EPFL
École
polytechnique
fédérale
de Lausanne

Institute of Materials - Institute of Bioengineering
sunmil.epfl.ch

SuNMIL
Supramolecular
NanoMaterials
and Interfaces
Laboratory

Surface and Interfacial Energy
Lesson 2

MSE 304

Francesco Stellacci

桑缪 썬밀 सानमिल ΣουNMιΛ سنمل CaHMПЛ

What is a Surface?

continuum

- Surfaces are the terminal limiting planes for objects, they are two-dimensional complex planes

classical TD

- Surfaces are two-dimensional defects in materials, specifically they are ***topological*** defects containing under-coordinated units.

statistical mechanics

atomistic view

Definition of Interfaces

$\alpha \mid \beta$

- When two surfaces come in atomic contact, they form an interface; hence interfaces are topological defects formed by the joining of two surfaces

- Interfaces are topological defects formed by the joining of two surfaces

Do Surfaces Exist?

or we have only interface

only in vacuum

Plan of the Course

Solid-Vapor Interfaces

α | β

solid | vapor

surface

$\lim_{P_r \to 0} \beta$

catalysis and electronics

Plan of the Course

Solid-Liquid Interfaces

α solid | β liquid

(α liquid | β vapor)

biology

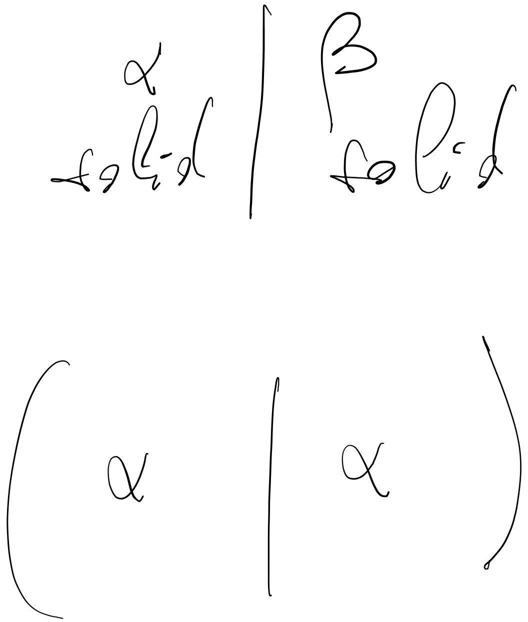
catalysis

sensing

corrosion

Plan of the Course

Solid-Solid Interfaces



all polycristalline material

electronic materials

The Point

What have we learned?

surface

interface

What is the background we really need?

→ thermodynamics

→ crystallography

Definition of Surface Energy

There are many definitions of surface energy, the reason is that the field has derived from various disciplines and has developed through the years in an incoherent way. There is still no real agreement on the terminology and the symbols to be used. As often in this case all definitions mostly converge to the same scientific concepts.

Already in 1878, Gibbs shows that surface energy is a thermodynamic quantity, and introduces the concept of '*excess surface free energy*'

Let's go in order.

First let's define the energy of a multi-component system (as done in a standard thermodynamic approach)

$$dG = dH - TdS = V\underline{dp} - S\underline{dT} + \sum_i \mu_i \underline{dn_i} + \underbrace{\vec{E}\,d\vec{D} + \vec{H}\,d\vec{B}}_{\simeq 0} + \gamma\, dA$$

$$dG = 0 \qquad \left(\frac{\delta G}{\delta A}\right)_{T,P,n_i} = \gamma$$

$$dG < 0$$

spontaneous process

$$\frac{J}{m^2} = \frac{N}{m}$$

Definition of Surface Energy

The initial definition of surface energy, is the free energy needed to create a surface of unit area.

$$\left(\frac{\delta G}{\delta A}\right)_{T,P,n_i} = \left(\frac{\delta U}{\delta A}\right)_{V,S,n_i} \equiv \gamma$$

Gibbs shows that this energy has to be positive. Hence the quantity γ was a quantity always positive and hence called it 'excess surface free energy' The unit are those of J/m2 or equivalently N/m

$$U = W + Q$$

$$\hookrightarrow \underset{\sim}{Q = 0} \quad [S \text{ const}]$$

$$dW = \gamma dA$$

$$dW > 0$$

$$\boxed{\gamma > 0}$$

$$dU\Big|_{V,S,n_i} = dW = (dG)_{T,P,n_i} = \gamma dA$$

Alternative Definitions for Excess Surface Free Energy

There are alternative definitions.

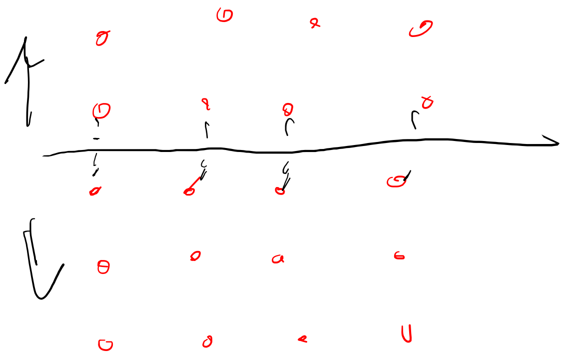
Surface Energy (γ)

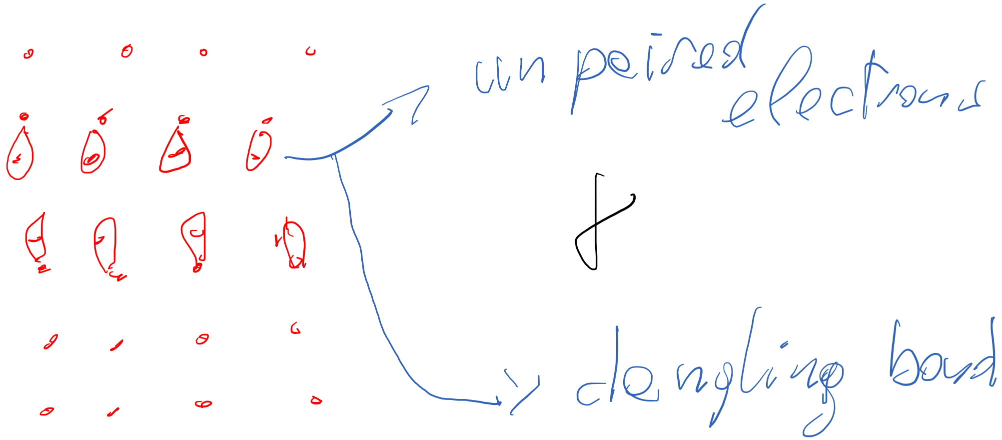
Surface Energy is the reversible work to create a surface of unit area at constant temperature and pressure, while keeping all of the atomic positions fixed to their bulk position.

An equivalent but probably more correct definition is:

Israelshvili

Surface Energy is half of the reversible work per unit area needed to reversibly separate an infinite material in two parts at constant temperature and pressure, without allowing for any atomic rearrangement.

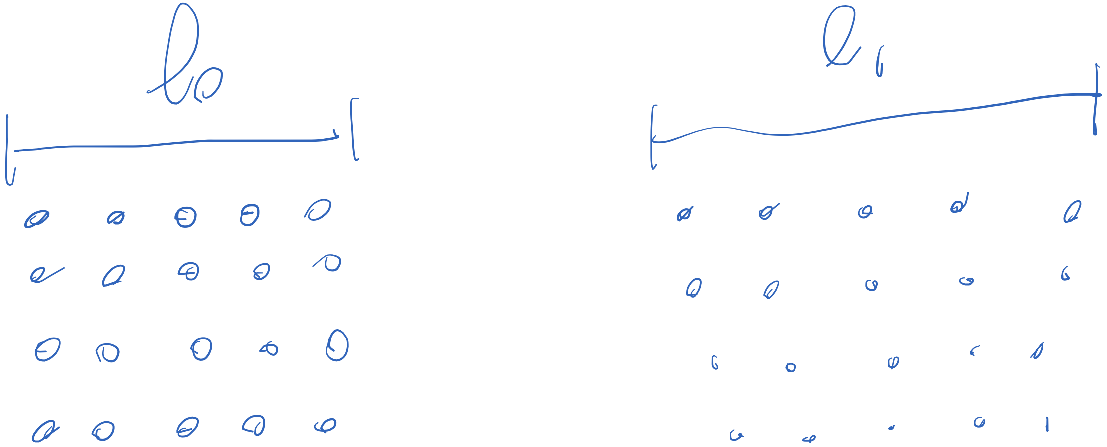




Alternative Definitions for Excess Surface Free Energy

Surface Tension σ

Surface tension is the homogenous and reversible work needed to extend the surface of a material of a unit area.
Here is a rationale:



The Key Problem in Understanding Surface Energy/Tension

How do we create new surface area in a material?

cut bonds

stretch bonds

Definition of Surface Stress

Surface Stress (f or f_{ij})

This is the more general definition.

Surface Stress is the energy required to reversibly create a unit area of surface at constant temperature and pressure.

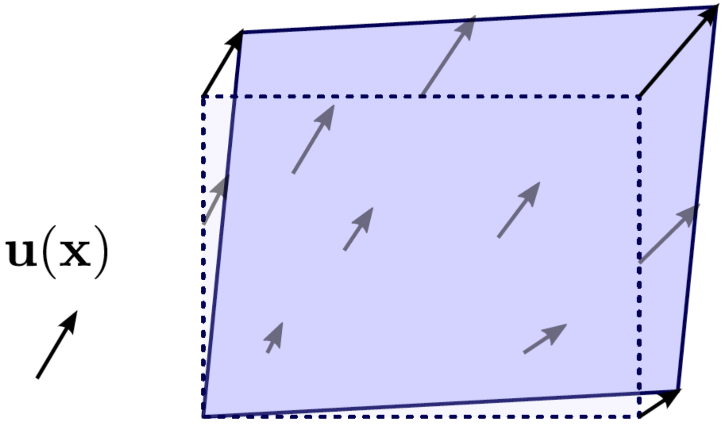
f_{ij}
surface
stress
tensor

$e \cdot f$

ε

$$\begin{bmatrix} e_{11} & e_{12} \\ e_{21} & e_{22} \end{bmatrix}$$

$$\begin{bmatrix} f_{11} & f_{21} \\ f_{12} & f_{22} \end{bmatrix}$$



$$\mathrm{d}e_{ij} = \partial u_i / \partial x_j$$

$$\underline{\mathrm{d}W} = A \sum_{ij} f_{ij} \mathrm{d}e_{ij}$$

surface stress tensor

strain tensor

Relationship between f_{ij} and γ

To understand the relationship between surface stress and excess surface free energy we need to better understand the thermodynamics of the problem.

Generic Definition of the Free Energy of a realistic system that contains one or multiple surfaces

∞ size

$$U = N_B \langle u_B \rangle$$

finite size

$$U = N_B \langle u_B \rangle + N_S \langle u_S \rangle = N_B u_B + A \cdot u_S$$

J/atom

J/m²

B terms are kept constant

$$S = N_B s_B + A S_s \qquad G = N_B g_B + A G_s$$

$$dW\Big|_{T,P,n_i} = dG\Big|_{T,P,n_i} = d\left(N_B g_B + A G_s\right)\Big|_{T,P,n_i} = d\left(A G_s\right)$$

Relationship between f_{ij} and γ

$$dW\Big|_{T,P,n_i} = d(AG_s)\Big|_{T,P,n_i}$$

surface energy → $d(AG_s) = G_s\, dA$ $\qquad G_s = \gamma$

↳ $\boxed{\underline{dG_s = 0}}$ → $dW = \gamma\, dA$

assumption

$$d(xy) = y\,dx + x\,dy$$

$$G = N_B g_B + \gamma A$$

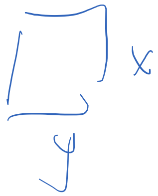
Relationship between f_{ij} and γ

$$d(AG_s)\Big|_{T,P,n_i} = \left(\underbrace{G_s\, dA}_{\text{cutting bonds}} + \underbrace{A\, dG_s}_{\text{changing the energy of a bond}}\right)_{T,P,n_i} = dW\Big|_{T,P,n_i}$$

$$dW\Big|_{T,P,n_i} = \vec{f}\,\underbrace{d\vec{A}} = A\underbrace{\sum_{ij} f_{ij}\, de_{ij}}$$

$$\delta_{ij} \begin{cases} \rightarrow 1 & i=j \\ \rightarrow 0 & i\neq j \end{cases}$$

$$dA = A\sum_{ij}\delta_{ij}\, de_{ij} = dA = A\sum_i de_{ii}$$



$$dA = A(\Delta x + \Delta y)$$

$$d(AG_s) = G_s A \sum_{ij}\delta_{ij}\, de_{ij} + A\sum_{ij}\left(\frac{\partial G_s}{\partial e_{ij}}\, de_{ij}\right)$$

Relationship between f_{ij} and γ

$$d(AG_s)_{T,P,n_i} = dW\big|_{T,P,n_i} = A\sum_{ij}\left(G_s\delta_{ij} + \frac{\delta G_s}{\delta e_{ij}}\right)de_{ij}$$

$$G_s = \gamma$$

$$= A\sum_{ij}\left(\gamma\delta_{ij} + \frac{\delta\gamma}{\delta e_{ij}}\right)de_{ij}$$

$$= A\sum_{ij} f_{ij}\, de_{ij}$$

$$f_{ij} = \gamma\delta_{ij} + \frac{\delta\gamma}{\delta e_{ij}}$$

$$\begin{bmatrix} f_{11} & f_{12} \\ f_{21} & f_{22} \end{bmatrix} = \begin{bmatrix} \gamma + \frac{\delta\gamma}{\delta e_{11}} & \frac{\delta\gamma}{\delta e_{12}} \\ \frac{\delta\gamma}{\delta e_{21}} & \gamma + \frac{\delta\gamma}{\delta e_{22}} \end{bmatrix}$$

$$f_{12} = f_{21}$$

A small parenthesis

Let’s recall now the Neumann’s principle:

The magnitude of a particular physical property of a material, when measured along a particular direction, is unchanged when the material is rotated, reflected or inverted into a new orientation corresponding to one of the symmetry elements of its point groups.

So what is the condition needed for having vanishing diagonal terms in the matrix that represents f?

C_3 or higher

$f_{12} = f_{21} = 0$

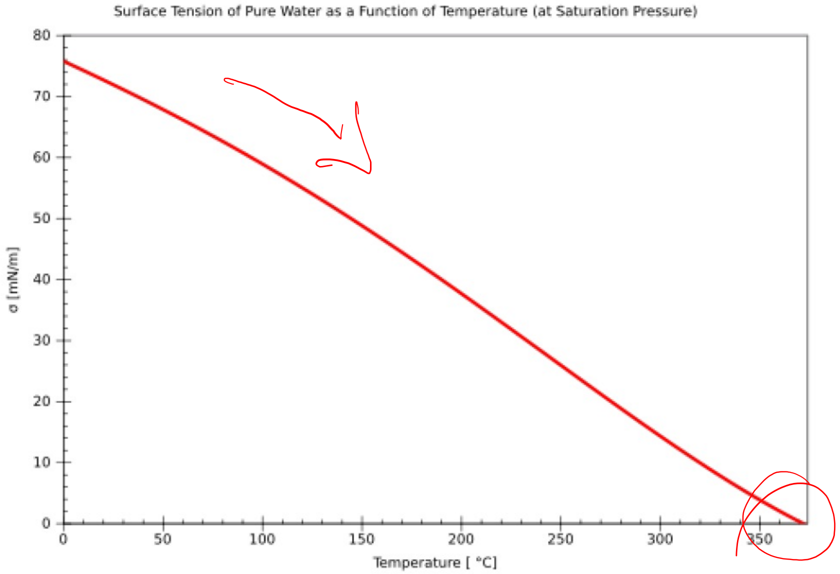
$f_{11} = f_{22}$

$f = \gamma + \frac{d\gamma}{d\ell} \rightarrow f - \gamma = \frac{d\gamma}{d\ell}$

Temperature Dependence of Excess Surface Free Energy

$\frac{\partial G}{\partial T}$

- Based on the definition $G_s = \overset{H}{E_s} - TS_s$, $(\partial\gamma/\partial T)_P = -S_s/A$.
- Typically the excess surface entropy is positive - atoms at the surface have more space to vibrate, and more ways to create defects
- γ is a decreasing function of temperature: at the critical temperature the liquid and the vapor become indistinguishable, and therefore $\gamma\,(T_c)$ must be zero.



Surface tension of water from the triple to the critical point [Stan J. Klimas at Wikipedia]

What is the equilibrium shape of a materials of finite dimensions?

(1) $U, p, T, n_i, S, V, \mu_i$
A^1, γ^1

(2) $U, p, T, n_i, S, V, \mu_i$
A^2, γ^2

$$G^1 = U + pV - TS + \sum_i \mu_i n_i + \gamma^1 A^1$$

$$G^2 = U + pV - TS + \sum_i \mu_i n_i + \gamma^2 A^2$$

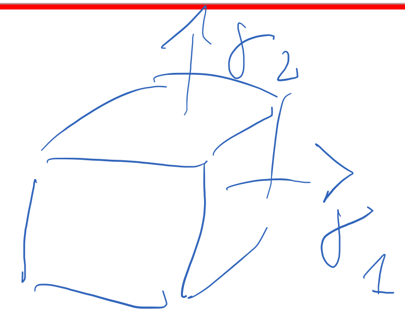
$$\Delta G = G^2 - G^1 = \gamma^2 A^2 - \gamma^1 A^1$$

a gas is a form of matter where $\gamma = 0$

$\Delta G < 0$ sponteneous event $\rightarrow$ $\min \gamma^i A^i$

for a liquid γ is constant with direction $\quad \Delta G = \gamma \Delta A \quad \min \Delta A$

What is the equilibrium shape of a materials of finite dimensions?



$$dG = \int_{\vec{n}} \gamma(\vec{n})\, dA$$

$$\min \underbrace{\int_{\vec{n}} \gamma(\vec{n})\, dA}$$

Stereographic Projections

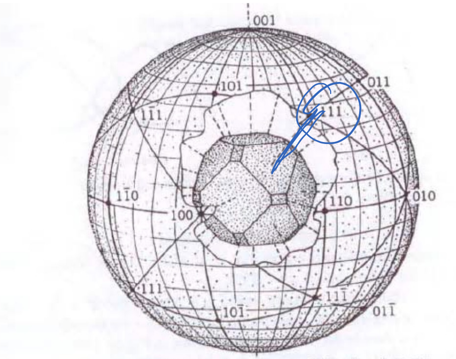
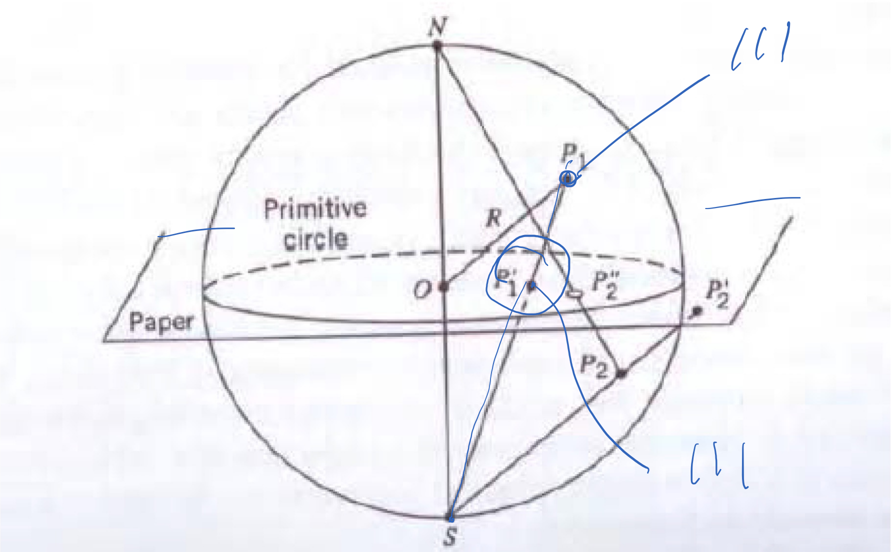
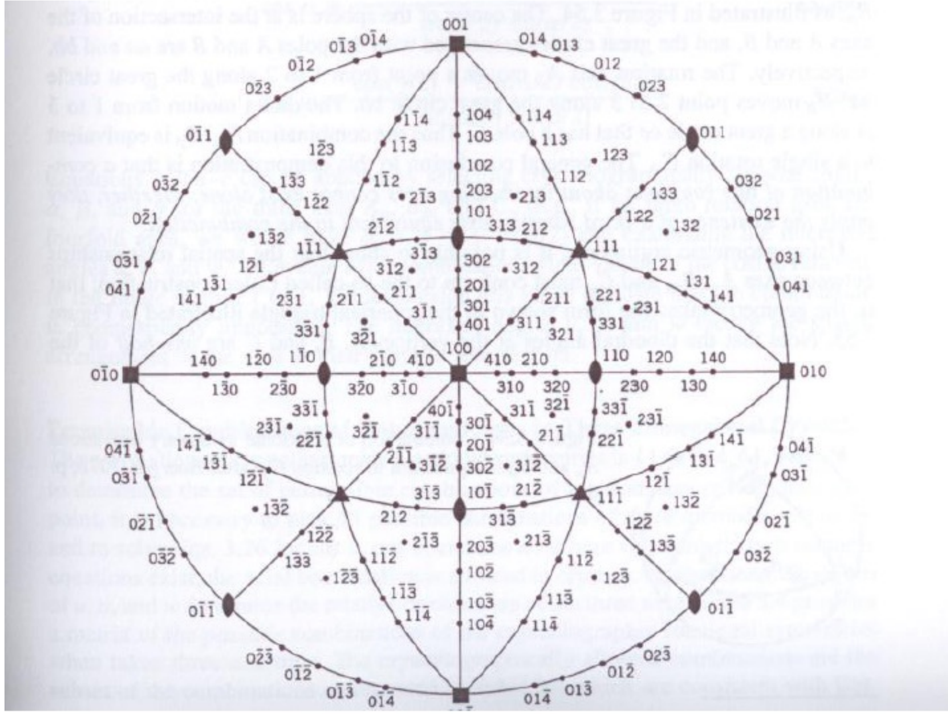


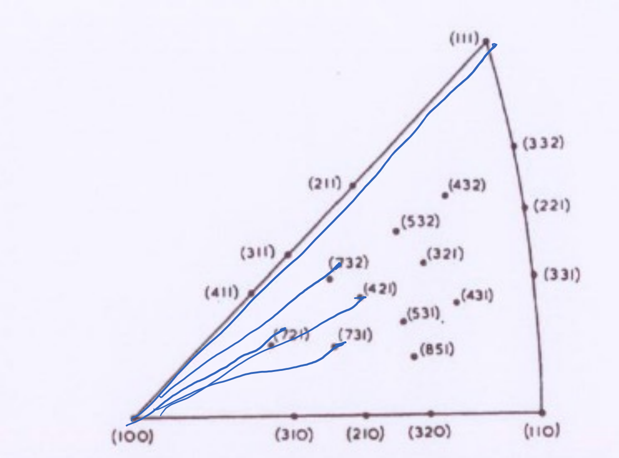
Figure 3.51 Spherical projection of directions in a truncated cube. (From E. Wahlstrom, 1979, p. 11.)



Stereographic Projections



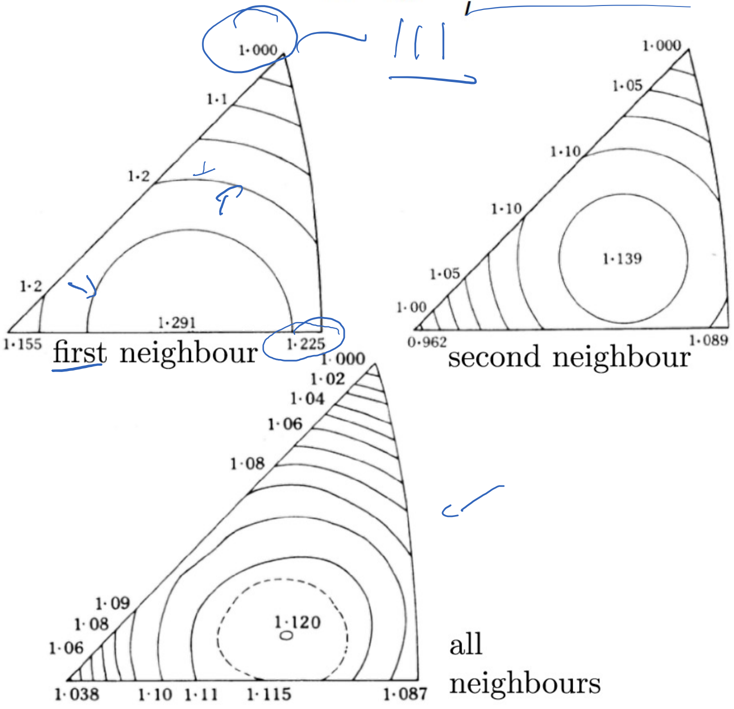
l = coeff · γ



Stereographic Projections

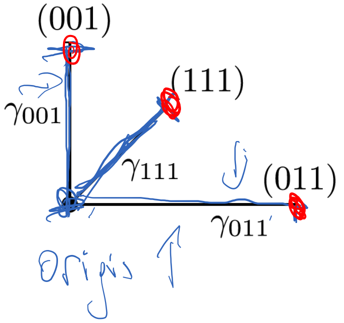
- Stereographic projections: a concise 2D representation of crystal directions
- Can be used to represent the dependence of γ on the orientation:

$$\gamma_{hkl} \approx -\frac{\epsilon_b}{2}\frac{d_{hkl}}{V_0}\sum_i \mathbf{u}_b^{(i)} \cdot \hat{\mathbf{n}}_{hkl}$$

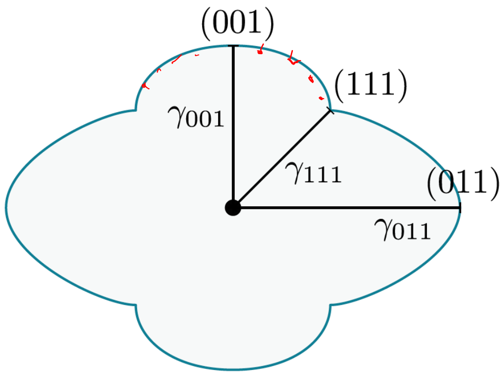


Wulff Construction and Wulf Plot

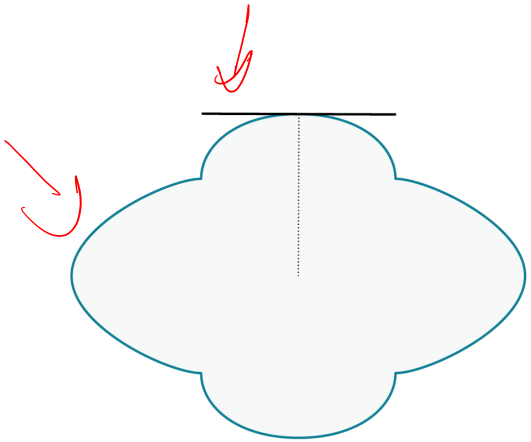
(1)



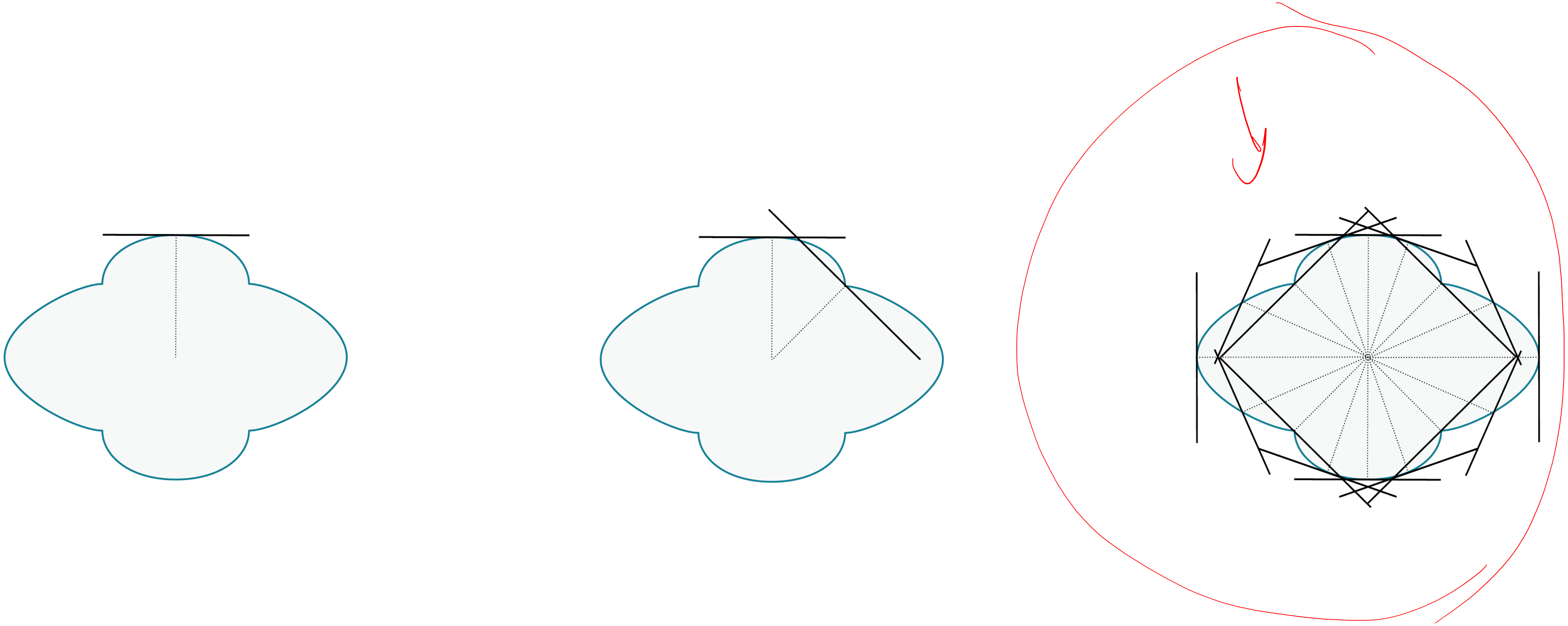
(2)



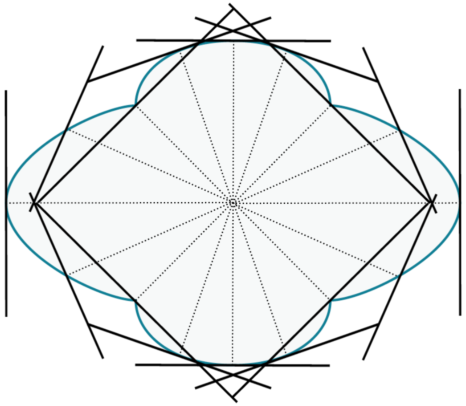
(3)

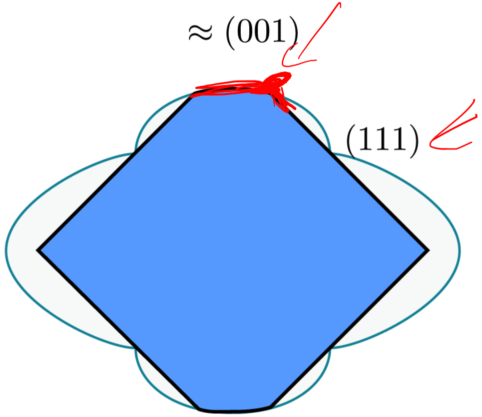


Wulff Construction and Wulf Plot



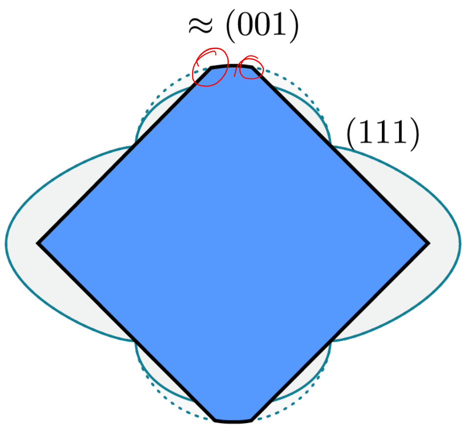
Wulff Construction and Wulf Plot



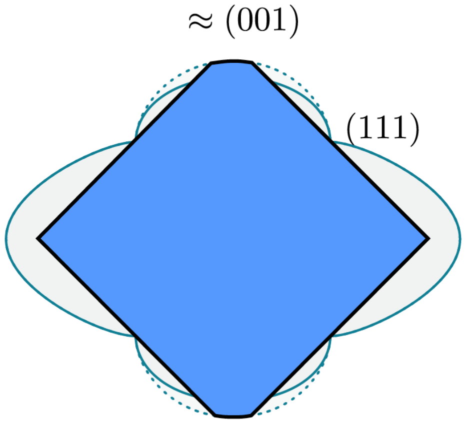


4 bonds

3 bond

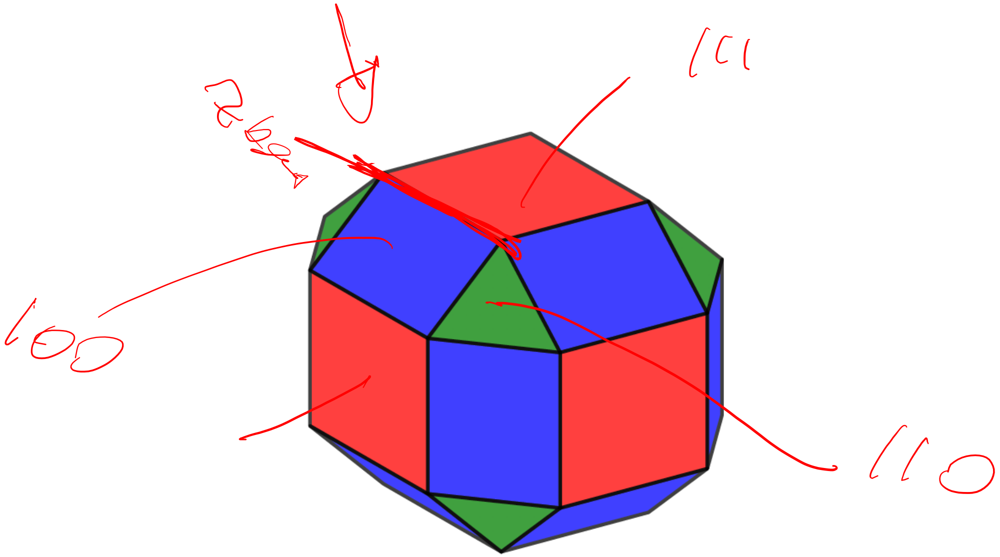


Wulff Construction and Wulf Plot



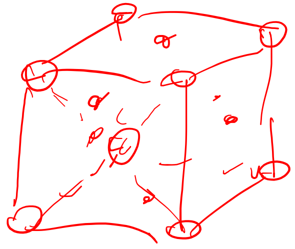
- In a liquid, γ is constant, so the system just want to minimize area at fixed volume ⟶ spherical droplets
- In a solid, the surface energy γ is orientation-dependent. Minimize total surface energy at constant volume

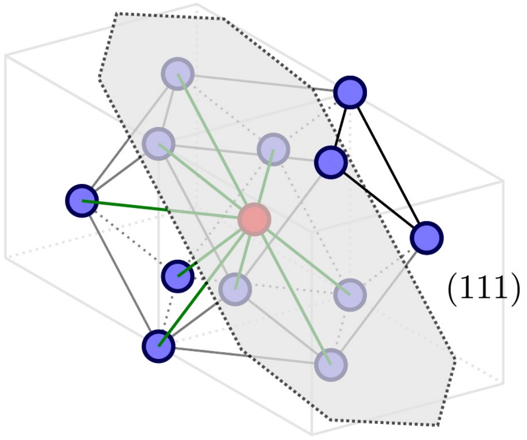
$$\min \int \underbrace{\gamma\left(\hat{\mathbf{n}}\right) dA}_{}$$

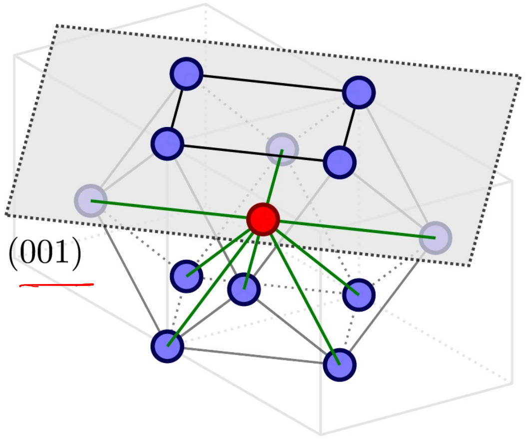


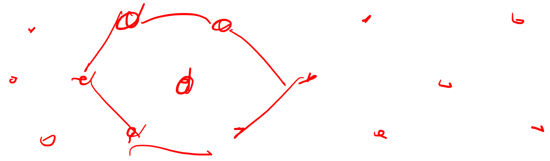
Key Questions to be addressed

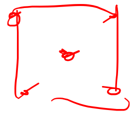
Why different crystallographic planes have different surface energies?











Conclusions

What have we learned?

What are the key questions to be addressed?