EPFL
École polytechnique fédérale de Lausanne

CHEMINA
Laboratory of Chemical Nanotechnology

Surface Energetics & Interfacial Phenomena Lesson 3

MSE 304

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Plan of the Course: Fundamentals, Characterization, and Applications

1: Intro to Surfaces & Interfaces

2: Surfaces in the Real World - Adsorption

3: Surface Energetics & Interfacial Phenomena

4: Atomic Structure of Real Surfaces

5: Characterization of Real Surfaces

6: Solid-Liquid Interfaces + Techniques

7: Solid-Solid Interfaces

8: Charged Solid-Liquid Interfaces

9: Surface Chemistry

10: Biological Processes at Surfaces

11: Electronic Properties of Surfaces

12: Thin Film Technologies

13: Biosensor Fundamentals

14: Biosensing applications

Things may be adapted in real time – thank you for your patience!
Midterm feedback (Week 5) – Recap session Week 7?

Recap from Lesson 2 - Applied

Contamination comes from air, humidity, residues, dust, handling, etc.

We can tackle contamination in controlled environments like the cleanroom

Different methods to clean the surface from the macroscale to atomic-scale

Scanning tunneling microscopy can visualize at atomic scales

Recap from Lesson 2 - Basics

Adsorption = surface, Absorption = bulk

Physisorption = weak and reversible
Chemisorption = strong and permanent

Crystal lattice structures of surfaces defines how adsorbates stick

Adsorbates are arranged on surfaces to minimize surface energy

What do we mean when we talk about “surface energy”

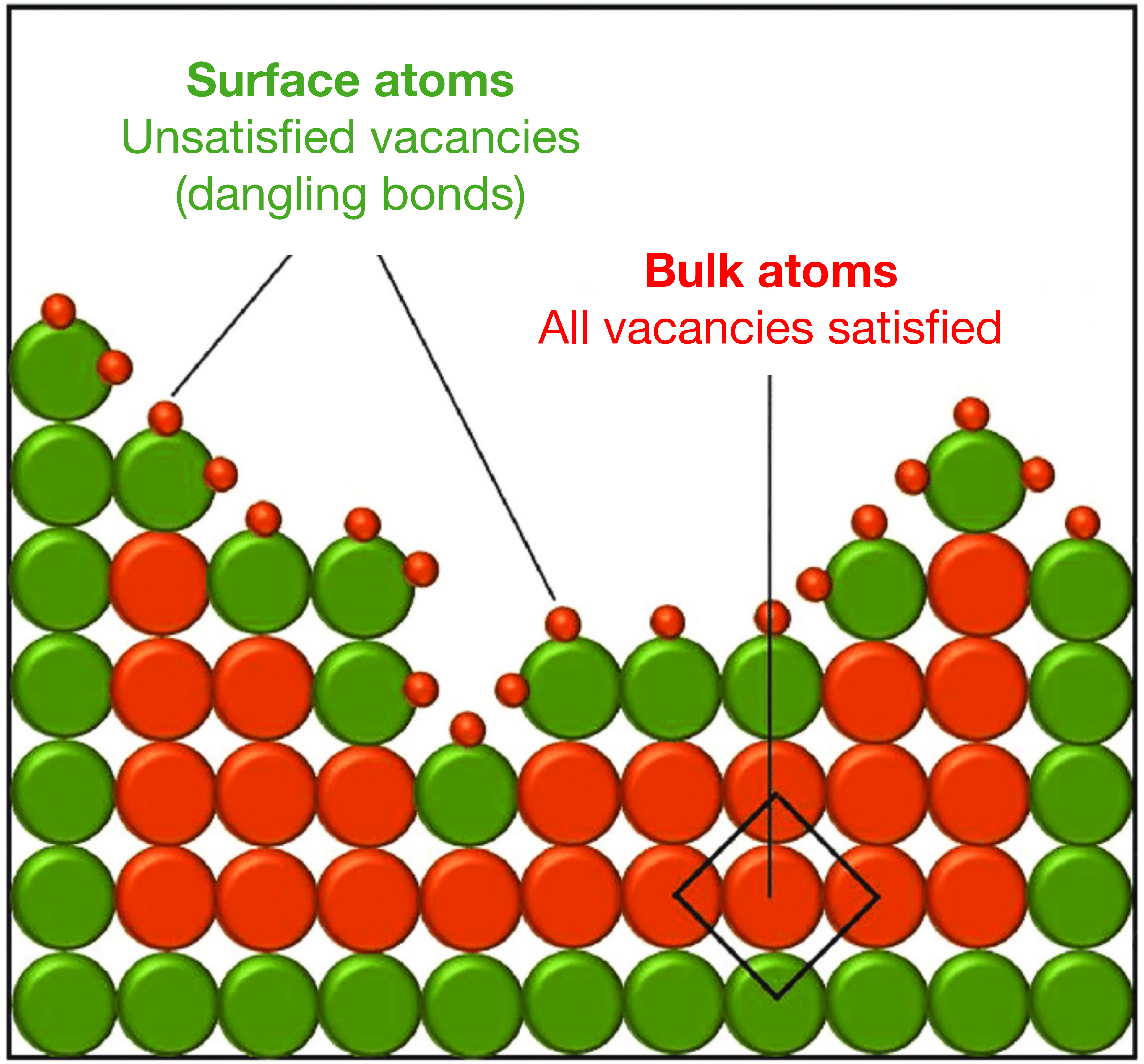
Outline of Lesson 2

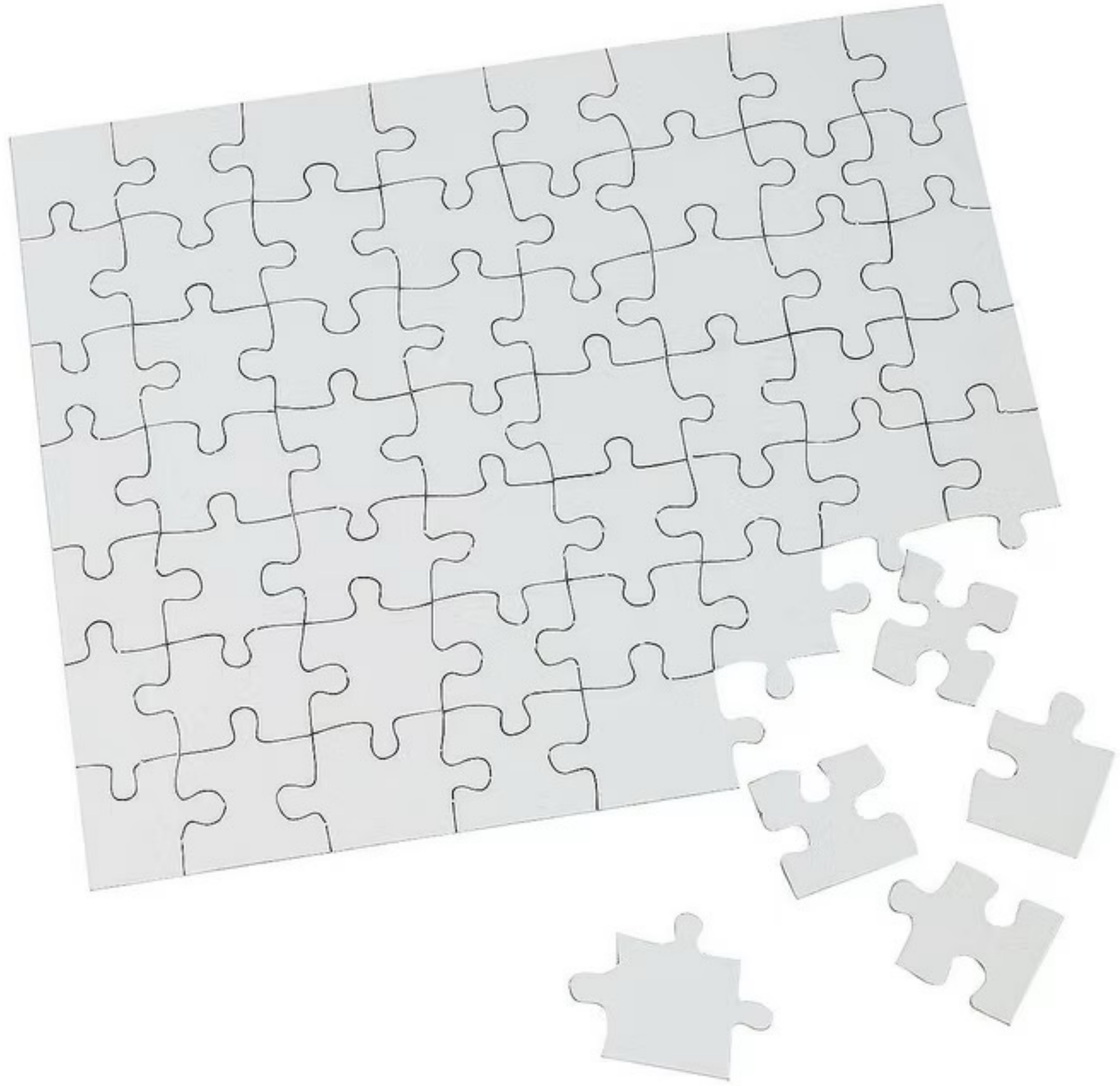
- Why surface energy matters – why we should study the basics
- Definitions of **surface free energy**
- Difference between **surface stress** and **surface tension**
- Contact angle - ideal to complex models of **wetting** on surfaces
- How to measure **contact angle**

Surfaces Adsorb Contaminants Due to High Surface Energy

At the surface, atoms are missing neighbors ➔ unsatisfied "dangling bonds"

Bulk crystal every atom fully bonded ➔ stable, low energy





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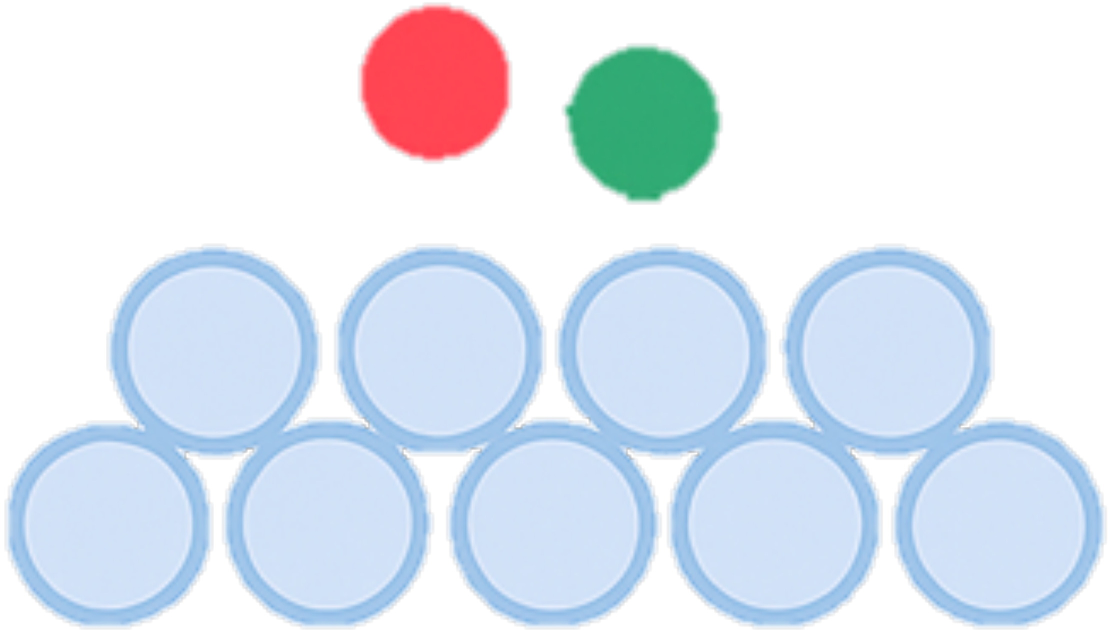
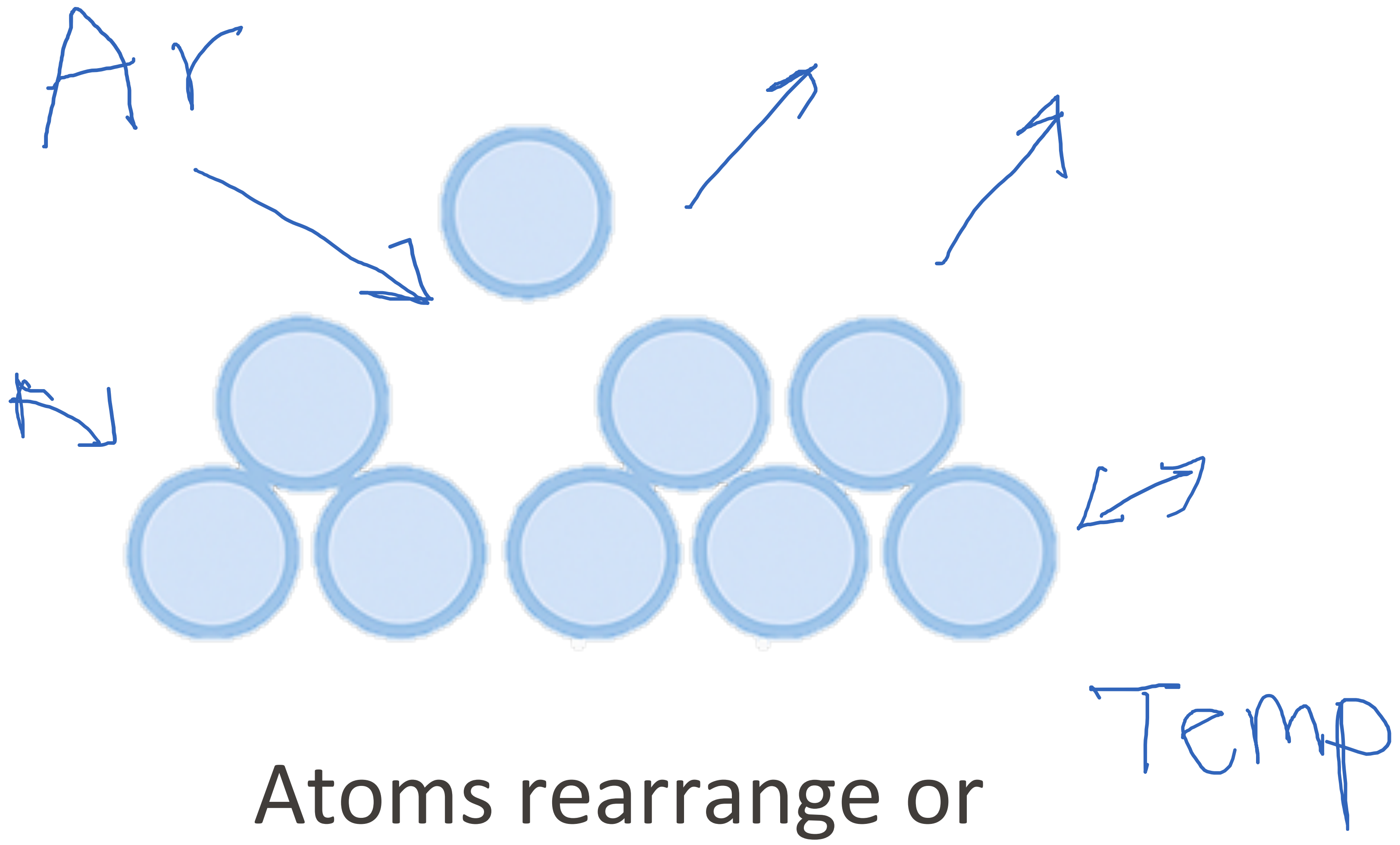
Surfaces Lower Their Energy Through Various Means

Adsorption of molecules



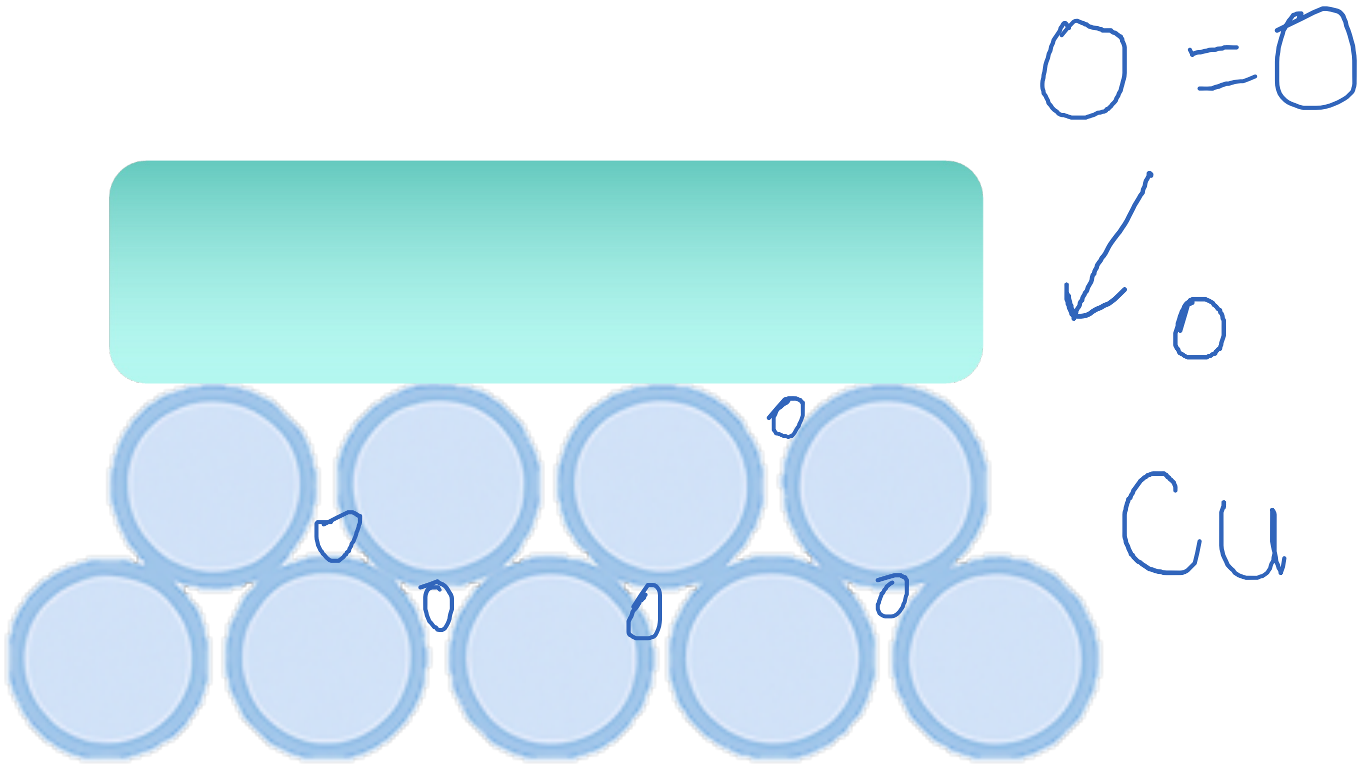
Contaminants binding to the surface

Surface reconstruction



Atoms rearrange or shift position

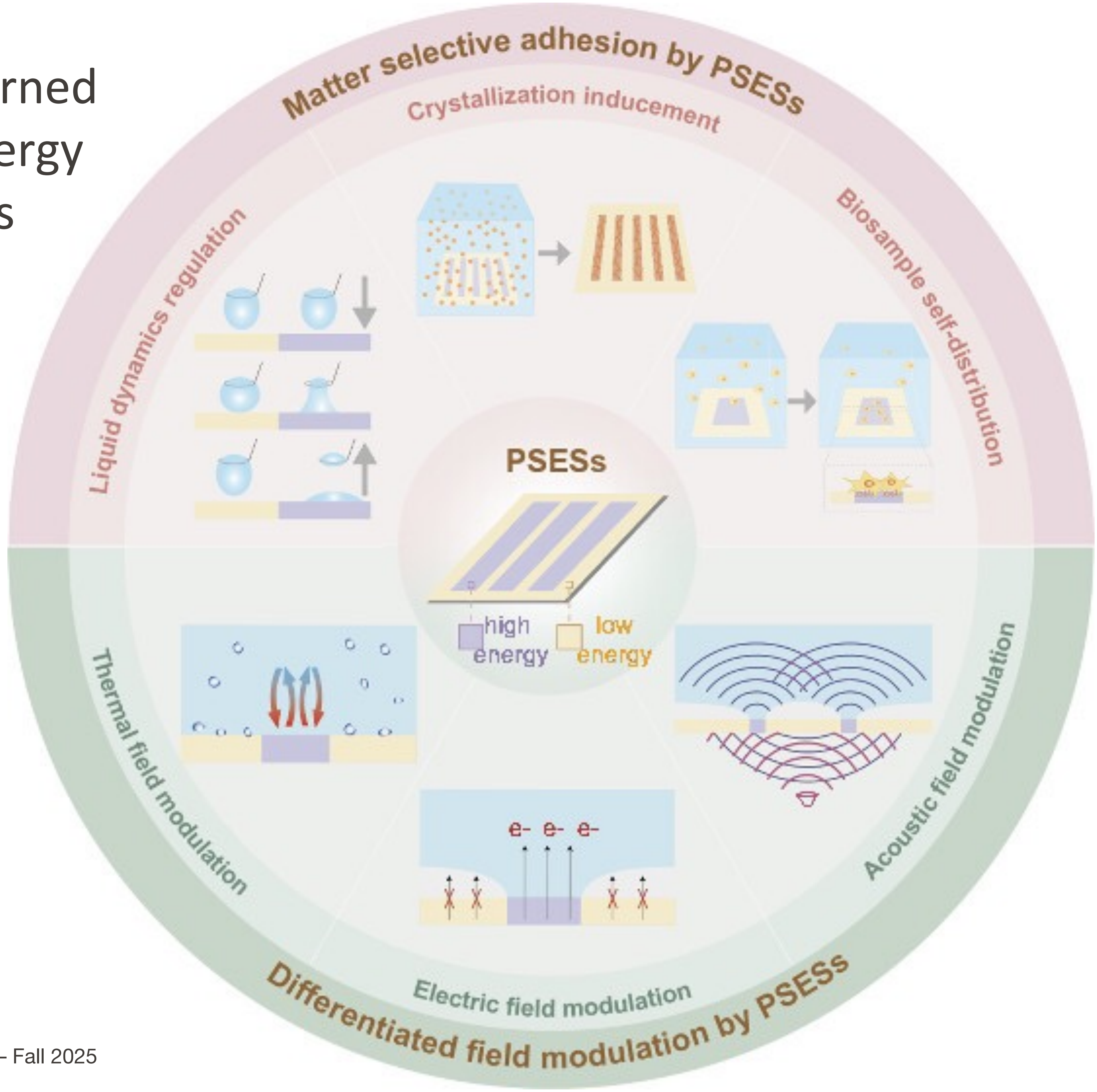
Formation of thin films/oxides



Passivation of surface

Why Surface Energy Matters

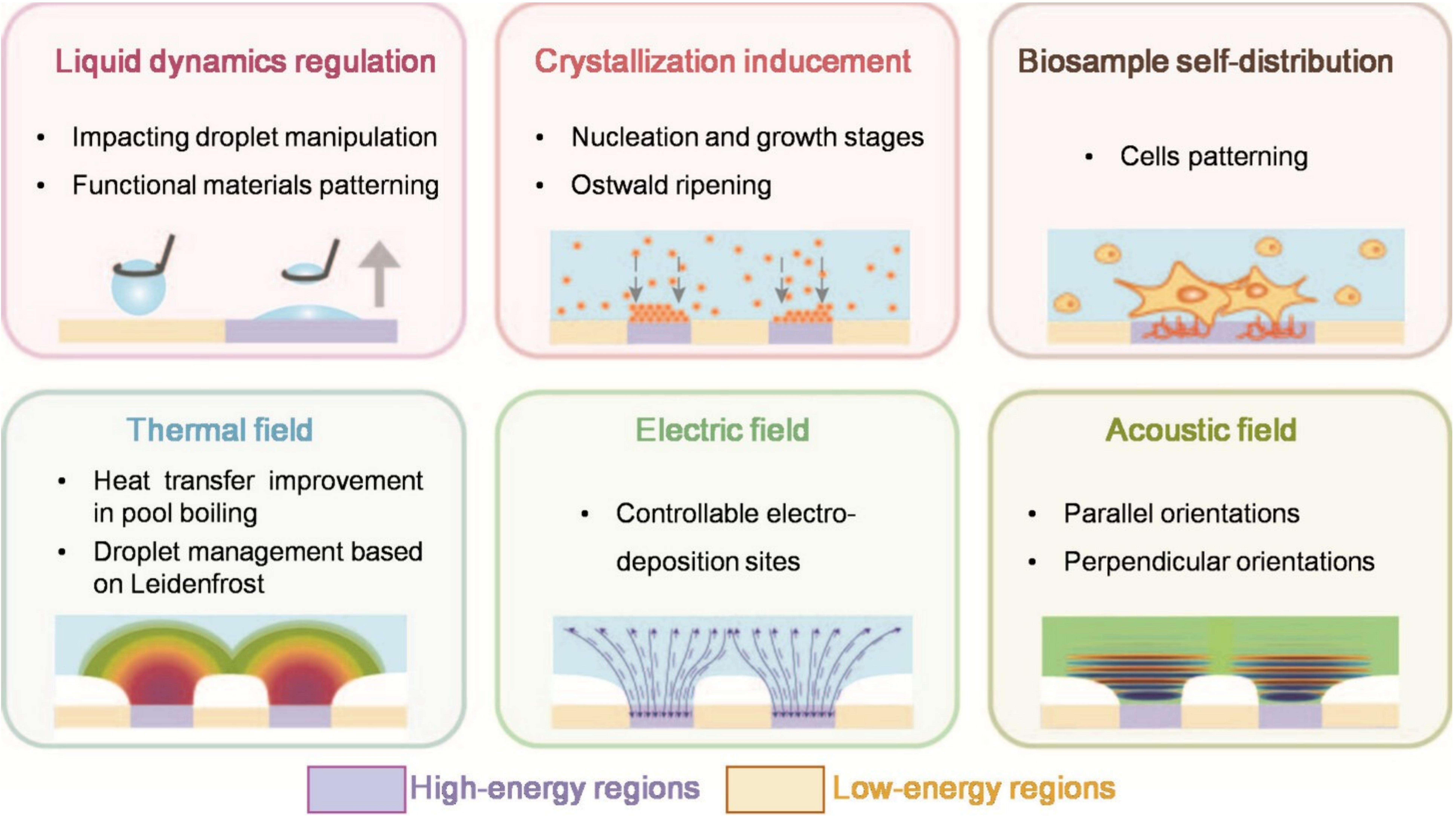
PSES: patterned surface energy surfaces



Abstract: Surface energy, as an intrinsic property of solids, plays a crucial role in **modulating the characteristics of solid surfaces**, especially of the **solid–liquid interface**. Due to inevitable processes such as surface **adsorption or contamination**, the surface energy of practical solids is usually nonuniform. However, if this nonuniformity is rationally designed and effectively utilized, it is capable of endowing great potential for **liquid manipulation**.

Liu *et al.* | *ACS Nano* | 2025

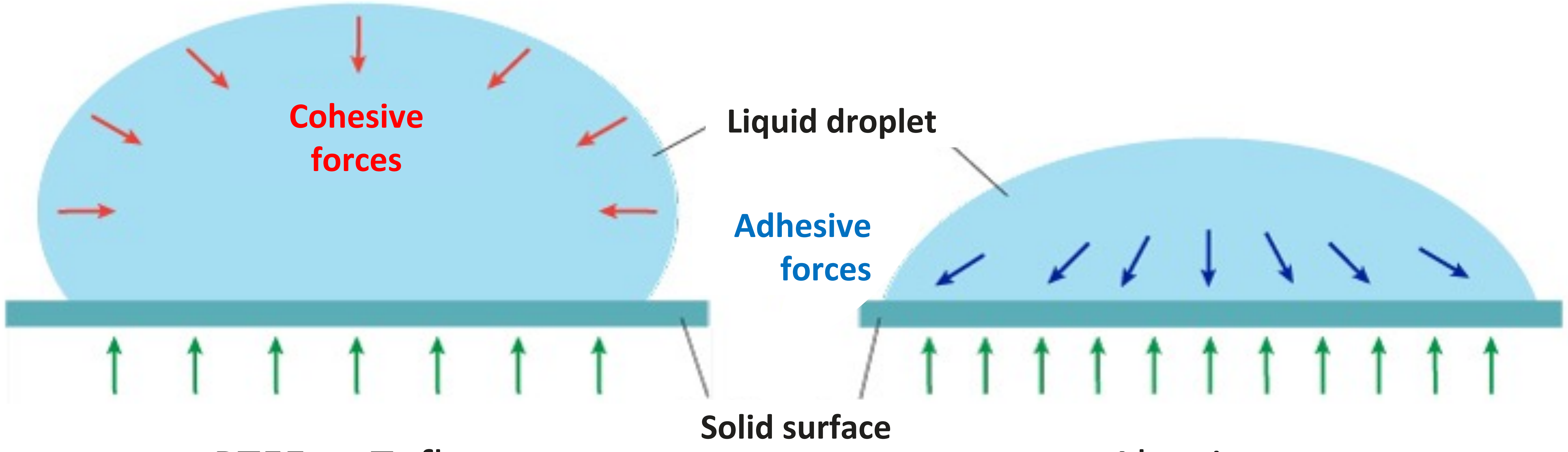
Why Surface Energy Matters



Liu *et al.* | *ACS Nano* | 2025

Choosing Different Surface Materials Based on Surface Energy

Low Surface Energy	**High Surface Energy**
Hard to adhere	Easy to adhere



Low Surface Energy	High Surface Energy
PTFE or Teflon	Aluminum
Silicone	Copper
Polyethylene	Alumina
Waxed surfaces	Pure silicon
Paraffin	Titanium dioxide

Surface energy not just an abstract thermodynamics concept but practical!

Difference Between Surface Energy and Surface Free Energy

Surface Energy (ɣ)
Mechanical definition

Work required to create a unit area of new surface (J/m^2)

Surface Free Energy ($\tilde{ɣ}$)
Thermodynamic definition

Excess Gibbs free energy per unit area at the surface relative to the bulk (J/m^2)

The two definitions are often used interchangeably in textbooks, literature, *etc.*

Definition of Surface Free Energy

Remember: Surface science is a relatively new field derived from various disciplines

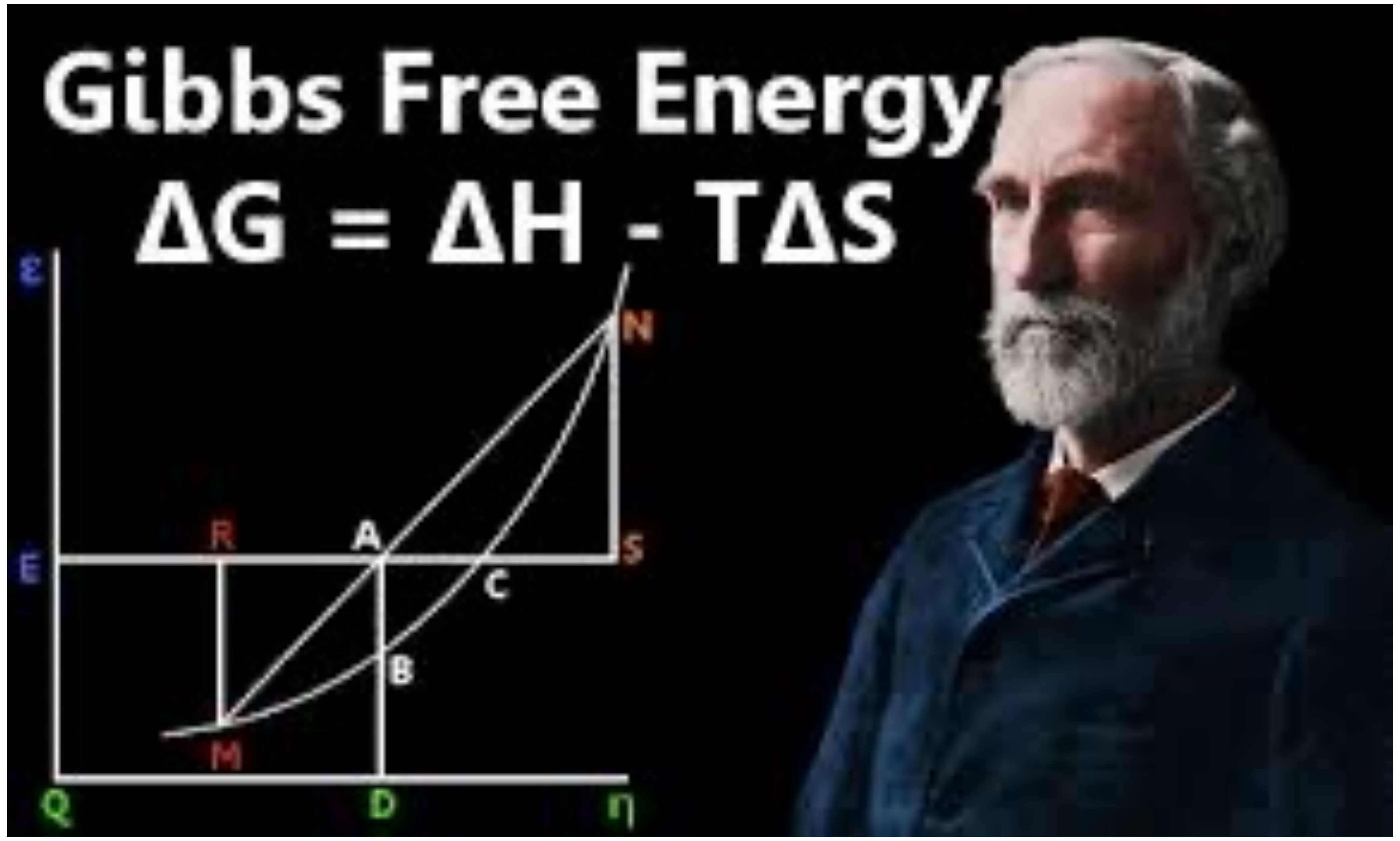
Therefore, there are many definitions of surface energy and no real agreement on the terminology or symbols

Already in 1878, Josiah Gibbs showed that surface energy is a thermodynamic quantity and introduced the concept of "**excess surface free energy**"

$dG = 0$ At equilibrium

$dG < 0$ Spontaneous process

Gibbs introduced the concept because surfaces are "different from the bulk" ➔ excess free energy



Classical Thermodynamic Definition of Surface Free Energy

Defining the energy of a multi-component system

$$dG = V\,dp - S\,dT + \sum_i \mu_i\,dn_i + \left(\sum_j \chi_j\,dQ_j\right) + \tilde{\gamma}\,dA$$

Pressure-volume work | Entropy | Chemical potentials | Generalized work term | Surface free energy

Generalized work term:

- Electrical work → potential x Δcharge
- Magnetic work → field x Δmagnetization
- Elastic work → stress x Δstrain

The surface free energy is the excess Gibbs free energy associated with the creation of a unit of surface

Thermodynamic Definition of Surface Free Energy

Surface free energy, γ, is defined as the free-energy cost per unit area of creating surface

$$\tilde{\gamma} = \left(\frac{\partial G}{\partial A}\right)_{T,P,n_i}$$

If I hold temperature, pressure, and composition fixed, how much does the Gibbs free energy increase when the surface area is increased?

$$\tilde{\gamma} = \left(\frac{\partial U}{\partial A}\right)_{V,S,n_i}$$

If I hold volume, entropy, and composition fixed, how much does the internal energy increase when the surface area is increased?

Gibbs contribution: **Surface energy is a positive quantity** it takes **work to create a surface**, which **increases the free energy** of the system. Surface never created spontaneously.

May seem obvious today: if we create a surface, we are always breaking bonds and need to put energy into the system. However, in 1878, concept of atoms and bonds didn't exist

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It Takes Work to Create a Surface

1st law of thermodynamics: energy not created nor destroyed, conserved

Change in internal energy of system

$$dU = \delta W + \delta Q$$

Heat added

Work done by system

$$dQ = 0$$

No heat exchange

$$dU = \delta W = \tilde{\gamma}\, dA$$

Excess surface free energy

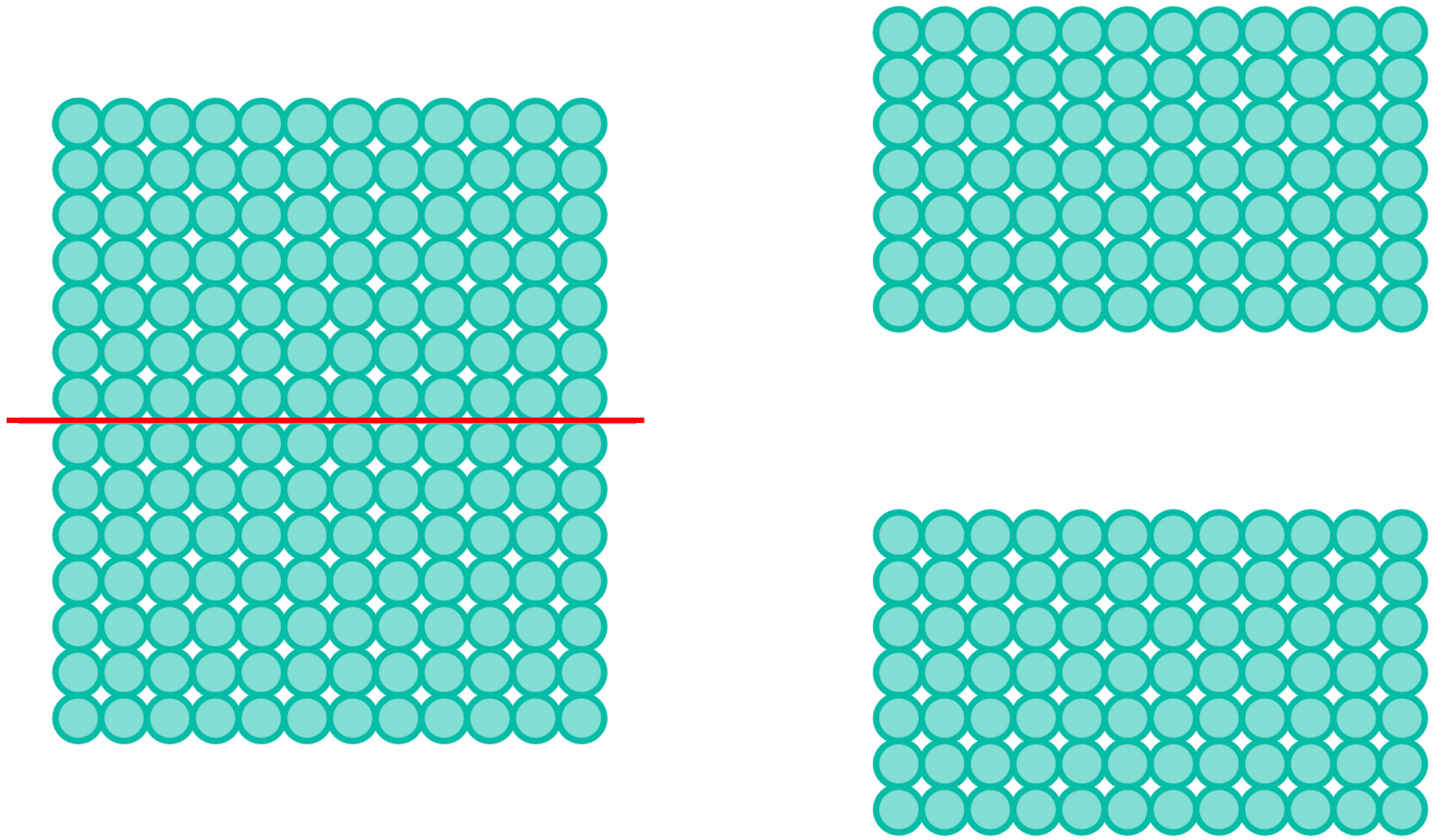
$$\delta W > 0 \qquad \tilde{\gamma} > 0$$

Gibbs contribution: **Surface free energy is a positive quantity** it takes **work to create a surface**, which **increases the free energy** of the system

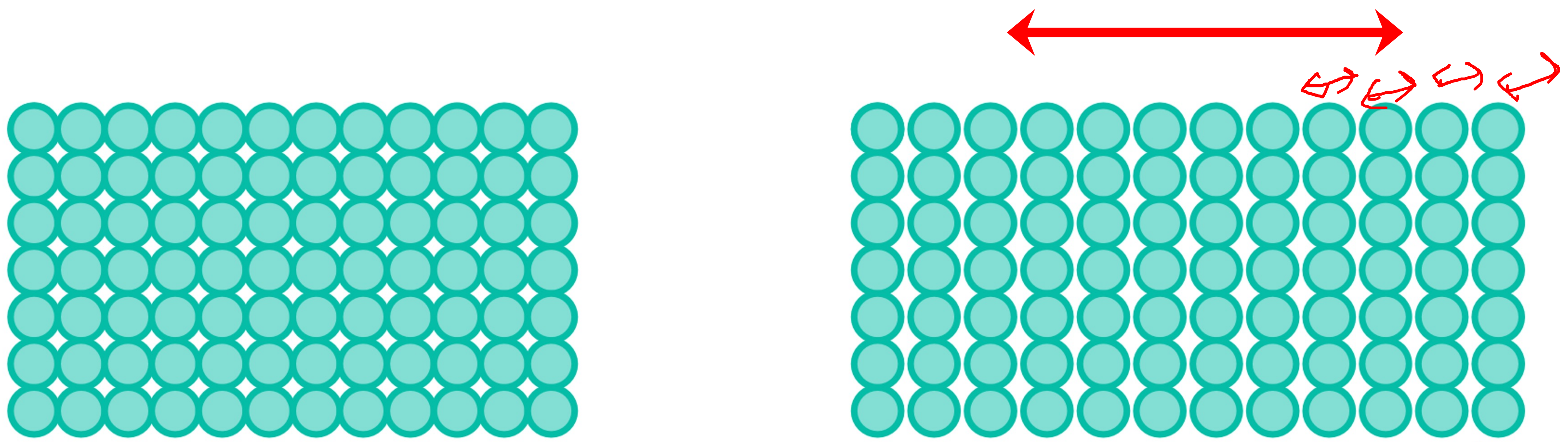
Surface never created spontaneously.

How Do We Create a New Surface Area in a Material?

Cutting bonds



Stretching bonds



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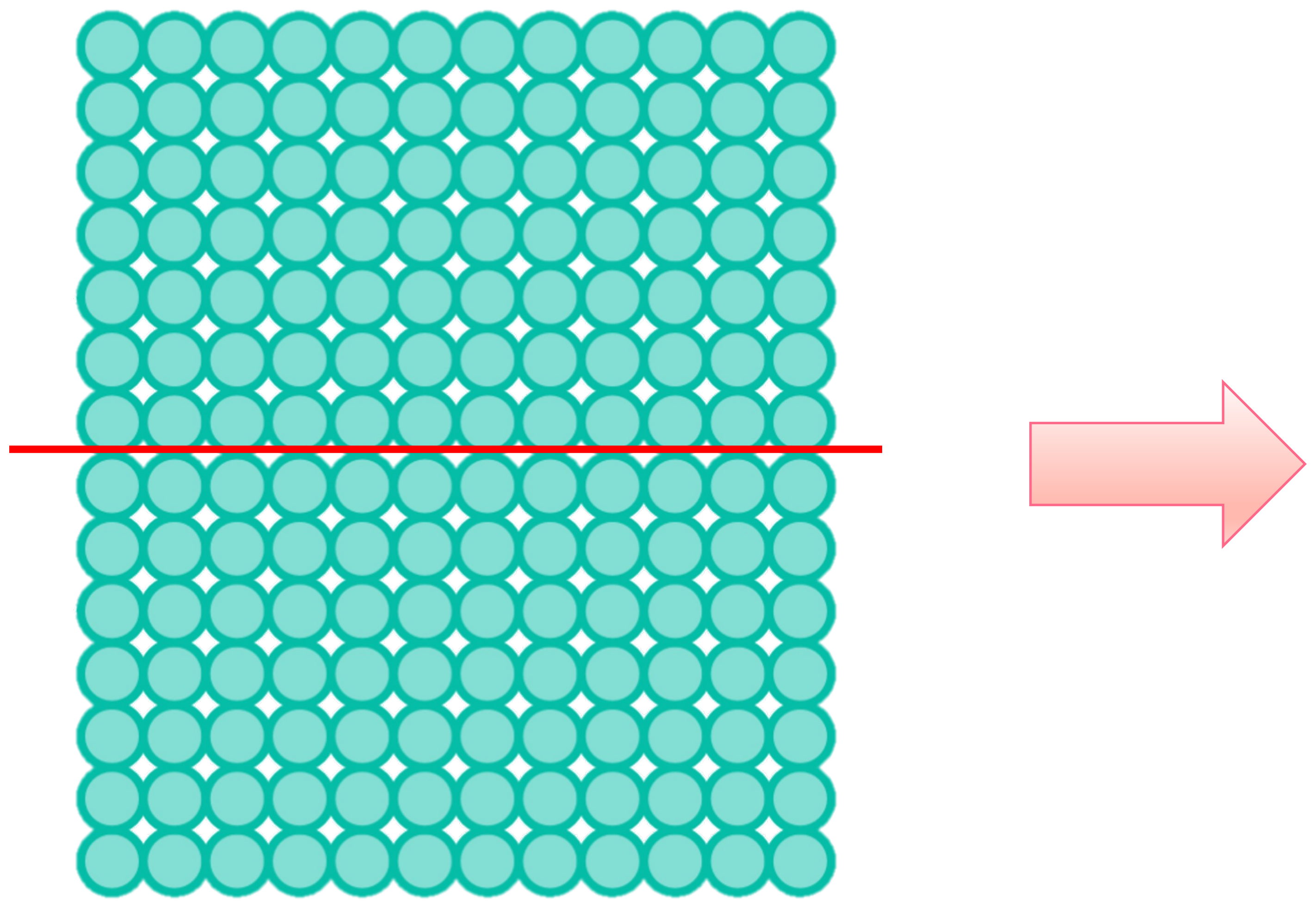
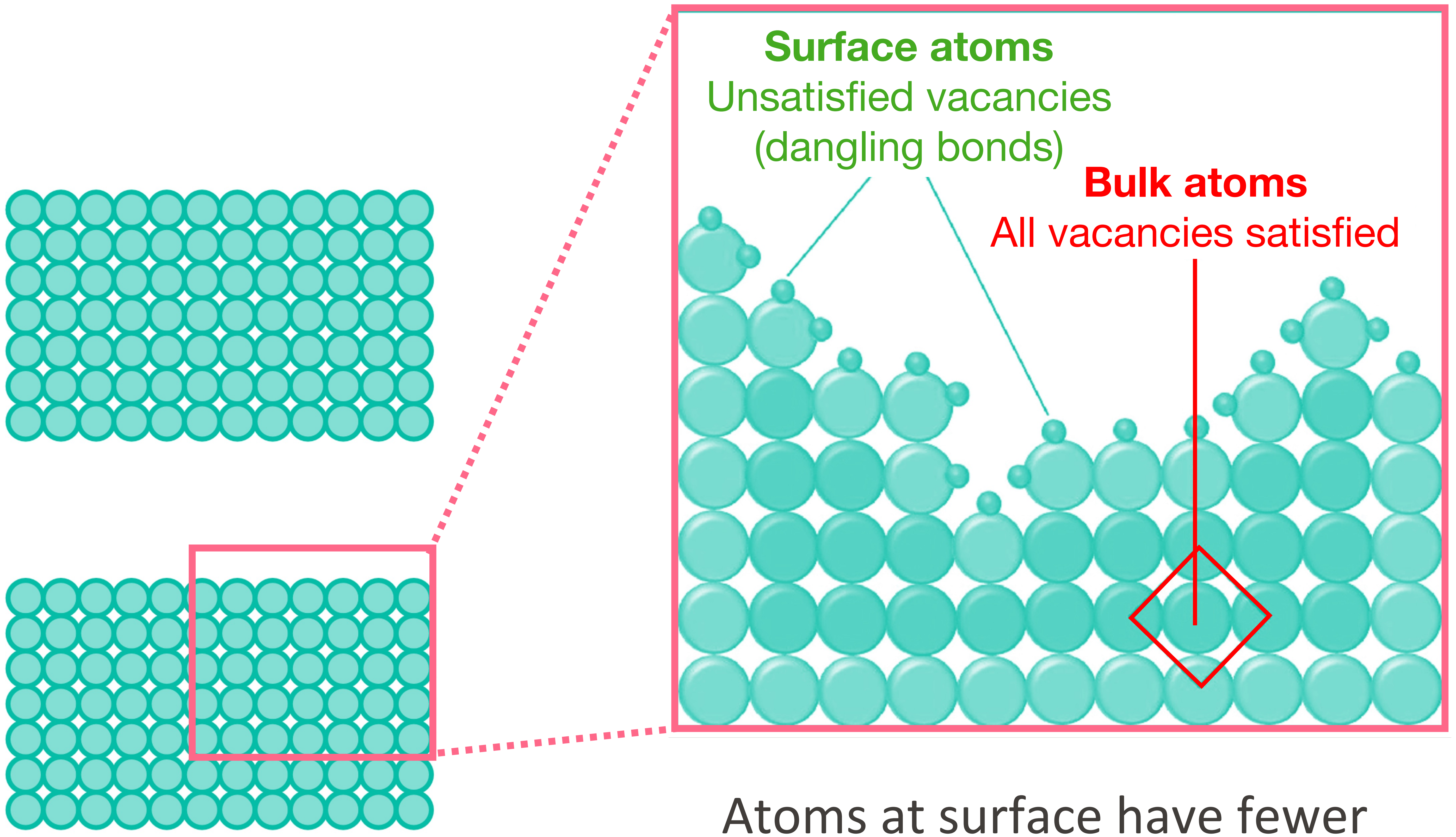
Cutting Bonds to Create New Surface Area

In a solid material, each atom is surrounded by neighbors so it's comfortable ☺





Create 2 new surfaces

Atoms at surface have fewer neighbors (missing bonds) = higher in energy

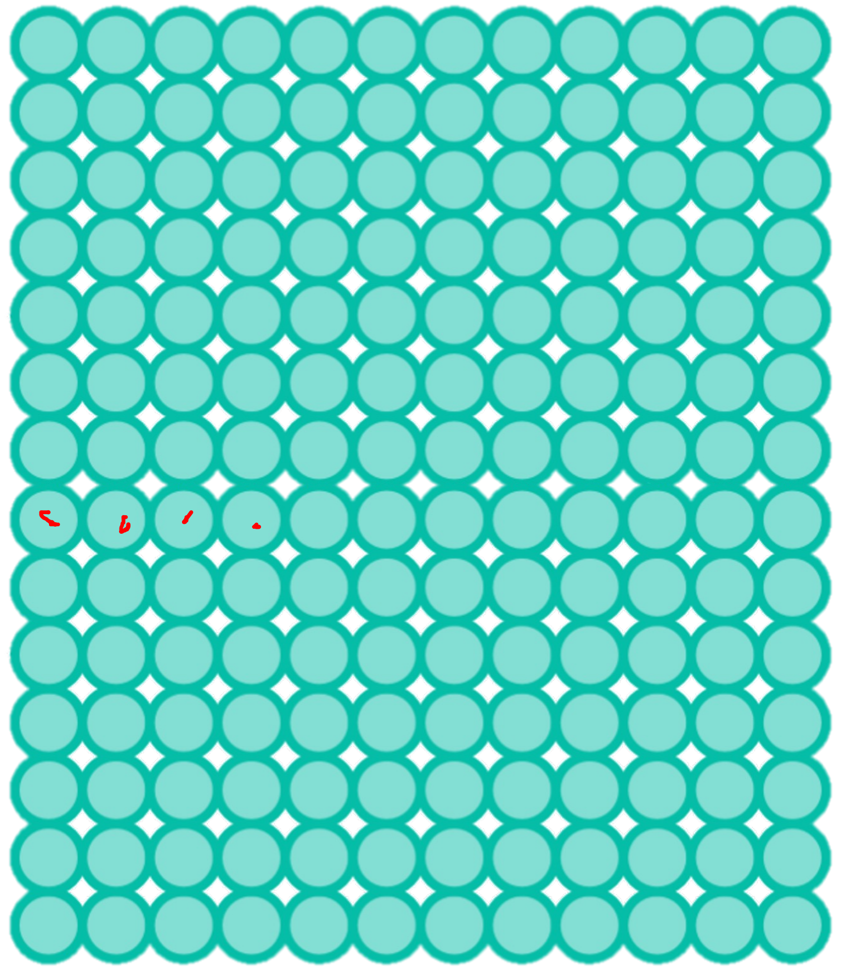
Energy cost of creating a unit area of new surface = **surface energy (ɣ)**

Thermodynamic Definition of Surface Energy (ɣ)

Surface Energy (ɣ): reversible work to create a surface of unit area at constant temperature and pressure, while keeping all the **atomic positions fixed** to their bulk position.

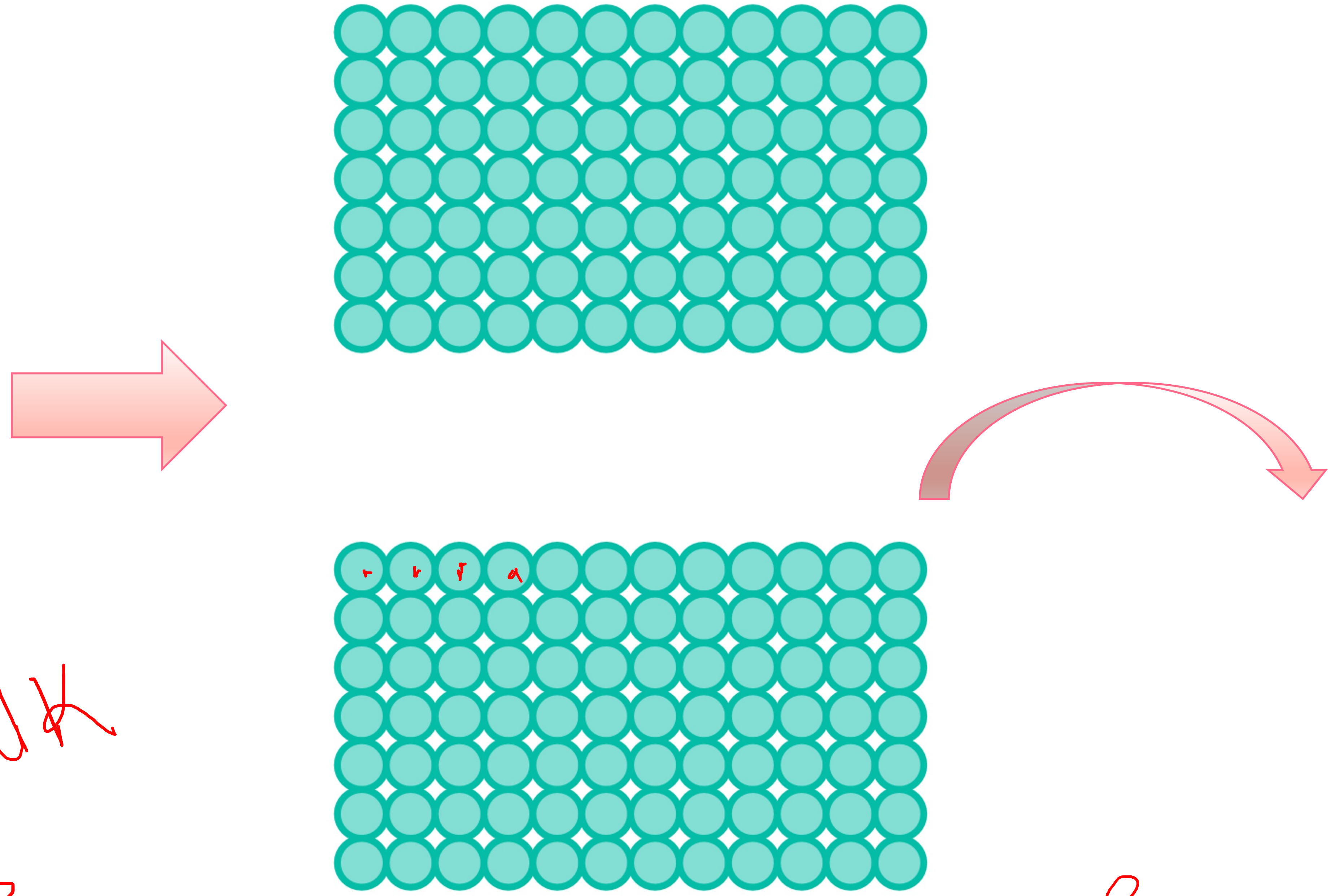
G_s: Gibbs free energy cost per unit area of surface
E_s: excess internal energy of the surface
T: temperature
S_s: excess entropy of the surface

Total Gibbs free energy of solid



Bulk atoms: NG_B

Bulk # atoms



Surface: G_sA

surface

Bulk surface

$$G_{total} = NG_B + G_SA$$

$$G_{total} = NG_B + \gamma A$$

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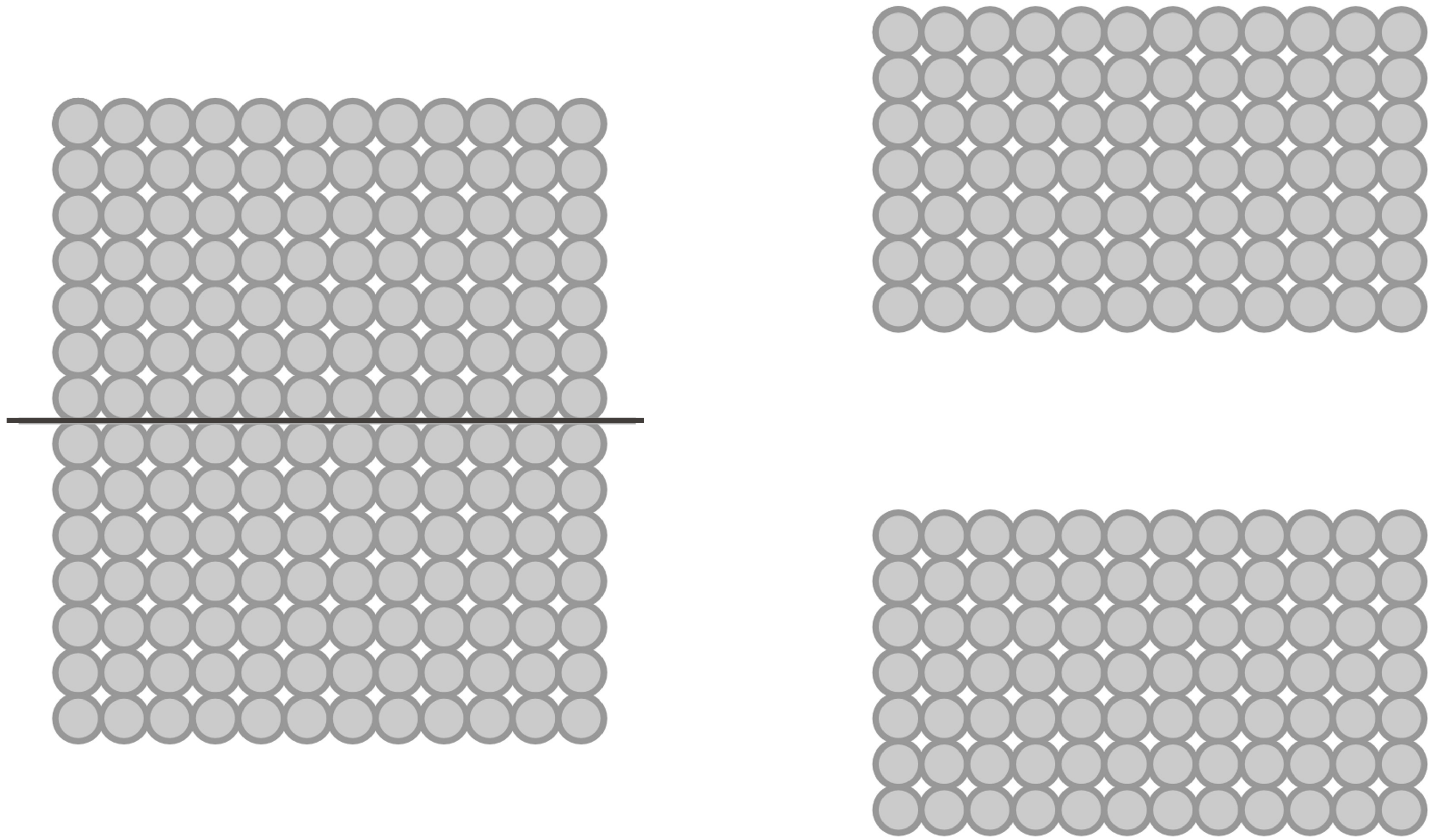
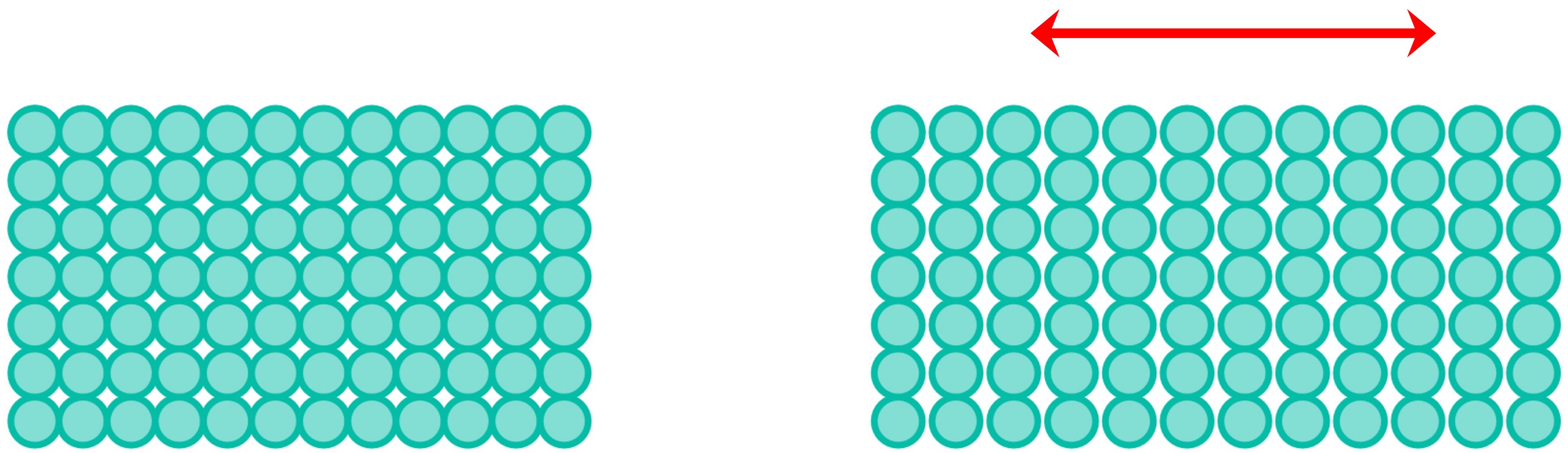
How Do We Create a New Surface Area in a Material?

Cutting bonds

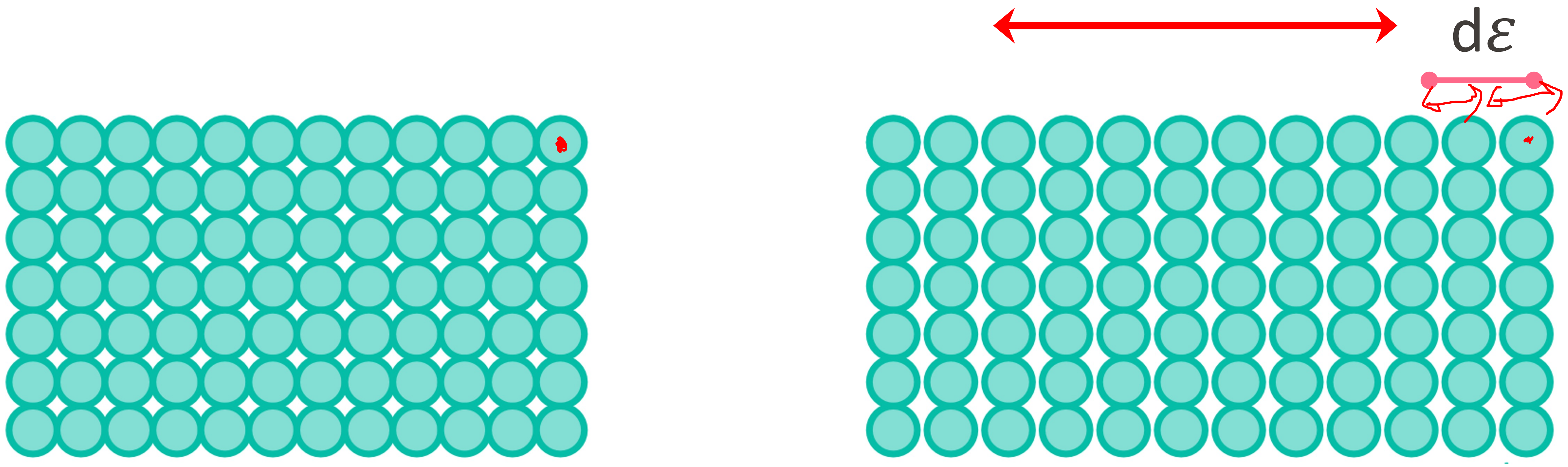


Stretching bonds



Definition of Surface Stress (*f*)

Surface Stress (*f*): reversible work per unit area needed to elastically deform the surface of a **solid** (stretch existing atoms)



f = surface stress
(force/unit length)

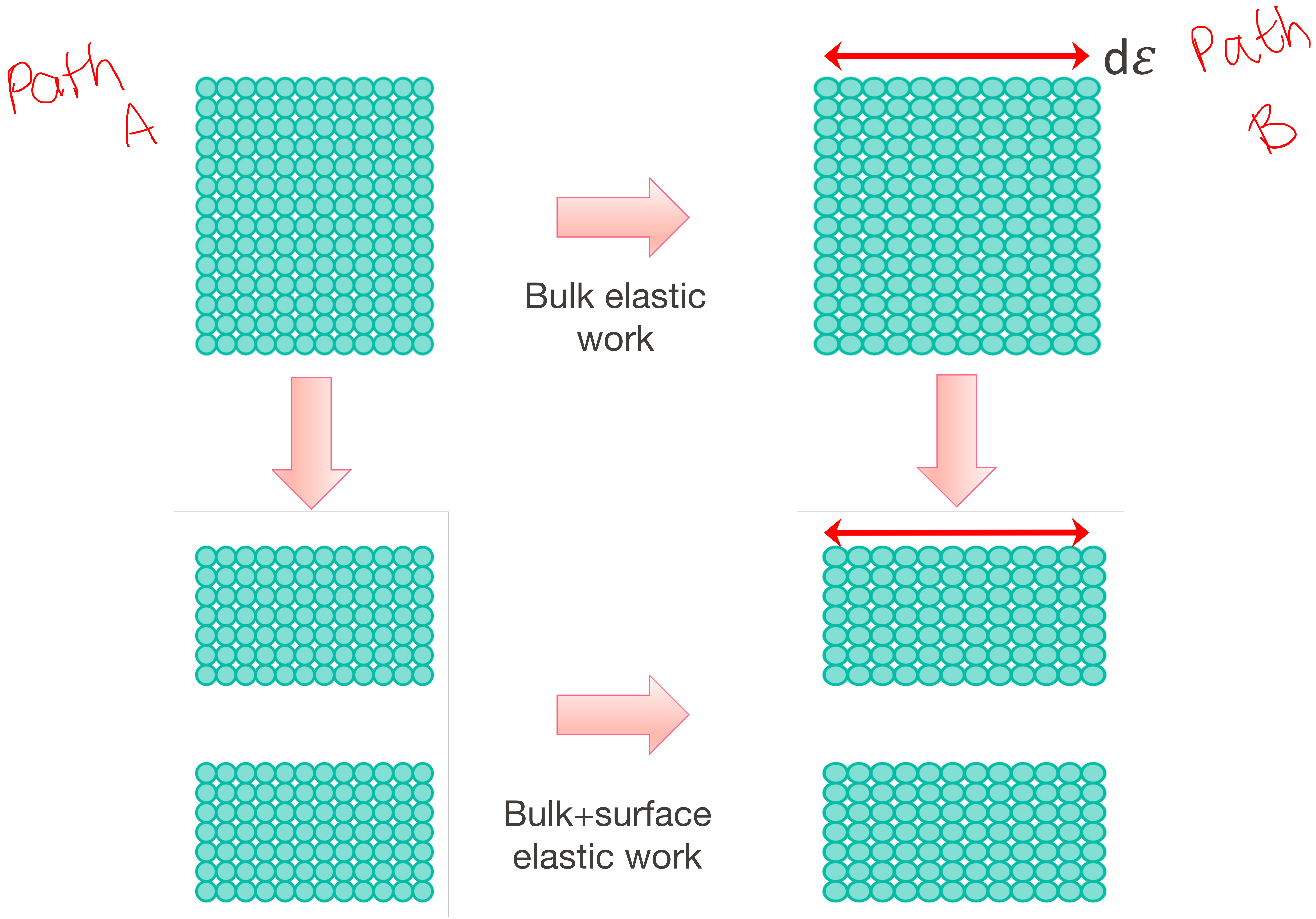
Strain (ε) is the relative deformation (change in length/original length)

So which definition is correct?

Both cutting and stretching bonds can happen at the same time to generate new surfaces

Both cases make the material less happy ➔ excess surface free energy ($\tilde{\gamma}$ contains both)

Careful: Surface Energy (ɣ) ≠ Surface Stress (*f*) in Solids



Path A (cut first, then stretch)

$$W_A = \gamma A + dW_{el} + dW_{el,s}$$

$$dW_{el,s} = A\, f\, d\varepsilon$$

Path B (stretch first, then cut)

$$W_B = dW_{el} + \gamma A + d(\gamma A)$$

The excess of elastic energy depends on the fact that atoms in the surface are held in place by the underlying bulk.

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Surface Energy (γ) ≠ Surface Stress (f) in Solids

(1) $$W_A = \gamma A + dW_{el} + A\,f\,d\varepsilon$$

(2) $$W_B = dW_{el} + \gamma A + d(\gamma A)$$

$$W_A = W_B$$

$$A\,f\,d\varepsilon = d(\gamma A)$$

$$f = \gamma + \frac{d\gamma}{d\varepsilon}$$

Shuttleworth equation

surface energy

ε (strain)
how much surface is stretched

↓

causes change in γ (surface energy)
thermodynamic cost of making/storing surface

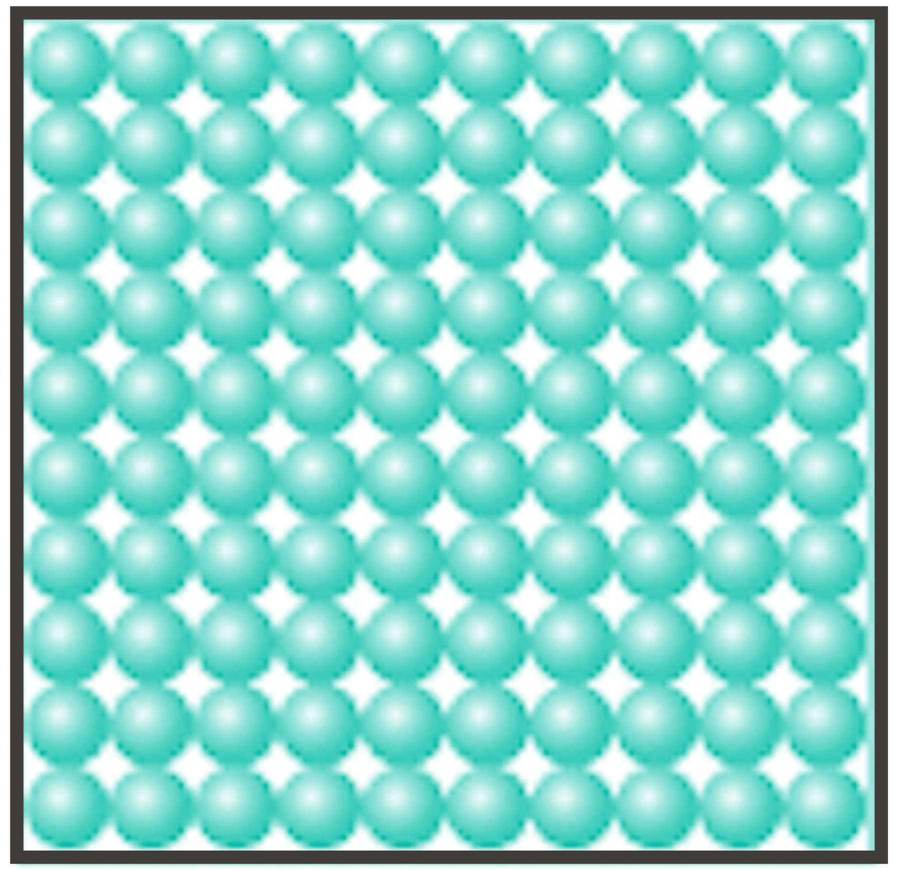
↓

shows up as f (surface stress)
mechanical force per unit length at surface

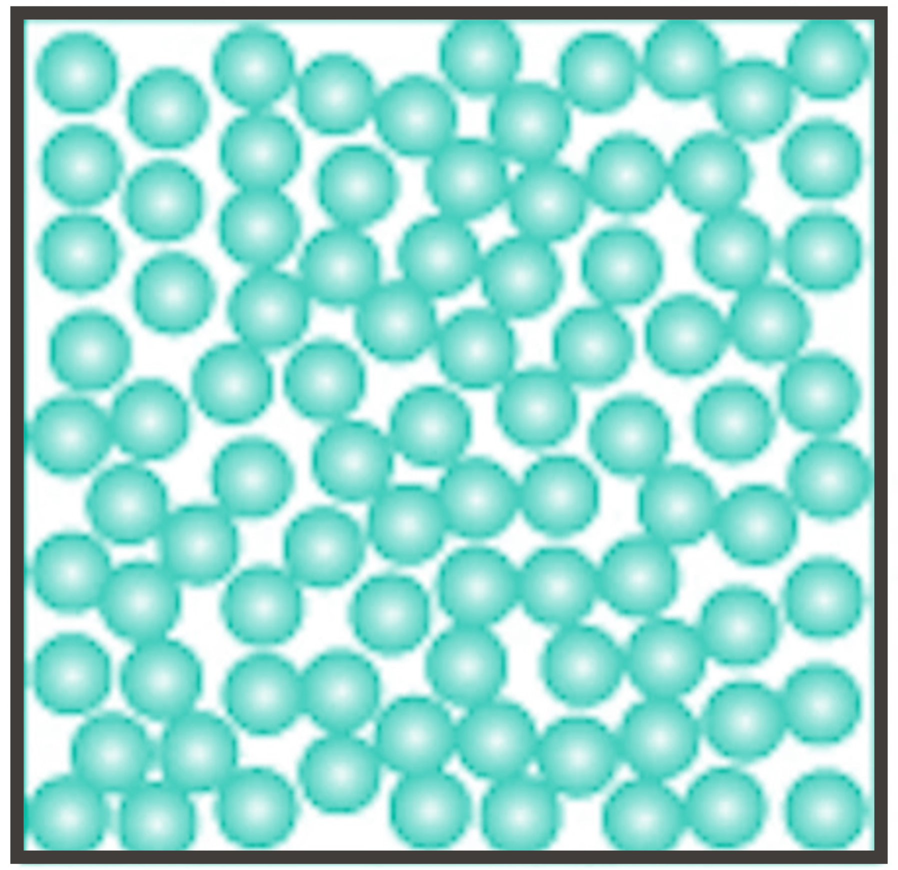
But what about liquids?

Liquids Have Surface Tension (σ) = Surface Energy (ɣ)

Surface tension (σ): homogenous and reversible work per unit area needed to extend the surface of a **liquid**



Solid



Liquid

Stretching ➔ Elastic strain

"Stretching" impossible

Molecules in a liquid are mobile so you can't "stretch" surface atoms like in a solid

The atoms just rearrange

Only way to increase surface is by creating more

$\sigma = \gamma$

Surface Tension (stress) = Surface Energy

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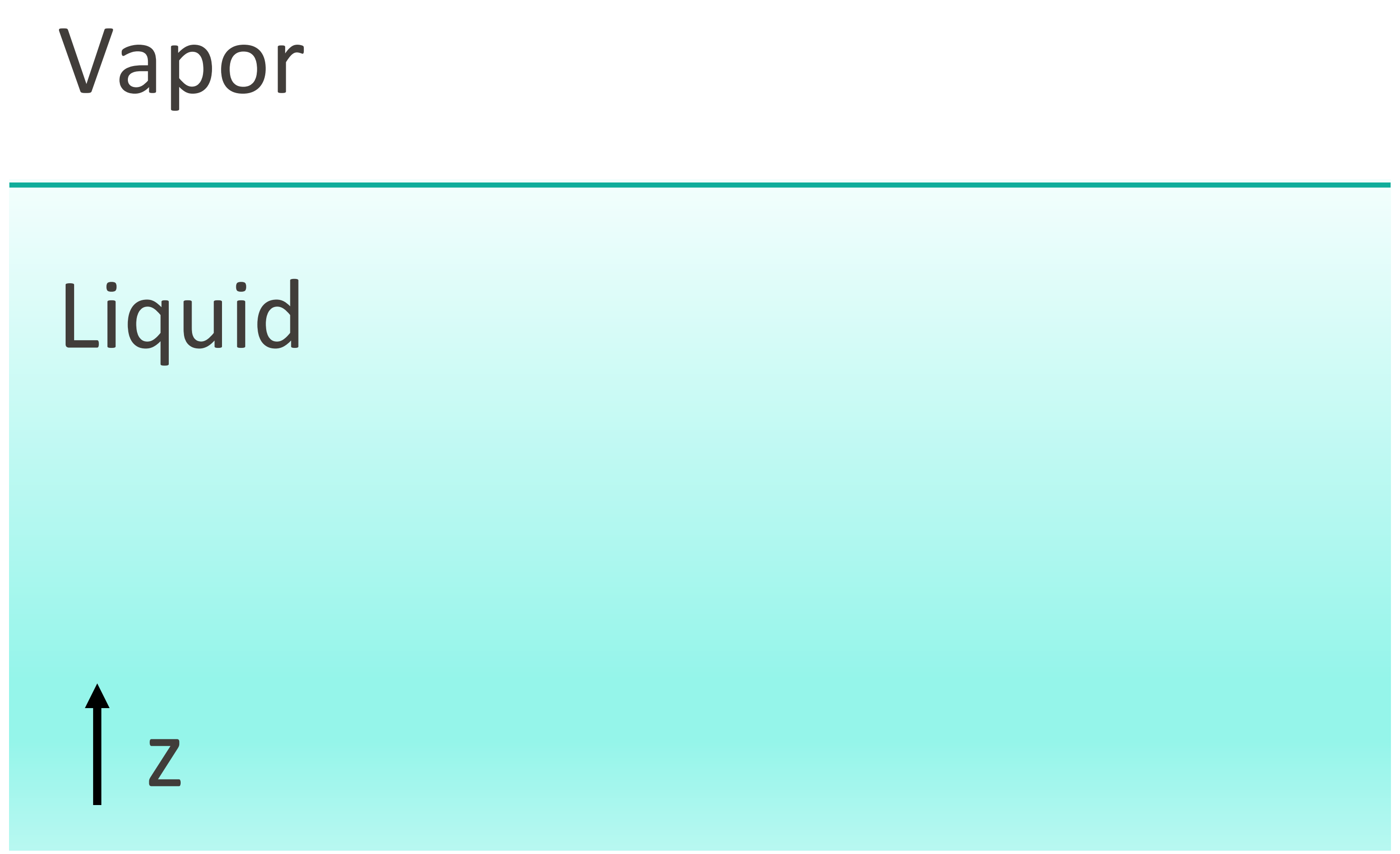
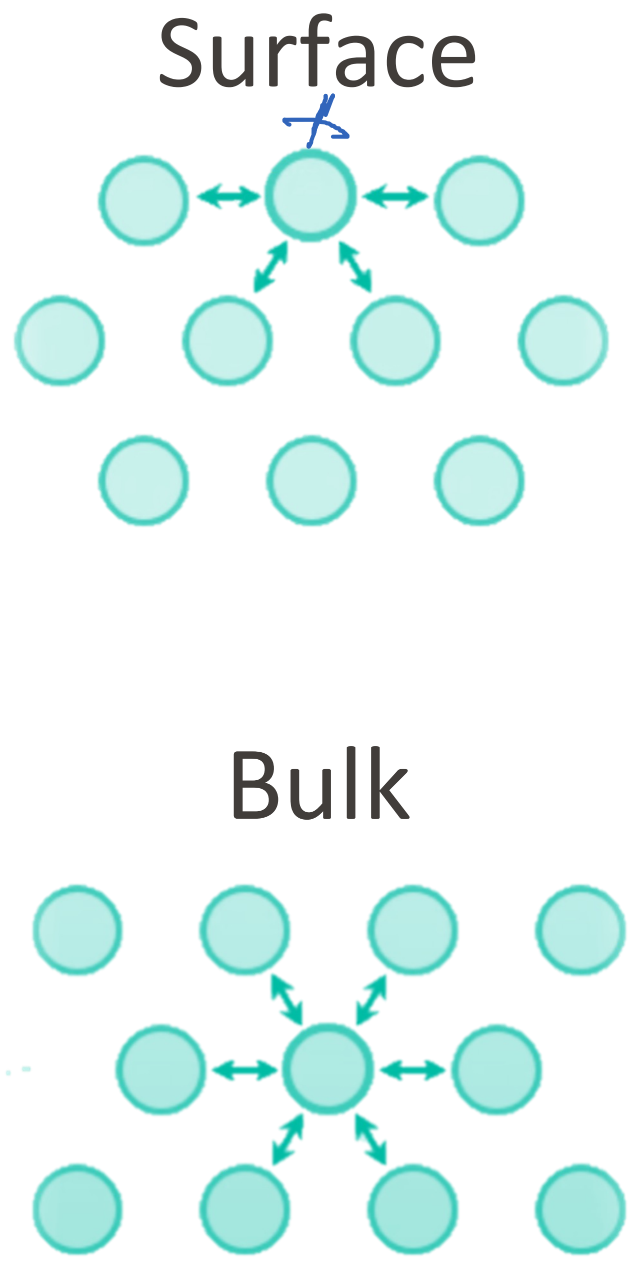
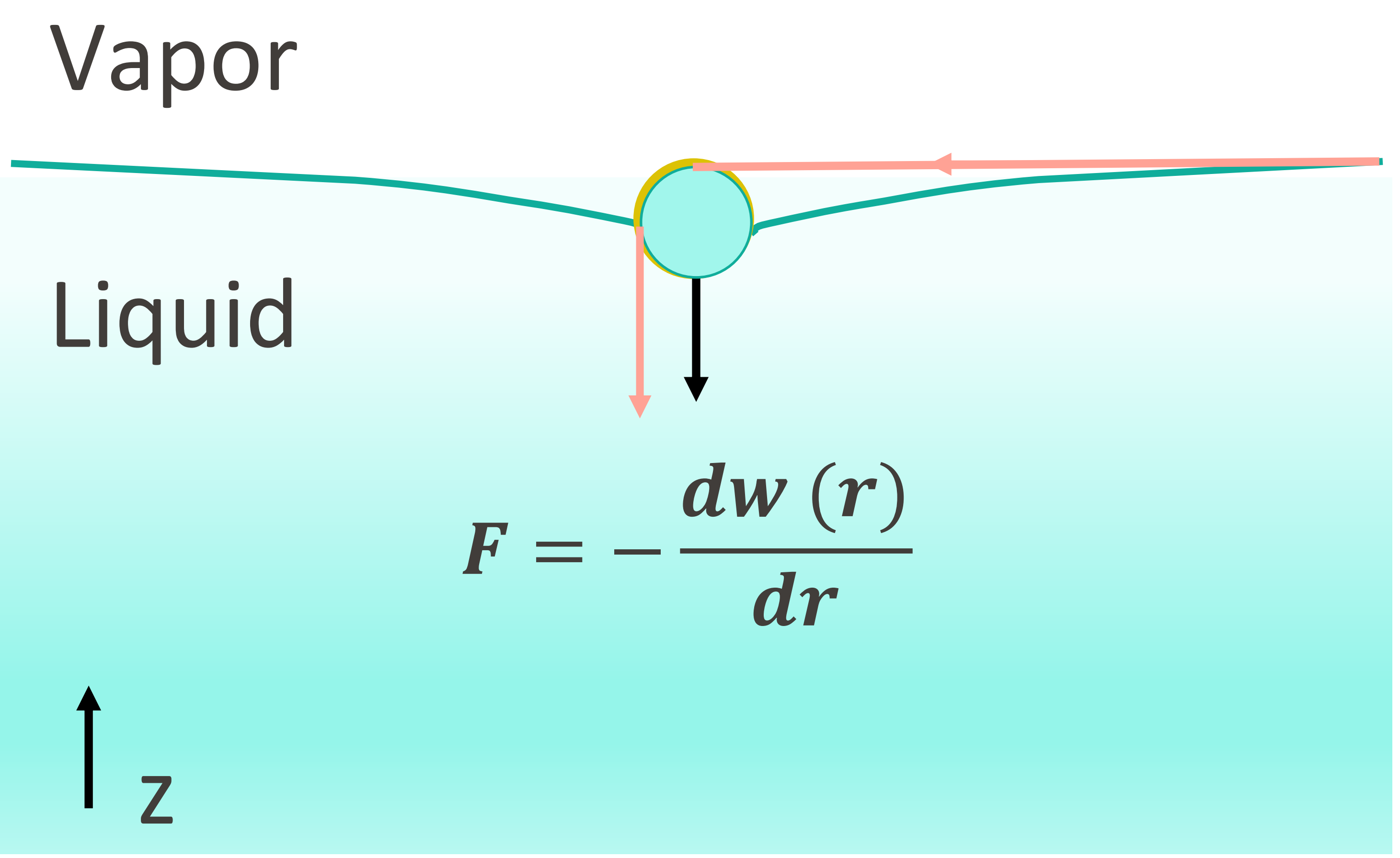
Molecular View of Surface Tension (σ)

Surface tension (σ): homogenous and reversible work per unit area needed to extend the surface of a **liquid**





Loss of stabilizing interactions

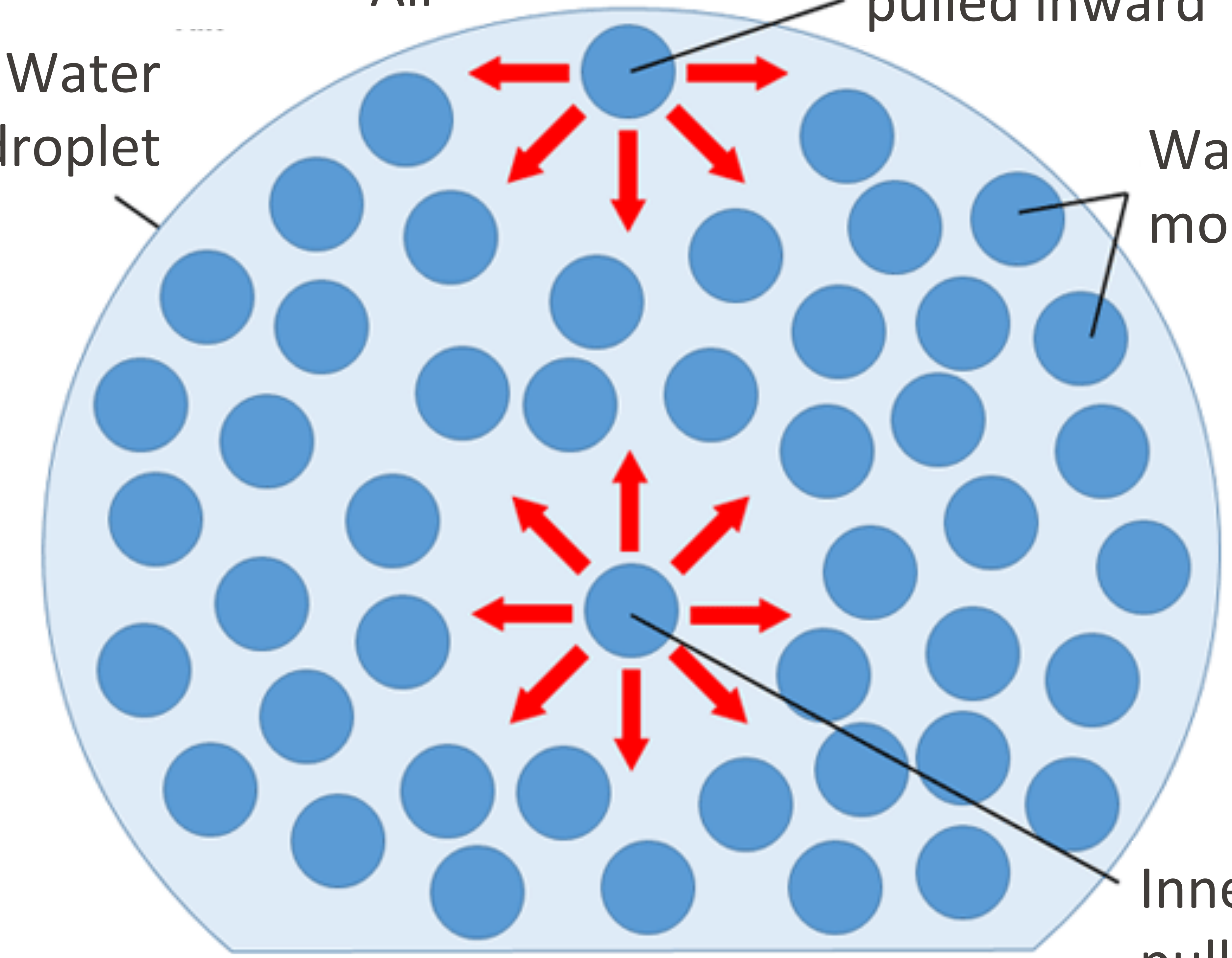


Molecular interaction potential between two molecules as a function of distance (r)

Surface energy (ɣ) = surface tension (σ)

Molecular View of Surface Tension (σ)

Surface tension (σ): homogenous and reversible work per unit area needed to extend the surface of a **liquid**



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Key Takeaway: Summarizing Terminology

Surface Energy (ɣ)

Work to create a surface of unit area at constant temperature and pressure, while keeping all the atomic positions fixed to their bulk position – mechanical definition.

Surface stress (*f*) – solids only

Mechanical stress when the surface is strained

In solids: $\gamma \neq f$

Surface Tension (σ) – liquids only

Work to extend the surface of a liquid of a unit area

In liquids: $\gamma = \sigma$

Surface free energy ($\tilde{\gamma}$)

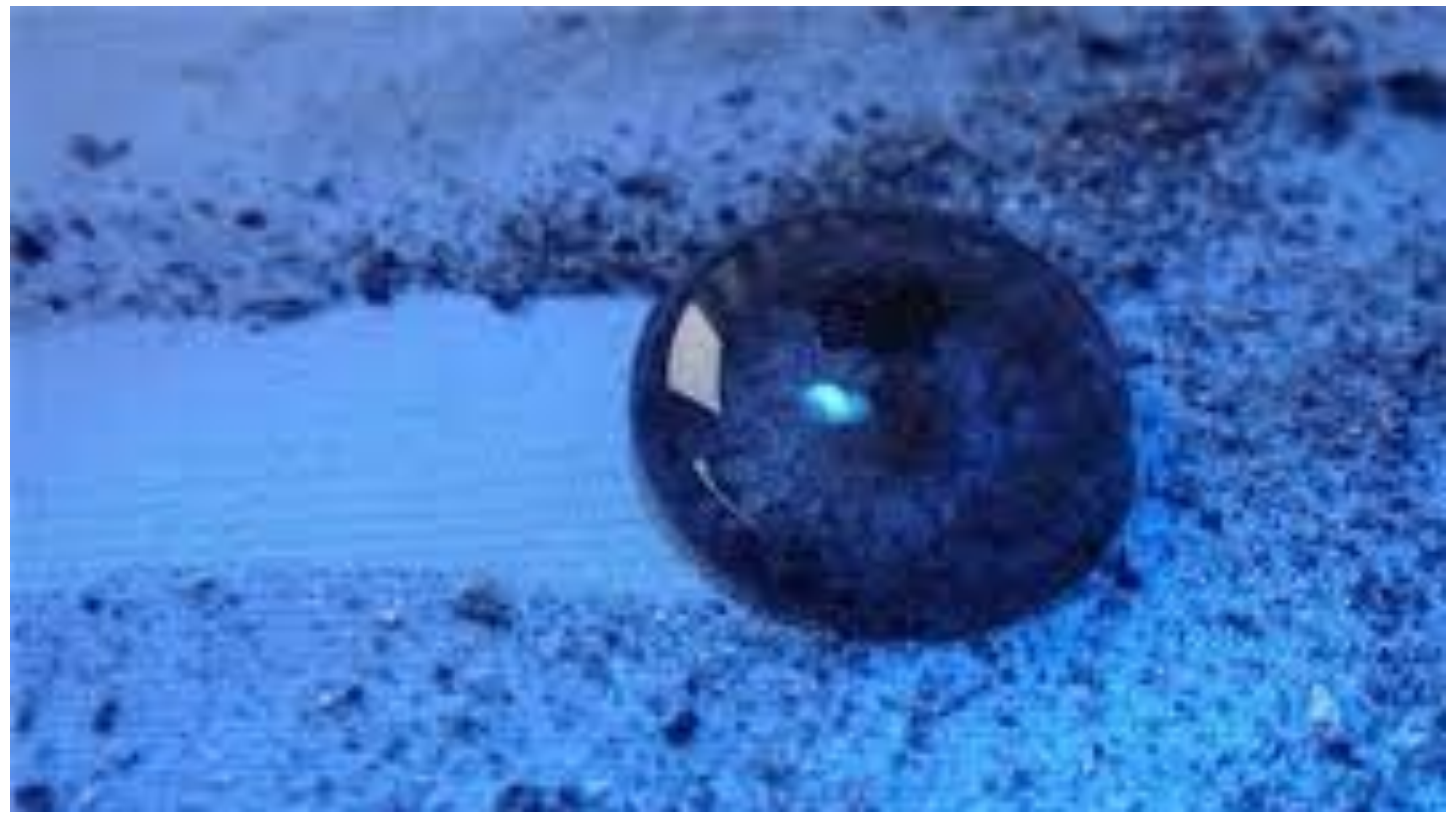
Excess Gibbs free energy per unit surface area relative to the bulk.

Combination of cutting bonds and stretching bonds – thermodynamic definition

From the idealized version of a surface to a more realistic plane

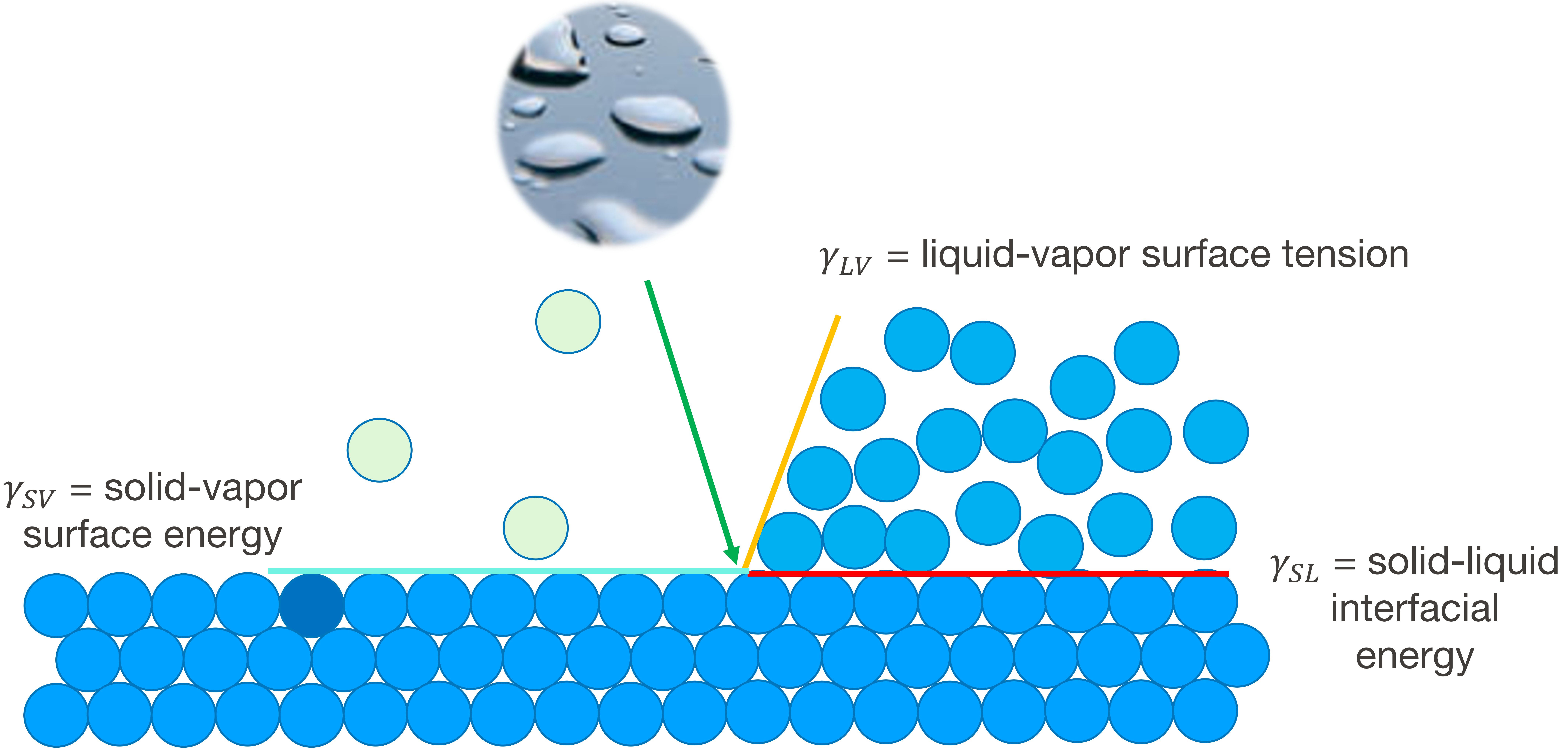
From Surface Energy to Wetting

Wetting is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together.



Droplets show us how surfaces balance forces and energies

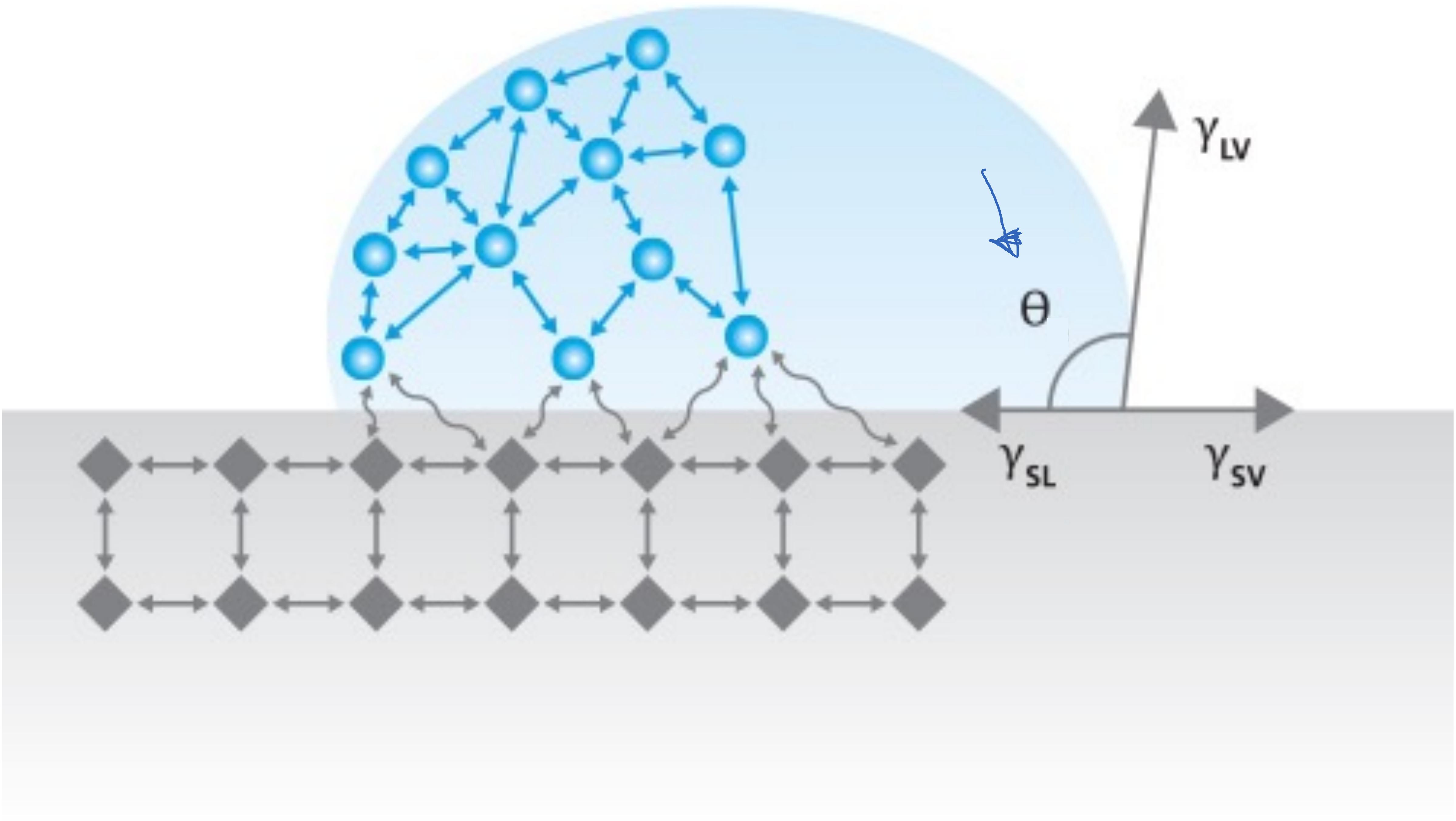
Surface *vs.* Interfacial Energy



The droplet is balancing the competition between three interfaces

Young's Equation for Contact Angle

Contact angle (θ): quantifies the wetting of a solid by a liquid. Angle formed by a liquid at the three-phase boundary point where the liquid, gas, and solid intersect (thermodynamic equilibrium)



Young's Equation

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

Relating interfacial energies with contact angle

Ideal surface assumptions:

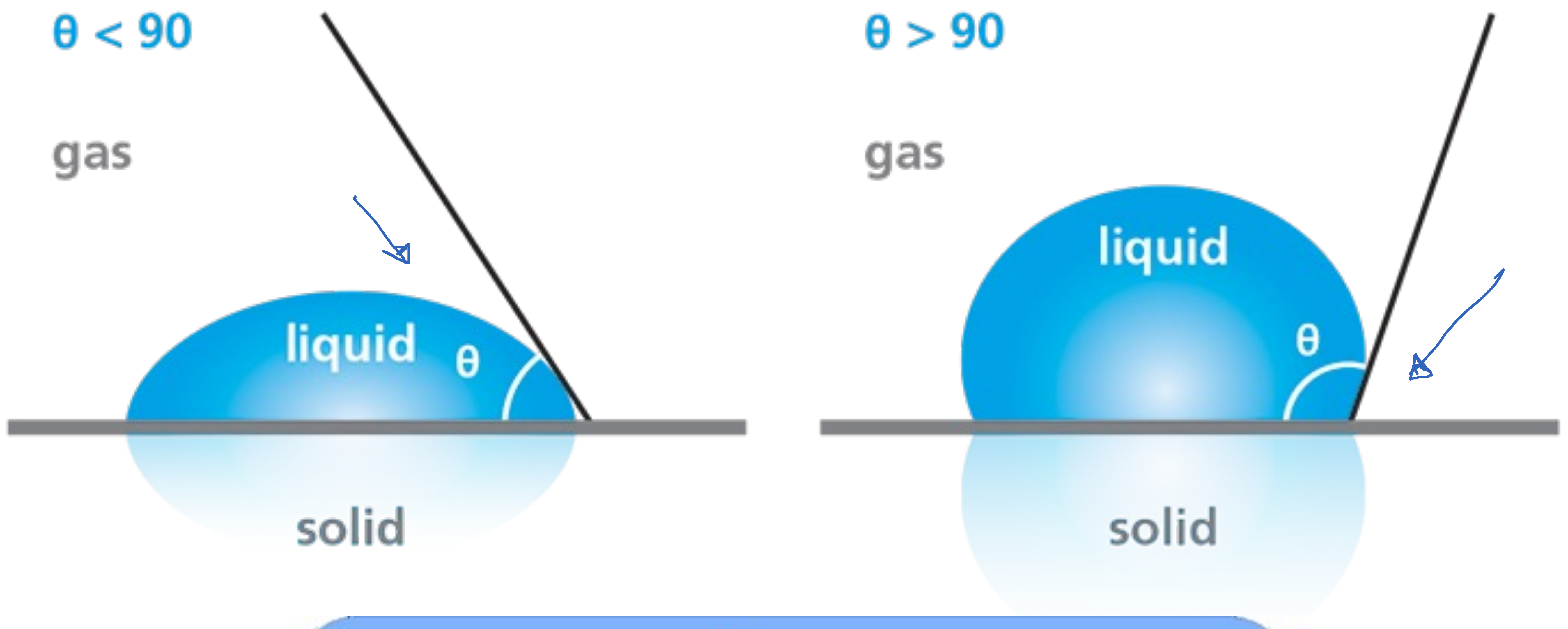
- Smooth
- Rigid
- Chemically homogeneous
- Insoluble
- Non-reactive

Young's equation bridges microscopic energies and what we can measure in the lab — the contact angle

Hydrophilic *vs.* Hydrophobic Surfaces

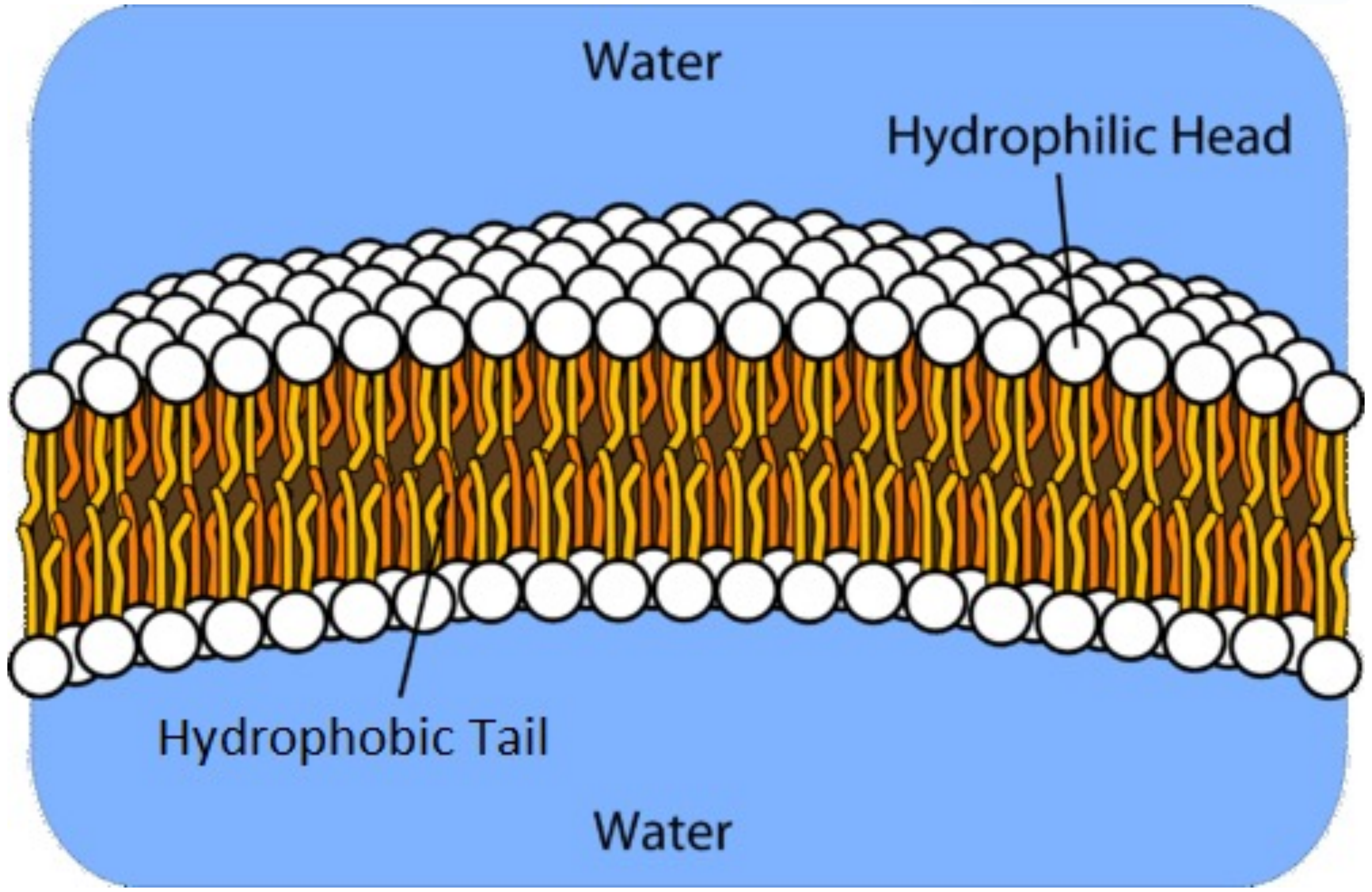
Hydrophilic

High wettability



Hydrophobic

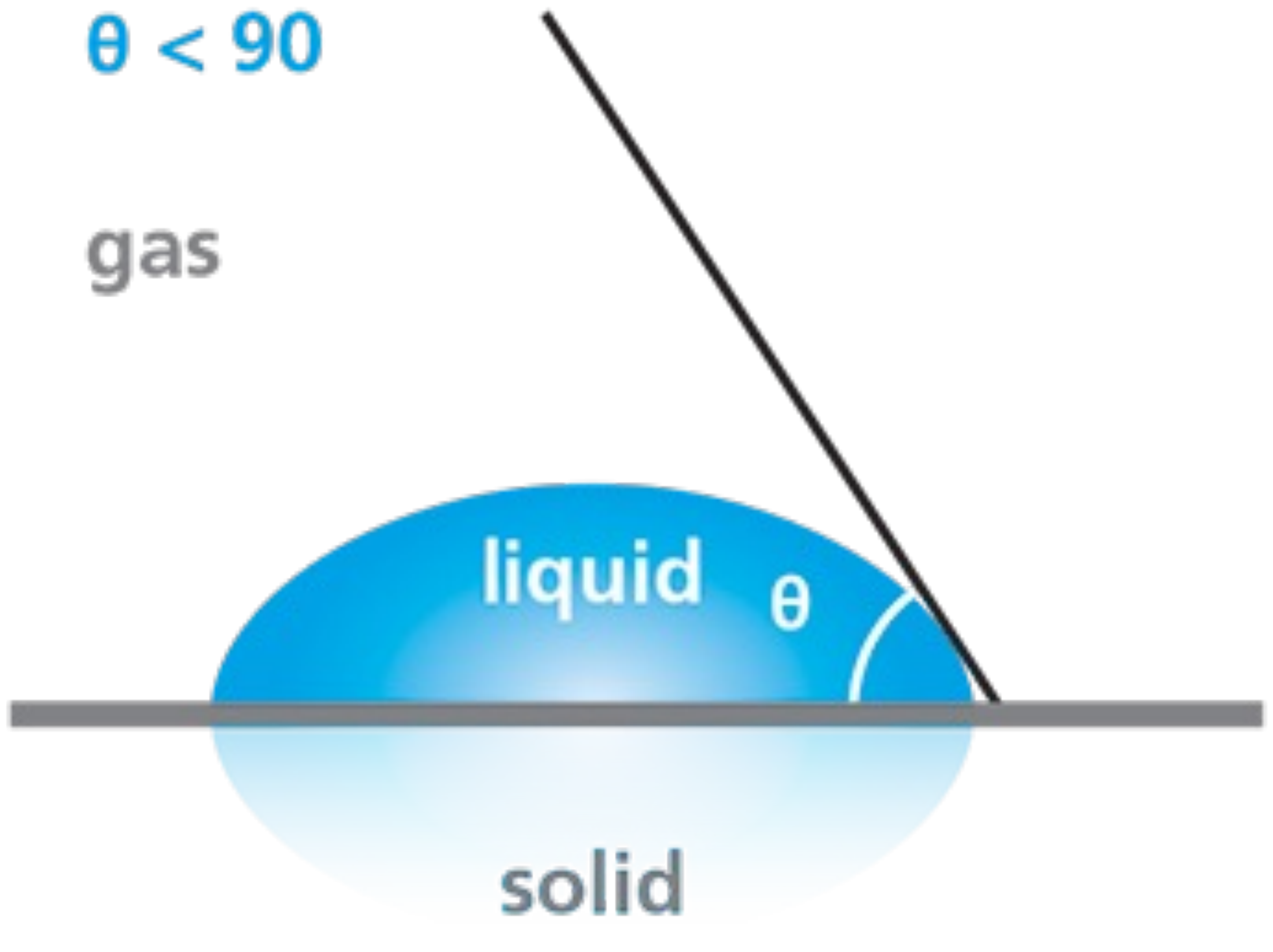
Low wettability

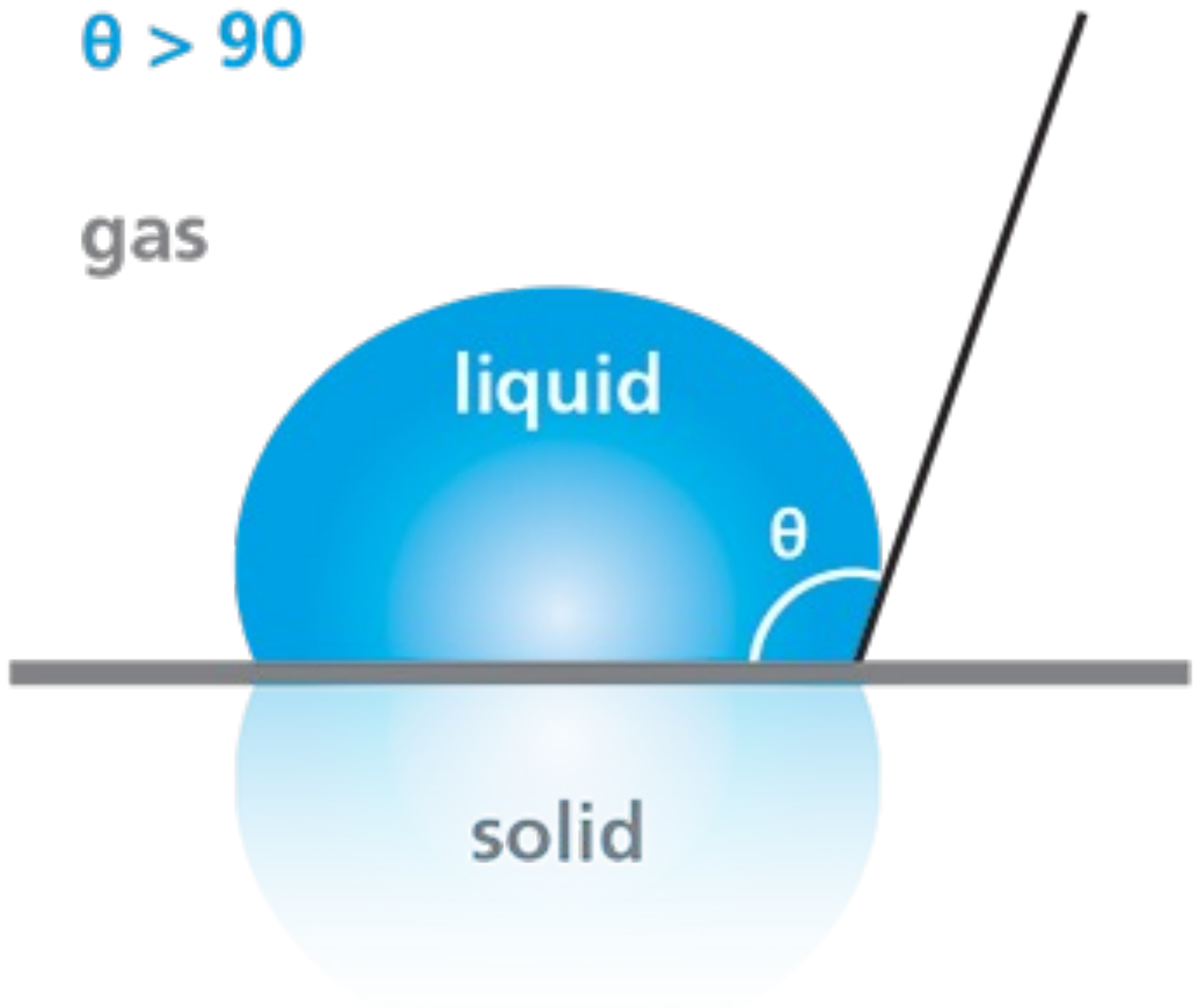


Hydrophilic *vs.* Hydrophobic Surfaces – Chemical Structure

Hydrophilic

High wettability



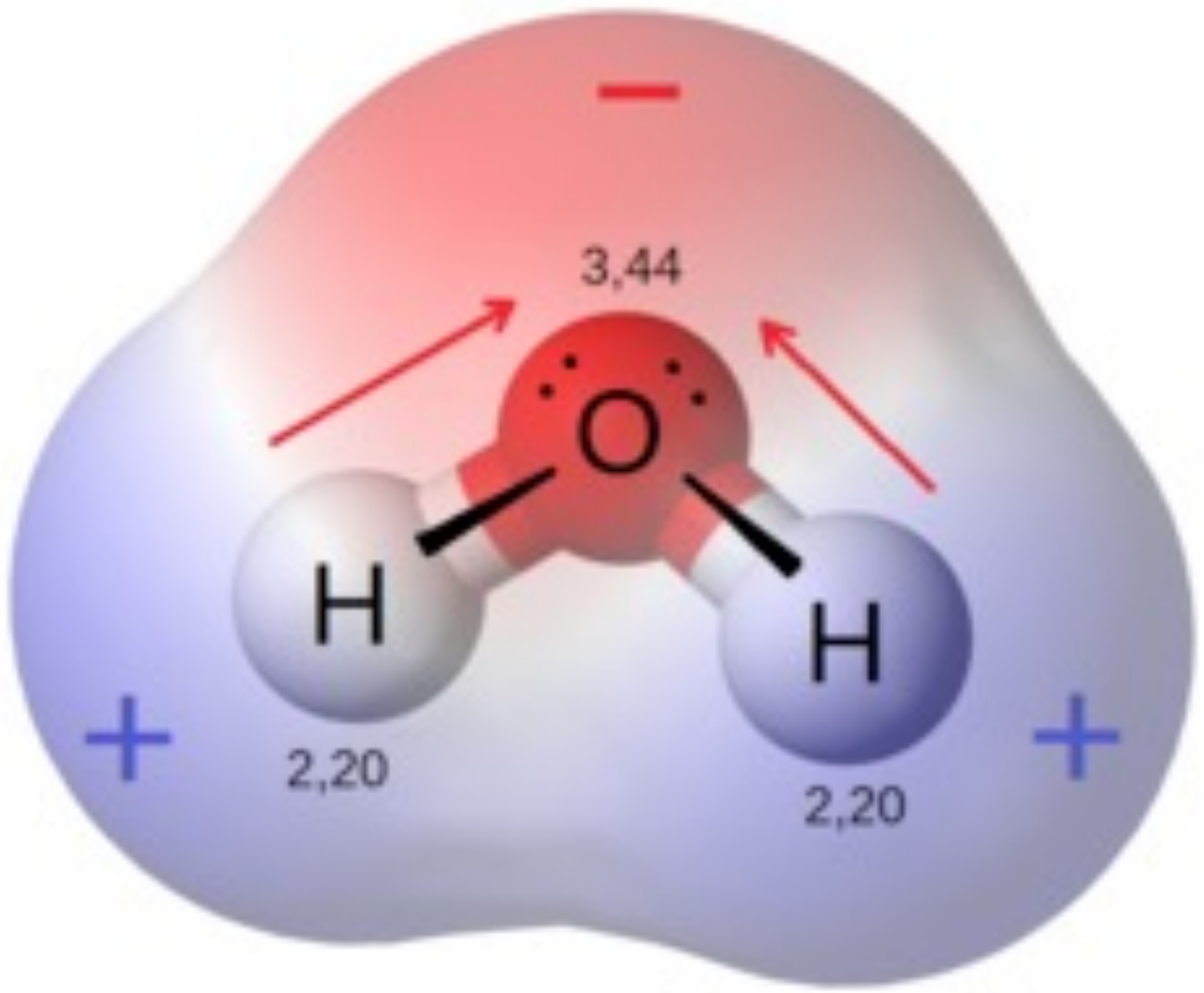


Hydrophobic

Low wettability

Polar

Non-polar



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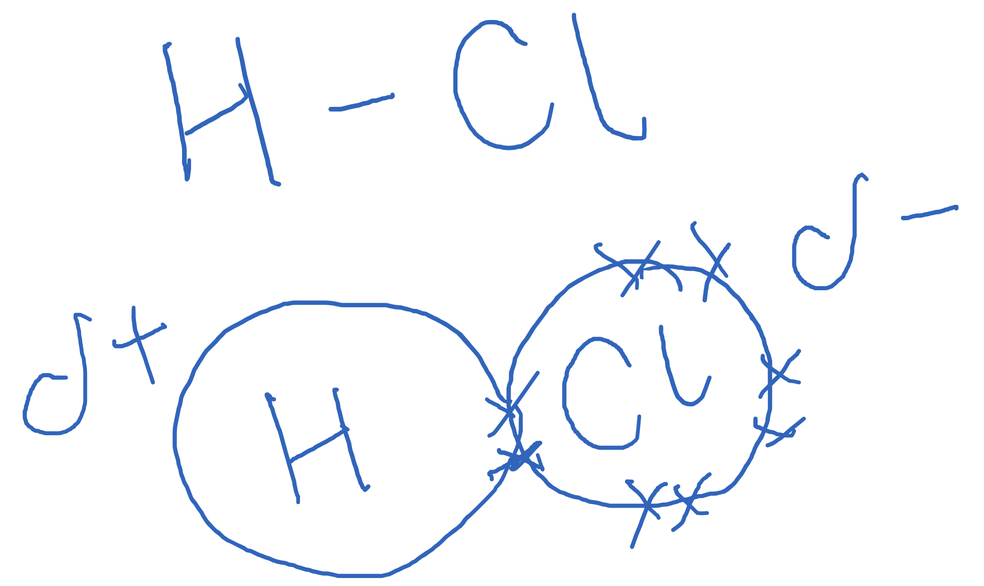
How to Determine if Molecule is Polar



1. Write Lewis structure of the molecule/compound

2. Determine the electronegativity difference of the bonds to the central atoms

Electronegativity Difference	Bond type
0	Nonpolar covalent
0 – 0.4	Slightly polar covalent
0.5-2.1	Polar covalent
>2.1	Likely ionic

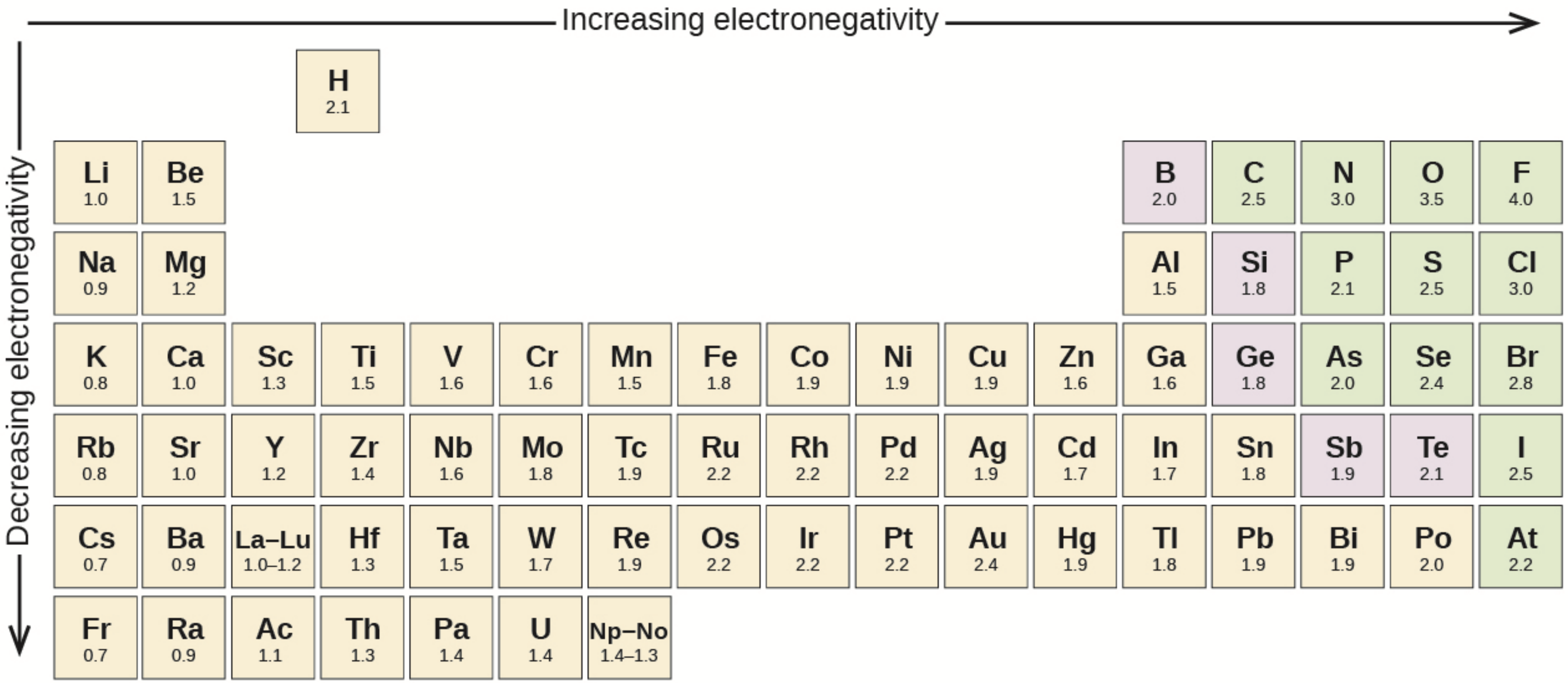
3. If more than 2 atoms, figure out molecular shape around central atom

4. Decide if environment around central atom is symmetric (net dipole?)

How to Determine if Molecule is Polar

1. Write Lewis structure of the molecule/compound
2. Determine the electronegativity difference of the bonds to the central atoms
3. Figure out molecular shape around central atom
4. Decide if environment around central atom is symmetric

NH_3



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How to Determine if Molecule is Polar

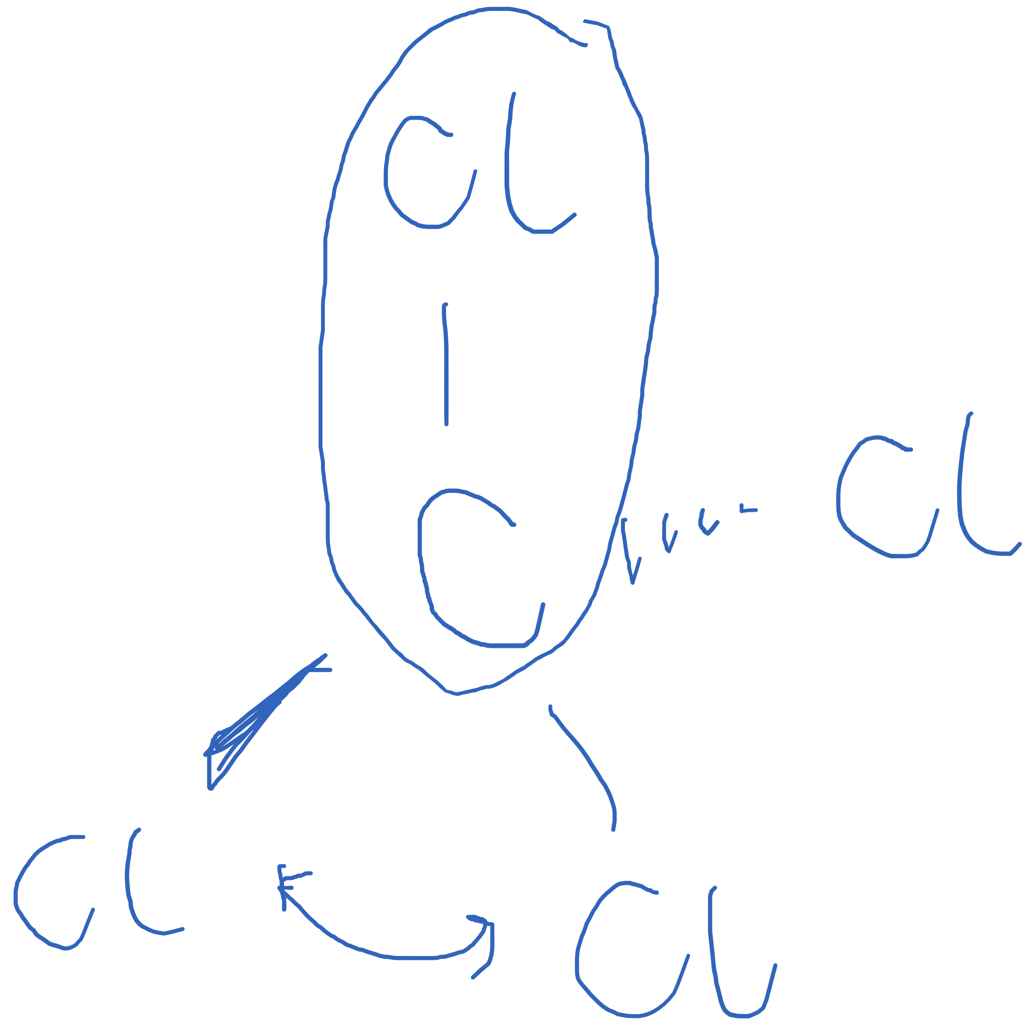
1. Write Lewis structure of the molecule/compound
2. Determine the electronegativity difference of the bonds to the central atoms
3. Figure out molecular shape around central atom
4. Decide if environment around central atom is symmetric

Increasing electronegativity →

Decreasing electronegativity ↓

		H 2.1														
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La–Lu 1.0–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac 1.1	Th 1.3	Pa 1.4	U 1.4	Np–No 1.4–1.3										

CCl_4



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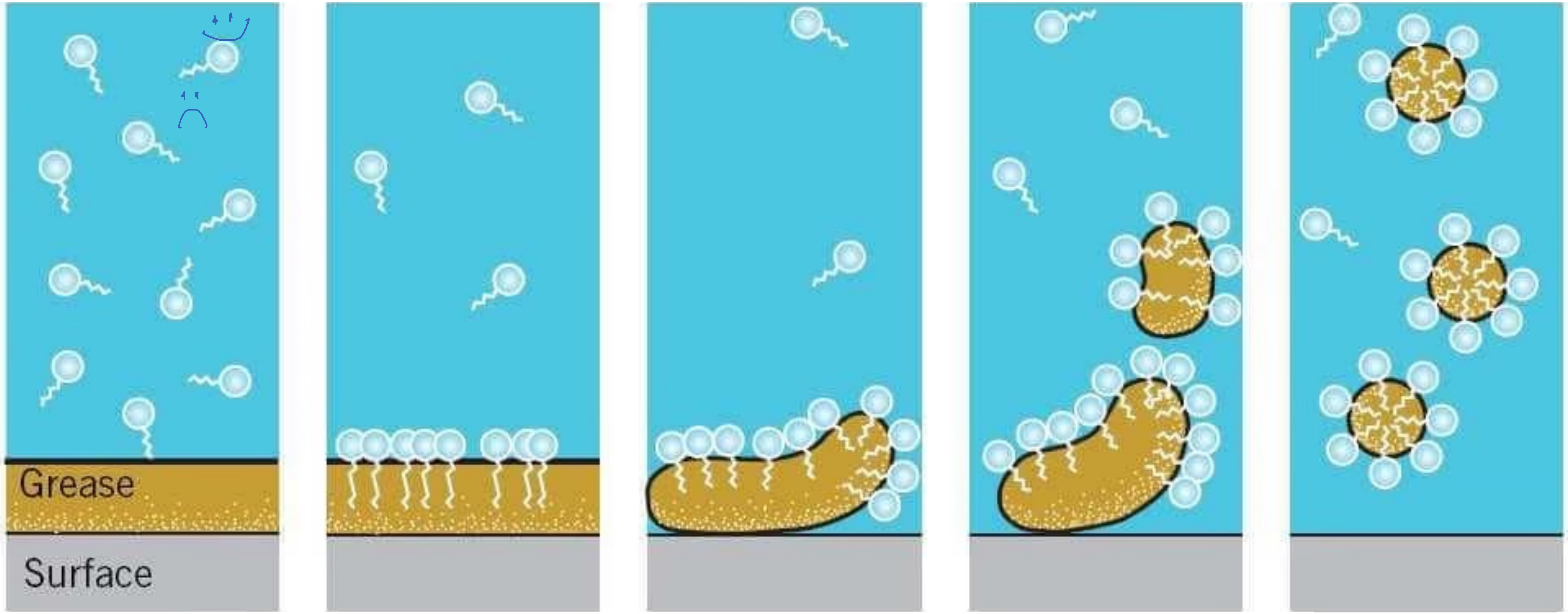
How Surfactants (Soap) Reduce Interfacial Energy

Surfactant molecules dissolve in water

With agitation, surfactants break up grease into small patches



Surfactants arrange at grease-water interface (Lowers γ)

Micelle formation

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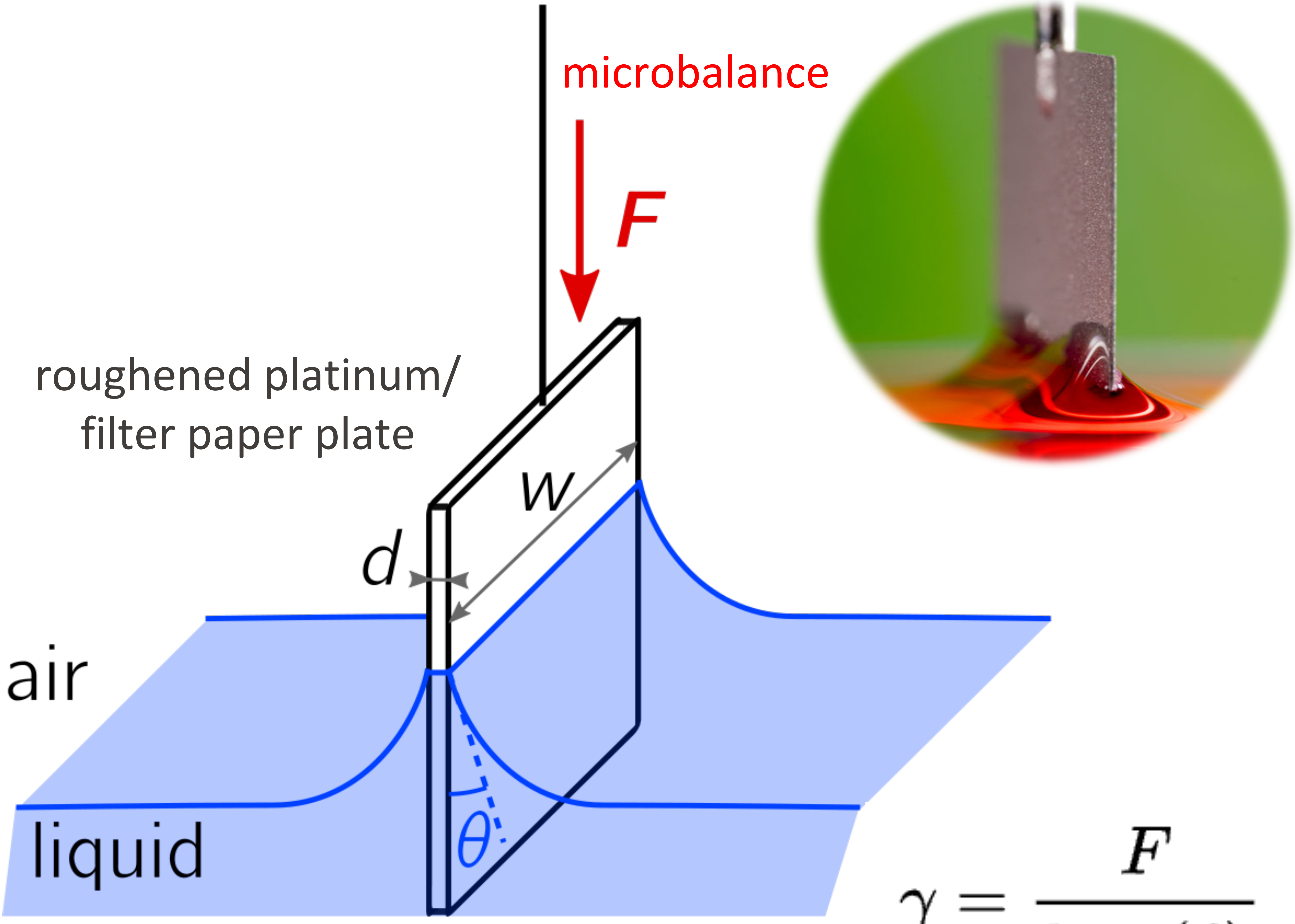
Measuring θ and γ (sometimes called σ)

Wilhelmy plate

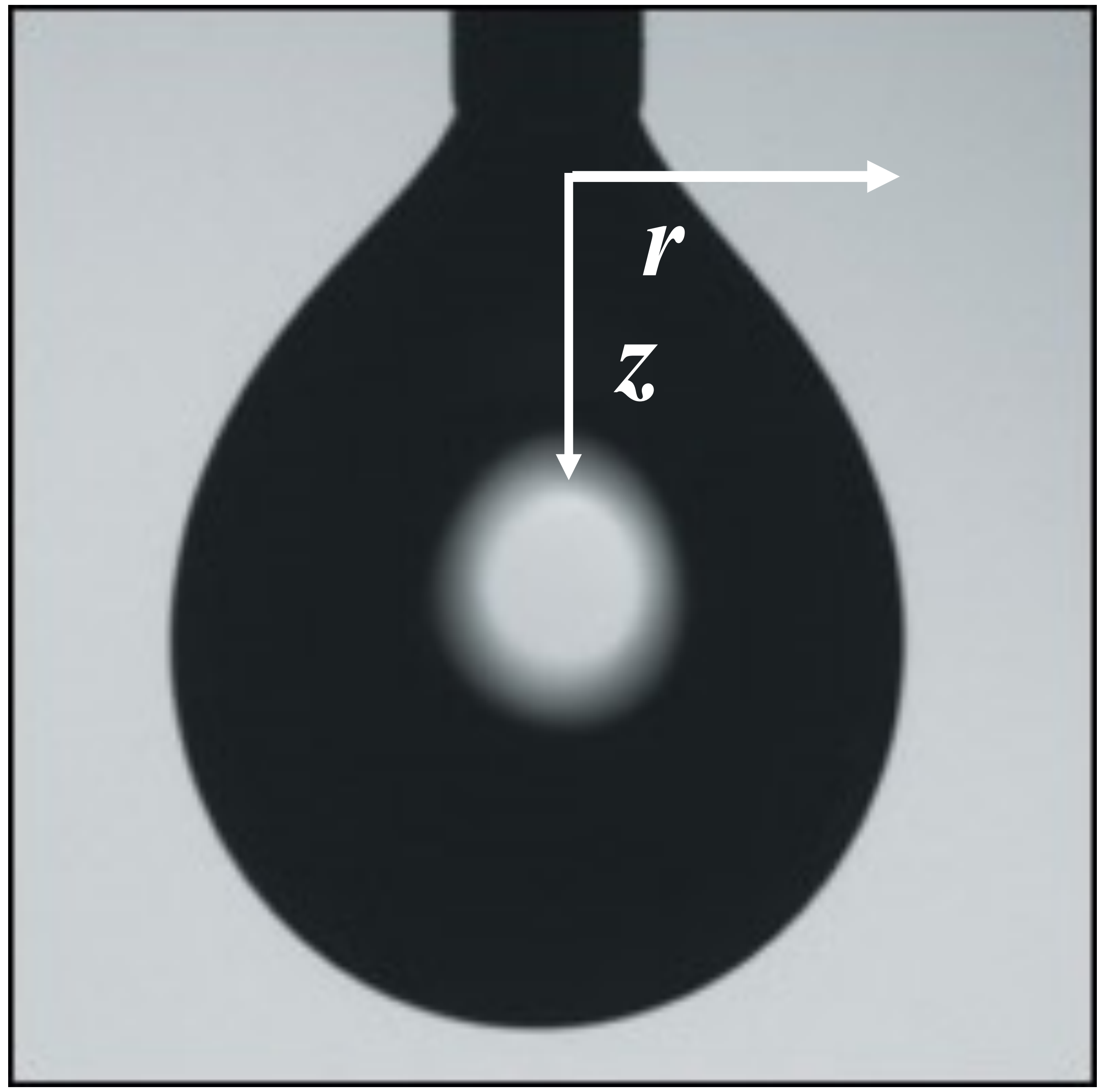


$$\gamma = \frac{F}{l\cos(\theta)}$$

Surface tension

↖ 2w + 2d

Pendant drop



Surface tension of the liquid measured by the optical drop profile under gravity

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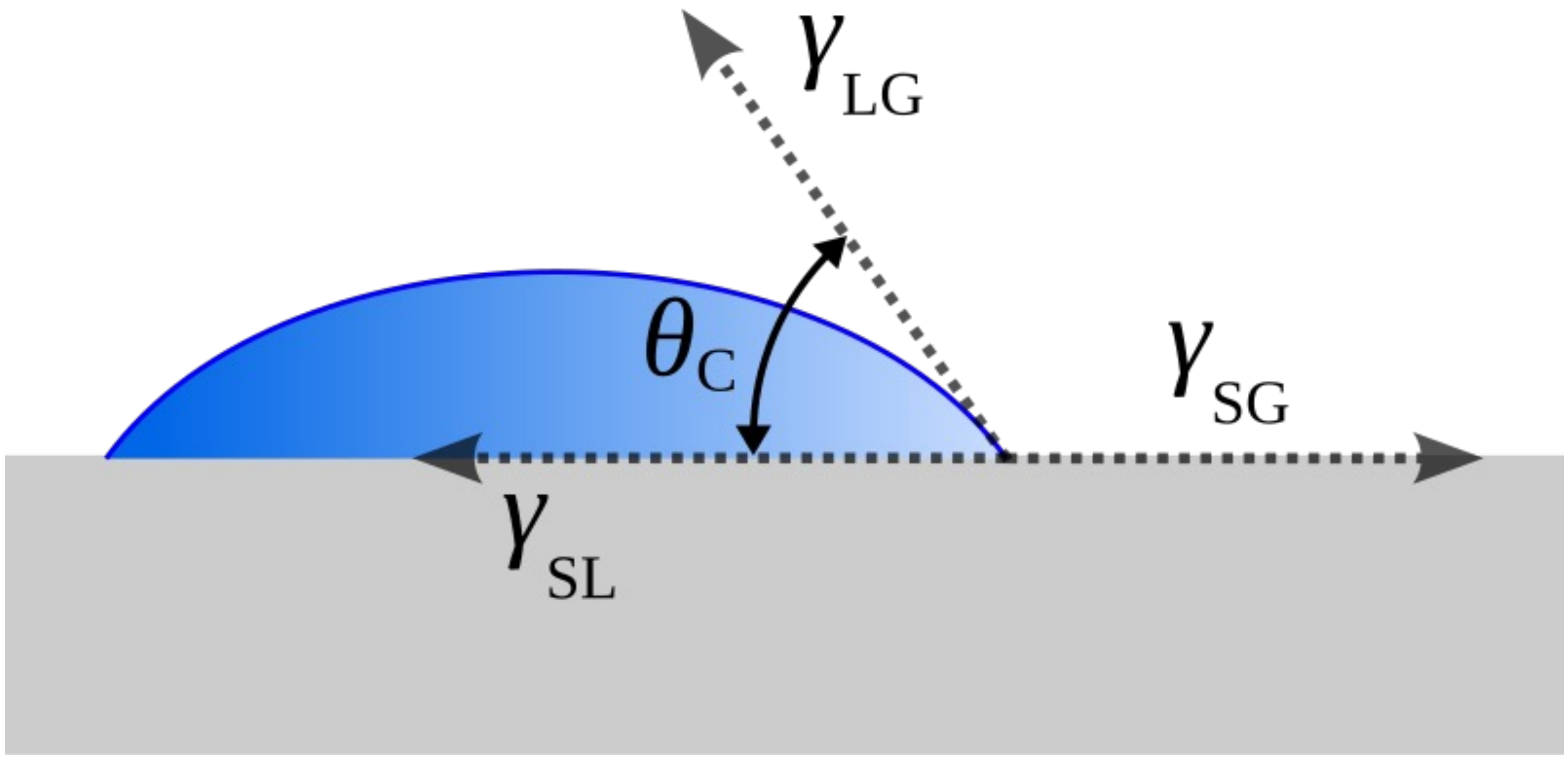
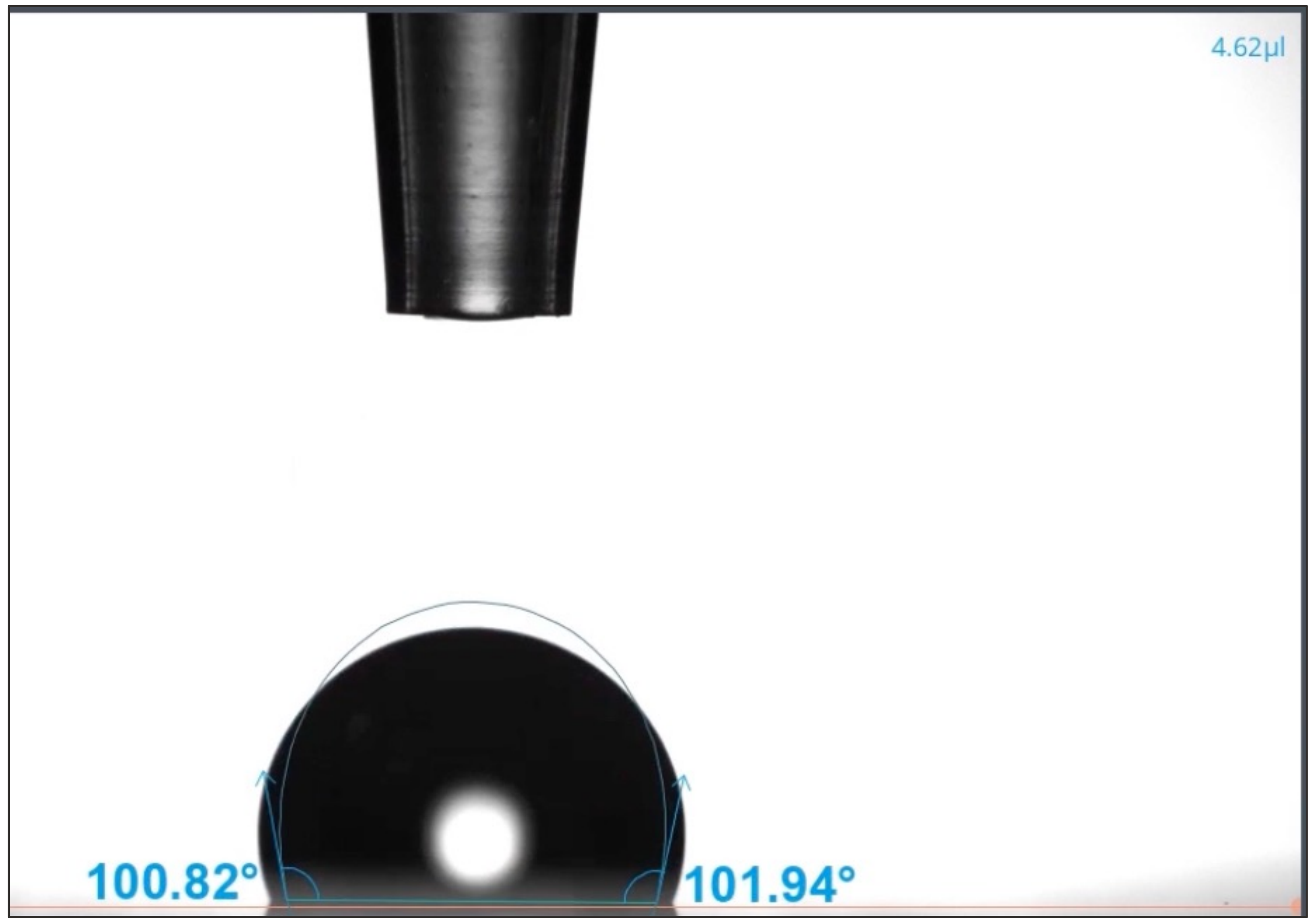
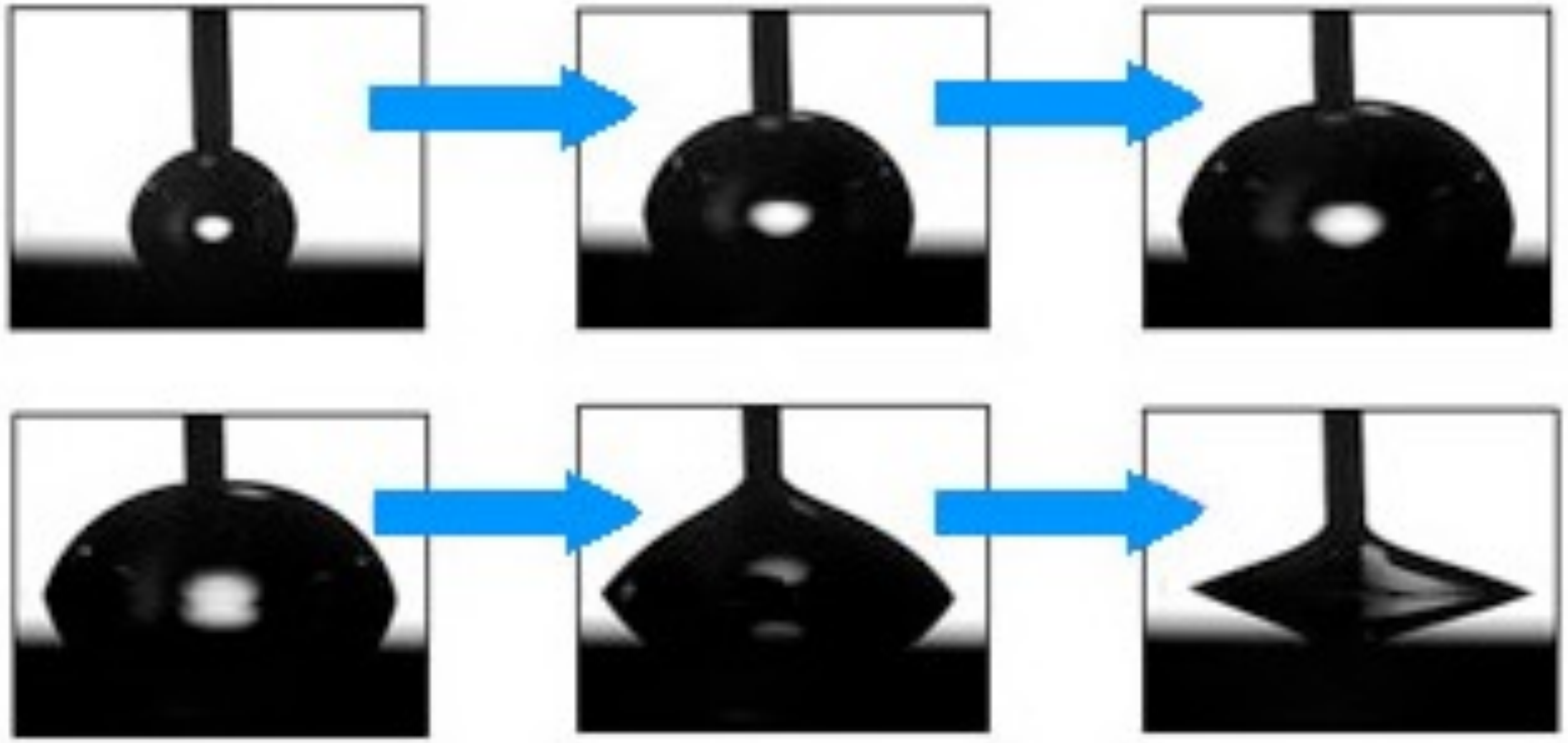
Measuring θ and γ (sometimes called σ)





Sessile drop

Direct contact angle measurement from drop or bubble shape shape



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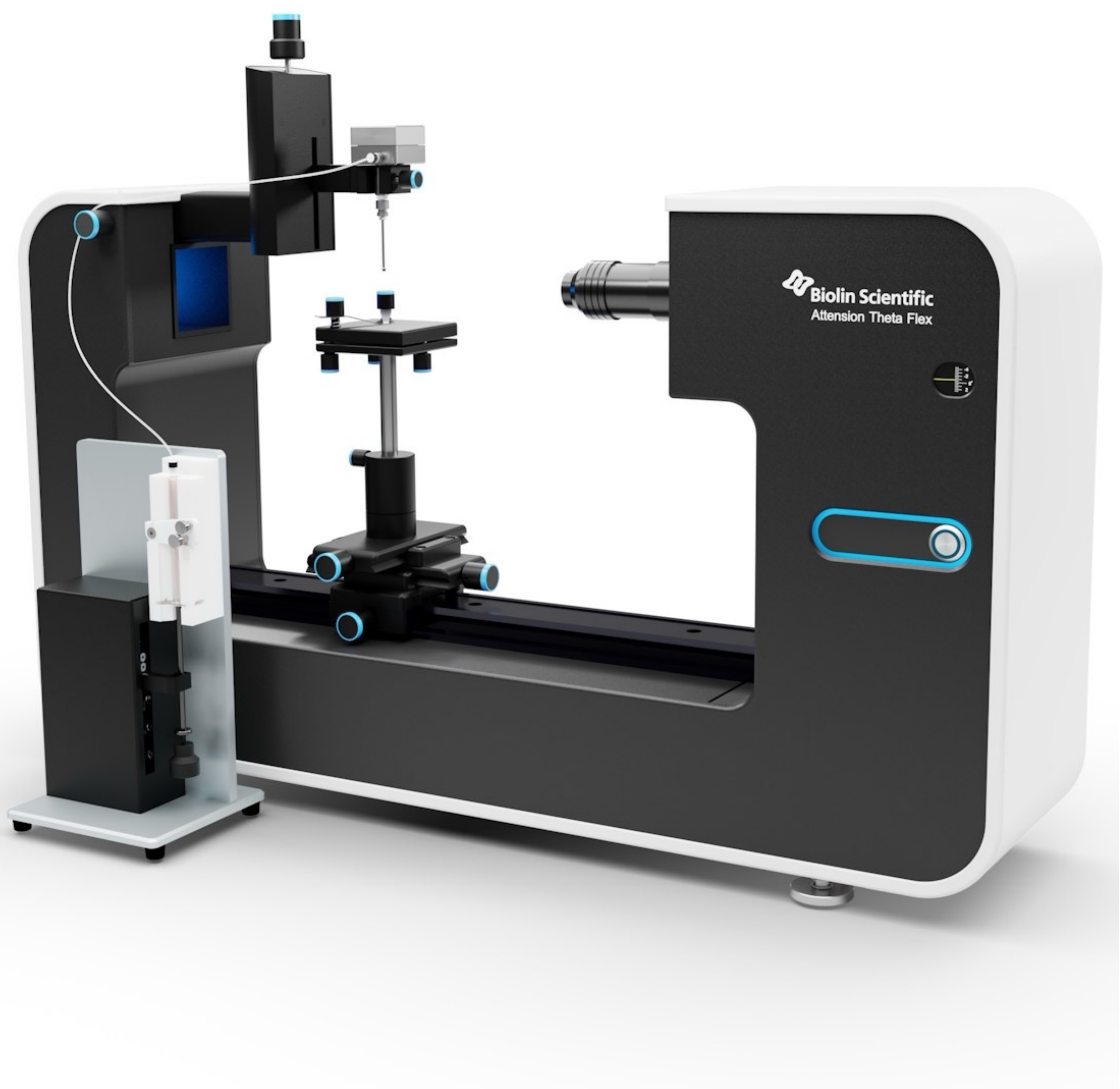
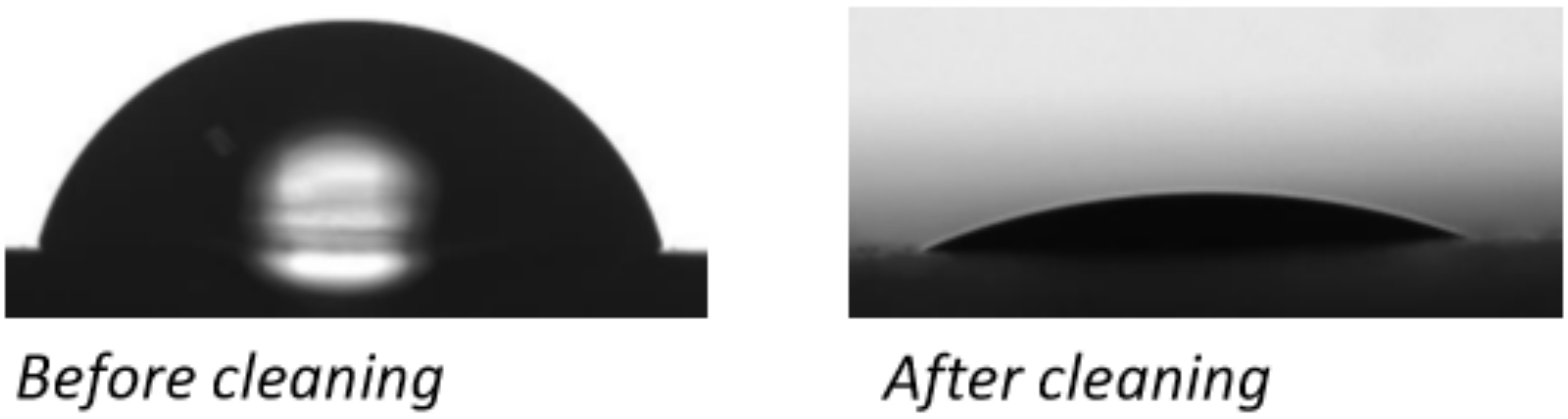
Contact Angle Instruments



Contact Angle on Glass Surface Higher with Contamination



Contact angle advantages: Quick, non-destructive

Contact angle limitations: Limited information

Biolin Scientific

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Key Takeaways

Young's equation bridges microscopic energies to something we can measure in the lab

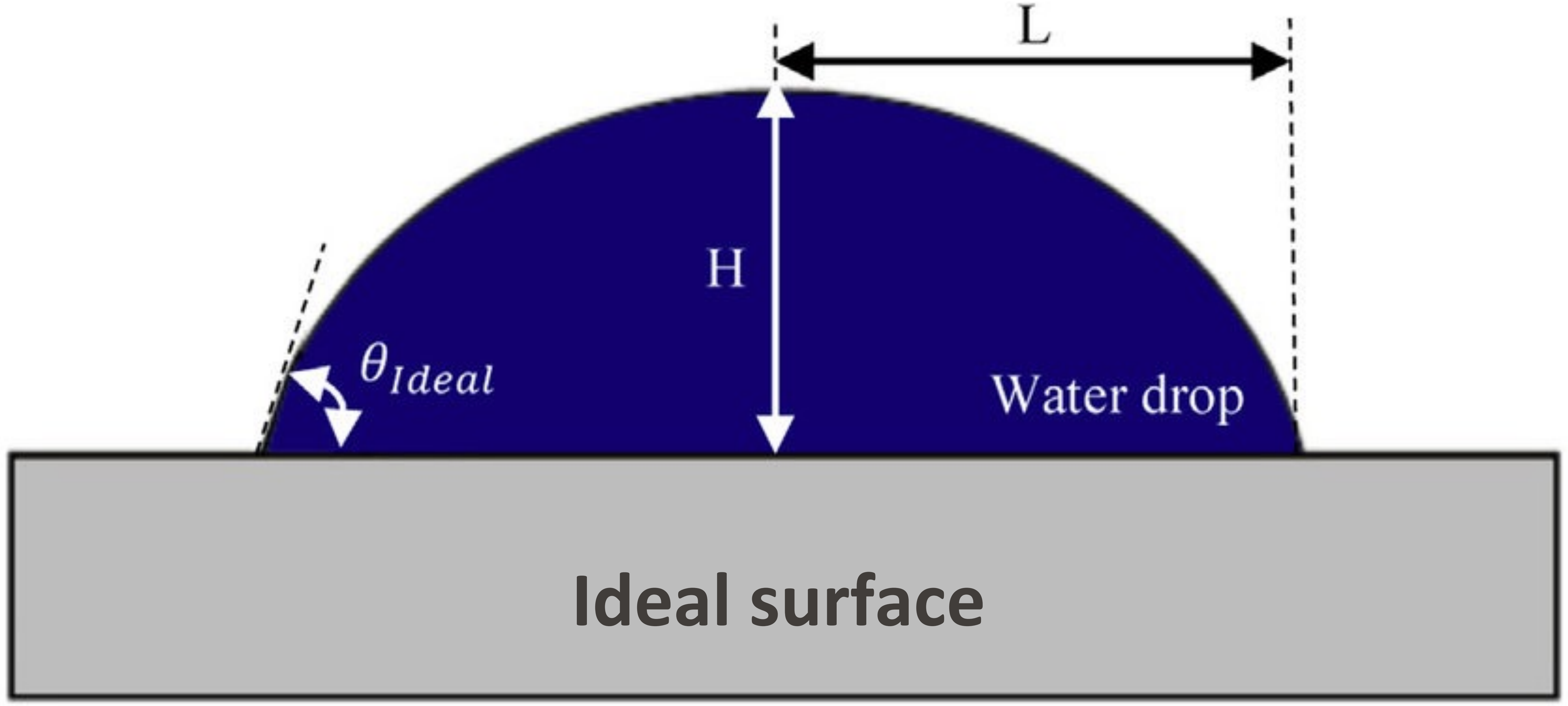
Basics of hydrophilic vs. hydrophobic molecules/interfaces

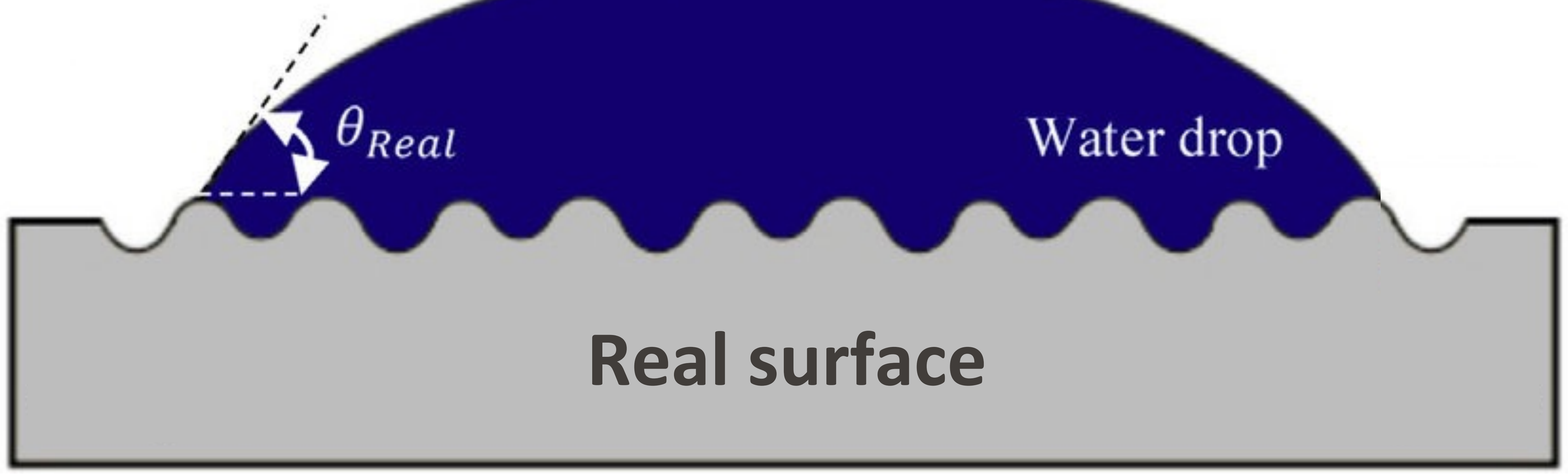
You can modulate interfacial energy using surfactants

There are various methods (Wilhelmy plate, pendant drop, sessile drop) to measure contact angle

Young's equation is for ideal surfaces – what happens on "real" surfaces?

Limits of Young's Equation – Complications in Real Systems





Ideal surface	Real surface
Perfectly flat and smooth	Rough
Rigid	Contaminated
Chemically homogeneous	Chemically heterogeneous
Contact angle well-defined and ideal	Contact angle hysteresis and deviations

Young

We need other models to describe wetting on real surfaces

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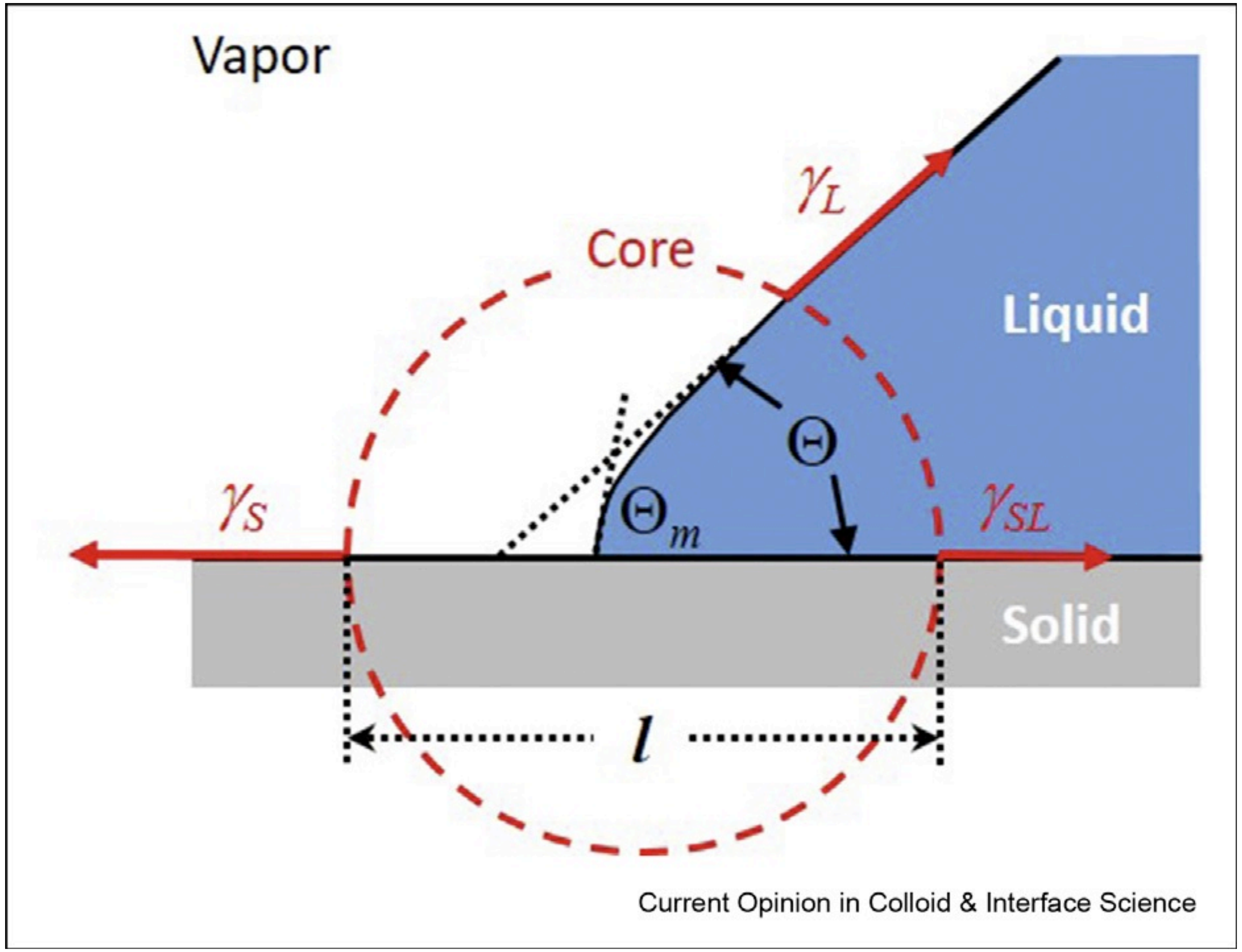
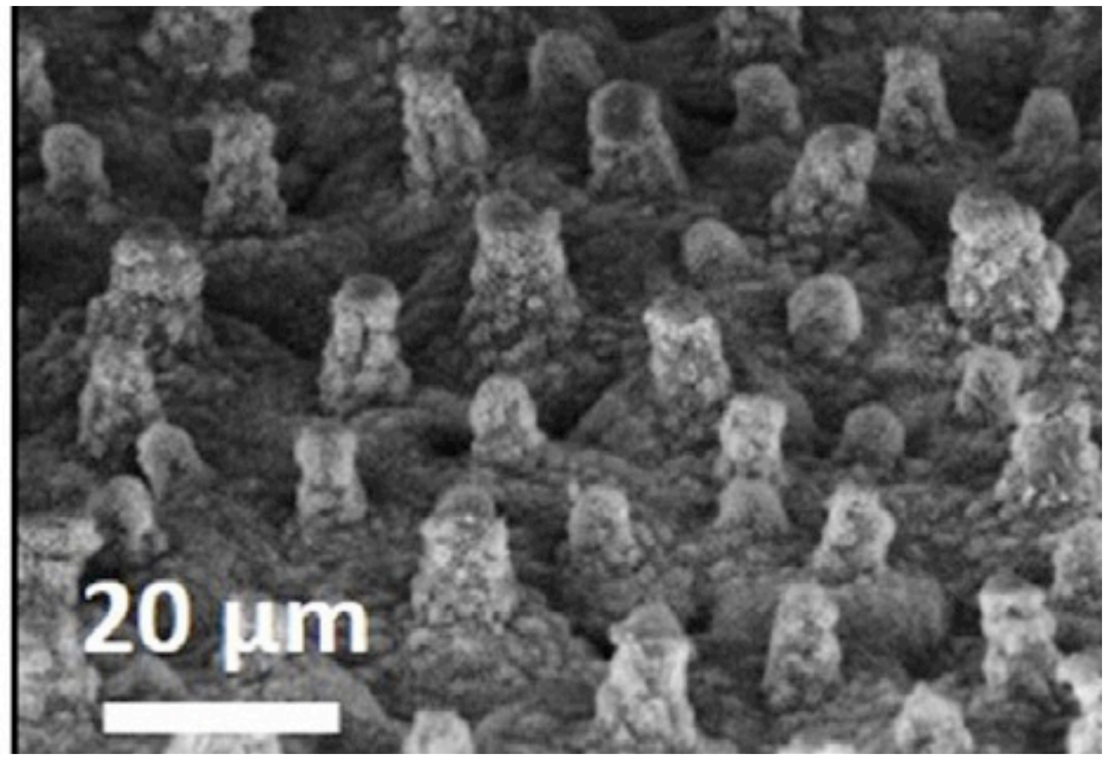
Macroscopic and Microscopic Contact Angles



The microscopic contact angle may be different from the macroscopic or "apparent" contact angle (length scale of measurement relative to molecular, heterogeneity or surface structure scale)



The contact angle is a static, equilibrium quantity that only depends on surface energies

During spreading of a liquid, the contact line moves over the surface

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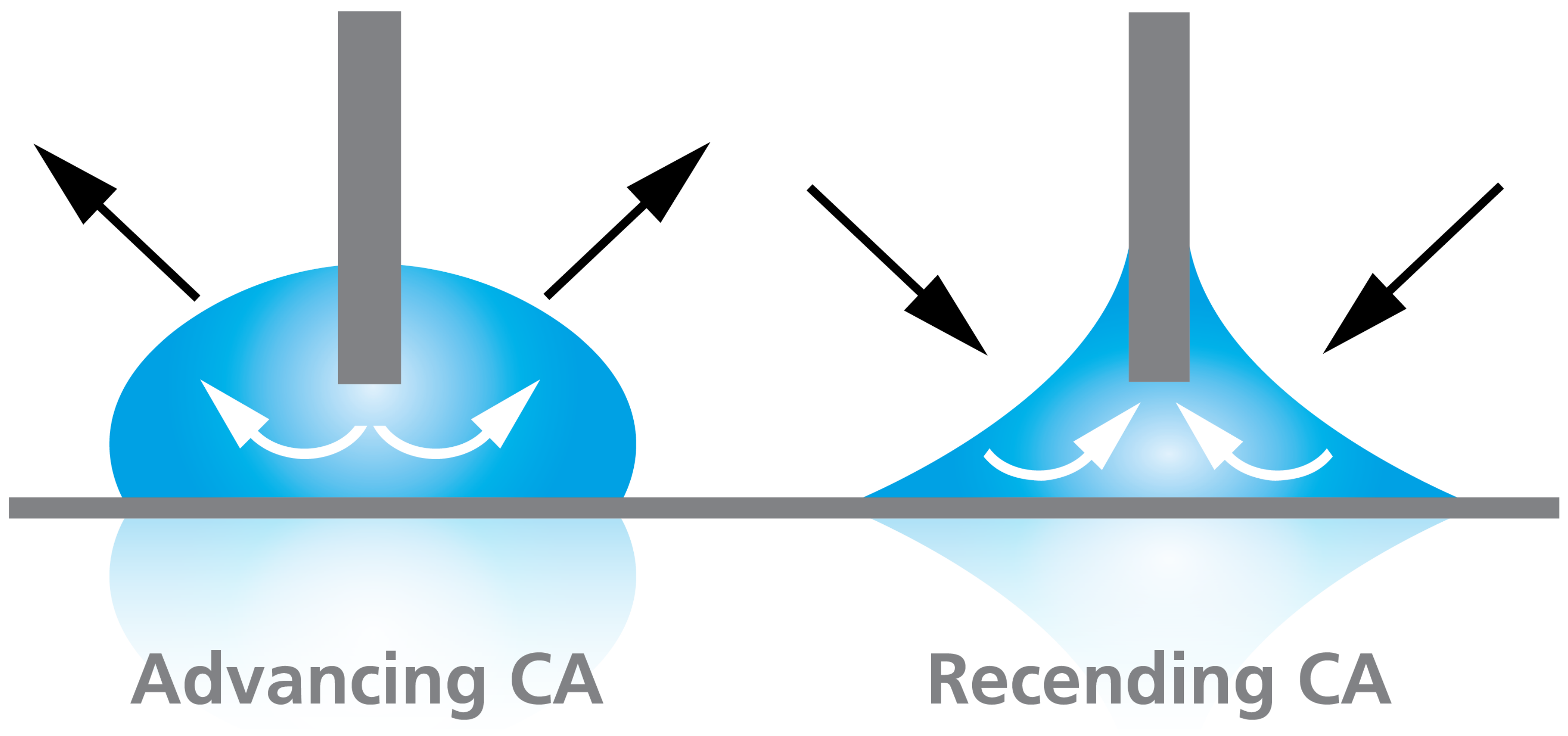
Dynamic Contact Angles

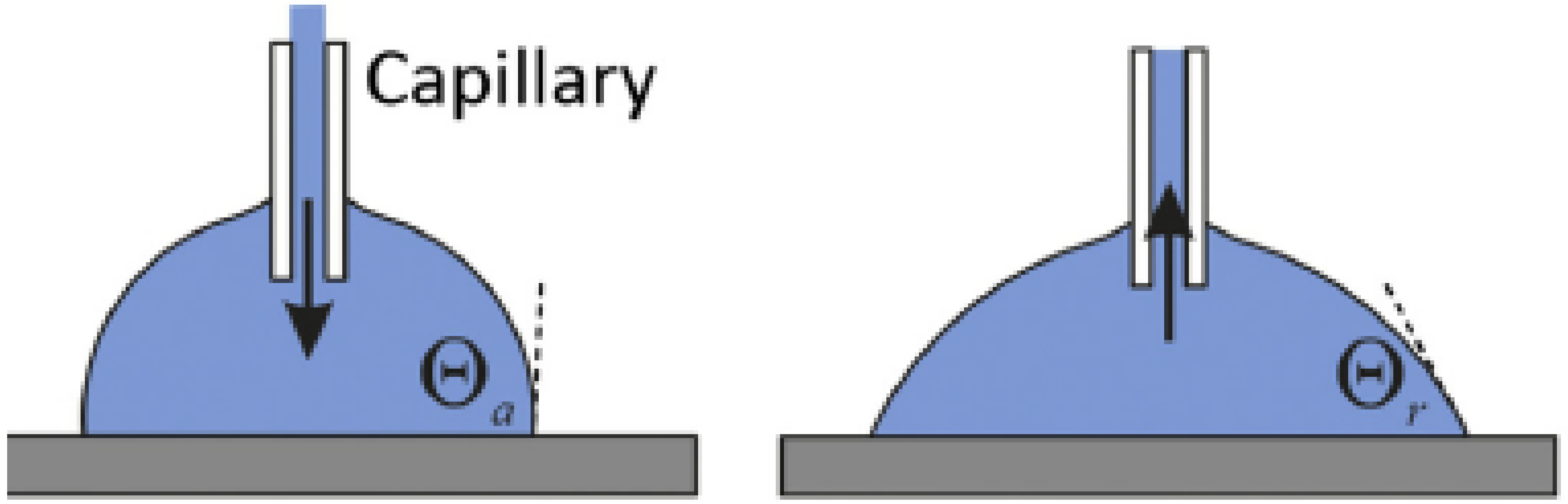
θ_a advancing contact angle

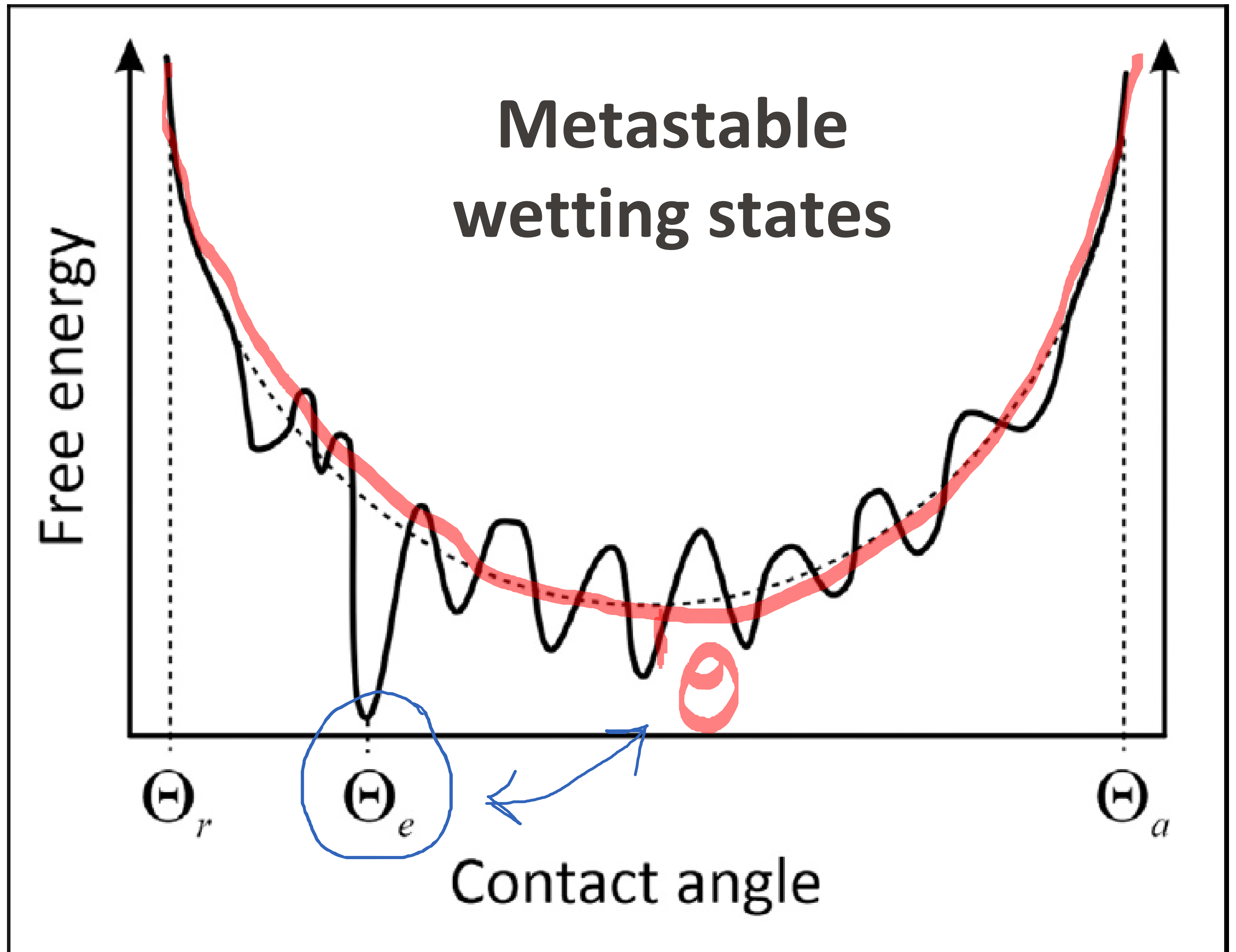
θ_r receding contact angle

$\Delta\theta = \theta_a - \theta_r$ **Contact angle hysteresis**



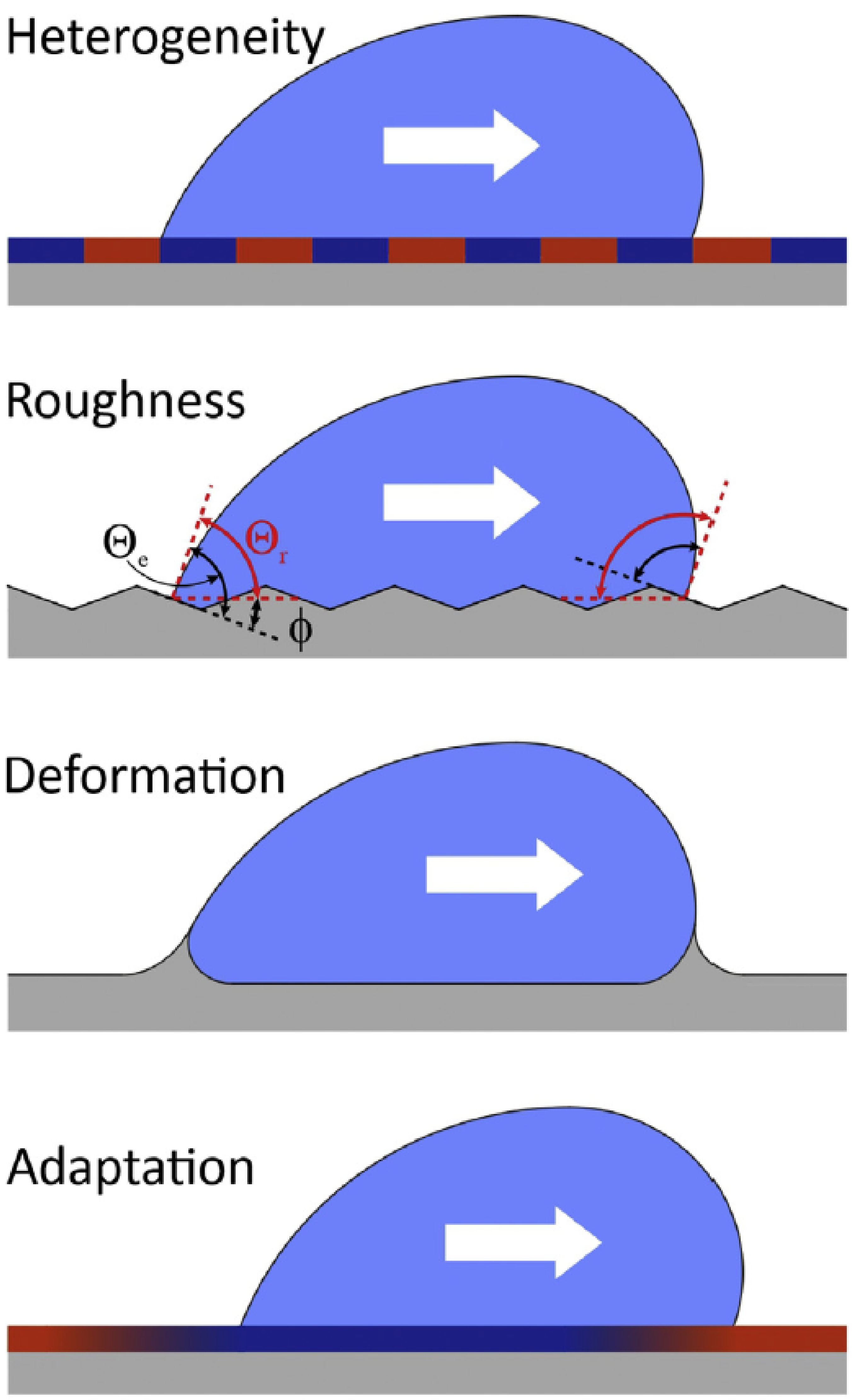
Contact line pinning: droplet edge gets stuck in metastable states leading to hysteresis





Current Opinion in Colloid & Interface Science

Causes of Contact Angle Hysteresis



Current Opinion in Colloid & Interface Science

Chemical heterogeneity ➔ different local regions with different surface energies

Topographical heterogeneity ➔ different local slope

Soft solids ➔ material deformation in response to wetting (compression and tension)

Evolution of surface properties exposed to the liquid ➔ reconfiguration, relaxation, dissolution of impurities

Contact Angles on Rough Surfaces: The Wenzel Model

Roughness enhances wettability

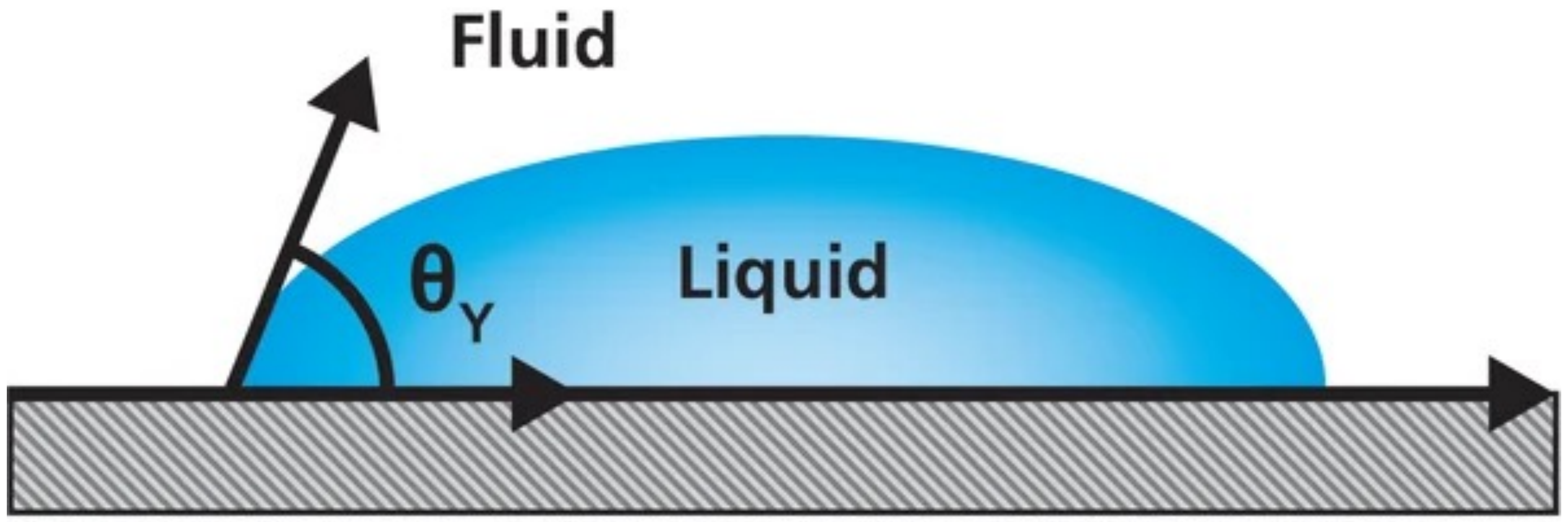
- ➢ Hydrophilic surfaces appear more hydrophilic
- ➢ Hydrophobic surfaces appear more hydrophobic

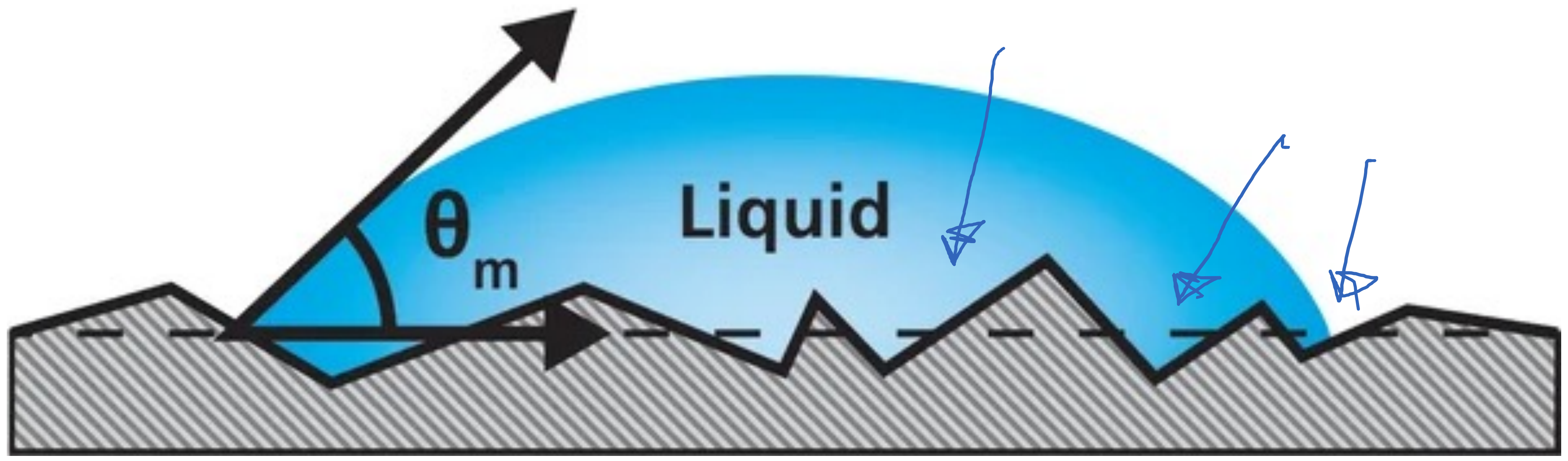
measured contact angle

$$\cos\theta_m = r\cos\theta_\gamma$$

thermodynamic contact angle

Roughness (*r*): geometrical factor representing ratio between the real contact area and the apparent (projected) area





This model is for when the liquid **penetrates** the roughness of the surface

Source: Lucio Isa, ETHZ

Contact Angles on Rough Surfaces: Cassie-Baxter Model

Incomplete coating of surfaces by a liquid – air pockets bounded between the surface and liquid

$$\cos\theta^*_{CB} = \phi_1 \cos\theta_1 + \phi_2 \cos\theta_2$$

Fraction on air vs. solid $\phi_1 + \phi_2 = 1$

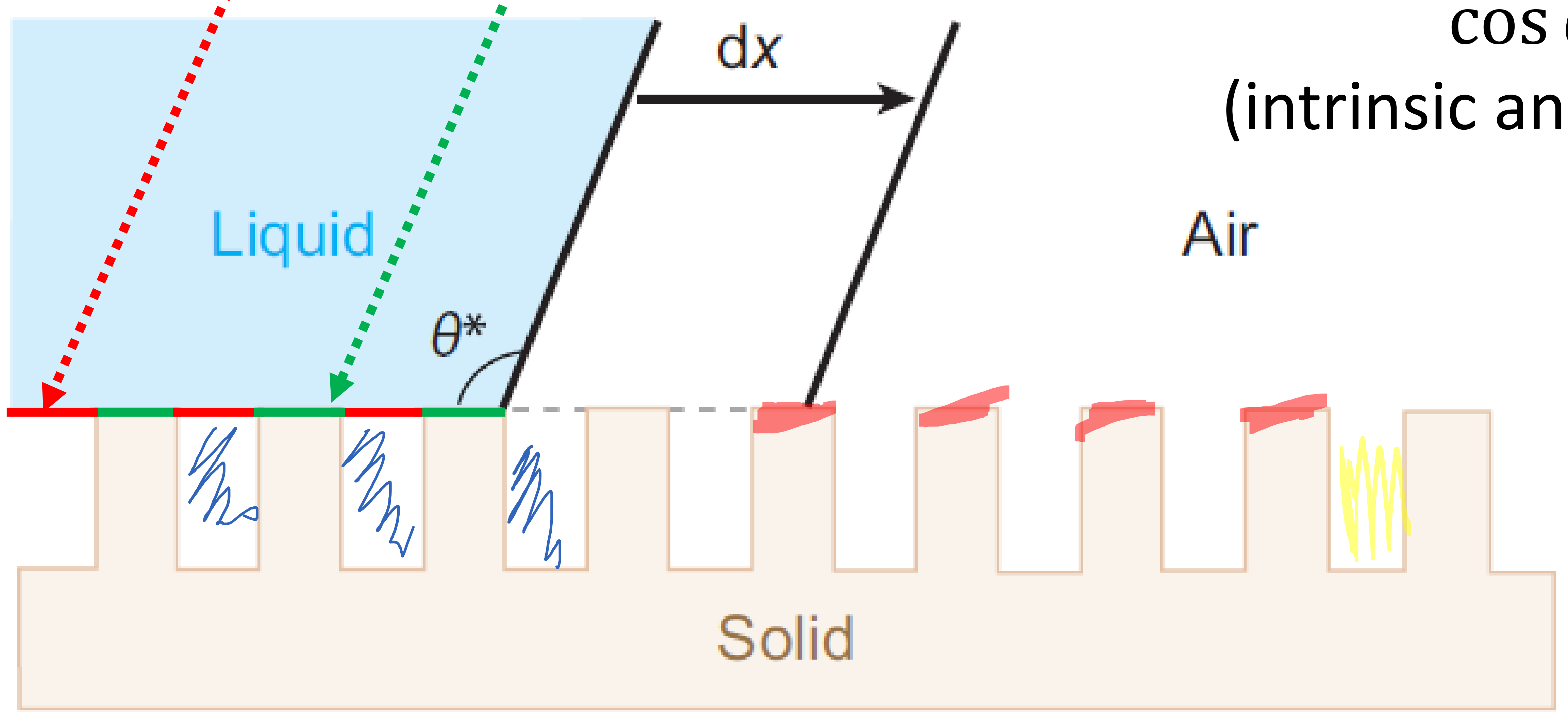
0.5 0.5

$\cos\theta_1 = -1$ for air

$(\theta_1 = 180°)$

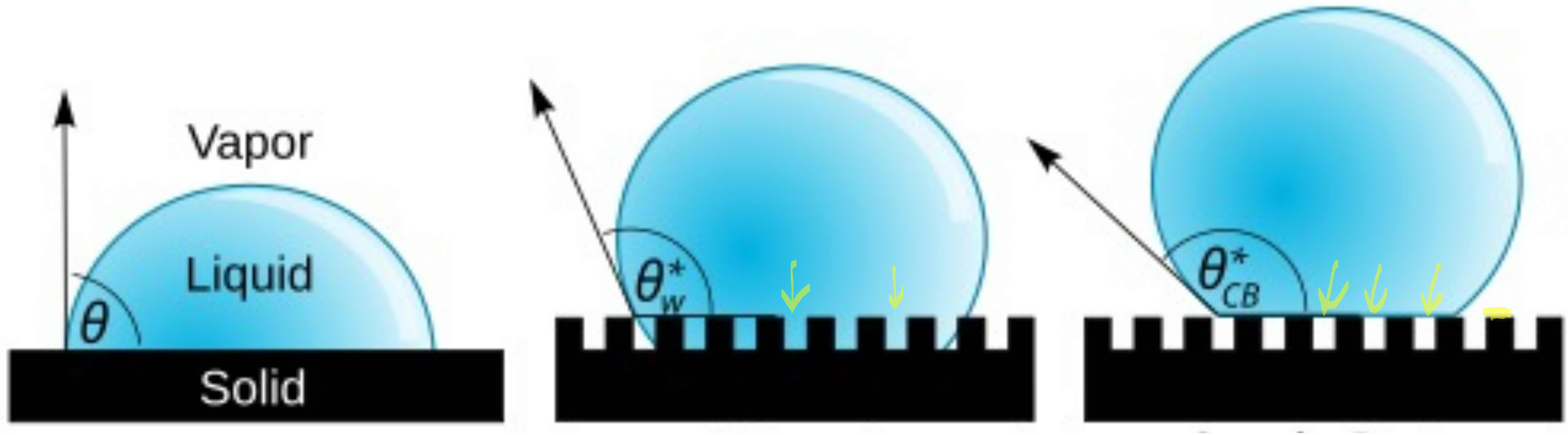
$\cos\theta_2 = \theta$

(intrinsic angle of material)



Less contributions from solid, apparent contact angle more hydrophobic

Various Models to Describe the Behavior of Drop on Surface



Young Model **Wenzel Model** **Cassie-Baxter Model**

Source: Wikipedia

Droplet Pinned at Edges Until Surface Forces Cause Motion

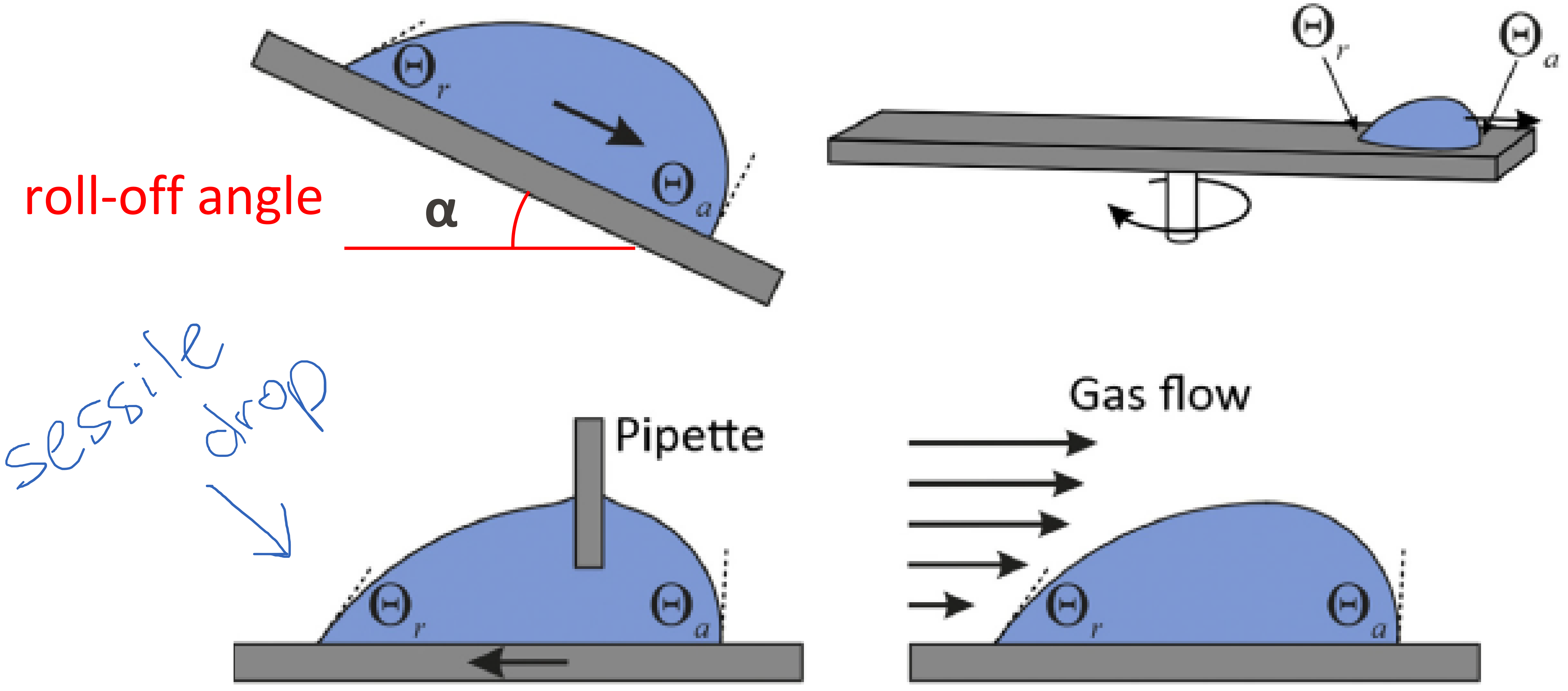
width of the contact area

Lateral force to initiate motion

$$F = kw\gamma_L(\cos\theta_r - \cos\theta_a)$$

geometrical factor ≈ 1

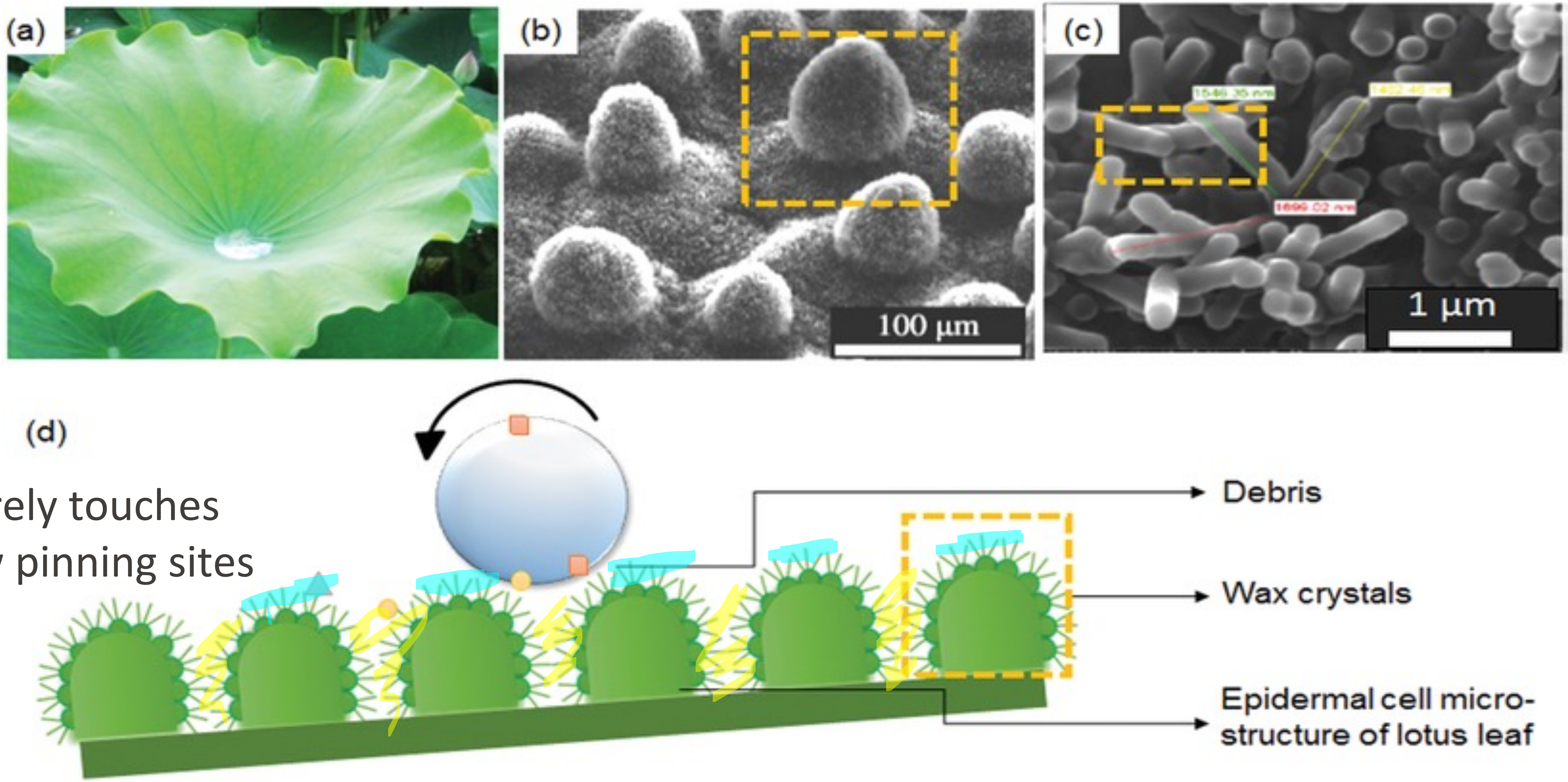
A drop won't move until the force overcomes pinning



Current Opinion in Colloid & Interface Science

How The Lotus Leaf Self-Cleans Its Surface

Rough microstructures amplify hydrophobicity ➔ superhydrophobicity (Cassie-Baxter)

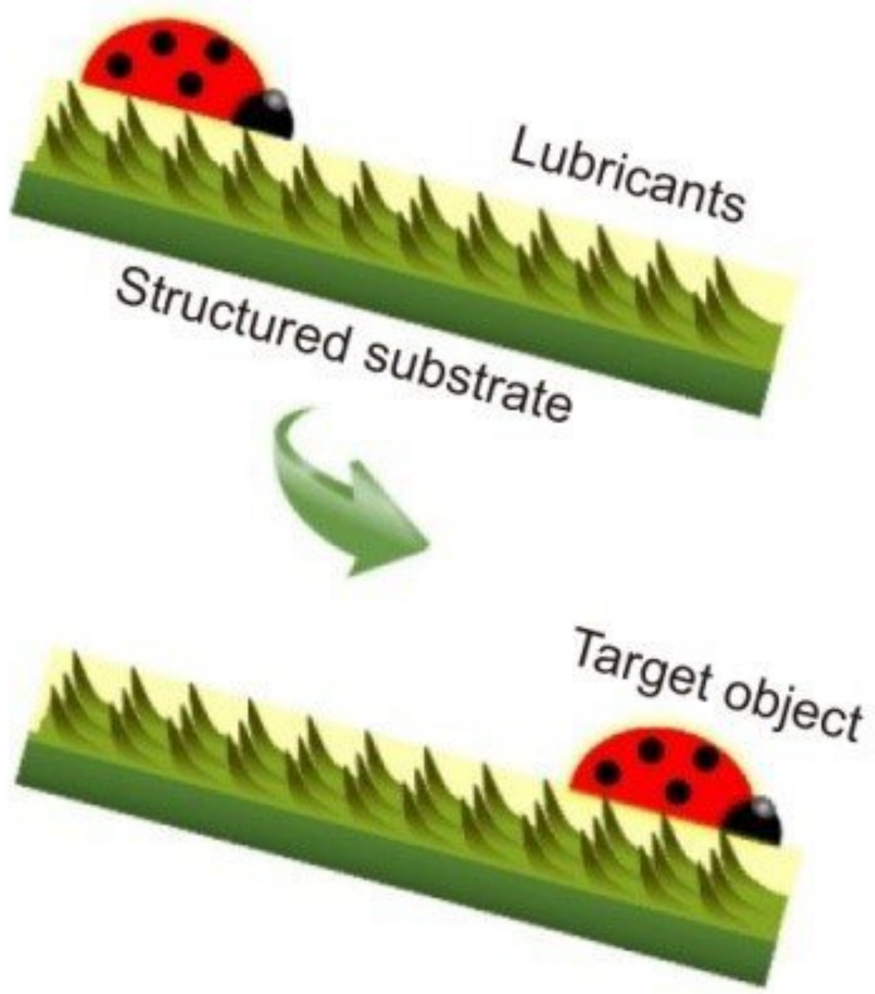


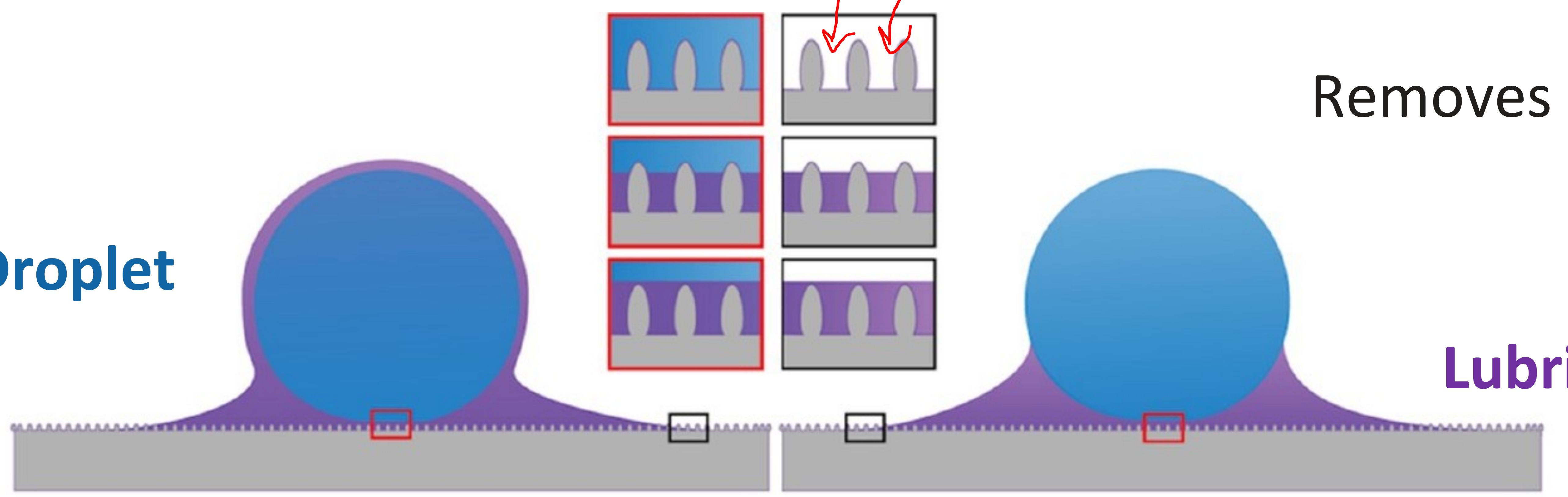
Droplet barely touches surface = few pinning sites

Konar *et al.* | Adv. Mater. Interf. | 2020

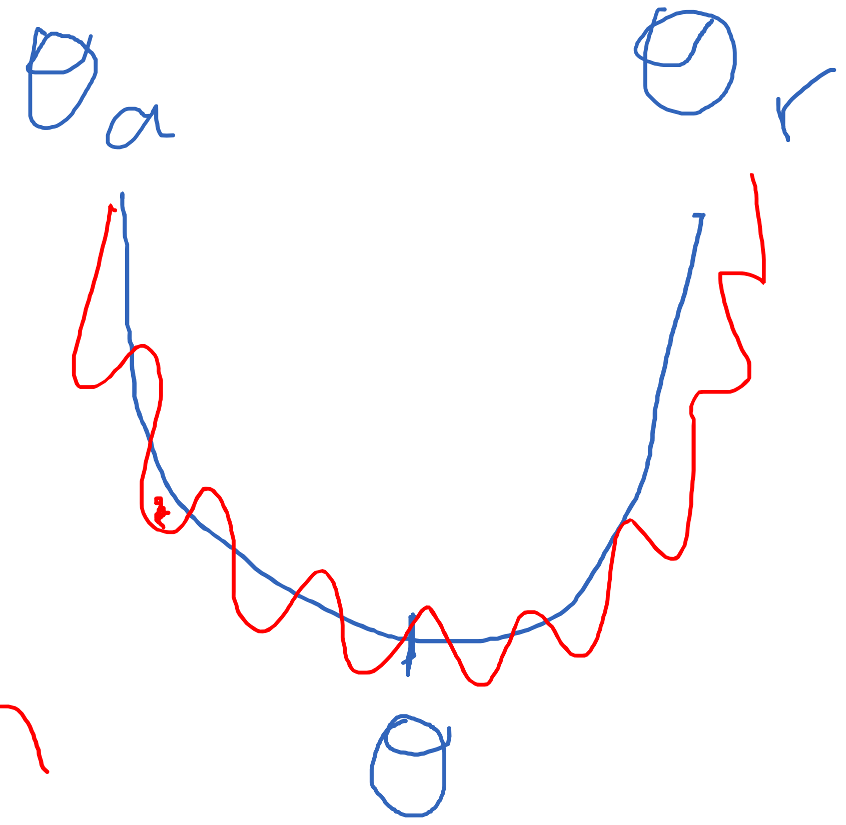
Surfaces with Low Contact-Angle Hysteresis (SLIPS)

Slippery surface model





Pitcher plant



Low friction
Lubrication

Coats surface and lowers surface free energy

Removes contact pinning

Slippery liquid-infused porous surface(s) (SLIPs)

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Gradient of Surface Tension at the Interface

Morgenthaler *et al.* | *Langmuir* | 2003

Imbalance of forces acts as a “force field” to drive droplet motion without tilting the surface

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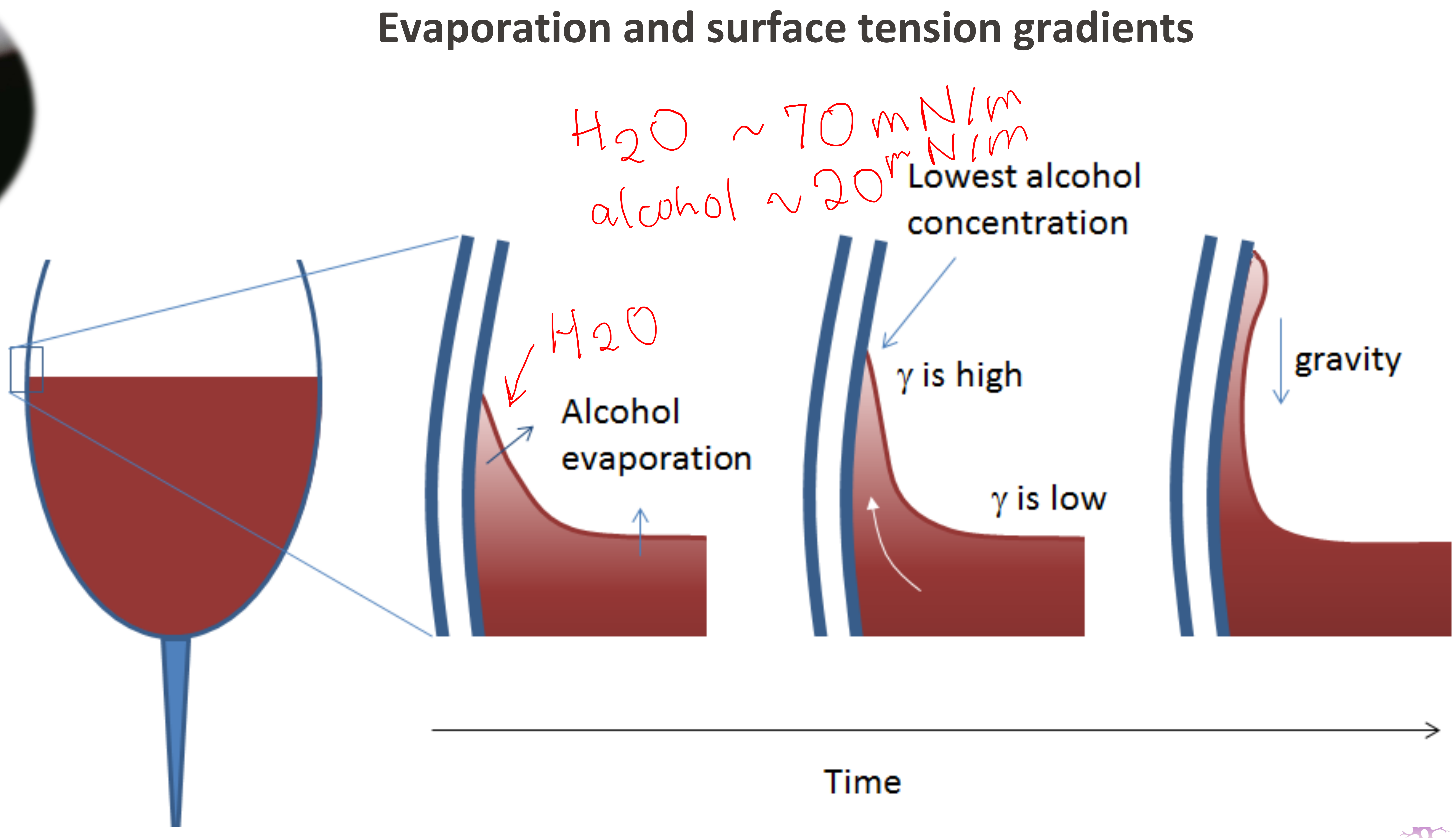
Surface Tension Gradients: Marangoni Flows

"Wine tears"



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Key Takeaways

Real surfaces are never ideal

Dynamic wetting is about pinning and motion – a droplet won’t move until surface forces overcome pinning

Roughness amplifies wetting behavior – modeled by Wenzel and Cassie-Baxter models

Nature provides great examples of these effects (pitcher plant, lotus effect)

Surface tension gradients can move liquid spontaneously

Summary of Today's Class

- Thermodynamic definitions of **surface free energy vs. surface energy**
- Interfacial energy – **wetting**
- **Hydrophobic** *vs.* **hydrophilic** molecules/surfaces
- Measuring these properties using **contact angle**
- Real surfaces cause contact angle **hysteresis**

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