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Universidade de São Paulo

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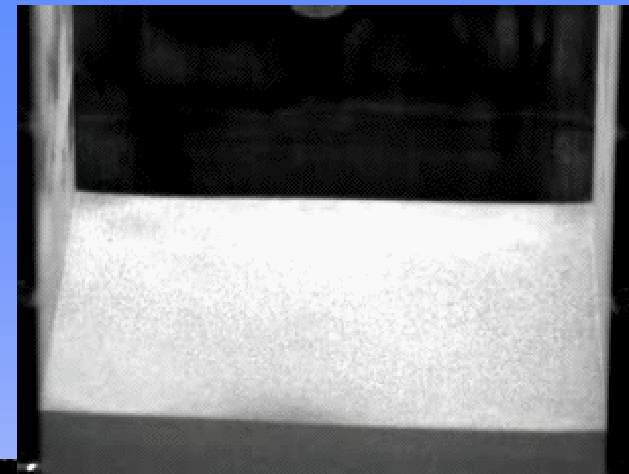
PhotoTech

The USP Research Consortium for Photochemical Technology

INCT catálise

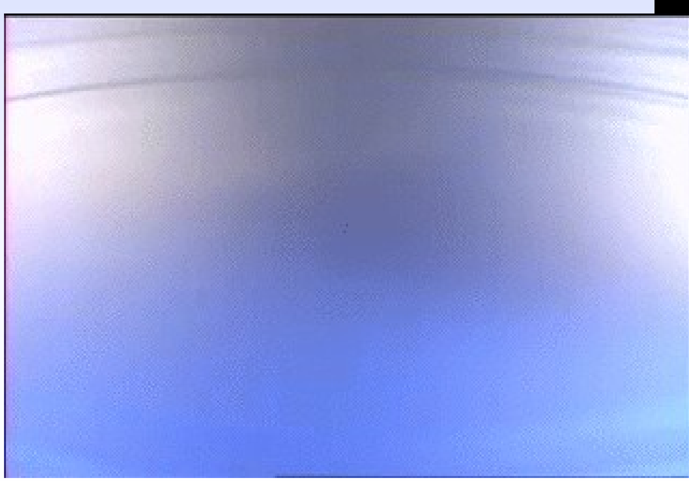
**Associated Laboratory**



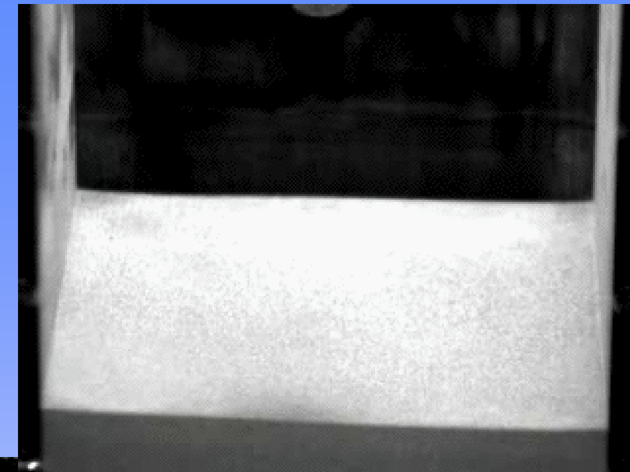


# INTRODUCTION TO

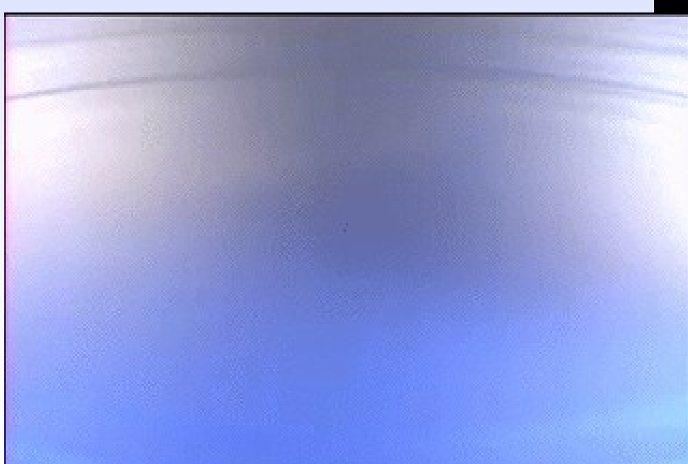
# SURFACES, INTERFACES



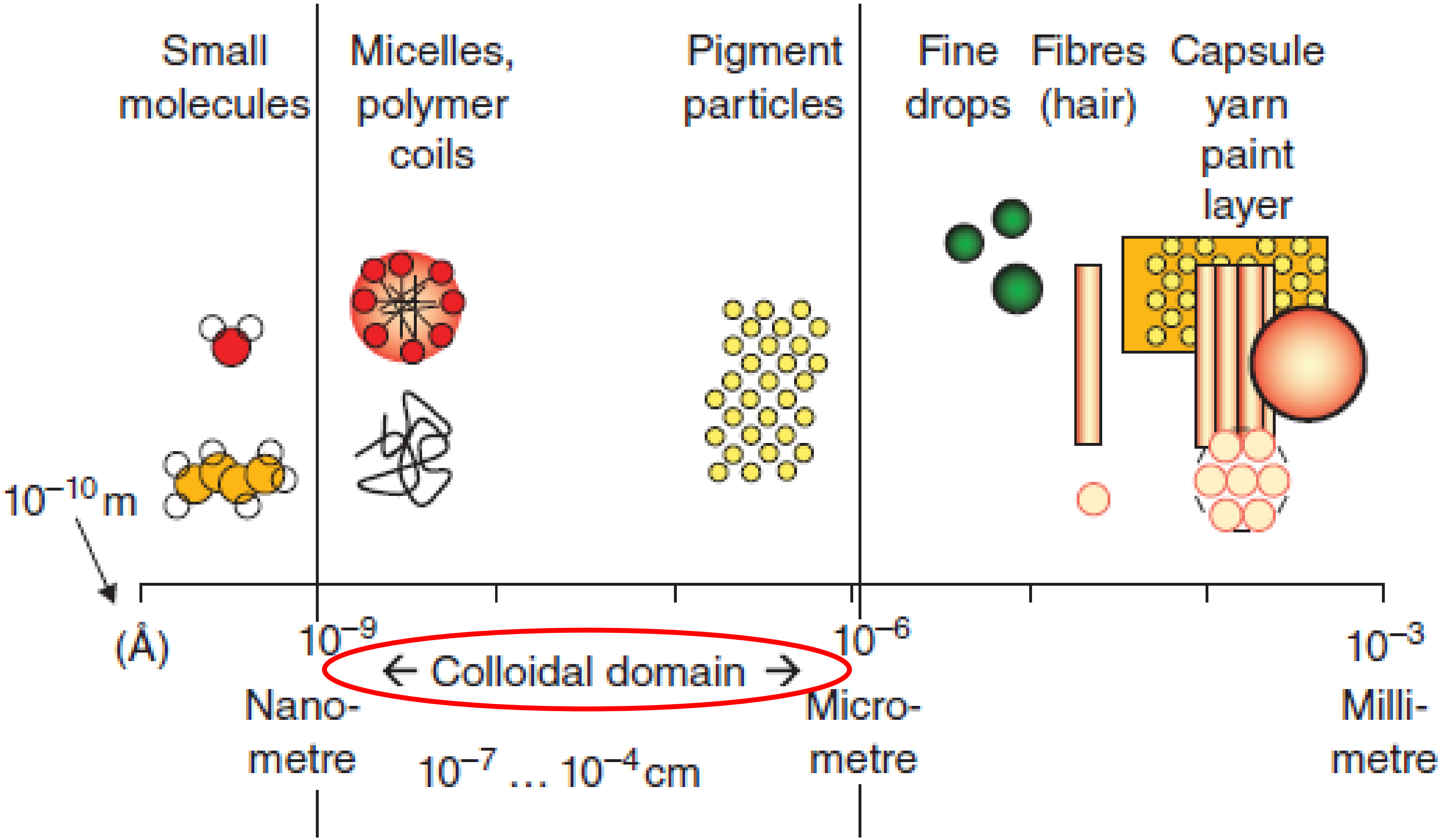
# EMULSIONS & FOAMS



# Fundamentals of Colloids and Interfaces



# The Colloidal Domain




Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

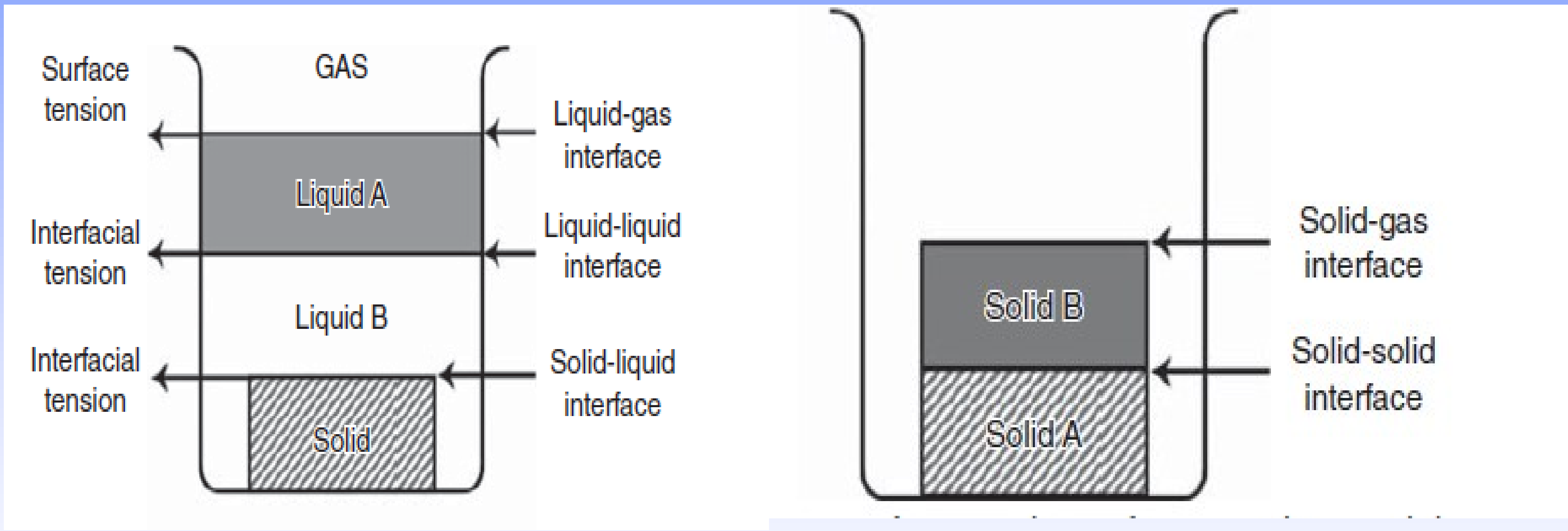
# Origin of the Term "Colloid"


***Figure 1.2*** *Thomas Graham (1805–1869), the pioneer in the study of colloidal systems, used the term "colloids" derived from the Greek word for glue ("*colla*"). He thought that their special properties were due to the nature of the compounds involved. Later, it was realized that the size of particles (of the "dispersed phase", as we call it) is solely responsible for the special properties of colloidal systems. (Right) T. Graham, H407/0106. Courtesy of Science Photo Library*

**Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)**

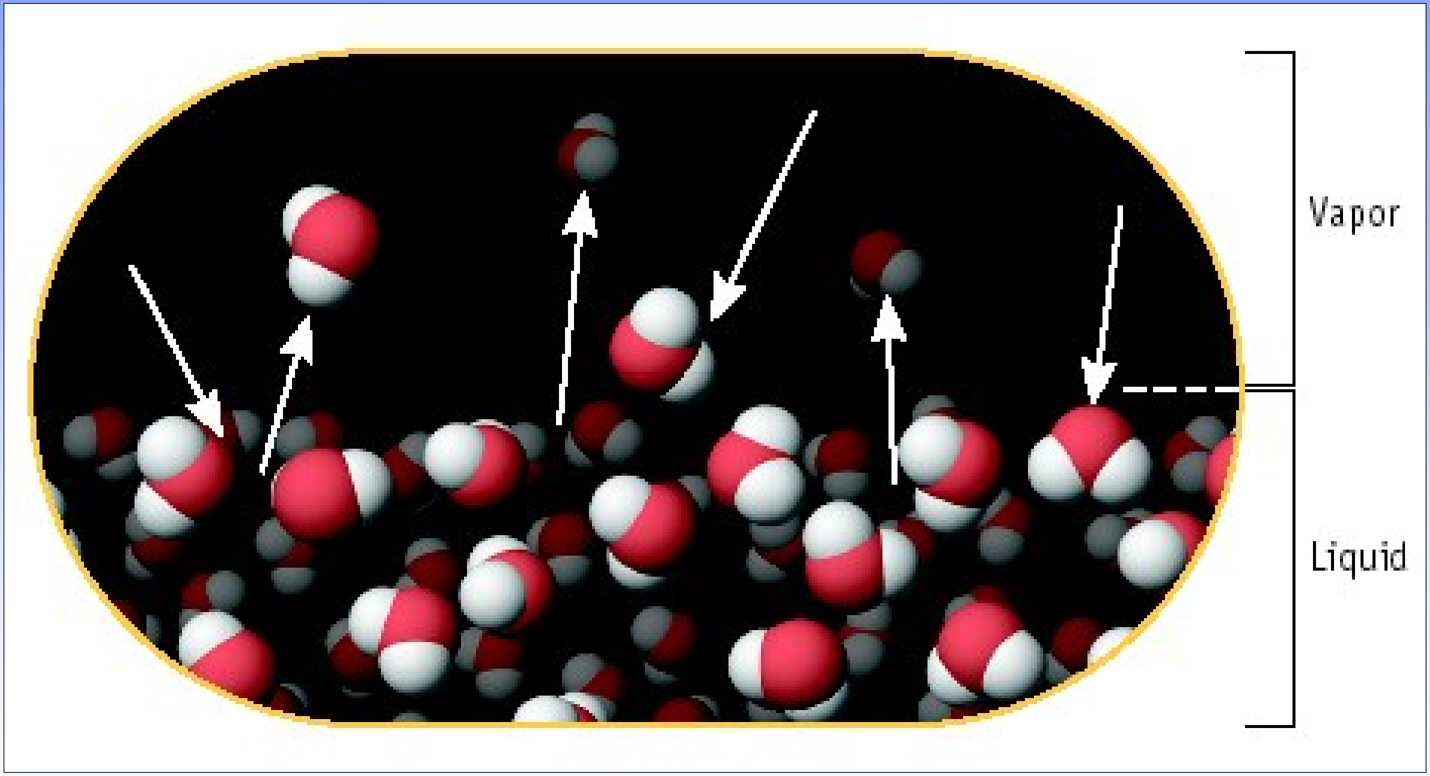
# Surfaces and Interfaces

# Types of Interfaces/Surfaces

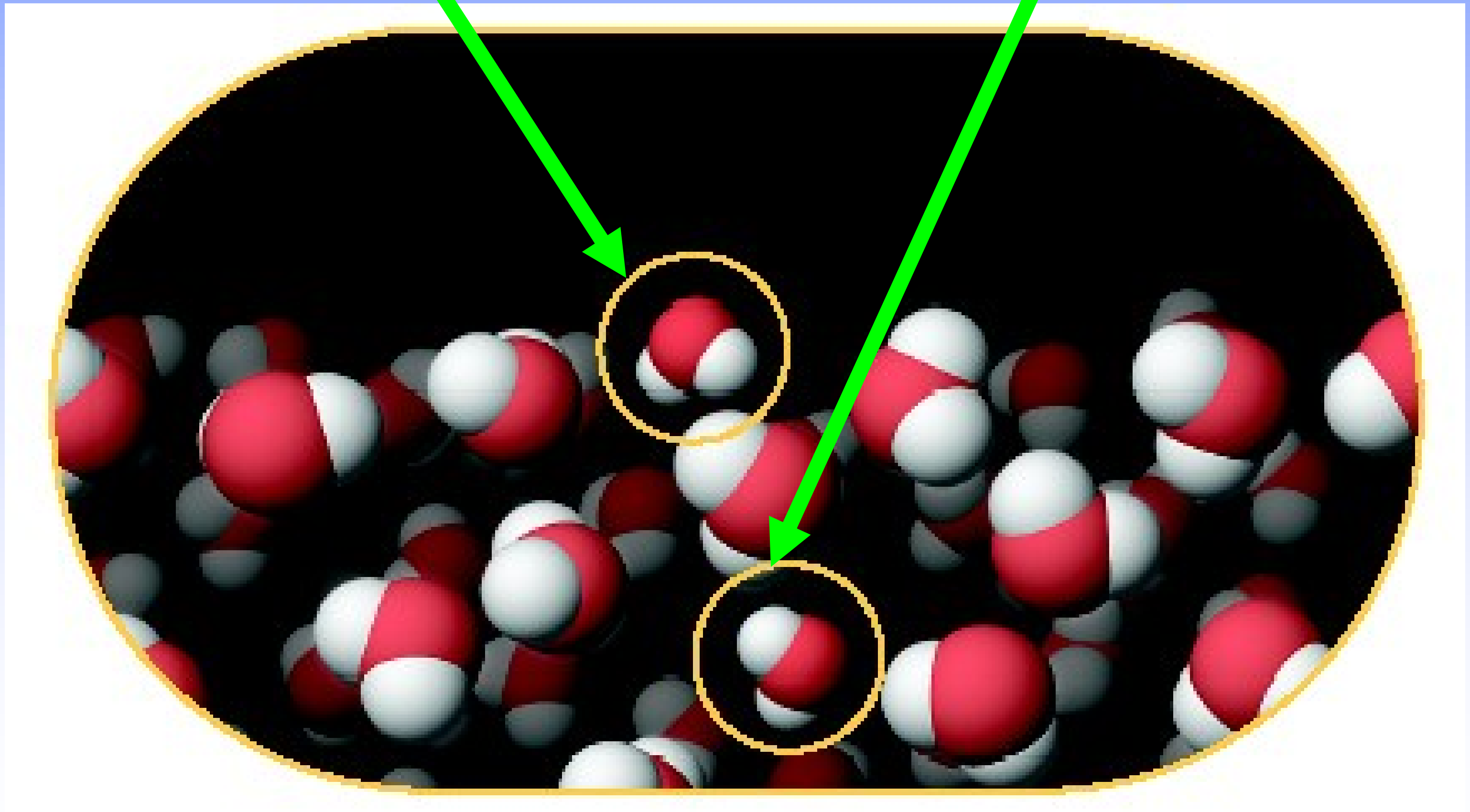



Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

# The Surface of a Liquid



# Molecules on the Surface and in the Interior (bulk) of a Liquid



# Surface Tension

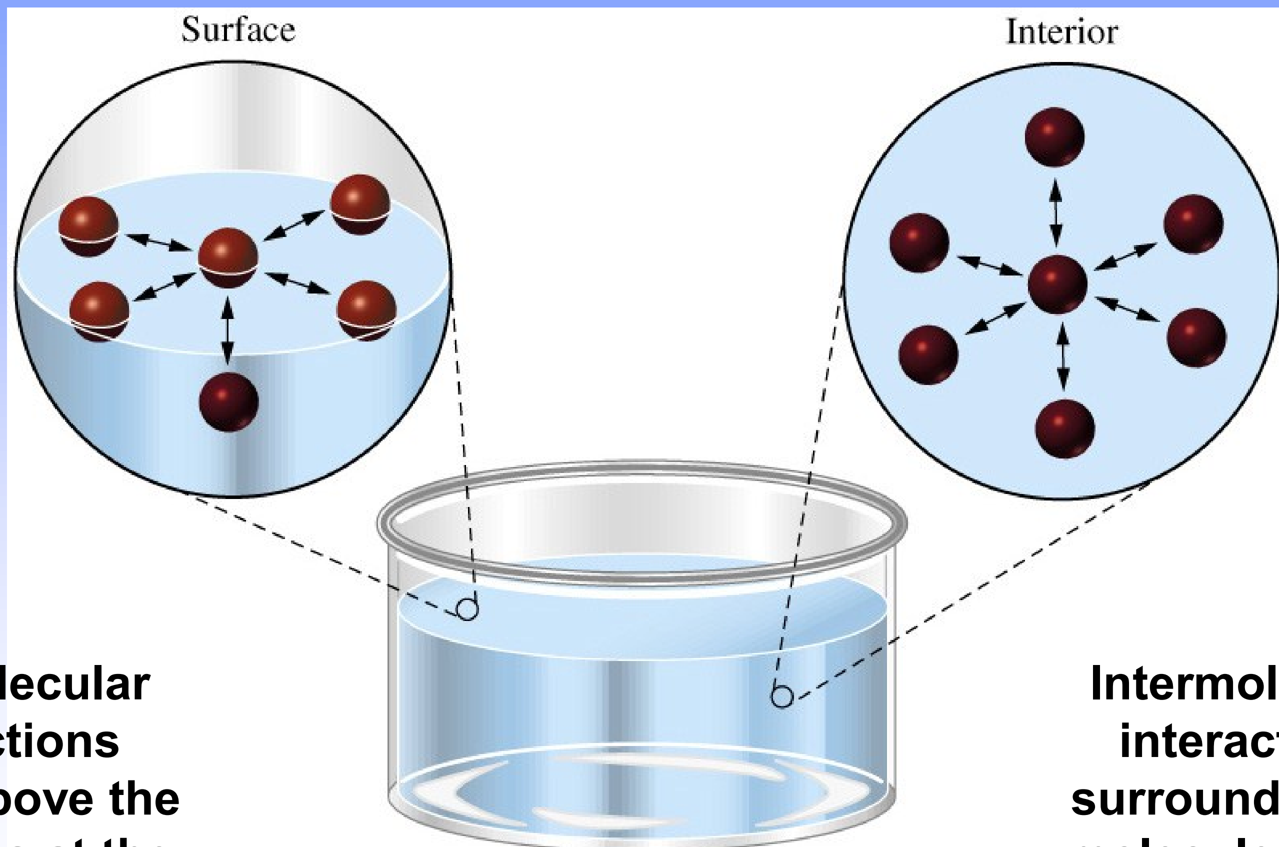
# Surface Tension

The Surface Tension

makes the water drops spherical.

Why?

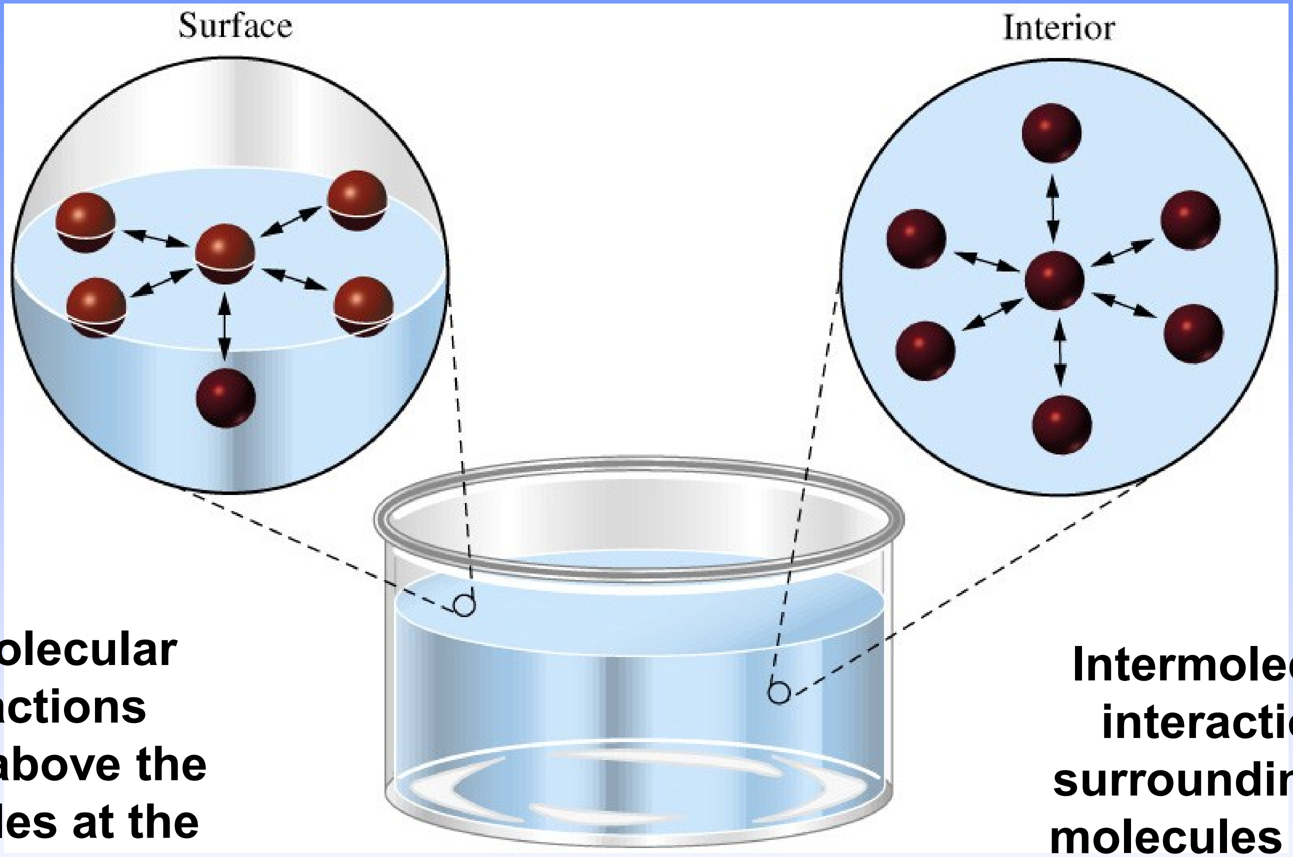
# Surface Tension




**Intermolecular Interactions absent above the molecules at the surface**

**Intermolecular interactions surrounding the molecules in the interior of the liquid.**

# Surface Tension

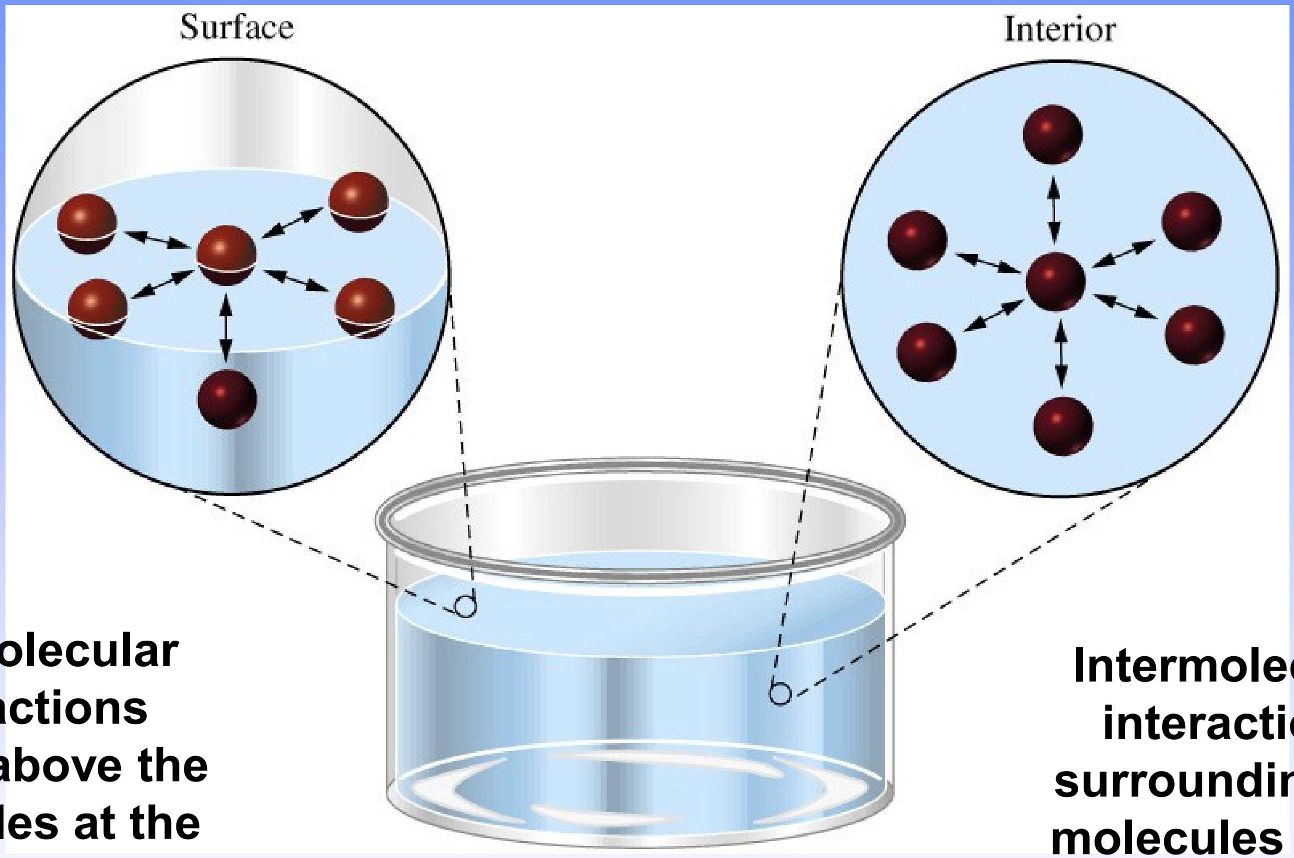



**Intermolecular Interactions absent above the molecules at the surface**

**Intermolecular interactions surrounding the molecules in the interior of the liquid.**

**The ENERGY of a molecule at the surface is HIGHER than that of a molecule in the interior of the liquid!**

# Surface Tension

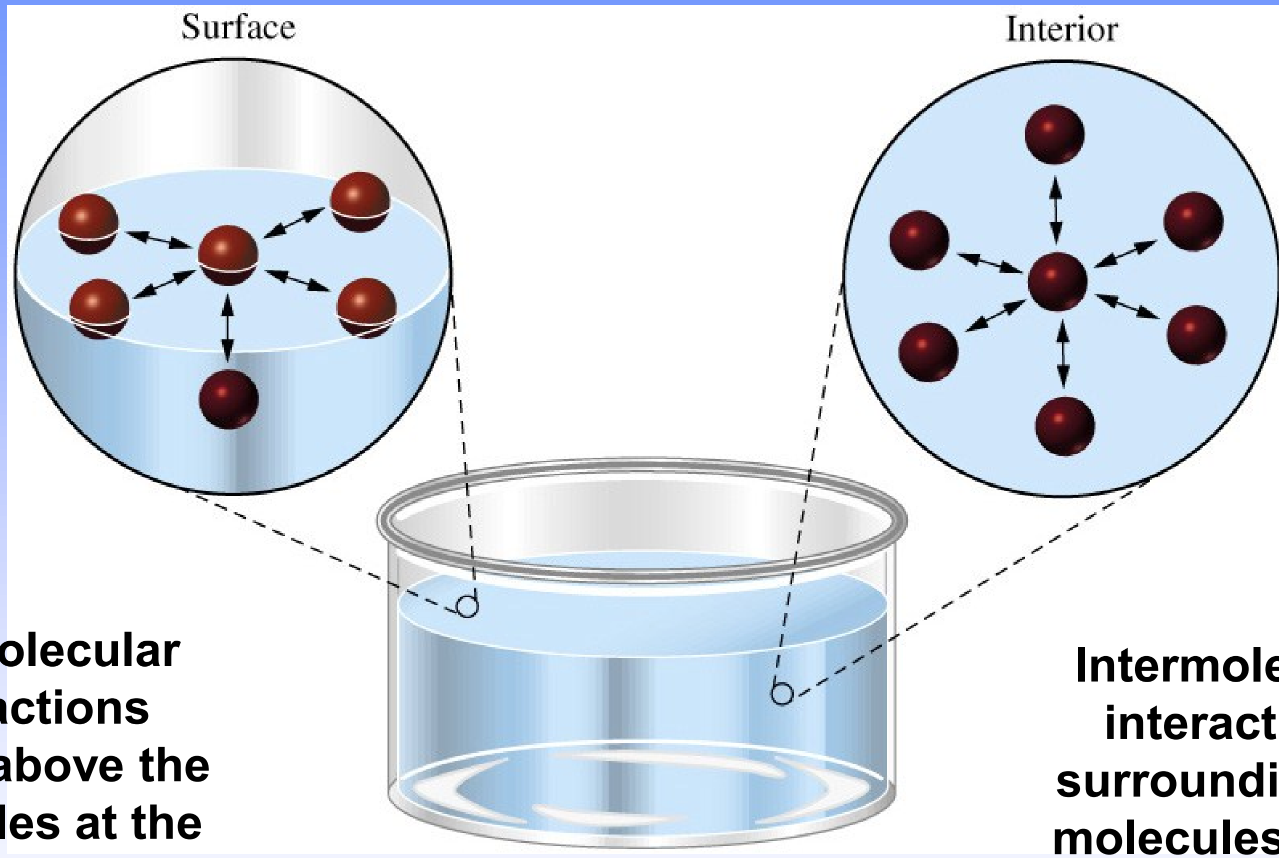



**Intermolecular Interactions absent above the molecules at the surface**

**Intermolecular interactions surrounding the molecules in the interior of the liquid.**

**What would happen if the ENERGY of a molecule at the surface were LOWER than that of a molecule in the interior of the liquid?**

# Surface Tension




Intermolecular Interactions absent above the molecules at the surface

Intermolecular interactions surrounding the molecules in the interior of the liquid.

**We have to do WORK to create a surface or interface!**

**Work = Surface (or interfacial) tension x Area of the Surface (or Interface)**

# Surface Tension

**The Surface Tension**

**makes the water drops spherical.**

**Why?**

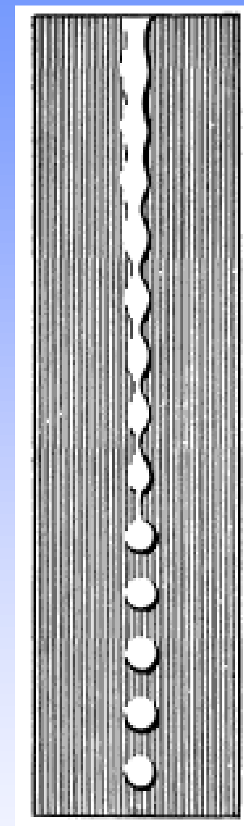
**Minimization of surface area.**

# Surface Tension

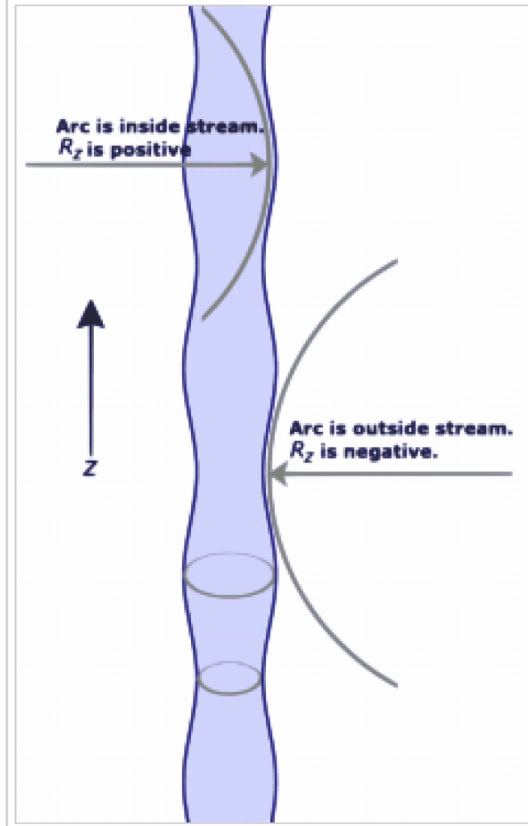
**The Surface Tension** makes the water drops spherical.

**Why?**

Minimization of surface area.

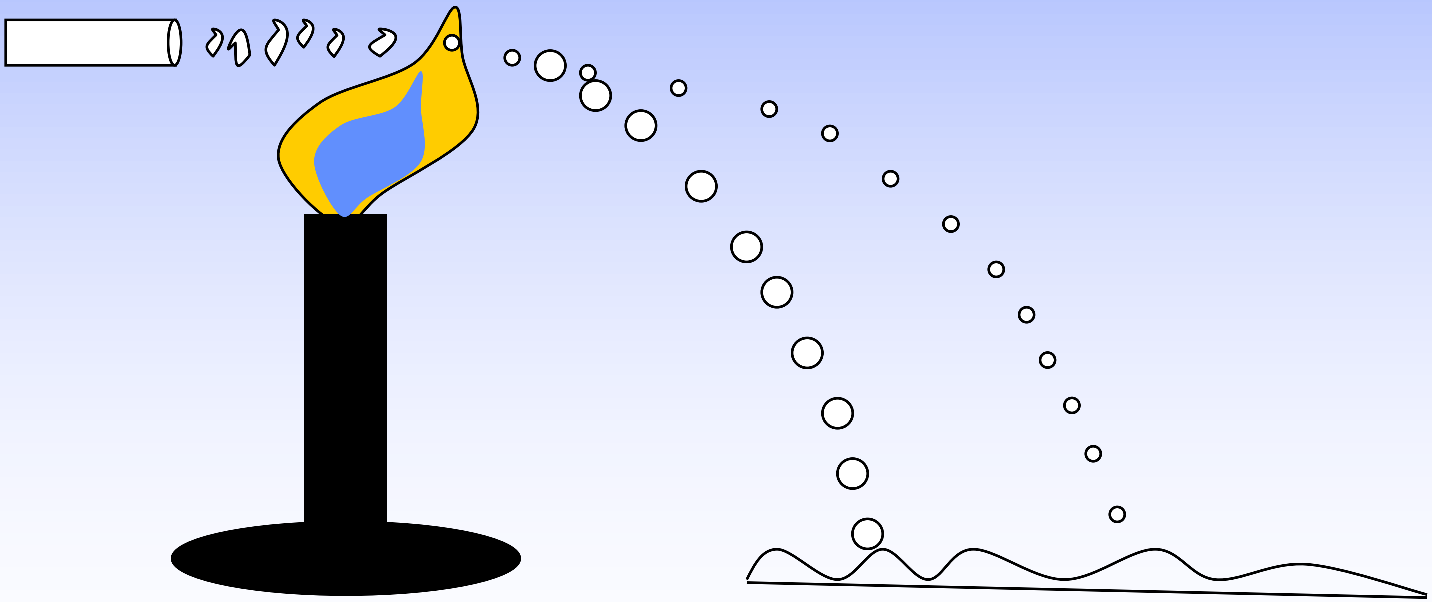


Plateau–Rayleigh instability

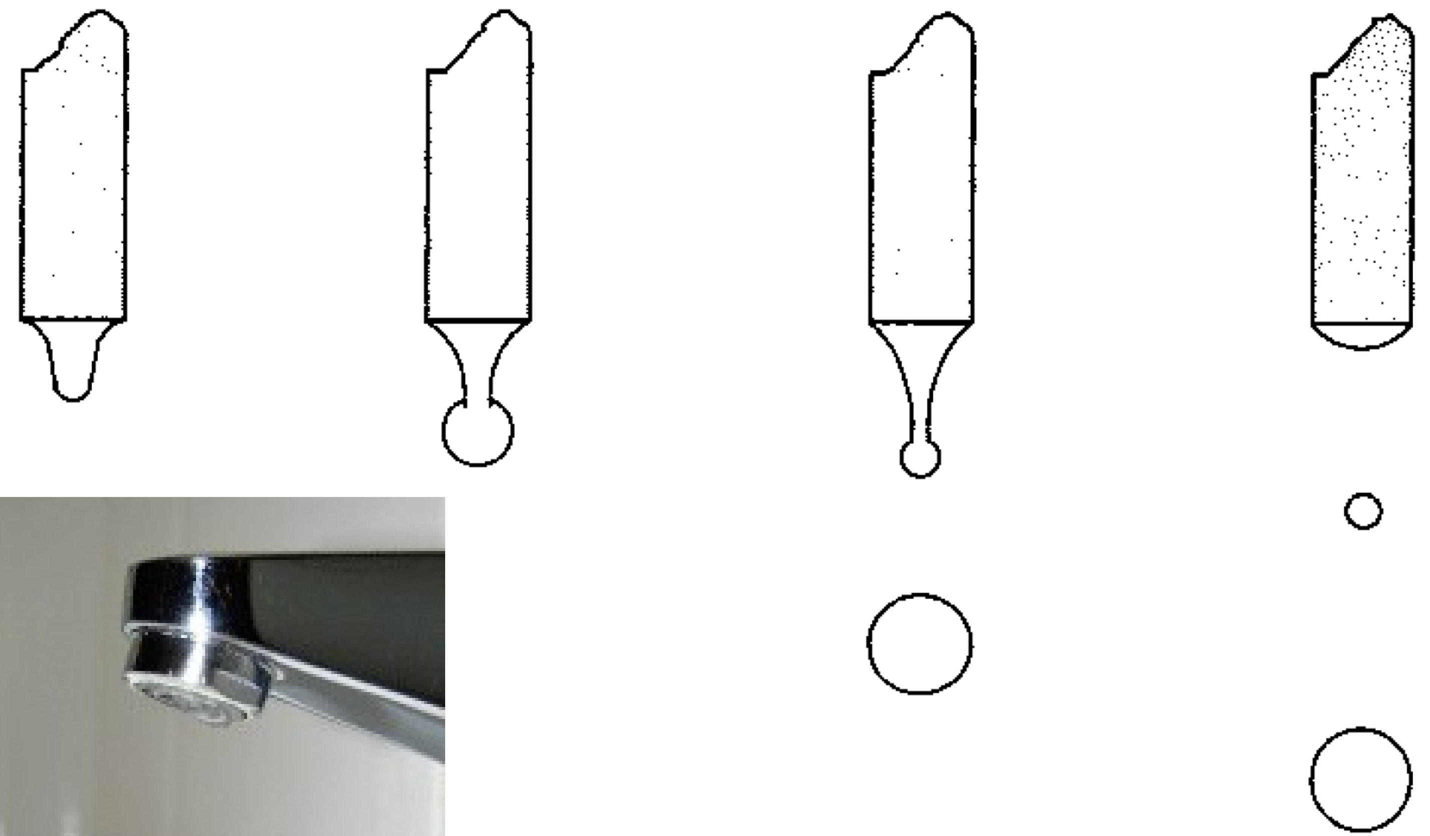



Intermediate stage of a jet breaking into drops. Radii of curvature in the axial direction are shown. Equation for the radius of the stream is $R(z)=R_0+A_k\cos(kz)$, where $R_0$ is the radius of the unperturbed stream, $A_k$ is the amplitude of the perturbation, $z$ is distance along the axis of the stream, and $k$ is the wave number

# Utilizing surface tension to produce perfect glass spheres (and sort them by size).

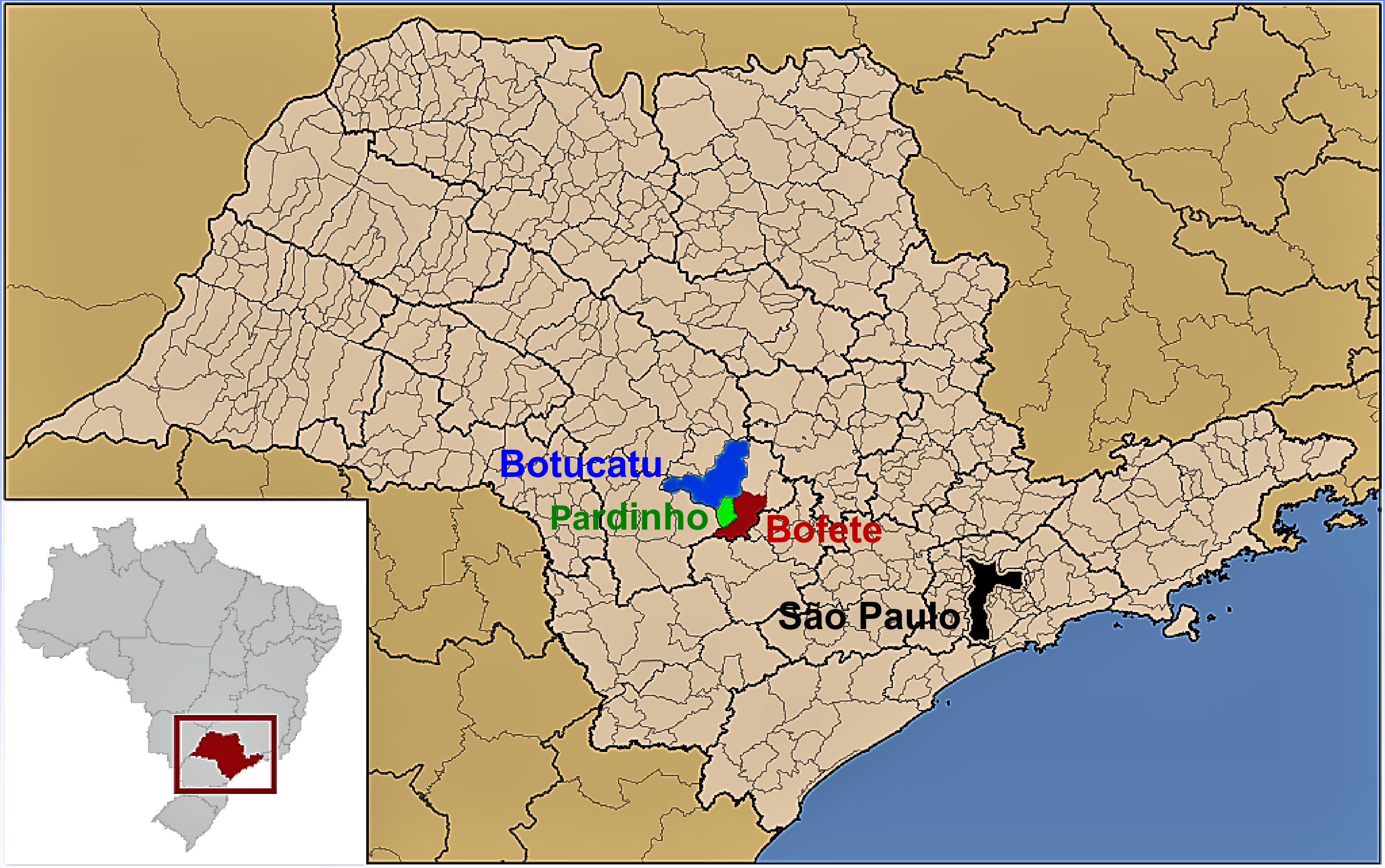


# Formation of a liquid drop



# Botucatu and Bofete, SP



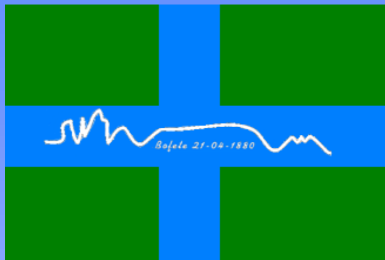


# Fazenda Anhumas, Botucatu, SP



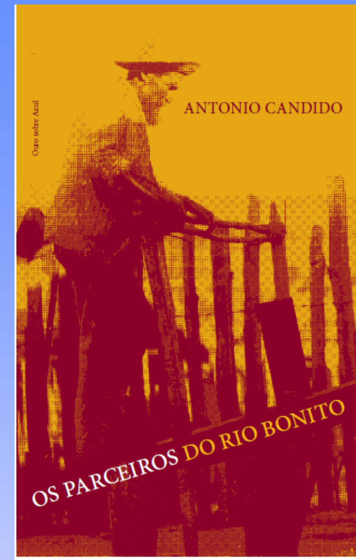
# Botucatu and Bofete, SP





**O Gigante Adormecido (Bofete)**

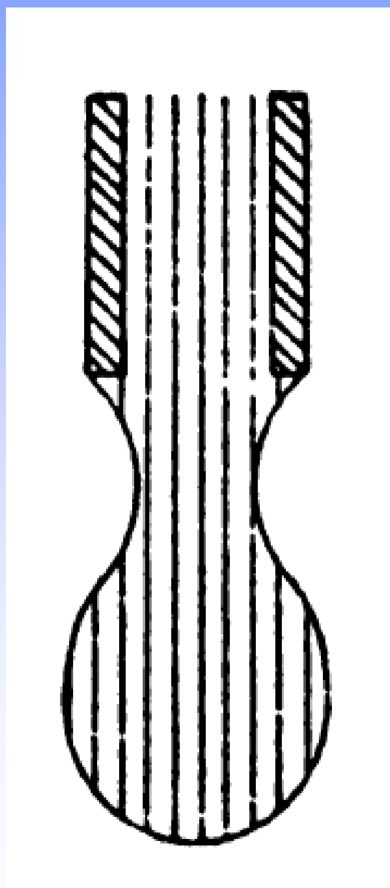

http://misteriosantiguidade.blogspot.com.br/2015/07/o-gigante-adormecido.html

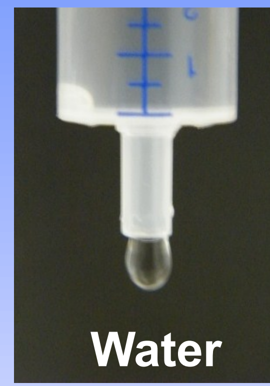



**As Três Pedras (Botucatu/Bofete)**


**Sítio Querência**
**(Bairro Anhumas, Botucatu)**

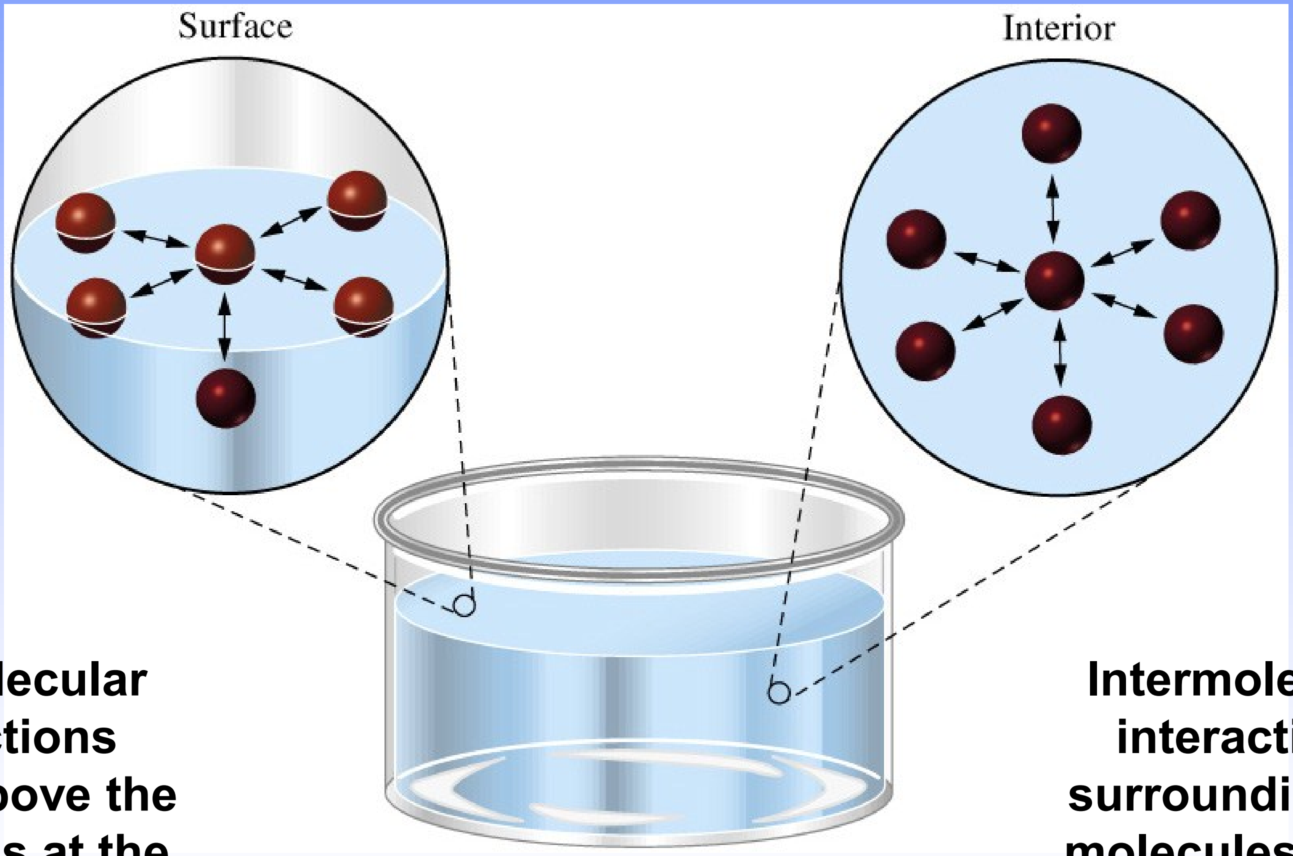
# Measuring the Surface Tension Stalagmometry






Pinga

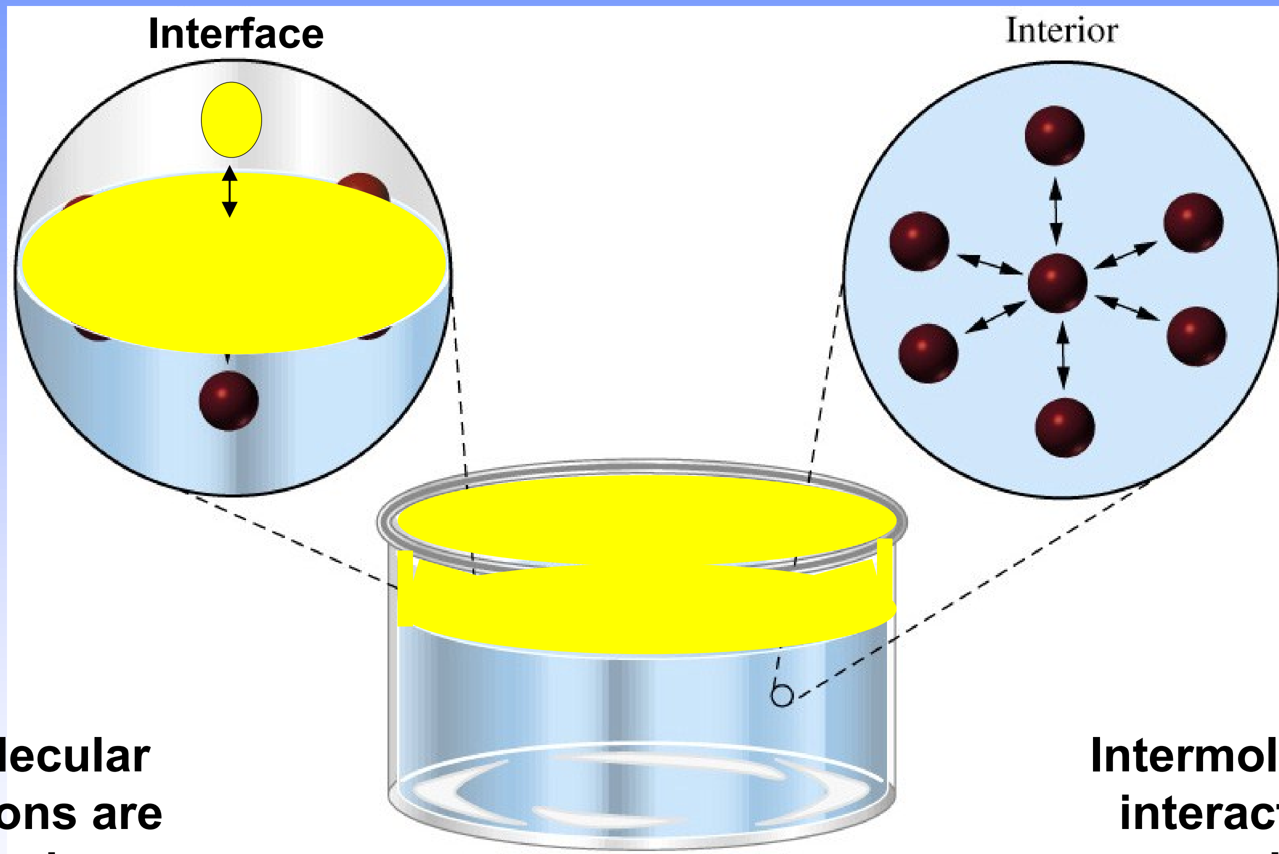

# Surface Tension




**Intermolecular Interactions absent above the molecules at the surface**

**Intermolecular interactions surrounding the molecules in the interior of the liquid.**

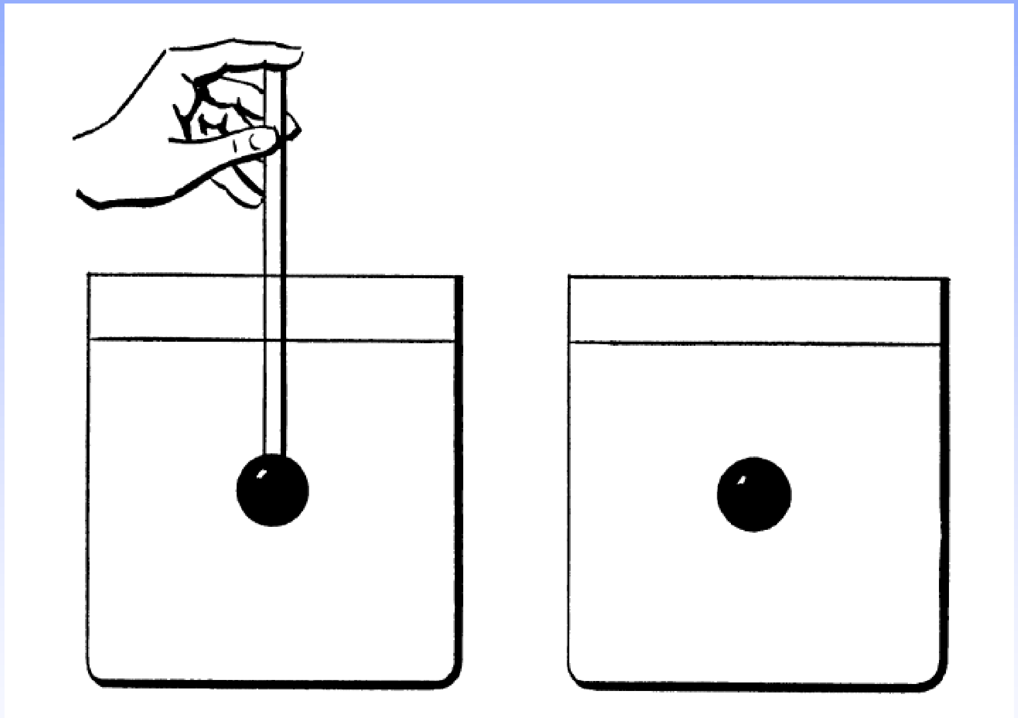
# Interfacial Tension

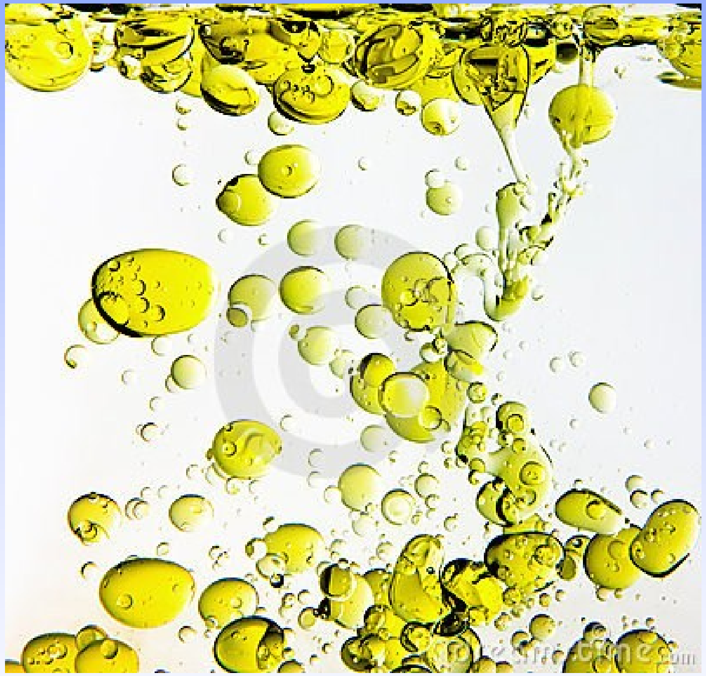



**Intermolecular Interactions are different above and below the molecules at the interface**

**Intermolecular interactions surrounding the molecules in the interior of the liquid.**

# Interfacial Tension
## also minimizes surface area



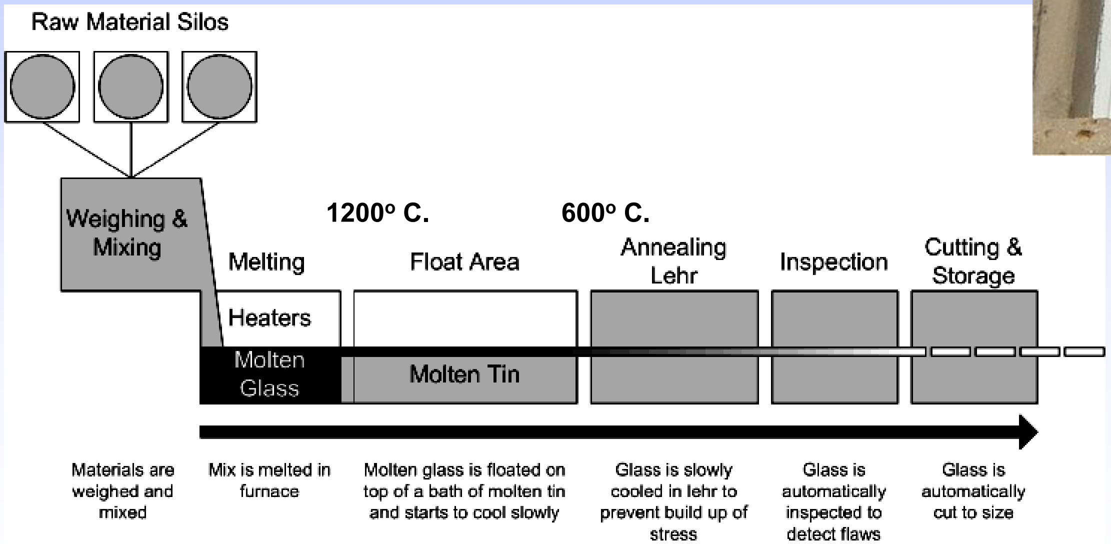


Olive Oil in Water

http://www.dreamstime.com/royalty-free-stock-photography-olive-oil-water-image6224407

# Float Glass: Using Interfacial Tension to make really flat glass surfaces.

Window in Jena (from Wikipedia)



# Interfacial Tension

## Adhesion, Wetting and Contact Angle

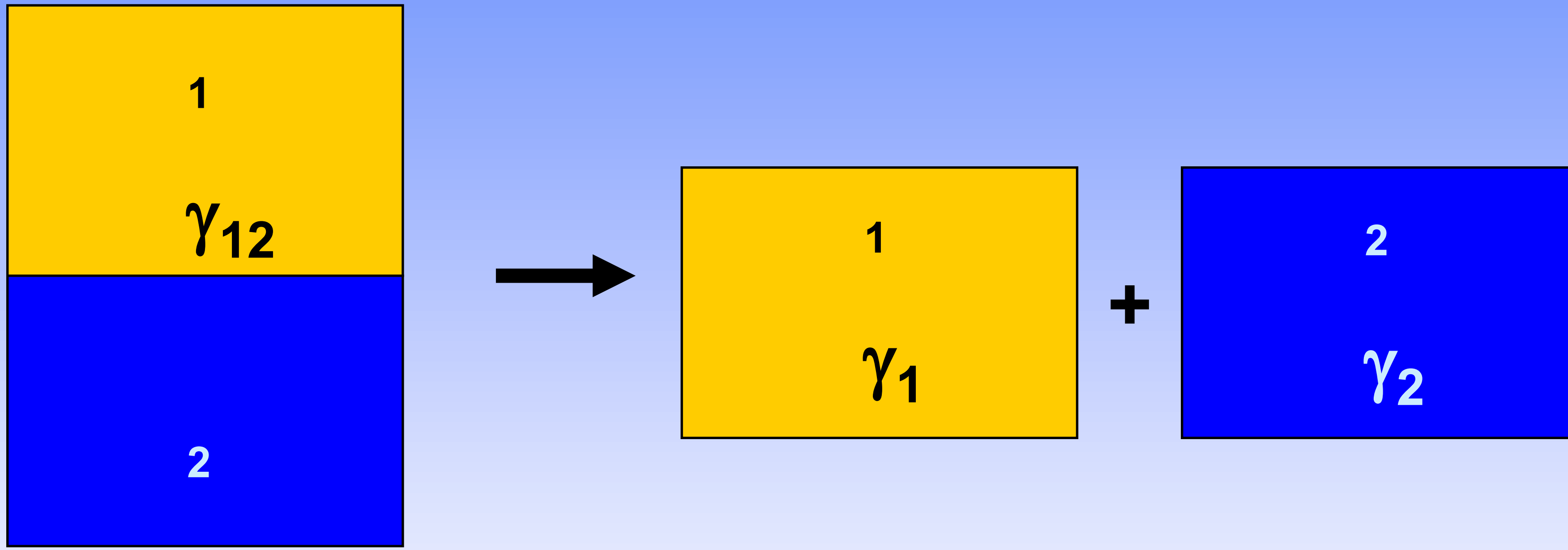
# Interfacial Tension

Hydrophilic Surface

Hydrophobic Surface

## Adhesion, Wetting and Contact Angle

# Work of Adhesion

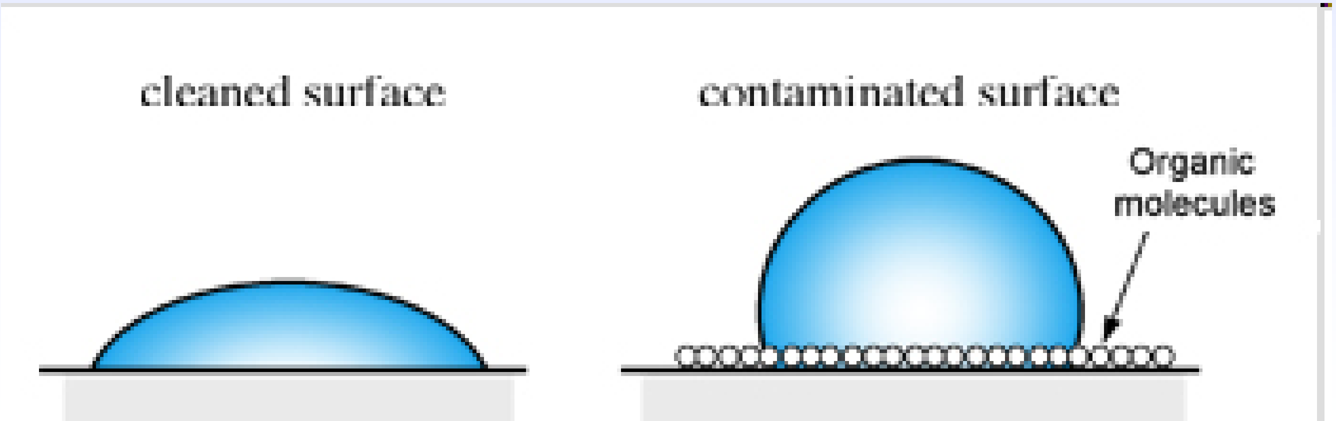



**We have to do WORK to separate surfaces at an interface!**

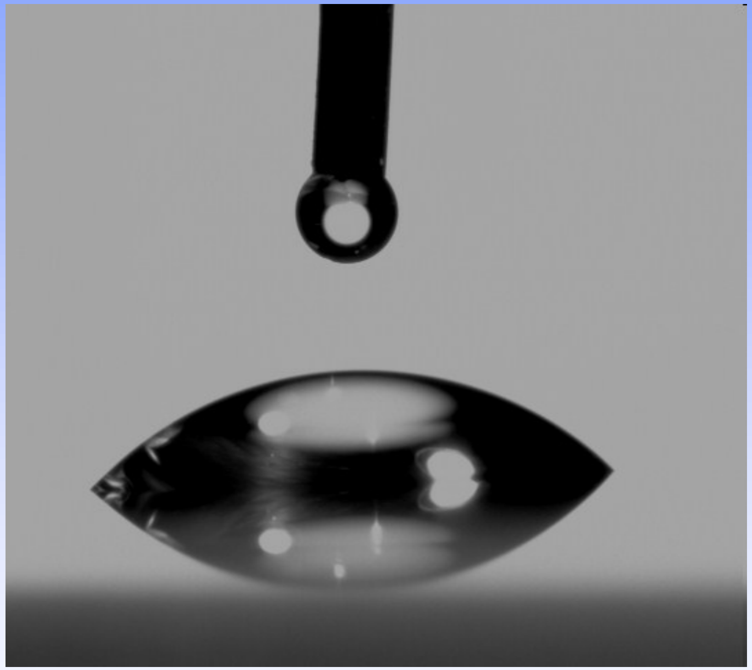
**Work of adhesion = $\gamma_1 + \gamma_2 - \gamma_{12}$**

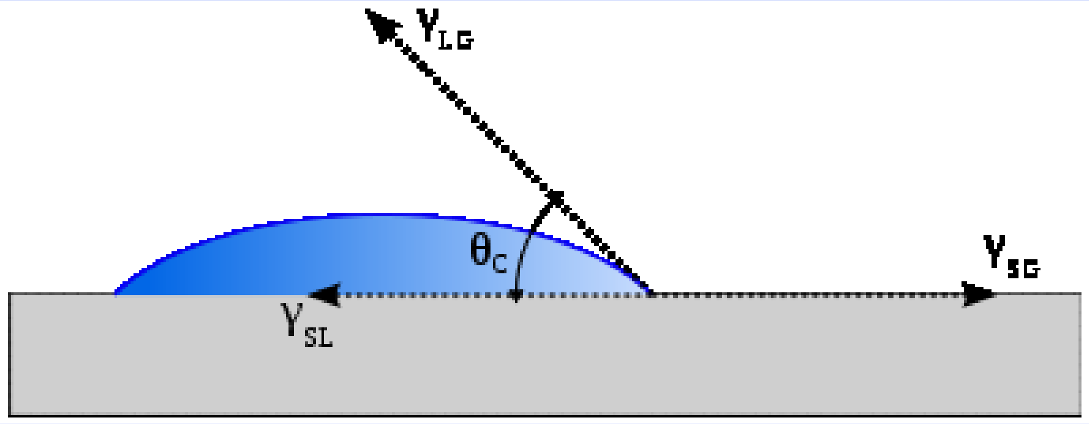
# Contact Angle

Hydrophilic Surface → Hydrophobic Surface



# Contact Angle Definition

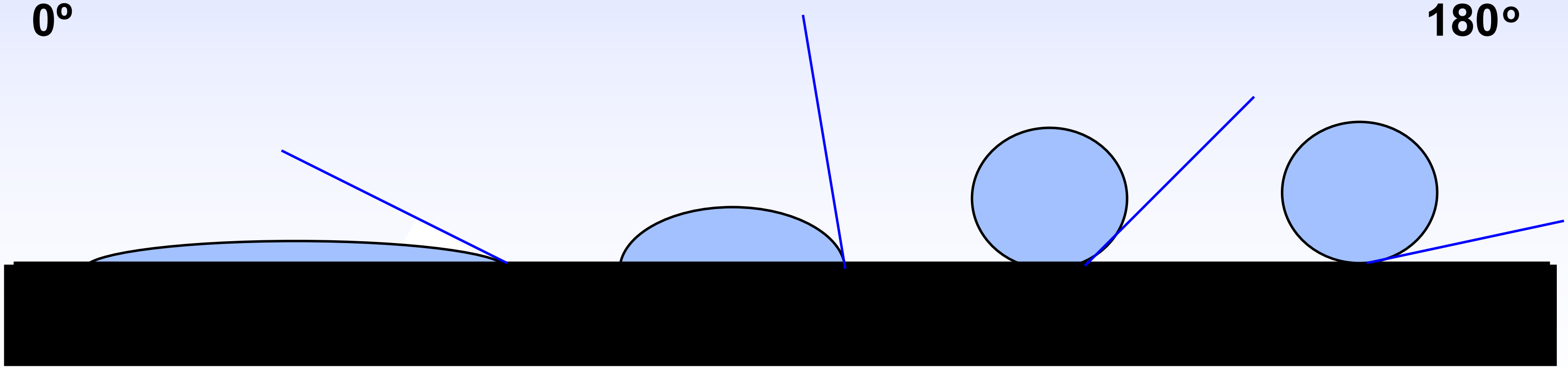




# Contact Angle

Hydrophilic Surface → Hydrophobic Surface

0º 180º



**Note: Higher contact angle = greater drop depth**

# Estimating Surface Tensions

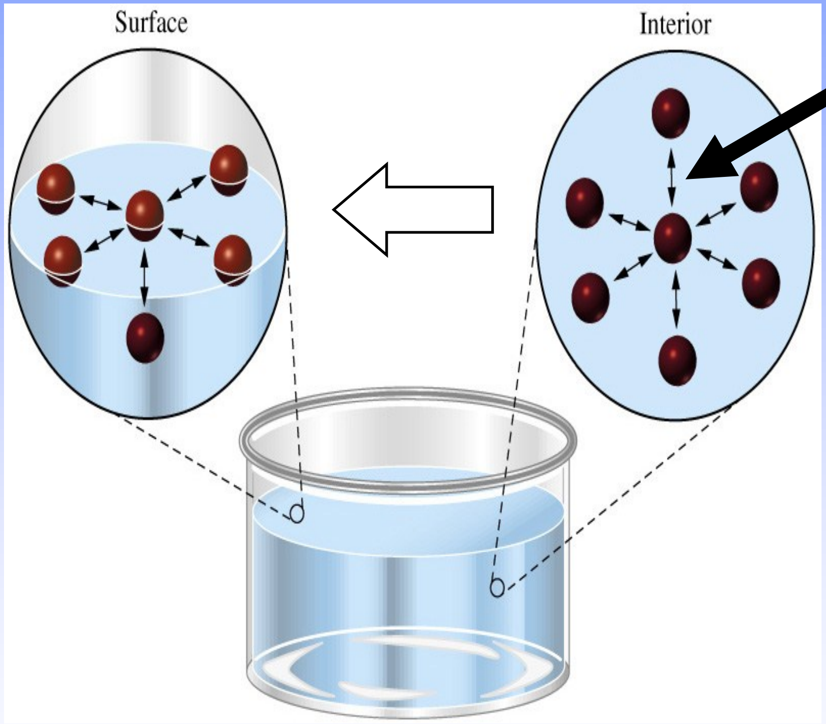
# from

# Molecular Structure

**Table 2.2.** The surface tensions of some common pure liquids at the vapour–liquid interface at 20 °C. (From Jasper, 1972.)

| Liquid | Surface tension, $\gamma$/mN m$^{-1}$ | Liquid | Surface tension, $\gamma$/mN m$^{-1}$ |
|---|---|---|---|
| Acetic acid | 27.6 | *n*-hexane | 18.4 |
| Acetone | 25.1 | Isobutyl alcohol | 22.9 |
| Benzene | 28.9 | Methanol | 22.5 |
| *n*-butyl alcohol | 25.4 | Mercury | 486.5 |
| Carbon tetrachloride | 27.0 | *n*-octane | 21.6 |
| Chloroform | 27.2 | Oleic acid | 32.5 |
| Cyclohexane | 25.2 | Propanoic acid | 26.7 |
| Ethyl acetate | 24.0 | *n*-propyl alcohol | 23.7 |
| Ethanol | 22.4 | Pyridine | 37.2 |
| Di-ethyl ether | 17.0 | Toluene | 28.5 |
| Glycerol | 63.4 | Vinyl acetate | 24.0 |
| Ethylene glycol | 48.4 | Water | 72.8 |

# Relationship between the chemical structure of the molecules of a pure liquid and its Surface Tension




What are the intermolecular interactions that are lost by the molecules at the surface?

An obvious component is van der Waals or dispersion forces.

**Table 2.2.** The surface tensions of some common pure liquids at the vapour–liquid interface at 20 °C. (From Jasper, 1972.)

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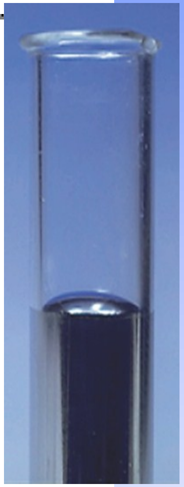
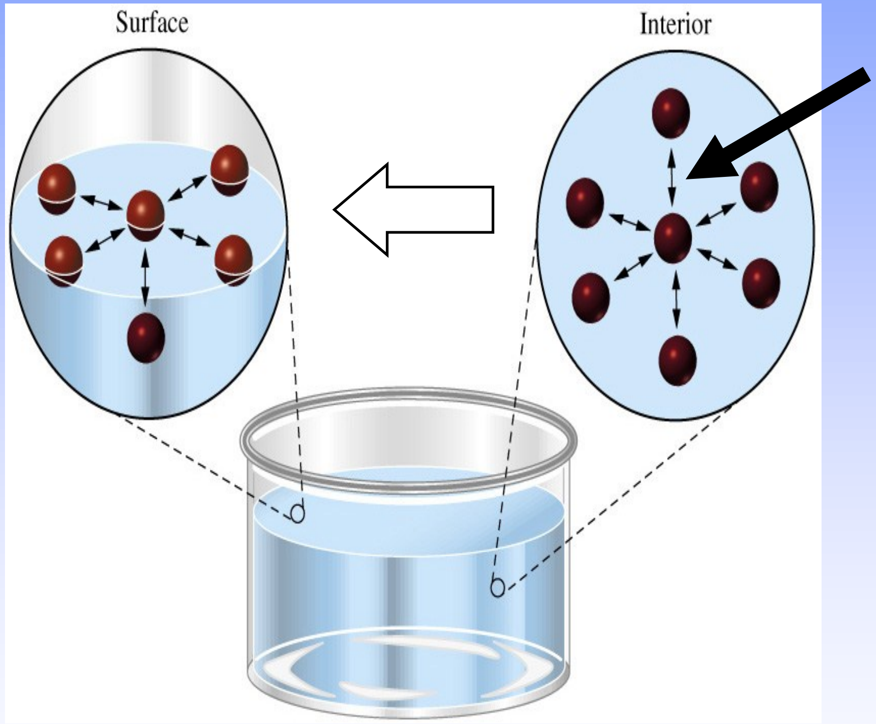


# Relationship between the chemical structure of the molecules of a pure liquid and its Surface Tension



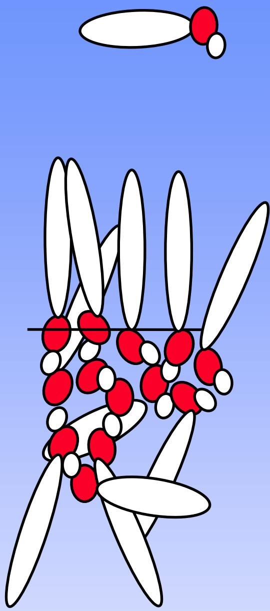

What are the intermolecular interactions that are lost by the molecules at the surface?

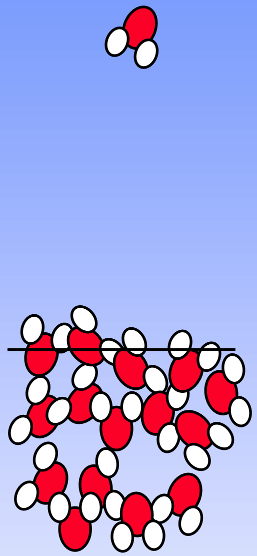
One obvious one are the van der Waals or dispersion forces.

The second are the dipole-dipole interactions.

But what about hydrogen bonds?

# Surface Tension of Ethyl Alcohol and Water





**Ethanol**
**22 dynes/cm**

**Water**
**72 dynes/cm**

**Table 2.2.** The surface tensions of some common pure liquids at the vapour–liquid interface at 20 °C. (From Jasper, 1972.)

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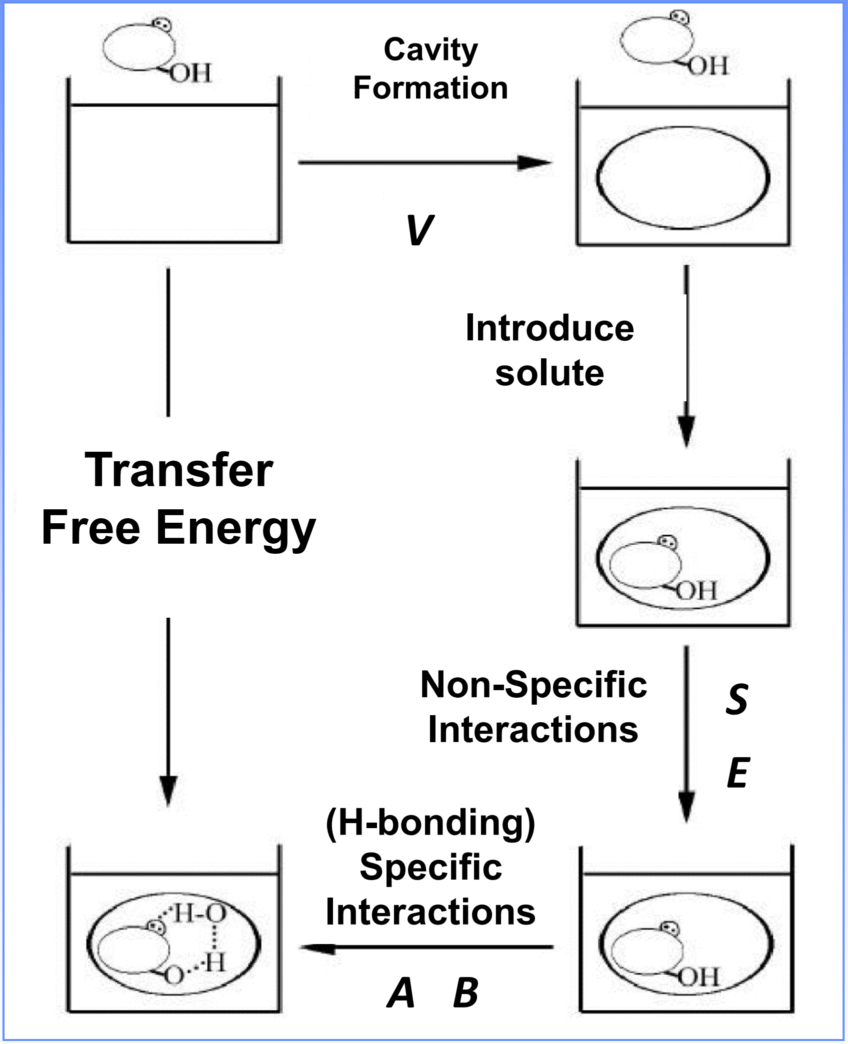
# LINEAR SOLVATION FREE ENERGY RELATIONSHIPS (LSERs)




**Solute Parameters:**

**V – solute molar volume**

- Solvent cohesion
- Dispersion effects (=alkane)
- Hydrophobicity

**S – solute dipolarity**

**E – solute excess polarizability**

**A – solute H-bond acidity**

**B – solute H-bond basicity**

**Coefficients:**

**Relative importance of each contribution**

$$\Delta G^0 = c + aA + bB + sS + rE + vV$$

# Relationship between the chemical structure of the molecules of a pure liquid and its Surface Tension

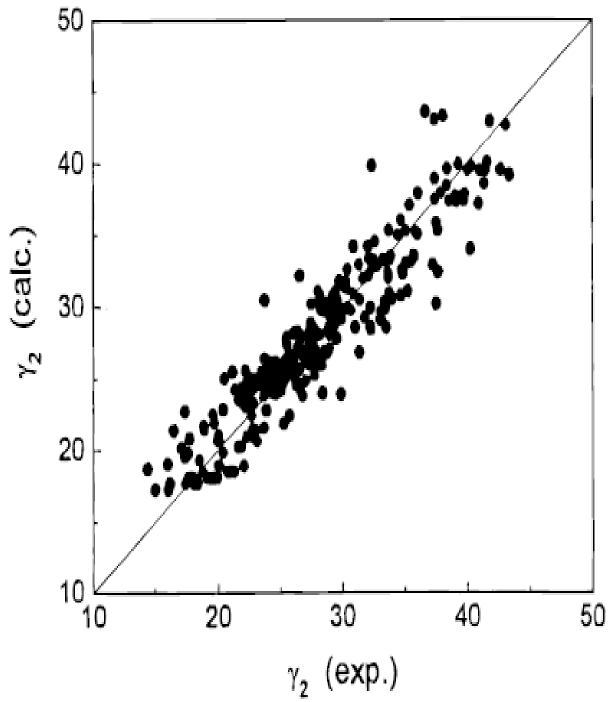



**Figure 1.** Comparison of calculated (eq 8) and experimental values of the surface tensions of 299 organic liquids at 20 °C.

$$\gamma = 14.8 + 11.4\,E + 10.6\,\mathrm{S} + 3.4\,(\mathrm{A} \times \mathrm{B})^{1/2} + 2.95\,V + 0.87\,N_{\mathrm{C}}$$

**Freitas, Quina & Carroll, *Langmuir*, 2000, *16*, 6689–6692**

# Relationship between the chemical structure of the molecules of a pure liquid and its Surface Tension

$$\gamma = 14.8 + 11.4\,E + 10.6\,S + 3.4\,(A \times B)^{1/2} + 2.95\,V + 0.87\,N_C$$

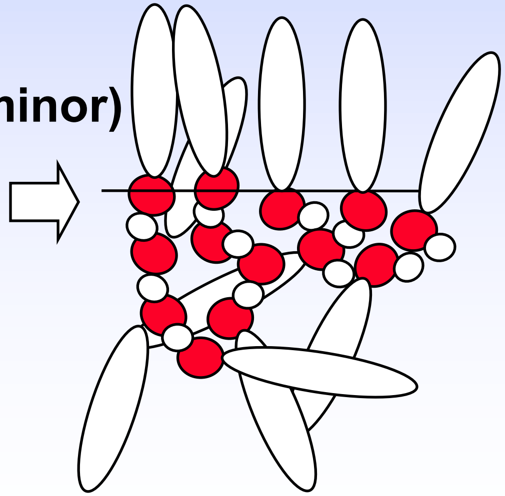
For linear alkanes only

Hydrogen bonding (minor)

<u>Major</u>:

Dispersion, Polarizability and Dipolarity

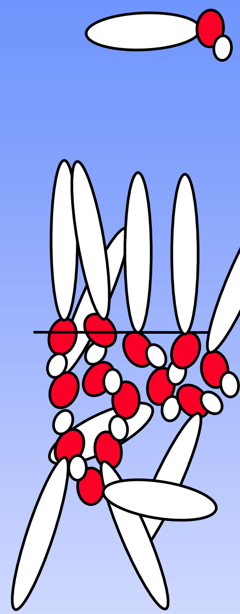
Fails for 3-D hydrogen bonded liquids!

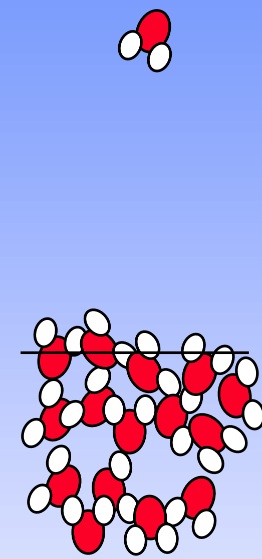


Ethanol

Freitas, Quina & Carroll, *Langmuir*, 2000, *16*, 6689–6692

# Surface Tension of Ethyl Alcohol and Water





Ethanol
22 dynes/cm

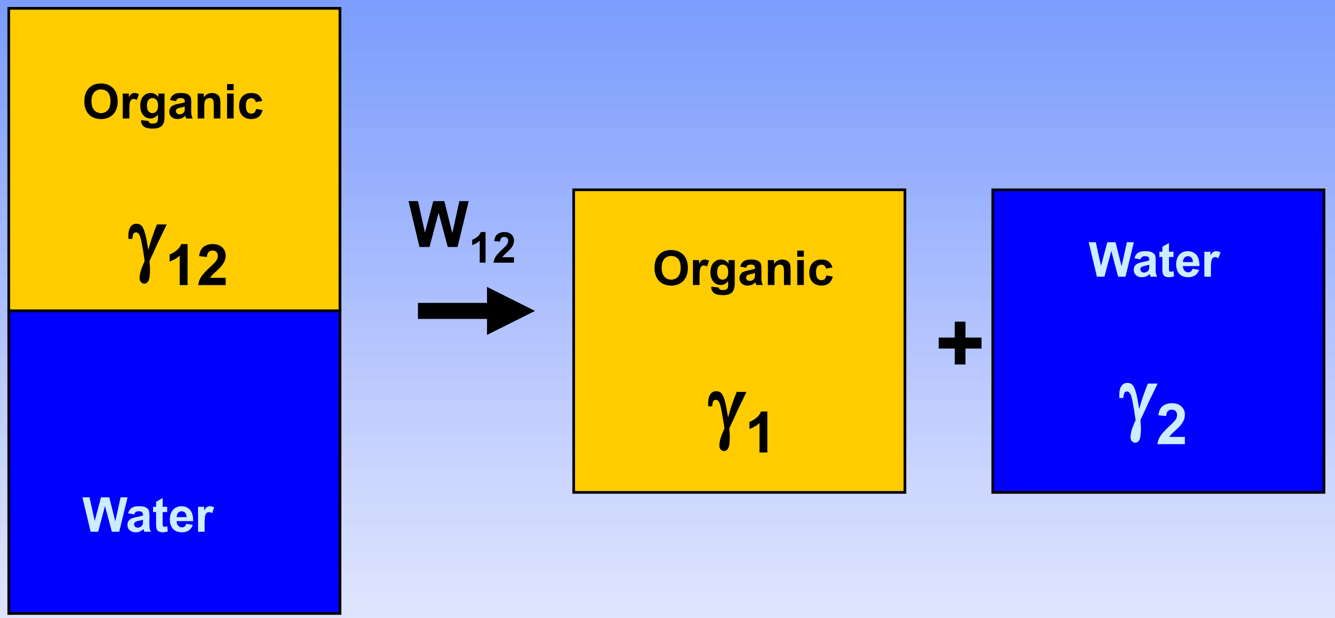
Water
72 dynes/cm

**Correlation works for 2-D or 1-D hydrogen bonded liquids,**

**but fails for 3-D hydrogen bonded liquids**

# Work of Adhesion between Organic Liquids and Water



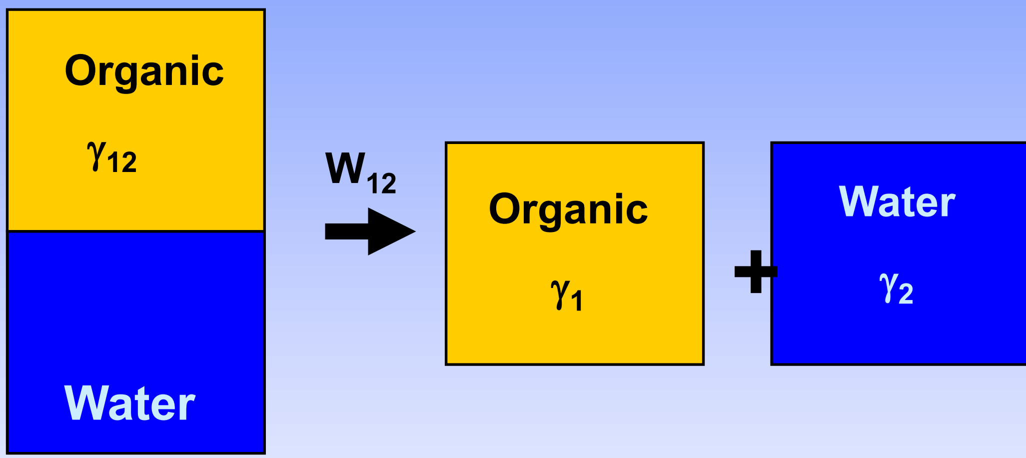



$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12}$$

Freitas, Quina & Carroll, *J. Phys. Chem. B*, 1997, *101*, 7488–7493.

# Work of Adhesion between Organic Liquids and Water





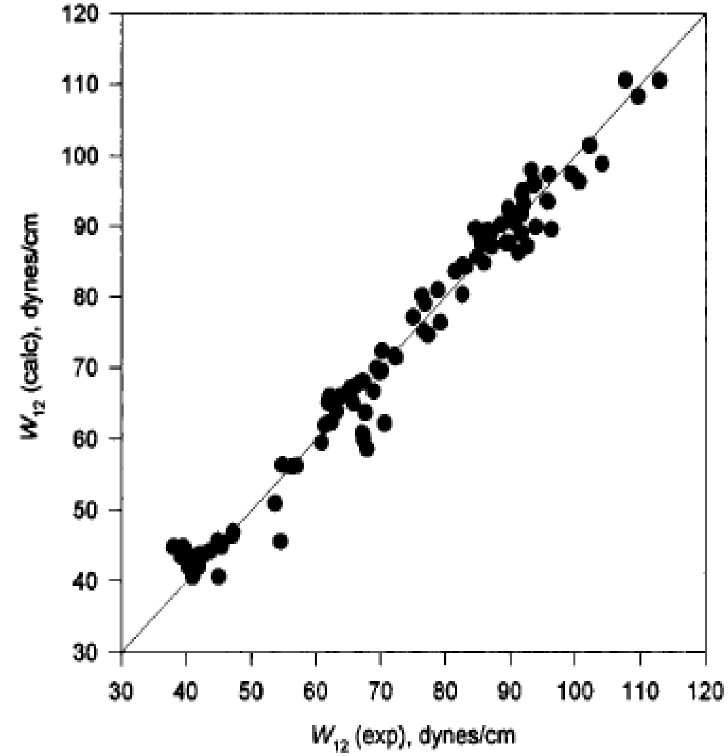



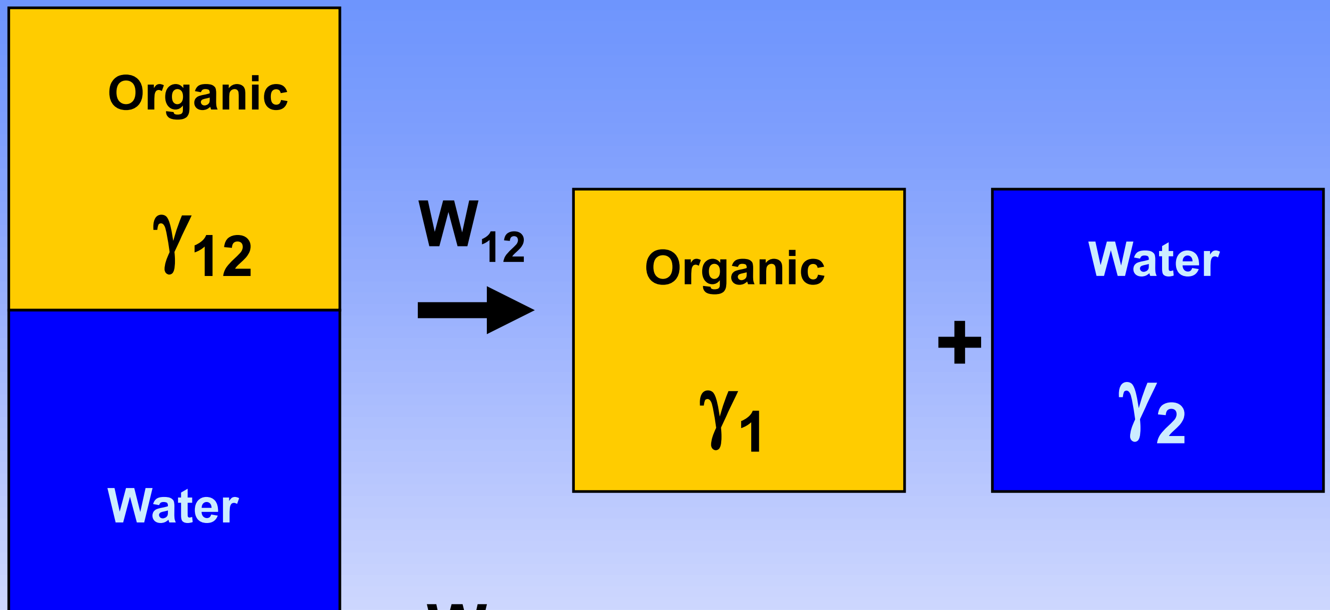

**Figure 1.** Correlation of $W_{12}$ calculated from eq 7 with experimental $W_{12}$ for compounds 1−103 in Table 1.

$$W_{12} = 53 + 31\,\mathrm{S} + 39\,\mathrm{A} + 51\,\mathrm{B} - 2.4\,E - 9.9\,V + 1.8\,N_{\mathrm{C}}$$

Freitas, Quina & Carroll, *J. Phys. Chem. B*, 1997, *101*, 7488–749

# Work of Adhesion between Organic Liquids and Water






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

$$W_{12} = 53 + 31\,S + 39\,A + 51\,B - 2.4\,E - 9.9\,V + 1.8\,N_C$$

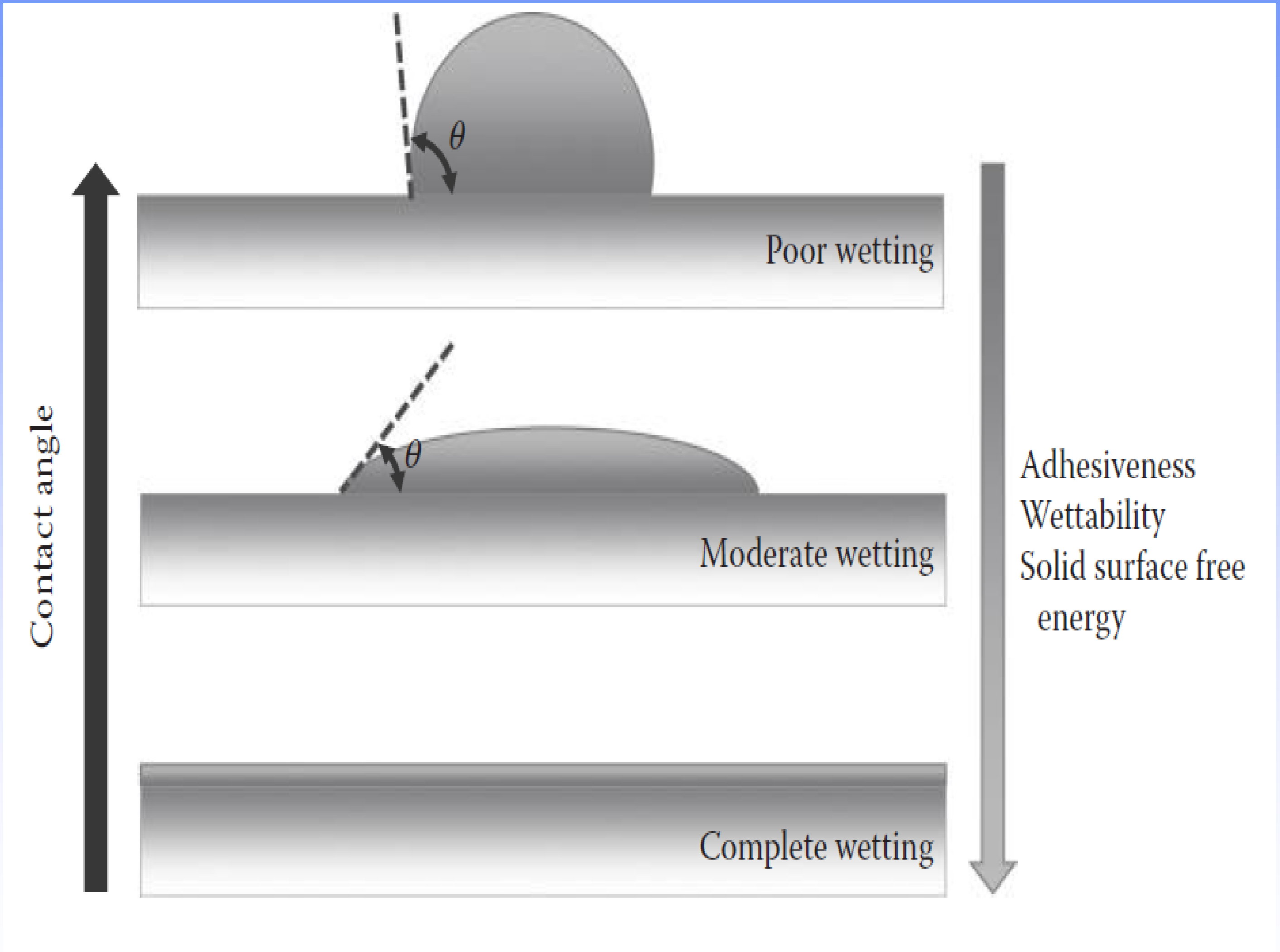
**Major:**

Dispersion + Dipolarity + Hydrogen bonding

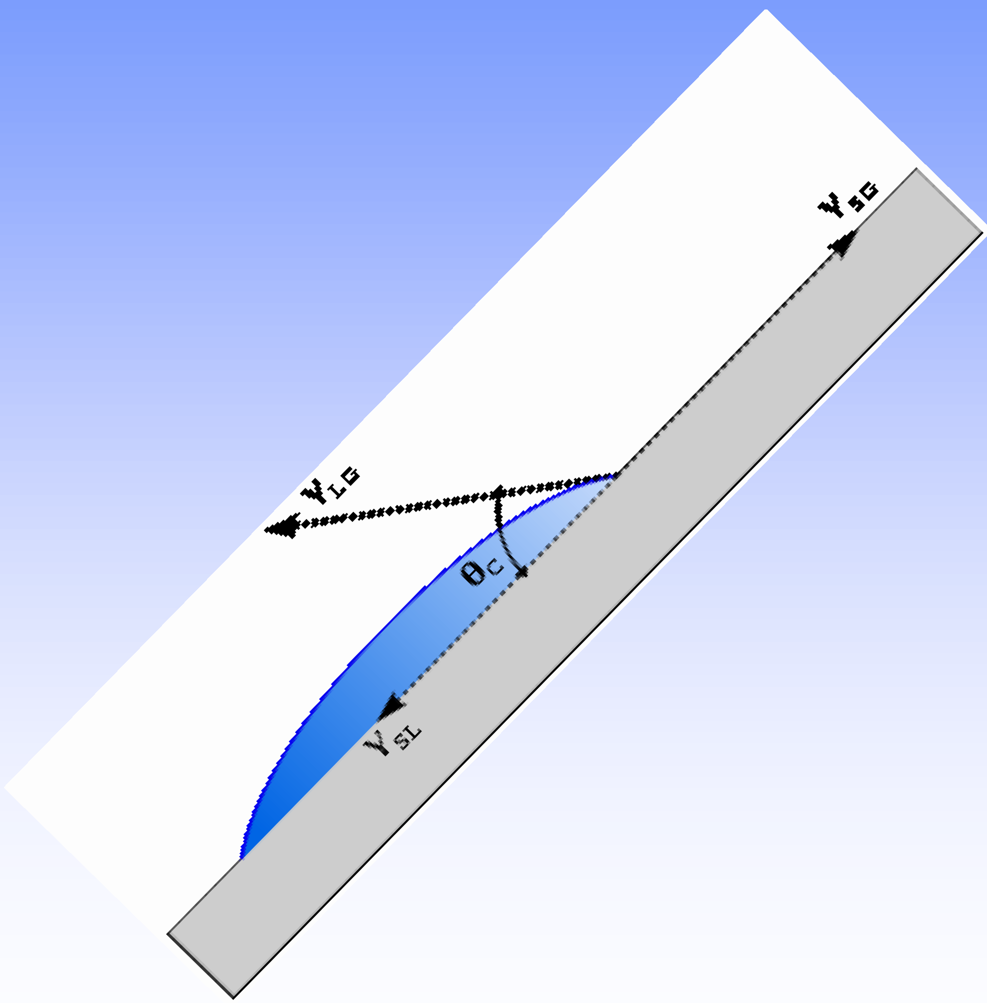
For linear alkanes only

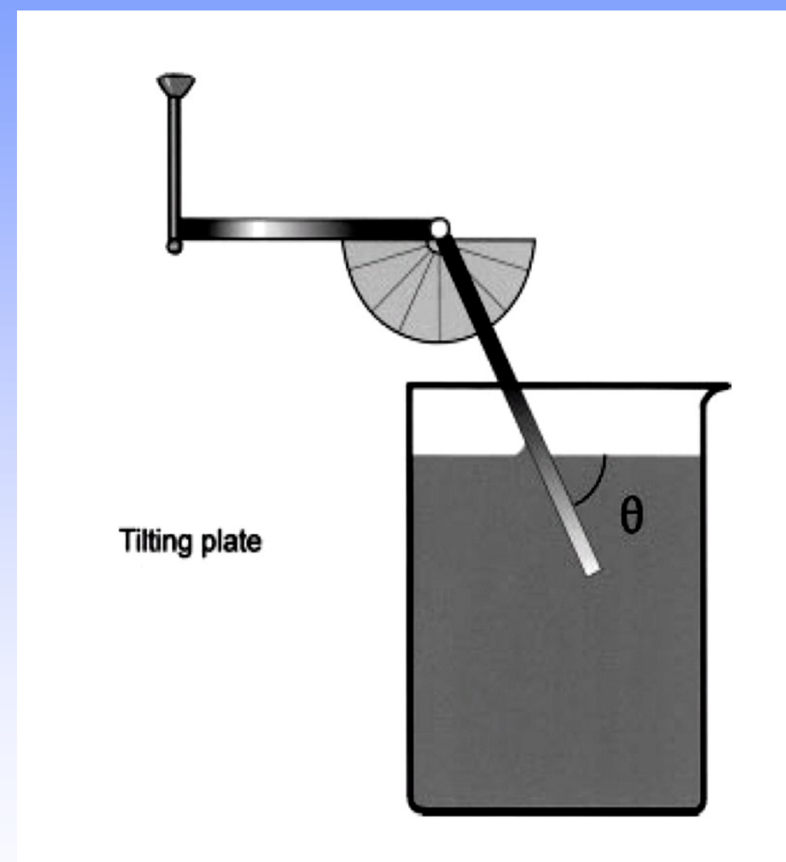
Freitas, Quina & Carroll, *J. Phys. Chem. B*, 1997, *101*, 7488–7493.

# Measuring Contact Angles

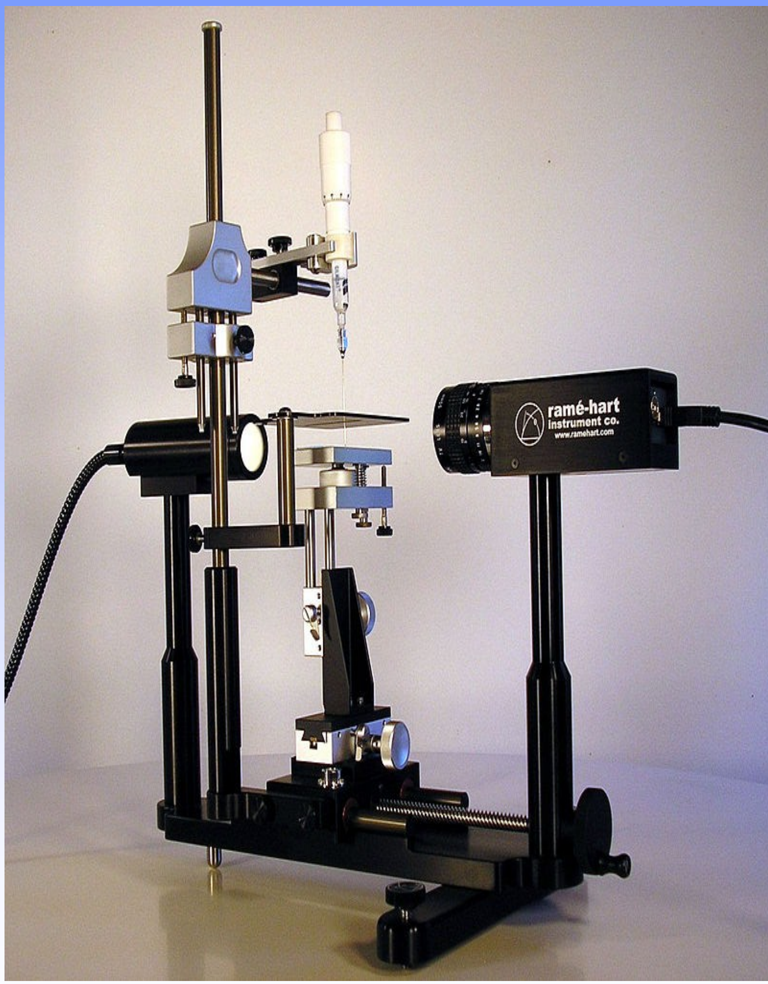


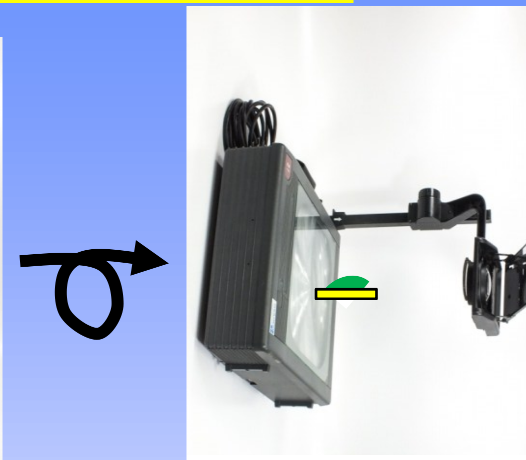
# Contact Angle Measurement: Tilting Plate Method

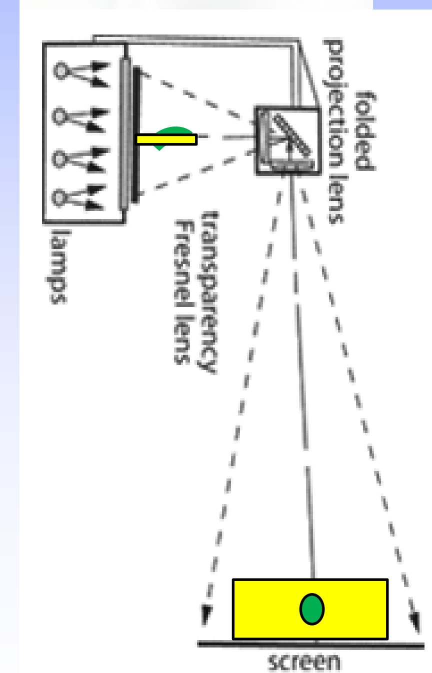


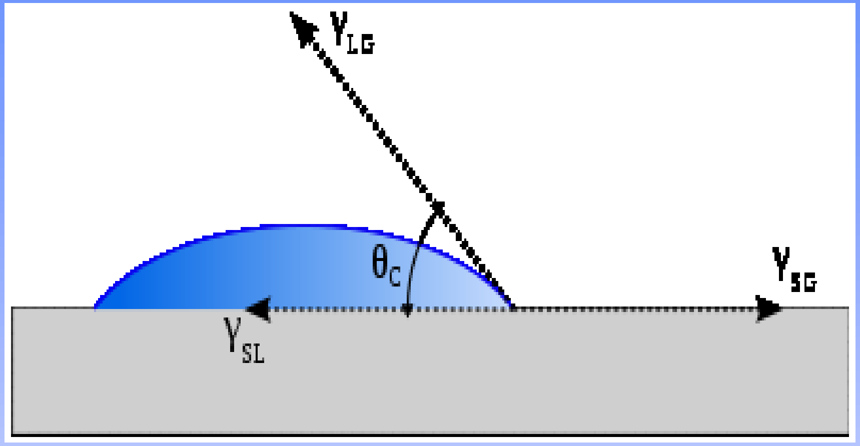
# Commercial Contact Angle Goniometer and an In-House Version if None is Available

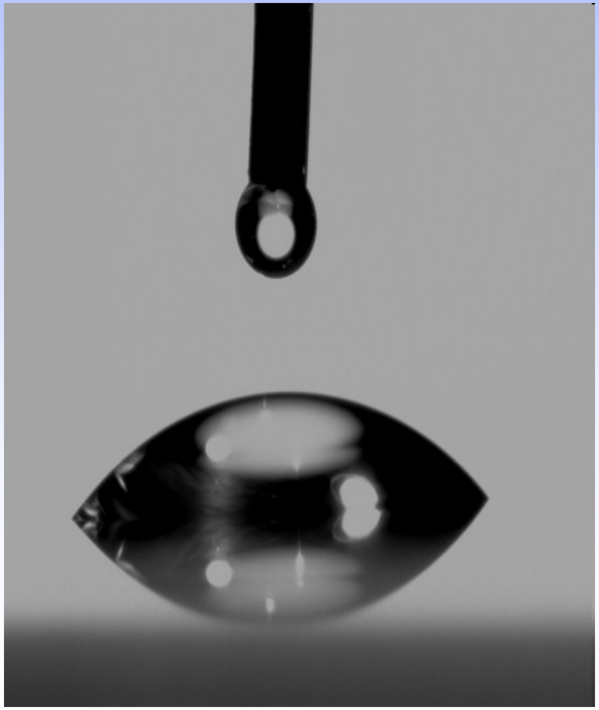


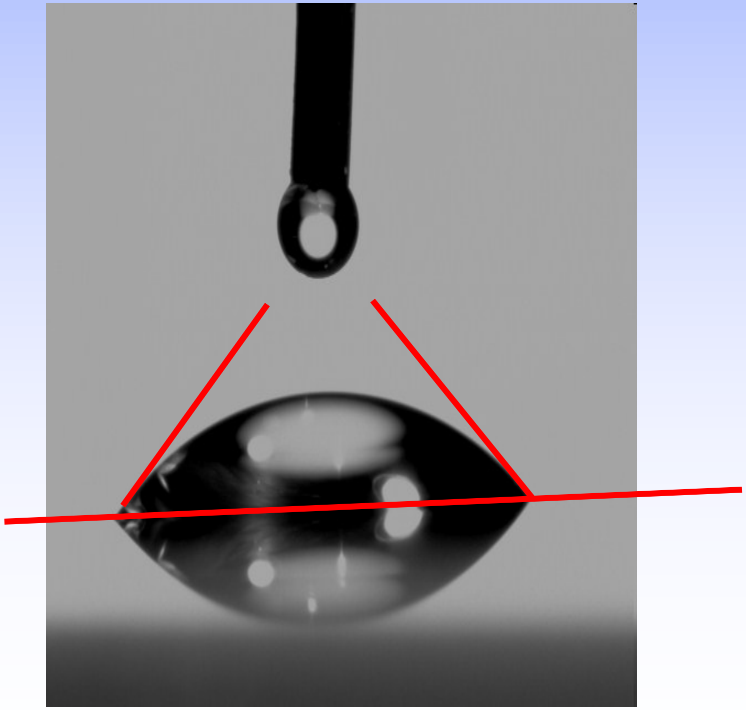





# Contact Angle Measurement

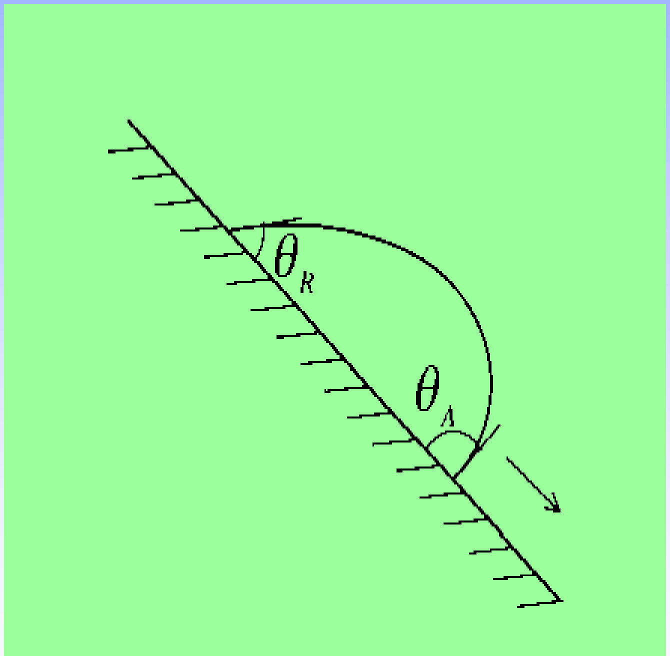


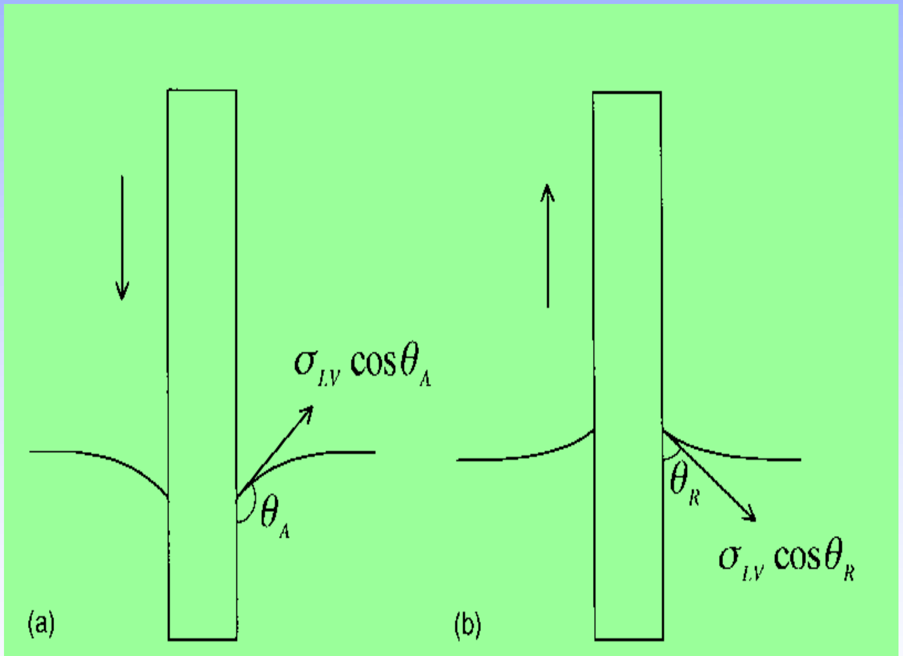





# Static Contact Angle Hysteresis of a Drop on an Inclined Surface or the Dynamic Contact Angle Hysteresis at a Surface Being Inserted and Withdrawn from a Liquid

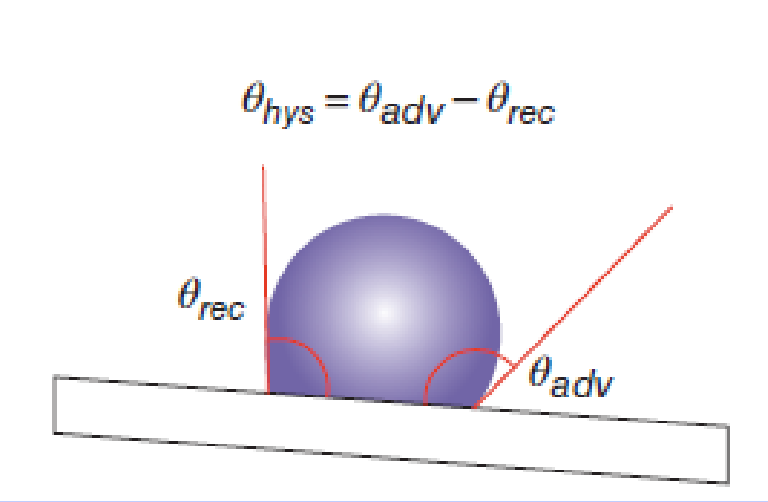
## Receding and Advancing Contact Angles




From: Stanley Hartland, *Surface and Interfacial Tension_ Measurement, Theory, and Applications*, CRC Press (2004)

# Causes of contact angle hysteresis:




- surfaces are not (almost never) absolutely smooth, i.e., they have some roughness (*perhaps the most important reason*);
- equilibrium is not reached;
- surfaces can be contaminated (adsorbed liquids or even solid particles, e.g., dust);
- surfaces may undergo some changes during contact with the test liquid;
- the spreading pressure may be significant for low values of contact angle.

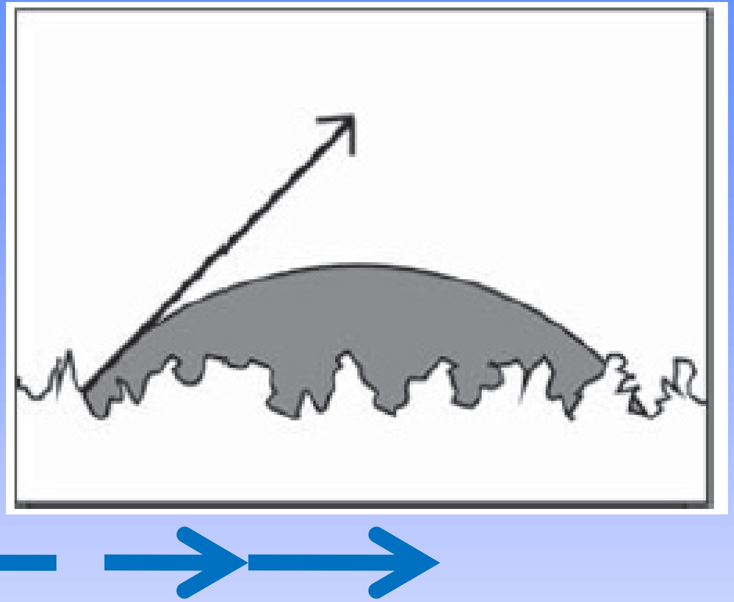
Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

# Contact Angle: The Young Equation



Thomas Young (1773–1829)

*Reproduced from http://commons.wikimedia.org/wiki/File:Thomas_Young_(scientist).jpg*

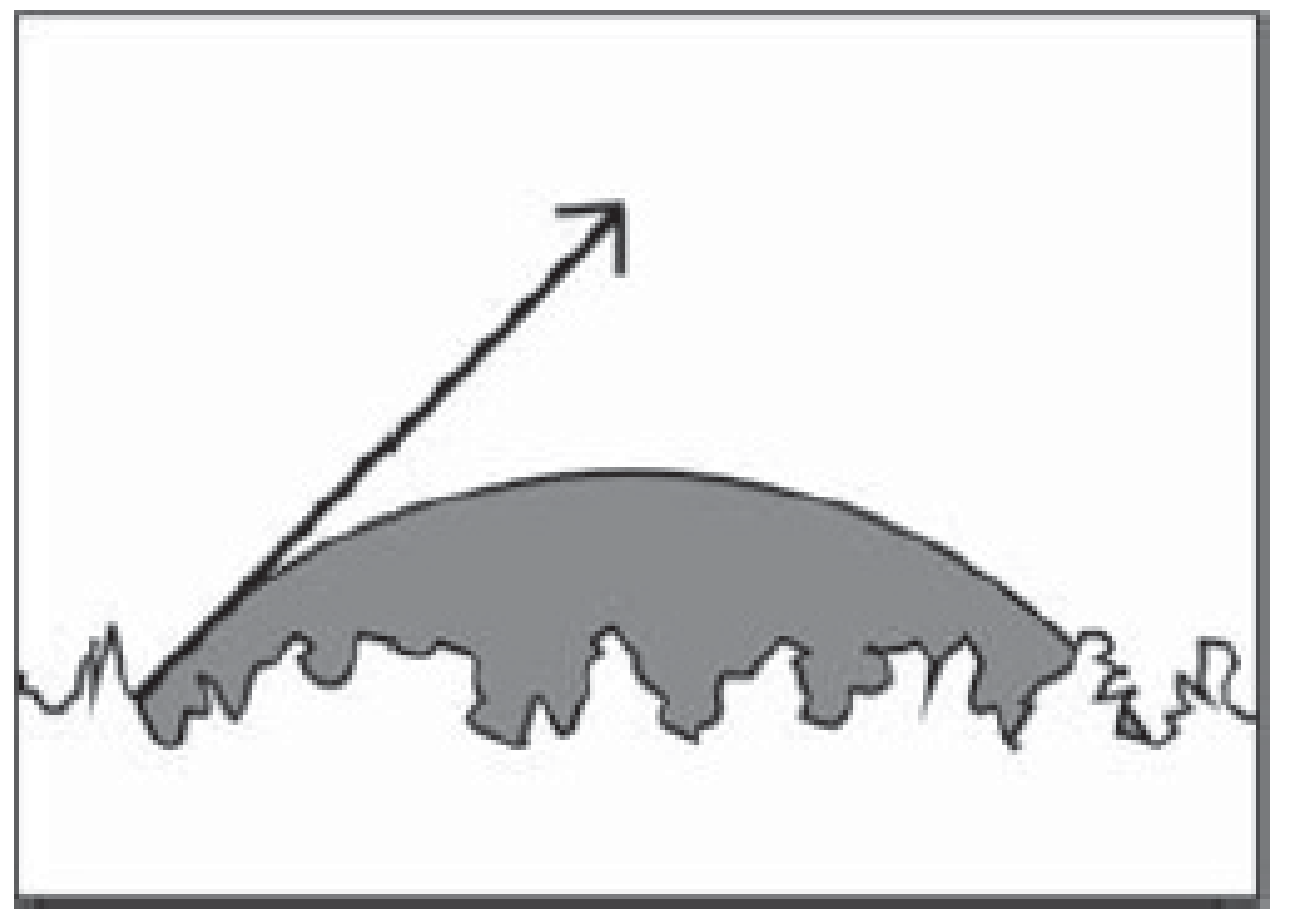


$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta$$

$$\cos\theta = (\gamma_S - \gamma_{SL})/\gamma_L$$

Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

# The Effect of Surface Roughness



Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

# The Wenzel Roughness Factor, $R_f$:

$$\cos \theta_{smooth} = (\gamma_S - \gamma_{SL})/\gamma_L \qquad \text{(Young Eq.)}$$

**Takes into account the effect of roughness on contact angle.**

$$\cos \theta_{rough} = R_f (\gamma_S - \gamma_{SL})/\gamma_L \qquad \text{(Wenzel)}$$

**where** $R_f = \cos \theta_{rough} / \cos \theta_{smooth} \geq 1$

**If** $\theta_{smooth} < 90^o$ **(partial wetting) then** $\theta_{rough} < \theta_{smooth}$ **(better wetting)**

**If** $\theta_{smooth} > 90^o$ **(partial non-wetting) then** $\theta_{rough} > \theta_{smooth}$ **(poorer wetting)**

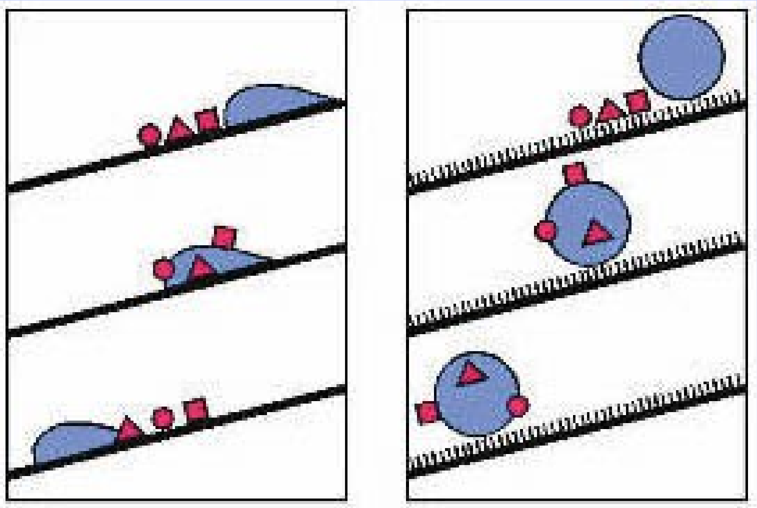
# Lotus Plants at Nankai University, Tianjin, China

# Superhydrophobicity:

## θ > 150º

# The Lotus Effect:

## Non-Wetting & Self-Cleaning Surfaces



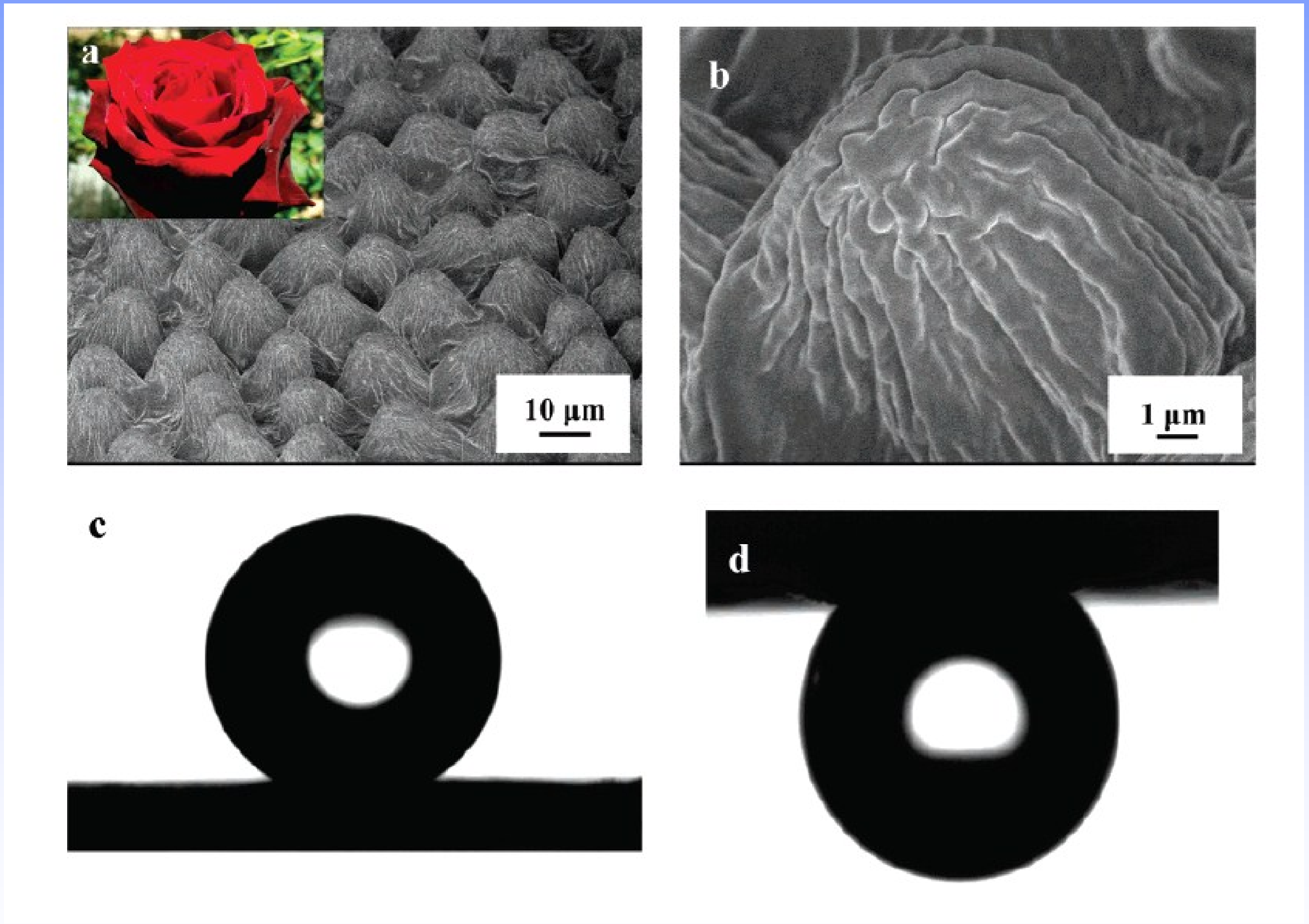
http://library.thinkquest.org/27468/images/fig_8_2.jpg

**Lotus e Taro**
**(http://plantsrescue.com/tag/green-taro/)_**

**Lotus effect on a taro leaf**
(Wikipedia "Lotus effect")

# The Rose Petal Effect:

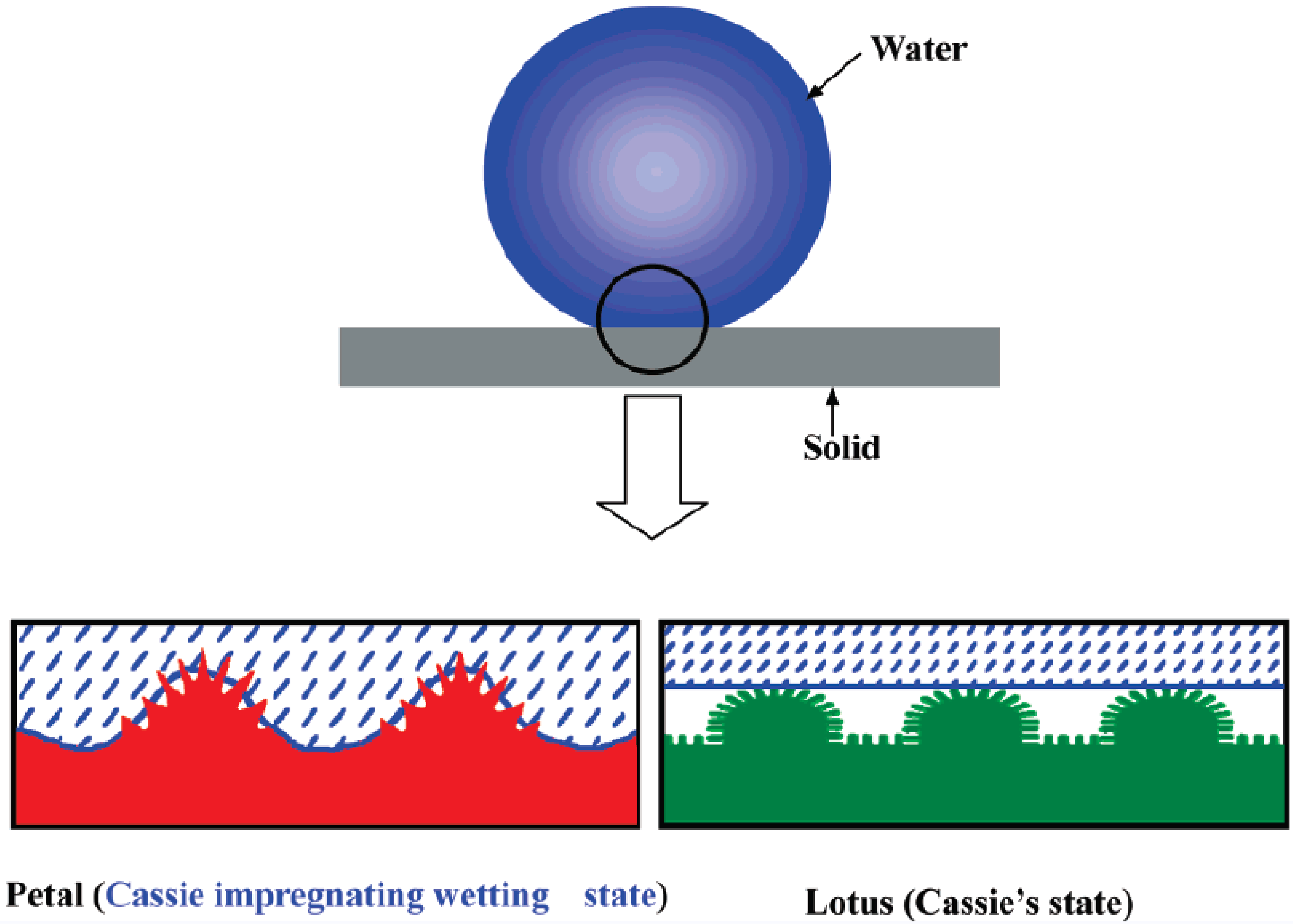
## Non-Wetting but Adhesive Surfaces



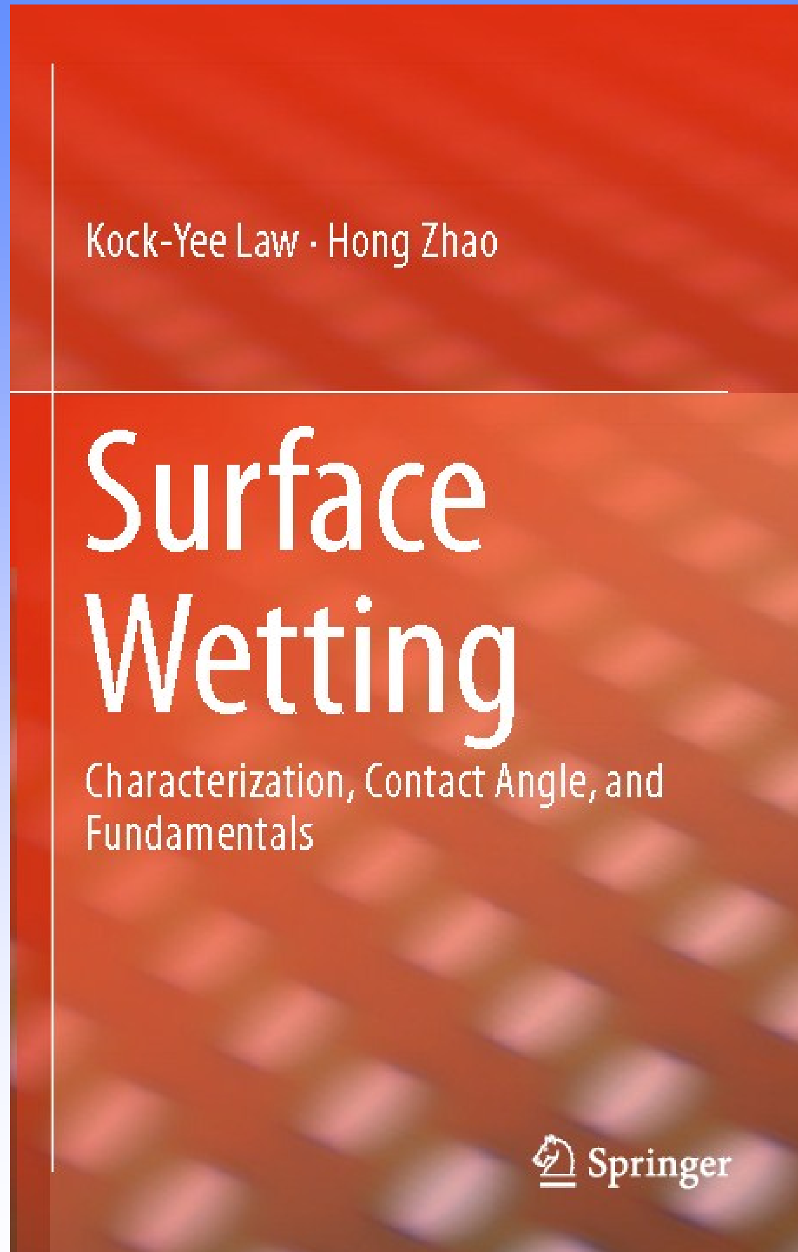

Feng et al., Petal Effect: A Superhydrophobic State with High Adhesive Force, *Langmuir*, **2008,** *24*, 4114-4119**.**

# Superhydrophobicity: Petal & Lotus Effect

# Superhydrophobicity: Petal vs. Lotus Effect

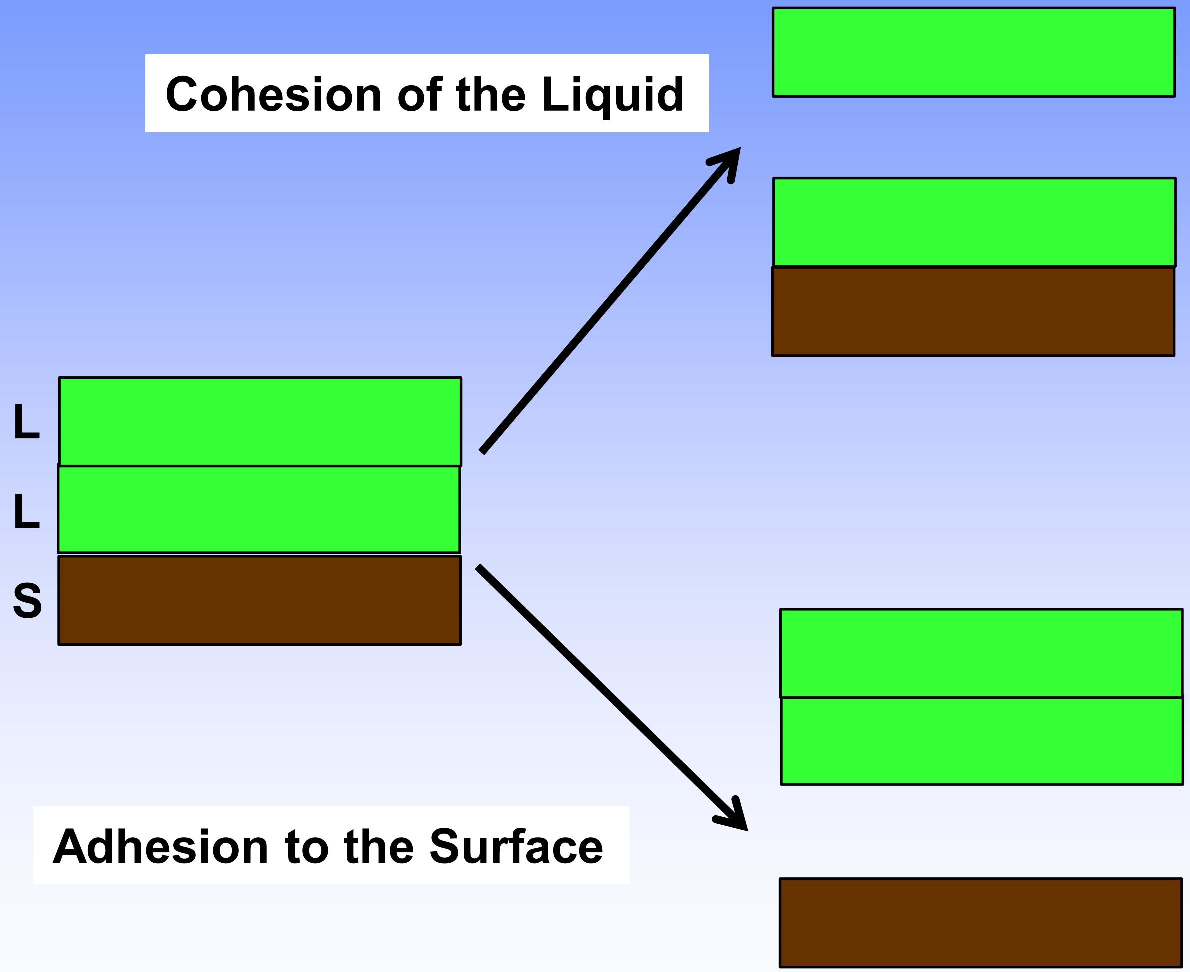



Feng et al., Petal Effect: A Superhydrophobic State with High Adhesive Force, *Langmuir*, **2008,** *24*, 4114-4119**.**


Kock-Yee Law · Hong Zhao
Surface Wetting
Characterization, Contact Angle, and Fundamentals
Springer

2016

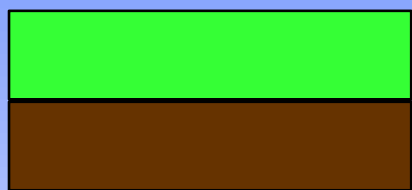
# Solids and Liquids: Work of Cohesion vs. Work of Adhesion




$W_C = 2\gamma_L$

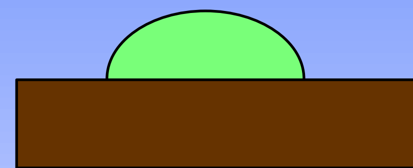
$W_A = \gamma_L + \gamma_S - \gamma_{SL}$

# Cohesion vs. Adhesion and Contact Angle



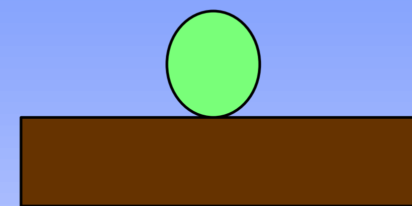
$\theta = 0^{o}$

$W_C = W_A$



$\theta = 90^{o}$

$W_C = 2W_A$

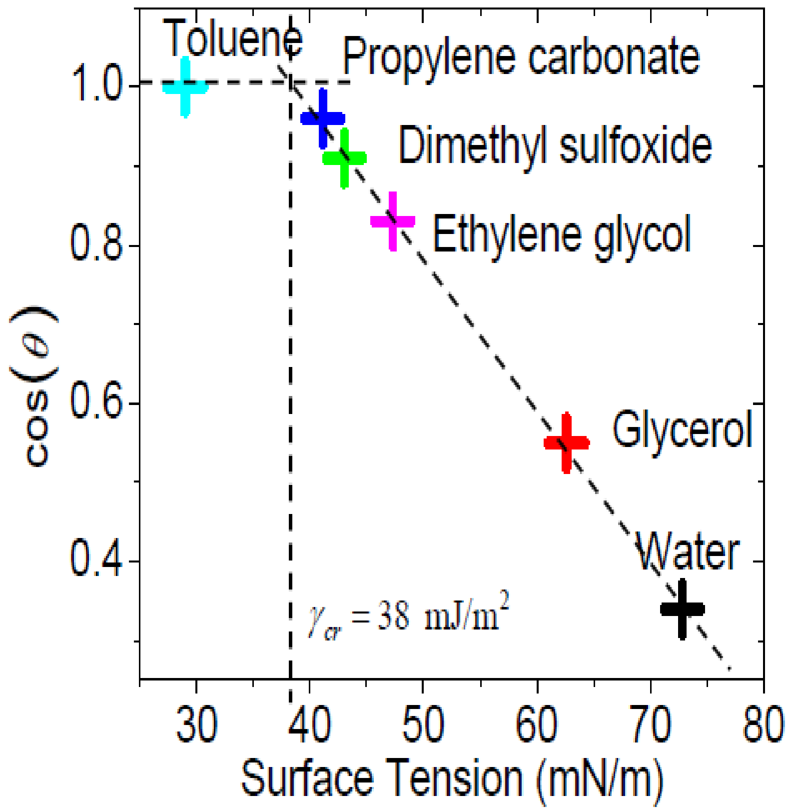


$\theta = 180^{o}$

$W_A = 0$

$$\cos\theta = 2(W_A / W_C) - 1$$

# Surface Tension of Solids: The Zisman approach




Zisman plot for PMMA using various testing liquids

Zisman found that $\cos\theta$ is usually a monotonic function of $\gamma_l$

$$\cos\theta = a - b\gamma_l = 1 - \beta(\gamma_l - \gamma_{cr})$$

$\gamma_{cr}$ is called the "critical surface tension" of a solid and is a characteristic property of any given solid

Any liquid with $\gamma_l < \gamma_{cr}$ will wet the surface

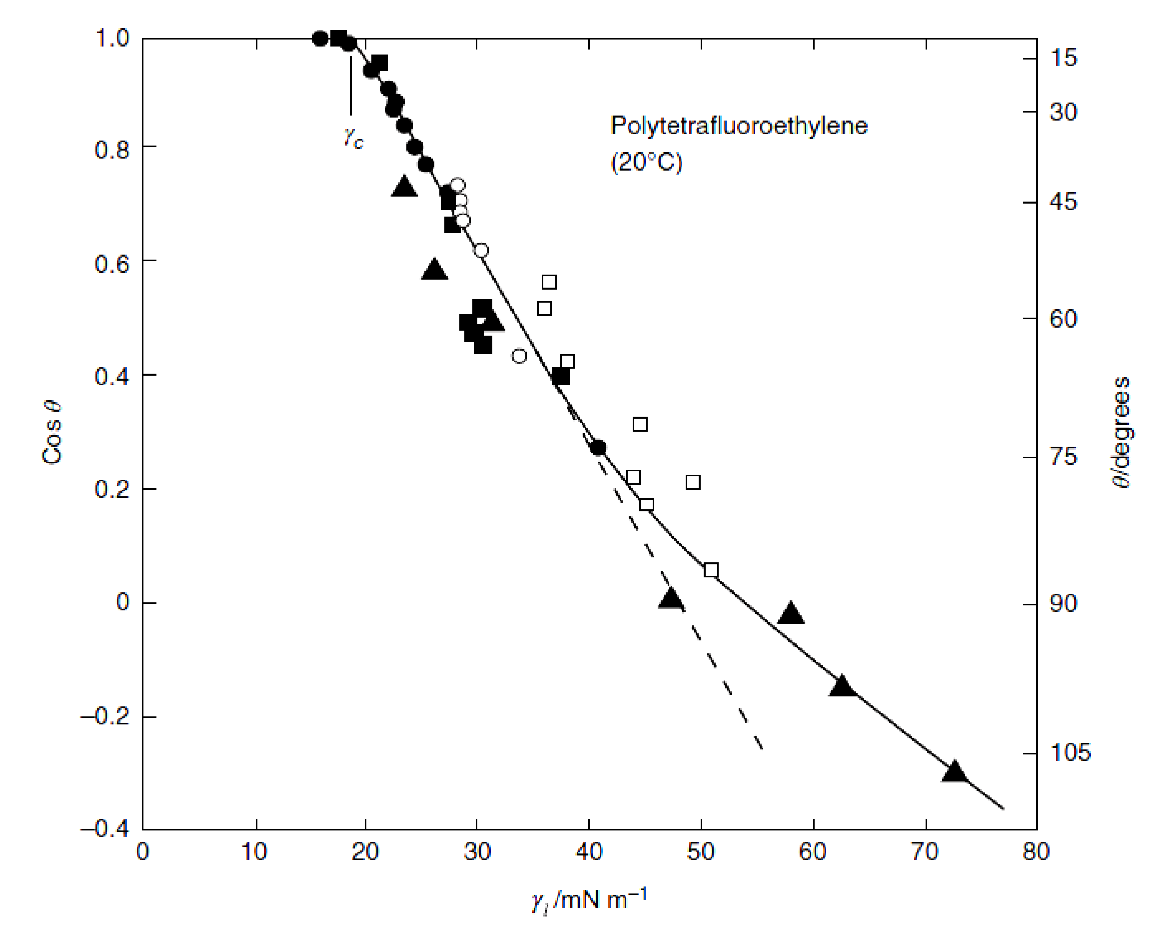
It is found that critical surface tension is close to the solid surface tension of polymer

$$\gamma_s \approx \gamma_{cr}$$

*web.mit.edu/nnf/education/wettability/summerreading-2005short.pdf*

# The Critical Surface Tension, $\gamma^{crit}$

**All liquids with $\gamma < \gamma^{crit}$, where $\cos\theta = 1$, totally wet the surface**




Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

# Table of Critical Surface Tensions, $\gamma^{crit}$

| Solid | $\gamma^{crit}$ | Solid | $\gamma^{crit}$ |
|---|---|---|---|
| Polyhexafluoropropylene | 16.2 | Poly(vinylidene chloride) | 40 |
| Polytetrafluoroethylene (PTFE, Teflon) | 18.5 | Poly(ethylene terephthalate) (PET) | 43 |
| Polytrifluoroethylene | 22.0 | Nylon 6,6 | 43 |
| Poly(dimethylsiloxane) | 24.0 | Poly(acrylonitrile) | 44 |
| Poly(vinylidene fluoride) | 25.0 | Cellulose – from wood | 36–42 |
| Poly(vinyl fluoride) | 28.0 | Cellulose – from cotton | 42 |
| Butyl rubber | 27.0 | Wool | 45 |
| Polyethylene (PE) | 31.0 | Urea-formaldehyde resin | 61 |
| *cis*-Polyisoprene | 31.0 | Polyamide–epichlorohydrin resin | 52 |
| *cis*-Polybutadiene | 32.0 | Casein | 43 |
| Polystyrene (PS) | 33.0 | Starch | 39 |
| Polyvinyl alcohol | 37.0 | Resorcinol adhesives | 51 |
| Poly(methyl methacrylate) (PMMA) | 39.0 | Aluminium | ~500 |
| Poly(vinyl chloride) (PVC) | 39.0 | Copper | ~1000 |

**Simple applications: Painting the Surface, Gluing surfaces**

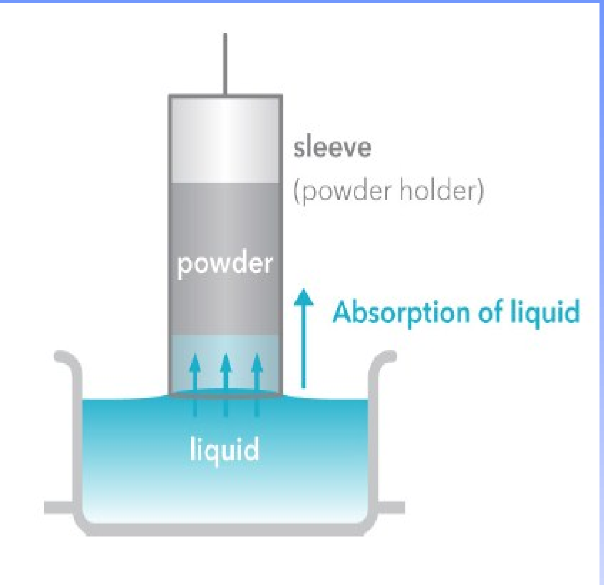
Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

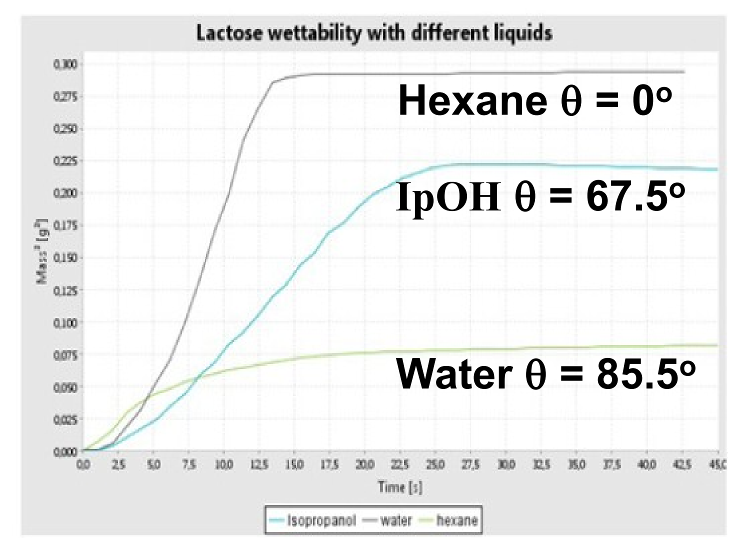
# Contact Angle of Powders

The Washburn Method measures the maximum weight gain due to absorption of liquids in a cylinder of the powder.

Comparison of the weight gain with that of a totally wetting liquid with contact angle zero.

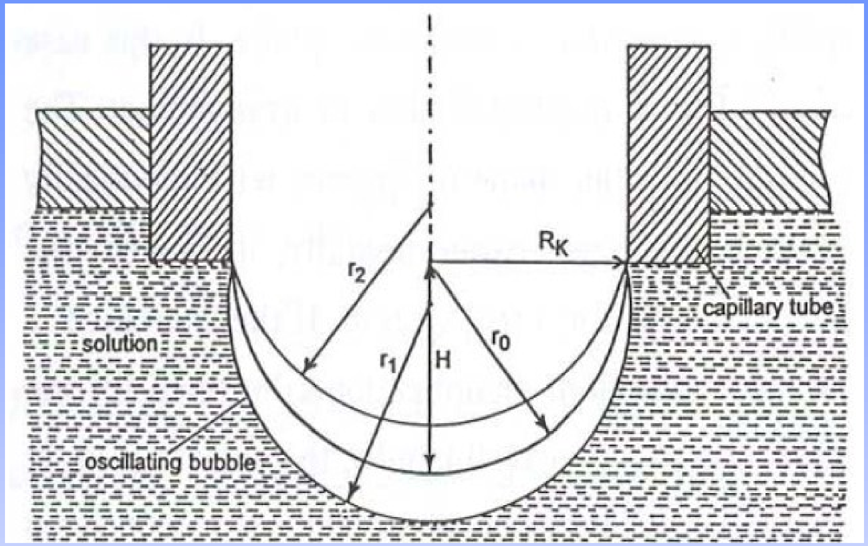
Powder size and packing must be reproducible. Wettability of the Tube, etc.

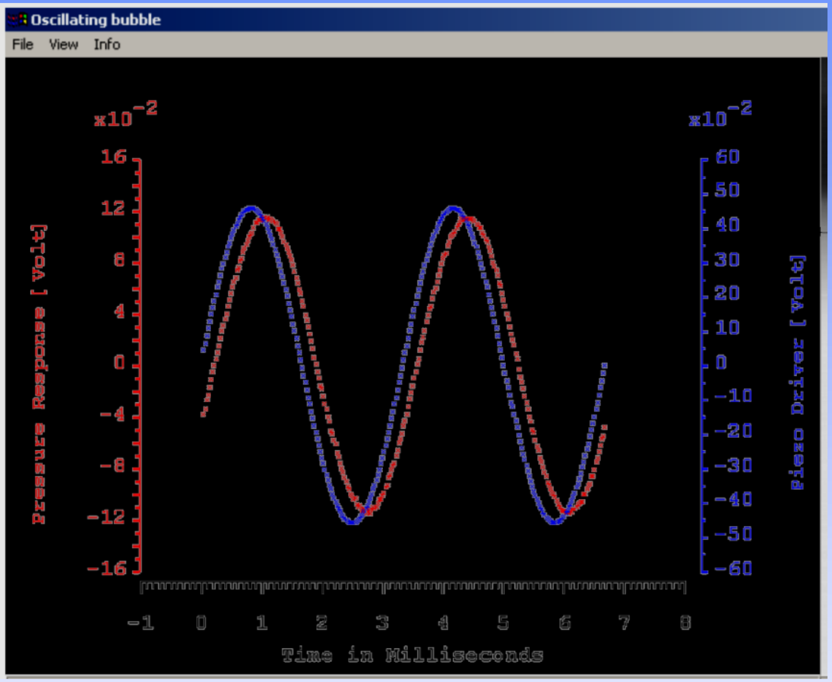


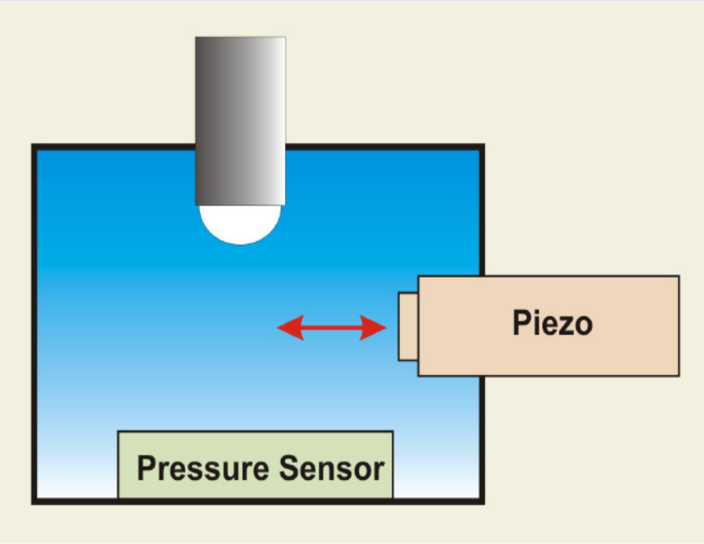




Review: Alghunaim et al., *Powder Technology* 2016, *287*, 201–215.
Alghunaim & Newby, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 2016, *492*, 79–87.

# Surface Rheology



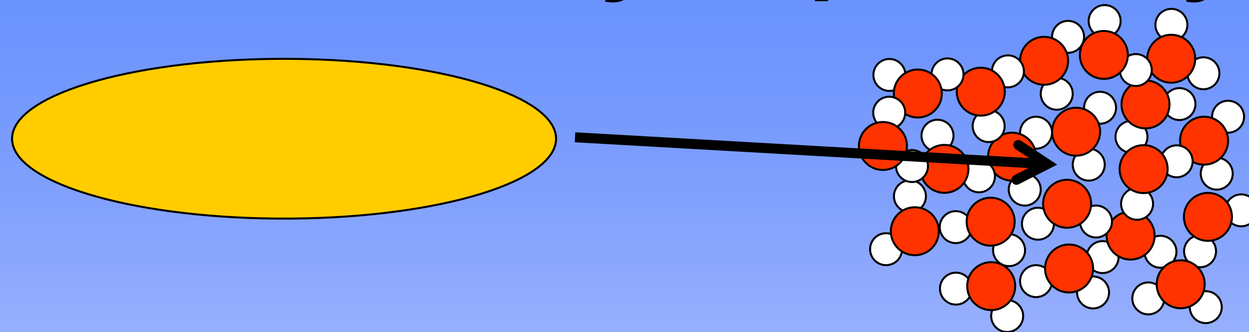

**Amplitude → Elasticity**

**Phase Shift → Surface Viscosity**

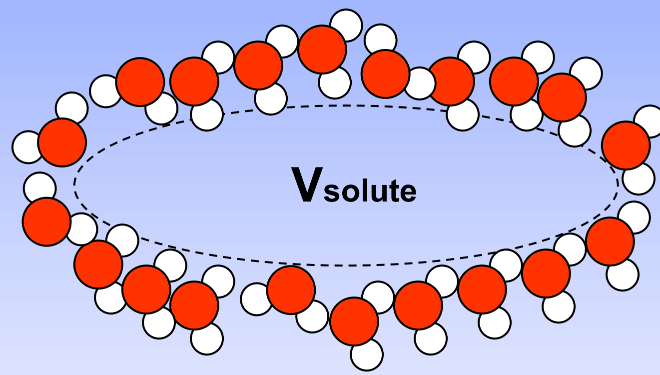
BUBBLEDROP ANALYZER

OPTREL GBR
WWW.OPTREL.DE

# What is Hydrophobicity?



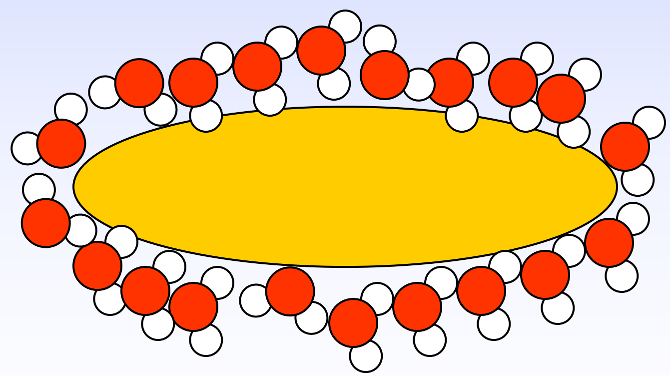
Make cavity the size of the solute:




**Cavitation energy:**

$$V_{solute} \times \underbrace{(\Delta\bar{H}_{vap}/\bar{V}_{solvent})}_{\text{(Hildebrand parameter } \delta_H^2\text{)}}$$

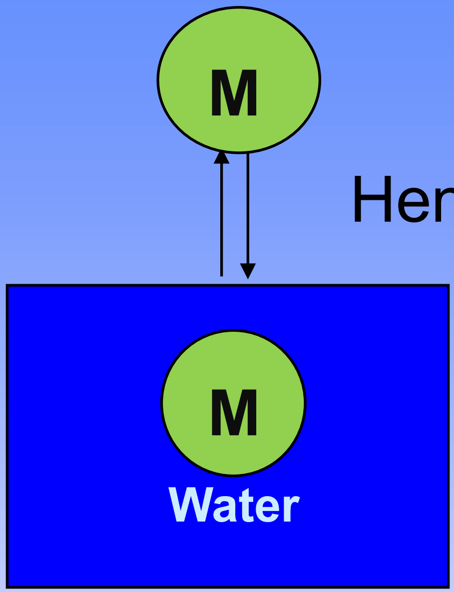
Insert solute in the cavity:



**Dispersion Energy**

**Energy Required to Insert the Solute = |Cavitation Energy| - |Dispersion|**

# Gas Phase-Water Partitioning Insensitive to Solute Volume!




Henry's constant ($L_W$) for air-water partitioning

$$\log L_W = -1 + 2.5\,S + 3.8\,A + 4.8\,B + 0.6\,E - 0.9\,V$$

**Dipolarity + Hydrogen bonding**

**Relatively insensitive to the size of the solute!**

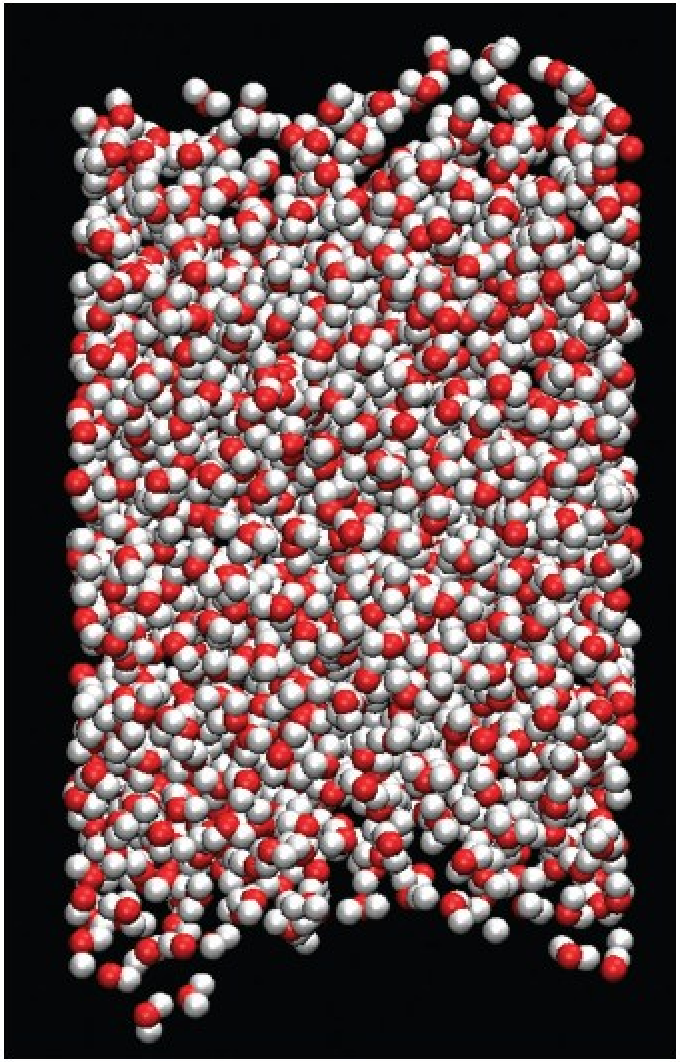
**Energy Required to Insert an Alkane (S = A = B = E = 0) into Water =**
**|Cavitation Energy| - |Dispersion| ≈ 0**

**Cavitation energy necessary to make the cavity in water ≈ energy gained from dispersion when an alkane solute is placed in the cavity!**

**Entropy much more important than Enthalpy in the Hydrophobic Effect**

Abraham *et al*., *J. Chem. Soc. Perkin 2,* **1994,** 1777-1789.

# Molecular Dynamics Simulations



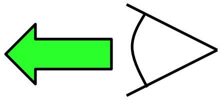
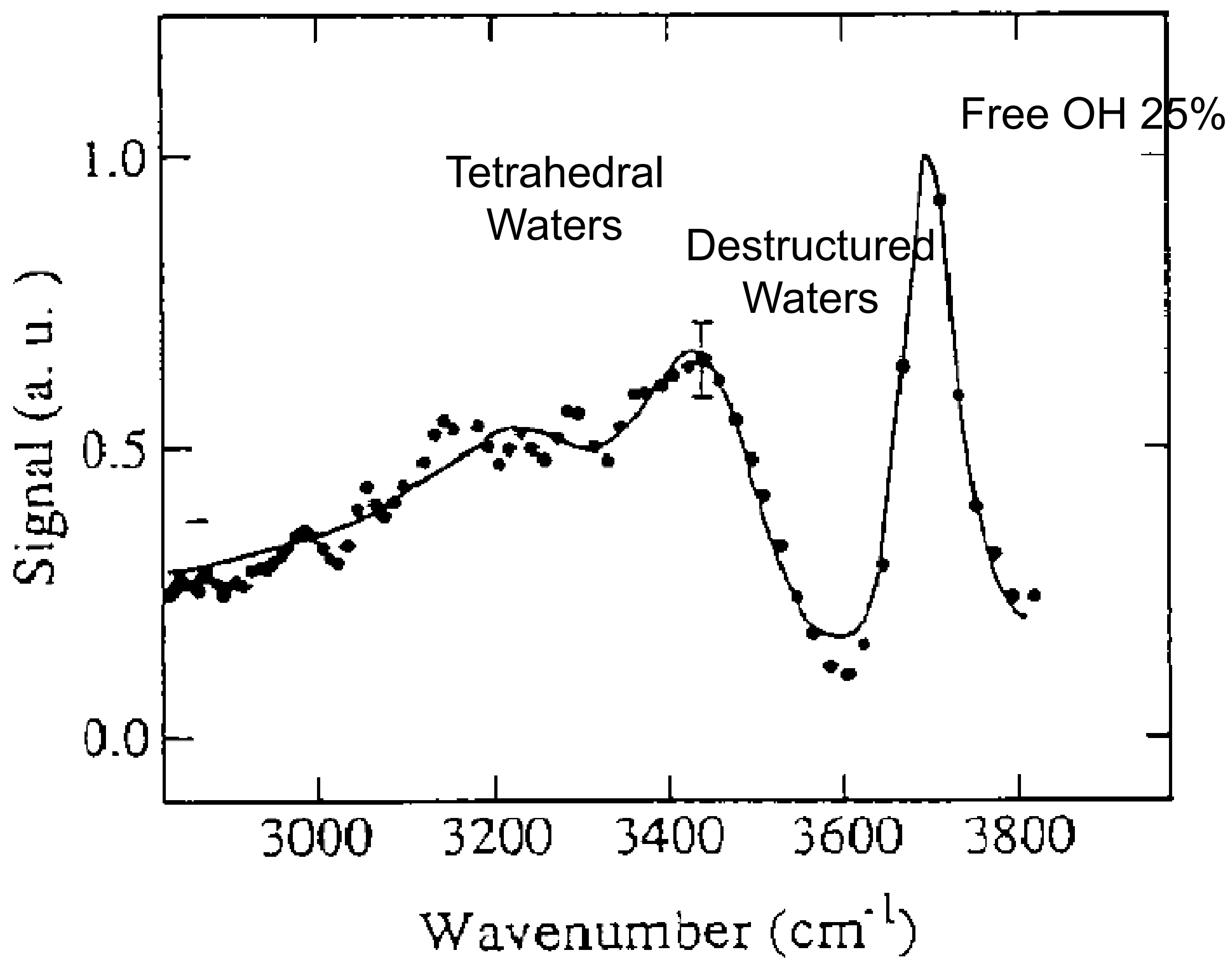
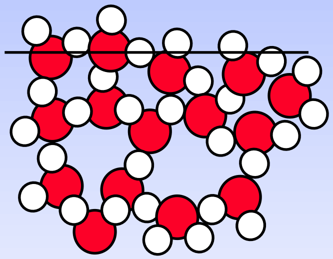



**Fig. 1** Snapshot of the simulated water/vacuum interfaces. Black spheres (red, online) represent oxygen atoms, and white ones represent hydrogen atoms.

Y. Wang, N. O. Hodas, Y. Jung and R. A. Marcus, Phys. Chem. Chem. Phys., 2011, **13**, 5388–5393

# Sum Frequency Generation (SFG) Vibrational Spectrum of the Air-Water Interface

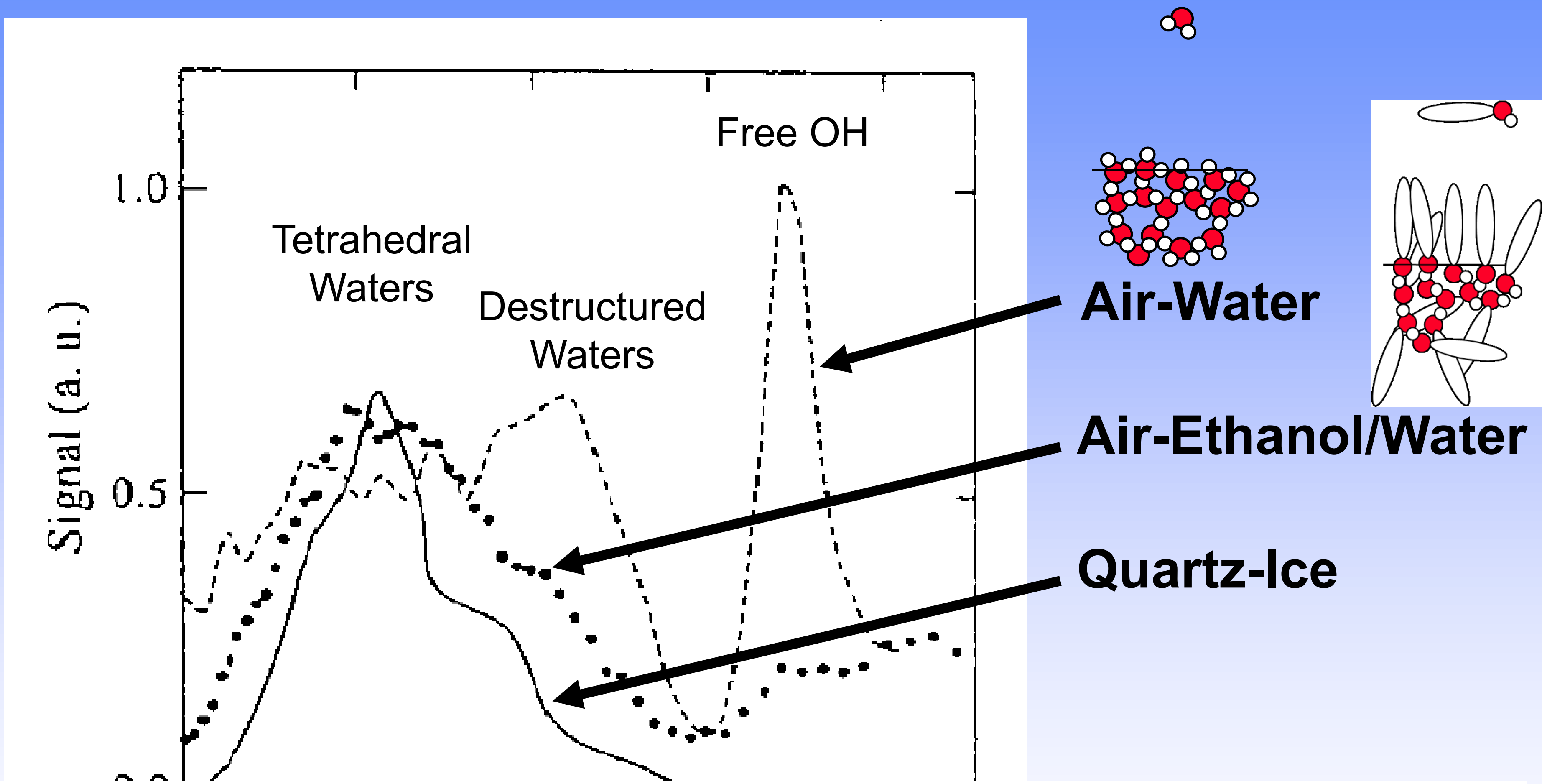


E. Freysz, Q. Du* and Y.R. Shen*

ANNALES DE PHYSIQUE
Colloque C1, supplément au n°5, vol. 19, octobre 1994

# SFG Spectra of Other Interfaces

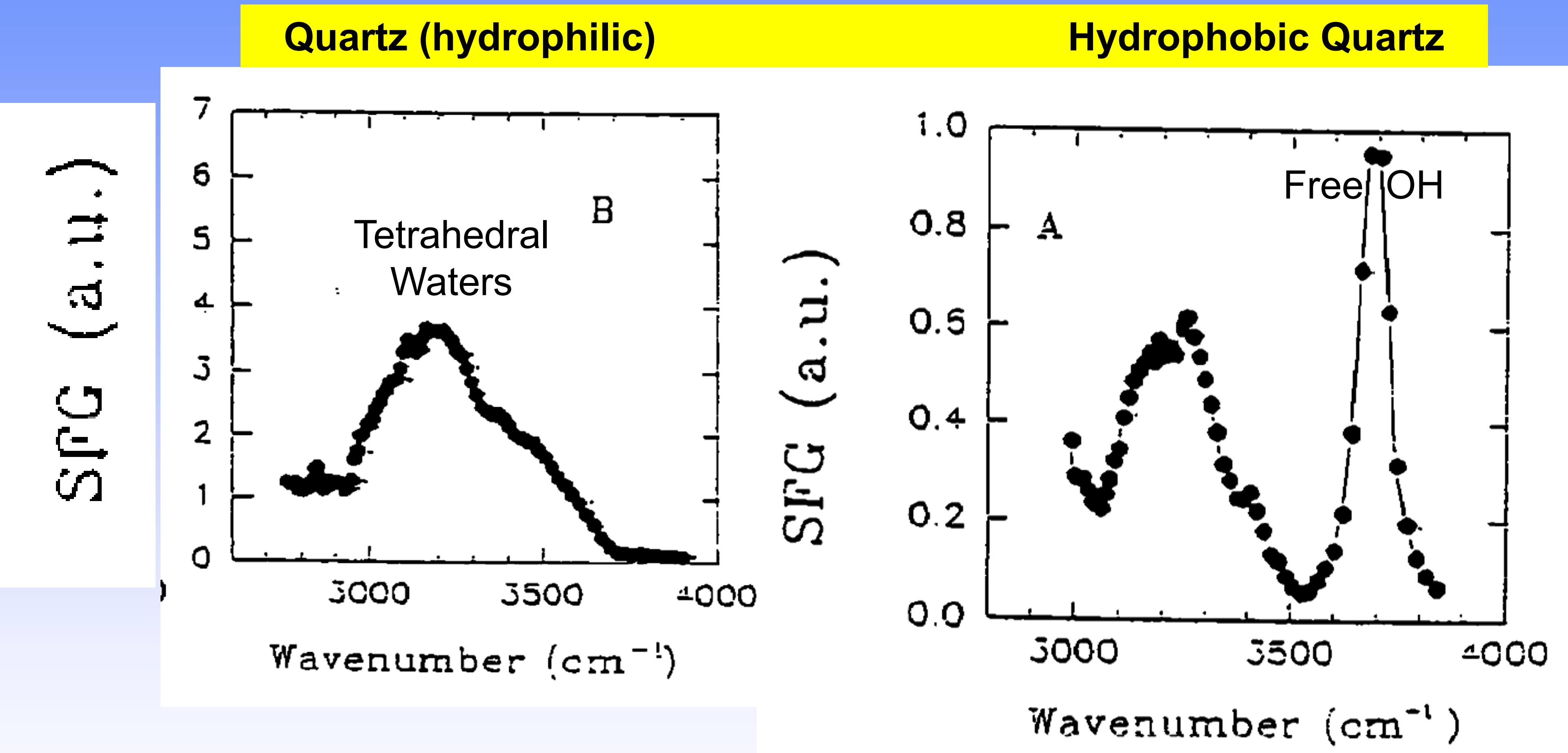



Spectrum of air-water interface (- - -), air-alcohol-water interface (•) and quartz-ice interface (___)


E. Freysz, Q. Du* and Y.R. Shen*

ANNALES DE PHYSIQUE
Colloque C1, supplément au n°5, vol. 19, octobre 1994

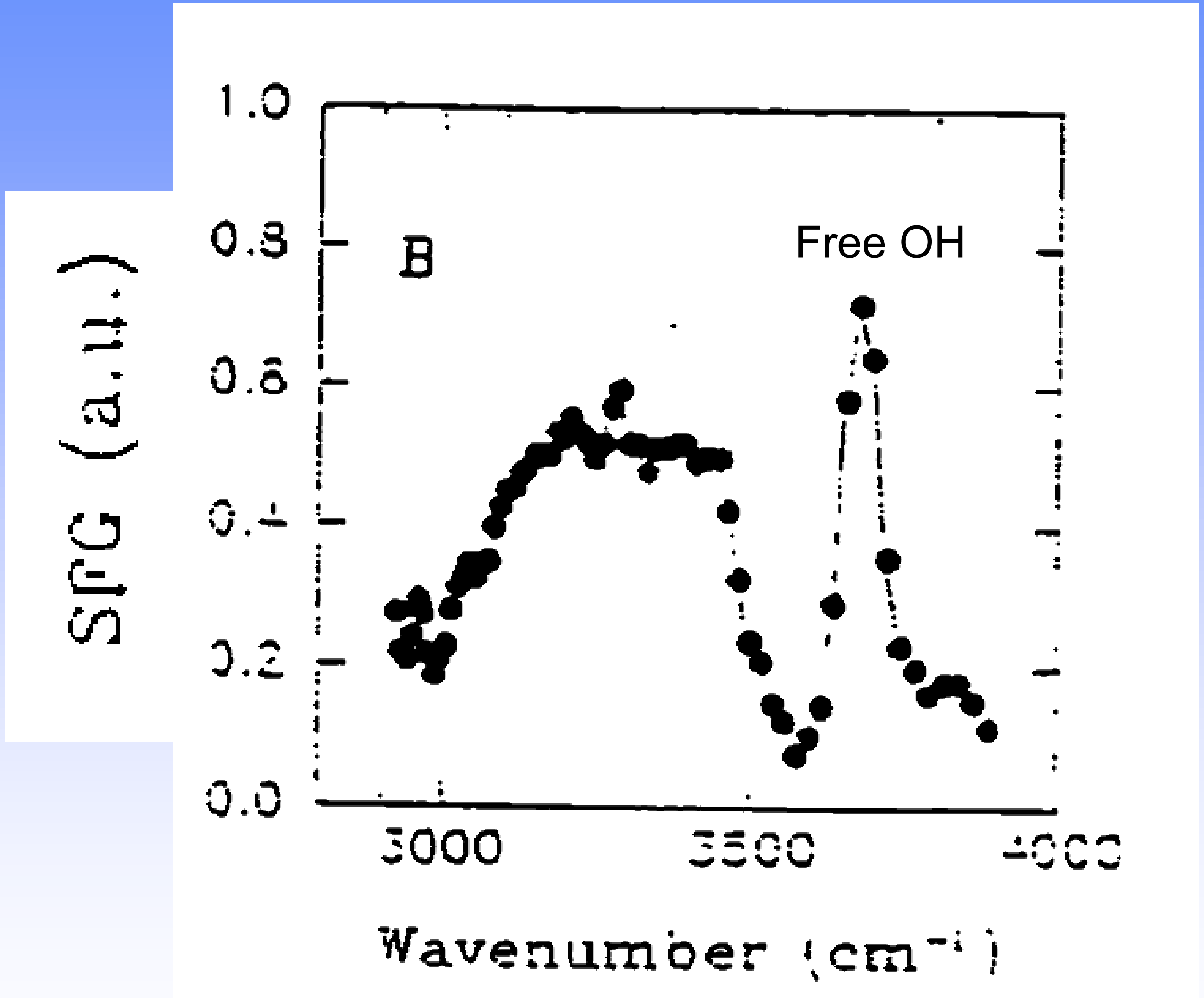
# SFG Spectra of Quartz-Water Interfaces




E. Freysz, Q. Du* and Y.R. Shen*

ANNALES DE PHYSIQUE
Colloque C1, supplément au n°5, vol. 19, octobre 1994

# SFG Spectra of the Hexane-Water Interface

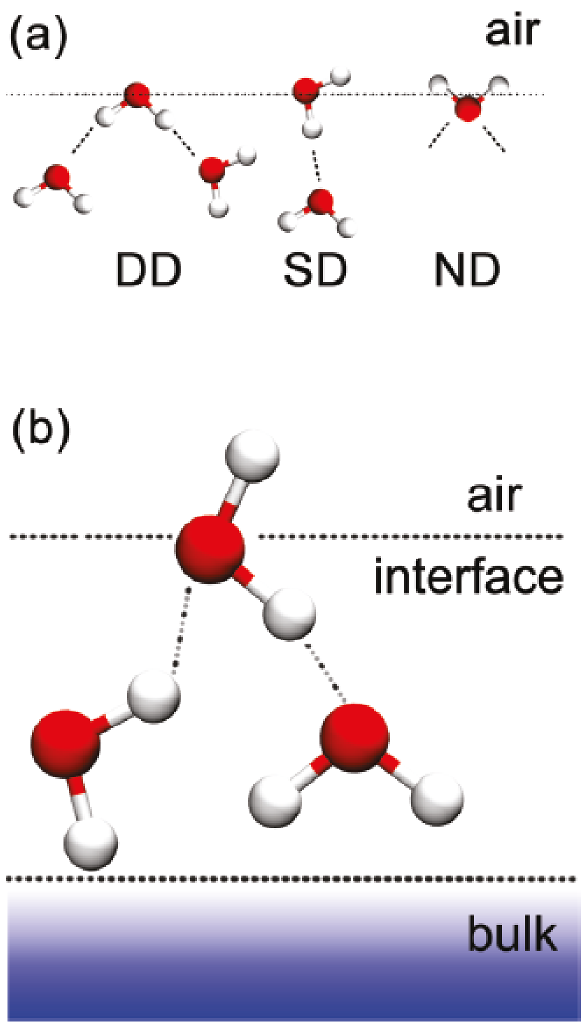



E. Freysz, Q. Du* and Y.R. Shen*

ANNALES DE PHYSIQUE
Colloque C1, supplément au n°5, vol. 19, octobre 1994

# *Ab initio* Molecular Dynamics Simulations

Scheme 1. (a) Depiction of Double Donor (DD), Single Donor (SD), and Non-donor (ND) Water Orientations at Air−Water Interface[a]; (b) Schematic of Structure of Water Molecules near the Air−Water Interface from Our Ab Initio MD Simulations[b].

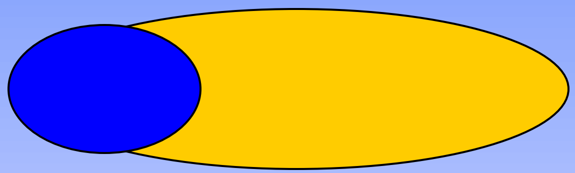


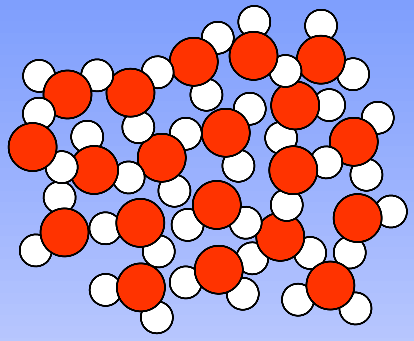

| — | bulk | surface | SFG experiment (ref 35) surface |
|---|---|---|---|
| DD | 0.84 | 0.49 | |
| SD | 0.15 | 0.45 | |
| ND | 0.01 | 0.06 | |
| $F$ (free OH) | 0.08 | 0.29 | 0.25 |
| $\langle n_{HB} \rangle$ | 3.7 | 2.9 | 3.0 |

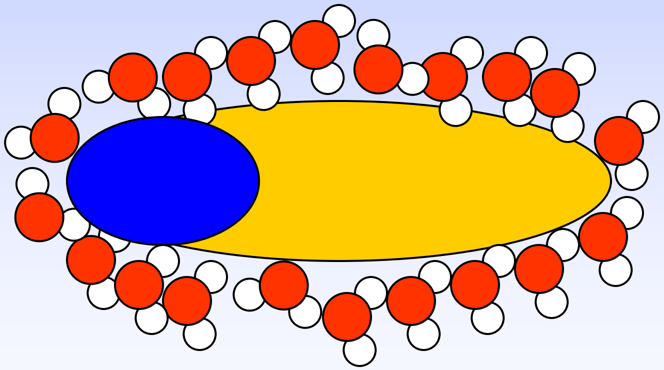
Thomas D. Keuhne, Tod A. Pascal, Efthimios Kaxiras, and Yousung Jung

J. Phys. Chem. Lett. 2011, 2, 105–113

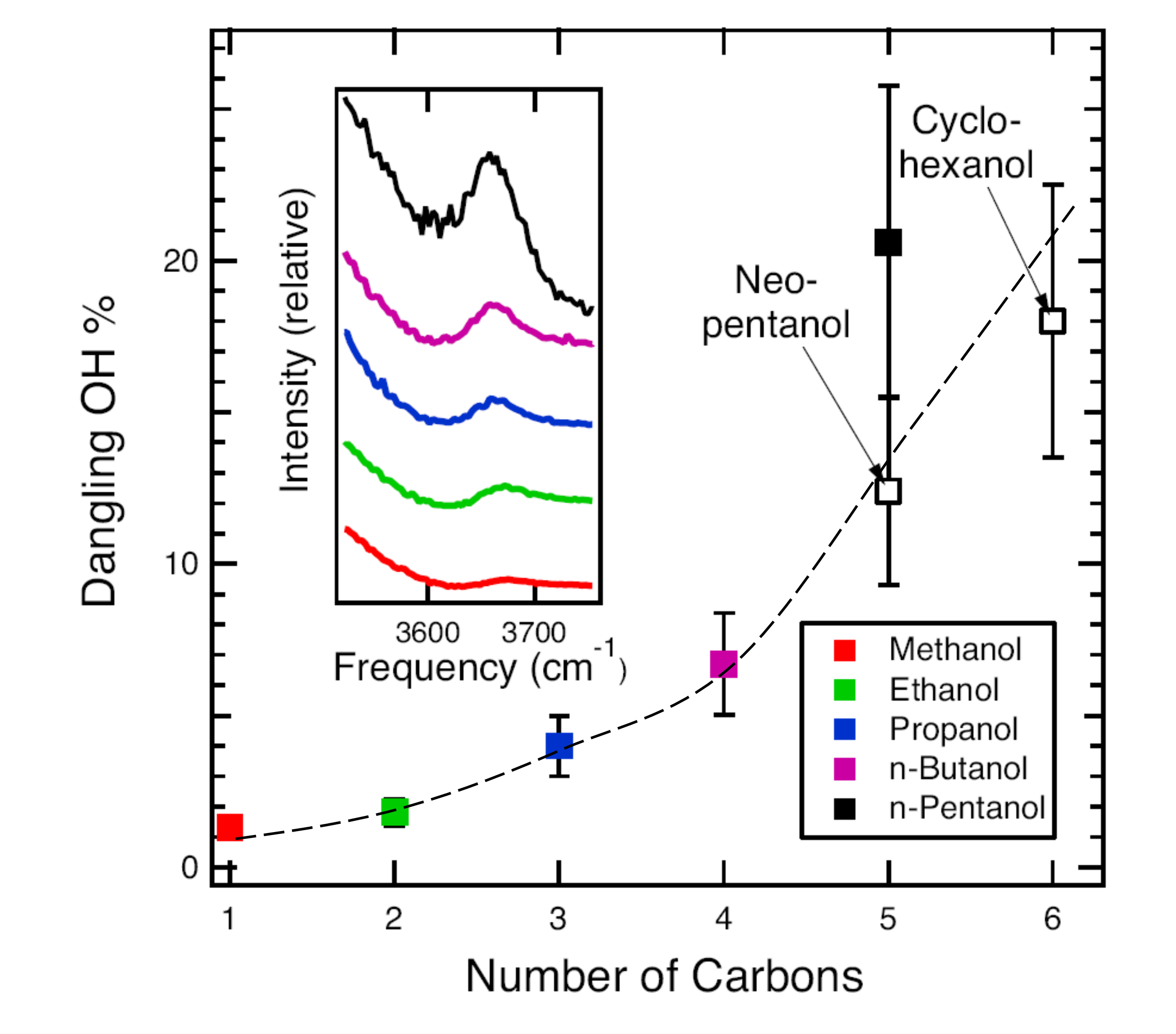
# Solvation in Water

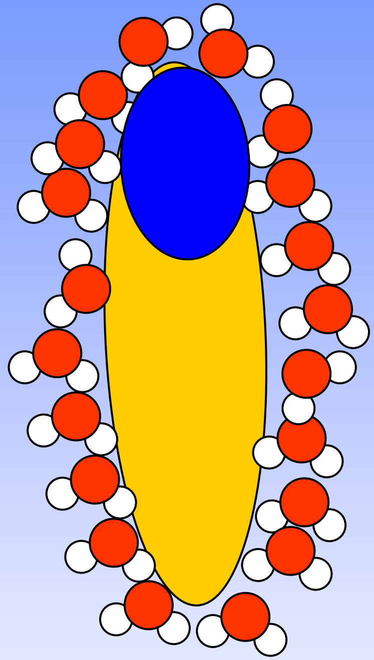






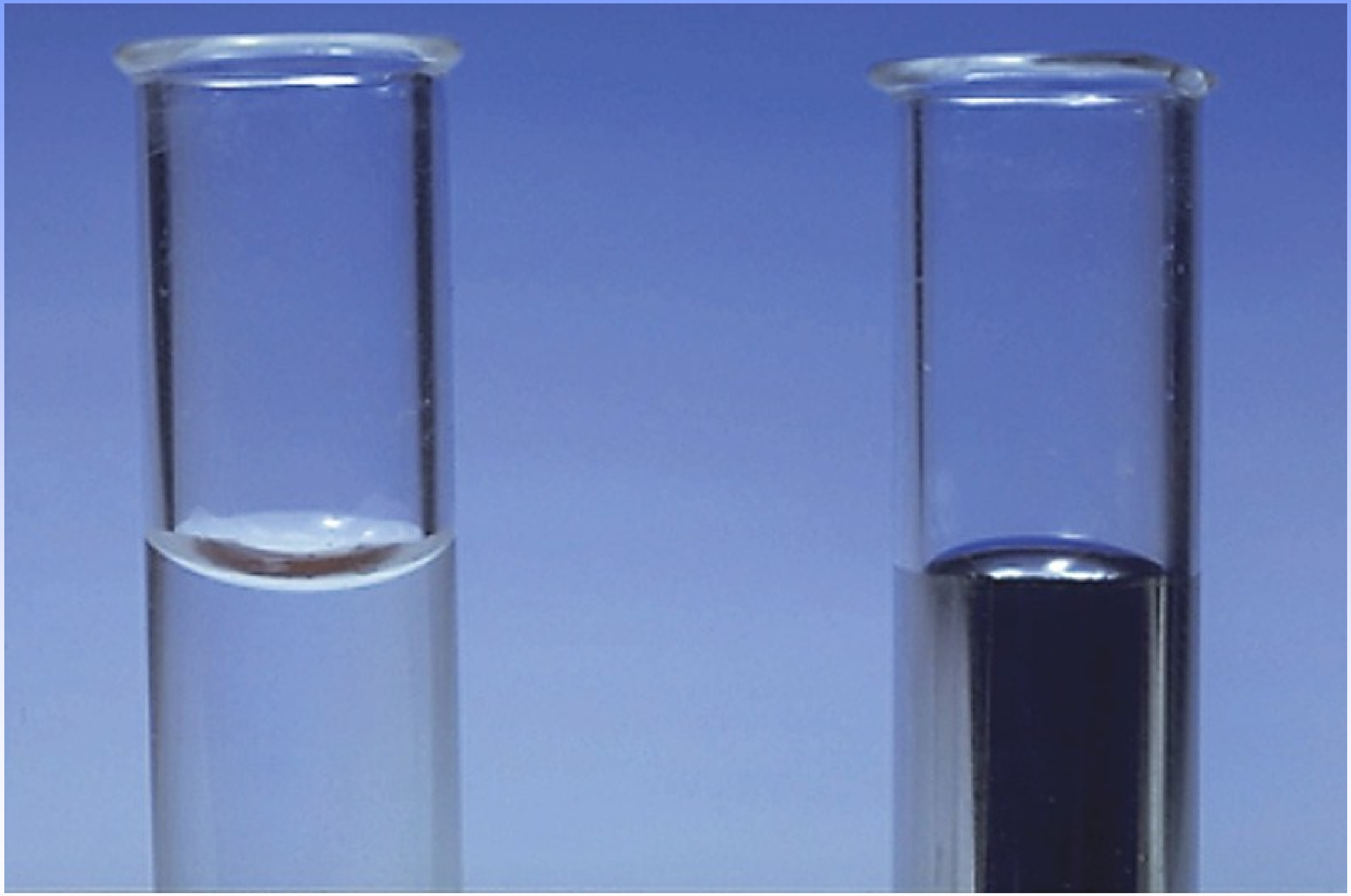
# Solvation of Alcohols in Water:
## Dangling OH-Bonds as a function of the alkyl portion of the alcohol



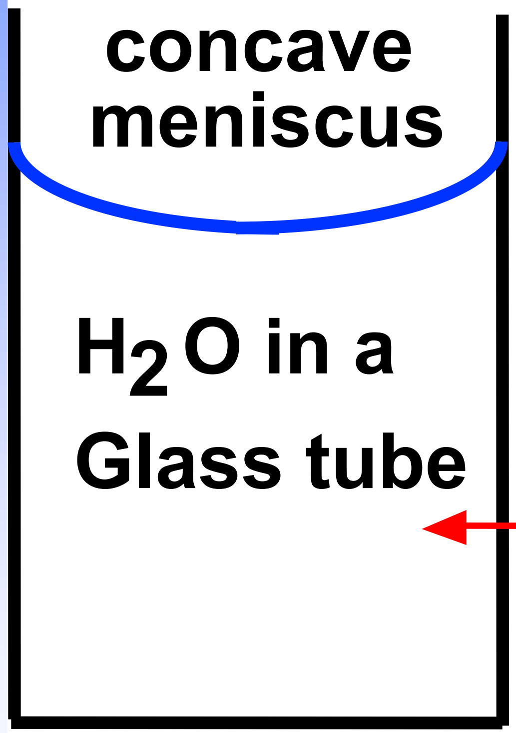



Perera et al., *PNAS*, **2009**, *106*, 12230

# Capillarity
## Glass-Water vs. Glass-Mercury



# Capillarity

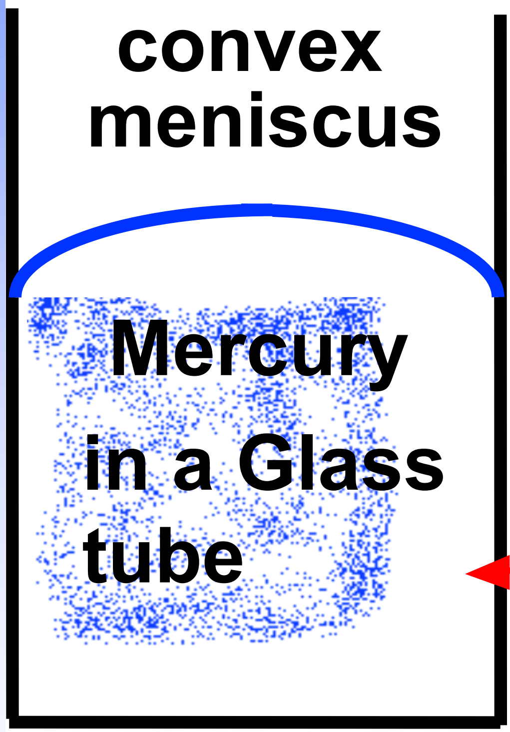



**Adhesion Forces**
Between Water and Glass

**Are GREATER than the**

**Cohesion Forces**
Between molecules of Water

# Capillarity




**Adhesion Forces**

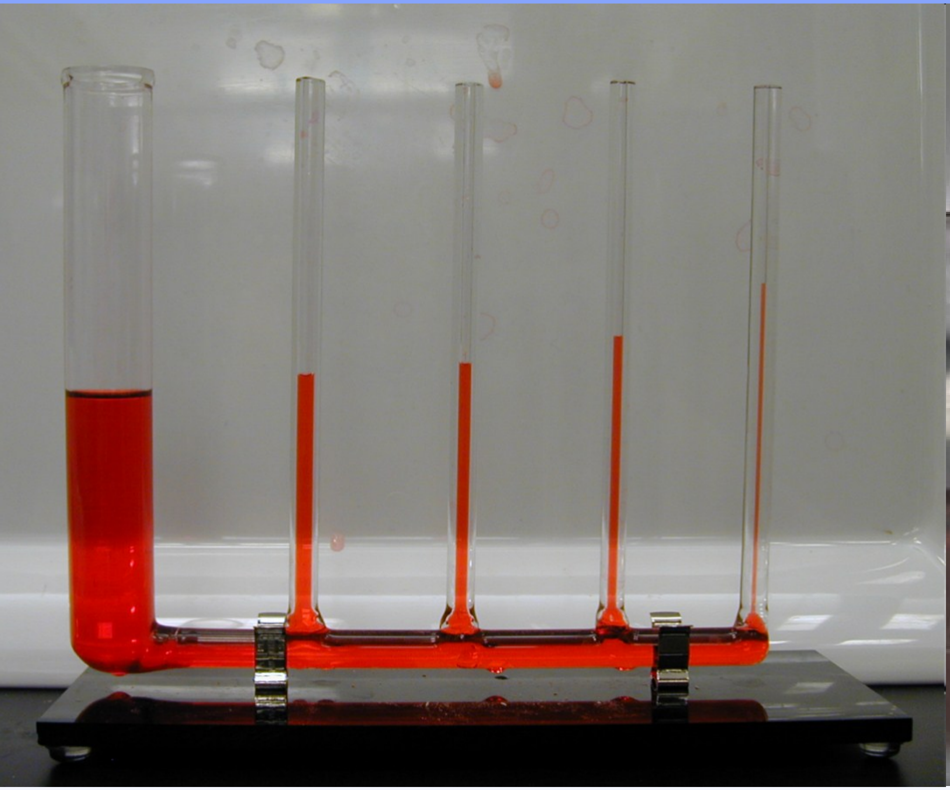
Between Mercury and Glass

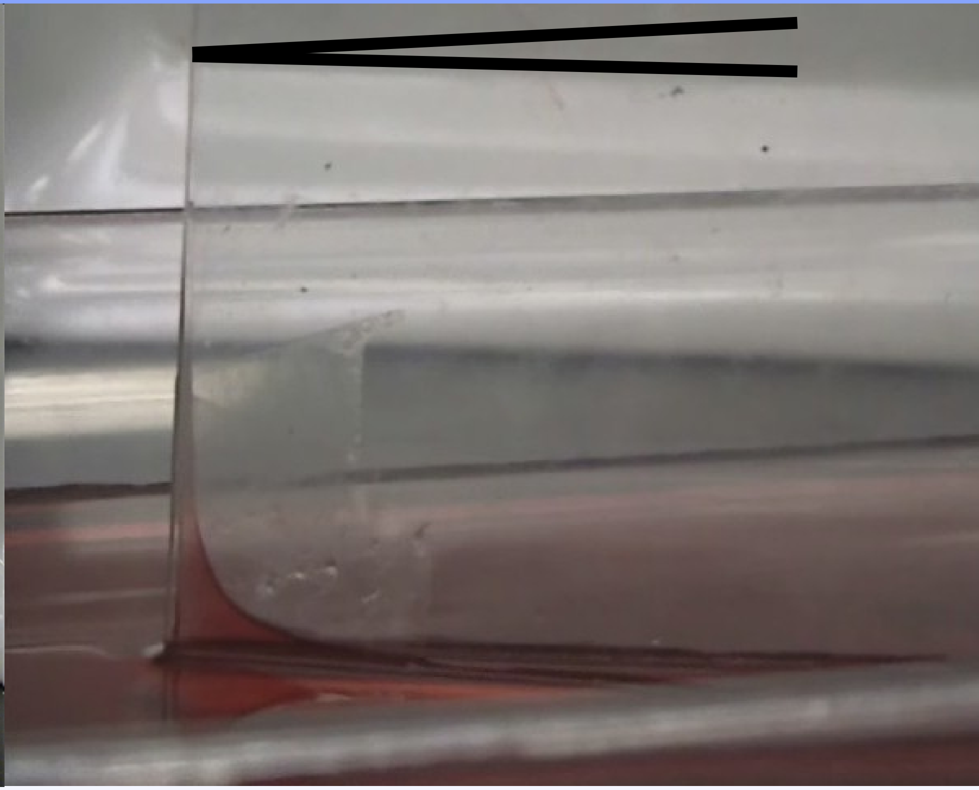
**Are SMALLER than the**

**Cohesion Forces**

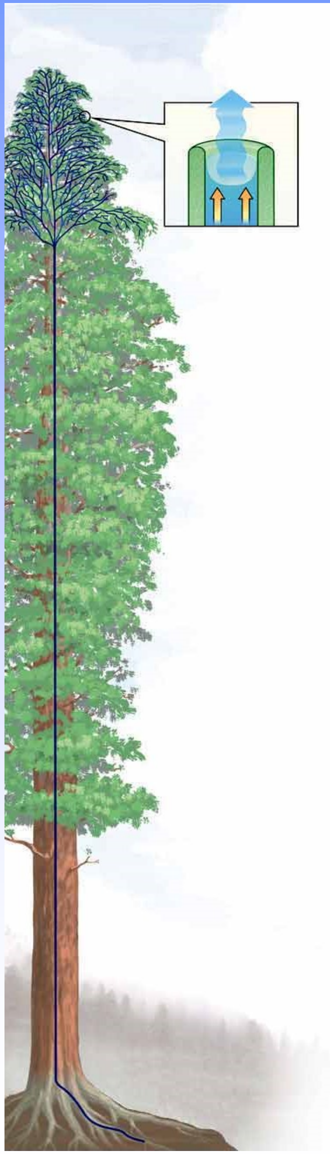
Between molecules of WaterMercury

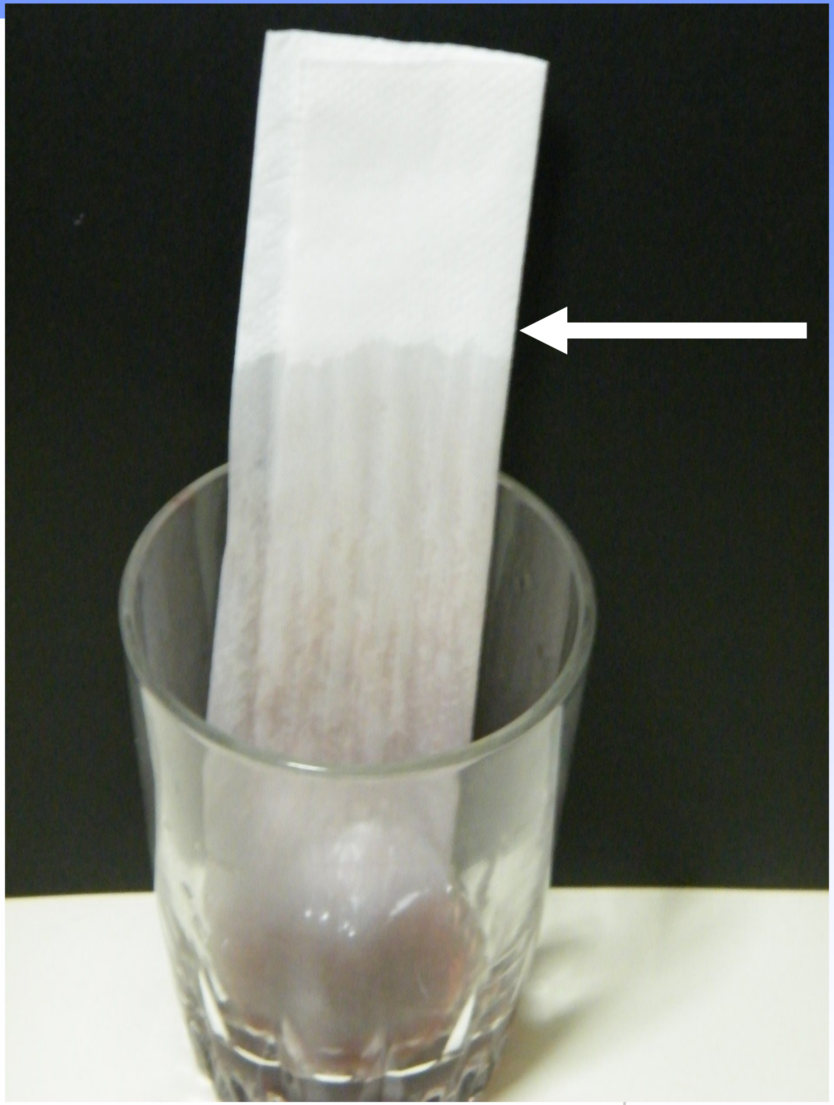
# Capillarity



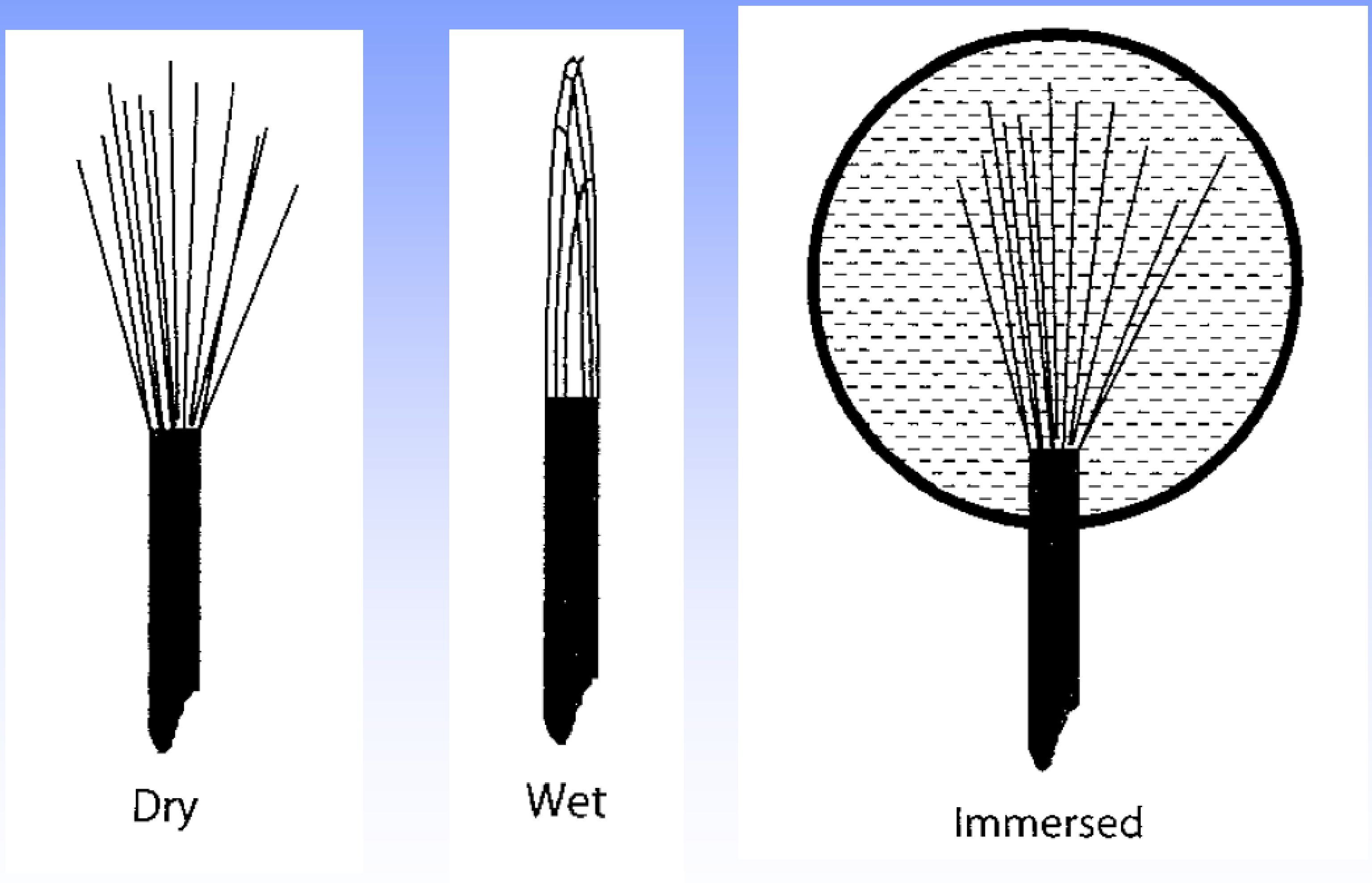


# Capillarity





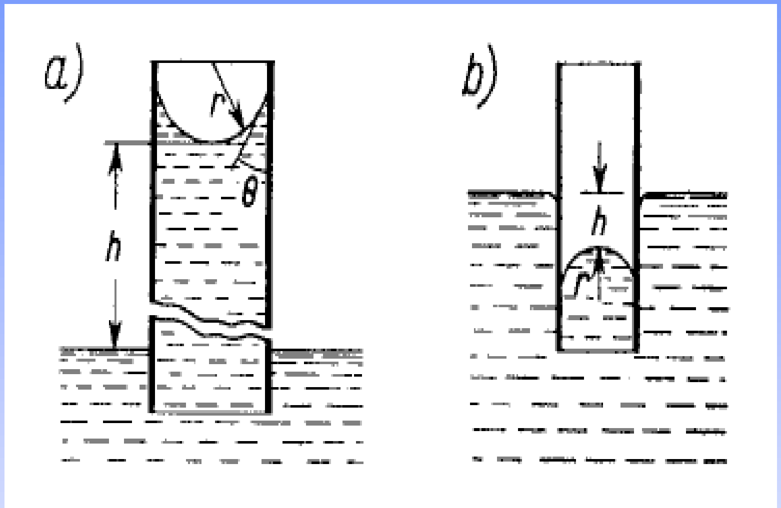
# Capillarity



# Capillarity

Try making a sand castle out of dry sand!

# Capillary Rise




$$f_1 = 2\pi r \gamma \cos\theta$$

$$f_2 = \pi r^2 h \rho g$$

$$2\pi r \gamma \cos\theta = \pi r^2 h \rho g$$

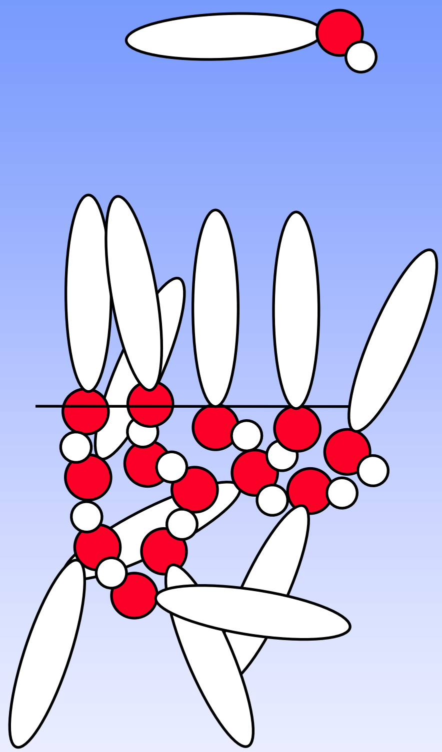
$$\gamma = \frac{r h \rho g}{2\cos\theta}$$

**For Water (θ = 0): h =14.8/r (in mm)**

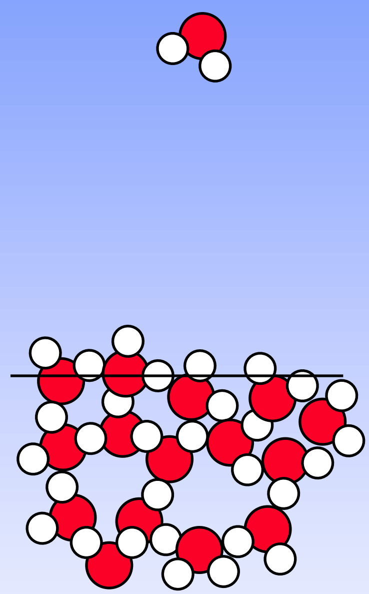
| Diam. | r | h |
|---|---|---|
| 1000 mm | 500 mm | 0.03 mm |
| 40 mm | 20 mm | 0.74 mm |
| 1 mm | 0.5 mm | 29 mm |
| 0.4 mm | 0.2 mm | 74 mm |
| 0.1 mm | 0.05 mm | 296 mm |

http://zzm.umcs.lublin.pl/Wyklad/FGF-Ang/2A.F.G.F.%20Surface%20tension.pdf

# Surface Tension of Ethyl Alcohol and Water

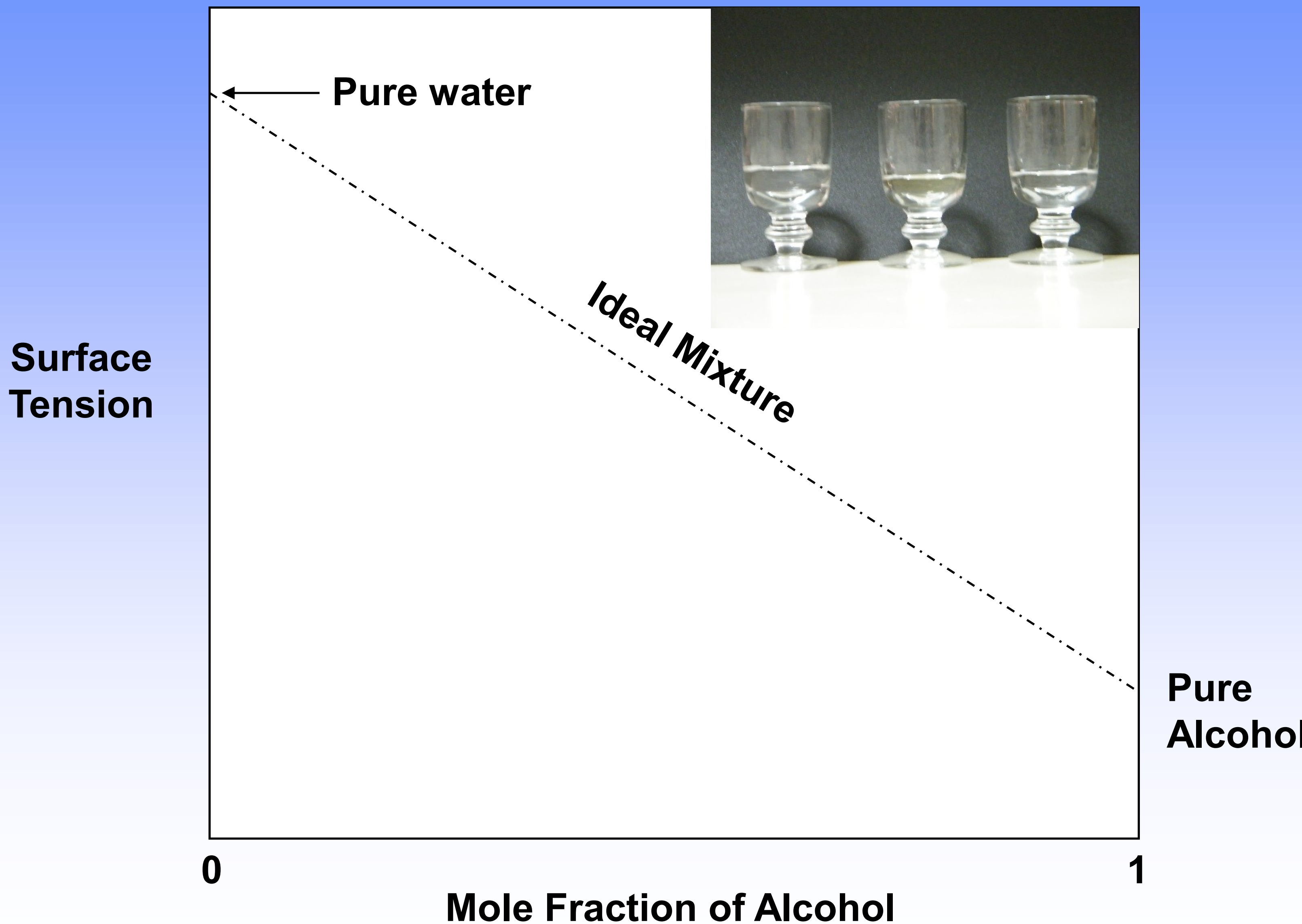


Ethanol
22 dynes/cm

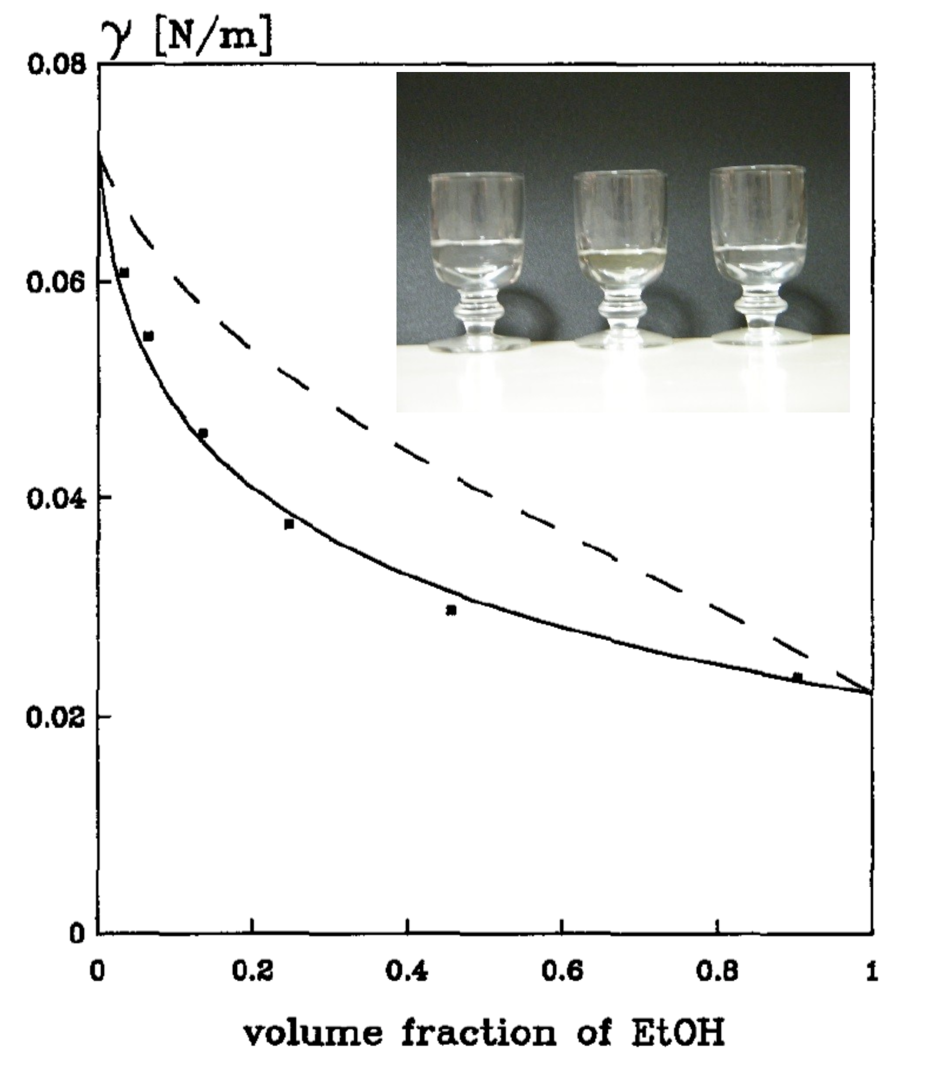


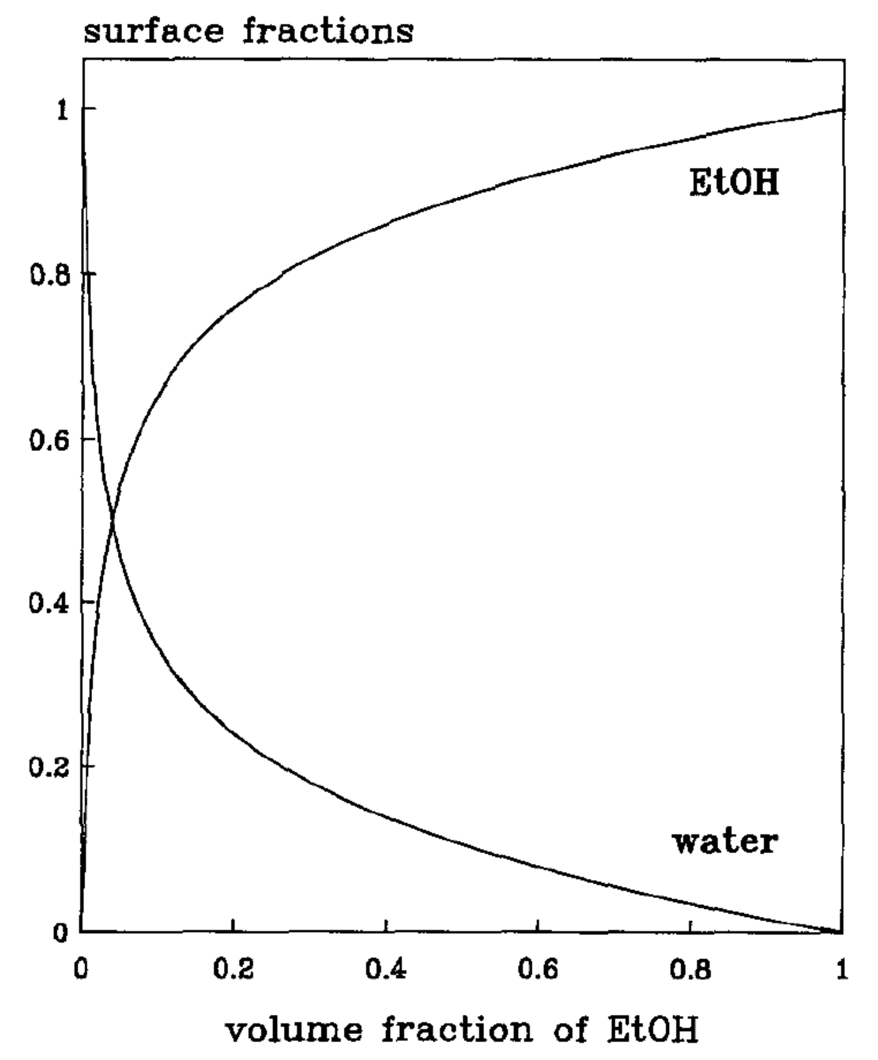
Water
72 dynes/cm

# Surface Tension of Alcohol-Water Mixtures



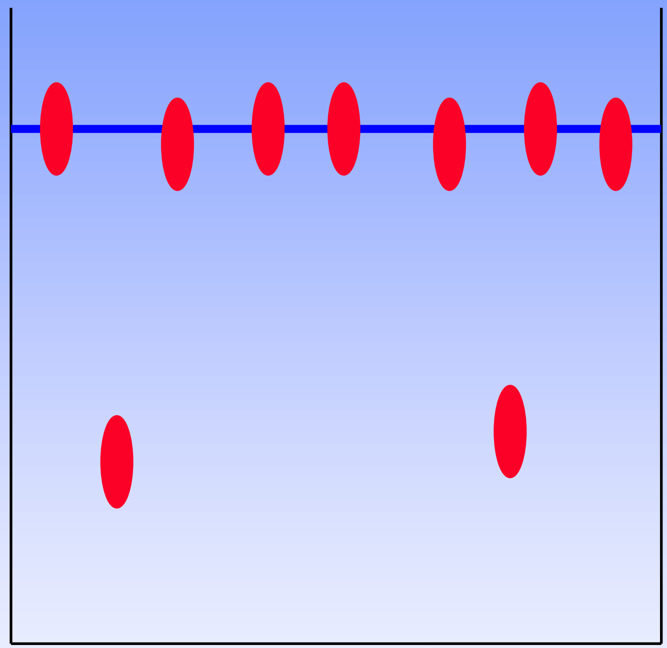
# Surface Tension of Alcohol-Water Mixtures




Lamperski, *JCIS*, **1991**, *144*, 153-158.

# Surface Tension of Alcohol-Water Mixtures

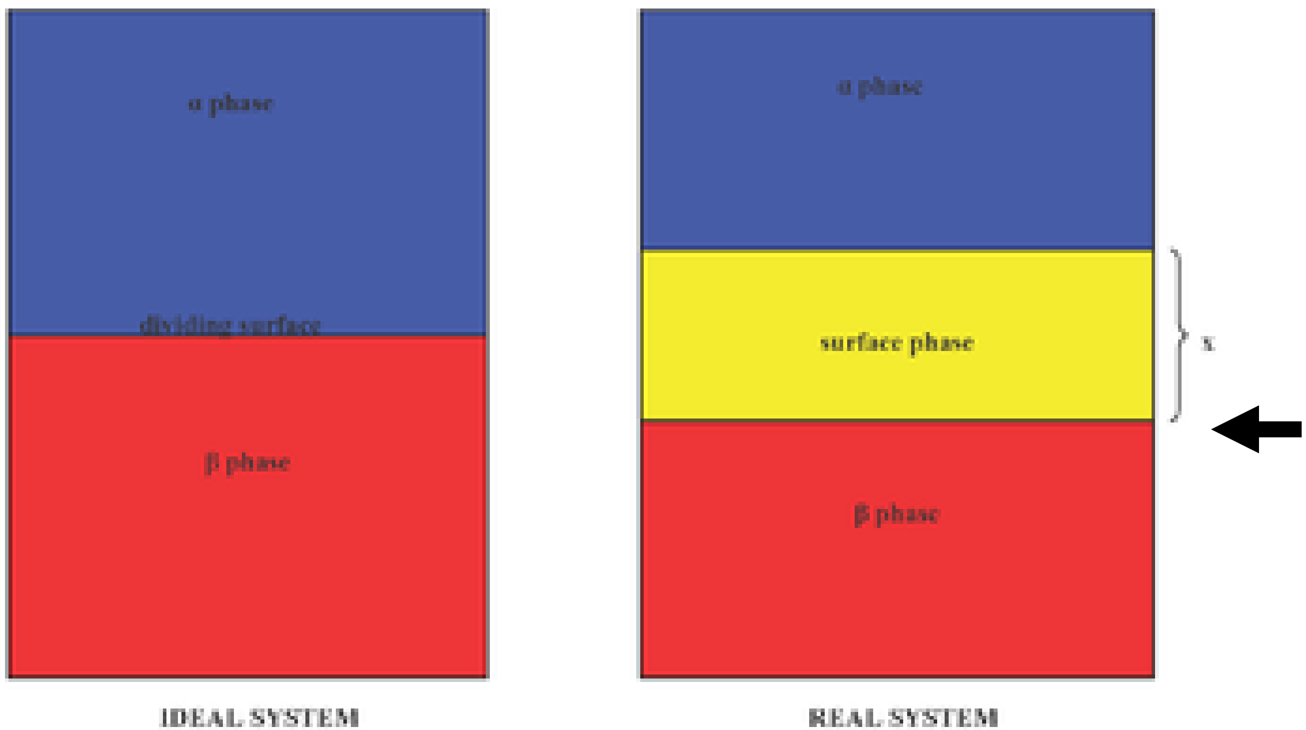


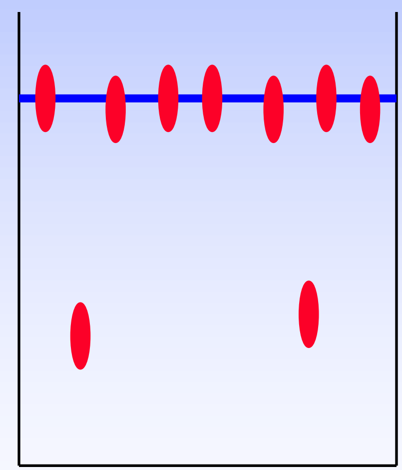
**The molecules of the liquid with the LOWEST surface tension concentrate at the surface (or interface).**

**Because they lower the surface (or interfacial) tension the most, they diminish the work required to create the surface (or interface) the most.**

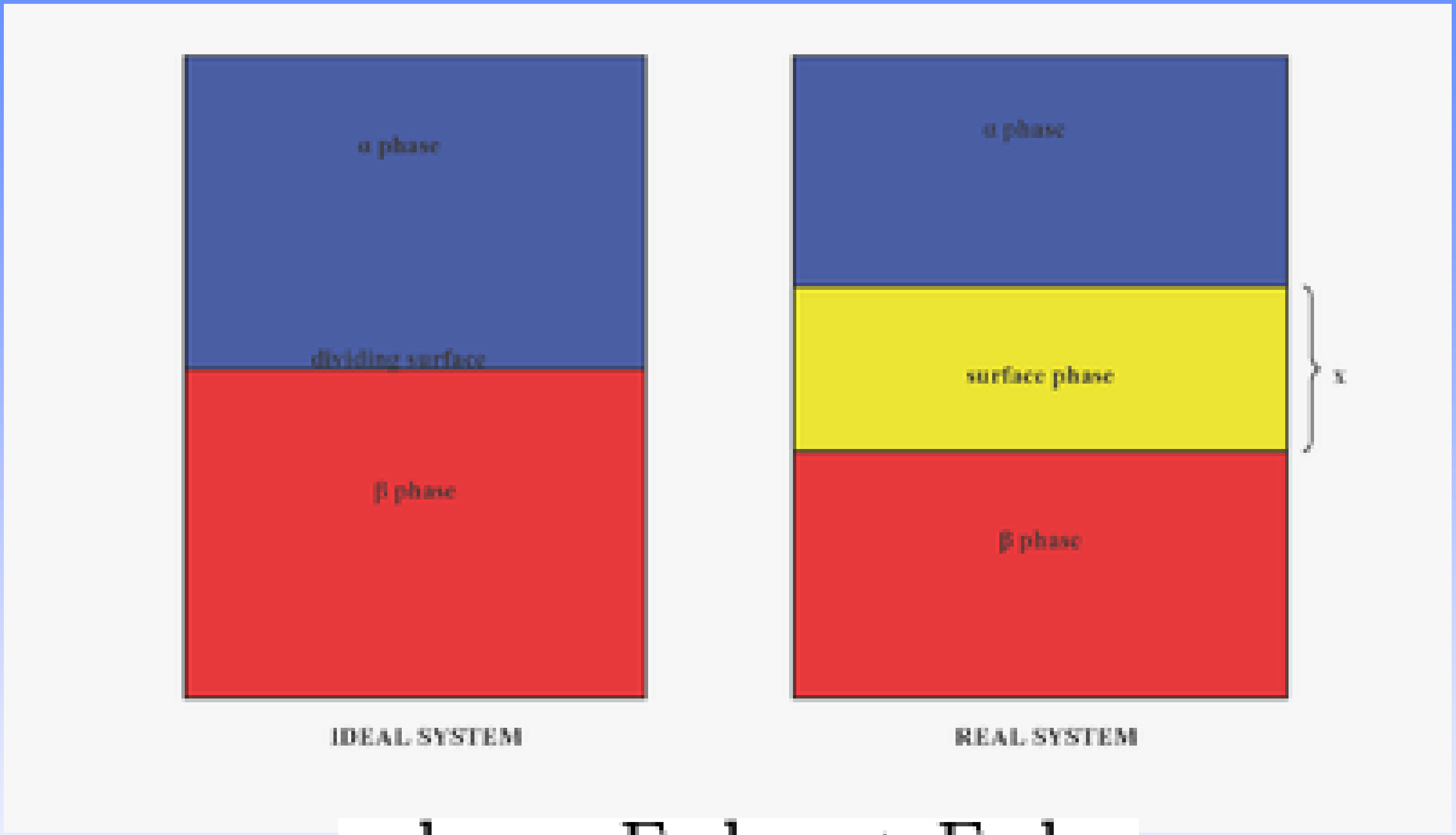
# Surface Tension and the Gibbs Adsorption Isotherm





# Surface Tension and the Gibbs Adsorption Isotherm




$$-\mathrm{d}\gamma = \Gamma_1 \mathrm{d}\mu_1 + \Gamma_2 \mathrm{d}\mu_2$$

**$\Gamma_i$ = Surface Excess** **$\mu_i = \mu_i^o + RT \ln a_i$**

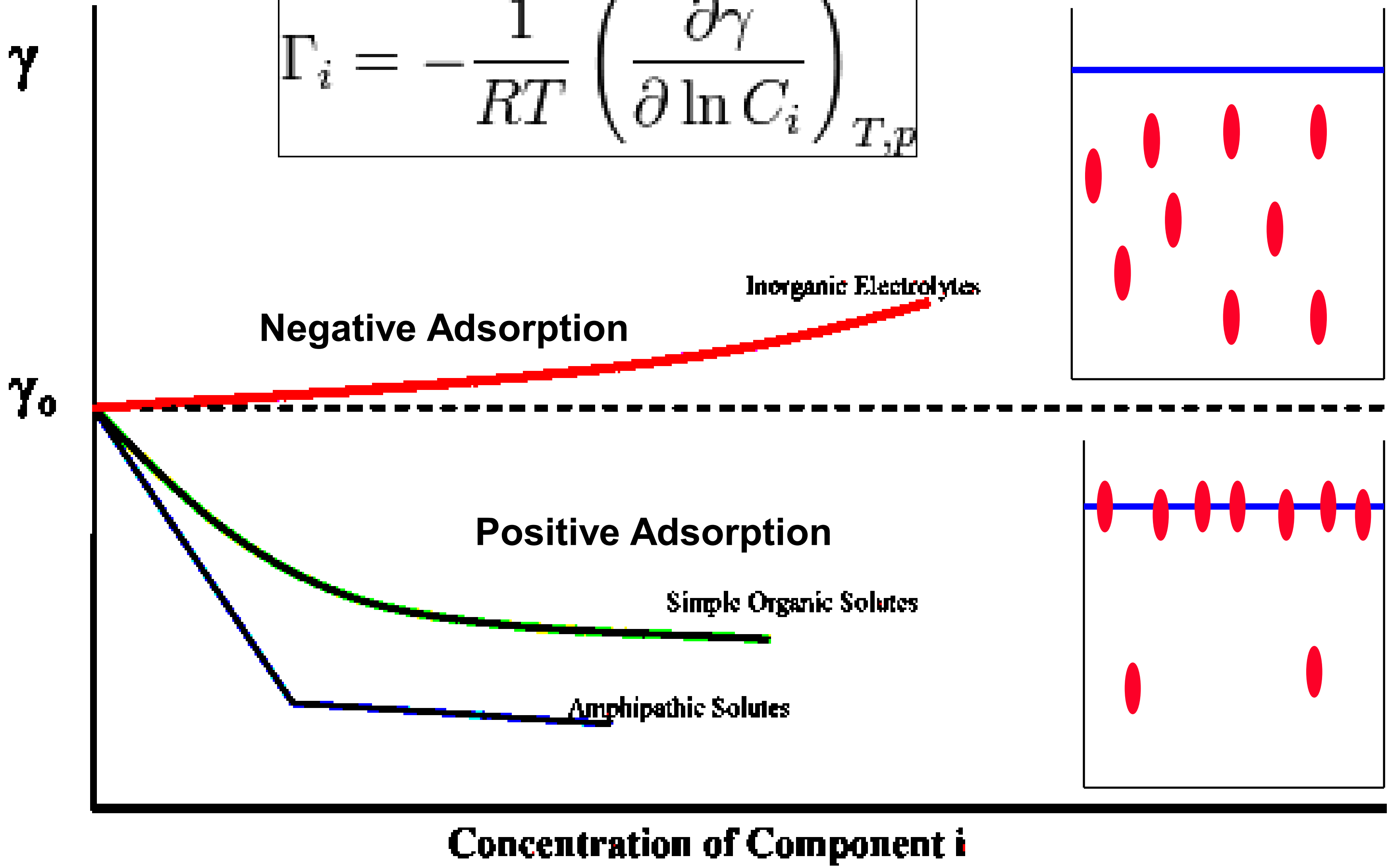
$$\Gamma_i = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln C_i}\right)_{T,p}$$

**Units of mol/m$^2$**

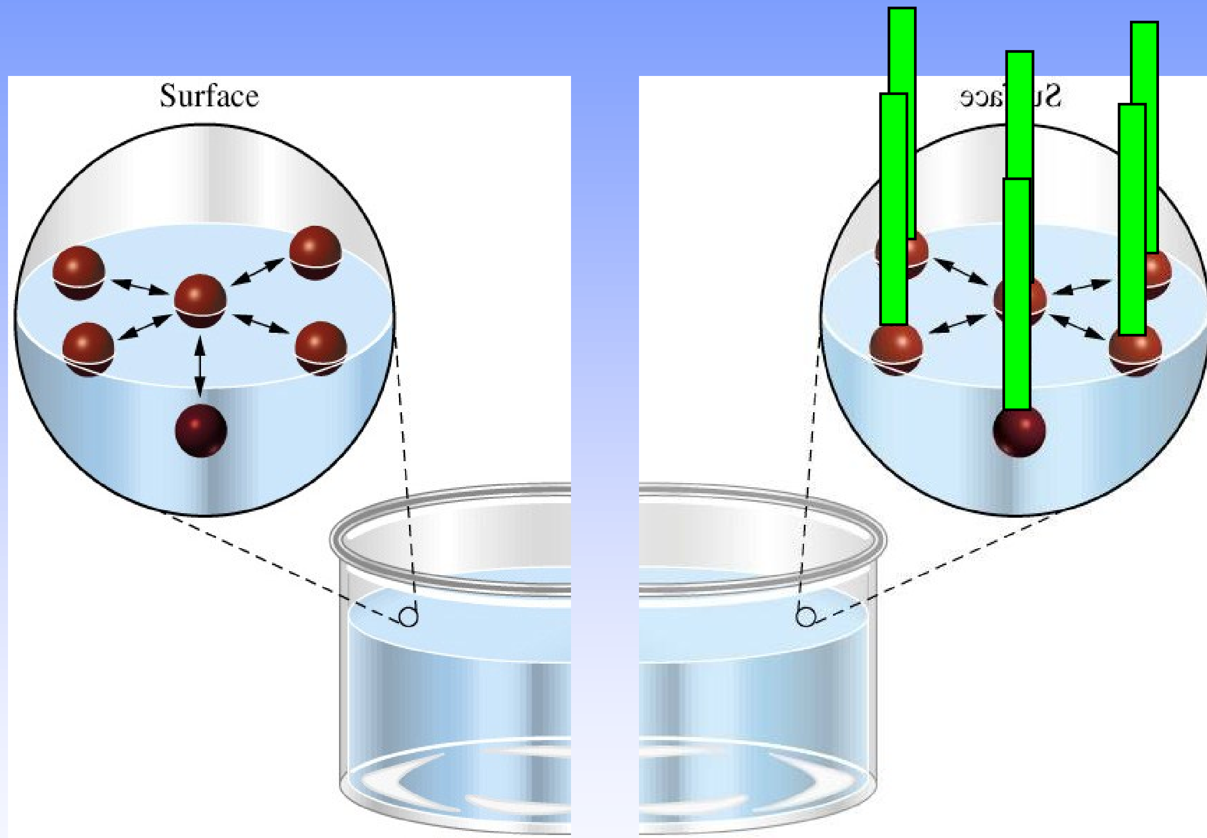
# Surface Tension and the Gibbs Adsorption Isotherm



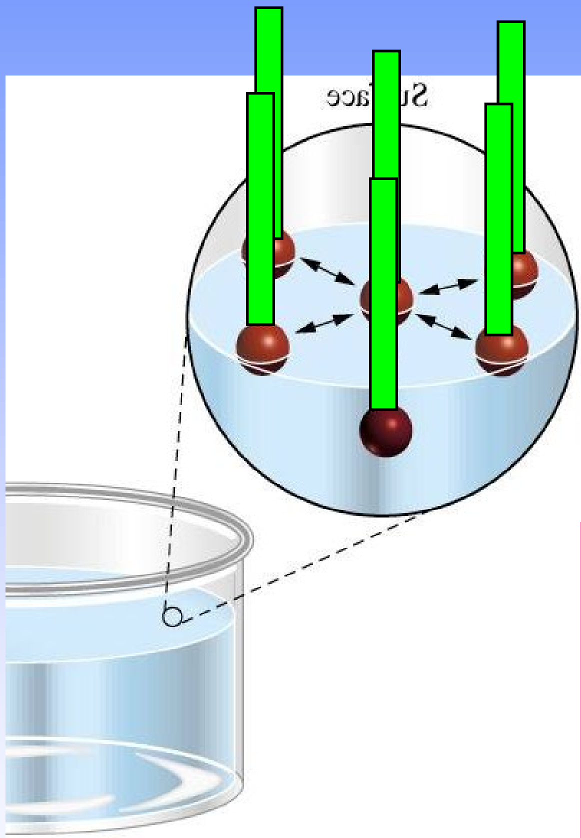
$$\Gamma_i = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln C_i}\right)_{T,P}$$

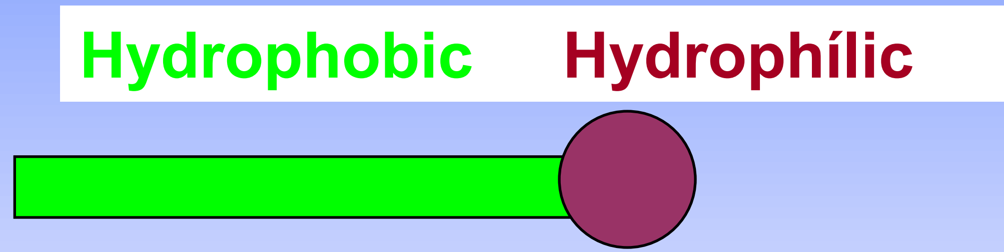


# Surface Tension of Detergents



# Detergents e Tensoatives






$CH_3(CH_2)_{11}$-$OSO_3^-$ $Na^+$ SDS

$C_{12}H_{25}$-Phenyl-$SO_3^-$ $Na^+$ SDBS

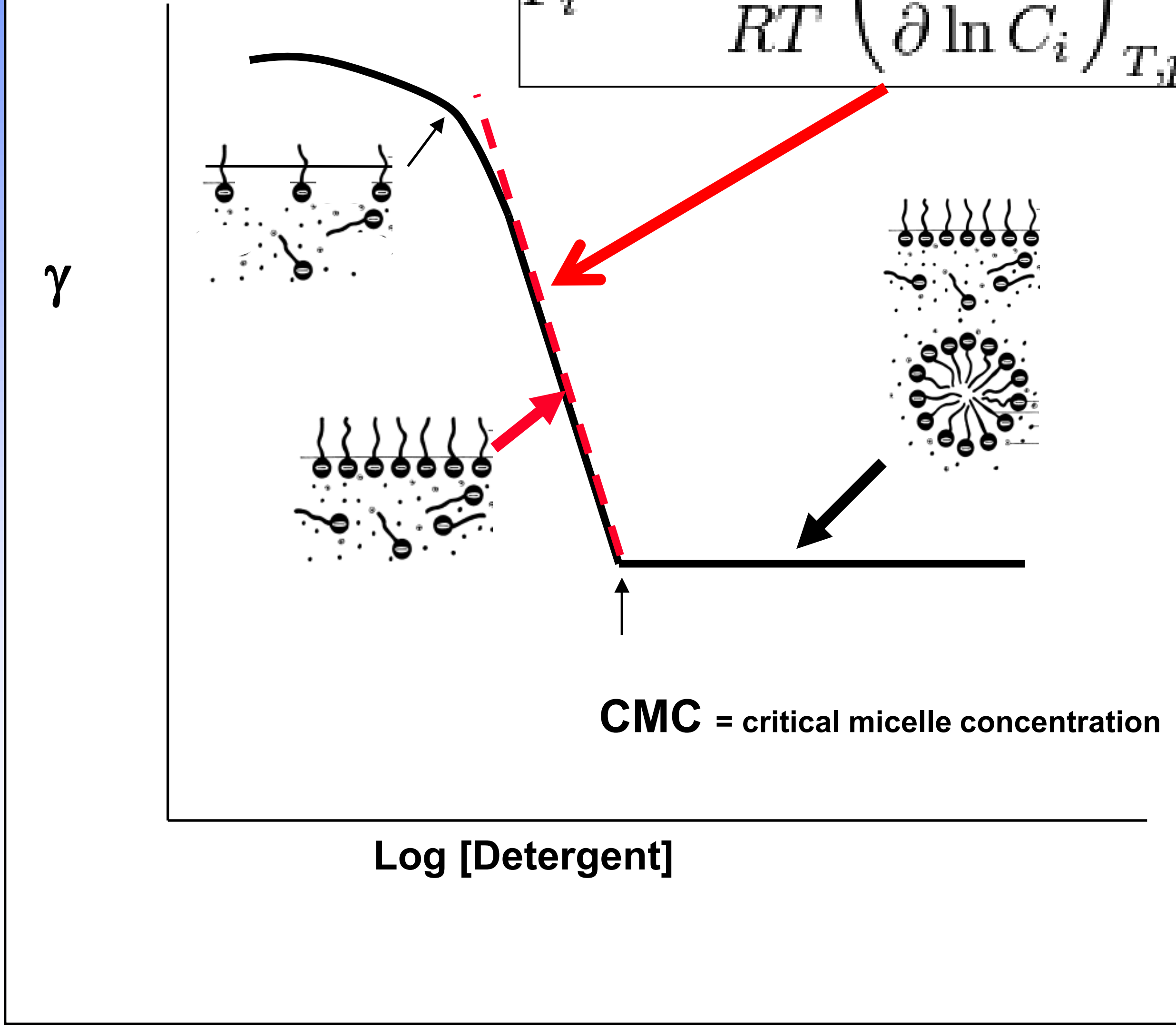
$C_{18}H_{37}$-$NMe_2^+$ $Cl^-$ DODAC

/

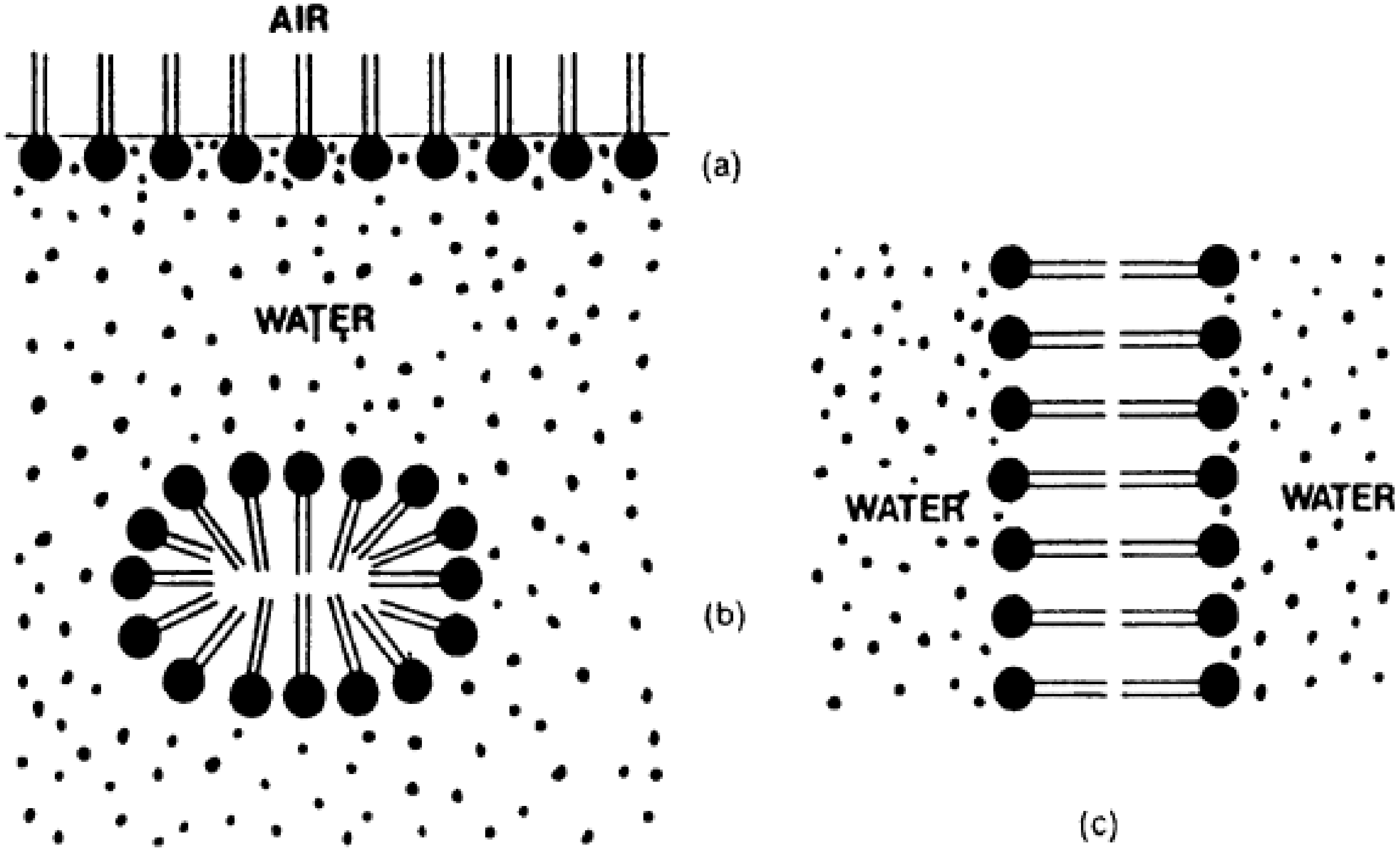
$C_{18}H_{37}$ Cream Rinse/Fabric Softener

# Surface Tension and Micellization

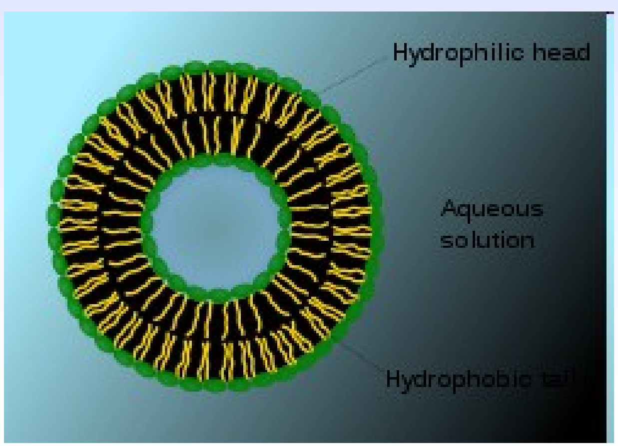
$$\Gamma_i = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln C_i}\right)_{T,p}$$

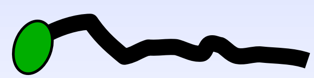


# Monolayers, Micelles and Bilayers

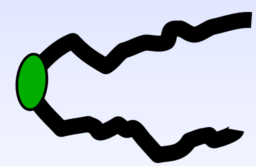


# Vesicles and Bilayers



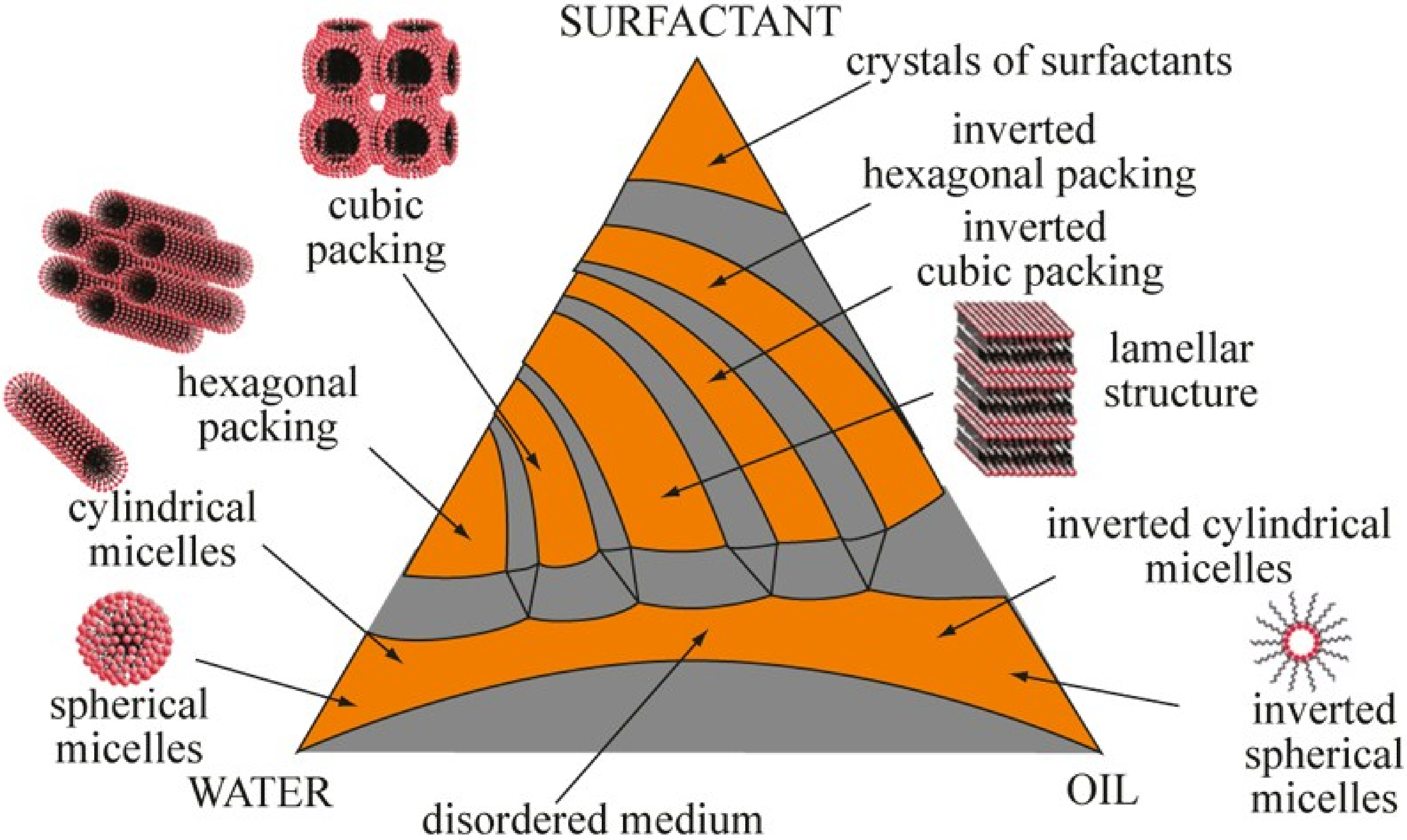
Form Micelles



Form Vesícles or Bilayers

**Packing (Radius of Curvature)**

# The Universe of Emulsions and Microemulsions

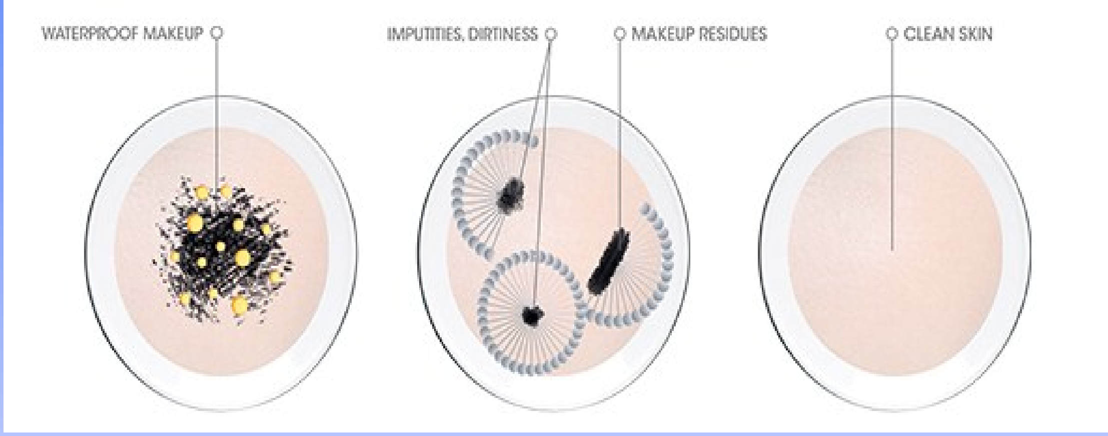



http://eng.thesaurus.rusnano.com/upload/iblock/a32/amfi1.jpg

WalMart, Ottawa, Canada, September, 2016




HOW DOES IT WORK?



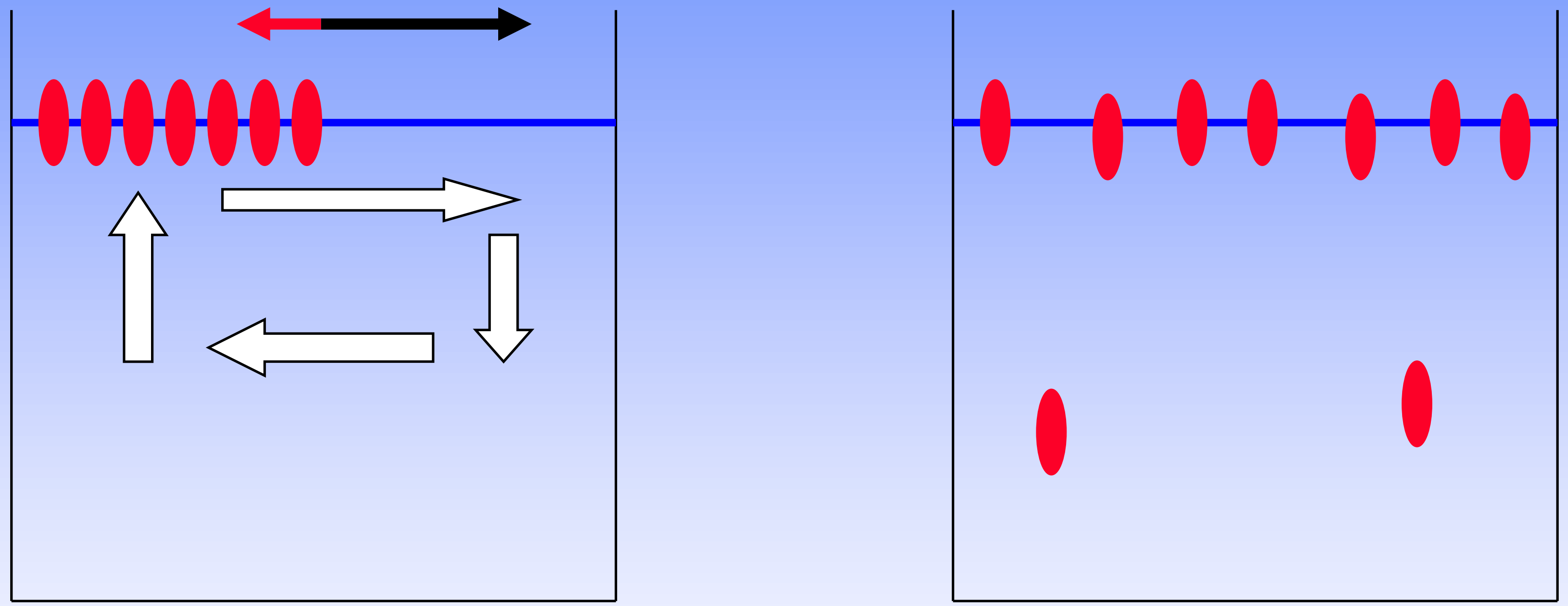

A multi-purpose cleanser that contains Micellar technology. Like a magnet, micelles capture and lift away dirt, oil and makeup without harsh rubbing, leaving skin perfectly clean, hydrated and refreshed without over-drying.

# Micelles


AQUA / WATER, HEXYLENE GLYCOL, GLYCERIN, DISODIUM COCOAMPHODIACETATE DISODIUM EDTA, POLOXAMER 184, POLYAMINOPROPYL BIGUANIDE, FIL B162919/3


AQUA/WATER, CYCLOPENTASILOXANE, ISOHEXADECANE, POTASSIUM PHOSPHATE, SODIUM CHLORIDE, HEXYLENE GLYCOL, DIPOTASSIUM PHOSPHATE, DISODIUM EDTA, DECYL GLUCOSIDE, POLYAMINOPROPYL BIGUANIDE

# The Marangoni Effect



Sometimes called the Gibbs-Marangoni effect

Mass transfer along an interface due to a surface tension gradient. A surface tension gradient causes the liquid to flow away from regions of low surface tension.

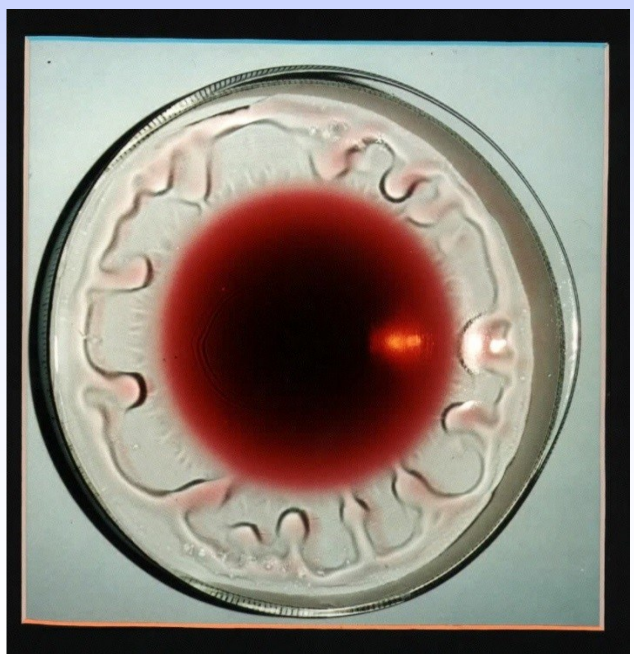
# The Marangoni Effect

**The Soap Boat propelled by Isopropanol**

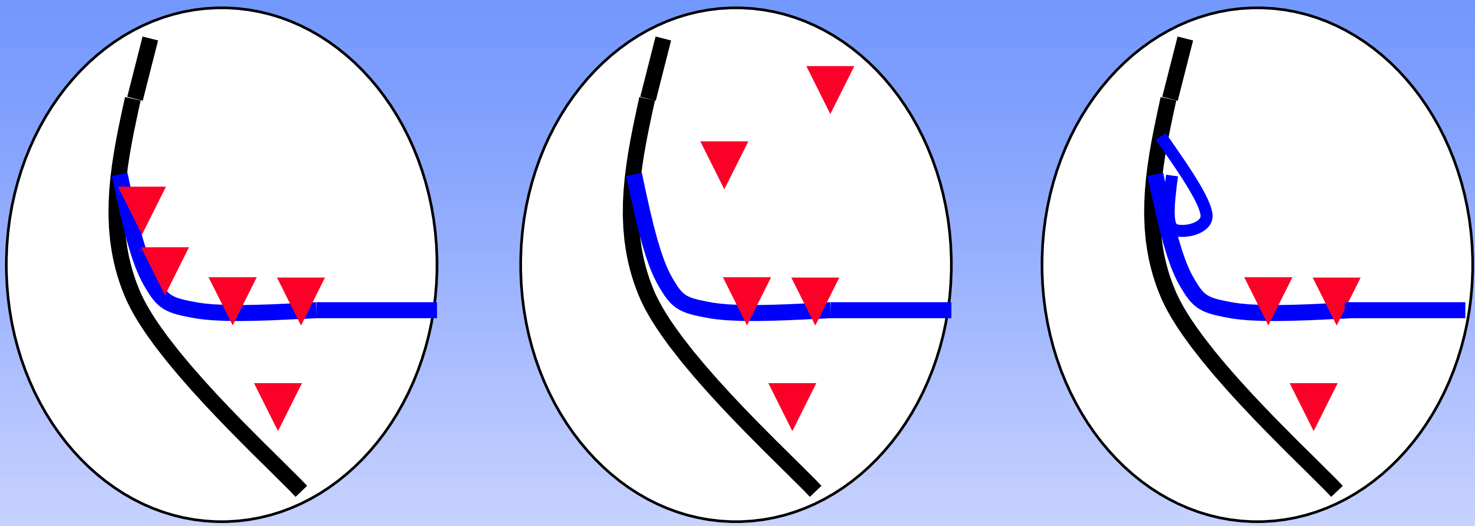
**Video from: http://www.jce.divched.org/blog/soap-boat-20**

C. Renney, A. Brewer, T. J. Mooibroek **Easy Demonstration of the Marangoni Effect by Prolonged and Directional Motion: "Soap Boat 2.0"** *J.. Chem. Educ.*, 2013, 90 (10), pp 1353–1357. **DOI: 10.1021/ed400316a**

# Tears of Wine



# Tears of Wine



*Not formed by:*

Pure water,

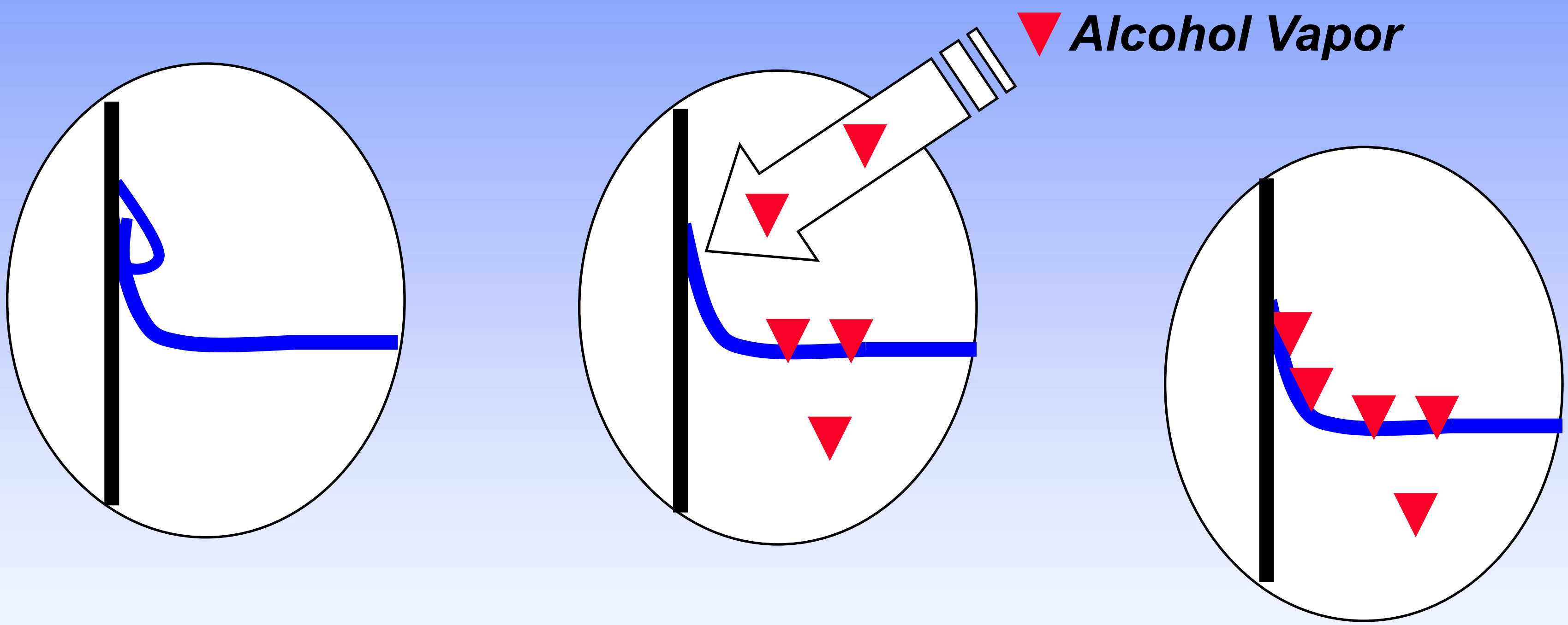
Pure alcohol

or

In a closed glass

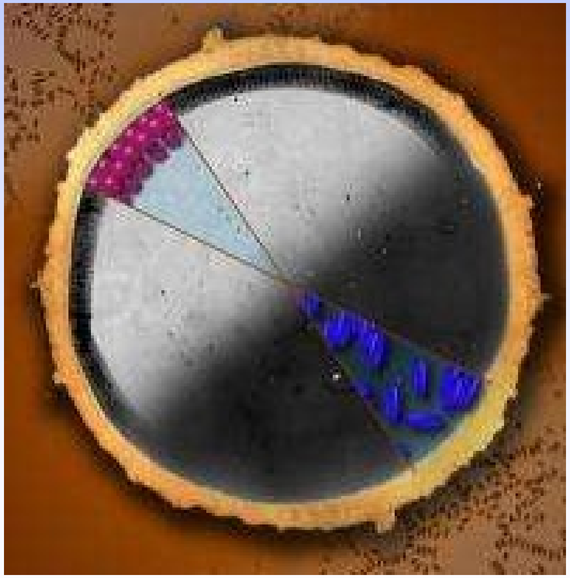
# https://youtu.be/m97odI-NEwk

# Avoiding Water-Spotting on Silicon Wafer after Cleaning




http://www.globalmanufacture.net/home/communities/engineering/dry.cfm

# The Coffee-Ring Effect vs. Dried Drops of Whiskey



**Coffee evaporates more quickly at the edges, which leads to a change in surface tension, which causes more coffee (and the bean residue) to be pulled to the edges, where it dries.**

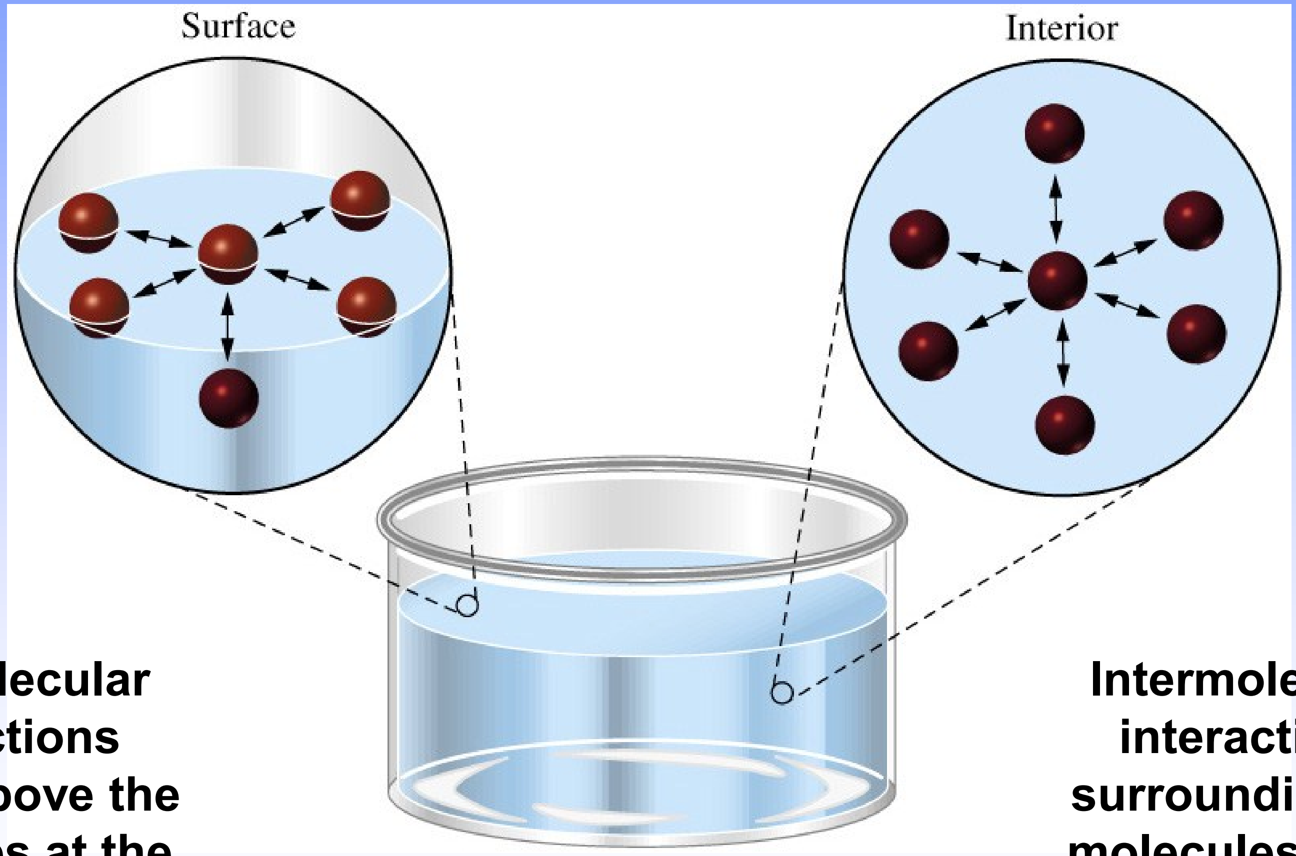
**Whiskies that did not leave behind a coffee ring type pattern when they evaporate have two important features:**

**(1) Tensoactive biomolecules - as the liquid evaporates they collect on the edges of the drying surface which in turn creates a surface tension gradient that pulled the liquid back inward;**

**(2) plant-derived biopolymers that channel particles in the liquid to the base material (the drinking glass) where they stick.**

**Hyoungsoo Kim et al. Controlled Uniform Coating from the Interplay of Marangoni Flows and Surface-Adsorbed Macromolecules, *Physical Review Letters* (2016). DOI: 10.1103/PhysRevLett.116.124501 ,**

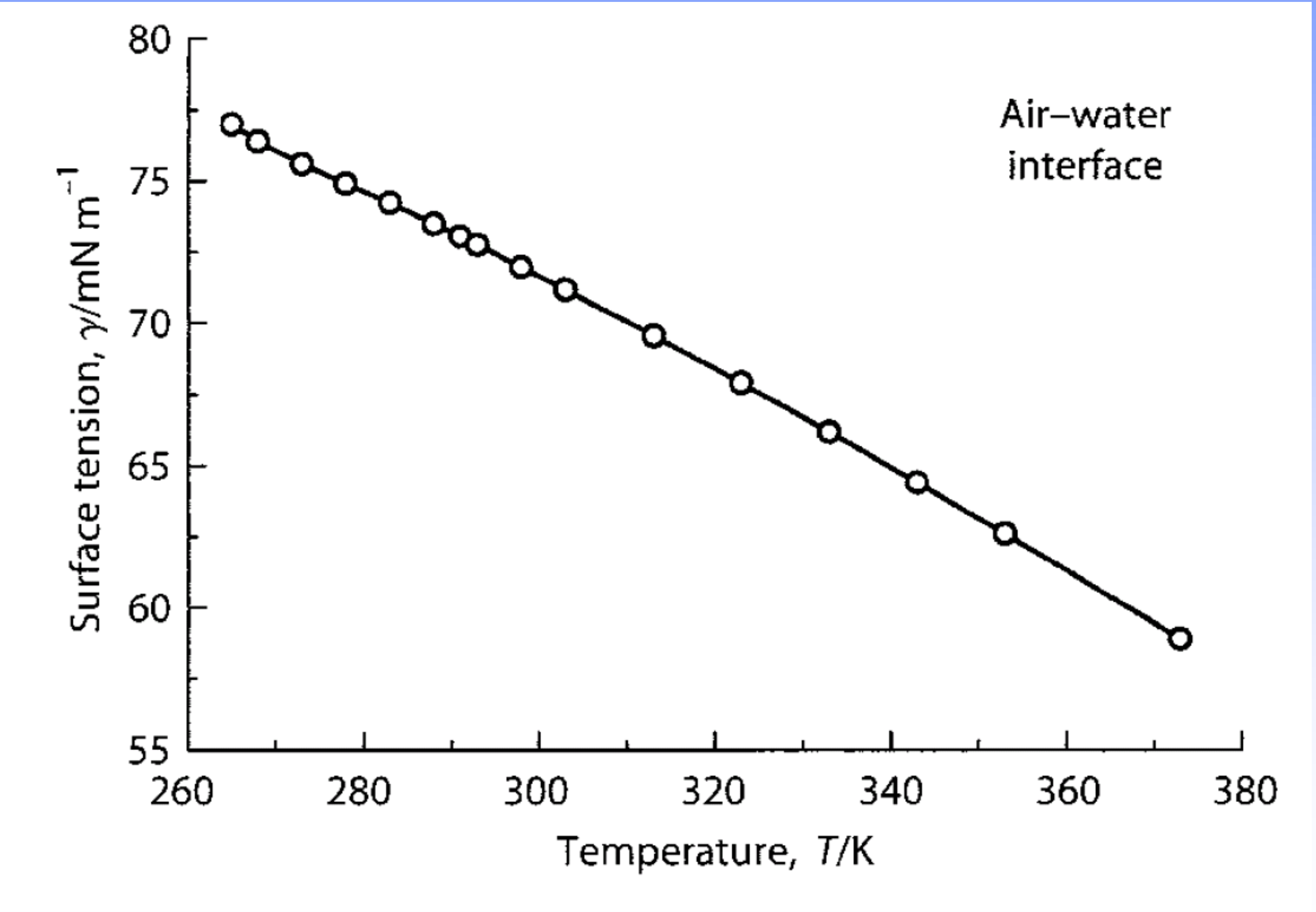
# Effect of Temperature on the Surface Tension?



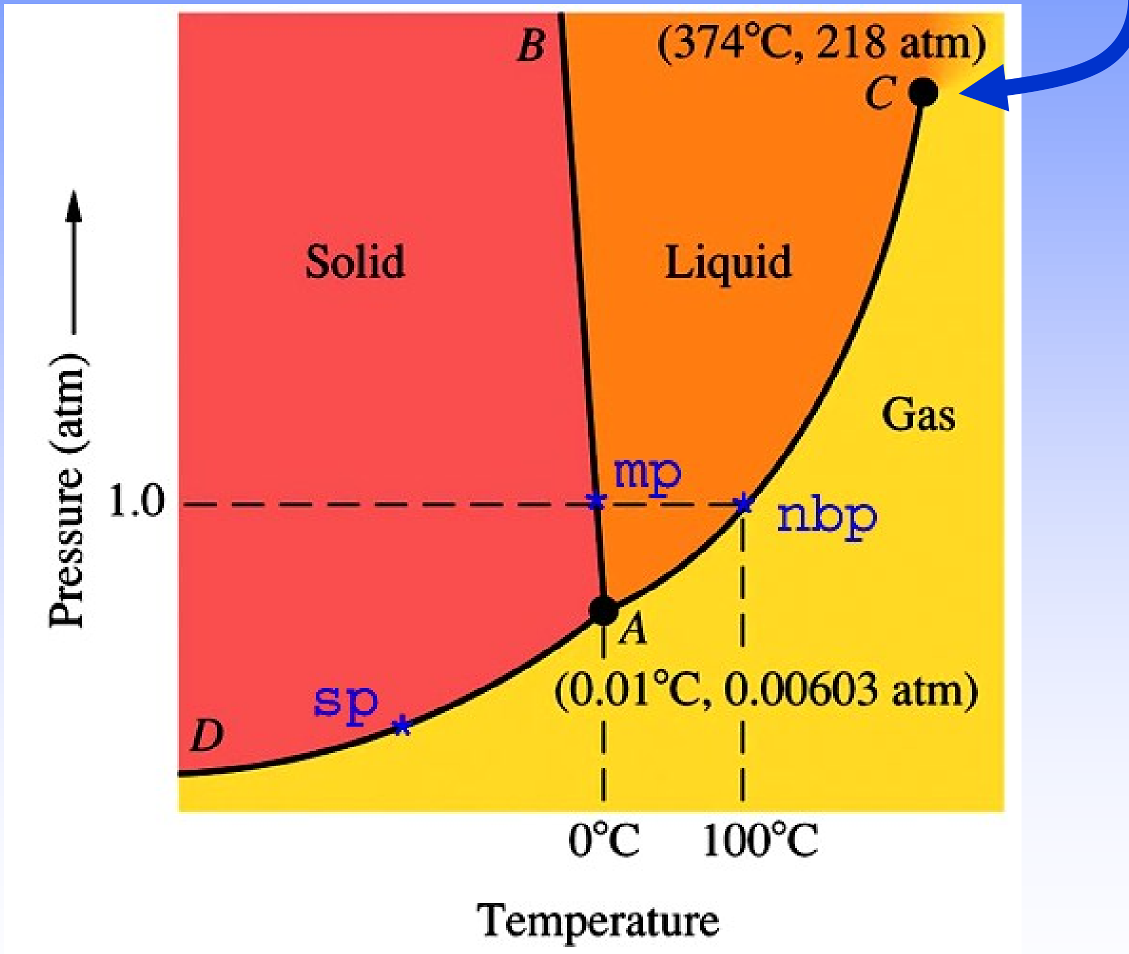

**Intermolecular Interactions absent above the molecules at the surface**

**Intermolecular interactions surrounding the molecules in the interior of the liquid.**

# Effect of Temperature on the Surface Tension:



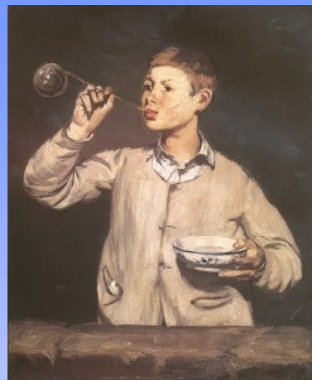
# Effect of Temperature on the Surface Tension - The surface tension goes to Zero at the Critical Point




**Supercritical Fluids**

# Soap Bubbles

I'm Forever Blowing Bubbles
by William Stephen Coleman



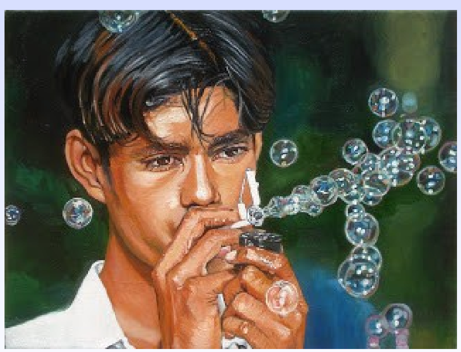
Boy Blowing Bubble
by Edouard Manet

Two Boys Blowing Bubble
by Adriaen Hanneman

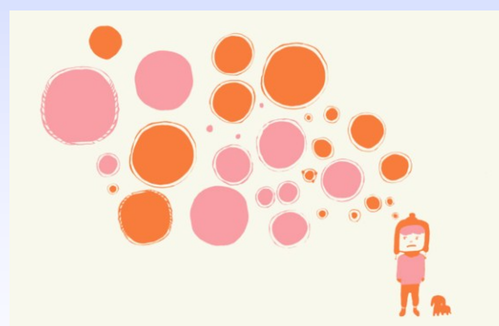
Still Life with a Boy Blowing Soap Bubbles
by Karel Dujardin

Soap Bubbles
by Jean Baptiste Siméon Chardin

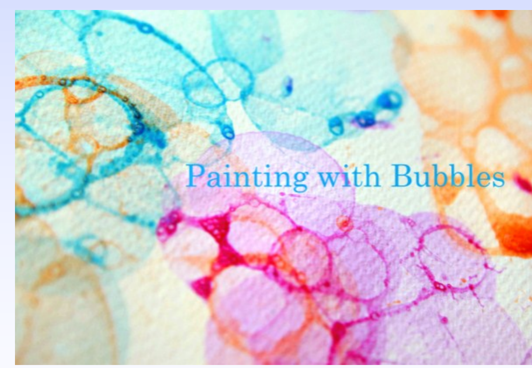
Bubbles
by John Everett Millais



Bubble Boy
by Sreenivasa Ram Makineedi

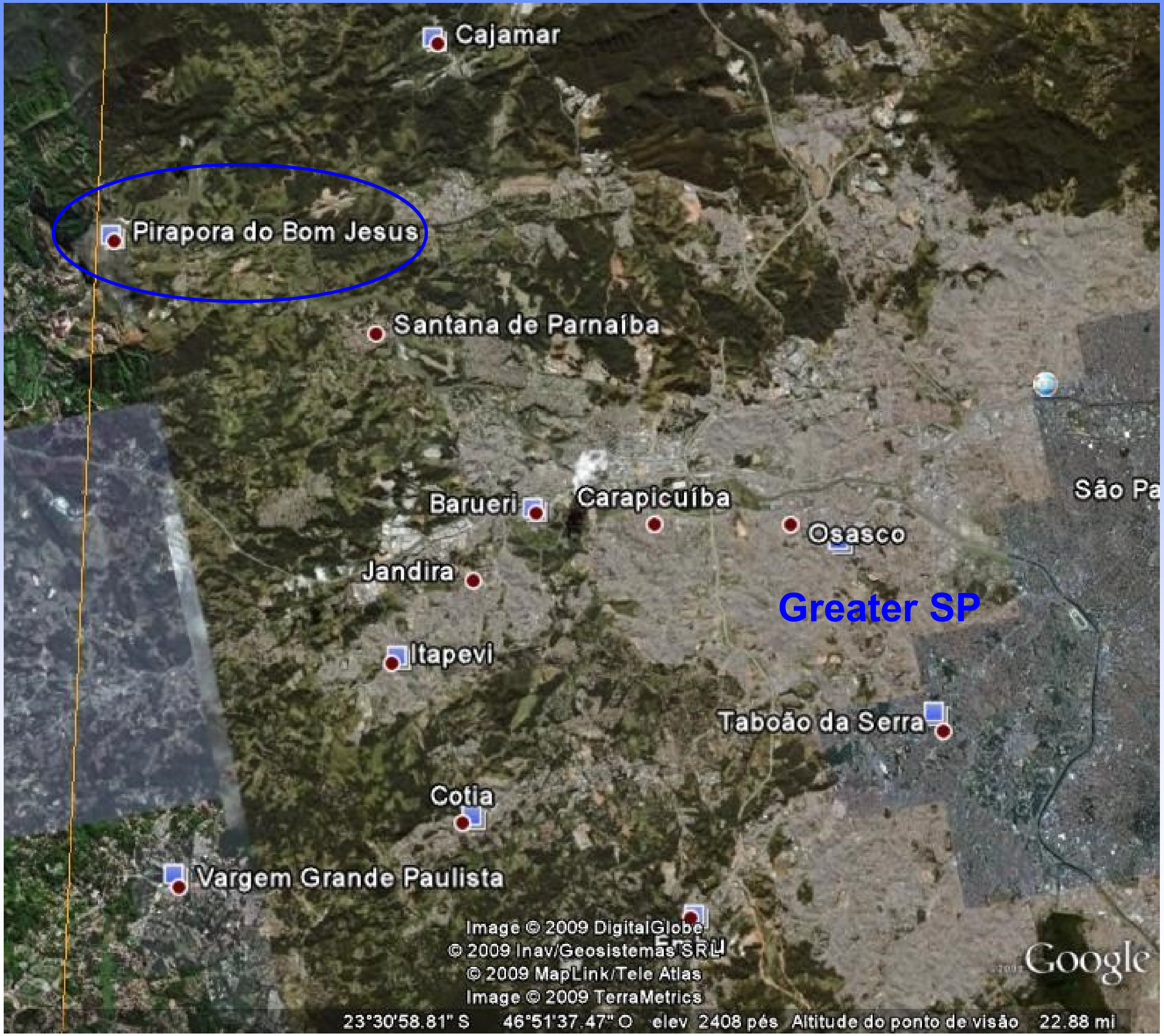


Bubble Boy
by Terri Fry Kasuba




http://www.ramblingsfromutopia.com/2012/06/diy-painting-with-bubbles.html

# Bubbles and Foams



# Pirapora do Bom Jesus

# Rio Tieté, Pirapora do Bom Jesus, August, 2003

# Bolhas e Espumas

# Bolhas e Espumas

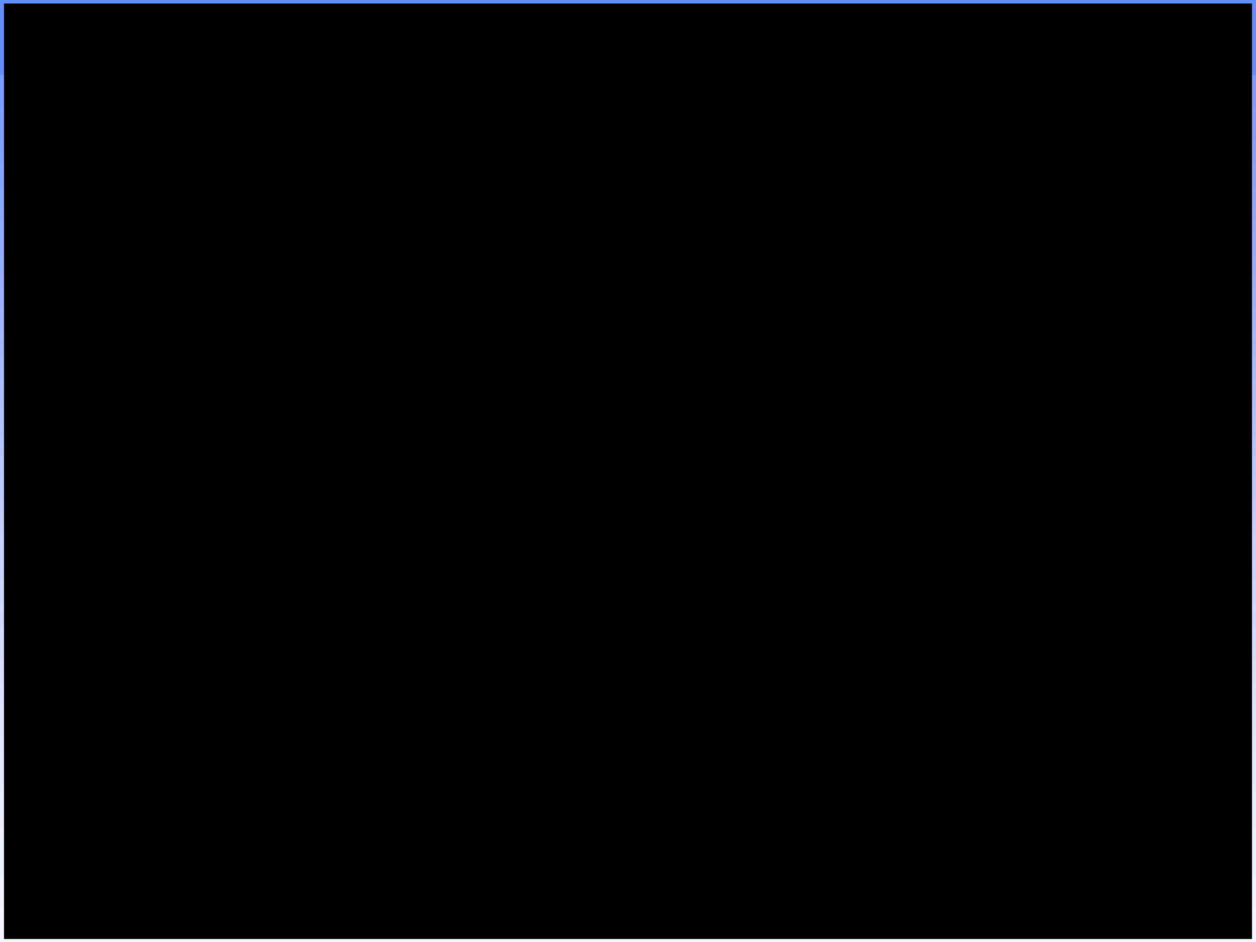
# https://youtu.be/3BKgB0YSpd4

# Esthetics of Foam in Beer

## Beer Foam:

- **Head (proteins)**
  - **Height**
  - **Whiteness**
  - **Persistence**
  - **Texture**
- **Lacing (Hops)**

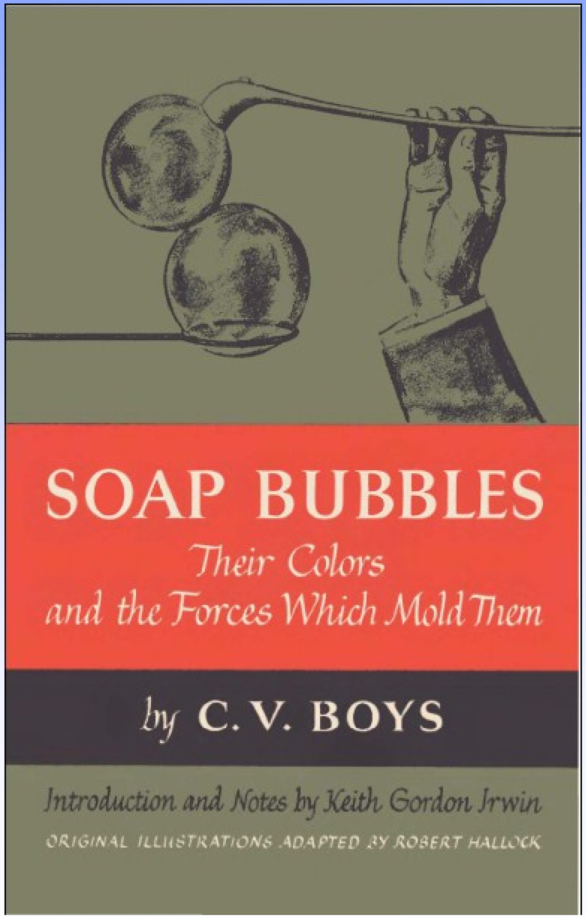
# Bubbles are unstable

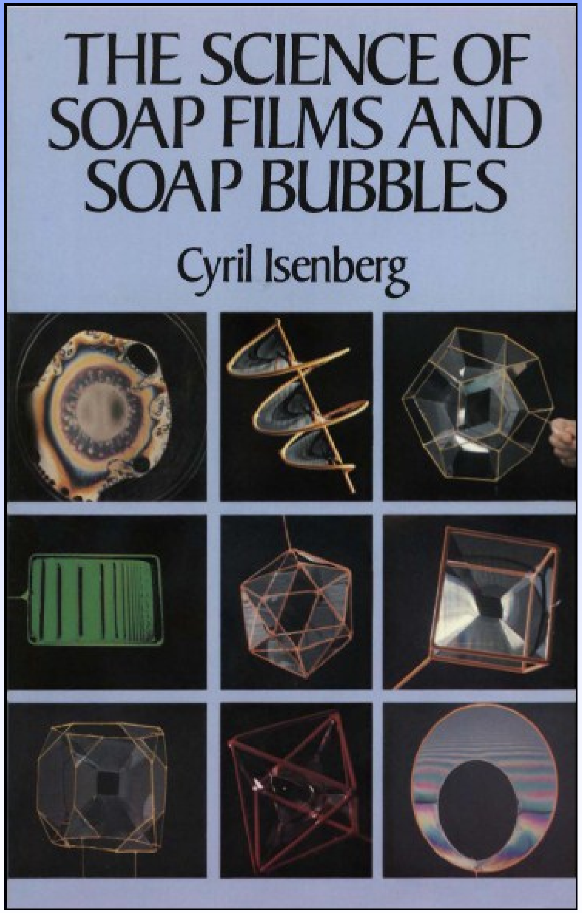


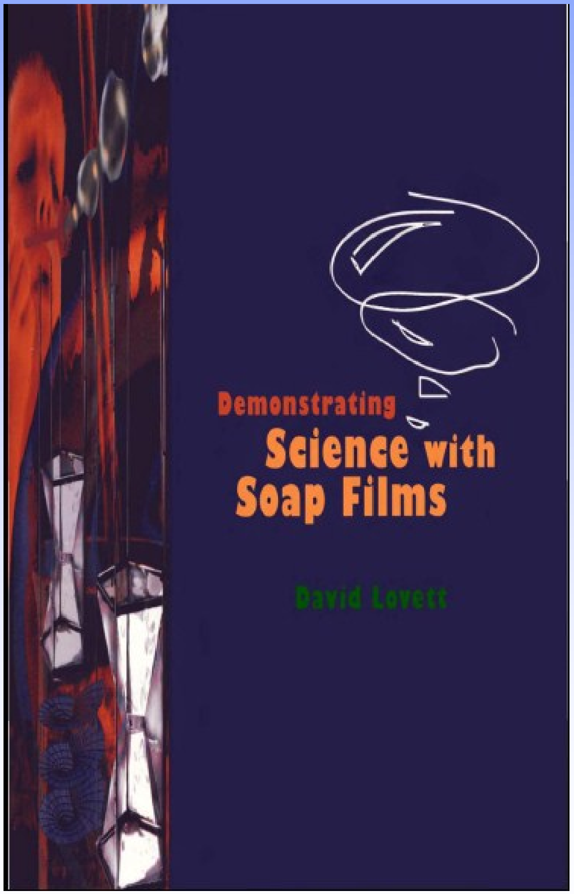
**Slow-Motion Video by**
**Dr. Edvaldo Sabadini**
**IQ-UNICAMP**

**https://youtu.be/Yx14dpeMArc**

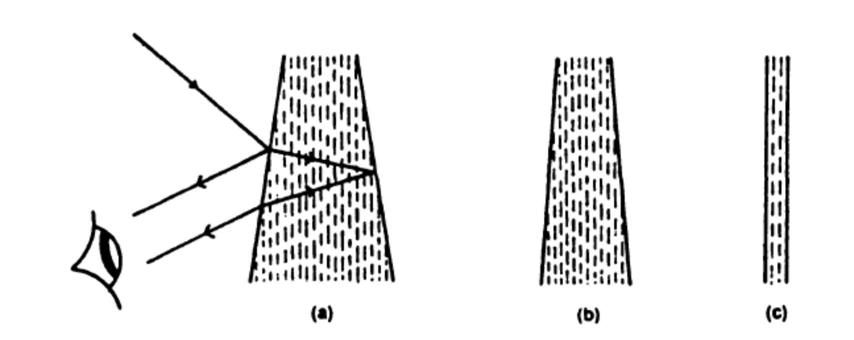
# Soap Bubble Science

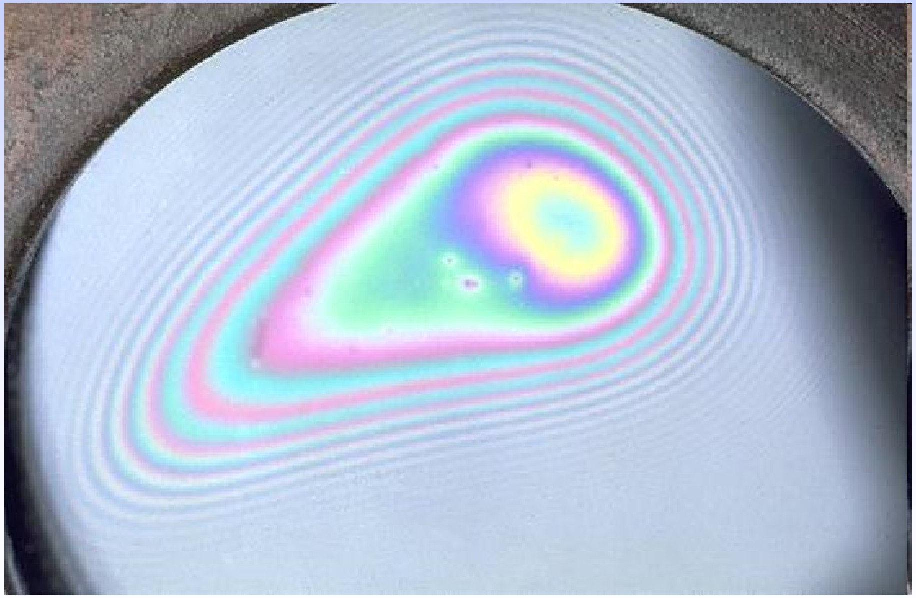


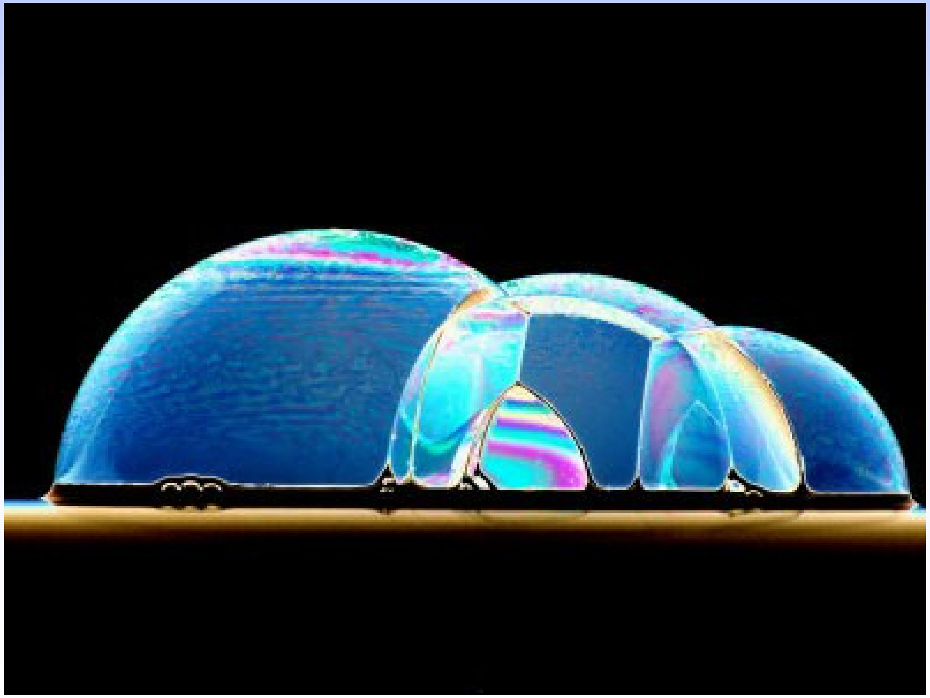



# Newton's Rings





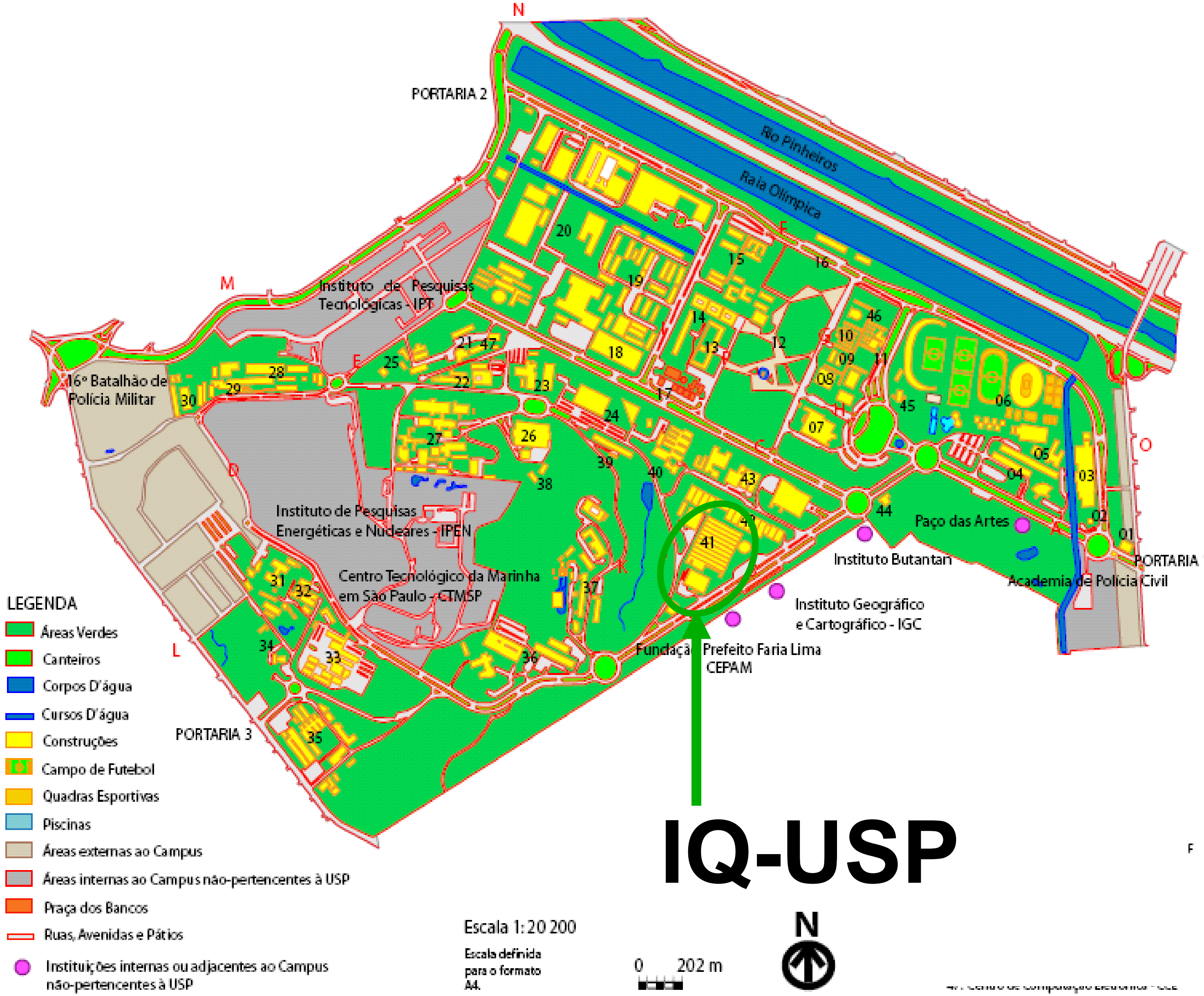
# Oil on Troubled Waters

The first to describe this phenomenon was Aristotle in his *Problemata Physica*:
*Now oil poured on the surface of water makes it more transparent, and the sea, having fat in it, is naturally more transparent.*

Plutarch, *Moralia: Quaestiones Naturales*
Pliny the Elder (77 A.D.), first experiment

Benjamin Franklin, *A Letter from Benjamin Franklin to William Brownrigg, 1773;*
*Repeated Pliny´s experiment at Clapham pond:*
*"The oil, though not more than a teaspoonful, produced an instant calm over a space several yards square which spread amazingly and extended itself gradually till it reached the lee side, making all that quarter of the pond, perhaps half an acre, as smooth as a looking glass."*

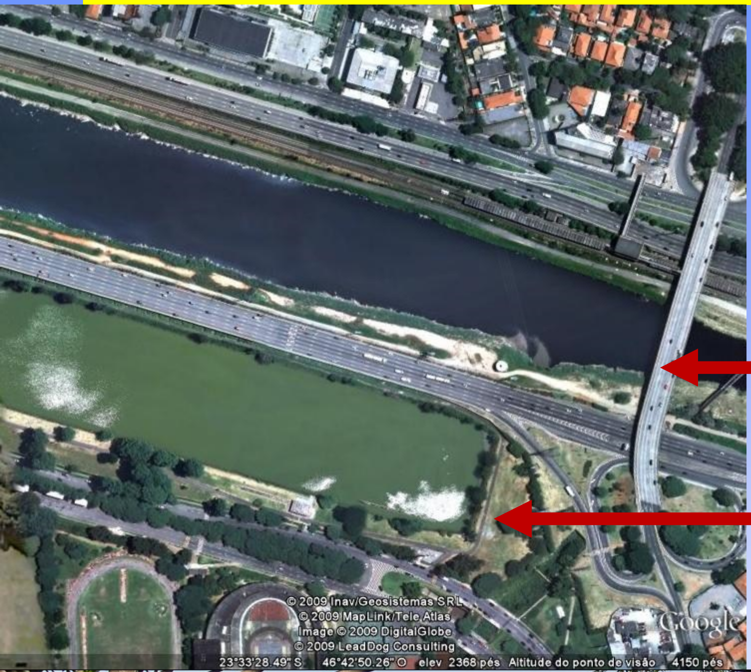
# USP Main Campus in the City of São Paulo



# Oil on Troubled Waters

# Oil on Troubled Waters

**Olympic Rowing Pond vs. Pinheiros River**
**24/01/2014**
**[photos Jair Menegon]**



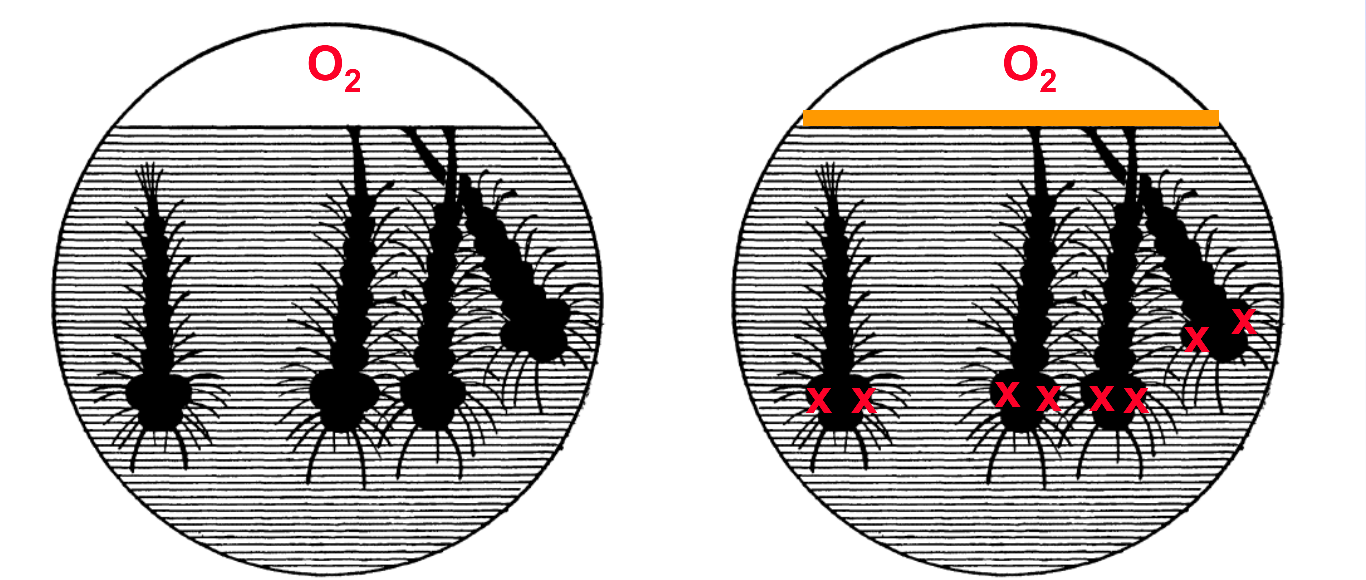

# Fish Pond at Fazenda Anhumas, Botucatu, SP

Before

After

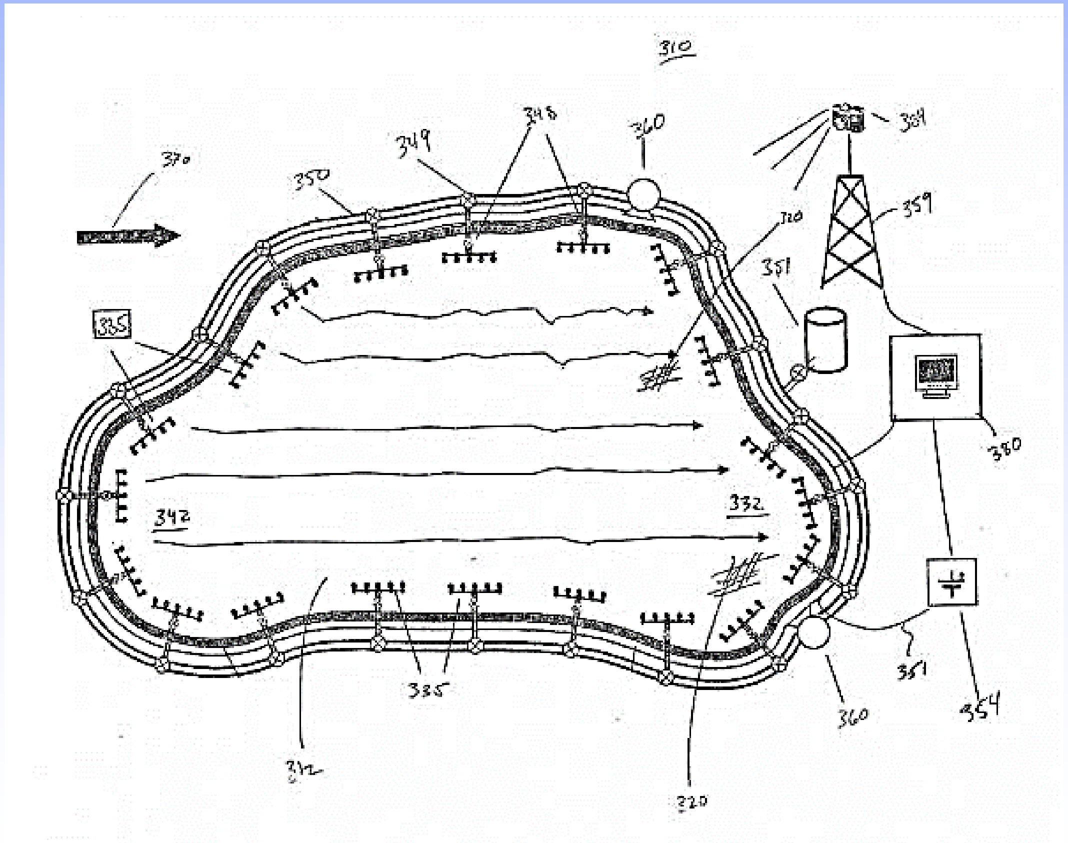
During Spreading

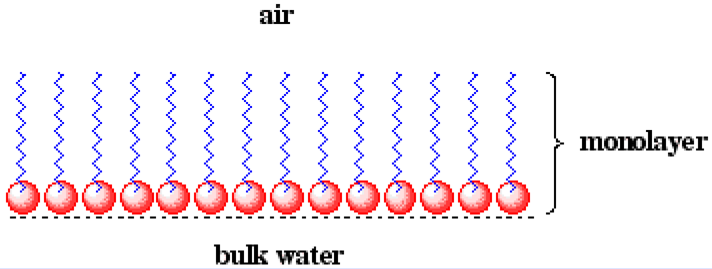
# Mosquito larvae breathing at the water surface



# Controlling Water Evaporation With Monolayers

A basic sketch of Alamaro's monolayer system developed by MIT. Skimmers and equipment to reapply monolayer along the reservoirs edge are controlled by a central hub, which also uses radar to monitor the coverage of the reservoir.

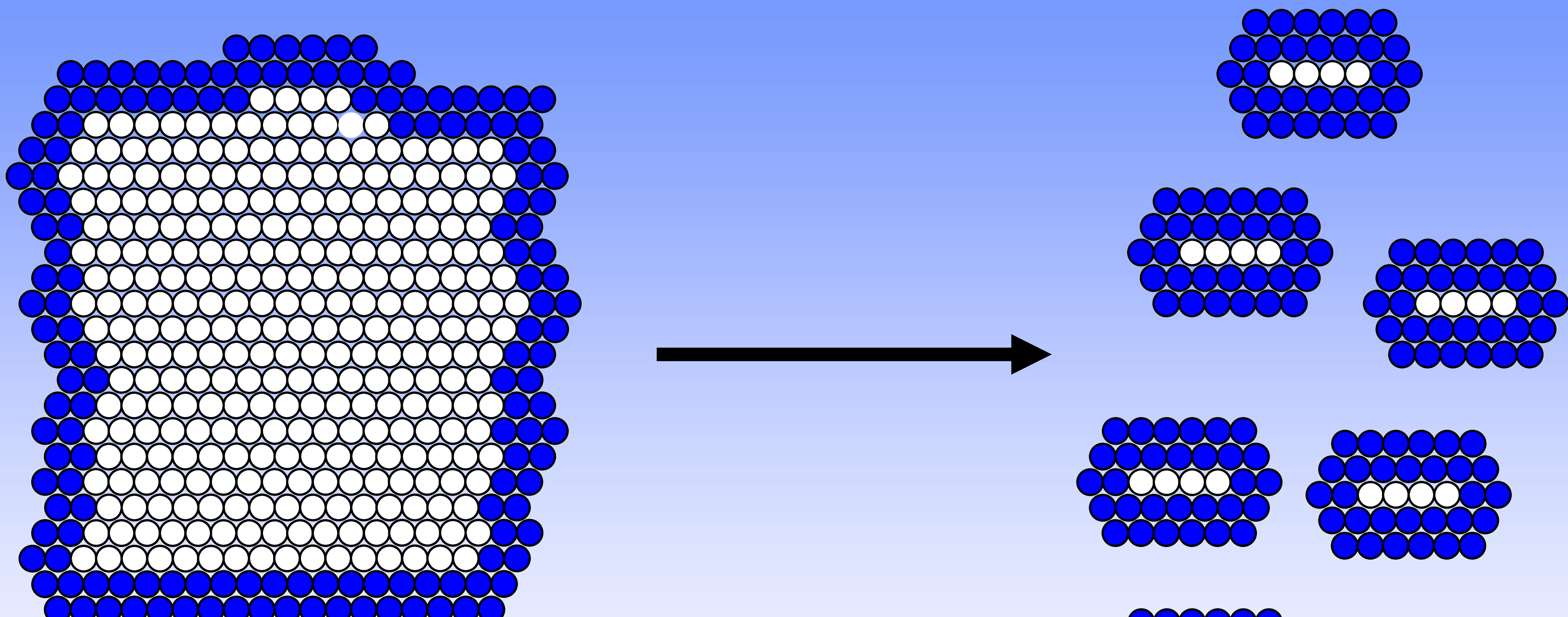


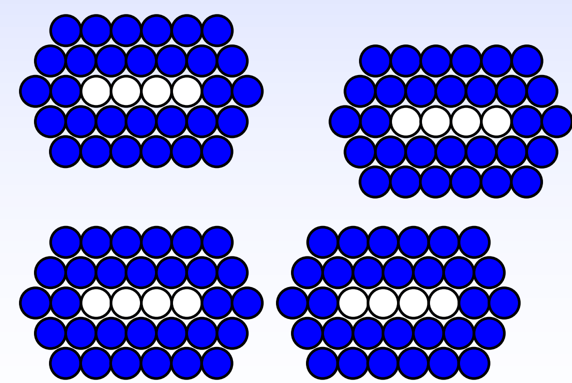



http://keranews.org/post/how-tiny-bit-vegetable-oil-could-save-texas-billions-gallons-water

Posted October 14, 2013

# Nanotechnology





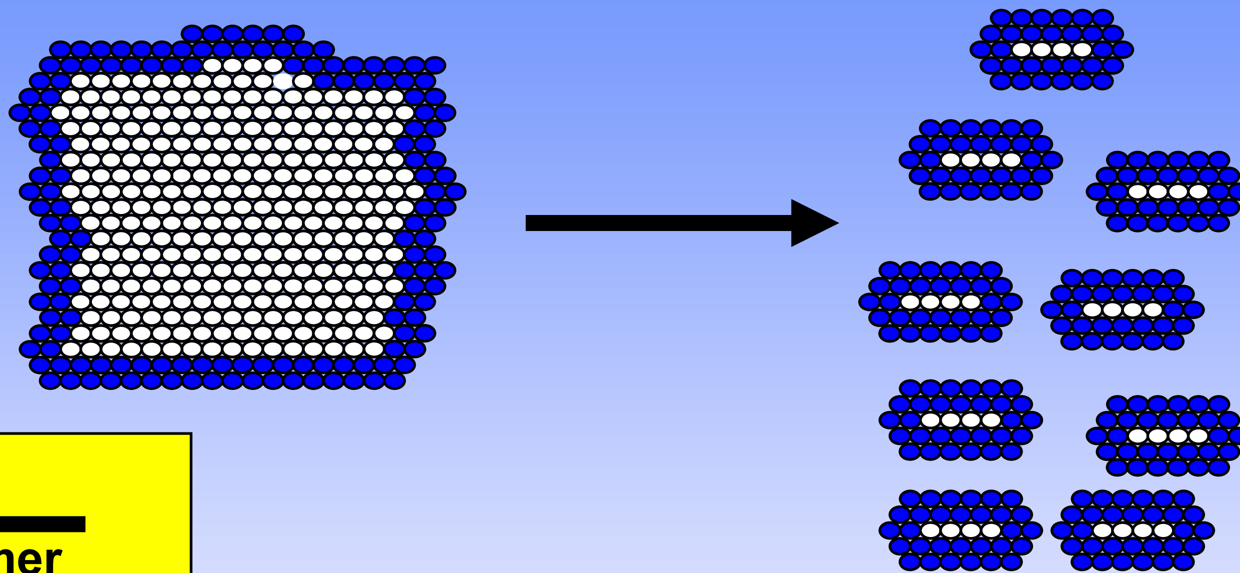
**Increase of the net surface area**

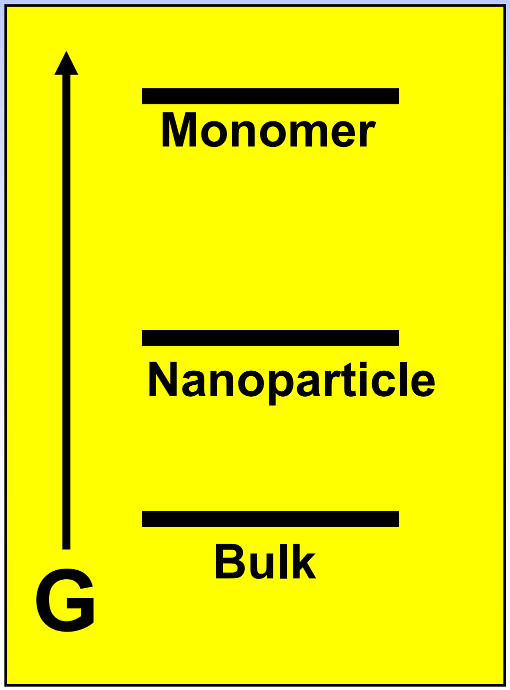
**Increase of the fraction of the material at the surface**

**Result:**

**The surface dominates the properties of the material**

# Nanodrops or Nanocrystals






Nanodrops and nanocrystals are less stable than the bulk.

Nanodrops have a higher vapor pressure than bulk drops (nucleation of rain).

Nanocrystals and nanodrops are more soluble than bulk solid or bulk liquid (nucleation in crystallization and Ostwald ripening of emulsions).

# The Kelvin Equation:

$$\ln (P_{drop}/P_{flat}) = (V_m^{liq}/RT)(2\gamma/R_C)$$

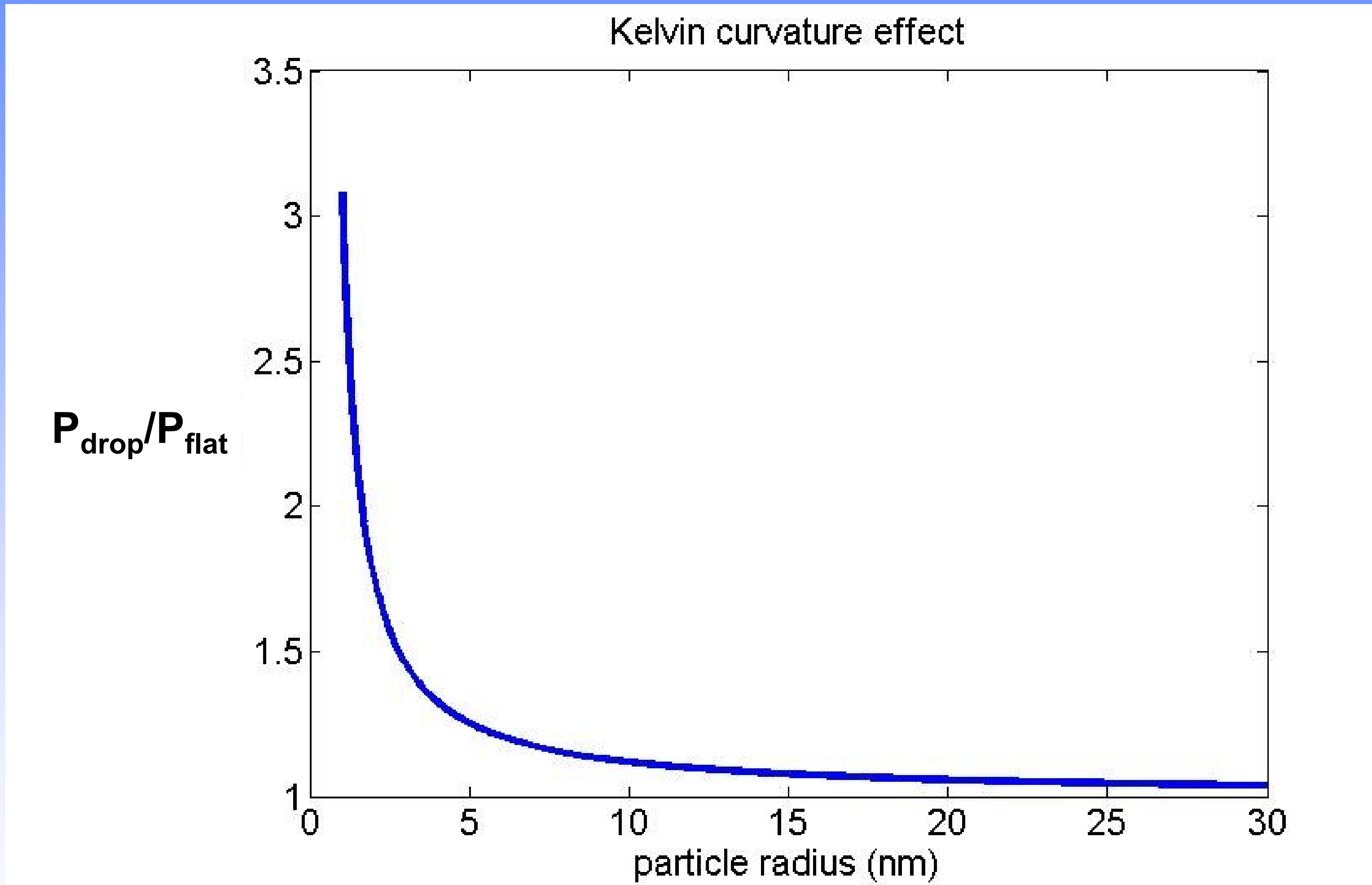
For the vapor pressure of a liquid drop relative to a flat surface.

**The fundamental difficulty of nucleation!**

| | | | | |
|---|---|---|---|---|
| $R_C$: | 1 mm | 100 nm | 10 nm | 1 nm |
| $P_{drop}/P_{flat}$ : | 1.001 | 1.011 | $1.11_4$ | 2.95 |

*[Valid down to at least 2.5 nm for organic liquids and 1.5 nm for water]*

Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)

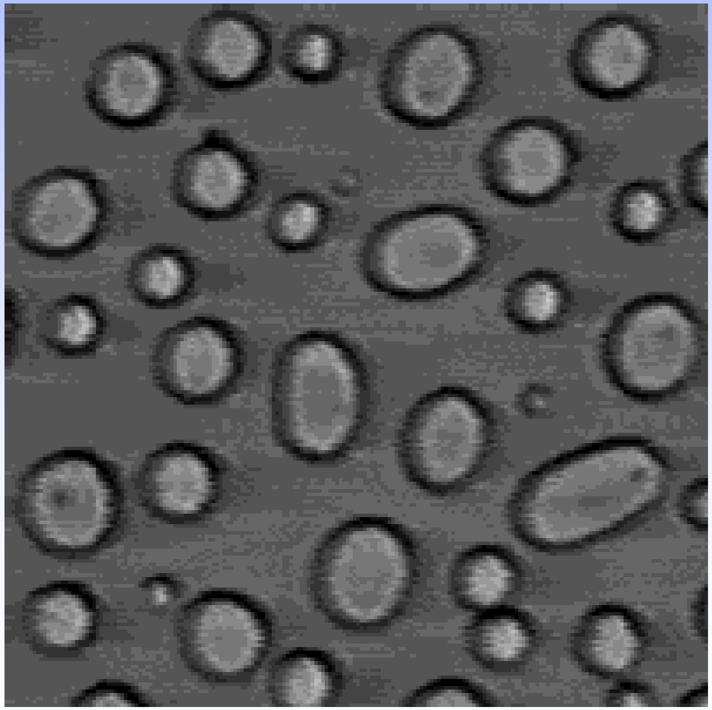



**Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)**

# Ostwald Ripening:

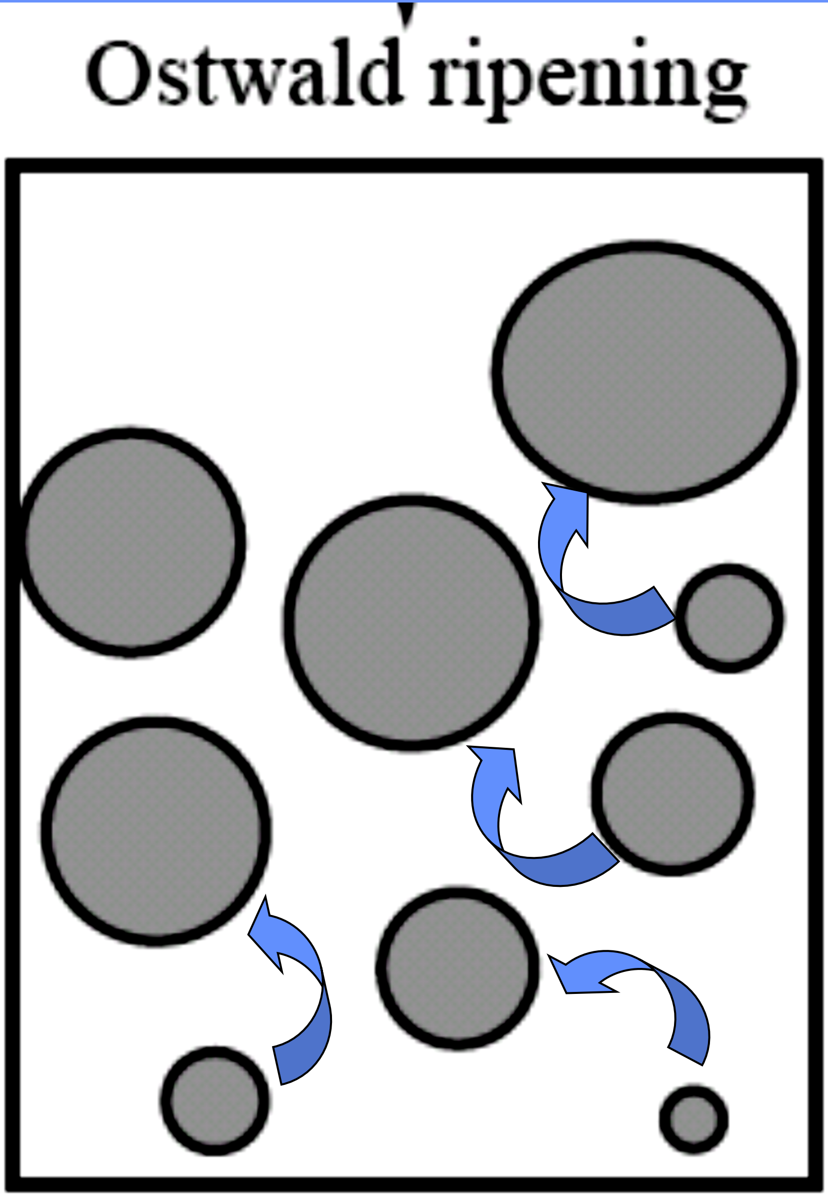
$$\ln [S(R_C)/S(R_C \rightarrow \infty)] = (V_m^{liq}/RT)(2\gamma_{SL}/R_C)$$

**Small crystals or drops are more soluble than large ones.**



**http://www.weizmann.ac.il/complex/stavans/ostwald-ripening-nonequilibrium-liquid-solid-thin-layers**

**Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*-John Wiley & Sons (2016)**



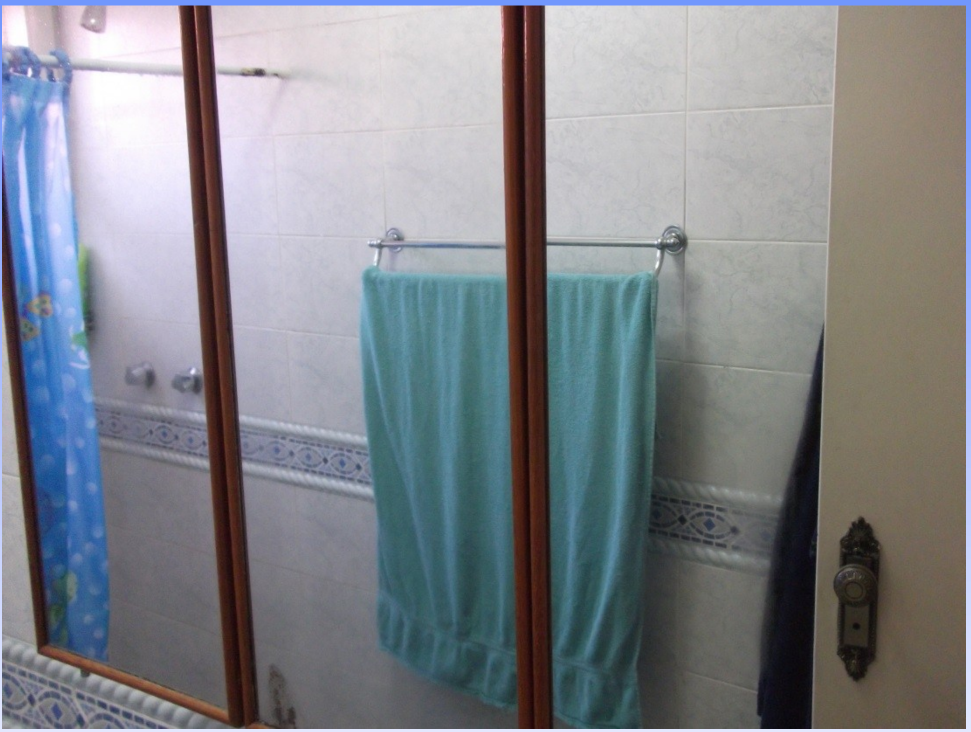

**Smaller Drops have a higher energy and hence are more soluble than large drops. Material migrates through the continuous phase and accumulates in the large drops.**

**Rate of Ostwald Ripening can be reduced by incorporating an insoluble oil into the oil phase in an O/W emulsion.**

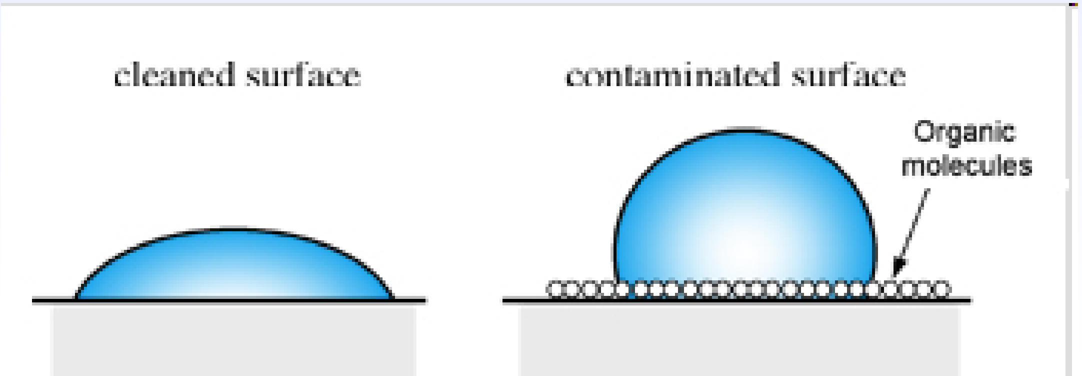
# Condensation

**Nucleation increases the radius of curvature and hence diminishes the Kelvin effect on condensation.**

# A Dry Soap Film Stops Steaming of Mirrors

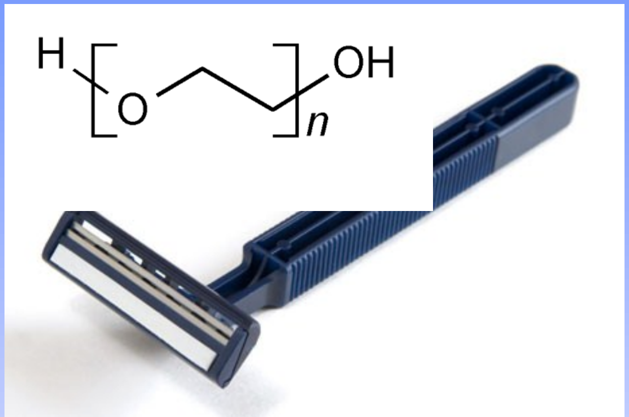


## Barrier to Nucleation and Drop Size



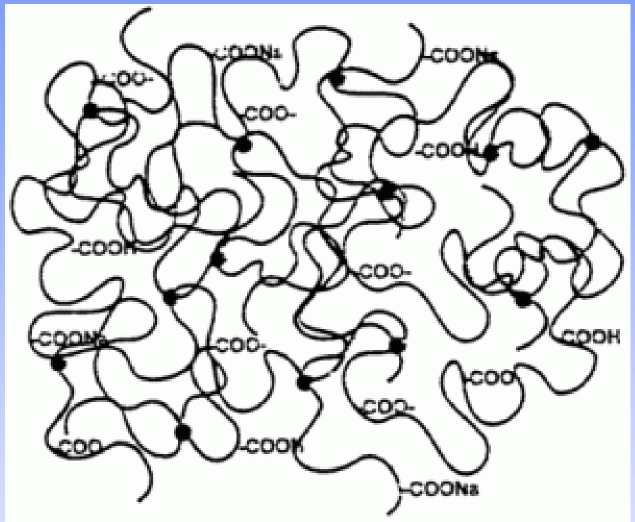
# Colloidal Polymers

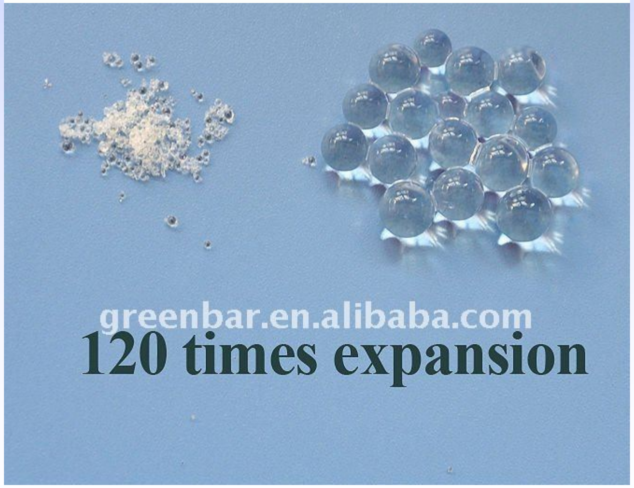
## Rheology Modification




http://www.businessinsider.com/this-amazing-liquid-flows-uphill-2013-12

## Superadsorbent Polymers




# Colloidal Polymers

**Slow-Motion Videos by**
**Dr. Edvaldo Sabadini**
**IQ-UNICAMP**

**Pure Water Drop**

**https://youtu.be/VudmLmjfgLQ**

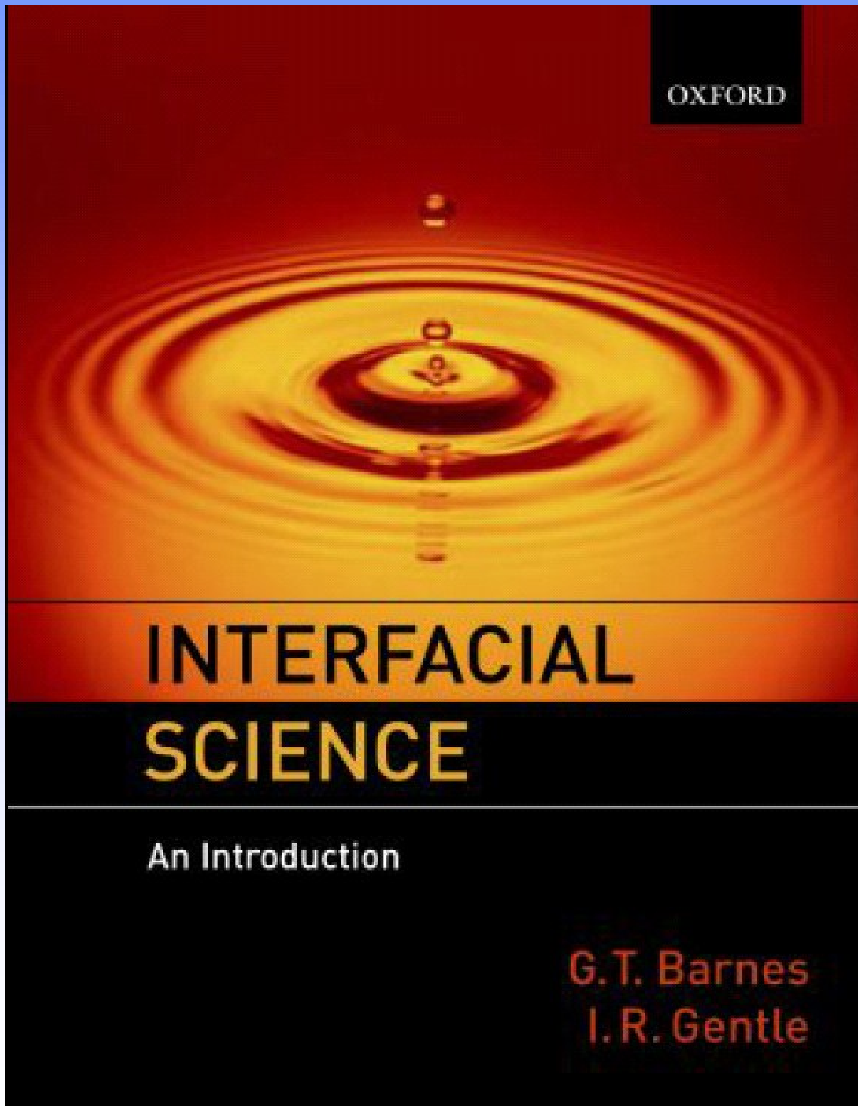
# Colloidal Polymers

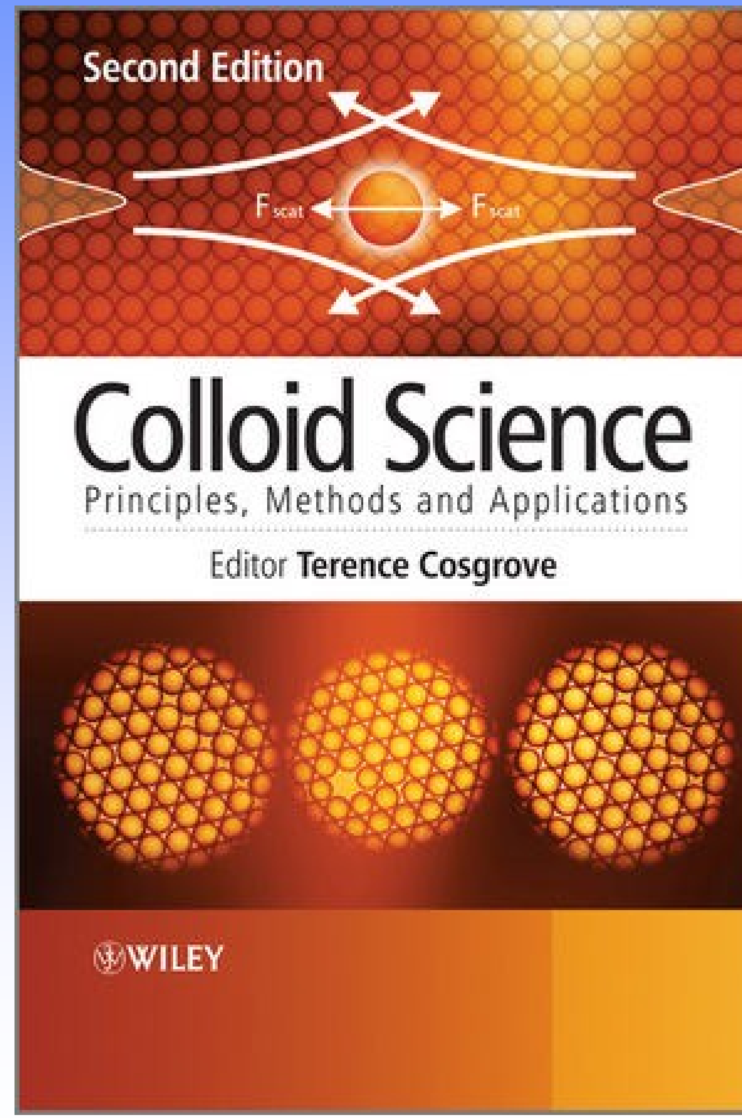
**Slow-Motion Videos by**
**Dr. Edvaldo Sabadini**
**IQ-UNICAMP**

**Drop with Poly(ethylene oxide)**

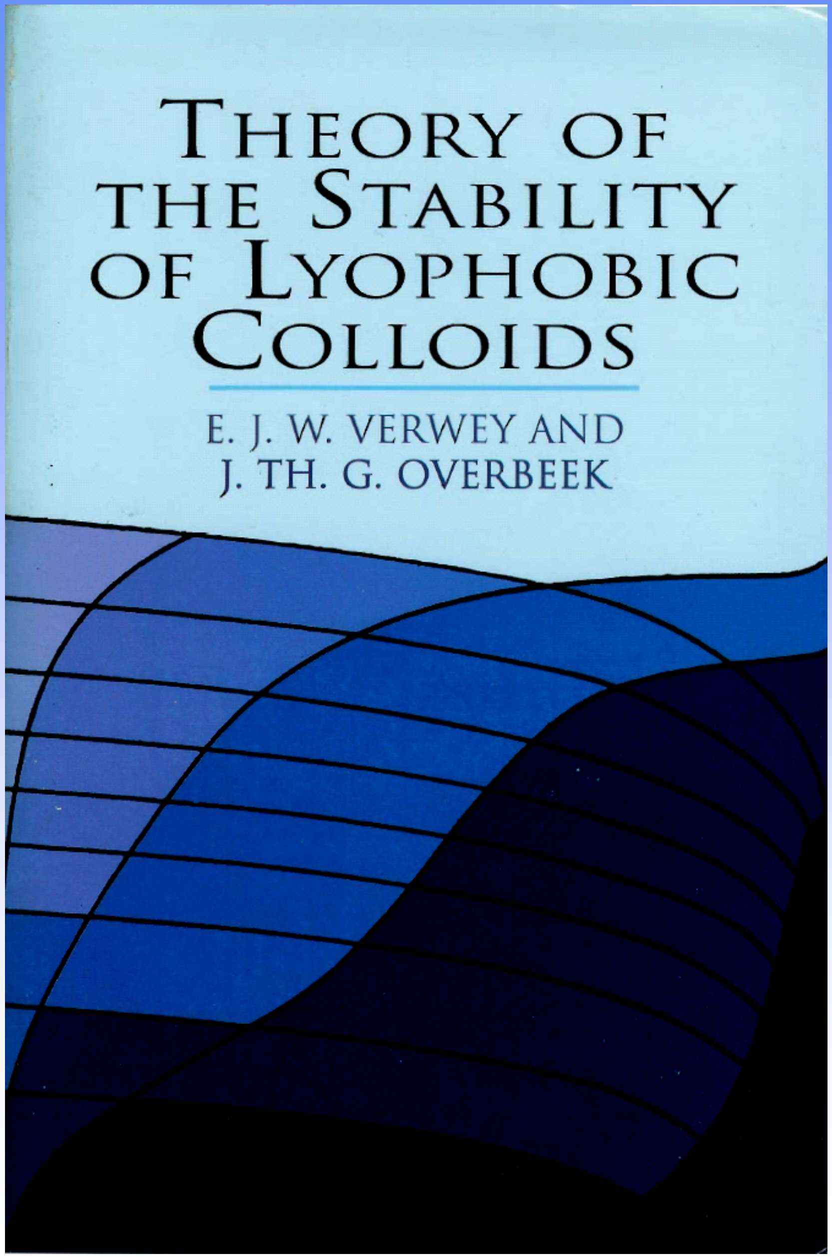
**https://youtu.be/XKnu-ZJe0L8**

# General Bibliography



# Colloid Stability




## DLVO Theory

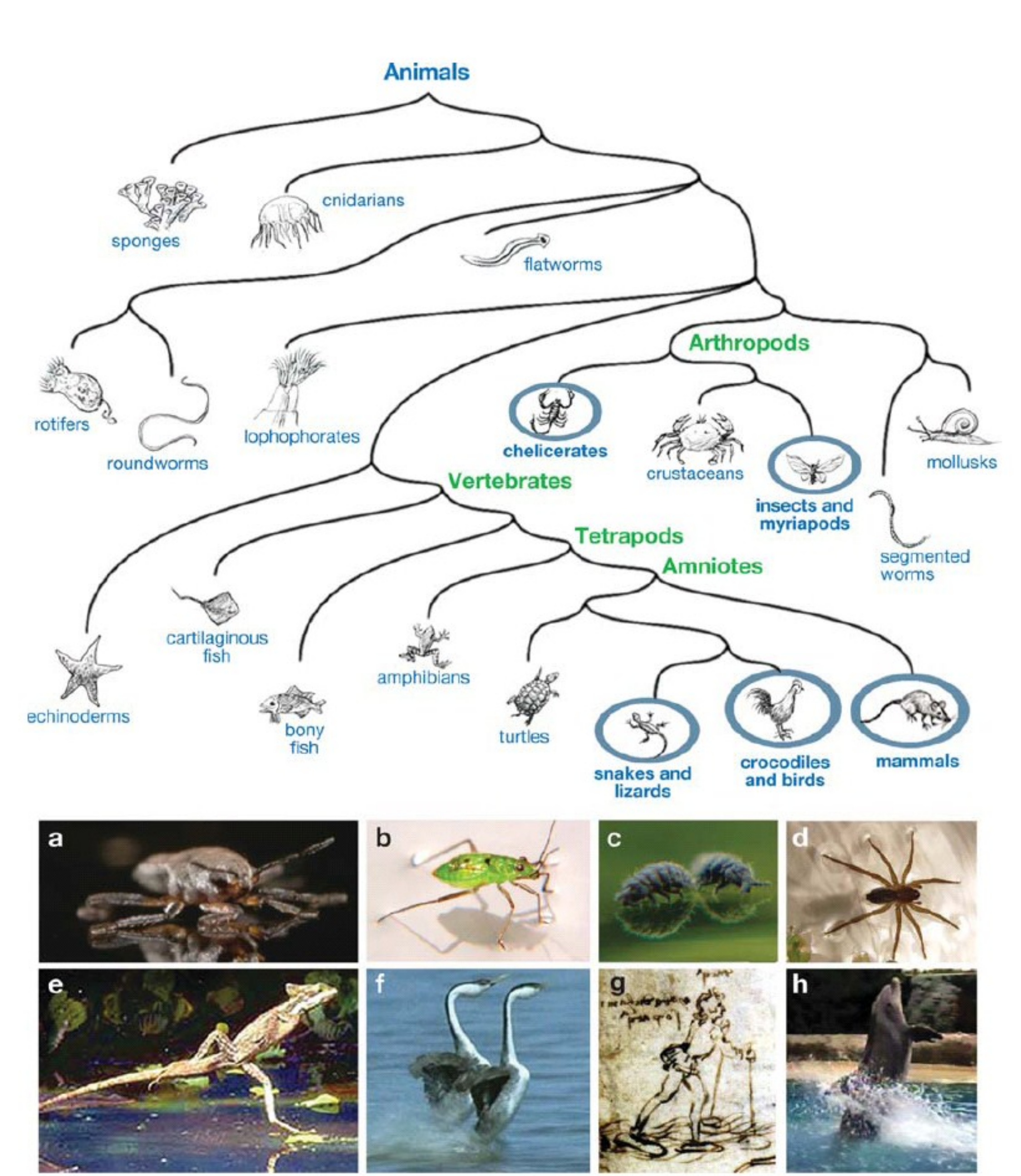
- **D**erjaguin
- **L**andau
- **V**erwey
- **O**verbeek

# Nature Uses Surface and Interfacial Tensions

## Walking on Water: Biolocomotion at the Interface

John W.M. Bush and David L. Hu

*Annu. Rev. Fluid. Mech.* **2006**.*38*:339-369.



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