



## Surfaces and interfaces

Definitions (external and internal surfaces)

Thermodynamics

Structure

**MAURO PALUMBO**

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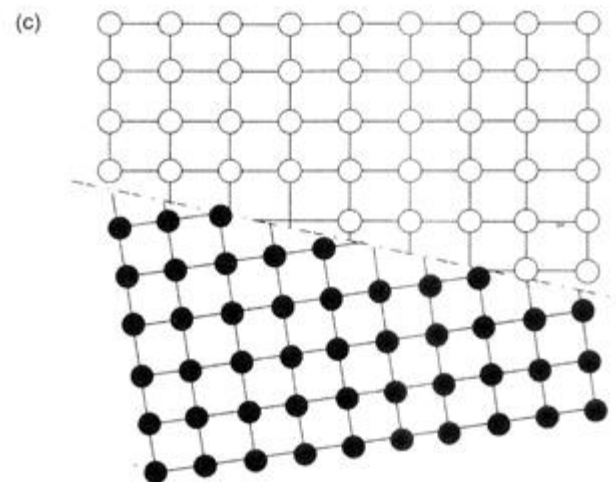
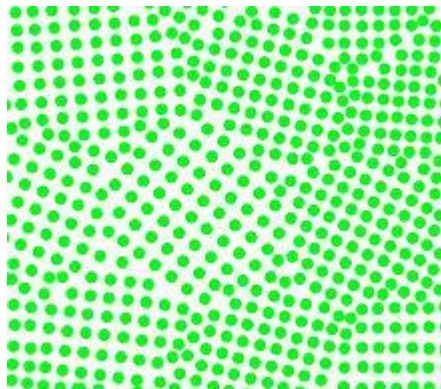
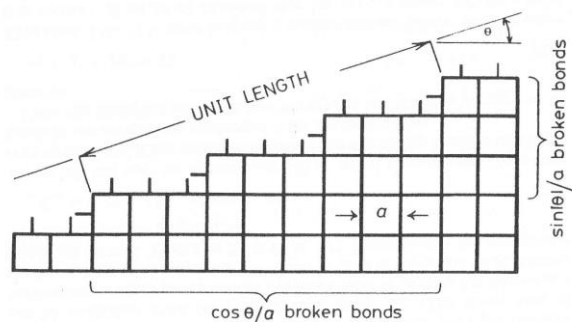
**mauro.palumbo@unito.it**

Dipartimento di Chimica

Università di Torino

Via Pietro Giuria 9 - 10125 Torino

1. Free surfaces of a solid or liquid (solid/vapour or liquid/vapour interfaces)
2. Grain boundaries ( $\alpha/\alpha$  interfaces)
3. Interphase interfaces ( $\alpha/\beta$  interfaces)



**Surface tension**, (refers to liquid surfaces, stress-free, N/m)

Surface tension is a phenomenon **observed at the liquid-air interface, attributable to the cohesive forces between liquid molecules**. It is the property of **the liquid surface** that causes it to **behave as an elastic sheet**. It can be thought of as **a manifestation of surface energy in liquids**, where it's the force per unit length or the energy per unit area required to expand the surface of the liquid.

**Surface/interface energy** (reversible work needed to create a unit surface/interface, J/m<sup>2</sup>)

Surface energy is **a measure of the excess energy at the surface of a material compared to its bulk**. It is defined as the work required to create a unit area of surface. For solids, surface energy quantifies the disruption of intermolecular bonds when a surface is created, which makes atoms at the surface more energetic than those in the interior.

$$dW_{S(T,P)} = \gamma dA$$

$$\gamma = \lim_{\delta A \rightarrow 0} \frac{\delta W_{S(T,P)}}{\delta A}$$

**Surface/interface stress** (work needed to deform reversibly a surface in solids, depends on direction, elastic regime), N/m)

Surface/interface stress **is a tensorial quantity** that describes the force per unit length acting along the surface of a solid due to the imbalance of intermolecular forces at the surface/interface. It is analogous to surface tension in liquids but applies to solid materials. Surface **stress includes both the distortive (change in shape) and dilatational (change in area) responses of a material's surface under stress.**

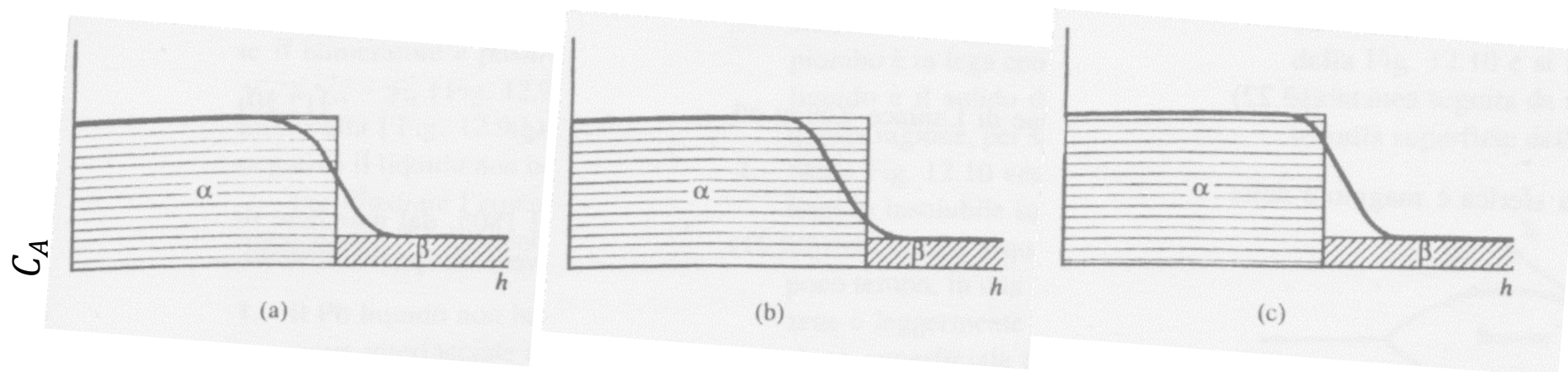
$$\sigma = \lim_{\delta l \rightarrow 0} \frac{\delta p'}{\delta l}$$

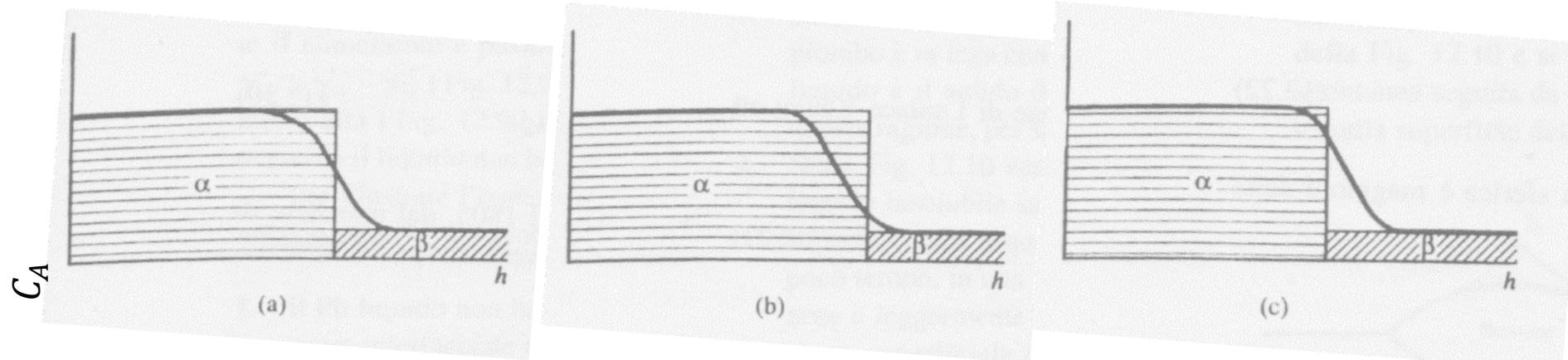
Notes:

- Units are equivalent (N/m and J/m<sup>2</sup>)
- Typical symbols are  $\gamma$  and  $\sigma$

**Sharp and diffuse interfaces** (change in atomic configuration at either very short or considerable distance)

**Surface phase** (surface atoms/molecules treated as a phase)/ **Gibbs dividing surface** (properties change at a single plane)





**Gibbs surface is a conceptual tool used in the thermodynamics of surfaces to simplify the analysis of interfacial phenomena.** In a phase boundary, the transition from one phase to the other is not abrupt but occurs over a finite distance with a gradient in properties. This gradual change poses challenges for thermodynamic analysis since properties like density vary continuously across the interface.

To facilitate the mathematical treatment of surface phenomena, **Gibbs introduced the concept of an imaginary dividing surface that separates the two phases.** This dividing surface is chosen such that certain conditions are satisfied, making it possible to assign surface excess quantities to the interface. The exact position of the Gibbs dividing surface depends on the convention chosen for its definition.

By using the Gibbs dividing surface, one can treat the interface as if it were a thin, distinct phase itself, with its own thermodynamic properties. This significantly simplifies the mathematical treatment of surfaces and interfaces in thermodynamics.

$$E = NE_b + AE_s$$

$E_b, S_b, G_b \rightarrow$  internal energy, entropy and Gibbs free energy of the bulk

$$S = NS_b + AS_s$$

$E_s, S_s, G_s \rightarrow$  internal energy, entropy and Gibbs free energy of the surface (per unit area)

$$G = NG_b + AG_s$$

$$G_s = H_s - TS_s = E_s + PV - TS_s$$

Gibbs free energy of the surface (per unit area) related to surface enthalpy and entropy

Solid surface energy can change in two ways:

1. By increasing or decreasing the physical area of the surface (for example by adding atoms from the bulk)
2. By changing the position of the atoms at the surface by elastic deformation (for example surface relaxation)



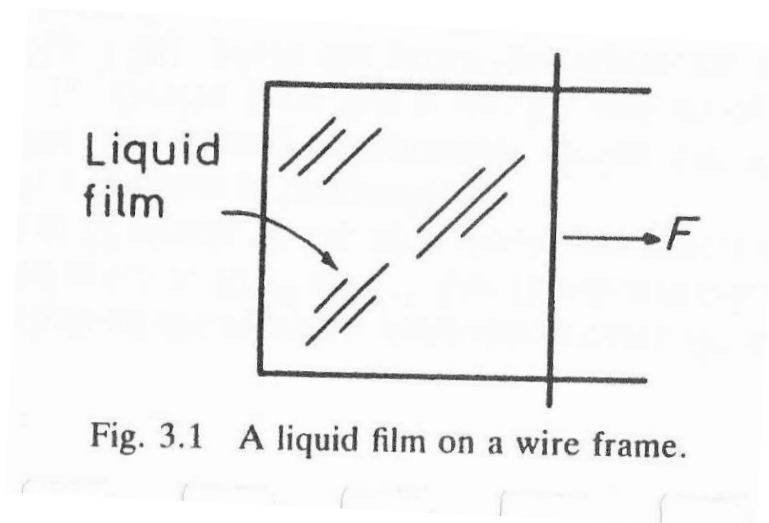
$$dW_{S(T,P)} = d(AG_S) = G_S dA + dG_S A$$

If we can neglect the surface stress (for example for a liquid),  $dG_S = 0$

$$dW_{S(T,P)} = G_S dA = \gamma dA$$

$\gamma$  is the most common symbol used for  $G_S$

$$G_S = \gamma$$



$$dW_{S(T,P)} = F dA = \gamma dA$$

$$F = \gamma \quad \text{force per unit length}$$

For a single component:

$$dG = -SdT + VdP + \gamma dA$$



**Creation of a surface:** the dark atom has less nearest neighbours with respect to bulk atoms → surface energy.

In liquids, no surface stress.

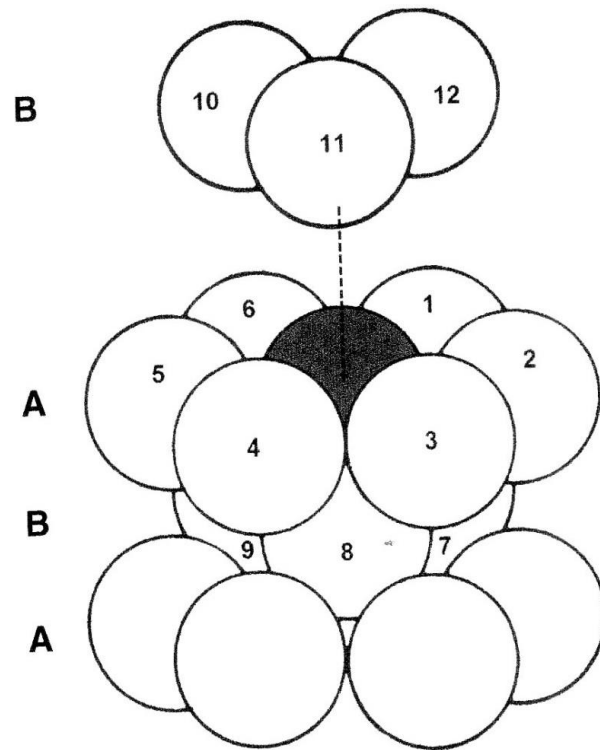
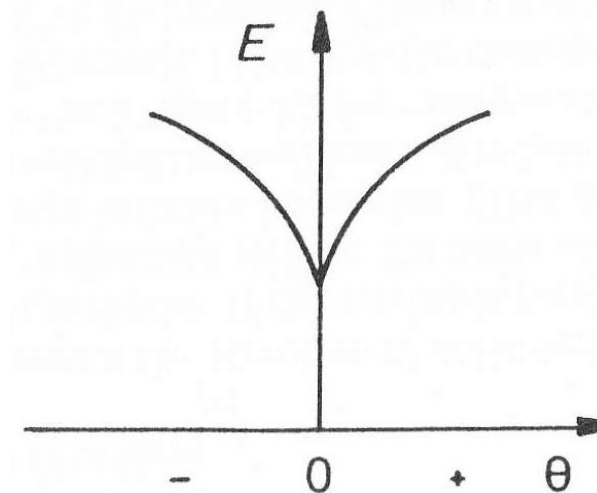
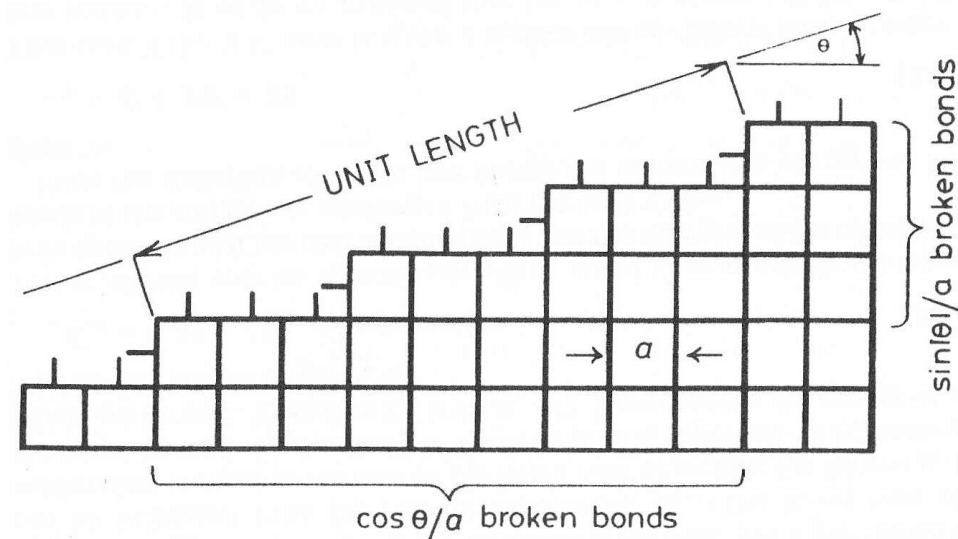


Table 2.1 *Experimental values of the surface energy ( $\gamma$ ) of liquids at the indicated temperature*

Liquid	$T$ (°C)	$\gamma$ (mJ/m <sup>2</sup> )
H <sub>2</sub> O	25	72.1
Ethanol	20	22.4
Benzene	20	28.9
Al	600	866
Al-33 wt% Cu	700	452
Cu	1,083	1,355
Au	1,063	1,138
Fe	1,535	1,855
Ni	1,455	1,780
Ni-20 wt% Cu	1,300	1,700
Ni-40 wt% Cu	1,300	1,460
Ni-60 wt% Cu	1,300	1,310
Ni-80 wt% Cu	1,300	1,125
Ag	951	910
NaCl	801	114
Na <sub>2</sub> SO <sub>4</sub>	884	196
Na <sub>2</sub> SiO <sub>3</sub>	1,000	250
Al <sub>2</sub> O <sub>3</sub>	2,080	700

## Energy of external surfaces

External surface of a 2-D crystal of pure component A in which the lattice parameter is  $a$  and the bond energy between A-A atoms is  $\epsilon_{AA}$



$$E_{SV} = (\cos \theta + \sin |\theta|) \epsilon_{AA} / 2a^2 \quad \text{Solid-vapour surface energy}$$

**Surface energy depends on the orientation** for solid phases.

In solids, surface energy depends on lattice plane.  
Average values are given below.  
Surface stress depends on lattice plane and direction of deformation.

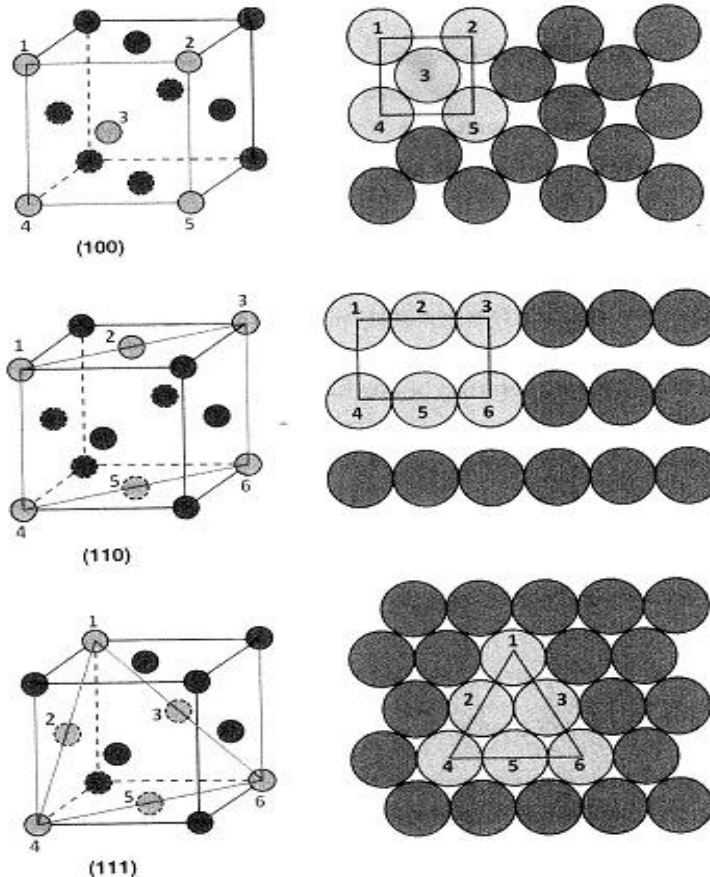


Table 2.2 *Experimental values of the surface energy ( $\gamma$ ) of solids at the indicated temperature*

Solid	$T$ (°C)	$\gamma$ (mJ/m <sup>2</sup> )
Al	450	980
Al-84 at% Cu	800	1,720
Cu	970	1,650
Cu-20 at% Au	850	1,160
Cu-40 at% Au	850	930
Cu-60 at% Au	850	910
Cu-80 at% Au	850	1,140
Au	1,000	1,400
Fe ( $\delta$ phase)	1,450	1,950
Fe ( $\gamma$ phase)	1,350	2,100
Ni	1,060	2,280
Ag	950	1,100
NaCl (100)	25	300
LiF (100)	-196	340
Al <sub>2</sub> O <sub>3</sub> (average)	1,850	905

***A grain boundary is a region that separates two grains, or crystallites, in a polycrystalline material.*** Grains are individual crystals within a material that have a specific lattice orientation; when multiple grains come together, they do not generally share the same orientation. The grain boundary is the interface between these differently oriented crystals.

They are divided in:

- **Small or low-angle grain boundaries** (misorientation angle  $<10-15^\circ$ )
- **High-angle grain boundaries** (misorientation angle  $>10-15^\circ$ )

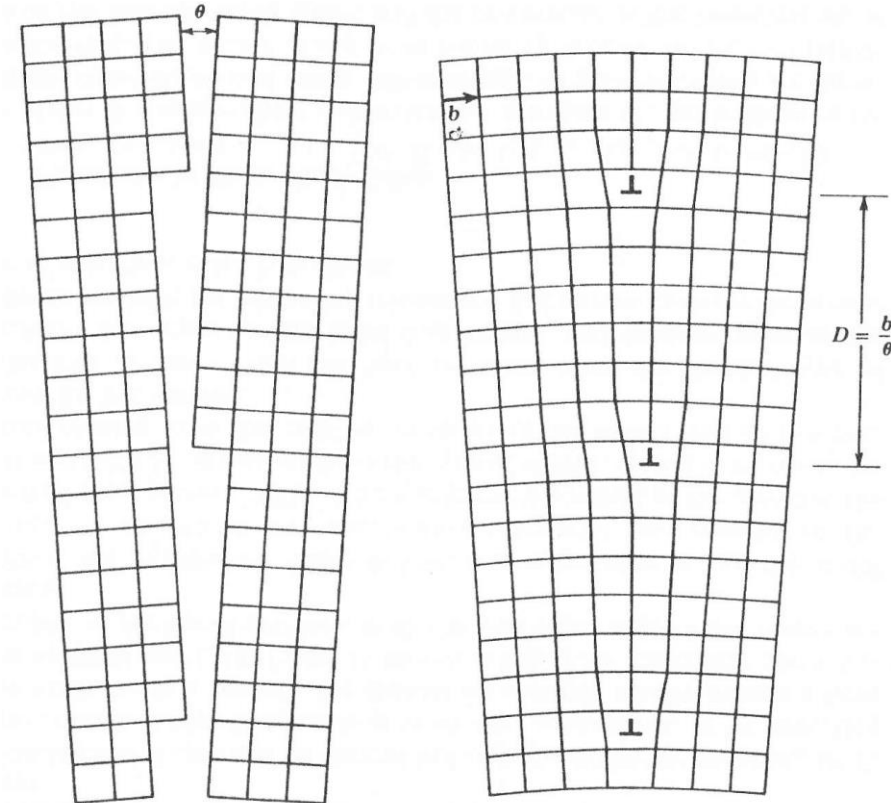
**Low-angle grain boundaries** (s.a.g.b.): figures depict two crystals joined to form a s.a.g.b. In real metallic crystals they often form by dislocation pile up (sub-grain boundaries).

Set of  $n$  interfacial dislocations at distance,  $D$ :  
modulus of Burgers vector,  $b$ , divided by  $\sin \theta$

$$D = \frac{b}{\sin \theta} \cong \frac{b}{\theta}$$

so the interfacial energy is approximately  
proportional to the density of dislocations:

$$\gamma \approx \frac{1}{D} \propto \theta$$



Note: the Burgers vector provides a quantitative measure of the magnitude and direction of the lattice distortion caused by a dislocation.



**High-angle boundaries** have misorientation  $> 10-15^\circ$  but may display site coincidence. Tend to have higher energy because of the less optimal atomic packing and greater atomic disorder. are generally more mobile than low-angle boundaries under the application of stress or thermal energy. Their mobility is a critical factor in processes like recrystallization and grain growth.

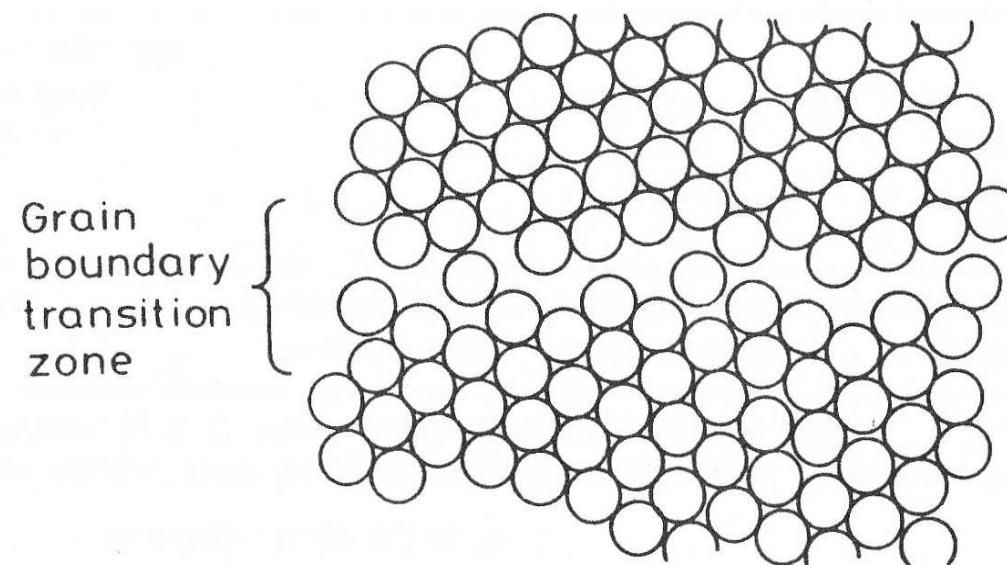
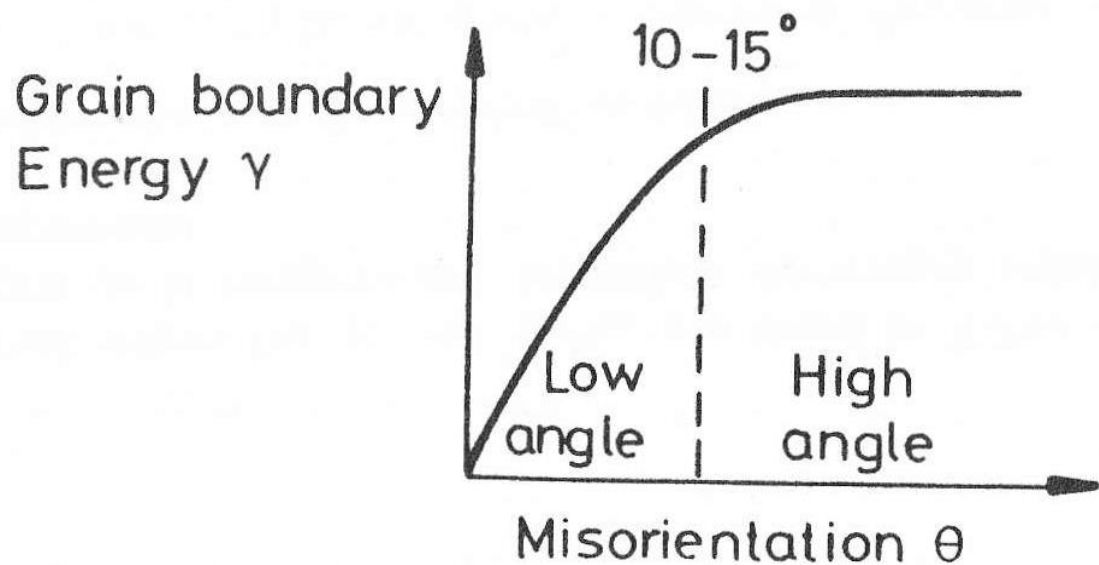


Fig. 3.10 Disordered grain boundary structure (schematic).

**Site coincidence:** *atoms from two adjacent grains (or crystallites) align or match at certain positions across the grain boundary.*

In some orientations, a fraction of the lattice sites from one grain will coincide with those of the neighboring grain, *leading to a reduction in the boundary energy.* These specific orientations are characterized by a higher degree of atomic matching across the boundary and tend to be more stable.

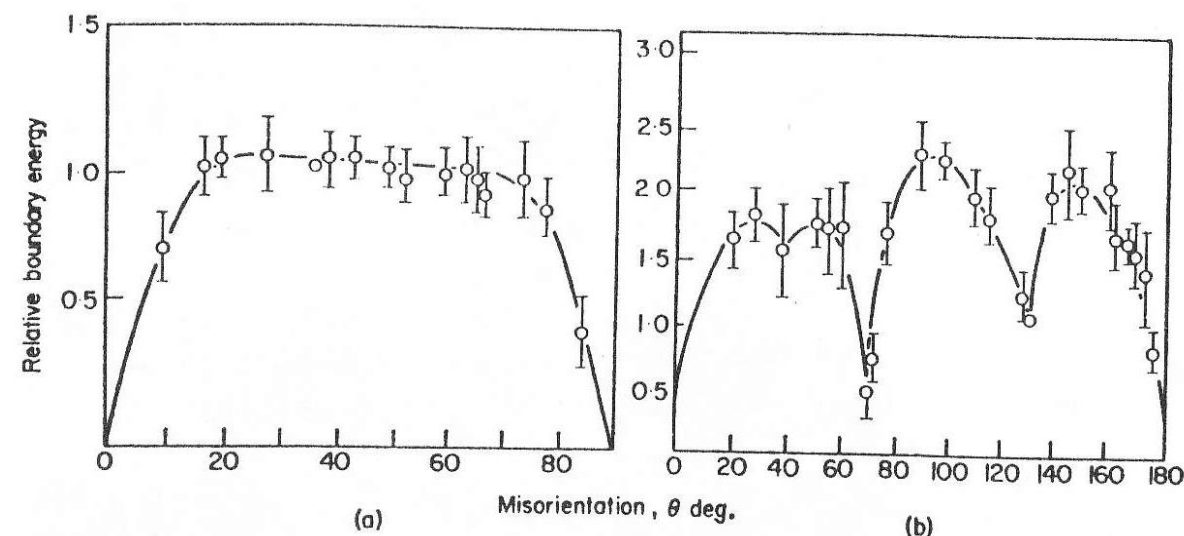
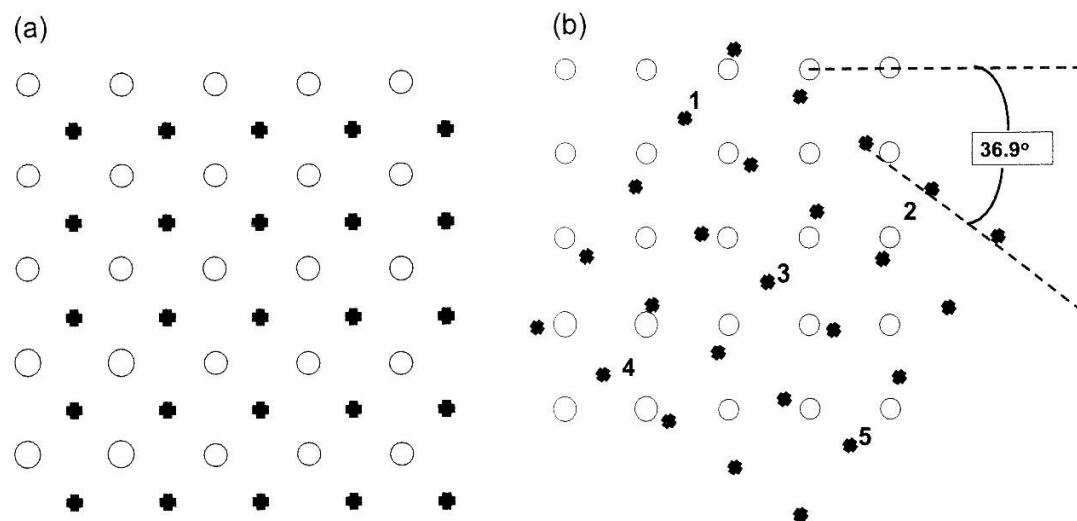
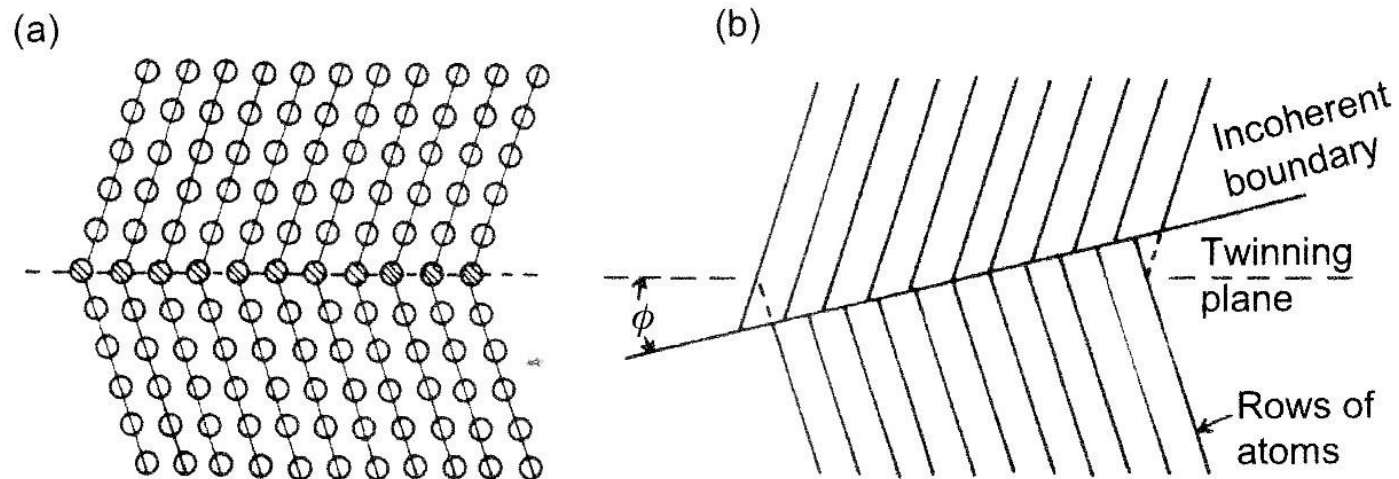


Fig. 3.13 Measured grain boundary energies for symmetric tilt boundaries in Al (a) when the rotation axis is parallel to  $\langle 100 \rangle$ , (b) when the rotation axis is parallel to  $\langle 110 \rangle$ . (After G. Hasson and C. Goux, *Scripta Metallurgica*, 5 (1971) 889.)



**Twin boundaries**: refer to a specific type of grain boundary that occurs **when two regions of a crystal share the same type of lattice structure but are mirrored reflections of each other across the boundary**. This phenomenon is known as twinning, and it results in a special crystallographic relationship between the two regions, making twin boundaries distinct from other types of grain boundaries.

Can be **coherent** and **incoherent** when twinning plane and boundary do not coincide



For coherent twins energy is low because of high symmetry; for incoherent twin is intermediate with respect to high angle boundaries.

Solid/vapor interface energies are higher.

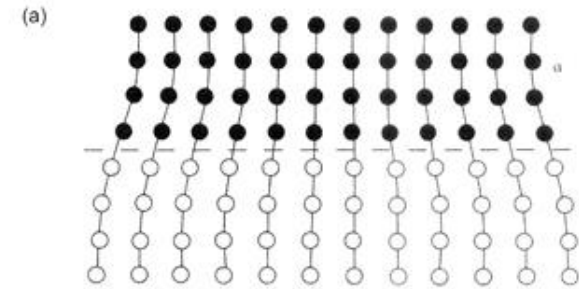
Table 4.3 *A comparison of values for several types of boundary in pure Cu*

Type of boundary	$\gamma$ (mJ/m <sup>2</sup> )
Solid/vapor (average)	1,400
High-angle grain boundary	450
Incoherent twin boundary	300
Coherent twin boundary	20

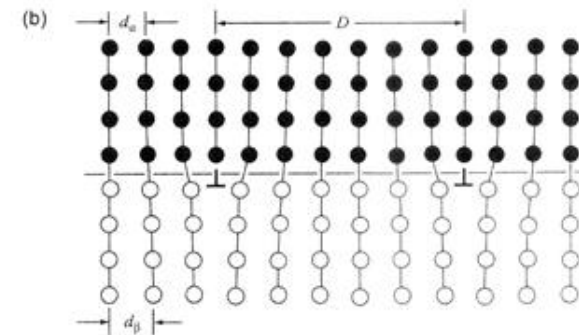
In metallic materials, interfaces between two different solid phases are crucial in determining the material's properties, especially its mechanical strength, ductility, and thermal stability. These interfaces can be classified based on their coherence, which describes the degree of atomic matching across the interface. The three main types of interfaces are **coherent**, **semi-coherent**, and **incoherent**.

**a) Coherent interfaces:** the atoms across the boundary are in a continuous lattice arrangement, with the crystallographic planes of the two phases perfectly aligned. This means there is a one-to-one match of atoms across the interface, maintaining the periodicity of the crystal lattice.

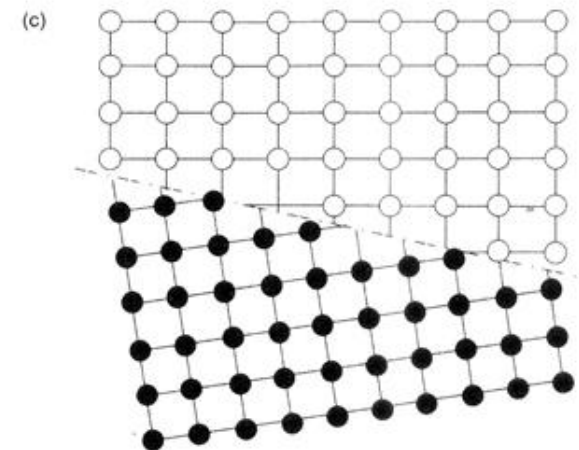
The **interfacial energy for coherent interfaces**  $\gamma_{chem}$  **depends on phase composition and is low**. They can be sources of strain because of the difference in lattice parameters (size and shape) between the two phases, leading to coherency strain. Coherent interfaces strongly influence mechanical strength and can lead to hardening effects in materials (ex. Al alloys).



coherent



semi-coherent



incoherent

**b) Semi-coherent interfaces** have partial alignment of the crystal lattices of the two phases, with some regions of good fit interrupted by misfit dislocations. These dislocations are defects that accommodate the lattice mismatch between the two phases, allowing for partial coherence.

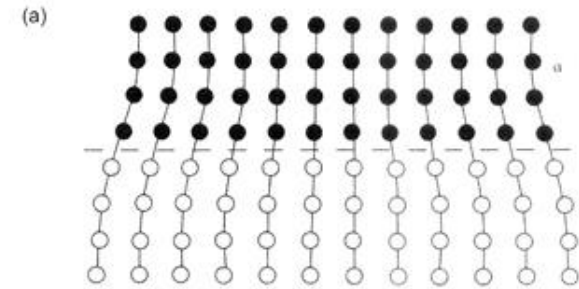
The energy of semi-coherent interfaces is higher than that of coherent interfaces due to the presence of misfit dislocations, separated by  $D = d_\beta / \delta$ , which introduce localized regions of strain and disorder:

$$\gamma_{semicoher} = \gamma_{chem} + \gamma_{disl}$$

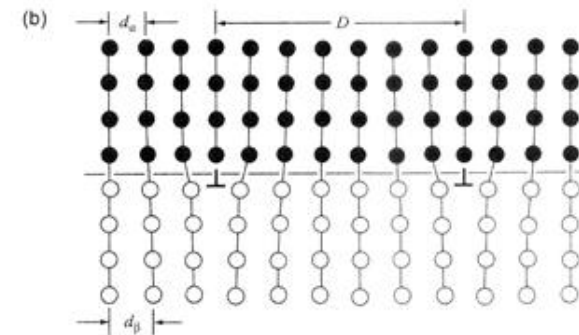
Misfit is defined as

$$\delta = \frac{d_\beta - d_\alpha}{d_\alpha}$$

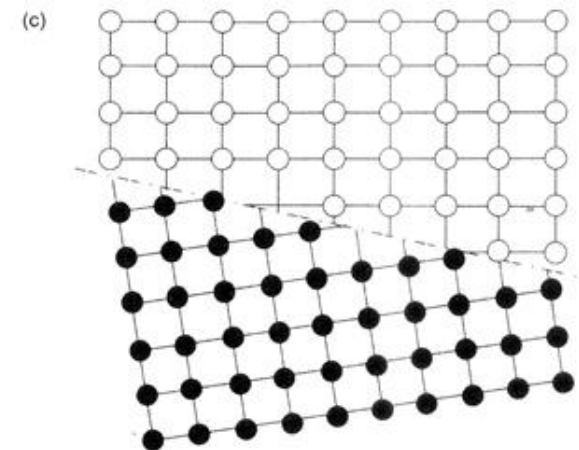
The presence of misfit dislocations at **semi-coherent interfaces** can strengthen the material by impeding the motion of dislocations. This can enhance the material's mechanical properties, such as yield strength.



coherent



semi-coherent



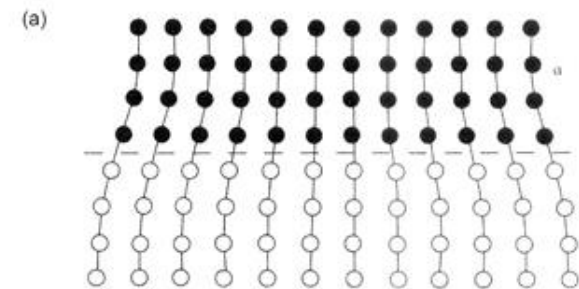
incoherent



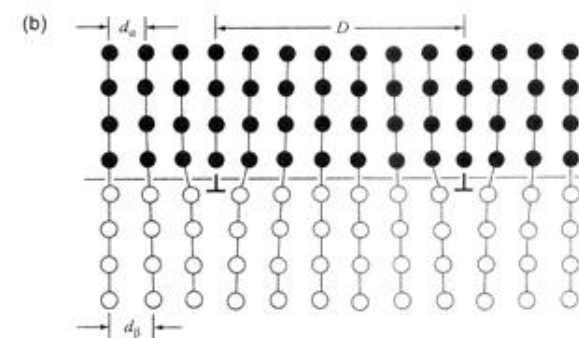
**c) Incoherent interfaces** lack any crystallographic relationship between the adjoining phases, meaning there is no continuity of the lattice planes across the boundary. The atomic arrangement is highly irregular, and there is no match between the atoms of the two phases.

**These interfaces have the highest energy** due to the significant lattice mismatch and disorder. The lack of a coherent structure leads to a high degree of atomic misfit.

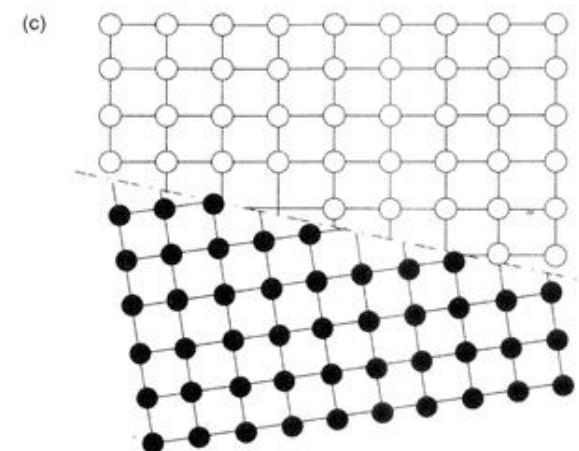
Incoherent interfaces **are less effective at blocking dislocation motion** than coherent or semi-coherent boundaries, which can influence the material's mechanical properties. However, they can be beneficial for properties like creep resistance, as they are stable at high temperatures and under mechanical stress.



coherent

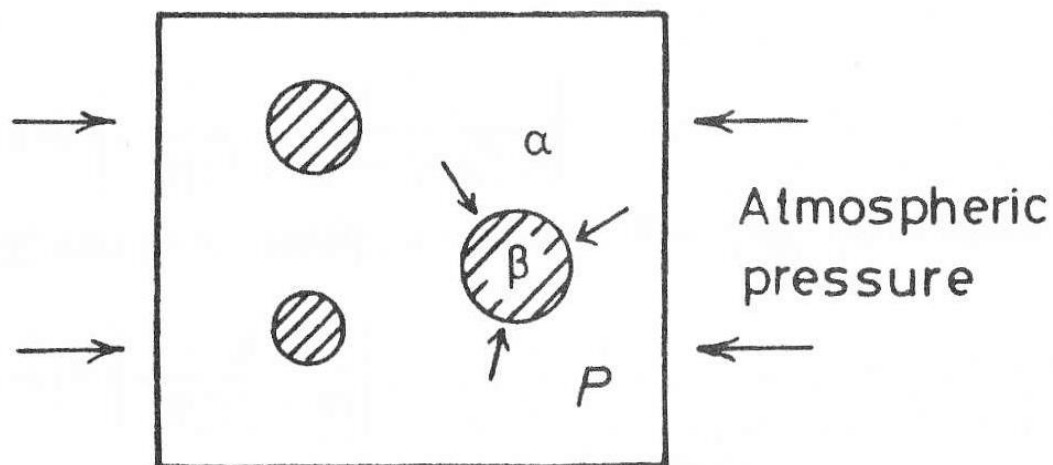


semi-coherent



incoherent

# Effect on interfaces on equilibrium: Laplace-Young equation



Laplace-Young equation

$$\Delta P = \gamma \left( \frac{\partial A}{\partial V} \right)_T$$

The **Laplace-Young equation** describes the pressure difference across the interface of two phases due to surface tension.

For a spherical particle\*

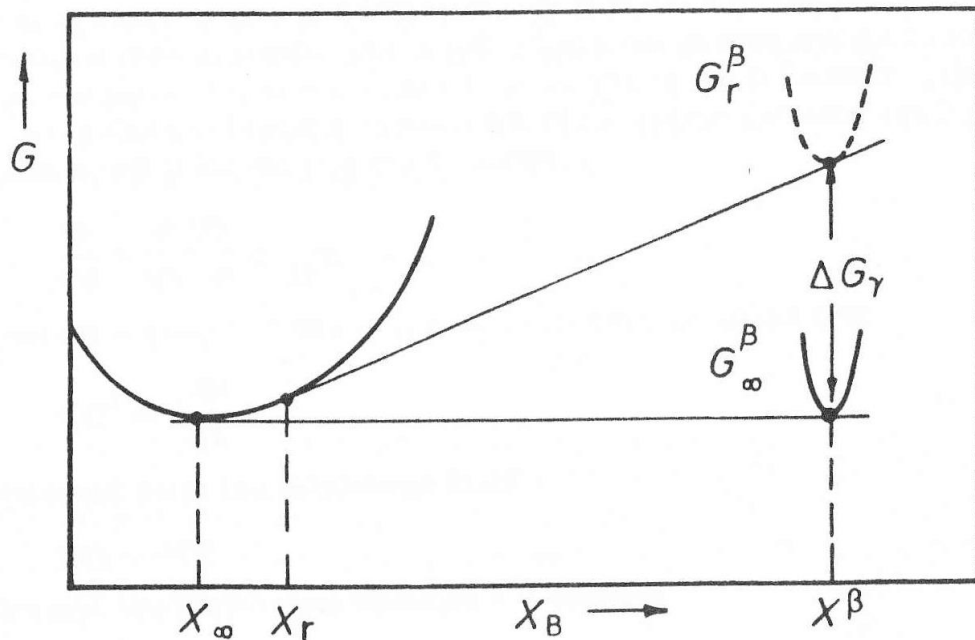
$$\Delta P = \frac{2\gamma}{r}$$

The **curvature of the surface leads to a pressure difference**, with higher pressure on the concave side (inside) and lower pressure on the convex side (outside) of the curvature. This pressure difference is what holds droplets or bubbles in their shape. The equation highlights that smaller droplets or bubbles (with smaller radii of curvature) have a larger pressure difference across their surface. This principle explains phenomena like the tendency of smaller droplets to merge into larger ones, reducing overall surface energy.

\*you can prove this by remember the chain derivation  
rule:  $\frac{\partial A}{\partial V} = \frac{\partial A}{\partial r} \frac{\partial r}{\partial V}$  and  $A = 4\pi r^2$ ,  $V = \frac{4}{3}\pi r^3$ ...

# Effect on interfaces on equilibrium:

## Gibbs-Thomson effect



The **Gibbs-Thomson effect** describes how the curvature of a surface affects the thermodynamic properties of a system.

$$\Delta G_\gamma = \Delta PV = \frac{2\gamma V_m}{r}$$

Small particles have higher free energies

It explains, for example, how the melting point of a material changes with the size of its particles.

**Materials with highly curved surfaces (small particles or thin films) have different thermodynamic properties than bulk materials.** For example, nanoparticles have a lower melting point than the same material in bulk form. This is because the excess surface energy of smaller particles affects the energy balance required for phase transformations.

The Gibbs-Thomson effect **is critical in understanding the stability of phases at the nanoscale, influencing phenomena like the nucleation, growth and dissolution of particles**, the behavior of catalysts, and the sintering of materials.