

Regarding the Young equation

Miguel A. Rodríguez Valverde

$$\sigma_{SV} - \sigma_{SL} = \gamma_{LV} \cos \theta_Y$$

In memory to Pierre Gilles De Gennes
prix Nobel de physique en 1991



Motivation

to avoid **misleading** interpretations of the Young equation

$$\sigma_{SV} - \sigma_{SL} = \gamma_{LV} \cos \theta_Y$$



Rusanov



Platikanov



Starov

Interfacial **tension** or interfacial **energy**?**TABLE 8.1. Typical Liquid Surface and Interfacial Tensions at 20°C (mN m⁻¹)**

Liquid	Surface Tension	Interfacial Tension versus Water
Water	72.8	—
Ethanol	22.3	—
<i>n</i> -Octanol	27.5	8.5
Acetic acid	27.6	—
Oleic acid	32.5	7.0
Acetone	23.7	—
Carbon tetrachloride	26.8	45.1
Benzene	28.9	35.0 (357 vs. mercury)
<i>n</i> -Hexane	18.4	51.1 (378 vs. mercury)
<i>n</i> -Octane	21.8	50.8
Mercury	485	375

TABLE 7.1. Reported Surface Energies of Commonly Encountered Solids

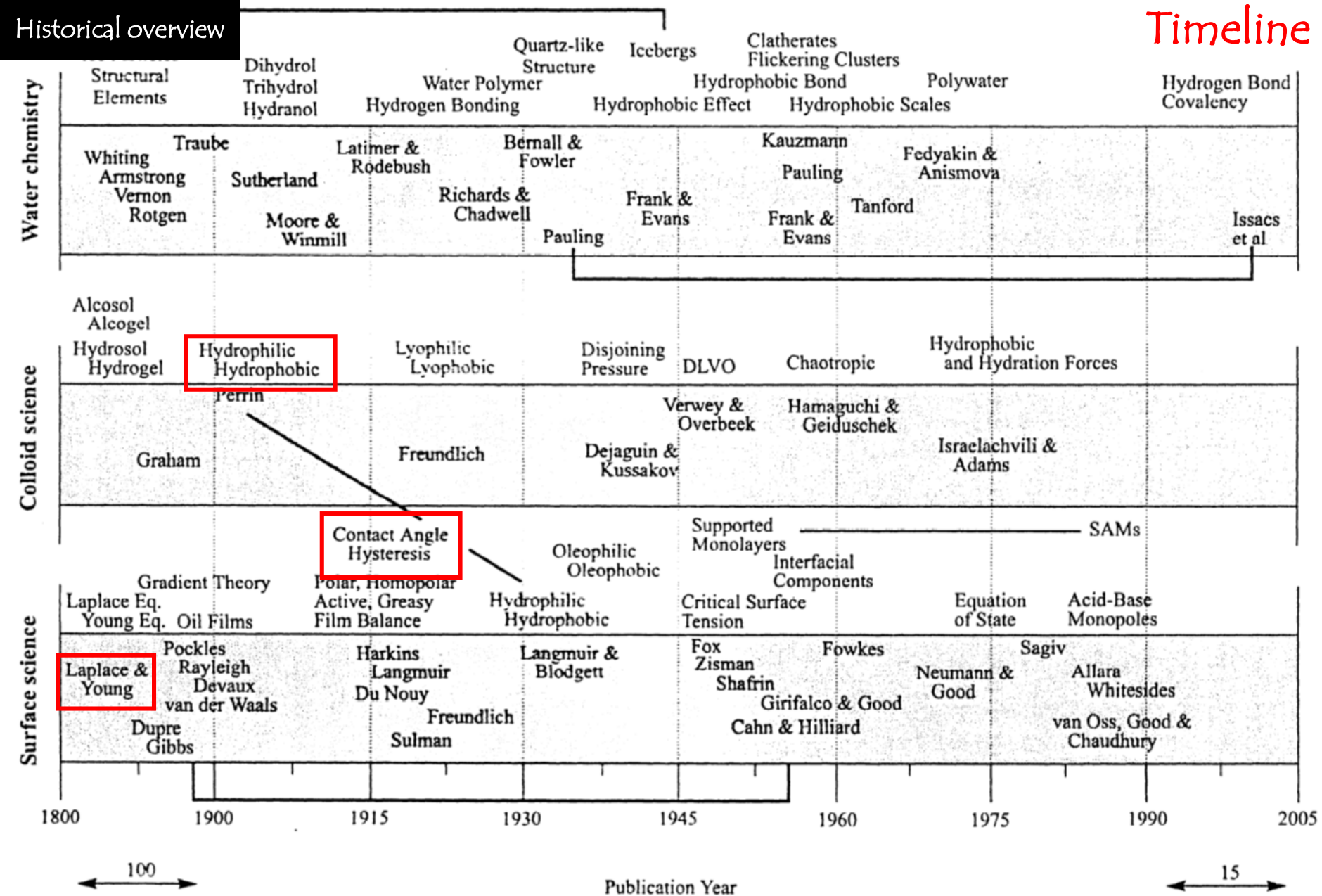
Material	Surface Energy (mJ m ⁻²)	Material	Surface Energy (mJ m ⁻²)
Teflon	20	Lead iodide (PbI ₂)	130
Paraffin wax	26	Silica	462
Polypropylene	28	Lead fluoride (PbF ₂)	900
Polyethylene	36	Iron	1360
Polystyrene	44	Gold	1500
Ice	82	Mica	4500

Outline

- ◇ Historical overview
- ◇ Revised Surface Thermodynamics
- ◇ The Solid Surfaces' evil
- ◇ Other controversial issues
- ◇ References

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📖 E. A. Vogler, *On the Origins of Water Wetting Terminology*, in *Water in Biomaterials Science*, M. Morra (ed.), John Wiley, pp. 149-182 (2001).



Thomas Young (1773–1829)

📖 "An Essay on the Cohesion of Fluids",
Philosophical Transactions of the Royal
Society of London, 95, 65–87, (1805).

<http://gallica.bnf.fr/ark:/12148/bpt6k55900p>

III. *An Essay on the Cohesion of Fluids.* By Thomas Young,
M. D. For. Sec. R. S.

Read December 20, 1804.

I. *General Principles.*

IT has already been asserted, by Mr. MONGE and others, that the phenomena of capillary tubes are referable to the cohesive attraction of the superficial particles only of the fluids employed, and that the surfaces must consequently be formed into curves of the nature of linteariæ, which are supposed to be the results of a uniform tension of a surface, resisting the pressure of a fluid, either uniform, or varying according to a given law. SEGNER, who appears to have been the first that maintained a similar opinion, has shown in what manner the principle may be deduced from the doctrine of attraction, but his demonstration is complicated, and not perfectly satisfactory; and in applying the law to the forms of drops, he has neglected to consider the very material effects of the double curvature, which is evidently the cause of the want of a perfect coincidence of some of his experiments with his theory. Since the time of SEGNER, little has been done in investigating accurately and in detail the various consequences of the principle.

It will perhaps be most agreeable to the experimental philosopher, although less consistent with the strict course of logical argument, to proceed in the first place to the comparison

Johann Carl Friedrich Gauss (1777–1855)

📖 "Principia Generalia Theoriae Figurae Fluidorum"
 Comment. Soc. Regiae Scient. Gottingensis Rec. 7
 (1830).

<http://gallica.bnf.fr/ark:/12148/bpt6k99405t>



Gauss used the Principle of Virtual Work to unify the achievements of Young and Laplace

Athanase Dupré (1808–1869)

📖 "Théorie mécanique de la chaleur". Paris, Gauthier-Villars, 1869

$$w_{adh} = \gamma_{LV} (1 + \cos \theta)$$

L'angle de raccordement

Controversy about the Young equation

1. **Experimental** verification
2. **Mechanistic** derivation/interpretation
3. Restrictive concept of **ideal** solid surface
4. Influence of **external field**, contact angle **hysteresis**, effect of drop **size**...

As result...the **delirious** renaming of the Young equation

📖 TOMINAGA HIROSHI, SAKATA GORO, ISHIBUCHI TOMOMI, OUMI MASAHARU, "Gamo Triangles of Wetting" (Provisional Name) and Re-verification of **Dupre-Gamo Equation**, Journal of the Adhesion Society of Japan (2000), 36(5) 176-178

Reply:

📖 VOLPE C D SIBONI S MANIGLIA D, About the Validity of the So-called Dupre-Gamo Equation, Journal of the Adhesion Society of Japan (2003), 39(2) 64-66

Experimental verification of the Young equation

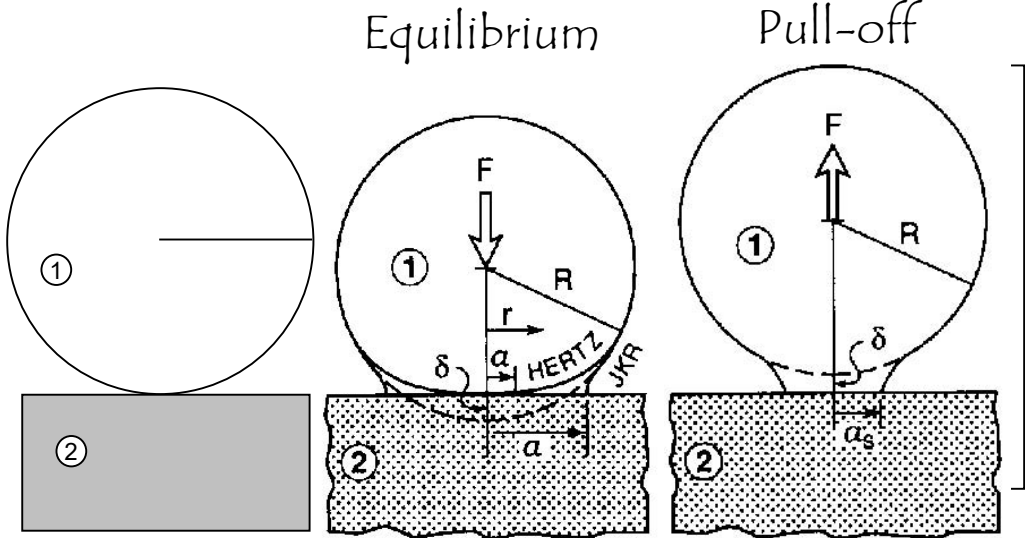
$$\sigma_{SV} - \sigma_{SL} = \gamma_{LV} \cos \theta_Y$$

No readily measurable quantities

Experimentally accessible quantities

📖 Erik Johnson, "The Elusive Liquid-solid Interface", Science 19 April 2002: Vol. 296. no. 5567, pp. 477 - 478

-Hertz and JKR theories (Contact Mechanics: adhesion, friction, and fracture)
-Adhesion (pull-off) forces by SFA
-Elastomeric solids



After ~ 200 years...

- 📖 A.I. Bailey, S.M. Kay, "A Direct Measurement of the Influence of Vapour, of Liquid and of Oriented Monolayers on the Interfacial Energy of Mica" *Proc. Roy. Soc. A*301 (1967), p. 47
- 📖 Johnson, K. L.; Kendall, K.; Roberts, A. D. "Surface Energy and the Contact of Elastic Solid" *Proc. R. Soc. London, A* 1971, A324, 301.
- 📖 R. M. Pashley, J. N. Israelachvili, "A Comparison of Surface Forces and Interfacial Properties of Mica in Purified Surfactant Solutions" *Colloids & Surfaces* 2 (1981) 169-187
- 📖 Manoj K. Chaudhury, George M. Whitesides, "Direct Measurement of Interfacial Interactions between Semispherical Lenses and Flat Sheets of Poly(dimethyl siloxane) and Their Chemical Derivatives," *Langmuir* 7 (1991):1013-1025

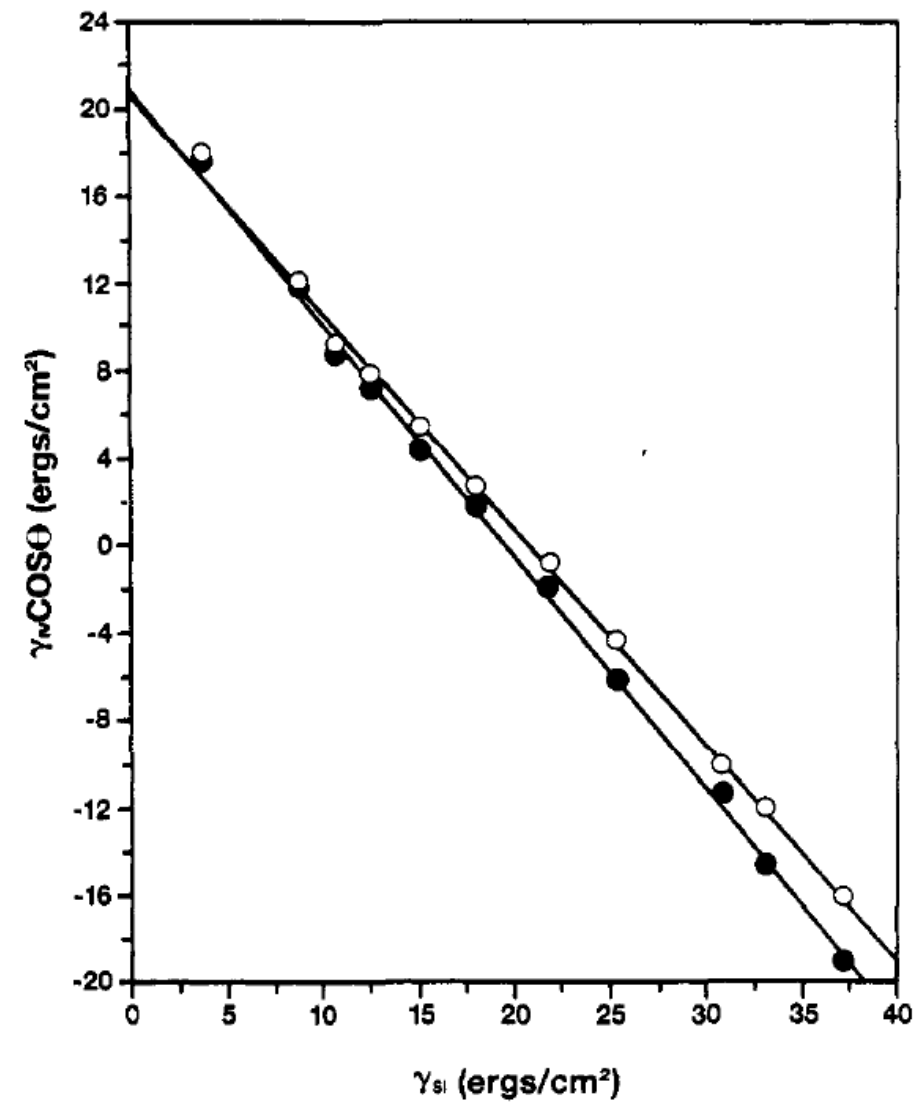


Figure 9. Plot of $\gamma_{lv} \cos \theta$ against γ_{sl} for the mixtures of water and methanol on PDMS obeying Young's equation (eq 5). Closed (●) and open (○) circles correspond to the data obtained from the advancing and receding contact angles, respectively. The values of γ_{sl} were obtained from Figure 8. The linear correlations between $\gamma_{lv} \cos \theta$ and γ_{sl} are in accordance with Young's equation. The intercepts in the $\gamma_{lv} \cos \theta$ axis yield the value of γ_{sv} of PDMS as 20.9 ergs/cm² (from θ_r) and 21.2 ergs/cm² (from θ_a), respectively.

Outline

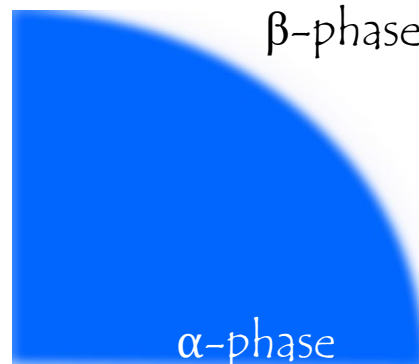
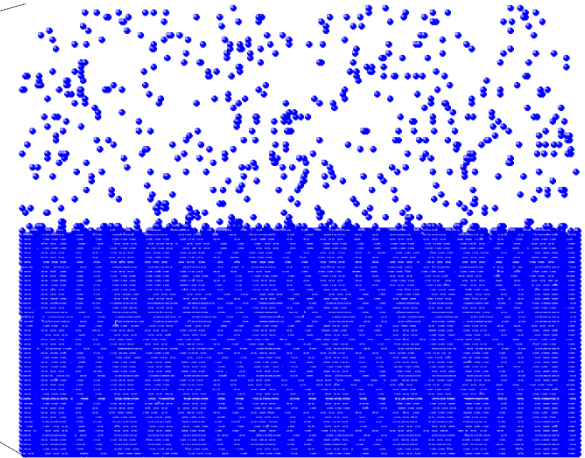
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Concept of *interface*

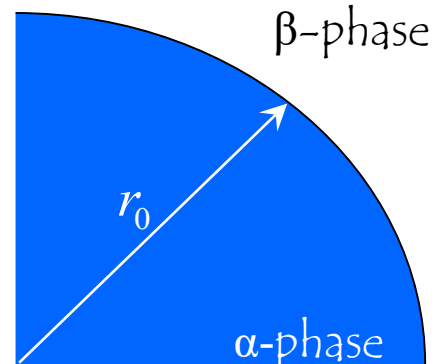
β -phase

α -phase


One-component system
(substance i)



Interphase



Interface

 Josiah Willard Gibbs, "On the Equilibrium of Heterogeneous Substances", The American Journal of Science and Arts Third Series, Vol. XVI, No. 96, December 1878, pp. 441-58

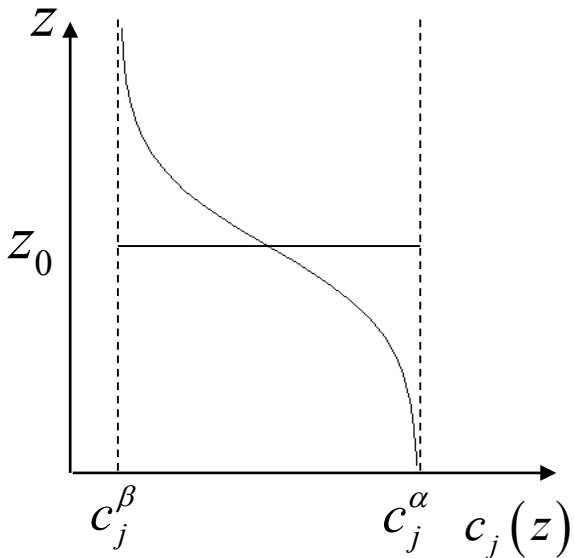
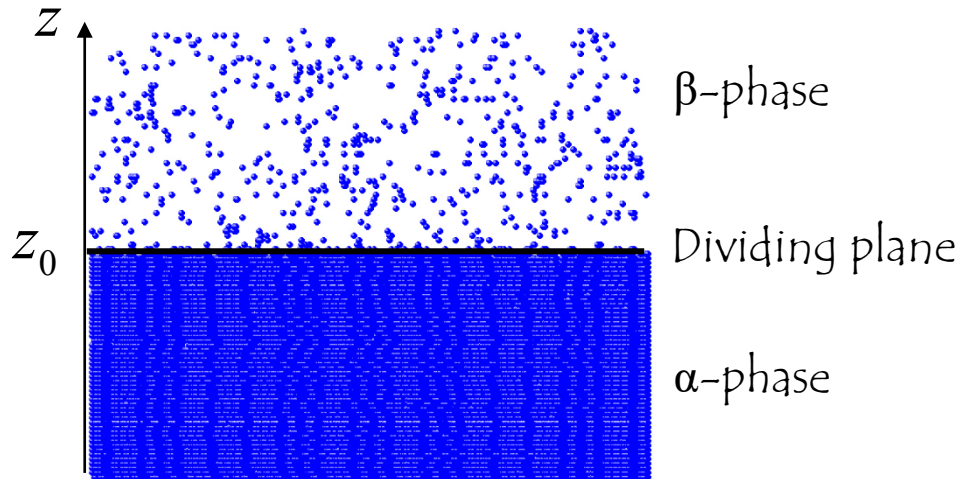
Position of the **Dividing** Plane

$c_j(z)$ Local concentration of the substance j

$c_j^\alpha = c_j(\infty)$ " in the bulk of α -phase

$c_j^\beta = c_j(-\infty)$ " in the bulk of β -phase

Normal coordinate
to the interface



$$\Gamma_j = \int_{-\infty}^{z_0} (c_j(z) - c_j^\alpha) dz + \int_{z_0}^{\infty} (c_j(z) - c_j^\beta) dz$$

$$\Gamma_j = 0 \Leftrightarrow \int_{-\infty}^{z_0} (c_j^\alpha - c_j(z)) dz = \int_{z_0}^{\infty} (c_j(z) - c_j^\beta) dz$$

How can we form a **new** interface $\alpha\beta$?

①

Stretching:

work against the forces of surface tension

dA



$$dW_\gamma = \gamma_{\alpha\beta} dA$$

Interfacial tension

Intensive tensorial quantity

②

Cutting-off:

work against the cohesive forces

dA



$$dW_\sigma = \sigma_{\alpha\beta} dA$$

Specific excess interfacial free energy

Intensive scalar quantity
(=surface grand thermodynamic potential)

$$\sigma_{\alpha\beta}(T, \mu_j) > 0$$

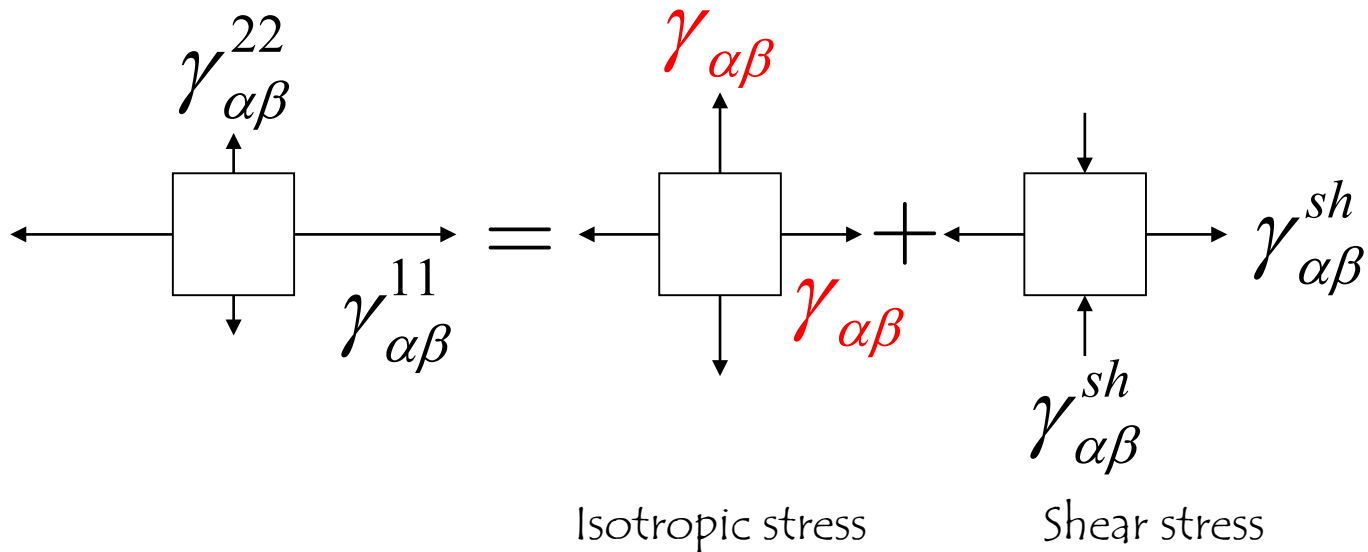
Anisotropic interfaces

$$\gamma_{\alpha\beta} = \frac{1}{2} \left(\vec{\gamma}_{\alpha\beta} : \vec{1} \right) \quad dW_\gamma = \left(\vec{\gamma}_{\alpha\beta} : d\vec{e} \right) A$$

Surface strain tensor

Interfacial stress **tensor** (principal directions)

$$\vec{\gamma}_{\alpha\beta} = \begin{pmatrix} \gamma_{\alpha\beta}^{11} & 0 \\ 0 & \gamma_{\alpha\beta}^{22} \end{pmatrix} = \gamma_{\alpha\beta} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \gamma_{\alpha\beta}^{sh} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

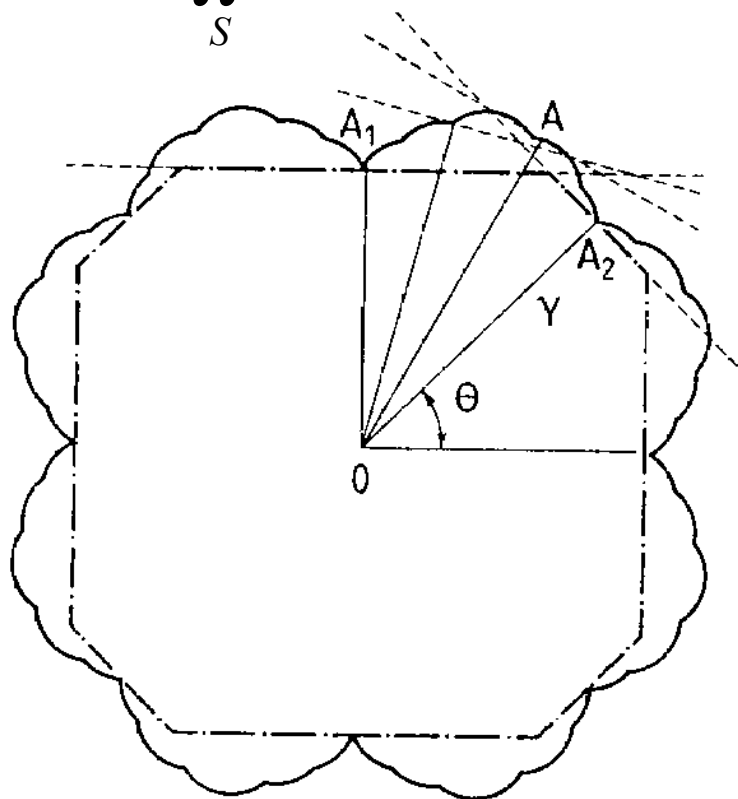


Wulff construction: the **shape** of things

-In **crystalline** solids, the surface tension depends on the crystal plane and its direction

-The equilibrium shape of a crystal is obtained by **minimizing** the integral

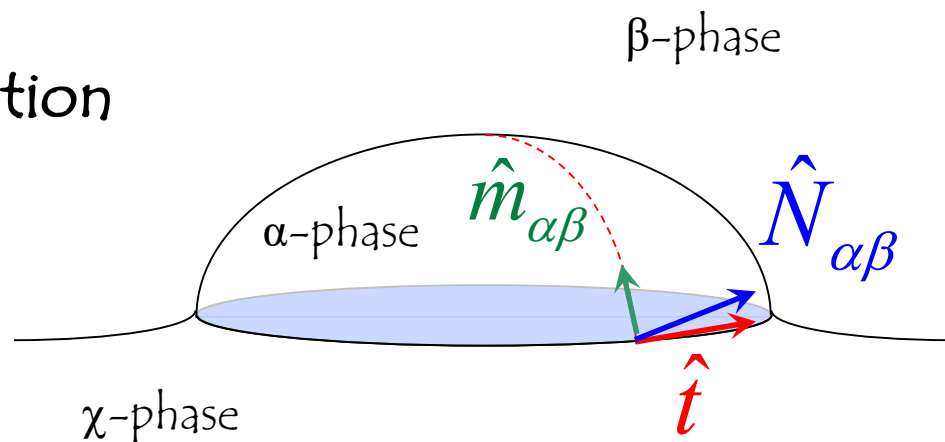
$$W_\gamma = A \iint_S \vec{\gamma}_{\alpha\beta} : d\vec{e}$$



Mechanical equilibrium condition (fluid interfaces)

$$\hat{m}_{\alpha\beta} = \hat{N}_{\alpha\beta} \times \hat{t}$$

conormal unit vector



$$\vec{\gamma}_{\alpha\beta} \equiv \vec{\gamma}_{\alpha\beta} \cdot \hat{m}_{\alpha\beta} = \frac{d\vec{F}_{\alpha\beta}}{dl}$$

$$W_\gamma = \int_C \vec{F}_{\alpha\beta} \cdot d\vec{r} = A \iint_S \vec{\gamma}_{\alpha\beta} : d\vec{e}$$

$\hat{m}_{\alpha\beta}$ Eigenvector

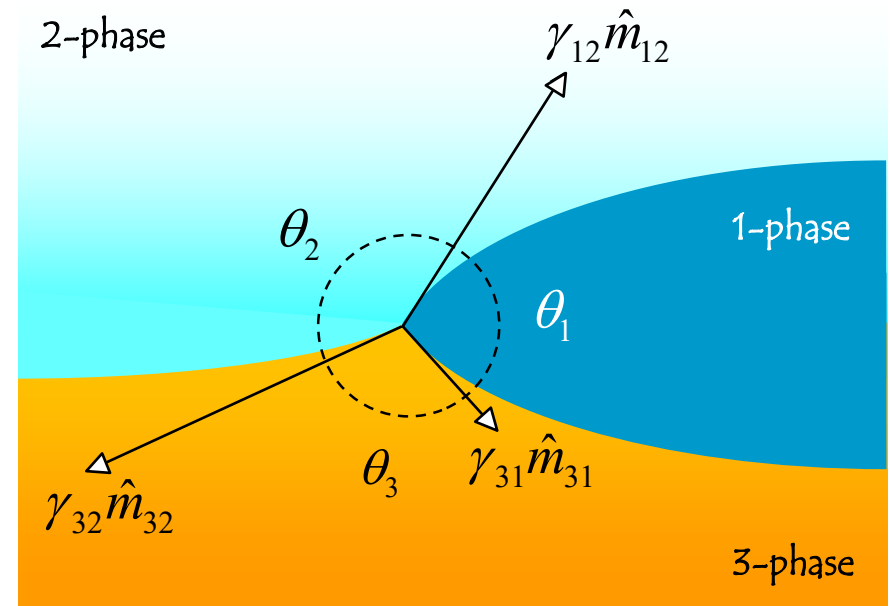
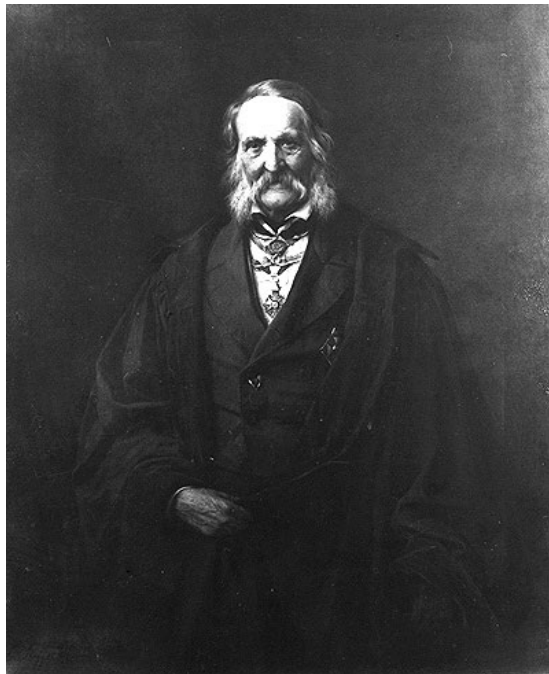
$\gamma_{\alpha\beta}$ Eigenvalue

$$\vec{\gamma}_{\alpha\beta} \cdot \hat{m}_{\alpha\beta} = \gamma_{\alpha\beta} \hat{m}_{\alpha\beta}$$

$$\sum_{[\alpha\beta\chi]} \vec{\gamma}_{ij} = \vec{0}$$

Neumann's **Triangle** equation (no generalized Young equation!)

$$\gamma_{12} \hat{m}_{12} + \gamma_{31} \hat{m}_{31} + \gamma_{32} \hat{m}_{32} = \vec{0} \quad \text{2-phase}$$



$$\frac{\sin \theta_3}{\gamma_{12}} = \frac{\sin \theta_2}{\gamma_{31}} = \frac{\sin \theta_1}{\gamma_{32}}$$

$$\theta_3 = \pi \Rightarrow \theta_1 = 0 \text{ or } \pi!!!$$

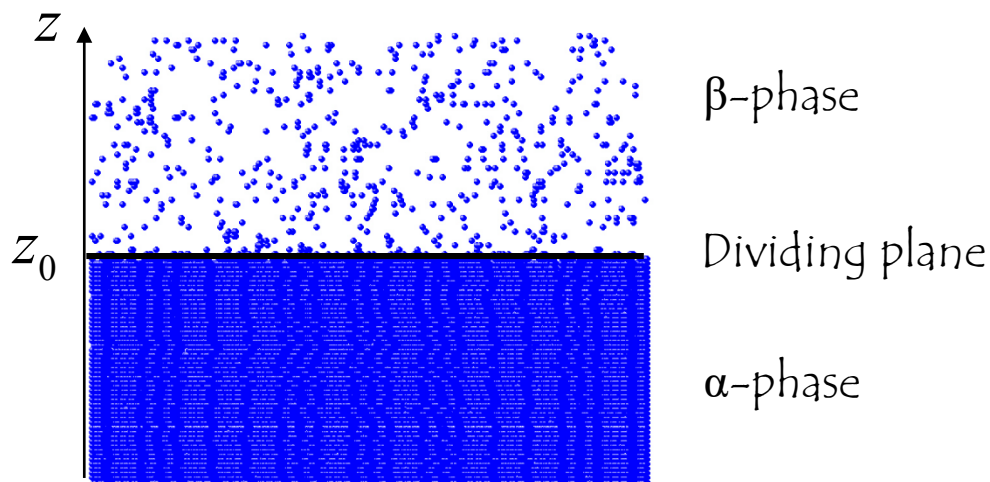
Franz Ernst Neumann (1798 -1895)

📖 Neumann, F. , "Vorlesungen über die Theorie der Capillarität", 152 (Teubner, Leipzig, 1894).

Relation between $\sigma_{\alpha\beta}$ and $\vec{\gamma}_{\alpha\beta}$

Local stress tensor

$$\vec{\gamma}_{\alpha\beta} = \int_{-\infty}^{z_0} (P_\alpha \vec{1} - \vec{P}(z)) dz + \int_{z_0}^{\infty} (P_\beta \vec{1} - \vec{P}(z)) dz$$

 Normal coordinate
to the interface


$$\sigma_{\alpha\beta} \vec{1} = \vec{\gamma}_{\alpha\beta} + \int_{-\infty}^{z_0} (\vec{\mu}_j(z) - \vec{\mu}_j^\alpha) c_j(z) dz + \int_{z_0}^{\infty} (\vec{\mu}_j(z) - \vec{\mu}_j^\beta) c_j(z) dz$$

 $\vec{\mu}_j(z)$ Chemical potential tensor of the substance j
 $\vec{\mu}_j^\alpha = \vec{\mu}_j(\infty)$ " in the bulk of α -phase

 $\vec{\mu}_j^\beta = \vec{\mu}_j(-\infty)$ " in the bulk of β -phase

 $c_j(z)$ Local concentration of the substance j

3D tensors

$$\gamma_{\alpha\beta} = \frac{1}{3} (\vec{\gamma}_{\alpha\beta} : \vec{1})$$

$$\vec{\gamma}_{\alpha\beta} = \frac{1}{A} \iiint_{V_\alpha} (P_\alpha \vec{1} - \vec{P}) dV + \frac{1}{A} \iiint_{V_\beta} (P_\beta \vec{1} - \vec{P}) dV$$

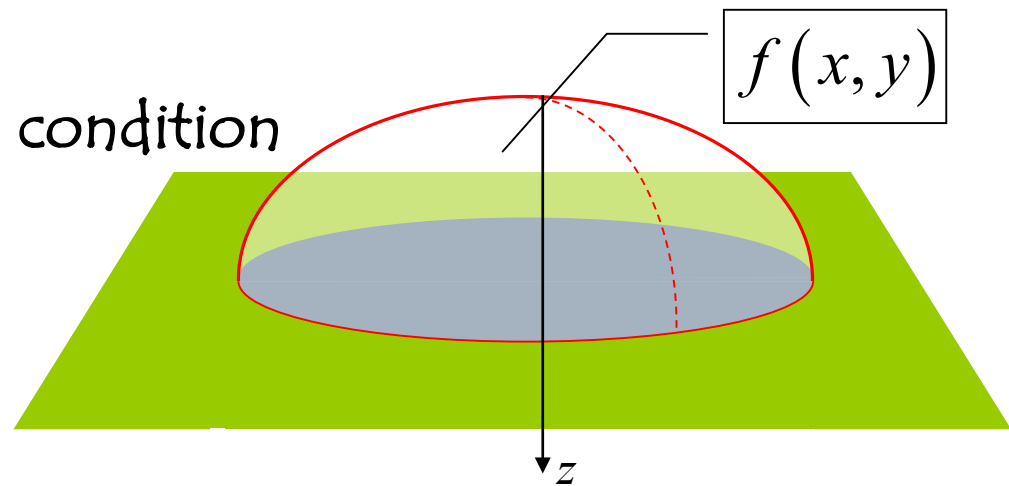
$$\sigma_{\alpha\beta} \vec{1} = \vec{\gamma}_{\alpha\beta} + \frac{1}{A} \iiint_{V_\alpha} (\vec{\mu}_j - \vec{\mu}_j^\alpha) c_j dV + \frac{1}{A} \iiint_{V_\beta} (\vec{\mu}_j - \vec{\mu}_j^\beta) c_j dV$$

Chemical equilibrium

$$\vec{\mu}_j = \vec{\mu}_j^\alpha = \vec{\mu}_j^\beta$$

$$\sigma_{\alpha\beta} = \gamma_{\alpha\beta}$$

Thermodynamic equilibrium condition (solid-liquid-fluid interfaces)



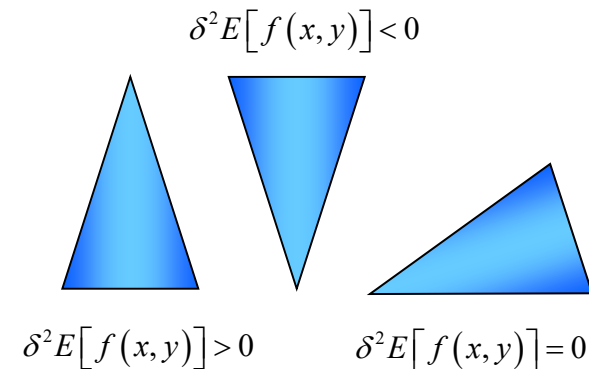
Energy functional of a solid-liquid-vapor (SLV) system (ideal solid surface)

$$E[f(x, y)] = \int_{A_{lv}} \sigma_{LV} dA - \int_{V_l} \Delta\rho g f dV + \int_{A_{sl}} (\sigma_{SL} - \sigma_{SV}) dA$$

Closure conds. $\int_{V_l \cup V_v} dV = \text{const.}; \int_{A_{sl} \cup A_{sv}} dA = \text{const.}$

Energy functional **minimization**

local minimum condition:
$$\begin{cases} \delta E[f(x, y)] = 0 \\ \delta^2 E[f(x, y)] > 0 \end{cases}$$



$$\delta E = \delta \Omega = 0$$

Conditioned minimization $V_l = \text{const}$

$$\Omega[f(x, y)] \equiv E[f(x, y)] - \lambda V_l$$

Grand canonical potential $\Omega(T, V_l, \mu)$ Pressure difference at $f = 0$ $\lambda = \Delta P_0$

 <http://www.iupac.org/publications/pac/2001/pdf/7308x1349.pdf>

$$\text{ext}_{f(x,y)} \left\{ \frac{\Omega}{\sigma_{LV}} \right\} = \text{ext}_{f(x,y)} A_{lv} - \frac{\Delta \rho g}{\sigma_{LV}} \text{ext}_{f(x,y)} \int_{V_l} f dV - \frac{\lambda}{\sigma_{LV}} V_l + \frac{\sigma_{SL} - \sigma_{SV}}{\sigma_{LV}} \text{ext}_{f(x,y)} A_{sl}$$

Young-Laplace Eq.
Young Eq.

1. The Young equation is **necessary** condition for the global equilibrium, but it is **not sufficient** condition. The Young equation is associated to whatever **metastate** of a **real** SLV system (local minima), instead of to the global equilibrium state (global minimum)
2. The Young equation is **independent** of the **interfacial** geometry and the **gravitational** field

Young equation: (local) **thermodynamic** equilibrium condition
(**NOT** force balance!)

$$\sigma_{SV} - \sigma_{SL} = \sigma_{LV} \cos \theta_Y$$

3. **Boundary** condition of the Young-Laplace equation, derived by thermodynamic arguments
4. Young contact angle is a **thermodynamic** quantity, a conceptual, unlocated angle

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- ◇ Revised Surface Thermodynamics
- ◇ *The Solid Surfaces' evil*
- ◇ Other controversial issues
- ◇ References

Chemical equilibrium

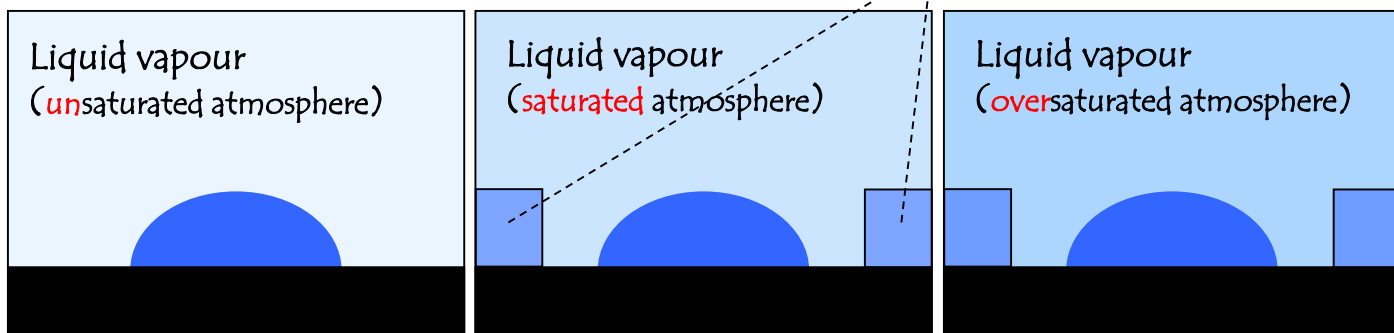
$$\vec{\mu}_j = \vec{\mu}_j^\alpha = \vec{\mu}_j^\beta$$

$$\sigma_{\alpha\beta} = \gamma_{\alpha\beta}$$

... although

In practice...

Air



$$\mu_j^L \neq \mu_j^V$$

$$\ln \frac{P_V}{P_V^{plane}} \approx \frac{2\gamma_{LV}v_L}{RT} H$$

$$\mu_j^L = \mu_j^V$$

Non-uniformity of chemical potentials near the solid surface:

Absence of diffusion equilibrium



-Diffusion in real solids proceeds **slowly**
(diffusion time \gg experiment time)

-**ill**-defined thermodynamic states

$$\sigma_{SF} \neq \gamma_{SF}$$

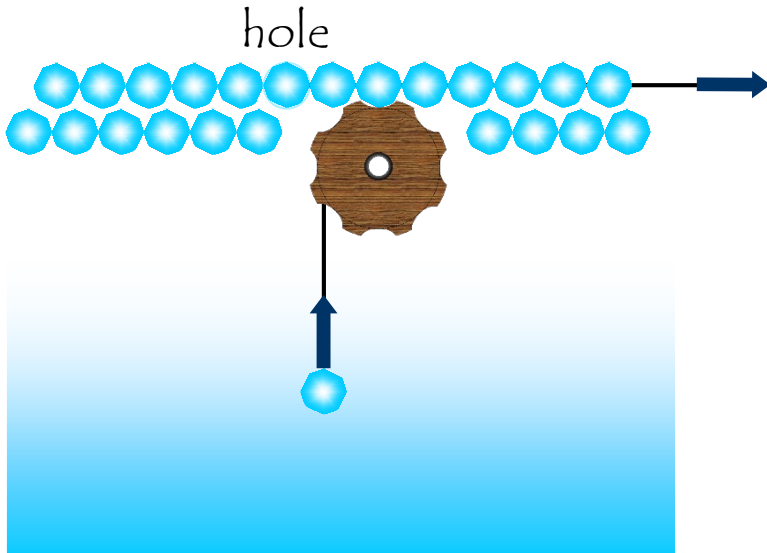
The Solid Surfaces' **evil** 🤖

"God made solids, but surfaces were the work of the devil"-----Wolfgang Pauli

Stretching of interfaces

Liquid-Fluid interface:

Variable number of interfacial molecules



Plastic deformation

$$\sigma_{LF} = \gamma_{LF}$$

Solid-Fluid interface:

Constant number of interfacial molecules



Elastic deformation

$$\sigma_{SF} \neq \gamma_{SF}$$

But if...

$$\vec{\mu}_j \approx \vec{\mu}_j^L \approx \vec{\mu}_j^F$$

$$(\sigma_{SF} - \sigma_{SL}) \vec{1} = \vec{\gamma}_{SF} - \vec{\gamma}_{SL} + \frac{1}{A} \iiint_{V_F} (\vec{\mu}_j - \vec{\mu}_j^F) c_j dV - \frac{1}{A} \iiint_{V_L} (\vec{\mu}_j - \vec{\mu}_j^L) c_j dV$$

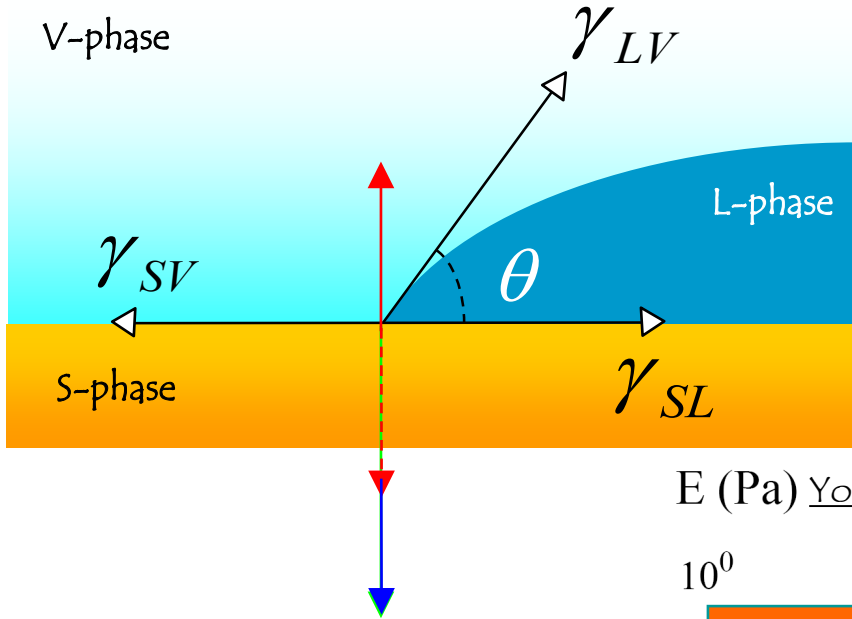
$$(\sigma_{SF} - \sigma_{SL}) \vec{1} \approx \vec{\gamma}_{SF} - \vec{\gamma}_{SL}$$

Equal principal directions

$$\sigma_{SF} - \sigma_{SL} \approx \gamma_{SF} - \gamma_{SL}$$

Mechanical equilibrium condition (solid-liquid-fluid interfaces)

$$\hat{m}_{32} = -\hat{m}_{31}$$



$$\begin{cases} \gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \\ \gamma_{LV} \sin \theta - w + r = 0 \end{cases}$$

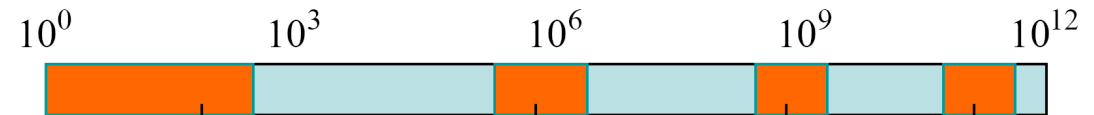
Gravity force (active)

Reaction force (passive)

Elastic restoring force (passive)

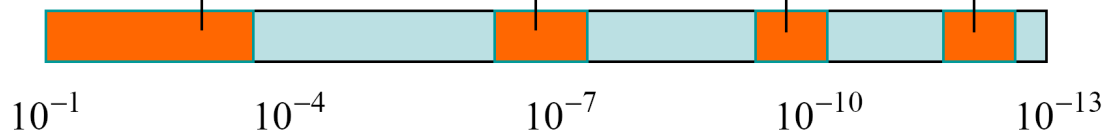
$$R = w - r \propto E$$

E (Pa) Young modulus



Cells, soft tissue Elastomers Engineering Thermoplastics Metals, Ceramic

γ/E (m)
($\gamma = 0.1 \text{ J/m}^2$) Ridge height

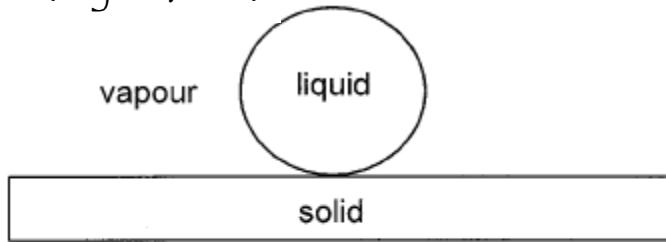


The **false** equilibrium of a sessile drop
(the Solid Surfaces' evil cont'd)

How **minimize** the solid stresses along the contact line?

Deformation of the solid surface: "Everything flows, nothing stands still"

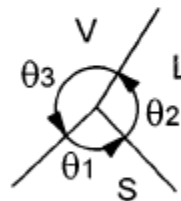
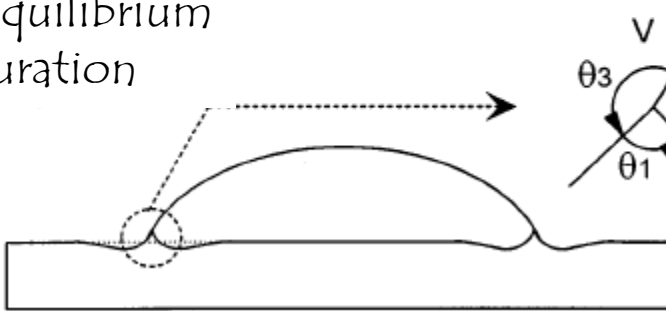
Initial configuration



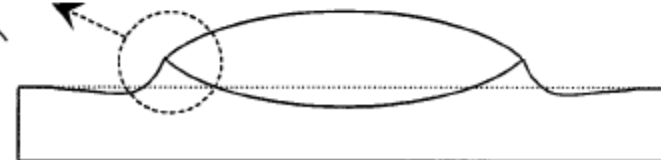
Non-equilibrium (but stable) configuration



Local equilibrium configuration



Both local and total equilibrium configuration

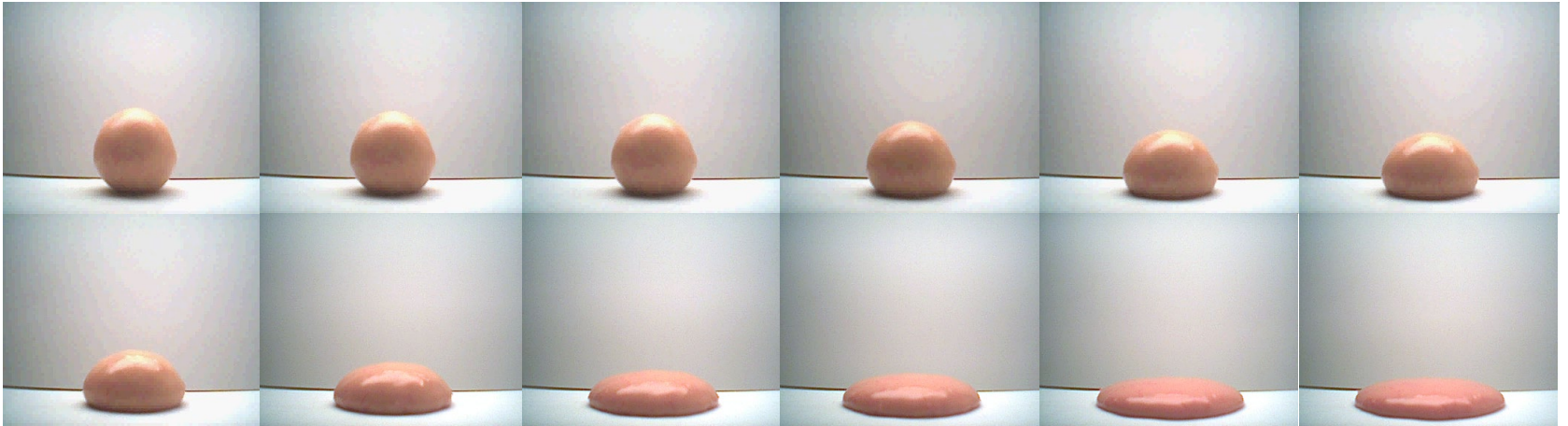


...after millions of years or minutes

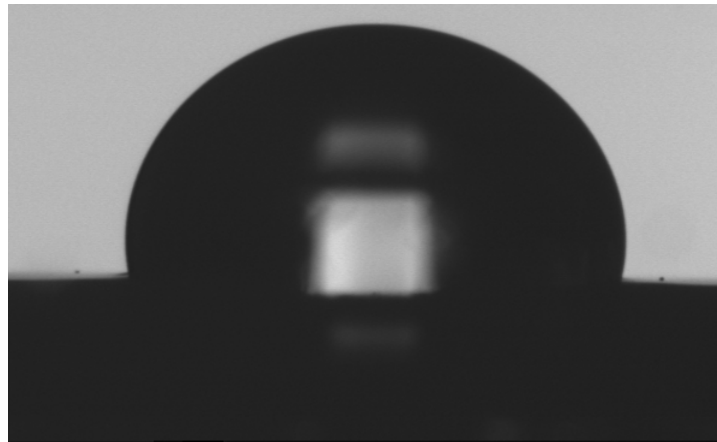
Hard matter versus Soft matter: timescales

$$Dh \equiv \frac{t_{rel}}{t_{obs}}$$

Deborah Number ~ 1 : viscoelastic



Silly putty

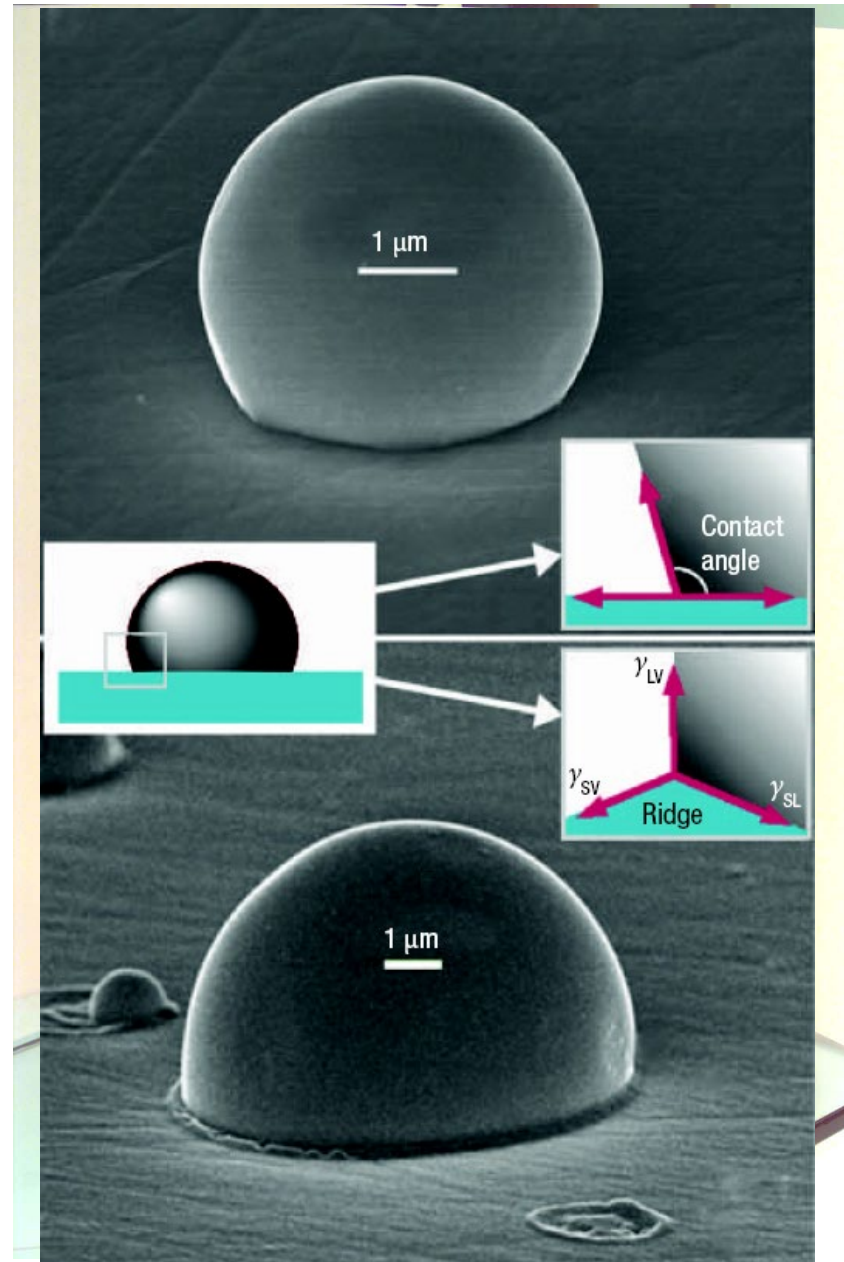


Bitumen film

Pitch drop experiment

Deborah Number $\gg 1$: solid-like

	Date	Event
	1927	Experiment set up
	1930	The stem was cut
December	1938	1st drop fell
February	1947	2nd drop fell
April	1954	3rd drop fell
May	1962	4th drop fell
August	1970	5th drop fell
April	1979	6th drop fell
July	1988	7th drop fell
November 28, 2000		8th drop fell



Huge landslide at the Dolomites in Italy

Deborah Number >>> 1: solid-like

October 12, 2007

This morning an overshadowing landslide collapsed from the Cima Una peak (2.598 meters) of the Dolomites in Southern Tyrol, which is situated in Northern Italy.

Teams of the Italian Civil Defense, of the Fire Department and of the Police Department are already working since a few moments after the fact, they affirmed that 60.000 cubic meters fell, obscuring the sky and complicating their work, but fortunately nothing makes think that there are injured people or victims.



"History" of solid surfaces (the Solid Surfaces' evil cont'd)

- ◇ Formative and environmental history of the sample

Cleaving, Grinding, Polishing, Etching, Sandblasting

- ◇ Presence (or absence) of adsorbed species and surface **contamination**

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Kinetic hysteresis (swelling)

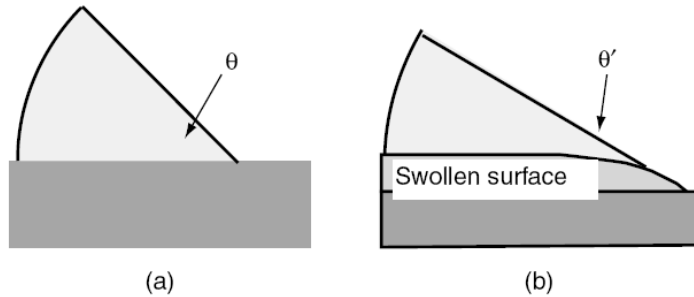


FIGURE 17.6. If the liquid used for measuring the contact angle is absorbed into the solid surface (i.e., it swells) the resulting contact angle will be smaller than the “true” value.

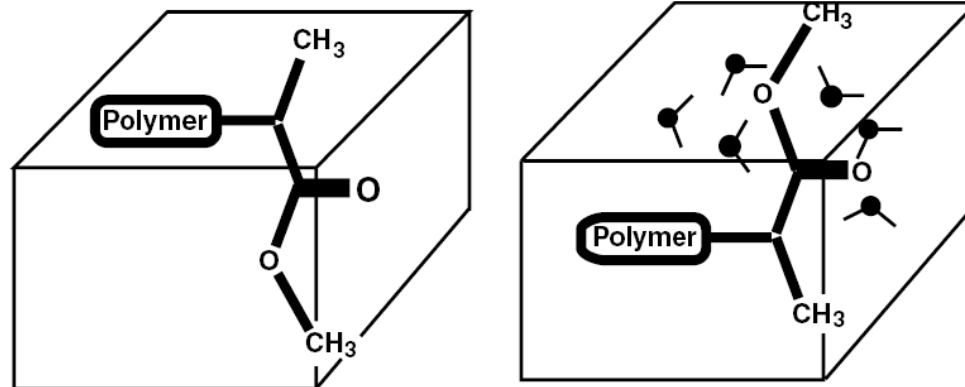
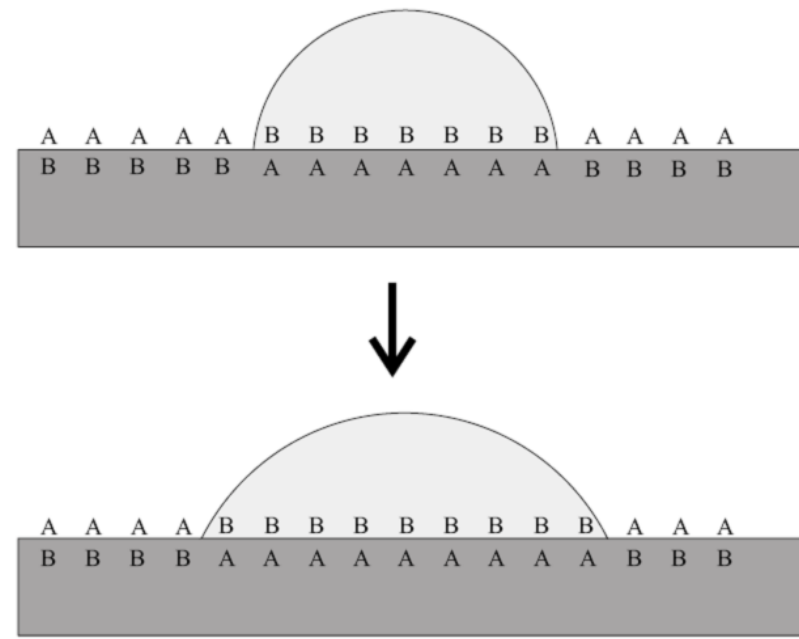


FIGURE 7.7. Rigid, hydrophobic polymers such as poly(methylmethacrylate) that contain somewhat hydrophilic ester side chains may, in prolonged contact with water, undergo surface molecular reorientation due to the interaction of water with the ester groups. The interfacial region may become plasticized or softened as a result of the water–ester interaction, liberating to some extent the side chains (or “lubricating” the interchain interaction region) and increasing their mobility.

Outline

- ◇ Historical overview
- ◇ Revised Surface Thermodynamics
- ◇ The Solid Surfaces' evil
- ◇ Other controversial issues
- ◇ References

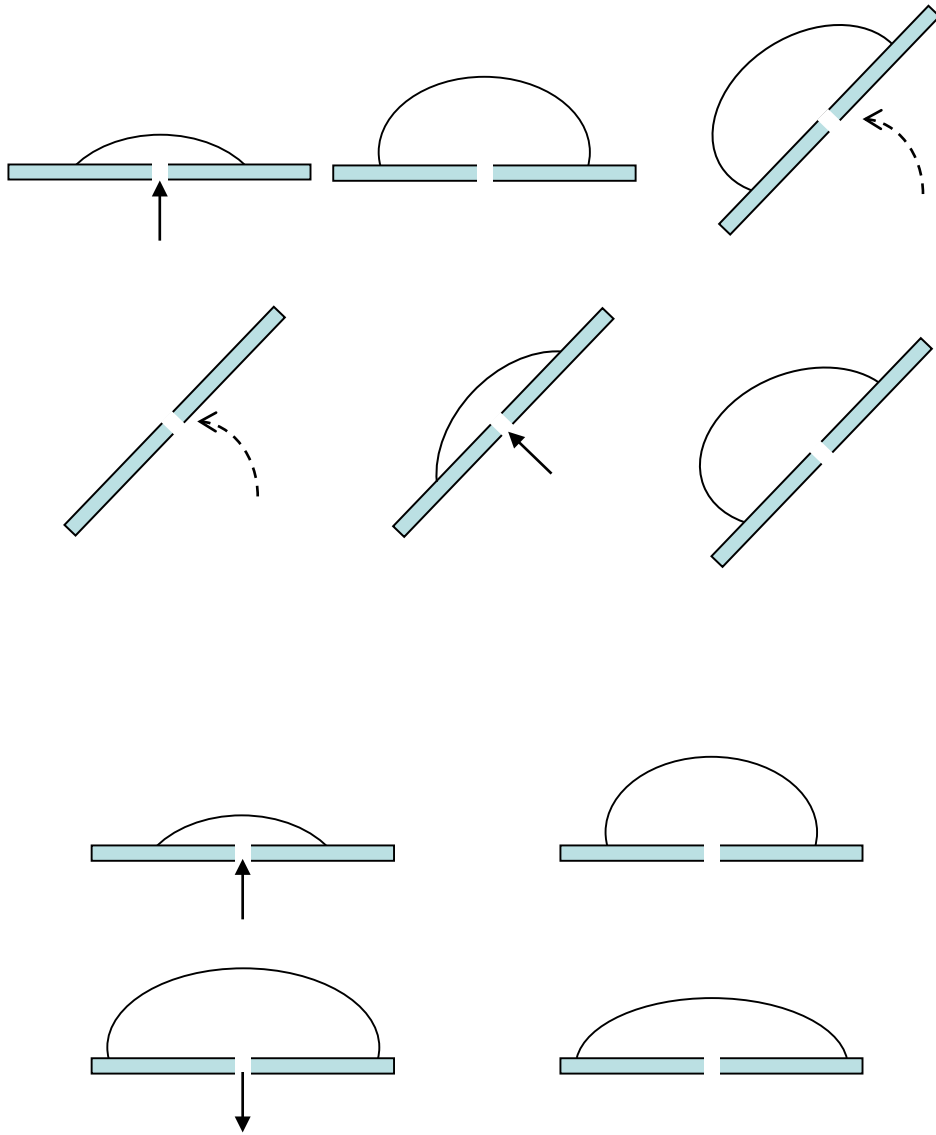
Curvature Corrections to specific interfacial free energy

$$\sigma_{\alpha\beta} = \gamma_{\alpha\beta} + C_H H + C_K K$$

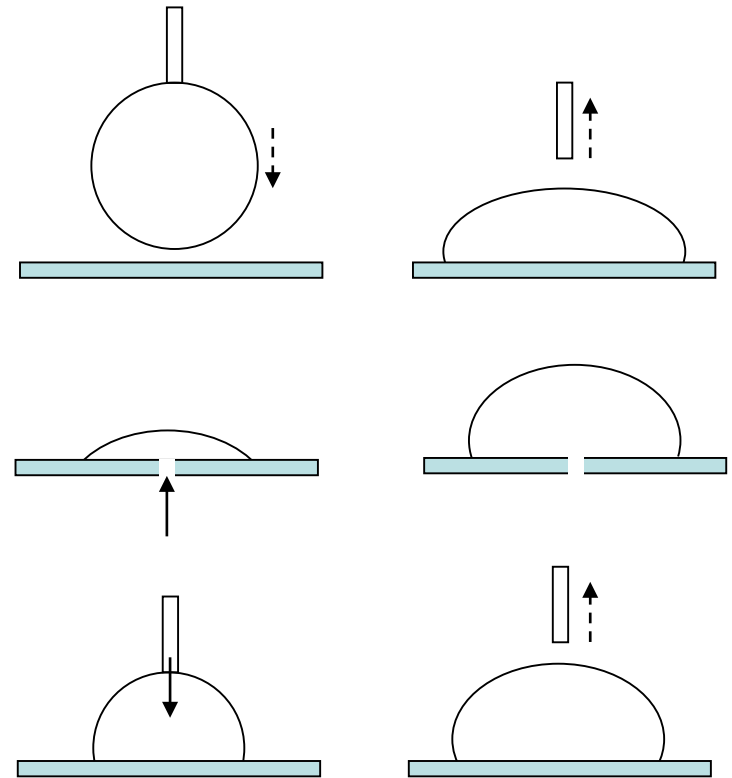
$$H = \frac{1}{2}(\kappa_1 + \kappa_2)$$

$$K = \kappa_1 \kappa_2$$

Moderately curved interface: $C_H \sim 10^{-5} \text{ J/m}$

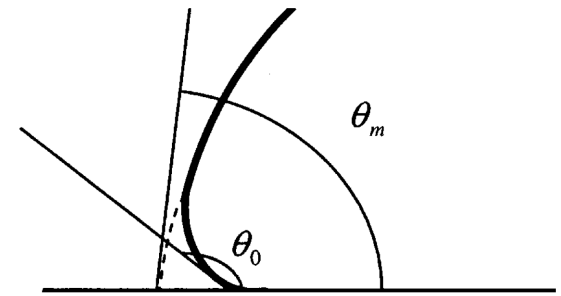


Contact angle hysteresis
("history" of the system)

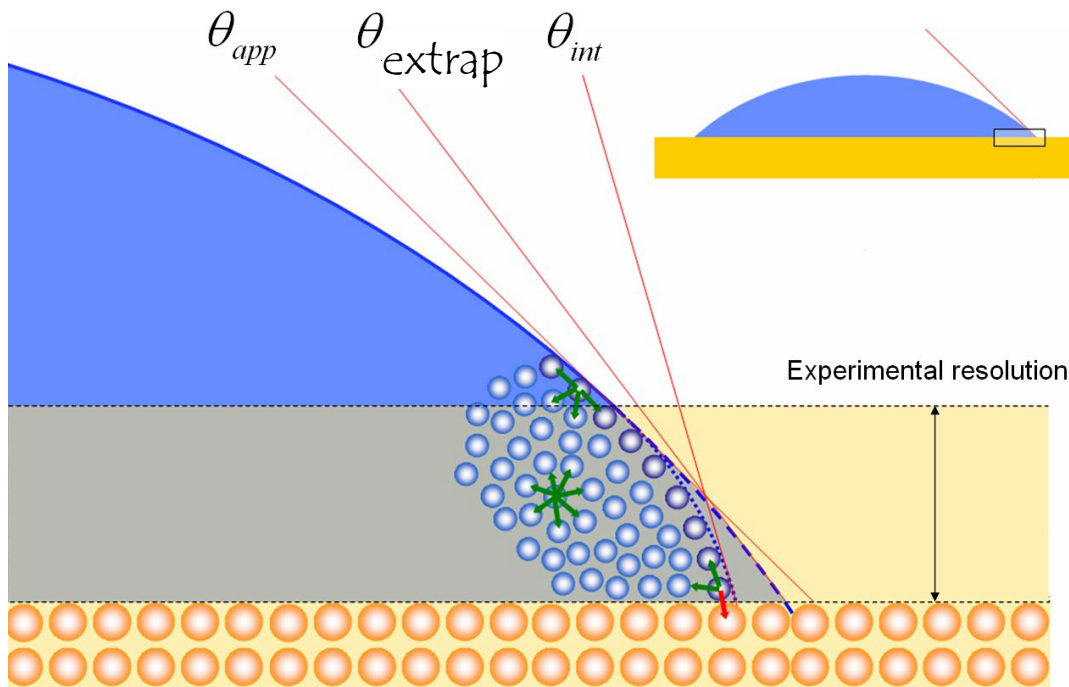


Scales of contact angle

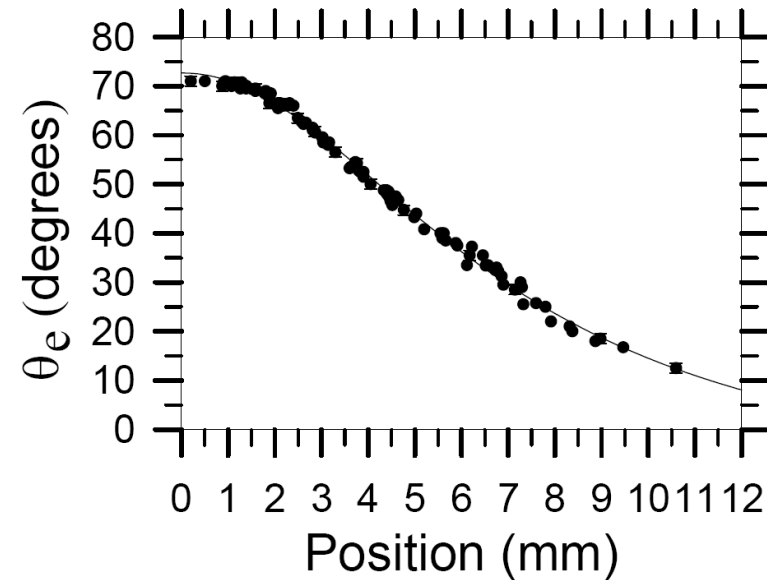
Optically or atomically ideal surface?



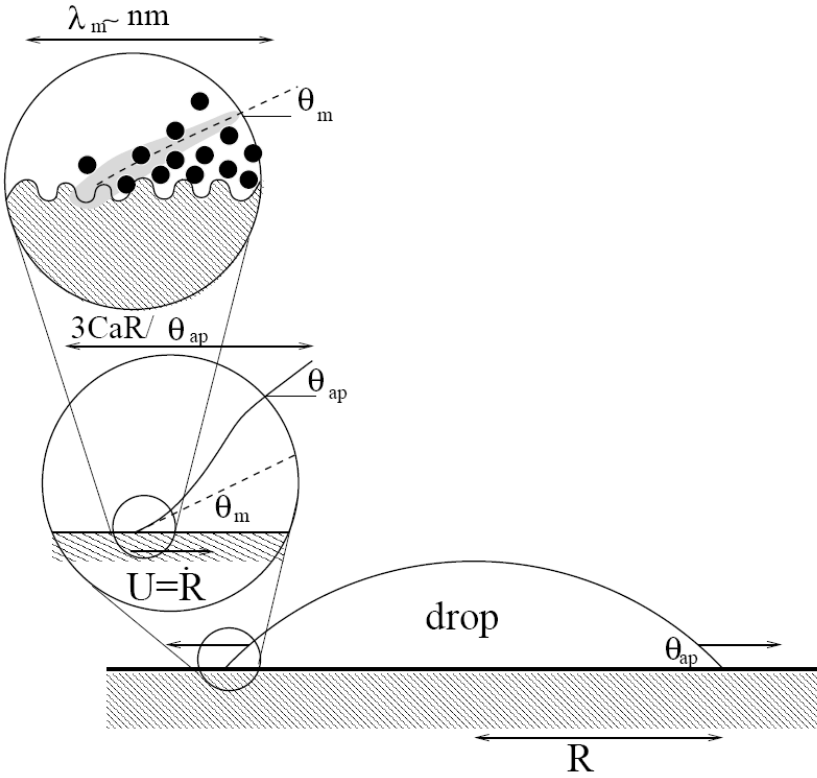
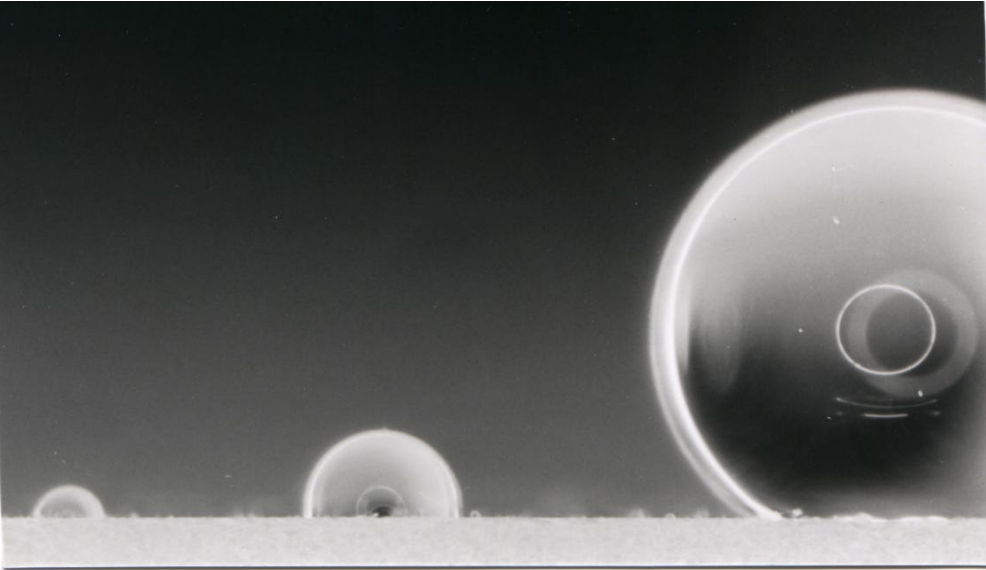
Macroscopic, θ_m , and microscopic, θ



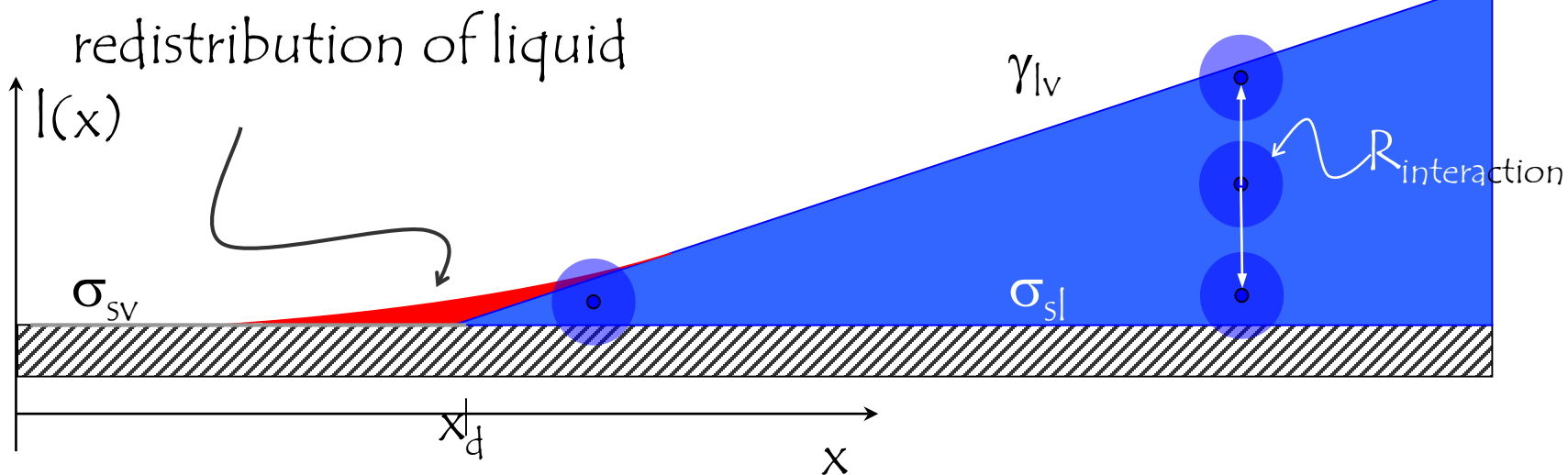
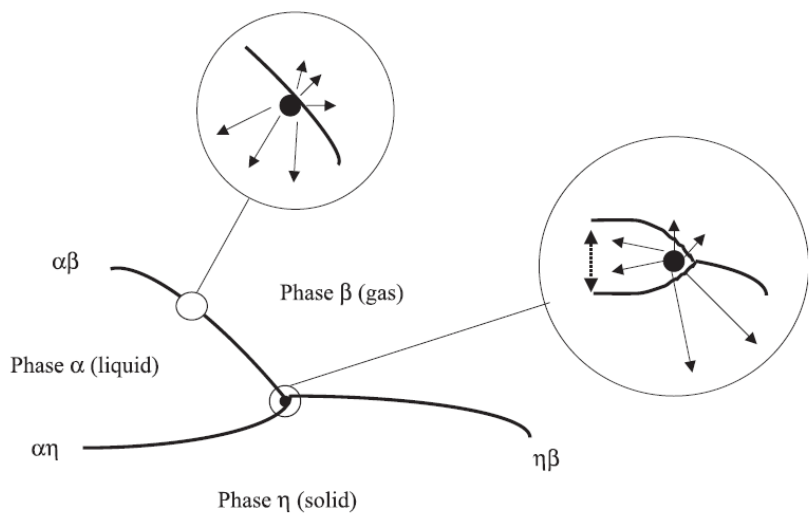
Static contact angle



Drop Size on contact angle: line tension, long-range forces...

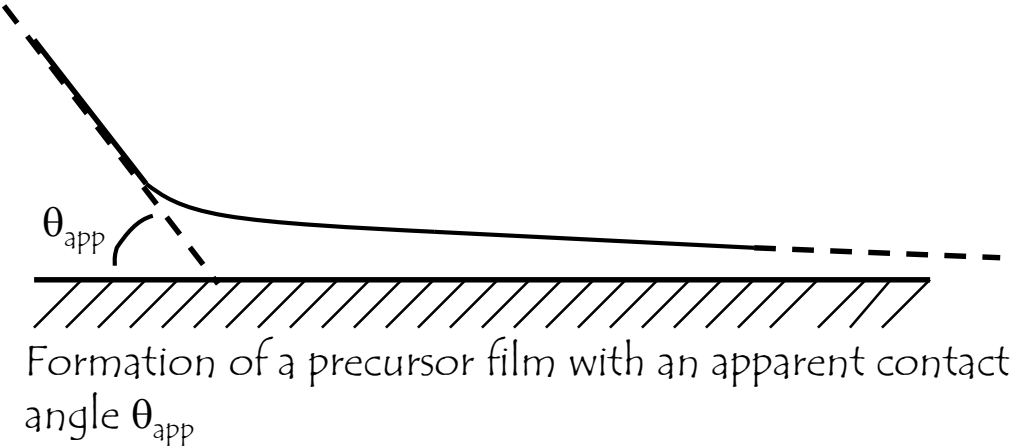


$$\cos \theta_{int} = \cos \theta_Y - \frac{\sigma_{slv}}{\gamma_{lv} r_c}$$



Schematic drop profile. In the vicinity of the three-phase contact line there is a redistribution of liquid from the spherical cap profile observable, which is caused by the effective interface potential.

Precursor film: surface pressure



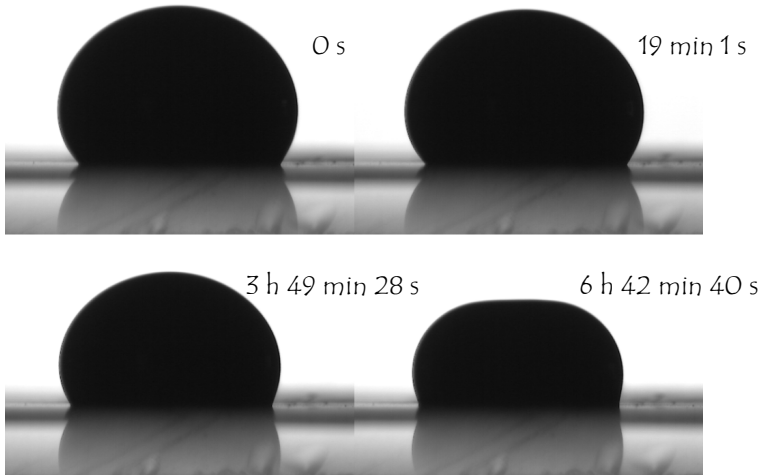
Young-Bangham equation

$$\sigma_S - \pi - \sigma_{SL} = \sigma_{LV} \cos \theta_Y$$

Drying, Soldering, Polymerization

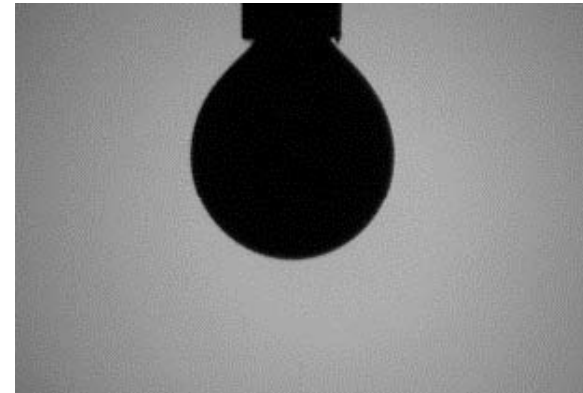
Shape of desiccated, solder, polymerized drops may **not** represent neither their surface tension nor their contact angle

Desiccation

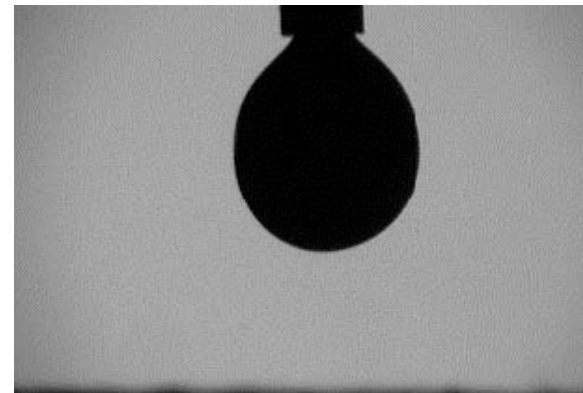


Bitumen emulsion

Surface oxidation

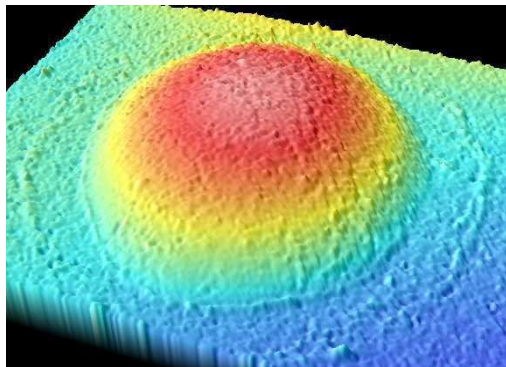


Unoxidized solder

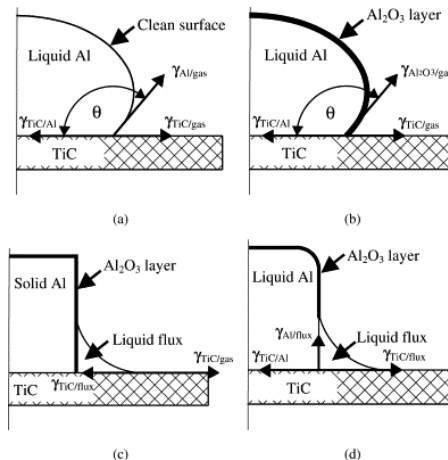


Oxidized solder

Polymerization shrinkage



Dental resin



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