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MATERIAIS NANOESTRUTURADOS E NANOTECNOLOGIAS

Physical Chemistry of Solid Surfaces

M. Clara Gonçalves

Summary

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- **Introduction**
- **Fundamentals of Surface Energy**
- **Chemical Potential as a Function of Surface Curvature**
- **Further Reading**

Introduction

CUBE OF 1 cm EDGE

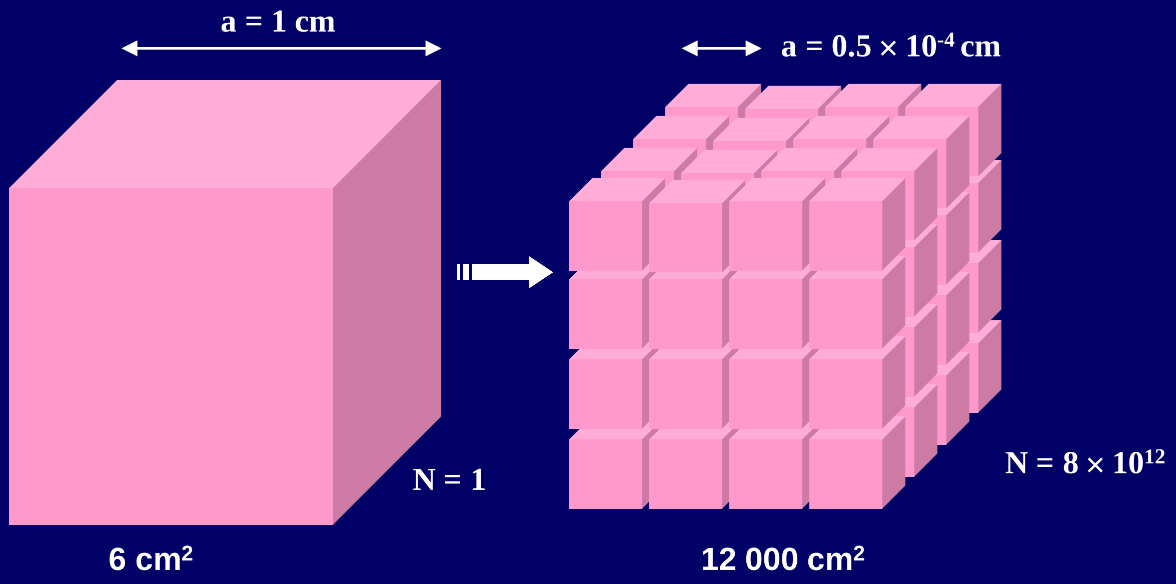
TOTAL SURFACE AREA = **6 cm^2**

PERCENTAGE OF SURFACE ATOMS **10^{-5} %**

CUBE OF 1 cm EDGE

DIVIDED INTO **8 × 10^{12}**

SMALL CUBES OF **0.5 µm EDGE**



CUBE OF 0.5 µm (0.5 × 10^{-4} cm) EDGE

AREA OF EACH FACE = 0.25 × 10^{-8} cm^2

TOTAL SURFACE AREA= 1.5 × 10^{-9} cm^2

$8 \times 10^{12} \times 1.5 \times 10^{-9}$ cm^2 = 12 000 cm^2

Surface Energy

- NANOSTRUTURES AND NANOMATERIALS POSSESS A **LARGE FRACTION OF SURFACE AREA PER UNIT VOLUME**.

- DUE TO THE **VAST SURFACE AREA** NANOSTRUTURES AND NANOMATERIALS POSSESS A **HUGE SURFACE ENERGY** .

- AND THUS, NANOSTRUTURES AND NANOMATERIALS ARE THERMODINAMICALLY **UNSTABLE** OR **METASTABLE**.

⇒ **ONE OF THE GREAT CHALLENGES IN FABRICATION AND PROCESSING OF NANOMATERIALS IS TO OVERCOME THE SURFACE ENERGY, AND TO PREVENT THE NANOSTRUCTURES OR NANOMATERIALS FROM GROWTH IN SIZE, DRIVEN BY THE REDUCTION OF OVERALL SURFACE ENERGY.**

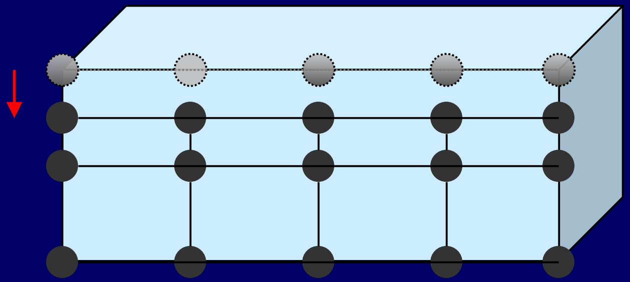
Surface Energy

- **ATOMS** OR **MOLECULES** ON A **SOLID SURFACE** POSSESS **FEWER NEAREST NEIGHBORS** OR **CN**, AND THUS HAVE UNSATISFIED BONDS EXPOSED TO THE SURFACE.

- BECAUSE OF THE DANGLING BONDS ON THE SURFACE, **SURFACE ATOMS** OR **MOLECULES** ARE **UNDER INWARDLY DIRECTED FORCE**.

- AND THUS, THE **BONF DISTANCE** BETWEEN THE SURFACE ATOMS OR **MOLECULES** AND **THE SUB-SURFACE ATOMS** OR **MOLECULES** IS **SMALLER** THAN THAT BETWEEN INTERIOR ATOMS OR MOLECULES.

Surface Energy



➡ **WHEN SOLID PARTICLES ARE VERY SMALL, SUCH A DECREASE IN BOND LENGTH BETWEEN THE SURFACE ATOMS AND INTERIOR ATOMS BECOMES SIGNIFICANT AND THE LATTICE CONSTANTS OF THE ENTIRE SOLID PARTICLES SHOW AN APPRECIABLE REDUCTION.**

Surface Energy

- FOR A GIVEN **SURFACE** WITH A FIXED **SURFACE AREA**, THE **SURFACE ENERGY** CAN BE **REDUCED** THROUGH:

SURFACE RELAXATION, THE SURFACE ATOMS OR IONS SHIFT INWARDLY WHICH OCCUR MORE READILY IN LIQUID PHASE THAN IN SOLID SURFACE.

➡ WHEN **SOLID PARTICLES** ARE **VERY SMALL**, SUCH A **DECREASE IN BOND LENGTH** BETWEEN THE SURFACE ATOMS AND INTERIOR ATOMS BECOMES SIGNIFICANT AND THE **LATTICE CONSTANTS** OF THE ENTIRE SOLID PARTICLES SHOW **AN APPRECIABLE REDUCTION**.

Surface Energy

- THE EXTRA ENERGY POSSESSED BY THE SURFACE ATOMS IS DESCRIBED AS **SURFACE ENERGY**, OR **SURFACE TENSION**.

- **SURFACE ENERGY**, **γ** , IS THE ENERGY REQUIRED TO CREATE A UNIT AREA OF NEW SURFACE:

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

γ- surface energy
G – Gibbs energy
A – surface area

- ON A **NEW CREATED SURFACE**, EACH **ATOM** IS LOCATED IN **AN ASYMMETRIC ENVIRONMENT** AND WILL MOVE TOWARDS THE INTERIOR DUE TO BREAKING OF BONDS AT THE SURFACE.

Surface Energy

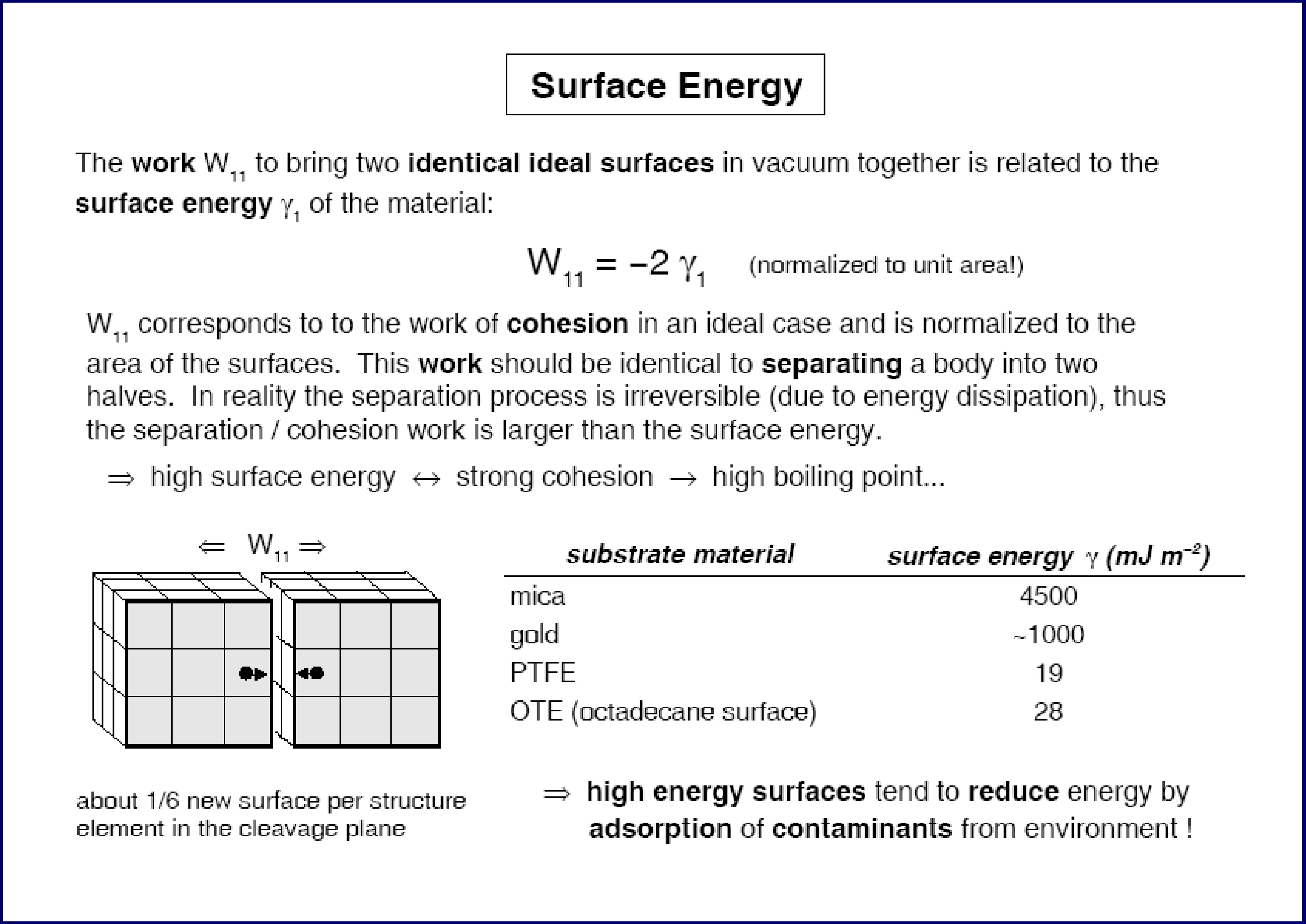
- ON A **NEW CREATED SURFACE**, EACH **ATOM** IS LOCATED IN **AN ASYMMETRIC ENVIRONMENT** AND WILL MOVE TOWARDS THE INTERIOR DUE TO BREAKING OF BONDS AT THE SURFACE.

- **AN EXTRA FORCE** IS REQUIRED **TO PULL THE SURFACE ATOMS** BACK TO ITS ORIGINAL POSITION. FOR EACH ATOM, THIS SURFACE ENERGY IS:

$$\gamma = \frac{1}{2} N_b \varepsilon \rho_a$$

γ - surface energy
N_b – number of broken bonds
ε – half of the bond strength
ρ_a – surface atomic density, i.e., the number of atoms of each area per area on the new surface

Surface Energy



Surface Energy

The **work** W_{11} to bring two **identical ideal surfaces** in vacuum together is related to the **surface energy** γ_1 of the material:

$$W_{11} = -2\,\gamma_1 \qquad \text{(normalized to unit area!)}$$

W_{11} corresponds to to the work of **cohesion** in an ideal case and is normalized to the area of the surfaces. This **work** should be identical to **separating** a body into two halves. In reality the separation process is irreversible (due to energy dissipation), thus the separation / cohesion work is larger than the surface energy.

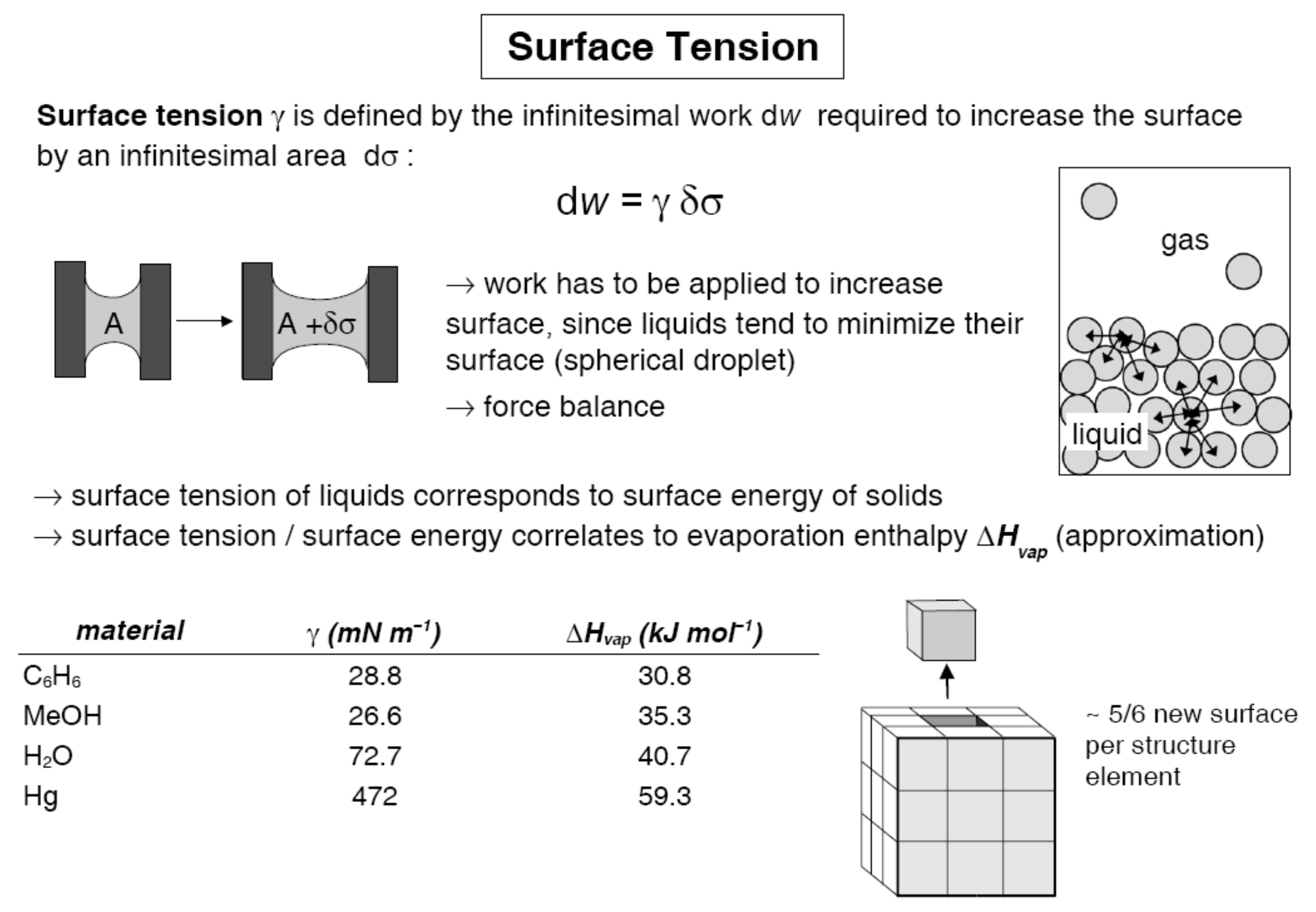
⇒ high surface energy ↔ strong cohesion → high boiling point...

about 1/6 new surface per structure element in the cleavage plane

substrate material	*surface energy* γ *(mJ m^{-2})*
mica	4500
gold	~1000
PTFE	19
OTE (octadecane surface)	28

⇒ **high energy surfaces** tend to **reduce** energy by **adsorption** of **contaminants** from environment !

Surface Energy



Surface Tension

Surface tension γ is defined by the infinitesimal work d*w* required to increase the surface by an infinitesimal area dσ :

$$dw = \gamma\, \delta\sigma$$

A → A +$\delta\sigma$

→ work has to be applied to increase surface, since liquids tend to minimize their surface (spherical droplet)

→ force balance

gas

liquid

→ surface tension of liquids corresponds to surface energy of solids

→ surface tension / surface energy correlates to evaporation enthalpy ΔH_{vap} (approximation)

material	γ *(mN m^{-1})*	ΔH_{vap} *(kJ mol^{-1})*
C_6H_6	28.8	30.8
MeOH	26.6	35.3
H_2O	72.7	40.7
Hg	472	59.3

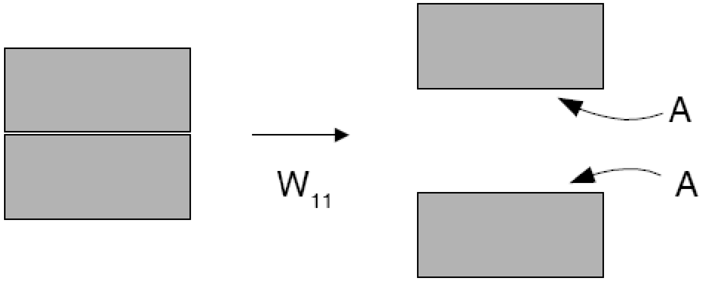
~ 5/6 new surface per structure element

Surface Energy

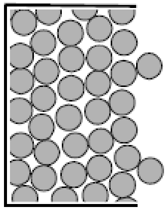
Cohesion

Cohesion forces act **within** a **condensed material** (liquid, solid) to keep it together.

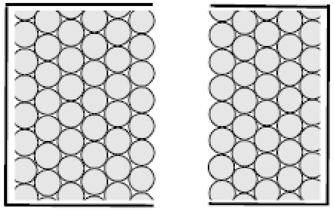
work of cohesion W_{11}: free energy change, or reversible work done, to cleave / separate a material from contact to infinity in vacuum



$$W_{11} = 2\,\overbrace{A}^{\text{new cleaveage area}}\,\underset{\text{surface (free) energy}}{\gamma}$$

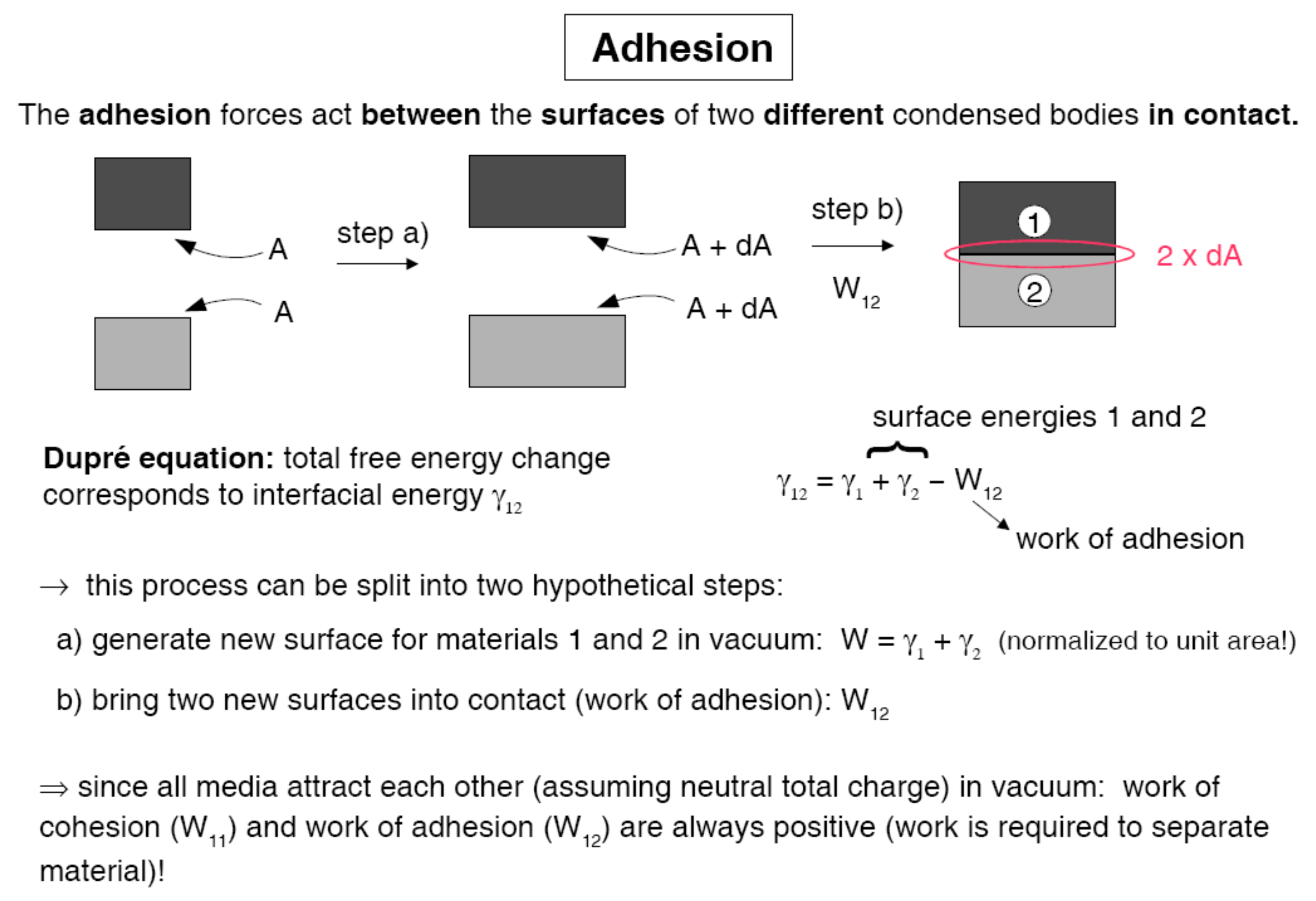


– cohesion in amorphous solids and liquids is isotropic:
→ random fracture plane (e.g. glass)



– cohesion in crystalline solids is anisotropic:
→ fracture along crystal planes (e.g. Si single crystal wafer)

Surface Energy



Adhesion

The **adhesion** forces act **between** the **surfaces** of two **different** condensed bodies **in contact.**

Dupré equation: total free energy change corresponds to interfacial energy γ_{12}

$$\gamma_{12} = \overbrace{\gamma_1 + \gamma_2}^{\text{surface energies 1 and 2}} - W_{12}$$

work of adhesion

→ this process can be split into two hypothetical steps:

a) generate new surface for materials 1 and 2 in vacuum: $W = \gamma_1 + \gamma_2$ (normalized to unit area!)

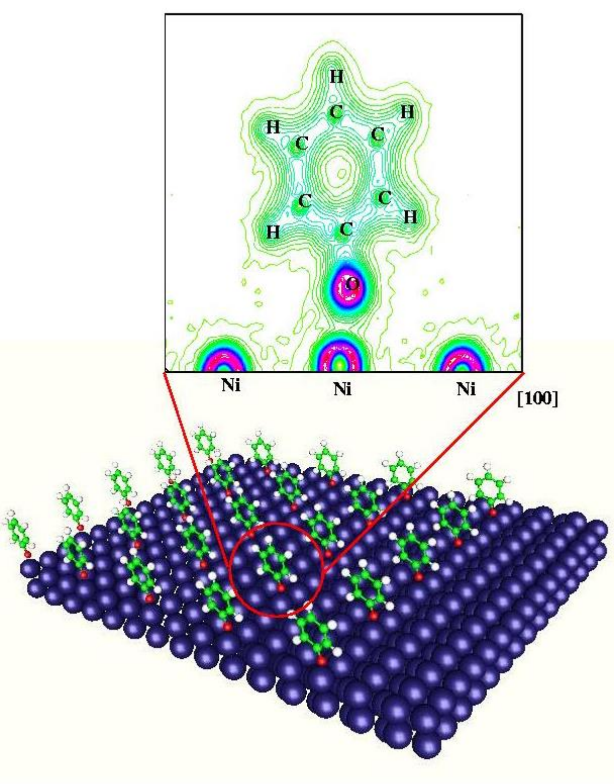
b) bring two new surfaces into contact (work of adhesion): W_{12}

⇒ since all media attract each other (assuming neutral total charge) in vacuum: work of cohesion (W_{11}) and work of adhesion (W_{12}) are always positive (work is required to separate material)!

Surface Energy

- FOR A GIVEN **SURFACE** WITH A FIXED **SURFACE AREA**, THE **SURFACE ENERGY** CAN BE **REDUCED** THROUGH:

CHEMICAL AND **PHYSICAL ADSORPTION** ON SOLID SURFACES;



Surface Energy

- FOR A GIVEN **SURFACE** WITH A FIXED **SURFACE AREA**, THE **SURFACE ENERGY** CAN BE **REDUCED** THROUGH:

COMPOSITION SEGREGATION OR **ENRICHMENT** OF IMPURITIES ON THE SURFACES;

➡ IN **NANOSTRUCTURES** AND **NANOMATERIALS PHASE SEGREGATION** MAY PLAY A SIGNIFICANT ROLE IN THE REDUCTION OF SURFACE ENERGY, CONSIDERING THE GREAT IMPACT OF SURFACE ENERGY AND THE SHORT DIFFUSION DISTANCE.

Surface Energy

- AT THE **INDIVIDUAL NANOSTRUCTURE LEVEL,** THE SURFACE ENERGY CAN BE REDUCED THROUGH:

REDUCE THE OVERALL SURFACE AREA, ASSUMING THE MATERIAL IS ENTIRELY ISOTROPIC

i) **COMBINING INDIVIDUAL NANOSTRUCTURES TOGETHER** TO FORM **LARGE STRUCTURES** SO AS TO REDUCE THE OVERALL SURFACE AREA;

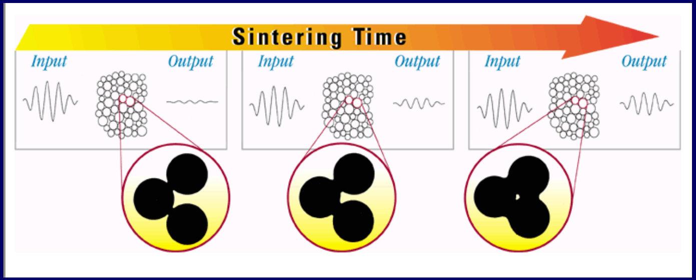
SINTERING

OSTWALD RIPENING

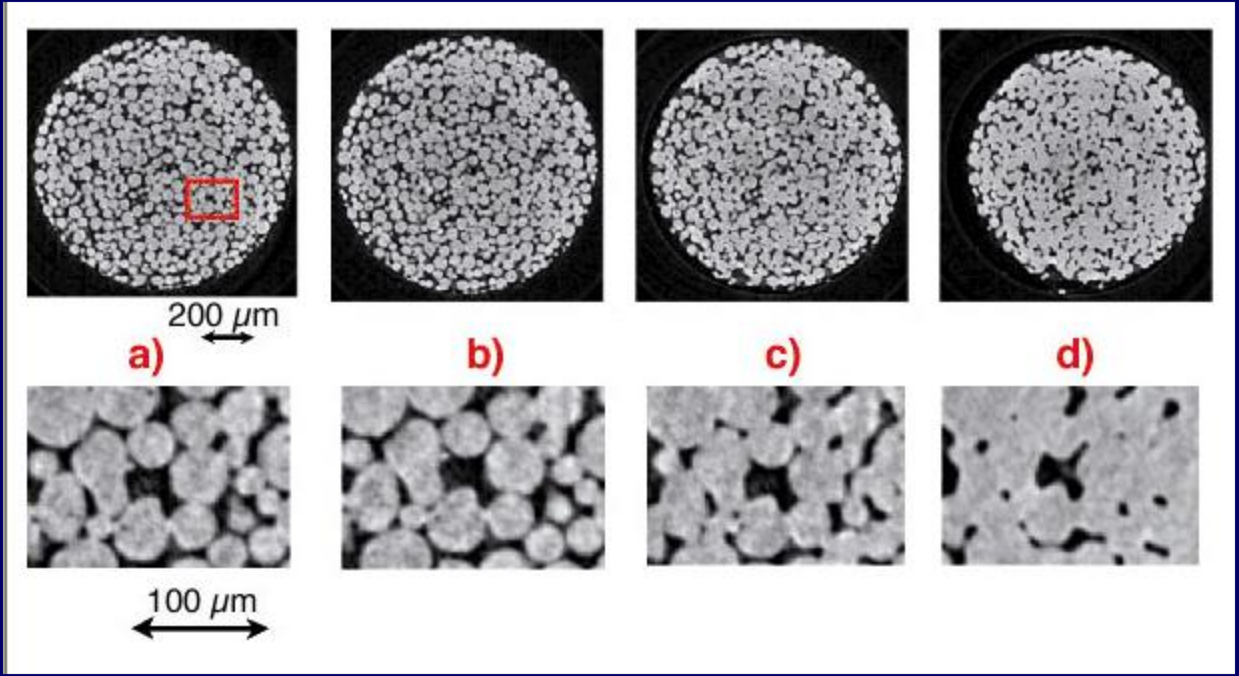
ii) **AGGLOMERATION OF INDIVIDUAL NANOSTRUCTURES** WITHOUT ALTERING THE INDIVIDUAL NANOSTRUCTURES;

Surface Energy

➡ **SINTERING**



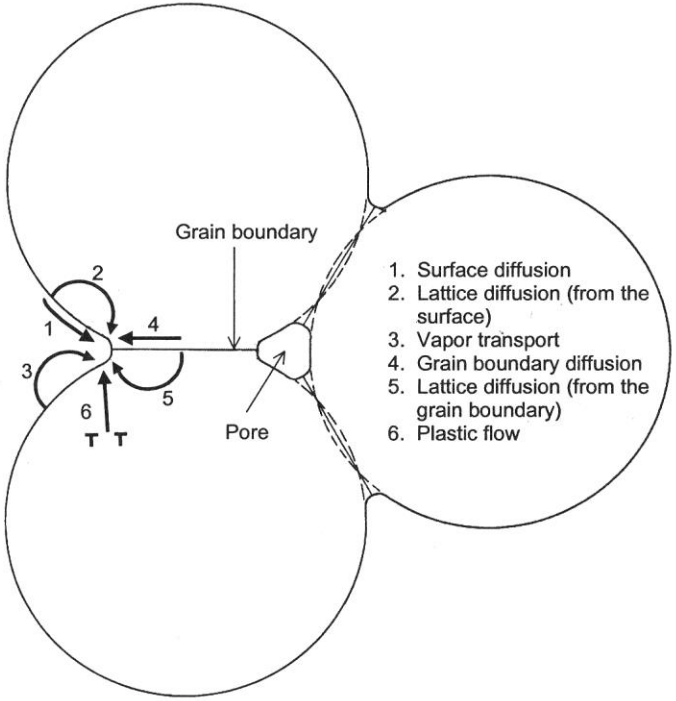
http://www.ameslab.gov/news/sinter.gif



http://www.esrf.eu/UsersAndScience/Publications/Highlights/2002/Materials/MAT3

Surface Energy

SINTERING

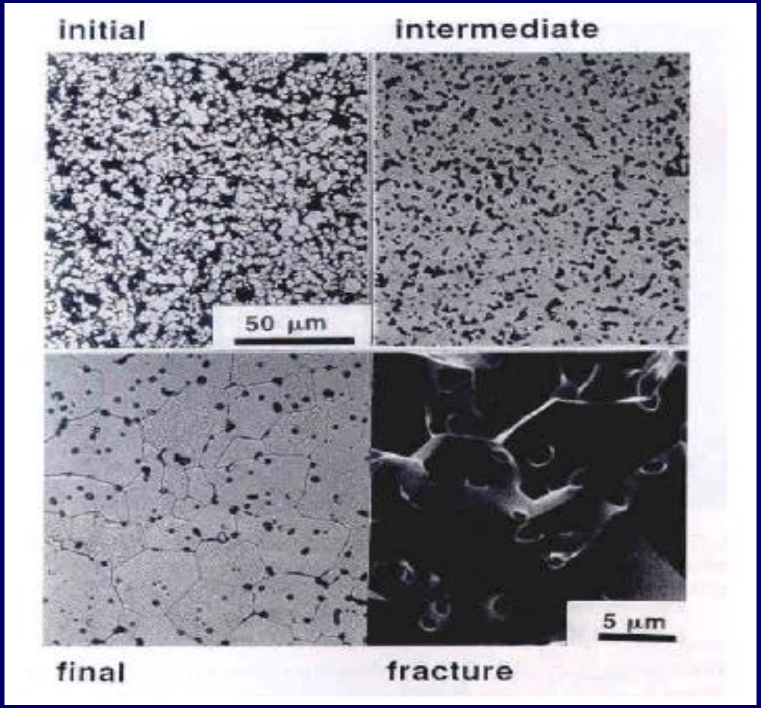


Six distinct mechanisms can contribute to the sintering of a consolidated mass of crystalline particles:(1) surface diffusion, (2) lattice diffusion from the surface, (3) vapor transport, (4) grain boundary diffusion, (5) lattice diffusion from the grain boundary, and (6) plastic flow. Only mechanisms 1 to 3 lead to densification, but all cause the necks to grow and so influence the rate of densification.

Introduction to Ceramics, W.D. Kingery, H.K. Bowen, D.R. Uhlmann, John Wiley & Sons, 1975, p. 475.

Surface Energy

SINTERING



http://www.emi.fraunhofer.de/images/MAVO/Sinter2.gif

Surface Energy

LET US CONSIDER TRANSFERING MATERIAL FROM AN **INFINITE FLAT SURFACE** TO A **SPHERICAL SOLID PARTICLE.**

AS A RESULT OF **TRANSFERRING** OF **dn ATOMS** FROM A **FLAT SOLID SURFACE** TO A **PARTICLE** WITH A **RADIUS** OF **R**, THE **VOLUME CHANGE** OF SPHERICAL PARTICLE, **dV**, IS EQUAL TO THE **ATOMIC VOLUME, Ω**, TIMES **dn**, THAT IS:

$$dV = 4\pi R^2 dR = \Omega dn$$

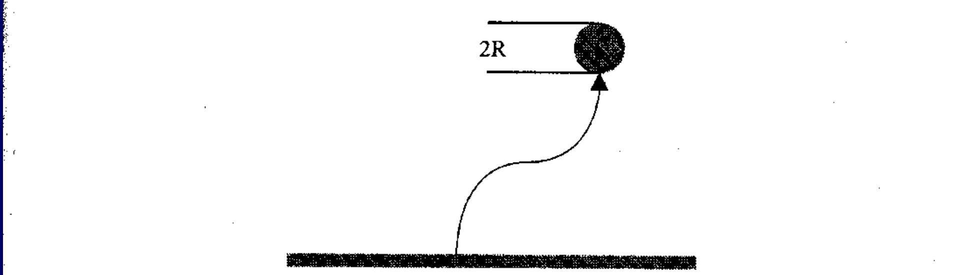


Fig. 2.10. Transport of *n* atoms from the flat surface of a semi-infinite reference solid to the curved surface of a solid sphere.

Nanostructures and Nanomaterials. Synthesis, Properties & Applications,
G. Cao, ICP Imperial College Press, 2007 (ISBN 1-86094-480-9), p. 27.

Surface Energy as a Function of Surface Curvature

- **CHEMICAL POTENTIAL** AS A FUNCTION OF **SURFACE CURVATURE**

THE **WORK** PER ATOM TRANSFERED, Δμ, EQUALS TO THE **CHANGE OF CHEMICAL POTENTIAL**, GIVEN BY:

$$\Delta\mu = \mu_C - \mu_\infty = \gamma \frac{dA}{dn} = \gamma 8\pi R dR \frac{\Omega}{dV}$$

m_c – chemical potential of the particle surface

m_∞ – chemical potential of the flat surface

Ω– atomic volume

Surface Energy as a Function of Surface Curvature

YOUNG-LAPLACE EQUATION

THE **YOUNG-LAPLACE EQUATION** DESCRIBES THE CHEMICAL POTENTIAL OF AN ATOM IN A SPHERICAL SURFACE, WITH RESPECT TO A FLAT REFERENCE SURFACE.

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

GENERALIZATION FOR ANY TYPE OF CURVED SURFACES:

$$\Delta\mu = \gamma\Omega\left(\frac{1}{R_1}+\frac{1}{R_2}\right)$$

Surface Energy as a Function of Surface Curvature

Concave curvature **Convex curvature**

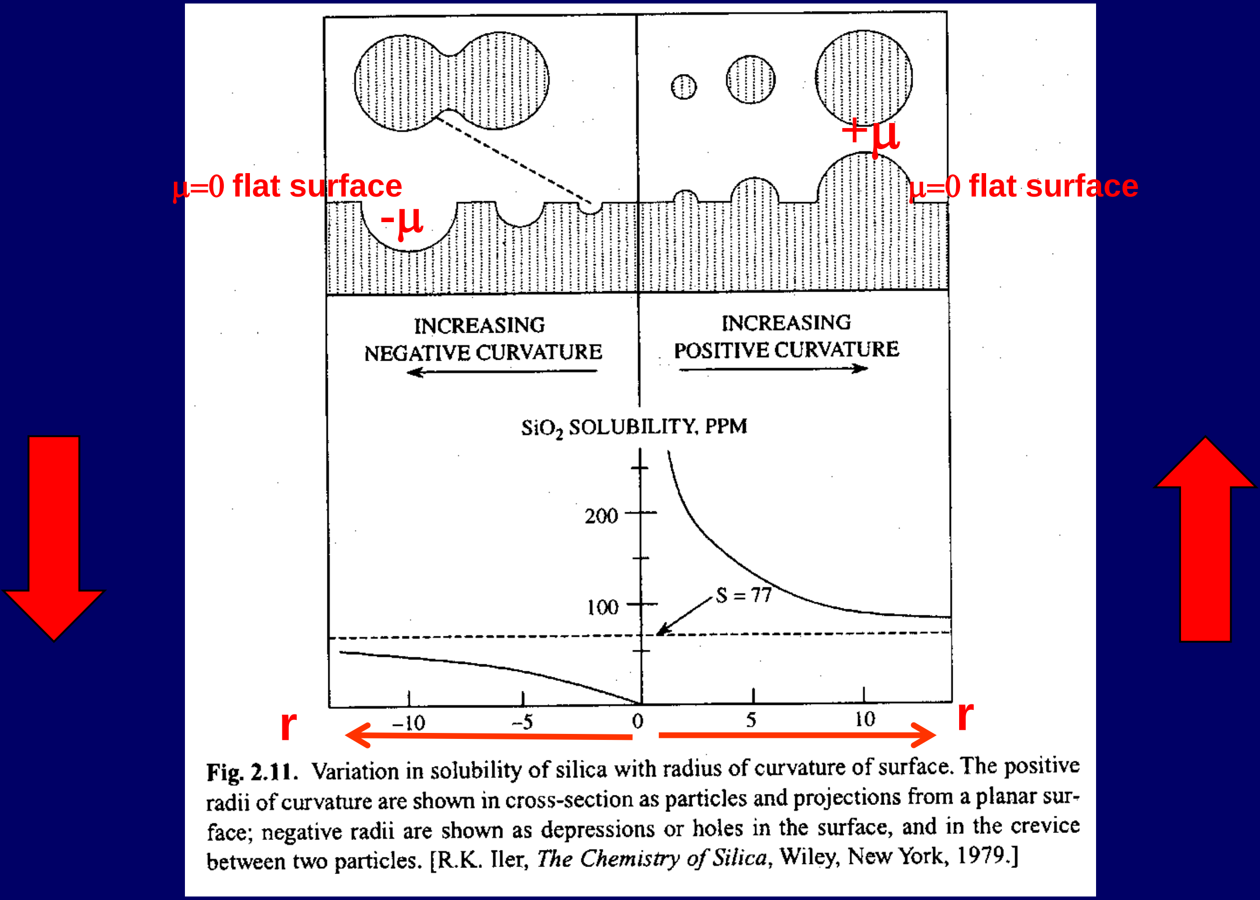


Fig. 2.11. Variation in solubility of silica with radius of curvature of surface. The positive radii of curvature are shown in cross-section as particles and projections from a planar surface; negative radii are shown as depressions or holes in the surface, and in the crevice between two particles. [R.K. Iler, *The Chemistry of Silica*, Wiley, New York, 1979.]

Nanostructures and Nanomaterials. Synthesis, Properties & Applications,
G. Cao, ICP Imperial College Press, 2007 (ISBN 1-86094-480-9), p. 28.

Surface Energy as a Function of Surface Curvature

FOR A **CONVEX SURFACE** , THE **CURVATURE** IS **POSITIVE**, AND THUS THE **CHEMICAL POTENTIAL** OF **AN ATOM** ON SUCH A SURFACE IS **HIGHER** THAN THAT ON A FLAT SURFACE.

MASS TRANSFER FROM A **FLAT SURFACE** TO A **CONVEX SURFACE** RESULTS IN AN **INCREASE IN SURFACE CHEMICAL POTENTIAL**.

FOR A **CONCAVE SURFACE** , THE **CURVATURE** IS **NEGATIVE**, AND THUS THE **CHEMICAL POTENTIAL** OF **AN ATOM** ON SUCH A SURFACE IS **LOWER** THAN THAT ON A FLAT SURFACE.

MASS TRANSFER FROM A **FLAT SURFACE** TO A **CONCAVE SURFACE** RESULTS IN AN **DECREASE IN SURFACE CHEMICAL POTENTIAL**.

Surface Energy as a Function of Surface Curvature

- AT THE **INDIVIDUAL NANOSTRUCTURE LEVEL**,

THE SURFACE ENERGY CAN BE REDUCED THROUGH:

REDUCE THE OVERALL SURFACE AREA, ASSUMING THE MATERIAL IS ENTIRELY ISOTROPIC

i) **COMBINING INDIVIDUAL NANOSTRUCTURES TOGETHER** TO FORM LARGE STRUCTURES SO AS TO REDUCE THE OVERALL SURFACE AREA;

Surface Energy as a Function of Surface Curvature

TWO PARTICLES, WITH DIFFERENT RADII, R_1 R_2, INTO A SOLVENT

GIBBS-THOMPSON EQUATION

$$\ln\left(\frac{S_c}{S_\infty}\right) = \gamma\Omega\frac{R_1^{-1}+R_2^{-1}}{kT}$$

S_c – solubility of a curved surface

S_∞ - solubility of a flat surface

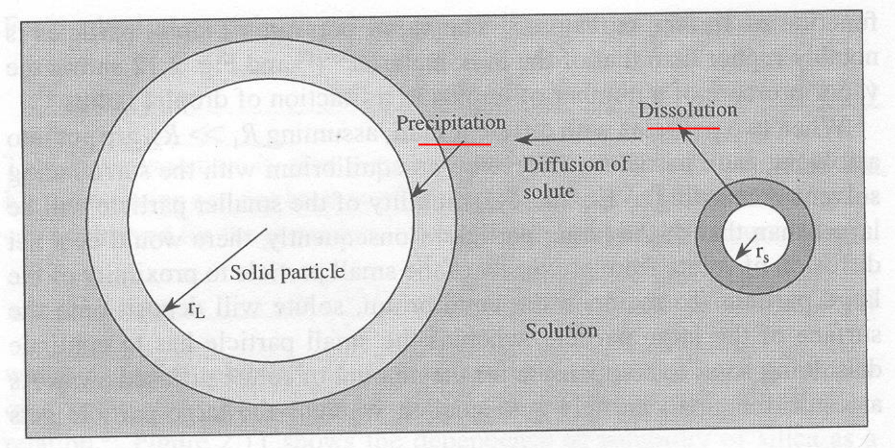
NOTE THAT THE VAPOR PRESSURE OF SMALL PARTICLES IS NOTABLY HIGHER THAN THAT OF THE BULK MATERIAL.

WHEN TWO PARTICLES WITH DIFFERENT RADII ARE PUT INTO A SOLVENT, EACH PARTICLE WILL DEVELOP AN EQUILIBRIUM WITH THE SURROUNDING SOLVENT.

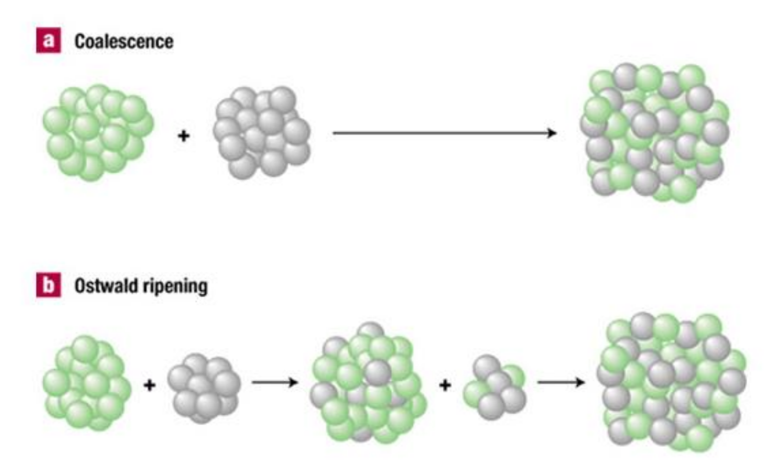
THE SOLUBILITY OF THE SMALLER PARTICLE WILL BE LARGER THAN THAT OF THE LARGER PARTICLE.

Surface Energy as a Function of Surface Curvature

OSTWALD RIPENING



Nanostructures and Nanomaterials. Synthesis, Properties & Applications, G. Cao, ICP Imperial College Press, 2007 (ISBN 1-86094-480-9), p. 27.



Michael Bowker
Nature Materials 1, 205 - 206 (2002).

Surface Energy as a Function of Surface Curvature

➡ **OSTWALD RIPENING**

THERE WOULD BE A NET DIFFUSION OF SOLUTE FROM PROXIMITY OF THE SMALL PARTICLE TO PROXIMITY OF THE LARGE PARTICLE.

TO MAINTAIN THE **EQUILIBRIUM**, SOLUTE WILL DEPOSIT ONTO THE SURFACE OF THE LARGE PARTICLE WHEREAS THE SMALL PARTICLE HAS TO CONTINUE DISSOLVING SO AS TO COMPENSATE FOR THE AMOUNT OF SOLUTE DIFFUSED AWAY.

THE SMALLER PARTICLE GETS SMALLER

THE LARGER PARTICLE GETS LARGER

Further Reading

- Nanostructures and Nanomaterials. Synthesis, Properties & Applications, G. Cao, ICP Imperial College Press, 2007 (ISBN 1-86094-480-9).

- Thin-Film Deposition. Principles & Practice, D. L. Smith McGraw-Hill, 1995 (ISBN 0-07-058502-4).