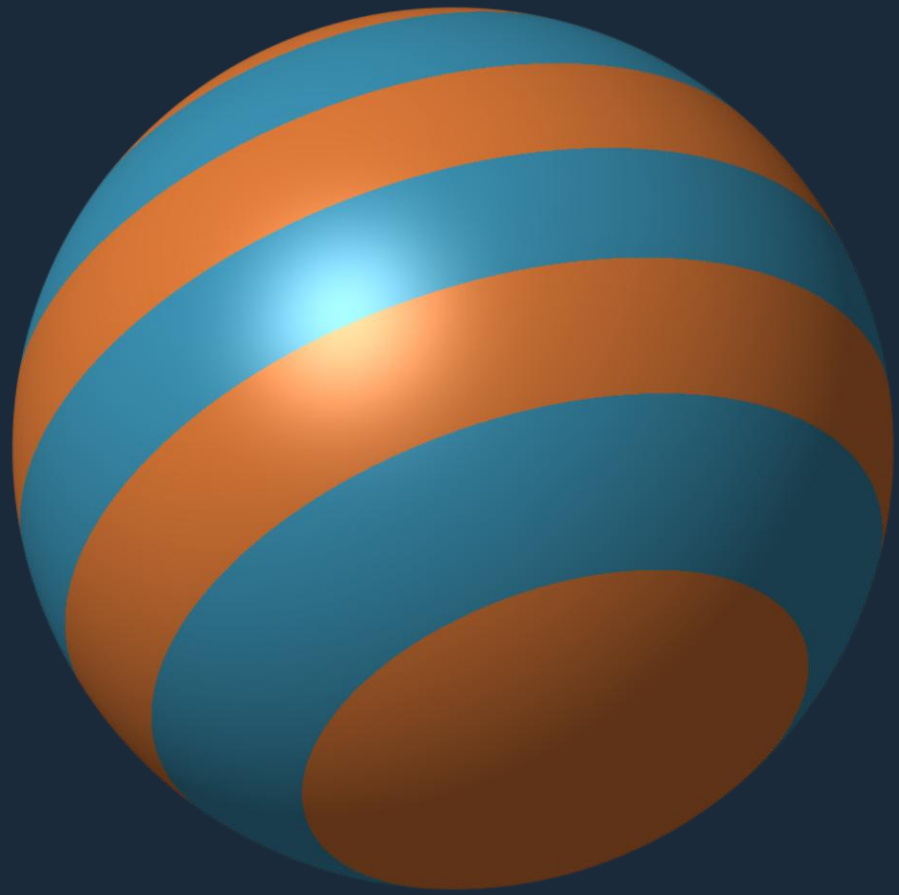
GUEST LECTURE 1 OF 3

Surface Science of Nanoparticles

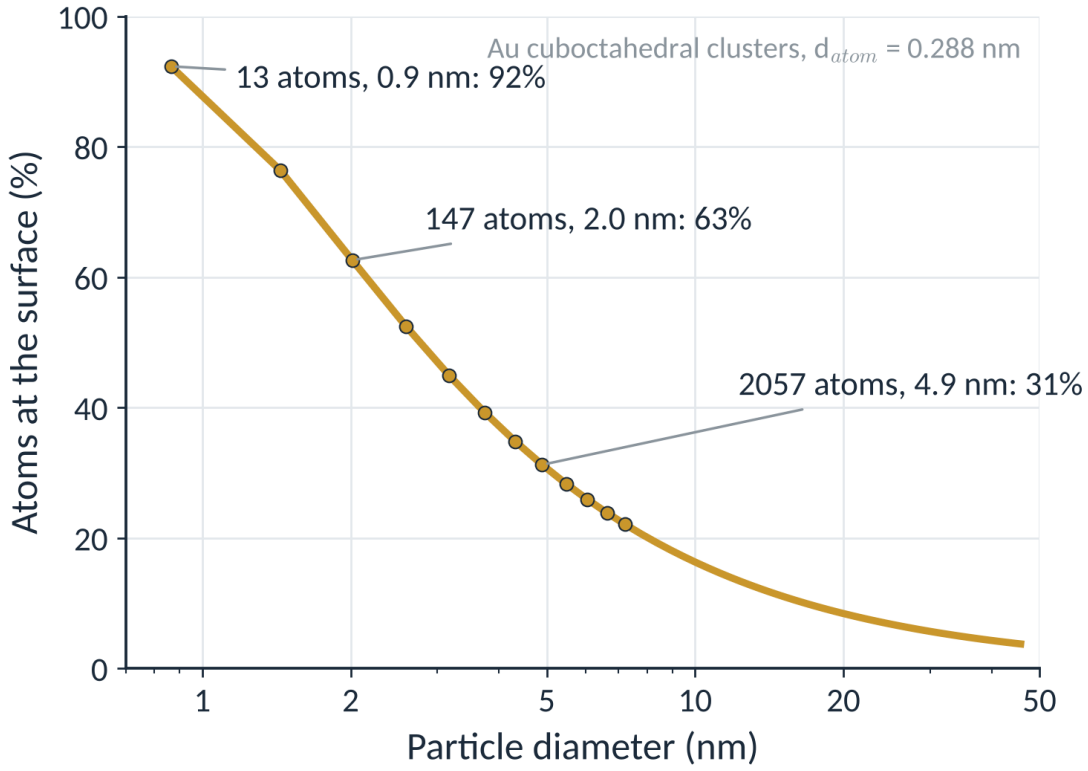
Interfacial energy, wetting and charged interfaces



Francesco Stellacci · EPFL

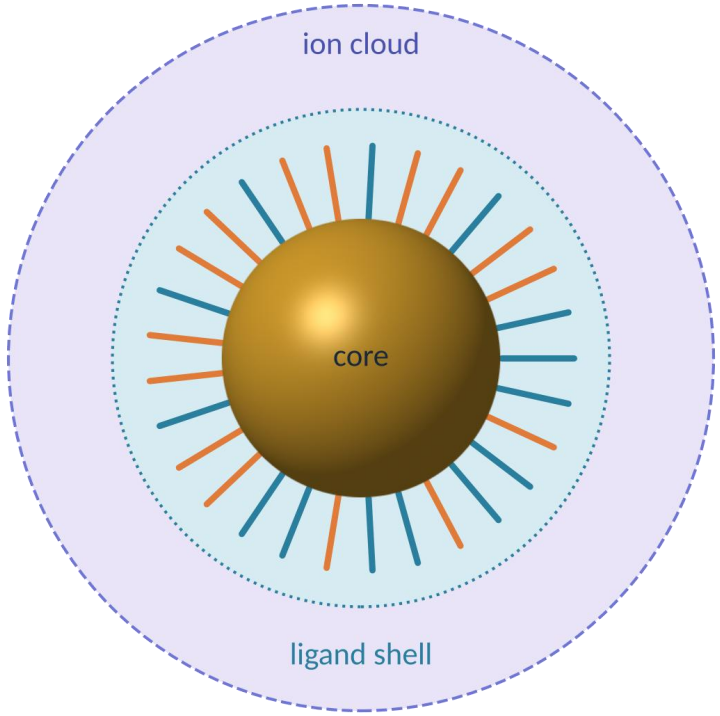
Why surfaces dominate at the nanoscale

- A 2 nm gold particle has about 60% of its atoms at the surface
- Surface atoms miss neighbours, so they carry an excess free energy: γ per unit area
- The term γA competes with bulk terms: it shifts phase equilibria and drives ripening and aggregation
- In a liquid, a nanoparticle is largely its interface: wetting, charge and ligands set its behaviour



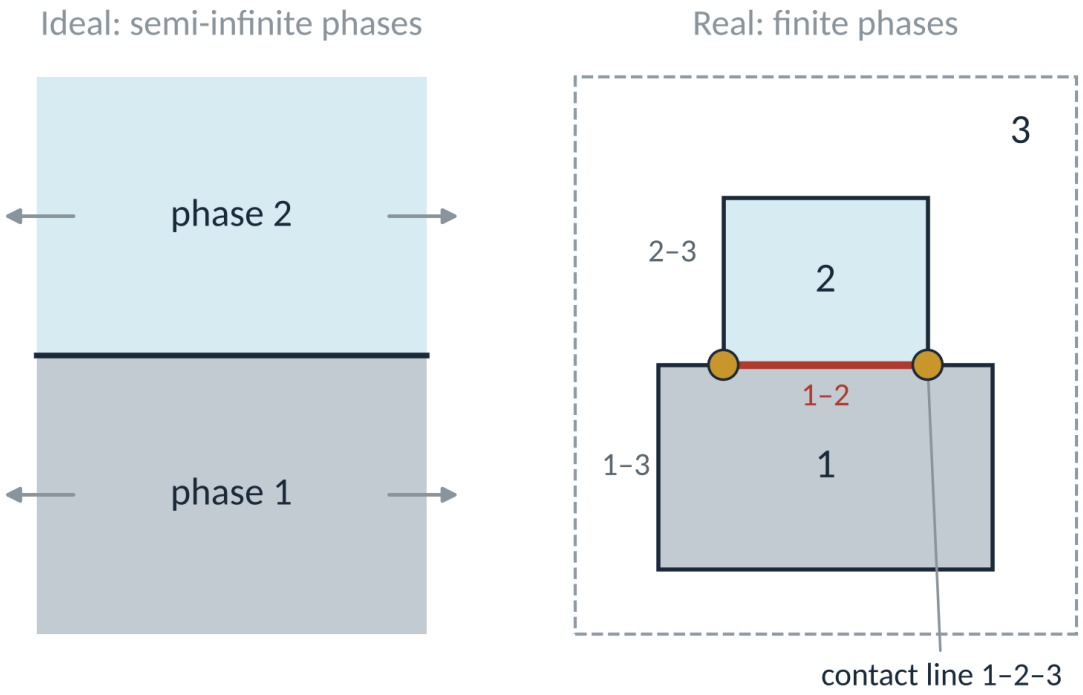
Outline

1. Interfaces and interfacial energy
2. Curvature: why size matters
3. Wetting: Young and Young–Dupré
4. Roughness, superhydrophobicity, hedgehog particles
5. Molecularly patchy surfaces
6. Charged solid–liquid interfaces
7. Colloidal stability: DLVO



What is an interface?

- An interface is the region where properties change from those of phase 1 to those of phase 2
- Ideal model: two semi-infinite phases and a single interface
- Real, finite systems: several interfaces (1–2, 1–3, 2–3) that meet at contact lines (1–2–3)
- A nanoparticle is finite in every direction



Reading: J. N. Israelachvili, Intermolecular and Surface Forces, 3rd ed., Academic Press (2011), Ch. 17

Interfacial energy: a thermodynamic definition

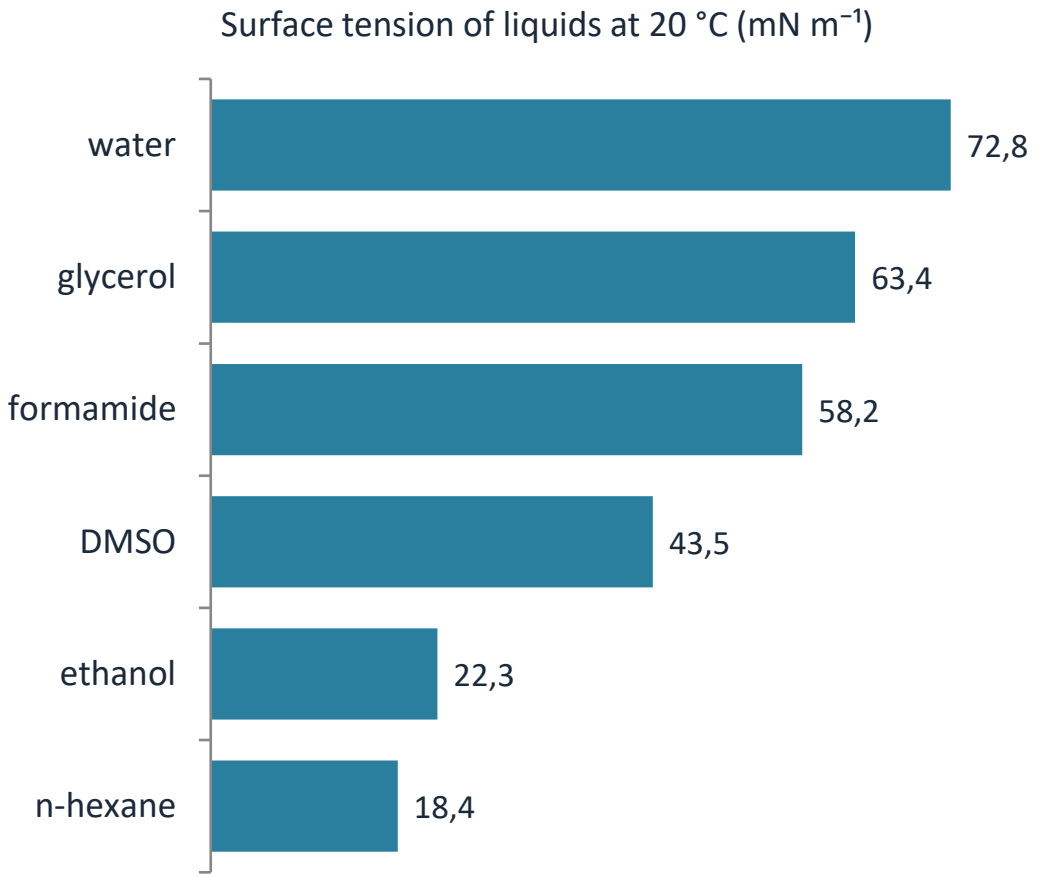
General: every facet (hkl), every pair of phases

$$G = \sum_i \mu_i^{\infty} N_i + \sum_{hkl} \sum_{ij} f_{ij}^{hkl} A_{ij}^{hkl}$$

Simplified: one γ per interface

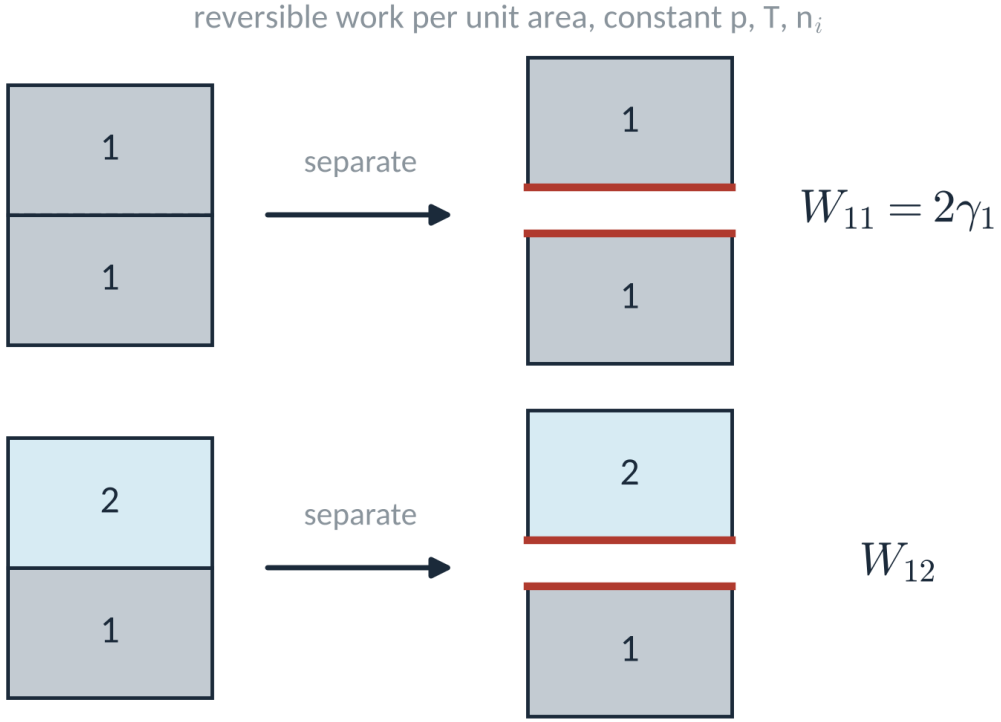
$$G = \sum_i \mu_i^{\infty} N_i + \sum_i \gamma_i A_i \qquad \gamma = \left(\frac{\partial G}{\partial A} \right)_{p,T,n_i}$$

- γ is an excess free energy per unit area (J m^{-2} = N m^{-1})
- Solids: γ depends on the facet (hkl), which sets nanocrystal shapes
- Liquids: γ is the surface tension

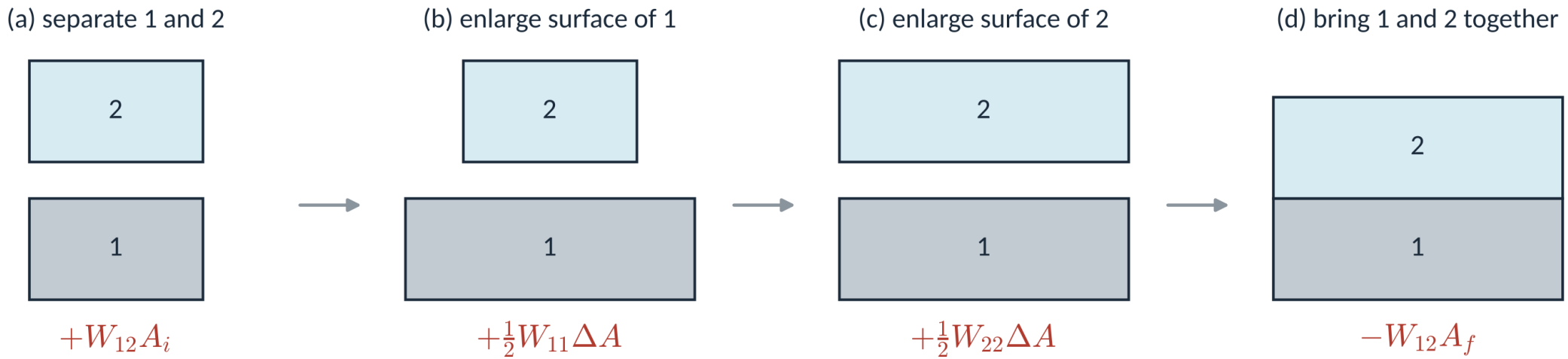


Work of cohesion and work of adhesion

- **W_{11}**: reversible work per unit area to separate phase 1 from itself (constant p, T, n_i)
- Two new surfaces are created: $W_{11} = 2\gamma_1$
- **W_{12}**: reversible work per unit area to separate phase 1 from phase 2
- In vacuum, W_{11} and W_{12} are always positive



From work of adhesion to interfacial energy



$$\gamma_{12}\,\Delta A = W_{12}A_i + \tfrac{1}{2}W_{11}\Delta A + \tfrac{1}{2}W_{22}\Delta A - W_{12}A_f$$

Dupré equation

$$\gamma_{12} = \tfrac{1}{2}W_{11} + \tfrac{1}{2}W_{22} - W_{12} = \gamma_1 + \gamma_2 - W_{12}$$

- Strong 1–2 adhesion means low interfacial energy
- $\gamma_{12} \rightarrow 0$ when phases 1 and 2 are alike

Three phases: adhesion in a medium and spreading

$$W_{132} = \gamma_{13} + \gamma_{23} - \gamma_{12} = W_{12} + W_{33} - W_{13} - W_{23}$$

Solid (1), liquid (2), vapour (3): $W_{33} \approx W_{13} \approx W_{23} \approx 0$

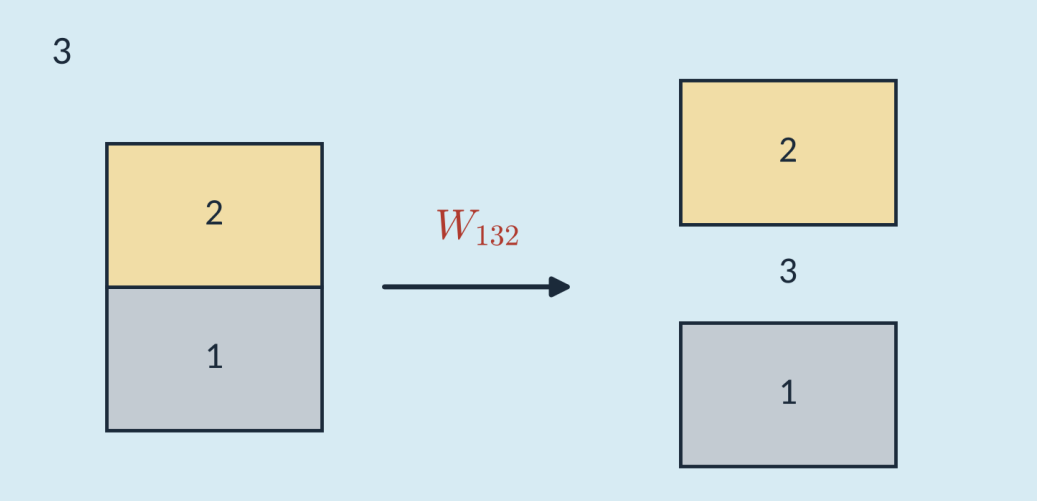
$$W_{SL} = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$

Dupré equation

Spreading coefficient:

$$S = \gamma_{SV} - \gamma_{SL} - \gamma_{LV} = W_{SL} - W_{LL}$$

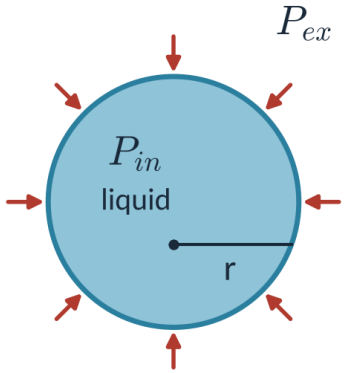
- S ≥ 0: the liquid spreads into a film
- S < 0: the liquid forms drops

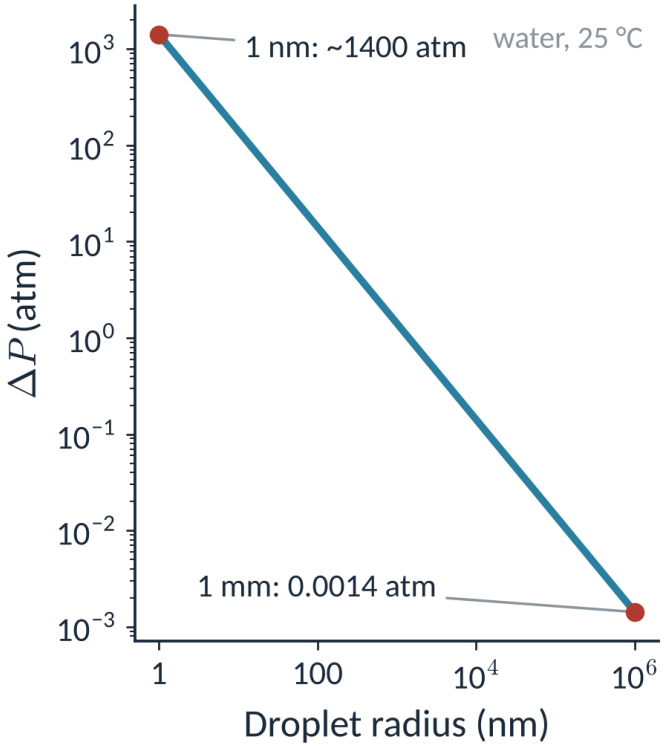


Laplace pressure

$$\Delta P = P_{\text{in}} - P_{\text{ex}} = \frac{2\gamma}{r}$$

- A curved interface pulls inwards; an excess pressure inside balances it
- General surface: $\Delta P = \gamma\,(1/R_1 + 1/R_2)$
- Water at 25 °C:
  - r = 1 mm: $\Delta P \approx 1.4 \times 10^{-3}$ atm
  - r = 1 nm: $\Delta P \approx 1.4 \times 10^{3}$ atm





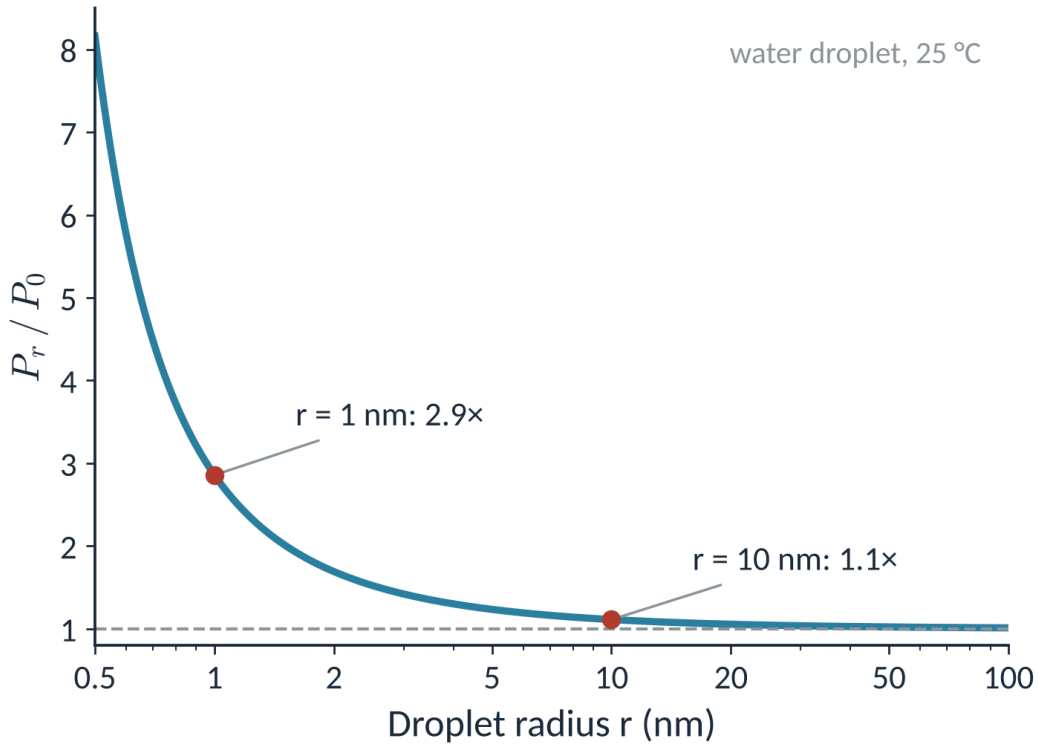
Chemical potential of a small phase: Kelvin equation

$$\mu = \mu^{\infty} + \frac{2\gamma V_m}{r} \qquad \ln\frac{P_r}{P_0} = \frac{2\gamma_{\mathrm{LV}} V_m}{RT\, r}$$

Particles in solution (Ostwald–Freundlich):

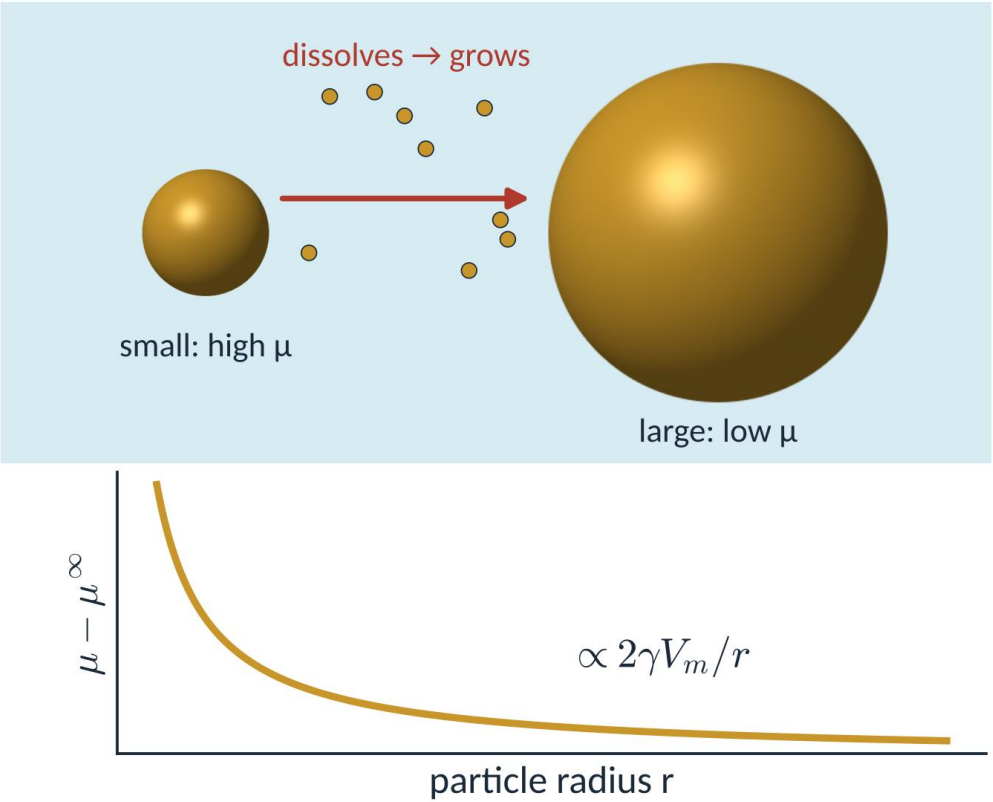
$$\ln\frac{c_r}{c_\infty} = \frac{2\gamma_{\mathrm{SL}} V_m}{RT\, r}$$

- Small droplets evaporate faster; small particles are more soluble
- Water: $P_r/P_0 \approx 2.9$ at r = 1 nm, 1.1 at r = 10 nm
- A droplet in a constant-pressure vapour is in unstable equilibrium



Ostwald ripening

- μ falls with r: material moves from small to large particles through the solution
- Small particles shrink and vanish; mean size grows, particle number falls
- Diffusion-limited (LSW) coarsening: $\langle r \rangle^3 - \langle r_0 \rangle^3 \propto t$
- Ligands, low solubility and surface charge slow ripening: essential in synthesis and storage



Nucleation: a surface-energy barrier

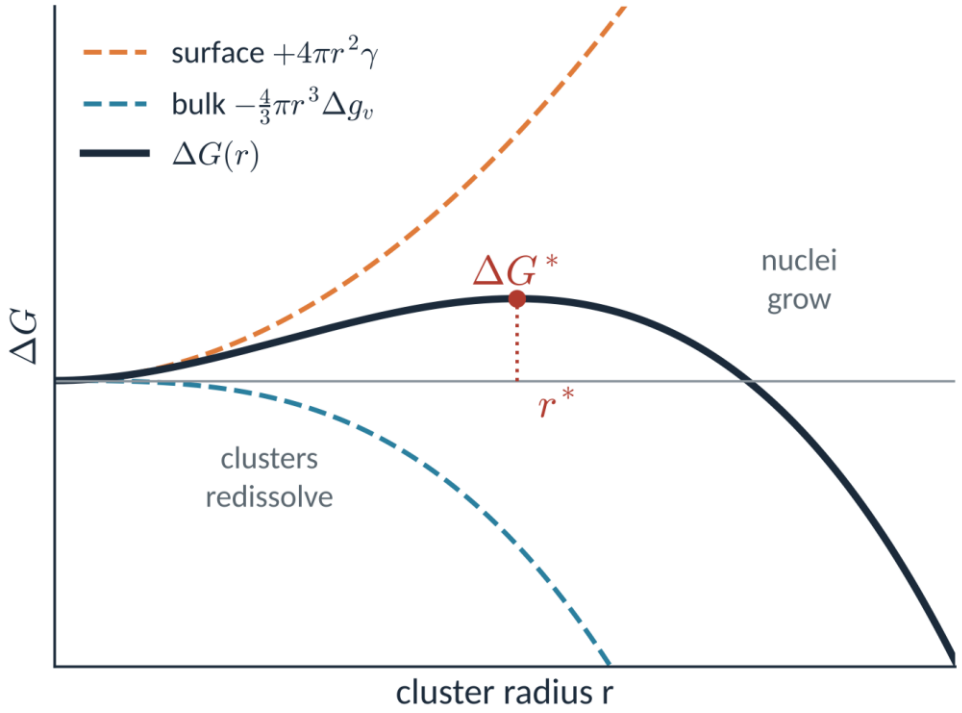
$$\Delta G(r) = -\frac{4}{3}\pi r^3 \Delta g_v + 4\pi r^2 \gamma$$

$$r^* = \frac{2\gamma}{\Delta g_v} \qquad \Delta G^* = \frac{16\pi\gamma^3}{3\,\Delta g_v^2} \qquad \Delta g_v = \frac{k_B T}{v} \ln S$$

- Below r^* clusters redissolve; above r^* they grow
- Higher supersaturation S lowers r^* and ΔG^*

On a substrate (heterogeneous nucleation):

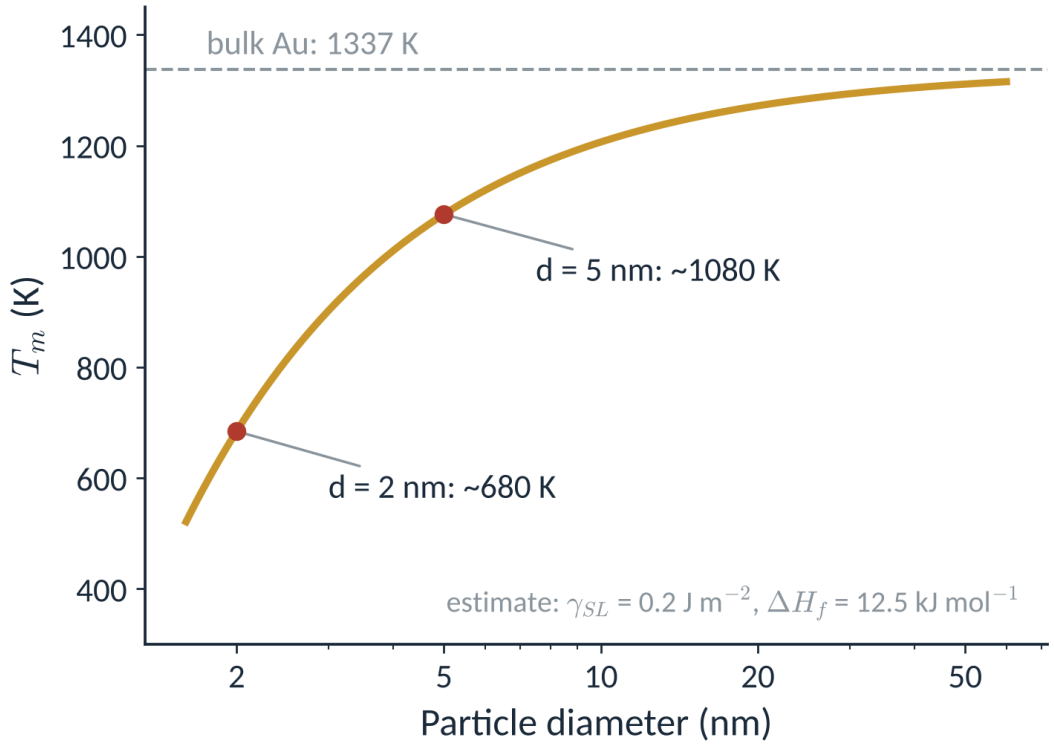
$$\Delta G^*_{\text{het}} = \Delta G^* f(\theta), \quad f(\theta) = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4}$$



Melting-point depression

$$\frac{T_m(r)}{T_m^{\infty}} = 1 - \frac{3\gamma_{SL}}{\Delta H_f \, r}$$

- A solid sphere melts when the bulk free-energy gain balances the cost of its γ_{SL} interface
- T_m falls as $1/r$ (ΔH_f per unit volume)
- Gold: 1337 K in bulk; particles of a few nm melt hundreds of kelvin lower
- Laplace, Kelvin, ripening, nucleation, melting: all γ/r effects



Ph. Buffat, J.-P. Borel, Phys. Rev. A 13, 2287 (1976)

Contact angle and Young's equation

At constant p, T, composition (no reactions):

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

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

Moving the contact line: $dA_{SV} = -dA_{SL}$

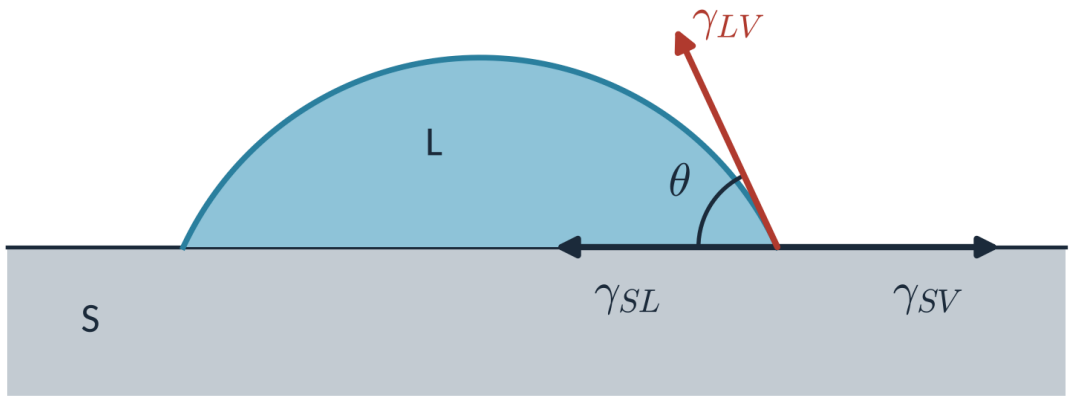
$$\left(\gamma_{\mathrm{SL}} - \gamma_{\mathrm{SV}}\right) dA_{\mathrm{SL}} + \gamma_{\mathrm{LV}}\, dA_{\mathrm{LV}} = 0$$

With $dA_{LV} = \cos\theta\, dA_{SL}$ (next slide):

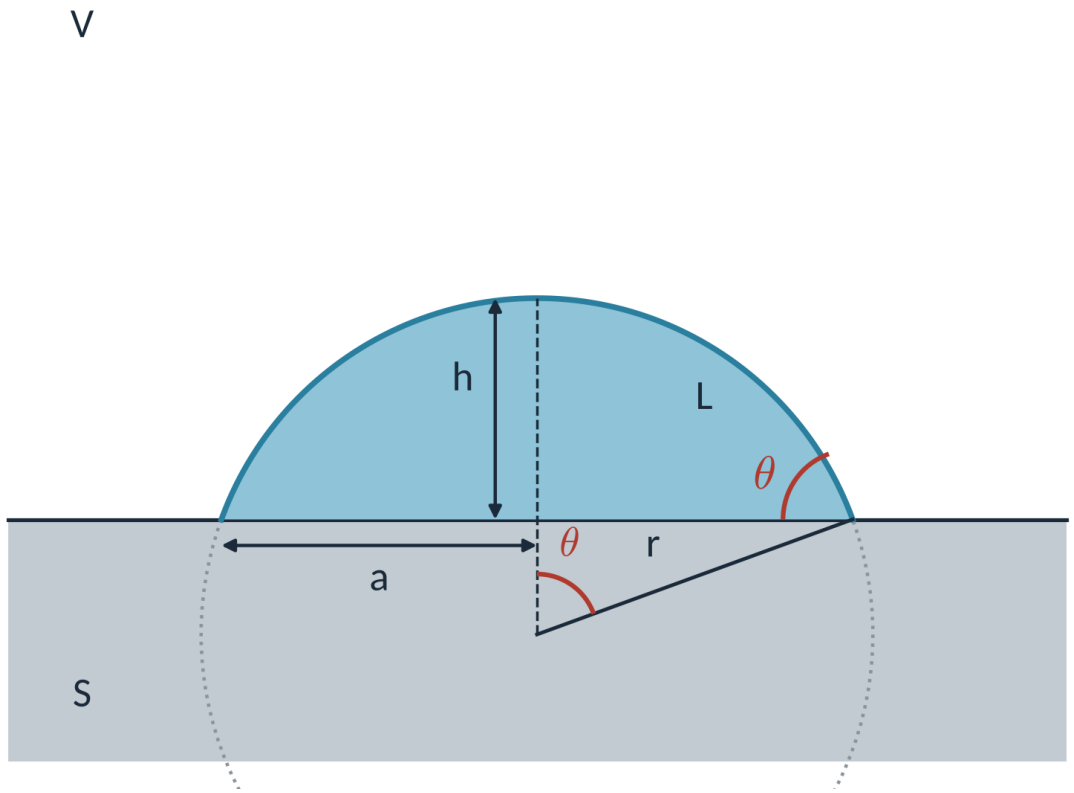
$$\gamma_{\mathrm{LV}} \cos\theta = \gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}}$$

Young's equation

V



Young's equation: the geometric step



Spherical cap, radius r, contact angle θ:

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

$$A_{\mathrm{LV}} = 2\pi r^2(1 - \cos\theta) \qquad A_{\mathrm{SL}} = \pi r^2 \sin^2\theta$$

Constant volume while the line moves:

$$\left.\frac{\partial V}{\partial \theta}\right| = 0 \;\Rightarrow\; \frac{dA_{\mathrm{LV}}}{dA_{\mathrm{SL}}} = \cos\theta$$

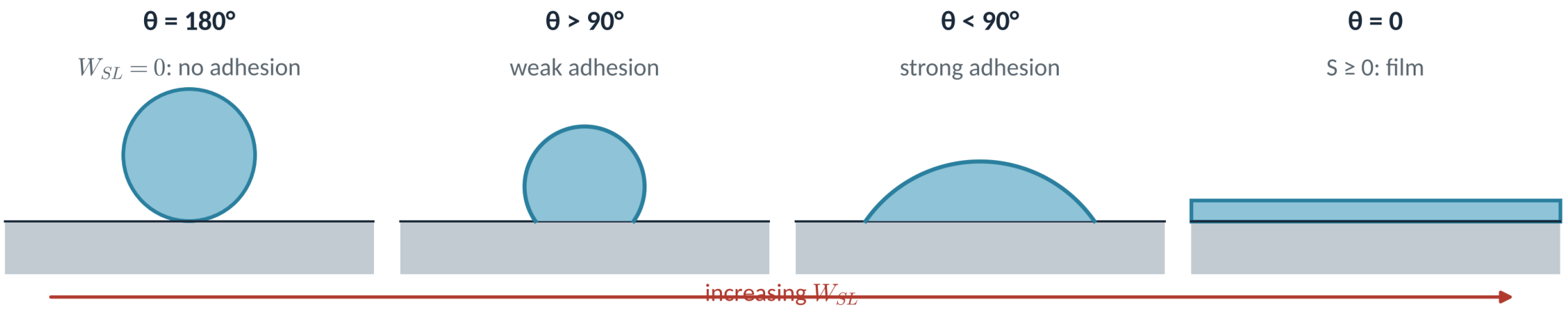
$$\gamma_{\mathrm{LV}} \cos\theta = \gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}}$$

Gravity neglected: drop smaller than the capillary length (≈ 2.7 mm for water)

Young–Dupré equation

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

Young–Dupré



- θ and γ_{LV} are measurable: together they give W_{SL}
- $\theta = 180° \Leftrightarrow W_{SL} = 0$; $\theta = 90° \Leftrightarrow W_{SL} = \gamma_{LV}$; $\theta = 0 \Leftrightarrow W_{SL} \geq 2\gamma_{LV} = W_{LL}$

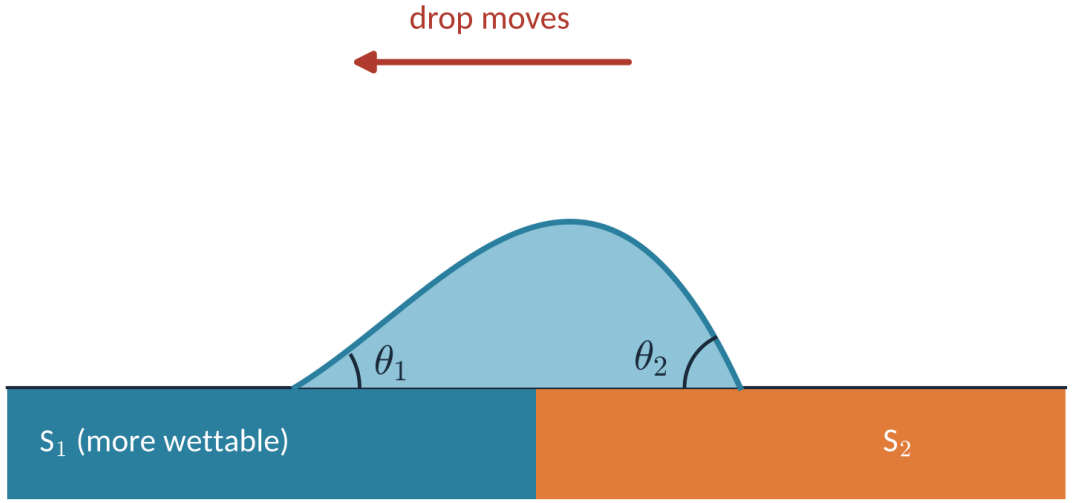
Drops on chemically patterned surfaces

- A drop straddling S_1 (θ_1) and S_2 ($\theta_2 > \theta_1$) is not at equilibrium

Advancing on S_1 while receding from S_2:

$$\frac{dG}{dA} = -\gamma_{LV}\left(\cos\theta_1 - \cos\theta_2\right) < 0$$

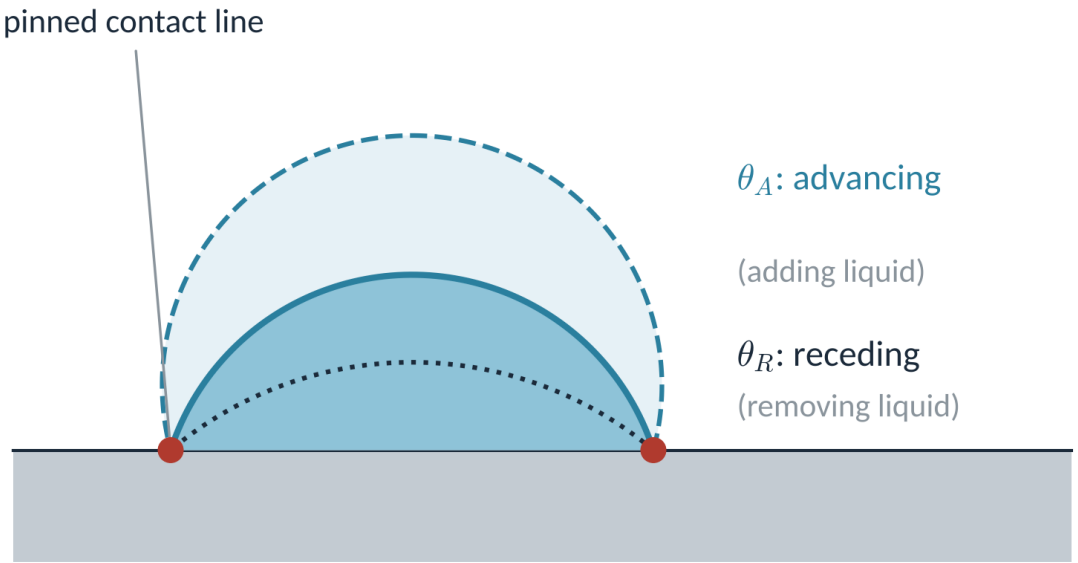
- Drops run towards the more wettable side
- Wettability gradients can drive drops uphill



M. K. Chaudhury, G. M. Whitesides, Science 256, 1539 (1992)

Measuring contact angles: hysteresis

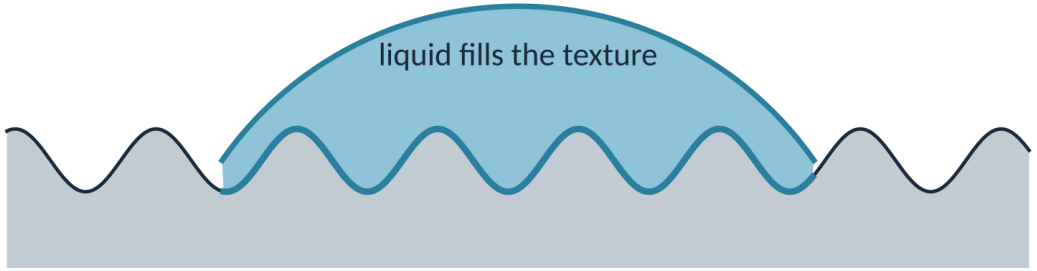
- Defects and heterogeneities pin the contact line
- Adding liquid: θ grows until the line advances at θ_A
- Removing liquid: θ falls until the line recedes at θ_R
- $\theta_R < \theta_{Young} < \theta_A$: report both, not one 'static' angle
- Hysteresis $\Delta\theta = \theta_A - \theta_R$ reflects heterogeneity

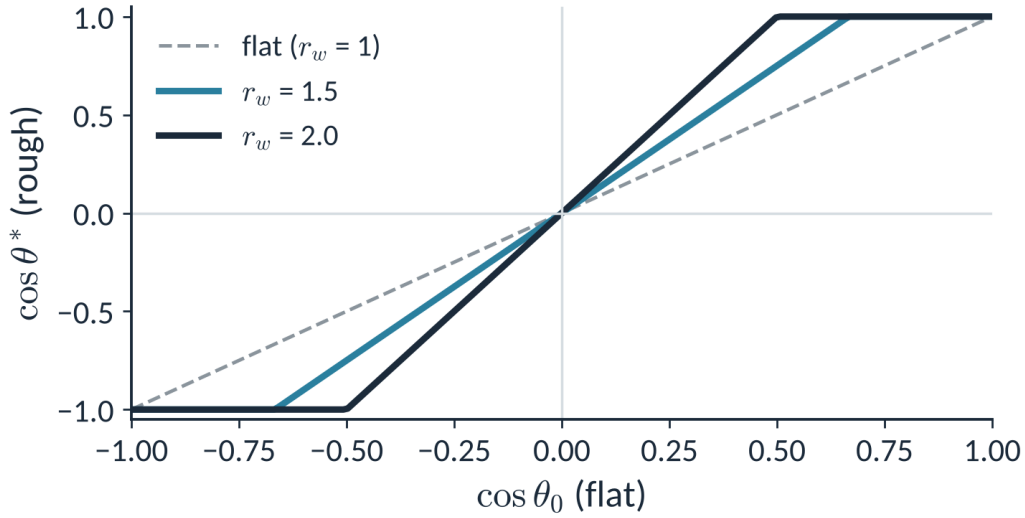


Rough surfaces: the Wenzel equation

$$\cos\theta^* = r_w \cos\theta_0 \qquad r_w = \frac{A_{\mathrm{SL}}^{\mathrm{micro}}}{A_{\mathrm{SL}}^{\mathrm{macro}}} \geq 1$$

- The liquid follows the texture: true contact area is r_w times larger
- Roughness amplifies the intrinsic behaviour:
  - $\theta_0 < 90°$: the rough surface wets more
  - $\theta_0 > 90°$: the rough surface repels more



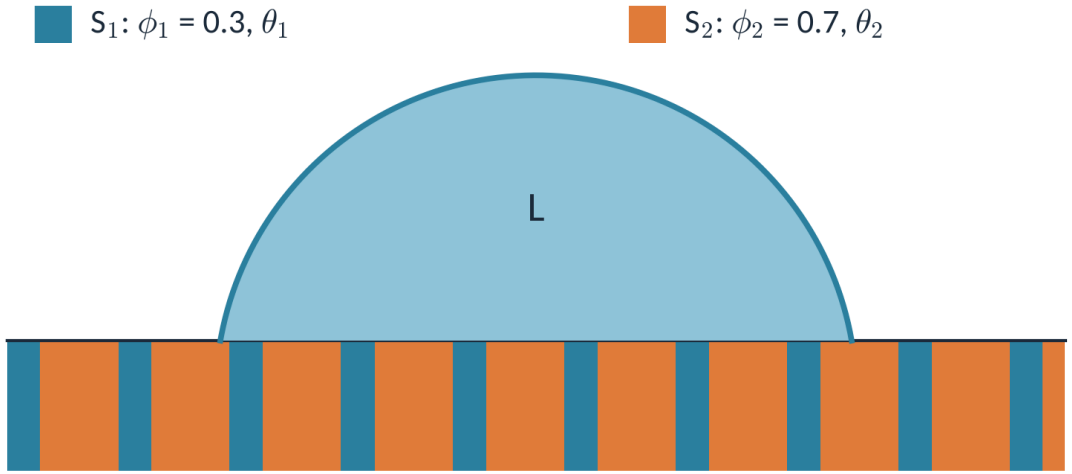


Mixed surfaces: the Cassie equation

$$\cos\theta^* = \sum_i \phi_i \cos\theta_i \qquad \sum_i \phi_i = 1$$

$$\Leftrightarrow \quad W_{\mathrm{SL}} = \sum_i \phi_i W_{\mathrm{SL},i}$$

- Example: $\phi_1 = 0.3$, $\phi_2 = 0.7$ gives
  - $\cos\theta^* = 0.3\cos\theta_1 + 0.7\cos\theta_2$
- Assumes domains much smaller than the drop and much larger than solvent molecules
- Additive W_{SL}: tested at the molecular scale in Section 5

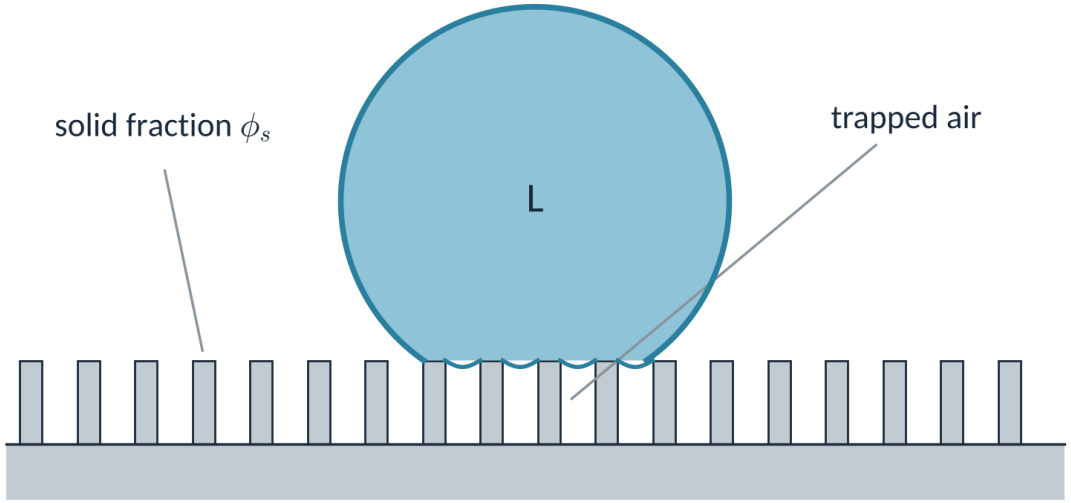


Air pockets: the Cassie–Baxter state

$$\cos\theta^* = \phi_s \cos\theta_0 + (1 - \phi_s)\cos 180°$$

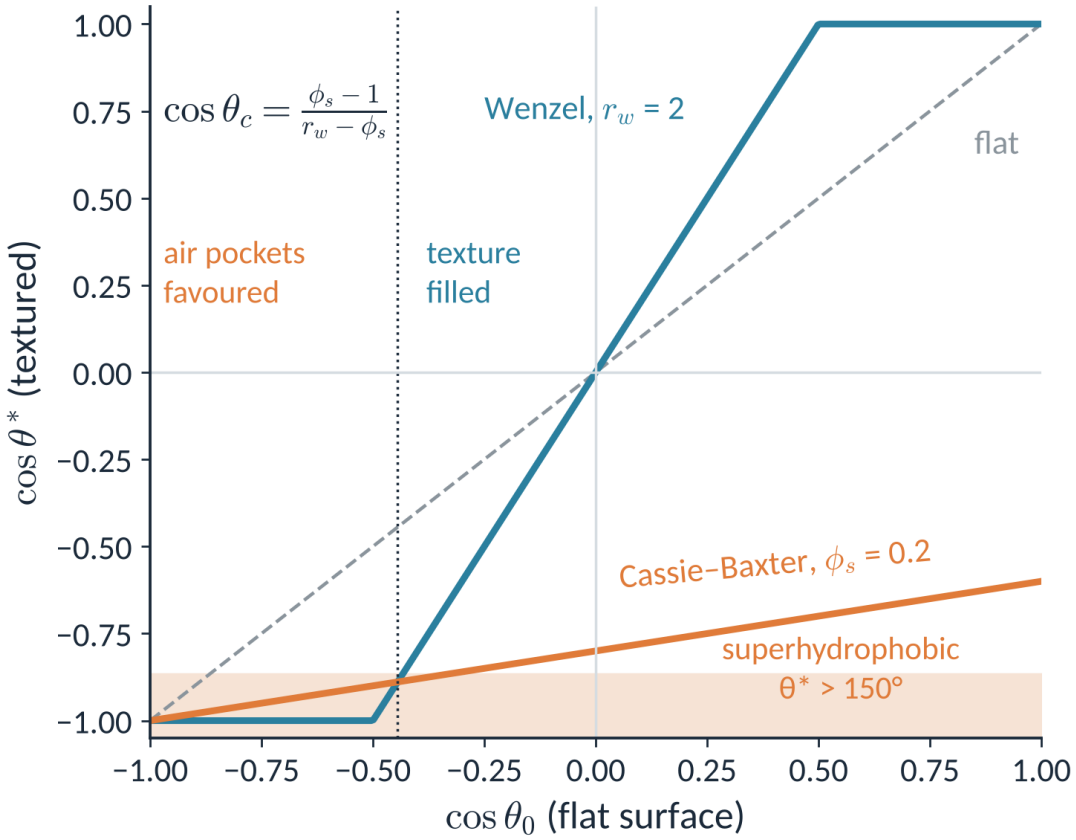
$$1 + \cos\theta^* = \phi_s\,(1 + \cos\theta_0)$$ **Cassie–Baxter**

- The liquid rests on the tops of the texture; trapped air acts as a component with θ = 180°
- A small solid fraction ϕ_s pushes θ^* towards 180°
- Little solid contact: low adhesion, low hysteresis



Superhydrophobicity and the lotus effect

- Superhydrophobic: $\theta^* > 150°$ and hysteresis < 10°; drops roll off and clean the surface
- Needs hydrophobic chemistry plus (hierarchical) roughness that holds air
- Air pockets are favoured when $\cos\theta_0 < \cos\theta_c$
- Porous alumina: θ rises from ≈60° to ≈130° as pores widen to ~400 nm



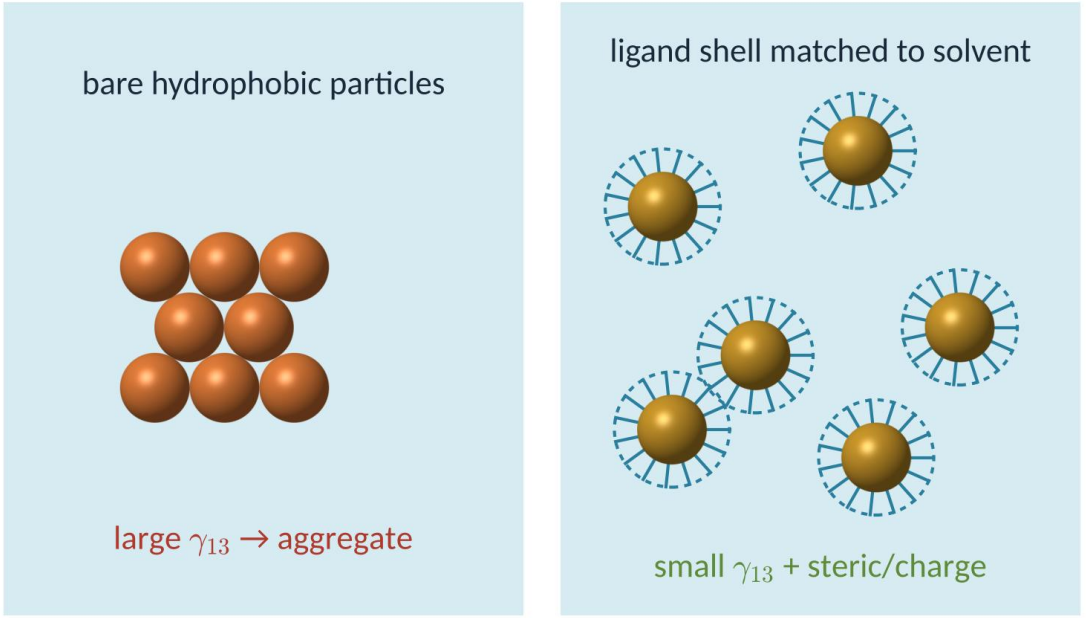
C. B. Ran, G. Q. Ding, W. C. Liu et al., Langmuir 24, 9952 (2008)

Dispersing particles: the classical view

$$W_{131} = 2\gamma_{13} > 0$$

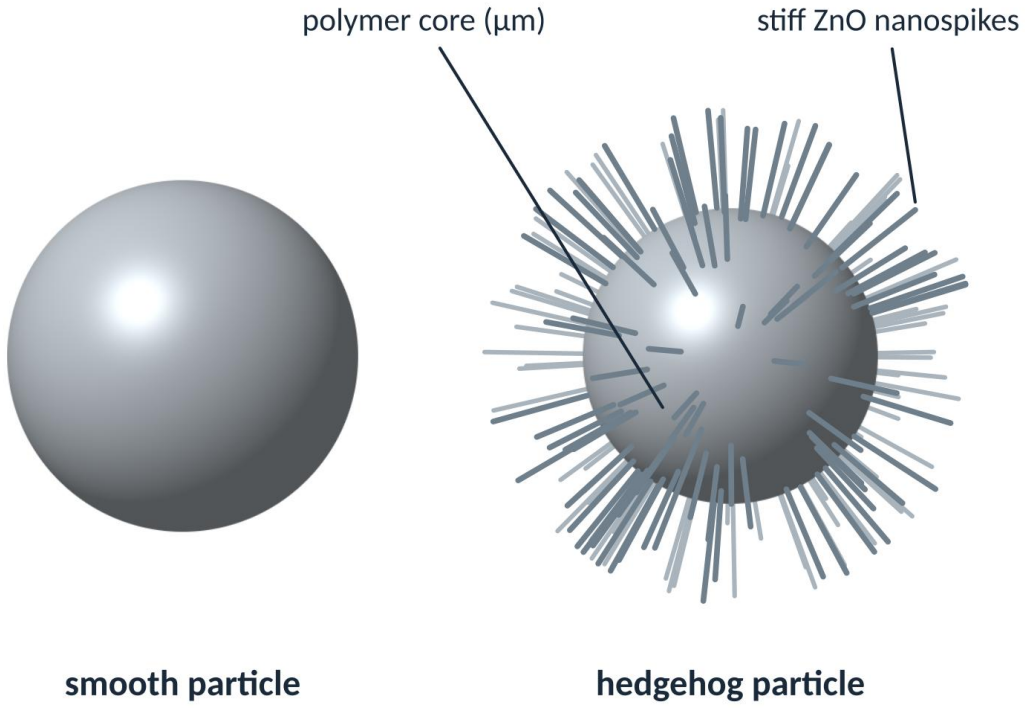
- Two identical particles in a solvent always attract: separating them costs $2\gamma_{13}$
- Hydrophobic particles in water (large γ_{13}) aggregate fast and irreversibly
- Classical cure: change the chemistry (ligands, surfactants, polymers) to lower γ_{13} and add repulsion

Can geometry do the job instead?



Hedgehog particles (Kotov and co-workers)

- Micrometre polymer spheres covered with stiff, radial ZnO nanospikes
- Hydrophobic (silane-treated) hedgehogs disperse in water
- Hydrophilic hedgehogs disperse in non-polar organic solvents
- Smooth particles with the same chemistry aggregate
- No surfactant needed: a route to low-VOC paints and coatings

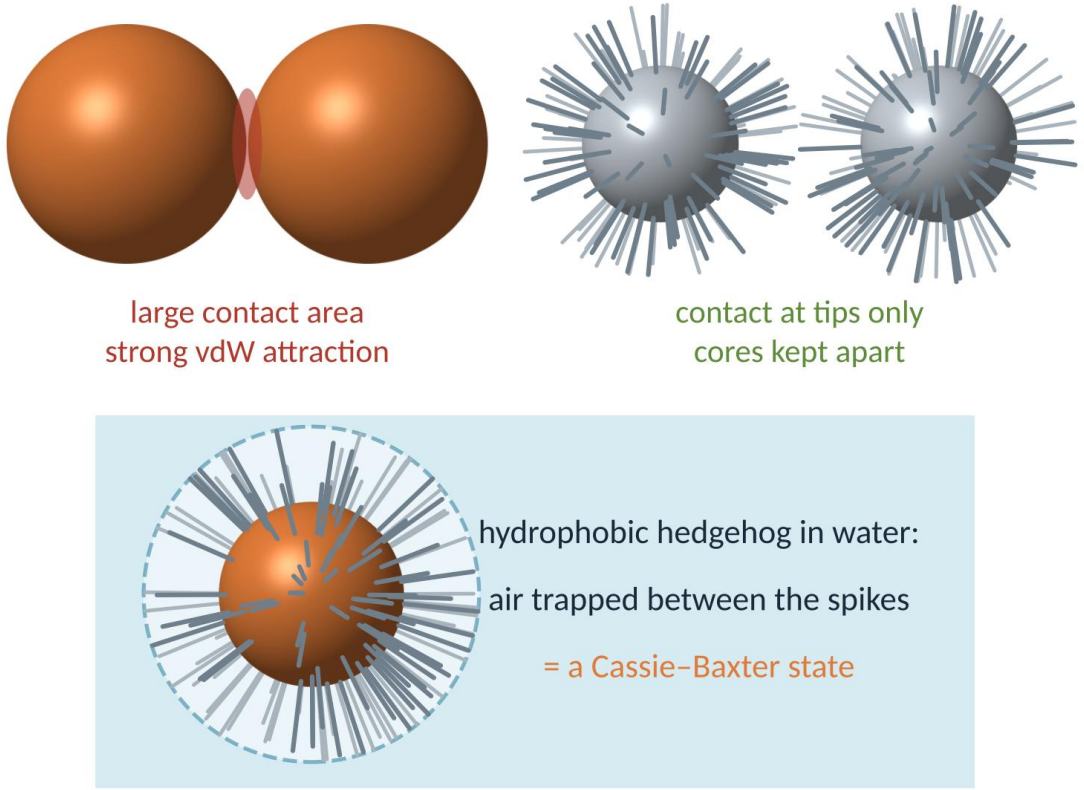


J. H. Bahng, B. Yeom, Y. Wang, S. O. Tung, J. D. Hoff, N. A. Kotov, Nature 517, 596 (2015)

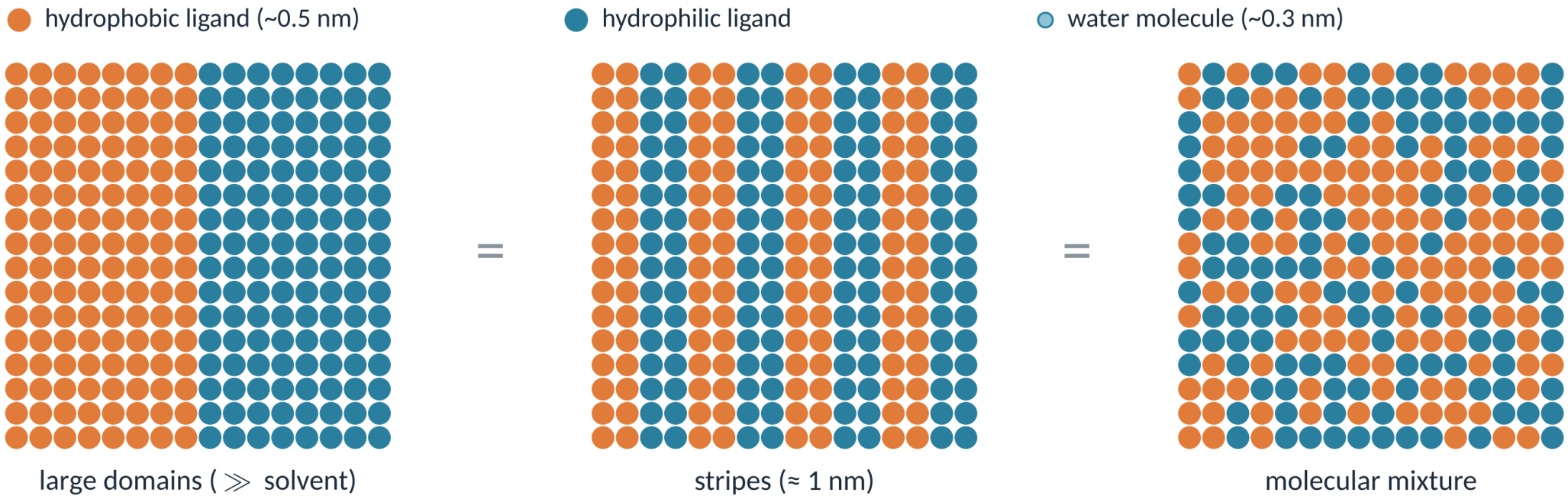
Why do hedgehogs stay dispersed?

- Spikes stop interpenetration: contact only at a few tips
- Small contact area and large core separation sharply reduce van der Waals attraction
- In water: air trapped between spikes (a Cassie–Baxter state) and charged air–water interfaces add repulsion
- In organic media: low ionic strength, long-range electrostatic repulsion

Topography can override surface chemistry



Does Cassie hold at the molecular scale?

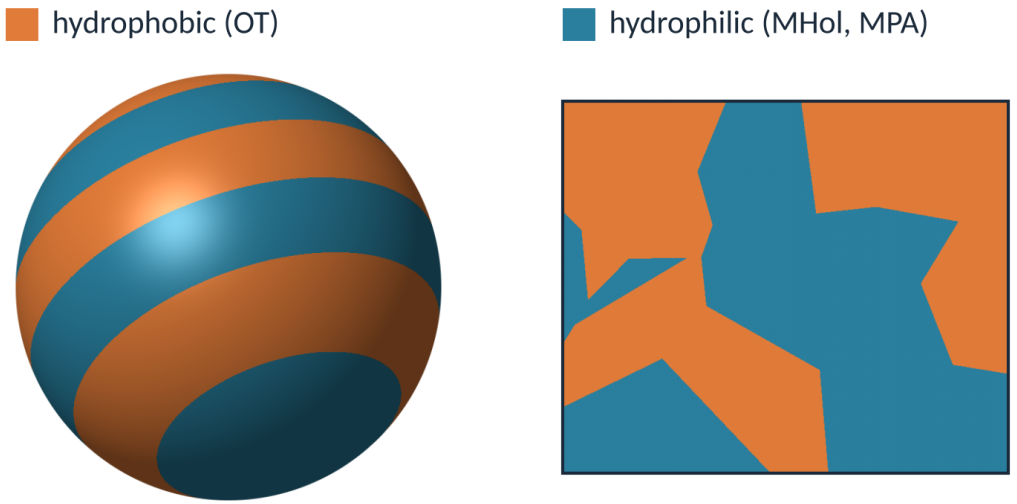


- Cassie: W_{SL} depends only on composition ϕ_i
- Hidden assumption: domains ≫ solvent molecules

- Proteins and ligand-coated nanoparticles have 0.5–2 nm domains
- Same composition, different arrangement: same γ_{SL}?

Mixed-ligand gold nanoparticles

- Au cores coated with two thiols: hydrophobic octanethiol (OT) plus hydrophilic mercaptohexanol (MHol) or mercaptopropionic acid (MPA)
- On small, faceted cores the ligands form stripe-like or patchy domains < 2 nm
- On flat gold the same mixtures form domains > 5 nm
- Model system: same chemistry, tunable nanoscale arrangement



mixed-ligand nanoparticle

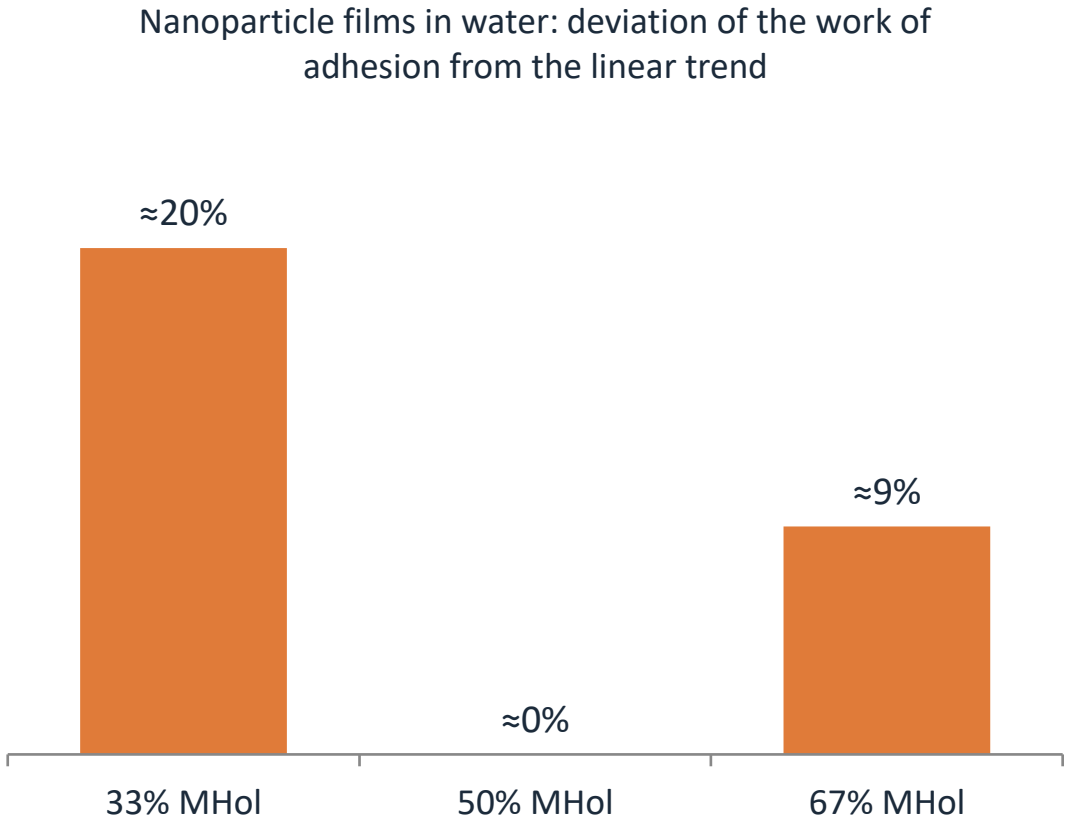
domains < 2 nm (stripes, patches)

same mixture on flat gold

domains > 5 nm

Interfacial energy depends on nanoscale structure

- W_{SL} vs composition from contact angles and small-amplitude AFM in liquid
- Flat SAMs (domains > 5 nm): linear in composition, as Cassie predicts
- Nanoparticle films (domains < 2 nm): non-monotonic, deviations up to ~20%
- 3 M NaCl changes the pattern of deviations

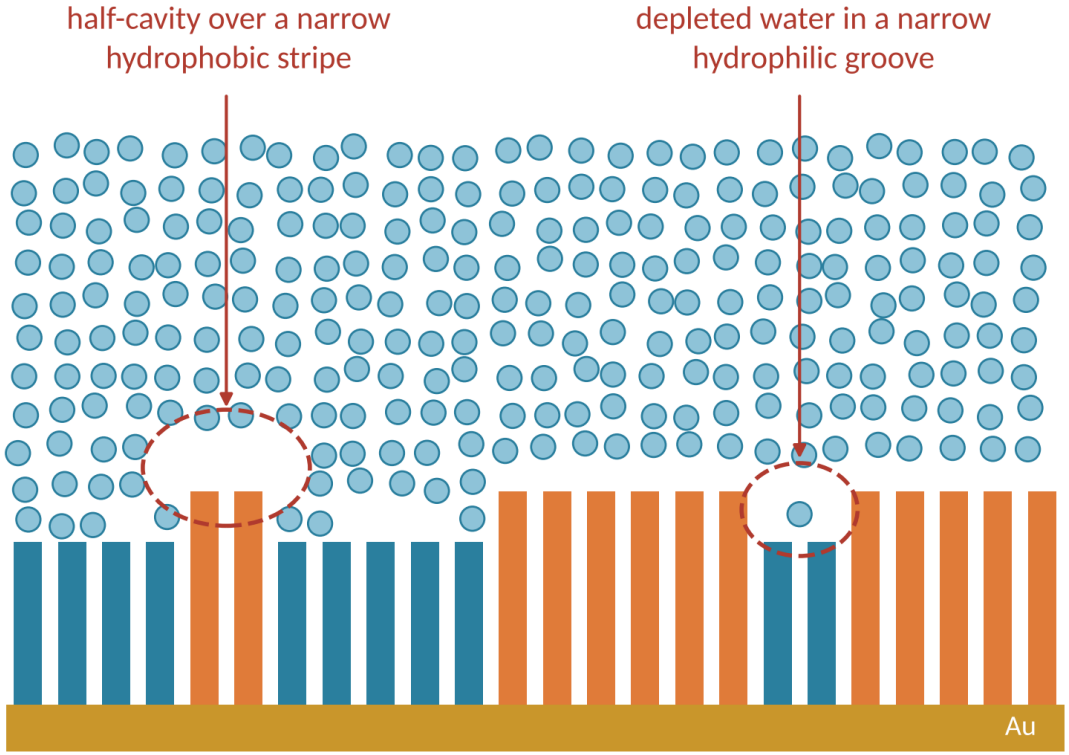


J. J. Kuna, K. Voïtchovsky, C. Singh, H. Jiang, S. Mwenifumbo, P. K. Ghorai, M. M. Stevens, S. C. Glotzer, F. Stellacci, Nat. Mater. 8, 837 (2009)

Molecular origin: solvent structure at the interface

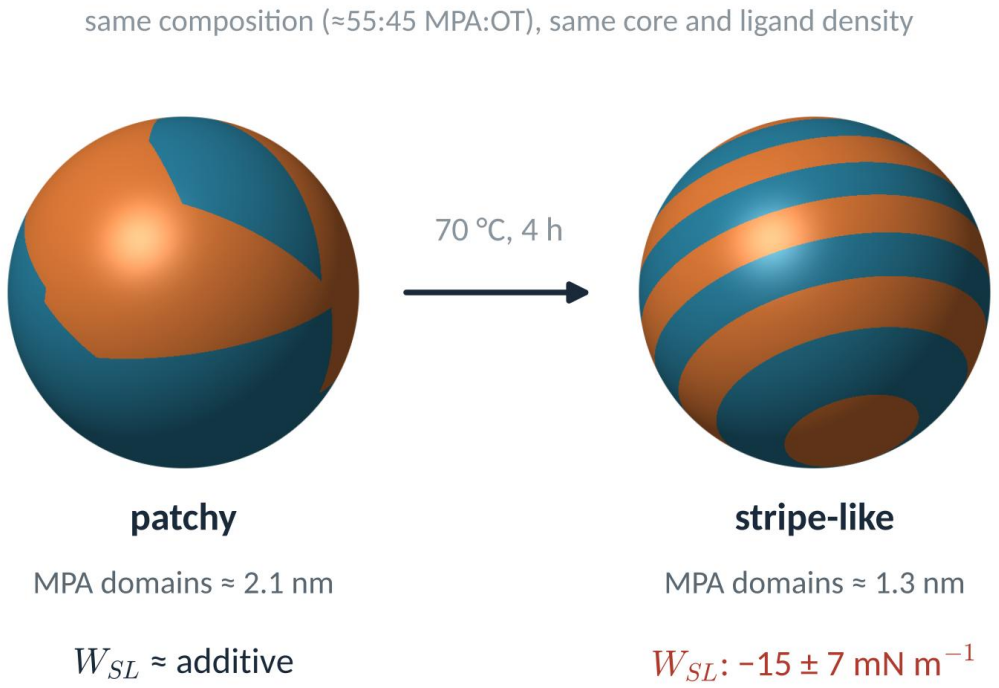
- Simulations: over narrow hydrophobic stripes water forms half-cavities bridged by hydrogen bonds
- Narrow hydrophilic grooves confine water and partly exclude it
- Both effects depend on stripe width, so W_{SL} varies non-monotonically

At the nanoscale, hydrophobicity is not a property of a molecule alone



Same composition, different patches

- Au nanoparticles (core ≈ 4.9 nm), ≈55:45 MPA:OT; annealing at 70 °C turns patches into stripes
- Morphology from small-angle neutron scattering; composition, size, density unchanged
- W_{SL} differs by 15 ± 7 mN m^{-1} (~20%): stripe-like particles are more hydrophobic
- Sum-frequency generation: interfacial water hydrogen-bonds differently



Z. Luo, A. Murello, D. M. Wilkins, F. Kovacik, J. Kohlbrecher, A. Radulescu, H. I. Okur, Q. K. Ong, S. Roke, M. Ceriotti, F. Stellacci, PNAS 116, 25516 (2019)

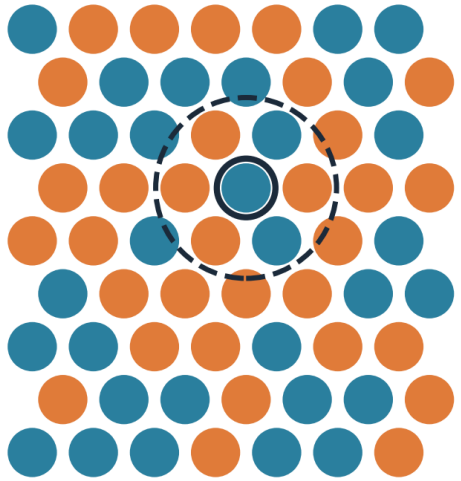
A nearest-neighbour model of wetting

$$\Delta f = \sum_i n_i \, f_i$$

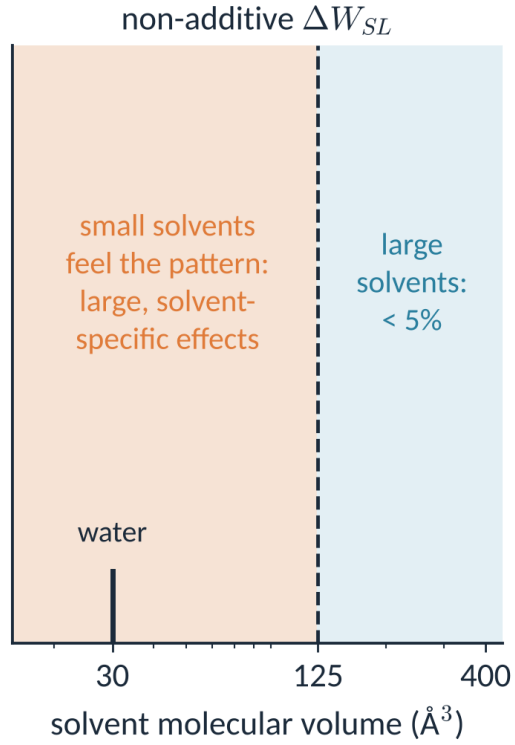
sum over ligand environments

- Excess water density and orientation over a ligand set by its first neighbours
- Cluster-expansion-like model reproduces both morphologies
- Confirmed: solvents > ~125 Å^3 span several ligands, < 5% effect

Wetting is non-additive when domains approach the solvent size



ligand + first neighbours set its local excess



Electrochemical equilibrium at an interface

Solid α (activity ≈ 1):

$$\tilde{\mu}_i^{\alpha} = \mu_i^{\infty,\alpha} + \mu_i^{s,\alpha\beta} + z_i F \psi_0$$

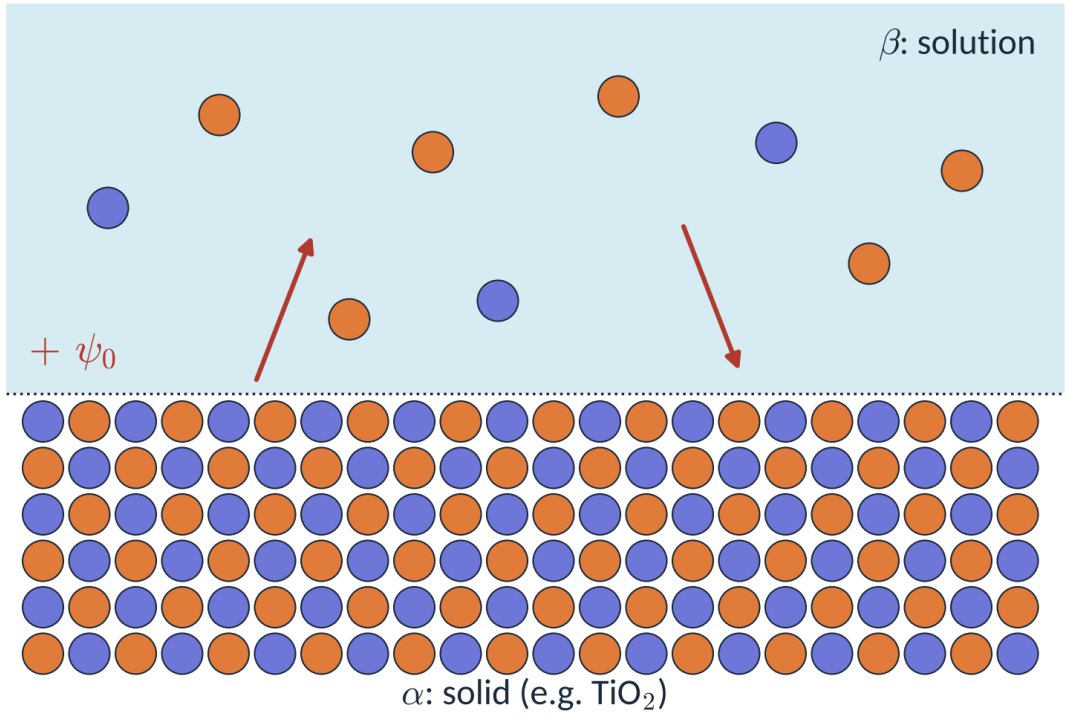
Solution β (reference, ψ = 0):

$$\tilde{\mu}_i^{\beta} = \mu_i^{0,\beta} + RT \ln c_i$$

$$\tilde{\mu}_i^{\alpha} = \tilde{\mu}_i^{\beta} \quad \forall\, i$$

for every species

- Ions and electrons exchange until their electrochemical potentials match
- Result: a net surface charge and a surface potential ψ_0

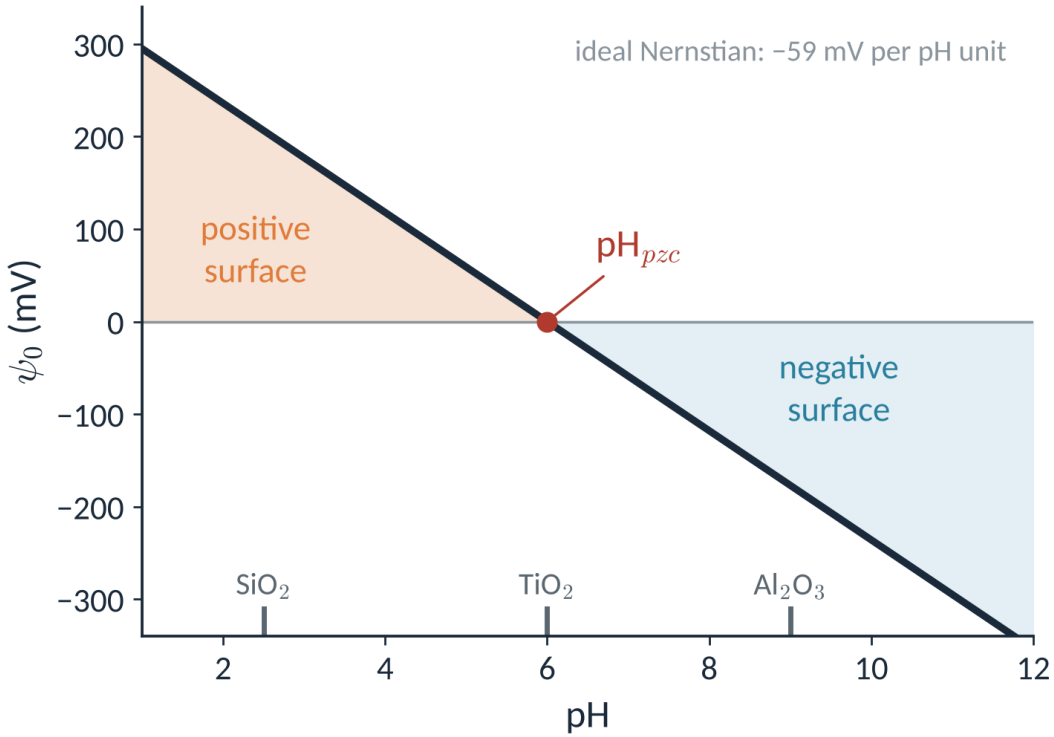


The point of zero charge

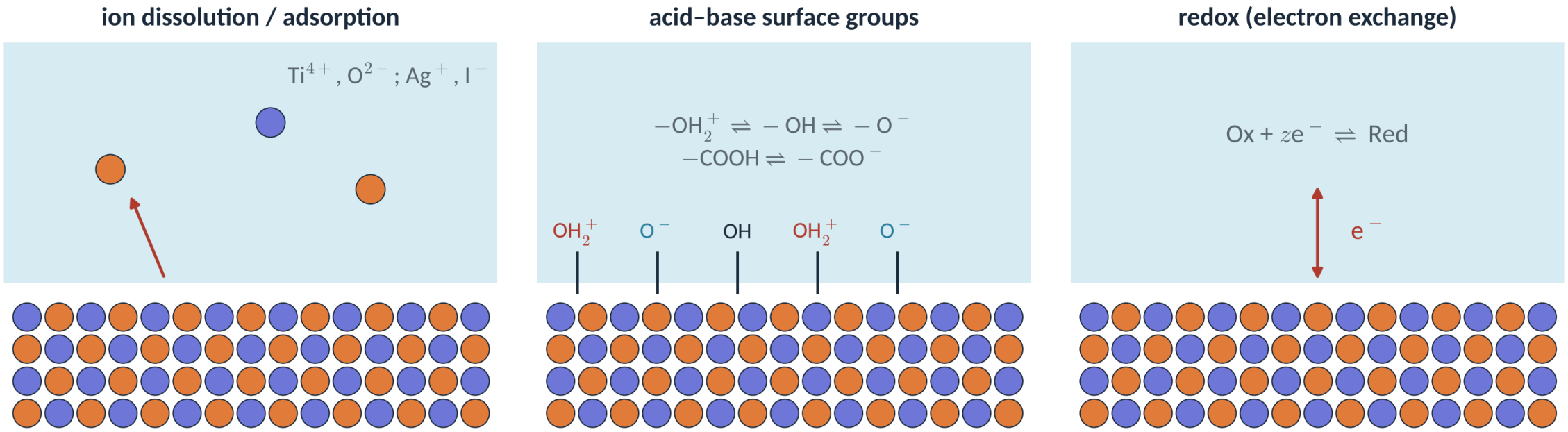
$$\psi_0 = \frac{RT}{zF} \ln \frac{c_i}{c_i^{\mathrm{pzc}}}$$

$$\psi_0 \approx 0.059\,(\mathrm{pH_{pzc}} - \mathrm{pH})\ \mathrm{V} \quad (H^+,\ 25\ °C)$$

- pzc: concentration of the potential-determining ion at which $\psi_0 = 0$
- Oxides: positive below pH_{pzc}, negative above
- Typical pH_{pzc}: SiO_2 ≈ 2–3, TiO_2 ≈ 6, α-Al_2O_3 ≈ 9



Atomistic origins of surface charge



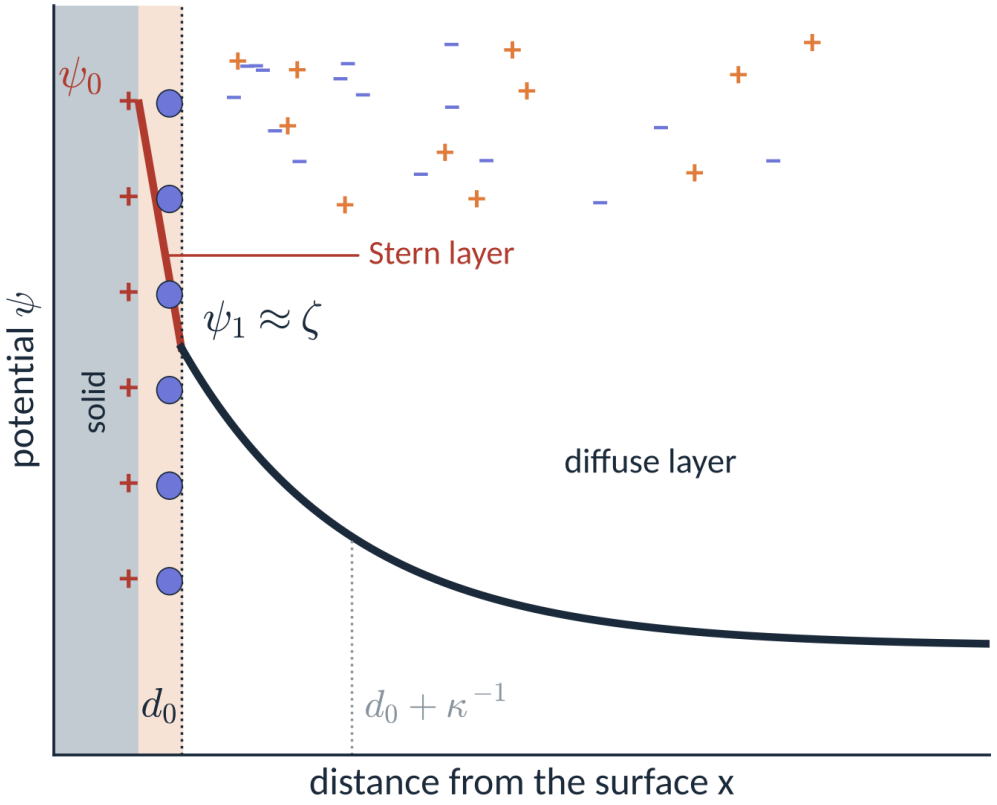
- Lattice ions dissolve or adsorb unequally (TiO_2, AgI)
- Surface groups protonate or deprotonate
- Metals exchange electrons with redox couples

ψ_0 depends on crystallography, shape and the composition of both phases

The Helmholtz (Stern) layer

$$\sigma_0 = \frac{\varepsilon_0 \varepsilon_r}{d_0}(\psi_0 - \psi_1) \qquad \psi_1 \approx \zeta$$

- Counter-ions bind at a plane d_0 from the surface (≈ hydrated ion radius)
- A molecular capacitor, $K = \varepsilon_0\varepsilon_r/d_0$: linear drop from ψ_0 to ψ_1
- $\psi_1 \approx \zeta$, the zeta potential measured by electrophoresis
- Beyond d_0: the diffuse layer



The diffuse layer: Poisson–Boltzmann

$$\nabla^2\psi = -\frac{\rho}{\varepsilon_0\varepsilon_r} \qquad n_i = n_i^\infty \exp\left(-\frac{z_i e\psi}{k_B T}\right)$$

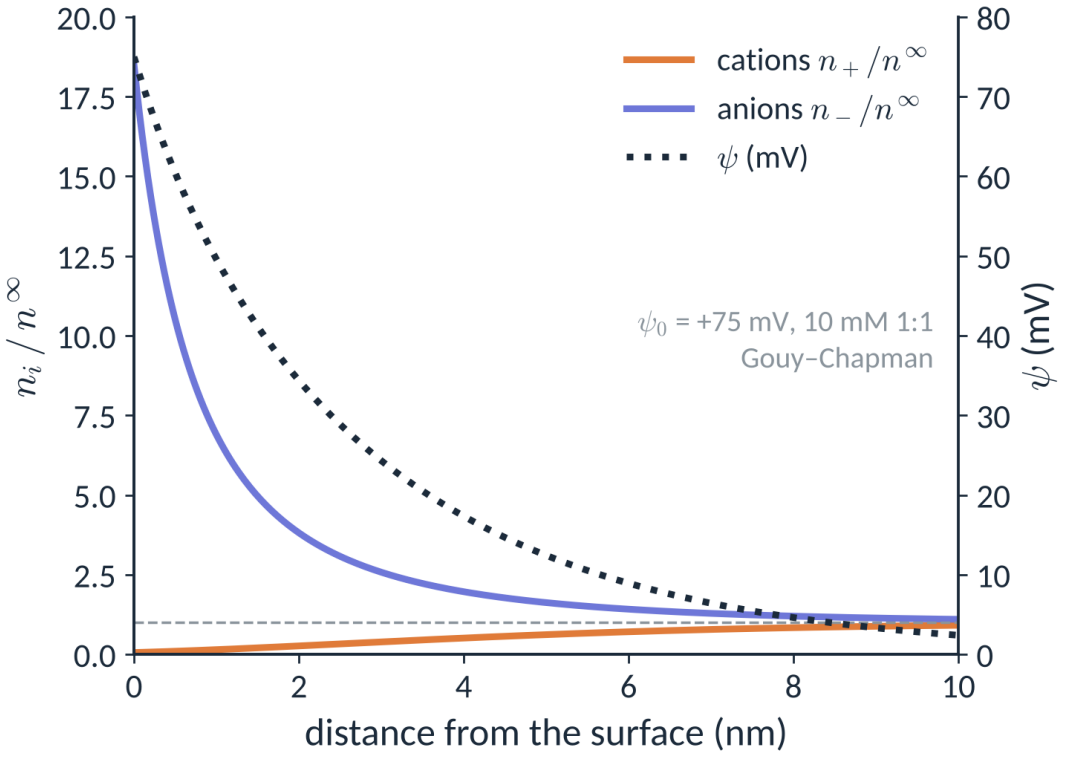
Symmetric z:z electrolyte:

$$\nabla^2\psi = \frac{2n^\infty ze}{\varepsilon_0\varepsilon_r}\sinh\left(\frac{ze\psi}{k_B T}\right)$$

Debye–Hückel limit:

$$\nabla^2\psi = \kappa^2\psi \qquad (ze\psi \ll k_B T)$$

- Mean field: point ions in a continuous dielectric
- Counter-ions accumulate, co-ions are depleted near the surface

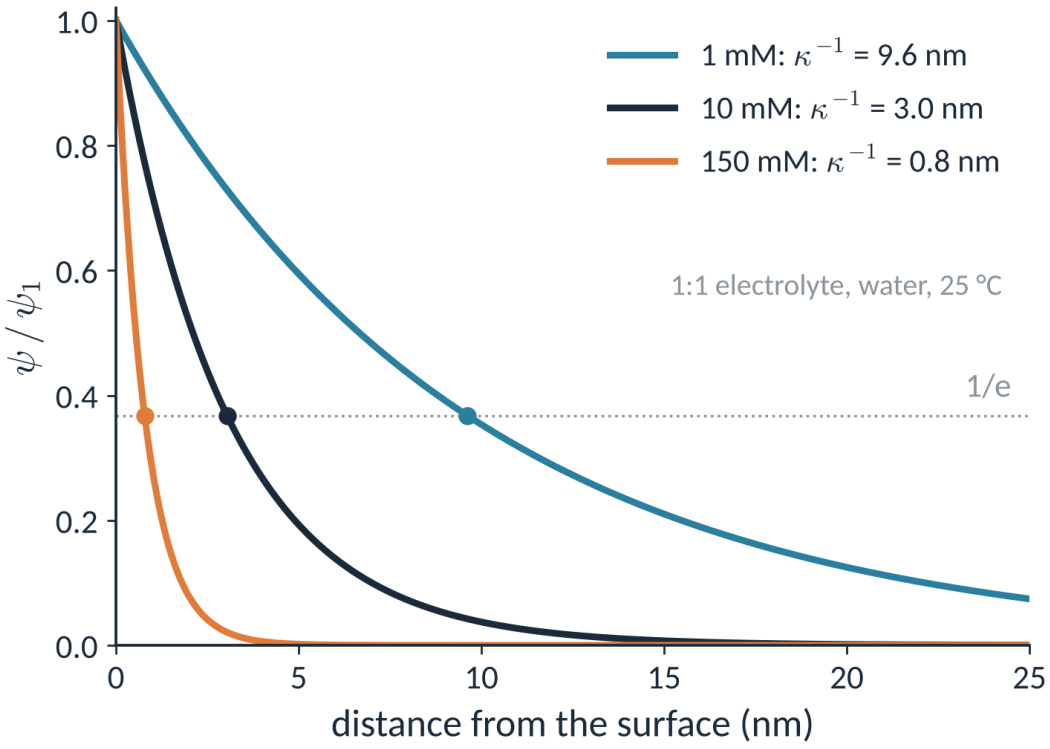


The Debye length

$$\kappa^2 = \frac{e^2 \sum_i n_i^\infty z_i^2}{\varepsilon_0 \varepsilon_r k_B T} \qquad \kappa^{-1} \approx \frac{0.304\ \text{nm}}{\sqrt{I\ [\text{M}]}}$$

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

- Flat surface, low potential: $\psi(x) = \psi_1\, e^{-\kappa x}$
- κ^{-1}: 9.6 nm at 1 mM, 3.0 nm at 10 mM, 0.8 nm at 150 mM (1:1)
- 1 M $CaCl_2$: $I = \frac{1}{2}(1 \cdot 2^2 + 2 \cdot 1^2) = 3$ M



Charged nanoparticles: curvature matters

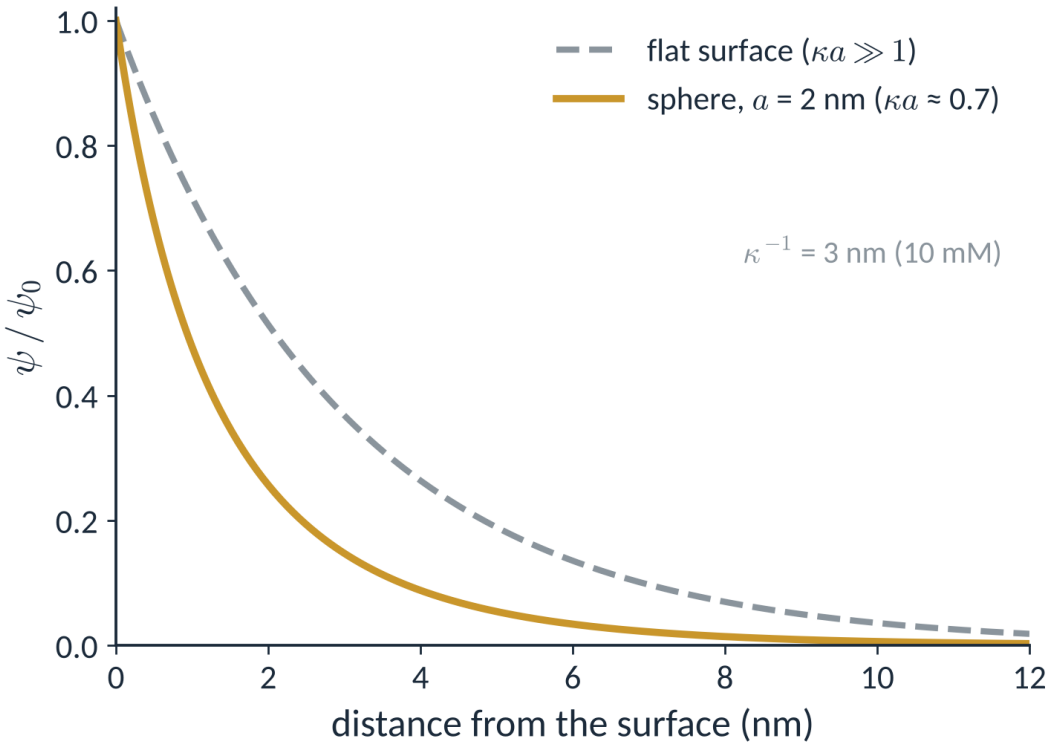
$$\psi(r) = \psi_0 \frac{a}{r} e^{-\kappa(r-a)} \qquad (\kappa a \ll 1)$$

$$\psi(x) = \psi_0 e^{-\kappa x} \qquad (\kappa a \gg 1)$$

Flat surface, any potential (Gouy–Chapman):

$$\tanh \frac{ze\psi}{4k_BT} = \tanh \frac{ze\psi_0}{4k_BT} e^{-\kappa x}$$

- Small particles: the potential decays faster than near a flat wall
- Typical NPs: a = 1–10 nm, κ^{-1} = 1–10 nm, so κa ≈ 1: neither limit is exact



Two competing interactions

Double-layer repulsion (low potential, weak overlap):

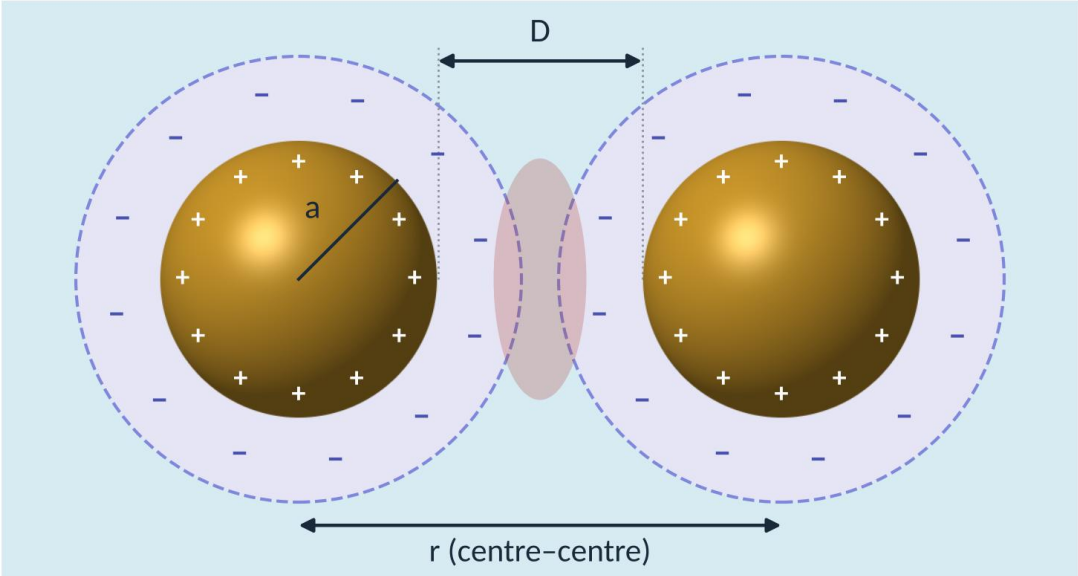
$$V_{\text{rep}} = 4\pi\varepsilon_0\varepsilon_r\,\psi_0^2\,\frac{a^2}{r}\,e^{-\kappa(r-2a)}$$

van der Waals attraction (Hamaker):

$$V_{\text{vdW}} = -\frac{A}{6}\left[\frac{2a^2}{r^2-4a^2} + \frac{2a^2}{r^2} + \ln\left(1-\frac{4a^2}{r^2}\right)\right]$$

$$V_{\text{vdW}} \approx -\frac{A\,a}{12D} \qquad (D \ll a)$$

- A: Hamaker constant, 10^{-20}–10^{-19} J (large for metals)
- Like particles always attract in a medium ($W_{131} = 2\gamma_{13} > 0$)

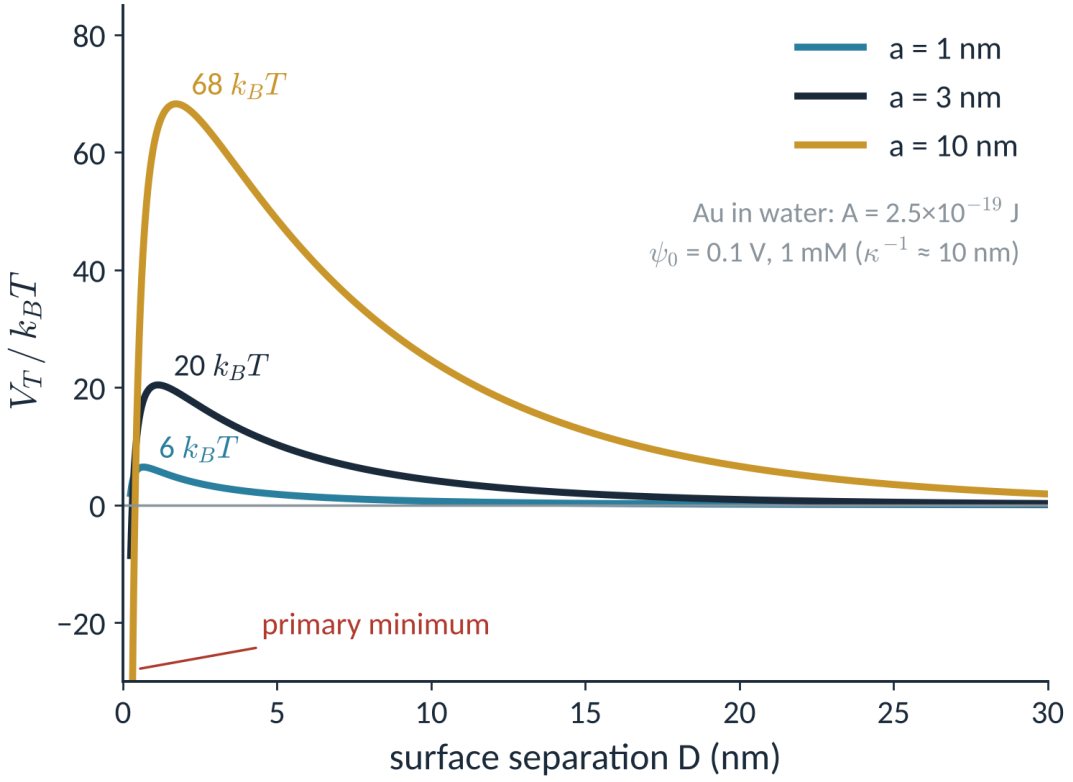


r: centre-to-centre distance; D = r − 2a: surface separation

The DLVO potential

$$V_T(D) = V_{\text{rep}} + V_{\text{vdW}}$$

- Energy barrier: colloids are kinetically, not thermodynamically, stable
- A barrier of $\gtrsim$ 15–20 $k_B T$ keeps particles dispersed for long times
- The barrier grows with particle size: small nanoparticles need ligands
- Exponential repulsion vs power-law attraction: attraction wins at very short range

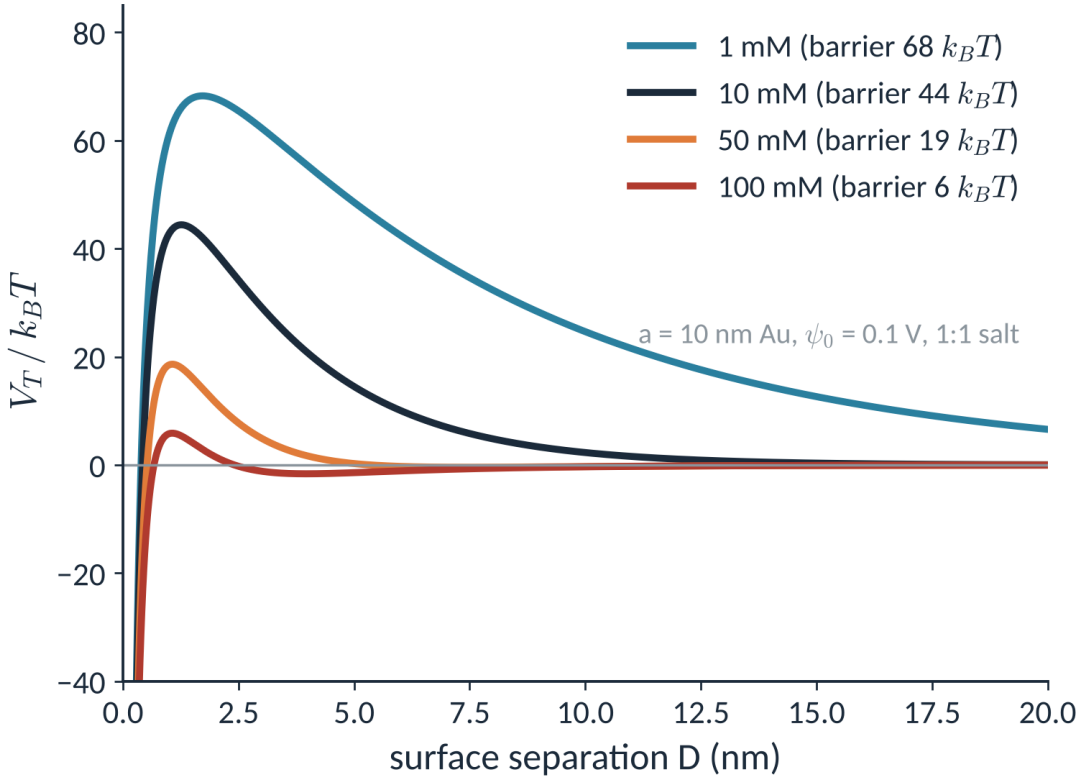


Salt destabilises colloids

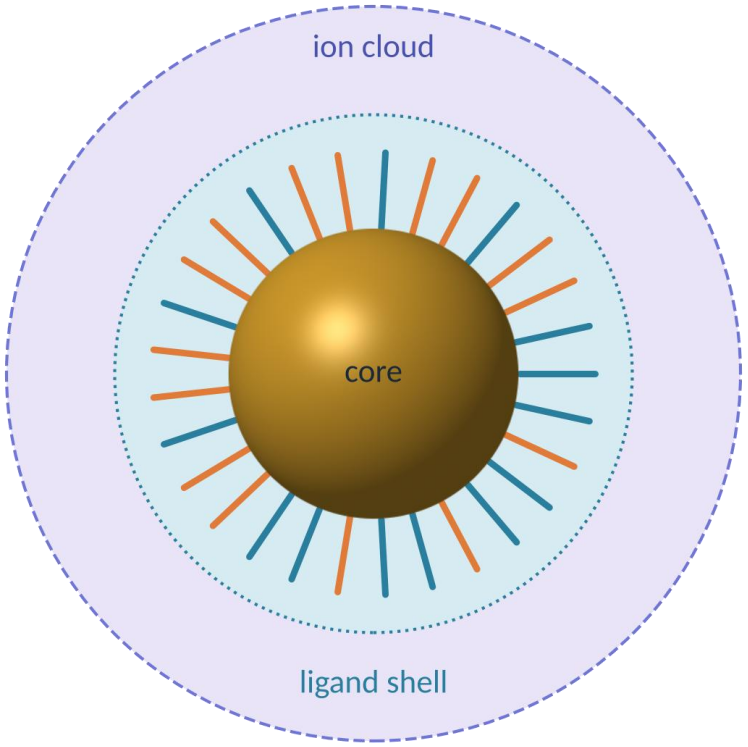
- Salt shortens κ^{-1} and lowers the barrier
- Critical coagulation concentration (CCC): barrier gone, fast aggregation

$$\mathrm{CCC} \propto z^{-6}$$ **Schulze–Hardy (high ψ_0)**

- Counter-ion valence matters far more than concentration
- Physiological media (150 mM, $\kappa^{-1} \approx 0.8$ nm) destabilise charge-stabilised nanoparticles



Beyond DLVO for nanoparticles



Ligand shells

Steric and hydration forces; structured solvent (Section 5)

Small κa

Few, discrete charges: continuum models strained

Geometry

Rough or spiky particles weaken vdW (Section 4)

Ion specificity

Hofmeister effects and charge regulation

DLVO remains the starting point for any stability argument

SUMMARY

One quantity, many consequences

1 Interfacial energy

γ is an excess free energy; Dupré links it to adhesion

2 Curvature

Laplace, Kelvin, ripening, nucleation, melting: all scale as γ/r

3 Wetting

Young and Young–Dupré turn contact angles into W_{SL}

4 Geometry

Wenzel, Cassie–Baxter, superhydrophobicity, hedgehog particles

5 Nanoscale patches

Wetting is non-additive when domains approach solvent size

6 Charge

pzc, Stern layer, Debye length; DLVO sets colloidal stability

Further reading

- J. N. Israelachvili, Intermolecular and Surface Forces, 3rd ed., Academic Press (2011): Ch. 17 (adhesion and wetting), plus the chapters on van der Waals and double-layer forces
- J. H. Bahng et al., Anomalous dispersions of 'hedgehog' particles, Nature 517, 596 (2015)
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- Z. Luo et al., Determination and evaluation of the nonadditivity in wetting of molecularly heterogeneous surfaces, PNAS 116, 25516 (2019)
- C. B. Ran et al., Langmuir 24, 9952 (2008)
- Ph. Buffat, J.-P. Borel, Phys. Rev. A 13, 2287 (1976)
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