EPFL

École polytechnique fédérale de Lausanne

Institute of Materials - Institute of Bioengineering

sunmil.epfl.ch

SuNMIL

Supramolecular NanoMaterials and Interfaces Laboratory

Solid-Liquid Interfaces
Lesson 4

MSE 304

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Key Topics in the Previous Class

1) adatoms
2) defects on surface
3) TLK
4) Reconstructions

Reading Material

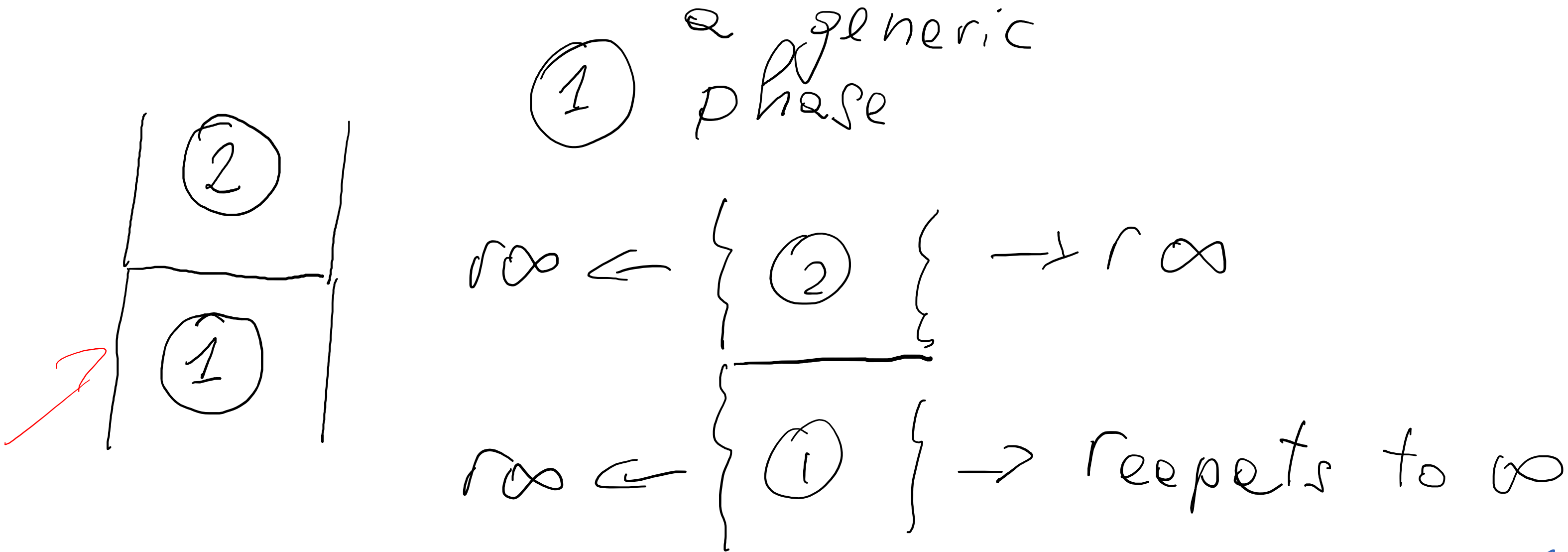
For this class please read Chapter 17 of J. Israelchvili, ”Intermolecular & Surface Forces” (Third Edition), Academic Press

In particular please read with attention paragraphs 17.1, 17.4, 17.5, 17.5

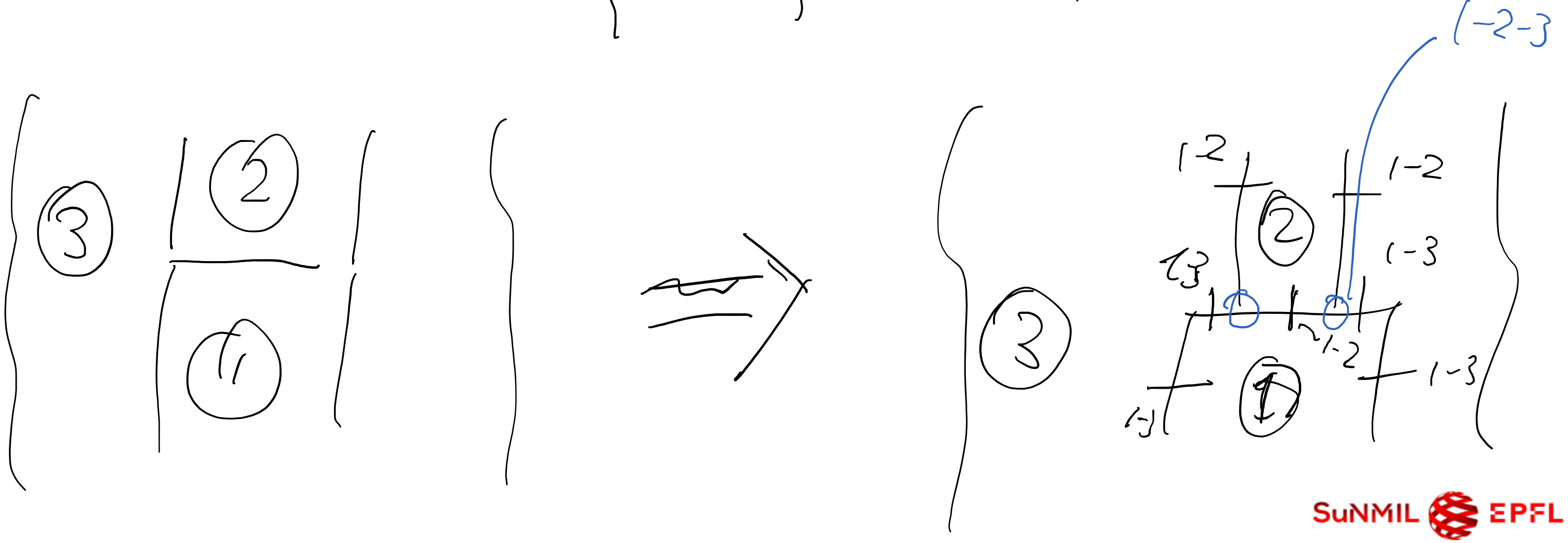
FIRST CLASS ON INTERFACES

Interfaces

What is an Interface?



Are they always that simple?



Interfacial Energy

General Definition (from previous classes and basic Thermodynamics knowledge)

$$G = \sum_i \mu_i^{\infty} N_i + \sum_{(hkl)}^{\text{all}} \sum_{ij} f_{ij}^{hkl} A_{ij}^{hkl} \quad \left(= \sum_i \mu_i^{r} N_i \qquad r = \text{real} \right)$$

Simplified Case

$$G = \sum_i \mu_i^{\infty} N_i + \underbrace{\sum_i^{\text{all phase}} \tilde{\gamma}_i A_i}$$

$$\text{free energy} \rightarrow \tilde{\gamma} \rightarrow \gamma \leftarrow \text{energy}$$

Interfacial Energy as Work to Create an Interface/Surface

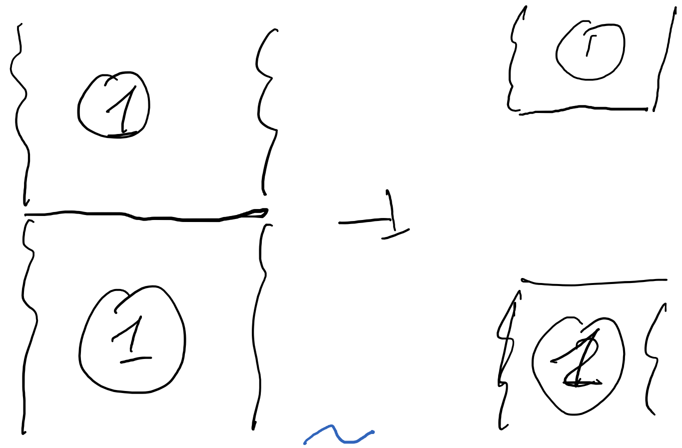
Work of Choesion

→ at constant p, T, and n_i

W_{11}

*reversible work per unit area

to separate 2 surface of phase 1



$$W_{11} = \frac{1}{2}\tilde{\gamma}_1$$

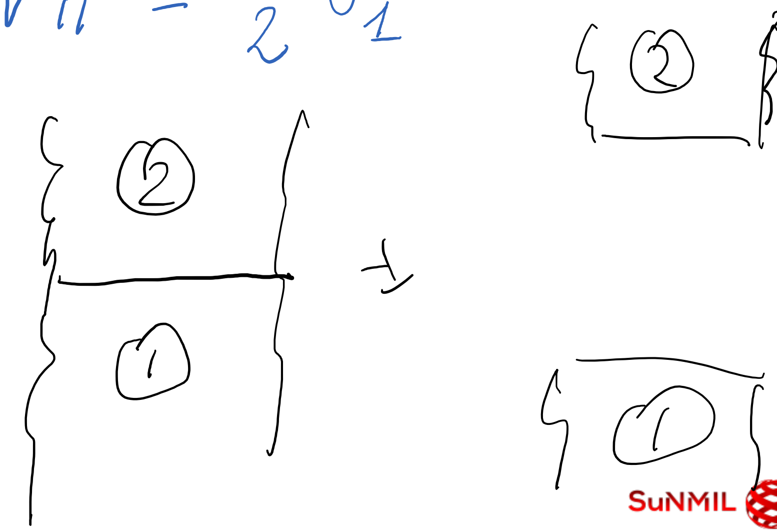
Work of Adhesion

→ at constant p, T, and n_i

W_{12}

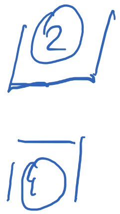
*reversible work per unit area

to separate a surface 1 from a surface 2



Interfacial Energy and the Work of Adhesion

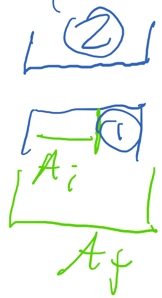
$\tilde{\gamma}_{12}$ reversible work to create a unit area (ΔA) of interface 1/2 at constant p, T, n_i



a) seperate 1 and 2 $\quad W_{12} \cdot A_i$

b) increase the surface area of 1 to A_f (from A_i) $\quad \frac{1}{2} W_{11}(A_f - A_i) = \frac{1}{2} W_{11} \Delta A$

c) increase the surface area of 2 to A_f $\quad \frac{1}{2} W_{22} \Delta A$



d) put 1 and 2 together $\quad - W_{12} A_f$

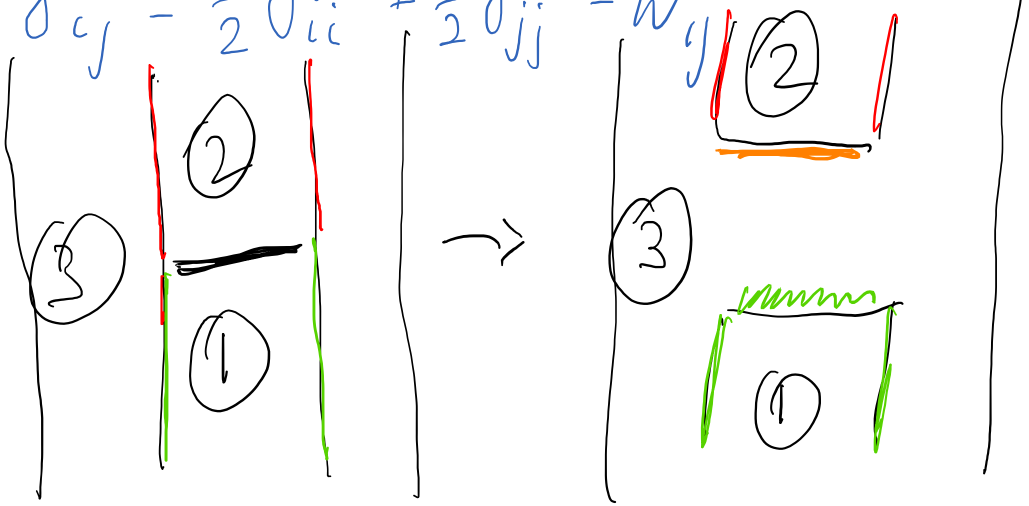
a + b + c + d

$$\tilde{\gamma}_{12} \cdot \Delta A = W_{12} A_i + \frac{1}{2} W_{11} \Delta A + \frac{1}{2} W_{22} \Delta A - W_{12} A_f = \underline{\left(\frac{1}{2} W_{11} + \frac{1}{2} W_{22} - W_{12}\right)} \Delta A$$

Multiple Interfaces, Generalization of the Model

$$\tilde{\gamma}_{12} = \frac{1}{2} W_{11} + \frac{1}{2} W_{22} - W_{12} = \tilde{\gamma}_1 + \tilde{\gamma}_2 - W_{12} \quad *$$

$$\gamma_{ij} = \frac{1}{2}\gamma_{ii} + \frac{1}{2}\gamma_{jj} - W_{ij}$$



$$W_{123} = \tilde{\gamma}_{13} + \tilde{\gamma}_{23} - \tilde{\gamma}_{12} =$$

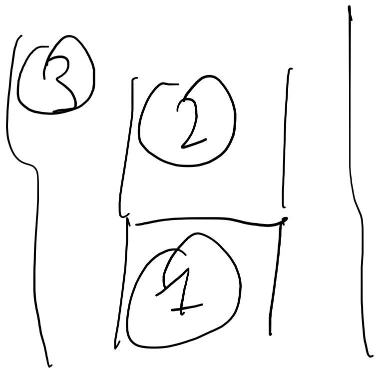
$$= \cancel{\tilde{\gamma}_1} + \tilde{\gamma}_3 - W_{13} + \cancel{\tilde{\gamma}_2} + \tilde{\gamma}_3 - W_{23} -$$

$$- (\cancel{\tilde{\gamma}_1} + \cancel{\tilde{\gamma}_2} - W_{23}) =$$

$$= 2\tilde{\gamma}_{33} + W_{13} + W_{23} - W_{12} = W_{123} \Rightarrow S \text{ or } \Pi$$

spreading coefficient

The case of a generic Solid-Liquid Interface of finite size



where

1 = solid

2 = liquid

3 = gas → vapor

$$W_{123} = 2\tilde{\gamma}_{33'} + W_{13} + W_{23} - W_{12} = W_{33'} + W_{13} + W_{23} + W_{12}$$

$$W_{SLV} = \underbrace{2\tilde{\gamma}_{V}}_{=0} + W_{SV} + W_{LV} - W_{SL} = W_{SV} + W_{LV} - W_{SL} =$$

$$W_{SLV} = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$ Dupré equation

Young's Theorem

$$dG = Vdp - SdT + \sum_\alpha \sum_i \mu_i^\alpha dn_i^\alpha + \underline{d(\gamma A)}$$

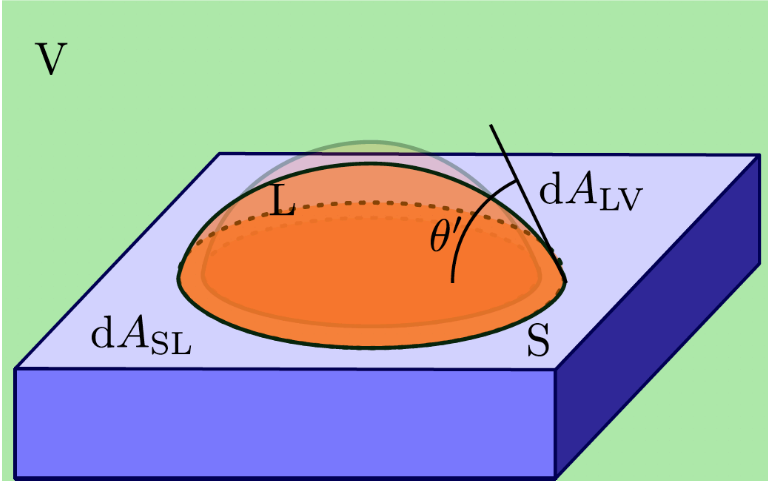
at constant p, T,

and constant n_i^α $\forall i$ and $\forall \alpha$

no chemical reaction allowed

$\hookrightarrow d\gamma = 0$ $\quad \left\{ \sum_\alpha \underline{\sum_{hkl}} d(\gamma^\alpha_{hkl} A^\alpha_{hkl}) \right\} \longrightarrow \sum_\alpha \gamma^\alpha dA^\alpha$

$$dG = 0 \Rightarrow \sum_\alpha \gamma^\alpha dA^\alpha = 0$$



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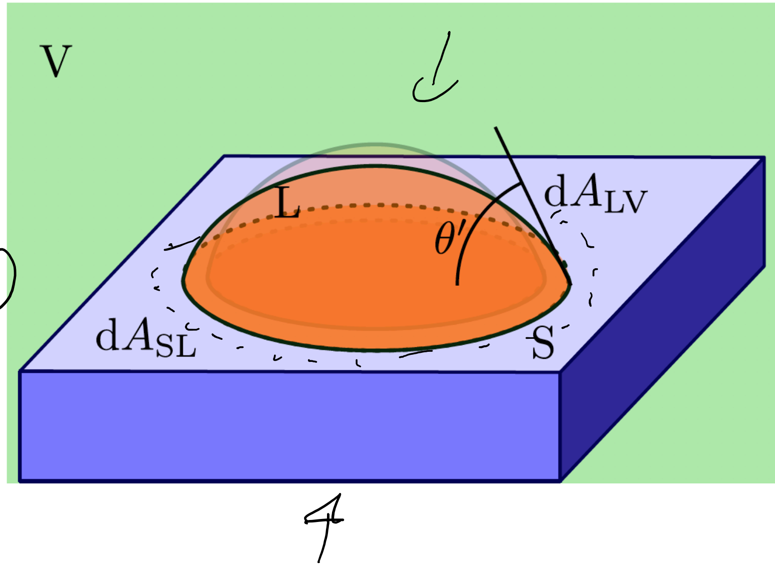
Young's Theorem

$$\sum_{\alpha} \gamma^{\alpha} dA^{\alpha} = 0$$

$$\gamma_{SL}\, dA_{SL} + \gamma_{SV}\, dA_{SV} + \gamma_{LV}\, dA_{LV} = 0$$

equilibrium condition



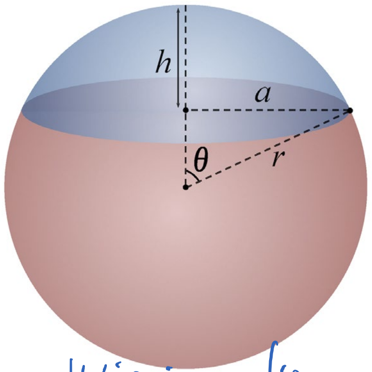
$$dA_{SV} = -dA_{SL}$$

$$(\gamma_{SL} - \gamma_{SV})\, dA_{SL} + \gamma_{LV}\, dA_{LV} = 0$$

Young's Theorem

the shape of the liquid is known

spherical cap (calotte)



wikipedia

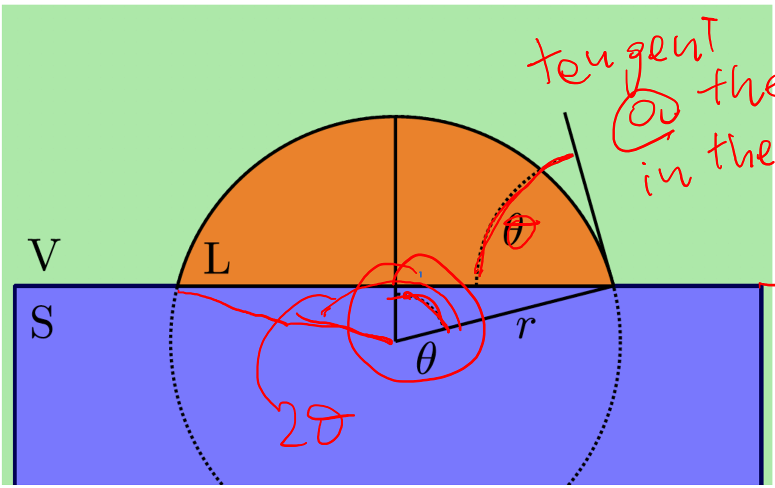
dn_i = constant
at constant volume of the liquid

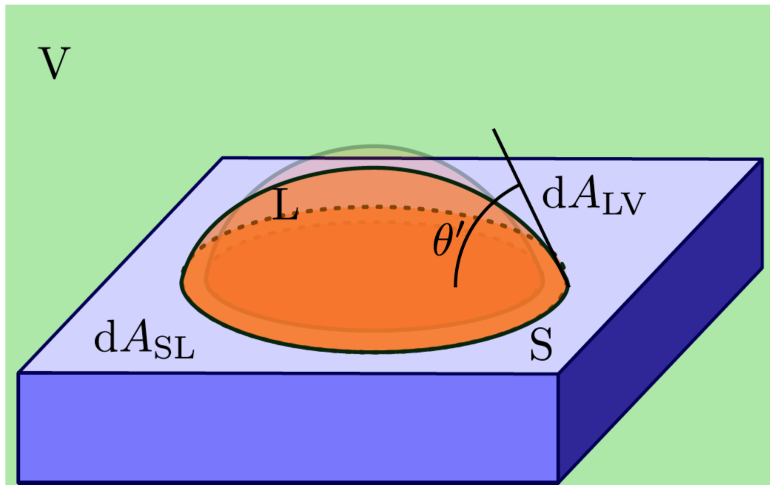
$$V = \frac{\pi h^2}{3}(3r - h) = \frac{\pi}{3} r^3 (2 + \cos\theta)(1 - \cos\theta)^2$$

$$A_{LV} = 2\pi r h = 2\pi r^2 (1 - \cos\theta)$$

$$A_{SL} = \pi a^2 = \pi r^2 \sin\theta^2$$

dA_{LV} $\quad$ dA_{SL}





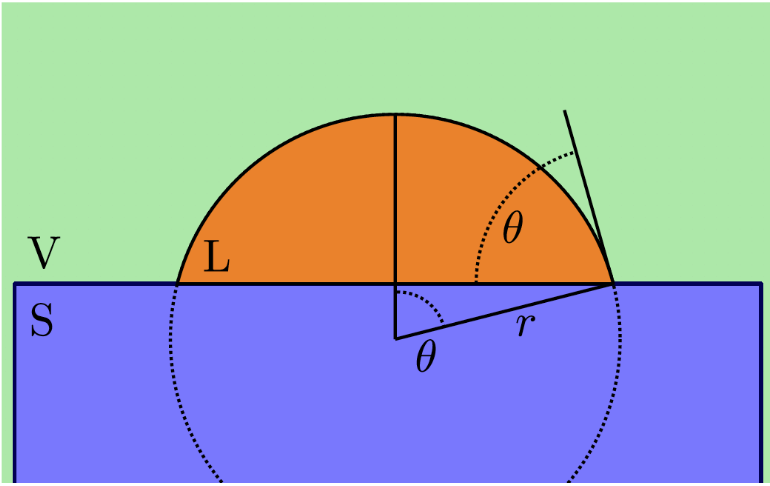
Young's Theorem

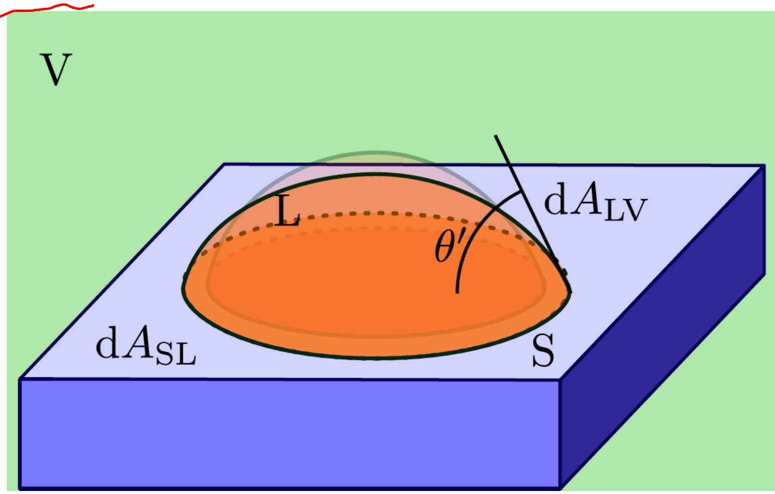
$$\frac{\partial V}{\partial \theta} = \frac{\pi}{3} 3r^2 \frac{dr}{d\theta}(2+\cos\theta)(1-\cos\theta)^2 - \frac{\pi}{3} r^3 \sin\theta\,(1-\cos\theta)^2 + \frac{\pi}{3} r^3 (2+\cos\theta)(1-\cos\theta)\sin\theta$$

boundary condition // $\frac{\partial V}{\partial \theta} = 0$

$$0 = 3\frac{dr}{d\theta}(2+\cos\theta)(1-\cos\theta) - r\sin\theta\,(1-\cos\theta) + r(2+\cos\theta)\sin\theta$$

$$\boxed{\frac{1}{r}\frac{dr}{d\theta} = \frac{\sin\theta\,(1+\cos\theta)}{(2+\cos\theta)(1-\cos\theta)}}$$





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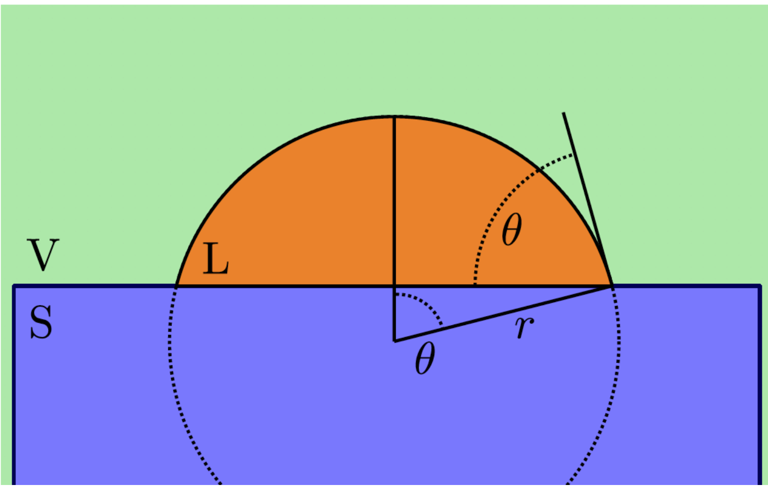
Young's Theorem

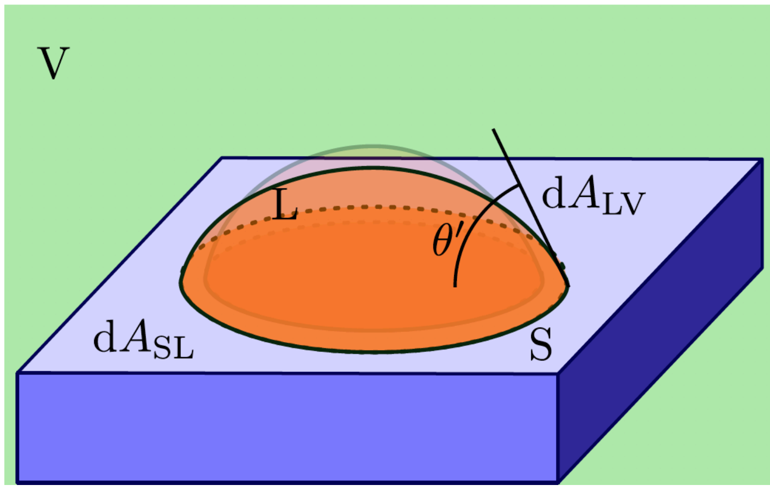
$(dA_{LV})_V \rightarrow (dA_{SL})_V$

$$\left(\frac{dA_{LV}}{dA_{SL}}\right)_V = \left(\frac{\left(\partial A_{LV}/\partial\theta\right)_V}{\left(\partial A_{SL}/\partial\theta\right)_V}\right)$$

$$A_{LV} = 2\pi rh = 2\pi r^2(1-\cos\theta) \longrightarrow \left(\frac{\partial A_{LV}}{\partial\theta}\right)_V = 4\pi r\frac{dr}{d\theta}(1-\cos\theta) + 2\pi r^2\sin\theta$$

$$A_{SL} = \pi a^2 = \pi r^2\sin\theta^2 \longrightarrow \left(\frac{\partial A_{SL}}{\partial\theta}\right)_V = 2\pi r\frac{dr}{d\theta}\sin\theta^2 + 2\pi r^2\sin\theta\cos\theta$$





Young’s Theorem

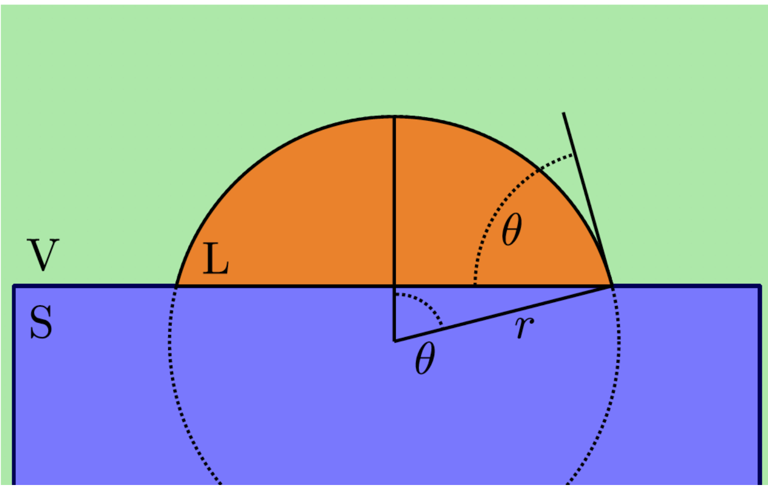
$$\left(\frac{\partial A_{LV}}{\partial \theta}\right)_V = 4\pi r \frac{dr}{d\theta}(1-\cos\theta) + 2\pi r^2 \sin\theta$$

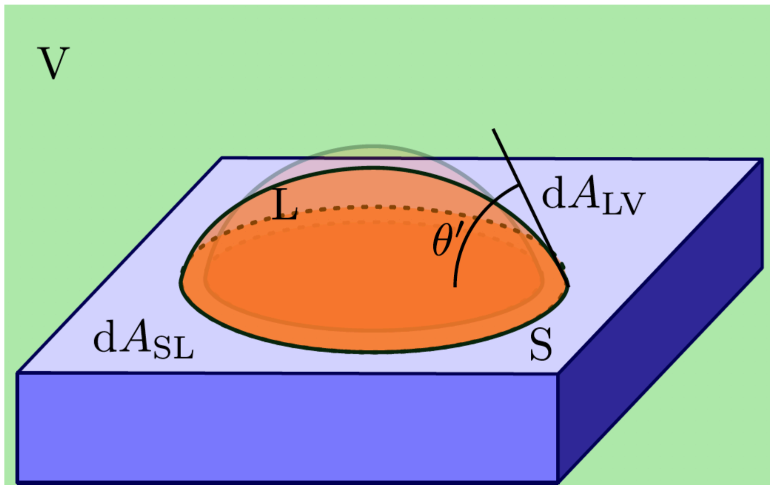
$$\left(\frac{dA_{LV}}{dA_{SL}}\right)_V = \left(\frac{\left(\partial A_{LV}/\partial\theta\right)_V}{\left(\partial A_{SL}/\partial\theta\right)_V}\right)$$

$$\left(\frac{\partial A_{SL}}{\partial \theta}\right)_V = 2\pi r \frac{dr}{d\theta}\sin\theta^2 + 2\pi r^2 \sin\theta\cos\theta$$

$$\left(\frac{dA_{LV}}{dA_{SL}}\right)_V = \left(\frac{\left(\partial A_{LV}/\partial\theta\right)_V}{\left(\partial A_{SL}/\partial\theta\right)_V}\right) = \frac{2\frac{dr}{d\theta}(1-\cos\theta) + r\sin\theta}{\frac{dr}{d\theta}\sin\theta^2 + r\sin\theta\cos\theta} = \frac{2\frac{1}{r}\frac{dr}{d\theta}(1-\cos\theta) + \sin\theta}{\frac{1}{r}\frac{dr}{d\theta}\sin\theta^2 + \sin\theta\cos\theta}$$

$\frac{1}{r^2}$



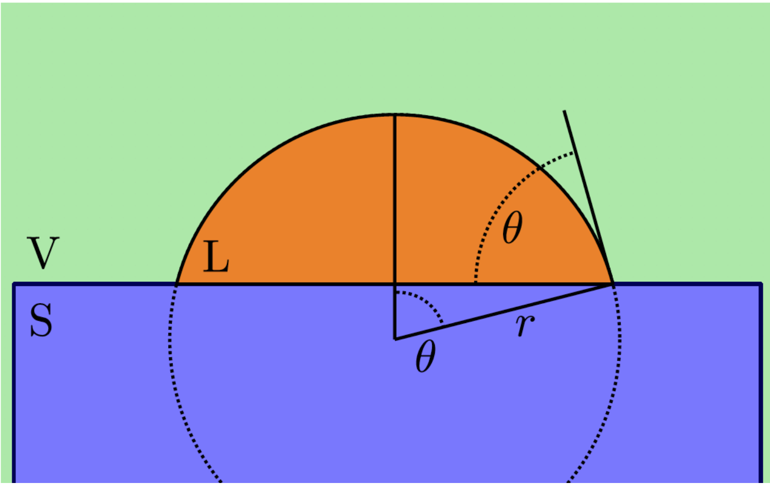


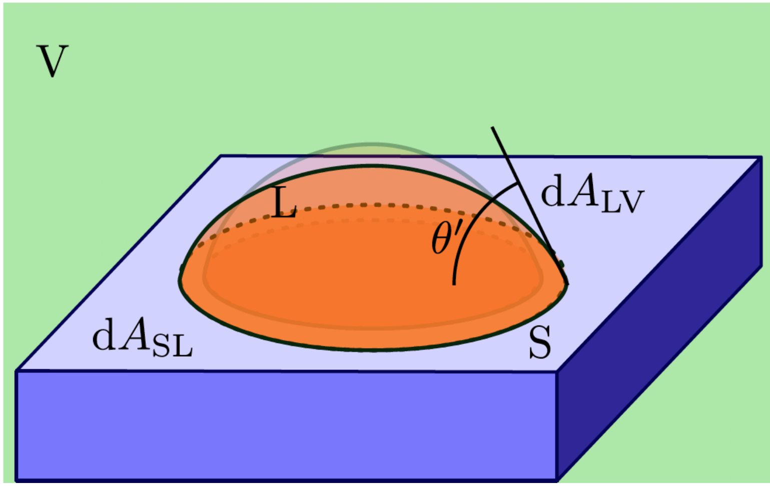
Young's Theorem

$$\left(\frac{dA_{LV}}{dA_{SL}}\right)_V = \left(\frac{\left(\partial A_{LV}/\partial\theta\right)_V}{\left(\partial A_{SL}/\partial\theta\right)_V}\right) = \frac{2\boxed{\frac{1}{r}\frac{dr}{d\theta}}(1-\cos\theta)+\sin\theta}{\boxed{\frac{1}{r}\frac{dr}{d\theta}}\sin\theta^2+\sin\theta\cos\theta}$$

$$\boxed{\frac{1}{r}\frac{dr}{d\theta}} = \frac{\sin\theta\,(1+\cos\theta)}{(2+\cos\theta)(1-\cos\theta)}$$

$$\left(\frac{dA_{LV}}{dA_{SL}}\right)_V = \left(\frac{\left(\partial A_{LV}/\partial\theta\right)_V}{\left(\partial A_{SL}/\partial\theta\right)_V}\right) = \frac{2\frac{\sin\theta\,(1+\cos\theta)}{(2+\cos\theta)(1-\cos\theta)}(1-\cos\theta)+\sin\theta}{\frac{\sin\theta\,(1+\cos\theta)}{(2+\cos\theta)(1-\cos\theta)}\sin\theta^2+\sin\theta\cos\theta} = \cos\theta$$





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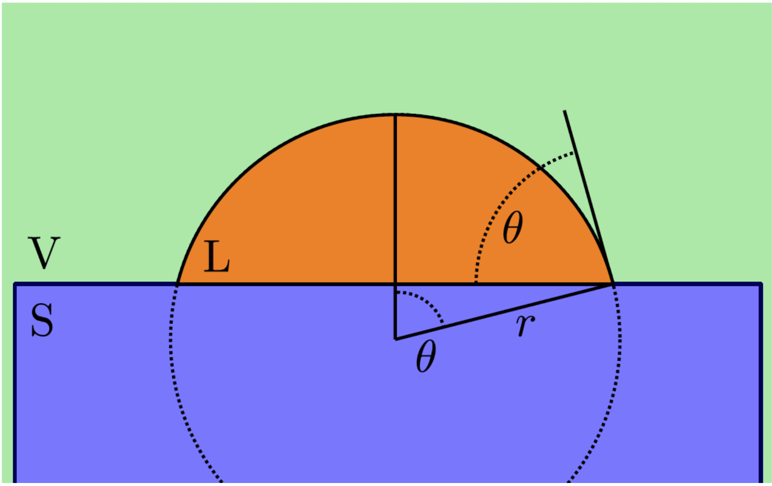
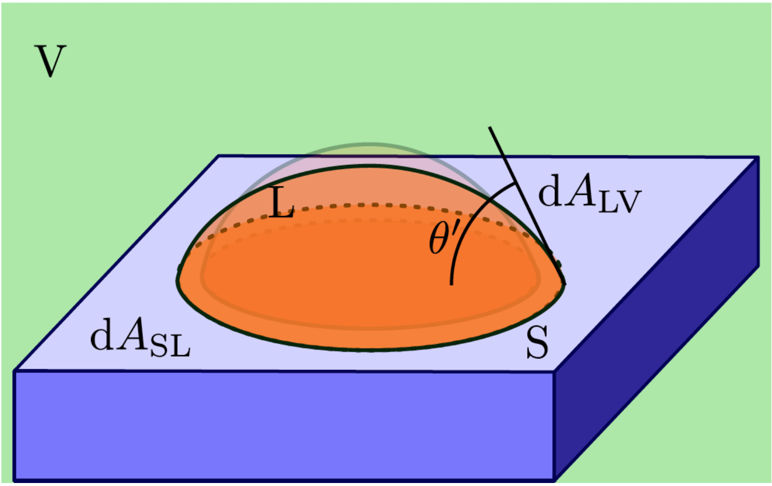
Young's Theorem

$$\left(\frac{dA_{LV}}{dA_{SL}}\right)_V = \left(\frac{\left(\partial A_{LV}/\partial\theta\right)_V}{\left(\partial A_{SL}/\partial\theta\right)_V}\right) = \frac{2\,\frac{\sin\theta\,(1+\cos\theta)}{(2+\cos\theta)(1-\cos\theta)}(1-\cos\theta)+\sin\theta}{\frac{\sin\theta\,(1+\cos\theta)}{(2+\cos\theta)(1-\cos\theta)}\sin\theta^2+\sin\theta\cos\theta} = \cos\theta$$

$$\boxed{\left(\frac{dA_{LV}}{dA_{SL}}\right)_V = \cos\theta}$$

$dA_{LV} = dA_{SL} \cdot \cos\theta$
@ constant V





Young’s Theorem

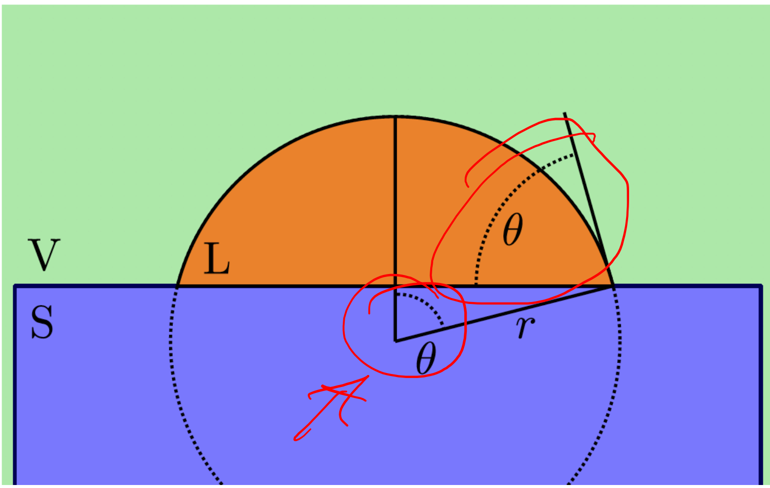
$$(\gamma_{SL} - \gamma_{SV})\, dA_{SL} + \gamma_{LV}\, dA_{LV} = 0$$

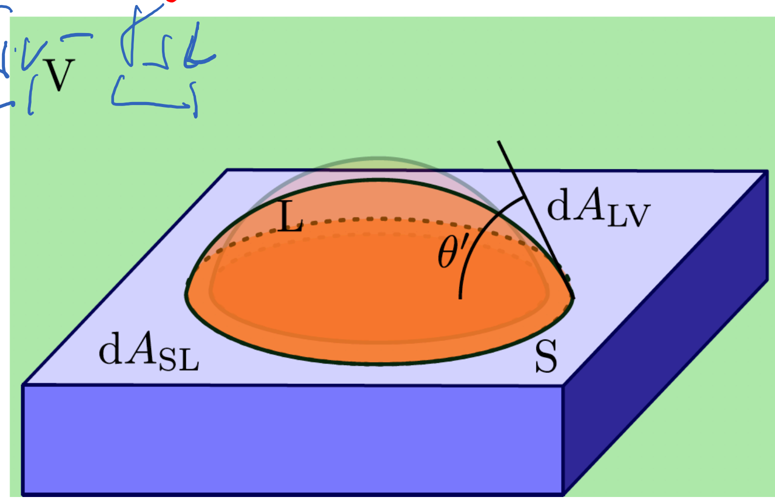
$$\rightarrow \quad (\gamma_{SL} - \gamma_{SV})\, \cancel{dA_{SL}} + \gamma_{LV}\, \cancel{dA_{SL}} \cos\theta_0 = 0$$

$$\gamma_{SL} - \gamma_{SV} + \gamma_{LV} \cos\theta = 0 \rightarrow$$

$$\tilde{\gamma}_{LV} \cos\theta = \tilde{\gamma}_{SV} - \tilde{\gamma}_{SL}$$

$$\cos\theta = \frac{\tilde{\gamma}_{SV} - \tilde{\gamma}_{SL}}{\tilde{\gamma}_{LV}}$$





Young-Dupré Equation

$$\gamma_{\mathrm{LV}} \cos\theta_0 = \underline{\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}}}$$

Young's theorem

$$W_{\mathrm{SVL}} = \gamma_{\mathrm{SV}} + \gamma_{\mathrm{LV}} - \gamma_{\mathrm{SL}}$$

Dupré Equation

$$\boxed{\gamma_{\mathrm{LV}}\left(\cos\theta_0 + 1\right) = \gamma_{\mathrm{SV}} + \gamma_{\mathrm{LV}} - \gamma_{\mathrm{SL}} = W_{\mathrm{SVL}}}$$

$$W_{SVL} = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} = \gamma_{LV} + \gamma_{LV}\cos\theta = \underline{\gamma_{LV}}(\cos\theta + 1)$$

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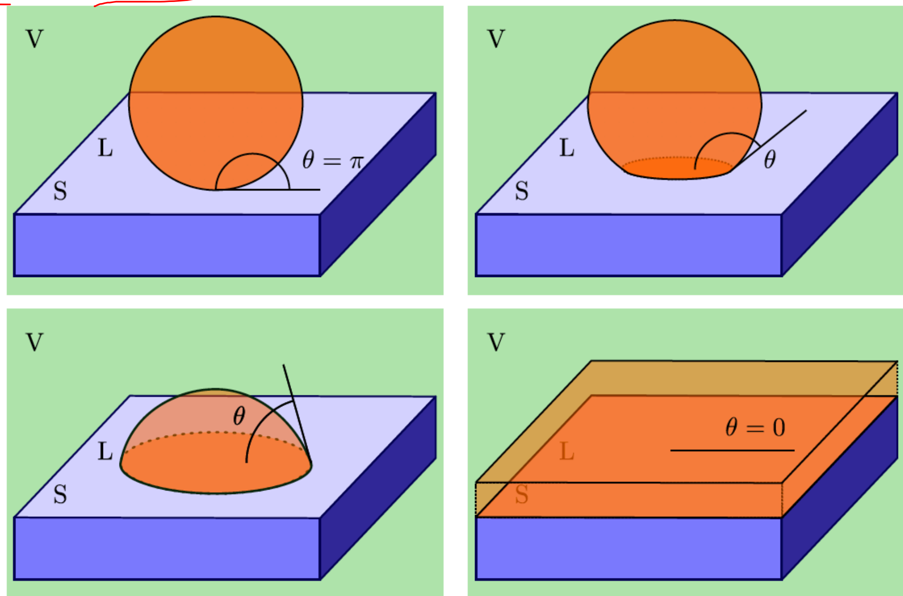
Young-Dupré Equation

$$\boxed{\gamma_{LV}\left(\cos\theta_0 + 1\right) = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} = W_{SVL}}$$

- When $W_{SVL} = 0$, $\theta_0 = \pi$, the droplet does not stick to the surface
- With growing W_{SVL}, θ_0 decreases and the droplet spreads more and more on the surface
- When $\gamma_{SV} \geq \gamma_{LV} + \gamma_{SL}$: complete wettability. The drop forms a film



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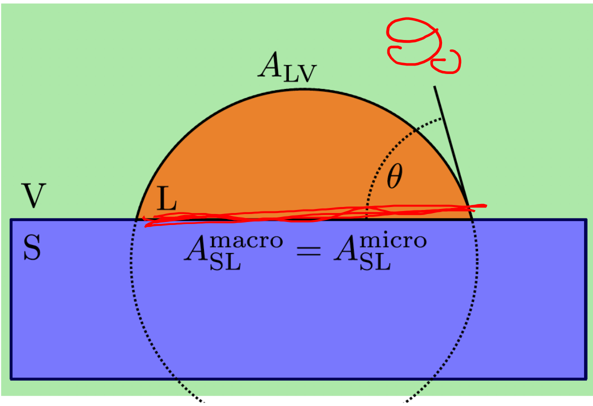
Wenzel Equation

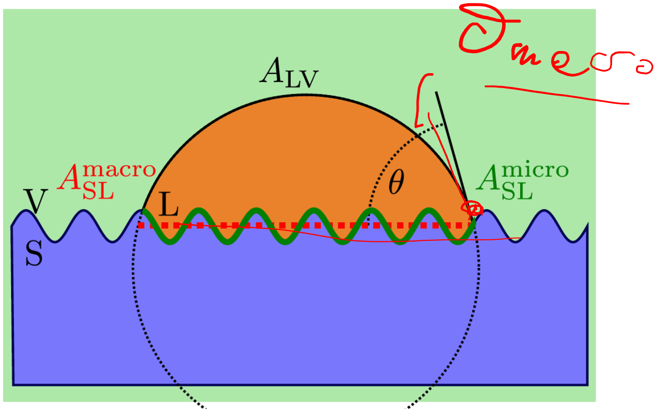
$$\phi = A_{SL}^{micro} / A_{SL}^{macro}$$

$$\gamma_{LV} \cos\theta_{macro} = (\gamma_{SV} - \gamma_{SL})\,\phi, \qquad \gamma_{LV} \cos\theta_0 = (\gamma_{SV} - \gamma_{SL})$$

$\phi \rightarrow rms$

$$\boxed{\cos\theta_{macro} = \phi\cos\theta_0}$$





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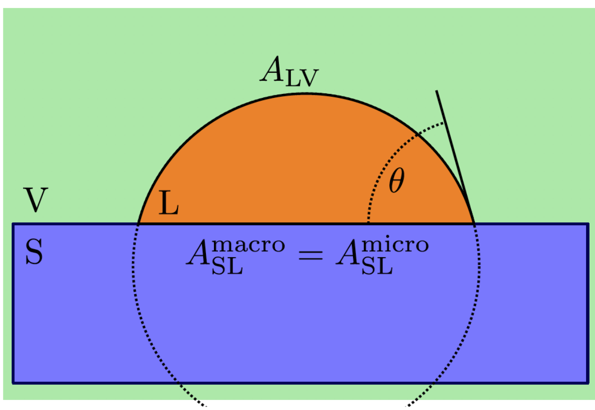
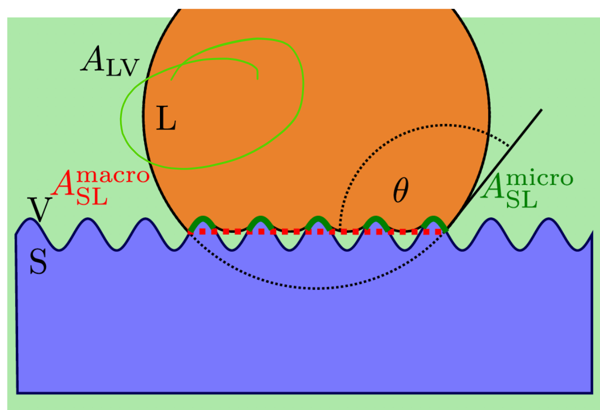
Cassie Equation





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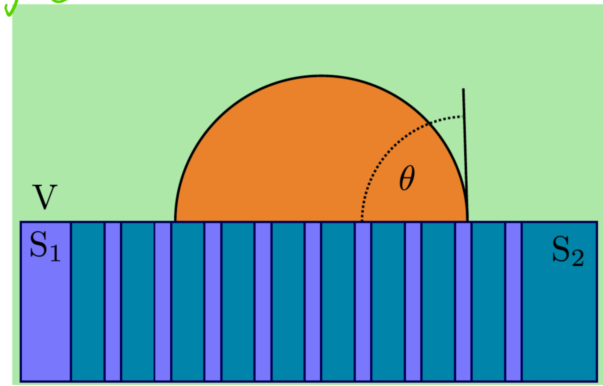
Cassie Equation

$\Phi_1 + \Phi_2 = 1$

$\cos\theta_{macro} = 0.3\cos\theta_1 + 0.7\cos\theta_2$

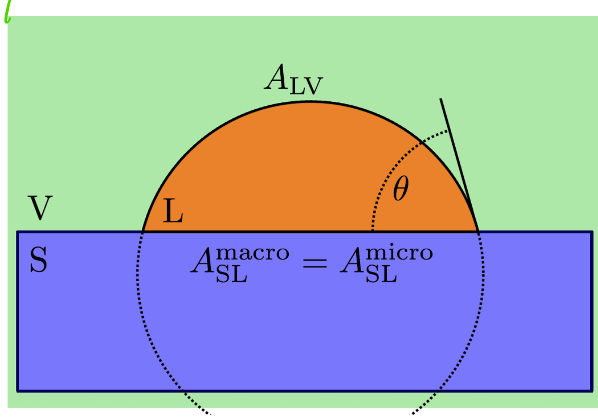
$$\boxed{\cos\theta_{\text{macro}} = \sum_i \phi_i \cos\theta_i}$$

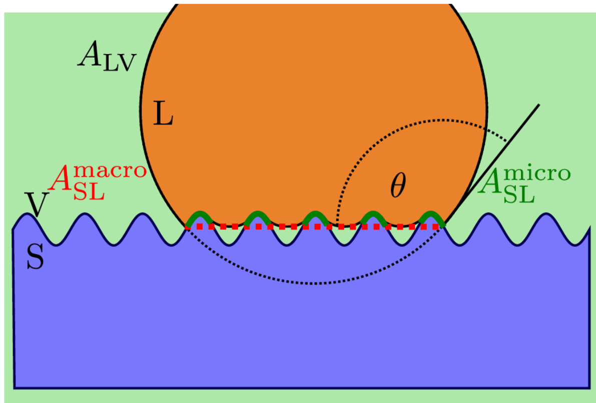
Multi-component surface



$\Phi_1 = 0.3$ $\quad S_1 \rightarrow \theta_1$

$\Phi_2 = 0.7$ $\quad S_2 \rightarrow \theta_2$





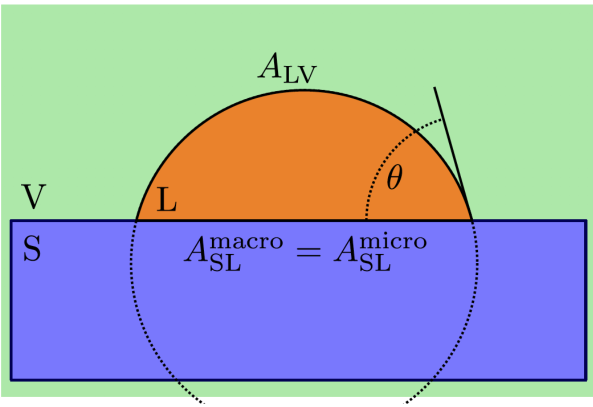
Cassie Equation

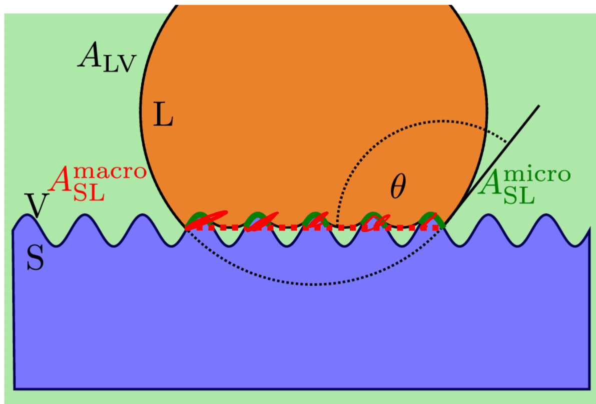
$$\boxed{\cos\theta_{\text{macro}} = \sum_i \phi_i \cos\theta_i}$$ Multi-component surface

$$\boxed{1 + \cos\theta_{\text{macro}} = \phi\,(1 + \cos\theta_0)}$$ Cassie equation

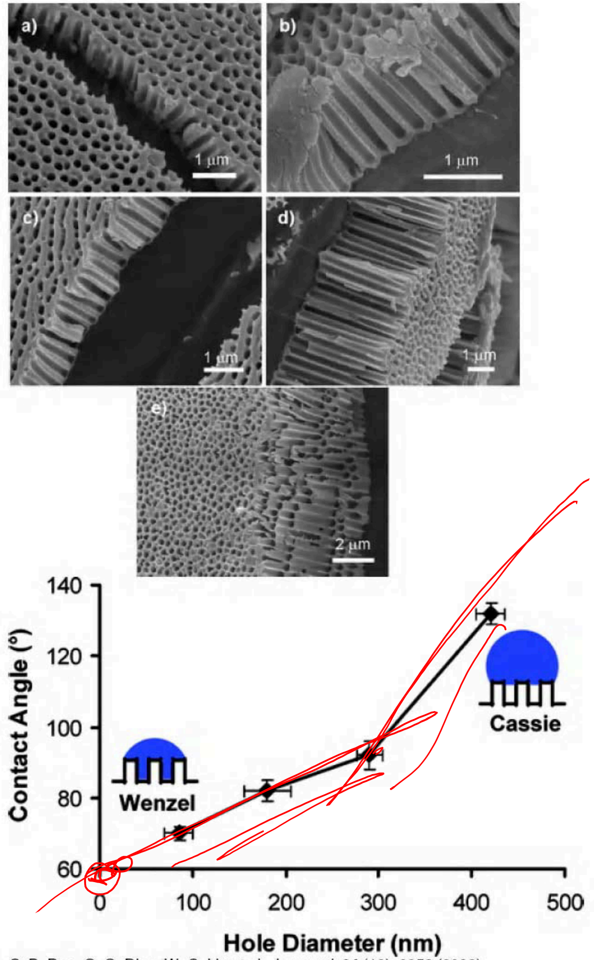
$\cos\theta_{air} = -1 \rightarrow \theta_{air} = \pi$

$\cos\theta_{macro} = \underbrace{\Phi_m}_{} \cdot \cos\theta_m + (1-\Phi_m)\cos\theta_{air} = \Phi_m \cos\theta_m + (1-\Phi_m)\cdot(-1)$

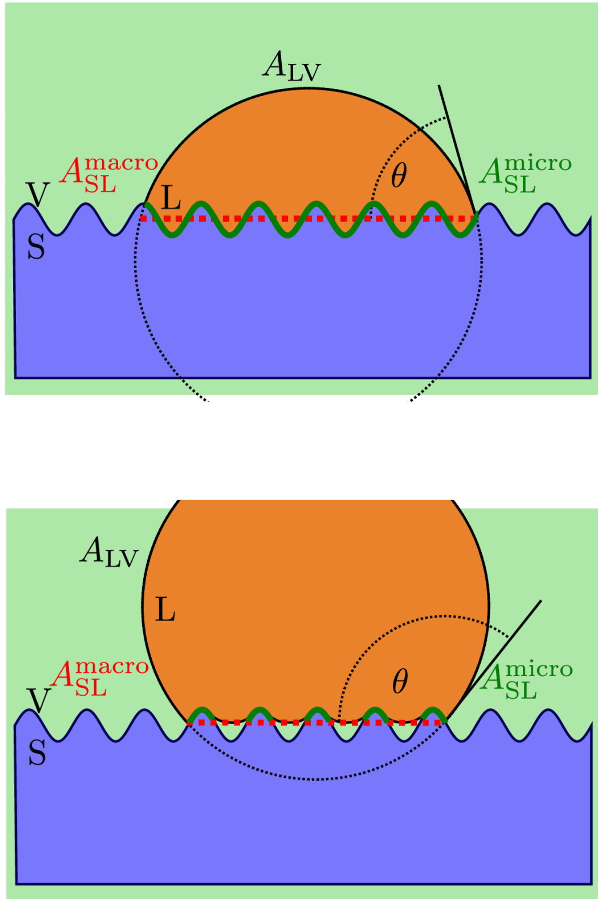




Cassie Equation



C. B. Ran, G. Q. Ding, W. C. Liu et al., *Langmuir* **24** (18), 9952 (2008).



the Lotus Leaf effect

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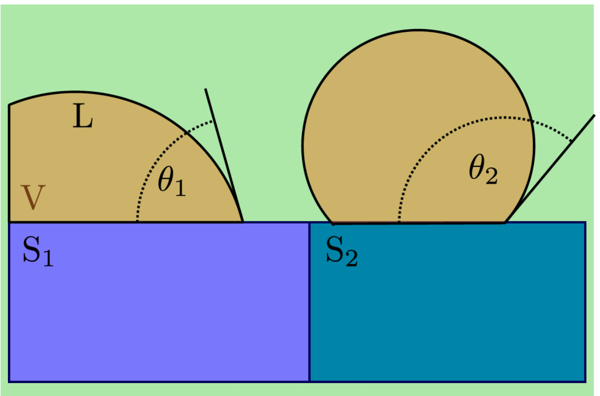
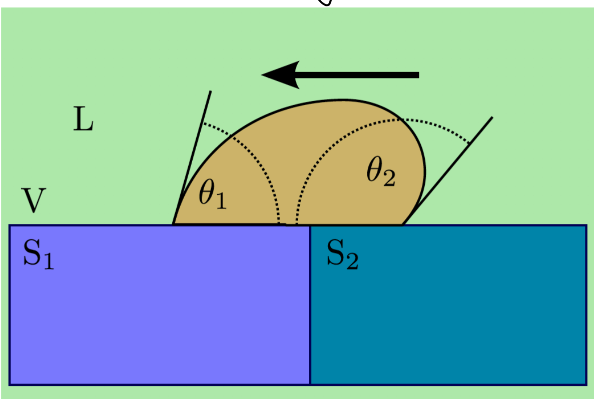
Considerations on Multicomponent Surfaces

Considerations on Multicomponent Surfaces

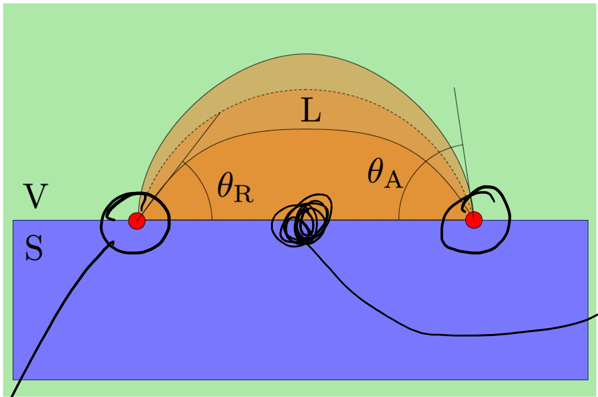
what happens
to this drop
here ?





why

Issues with Contact Angle Measurements



what happen here?

pinned

receding
advancing } average

SuNMIL EPFL