Last Weeks

Surface curvature vs. chemical potential

Self-assembly
SAMs
Adsorption

Ostwald ripening

Interaction forces & stability

Different types of nanomaterials

Physical Properties at Nanoscale I

26TH SEPTEMBER 2016

KIRSI YLINIEMI

Properties at Nanoscale Differ from Macro- or Atomic Scale

Surface-to-volume ratio large

Huge surface energy

Spatial confinement

Reduced imperfections

Properties at Nanoscale Differ from Macro- or Atomic Scale

Surface-to-volume ratio large
- Lower melting point

Huge surface energy
-Superparamagnetism

Spatial confinement
- Colour changes vs. size

Reduced imperfections
- Higher mechanical strength

One Size Does Not Fit All

Spatial confinement depends on the characteristic length scale of studied property

- **In the end, depends on the material property**

Properties at Nanoscale I & II

Property at Nanoscale	Application	
1. Electric	*Single-electron devices* *Nanopiezoelectric materials*	**Properties I**
2. Optical	*Optical Ruler* *Optical Antenna* *Local Heat Formation*	
3. Mechanical	*High-Strength Alloys* *Nanocrystals* *Nanolaminates*	
4. Thermal	*Thermoelectric materials* *Printed electronics*	**Properties II**
5. Magnetic	*Superparamagnetism*	

After This Lecture You Can

Describe the effect of size on electronic properties

Explain the concept "exciton"

Predict the shift in absorbance peaks of semiconductor nanomaterials

Explain localised surface plasmon resonance

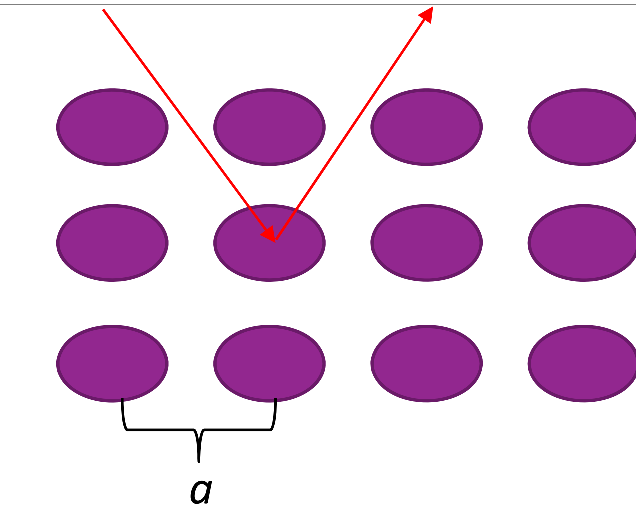
Use Hall-Petch equation in hardness estimations

1st Part: Electrical Properties at Nanoscale

METALS and SEMICONDUCTORS

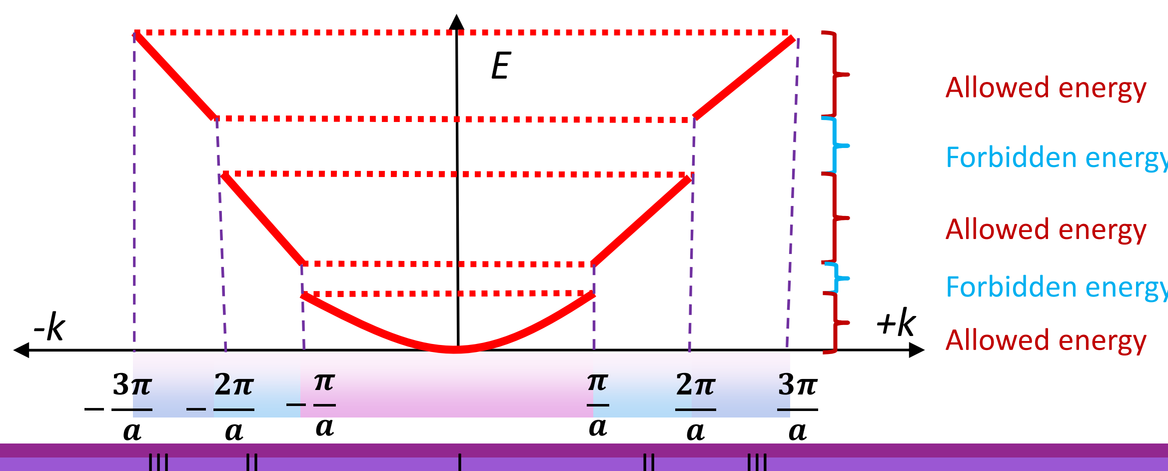
Electrons in Macroscopic Material (Bloch Functions & Brillouin Zones)

Bloch Wave Functions

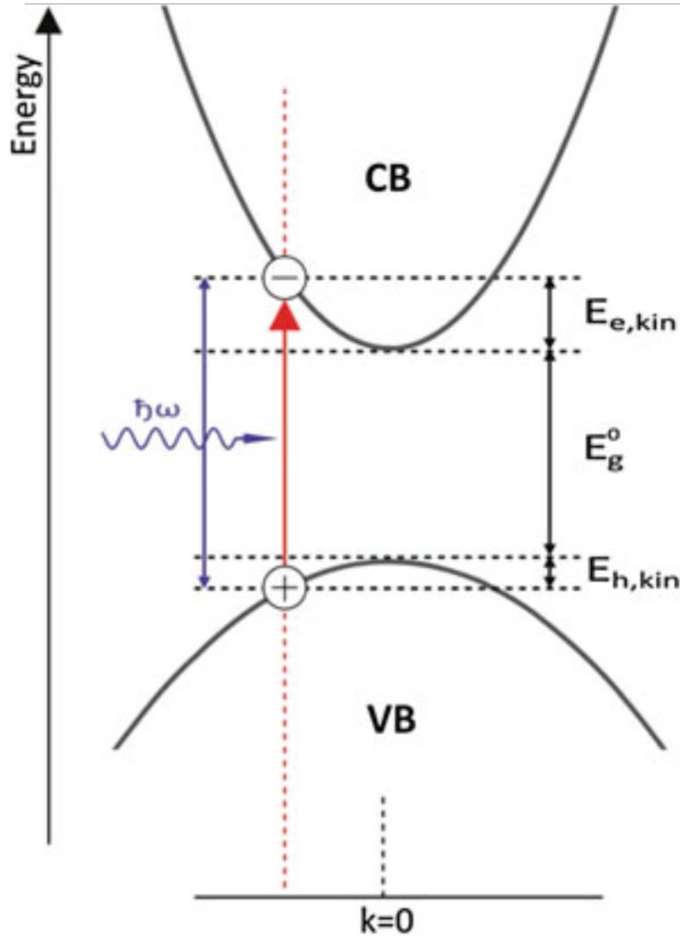


$$k = \pm\frac{n\pi}{a}$$

Brillouin Zones



Semiconductors: Bulks



$$E = E_g + E_{e,kin} + E_{h,kin}$$

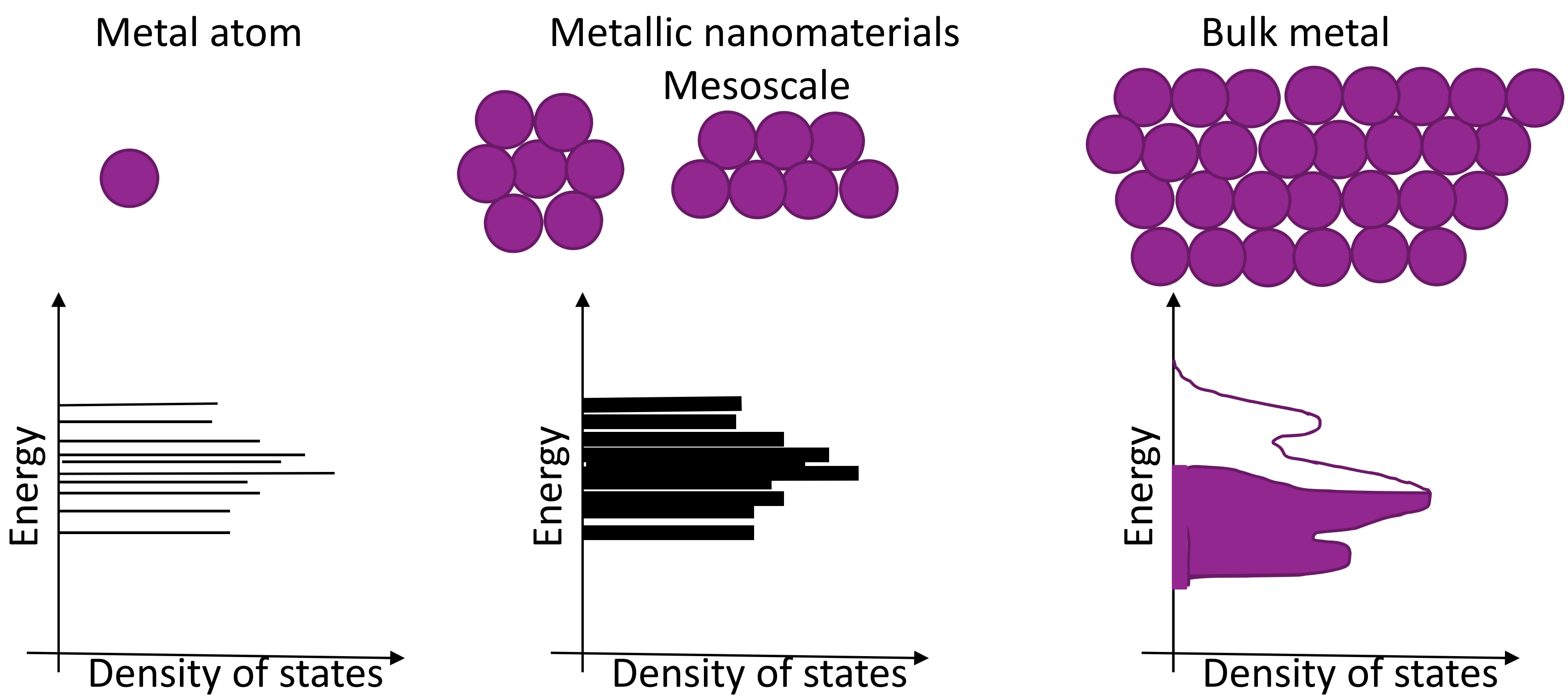
R. Koole, E. Groeneveld, D. Vanmaekelbergh,
A. Meijerink, C. de Mello Donegá, Ch. 2- p. 20 (2014), Springer

Two Effects at Nanoscale

1. Quantum Effect
Energy bands → discrete energy levels due to confinement to small space

2. Classical effect
Random walk → mean-free path of collisions at the same level with teh size of the system

Quantum Effect: Metals

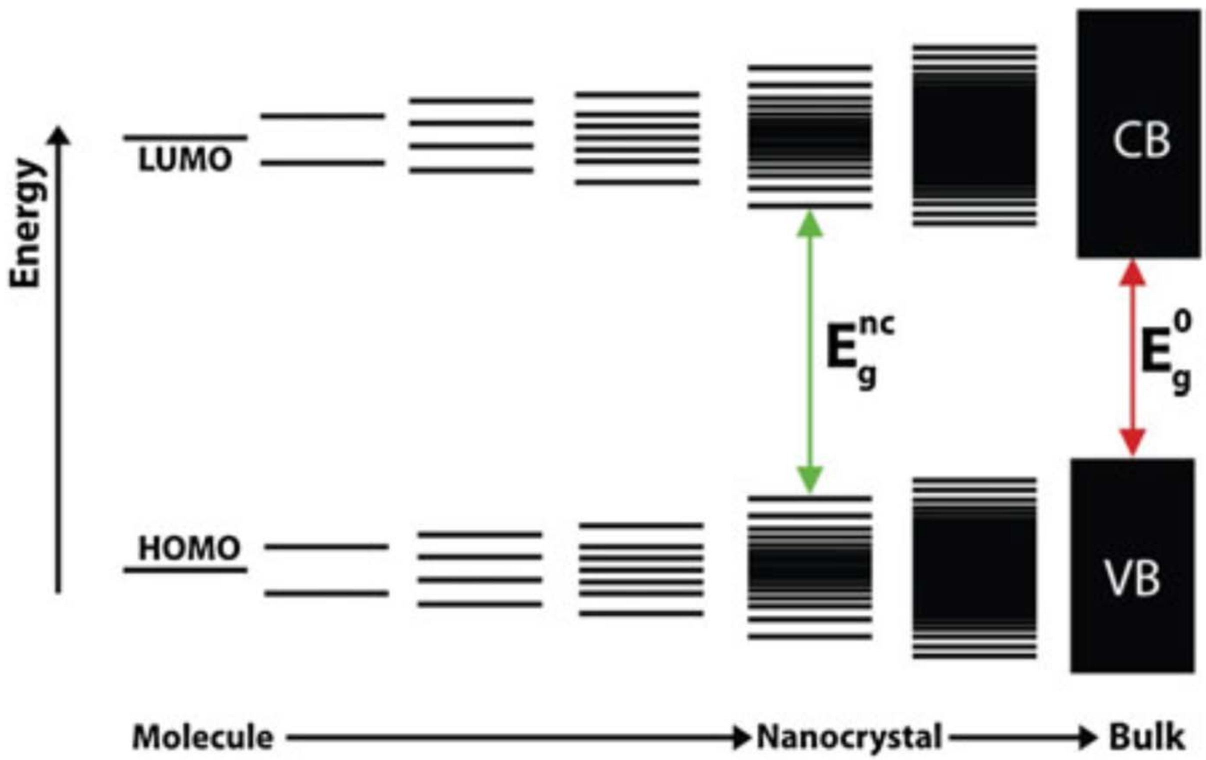


Quantum confinement:

- Discreet energy levels of electrons

➢ electrons in conductive nanomaterials behave more like in molecules

Quantum Effect: Semiconductor



R. Koole, E. Groeneveld, D. Vanmaekelbergh, A. Meijerink, C. Mello Donegá: Size effects on semiconductor nanoparticles, In Book: C. de Mello Donegá (Ed.), Nanoparticles: Workhorses of Nanoscience, Springer, Berlin Heidelberg, Berlin, Heidelberg (2014), p. 29

In bulk

- Electron in periodic potential wells, caused by positive nucleus

In nanoparticle (metal) / quantum dot (semiconductor)

- Electron in spherical potential well, radius = l
- Outside the sphere, potential = 0

Movement of Electrons (Conductivity)

At mesoscale (nanomaterials) electrons moving

1. In a confined space (QF) to certain direction(s)

- **Energy from Particle-in-a-box**

$$E_{Conf} = \left[\frac{\pi^2 \hbar^2 n^2}{2ml^2}\right]$$

2. Unrestricted to certain direction(s)

- **Fermi Energy (E_F)**

The type & size of nanomaterial affects how much quantum effect dominates : 2D, 1D, 0D

Watch **Video Lecture A: Particle-in-a-box** and Video **Lecture B: Density of States and Fermi Energy**

Total energy at 2D

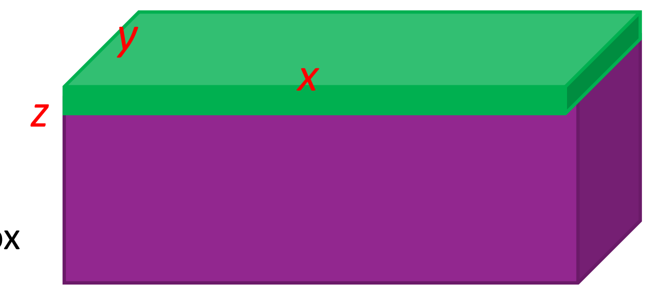
$$E_{Total} = \underbrace{\left[\frac{\pi^2\hbar^2 n^2}{2ml^2}\right]}_{\text{Quantum confinement in the thickness direction (z)}} + \underbrace{\left[\frac{\hbar^2 k_F^2}{2m}\right]}_{\text{Unrestricted movement to other directions (x, y)}}$$

$\hbar$ = reduced Planc'ks constant

n = quantum number

m= mass of electron

l = thickness of the film (i.e. "length of the box" in particle-in-a-box problem

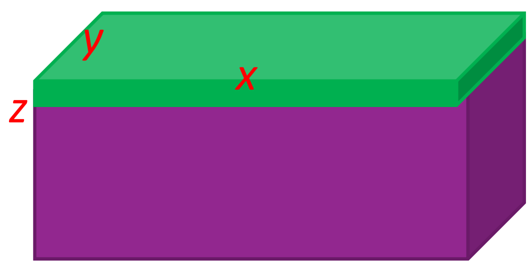


k_F = wave vector = $k_F = \sqrt{k_x^2 + k_y^2}$

k_x and k_y are related to electron's momentum

Total energy at 2D

$$E_{Total} = \underbrace{\left[\frac{\pi^2\hbar^2 n^2}{2ml^2}\right]}_{\text{Quantum confinement in the thickness direction (z)}} + \underbrace{\left[\frac{\hbar^2 k_F^2}{2m}\right]}_{\text{Unrestricted movement to other directions (x, y)}}$$



Electrons in z direction are ”trapped”

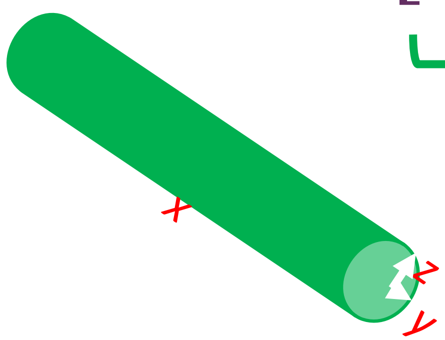
- **2D electrons are the conductive ones**
- Scattering (by grain boundaries, impurities & phonons) can also take in-plane direction (x,y)
- Smaller the grain, lower the conductivity

Total energy at 1D

$$E_{Total} = \underbrace{\left[\frac{\pi^2\hbar^2 n_y^2}{2ml_y^2}\right] + \left[\frac{\pi^2\hbar^2 n_z^2}{2ml_z^2}\right]}_{\text{Quantum confinement in two directions (y and z)}} + \underbrace{\left[\frac{\hbar^2 k_x^2}{2m}\right]}_{\text{Unrestricted movement to x directions}}$$

Total energy at 1D

$$E_{Total} = \underbrace{\left[\frac{\pi^2\hbar^2 n_y^2}{2ml_y^2}\right] + \left[\frac{\pi^2\hbar^2 n_z^2}{2ml_z^2}\right]}_{\text{Quantum confinement in two directions (y and z)}} + \underbrace{\left[\frac{\hbar^2 k_x^2}{2m}\right]}_{\text{Unrestricted movement to x directions}}$$



Quantum confinement in two directions (y and z)

Unrestricted movement to x directions

1D (z, y) act as ”reflectors” for electron movement

- **Electrons forced to stay on the surface**

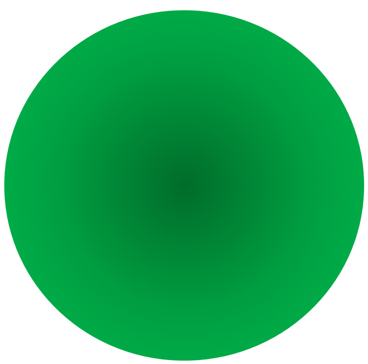
Scattering is also more restricted along the long-axis

- **Movement of electrons along the tube ”without” restrictions**

Curiosity – conductivities:
Carbon nanotube 10^9 A/cm^2
Copper 10^6 A/cm^2

Total energy at 0D

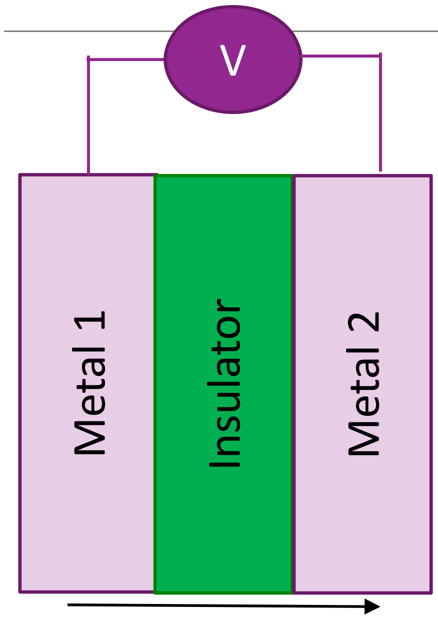
$$E_{Total} = \underbrace{\left[\frac{\pi^2\hbar^2 n_x^2}{2ml_x^2}\right] + \left[\frac{\pi^2\hbar^2 n_y^2}{2ml_y^2}\right] + \left[\frac{\pi^2\hbar^2 n_z^2}{2ml_z^2}\right]}_{\textit{Quantum confinement in all directions (x, y and z)}}$$



Restriction to all directions

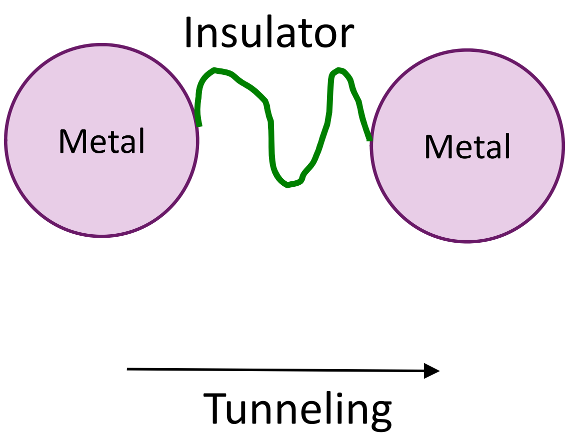
- **Even metallic nanoparticles behave like insulators or semiconductros (when on their own)**

Connected Nanoparticles



For tunneling

- Metal 2 needs to have unoccupied energy levels
  - Can be controlled by applying voltage



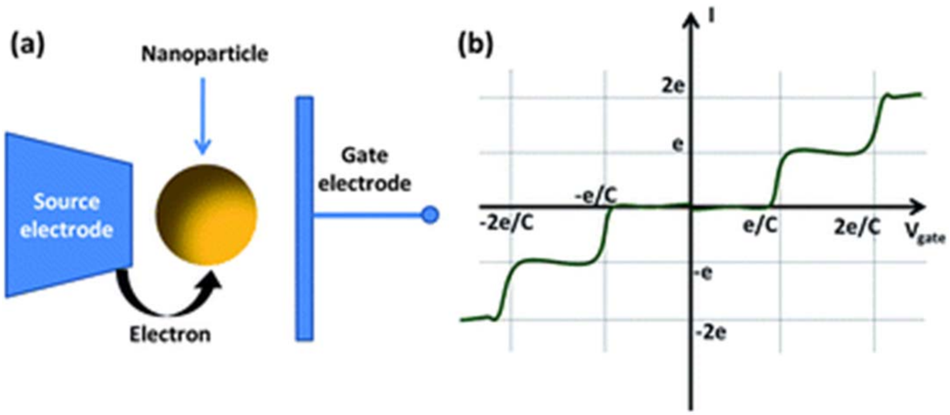
$$C = \frac{I}{V}$$

Conductance due to tunneling

Single-electron Devices

Discreet energy levels of nanoparticles

Transistors

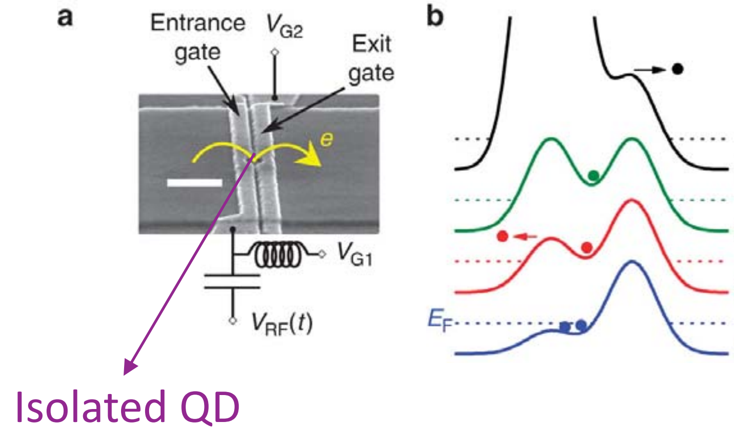


S. Singamaneni, V. N. Bliznyuk, C. Binek, Evgeny Y. Tsymbal, *J. Mater. Chem.* **21** (2011) 16819-16845.

Electron increases the charge of NP by $E = \frac{e^2}{2C}$ which the next electron has to overcome

- ➢ Coulomb staircase

Pumps



By manipulating the entrance gate and exit gate voltages, QD will be excited one electron / time

S.P. Giblin, M. Kataoka, J.D. Fletcher, P. See, T.J.B.M. Janssen, J.P. Griffiths, G.A.C. Jones, I. Farrer, D.A. Ritchie, *Nature Communications* **3** (2012) 1-6.

INSULATORS (DIELECTRICS)

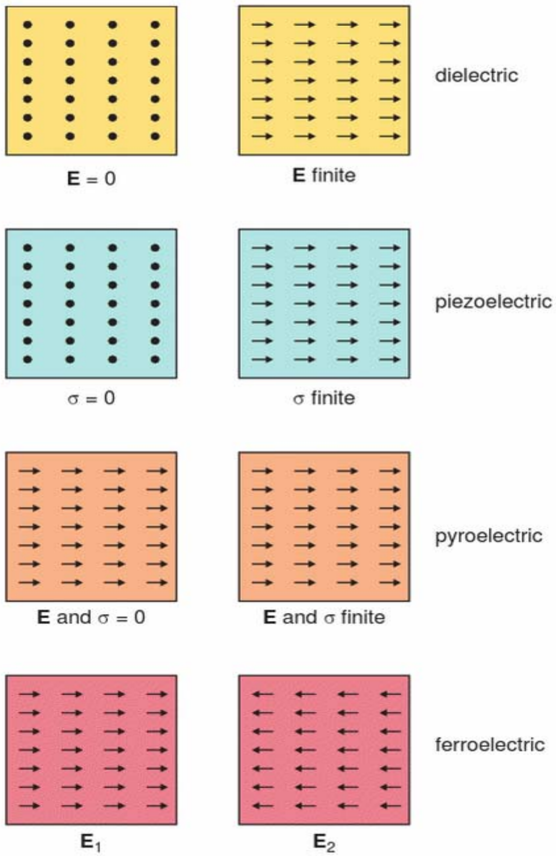
Ferro- and Piezoelectrocity

Ferroelectricity

- **Spontaneous polarisation** due to crystallographic features and surface terminations
- ”Electric field inside the material can be changed by **applied electric field**”

Piezoelectricity

- **Polarisation** due to **mechanical** stress/strain
- ”Electricity by pressing/pulling the material”



R.J.D. Tilley Understanding Solids – The Science of Materials, 2nd Ed., Wiley (2013), p.334.

Ferro- and Piezoelectrocity

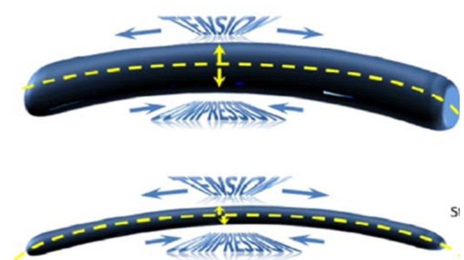
Surface becomes more dominant at nanoscale

Ferroelectricity

- Critical size (≈ 5 nm) when ferrolectricity disappears
- But also strain effects change: some atoms ”freezed” → ferroelectricity reappears when size decreases further

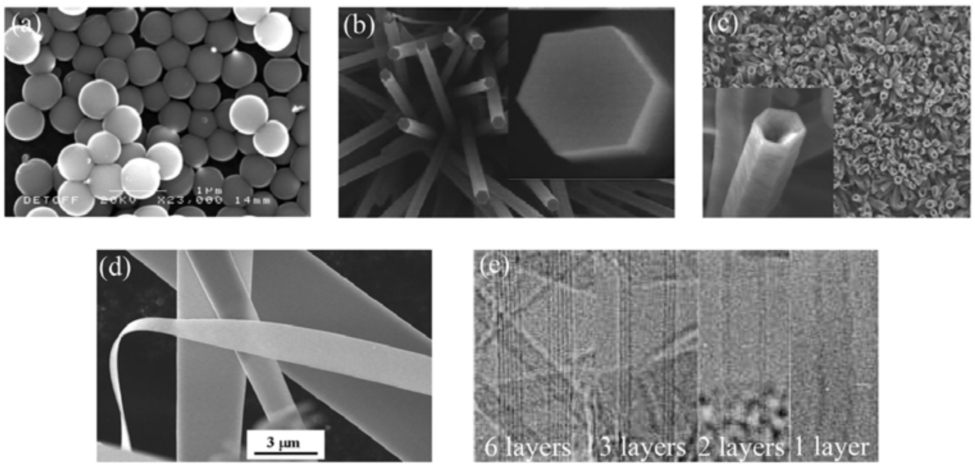
Piezoelectricity

- ”Increased” movement
- Temperature effect pronounced
- Single crystals?



Nanopiezoelectric Materials

TYPICAL MATERIALS

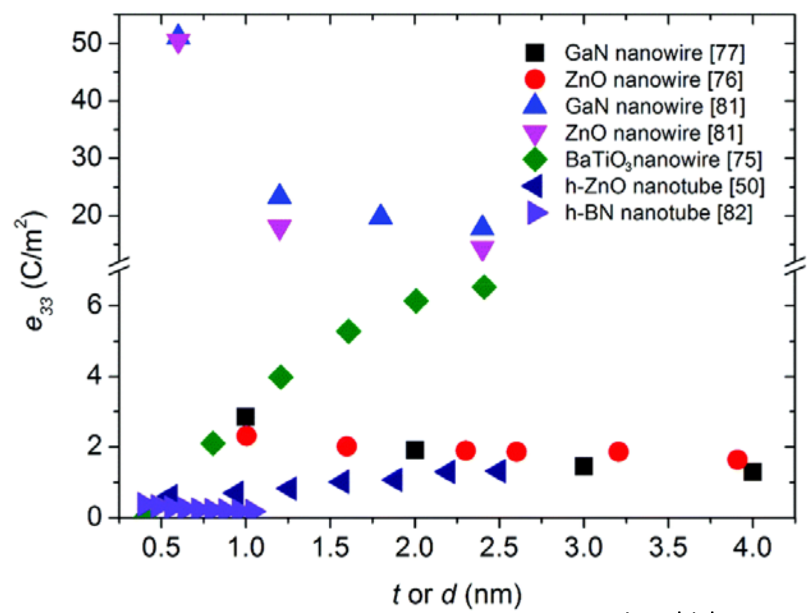


(a) ZnO nanoparticles,(b) ZnO nanowires, (c) ZnO nanotubes,(d) ZnO nanobelts,and (e) hexagonal Boron Nitride (h-BN) nanotubes.

$$e_{33} = \frac{\partial P}{\partial \varepsilon}$$

Polarisation P vs. strain ε along the axis

POLARISATION VS. STRAIN



t = cross-section thickness
d = radius

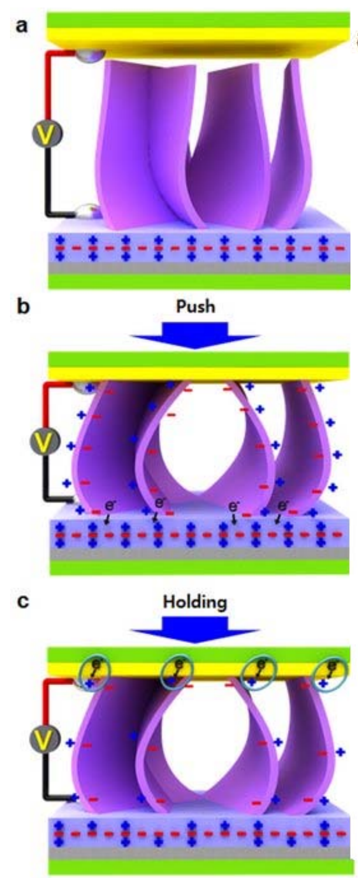
In bulk:

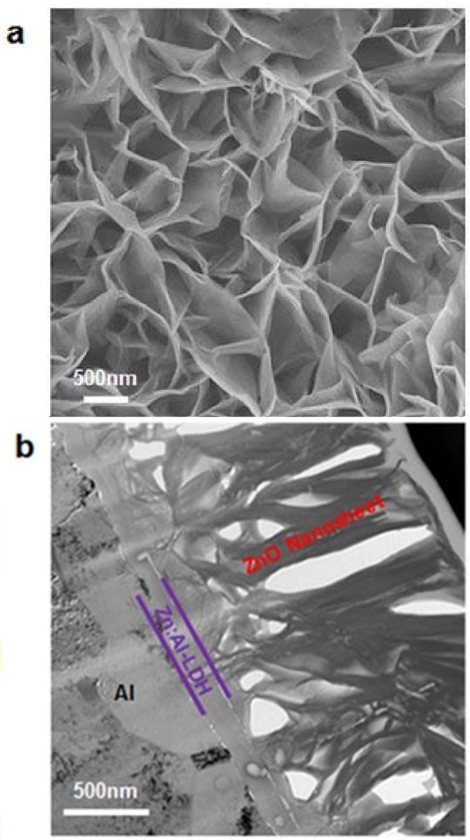
e_{33} (ZnO) ≈ 1.22 C/m^2

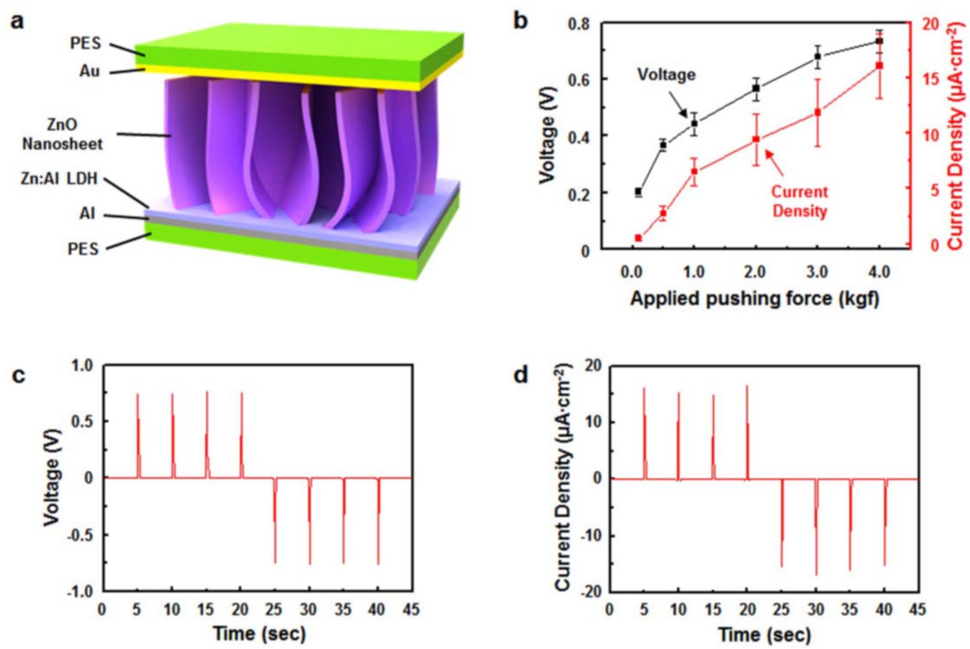
e_{33} (h-BN) ≈ 0.20 C/m^2

J. Zhang, C. Wang, C. Bowen, *Nanoscale* **6** (2014) 13314-13327.

Nanopiezoelectric Materials







Concept Checks

True or False

1. Carbon nanotubes are conductive along the tube length
2. The electrons in 2D structures can move on the plane only at wavelengths with multiple integer of thickness

Concept Checks

Which one is correct

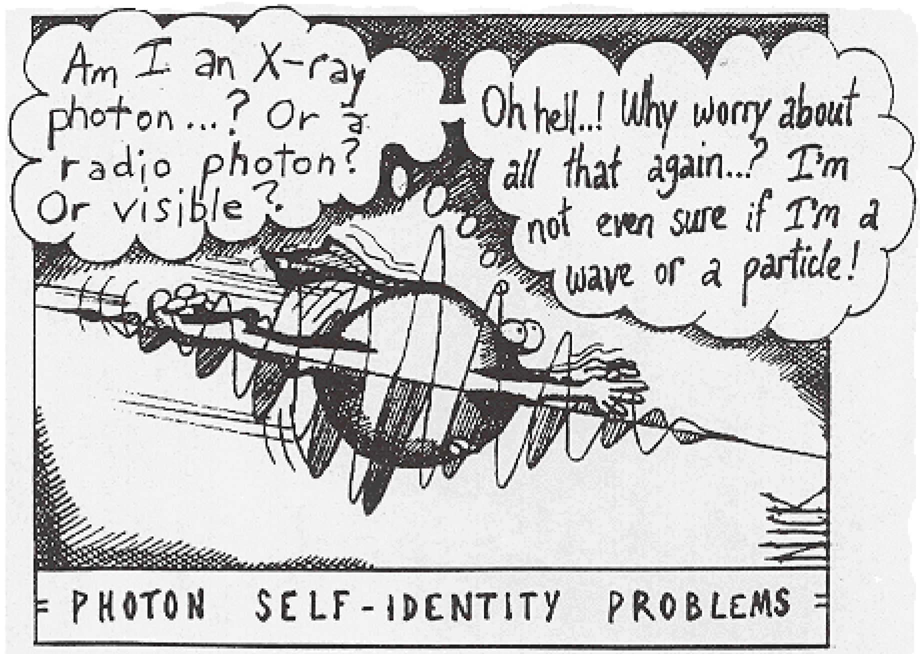
A) Quantum confinement increases the conductivity of 0D materials

B) 1D materials are typically more conductive than their bulk counterparts

C) Scattering in the non-confined direction increases the conductivity of 2D materials

2^{nd} Part: Optical Properties at Nanoscale

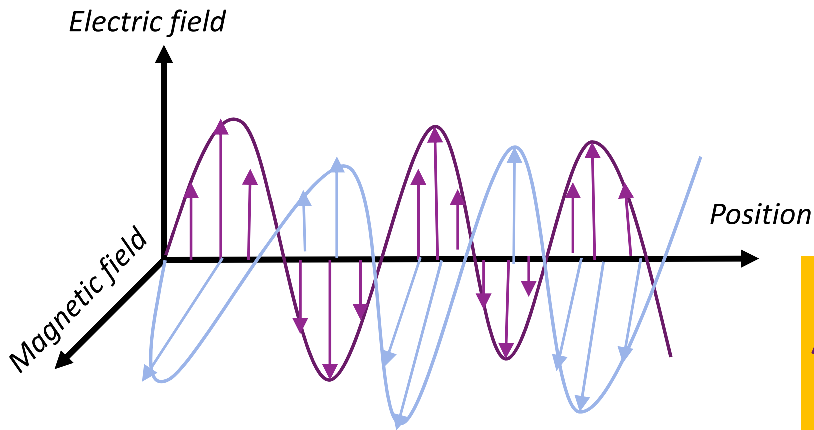
Optical Properties

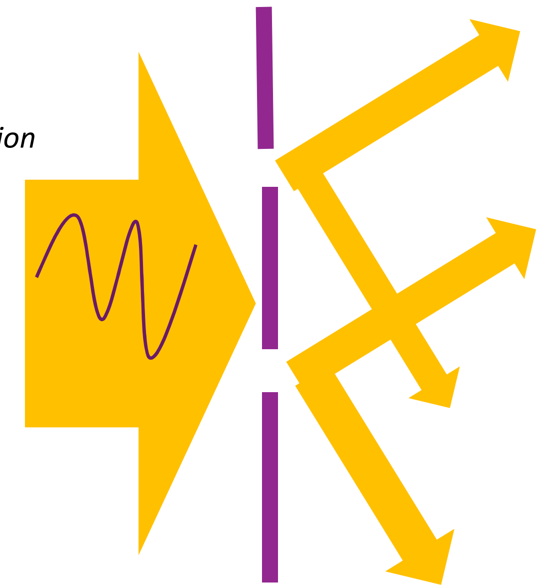


http://www.conversationswithanoldone.com/albert-einstein-surprises-robert-lanza-in-the-night

Electromagnetic Radiation

WAVE OR PARTICLE?

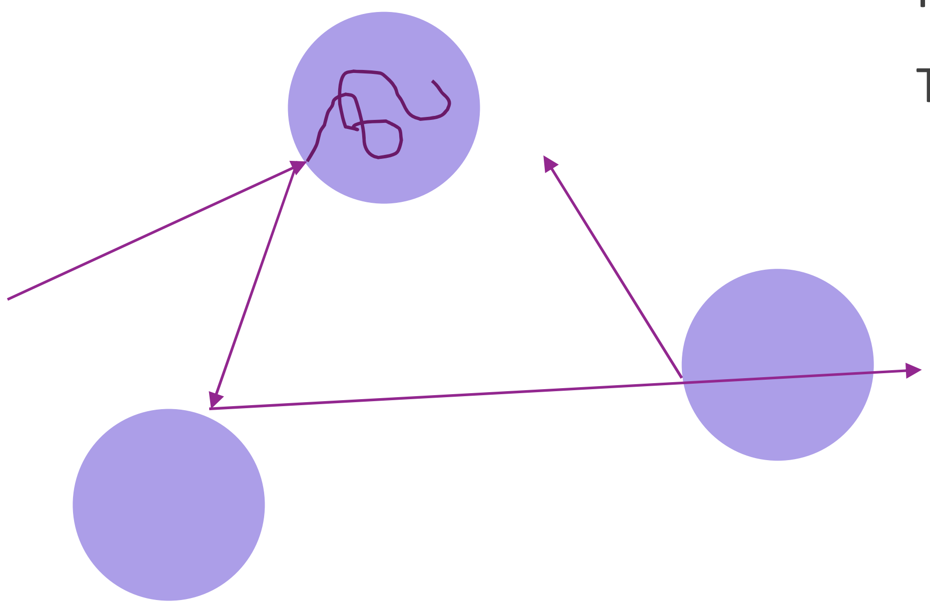




$$c = \frac{1}{\sqrt{\epsilon_0 \mu_0}} \qquad c = \lambda \nu$$

$$E = h\nu = \frac{hc}{\lambda}$$

Light vs. Solid

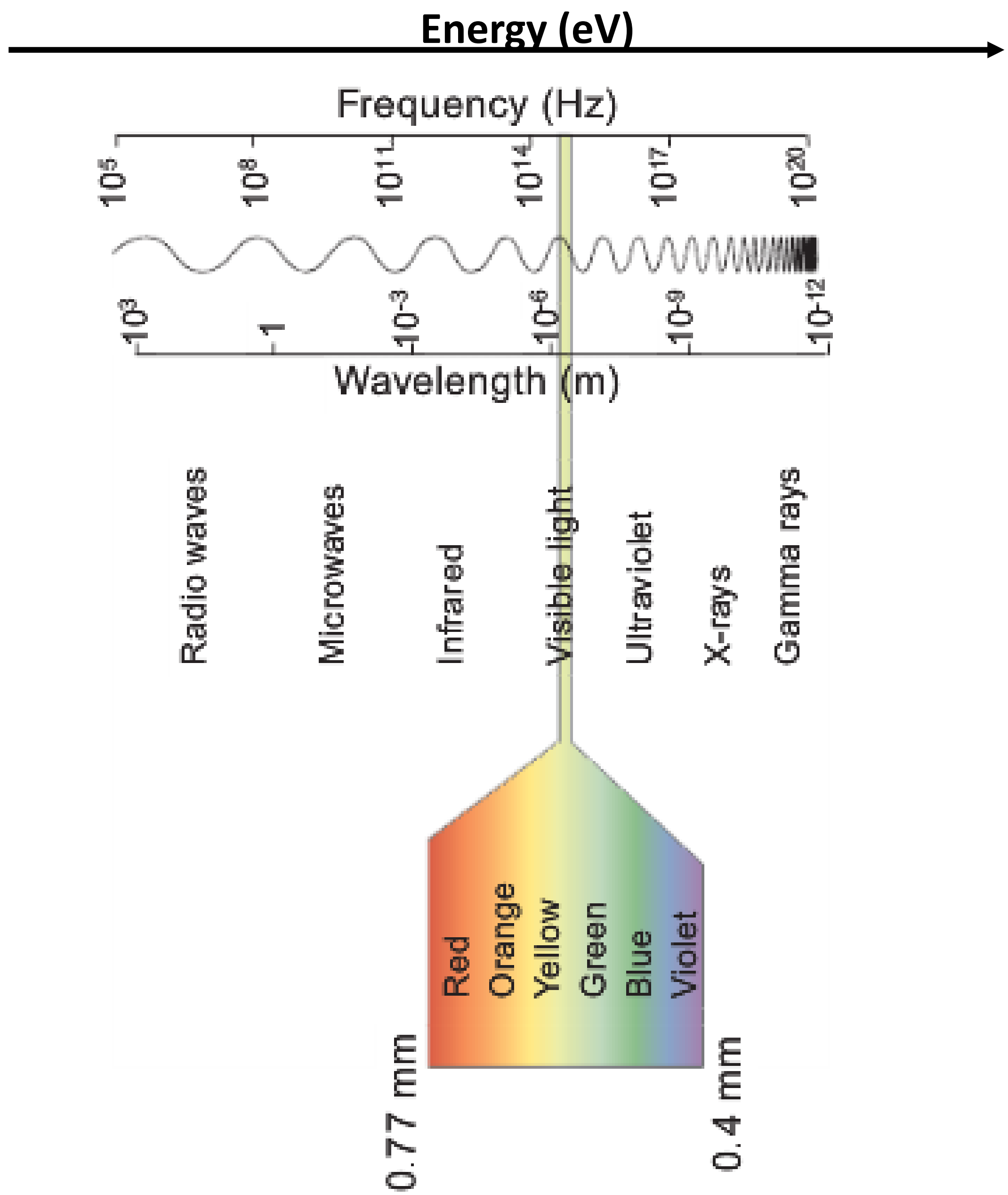


Absorbance

Reflectance (and scattering)

Transmission

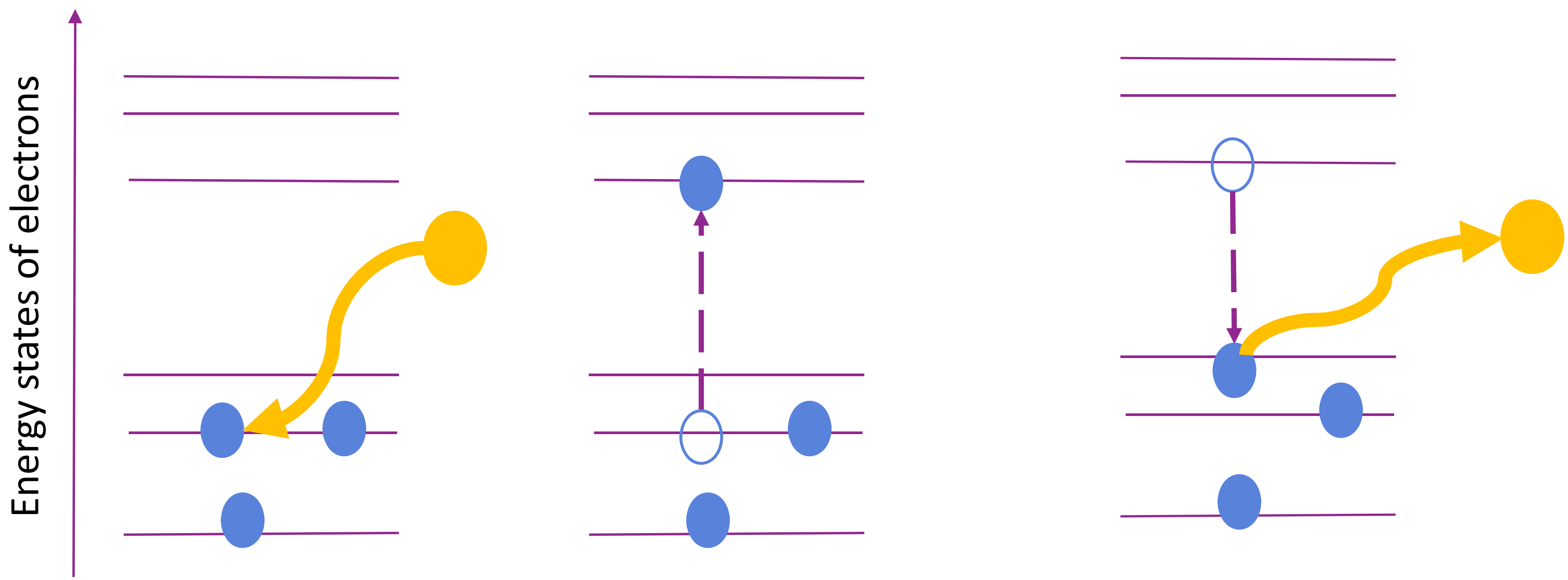
$$I_{tot} = I_A + I_R + I_T$$



From: M.F Ashby, P.J. Ferreira, D.L. Schodek, Nanomaterials, Nanotechnologies and Design – An Introduction to Engineers and Architects (2009) Elsevier, p.230.

Electromagnetic Radiation

WAVE ≈ PHOTONS

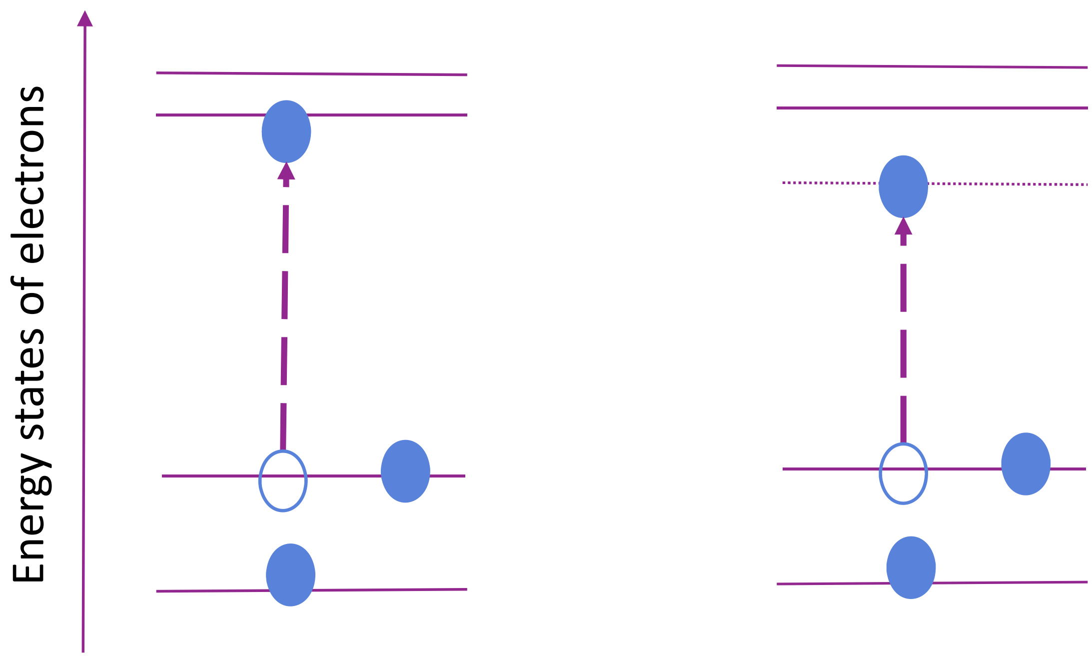


Energy of photon absorbed
- ➢ Absorbance

Energy of photon emitted
- ➢ luminesence

In bulk

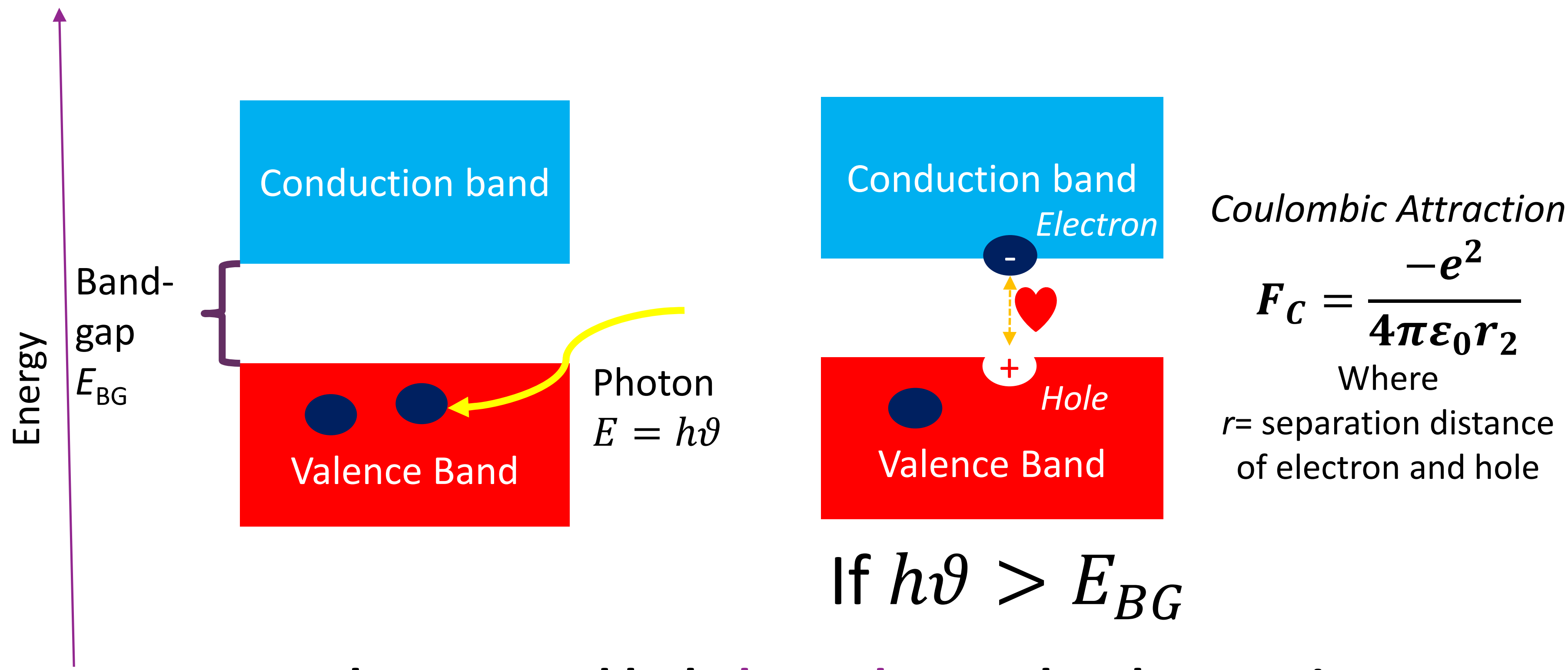
NORMAL T **LOW T**



Absorbance matches EXACTLY the band-gap

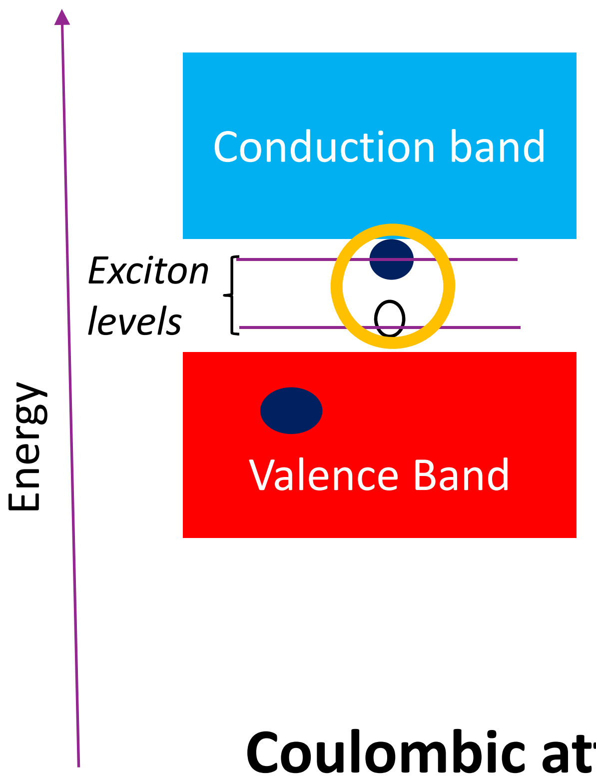
Absorbance slightly LOWER than the band-gap

Quasi-Particle: Exciton



Electron and hole bound to each other: exciton

Semiconductor



Coulombic Attraction

$$F_C = \frac{-e^2}{4\pi\varepsilon_0 r_2}$$

Bohr radius

$$r_B^{ex} = \frac{\varepsilon r_B m_o[1 + (m_e/m_h)]}{\varepsilon_0 m_e}$$

Coulombic attraction

1. Brings exciton levels closer to each other

2. Increases Bohr radius of exciton

Binding energy of exciton (formation of exciton)

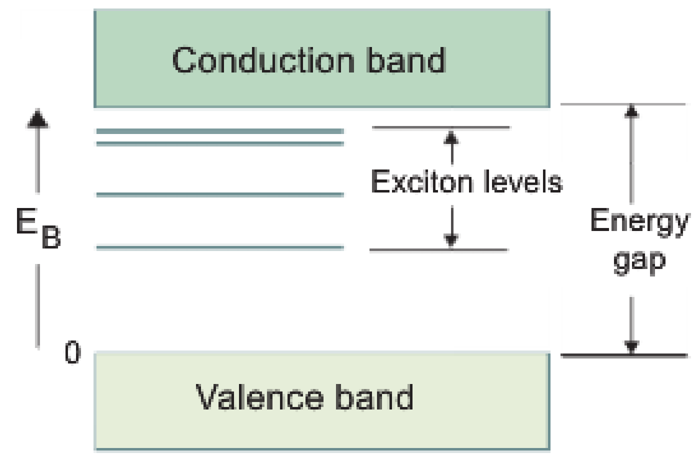


FIGURE 7.30

Energy levels of an exciton. The binding energy E_B of an exciton is equal to the difference between the energy required to create a free electron and free hole and the energy to create an exciton. (Adapted from C. Kittel, Introduction to Solid State Physics, *John Wiley & Sons Inc, New York.)*

M.F Ashby, P.J. Ferreira, D.L. Schodek, Nanomaterials, Nanotechnologies and Design – An Introduction to Engineers and Architects (2009) Elsevier., p. 206.

Exciton Diameter

Table 7.1 Exciton Bohr Diameters and Band-Gap Energies for Various Semiconductors

Material	Exciton Diameter	Band-Gap Energy
CuCl	1.3 nm	3.4 eV
CdS	8.4 nm	2.58 eV
CdSe	10.6 nm	1.74 eV
GaAs	28 nm	1.43 eV
Si	3.7 nm (longitudinal) 9 nm (transverse)	1.11 eV

Conclusion: At nanoscale, excitons come confined!

Excitons in Nanomaterials

- Exciton radius is at nanoscale

  - **Quantum confinement of excitons in nanomaterials**

0D > 1D > 2D (> 3D)

More QF, exciton levels higher & more quantized

(as the density of states becomes more discrete)

Confinement regions

WEAK and HIGH

- degree of coupling electron-hole (→Coulombic energy)
  - Dimensions of nanomaterial
  - Dimensions of electron & hole

Regimes

1. Strong Confinement Regime ($r << r_{Bohr}$)

- No excitons: Quantum confinement energy >> Coulomb energy
  - The kinetic energy of electron and hole so large that they move independently

$$E_{binding} = E_{bg}^{0} + E_{conf} = E_{bg}^{0} + \frac{2\hbar^2 \chi_e^2}{m_e^* D} + \frac{2\hbar^2 \chi_h^2}{m_h^* D}$$

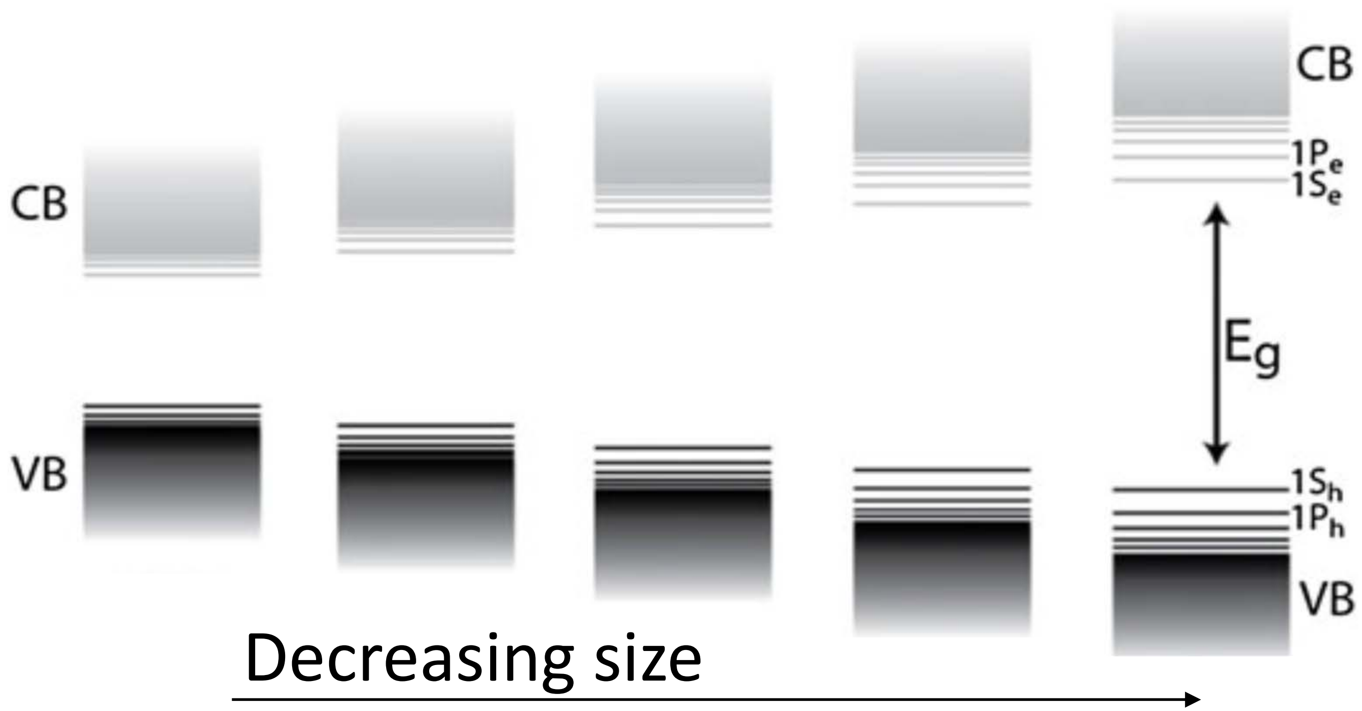
where D = size of the sphere, χ = Bessel function including quantum numbers (n, l, s)

2. Weak Confinement Regime ($r > r_{Bohr}$)

- Excitons exists

$$E_{binding} = E_{bg}^{0} + \frac{\pi^2 \hbar^2}{2r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - E_{Coulomb} + E_{polarisation} + E_{Rydberg}$$

Quantum Confinement

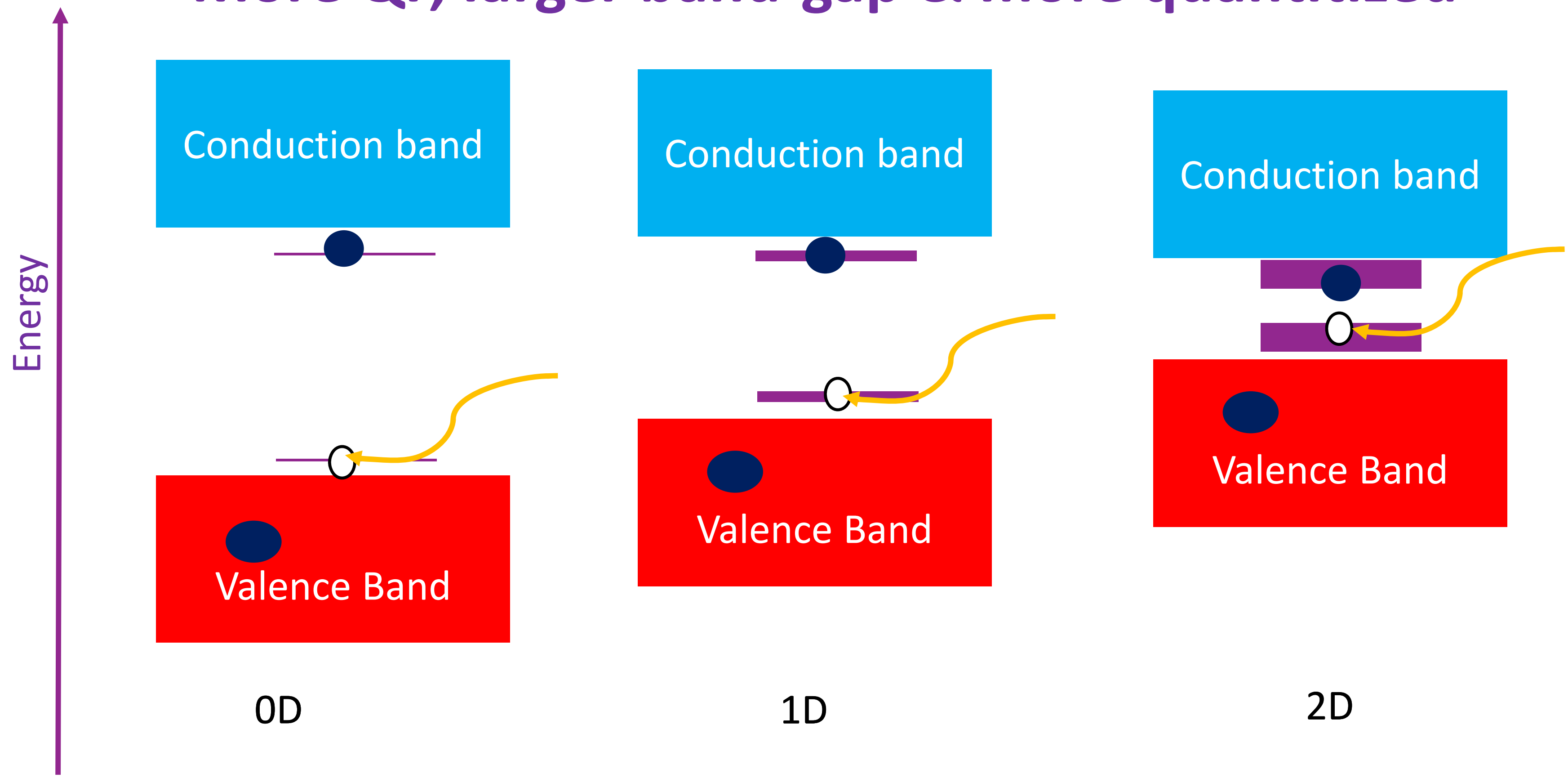


$$E_{binding} = E_{bg}^{0} + \frac{\pi^2\hbar^2}{2r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - E_{Coulomb} + E_{polarisation} + E_{Rydberg}$$

R. Koole, E. Groeneveld, D. Vanmaekelbergh, A. Meijerink, C. Mello Donegá: Size effects on semiconductor nanoparticles, In Book: C. de Mello Donegá (Ed.), Nanoparticles: Workhorses of Nanoscience, Springer, Berlin Heidelberg, Berlin, Heidelberg (2014), p. 24

Excitons in Nanomaterials

More QF, larger band-gap & more quantitized

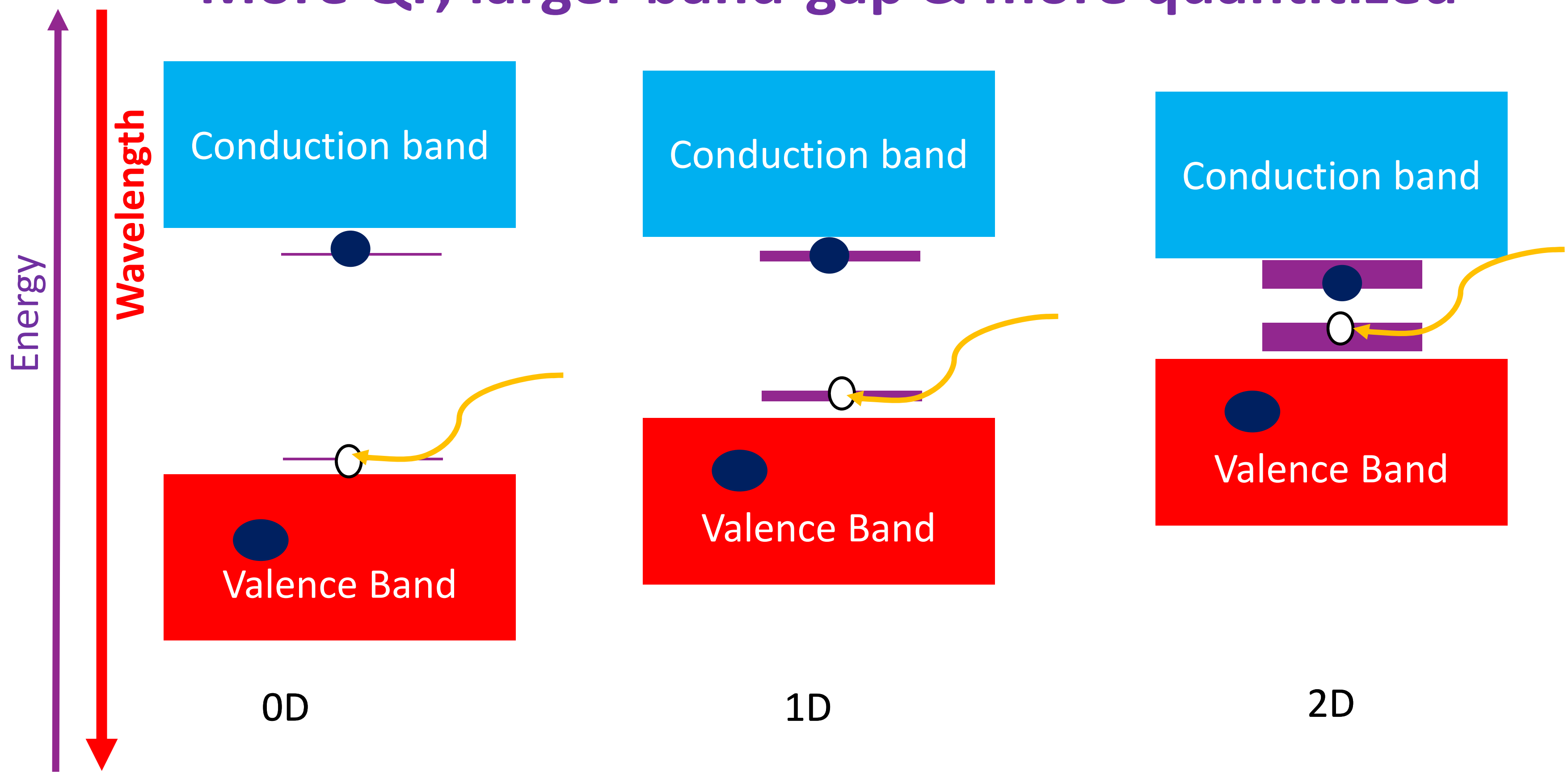


Remember!
Wavelength and energy are combined

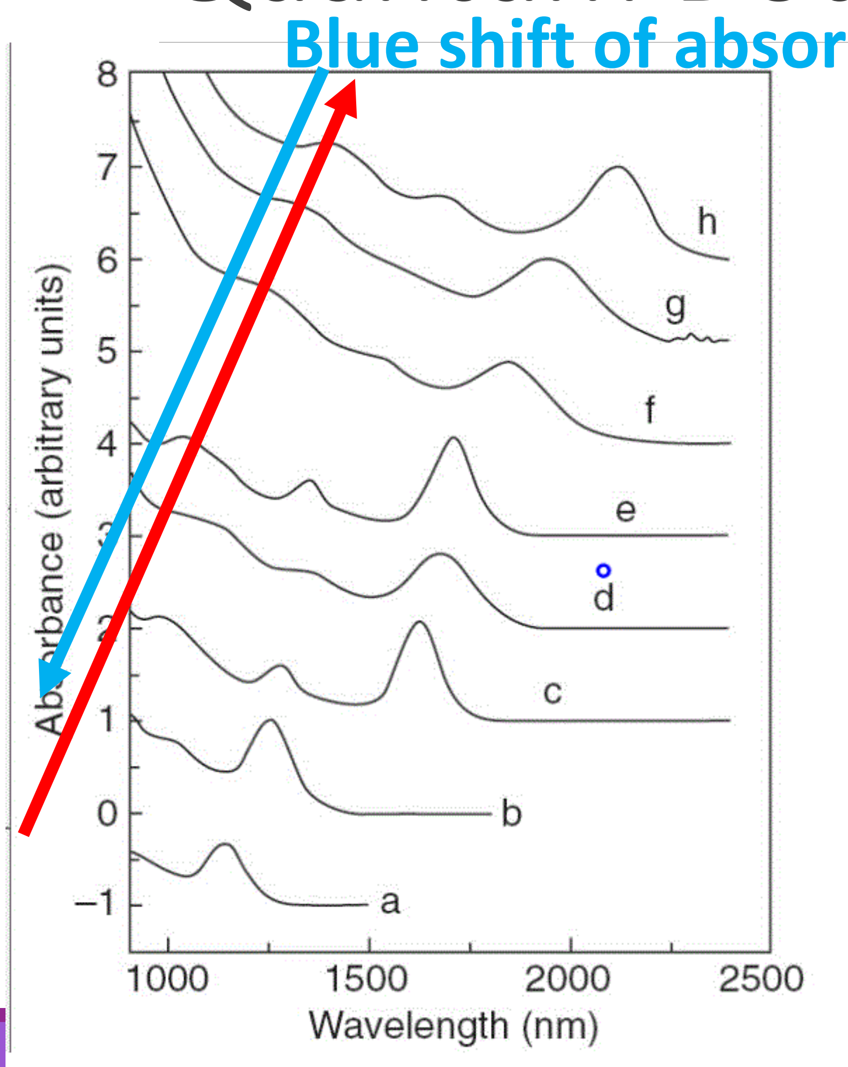
$$\lambda_{particle} = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$$

Excitons in Nanomaterials

More QF, larger band-gap & more quantitized



Absorbance Spectra of PbSe Quantum Dots



Diameters of

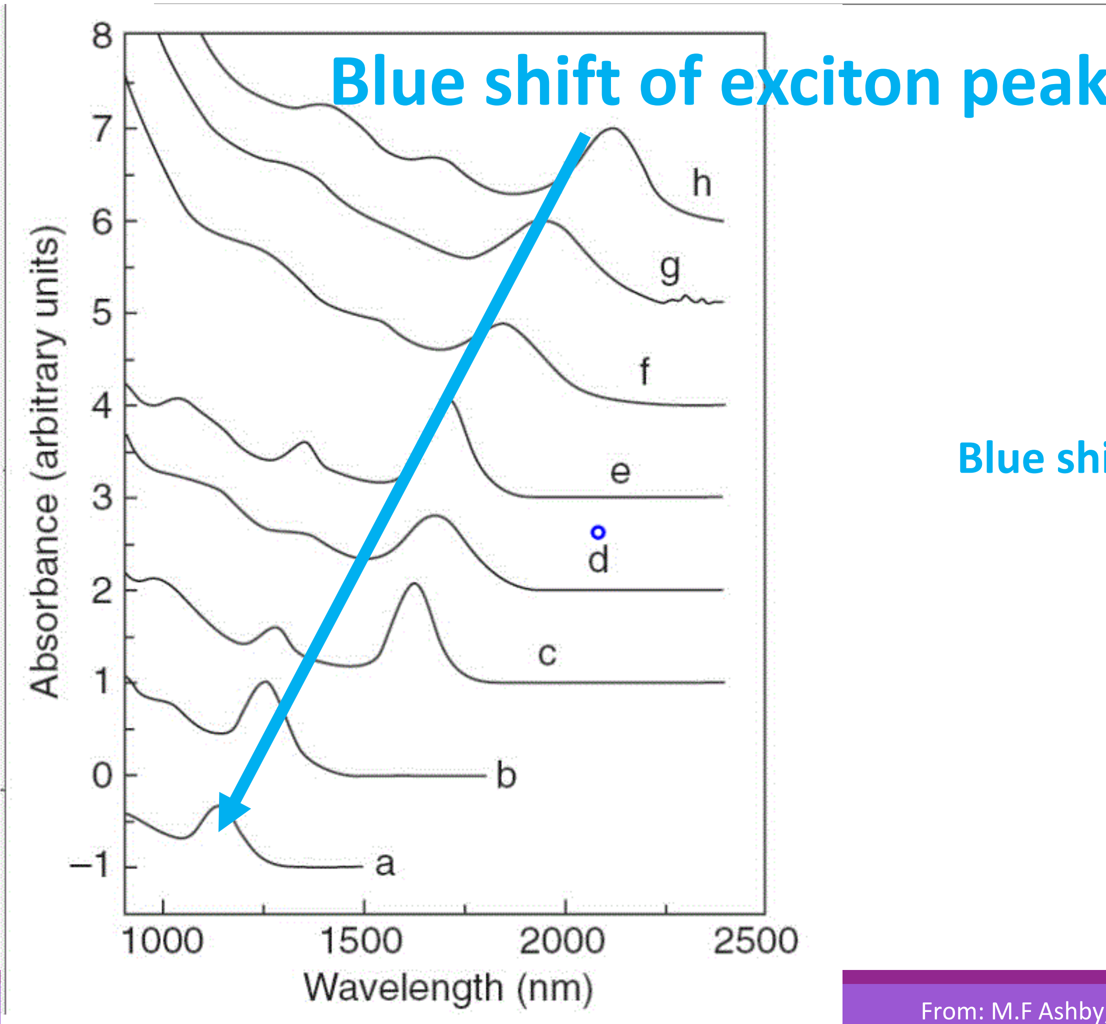
- a) 3 nm
- b) 3.5 nm
- c) 4.5 nm
- d) 5 nm
- e) 5.5 nm
- f) 7 nm
- g) 8 nm
- h) 9 nm

Blue shift

Red shift

From: M.F Ashby, P.J. Ferreira, D.L. Schodek, Nanomaterials, Nanotechnologies and Design – An Introduction to Engineers and Architects (2009) Elsevier, p.229.

Absorbance Spectra of PbSe Quantum Dots



Diameters of

Blue shift

a) 3 nm

b) 3.5 nm

c) 4.5 nm

d) 5 nm

e) 5.5 nm

f) 7 nm

g) 8 nm

h) 9 nm

Red shift

From: M.F Ashby, P.J. Ferreira, D.L. Schodek, Nanomaterials, Nanotechnologies and Design – An Introduction to Engineers and Architects (2009) Elsevier, p.229.

Two Regimes

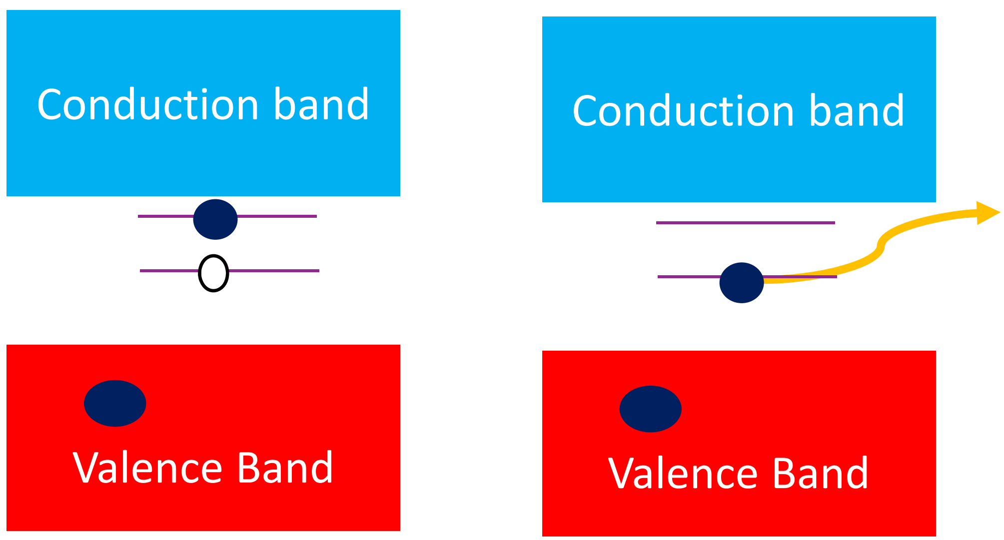
1. **Nanomaterial size ≈ few times exciton size**

- **Weak confinement**
- **Smaller particles have exciton absorbance peak at lower WLs**
- **0D has exciton peak at lower WLs than 2D**

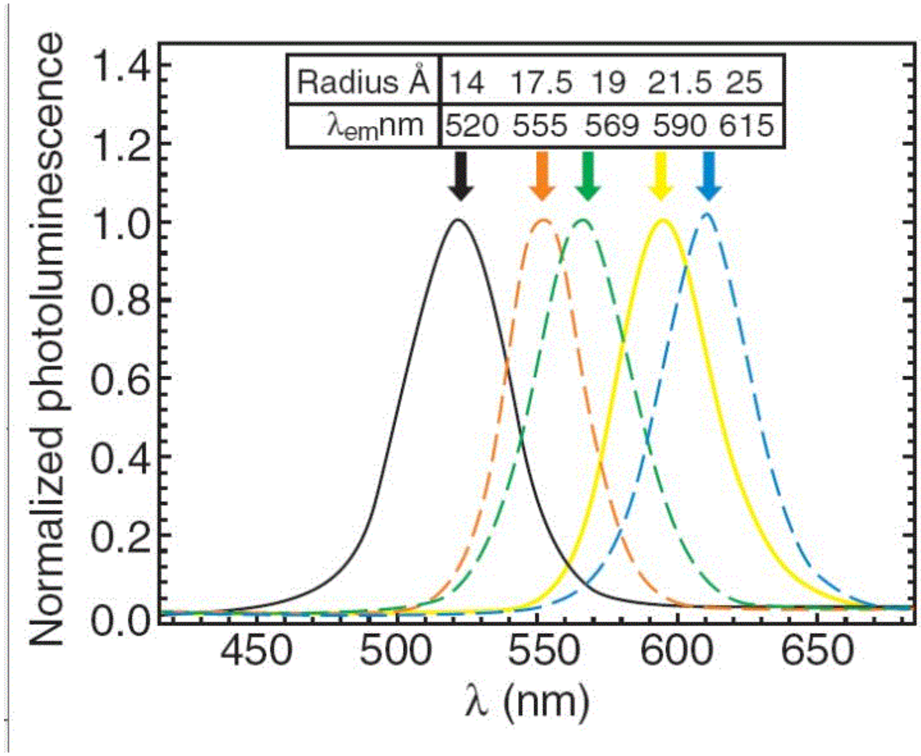
2. **Nanomaterial size < exciton radius**

- **Strong confinement**
  - No coupling – excitons do no exist
  - No exciton peak

Luminesence

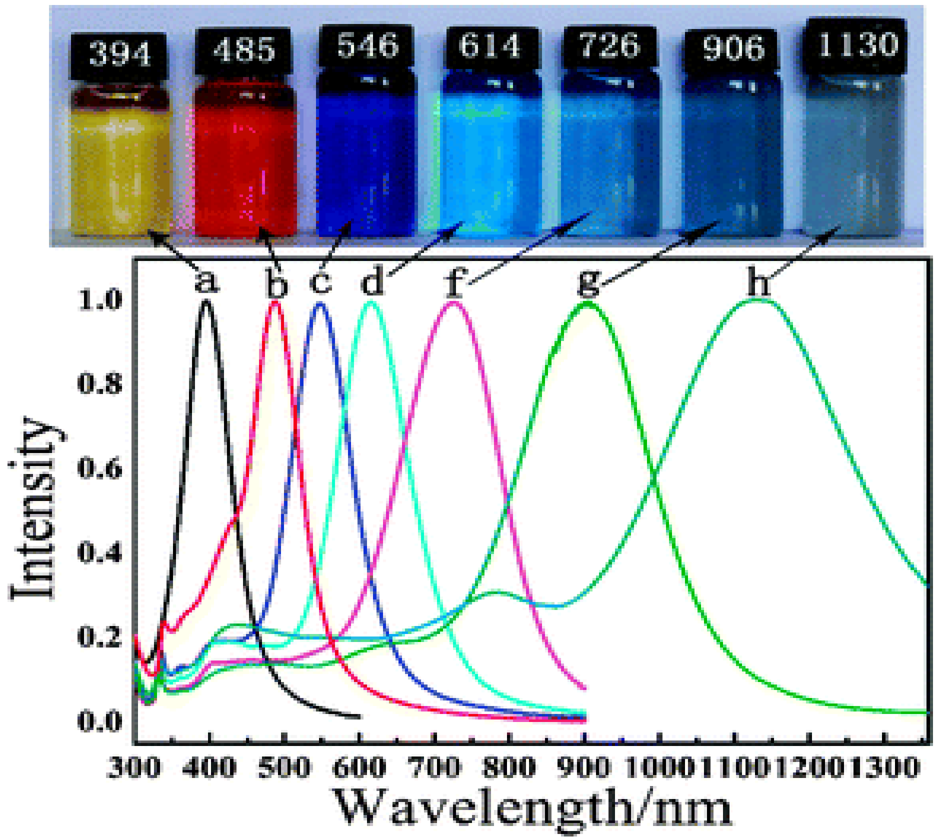


Luminesence



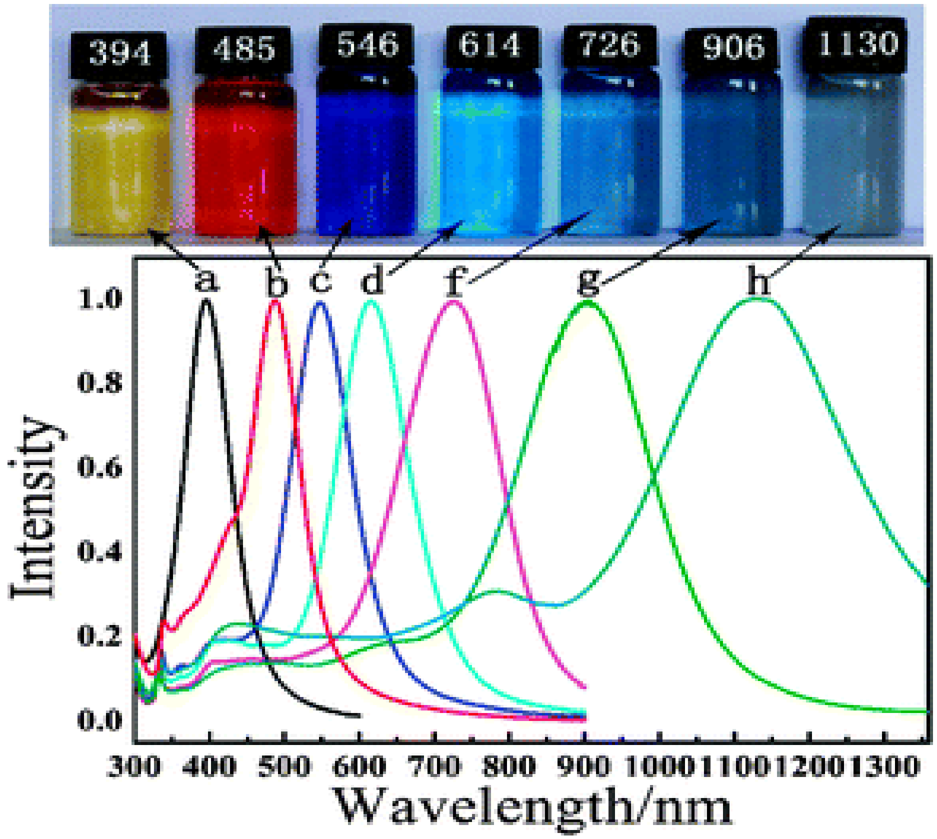
From: M.F Ashby, P.J. Ferreira, D.L. Schodek, Nanomaterials, Nanotechnologies and Design – An Introduction to Engineers and Architects (2009) Elsevier, p.230.

Nanoscale Observation



T. Tan, C. Tian, Z. Ren, J. Yang, Y. Chen, L. Sun, Z. Li, A. Wu, J. Yin, H. Fu, *Phys.Chem. Chem. Phys.*, **15** (2013) 21034-21042.

Nanoscale Observation



Localised Surface Plasmon Resonance

T. Tan, C. Tian, Z. Ren, J. Yang, Y. Chen, L. Sun, Z. Li, A. Wu, J. Yin, H. Fu, *Phys.Chem. Chem. Phys.*, **15** (2013) 21034-21042.

Localised Surface Plasmon Resonance (Metal NPs)

Mobile electrons create a collections of waves

➢ **Plasmons**

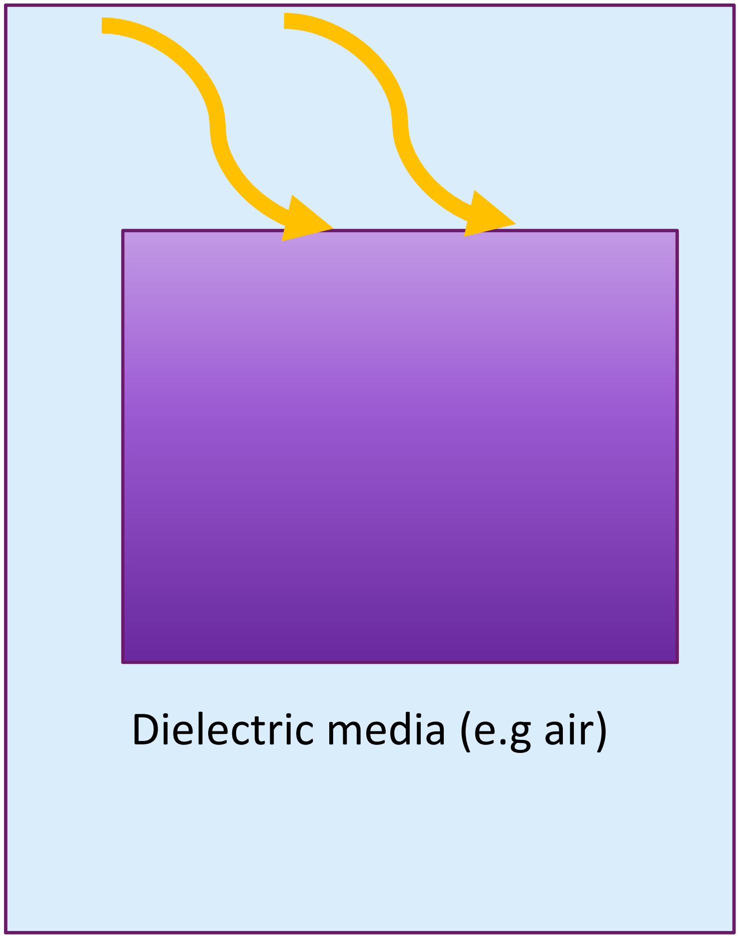
In bulk

- Not affected by light

At surface

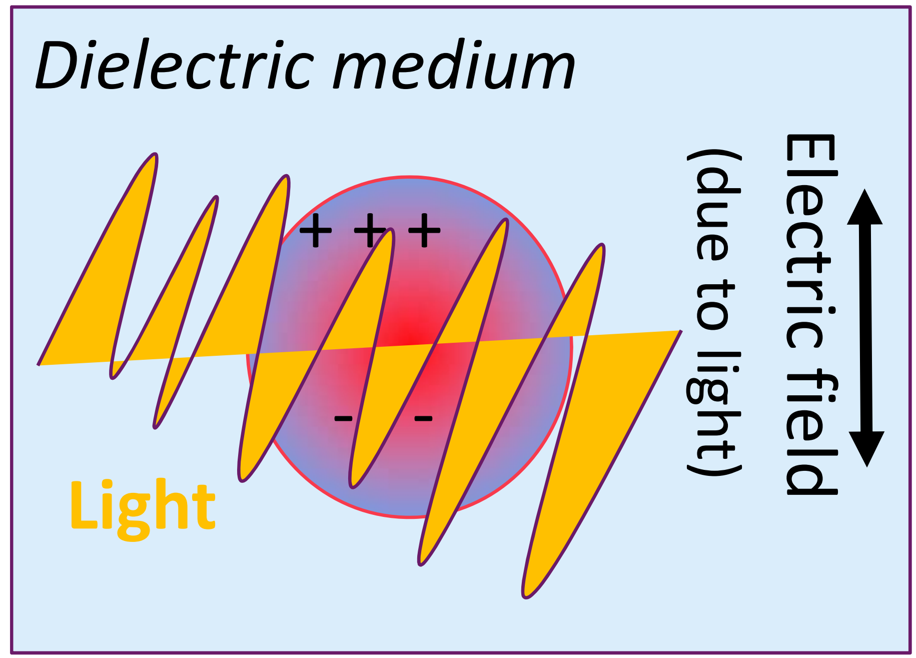
- Interaction with light

The interaction polarises the plasmons vs. the cationic cubic lattice



Localised Surface Plasmon Resonance (Metal NPs)

Surface plasmons oscillate with electromagnetic wave

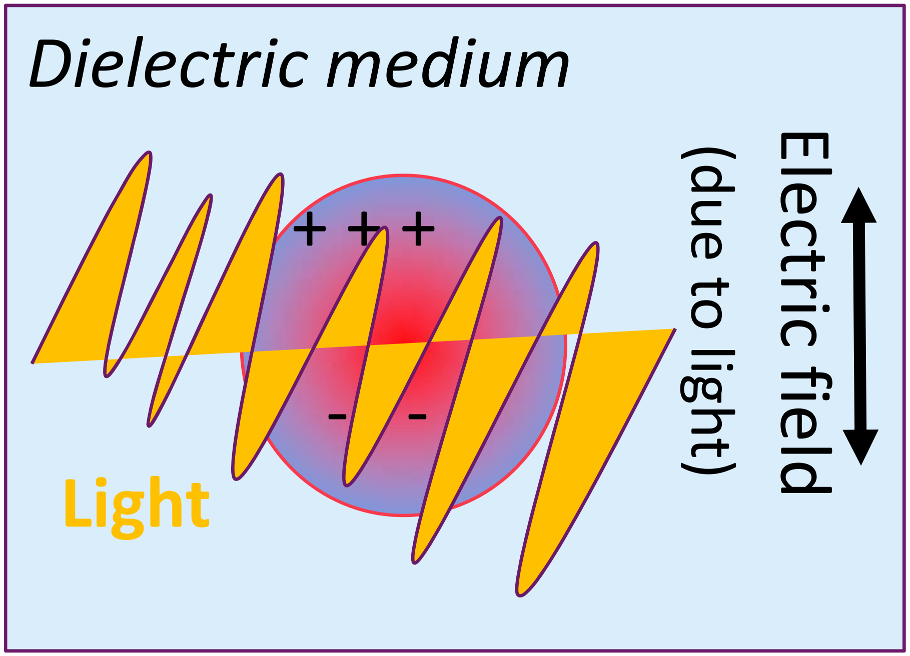


Localised Surface Plasmon Resonance (Metal NPs)

Surface plasmons oscillate with electromagnetic wave

At certain wavelength

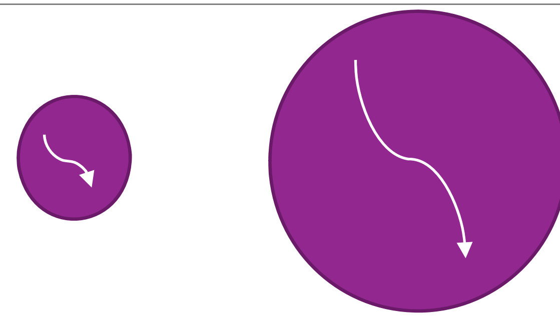
→Resonance between plasmon and light



Localised Surface Plasmon Resonance (Metal NPs)

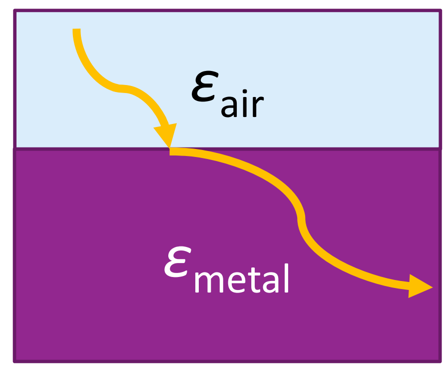
1. Size

Electron mean free path



2. Material Properties

Dielectroc constant:
metal|air interface has a large difference



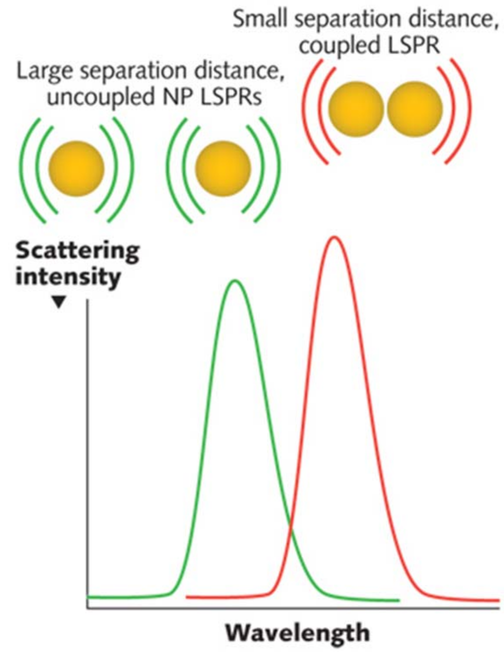
Localised surface plasmon resonance**

***localised in the nanoparticle*

Example: Optical Ruler

LSPR RULER

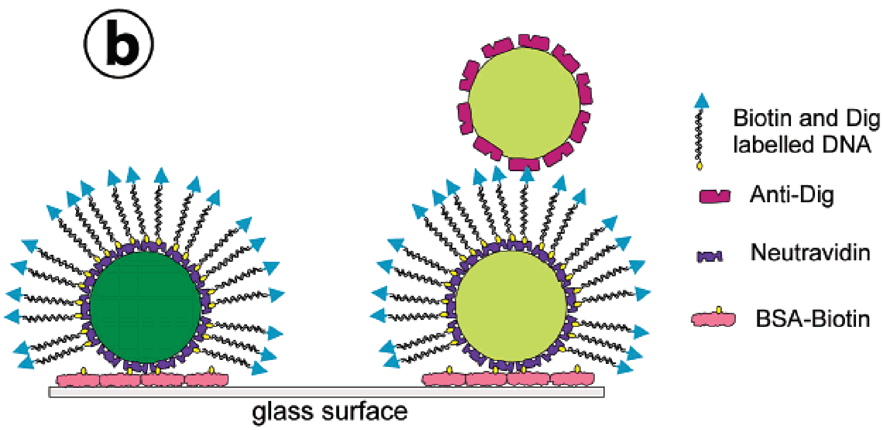
The red shift in the spectrum depends on the distance between the particles

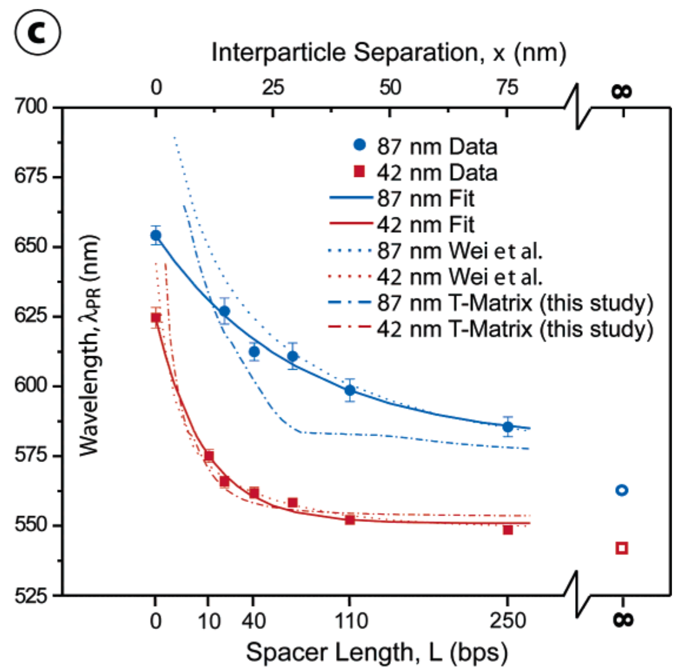


http://www.laserfocusworld.com/articles/print/volume-50/issue-09/features/nanometrology-plasmon-rulers-the-optical-angstrometers.html

Example: Optical Ruler

- Calibrated by coupling particles with known separation
  - Double stranded DNA as the linker





B. M. Reinhard et al. Nano Letters, **2005**, *5*, 2246.

Example: Optical Antenna

Antenna = mediator between far-field radiation and local fields (current)

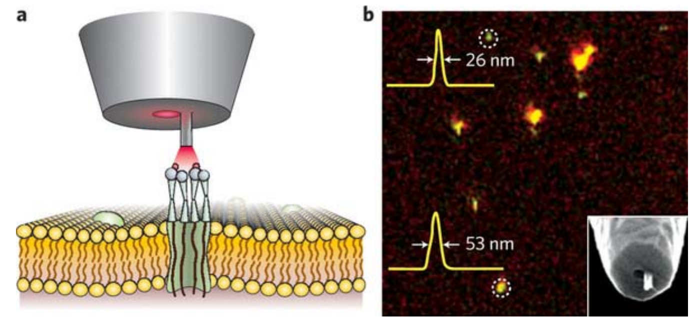
E. A. Coronado, E. R. Encina,F. D. Stefani, *Nanoscale* **3** (2011) 4042-4059.

Light → Far-field radiation

LSPR → Local field

Example

Detecting flurophores with optical antenna



L. Novotny, N. van Hulst, *Nature Photonics* **5** (2011) 83-90.

- LSPR transmits light to fluorophore very efficiently

- Smaller amounts and smaller scales detected

Example: Local Heat Generation

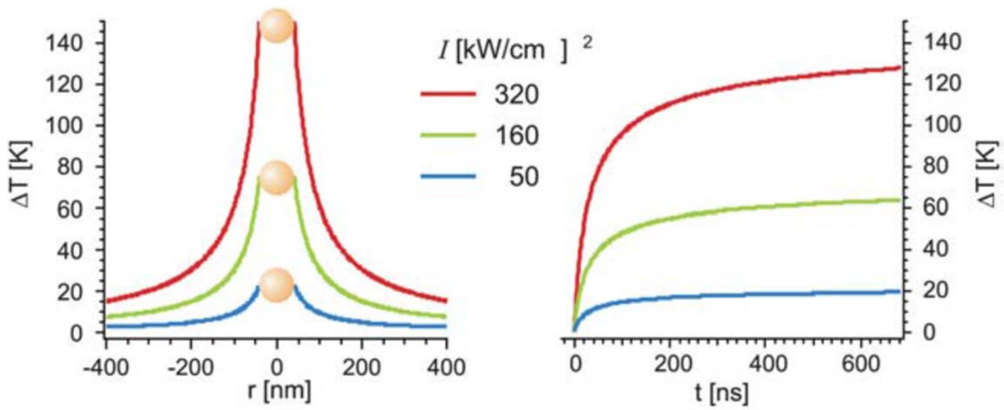
- Metal nanoparticles are poor light emitters but effective light absorbers

➢ After excitation (LSPR), the heat is conducted to metal crystal

➢ High local temperature's by light

$$\Delta T = \frac{I\sigma_{abs}}{4\pi kr}$$

I = intensity of light
σ_{abs}= absorbance cross-section
k = thermal conductivity of the medium
r = distance from nanoparticle



Concept checks

True of false

1. Excitons exist in weak confinement region
2. Surface plasmon resonance is due to confinement of electrons
3. Higher the wavelength, higher the energy

Concept checks

Which statement is correct

A) Binding energy of exciton increases with decreasing bad-gap

B) Binding energy of exciton increases with increased Coulomb energy

C) Binding energy of exciton increases with decreasing particle size

3rd Part: Mechanical Properties

Scale (In)Dependce

Continuum of Materials

- Properties of crystals / grains can be averaged to get the bulk material property
- ➢ Material properties are **Scale Independent**

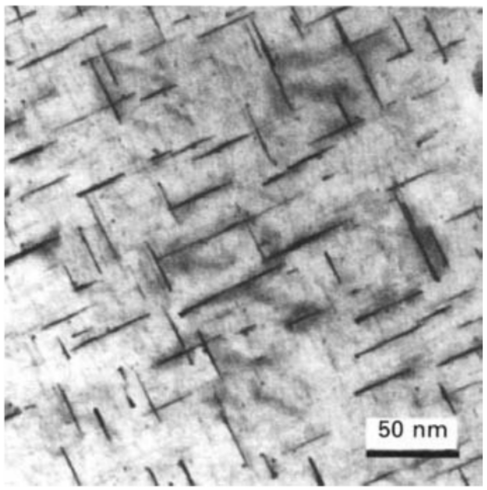
Higher Strength Steel and Aluminium Alloys (the latter half of 20th century)

- The above does not hold
- Material Properties are **Scale Dependent**

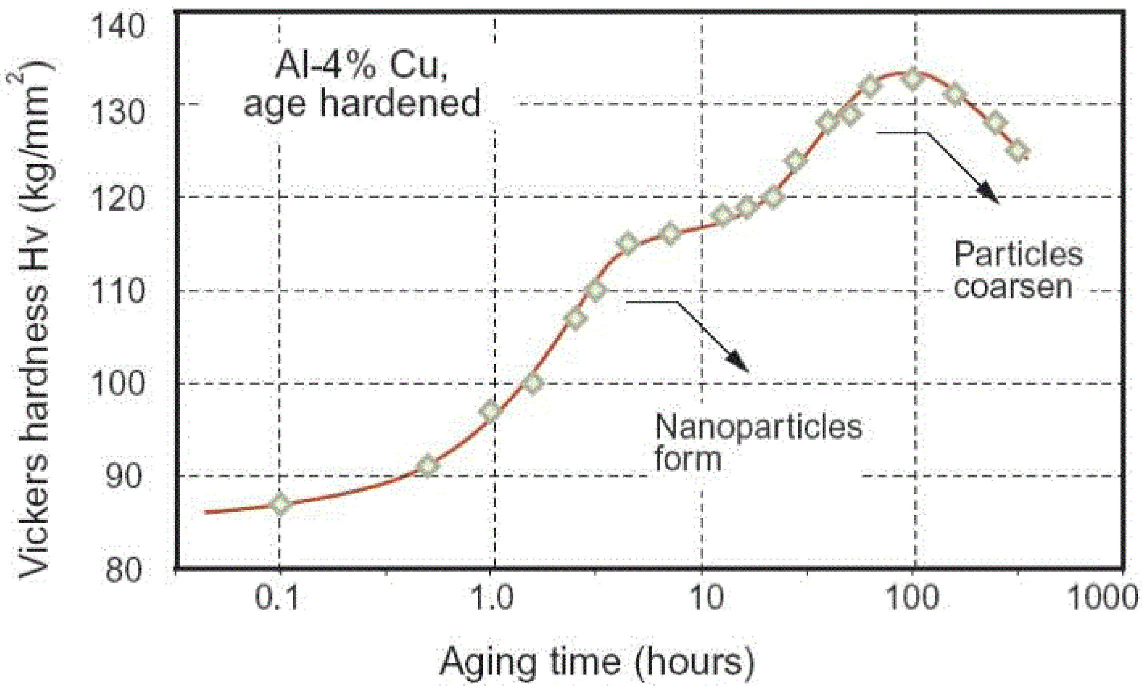
Mechanical Properties of

1. **Nanodispersions**
2. **Nanocrystals**
3. **Nanolaminates**

Nanodispersions (High-strength Steel & Al Alloys)



The oldest mechanical application of controlled nanoscale structuring



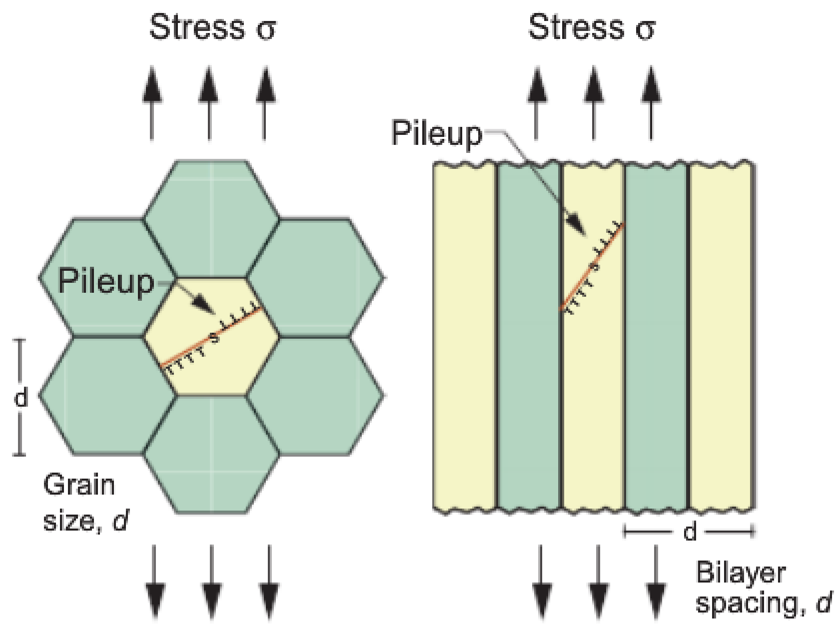
M.F Ashby, P.J. Ferreira, D.L. Schodek, Nanomaterials, Nanotechnologies and Design – An Introduction to Engineers and Architects (2009) Elsevier., pp. 201-202.

Nanocrystalline Solids: Hall-Petch Equation

Grain boundaries = **obstacles** for dislocations

Pileups can form between boundaries

- Grain size
- Applied Shear Stress



M.F Ashby, P.J. Ferreira, D.L. Schodek, Nanomaterials, Nanotechnologies and Design – An Introduction to Engineers and Architects (2009) Elsevier., p. 204.

Nanocrystalline Solids: Hall-Petch Equation

$$\sigma = \sigma_0 + k * \left(\frac{b}{d}\right)^{\frac{1}{2}}$$

$$= \sigma_0 + \left(\frac{2f * E}{C\mathrm{b}}\right)^{1/2} \left(\frac{\mathrm{b}}{d}\right)^{\frac{1}{2}}$$

Where

σ tensile stress

σ_0 lattice friction stress (constant)

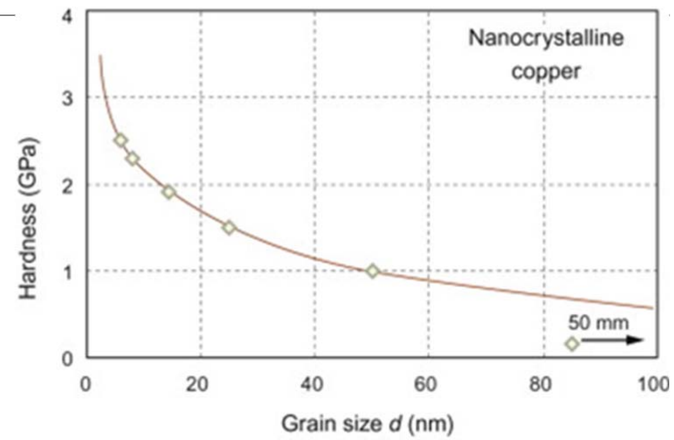
b Burgers vector

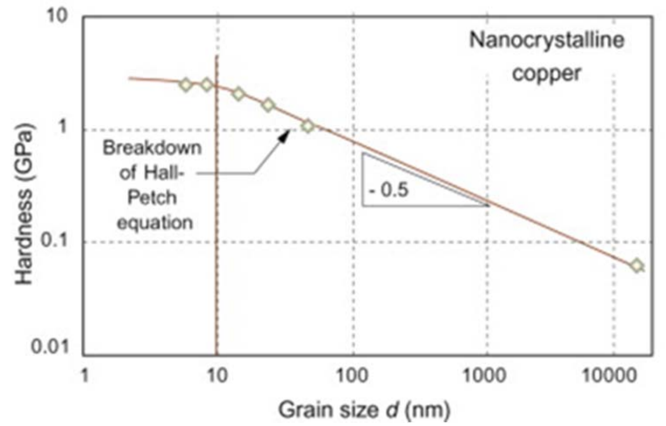
d grain size

E Elastic modulus (Young's modulus)

*f** force / unit length

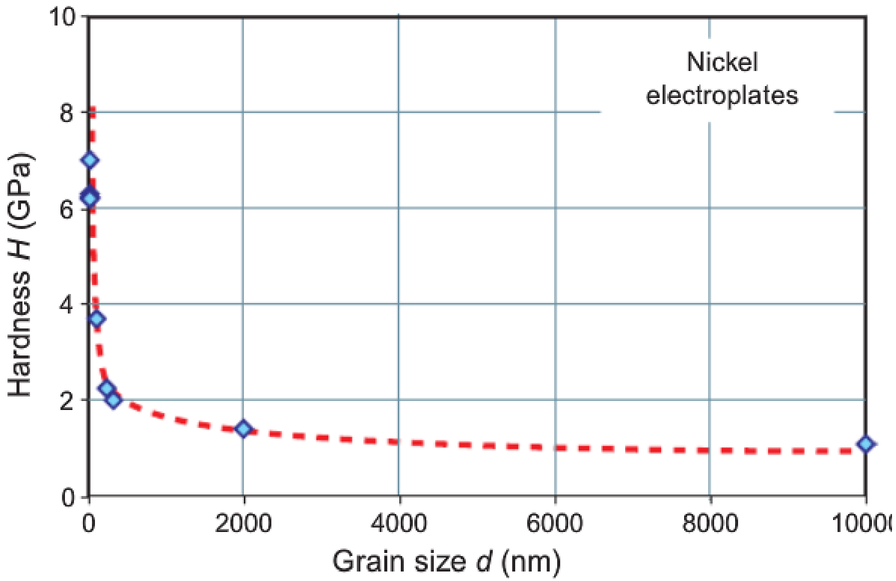
C constant

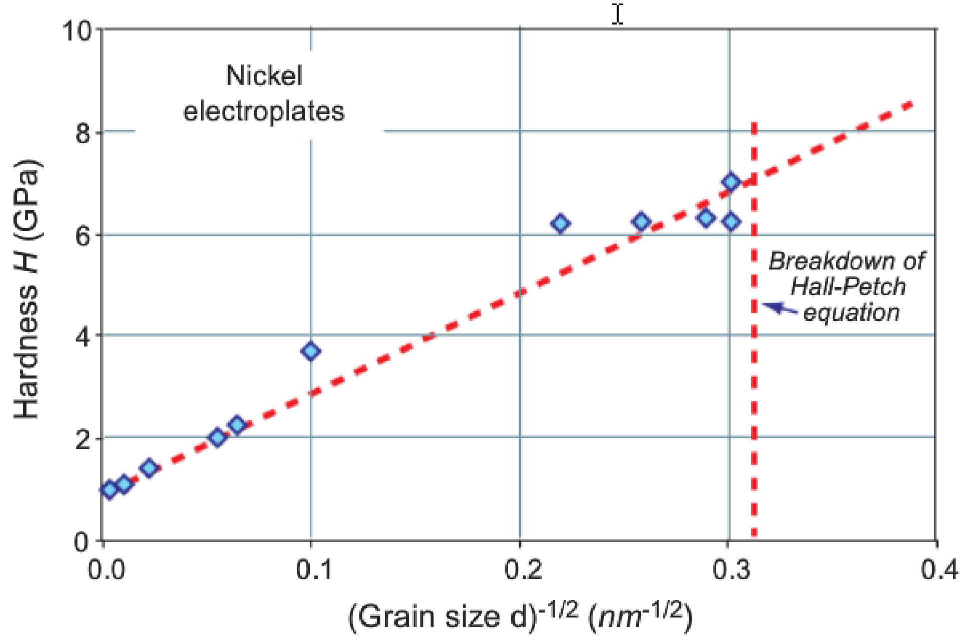




M.F Ashby, P.J. Ferreira, D.L. Schodek, Nanomaterials, Nanotechnologies and Design – An Introduction to Engineers and Architects (2009) Elsevier., p. 203.

Example: Electrodeposited Ni





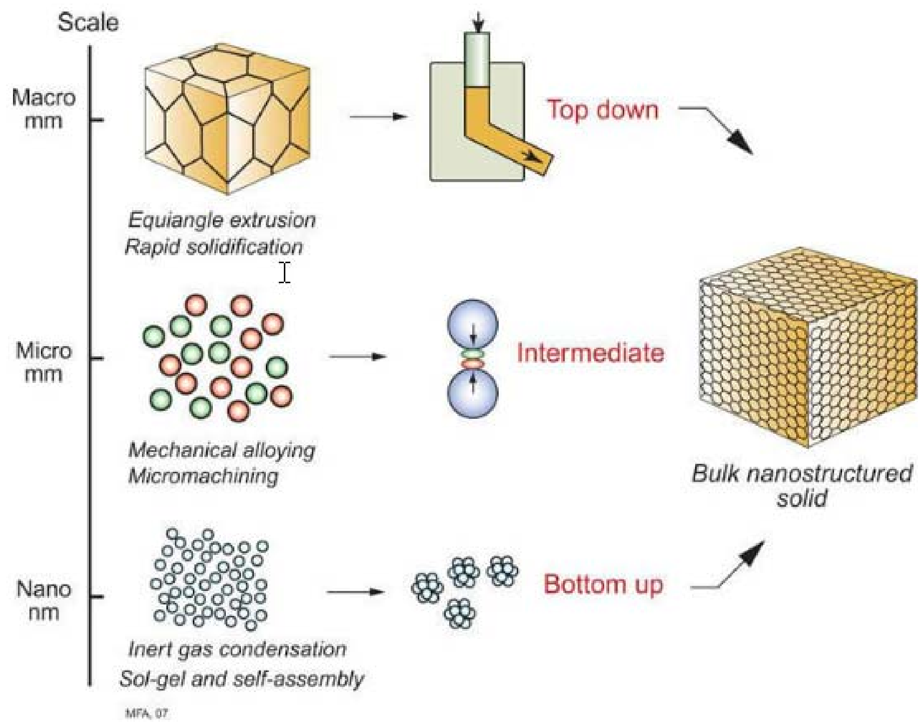
M.F Ashby, P.J. Ferreira, D.L. Schodek, Nanomaterials, Nanotechnologies and Design – An Introduction to Engineers and Architects (2009) Elsevier., p. 205.

Nanocrystallines

Glass stays amorphous due to its viscosity, same goes with most polymers

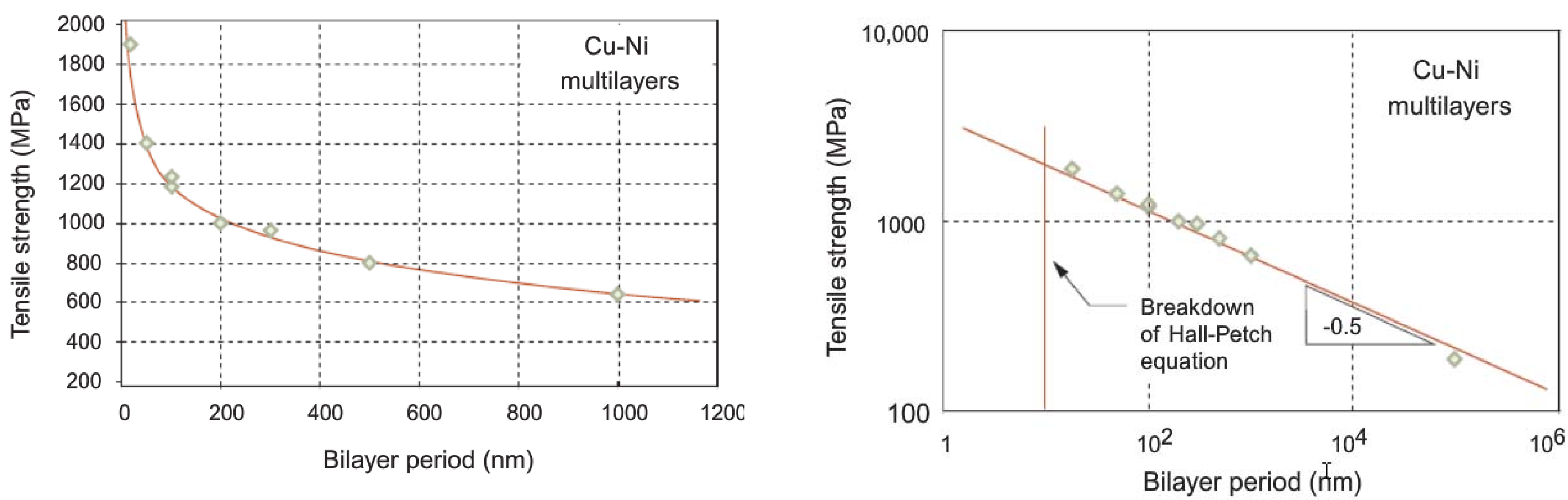
- ➢ Plenty of “obstacles”

But metals & ceramics → “familiar” crystals which are difficult to control



M.F Ashby, P.J. Ferreira, D.L. Schodek, Nanomaterials, Nanotechnologies and Design – An Introduction to Engineers and Architects (2009) Elsevier., p. 268.

Example: Nanolaminates



M.F Ashby, P.J. Ferreira, D.L. Schodek, Nanomaterials, Nanotechnologies and Design – An Introduction to Engineers and Architects (2009) Elsevier., p. 206.

Reading Material

For Exam

M.F Ashby, P.J. Ferreira, D.L. Schodek, Nanomaterials, Nanotechnologies and Design – An Introduction to Engineers and Architects (2009) Elsevier:

1. Electric Properties, pp. 218-222.

2. Optical Properties, pp. 227-232.

3. Mechanical Properties, pp. 199-211.

For Interested Reader (optional)

G. Cao, Y. Wang, Nanostructures and Nanomaterials – Synthesis, Properties and Applications, World Scientific:

- 1st Edition: Physical Properties (mechanical, optical, electric): pp. 357-382

- 2nd Edition: Physical Properties (mechanical, optical, electric): pp. 467-496

C. de Mello Donegá (Ed.), Nanoparticles: Workhorses of Nanoscience, Springer, Berlin(2014):

- Chapter 2: R. Koole, E. Groeneveld, D. Vanmaekelbergh, A. Meijerink, C. Mello Donegá: Size effects on semiconductor nanoparticles