Solid-liquid interfaces

M. Ceriotti - MX304

EPFL

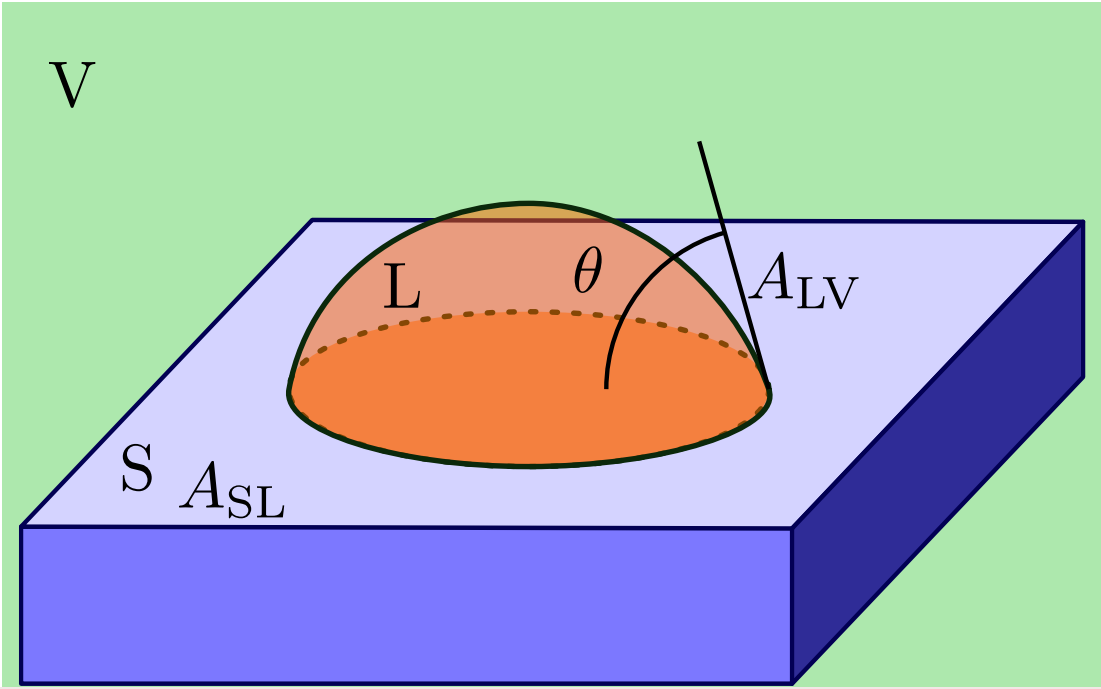
Outline

- Chapters 17.1, 17.4, 17.5, 17.6 of J. Israelchvili, “Intermolecular & Surface Forces” (third edition) Academic Press
- Equilibrium of a liquid droplet at a solid surface. Young equation
- Rough surfaces. Wenzel and Cassie models, super-hydrophobicity

Equilibrium Shape of a Droplet

- Consider a liquid droplet on top of a flat solid surface. Optimize the geometry **at constant volume.**
- Consider a 2D slice of the droplet

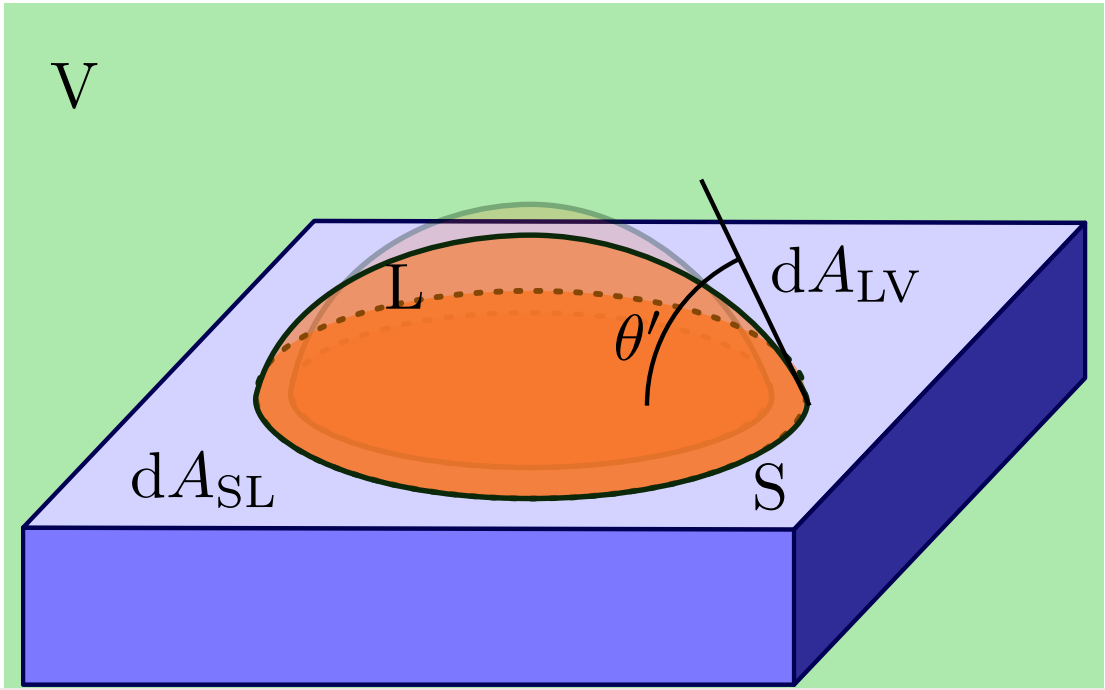
$$W_{\text{tot}} = (\gamma_{\text{SL}} - \gamma_{\text{SV}})\, A_{\text{SL}} + \gamma_{\text{LV}} A_{\text{LV}}$$



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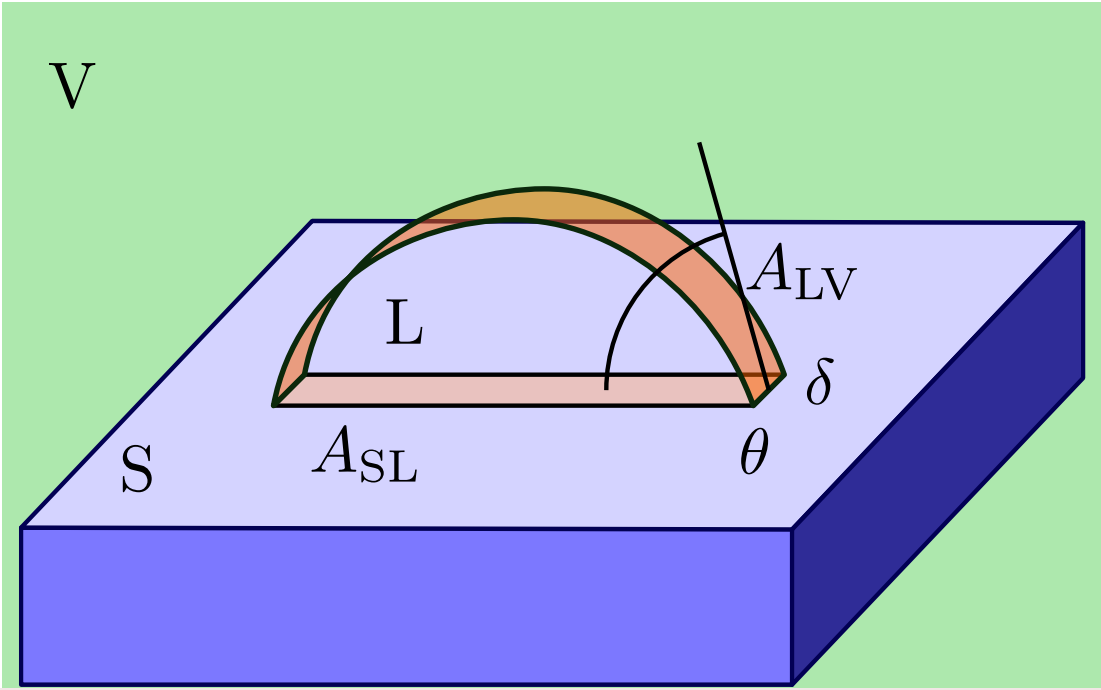
$$\mathrm{d}W_{\mathrm{tot}} = (\gamma_{\mathrm{SL}} - \gamma_{\mathrm{SV}})\,\mathrm{d}A_{\mathrm{SL}} + \gamma_{\mathrm{LV}}\mathrm{d}A_{\mathrm{LV}} = 0$$



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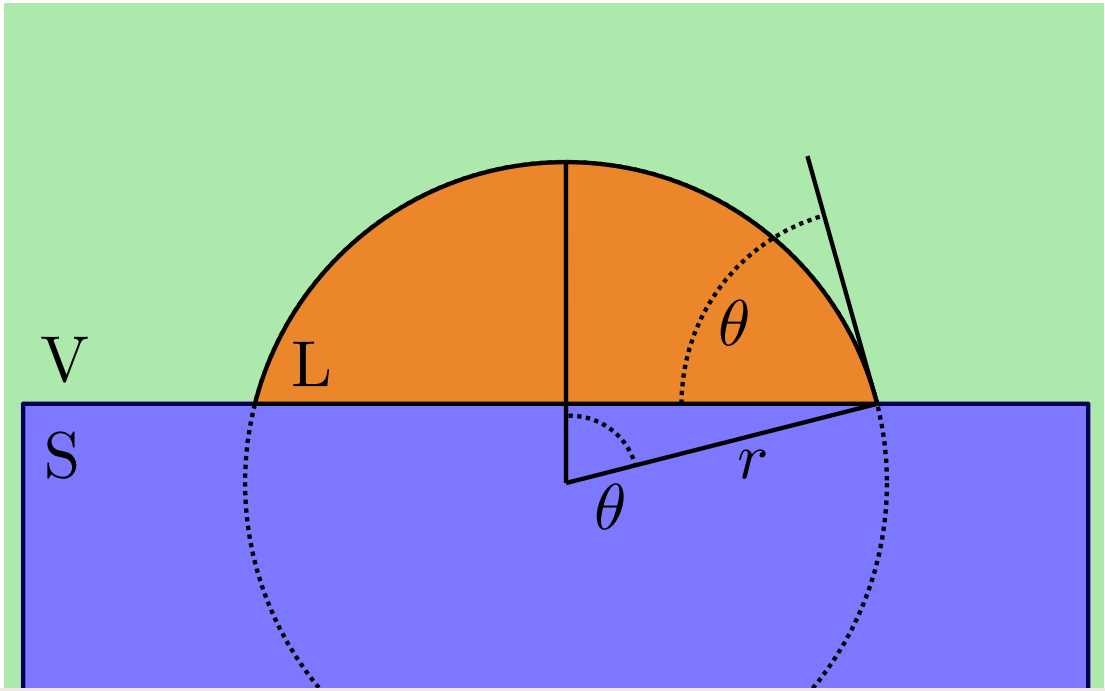
$$A_{SL} = 2r\delta \sin\theta, \quad A_{LV} = 2r\delta\theta, \quad V = r^2\delta\left(2\theta - \sin 2\theta\right)/2$$



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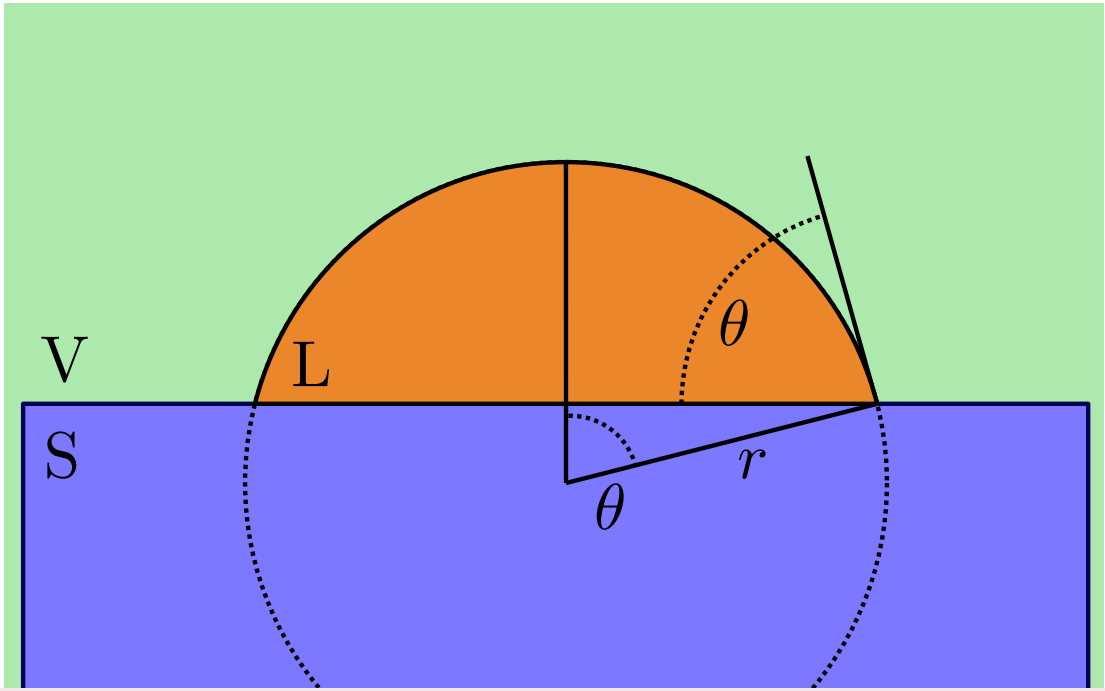
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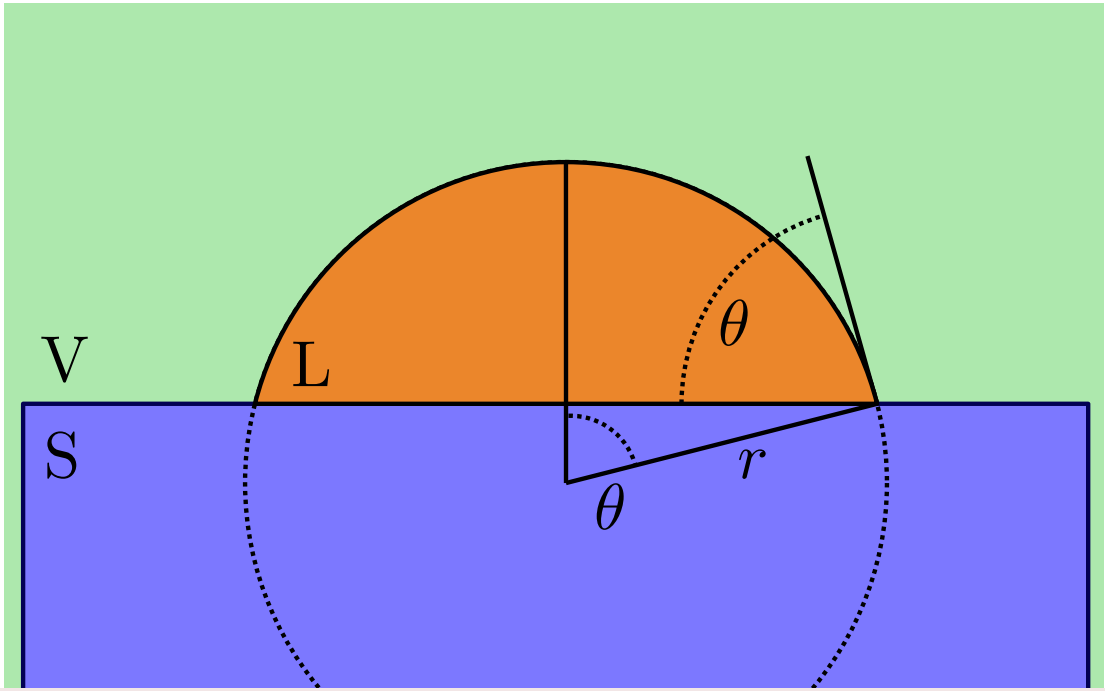
$$\left(\frac{\partial A_{LV}}{\partial A_{SL}}\right)_V = \frac{(\partial A_{LV}/\partial\theta)_V}{(\partial A_{SL}/\partial\theta)_V} = \frac{2\delta\left[1+\theta\left(\partial r/\partial\theta\right)_V/r\right]}{2\delta\left[\cos\theta+\sin\theta\left(\partial r/\partial\theta\right)_V/r\right]}$$



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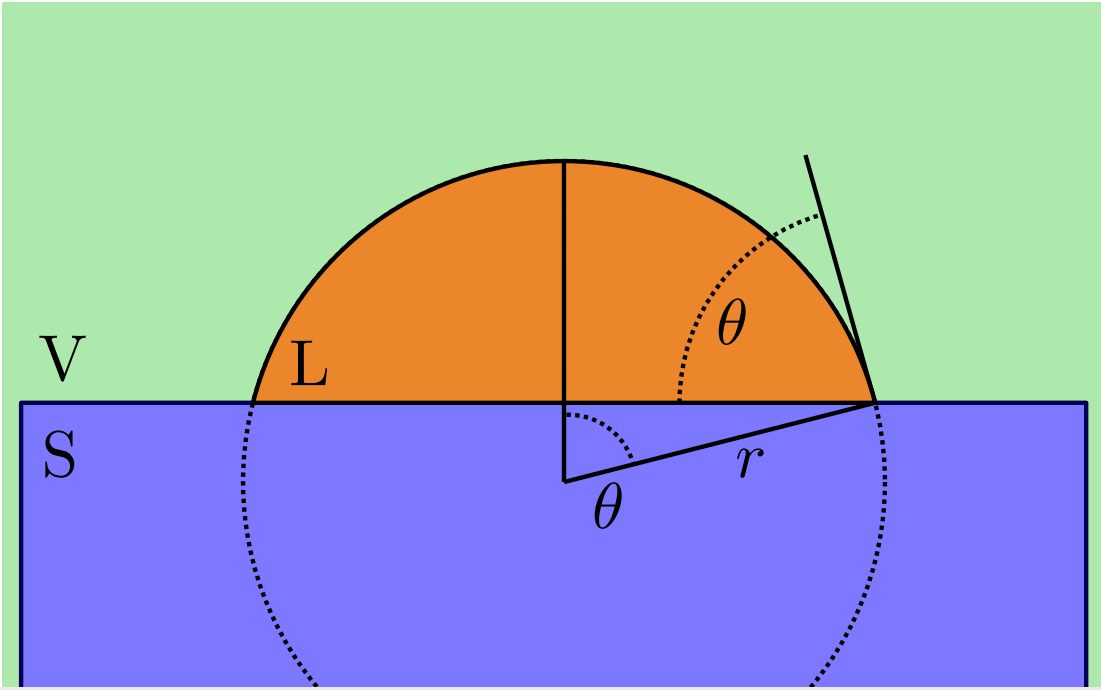
$$\frac{\partial V}{\partial \theta} = r\delta\left(2\theta - \sin 2\theta\right)\frac{\partial r}{\partial \theta} + \delta r^2\left(1 - \cos 2\theta\right) = 0$$



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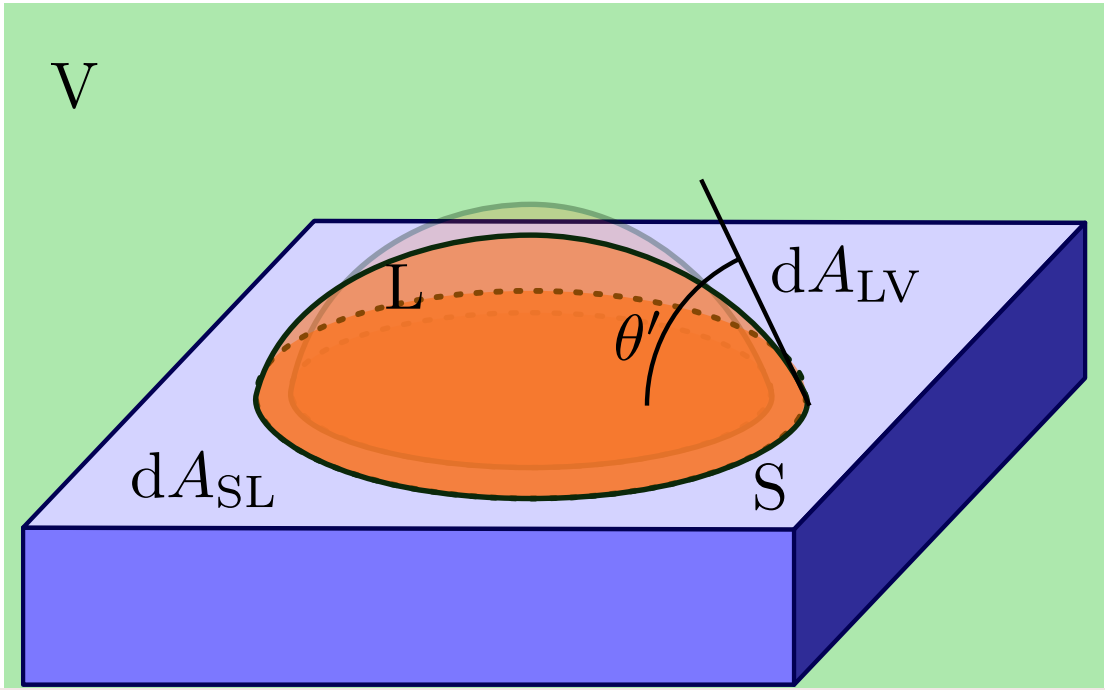
$$\frac{1}{r}\left(\frac{\partial r}{\partial \theta}\right)_V = -\frac{\sin^2\theta}{\theta - \sin 2\theta/2}$$



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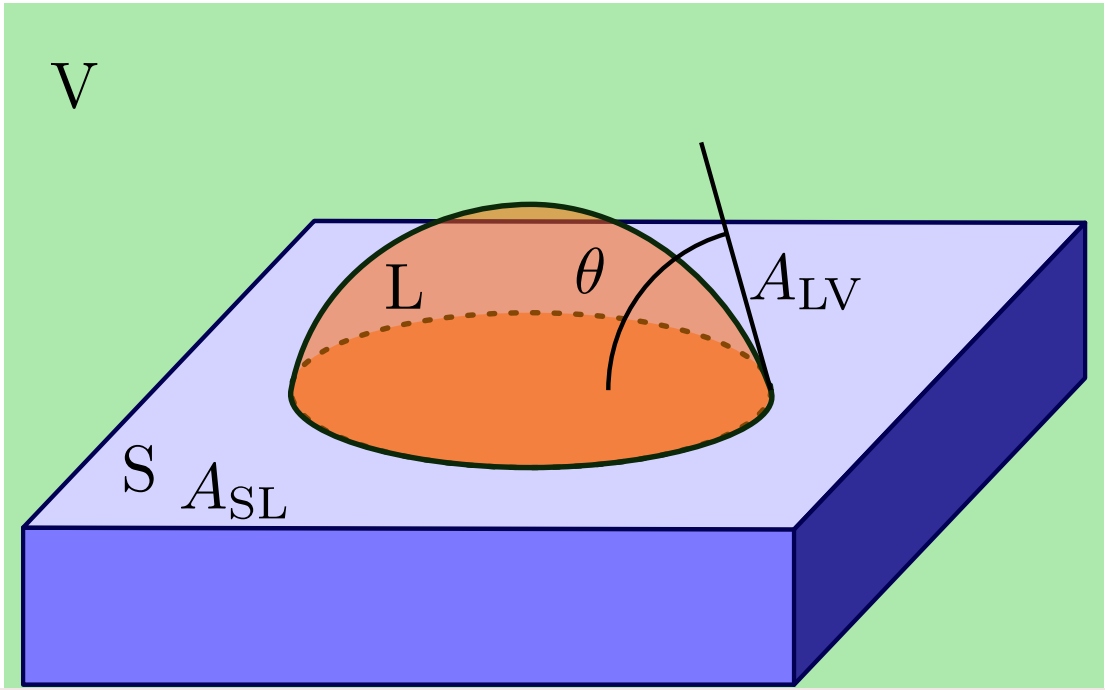
$$\left(\frac{\partial A_{LV}}{\partial A_{SL}}\right)_V = \frac{\theta - \sin 2\theta/2 - \theta \sin\theta}{\cos\theta\,(\theta - \sin 2\theta/2) - \sin\theta \sin^2\theta}$$



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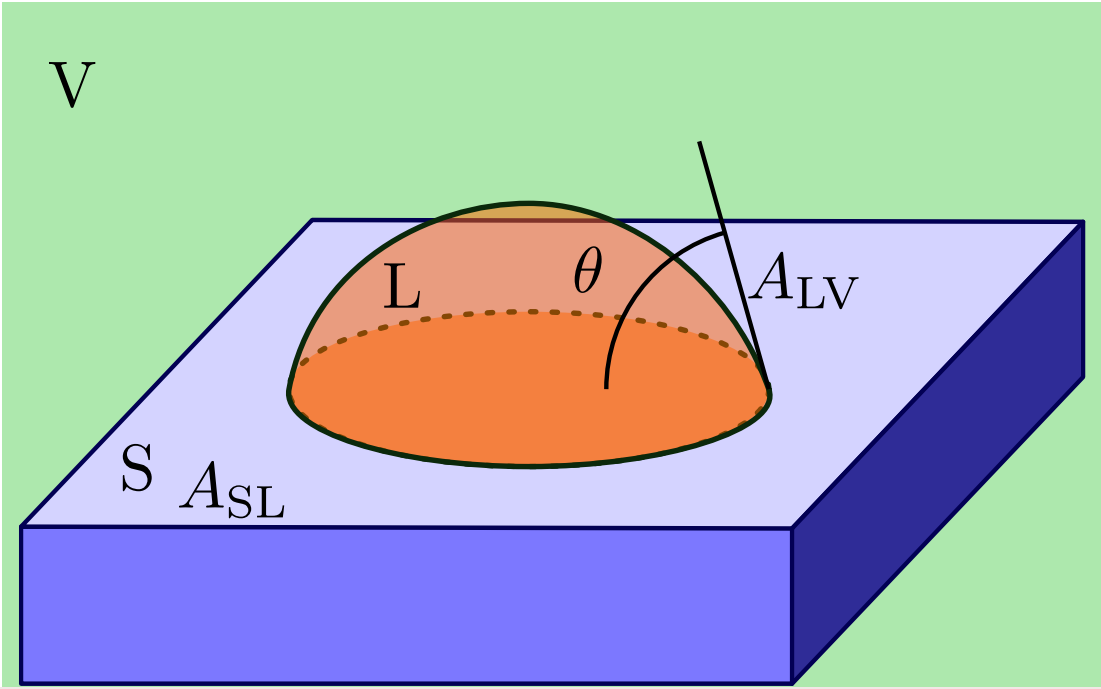
$$(\gamma_{SL} - \gamma_{SV})\, dA_{SL} + \gamma_{LV} dA_{SL} \cos\theta_0 = 0$$



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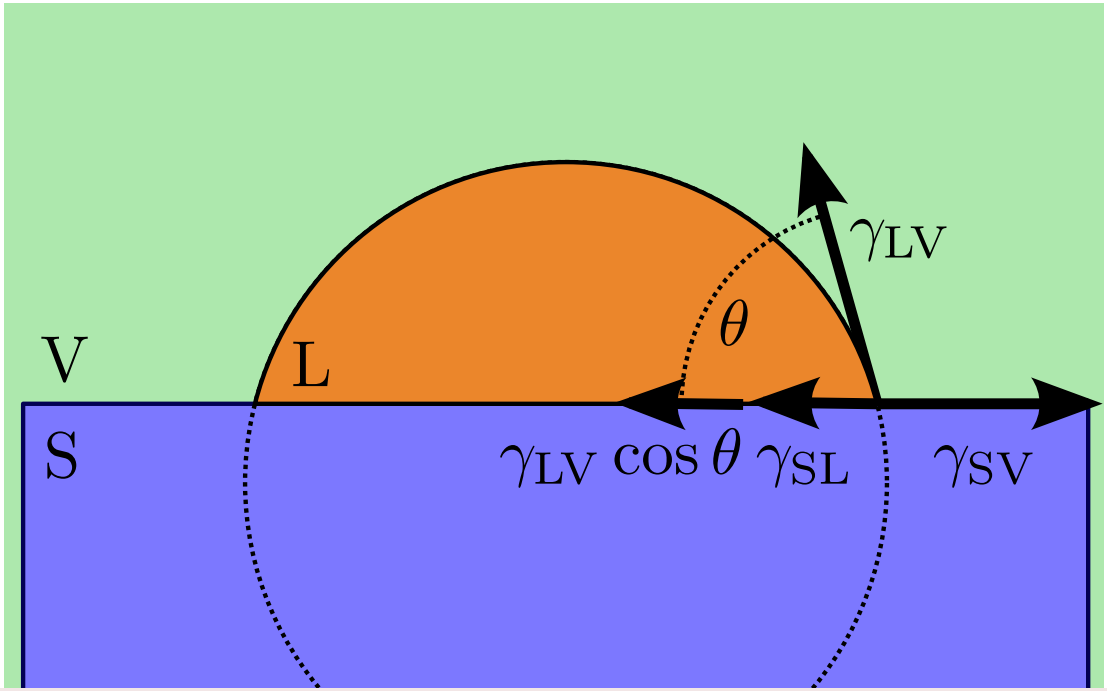
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Young-Dupré Equation

- Let's combine Young equation and Dupré Equation...

$$\gamma_{LV}\cos\theta_0 = \gamma_{SV} - \gamma_{SL} \qquad W_{SVL} = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$

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

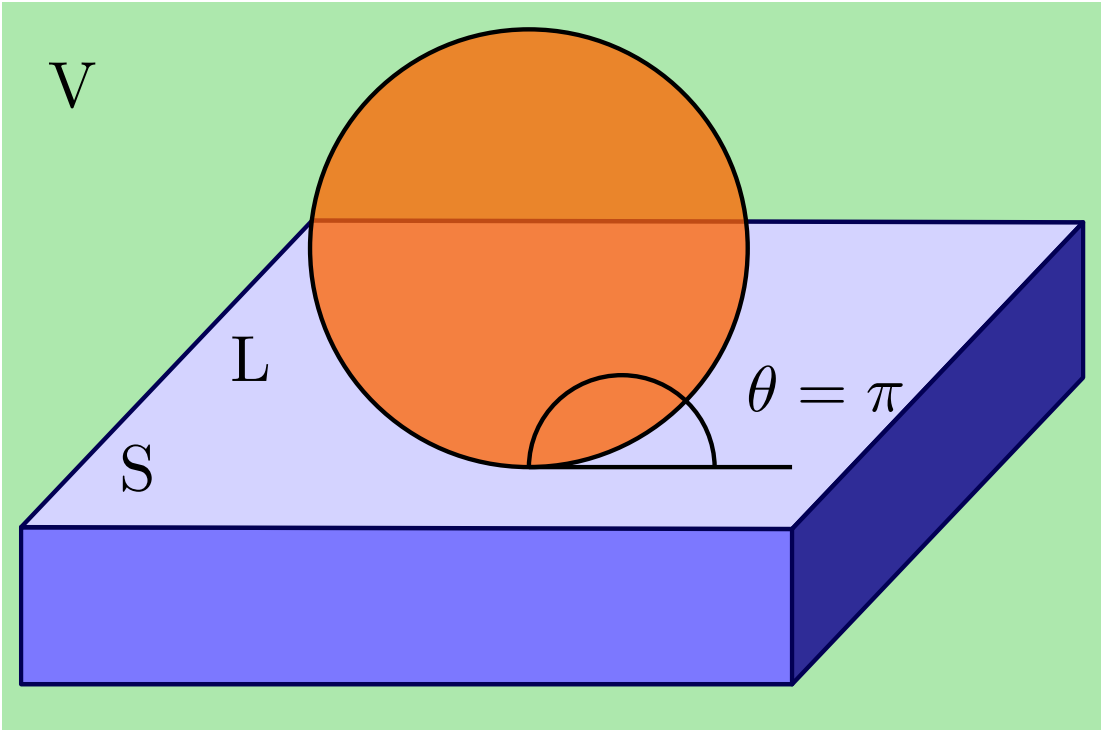
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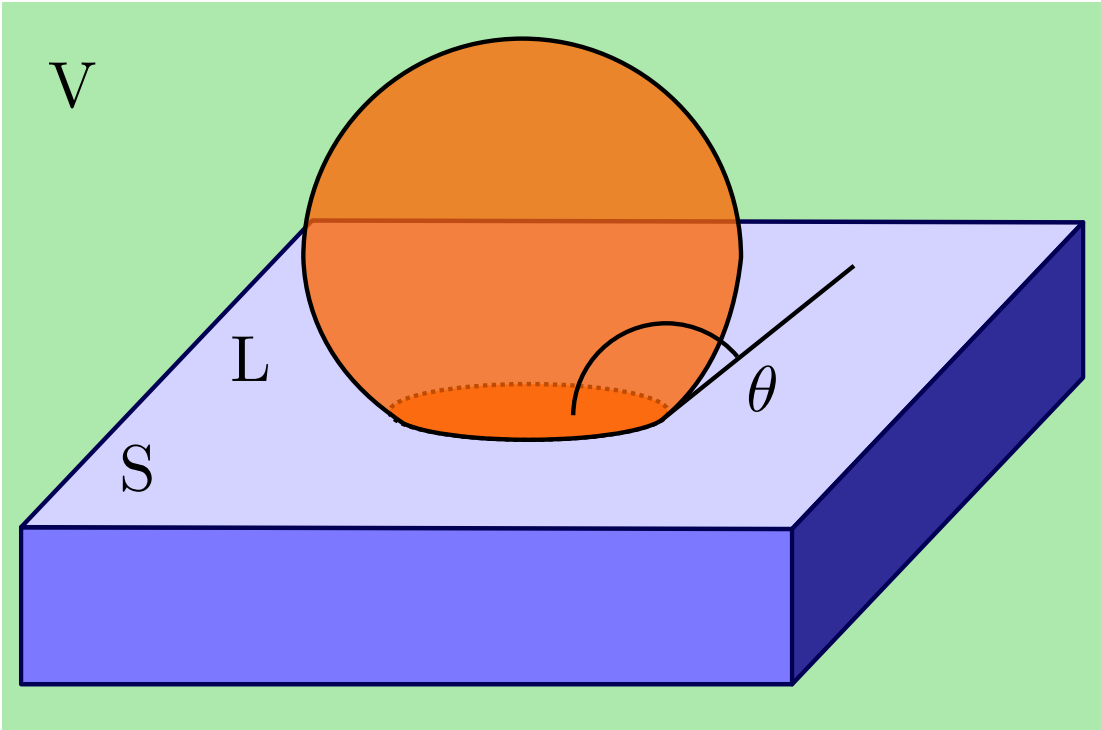


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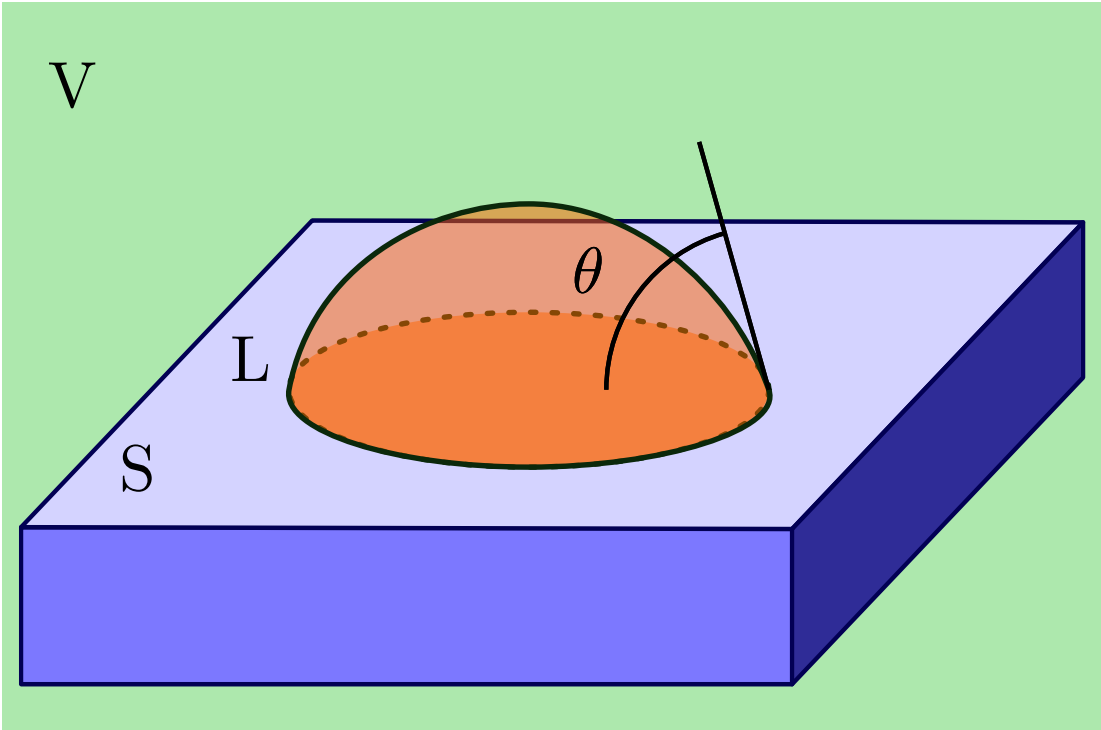


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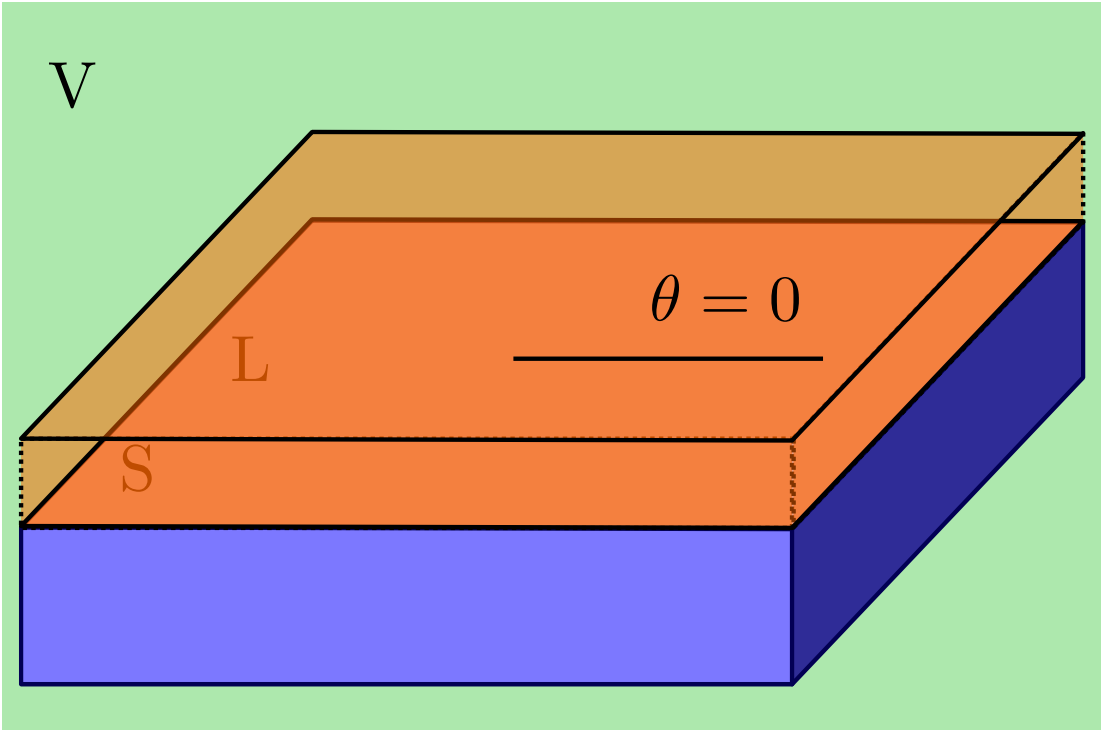


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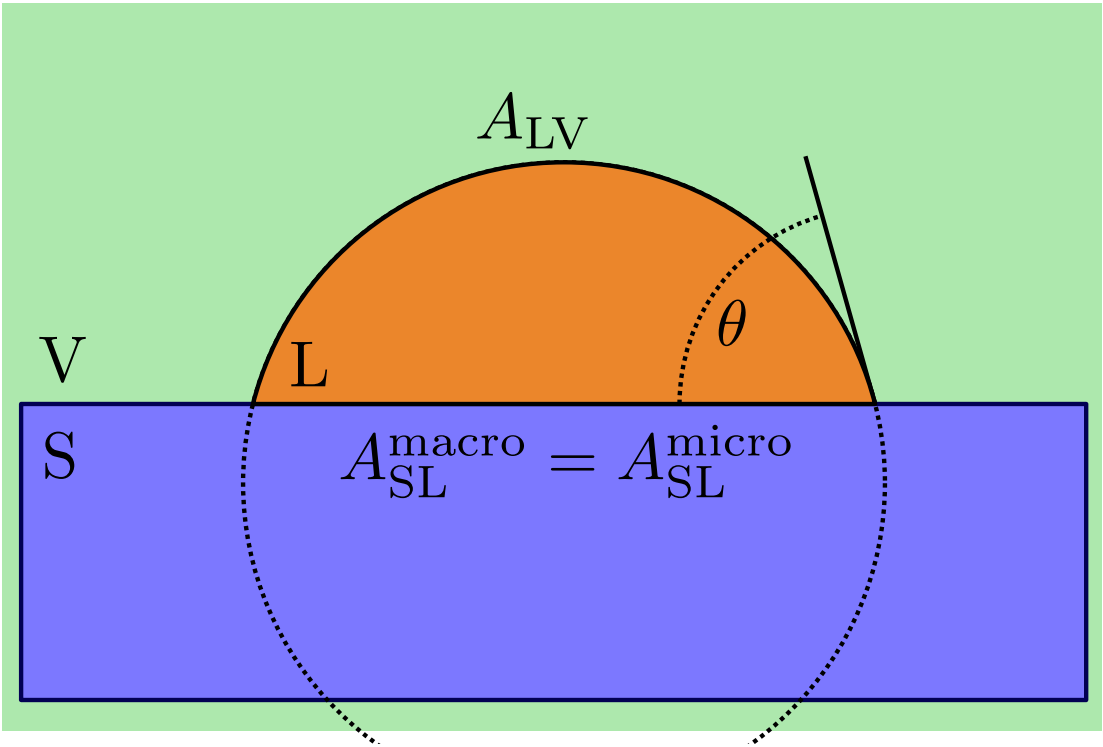
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Rough Surfaces: Wenzel equation

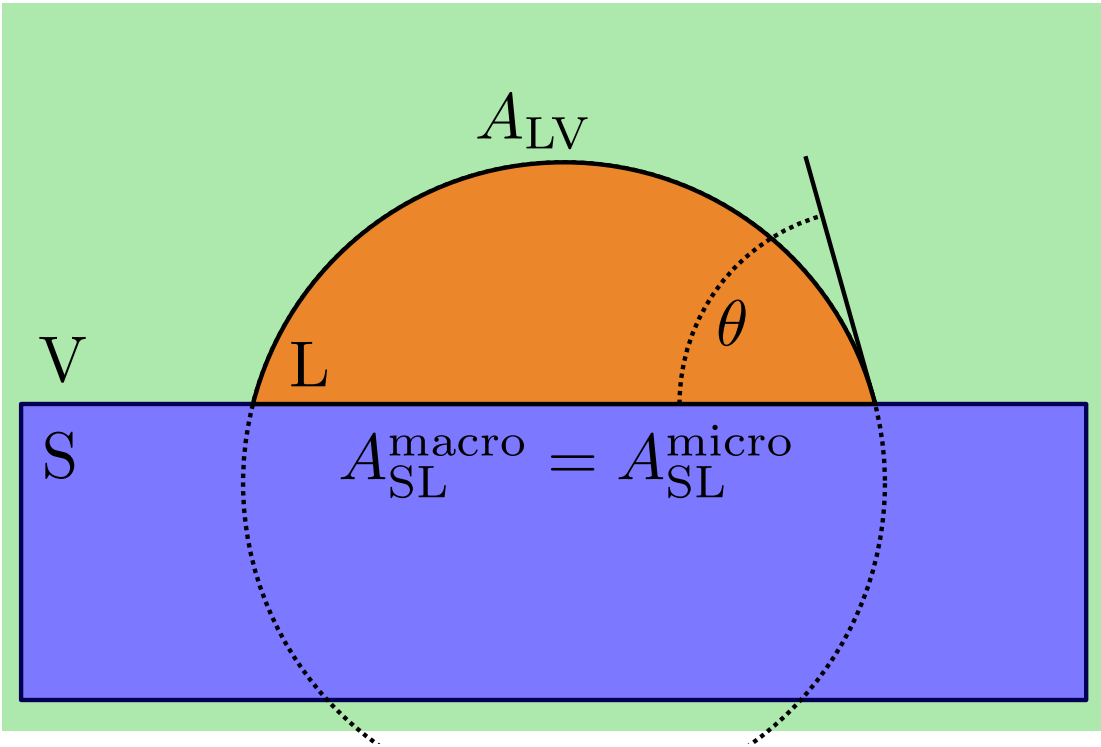
- What if the surface is rough? Then the microscopic surface contact A_{SL}^{micro} is larger than the macroscopic area A_{SL}^{macro}, depending on the roughness $\phi = A_{SL}^{micro} / A_{SL}^{macro}$



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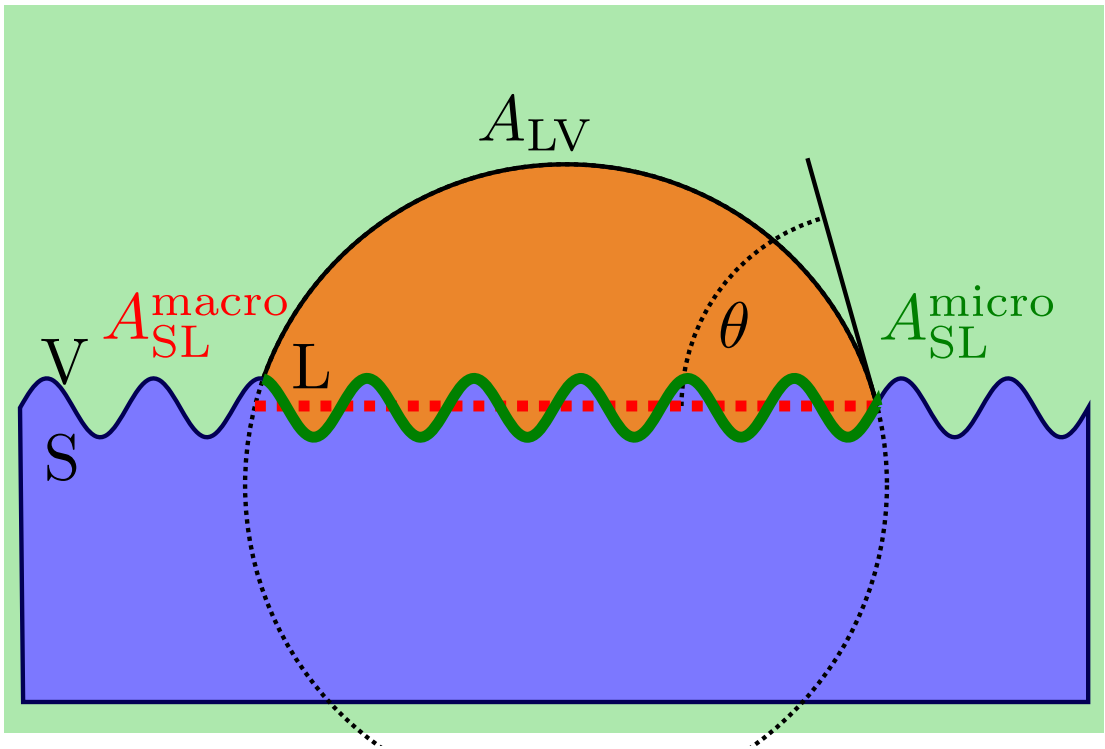
$$\gamma_{LV} \mathrm{d}A_{SL}^{macro} \cos\theta_{macro} = (\gamma_{SV} - \gamma_{SL})\, \phi \mathrm{d}A_{SL}^{macro}$$



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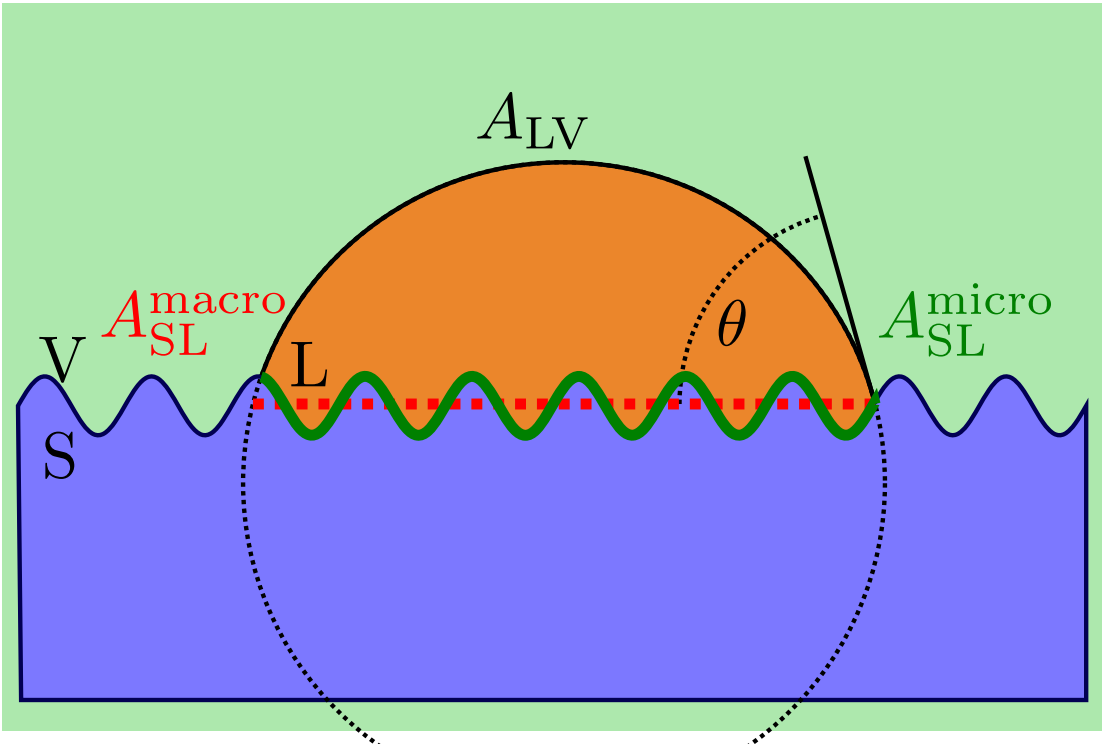
$$\gamma_{LV} \cos\theta_{macro} = (\gamma_{SV} - \gamma_{SL})\,\phi, \qquad \gamma_{LV} \cos\theta_0 = (\gamma_{SV} - \gamma_{SL})$$



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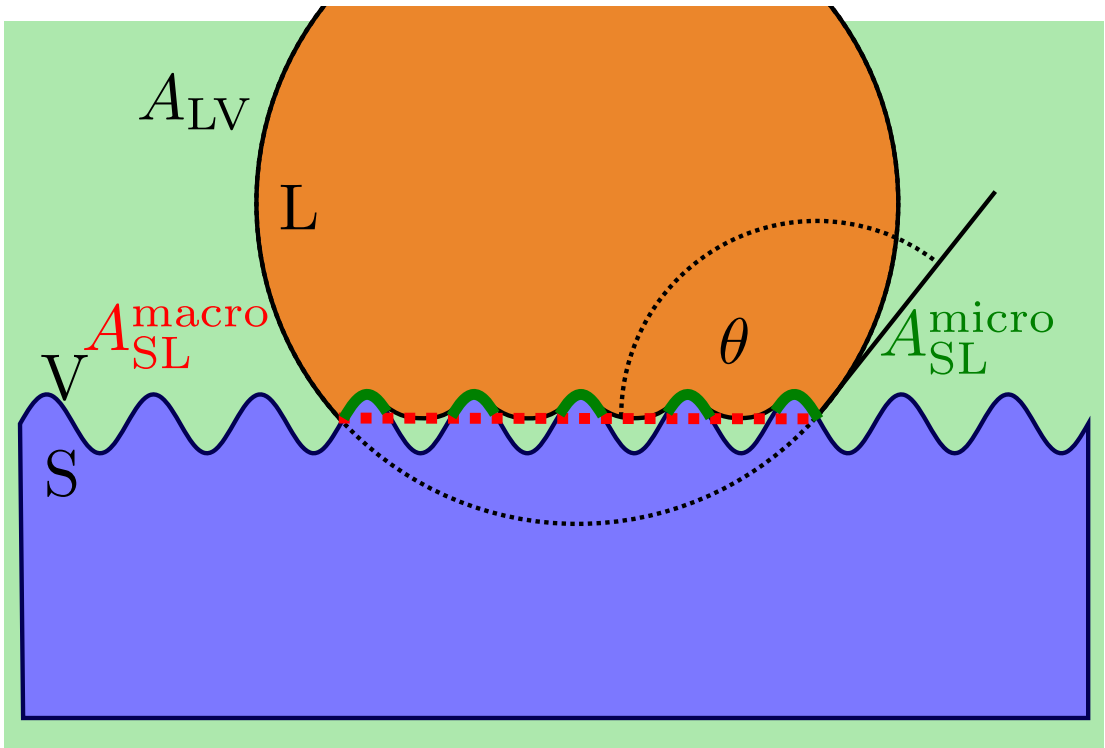


Rough Surfaces: Cassie equation

- If the contact is non-wetting, there can be air pockets! Now A_{SL}^{micro} only counts **contact** area, so $\phi = A_{SL}^{micro} / A_{SL}^{macro}$ also depend on θ_0!

$$\gamma_{LV} \mathrm{d}A_{SL}^{macro} \cos\theta_{macro} = \left[(\gamma_{SV} - \gamma_{SL})\,\phi - (1-\phi)\,\gamma_{LV} \right] \mathrm{d}A_{SL}^{macro}$$

- "Lotus effect", self-cleaning surfaces

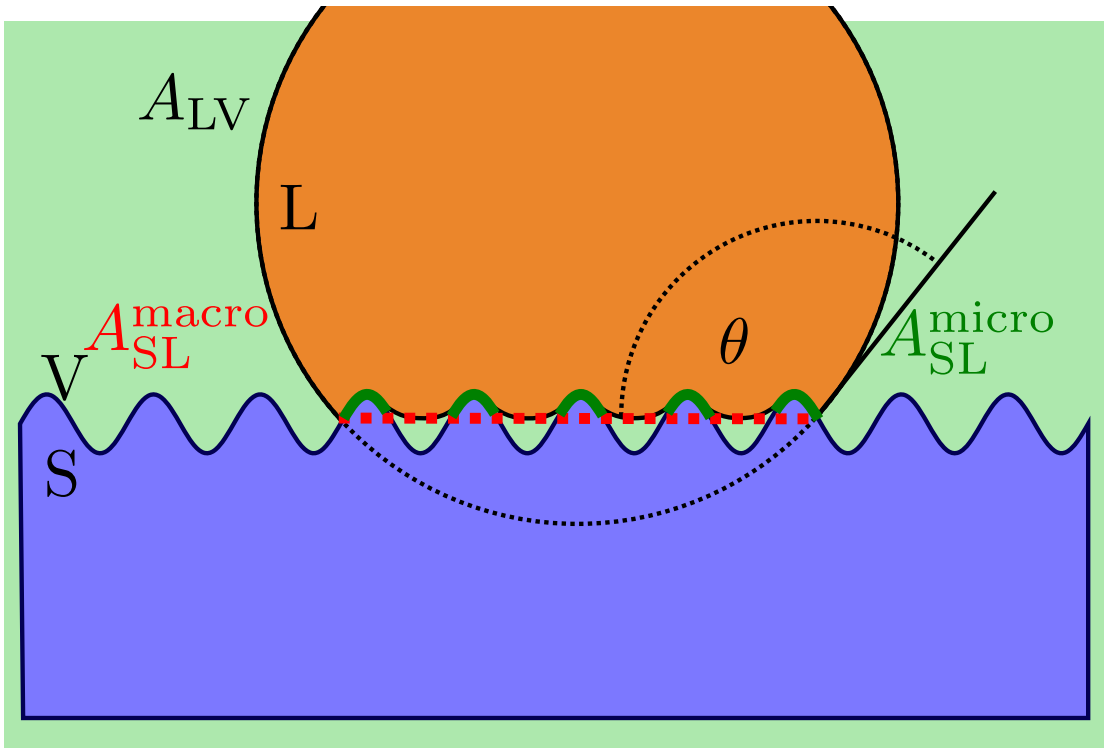


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$$\gamma_{LV}\left(1+\cos\theta_{macro}\right) = \left[\left(\gamma_{SV}-\gamma_{SL}\right)+\gamma_{LV}\right]\phi, \qquad \gamma_{LV}\cos\theta_0 = \left(\gamma_{SV}-\gamma_{SL}\right)$$

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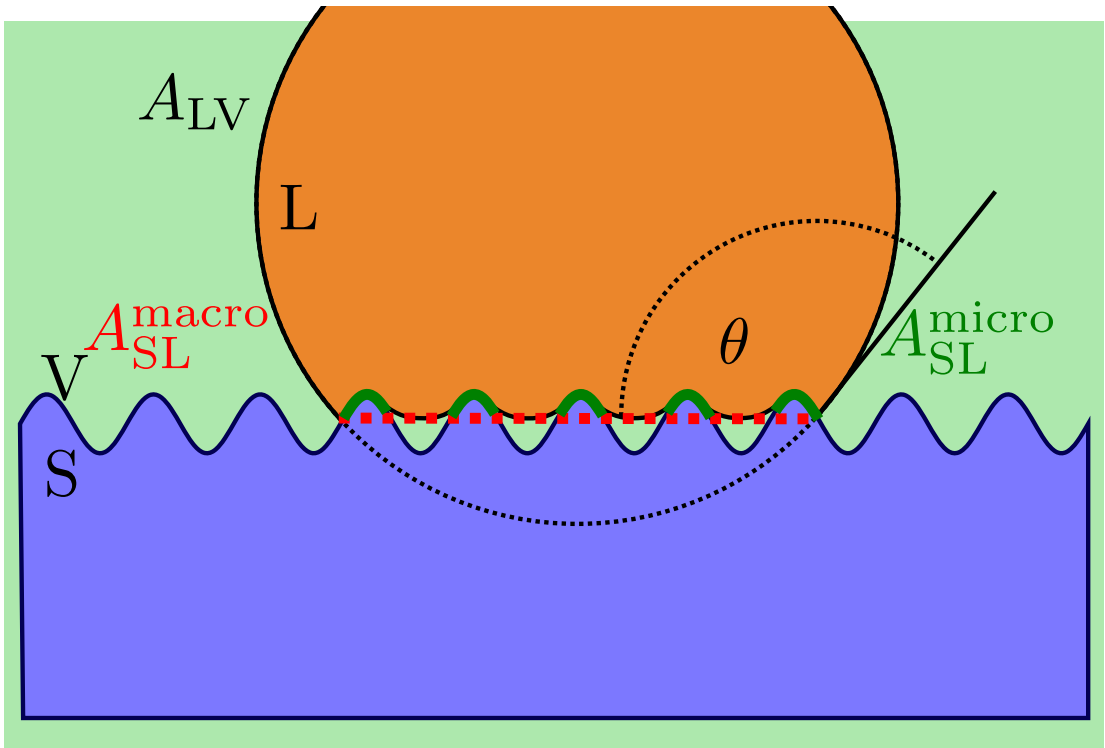


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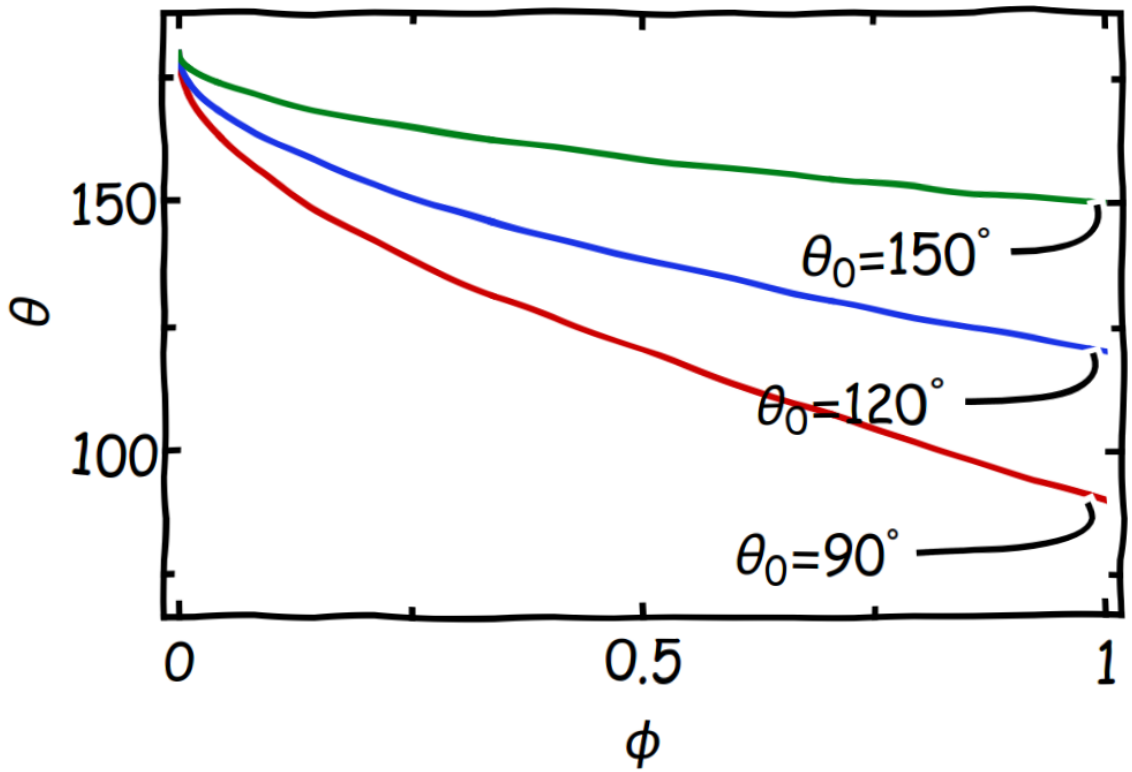


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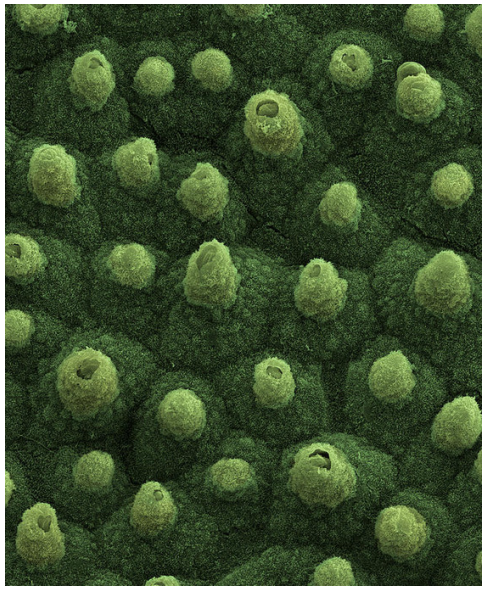
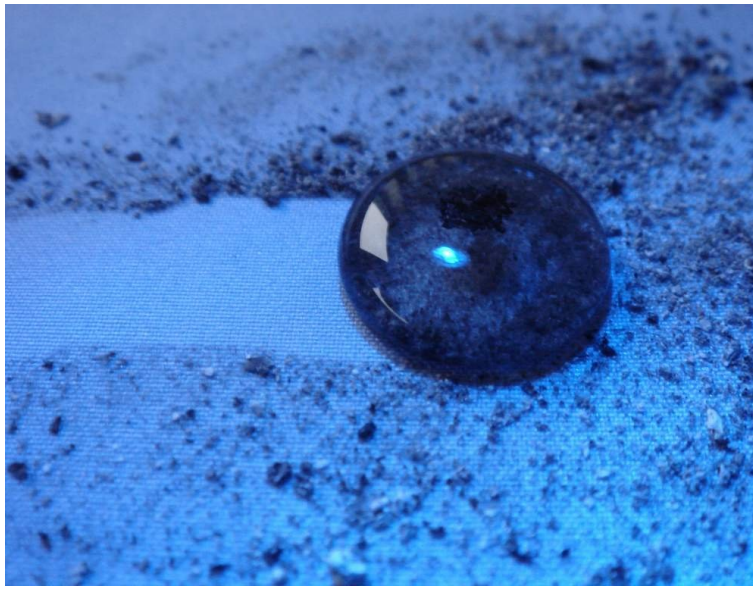


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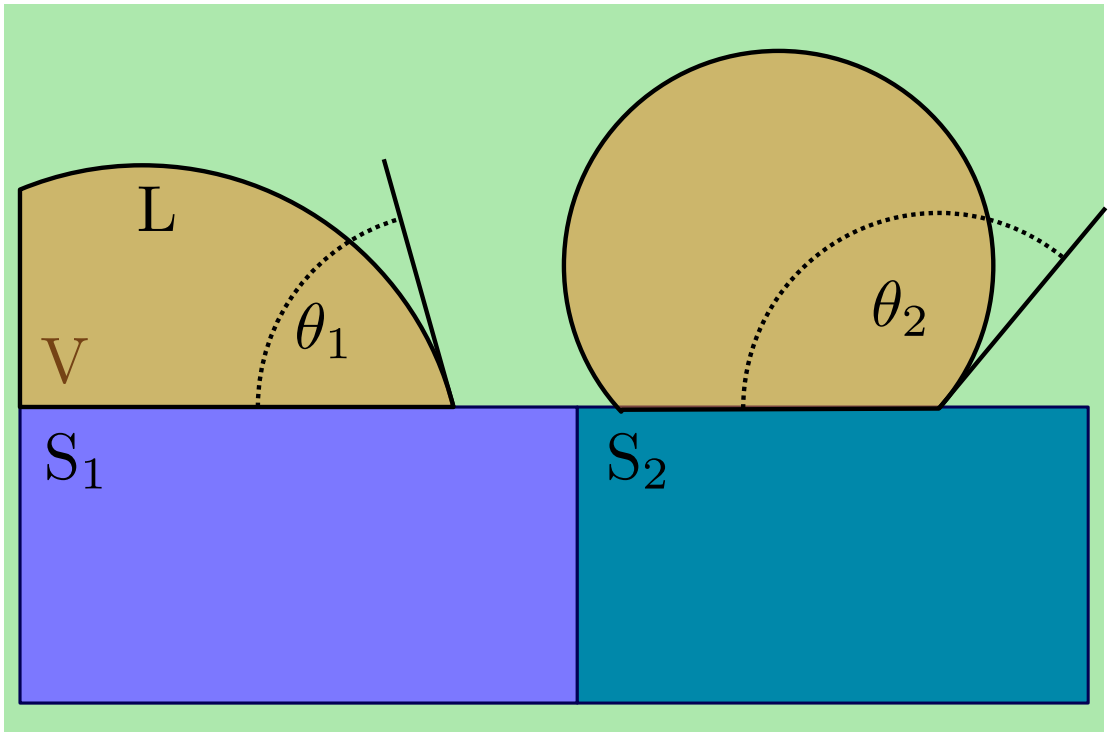
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Non-uniform Surfaces

- At a sharp interface there is a discontinuity in θ_0
- Droplets can move to reach global equilibrium
- "Generalized" Cassie equation: effective contact angle is a weighed average of the surface fractions and the ideal contact angle cosines

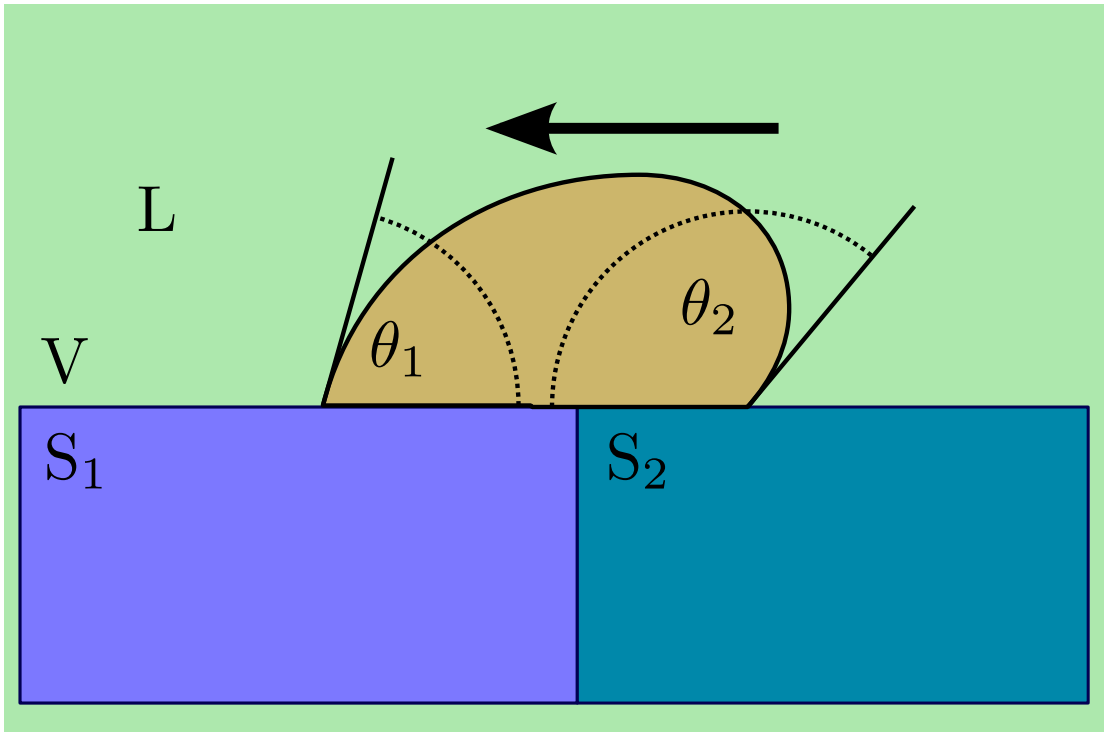
$$\cos\theta_{\text{macro}} = \sum_i \phi_i \cos\theta_i$$ Multi-component surface



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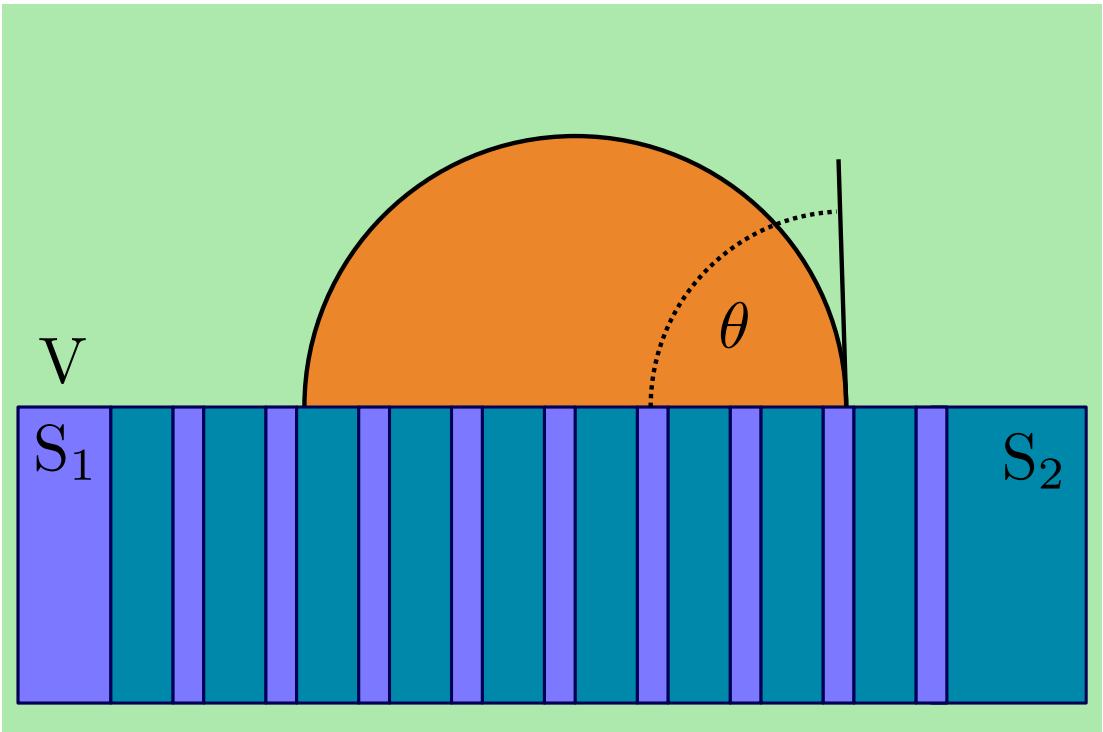


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Contact Angle Hysteresis

- In real surfaces, the triple line is "pinned", so in practice there is a range of meta-stable contact angles ("contact angle hysteresis")
- The maximum and minimum meta-stable angles are called *advancing* and *receding* contact angles

