Properties at Nanoscale II

27TH SEPTEMBER 2017

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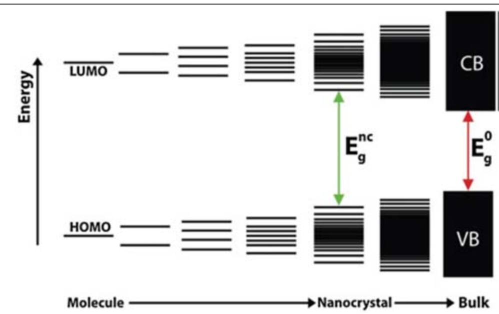
Last Lecture

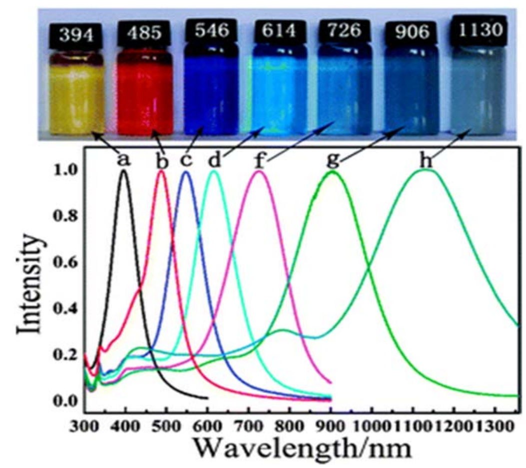
1) Electric Properties
- Metals
- Semiconductors
- Insulators (dielectrics)

2) Optical Properties
- Excitons and WL
- Localised Surface Plasmon Resonance

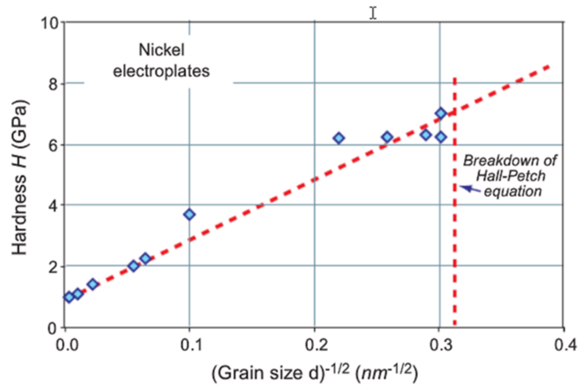
3) Mechanical Properties
- Nanodispersions
- Nanocrystalline solids
- Nanolaminates



Groeneveld, E.: Synthesis and optical spectroscopy of (hetero)-nanocrystals. Ph.D. Thesis, Utrecht University, Utrecht (2012) (From Book R. Koole)



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.



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

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* *Magentoresistance*	

After This Lecture You Can

Estimate the melting point of nanomaterials and explain its' behaviour vs. size

Explain the concept superparamagnetism

Estimate blocking temperature and Neel relaxation time

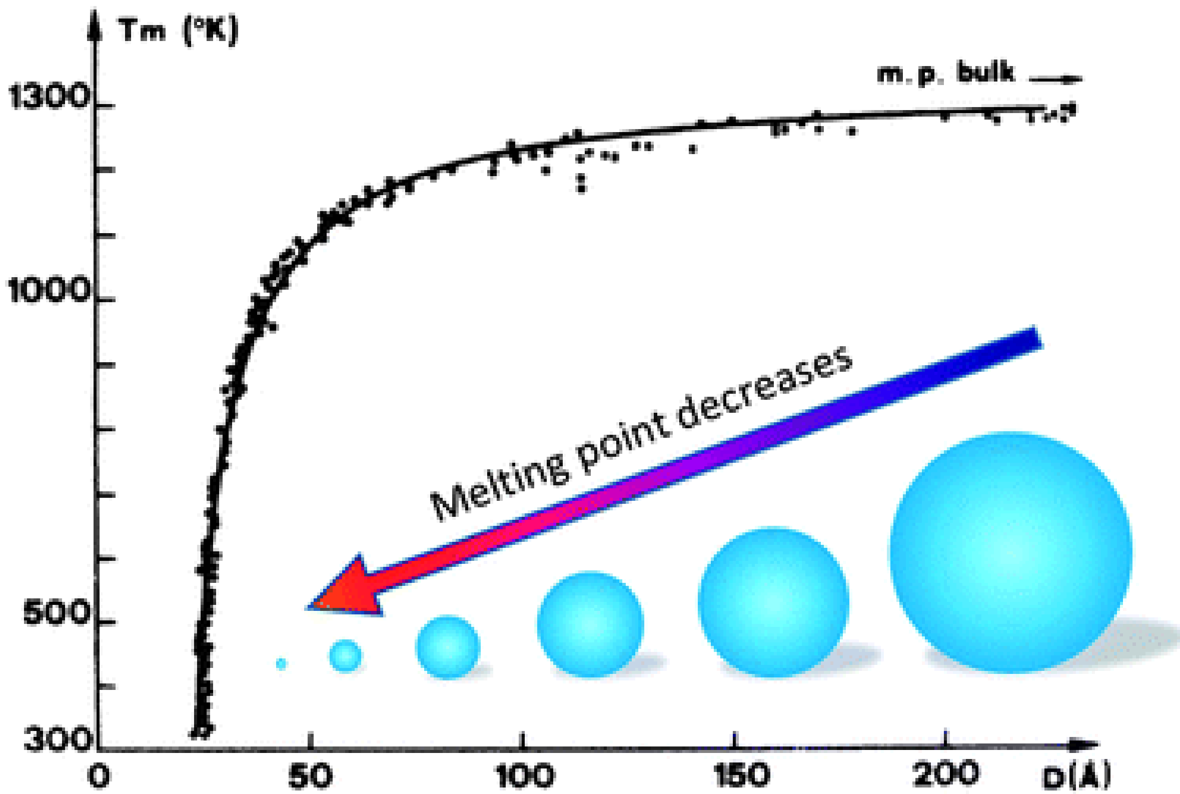
1^{st} Thermal Properties at Nanoscale

Thermal Properties

MELTING POINT

THERMAL TRANSPORT

Melting Point: Intuitive Explanations



P. Buffat and J. P. Borel, Phys. Rev. A: At., Mol., Opt. Phys., 1976, 13, 2287–2298.

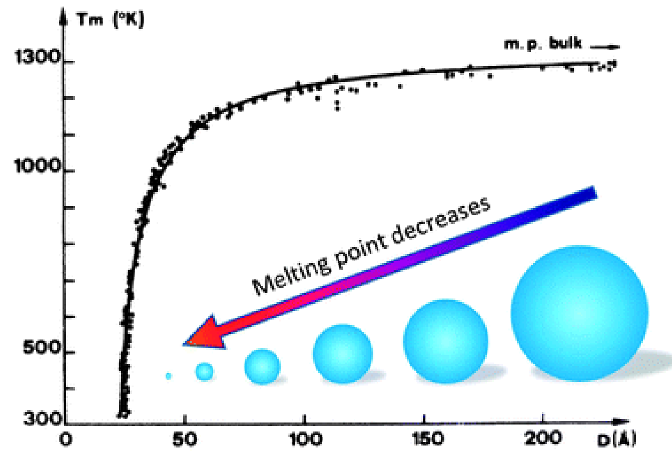
Melting Point: Intuitive Explanations

1) Atom binding:

- Surface atoms bind with less cohesive energy to the neighbouring atoms
  - Easier to "release" surface atoms than bulk atoms

2) Thermodynamic :

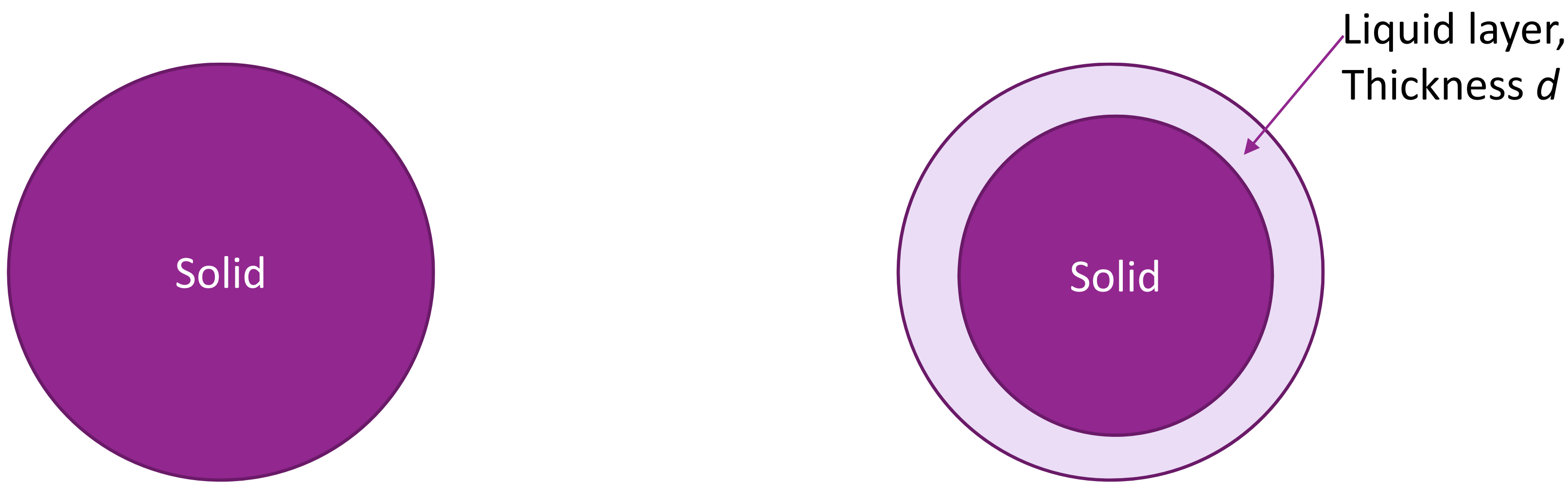
- "Melting opposite to nucleation"
- Change in the volume energy vs. surface energy
- *Predicted 1909 [1], first proved 1954 [2]*



P. Buffat and J. P. Borel, Phys. Rev. A: At., Mol., Opt. Phys., 1976, 13, 2287–2298.

[1] P. Pawlow. Z. Phys. Chemie, 65(1):545, 1909
[2] M. Takagi (1954). "Electron-Diffraction Study of Liquid-Solid Transition of Thin Metal Films". J Phys. Soc. Jpn. 9: 359.

Melting of Nanoparticle



As a function of time

- The solid|liquid interface changes

Melting Changes Gibbs Energy

$$\Delta G_{TOTAL} = \Delta G_{Bulk} + \Delta G_{Surface}$$

$$\Delta G_{Bulk} = \frac{L_0(T_0 - T)}{T_0} V_L \qquad \Delta G_{Surface} = \gamma \Delta A$$

Where

L_0= latent heat of melting

T_0= melting point of bulk

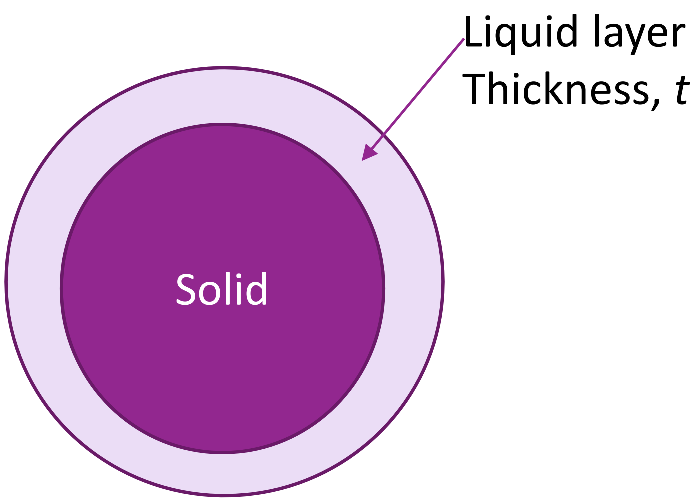
T= melting point of extended system

V_L=volume of liquid

γ = surface energy

ΔA= increment of surface area

Melting of Nanoparticle



$$\Delta G_{Surface} = A_L\gamma_L + A_{SL}\gamma_{SL} - A_S\gamma_S$$

Where

A_L = new liquid surface area

A_{SL} = new solid-liquid interface area

A_S = destroyed solid interface

γ_L = surface energy of liquid (per unit area)

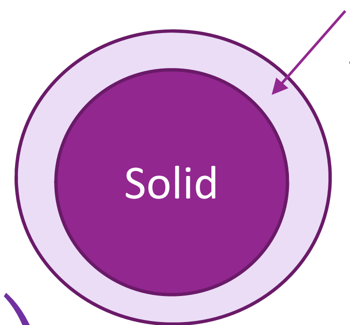
γ_{SL} = surface energy of solid|liquid (per unit area)

γ_S = surface energy of solid (per unit area)

Melting of Nanoparticle

At equilibrium

$$\frac{\partial G}{\partial t} = 0$$



Liquid layer
Thickness, t

$$\boldsymbol{T_M = T_0\left(1 - \frac{2\gamma_{SL}}{L_0 r}\right)}$$

Melting of Nanoparticles in Matrix

Young's theorem

$$\gamma_{SL}\cos\theta = \gamma_{LM} - \gamma_{SM}$$

LM = liquid|matrix

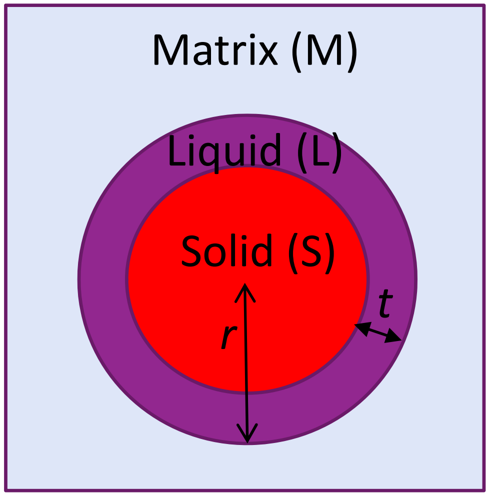
SM = solid | matrix

SL = solid |liquid

0< θ < 90°

If $\gamma_{SL} > \gamma_{LM}$ → $T_m < T_0$

If $\gamma_{SL} < \gamma_{LM}$ → $T_m > T_0$



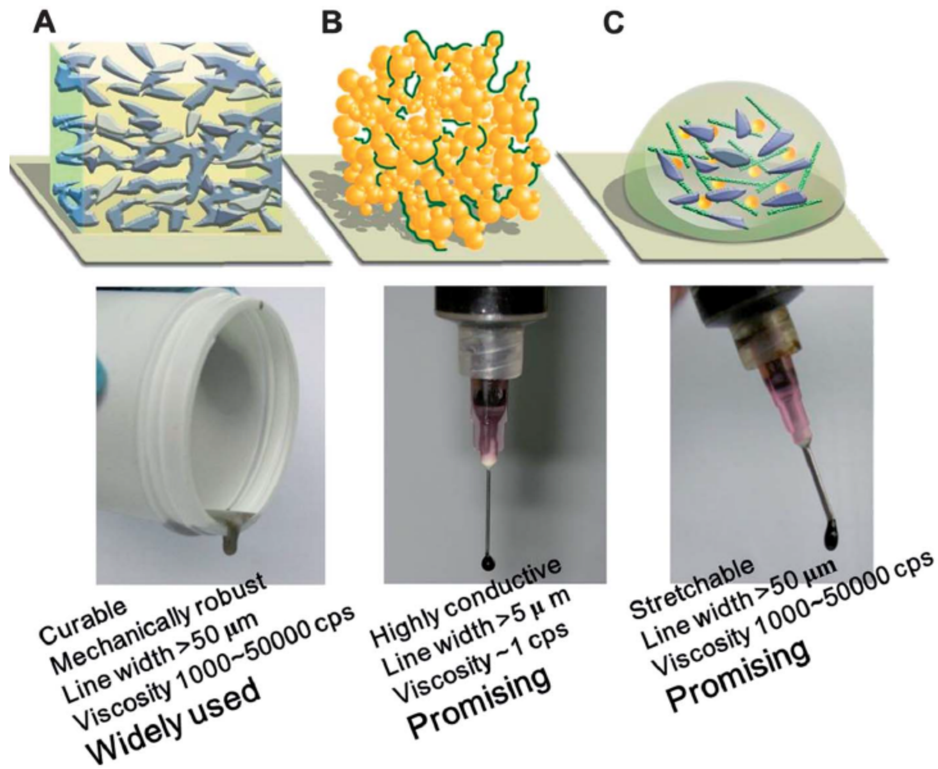
$$\Delta G_{bulk} = \frac{L_0(T_0 - T)}{T_0} V_L$$

$$\Delta G_{surf} = A_{LM}\gamma_{LM} + A_{SL}\gamma_{SL} - A_{SM}\gamma_{SM}$$

$$\Delta G_{tot} = \Delta G_{bulk} + \Delta G_{surf}$$

Example: Flexible Electronics

- Low melting point = Advantage in flexible electronics



C. Yang,C. Ping Wong, M. M. F. Yuen, *J. Mater. Chem. C*, **1** (2013) 4052-4069.

Thermal Transport (Thermal Conductivity)

1. Lattice wave vibrations (phonons)
   - More pronounced in non-metals
2. Free electrons
   - More pronounced in metals

Thermal Transport (Thermal Conductivity)

1. Lattice wave vibrations (phonons)

- More pronounced in non-metals

2. Free electrons

- More pronounced in metals

- **Quantum confinement when size close to the phonon wavelength**

0D → QF in **three** dimensions

1D → QF in **two** dimensions

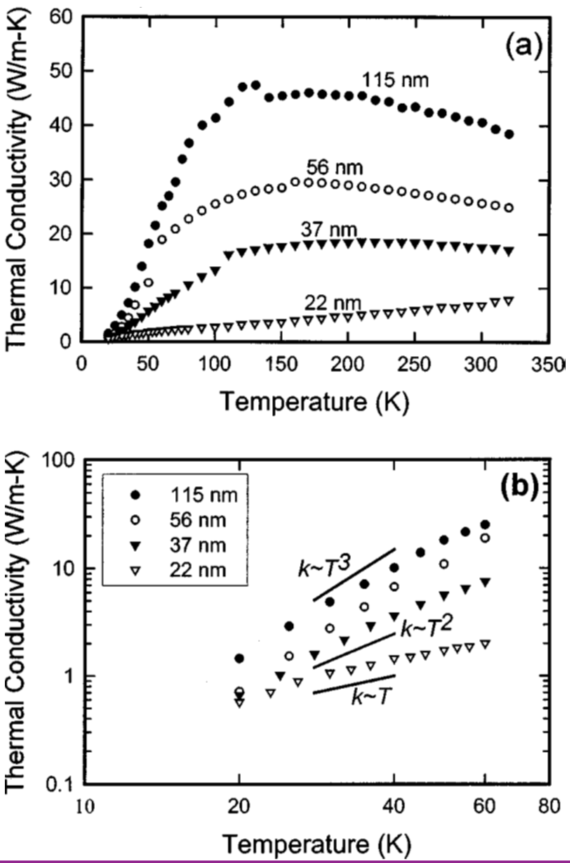
2D → QF in **one** dimension

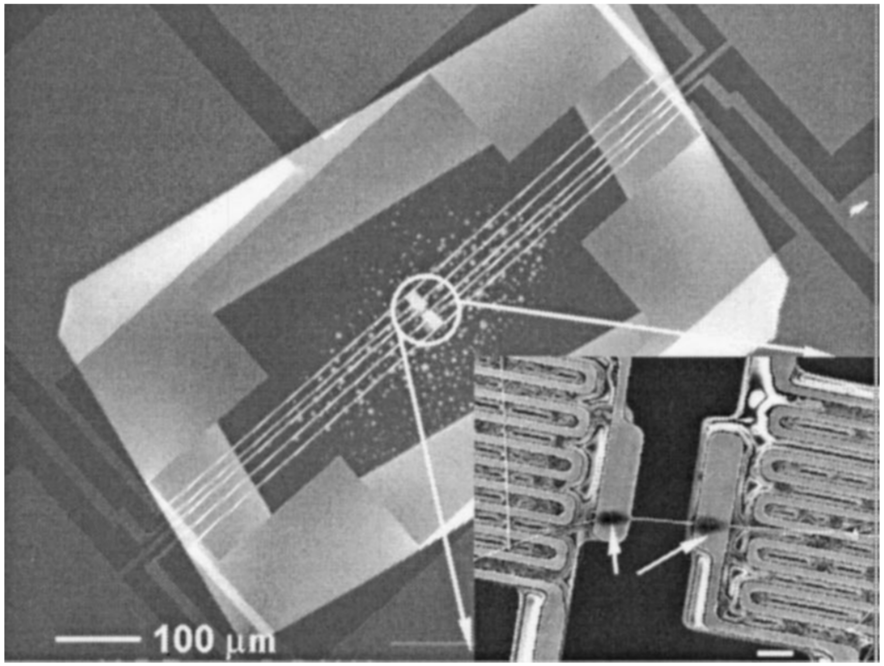
Effect on thermal conductivity

Note!
CNT 3000 W/mK
Bulk Cu 400 W/mK

Thermal Conductivity

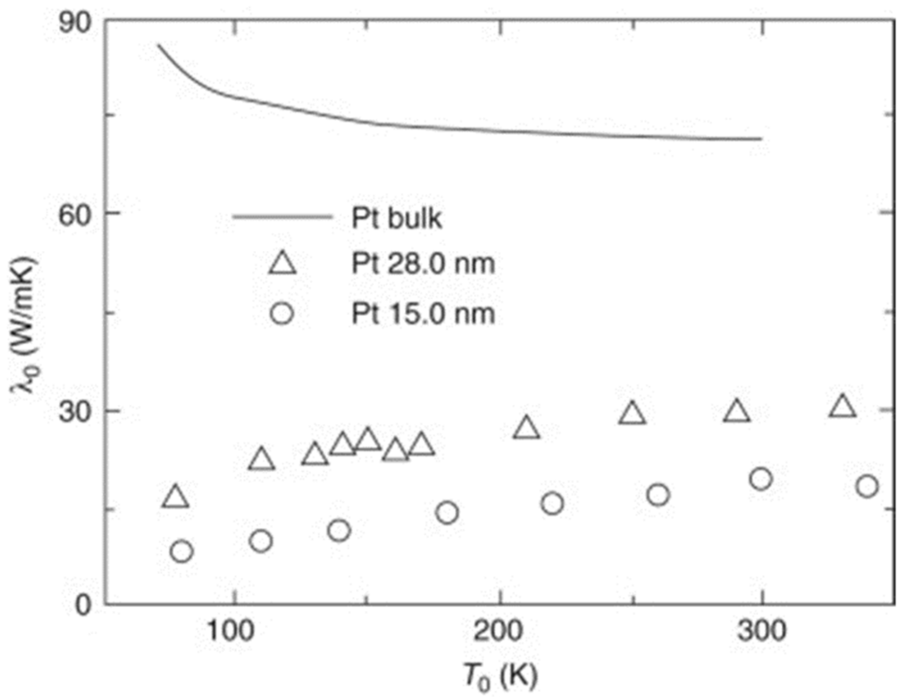
- First observed 2003 [1] for a individual silicon nanowire

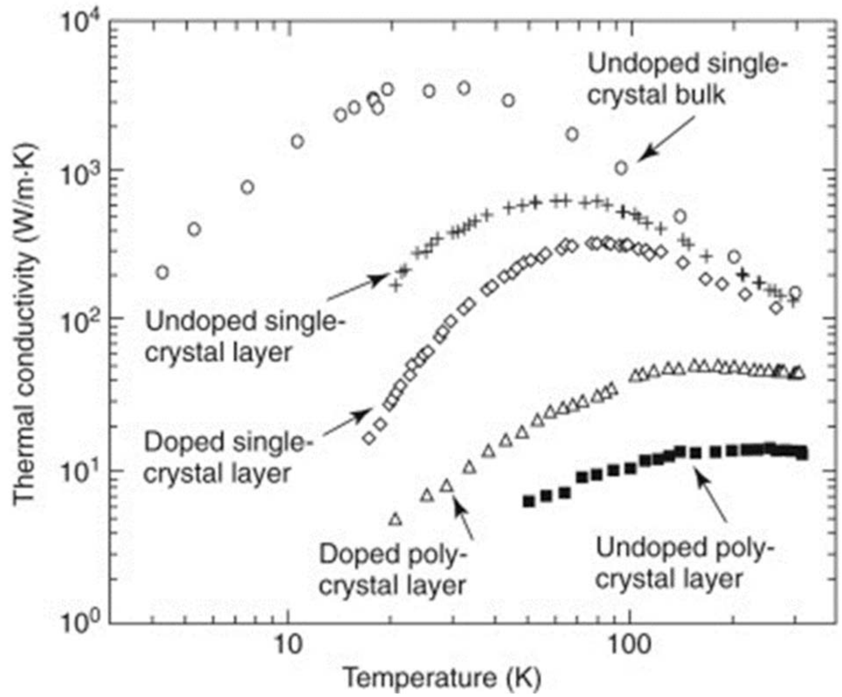




[1] Li, D.; Y. Wu; P. Kim; L. Shi; P. Yang; A. Majumdar (2003). "Thermal conductivity of individual silicon nanowires". *Applied Physics Letters* **83** (14): 2934–6

Example: 2D Materials



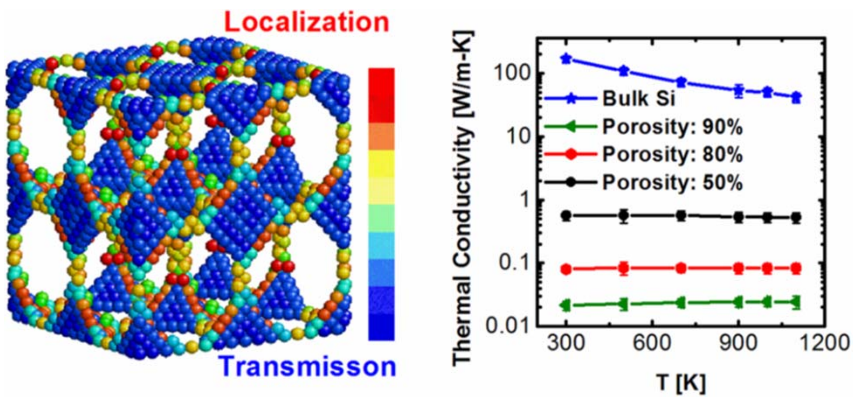


M. F. Ashby, P. J. Ferreira, D. L. Schodek, Nanomaterials, Nanotechnologies and Design (2009) pp. 216-217.

Example: Thermoelectric Materials

Lower Thermal Conductivity = Advantage in thermoelectric materials
(i.e. materials changing heat to electricity)

- Thermoelectric material should be a good electrical conductor and bad thermal conductor



L. Yang, N. Yang, B. Li, *Nano Lett.* **14** (2014) 1734–1738.

Figure of merit

$$ZT = \frac{\sigma S}{k}$$

σ =electrical conductivity
S = Seebeck coefficient
k = thermal conductivity

Heat Capacity and Thermal Expansion

HEAT CAPACITY

- Nanocsytalline iron > “normal” iron

➢ entropy effect

BUT

- ZnO flakes < bulk ZnO

THERMAL EXPANSION

- 3.2 nm AgNP in glass > bulk Ag

BUT

- 5.1 nm AgNP in glass ≈ bulk Ag
- SWCNT very very low

Conflicting results....

Concept Checks

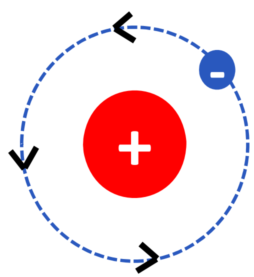
True or false

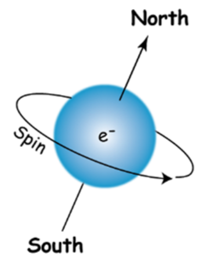
1) Thermoelectric materials is a lousy electric conductor and good thermal conductor.
2) Lower melting point of nanomaterials can be assumed to be due to the fact that small nanoparticles are thermodynamically less stable than their bulk counterparts.
3) Heat transfer in single layered, metallic 2D materials is lower due to lower freedom of electrons

2nd Part: Magnetic Properties at Nanoscale

Magnetic Properties

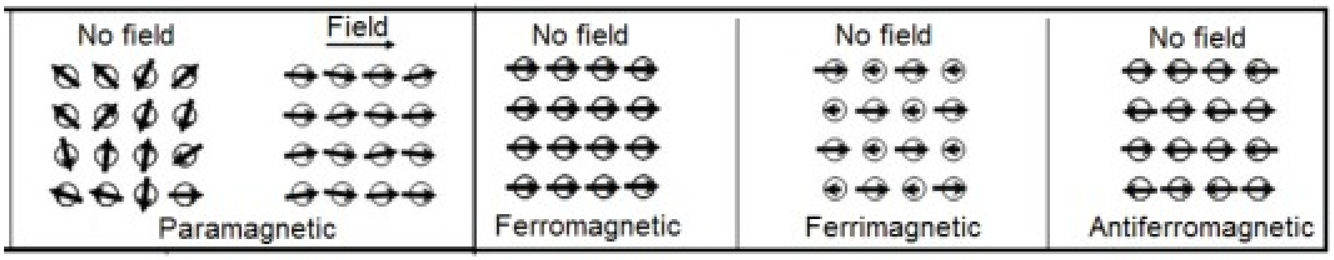
- All magnetic properties are related to magnetic moment of electrons
  1. Electron’s movement around the positive nucleus
  2. Spinning around its own axis





- Macsrocopic magnetism depends on how the atoms are in the bulk and how freely electrons’ magnetic moment can change
  - Domains

Magnetic Properties

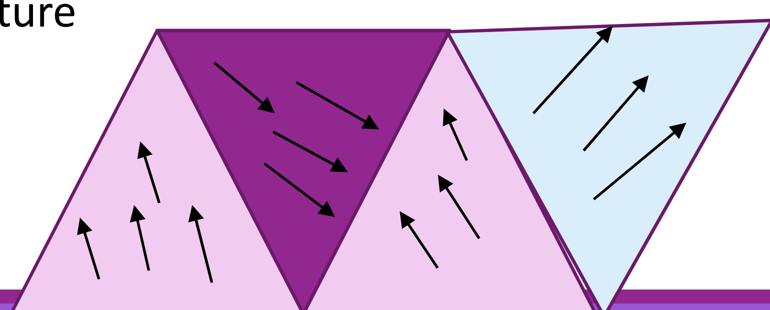


A. G. Kolhatkar, A. C. Jamison, D. Litvinov, R. C. Willson, T. R. Lee, *Int J Mol Sci.* **14** (2013) 15977–16009.

Properties are affected by

- Size
- Shape
- Composition
- Core-Shell structure

Research is concentrated on optimisation the response to the external magnetic field



Total Energy of Ferromagnetic

$$E_{Total} = E_{exc} + E_{ani} + E_{dem} + E_{app}$$

E_{exc} = energy related to an atomic magnetic moment

E_{ani} = energy related to the electron alignment in anisotropic crystals

E_{dem} = energy related to magnetic domains (dipole-dipole interactions)

E_{app} = energy related to an applied field

Total Energy of Ferromagnetic

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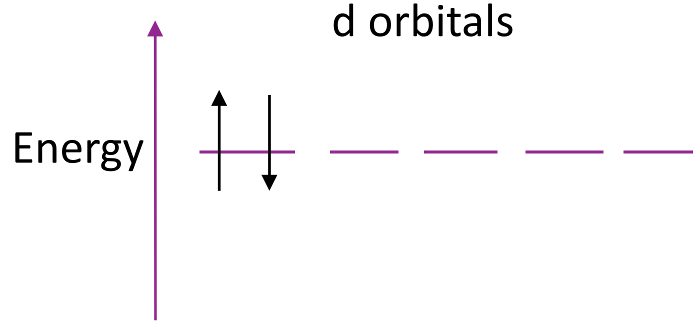
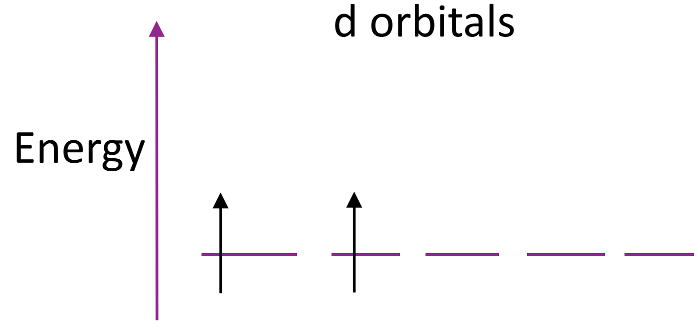
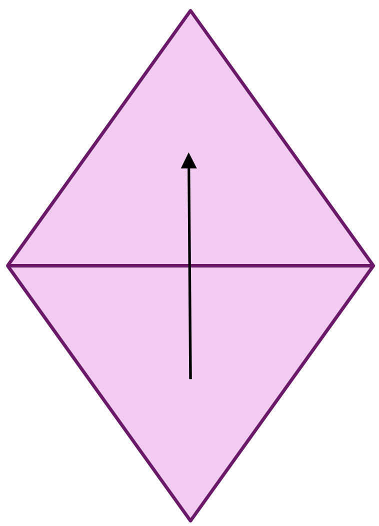




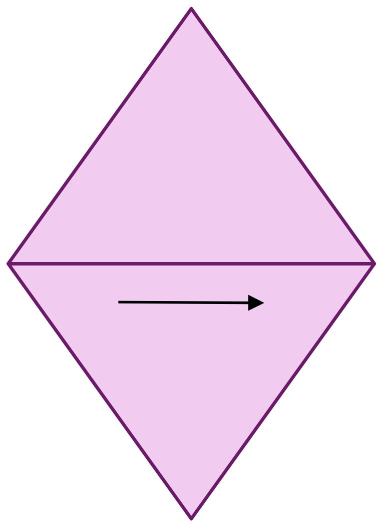
Total Energy of Ferromagnetic

$$E_{Total} = E_{exc} + \boldsymbol{E_{ani}} + E_{dem} + E_{app}$$

E_{ani} = energy related to the electron alignment in anisotropic crystals ("easy-axis")



OR



Total Energy of Ferromagnetic

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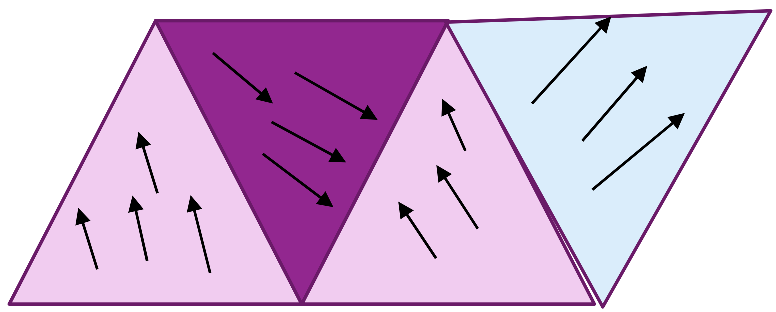
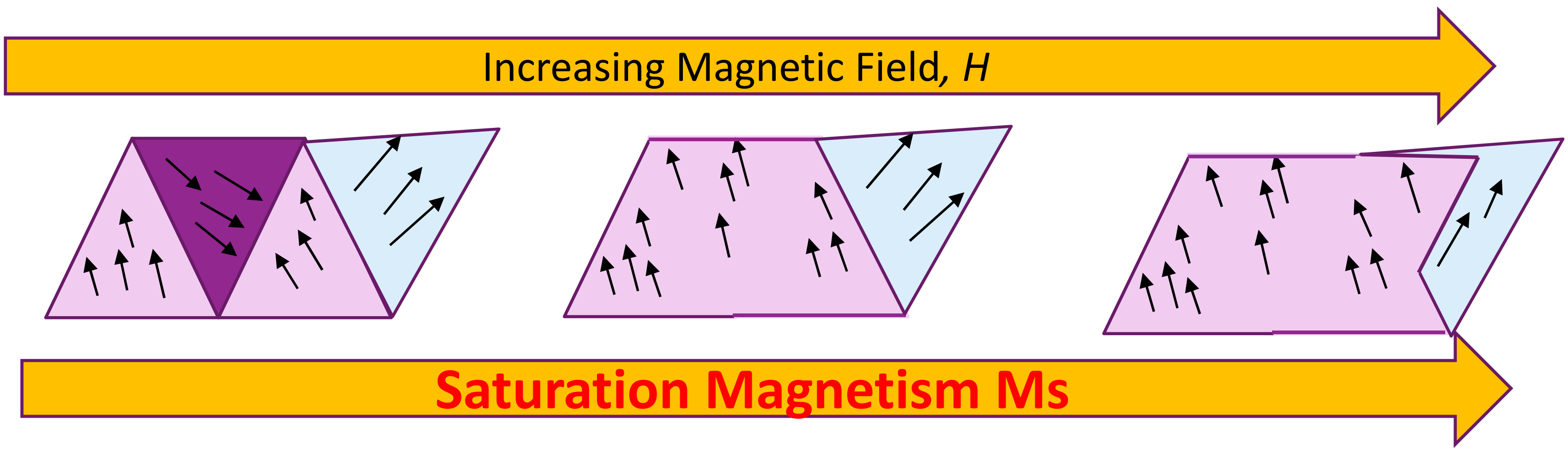


Total Energy of Ferromagnetic

$$E_{Total} = E_{exc} + E_{ani} + E_{dem} + \boldsymbol{E_{app}}$$

E_{app} = energy related to an applied field



Magnetic Properties in Bulk

Field is increased, ***magnetization*** increases

- **Saturation (Ms)**

- ***Field*** *is* decreased

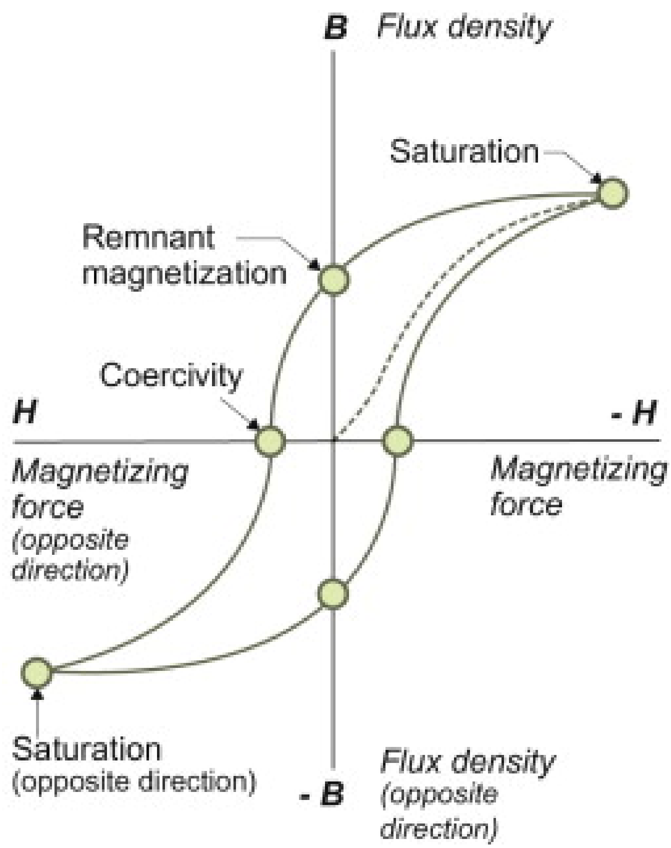
- **Hysteresis**

- **Remanence (Mr)**

  = magnetization left when the ***field is back to zero***

- **Coecervity (-Hc)**

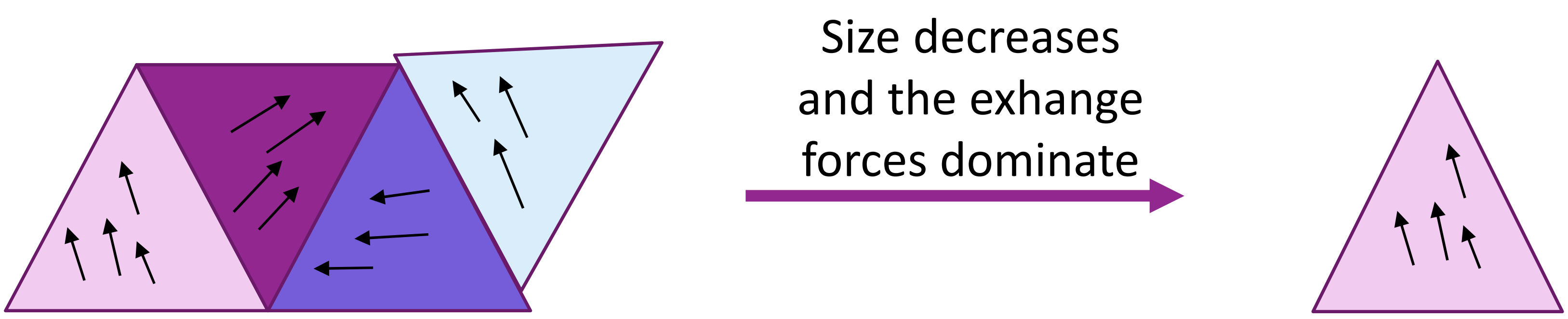
  = field needed to get back to ***zero magnetization***



M. F. Ashby, P. J. Ferreira, D. L. Schodek, Nanomaterials, Nanotechnologies and Design (2009) pp. 224

Ferromagnetics at Nanoscale

Critical size for single domain

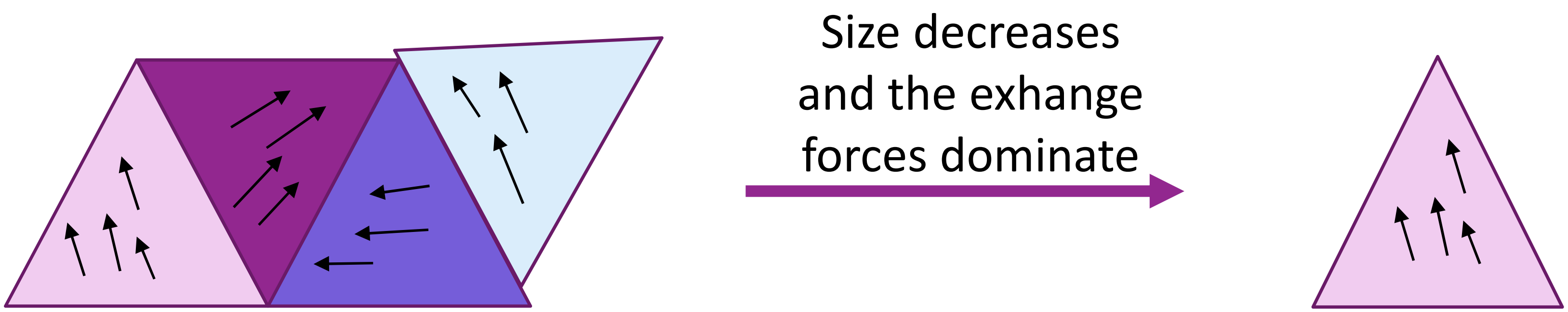


Ferromagnetics at Nanoscale

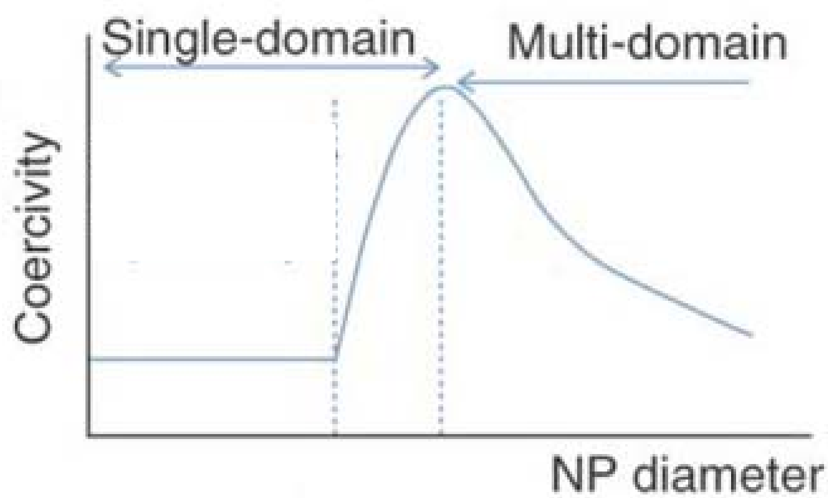
Critical size for single domain

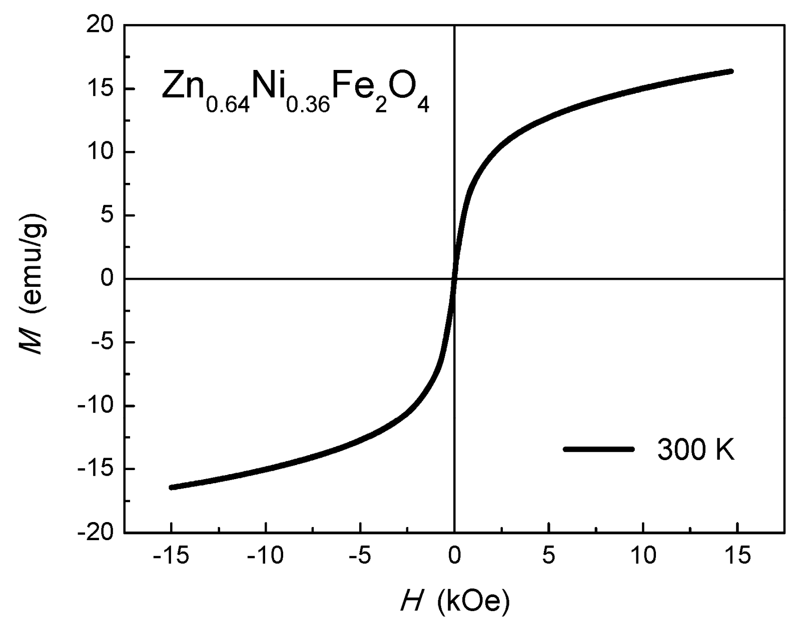
$$D_{cri} = \frac{9\gamma_B}{\mu_0 M_s^2} = \frac{9 \cdot 4(AK_1)^{1/2}}{\mu_0 M_s^2}$$

Where γ_0 = wall energy of materials, A is an exchange constant (exchange stiffness), K_1 anisotropic constant, μ_0 permittivity of free space and M_s saturation magnetimism



Single-Domain: Coecervity and Hysteresis

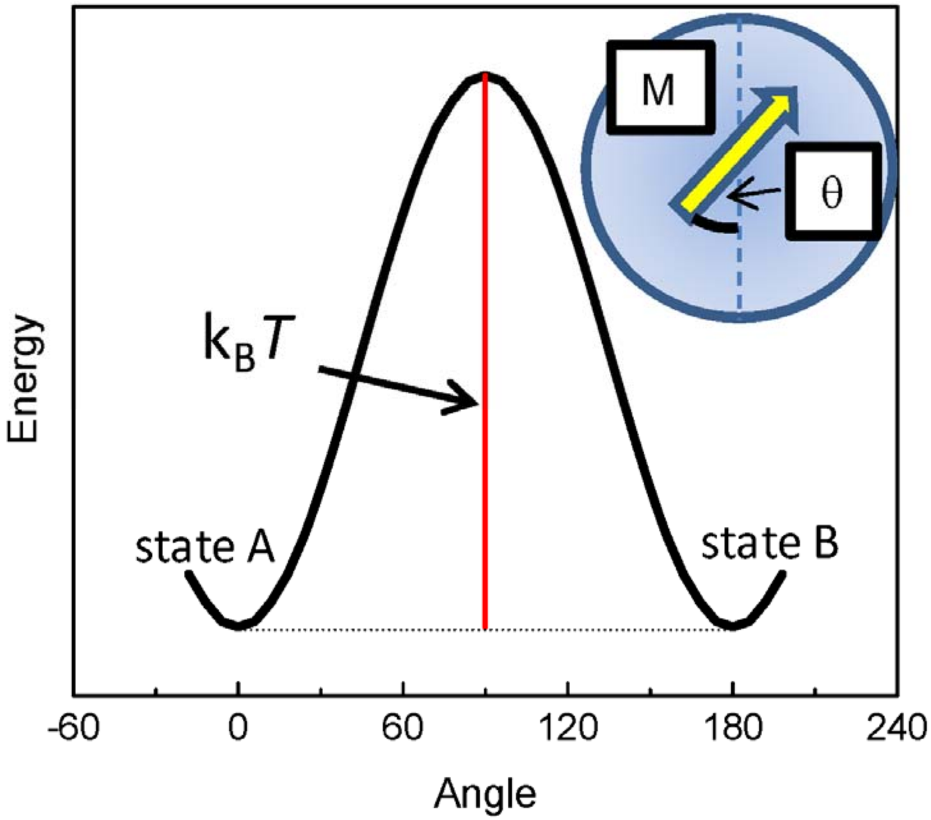




T. Trindade, A. L. Daniel-Da-Silva , *Biofunctional Composites of Polysaccharides Containing Inorganic Nanoparticles*, **Chapter 12** in Book Advances in Nanocomposite Technology", Ed. by A. Hashim, Intech (2011).

R. Díaz-Pardo, R. Valenzuela, *Characterization of Magnetic Phases in Nanostructured Ferrites by Electron Spin Resonance*, **Chapter 6** in Book: Advanced Electromagnetic Waves, Ed. by S. O. Bashir, Intech (2015).

Single-Domain: Spin Flip



$$E_a = KV\sin^2\Theta$$

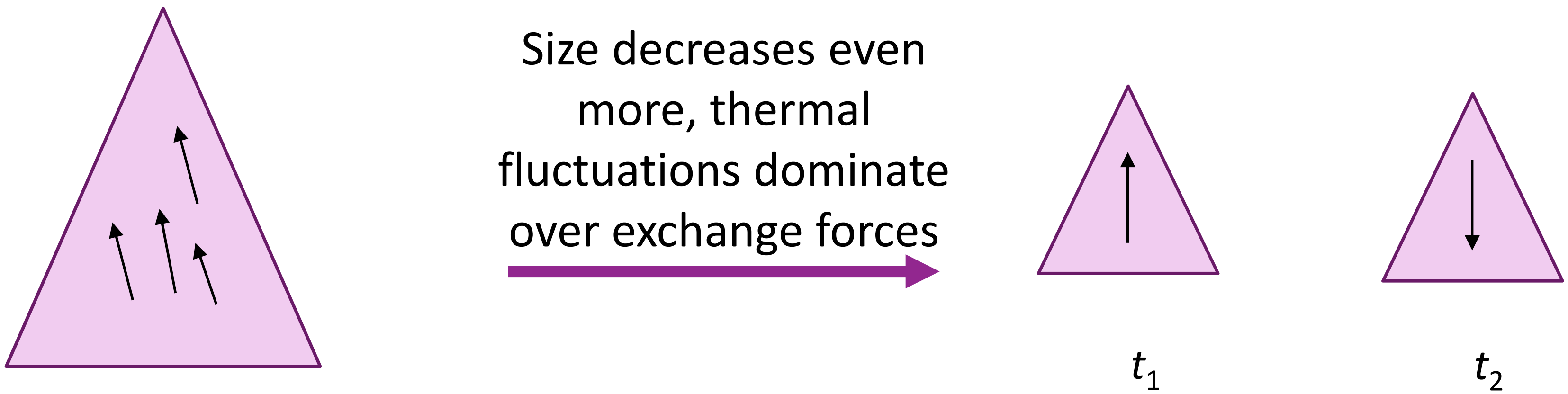
Where

K = magnetic anistropic constant

V = volume of the particle

Θ = angle between magnetization vector and easy axis of magnetization

Ferromagnetics at Nanoscale

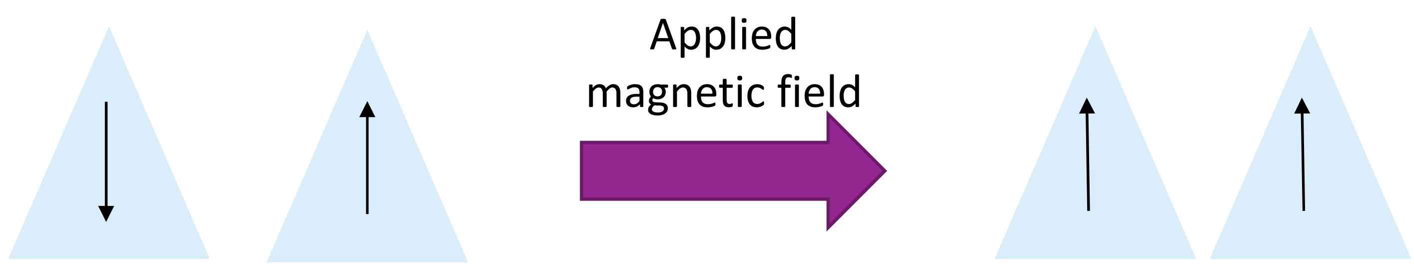


Thermal fluctations flip the spin so fast that ferromagnetic material ”feels and looks” from outside as paramagnetic

Superparamagnetism

Superparamagnetism

- *Single-domain*
- *No hysteresis*
- *Paramagnetic without external field*
- *Immediate response to magnetic field*
- *High saturations magnetism*



Without field, spin up/down (thermal fluctations)

With field, spin up or down

Superparamagnetism

BLOCKING TEMPERATURE T_B

$$T_B = \frac{KV}{25k_B} = \frac{K\left(\frac{4\pi r_0^3}{3}\right)}{25k_B}$$

K = anisotropic constant
V= volume of single-domain particle
k_B = Boltzmann constant
r_0 = radius of the single-domain particle

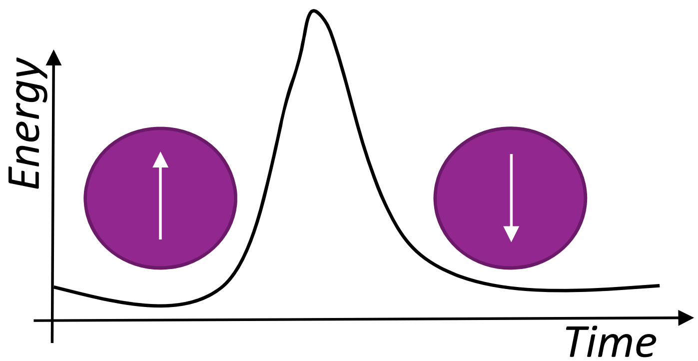
Above T_B (superparamagnetism)

- No field = magnetism is zero
  - Enough energy to flip the spin back and forth (randomly and quickly)
- With field = magnetism
  - particle spins follow the external magnetic field

Below T_B

- "Blocked" to one spin orientation
  - One domain = one spin direction (easy axis) = magnetism
  - Not enough energy to follow the external field
- Permanent magnetism

Superparamagnetism



NEEL RELAXATION TIME (T_N)

- Time between the spin flip (up/down) = Neel relaxation time

$$T_B = \frac{KV}{k_B \ln(\frac{\tau_N}{\tau_0})}$$

τ_N = Neel relaxation time
τ_0 = observation time

Superparamagnetic Nanoparticles

Strong response to the external field

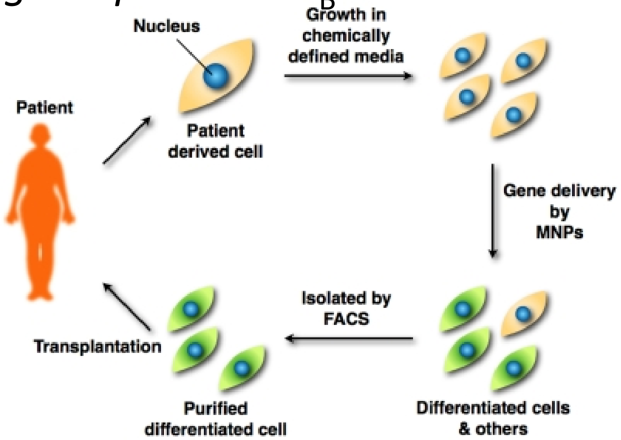
- **No magnetism without the field**
  - Paramagnetic behaviour without the field
- **Immediate response to magnetic field**
  - no hysteresis
- **With field, high saturation magnetism**
  - Ferri- or ferromagnetic materials (“supermagnetic” behaviour)

Biomedical Application

- No magnetism without the field
- ➢ **Reduces aggregation in body**
- Immediate response to magnetic field
- ➢ **Fast response time (for example in imaging)**
- High saturation magnetism
- ➢ **Lower concentrations needed / better contrast (in imaging)**

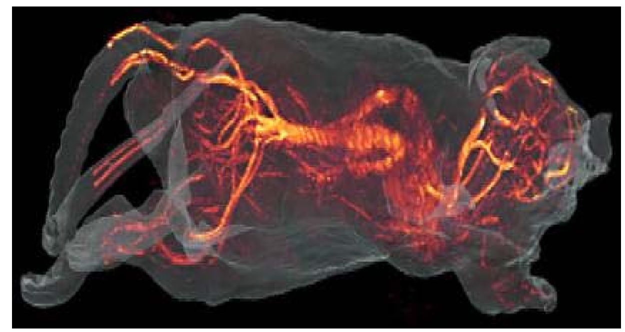
Biomedical Applications of Superparamagnetic Nanoparticles

Blocking temperature T_B



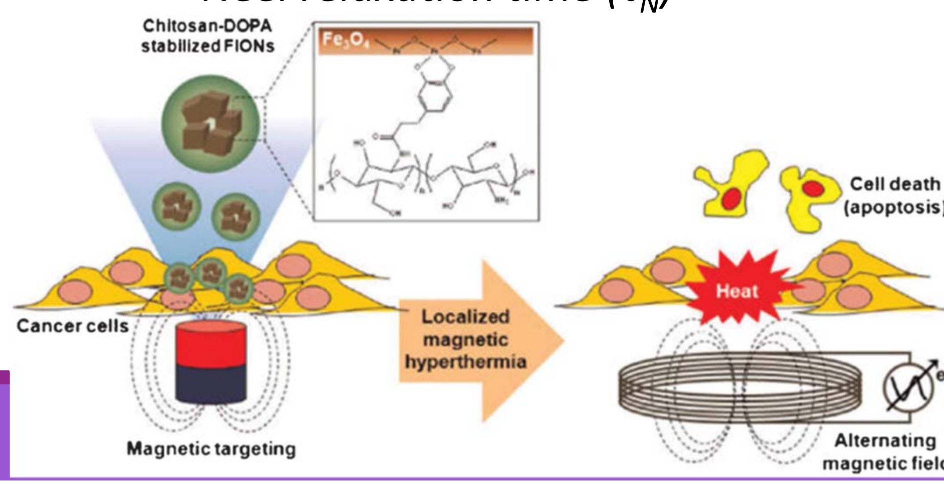
D. Kami, S. Takeda, Y. Itakura, S. Gojo, M. Watanabe, M. Toyoda, *Int. J. Mol. Sci.* **12** (2011) 3705-3722.

High saturation magnetization Ms
- high contrasts in MRI



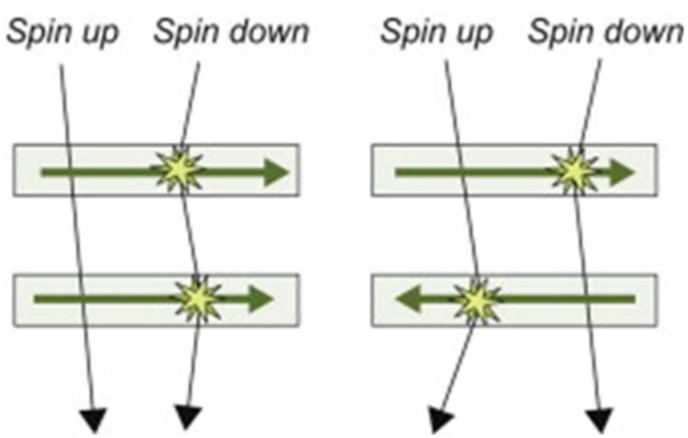
http://www.theamedical.com/index.php?r=web/view&id=125&action=Product

Neel relaxation time (τ_N)

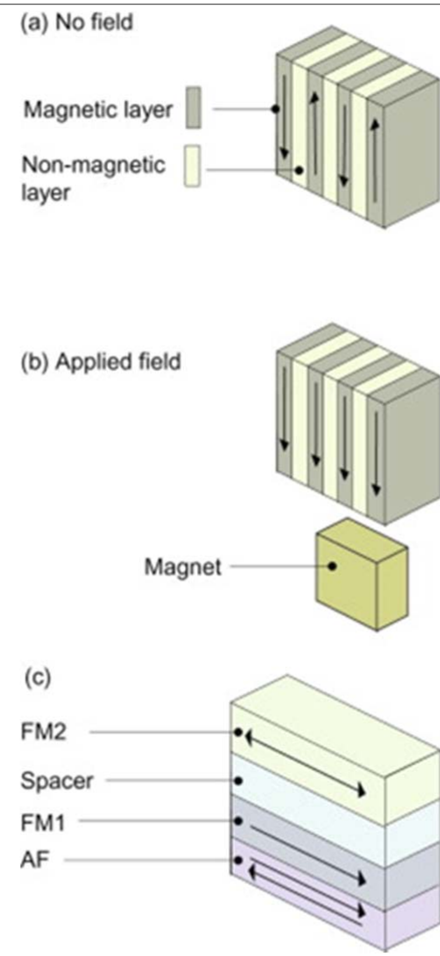


K. Yan, P. Li, H. Zhu, Y. Zhou, J. Ding, J. Shen, Z. Li, Z. Xu, P. K. Chu, *RSC Advances* **3** (2013) 10598-10618.

Giant & Colossal Magnetoresistance (GMR, CMR)



Low *R* **High *R***



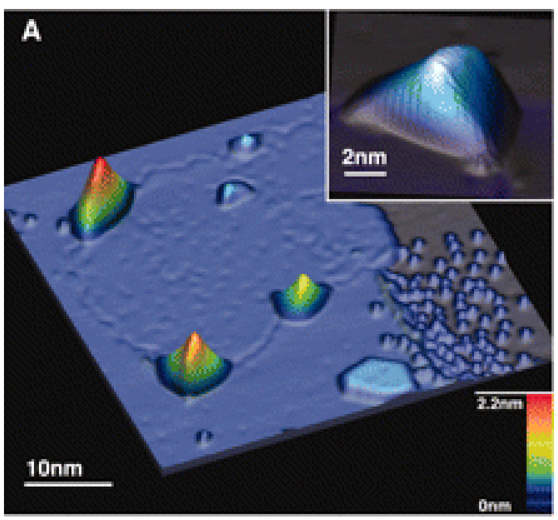
Antiferromagnetic coupling

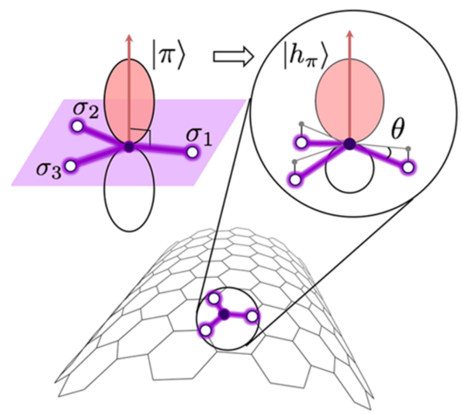
Exchange bias

M. F. Ashby, P. J. Ferreira, D. L. Schodek, Nanomaterials, Nanotechnologies and Design (2009) pp. 226-227.

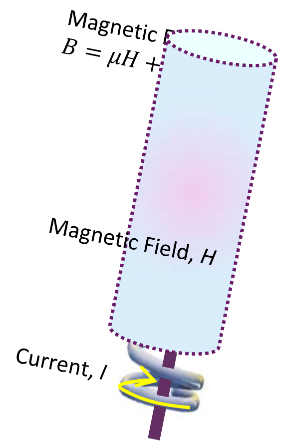
Curiosity: Graphene

- Straining of graphene can give even 300 T pseudomagnetic fields
- Before graphene, largest strain induced field observed was 85 T!





T. Dumitrica et al., *J. Nanophoton*. **6** (2012) 064501.



N. Levy et al., *Science* **329** (2010) 544-547.

Concept Checks

True of false

1) Below T_B (blocking temperature) superparamagnetic is not magnetic.
2) Spin-flipping takes place only at high temperatures.
3) Nanomaterials which are below critical size are superparamagnetic.
4) Neel relaxation time does not depend on the observation time.

Review of Physical Properties

Reading Material

<u>For the exam</u>

M.F. Ashby, P.J. Ferreira, D.L. Schodek*: Nanomaterials, Nanotechnologies and Design*

- *Thermal Properties: pp. 211-218*
- *Magnetic Properties: pp. 222-227*

<u>For Interested Reader (optional)</u>

G. Cao, Y. Wang: *Nanostructures and Nanomaterials - Synthesis, Properties, and Applications*

- 1st Edition (thermal, magnetic): pp. 353-357, 382-384.
- 2nd Edition (thermal, magnetic): pp. 462-467, 496-499.

Tomorrow is the deadline for abstract submission!

Conference Abstract

- Different from the abstract of a scientific paper
- One A4 (no more!)
- Usually contain image(s)
- Proper references

Short background, main findings, possibilities/future prospects

A lure for your poster!

6th Baltic Electrochemistry Conference, Helsinki, 15th – 17th June, 2016

Photogeneration of Hydrogen at Liquid-Liquid Interface

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ABSTRACT

Electron transfer reactions at liquid-liquid interfaces have been extensively studied for their promising use in the fuel production processes. Recently, Girault and co-workers [1] reported hydrogen photogeneration at polarized 1,2-dichloroethane(DCE)-water interface with decamethylruthenocene (DMRc) as the organic electron donor capable of reducing protons to hydrogen.

To further improve this process, we made an attempt to regenerate DMRc after hydrogen formation, by re-reduction of $DMRc^+$ in the organic phase. In our experiments, we used two Pt microelectrodes, one above each other, (Fig 1, left) and applied negative potential to the bottom one to re-reduce $DMRc^+$. At the same time, we did amperometric scan with the upper electrode polarized to potential sufficiently positive to oxidize DMRc. We observed an increase of the anodic current on the upper electrode (Fig. 1, right), indicating that regeneration of DMRc is indeed possible. To detect photogenerated hydrogen, we used scanning electrochemical microscope tip to measure the open circuit potential in the vicinity of the DCE-water interface [2].

Fig. 1. Left: Scheme of a system for DMRc regeneration. Right: Anodic current recorded on the upper electrode during the amperometric SECM scan above the bottom electrode.

We believe that light-induced processes, like hydrogen photogeneration at liquid-liquid interface, can be used in the future for energy storage systems which produce fuel during the day, whereas at night, they use surplus energy for electrochemical self-regeneration.

REFERENCES

[1] L. Rivier et al. *Decamethylruthenocene Hydride and Hydrogen Formation at Liquid|Liquid Interfaces* J. Phys. Chem. C, 119 (2015) 25761-25769.
[2] J. Jedraszko et al. *Scanning Electrochemical Microscopy Determination of Hydrogen Flux at Liquid|Liquid Interface with Potentiometric Probe*, Electrochem. Commun. 43 (2014) 22-24.