Università degli Studi di Trieste
Dipartimento di Ingegneria e Architettura
A.A. 2021-2022

Scienza e Tecnologia dei Materiali Ceramici

Modulo 2: Materiali Nanostrutturati

- Lezione 2 -

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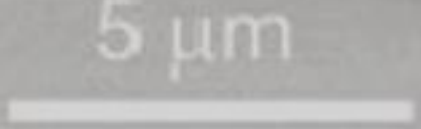


Esame e criteri di valutazione

Modalità d'esame e criteri di valutazione

- Ricerca bibliografica su argomento a scelta
- Homework
- Valutazione finale:
  - Presentazione e discussione della ricerca bibliografica (10 punti)
  - Partecipazione e homework (5 punti)
  - Domanda a scelta dello studente (5)
  - Domanda a scelta del docente (10 punti)

Appelli

- Ufficiali (previa conferma)
- Su appuntamento (collettivo)

Previous lectures: Review

- Course “instructions”

- Definition of objectives and overview of course content

Homework #1

Identify «hot topics» in the nanoworld. Classify them according to: societal challenges, key enabling technologies, applications

Societal Challenges:

- **Health and Wellbeing**
- **Secure, green, efficient energy**
- **Food and Waste**

Key Enabling Technologies

- Micro- and nanoelectronics
- Advanced Materials and Advanced Manufacturing
- Photonics
- Biotechnology (industrial)

This lecture: Content

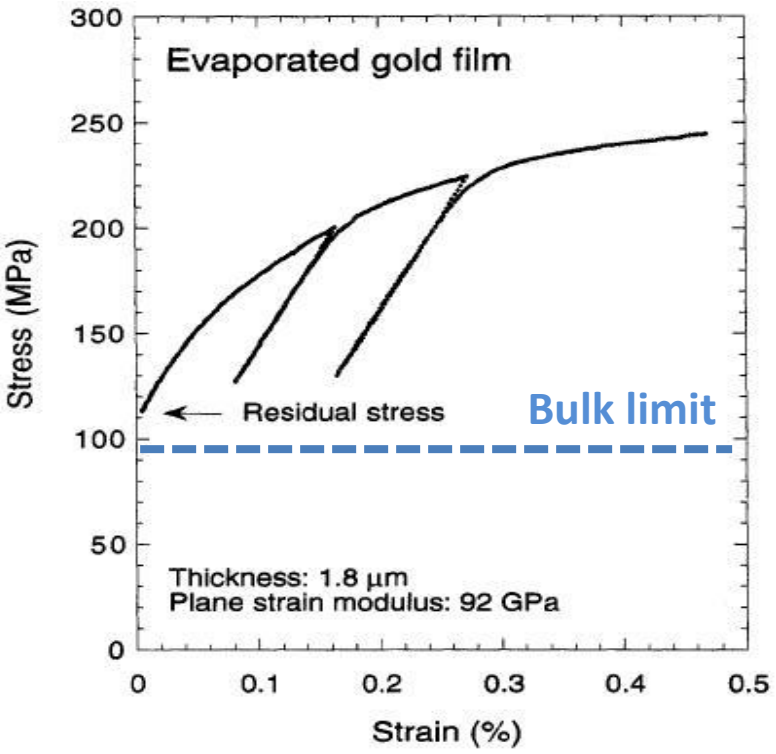
- Examples of what is nano and what is not

- Surfaces and interfaces (see lecture notes)
  - Review of relevant thermodynamic definitions
  - Fundamentals on surface energy and chemical potential

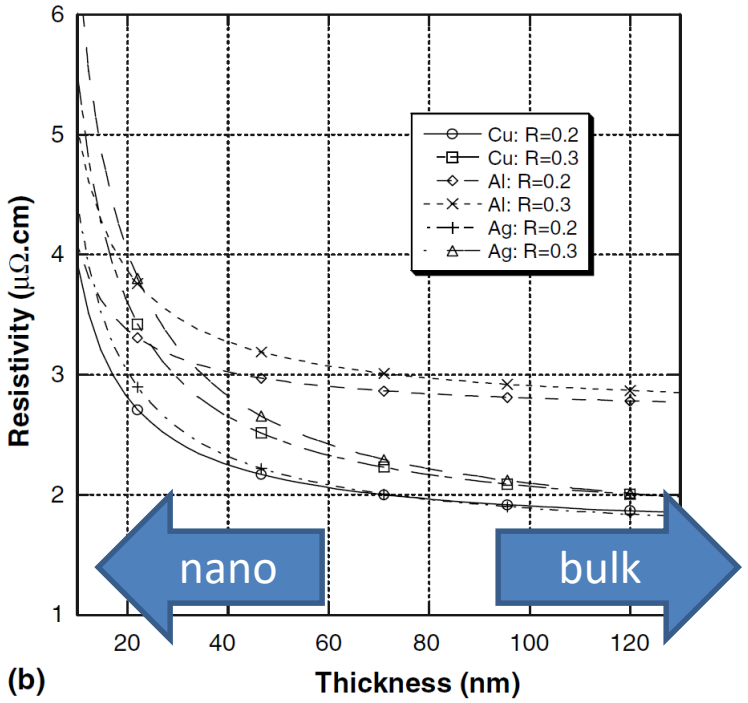
When “nano” is actually “nano”?

- Example 1: Thin films

Mechanical properties (e.g. strength)



Electrical properties (e.g. resistivity)

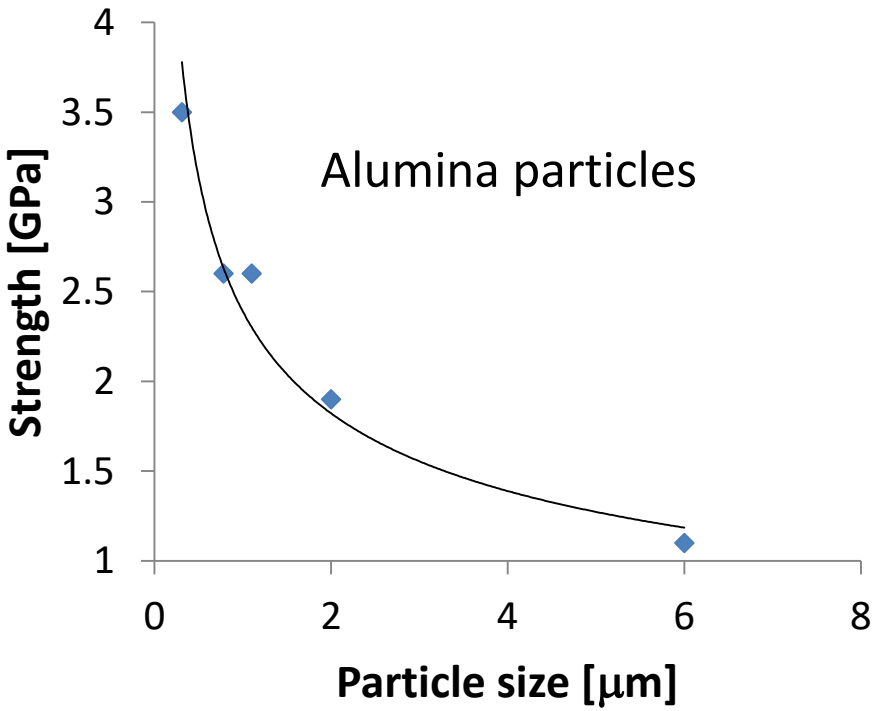


The “nano” limit is different for different materials properties

When “nano” is actually “nano”?

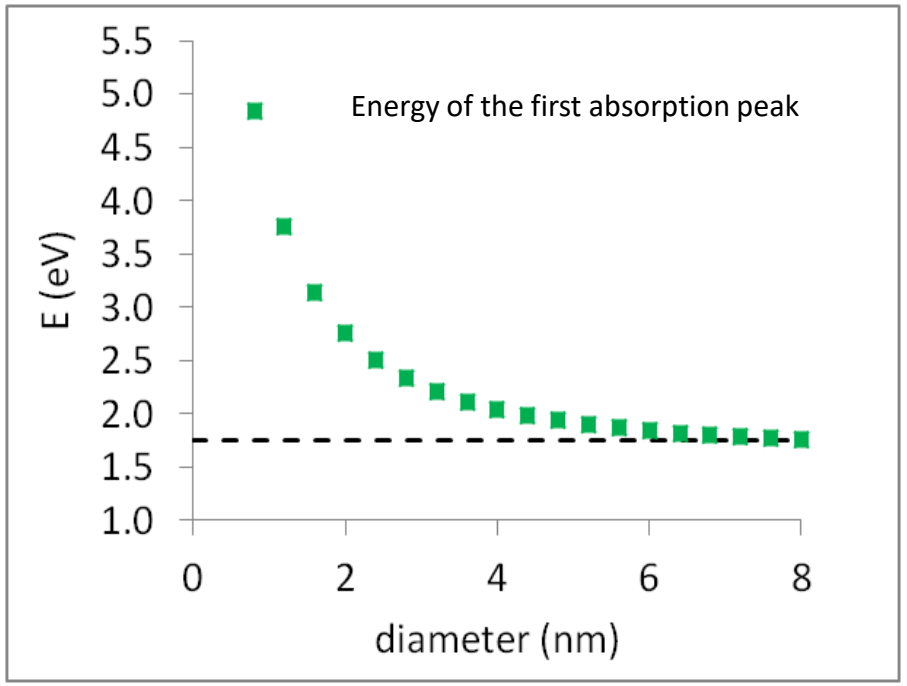
- Example 2: Spherical particles

Mechanical properties (e.g. strength)



Yoshida M et al., Rev. Sci. Instrum. 76, 093905 (2005)

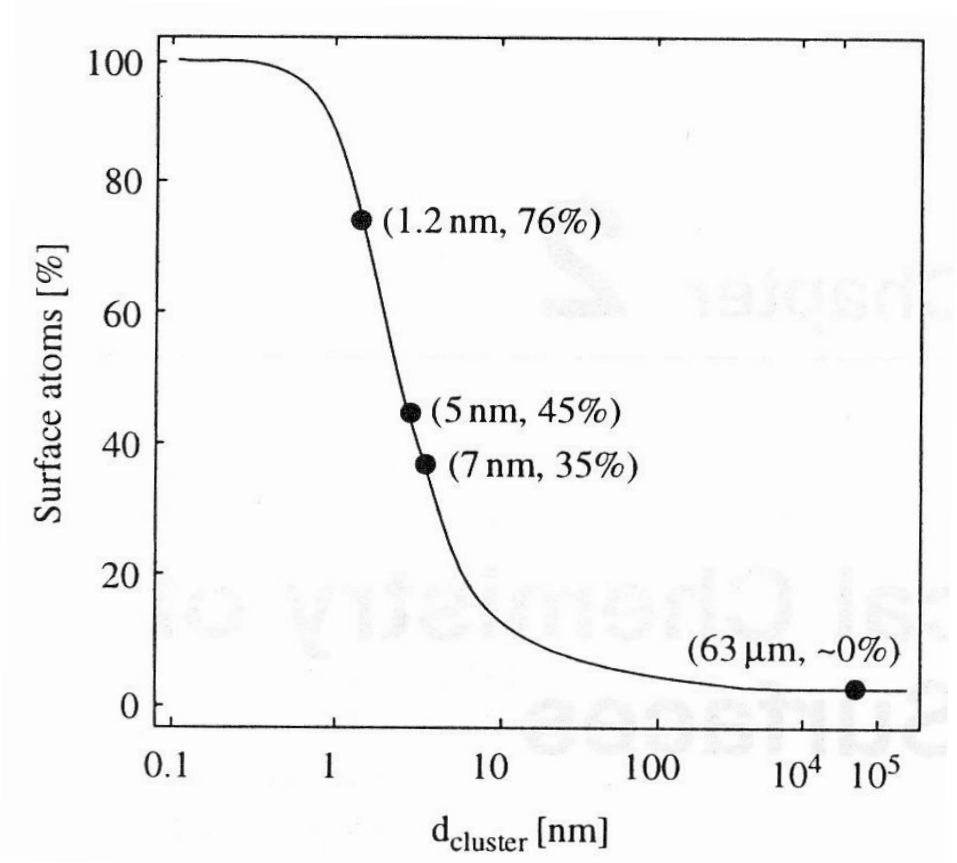
Optoelectronic properties (e.g. color)



L. Cozzarini, PhD Thesis, 2012

Importance of Surface

- Fraction of surface atoms increases rapidly when size drops



Importance of Surface

For a compact structure with coordination 12:

Number of surface atoms, *S*:

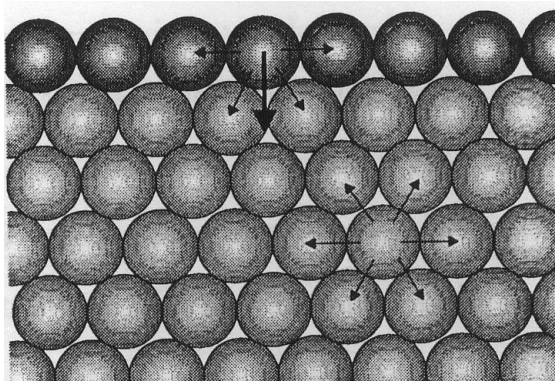
$$S = 10n^2 + 2$$

(*n* is the number of shells)

Full-shell Clusters	Total Number of Atoms	Surface Ato (%)
1 Shell	13	92
2 Shells	55	76
3 Shells	147	63
4 Shells	309	52
5 Shells	561	45
7 Shells	1415	35

Importance of Surface

Surface energy



Forces acting on bulk and surface atoms

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

Importance of Surface

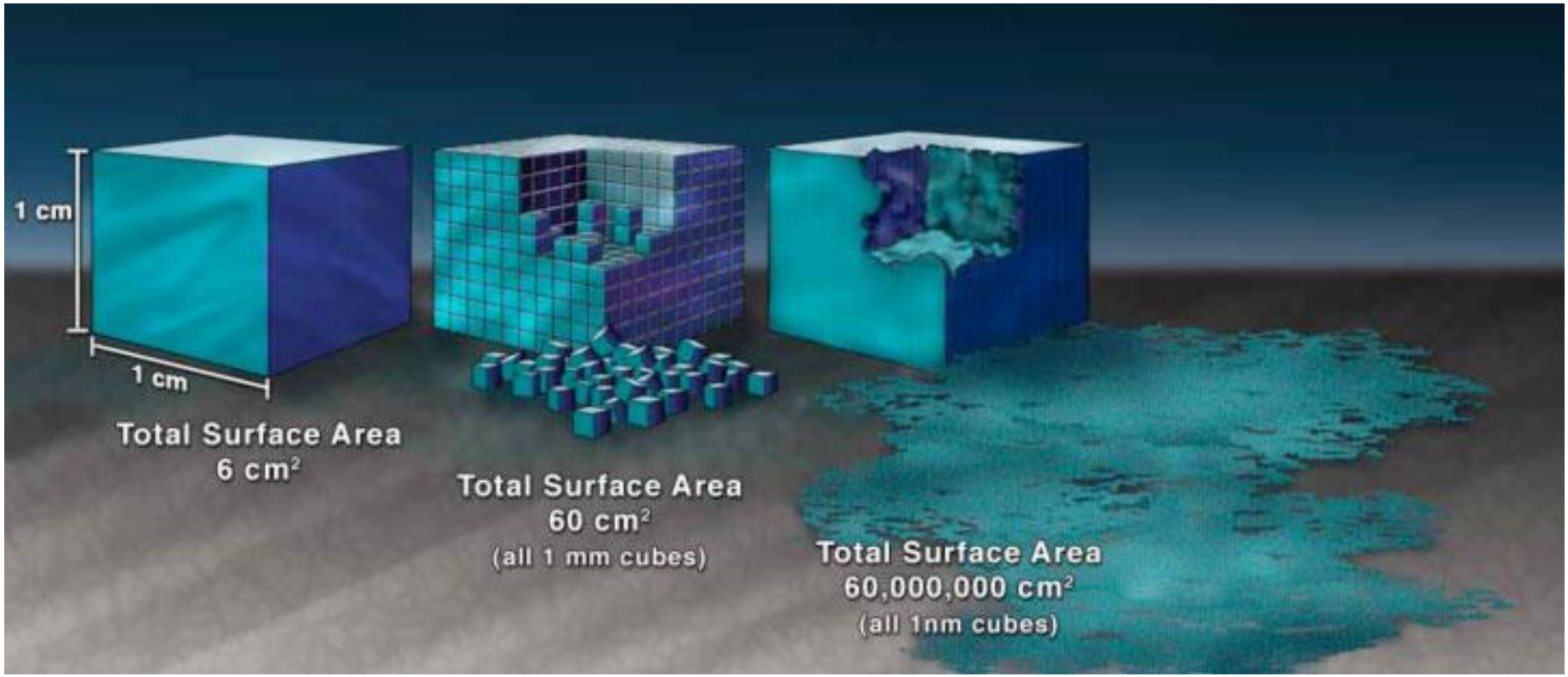
Total surface energy increase

Table 2.1. Variation of surface energy with particle size.[22]

Side (cm)	*Total surface area* (cm^2)	*Total edge* (cm)	*Surface energy* (J/g)	*Edge energy* (J/g)
0.77	3.6	9.3	7.2×10^{-5}	2.8×10^{-12}
0.1	28	550	5.6×10^{-4}	1.7×10^{-10}
0.01	280	5.5×10^{4}	5.6×10^{-3}	1.7×10^{-8}
0.001	2.8×10^{3}	5.5×10^{6}	5.6×10^{-2}	1.7×10^{-6}
10^{-4} (1 μm)	2.8×10^{4}	5.5×10^{8}	0.56	1.7×10^{-4}
10^{-7} (1 nm)	2.8×10^{7}	5.5×10^{14}	560	170

Importance of Surface

Total surface energy increase



Where are we?

2. **Design di materiali nanostrutturati**
   - **Fondamentali: stato solido, approfondimenti di fisica e chimica (anche sparsi durante il corso)**
   - Proprietà alla nanoscala
   - Attività seminariale sulla modellazione
   - Esempi in cui la nanostruttura determina le proprietà e di come queste possono essere "previste“:
     - quantum wells; banda intermedia; nanocompositi; opali artificiali; modificazione dell'energia superficiale mediante nanocoatings; etc.

Importance of Surface – Properties at the Nanoscale

- Effect of size on vapor pressure

(This is a curvature effect!)

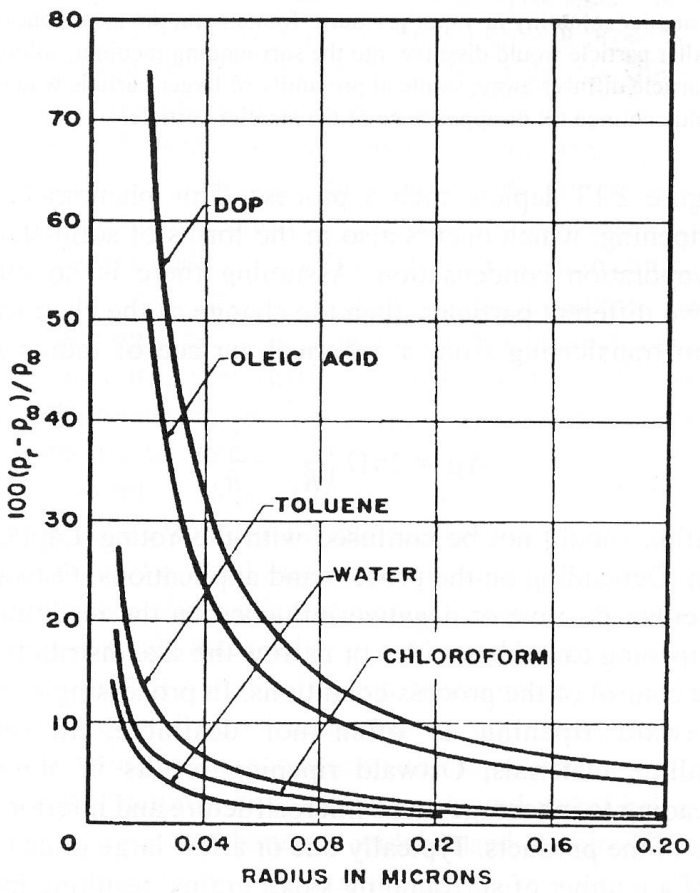
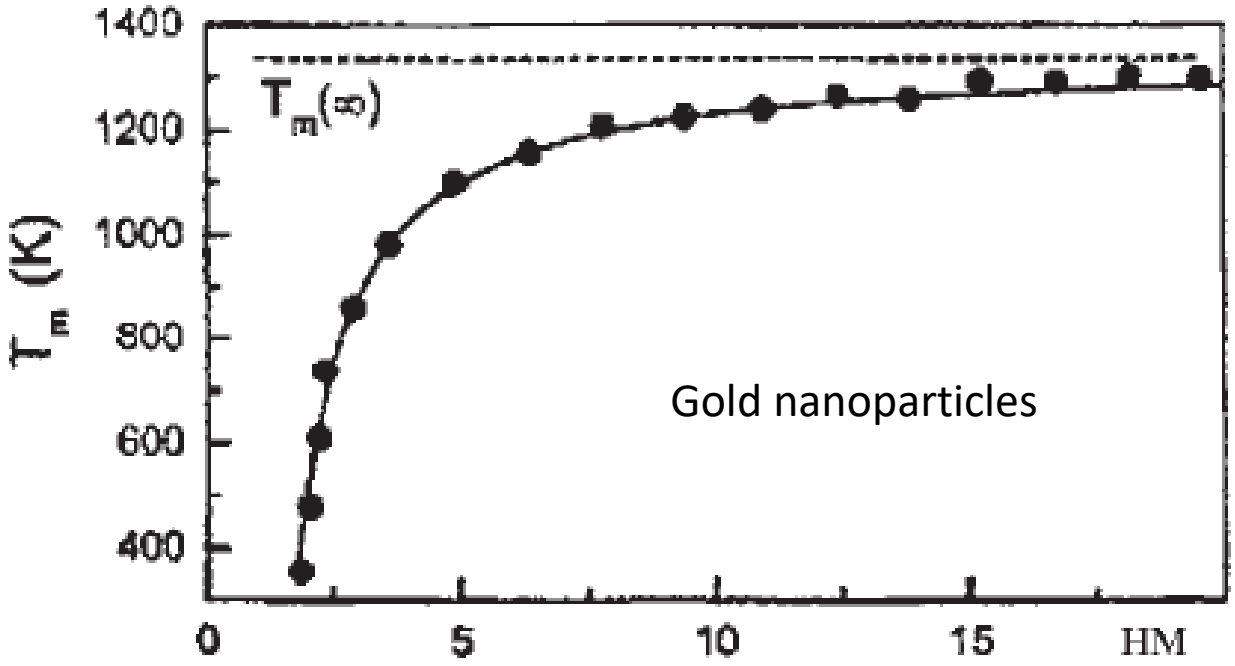


Fig. 2.12. Vapor pressure of a number of liquids as a function of droplet radius. [V.K. La Mer and R. Gruen, *Trans. Faraday Soc.* **48**, 410 (1952).]

Importance of Surface – Properties at the Nanoscale

- Melting point vs size

$$T_b - T_m = \left(\frac{2T_b}{\Delta H \rho_s r_s}\right)\left(\gamma_s - \gamma_l \left(\frac{\rho_s}{\rho_l}\right)^{\frac{2}{3}}\right)$$



Importance of Surface – Properties at the Nanoscale

- Inhibition of phase transformation in zirconia

Driving force to transformation:

$$\Delta G_{t-m} = \Delta G_{t-m}^{CHEM} + \cancel{\Delta G_{t-m}^{STRAIN}} + \Delta G_{t-m}^{SURF}$$

where $\Delta G_{t-m}^{SURF} = A_m \gamma_m - A_t \gamma_t$

For stress-free, undoped spherical zirconia particles:

$$\Delta G_{t-m} = \frac{4}{3}\pi r^3 (g_m - g_t) + 4\pi r^2 (\gamma_m - \gamma_t)$$

A critical particle radius exist, for which the tetragonal phase is thermodynamically stable

$r_c = -3\frac{\gamma_m - \gamma_t}{g_m - g_t}$ (5 to 10 nm for pure zirconia powders, 30 nm for solid ceramics)

Thermodynamics of surface-intensive systems

$$G = U - TS + PV + \mu N + \gamma A$$

ad-hoc term

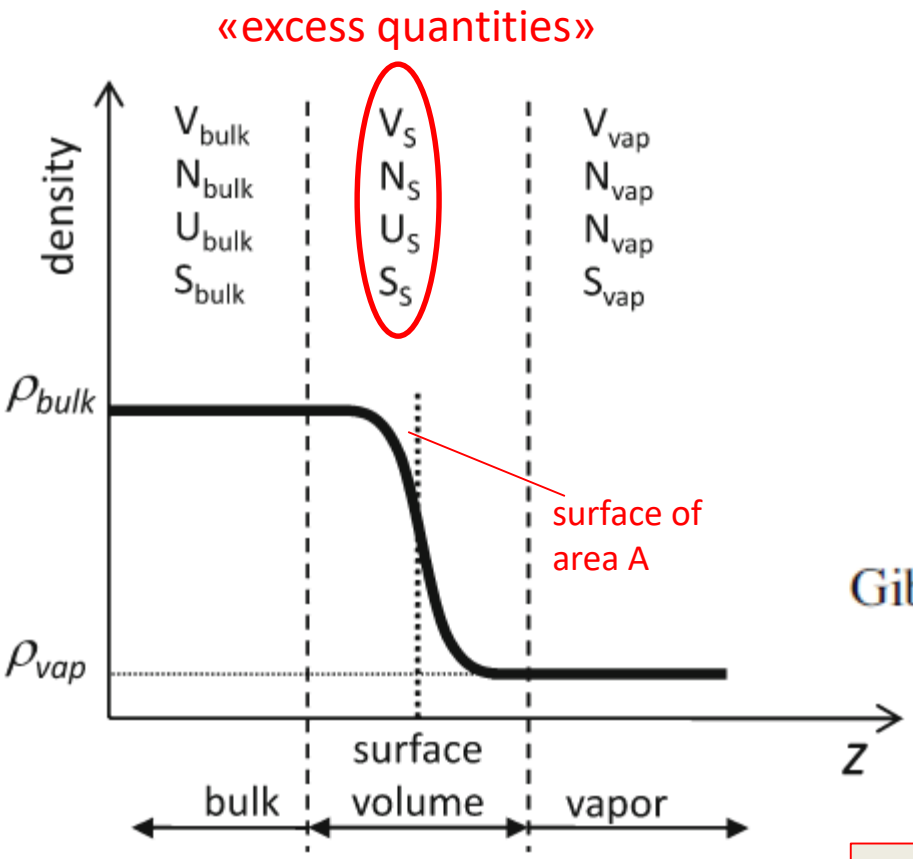
$$\gamma = \left.\frac{\partial G}{\partial A}\right|_{T,P,N}$$

Surface tension
(also: surface energy, surface free energy, etc.)

$$\mu = \left.\frac{\partial G}{\partial N}\right|_{T,P,A}$$

Chemical potential

Surface thermodynamics
- Gibbs' approach -



$$G_S = U_S - TS_S + PV_S$$

Surface energy $\quad u_S = \frac{U_S}{A}$

Gibbs surface free energy $\quad g_S = \frac{G_S}{A}$

In general $g_s = \gamma$
only in pure single component systems

Estimates of surface energy

Surface energy γ is of the same order of the surface tension F_L:

$$F_L \sim \gamma$$

Estimate of γ for a (111) surface in a compact structure leads to:

$$u_s = 0.25\ L_s/N_a \ \ [J/surf.\ atom]$$

L_s: sublimation latent heat
N_a: Avogadro

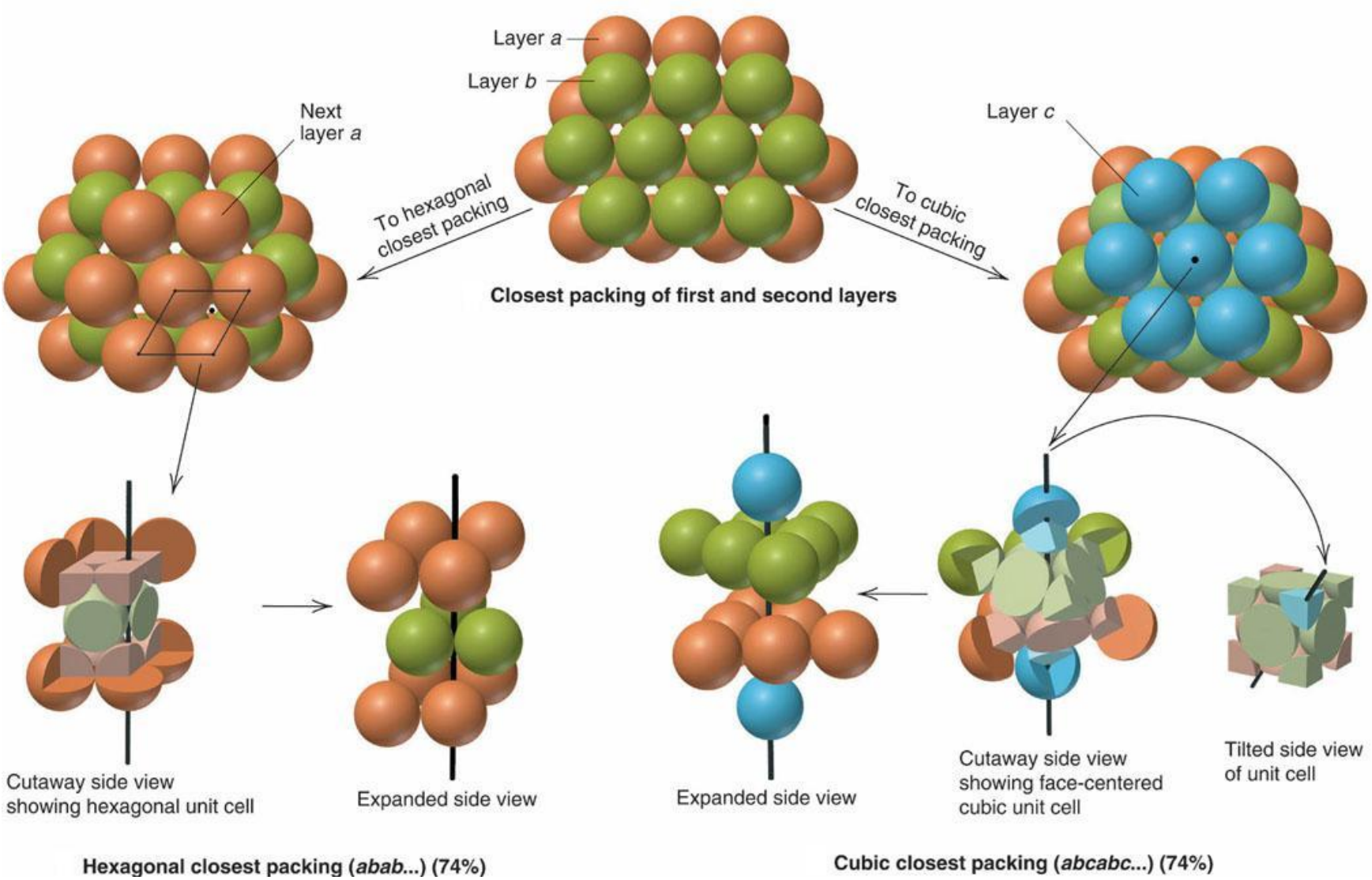
Considering that $\gamma = u_s + Pv_s - Ts_s$

we need to take into account entropy effects:

$$\gamma = 0.15\ L_s/N_a \ \ [J/surf.\ atom]$$

$$\left(\frac{\partial \gamma}{\partial T}\right)_P = -S$$

Close-packed Structures



Corrections to surface energy estimates: Surface reconstruction

Minimization of energy - Entropy increases

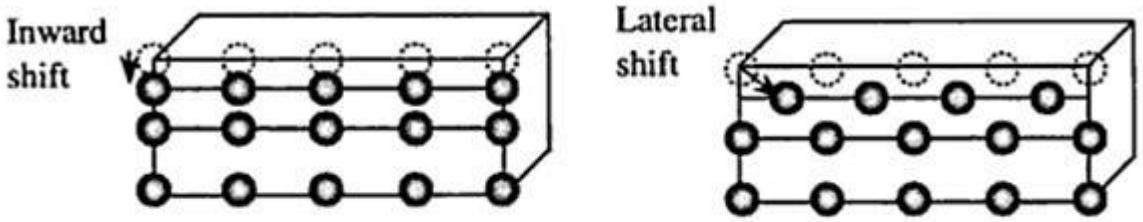
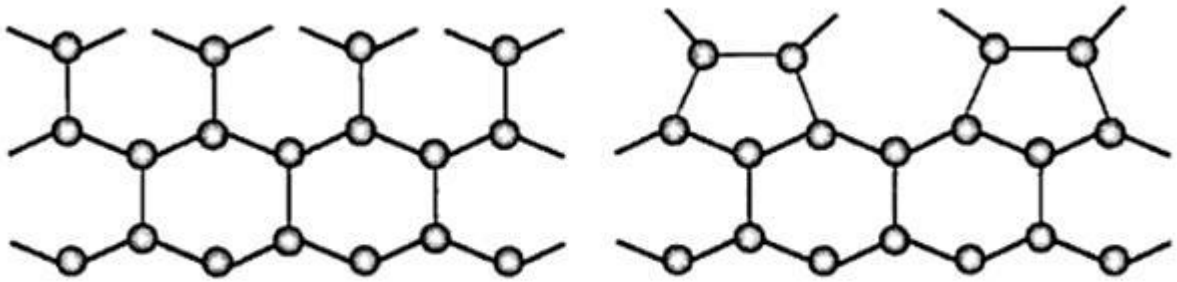


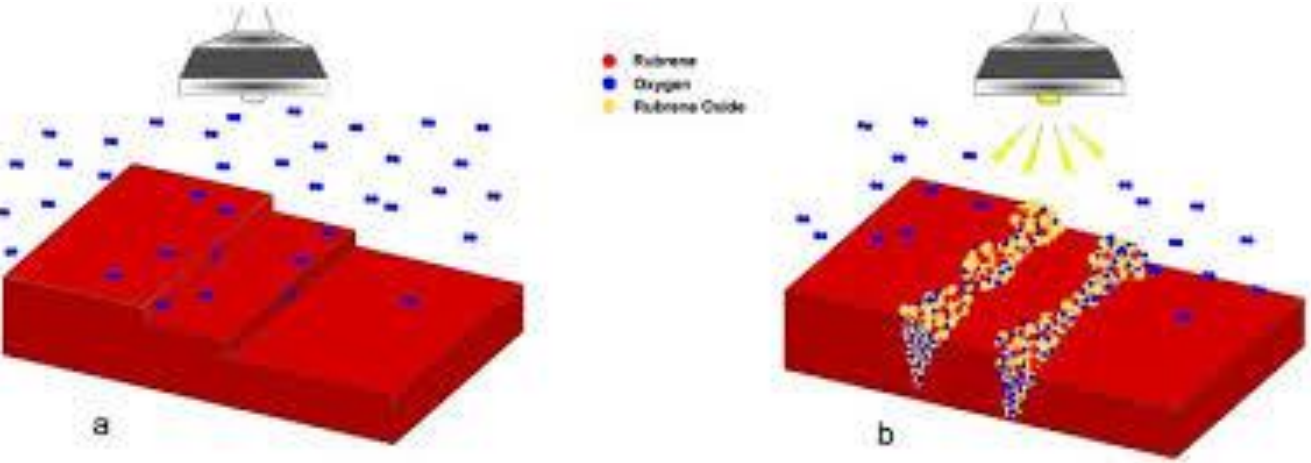
Fig. 2.4. Schematic showing surface atoms shifting either inwardly or laterally so as to reduce the surface energy.

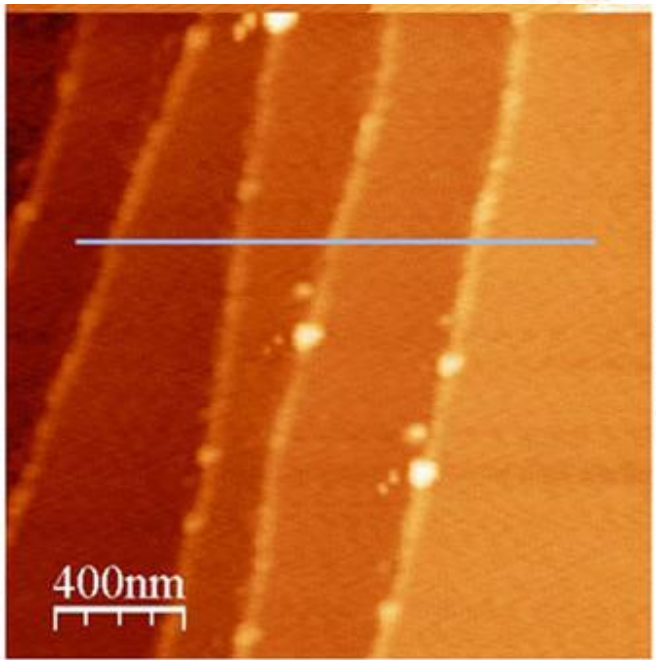


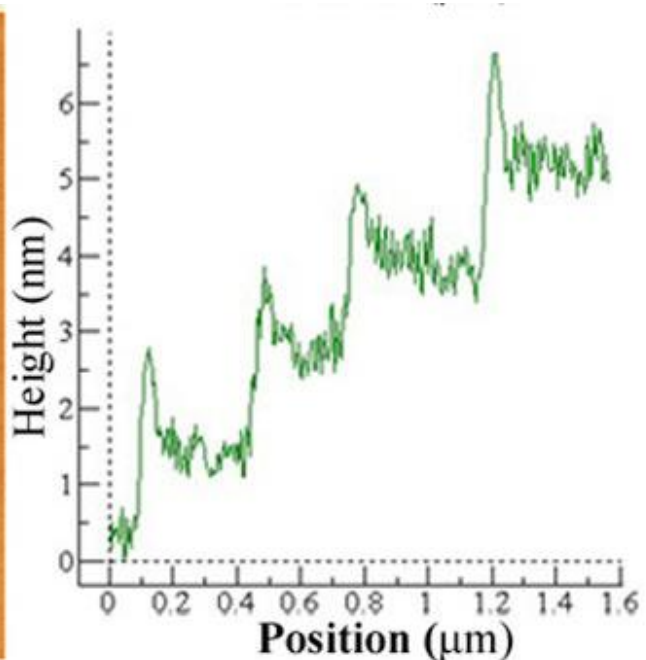
Original {100} surface

(2×1) restructured {100} surface

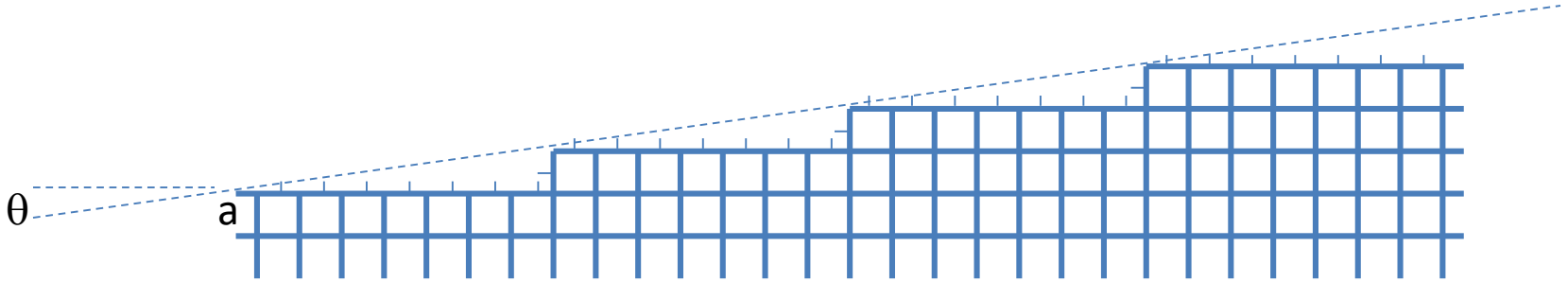
High Index Planes (Vicinal Surfaces)



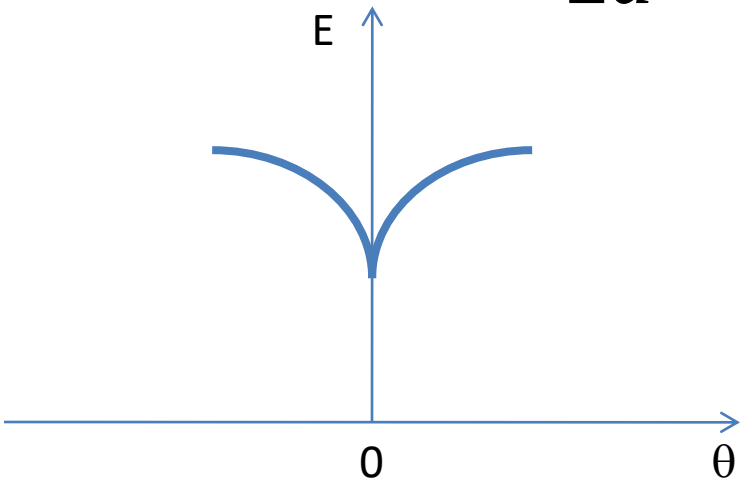




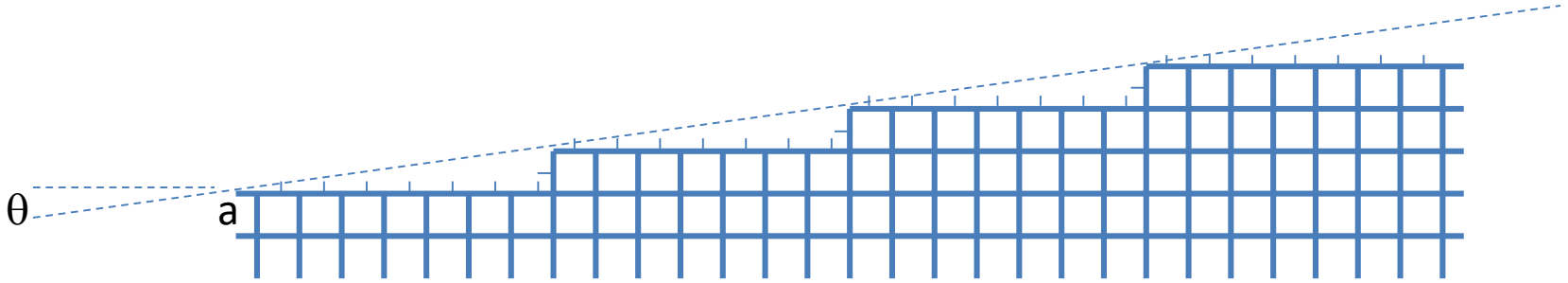
Surface Energy of High Index Planes



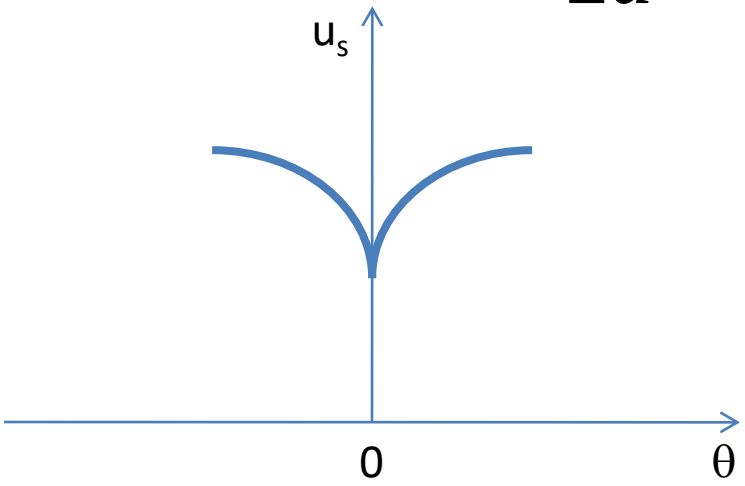
$$u_S = (\cos\vartheta + \sin|\vartheta|)\frac{\varepsilon}{2a^2}$$



Surface Energy of High Index Planes

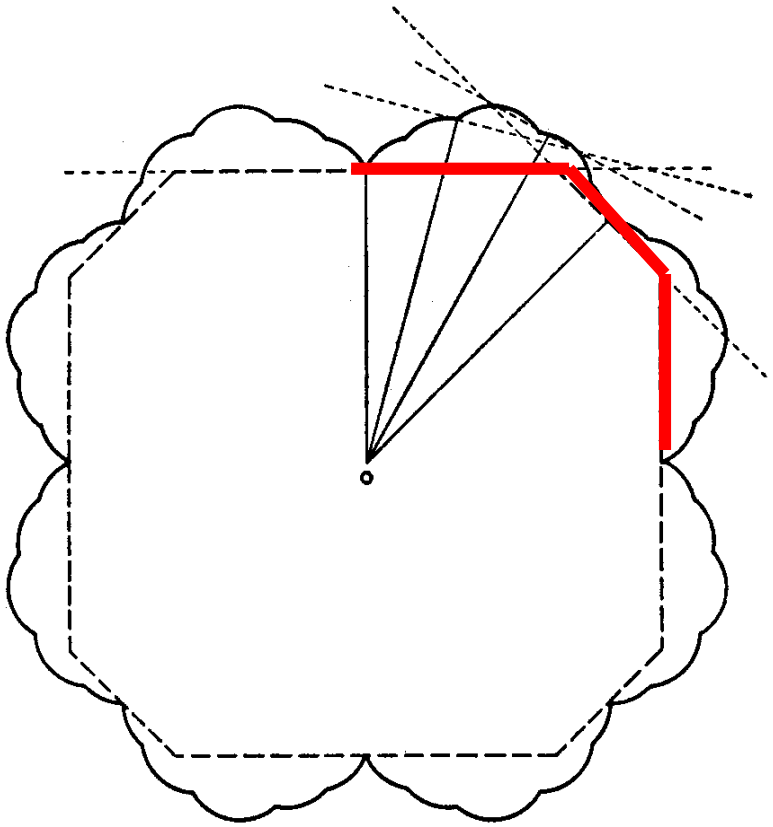


$$u_S = (\cos\vartheta + \sin|\vartheta|)\frac{\varepsilon}{2a^2}$$



Wulff Construction

Equilibrium shape of an isolated crystal

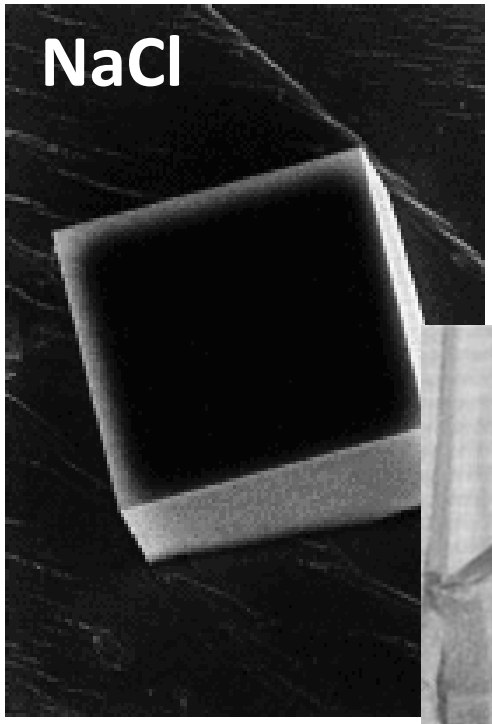


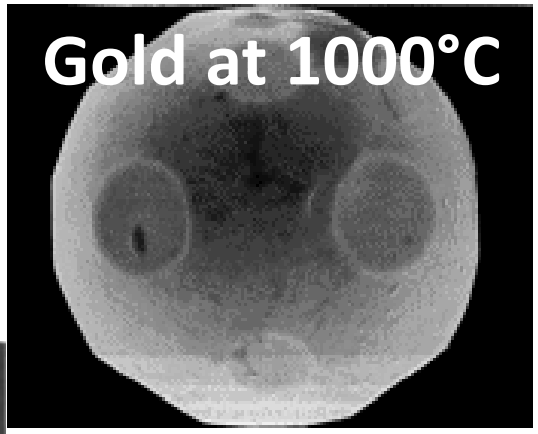
Gibb's theorem:

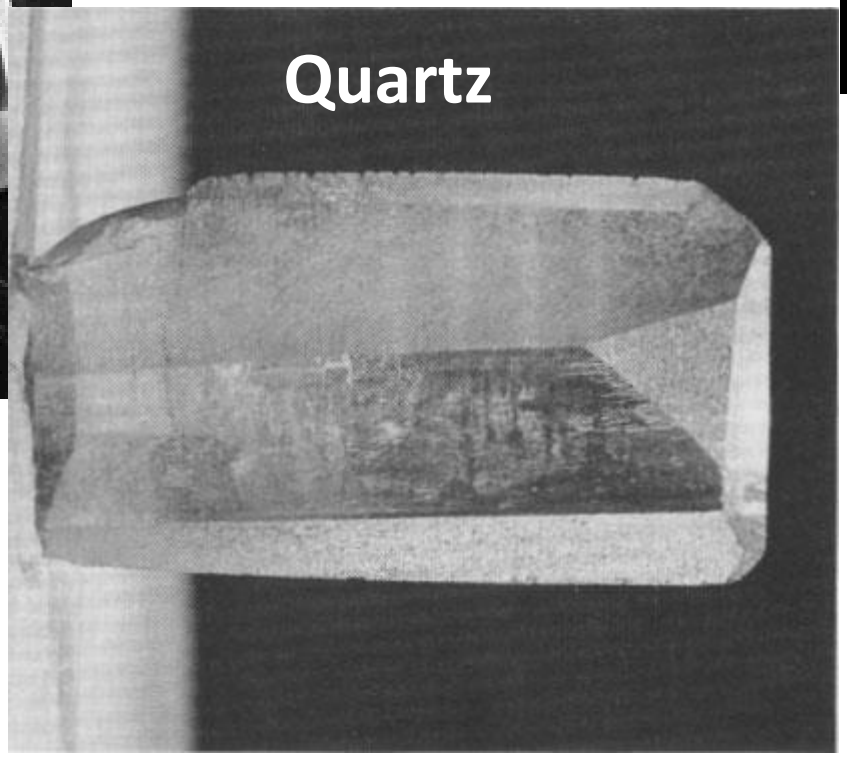
Minimize $\sum_i \gamma_i A_i$

Also a way to find the surface energy when the shape of a crystal is known

Equilibrium shape of an isolated crystal





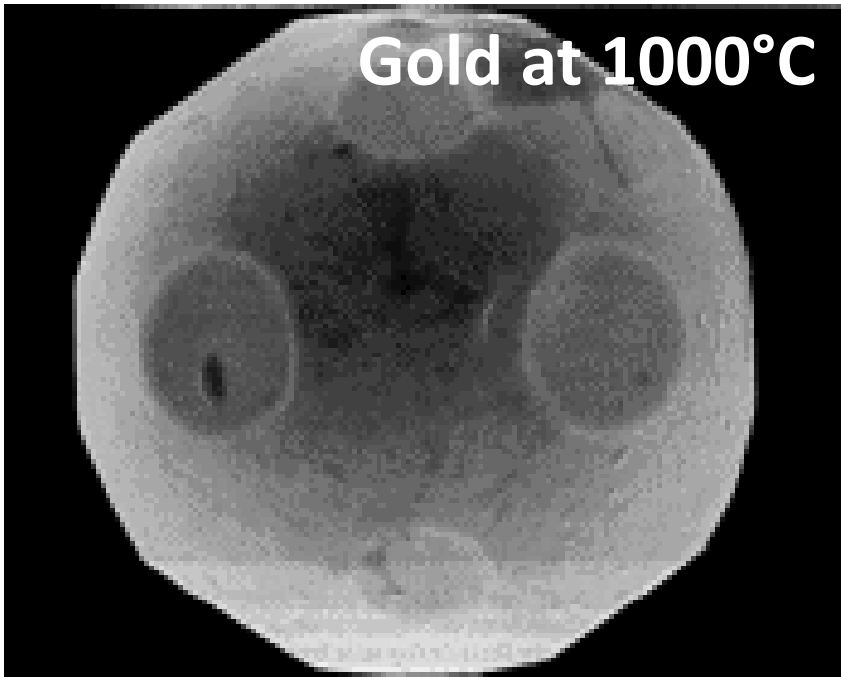


Equilibrium shape: Roughening Temperature

- The surface energy depends on temperature :

$$\left(\frac{\partial \gamma}{\partial T}\right)_P = -S$$

Facets tend to disappear upon increasing temperature



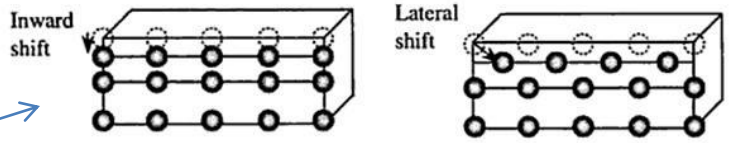
Take-home message

- Importance of the surface

- Homegame: for a system containing a given amount of material, calculate how the surface area increases when the size of the system's element decrease

Surface energy minimization

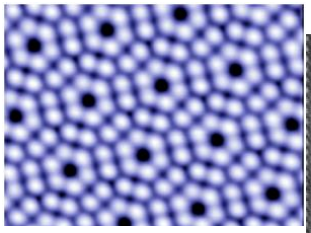
1. Surface mechanisms



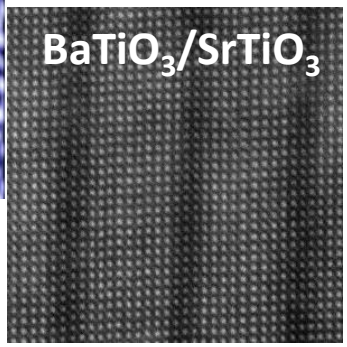
- Surface relaxation

- Surface reconstruction

  More than one dangling bond per atom



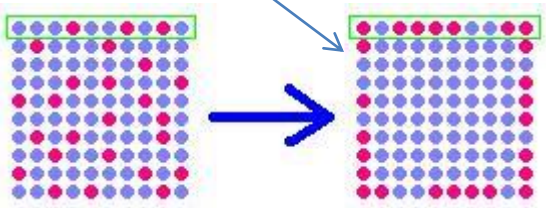
Si (111), 7x7 reconstruction



- Chemi- or physisorption of species at the surface

- Surface segregation

Important consequences on doping of nanostructures



Surface mechanisms of energy minimization are of major importance in nanostructures

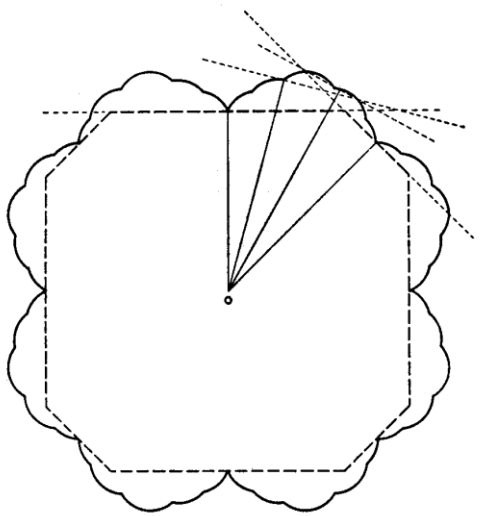
Surface energy minimization

2. Individual structure mechanisms

- Isotropic systems (liquids, amorphous solids):
  Total surface area minimization

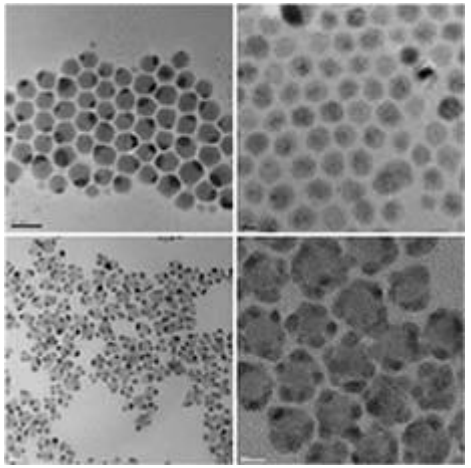
- Anisotropic systems (solid crystals): Minimize $\sum_i \gamma_i A_i$

  → Wulff's theorem



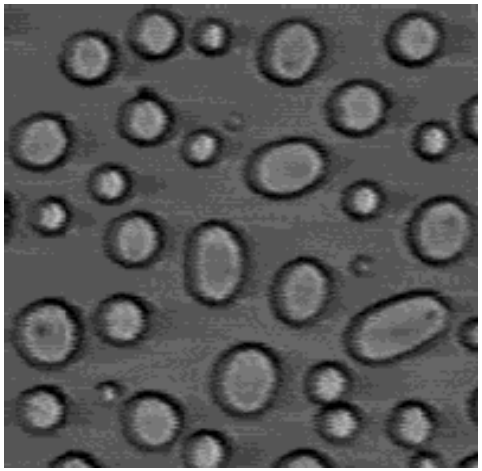
Surface energy minimization

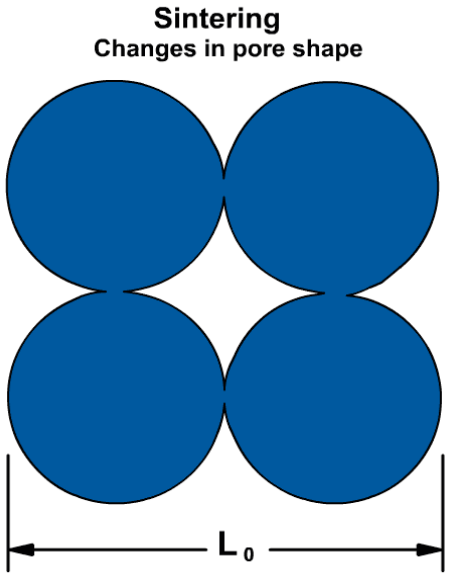
3. Overall system mechanisms



- Aggregation of individual structures

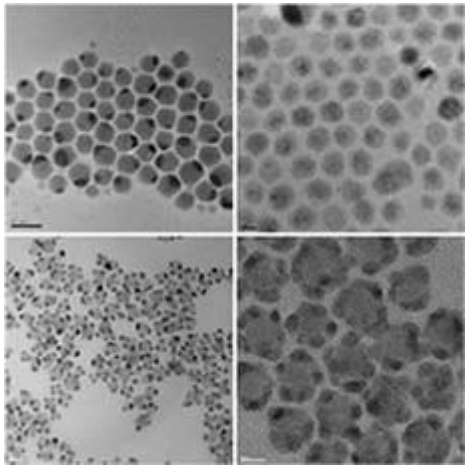
- Formation of new structures
  - Sintering
  - Ostwald ripening





Agglomeration - aggregation

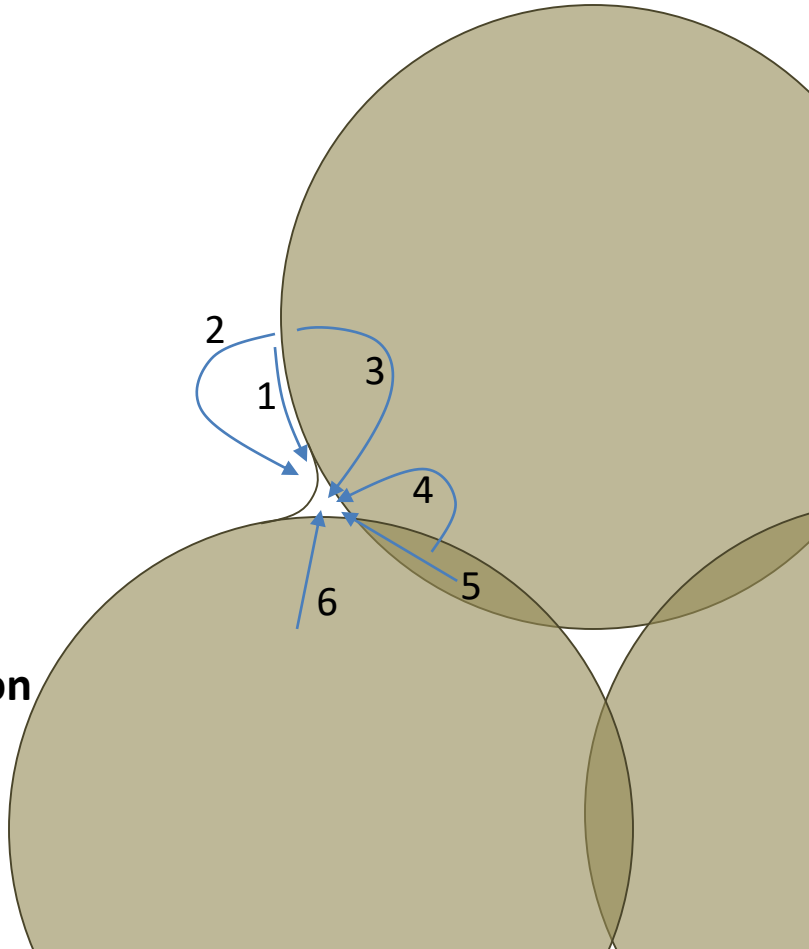
- Chemical bonds
- Physical bonds (Van der Waals)



Sintering

Mechanisms in diffusion controlled sintering:

	Mechanism	Source of matter
1.	Surface diffusion	Surface
2.	Vapor transport	Surface
3.	Lattice diffusion	Surface
4.	Lattice diffusion	Grain boundary
5.	Boundary diffusion	Grain boundary
6.	Lattice diffusion	Dislocations



- All mechanisms are driven by **surface area reduction**
- All lead to **neck growth**
- Only mechanisms 4, 5, and 6 lead to **densification**

Sintering

- **Stage 1:**

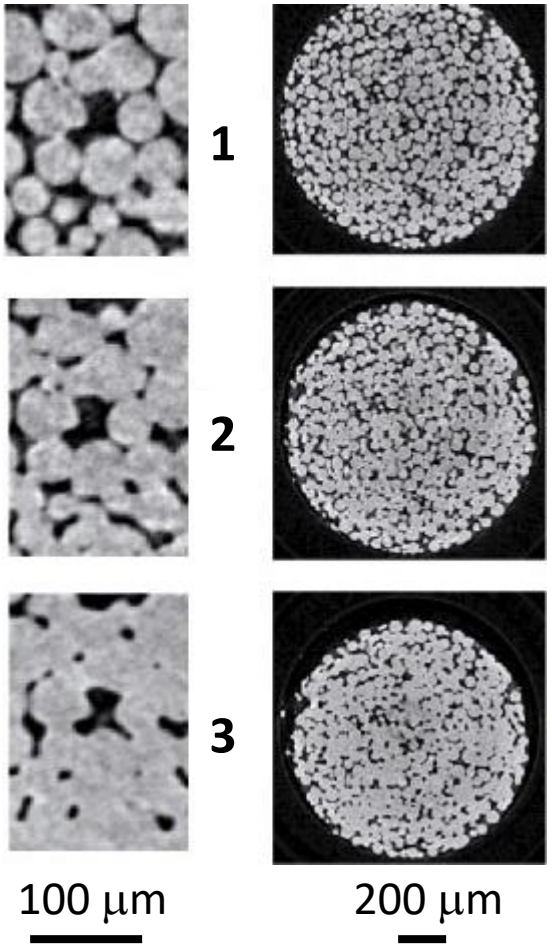
  Initial neck growth

- **Stage 2:**

  Large necks, cylindrical interconnected pores

- **Stage 3:**

  Isolated, spherical pores

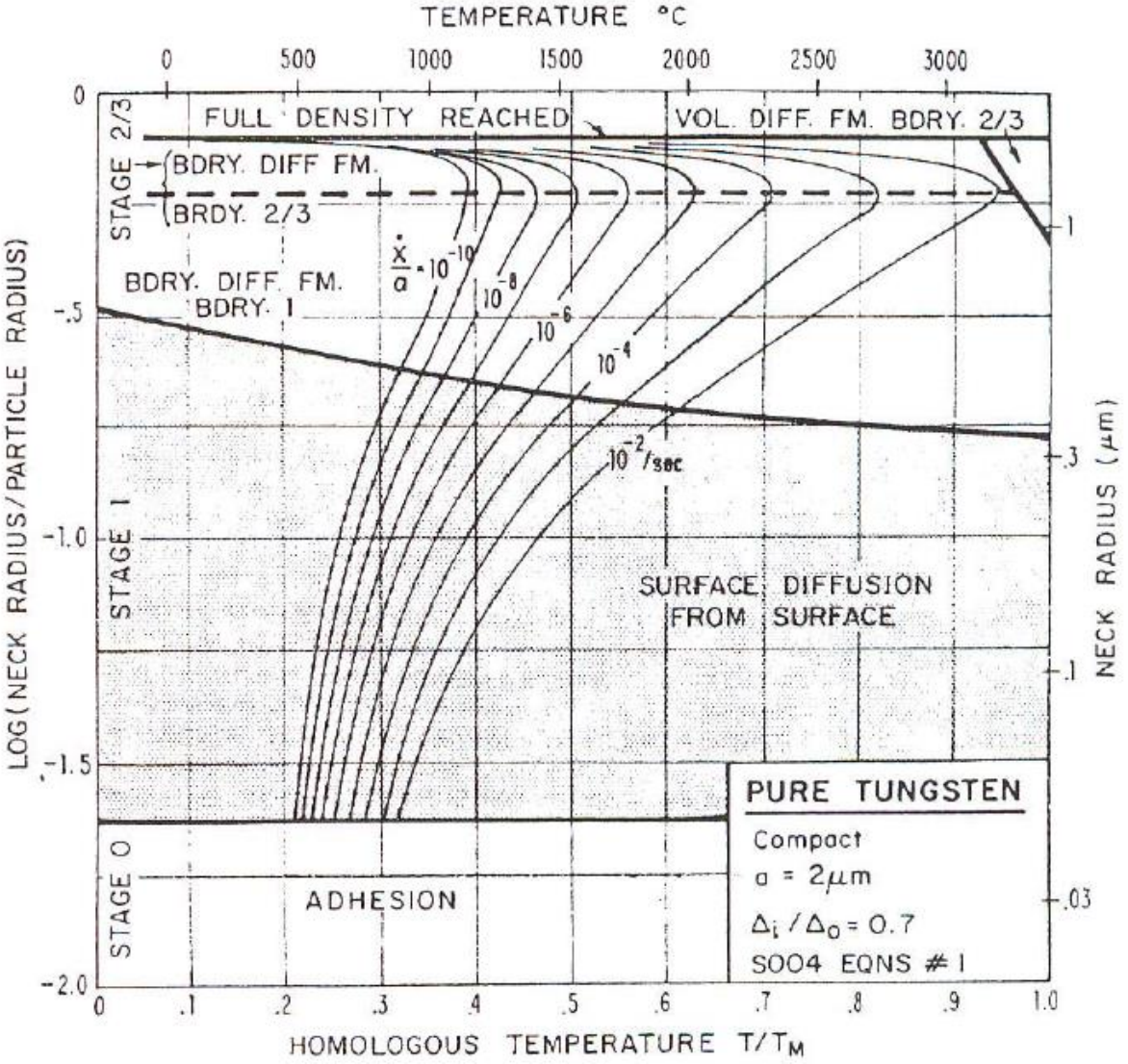


Sintering rate (time) diagrams

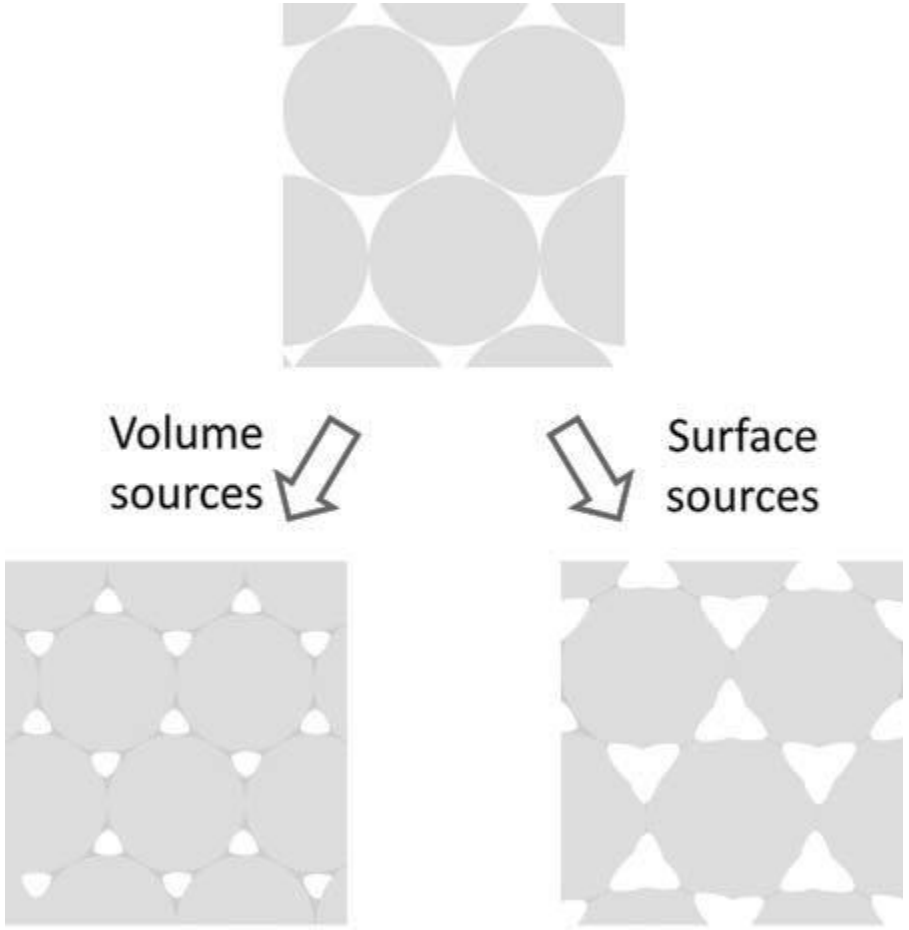
Rates are driven by the curvature difference

$$\frac{dr}{dt} = A \cdot D \cdot K^n$$

More to come!



Sintering conditions



- Low porosity
- Densification

- High porosity
- No Densification

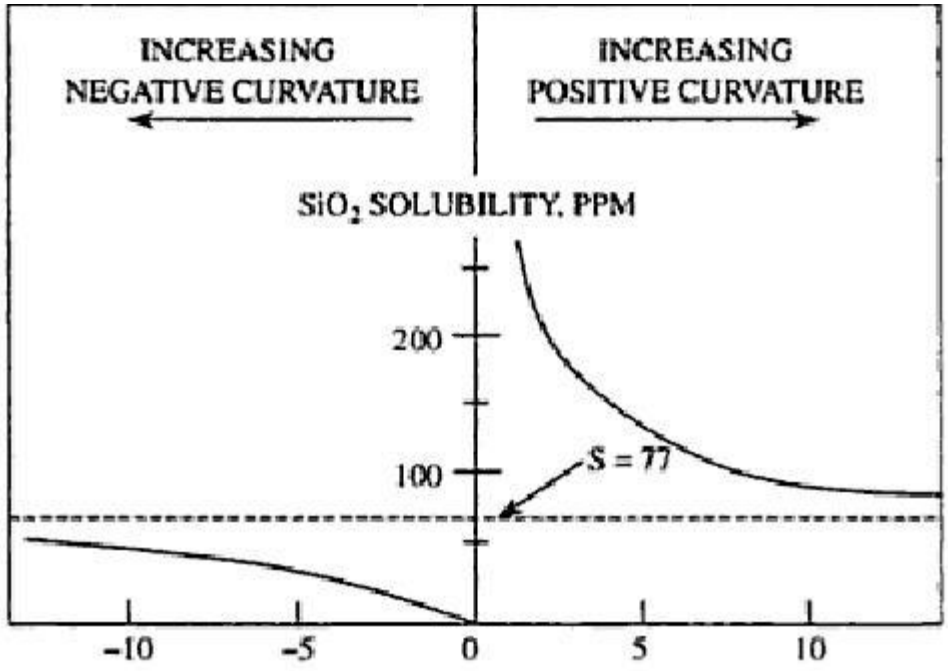
Ostwald ripening
- curvature and chemical potential -

Young – Laplace equation

$$\Delta\mu = \frac{2\gamma\Omega}{r}$$

Gibbs – Thompson equation

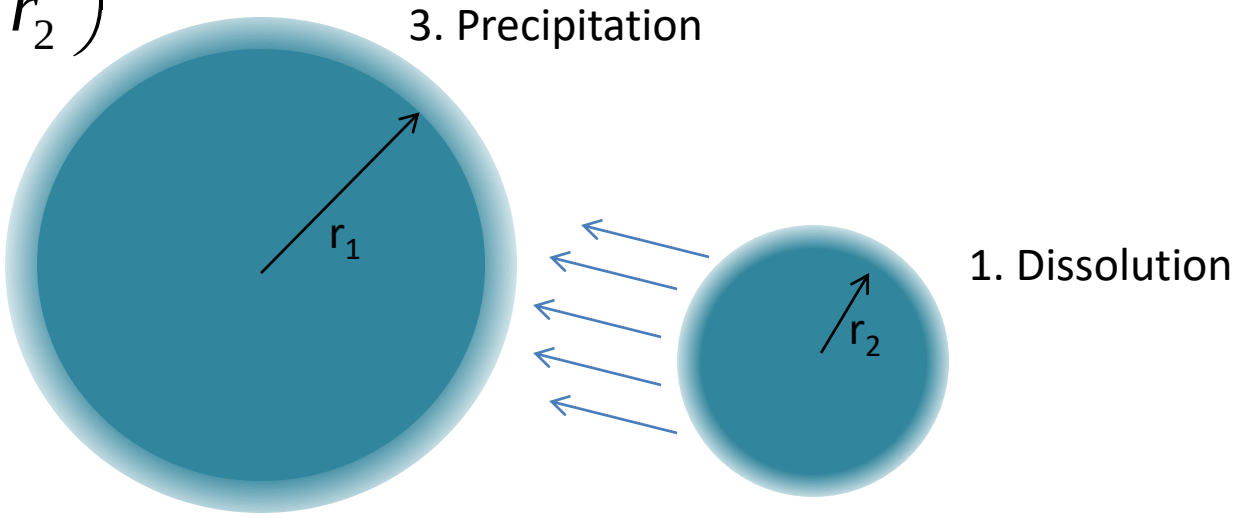
$$k_B T \ln \frac{S_c}{S_\infty} = \frac{2\gamma\Omega}{r}$$



Ostwald ripening
- curvature and chemical potential -

Driving force for Ostwald ripening

$$\Delta\mu = 2\gamma\Omega\left(\frac{1}{r_1} - \frac{1}{r_2}\right)$$



Ostwald ripening

Consequences:

- Exaggerated grain growth in sintering

- Growth of nanocrystals in solution:
  - Can either focus or broaden the size distribution