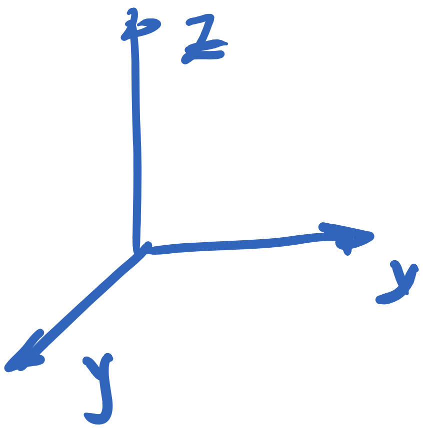
ECE5320

Lecture #3

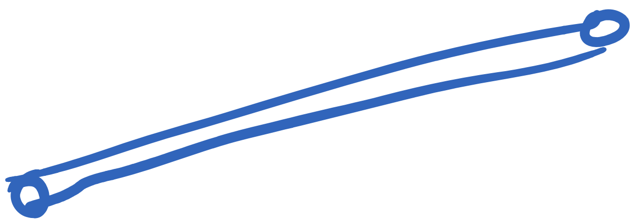
DIMENSIONALITY OF NANOMATER.



- NANO PARTICLE

  0-D

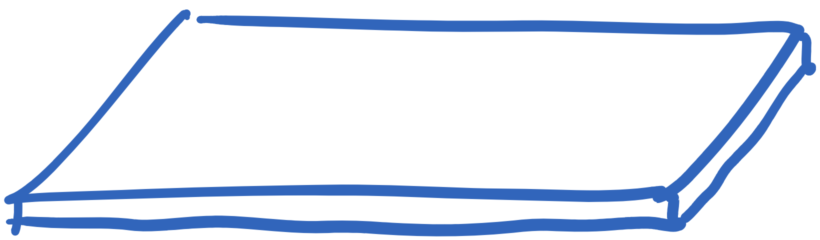
  $\delta_x, \delta_y, \delta_z << 100 nm$



- NANOWIRE (ROD, TUBE)

  1-D

  $\delta_x, \delta_y << \delta_z$

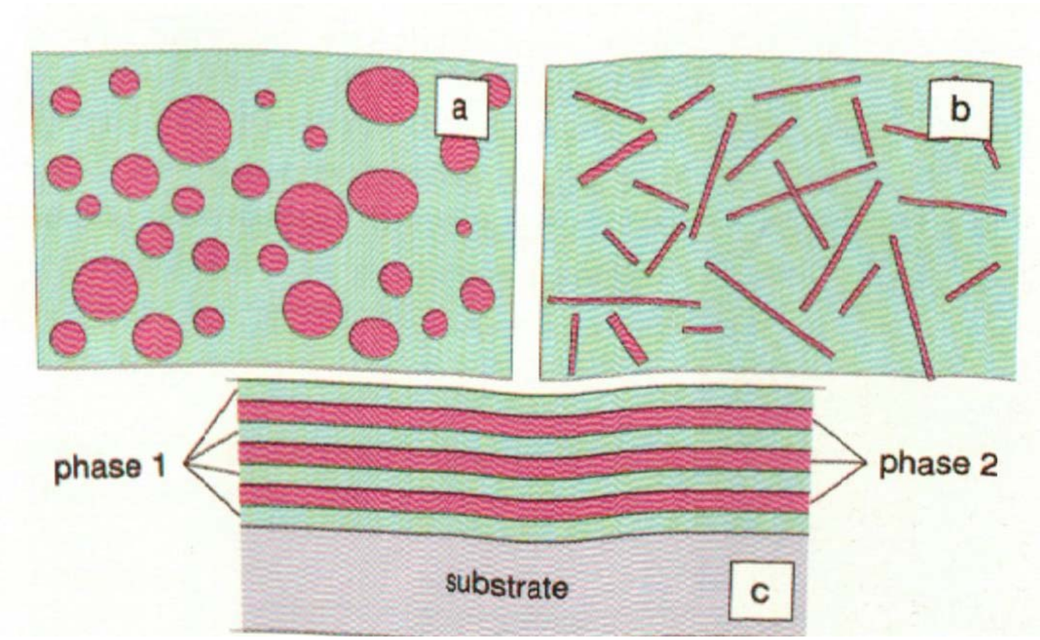


- THIN FILMS (NANOPLATES)

  2-D $\delta_x << \delta_y, \delta_z$

NANOCOMPOSITE

- NANOMATERIAL IN MATRIX

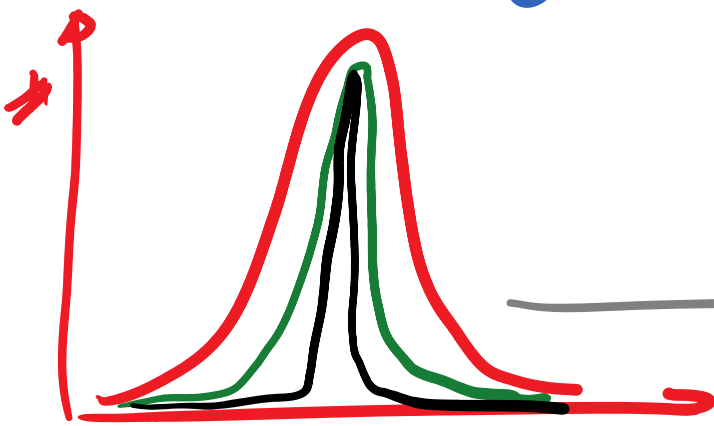


- THIS IS THE EASY WAY TO RELIZE THE PROPERTY OF NANOM.
- MECHANICAL
- ELECTRICAL
- MAGNETIC
- CHEMICAL

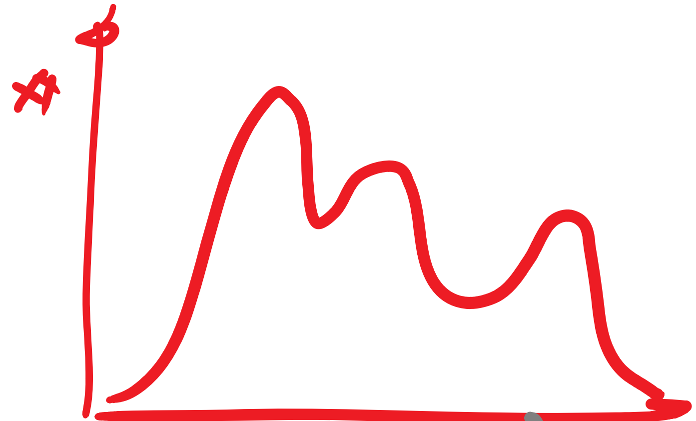
- PHASE 1 AND PHASE 2

Nanocomposite

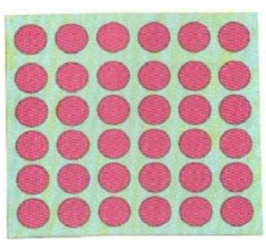
- CHALLENGE: UNIFORM SIZE AND DISTR.

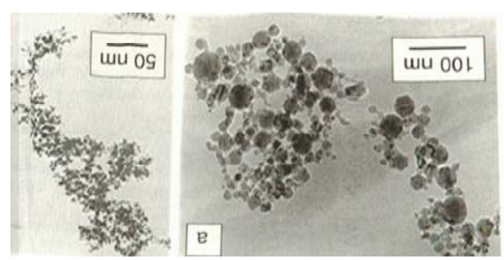


VS



- GRAINS
- NANOP. IN POLYMERS
- C. NANOTUB. IN POLYMERS
- Fe_2O_3, Al_2O_3 IN GLASS
- Au NP IN GLASS





ELEMENTARY CONSEQUENC. OF SMALL PARTICLE SIZE

- SURFACE:

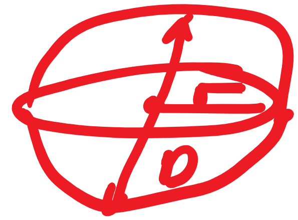
SURFACE / VOLUME

$4r^2\pi \,/\, \frac{4}{3}r^3\pi$

$$\boxed{\frac{A}{V} = \frac{3}{r}}$$

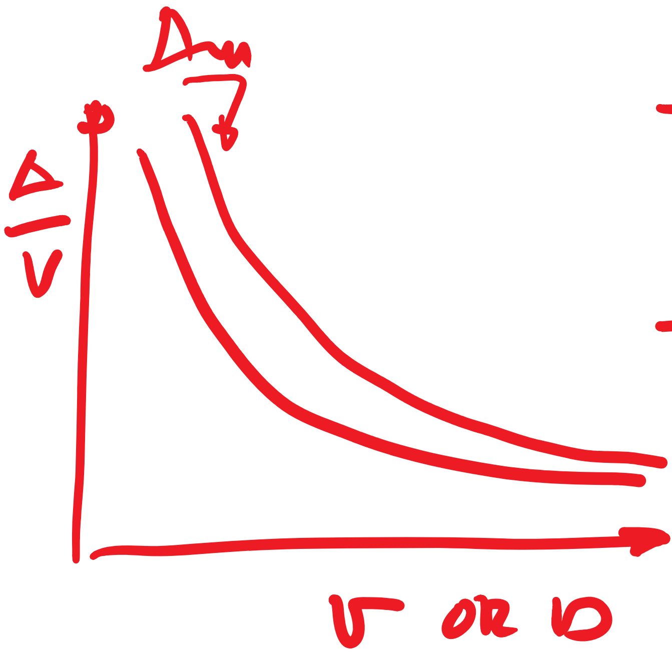
$r = \frac{D}{2}$

$$\boxed{\frac{A}{V} = \frac{3}{r} = \frac{6}{D}}$$



- D - DIAMETER OF NP.
- r - RADIUS OF NP.

ELEMENT. CONSEQ. OF SMALL SIZE



- EXTREMLY LARGE AREA PER VOLUME; D<10 nm ~ 10^8 FAC.
- CATALYSIS, CHEMISTRY, SENSING, COROSSION, OPTICS, TRANSPORT ...

A_m - SURFACE PER MOLE OF SUBST. M - MOLAR WEIGHT

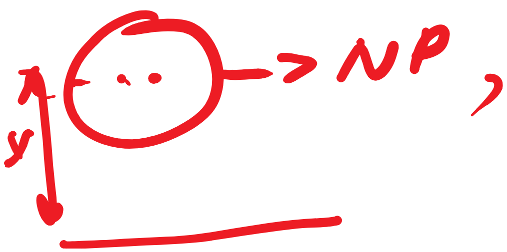
$$A_m = n \cdot A = \frac{M}{\rho \cdot D^3 \pi} \cdot \pi D^2 = \frac{6M}{\rho D}$$

ρ - DENSITY

THERMAL PHENOMENA

- kT (Boltzmann) $k = 1.38 \times 10^{-23}\ \frac{J}{K}$

MEASURE OF THERMAL FLUCTUATIONS



$$kT = \rho_{NP} \cdot v_{NP} \cdot g \cdot x = kT$$

FOR ZIRCONIA NP OF 5nm ⟹
$x = 1m$!

→ NP ARE VERY MOBILE AT ROOM T.

THERMAL PHENOMENA

c - speed of light

h - Planck's const $(6.63 \times 10^{-34}\ Js)$ v. small

λ - wave lenght

$$h\nu = h \cdot \frac{c}{\lambda}$$

$$V_{NP} = \frac{D^3 \pi}{6} \qquad D = 3\ nm$$

$$h \cdot \nu = C_p \cdot \rho \cdot V_{NP} \cdot \Delta T \Longrightarrow \boxed{\Delta T = 20K}$$

$C_p \rightarrow 457\ \frac{J}{kg K}$

$\rho \rightarrow 5.6 \times 10^3\ \frac{kg}{m^3}$ } Zirconia NP

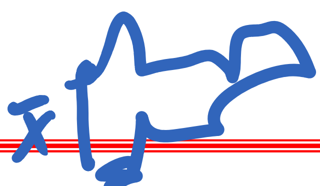
Diffusion and Thermal Phenomena

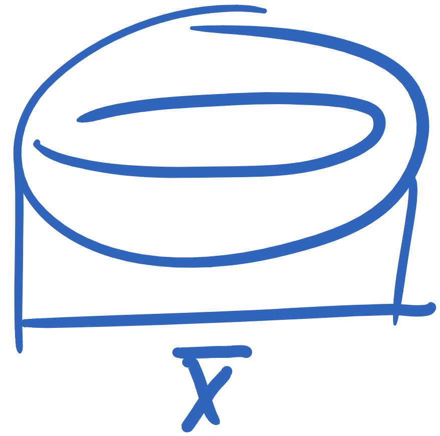
$$\bar{X}^2 = Dt$$

D - Diff. const.

t - Time

$\bar{X}$ - average displ. by random walk





} instantaneous homogenization (alloying)

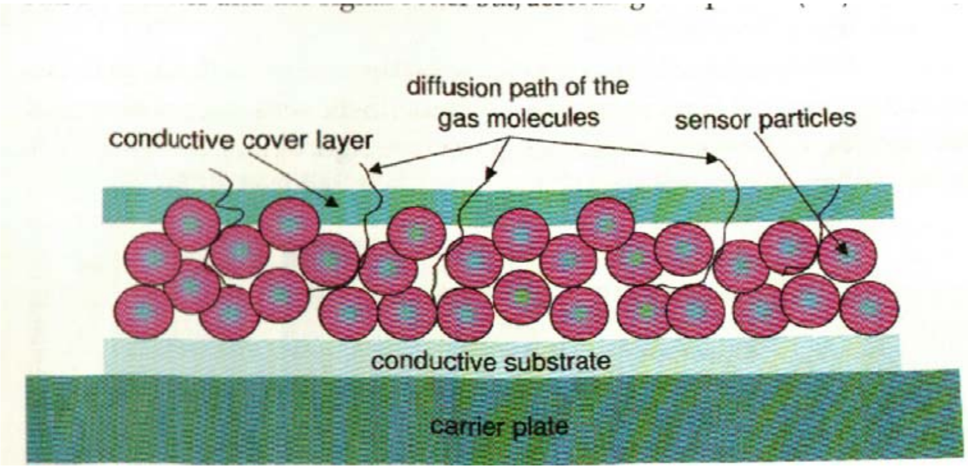
$\bar{X} \sim$ few nanom.

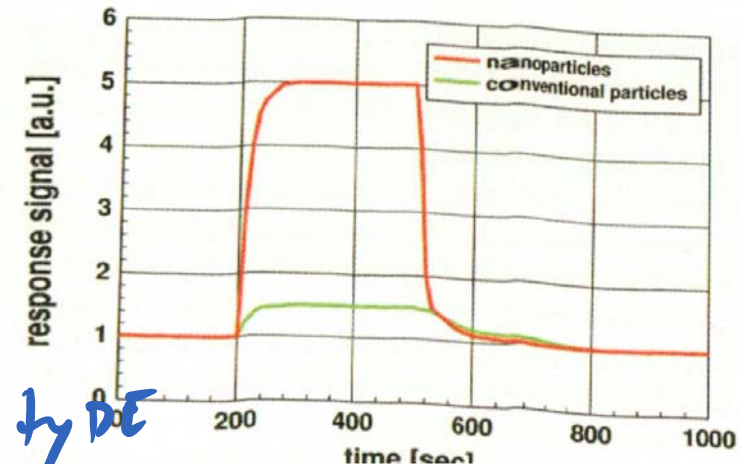
$D \cdot t \sim (10^{-9})^2 \; m^2$

$D \sim 10^{-10} \frac{m^2}{s} \Rightarrow t \sim 10^{-8} \; s$!

Diffusion of Nanoscale

Example: Sensors based on Nanoparticles (NP)





Amplitude and response time

NP: TiO_2, SnO_2, Fe_2O_3

Gas: O_2, CO, CO_2 ....

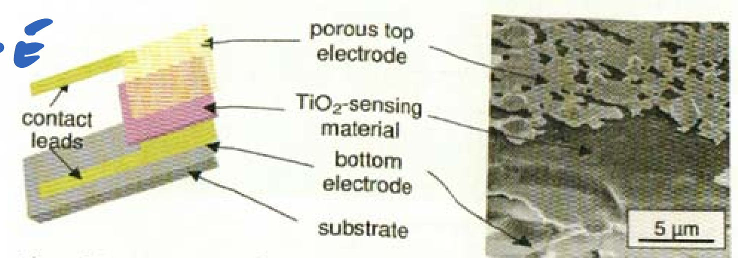
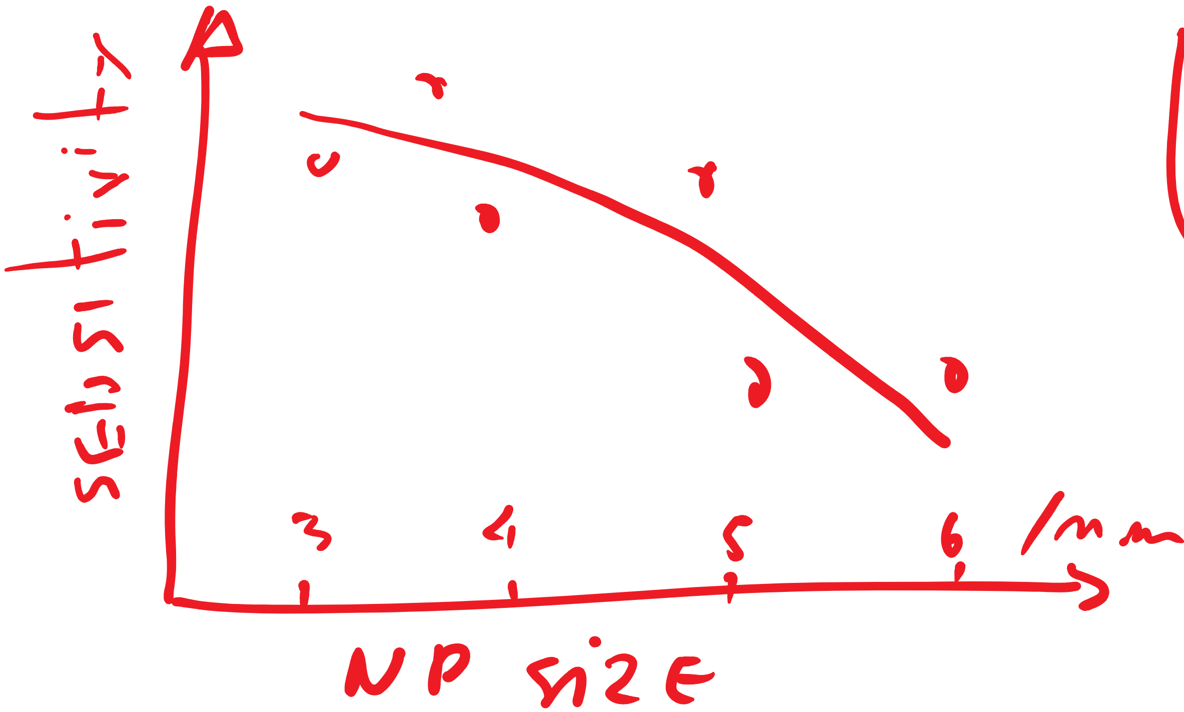


Figure 1.17 A gas sensor following the desi...

Diffusion at Nanoscale

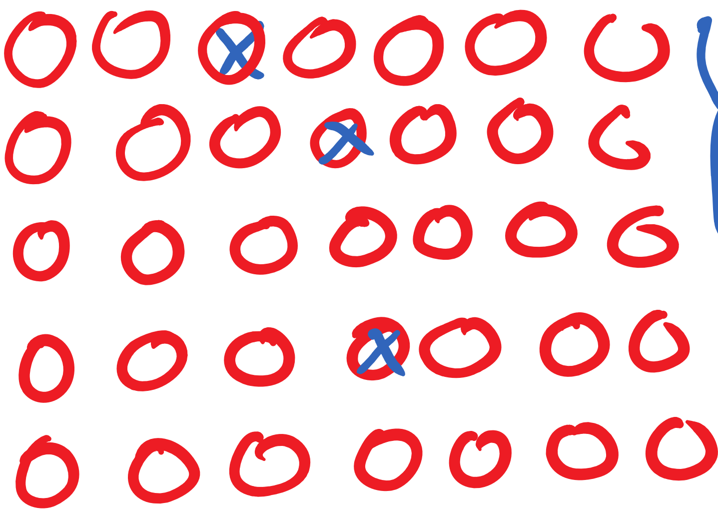
Sensors with NP / VERY CHEAP!



- HEALTH / TUMOR detection
- CHEMICAL
- HOMELAND
- PROCESS CONTROL
- OTHER.

NANOMATERIALS – SURFACES

– NEAR SURF. REGION



* 1st NEAREST NEIGHBOR
* δ * 2nd NN
* 3rd NN

– IN THE REGION δ ↕ FROM THE SURF.

– # 1st, 2nd AND 3rd NN IS DIFFERENT.

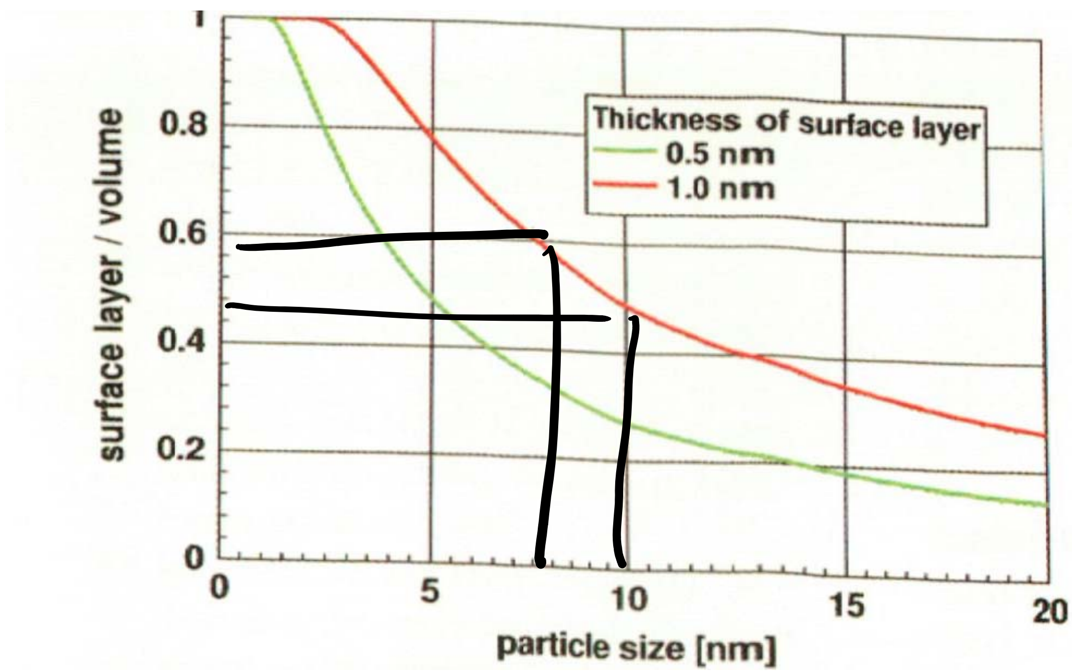
NANOMATERIALS - SURF.

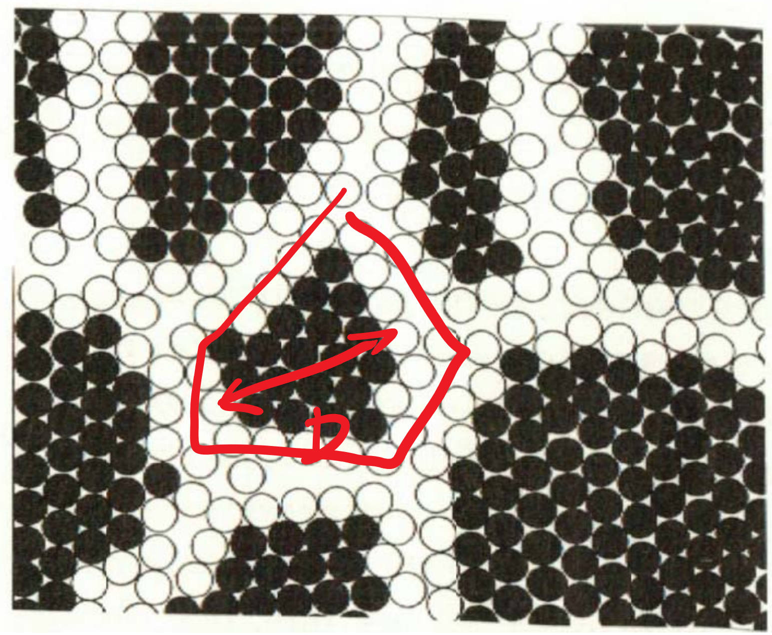
$$R^{*} = \frac{D^3 - (D-2\delta)^3}{D^3} = 1 - \left(\frac{D-2\delta}{D}\right)^3$$

$\delta \approx 0.5 - 1.5 \times 10^{-9}$ m

THE VOLUME % OF MATERIAL AFFECTED IS VERY DEPENDENT ON D, OR r OF NP.

REGION NEAR SURFACE
(AFFECTED BY SURFACE)

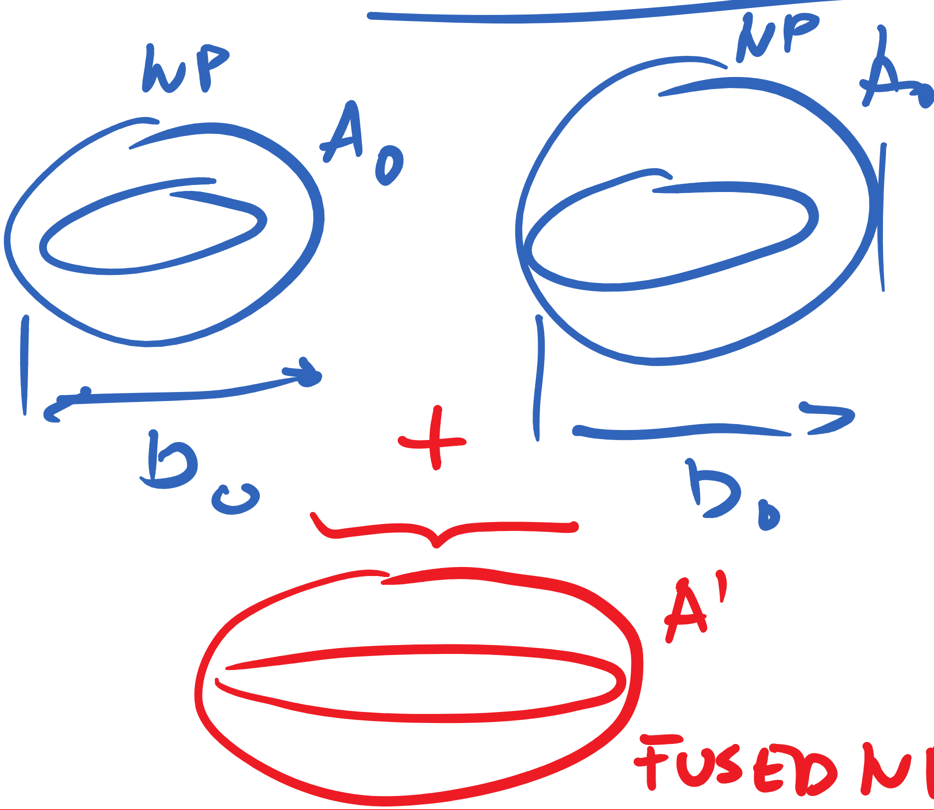




50% OF VOLUME AFFECT.
BY SURF FOR NP<10nm

NANOGRAINED
MATERIALS

NP – AGLOMERATION, FUSION, CO-AGULATION



TOTAL ENERGY OF NP RELATED TO SURFACE

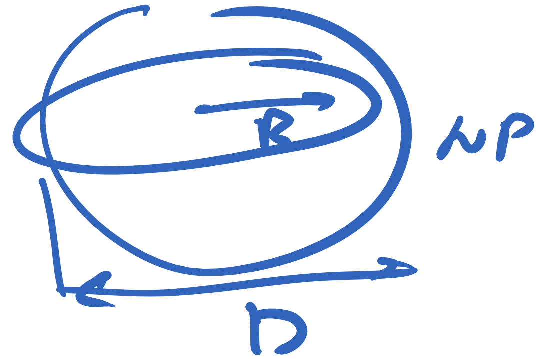
$$E_0 = \gamma \cdot A_0$$

2NP; $2E_0 = E_{TOT} = 2\gamma A_0$

FNP, $E_{FNP} = \gamma A'$

NP- FUSION, AGLOMERATION...

$E_{T,FNP} < E_{TOT}$



$\gamma A' < 2\gamma A_0$

$\Delta E = \gamma (A' - 2A_0)$

$\Delta E = \gamma (4R'^2\pi - 8R_0^2\pi)$

$\Delta E = ?$ $\Delta E < 0$; FUSION IS SPONTANEOUS

- AFECTS NP STABILITY

NP FUSION . . . . .

HOW MUCH IS ΔE?

$$\Delta E = \gamma \pi \left(D_{FNP}^2 - 2D_0^2 \right) \Rightarrow \Delta E = \gamma \pi D_0^2 \left(2^{2/3} - 2 \right)$$

$$V_{FNP} = 2V_0$$

$$\frac{4}{3} R_{FNP}^3 \pi = \frac{8}{3} R_0^3 \pi$$

$$\Rightarrow R_{FNP}^3 = 2 R_0^3 \; ; \; R_{FNP} = R_0 \sqrt[3]{2} \; ; \; D_{FNP} = D_0 \sqrt[3]{2}$$

NP FUSION ....

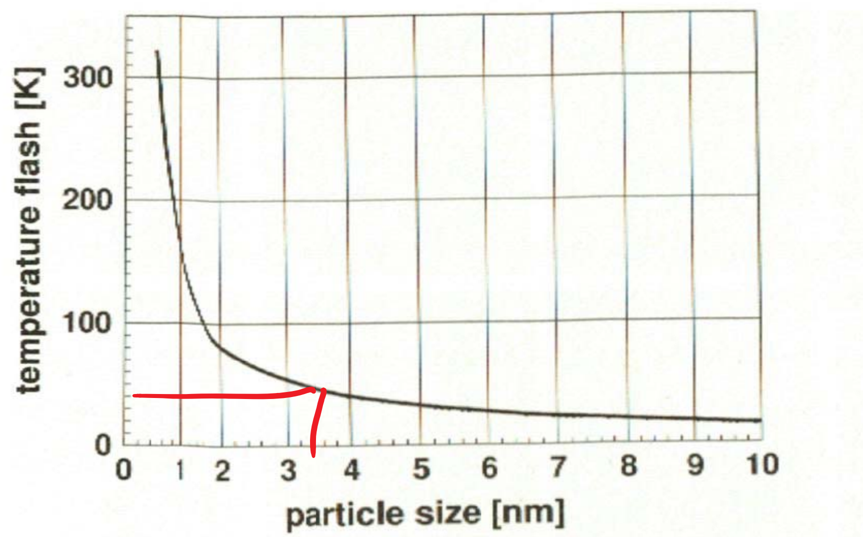
$$\Delta E = \rho \cdot V_{NP} C_p \cdot \Delta T$$

$$\Rightarrow \Delta T = \frac{\Delta E}{\rho V_{NP} C_p}$$

$$\Delta T = \frac{\gamma \pi D_0 (2^{2/3} - 2)}{\rho \frac{D_0^3}{6} \pi \cdot C_p}$$

$$\Delta T = \frac{\gamma 6}{\rho C_p} \cdot \frac{0.41}{D}$$

TEMPERATURE FLASH

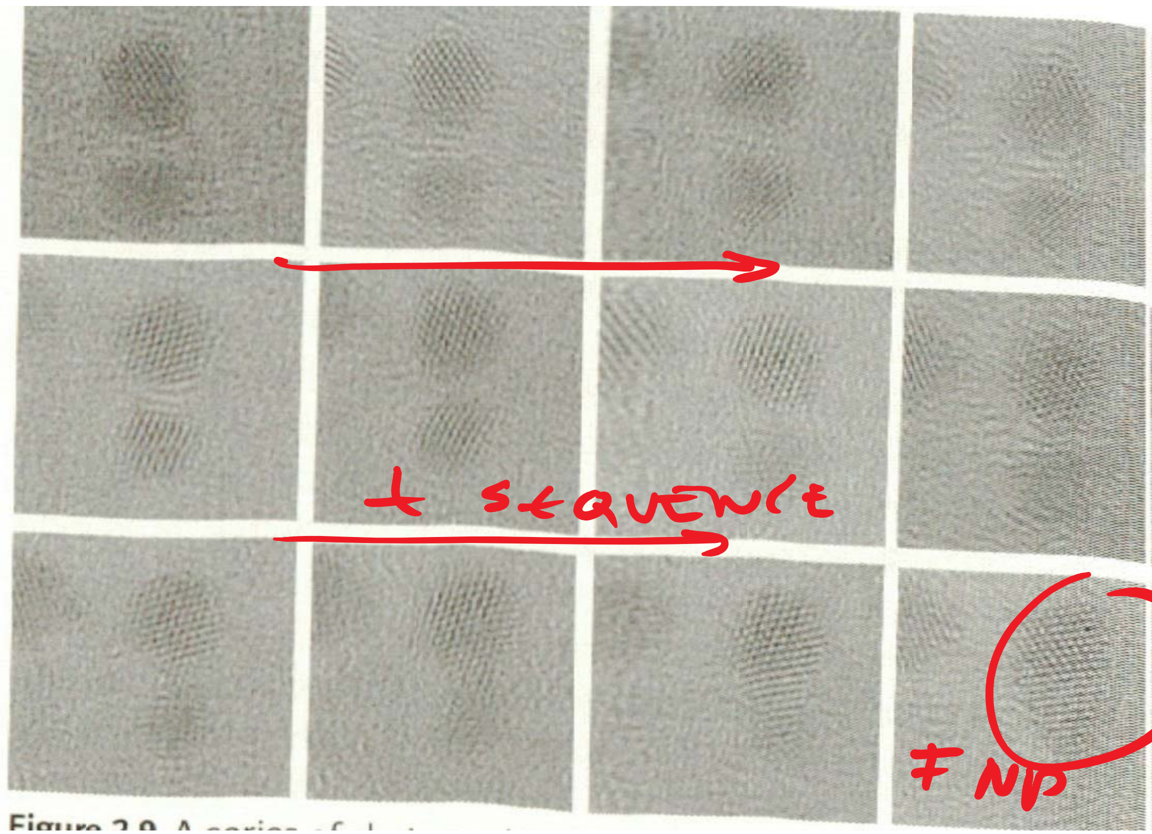


ZrO_2 NP

NP FUSION ....

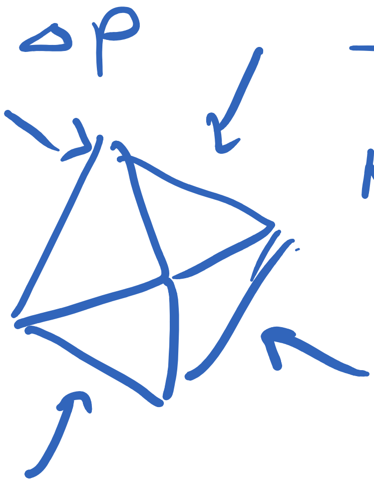
2 NPs →

TEM in situ → of NP FUSION



NP ARE UNDER PRESURE

FROM PREVIOUS LEC:



LIQUID NP

$$\Delta P = \frac{4\gamma}{D} = \frac{4f}{D} \text{ (SOLID)}.$$

NP ARE UNDER EXTRA PRESURE DUE TO A FINITE SIZE! (HYDROSTATIC STATE OF STRESS)

Hook's Law: $\varepsilon = \frac{\Delta P}{K_v}$ — HYDROSTATIC MODLE OF ELAST.

NPs ARE STRAINED

$$\varepsilon = \frac{\Delta a}{a} = \frac{4\gamma}{D K_v} ; \frac{4f}{D K_v}$$

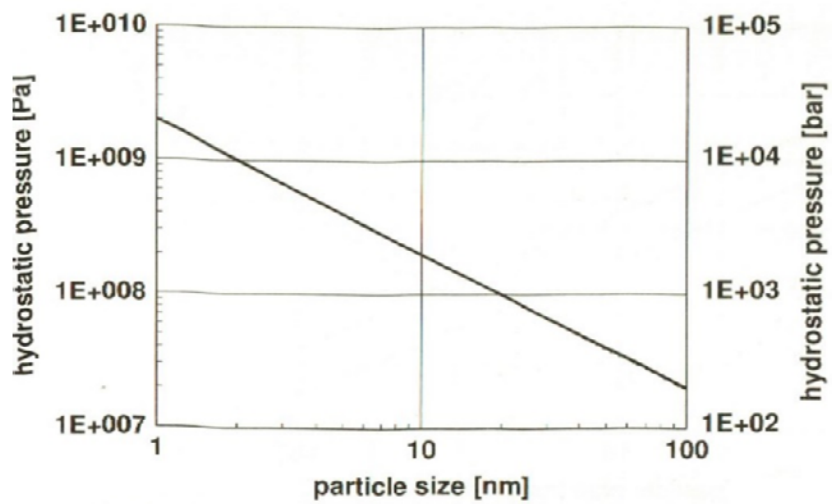


Figure 2.13 Hydrostatic pressure in nanoparticles as a function of particle size. The surface stress $\bar{\sigma}$ was assumed to be 1 N m^{-1}.

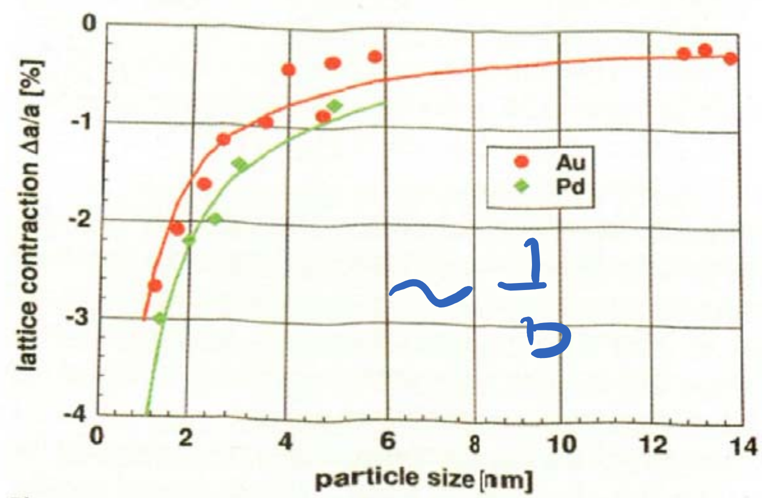


Figure 2.15 Experimental values for the lattice constant of gold [11] and palladium [12] nanoparticles. Due to hydrostatic pressure originating from surface tension, decreasing lattice parameters are observed with decreasing particle size.

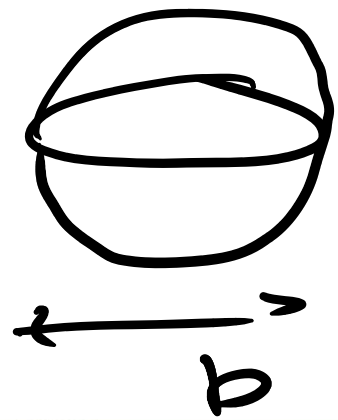
NPs HAVE EXTRA "STRAIN" ENERGY

$$E_{STRAIN} = \frac{1}{2}\Delta p \cdot \varepsilon \quad \left[\frac{J}{m^3}\right]$$

$$= \frac{1}{2}\Delta p \cdot \varepsilon \cdot V_{NP} \quad [J]$$

$$= \frac{1}{2}\,\frac{4\gamma}{D}\cdot\frac{4\gamma}{D K_v}$$

$$E_{STRAIN} = \frac{1}{2K_v}\left(\frac{4\gamma}{D}\right)^2 \quad \left[\frac{J}{m^3}\right]$$



NP

$$V_{NP} = \frac{D^3\pi}{6}$$

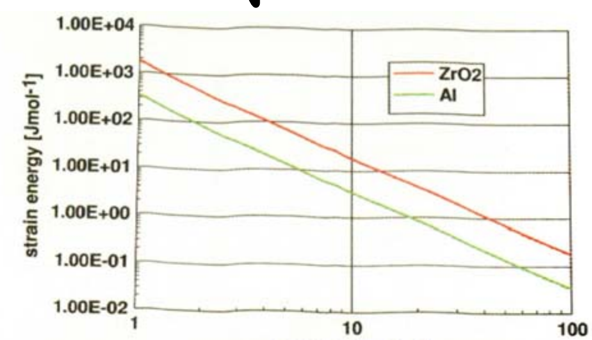


Figure 2.14 Strain energy of aluminum and zirconia nanoparticles calculated according to Equation (2.9).

METAL vs OXIDE NPs

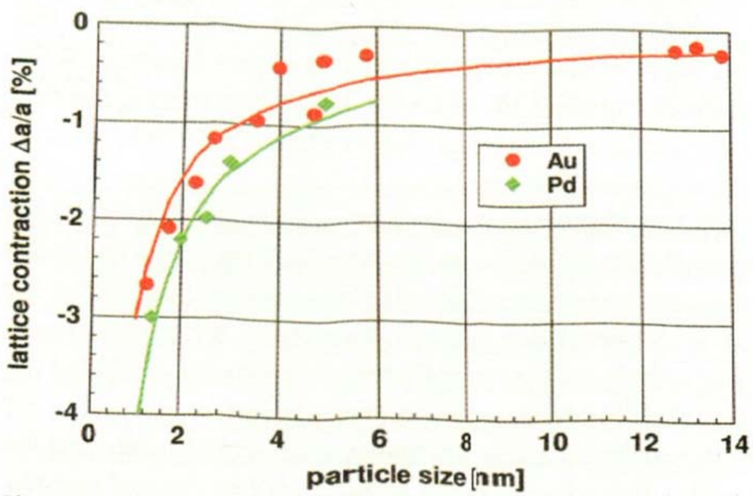


Figure 2.15 Experimental values for the lattice constant of gold [11] and palladium [12] nanoparticles. Due to hydrostatic pressure originating from surface tension, decreasing lattice parameters are observed with decreasing particle size.

VS

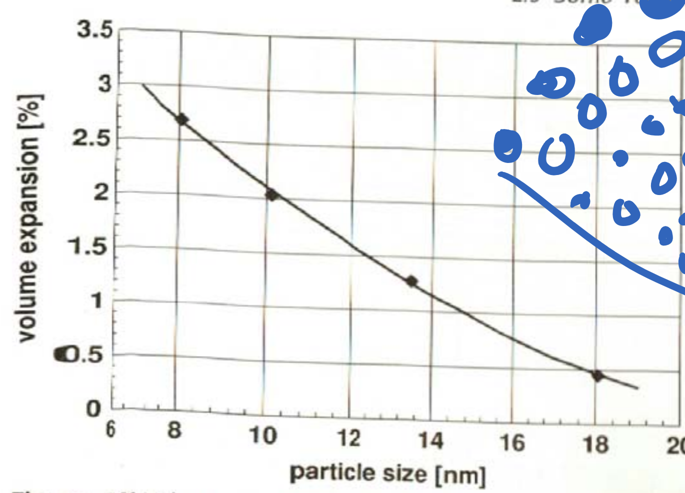
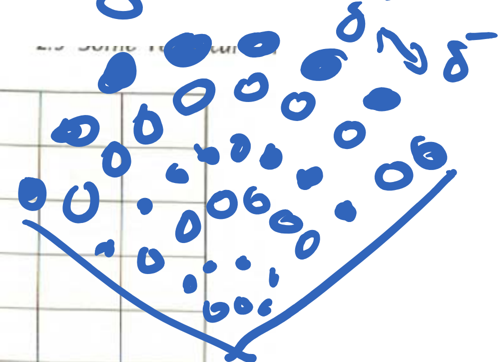


Figure 2.16 Volume expansion of γ-Fe_2O_3 nanoparticles [14] as a function of particle size. In oxides, in contrast to metallic particles, a volume increase is observed with decreasing particle size. This is a consequence of electrostatic repulsion due to the termination of metal cations by anions with electric charges of equal sign at the surface.



CHARGE TERMINAT-
-ION
δ^- vs δ^-
(REPULS-
-ION)

It is not so simple as we discussed.