École polytechnique fédérale de Lausanne

Institute of Materials - Institute of Bioengineering

sunmil.epfl.ch

Supramolecular NanoMaterials and Interfaces Laboratory

# Solid-Liquid Interfaces
# Lesson 3

## MSE 304

Francesco Stellacci

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# Key Topics in the Previous Class

# 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**

# Interfaces

**What is an Interface?**

**Are they always that simple?**

# Interfacial Energy

**General Definition (from previous classes and basic Thermodynamics knowledge)**

**Simplified Case**

# Interfacial Energy as Work to Create an Interface/Surface

**Work of Choesion**

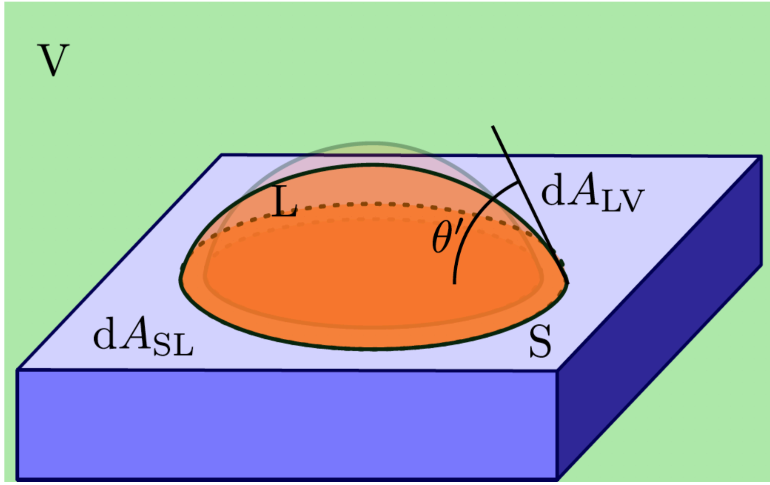
**Work of Adhesion**

# Interfacial Energy and the Work of Adhesion

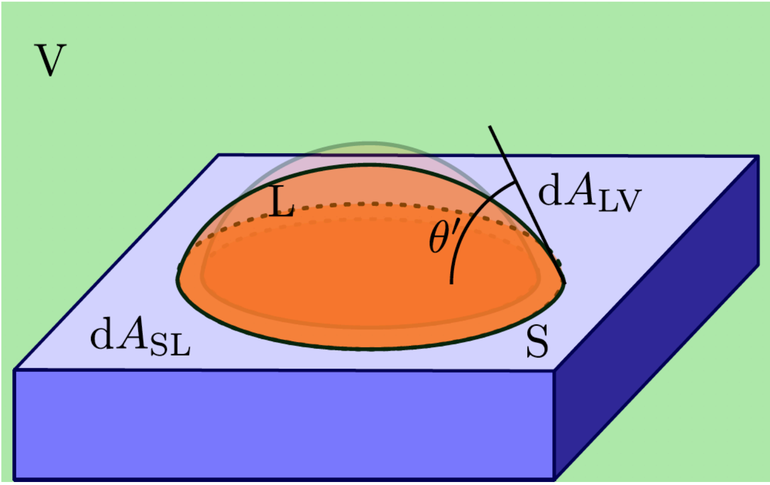
# Multiple Interfaces, Generalization of the Model

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

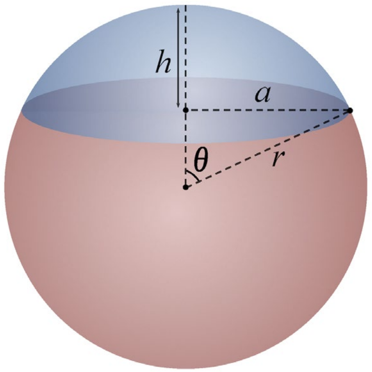
# Young's Theorem



# Young's Theorem



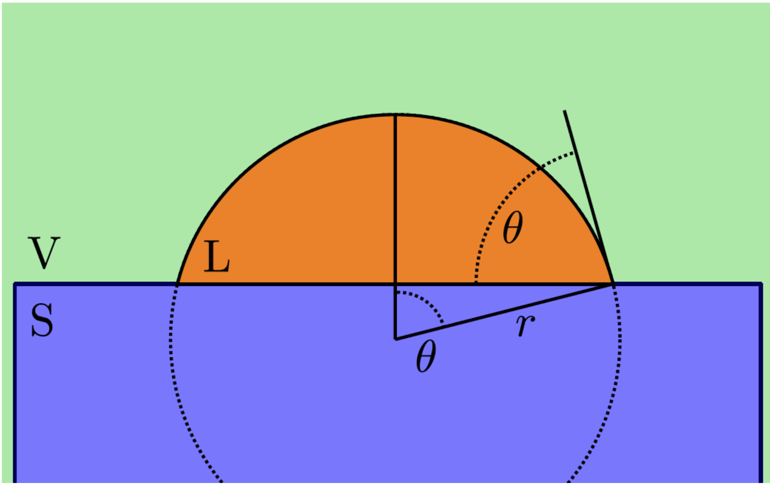
# Young's Theorem

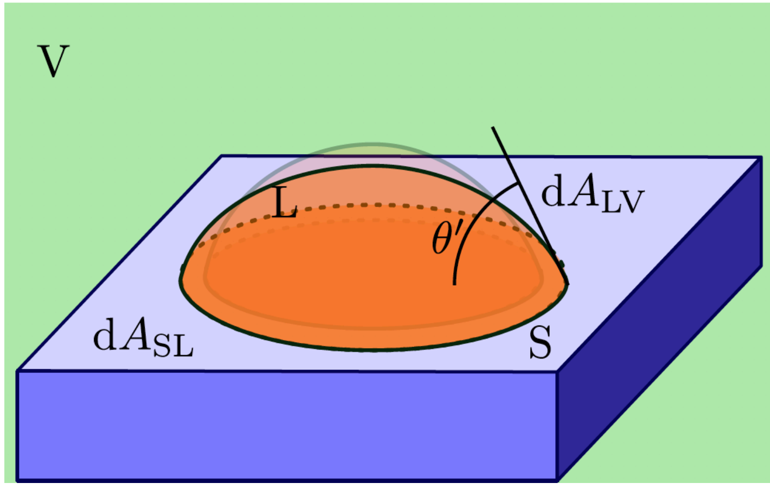



$$V = \frac{\pi h^2}{3}(3r - h) = \frac{\pi}{3} r^3 (2 + \cos\theta)(1 - \cos\theta)^2$$

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

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



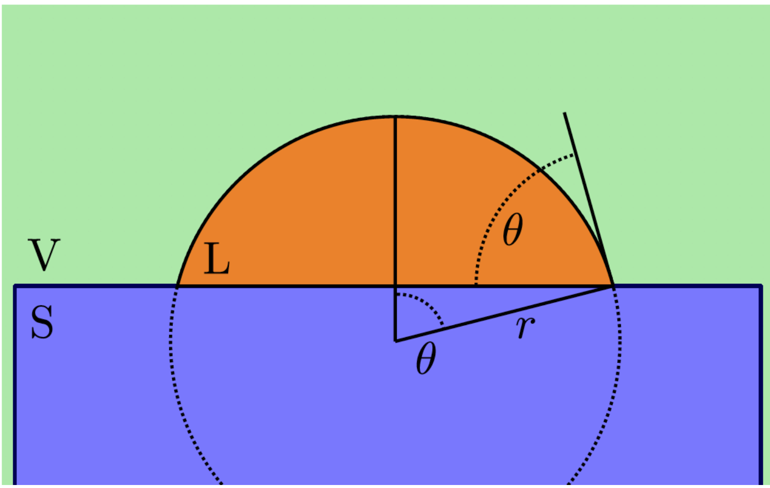
# Young's Theorem

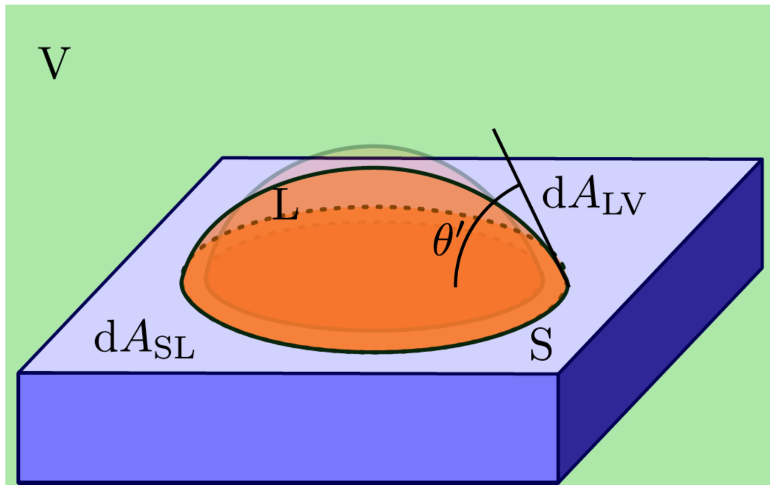
$$\frac{\partial V}{\partial \theta} = \frac{\pi}{3}3r^2\frac{dr}{d\theta}(2+\cos\theta)(1-\cos\theta)^2 - \frac{\pi}{3}r^3\sin\theta\,(1-\cos\theta)^2 + \frac{\pi}{3}r^3(2+\cos\theta)(1-\cos\theta)\sin\theta$$

$$\frac{\partial V}{\partial \theta} = 0$$

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

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



# Young's Theorem

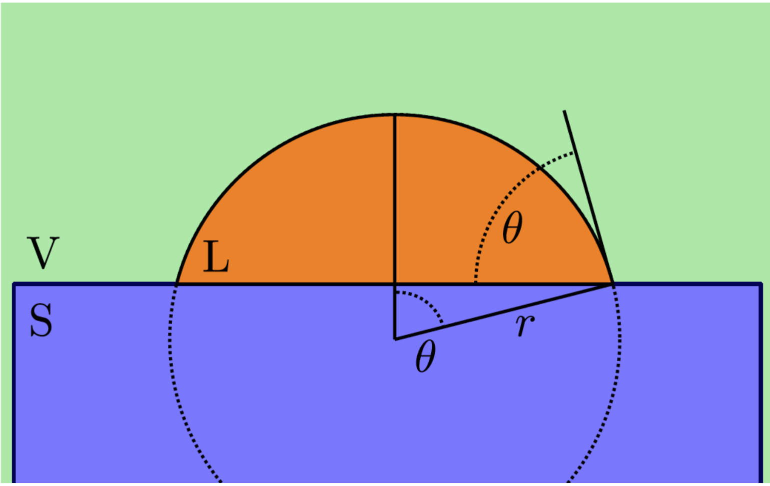
$$\left(\frac{dA_{LV}}{dA_{SL}}\right)_V = \left(\frac{\left(\partial A_{LV}/\partial\theta\right)_V}{\left(\partial A_{SL}/\partial\theta\right)_V}\right)$$

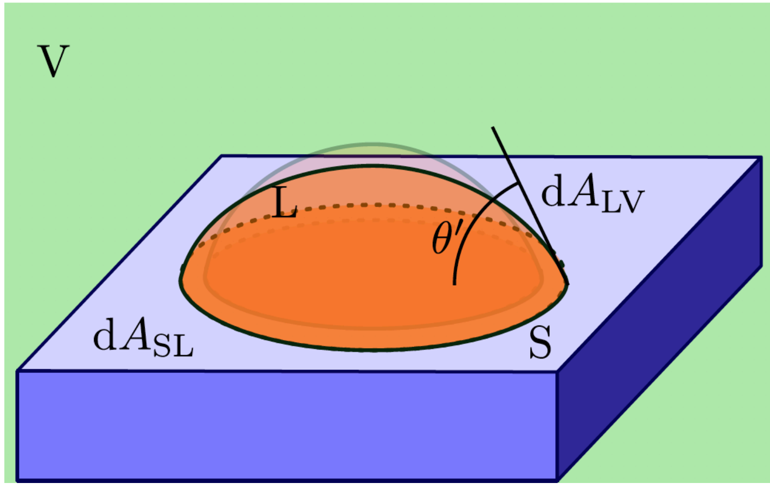
$$A_{LV} = 2\pi rh = 2\pi r^2(1-\cos\theta)$$

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

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

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



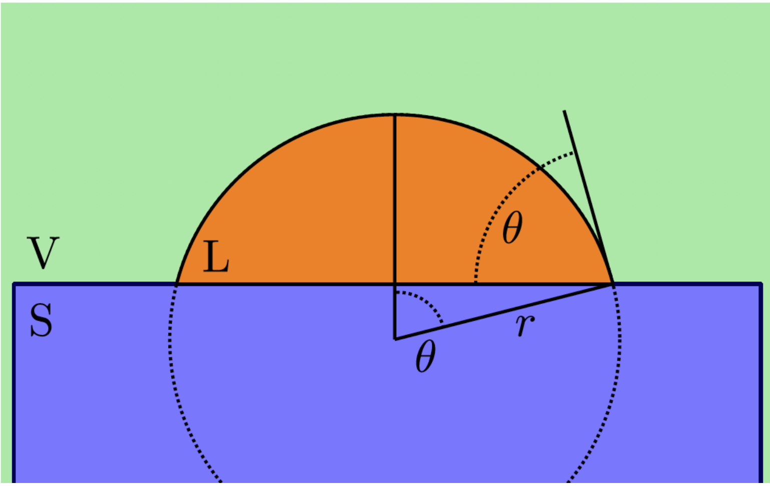
# Young's Theorem

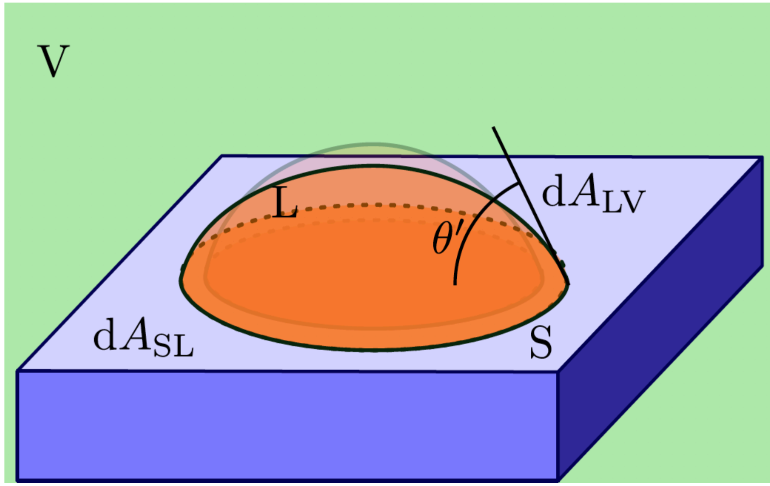
$$\left(\frac{dA_{LV}}{dA_{SL}}\right)_V = \left(\frac{\left(\partial A_{LV}/\partial\theta\right)_V}{\left(\partial A_{SL}/\partial\theta\right)_V}\right)$$

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

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

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





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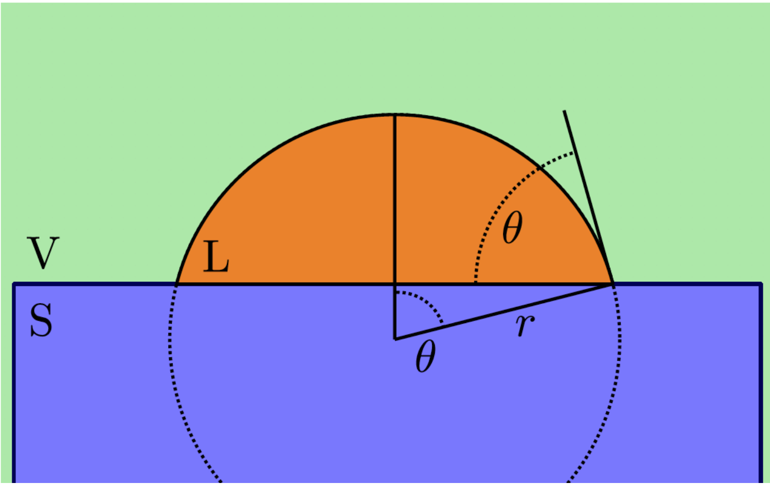
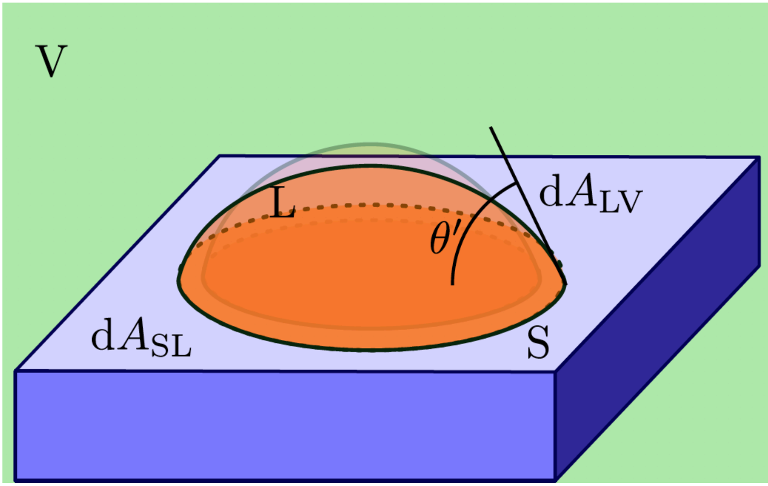
# Young's Theorem

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

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

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

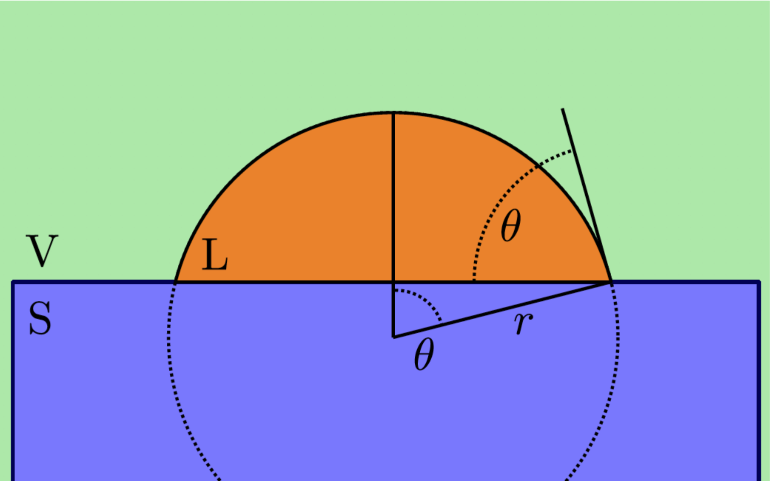


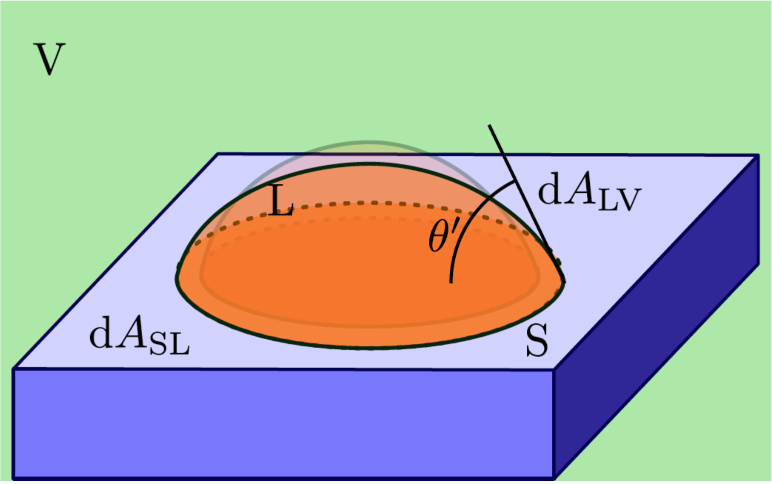



# Young's Theorem

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

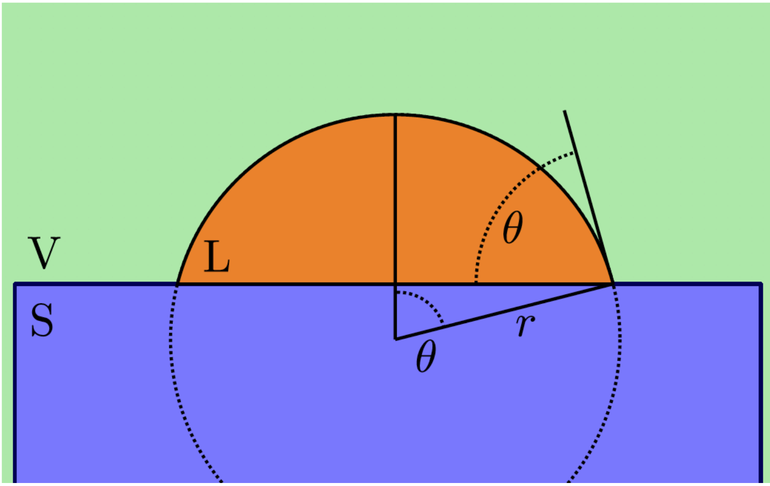
$$\left(\frac{dA_{LV}}{dA_{SL}}\right)_V = \cos\theta$$

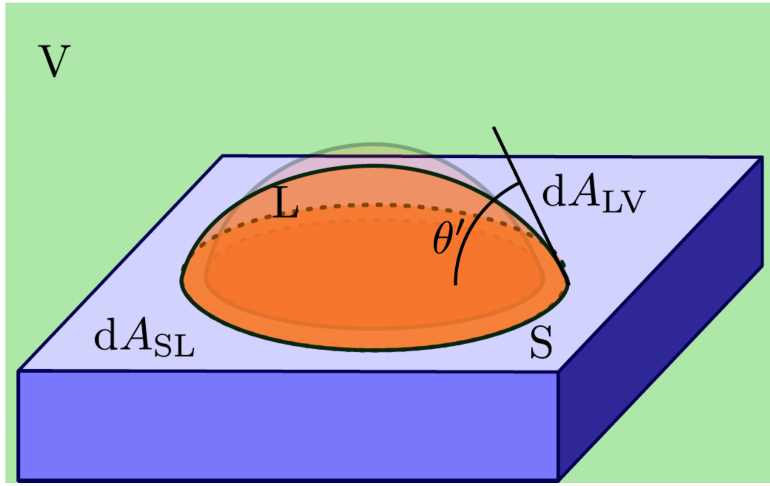


# Young's Theorem

$$(\gamma_{\mathsf{SL}} - \gamma_{\mathsf{SV}})\, \mathsf{d}A_{\mathsf{SL}} + \gamma_{\mathsf{LV}} \mathsf{d}A_{\mathsf{SL}} \cos\theta_0 = 0$$



# Young-Dupré Equation

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

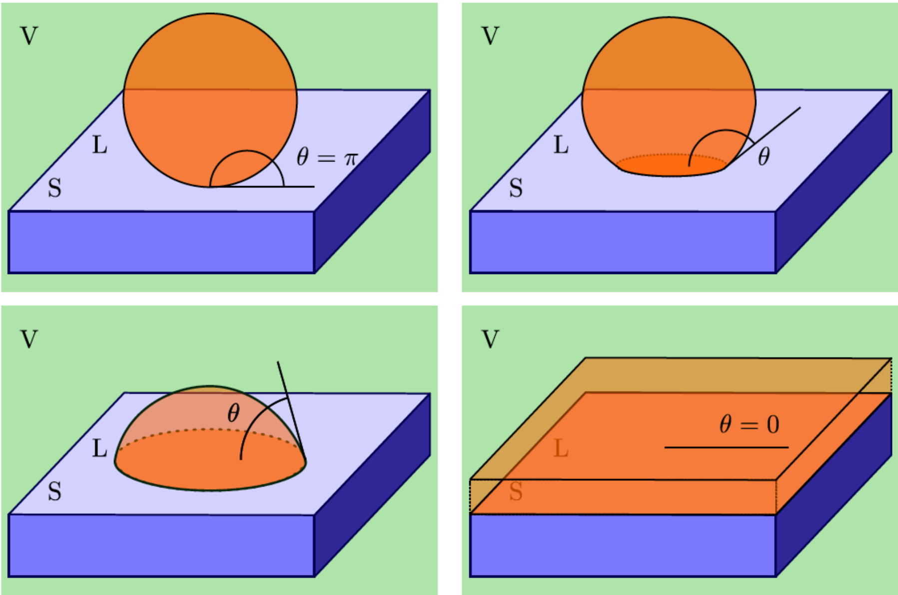
$$W_{SVL} = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$

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

# 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 $W_{SVL}$, $\theta_0$ 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

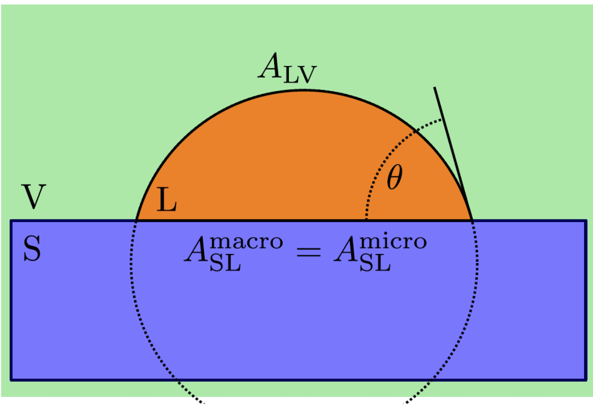


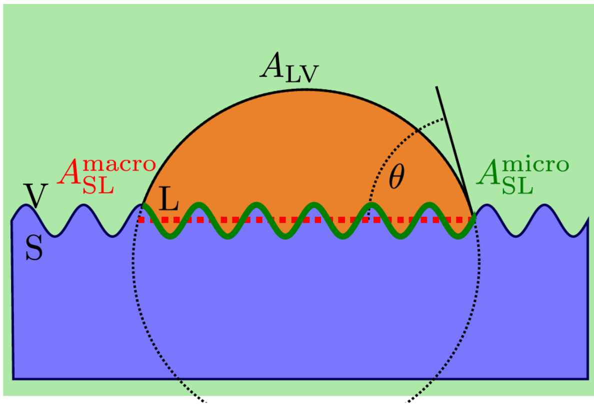
# Wenzel Equation

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

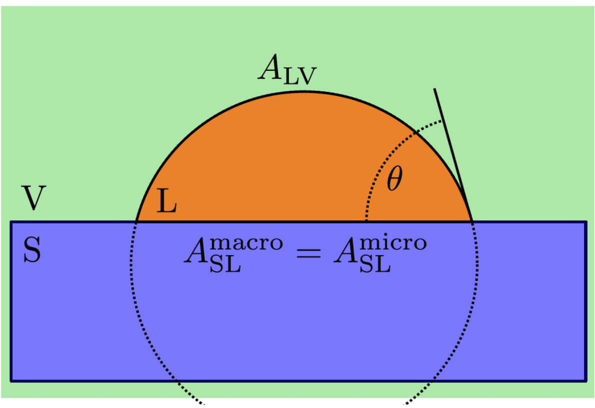
$$\gamma_{\mathrm{LV}} \cos\theta_{\mathrm{macro}} = (\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}})\,\phi, \qquad \gamma_{\mathrm{LV}} \cos\theta_0 = (\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}})$$

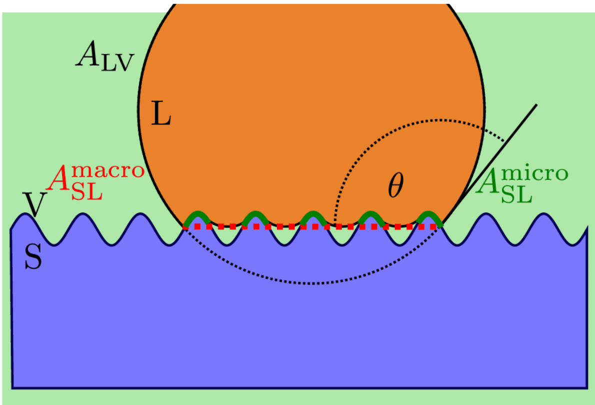
$$\boxed{\cos\theta_{\mathrm{macro}} = \phi \cos\theta_0}$$



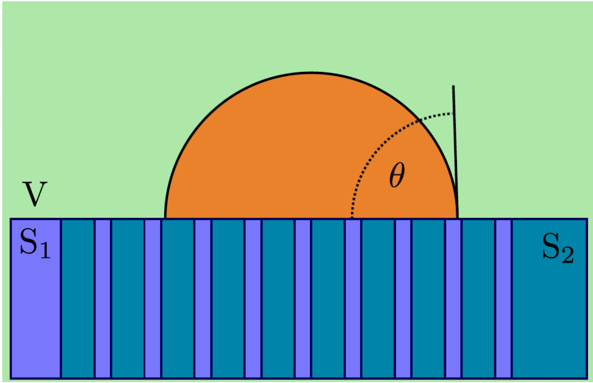
# Cassie Equation

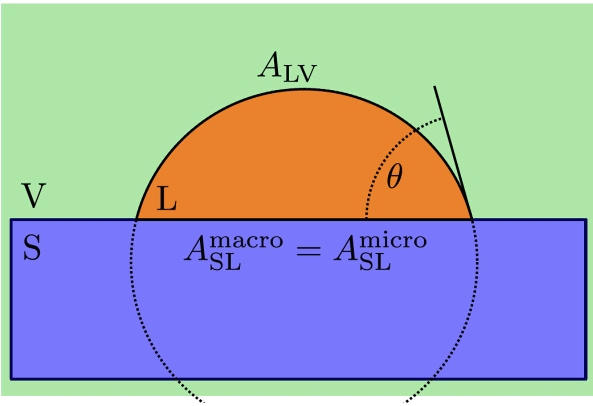


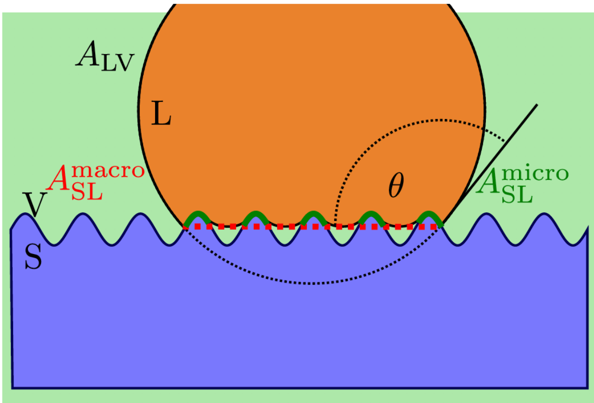



# Cassie Equation

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



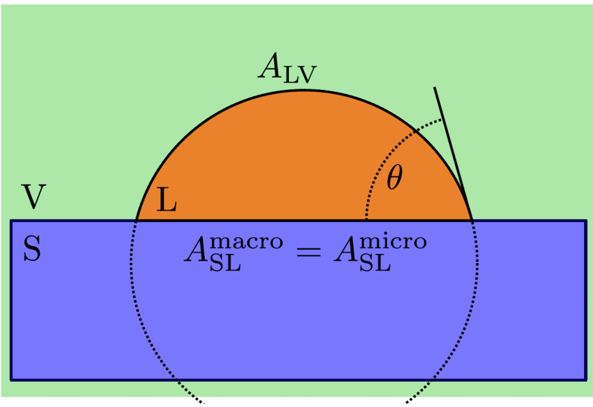



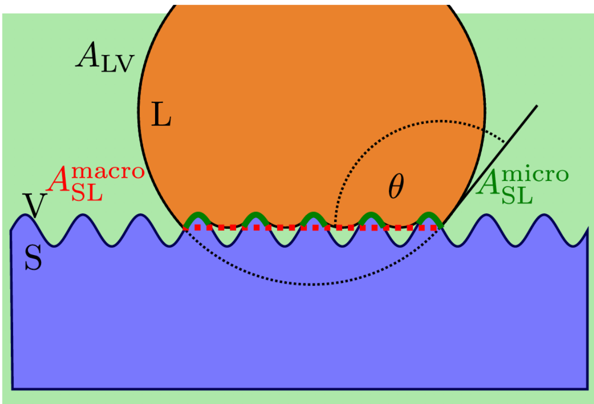



# Cassie Equation

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

$$\boxed{1 + \cos\theta_{\mathrm{macro}} = \phi\left(1 + \cos\theta_0\right)}$$ Cassie equation



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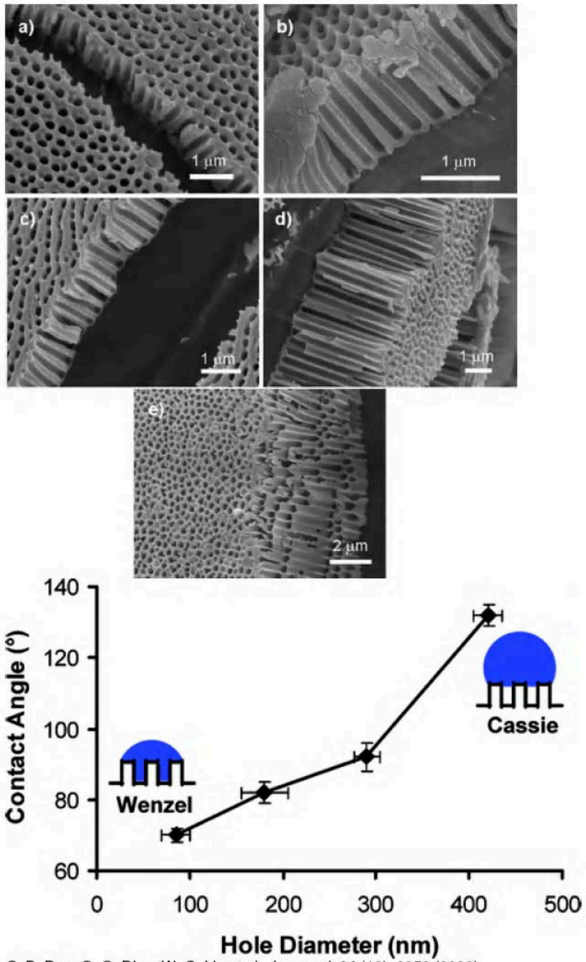
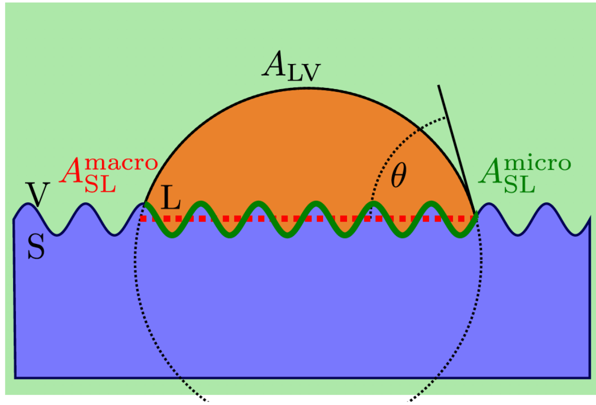
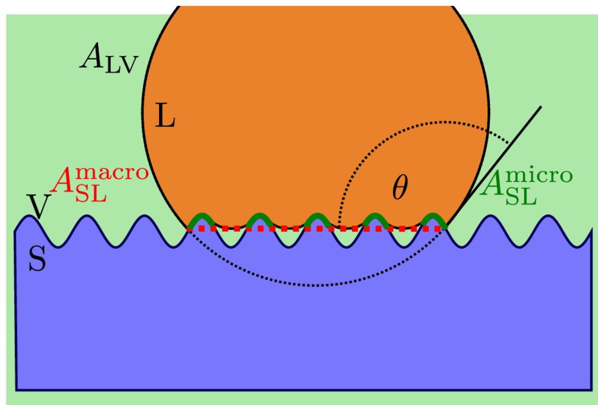



C. B. Ran, G. Q. Ding, W. C. Liu et al., *Langmuir* **24** (18), 9952 (2008).



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# Considerations on Multicomponent Surfaces

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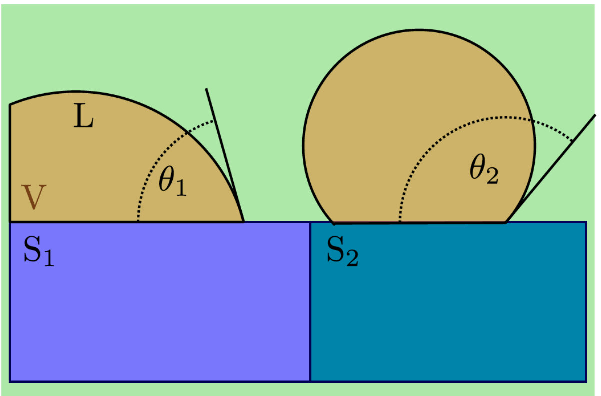


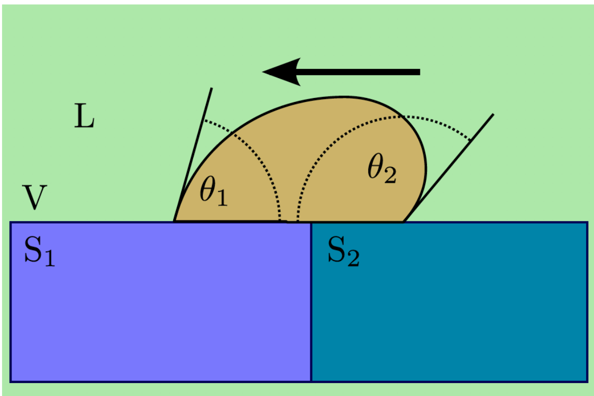

# Issues with Contact Angle Measurements