École polytechnique fédérale de Lausanne

Laboratory of Chemical Nanotechnology

Surfaces & Interfaces: From Ideal Planes to Real Materials

Lesson 6

MSE 304

Nako Nakatsuka

Nako.Nakatsuka@epfl.ch

October 17th 2025

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: Solid-Solid Interfaces

6: Surfaces & Interfaces: From Ideal to Real

7: Characterization of Real Surfaces

8: Solid-Liquid Interfaces

9: Surface Chemistry

10: Biological Processes at Surfaces

11: Electronic Properties of Surfaces

12: Thin Film Technologies

13: Biosensor Fundamentals

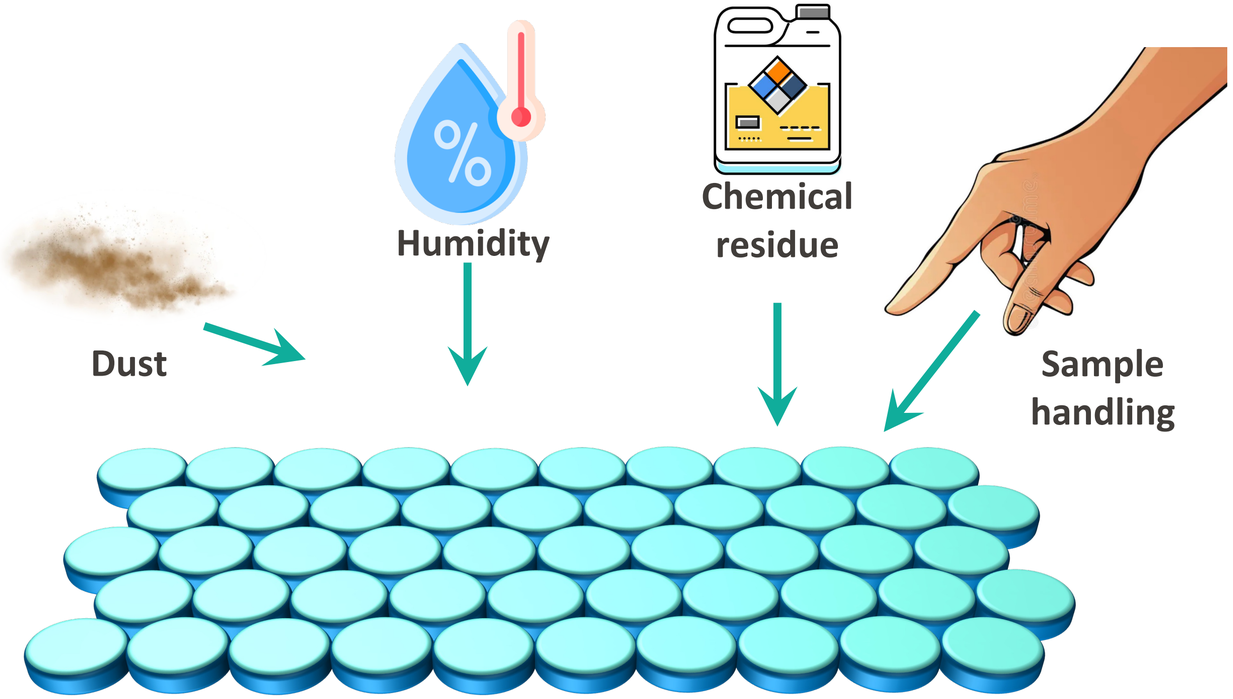
14: Biosensing applications

Central Theme: From Ideal to Real Systems

Perfect crystal

Broken symmetry
Impurities/defects
Reconstructions
Grain boundaries

Perfectly clean surface



Adsorption, contamination
Impurities/defects
Coatings at interfaces

CHEMINA

Fundamental Concepts You Should Recall

- Intermolecular interactions/forces
- Polarity of molecules – polar *vs.* nonpolar
- Hydrophilicity *vs.* hydrophobicity – wetting
- Crystal lattice structures – Miller indices, unit cell
- Basic thermodynamics – energy minimization and equilibrium

CHEMINA

Thermodynamics 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

Energy Landscape of Surfaces & Interfaces

Surfaces & Interfaces

Interfacial Energy (γ)
Source of surface-driven phenomena

Adsorption

Surface wants to lower energy by binding molecules
Physisorption *vs.* Chemisorption

Lectures 1-2

Surface Tension & Wetting

Balance between interfacial energies defines droplet behavior
Young's, Wenzel, Cassie-Baxter

Lecture 3

Surface Morphology

Different crystallographic planes have different surface energies
Wulff construction, crystal planes

Lecture 4

Interfaces

Polycrystalline materials form grain boundaries
Interfaces are structured defects minimizing global energy

Lecture 5

Defects

Perfect crystals are impossible – entropy favors defects
0-D to –D defects

Lectures 4-5

CHEMINA

Energy Minimization as the Unifying Principle

Adsorption

Surface wants to lower energy by binding molecules
Physisorption *vs.* Chemisorption

Lectures 1-2

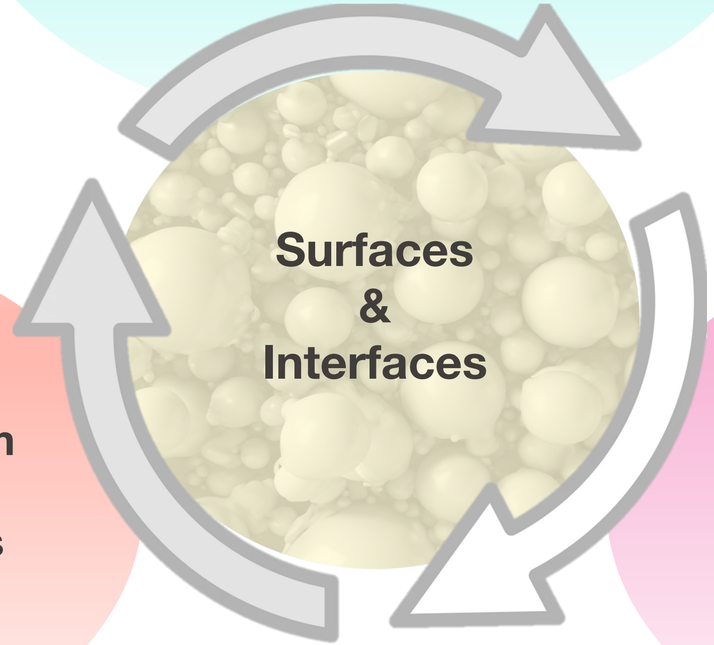
Surface Tension & Wetting

Balance between interfacial energies defines droplet behavior
Young's, Wenzel, Cassie-Baxter

Surface Morphology

Different crystallographic planes have different surface energies
Wulff construction, crystal planes

Lecture 4



Interfaces

Polycrystalline materials form grain boundaries
Interfaces are structured defects minimizing global energy

Lecture 5

Defects

Perfect crystals are impossible – entropy favors defects
0-D to –D defects

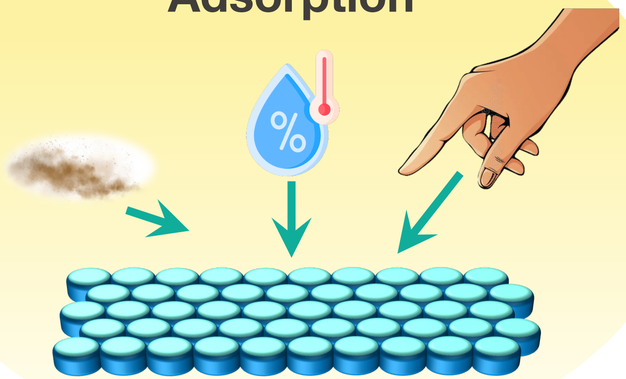
Lectures 4-5

CHEMINA

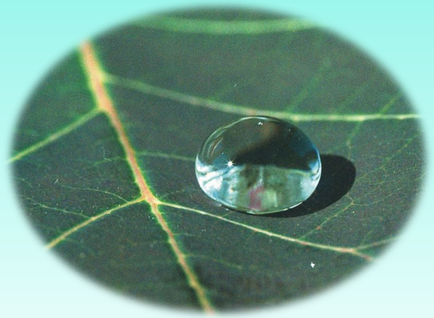
Why Surfaces Matter

Surfaces & Interfaces

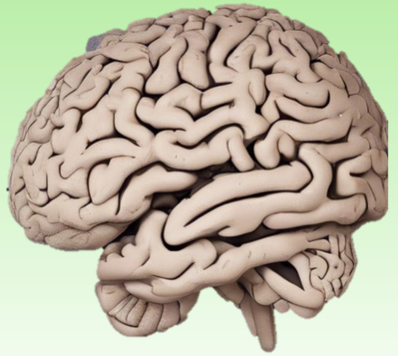
Adsorption



Surface Tension & Wetting

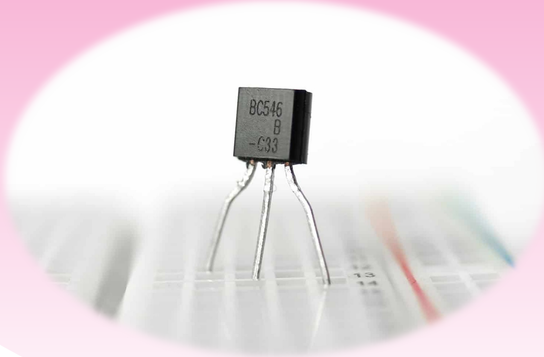


Surface Morphology



Interfaces

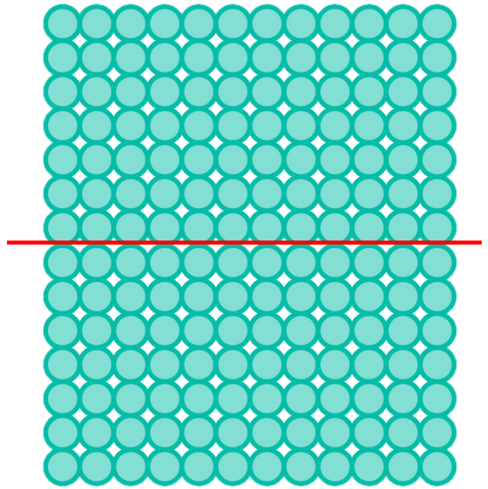
Defects



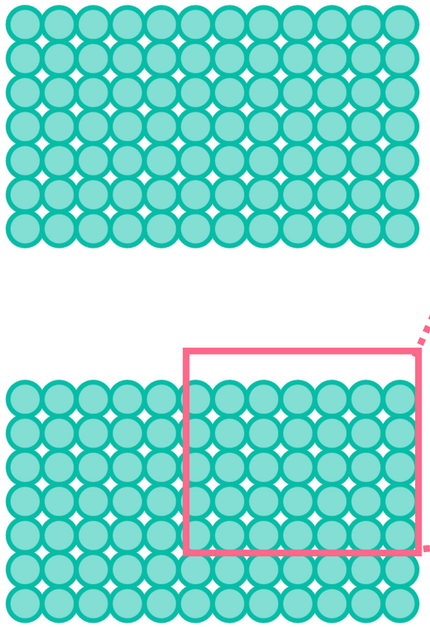
CHEMINA

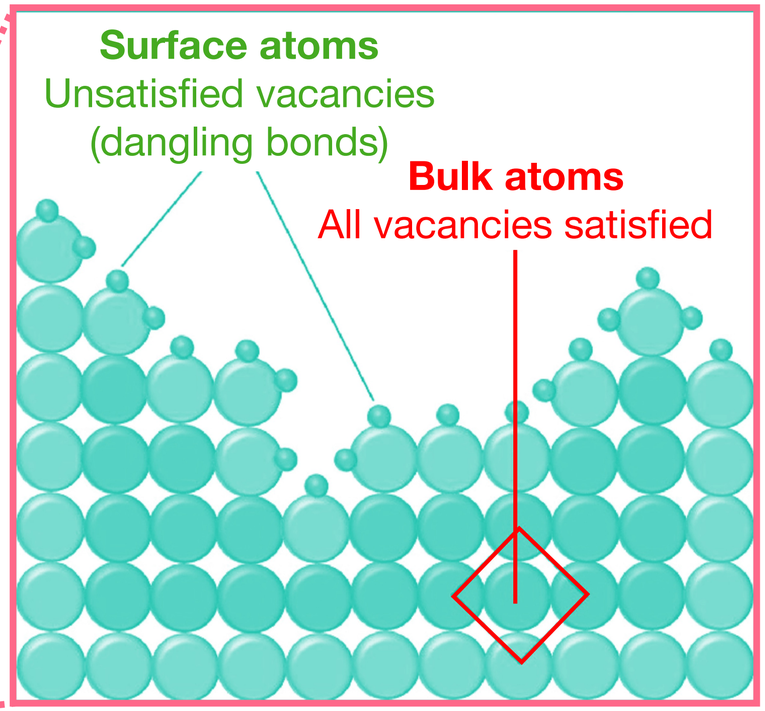
From Broken Bonds to Function

In a solid material, each atom is surrounded by neighbors ☺



Broken bonds ☹





Atoms at surface have fewer neighbors = higher in energy

Adsorption **Wetting** **Morphology** **Defects** **Interfaces**

CHEMINA

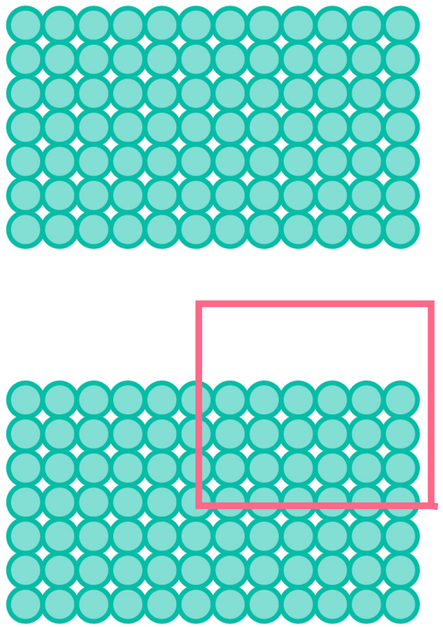
Different Forms of Intermolecular Interactions/Forces

Interaction Type	Strength (kJ/mol)	Mechanism	Examples in Surfaces
Covalent	100–1000	Shared electron pairs	Chemisorption, Si–O bonds on oxides
Ionic	400–800	Electrostatic between full charges	Adsorption of ions on mineral surfaces
Metallic	100–400	Electron delocalization	Grain boundaries (Au)
Hydrogen bonding	10–40	Polar–polar interaction via H	Water adsorption on glass, protein binding
Dipole–Dipole / Debye	1–20	Permanent ⇔ induced dipoles	Adsorption of polar molecules
Van der Waals (London dispersion)	0.1–10	Induced dipole–induced dipole	Physisorption of gases, surface contamination

CHEMENA

From Molecular Interactions to Surface Energy

Atomic scale – individual interactions

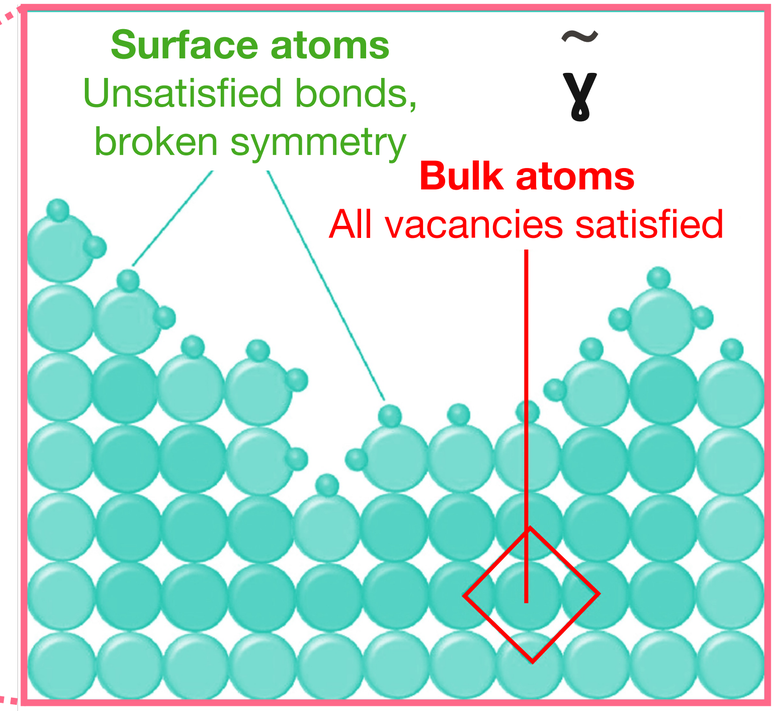


Forces acting between atoms

Local attractive and repulsive interactions between atoms determines how strongly matter adheres (bond formation vs. bond breaking)

Sum of all microscopic forces = surface free energy

Macroscopic scale – collective effect

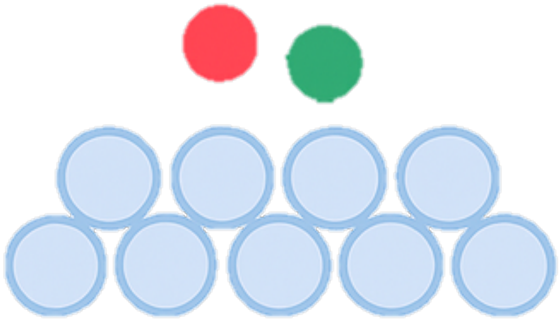


Surface free energy: excess free energy per unit area caused by unsatisfied atomic interactions at surface

CHEMENA

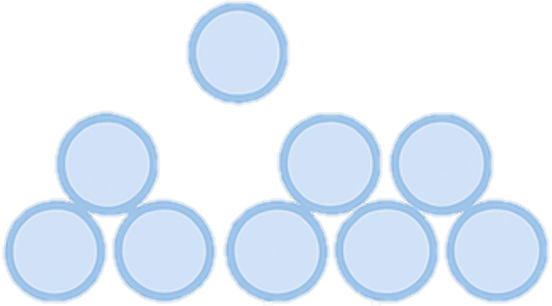
How Surfaces Lower Their Energy

Adsorption of molecules



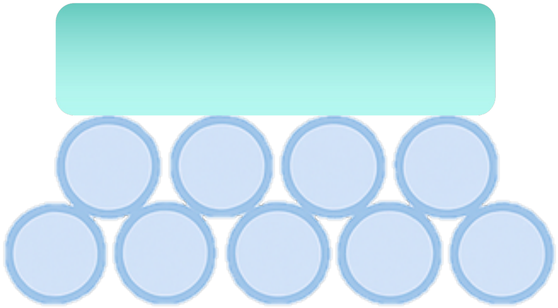
Physisorption/chemisorption to satisfy dangling bonds

Surface reconstruction



Atoms rearrange or shift position

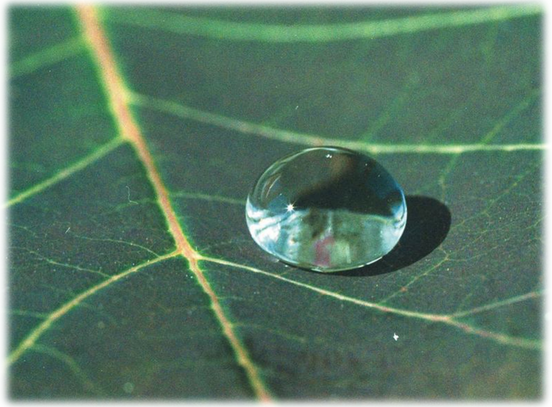
Interface formation



New interfaces form and energy redistributed between phases

CHEMINA

Careful: Adsorption *vs.* Absorption



Adsorption

Sticking to the surface of the other phase

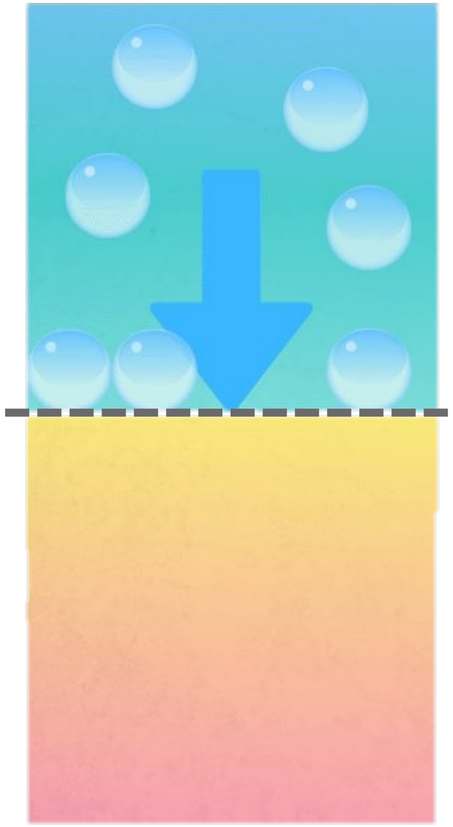
Absorption

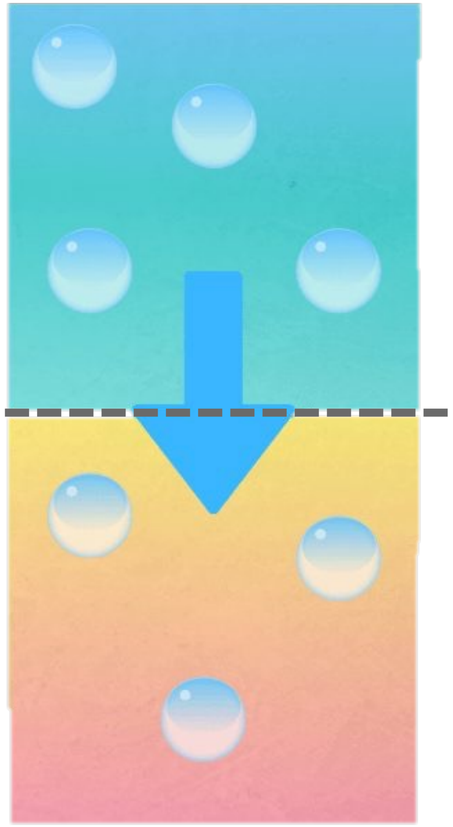
Soaking into the bulk of the other phase

Mass transfer **into** another matrial

Surface

Interface

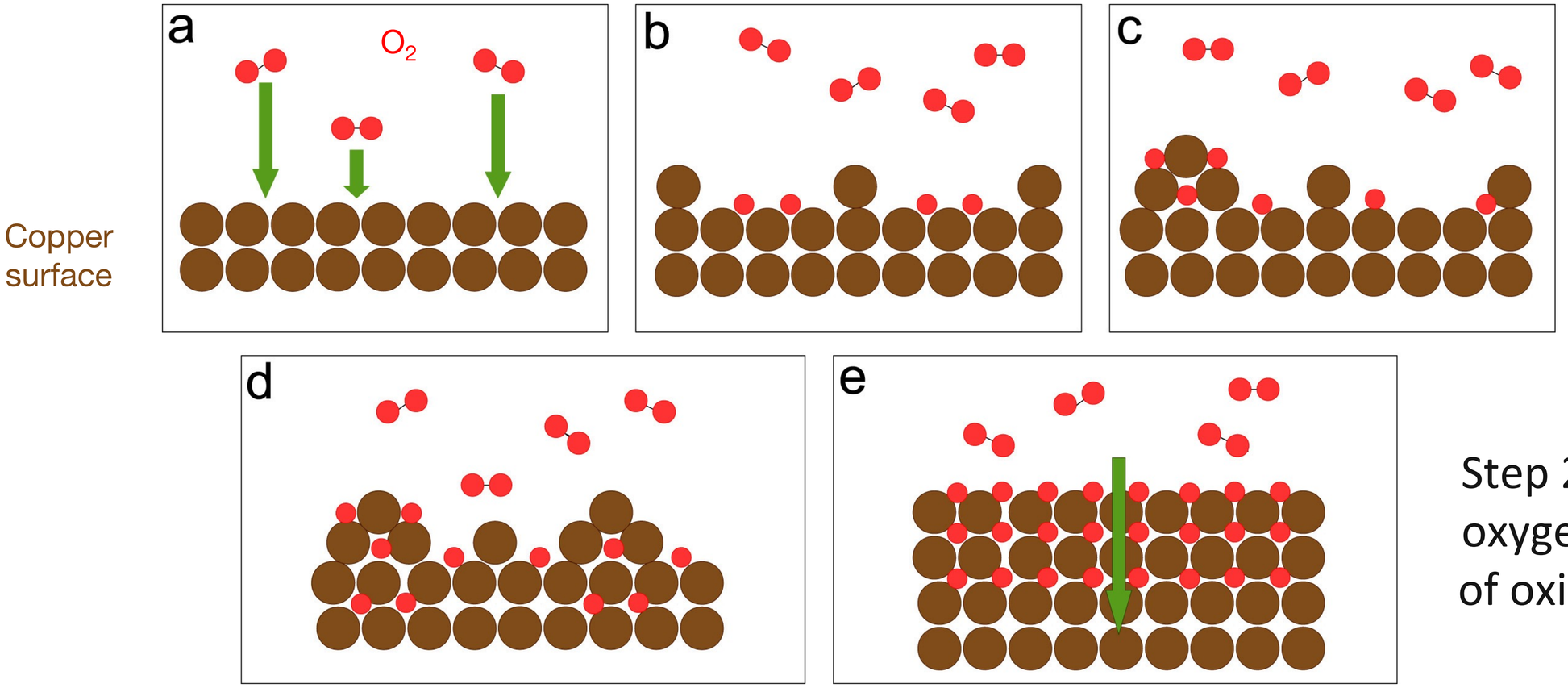




SCIENCE NOTES

CHEMINA

Metal Oxidation – Adsorption + Absorption



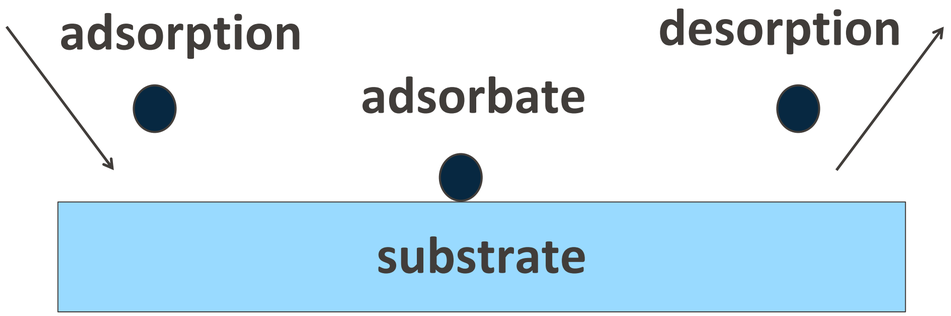
Step 1: **Adsorption** of O_2 onto copper surface

Step 2: **Absorption** of oxygen drives growth of oxide film into bulk

Gattinoni & Michaelides | *Surf. Sci. Rep.* | 2015

CHEMINA

The Different Forms of Adsorption on Surfaces



$$\theta = \frac{\text{Number of occupied adsorption sites}}{\text{Number of adsorption sites present}}$$

θ = 0 clean surface

θ = 1 monolayer

Physisorption

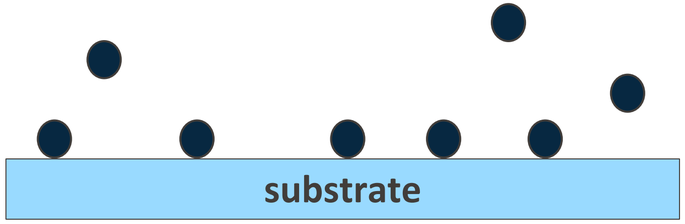
Van der Waals interactions between adsorbate and substrate

non-specific and weak

$\Delta H_{des} \approx 20$ kJ/mol

multilayer growth possible

observed mostly at low temperatures



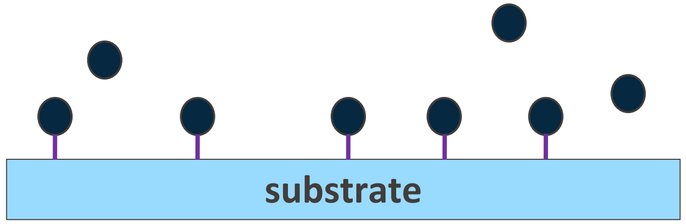
Chemisorption

Chemical bond between adsorbate and substrate

Generally kinetically stable at RT

$\Delta H_{des} \approx 200$ kJ/mol

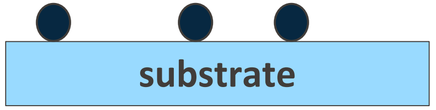
maximum coverage is 1 monolayer (θ = 1)



CHEMINA

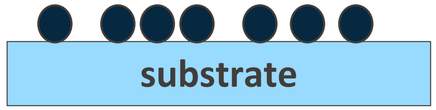
Ordered Adsorbate Layers

Small 2-D islands possibly ordered or completely disordered layers



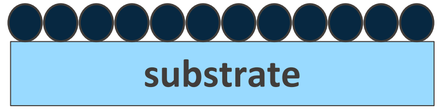
Low surface coverage

Crowding and interactions

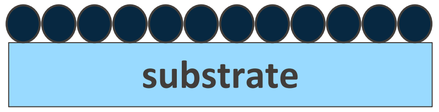


Medium surface coverage
(5-10 Å between atoms)

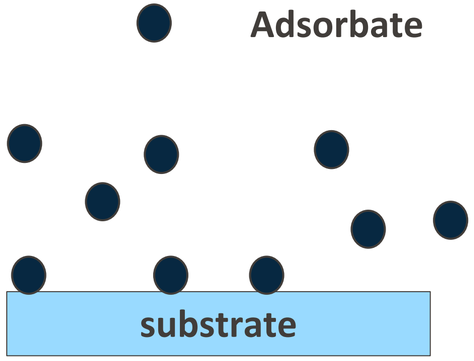
Adsorbate-substrate
Adsorbate-adsorbate



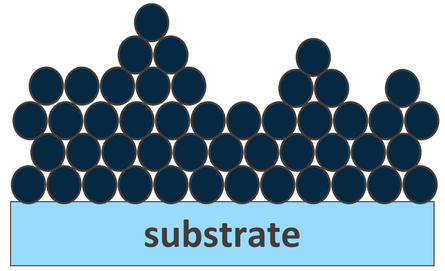
High surface coverage
Arranged to minimize energy



Monolayer adsorption



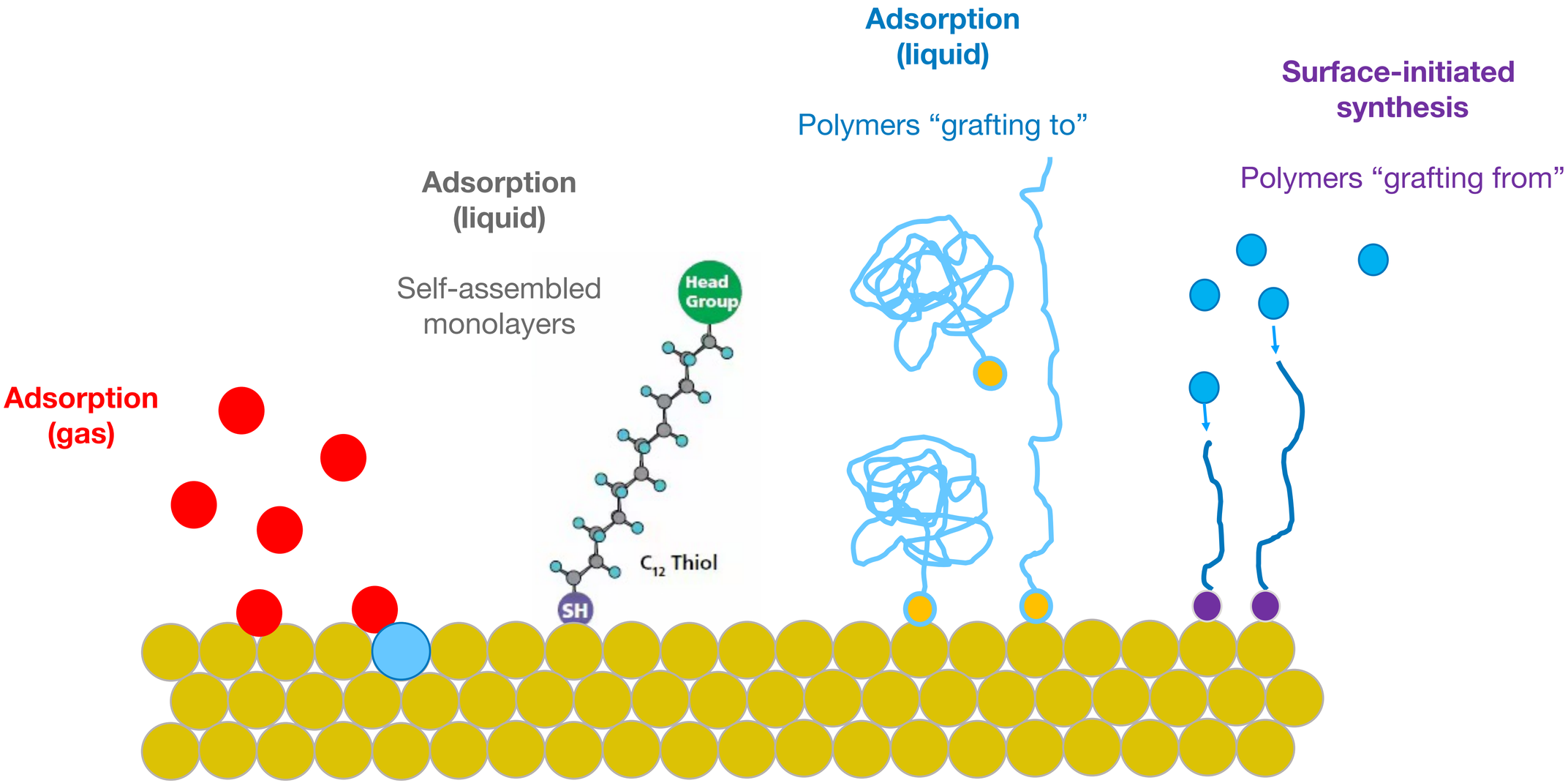
Multilayer adsorption



Crystal structure of the surface dictates where molecules adsorb

CHEMINA

Chemisorption (Surface Chemistry) In Future Lessons



CHEMINA

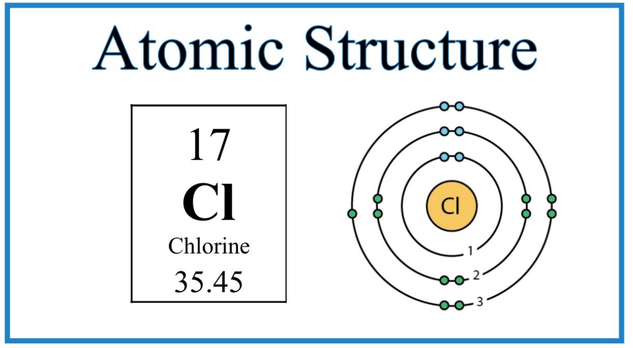
Surface Chemisorption Often Occurs Post Physisorption

Spontaneous process: ΔG<0

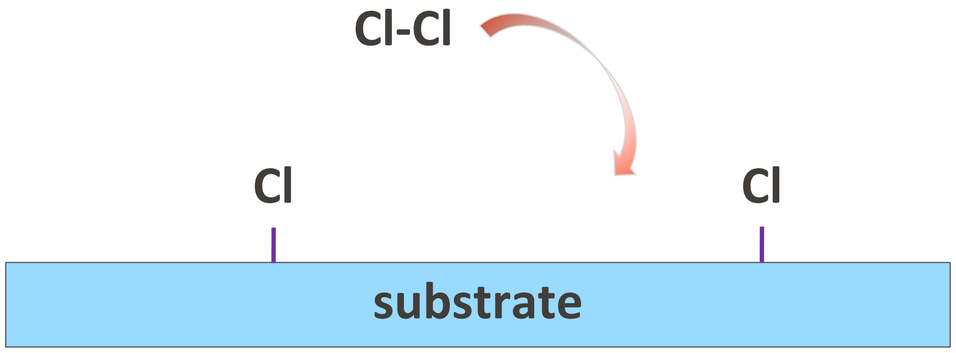
Adsorbate loses degrees of freedom upon adsorption: ΔS<0

$\Delta G = \Delta H - T\Delta S$ → **+**

Almost always exothermic: ΔH<0



Dissociation energy (strength of chemical bond) high in gas phase

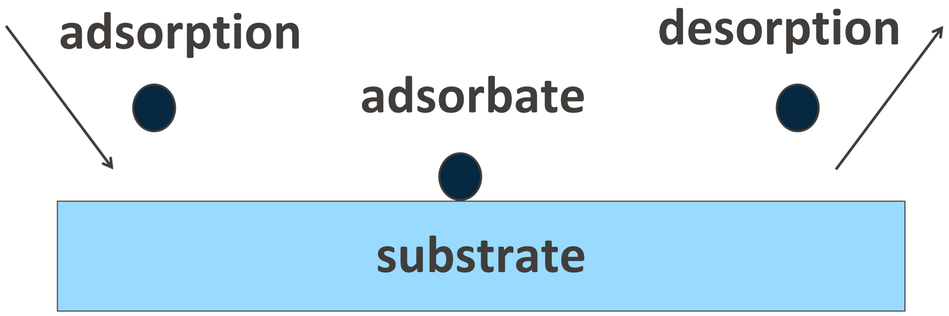


Surface interactions reduce energy required to break Cl-Cl bond

Catalytic surfaces inherently promote bond breaking!

CHEMINA

Desorption from the Surface



Breaking of chemical bonds and removal of adsorbed species from the surface

Molecule requires sufficient energy to activate the desorption (E_d)

Desorption is temperature dependent and is described by:

$$-\frac{dN_i}{dt} = \nu_i N_i^m \cdot \exp\left(\frac{-E_{d,i}}{RT}\right)$$

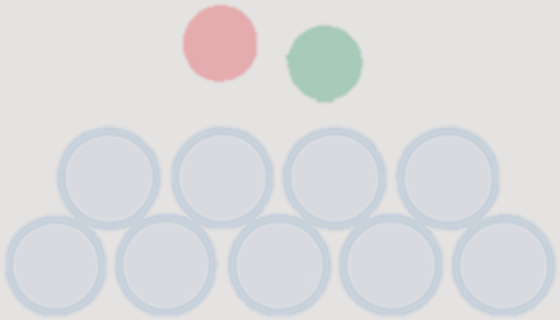
Polanyi-Wigner equation

***N_i*: surface concentration of the adsorbate**
***ν_i*: frequency factor – how often molecules try to escape**
***E_{di}*: desorption activation energy**
***m*: order of the desorption reaction**

CHEMINA

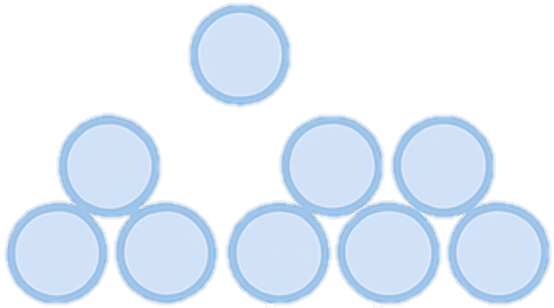
How Surfaces Lower Their Energy

Adsorption of molecules



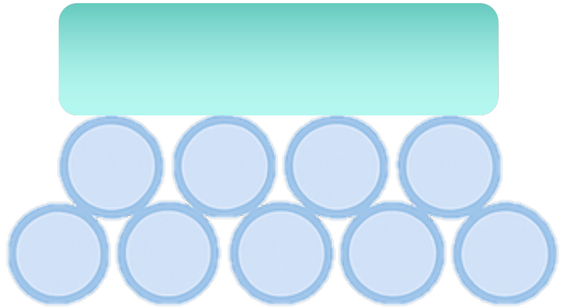
Physisorption/chemisorption to satisfy dangling bonds

Surface defects/ reconstruction



Atoms rearrange or shift position

Interface formation



New interfaces form and energy redistributed between phases

CHEMINA

Surface *vs.* Bulk Defects

	Surface Defects	Bulk Defects
Location	At or near top few atomic layers	Inside the crystal lattice
Type	Local atomic rearrangement (2D)	Bulk imperfection (0D–2D)
Goal	Minimize surface free energy (γ)	Minimize total free energy (G = H – TS) Accommodates stress, impurities, entropy
Examples	Adatoms, surface vacancies, TLK, reconstructions	Point defects (vacancies, interstitials), line defects (dislocations), grain boundaries, volume defects

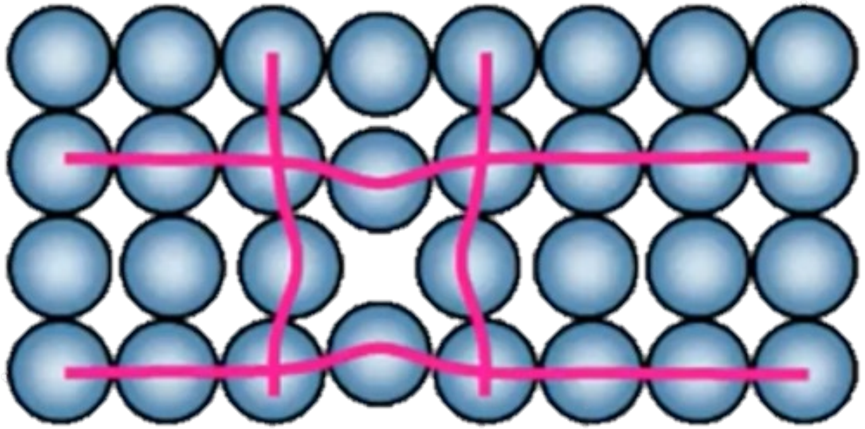
CHEMINA

Defects at Different Dimensions

- **Point Defects** - vacancies, interstitials, adatoms
- **Line Defects** – dislocations leading to terrace, ledges, kinks (TLK)
- **Surface reconstructions**
- **Bulk (volume) Defects** – voids, inclusions, pores

Basic Point Defects 1: Intrinsic Defects

Vacancies



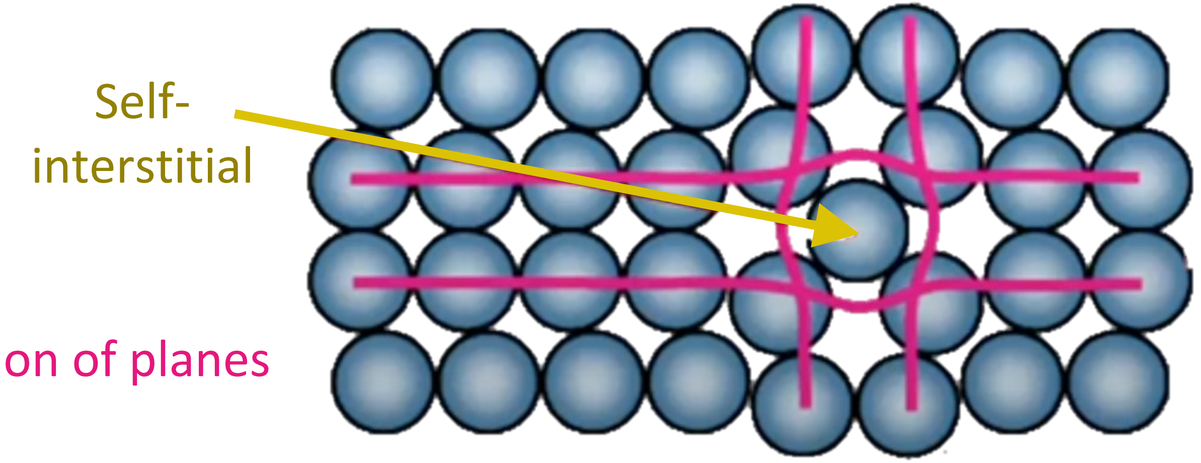
Missing atom on lattice

Surrounding vacancy, lattice is in:

- Tension (bond stretching)
- Compression

Distortion of planes

Interstitials



Additional atom in lattice

Surrounding interstitials, lattice is in:

- Compression

Where Do Intrinsic Defects Come From?

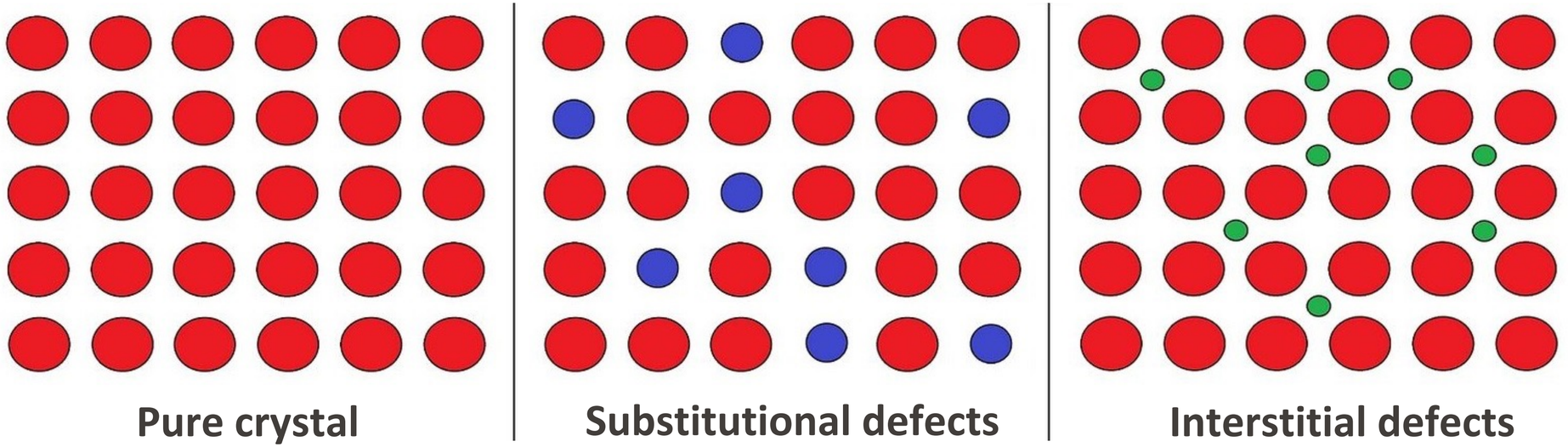
1. Thermal vibrations: at high temperatures, atoms vibrate with significant energy leading to creation of vacancies or shifting into interstitial positions

2. Crystal growth conditions: atoms can shift or move from ideal lattice positions during crystal building process leading to structural imperfections preserved as crystal cools

3. Ionizing radiation: High energy particles can knock atoms out of their positions

4. Mechanical stress and impact: physical forces can displace atoms from ideal lattice positions

Basic Point Defects 2: Extrinsic Defects



Extrinsic atoms sitting on the lattice site, lattice conserved

Small atoms can occupy interstitial sites

CHEMINA

Where Do Extrinsic Point Defects Come From?

Foreign atoms within a material's crystal structure – can be intentional or unintentional

Intentional: Doping

Deliberate introduction of impurity atoms into a crystal lattice to modify properties. Small amounts of dopants in semiconductors can significantly change their electrical behavior

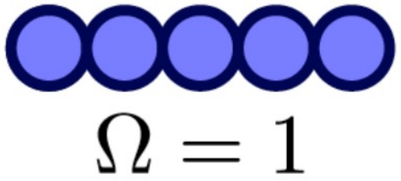
Unintentional: Impurities

Unwanted foreign atoms incorporated into the material during its formation or processing

- Impurities can be present in the original raw materials or introduced during extraction
- Manufacturing steps like welding can also introduce defects and impurities

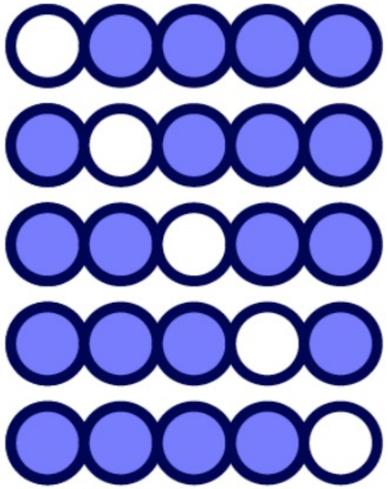
Point Defects Always Exist in Real Crystals

Point defects are unique – they are "**thermodynamic defects**", even in a perfect crystal grown under equilibrium conditions, they will exist

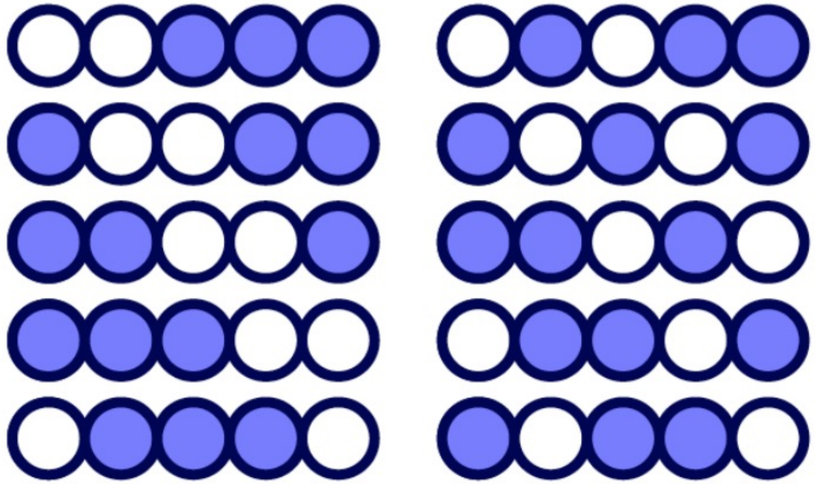


$\Omega = 1$

microstate



$\Omega = 5$



$\Omega = 5 \cdot 4/2 = 10$

Boltzmann entropy equation

$$S = k\, ln(\Omega)$$

CHEMINA

Energy-Entropy Balance for Vacancy Formation

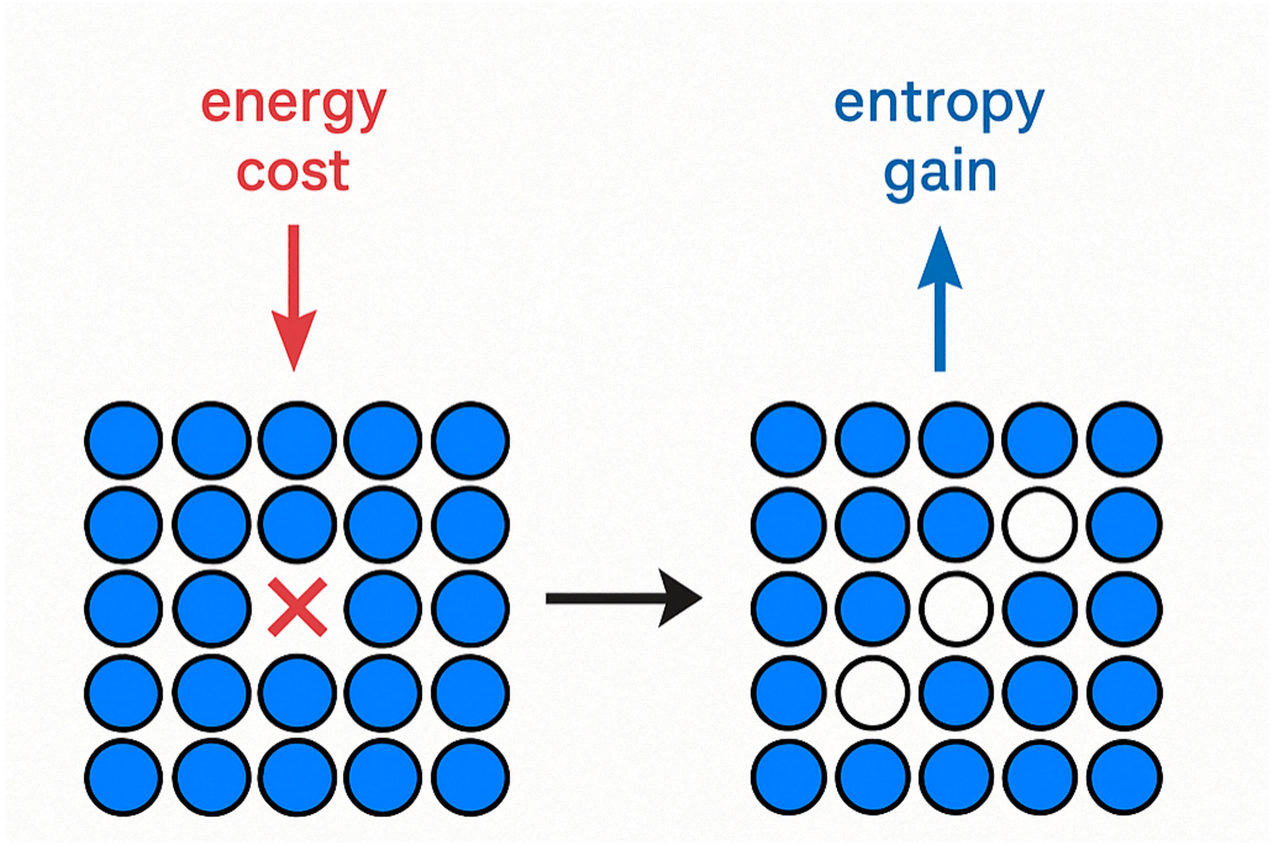
Creating a vacancy costs energy (breaking bonds) but system also gains entropy.

At equilibrium, the crystal balances these two effects.

Vacancy formation

Bonds broken

Energy penalty



More possible microstates (Ω)

Entropy gain

CHEMINA

Surface Defects by Dimensionality (0-D to 3-D)

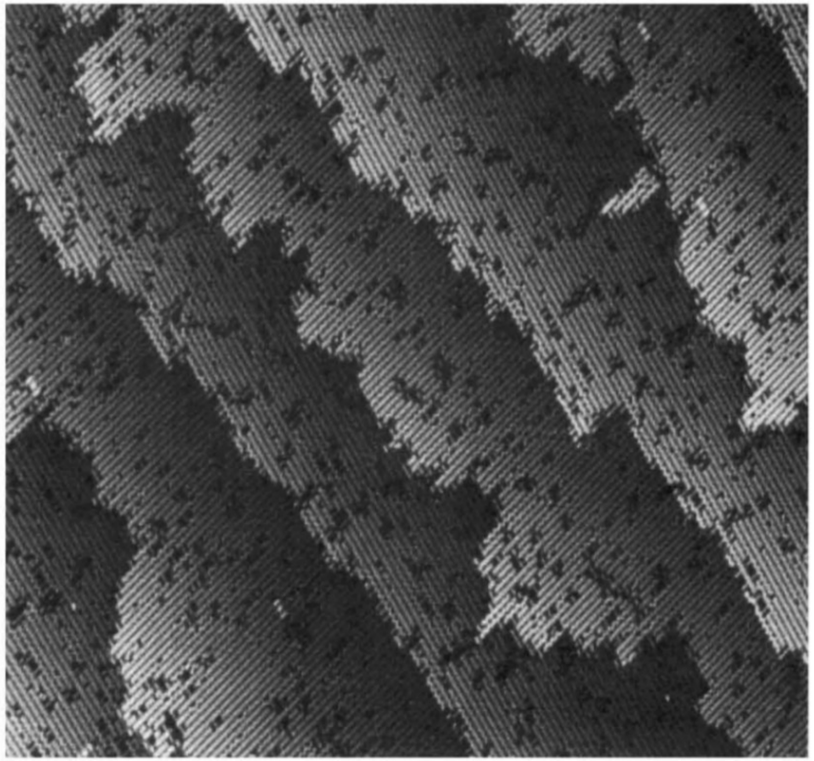
- **Point Defects** - vacancies, interstitials, adatoms
- **Line Defects** – dislocations leading to terrace, ledges, kinks
- **Surface reconstructions**
- **Bulk (volume) Defects** – voids, inclusions, pores

Line Defects (Dislocations) Arise in High Energy Planes

Not all surfaces of a crystal are perfectly flat

Singular surfaces ➔ atomically flat, very stable (lowest-energy crystal face)

Vicinal surfaces ➔ slightly tilted surfaces exhibit faceting: flat, terraces separated by ledges



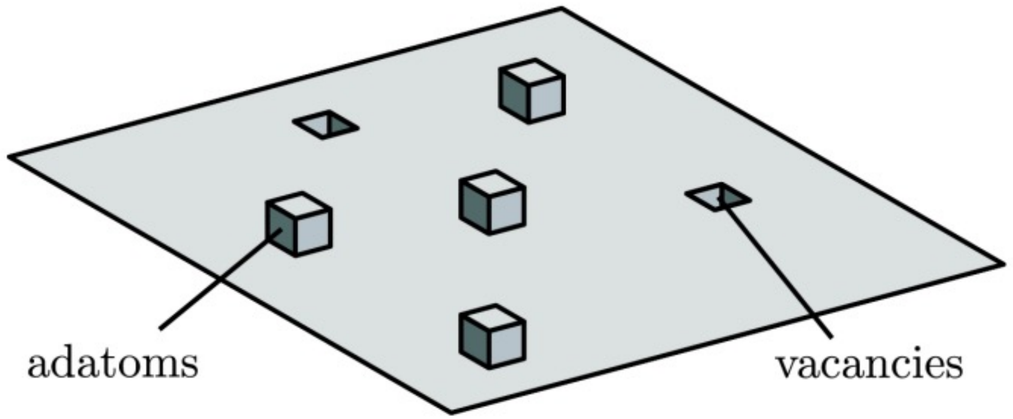
10nm

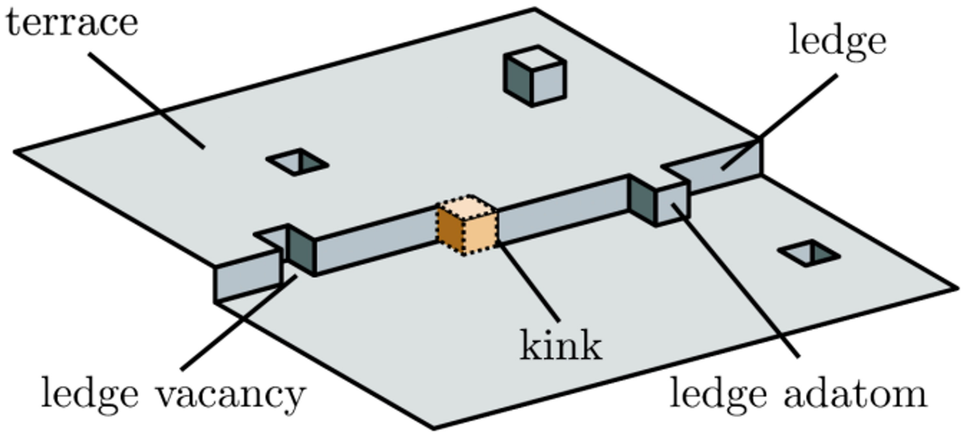
10 m

CHEMINA

Complexity of Line Defects in Real Surfaces (TLK Model)

In a real surfaces with ledges and kinks in addition to vacancies and adatoms…the story is complex





Terraces ➔ atoms fully coordinated ➔ low reactivity

Ledges ➔ atoms at a step edge have fewer neighbors than terraces ➔ moderate reactivity

Kinks ➔ atoms at a kink are the least coordinated ➔ highest reactivity

CHEMINA

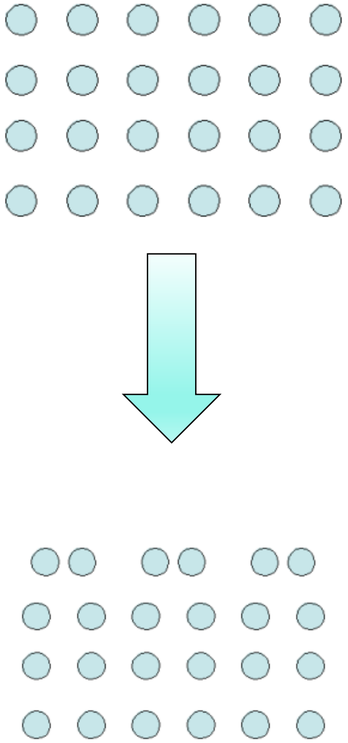
Surface Defects by Dimensionality (0-D to 3-D)

- **Point Defects** - vacancies, interstitials, adatoms
- **Line Defects** – dislocations leading to terrace, ledges, kinks
- **Surface reconstructions**
- **Bulk (volume) Defects** – voids, inclusions, pores

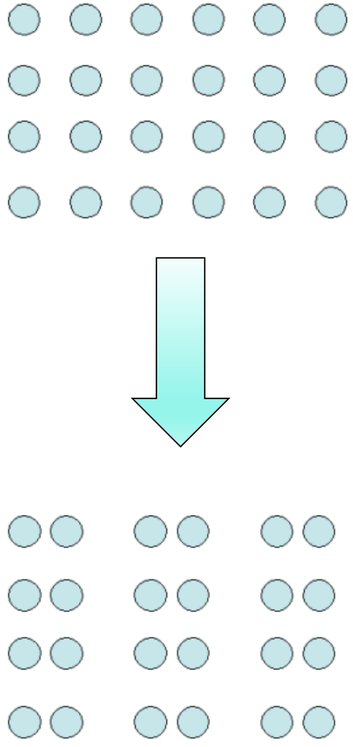
CHEMINA

Reconstructions in Real Surfaces – Dangling Bonds

Side view



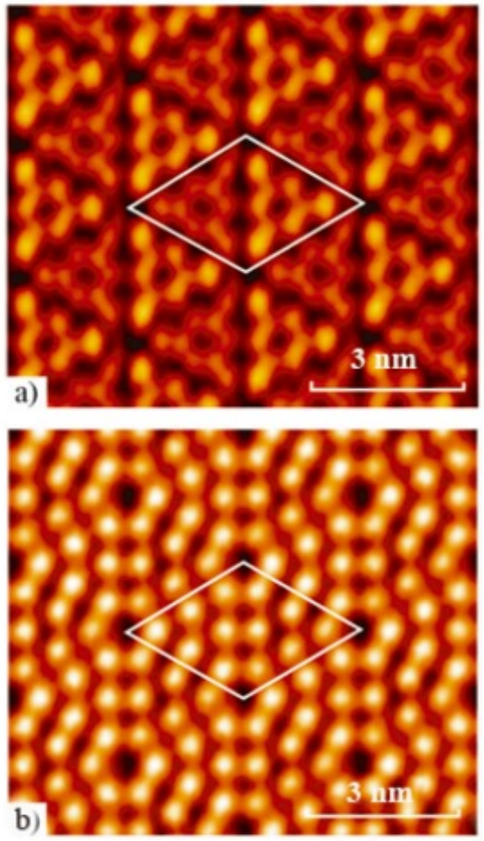
Top view



Problem: Now we broke symmetry at the surface

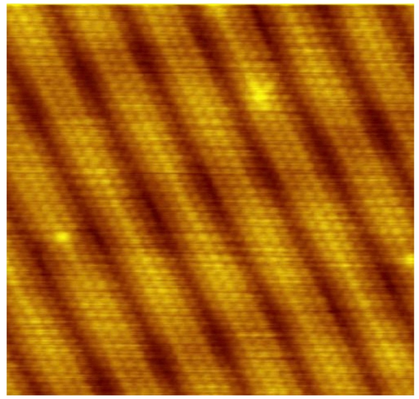
Surface Reconstruction: Energy penalty from unsymmetric pulling of surface bonds compensated by gain of forming bonds with two dangling orbitals

Reconstructions in Real Surfaces – Why They Matter



Si (111) – surface reconstructions determines electrical properties of semiconductors

Silicon	Gold
Covalent bonds	Metallic bonds
Dangling bonds at the surface high in energy	Delocalized electrons screen dangling bonds
Complex reconstruction to minimize surface energy	Small relatively uniform rearrangement



Au (100) – simpler reconstructions
Flat, stable surfaces for experiments

CHEMINA

Surface Defects by Dimensionality (0-D to 3-D)

- **Point Defects** - vacancies, interstitials, adatoms
- **Line Defects** – dislocations leading to terrace, ledges, kinks
- **Surface reconstructions**
- **Bulk (volume) Defects** – voids, inclusions, pores

Bulk (Volume) Defects in Crystals

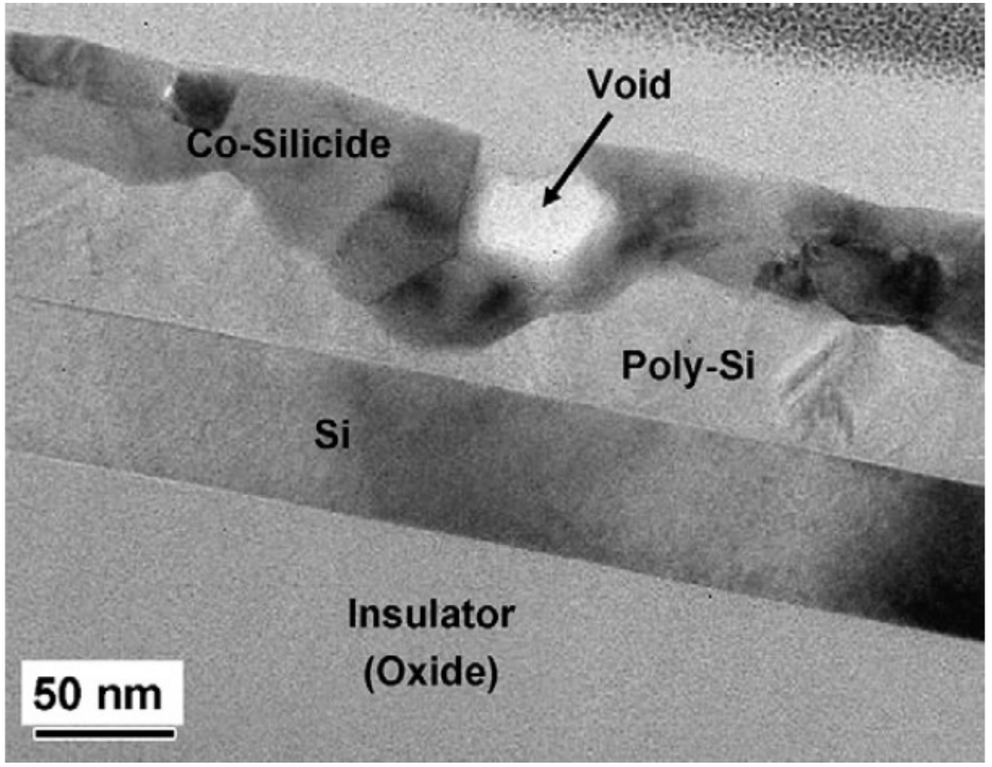
Extend over large regions of a crystal (not just a few atoms)

Caused by processing, impurities, or stresses

Types of bulk defects:

- **Voids**: empty regions
- **Inclusions**: foreign particles or phases inside
- **Cracks**: micro- or macroscale
- **Porosity**: many small voids

Voids in silicon

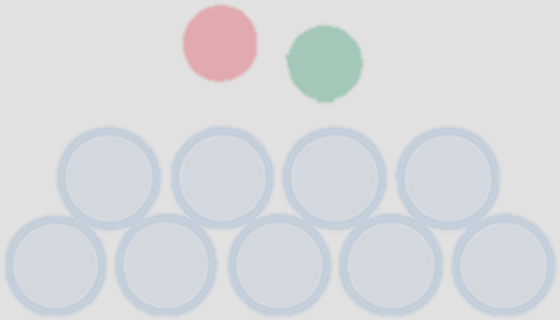


Raghaw & Swaminathan | Progress in Crystal Growth and Characterization of Materials | 2009

CHEMINA

How Surfaces Lower Their Energy

Adsorption of molecules

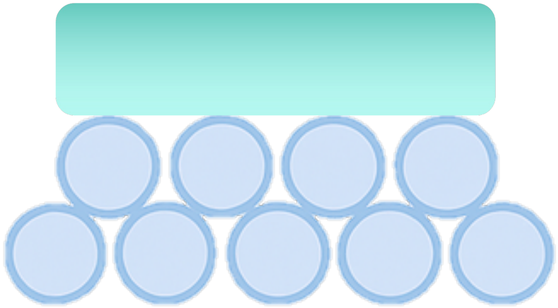


Physisorption/chemisorption to satisfy dangling bonds

Surface defects/ reconstruction

Atoms rearrange or shift position

Interface formation



New interfaces form and energy redistributed between phases

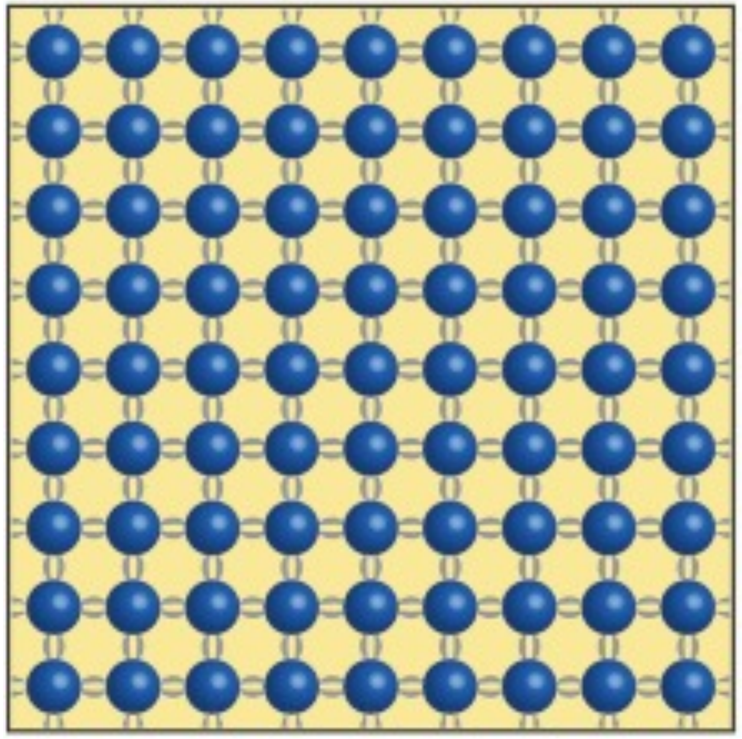
CHEMINA

How Surfaces Lower Their Energy

Type	Example	Key Driving Forces	Characteristic Features
Solid–Solid	Grain boundaries	Crystallographic mismatch, bonding strength	Misorientation, dislocations, segregation
Solid–Liquid	Wetting, adhesion, corrosion, biomolecular layers	Polar vs nonpolar interactions, hydrogen bonding	Contact angle, adsorption layers
Solid–Gas	Oxidation, catalysis, passivation	Chemisorption, reaction kinetics	Surface films

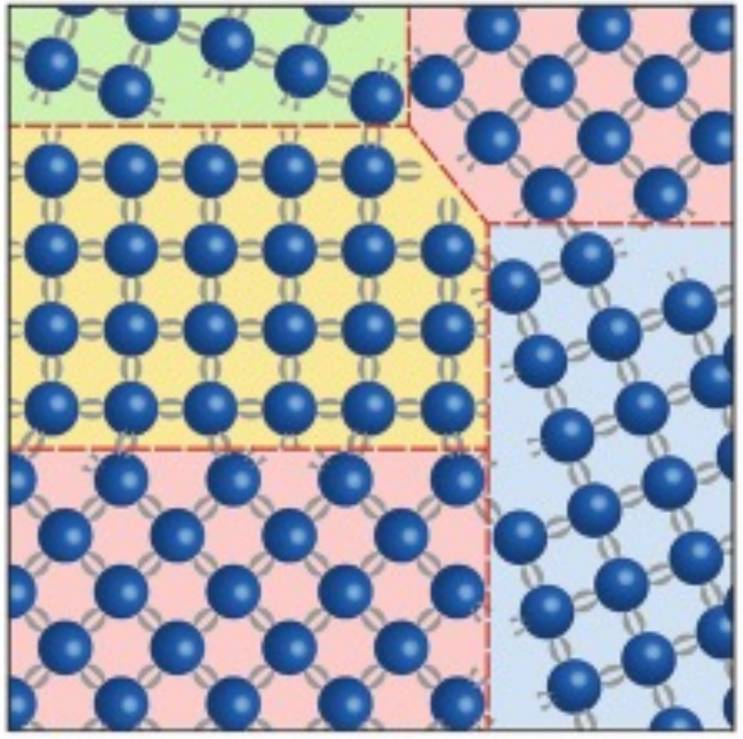
Real Materials Made of Many Small Crystals

Single crystals
(monocrystalline solids)



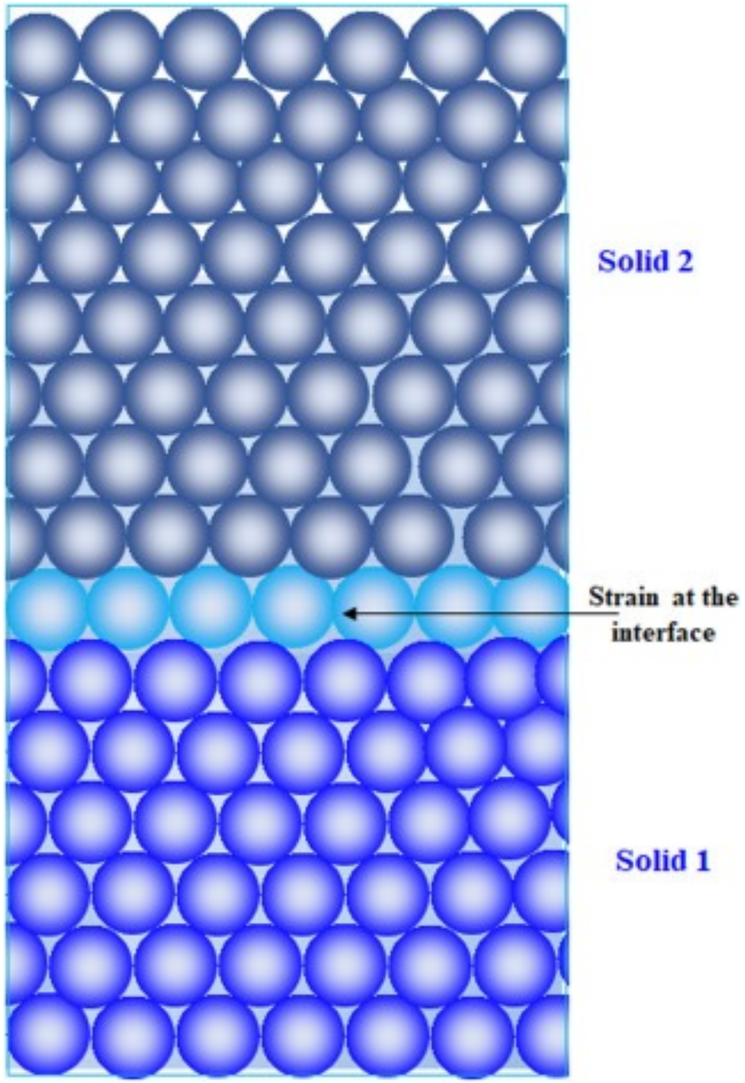
Relative spacing and orientation of neighboring atoms governed by chemical bonding

Patchwork of individual crystals (grains)
(Polycrystalline solids)



Individual grains differ in size and orientation and joined by planar interfaces called grain boundaries

Solid-Solid Interfaces are Common in Nature



$\alpha \mid \beta$

$\alpha \mid \alpha$

α ➔ solid crystalline phase

Any pure material that is in a single phase but in a polycrystalline solid, will have plenty of $\alpha \mid \alpha$ interfaces

CHEMINA

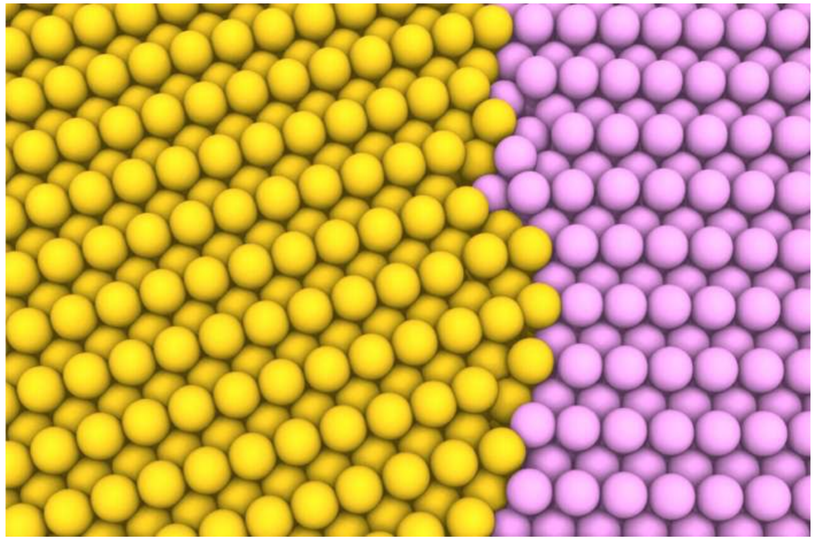
Grain Boundaries Are 2-D Defects

Grain boundaries cause a disruption in periodicity (atoms are in the wrong positions):

Higher energy

Broken distorted bonds

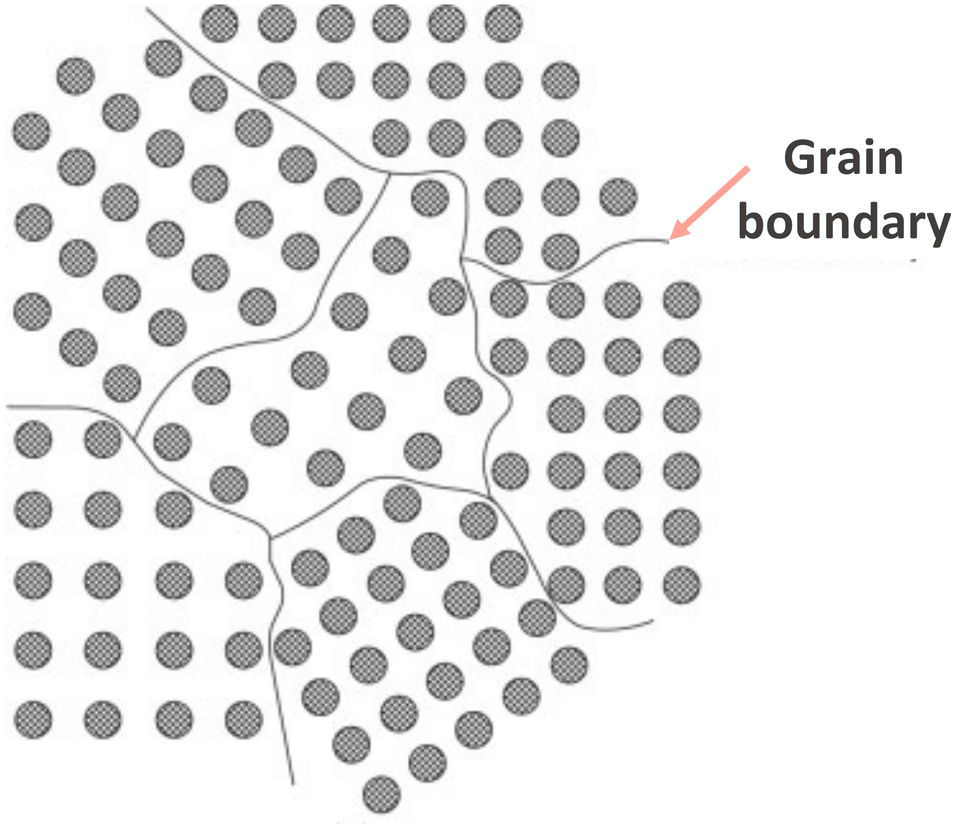
Material is at a slightly lower density

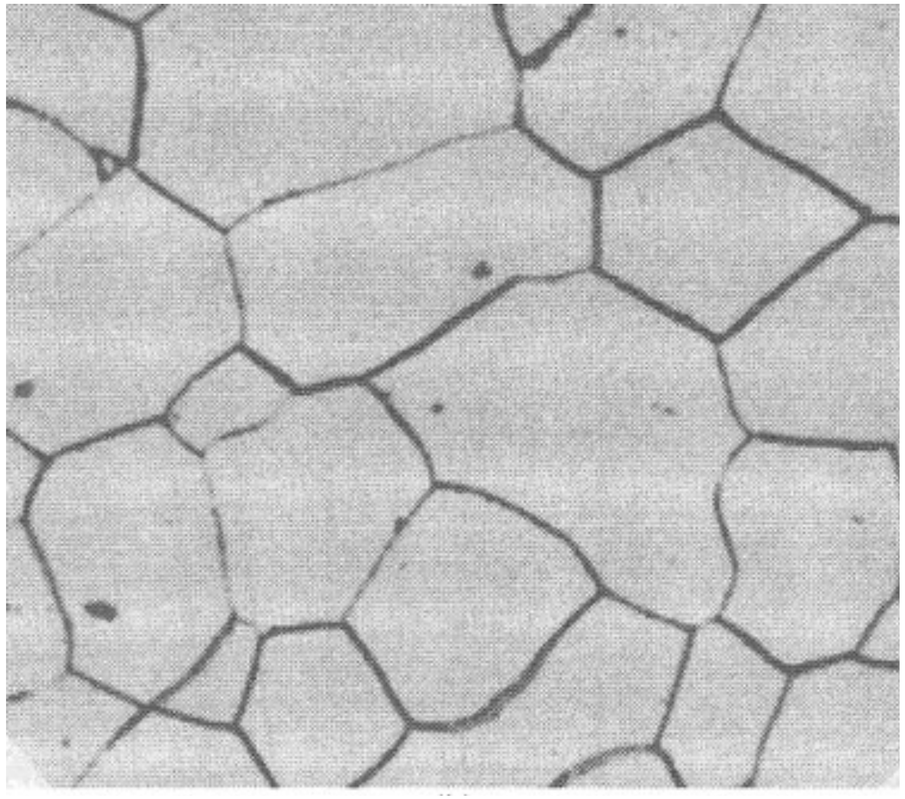


Atoms at a grain boundary **lower the energy** by arranging themselves so their rows line up better and match the atomic pattern on the other side

Grain Boundaries Form Microstructure

Grain boundaries are planar defects across which the crystal orientation changes



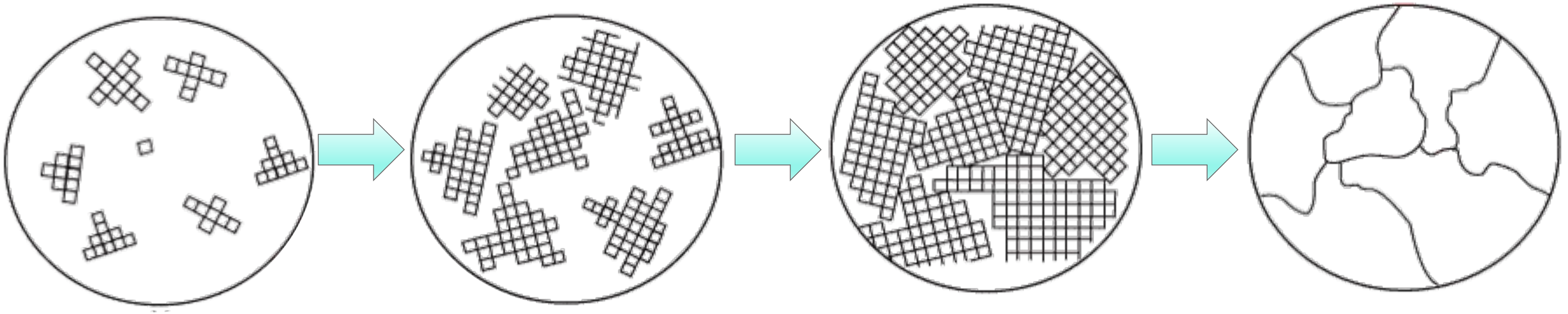


Microstructure influences properties: strength, toughness, corrosion, resistance, electrical

CHEMENA

Why do Grain Boundaries Form?

In engineering materials, a crystal is usually referred to as a “grain”



Nucleation of crystals

Crystal growth

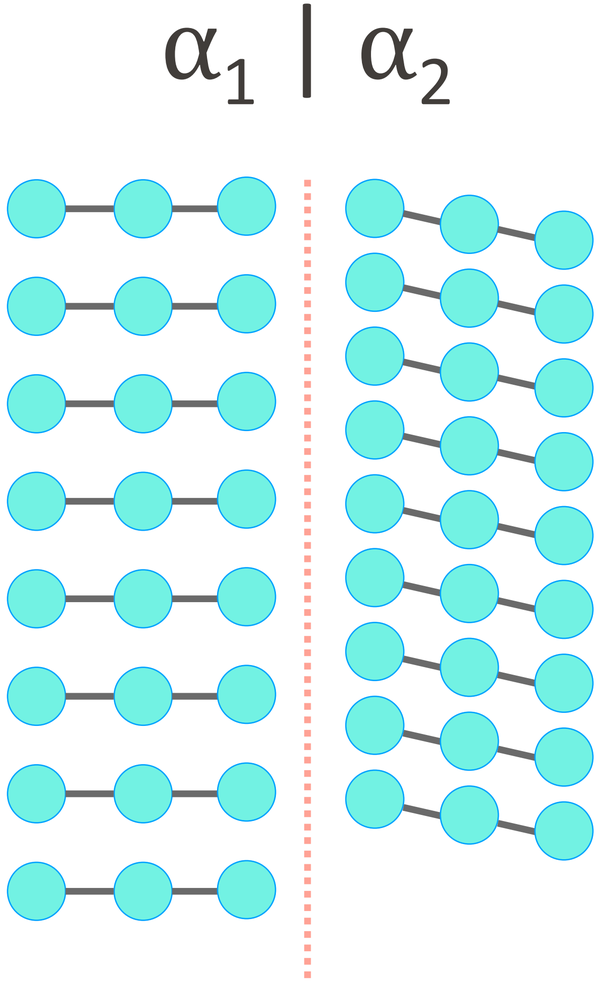
Irregular grains form as crystals grow together

Grain boundaries form

Rapid cooling ➔ more nucleation points and smaller grains, stronger material

Slow cooling ➔ larger grains with lower strength, hardness, and ductility

Thermodynamics of Homophase Solid-Solid Interfaces



Energy of a single bond broken + elastic energy to stretch all the reformed bonds past their equilibrium length

$$\boldsymbol{\gamma}_{\propto_1 \propto_2} = \boldsymbol{\gamma}_{\propto_1} + \boldsymbol{\gamma}_{\propto_2} - \boldsymbol{W}_{\propto_1 \propto_2}$$

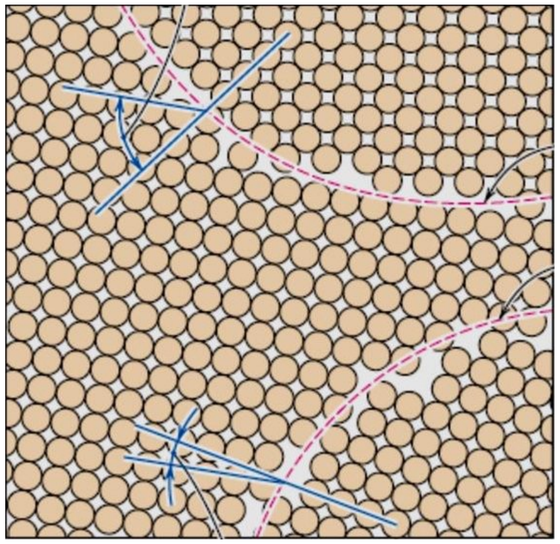
Different Types of Grain Boundaries

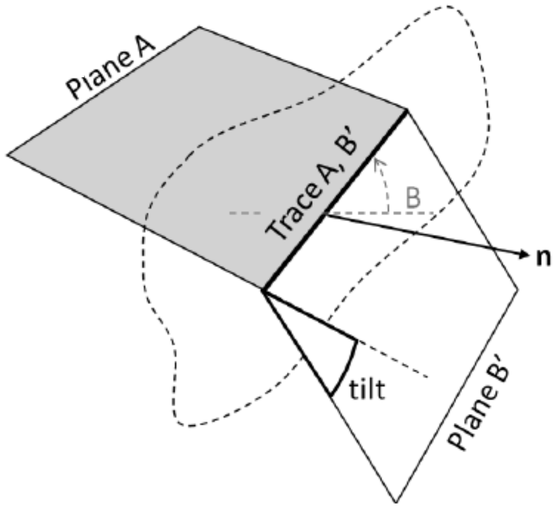
Different types of grain boundaries (GB)

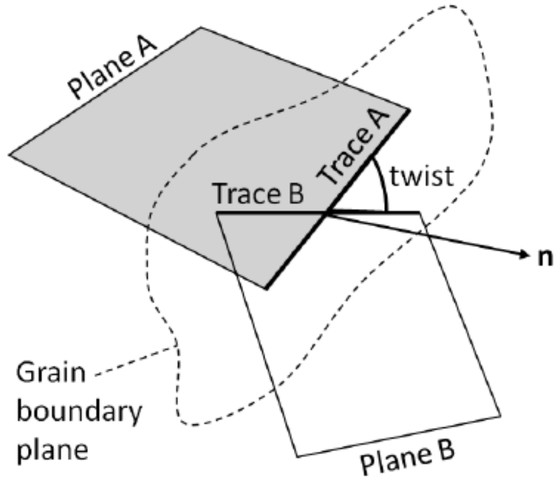
- Low-angle GB ≤5° rotation
- High angle GB
- Tilt boundary
- Twist boundary

High angle GB

Low angle GB







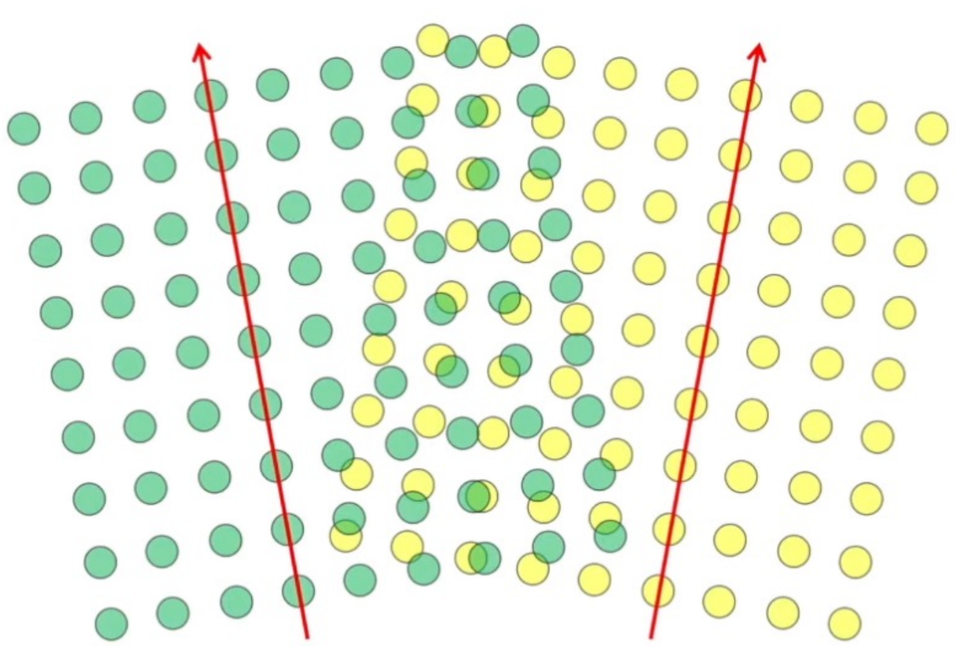
King *et al.* | Acta Materialia| 2011

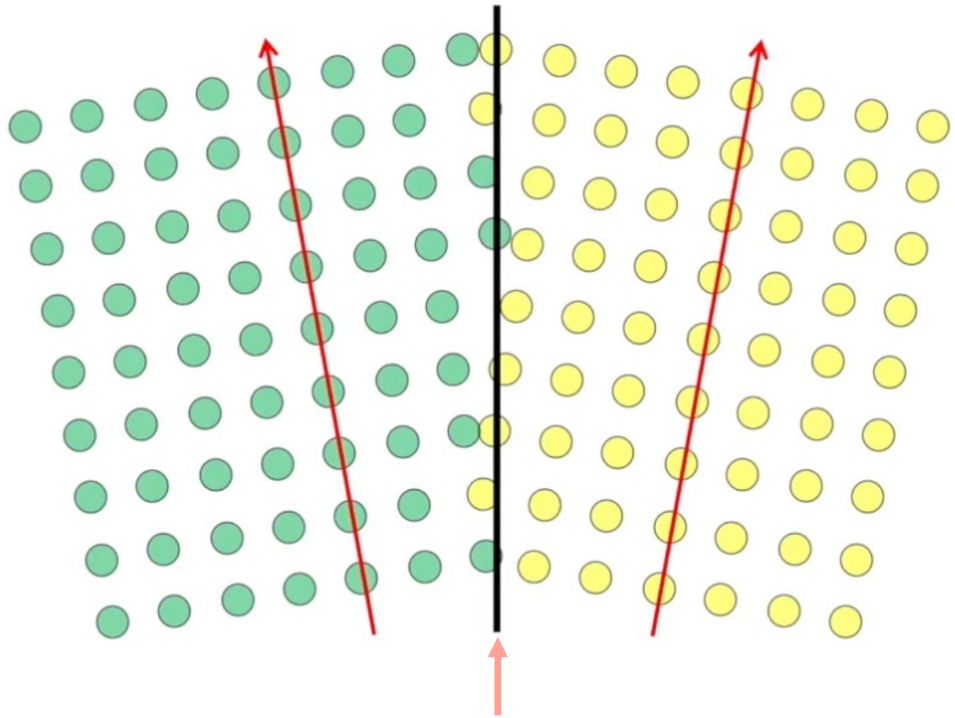
CHEMINA

High Angle Tilt Grain Boundaries

Adjacent grain rotated with respect to each other

Can cause major disruptions in both lattices at the grain boundary

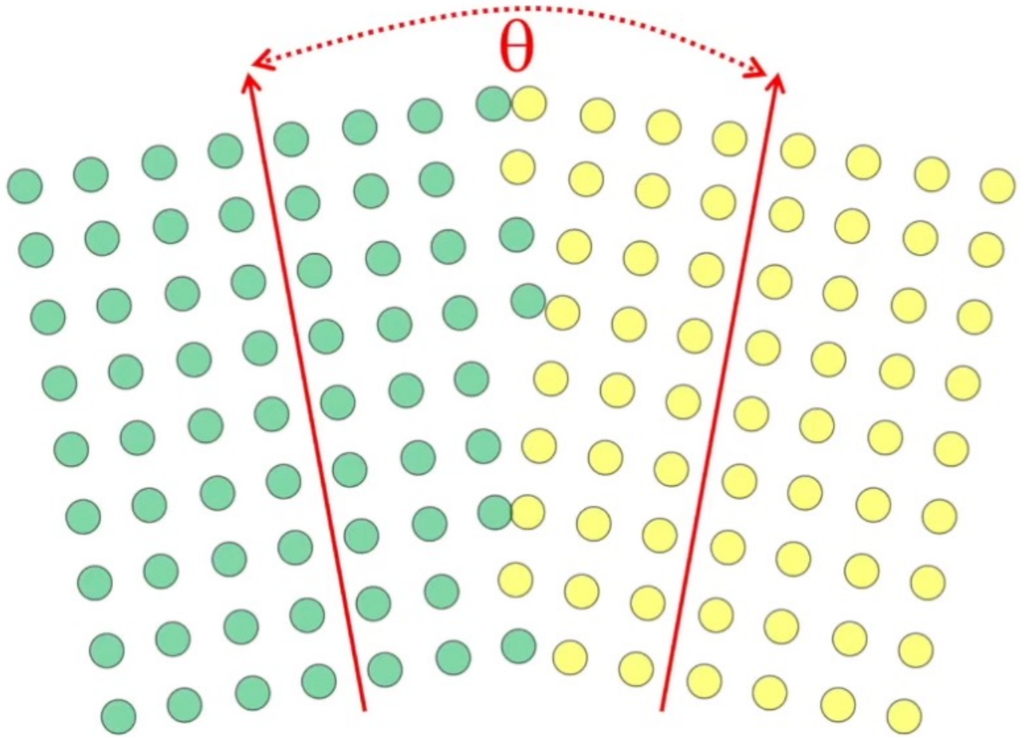




Greater disruption ➔ Higher grain boundary energy

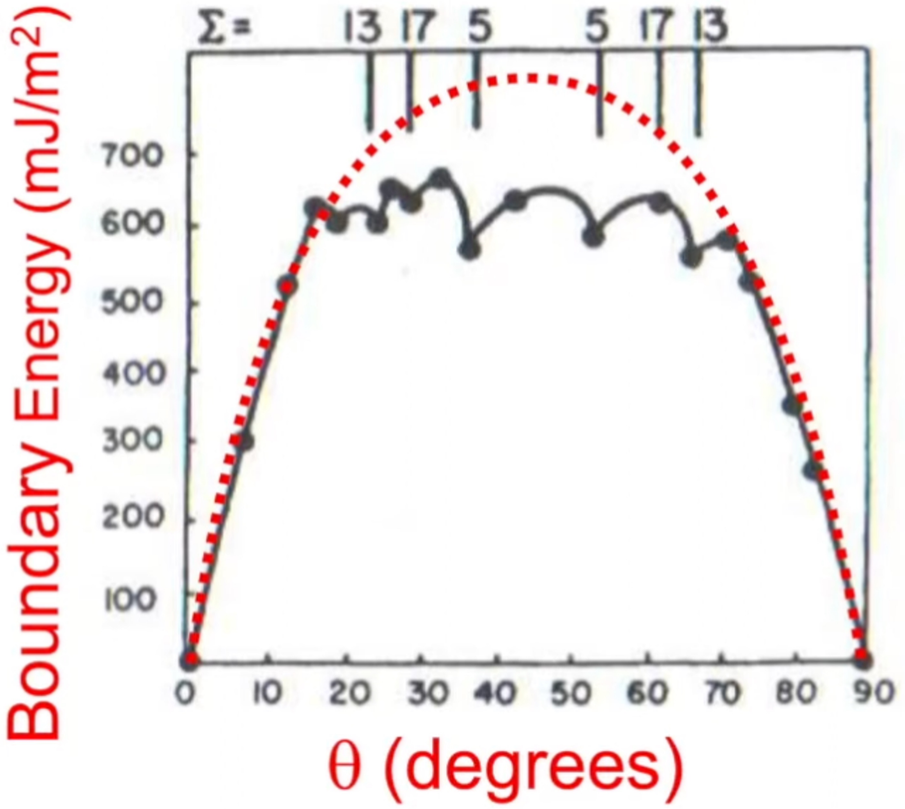
Grain Boundary Energy

Greater misorientation – energy of boundary systematically increases



Square lattice or simple cubic lattice

Maximum misorientation at 45° - highest energy?



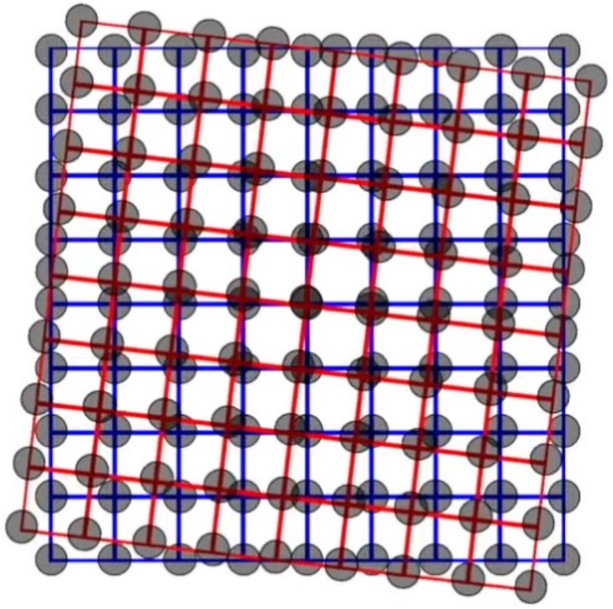
Lower energies at certain rotation angles

CHEMINA

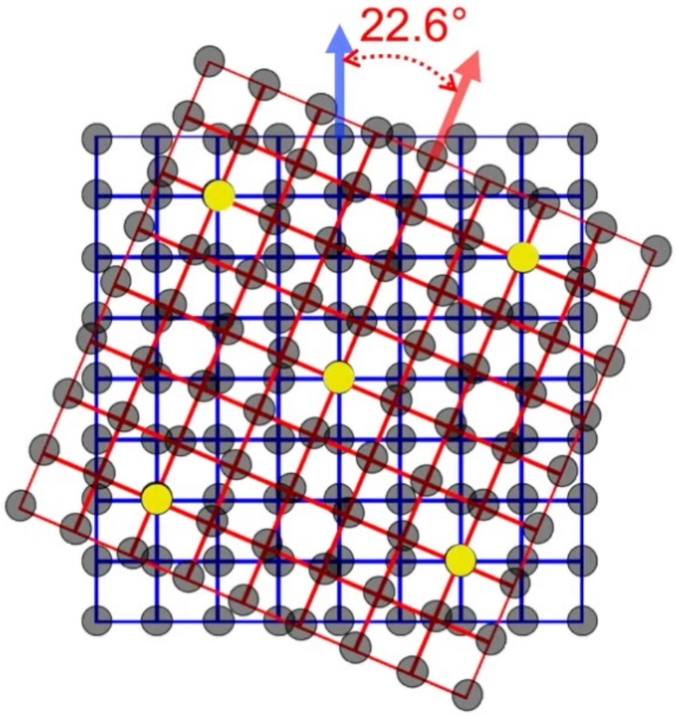
Grain Boundaries: Coincidence Site Lattice

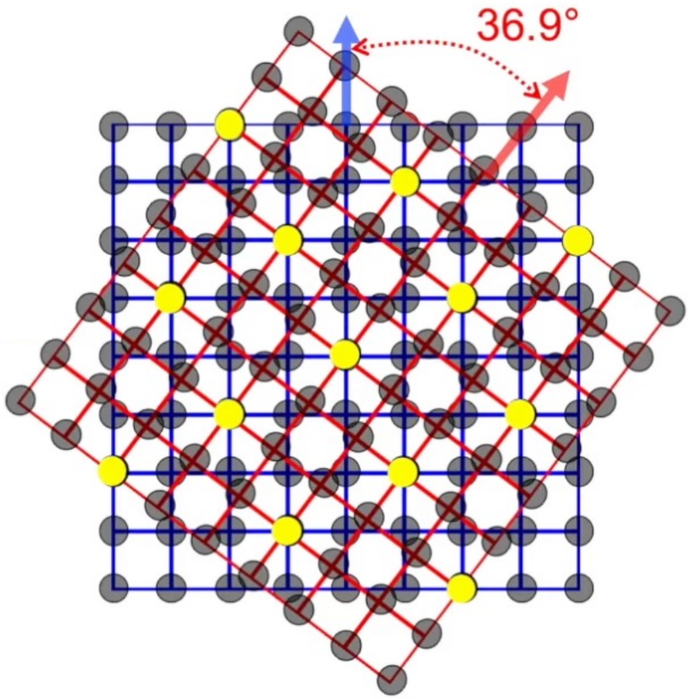
At certain angles, some lattice sites in rotated grains coincide at the boundary

Coincidence site lattice: at certain angles sites in both grains coincide ➔ more stable boundary



Superimposed grains



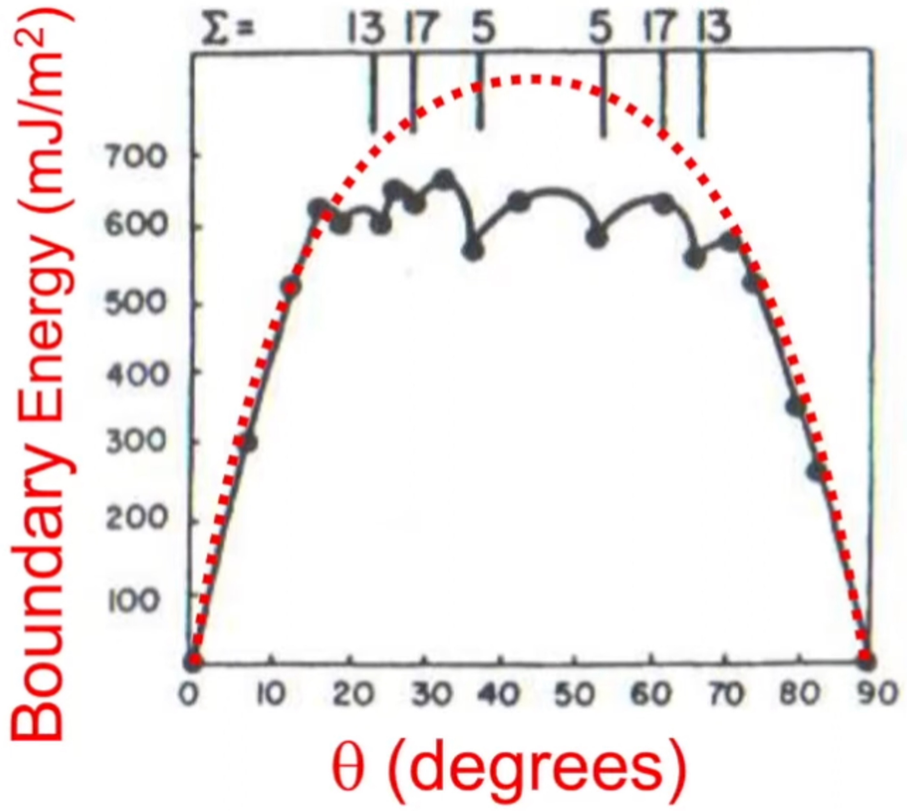


Some atoms in red and blue grains superimpose (yellow points)

Coincident site (super) lattice

CHEMINA

Grain Boundaries are Essentially Organized Defects



Lower energies correspond to angles for forming coincidence site lattices

As Σ increases ➔ less sites overlap ➔ less stabilization

Σ=1 ➔ perfect fit of all sites (no rotation)

Nature prefers order even when the structure is imperfect

The **coincidence site lattice** is a way the crystal partially restores order at an interface

CHEMINA

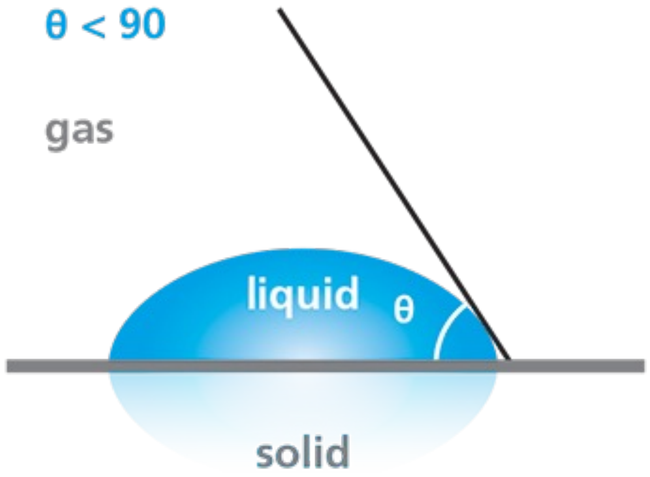
How Surfaces Lower Their Energy

Type	Example	Key Driving Forces	Characteristic Features
Solid–Solid	Grain boundaries	Crystallographic mismatch, bonding strength	Misorientation, dislocations, segregation
Solid–Liquid	Wetting, adhesion, corrosion, biomolecular layers	Polar vs. nonpolar interactions, hydrogen bonding	Contact angle, adsorption layers
Solid–Gas	Oxidation, catalysis, passivation	Chemisorption, reaction kinetics	Surface films

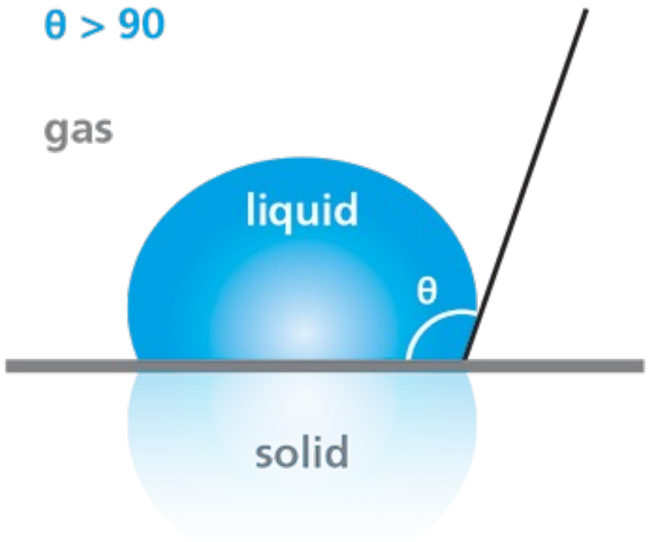
Hydrophilic *vs.* Hydrophobic Surfaces

Hydrophilic

High wettability



Polar



Non-polar

Hydrophobic

Low wettability

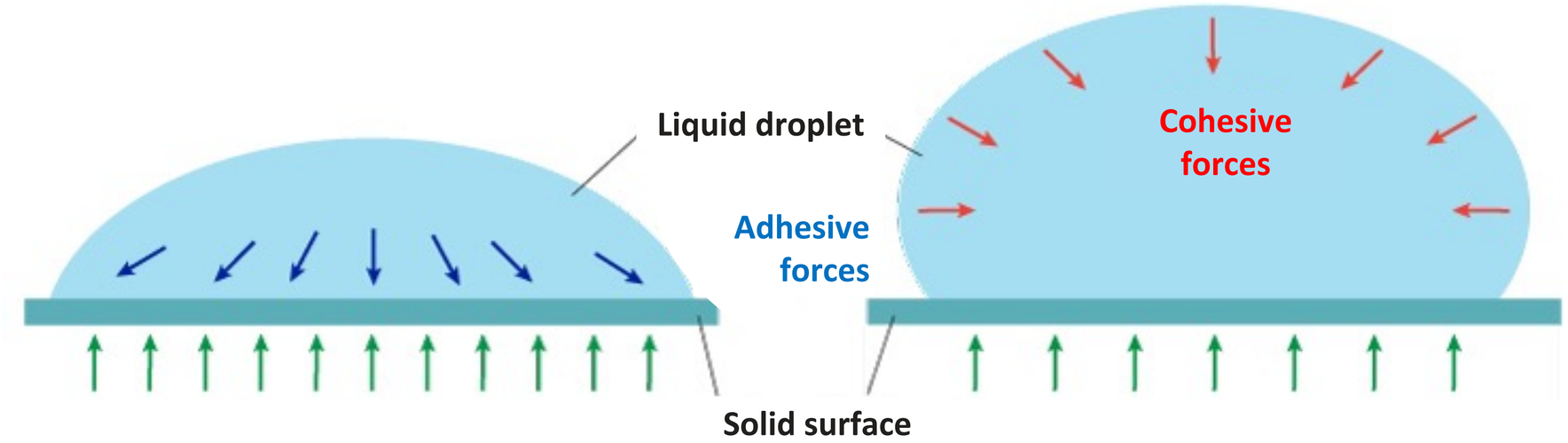
- Strong H-bonding/dipole–dipole interactions with water
- High surface energy (γ_{SV})
- Promotes *wetting* to maximize favorable interactions

- No H-bonding, dominated by weak van der Waals forces
- Low surface energy (γ_{SV})
- Water minimizes contact, droplets reduce interfacial area

Surface Materials Define Surface Energy

High Surface Energy

Easy to adhere



Low Surface Energy

Hard to adhere

Aluminum
Copper
Alumina
Pure silicon
Titanium dioxide

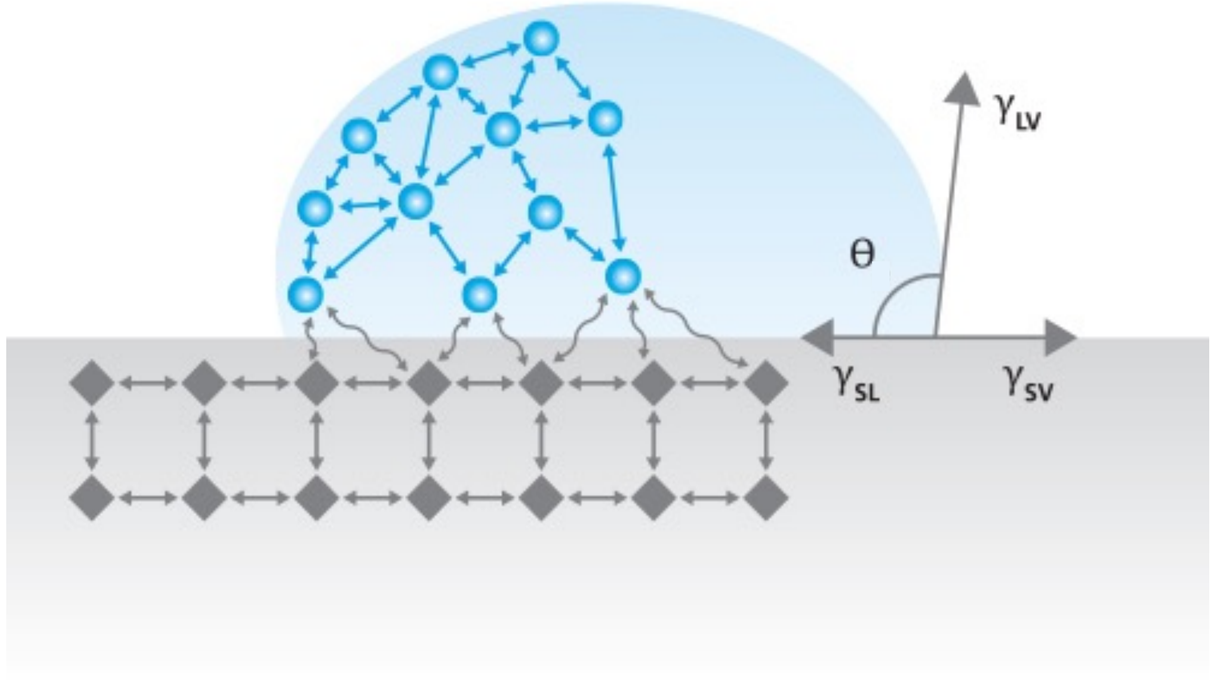
PTFE or Teflon
Silicone
Polyethylene
Waxed surfaces
Paraffin

Surface energy not just an abstract thermodynamics concept but practical!

CHEMINA

Contact Angle Visualizes Solid-Liquid Interactions

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

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

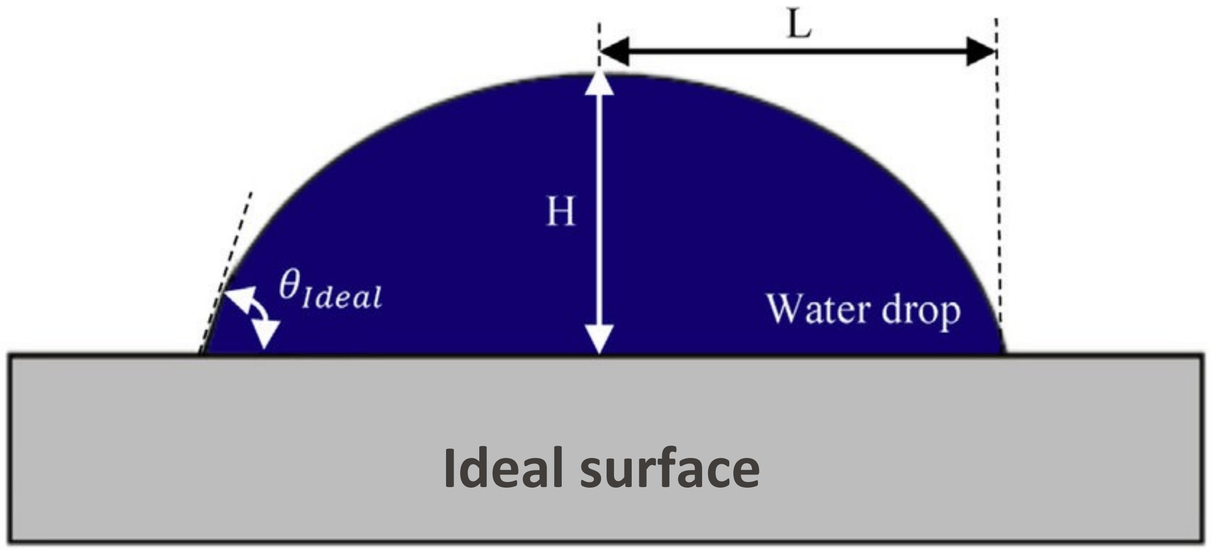
Relating interfacial energies with contact angle

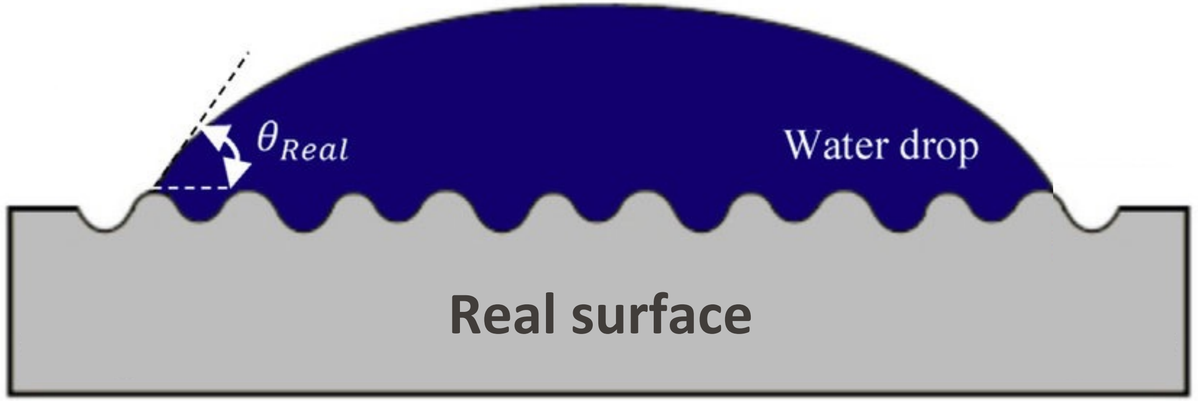
Ideal surface assumptions:

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

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

Limits of Young's Equation in Real Systems





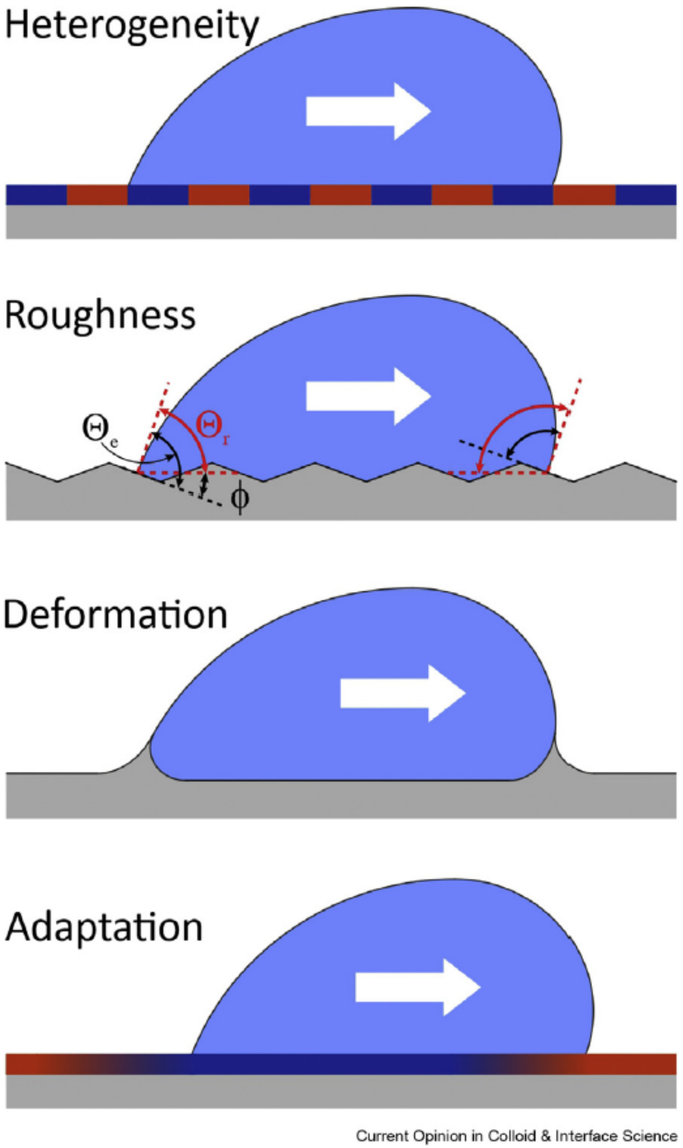
Perfectly flat and smooth
Rigid
Chemically homogeneous
Contact angle well-defined and ideal

Rough
Contaminated
Chemically heterogeneous
Contact angle hysteresis and deviations

We need other models to describe wetting on real surfaces

CHEMINA

Causes of Contact Angle Hysteresis



Current Opinion in Colloid & Interface Science

Chemical heterogeneity ➔ different local regions with different surface energies

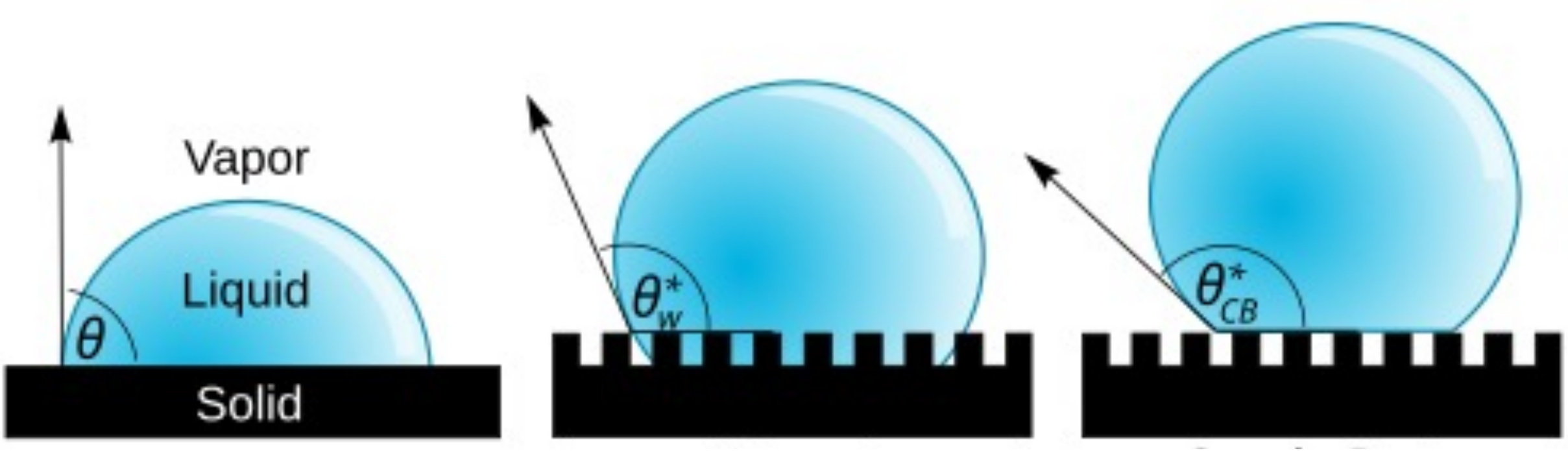
Topographical heterogeneity ➔ different local slope

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

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

CHEMINA

Models to Describe the Behavior of Drop on Surface

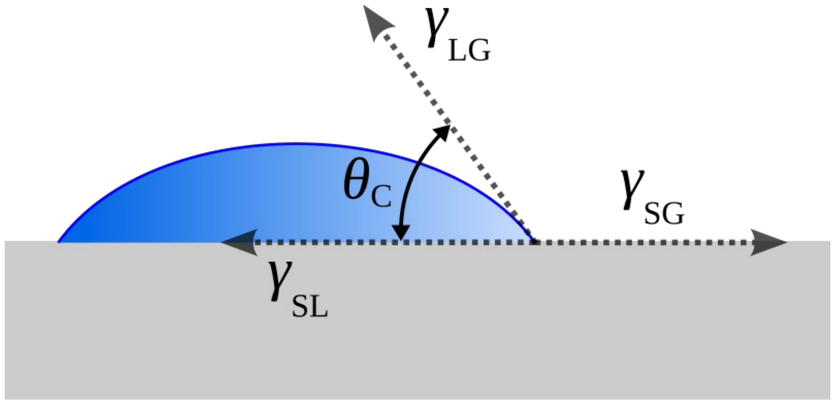


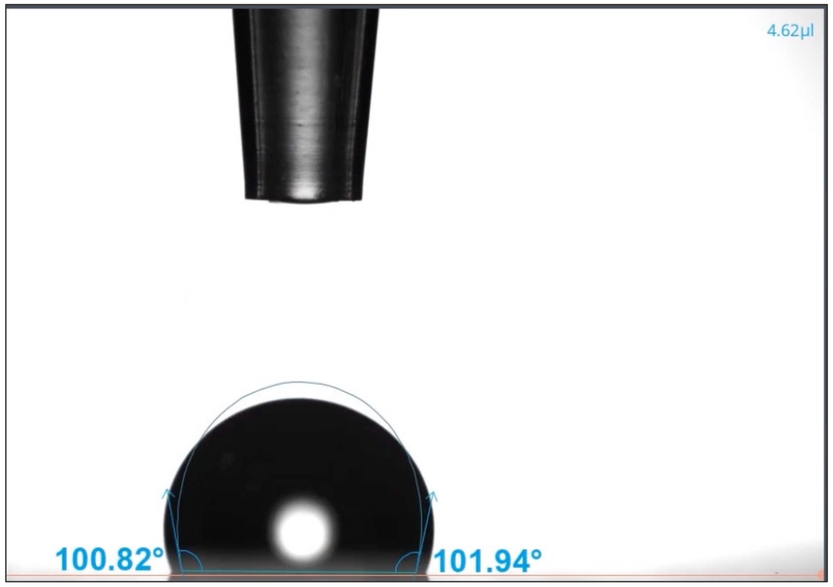
Young Model | **Wenzel Model** | **Cassie-Baxter Model**

Source: Wikipedia

CHEMINA

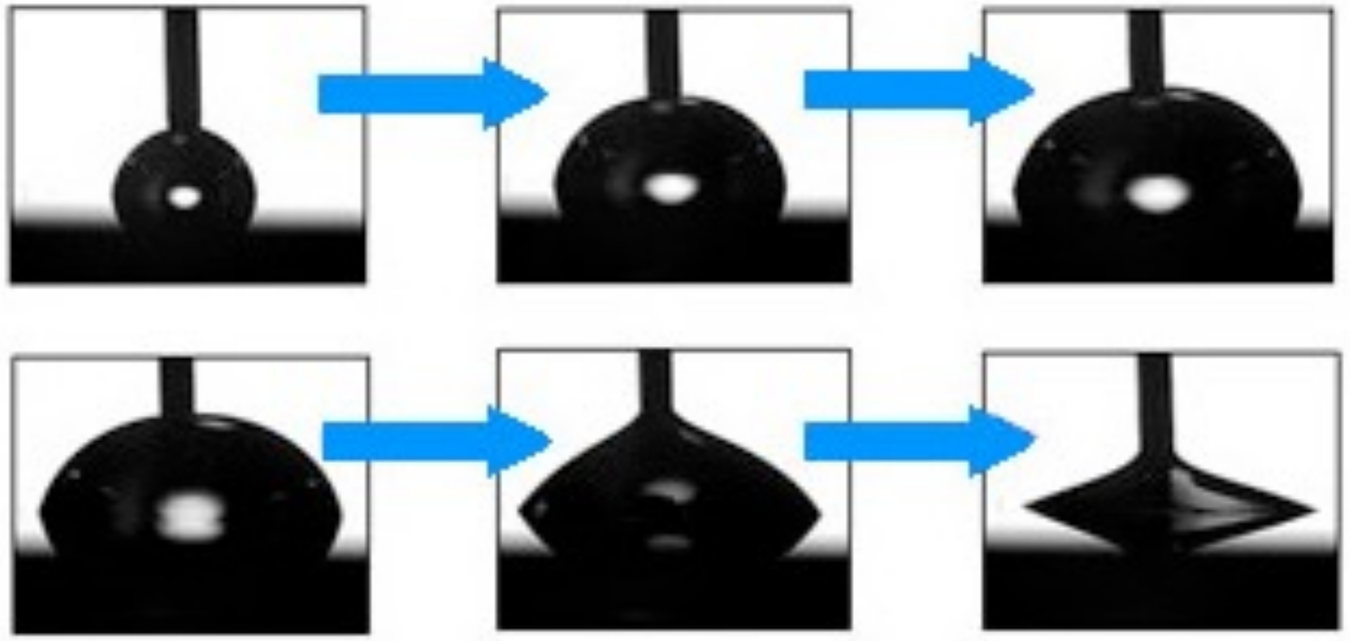
Contact Angle: Measuring θ and γ (sometimes called σ)





Sessile drop

Direct contact angle measurement from drop or bubble shape shape



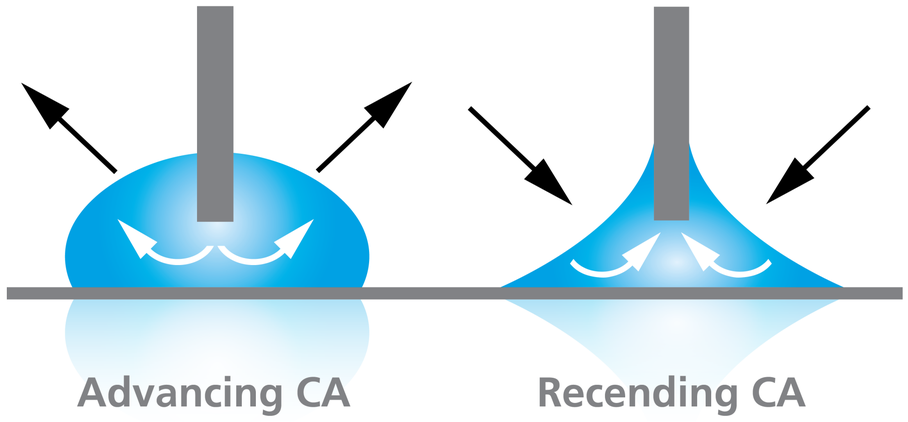
CHEMINA

Dynamic Contact Angles

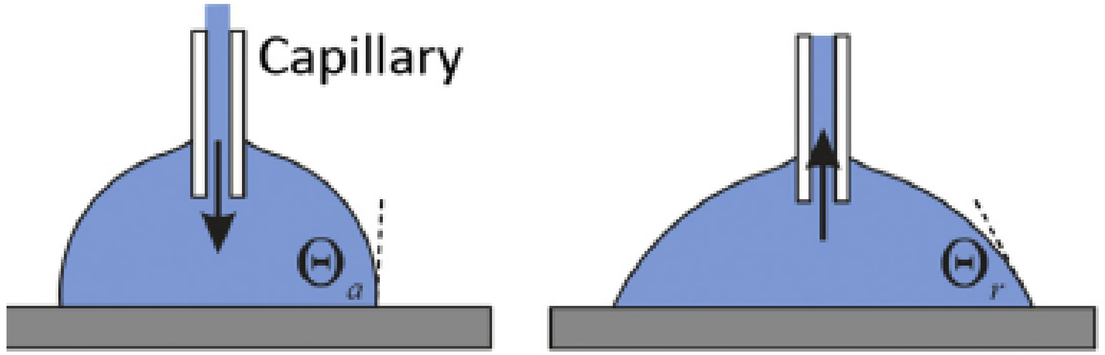
θ_a advancing contact angle

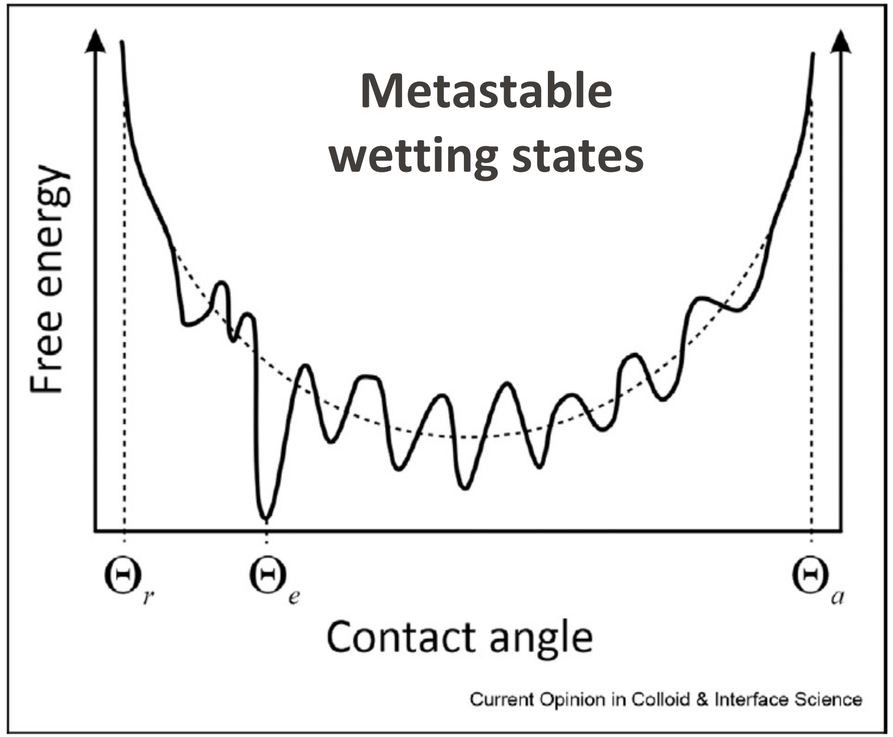
θ_r receding contact angle

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



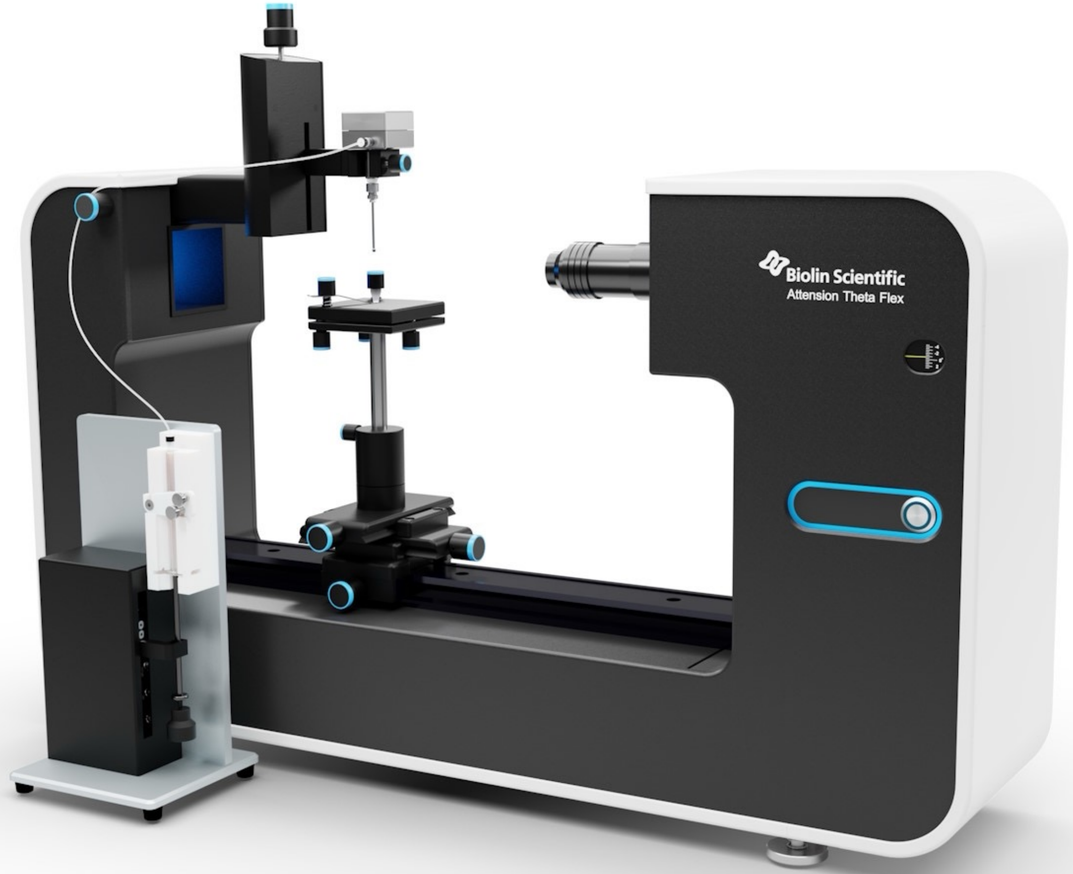
Contact line pinning: droplet edge gets stuck in metastable states leading to hysteresis





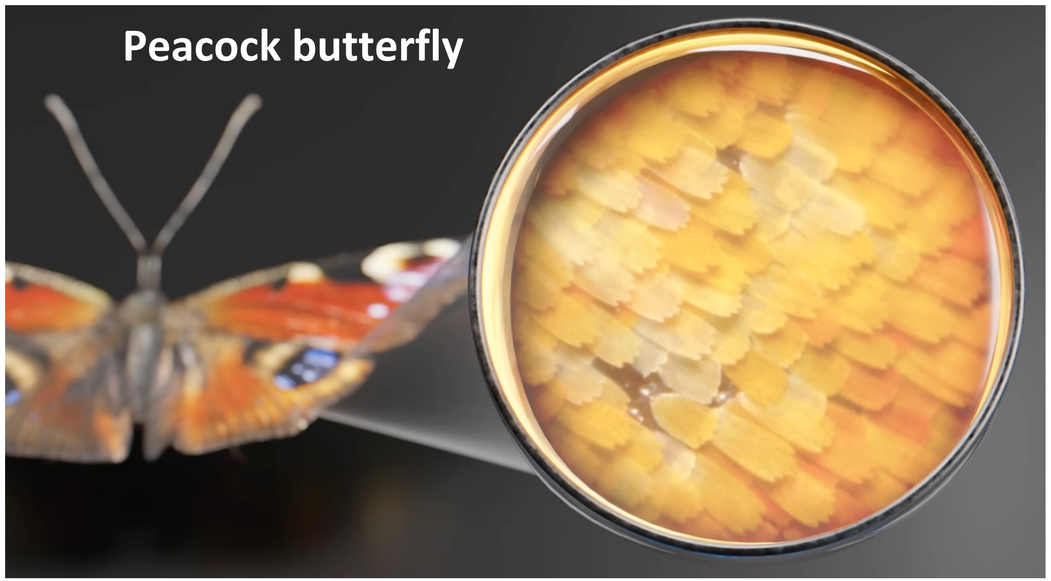
CHEMINA

Contact Angle Instruments

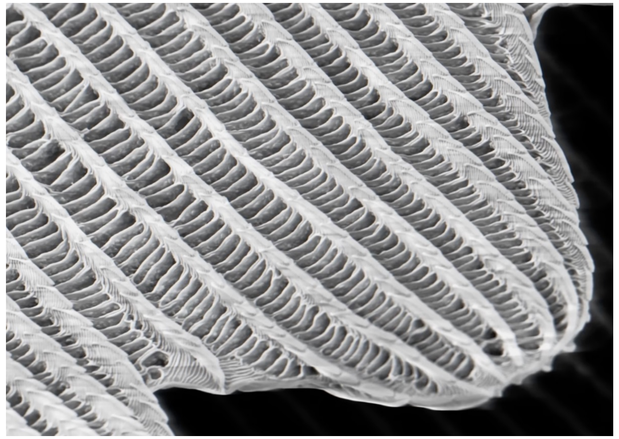


Techniques to Visualize Real Surfaces

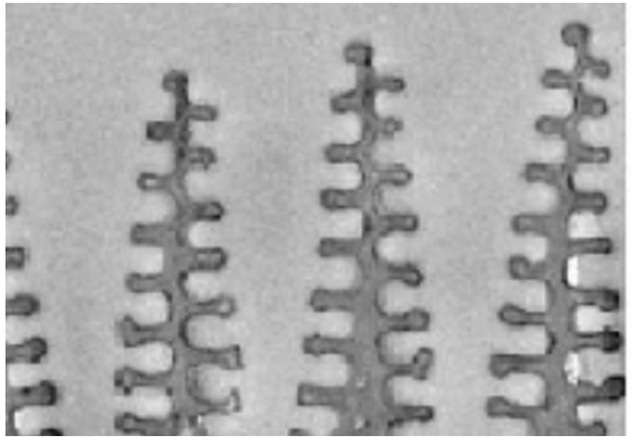
Light Microscopy



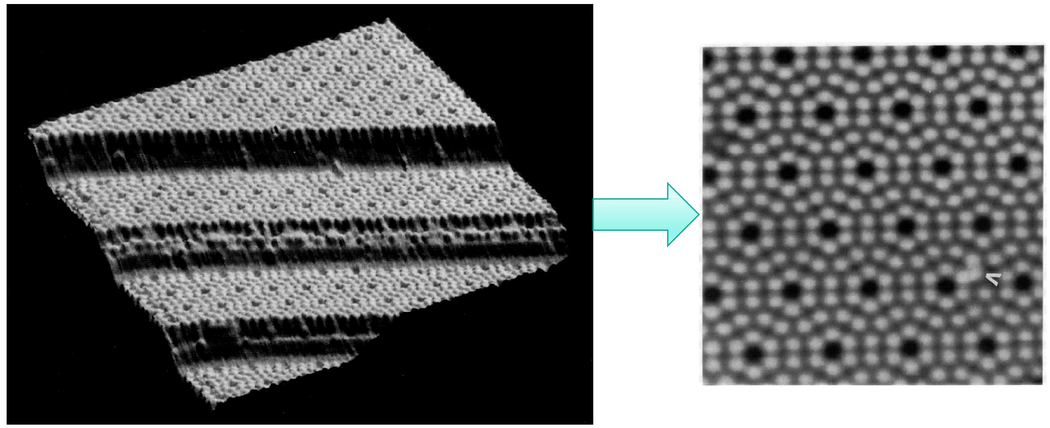
Scanning electron microscopy (SEM)



Transmission electron microscopy (TEM)

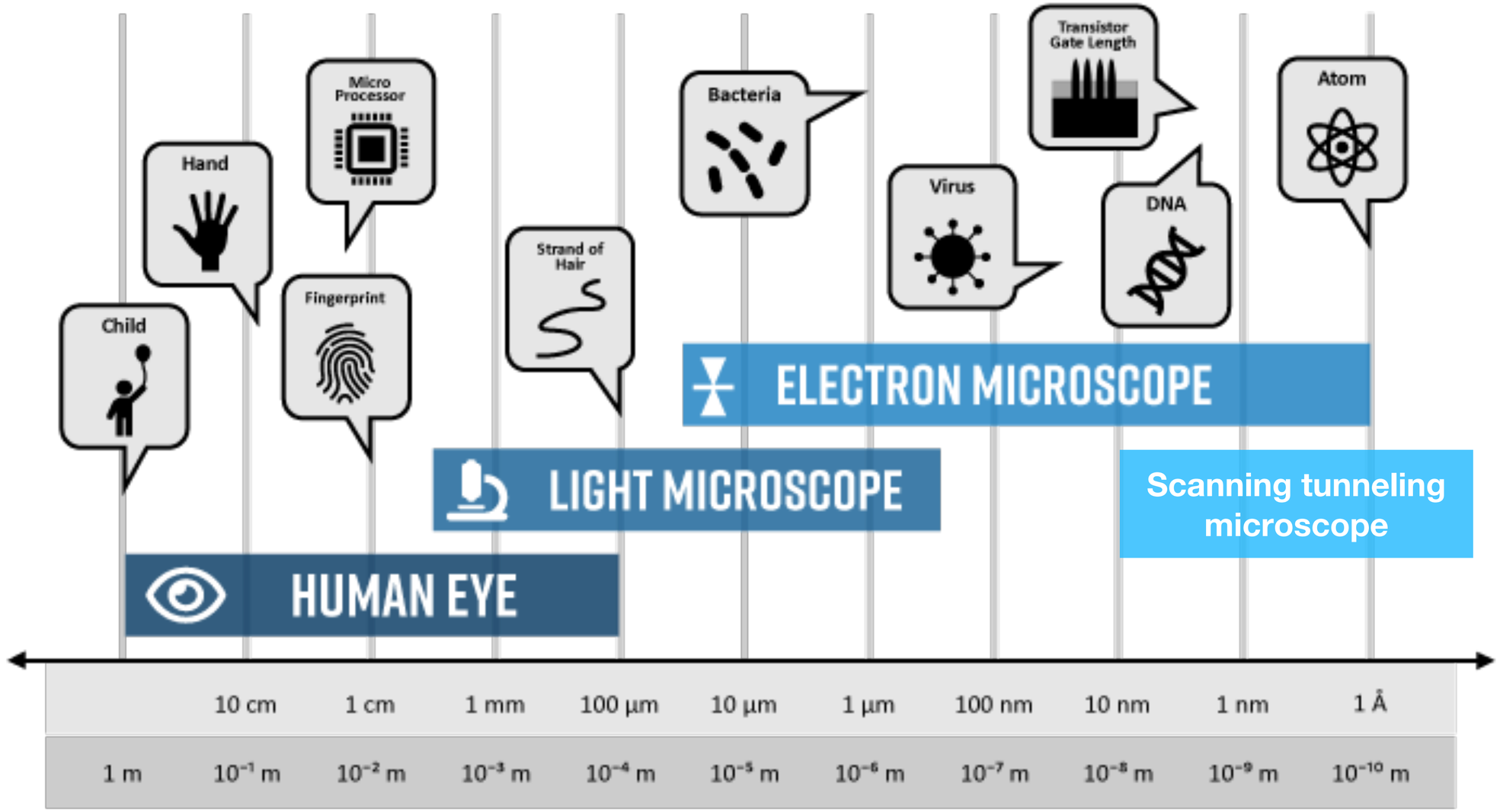


Scanning tunneling microscopy (STM)



CHEMINA

Length Scales Accessible with Different Microscopes

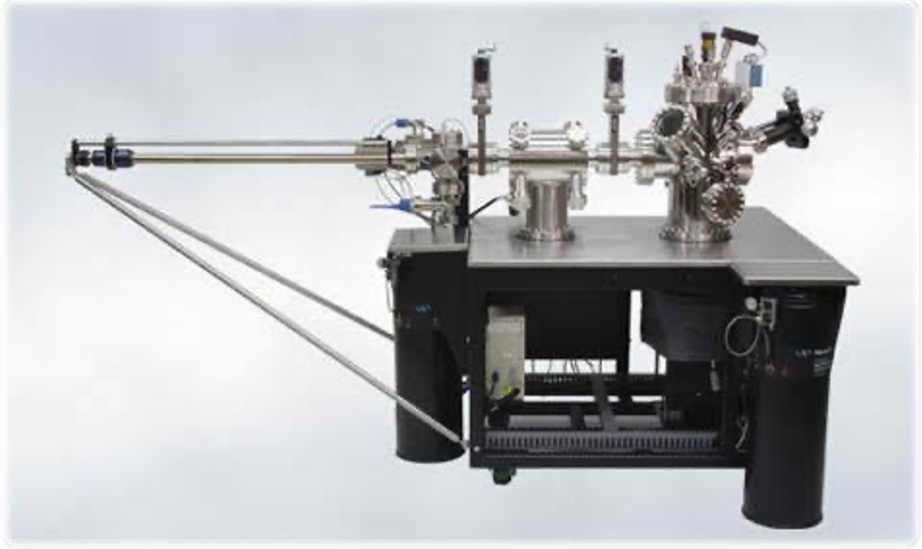


Why Do We Need Ultra-High Vacuum?

Instrumentation

Ion and electron beam instruments

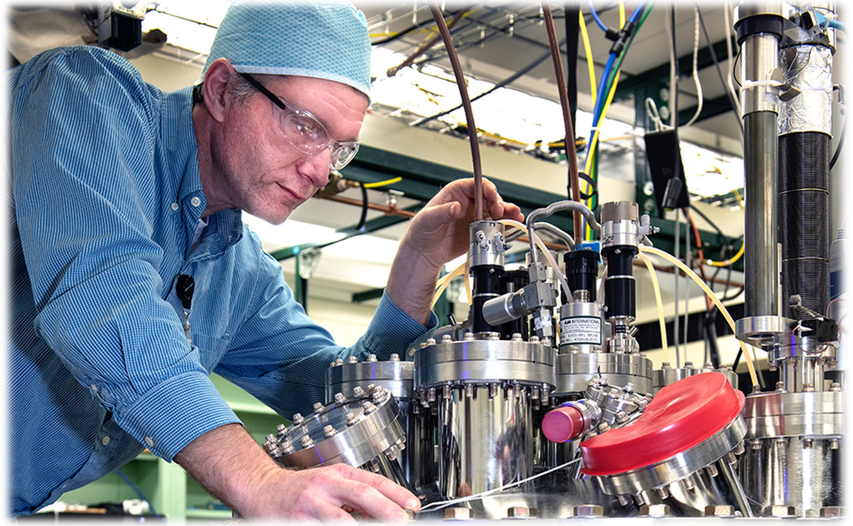
Need low pressure to avoid collisions with gas molecules



Depositions

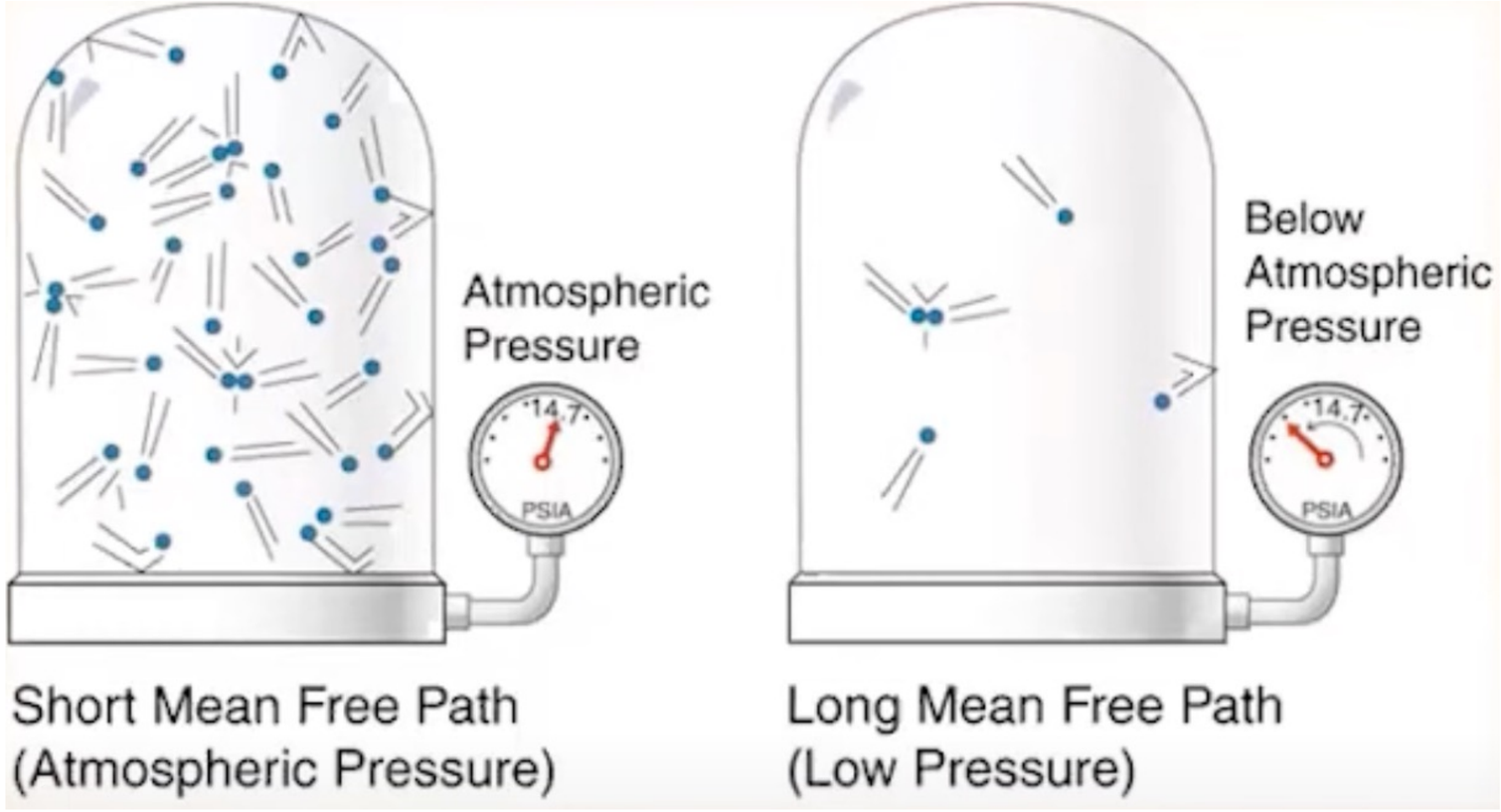
Chamber atmosphere can affect surface of specimen

Gas in chamber can adsorb onto surface



Why Do We Need Ultra-High Vacuum?

Lower pressure to decrease the mean free path – the average distance a particle travels before undergoing a significant collision with another particle

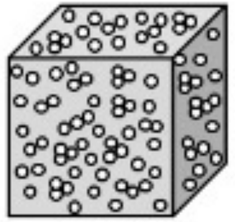
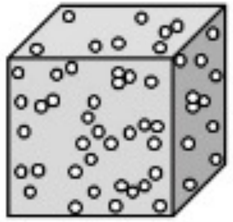
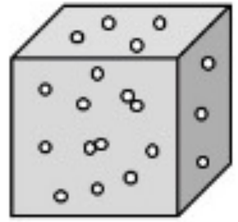


$$\Lambda = \frac{k_B T}{\sqrt{2}\,\pi d^2 p}$$

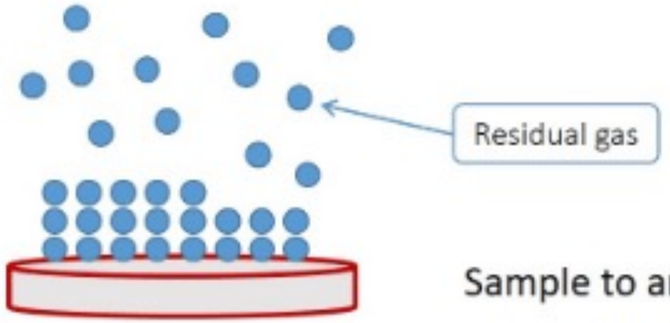
Λ: mean free path
k_B: Boltzmann's constant
T: Temperature
d: diameter of particle
p: pressure

CHEMINA

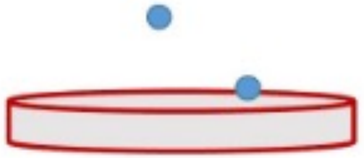
Vacuum Levels Significantly Impacts Monolayer Formation

Rough Vacuum	High Vacuum	Ultra High Vacuum
1 atm – 10^{-3} Torr	10^{-3} Torr - 10^{-8} Torr	10^{-8} Torr - 10^{-12} Torr
		
1 x 10^{-3} Torr **10^{13} atoms/cm^3**	**1 x 10^{-6} Torr** **10^{10} atoms/cm^3**	**1 x 10^{-11} Torr** **10^{5} atoms/cm^3**
1 residual gas **monolayer** every **4 SECONDS**		**1** residual gas **monolayer** every **4 DAYS**

High Vacuum



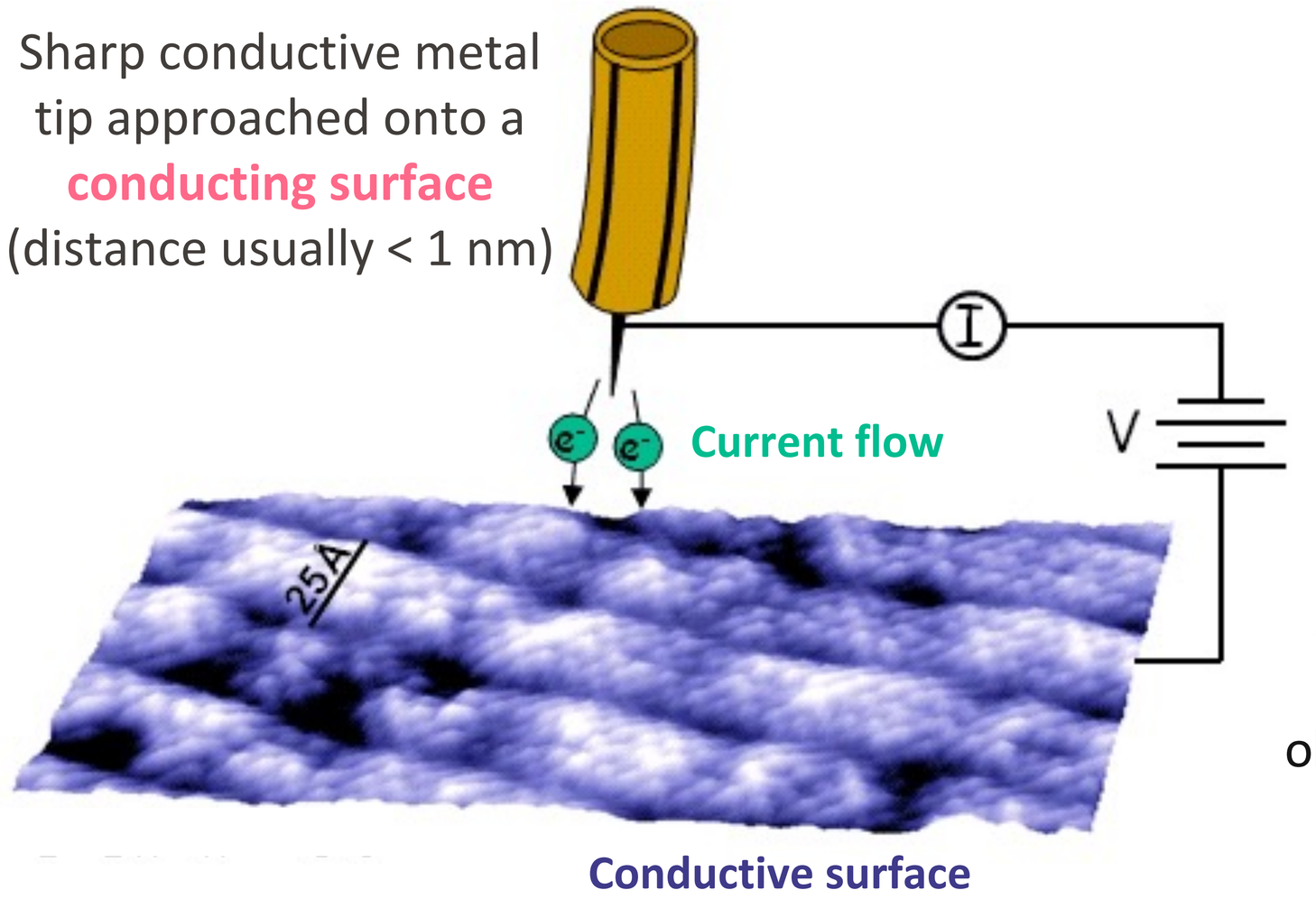
UHV



Seeing Surfaces with Atomic-Scale Resolution

Scanning Tunneling Microscopy (STM)

Sharp conductive metal tip approached onto a **conducting surface** (distance usually < 1 nm)



STM provides information on:

1) Electron-density distribution

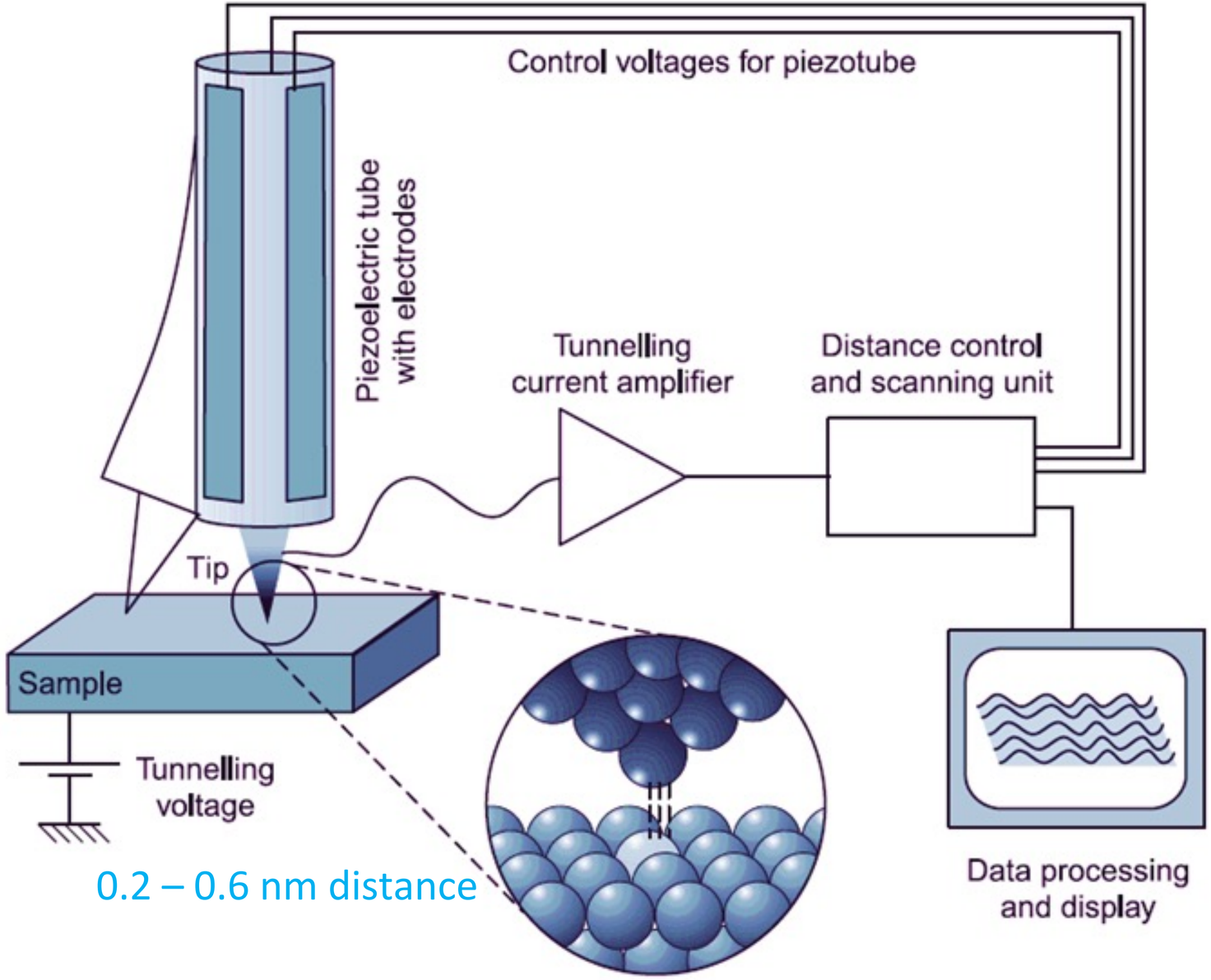
2) Electronic work function

3) Surface topography

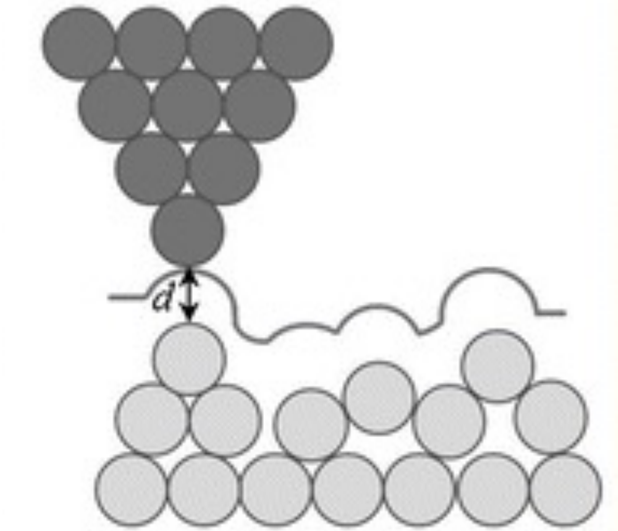
A 3-D image of the "surface" can be obtained with atomic resolution

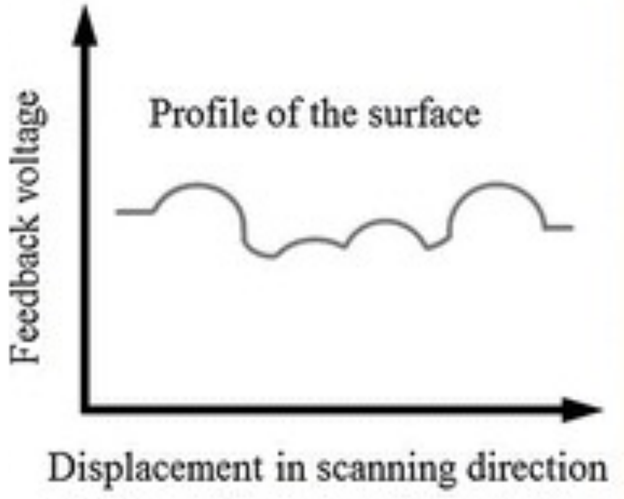
CHEMINA

STM Uses a Tunneling Current to Map Atoms on Surfaces



0.2 – 0.6 nm distance

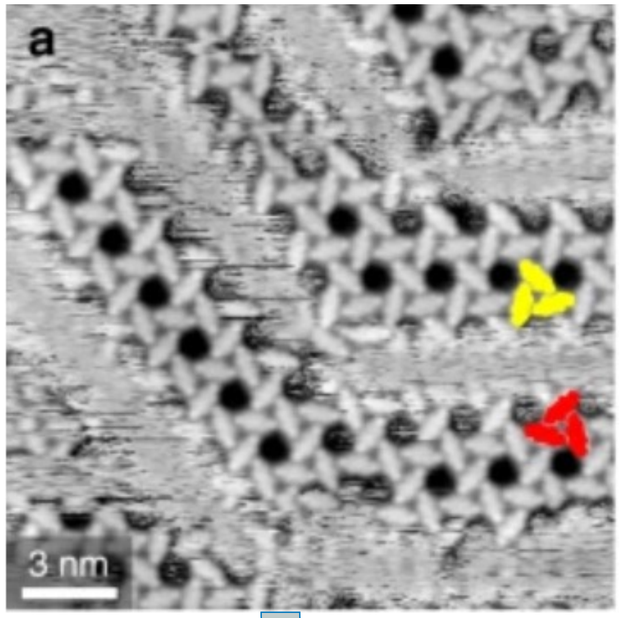




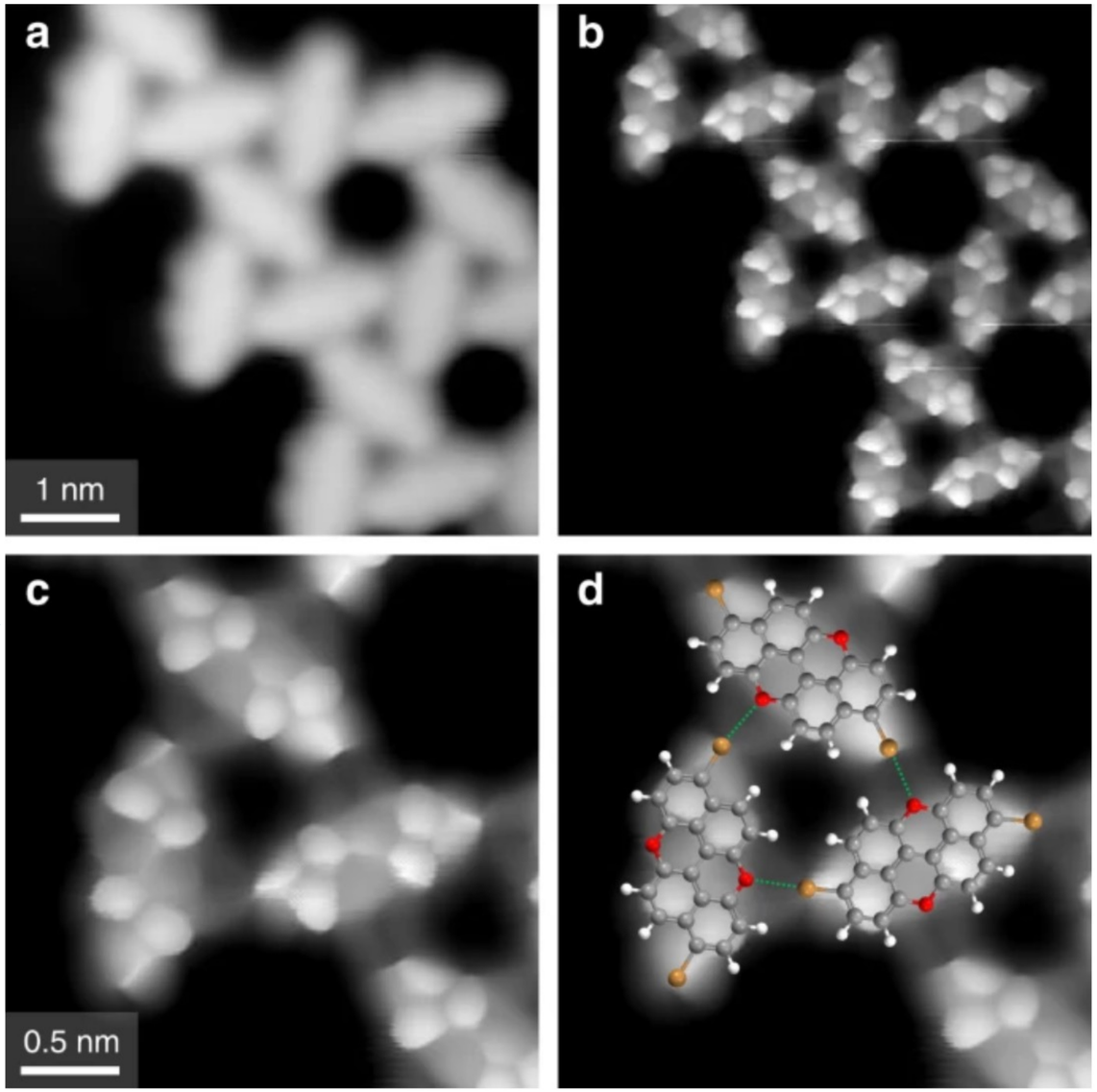
Source: Wikipedia

CHEMINA

The Power and Limitations of STM



Predicting intermolecular interactions with high-resolution STM



Lawrence *et al.* | *Nat. Commun.*| 2020

High resolution

Requires UHV and low temperature

Only conducting surfaces

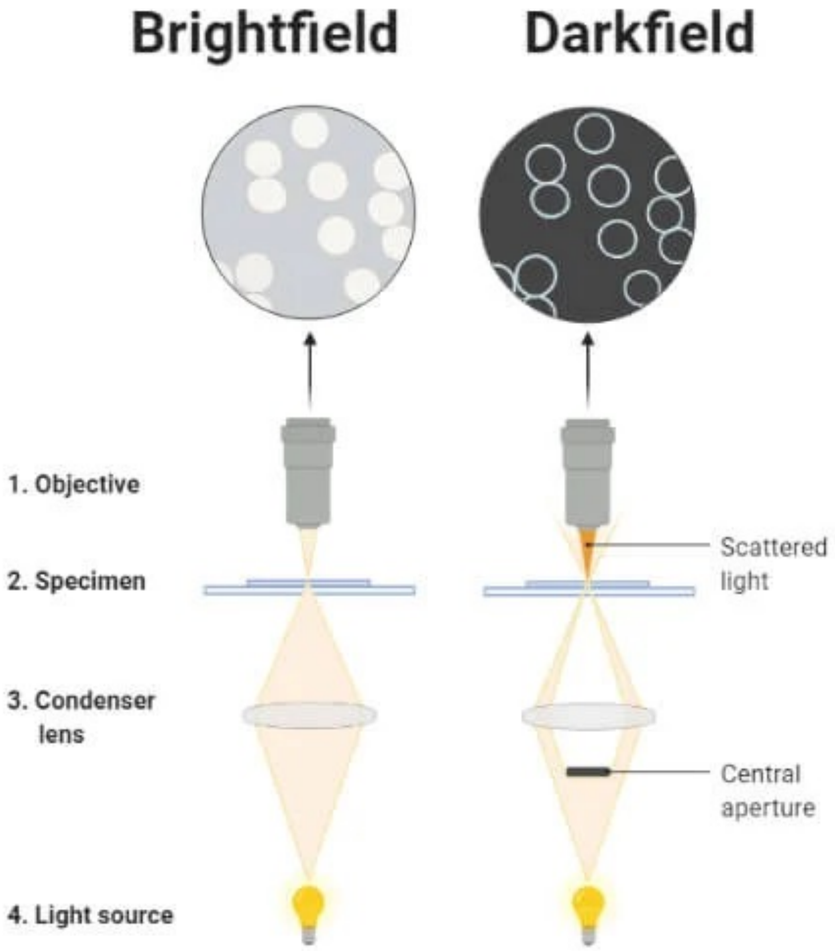
Slow scanning

Sensitive to vibration

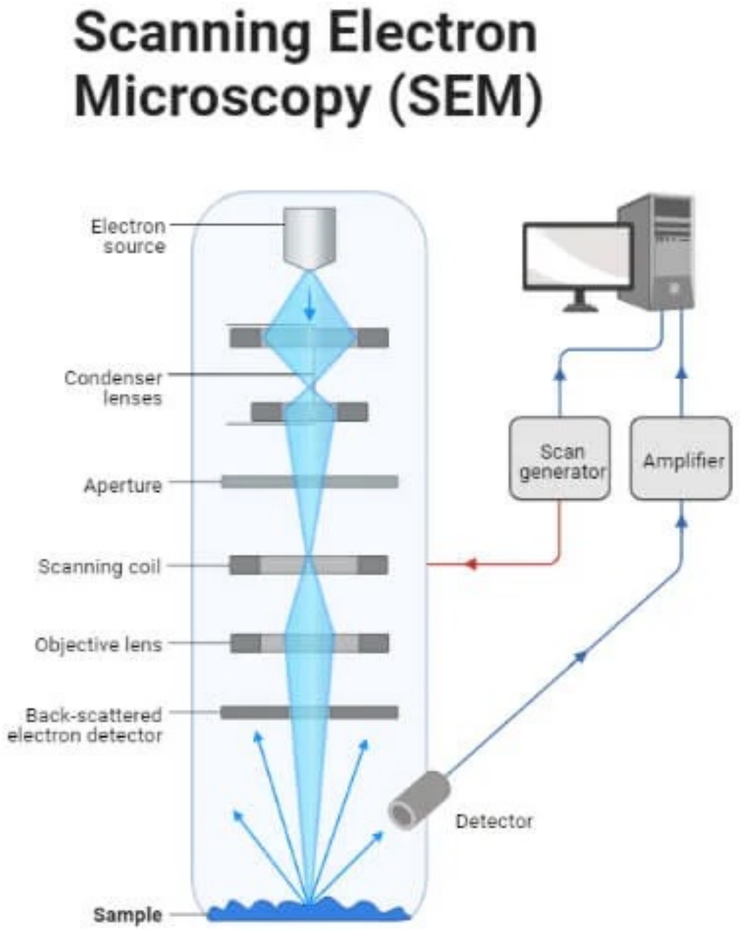
CHEMINA

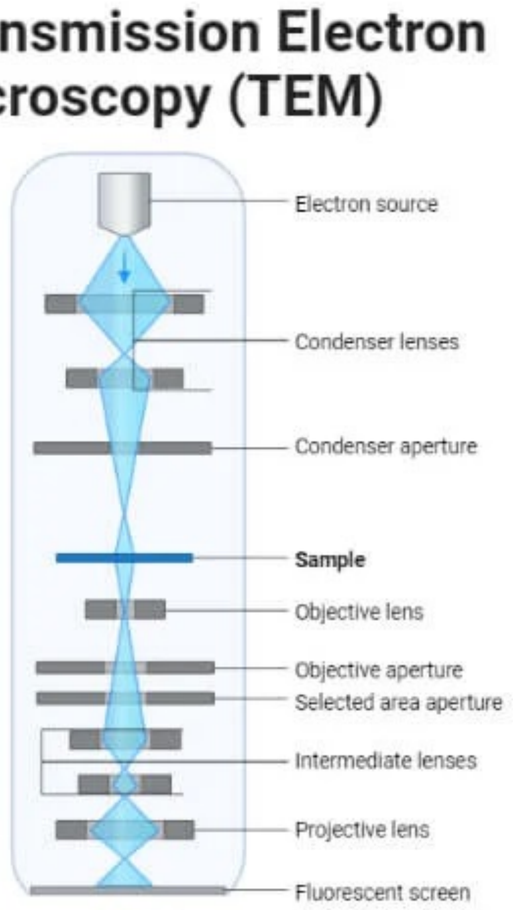
Electron Microscopy to Visualize Real Surfaces and Materials

Light Microscopy



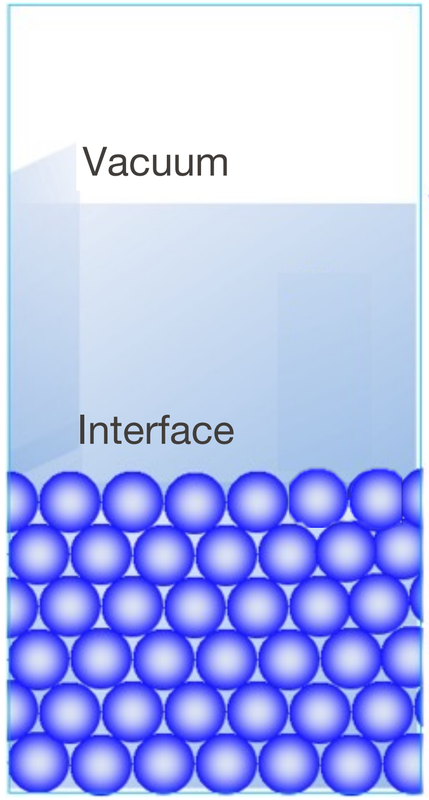
Electron Microscopy





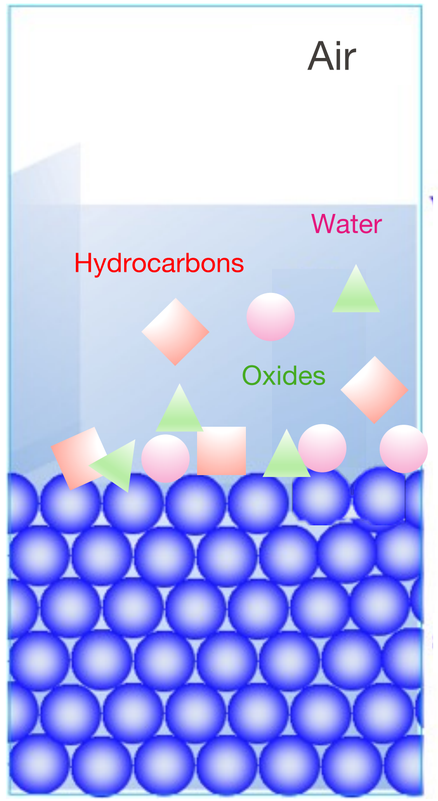
Energy Minimization as the Unifying Principle

Vacuum interface (Ideal surface)

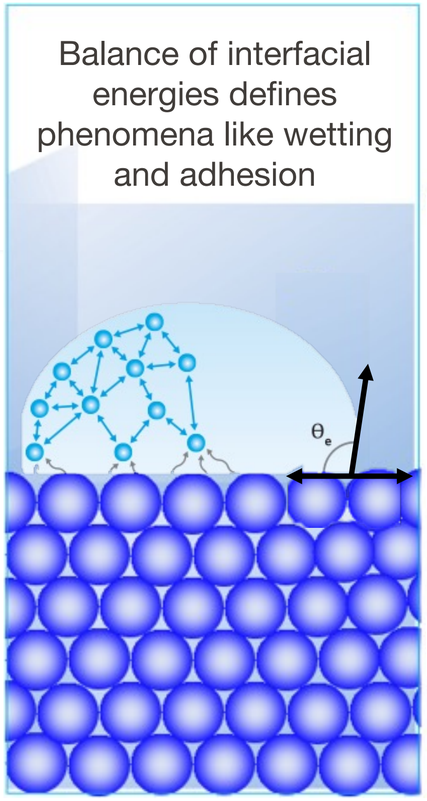


Perfect crystal lattice

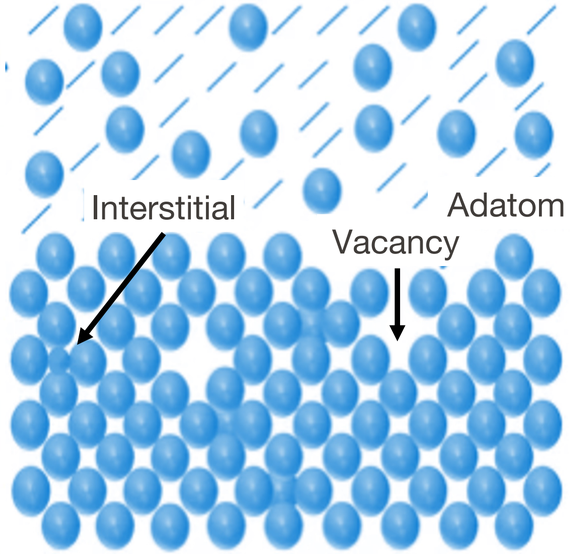
Contaminated surface (Real surface)



Real surfaces exist at interfaces

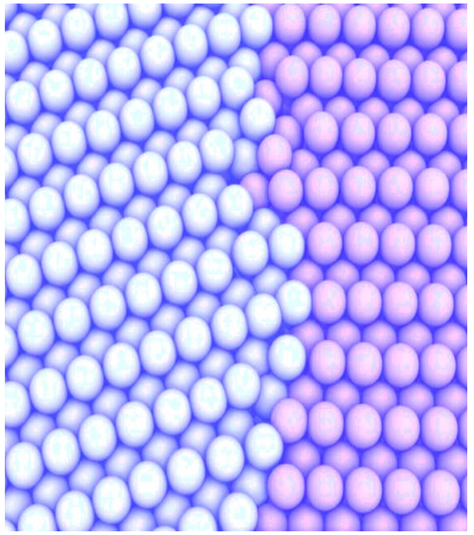


Defects at the interface



No interface is perfectly ordered – defects appear at multiple scales

Interface between polycrystals



Grain boundaries where atomic orientation changes

CHEMENA

Prof. Nako Nakatsuka
nako.nakatsuka@epfl.ch

EPFL
Laboratory of Chemical Nanotechnology
Campus Biotech
Chemin des Mines 9
1202, Geneva

https://www.epfl.ch/labs/chemina/