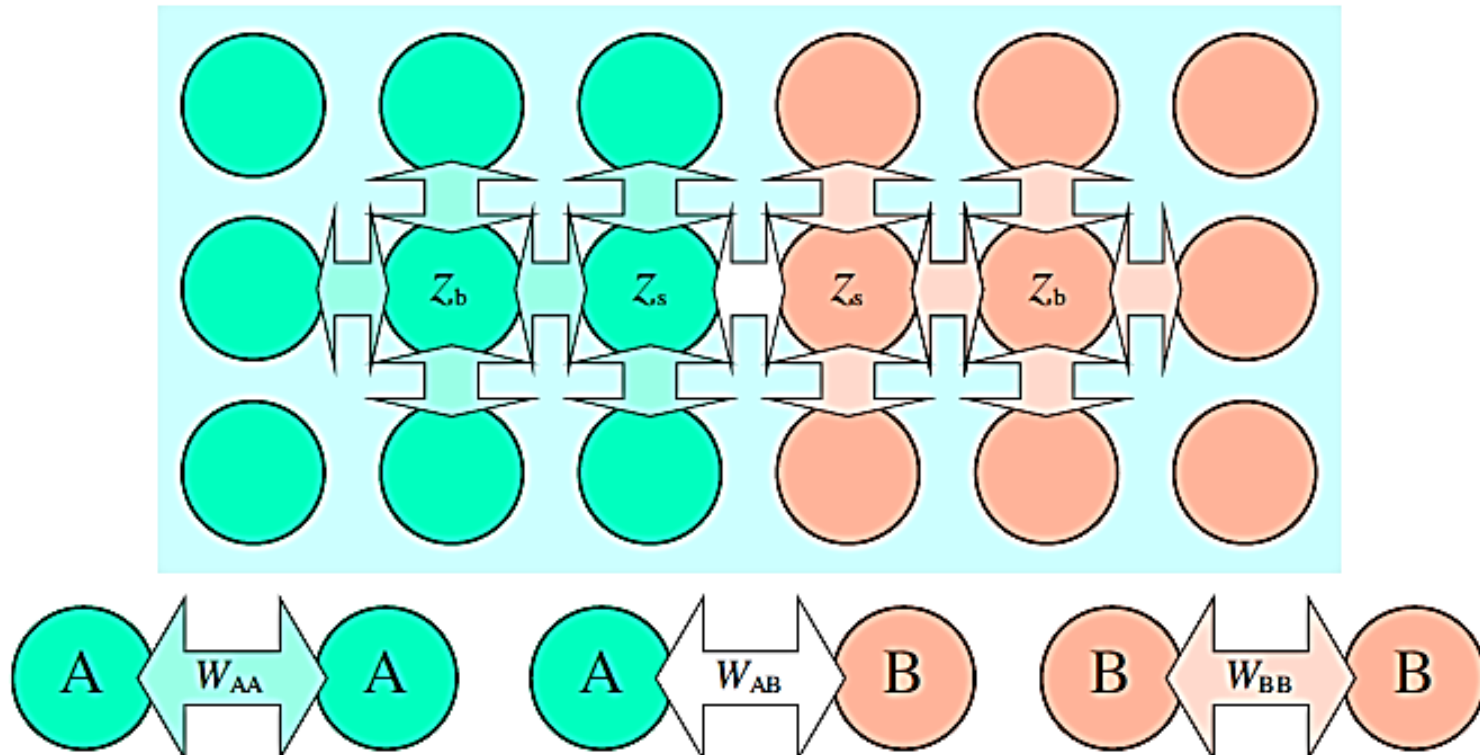


NB : Le film de savon a 2 faces

Soap film = 2 interfaces

Surface Tension / Interfacial Energy

- ❖ Surface tension - Interfacial Energy
 - Work of transferring a molecule to the AB interface



Surface Tension / Interfacial Energy

❖ Surface Tension - Interfacial Energy

- Creation of an interface between phases A and B

Interaction energy between molecules A and B at the interface

$$\begin{aligned}
 E_S &= N_S(z_b - z_s) \left[(W_{AA} + W_{BB})/2 - W_{AB} \right] \\
 &= N_S(z_b - z_s) w / (N_{Av} z_b)
 \end{aligned}
 \tag{2.1.4}$$

N_S : number of molecules of each species at the interface

N_{Av} : Avogadro number

w : interaction parameter (cf. Eq. 1.4.16)

$$w = z_b N_{Av} (W_{AB} - \frac{1}{2} W_{AA} - \frac{1}{2} W_{BB})$$

Energy per unit interfacial area

Results from the difference between the coordination numbers in the bulk and at the surface:

$$E_S/A = (z_b - z_s) w / (a_0 N_{Av} z_b) \tag{2.1.5}$$

A: surface area created. **a_0** : area of occupancy of molecule A at the surface.

Electrolyte Solutions

❖ A special solvent: water

– Structure of the water molecule

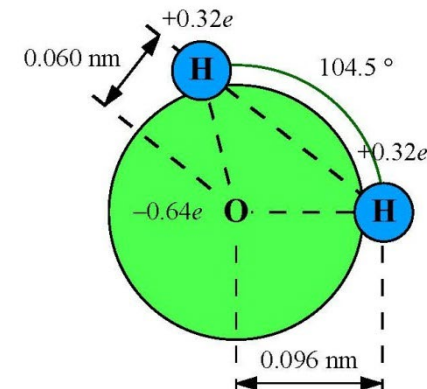
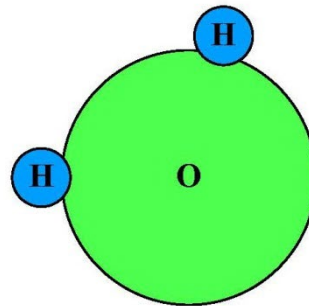
- The molecule is *asymmetric* ; the angle H – O – H = 104.25° .
- Each H carries a positive (partial) charge ($+0.32e$),
- O a negative charge ($-0.64e$).
- This results in a *permanent dipole moment* ($\mu = 1.84$ [D]).

– Hydrogen bond

$$1\text{D (Debye)} = 3.33564 \times 10^{-30} \text{ C}\cdot\text{m}$$

The “hydrogen bond” results from a Coulomb interaction with a *hydrogen atom* bonded to a very electronegative atom (O, N or F). Its low electron density allows it to get very close (0.15 to 0.2 [nm]) to other atoms with high electron density.

Recall: hybridization of orbitals sp^3 , ideal angle 109.5° , but in O two unshared couples of electrons, so...



Electrolyte Solutions

- Dissociation of electrolytes in solution

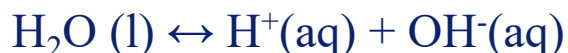
Solvolysis - Hydrolysis

- The dipole moment of water gives it a *dielectric permittivity* very high ($\epsilon_r = 78.3$ at 25°C).
- It has the effect of strongly attenuating the electric field around the dissolved ions.
- At the molecular level, water molecules strongly associate with dissolved ions (*solvation*), orienting itself in such a way as to minimize the electrostatic interaction energy.
- The *hydrolysis* is the separation by water of electrolytes into constituent ions.

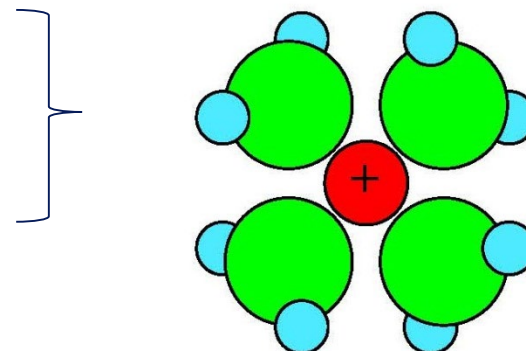
Examples:



Self-protolysis of water :



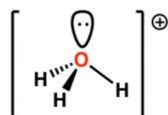
$$\log K_w = 14, \text{ at } T=25^\circ\text{C}$$



Cation solvaté

$\text{H}_3\text{O}^{\oplus}$ (Hydronium ion)

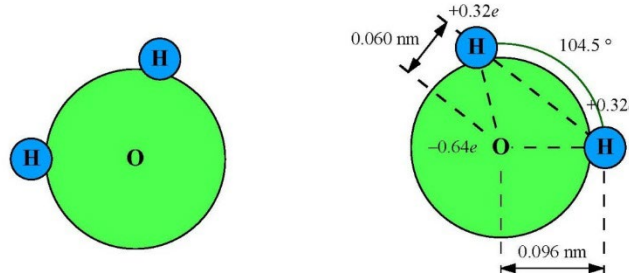
Remember:



Wetting - Dispersion of Ceramic Powders

- ❖ Wet a surface - oxides
- ❖ *Polar surfaces* - dispersed in - *Polar liquids*

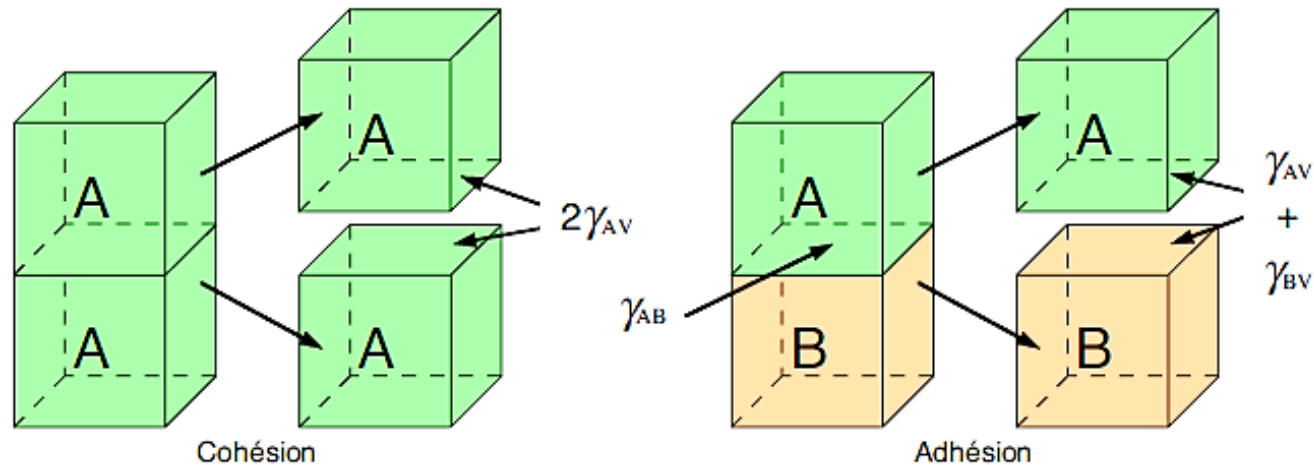
❖ H₂O



- ❖ a great advantage - economic and environmental cost
- ❖ More covalent bonds, Si₃N₄ , SiC
- ❖ Often uses organic solvents (e.g. n-hexane, C₆H₁₄)
- ❖ Even for ceramic oxide tape casting - H₂O not as good as organic.
- ❖ But last -10 years starting to use water industrially
- ❖ Good wetting but be careful with the dissolution which would modify either the stoichiometry of the powder or its surface properties (e.g. BaTiO₃) fn of pH as seen in previous courses.

Cohesion and Adhesion

❖ Work of cohesion, adhesion



Work of *cohesion*

Creation of an A-vapour interface:

$$\Delta G_{AV} = W_{AA} = 2\gamma_{AV} \quad (2.1.11) \quad \dots \text{ with perfect crystalline match}$$

Work of *adhesion*

Creation of an AB interface:

$$\Delta G_{AB} = W_{AB} = \gamma_{AV} + \gamma_{BV} - \gamma_{AB} \quad (2.1.12)$$

Cohesion and Adhesion

❖ Wetting

- Spreading coefficient S_{SL}

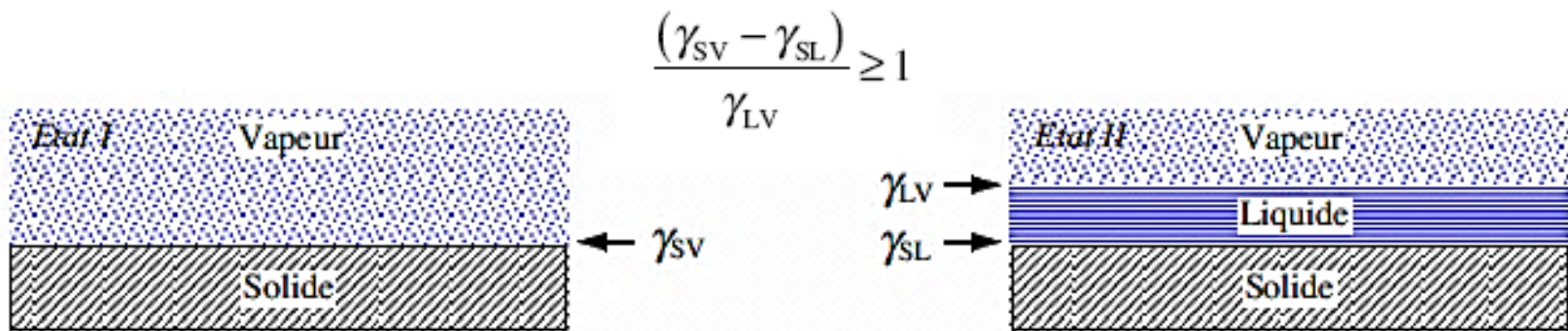
It is the decrease in surface energy $-\Delta G_{SL}$ obtained when the solid is completely covered with liquid:

$$\Delta G_{SL} = (\gamma_{LV} + \gamma_{SL}) - \gamma_{SV} \quad (2.1.15a) \quad \text{(Energy per unit of area)}$$

- where γ_{SV} , γ_{SL} and γ_{LV} are respectively the interfacial energies of the solid/vapor, solid / liquid and liquid / vapor, interfaces.

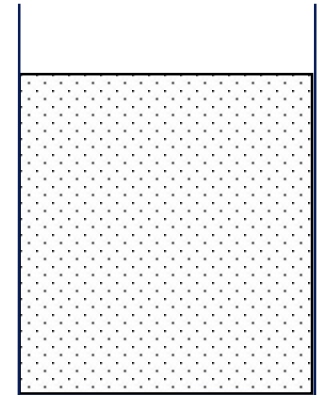
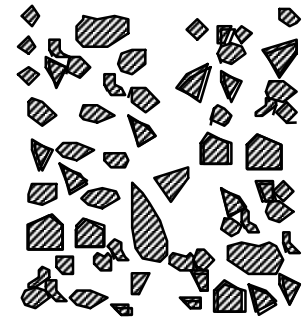
$$S_{SL} = -\Delta G_{SL} = (\gamma_{SV} - \gamma_{SL}) - \gamma_{LV} \quad (2.1.15b, \text{Dupr\'e equation})$$

The liquid spreads *spontaneously on the solid* if $S_{SL} \geq 0$, i.e. when:



Work of Dispersion, W_D

- ❖ The work required to go from a dry powder
 - all surfaces being exposed to the vapor phase,
- ❖ to a powder totally submerged and wetted by a liquid
 - only solid-liquid interfaces remain

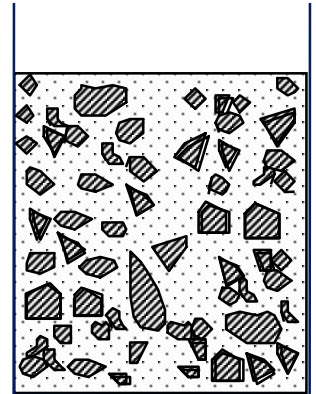


Work of Dispersion, W_D

- ❖ The work required to go from a dry powder
 - all surfaces being exposed to the vapor phase,
- ❖ to a powder totally submerged and wetted by a liquid
 - only solid-liquid interfaces remain

$$W_D = -(\gamma_{SV} - \gamma_{SL}) \cdot A$$

- ❖ When W_D is negative, then the dispersion of the powder in the liquid is a spontaneous process.



Wetting – Contact angle – Young's Law

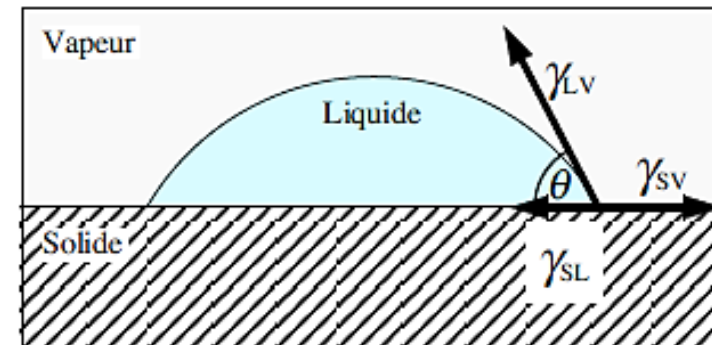
❖ Wetting

Young's Law (theorem)

- When the spreading of the liquid on the solid is not perfect, the liquid condenses in the form of droplets. If the droplets are small enough to neglect the influence of gravity, they take the form of a spherical cap.
- The balance of forces at the solid-liquid-vapor junction gives:

$$\left. \begin{aligned} \gamma_{SV} - \gamma_{SL} - \gamma_{LV} \cos\theta &= 0 \\ \Downarrow \\ \cos\theta &= \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \end{aligned} \right\} \quad (2.1.13)$$

θ is the *wetting angle* or *contact angle* of a liquid on solid.



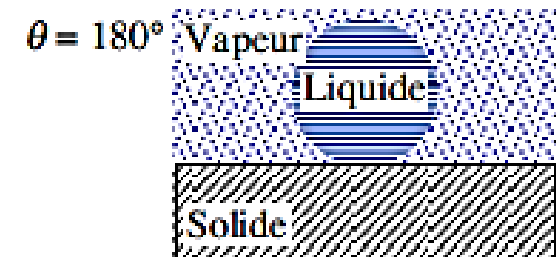
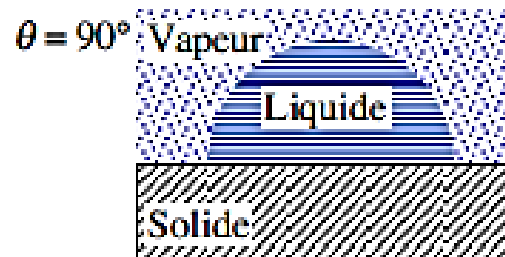
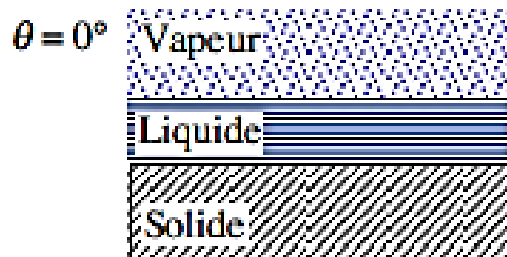
Wetting – Contact Angles

❖ Wetting

❖ Characteristic contact angles

θ	$\cos \theta$	γ_{SL}	S_{SL}
0°	1	$\gamma_{SV} - \gamma_{LV}$	0
90°	0	γ_{SV}	$-\gamma_{LV}$
180°	-1	$\gamma_{SV} + \gamma_{LV}$	$-2\gamma_{LV}$

- $\theta = 0^\circ \rightarrow$ wetting *perfect*, the solid is perfectly **lyophilic**
- $\theta = 90^\circ \rightarrow$ wetting *average*
- $\theta = 180^\circ \rightarrow$ *no* wetting, the solid is perfectly **lyophobic**



Wetting – Surface Roughness

❖ Wetting

– Influence of *surface roughness*

When the surface of the solid is not ideally smooth, its *thermodynamic roughness* f_R is defined as:

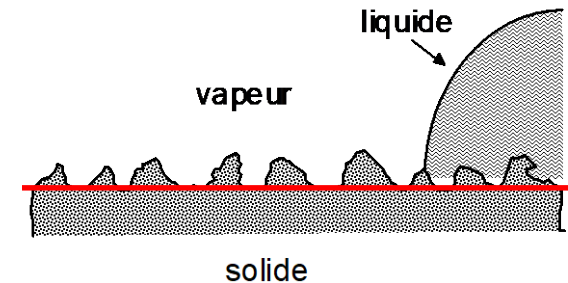
$$(2.1.16) \quad f_R = \frac{\text{real area of contact}}{\text{apparent area of contact}} \geq 1$$

It follows that:

$$(2.1.17) \quad \Delta G_{SL,R} = (\gamma_{SL} - \gamma_{SV})f_R + \gamma_{LV}$$

$$(2.1.18) \quad S_{SL,R} = (\gamma_{SV} - \gamma_{SL})f_R - \gamma_{LV}$$

$$(2.1.19) \quad \left. \begin{aligned} \cos\theta_R &= \frac{(\gamma_{SV} - \gamma_{SL})f_R}{\gamma_{LV}} \\ \cos\theta_R &= f_R \cos\theta \end{aligned} \right\}$$

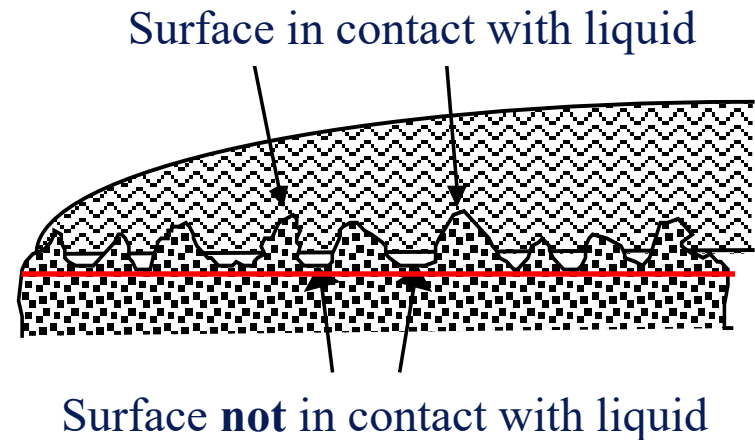


Wetting – Surface Roughness

❖ Wetting

- Effect of roughness on contact angle

θ	$\cos \theta$	$\cos \theta_R$	θ_R
$< 90^\circ$	> 0	$> \cos \theta$	$< \theta$
$= 90^\circ$	$= 0$	$= \cos \theta$	$= \theta$
$> 90^\circ$	< 0	$< \cos \theta$	$> \theta$



- $\theta < 90^\circ \rightarrow$ Roughness *increases* wetting and makes the solid **more lyophilic**
- $\theta = 90^\circ \rightarrow$ *No effect* of roughness on the wetting
- $\theta > 90^\circ \rightarrow$ Roughness *decreases* wetting and makes the solid **more lyophobic**

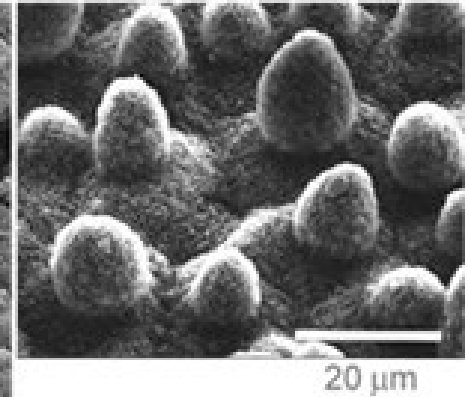
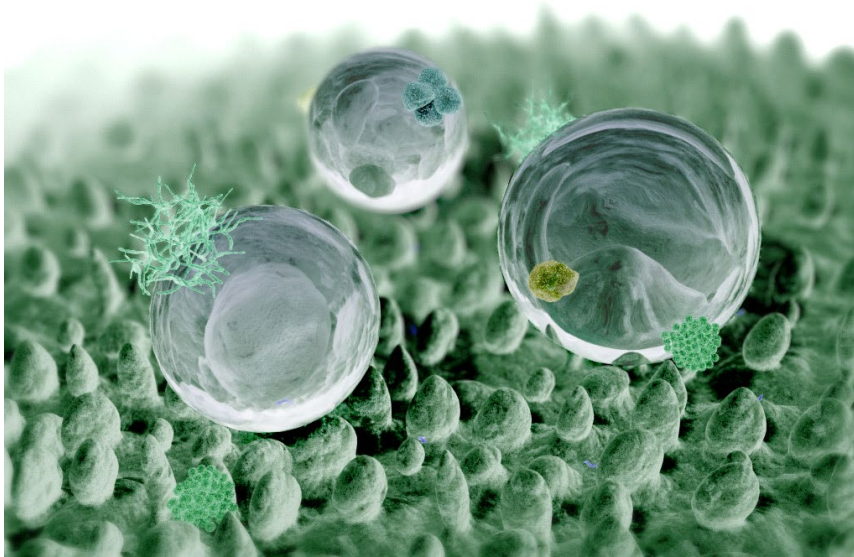
Lotus Leaf Effect



This phenomenon was studied in [1975](#) by Barthlott and Neinhuis, [botanists](#) of the [University of Bonn](#). Until their discovery, obtained by electron microscope analysis, it was mistakenly believed that the phenomenon was caused by the complete absence of roughness on the leaves.

http://en.wikipedia.org/wiki/Lotus_effect

Lotus leaf effect



Left: SEM image of surface produced within the project.
 Right: SEM image of the surface of a Lotus leaf.
 (D. Chakarov, P. Holgerson)

One technique to render a surface of [aluminum superhydrophobic](#) is by immersing it in a solution of [sodium hydroxide](#) for several hours, then applying a layer of [perfluorononan](#) with a thickness of 2 nanometers. This operation increases the contact angle from 67° to 168° .

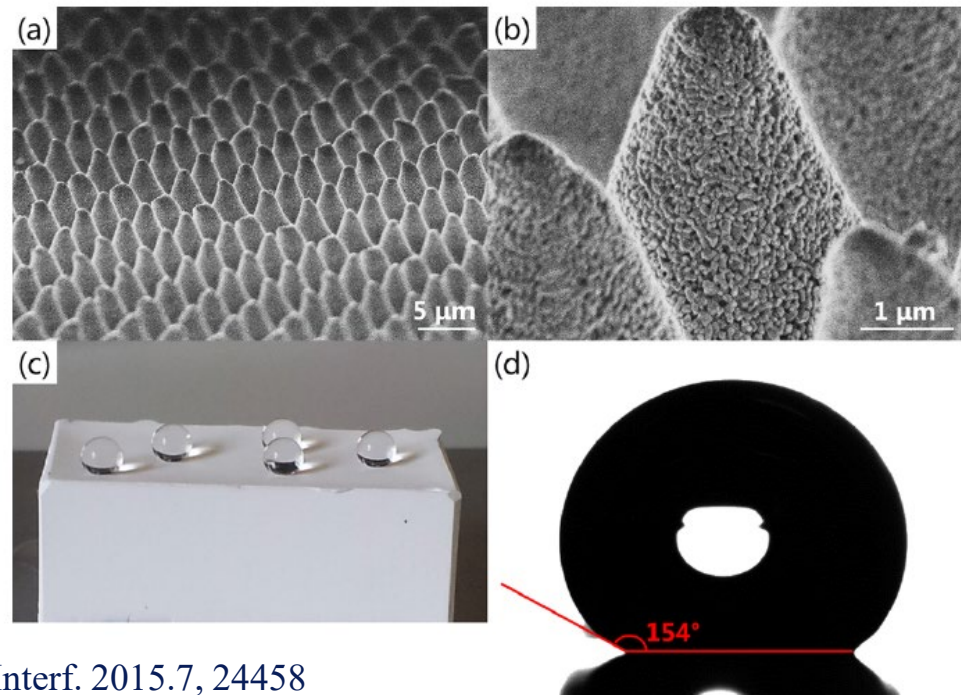
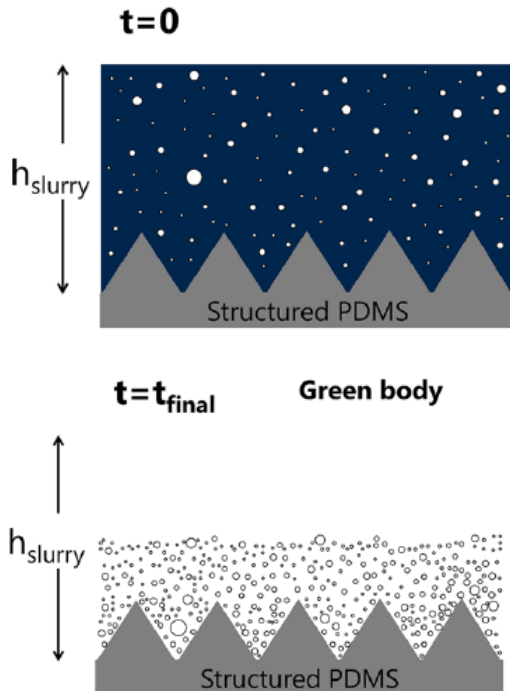
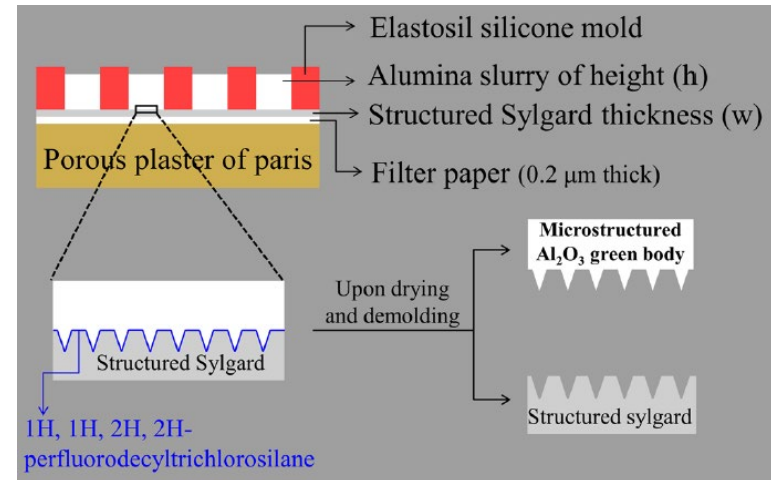
The lotus effect, M Reyssat, D Quéré, Pour la science, September 2006, p 34-40

Textile applications...



Superhydrophobic alumina surfaces - EMPA, Thun

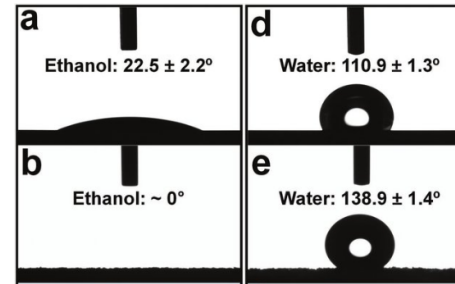
- *Surface 3D Micro Free Forms: Multifunctional Microstructured Mesoporous α -Alumina by in Situ Slip Casting Using Excimer Laser Ablated Polycarbonate Molds (EMPA-EPFL)**
- **Towards multifunctional ceramics or ceramic matrix composites for tribology and wetting, as well as biology and photovoltaics.**
- **120 cm² but... can scale up to 3 m²!!**



*Rowthu et al ACS Appl. Mater. Interf. 2015.7, 24458

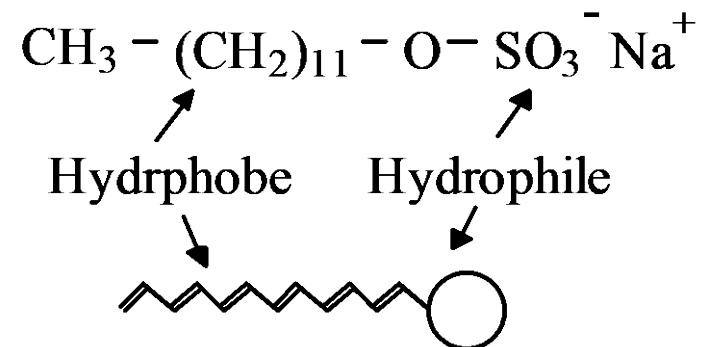
Contact angle - Surfactants

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$



Contact angle on PDMS
and roughness effect

- ❖ Mixing with ethanol, $\gamma_{LV} = 23 \text{ mN / m}$; water $\gamma_{LV} 73 \text{ mN / m}$
- ❖ To reduce γ_{SL} a surfactant is adsorbed at the solid-liquid interface.
- ❖ Surfactant = surface active agent
- ❖ An ionic surfactant - hydrophilic head - hydrophobic tail e.g.
- ❖ Sodium Dodecyl Sulfonate (SDS) or
- ❖ Soap - sodium stearate $\text{C}_{17}\text{H}_{35}\text{COONa}$,



Surface tension measurement

❖ Capillary rise

- Balance of forces at meniscus

The balance between the capillary rise force and the weight of the liquid column (mgh): gives,

$$\left. \begin{array}{l} W = \pi r^2 h g \Delta \rho \\ F = 2 \pi r \gamma \cos \theta \end{array} \right\} \rightarrow F = W \Rightarrow \gamma = \frac{r h g \Delta \rho}{2 \cos \theta} \quad (2.2.4)$$

With:

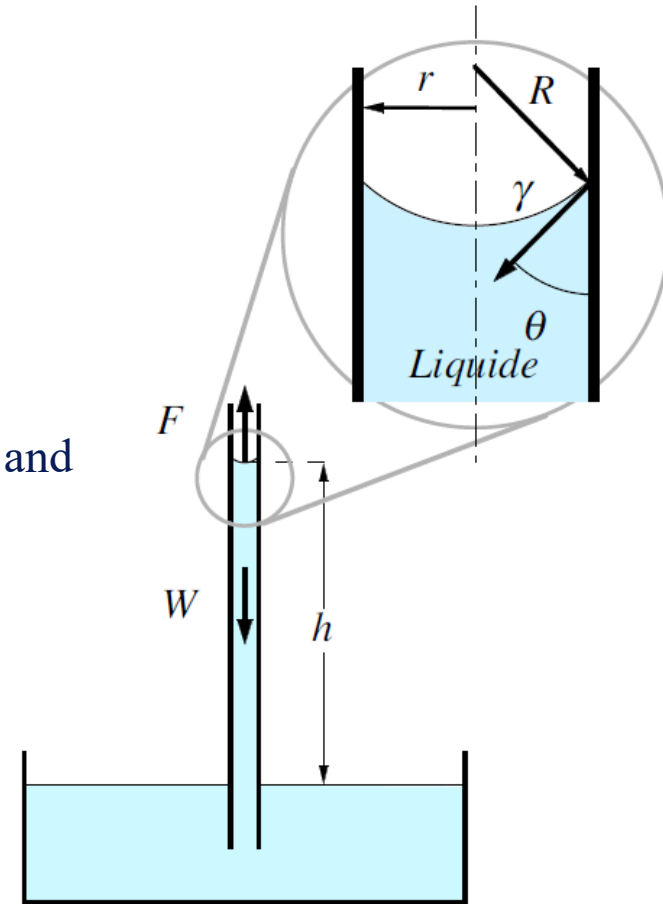
$\Delta \rho = \rho_L - \rho_V \cong \rho_L$: density difference between liquid and vapor (1 and 0.0012 g / cm³)

g : gravitational force

h : height of capillary rise

r : Inner radius of capillary tube

θ : Contact angle of the liquid in the capillary with the solid surface



Surface tension measurement

❖ Wilhelmy Balance

- Balance of forces

Increased apparent weight ΔW of a plate immersed in a liquid:

$$\Delta W = 2L\gamma_{LV}\cos\theta \Rightarrow \gamma_{LV} = \frac{\Delta W}{2L\cos\theta}$$

(2.2.11)

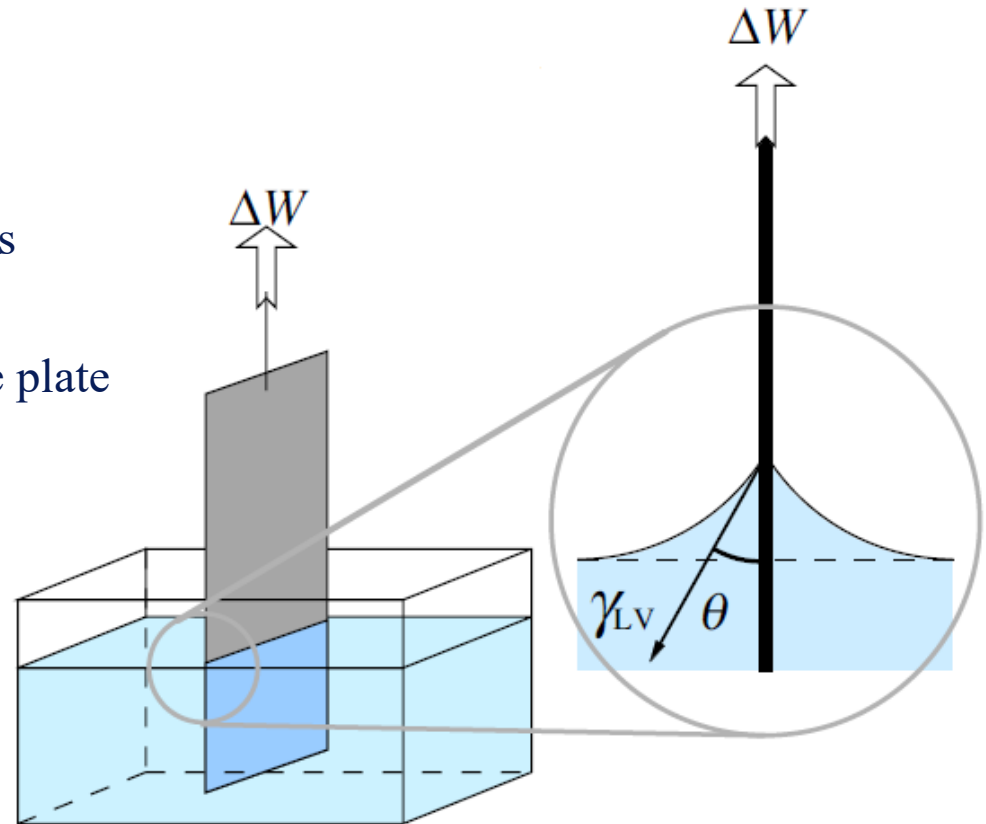
ΔW : Additional weight of the meniscus

L : Plate width (negligible thickness)

θ : Angle of wetting of the liquid on the plate

Advantage:

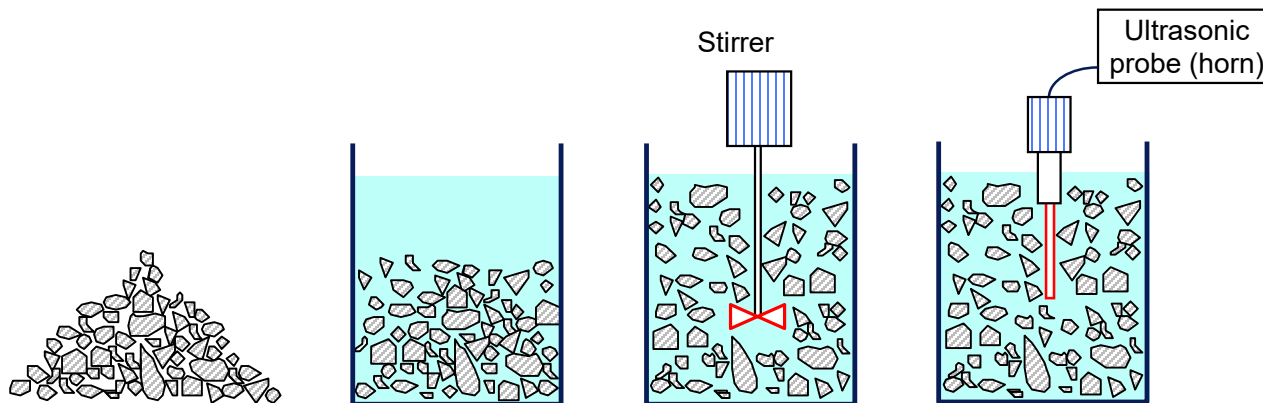
Possibility of continuous measurement, by modifying certain characteristics liquid (temperature, composition, etc.)



Dispersion – Suspensions and Pastes

The key factors in producing a dispersion either a suspension or paste are:

- ❖ wetting the surface of the powder with the liquid;
- ❖ the dispersion of the powder in the volume of this liquid by mixing or stirring;
- ❖ breaking up agglomerates (soft) or aggregates (hard) by ultrasonic treatment or by milling (week 6)
- ❖ agglomerates (soft) - no chemical bond
- ❖ aggregates (hard) - chemical bond
- ❖ the ability to keep the powder well dispersed and to avoid agglomeration or phase separation by sedimentation – colloidal stability...



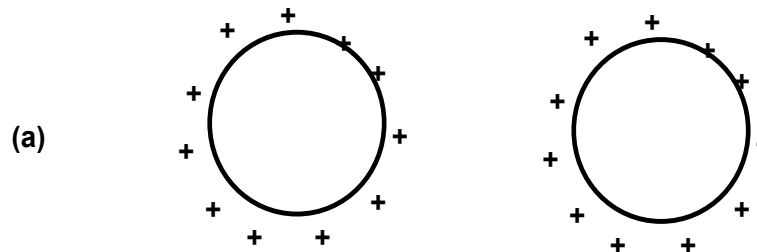
Colloidal Stability - Interparticle Forces

◆ Attractive

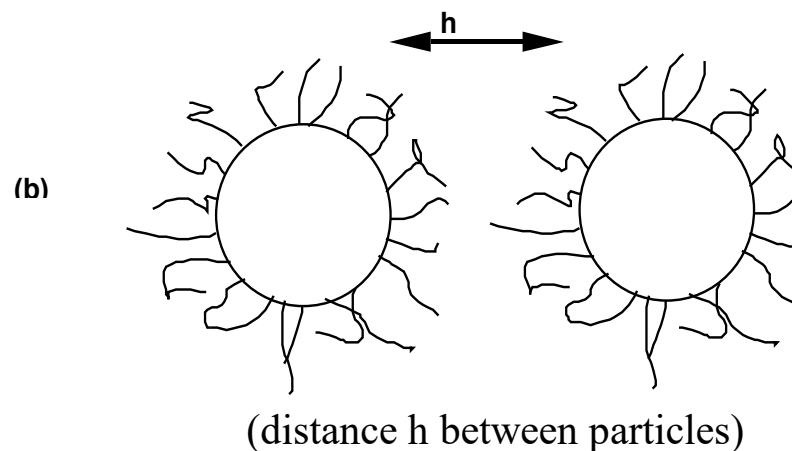
Van der Waals forces V_A

◆ Repulsive

(a) electrostatic, V_E
charged surfaces



(b) steric repulsion, V_S
polymer adsorption
soluble polymers -



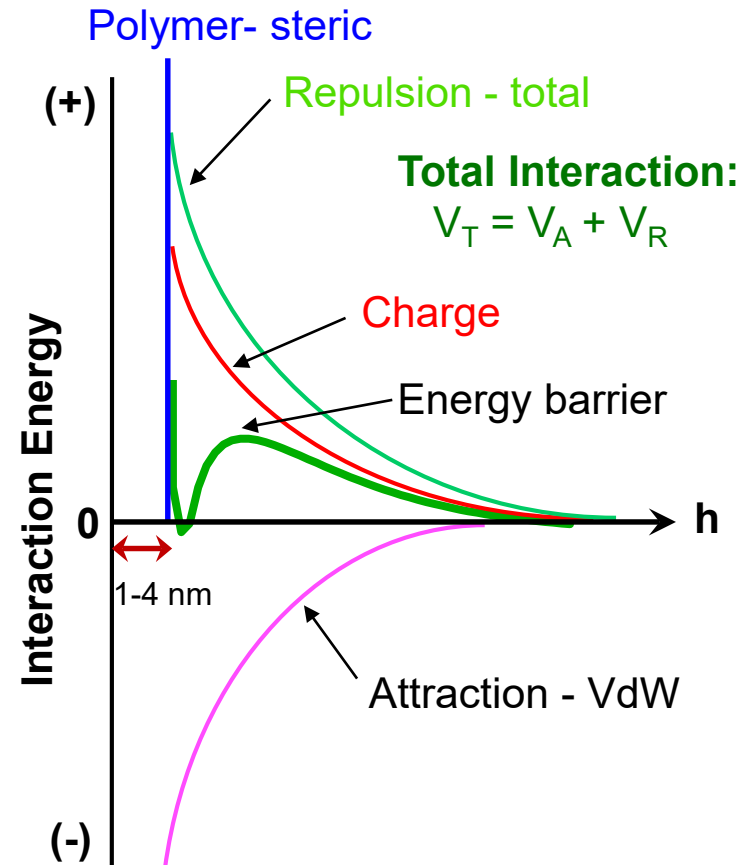
.R.G. Horn, J.Am.Ceram.Soc., 73(5) 1117-35 (1990).

Overall Interaction Energy

- ◆ Total Interaction (Potential) Energy $V(h)_T$:
- ◆ DLVO theory
- ◆ Derjaguin/Landau et Verveij/Overbeck = algebraic sum....

$$V(h)_T = V(h)_A + \underbrace{V(h)_E (+ V(h)_S)}_{V(h)_R}$$

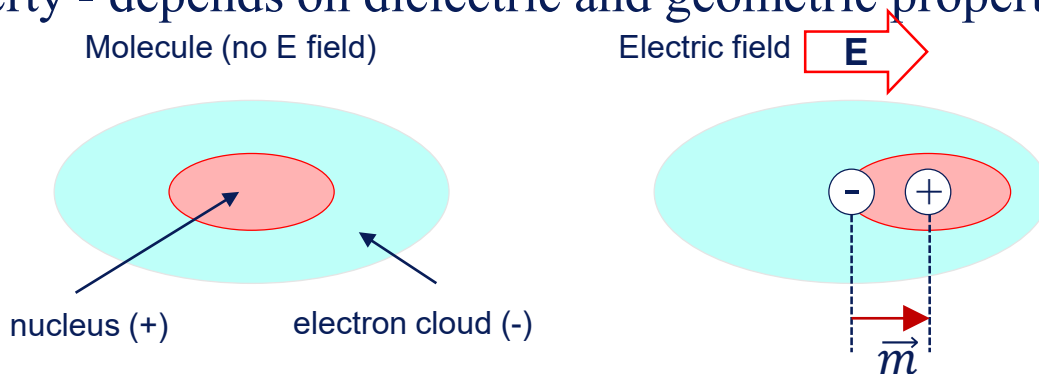
- ◆ Influences:
 - Rheology (flow of suspension)
 - Particle packing
 - Green body density
- ◆ Which in turn influences:
 - Sintering
 - Microstructure and
 - Properties



Attractive Forces - Intermolecular Forces

https://youtu.be/S8QsLUO_tgQ *

- ❖ Van der Waals
 - Always attractive between particles of the same nature
 - Interaction between dipoles * (induced e.g. CH₄) or permanent (e.g. H₂O - hydrogen bond)
- 3 types
 - Dipole - Dipole - interaction between permanent dipoles (Keesom forces)
 - Dipole - Induced Dipoles – induced from permanent dipoles (Debye forces)
 - Induced Dipole - Induced Dipole - instantaneous dipoles from electron cloud fluctuations (London or dispersion forces)
- ❖ Material property - depends on dielectric and geometric properties of the system



Useful videos

[*https://youtu.be/S8QsLUO_tgQ](https://youtu.be/S8QsLUO_tgQ) | <https://youtu.be/nvJv6mCmk68> | <https://youtu.be/ODnqtf3aAvw>

Dispersion Interaction- Fundamentals

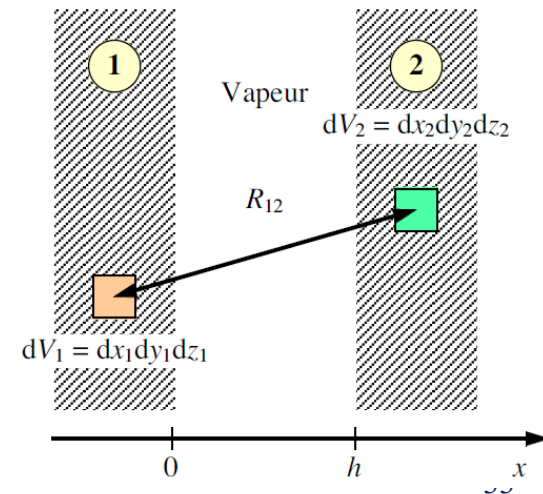
- ❖ Interaction between instantaneous dipole and induced dipole
 - Description
- ❖ A neutral molecule *without a permanent* dipolar moment present a *instantaneous* dipolar moment due to the movement of its electrons (e.g. CCl₄)
- ❖ An *attractive interaction* between any two molecules is established due to the correlated electronic movements of molecules (instantaneous dipole-induced dipole interaction).
- ❖ In quantum formalism, the potential energy for the interaction between the two molecules is given by:

$$V_{12}^{disp} = -\frac{1}{24(\pi\epsilon_0)^2 R_{12}^6} \sum_i \frac{|\langle n | \vec{m} | 0 \rangle_1|^2 |\langle k | \vec{m} | 0 \rangle_2|^2}{(E_1^n - E_1^0) + (E_2^k - E_2^0)} \cong -\frac{C_{12}}{R_{12}^6} \quad (5.2.1)$$

The amount $\langle n | \underline{m} | 0 \rangle_i$ represents the *instantaneous dipole moment* due to the energy transition $E_i^0 \rightarrow E_i^n$ in the molecule i .

This transient dipole moment gives the amplitude of the optical transition between the two states.

\mathbf{R}_{12} – is the distance between dipoles



Dispersion Interactions

- ❖ Dispersion Interaction
- ❖ Relationship with the optical properties of molecules

The *dispersion* interaction is linked to the *electrical polarizability* of molecules $\alpha(\omega)$, itself linked to their *refractive index* and is dependent on the frequency of light, ω ;

$\hbar = h / 2\pi$, h is the constant of *Planck*):

$$\alpha(\omega) = \frac{2}{3} \sum_i \frac{(E^n - E^0) |\langle n | \vec{m} | 0 \rangle|^2}{(E^n - E^0)^2 - \hbar^2 \omega^2} \quad (5.2.2) \quad \text{electrical polarizability}$$

For $\omega = 0$, the interaction potential between two molecules can be linked with their first ionization potentials (I_1 and I_2), as derived by *London* :

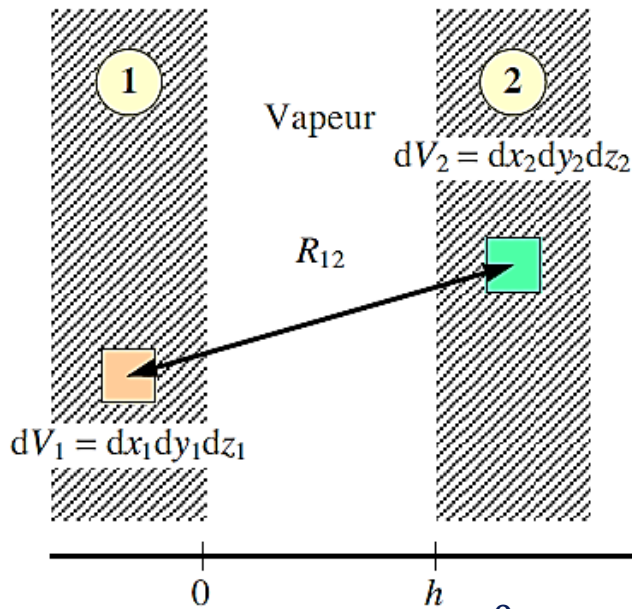
$$V_{12}^{disp}(R) = - \frac{3}{32(\pi\epsilon_0)^2} \frac{I_1 I_2}{I_1 + I_2} \frac{\alpha_1(0)\alpha_2(0)}{R_{12}^6} \quad (5.2.3)$$

The dispersion interaction is the *main* origin of the *cohesion* of condensed molecular phases (solid and liquid); it decreases very quickly with increasing distance R_{12} between the molecules. i.e. ***it is a short range interaction.***

Dispersion Interaction between Particles

- ❖ Semi-Infinite plates in vacuum
 - Approach of *Hamaker*

The interaction potential is obtained by *summing up* all interactions between all *pairs* of molecules belonging respectively to the two particles (plates) :



$$dU_{12} = \frac{C_{12}\rho_1\rho_2 dV_1 dV_2}{[(x_2-x_1)^2+(y_2-y_1)^2+(z_2-z_1)^2]^3} \quad (5.2.4)$$

Where ρ_i is the density of the phase i .

The total interaction energy is obtained by integration over the whole volume of the particles (considered as semi-infinite):

Where $H_{12} = \pi^2 C_{12} \rho_1 \rho_2$ is defined as the *Hamaker* constant

$$U_{12} = -\frac{H_{12}}{\pi^2} \int_{-\infty}^0 \int_h^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{dx_1 dx_2 dy_1 dy_2 dz_1 dz_2}{[(x_2-x_1)^2+(y_2-y_1)^2+(z_2-z_1)^2]^3} \quad (5.2.5)$$

Interaction potential

Dispersion interaction between semi-infinite plates

- ❖ Semi-Infinite plates in vacuum
 - Potential for interaction
- ❖ Full integration of Eq. (5.2.5) leads to the very simple expression for the interaction between two semi-infinite solids:

$$\frac{U_{12}}{Area} = -\frac{H_{12}}{6\pi} \int_h^\infty \frac{dx_2}{x_2^3} = -\frac{H_{12}}{12\pi h^2} \quad (5.2.7) \quad \begin{array}{l} \text{Potential energy} \\ \text{between the two} \\ \text{plates} \end{array}$$

- ❖ The **force** of interaction between **two semi-infinite solids** (1) and (2) is the derivative of the potential interaction U_{12} with respect to the separation distance h :

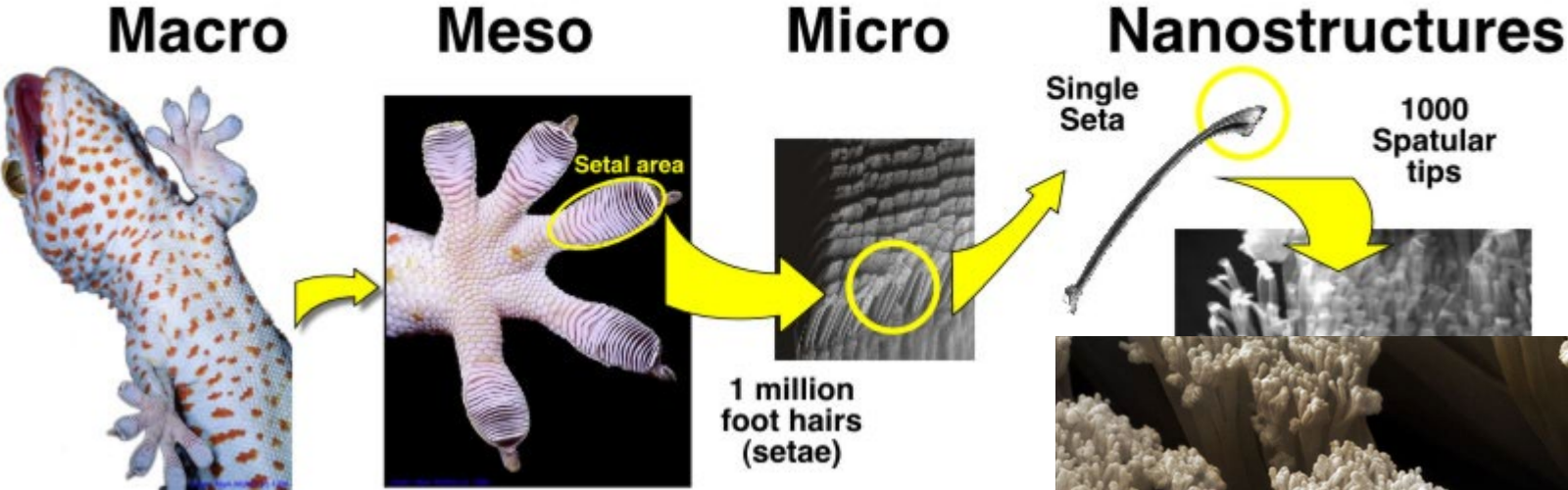
$$F_{12} = -\frac{dU_{12}}{dh} = -Area \times \frac{H_{12}}{6\pi h^3} \quad (5.2.9)$$

- ❖ While $U_{12}/Area$ varies as the inverse of *square* distance $1/h^2$, and F_{12} varies as $1/h^3$.
- ❖ The forces are ubiquitous ...and even used by the Gecko....

EXAMPLE - Gecko video... [Http: //www.youtube.com/watch? V = gzm7yD-JuyM](http://www.youtube.com/watch?V=gzm7yD-JuyM)

Gecko or «Spiderman» Van der Waals forces in action!

Gecko adhesive system



Video: EXAMPLE - Gecko

<http://www.youtube.com/watch?v=gzm7yD-JuyM>

Biomimetic Millisystems Lab, UC Berkley

<http://robotics.eecs.berkeley.edu/~ronf/Biomimetics.html>



Dispersion Interaction between Particles

❖ Infinite plates in a solvent

- Insertion of a liquid between two flat plates
- The combination of Eq. (5.2.1) and (5.2.2) leads to the expression:

$$H_{12} = \pi^2 C_{12} \rho_1 \rho_2 \quad (5.2.23)$$

- H_{12} is therefore approximately proportional to the polarizabilities of the media:

$$H_{12} \approx \rho_1 I_1 \alpha_1 \rho_2 I_2 \alpha_2 \quad (5.2.24)$$

- This allows us to write:

$$H_{12}^2 \cong H_{11} H_{22} \quad (5.2.25)$$

H_{11} : material 1 resp. vacuum

and for liquid (2) bounded by two plates of solid (1):

$$H_{121} \cong (\sqrt{H_{22}} - \sqrt{H_{11}})^2 \quad (5.2.26)$$

Two materials of the same nature: always attractive

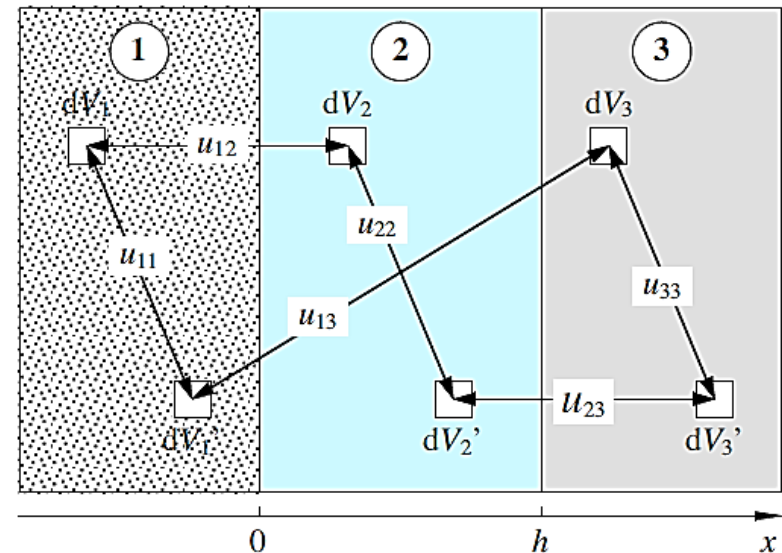
- ❖ This expression clearly demonstrates the intrinsically positive character of the constant H_{121} .

In the case of *three different* environments, we find :

$$H_{123} \cong (\sqrt{H_{22}} - \sqrt{H_{11}})(\sqrt{H_{22}} - \sqrt{H_{33}}) \quad (5.2.27)$$

We therefore see that $H_{123} < 0$ if $H_{11} < H_{22} < H_{33}$, or if $H_{33} < H_{22} < H_{11}$.

i.e. can be negative between materials of a different nature for these conditions – see slide 42



Dispersion Interaction between curved surfaces

❖ Interaction between curved surfaces

- Sphere-plane interaction:
- *Derjaguin* Approximation
- Consider the interaction between a solid plane and a sphere of radius R separated by a distance h such that $h \ll R$. By definition :

$$F = -\frac{dU(h)}{dh} \quad (5.2.28)$$

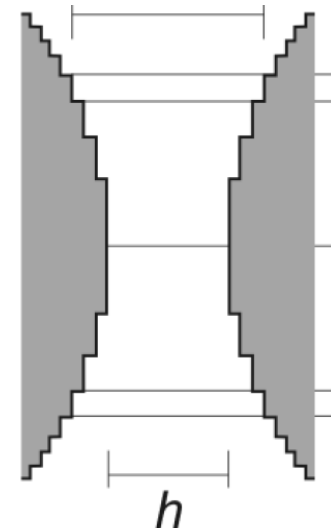
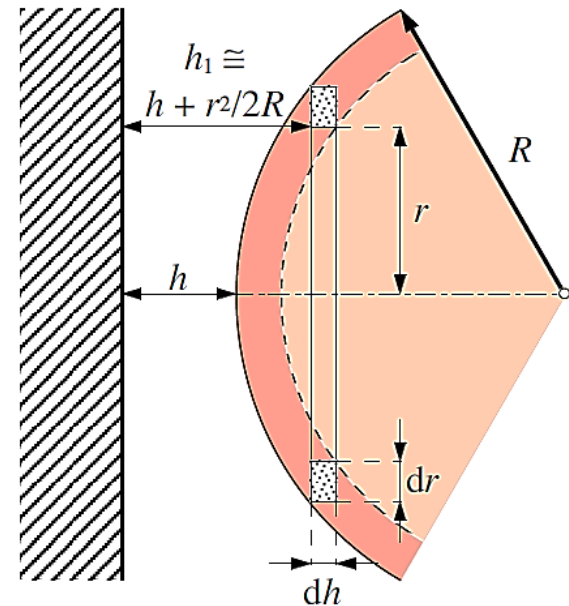
Which ultimately leads to the result:

$$F_{12}(h) = 2\pi R \frac{U_{12}(h)}{Area} = -2\pi R \frac{H_{12}}{12\pi h^2} \quad (5.2.31)$$

as $U_{12}(h)$ represents the interaction energy between two semi-infinite planes at a distant h , given by the

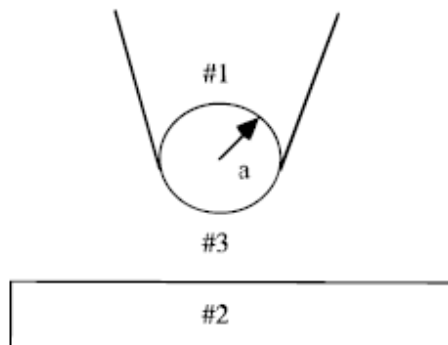
$$\text{Eq. (5.2.7)} \quad \frac{U_{12}}{Area} = -\frac{H_{12}}{12\pi h^2}$$

This geometry is particularly relevant for Atomic Force Microscopy (AFM) experiments where interparticle forces can be measured.



Van der Waals Forces - Measurement by AFM

- ❖ Measurement of interparticle forces between the same material or different materials
- ❖ A. Meurk, P. F. Luckham and L. Bergstrom, *Langmuir* **1997**, *13*, 3896-99



(a) Si_3N_4 -diiodomethane- SiO_2
Repulsive

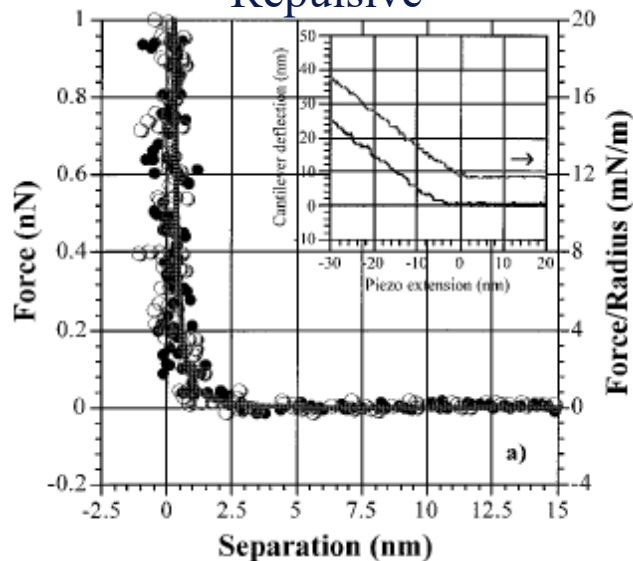
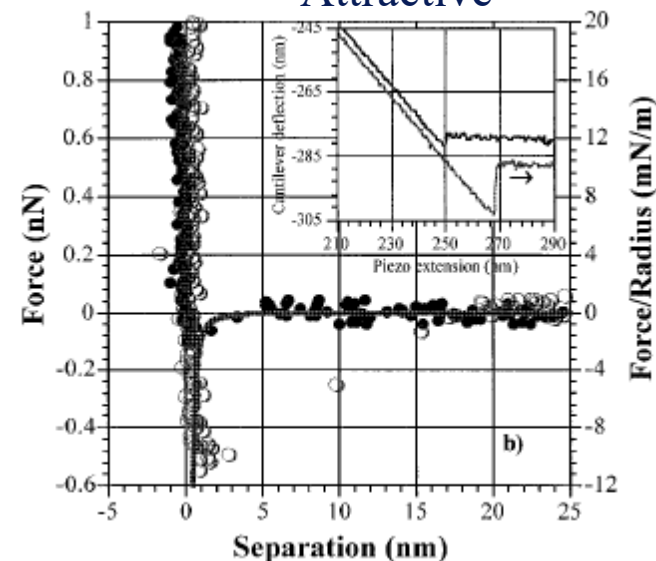


Table 2. Nonretarded Hamaker Constants

system (tip-medium-substrate)	A_{132} / 10^{-20} J	resulting interaction
Si_3N_4 -diiodomethane- β - Si_3N_4	1.0	attractive
Si_3N_4 -1-bromonaphthalene- β - Si_3N_4	2.8	attractive
Si_3N_4 -diiodomethane- SiO_2	-0.8	repulsive
Si_3N_4 -1-bromonaphthalene- SiO_2	-0.2	repulsive

(b) Si_3N_4 - diiodomethane- Si_3N_4 .
Attractive



filled circles denote approach, open circles denote retraction,

Dispersion Interaction between curved Surfaces

- ❖ Interaction between curved surfaces
 - Other interactions between curved surfaces

A derivation similar to the previous cases gives for two *orthogonal cylindrical surfaces* (h being the smallest distance between surfaces):

$$F_{12}(h) = 2\pi\sqrt{R_1R_2} \frac{U_{12}(h)}{Aire} \quad (5.2.32)$$

For two spheres:

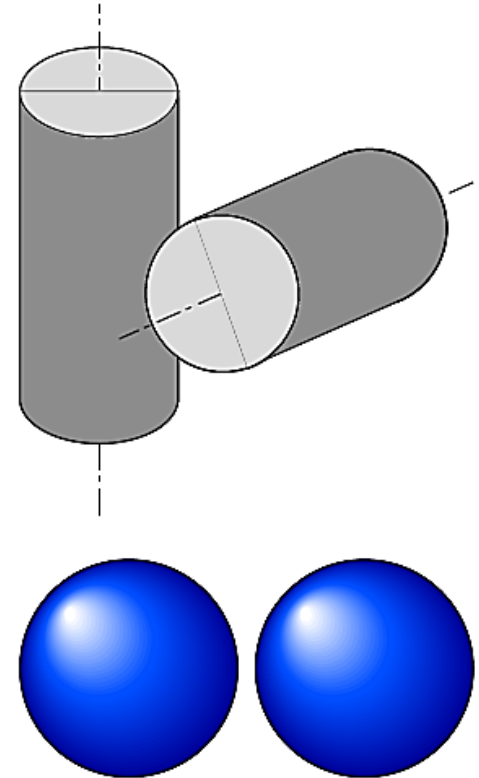
$$F_{12}(h) = 2\pi \frac{R_1R_2}{R_1+R_2} \frac{U_{12}(h)}{Aire} \quad (5.2.23)$$

If $h \ll R_1 < R_2$:

$$U_{sphère}(h) = -\frac{R_1R_2}{6(R_1+R_2)} \frac{H_{12}}{h} \quad (5.2.34)$$

If $h \gg R_1 > R_2$:

$$U_{sphère}(h) = -\left(\frac{4}{3}\right)^2 \frac{R_1^3R_2^3}{(h+R_1+R_2)^6} H_{12} \quad (5.2.35)$$



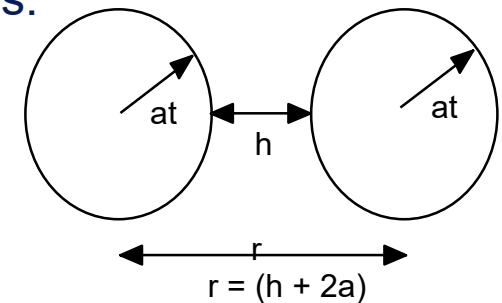
Traite de Matériaux - Van der Waals - Hamaker approach*

- ❖ Attractive Interaction Potential V_A
- ❖ Hamaker Constant A , form factor H !!!
- ❖ Dispersion forces (instantaneous dipoles - induced dipoles)
- ❖ Permanent Dipoles and Induced by permanent dipoles
- ❖ A - depends on dielectric properties (\sim polarizability)
 - particles and the continuous medium separating them,
 - over the entire spectral range of electromagnetic waves.
- ❖ For identical particles - size and chemistry in vacuum

$$V_A(h) = - A \cdot H(h, \text{form})$$

Van der Waals

$$A = \frac{3}{8} N^2 kT \sum_{n=0}^{\infty} \alpha^2 (i\xi_n)$$



N - number of molecules per unit volume of the material,

α is the polarizability of these molecules (dielectric constant), ξ_n is the electromagnetic frequency

Al_2O_3 in water is $A \sim 36.7 \times 10^{-21}$ J, under vacuum $A \sim 152 \times 10^{-21}$ J,

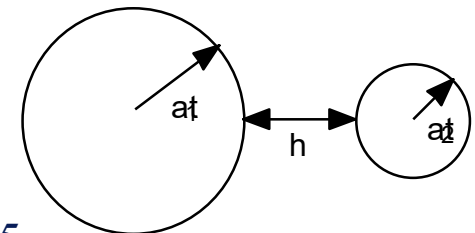
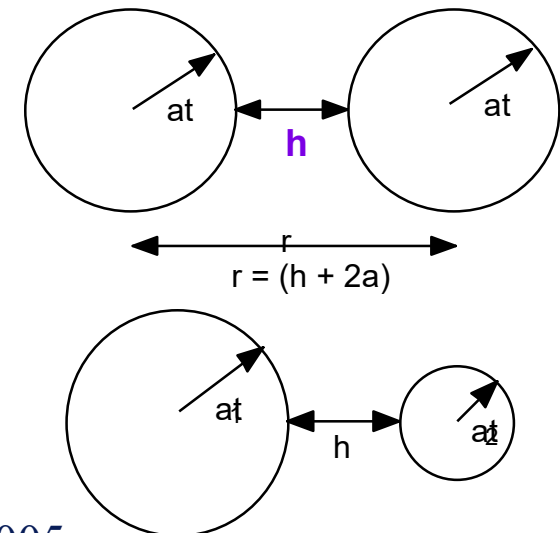
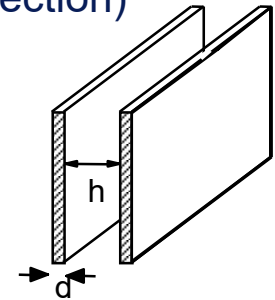
SiO_2 (silica) in water is $A \sim 4.6 \times 10^{-21}$ J, under vacuum $A \sim 65 \times 10^{-21}$ J

Summary - Van der Waals - Hamaker*

- ❖ A – Hamaker constant – function of dielectric properties of the material
- ❖ H, encompasses the morphology of the particles, their size, their separation and orientation
- ❖ Limitations
- ❖ Retardation
 - multi-body effects - phase shift of dipole correlation (decreased interaction)
- ❖ Screening
 - in the presence of a high concentration of electrolyte (p253)

$$V_A(h) = - A \cdot H(h, \text{form})$$

Shape	H geometric factor
Flat plates parallel - (semi-infinite)	$-\frac{1}{12\pi h^2}$
Identical spheres, radius a	$-\frac{1}{6} \left[\frac{2a^2}{r-4a^2} + \frac{2a^2}{r^2} + \ln \frac{r-4a^2}{r^2} \right]$
Spheres of radius, a_1 and a_2	$-\frac{1}{6} \left[\frac{2a_1a_2}{r^2 - (a_1 + a_2)^2} + \frac{2a_1a_2}{r^2 - (a_1 - a_2)^2} + \ln \frac{r^2 - (a_1 + a_2)^2}{r^2 - (a_1 - a_2)^2} \right]$



Attractive forces - magnetic *

- ❖ Ceramics with Fe, Ni, Co or Cr can have attractive interparticle magnetic forces .
- ❖ For cubic particles (approx. plates), the magnetic attraction energy is given by (Ozaki et al, 1988):

$$V_m = - \frac{\rho M^2}{4\pi\mu_0 (a+h)^3} \quad \text{Eq 3.4.12}$$

ρ is a constant depending on the orientation of the magnetic moments (from -2 to $+2$),

M is the dipole of the magnetic moment, μ_0 is the magnetic permeability,

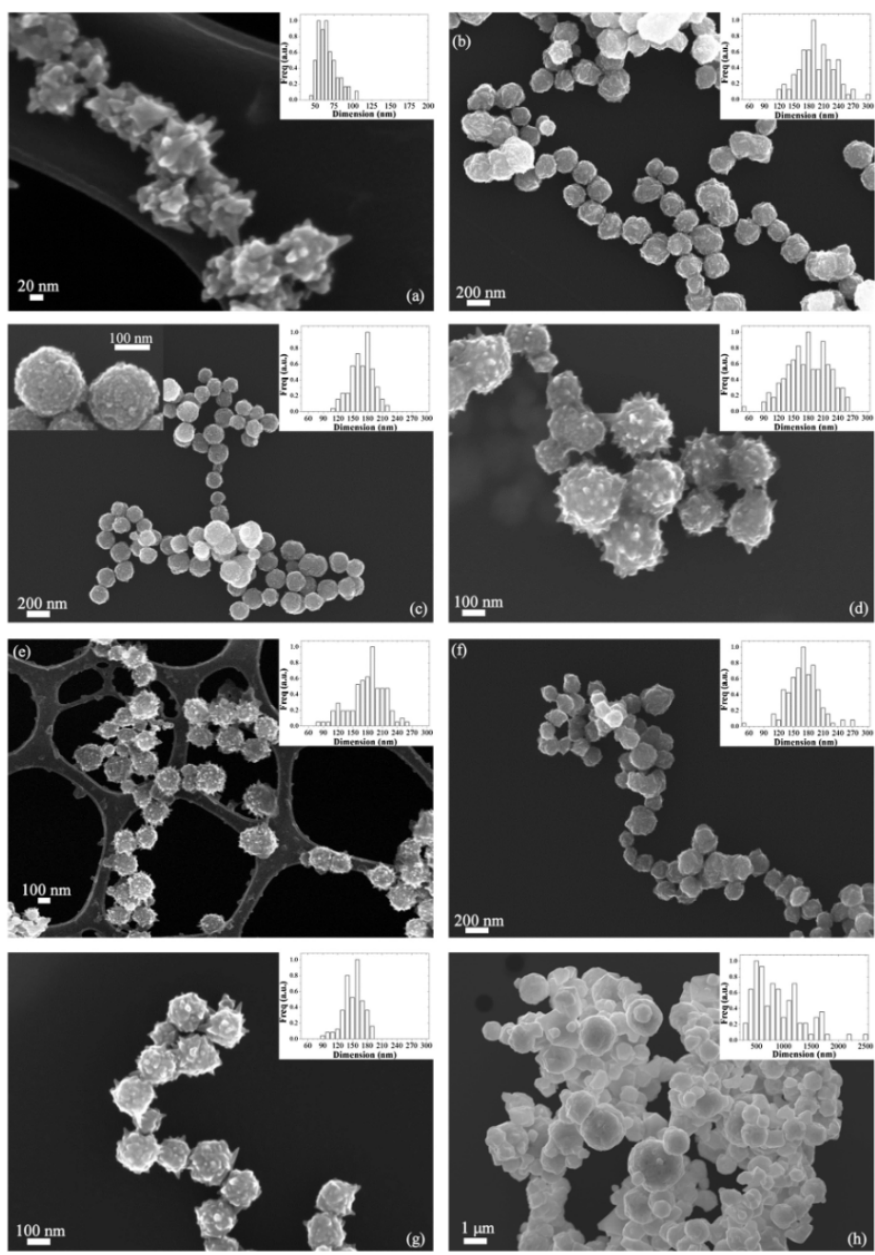
h is the separation distance between particles a is the size of the edge of the cube.

- ❖ When the particles are very small (10-15nm), they become superparamagnetic - many bio-medical applications...e.g. cancer treatment...Superparamagnetic iron oxides – SPIONS...

* **Les Céramiques**, Les Traités des Matériaux, Volume 16, PPUR, 2005

Ni nanoparticles

Applied Catalysis B: Environmental 156–157 (2014) 404–415



← Commercial Ni

Repulsive forces

- ❖ **Electrostatic – week 8**
 - dissociation of species at the surface
 - adsorption of charged species
 - dissociated ions, molecules or polymers
- ❖ **Steric – week 9**
 - molecules - often adsorbed polymers

