Introduction to Nanoscale Science

CHEM-E5120 INTERFACES AND NANOMATERIALS

ASSISTANT PROFESSOR PÄIVI LAAKSONEN - PAIVI.LAAKSONEN@AALTO.FI

UNIVERSITY TEACHER KIRSI YLINIEMI – KIRSI.YLINIEMI@AALTO.FI

Getting to know each other

Only to get 5 cr?

New friends?

What do you expect from this course?

Learn where nanomaterials can be used?

Learn about carbon nanomaterials?

Learn about properties of nanomaterials?

Learn about research in the field?

Which grade do you aim at?

5

1

Feedback from Last Year (2016)

General grade ≈ 3.8

Main Criticism

1. Too much, too little

➢ **We have adjusted topics in the lectures and try to get deeper**

➢ **Nevertheless, this is an introduction course**

2. 2^{nd} set of exercise answers too late

➢ **Timetable organised better**

Course Information

After this course you can

1. Combine **physical and chemical principles** that lead to the **characteristics of nanoscale materials**

2. Understands the origin of **self-assembly**

3. Determine the suitable **characterization methods** at nanoscale

4. **Analyse** measurement data at basic level

Before this course you should know

CHEM-A2120 Termodynamiikka (=”thermodynamics” or similar)

- Basic of thermodynamics: Gibb’s energy, enthalpy, entropy (1st and 2nd law of thermodynamics)

PHYS- A2140 Aineen rakenne (=“structure of matter” or similar course)

- Basics of Modern Physics: Schrödinger’s equation, particle-in-a-box problem, quantum numbers and electron configurations

CHEM- C2410 Materiaalit rakenteesta ominaisuuksiin(=“from stuctures to properties” or similar)

- Basics of material science: crystal structures, basics of electric, optic, magnetic, thermal and mechanical properties

Before this course it benefits if you know

CHEM- C2230 Pintakemia (= “surface science” or similar course)

- Basics of surface science: Van der Waal forces, electrostatic forces, DLVO theory, colloids & stability, contact angle & surface energy, adsorption isotherms

Lecture Schedule

THEME	LECTURE 1	LECTURE 2	EXERCISE SESSION
Introduction & Nanochemistry	**11.9.** Introduction to Nanoscale Science	**13.9.** Stability of Nanomaterials	**14.9.** Exercises
Self-assembly & Nanocarbons	**18.9.** Adsorption and self-assembly	**20.9.** Nanocarbons	**21.9.** Exercises
Properties at Nanoscale	**25.9.** Properties at Nanoscale I: Thermal, optical and mechanical	**27.9.** Properties at Nanoscale II: Electrical and magnetic	**28.9.** Exercises + **Abstract submission**
Characterization	**2.10.** Characterisation	**4.10**. Atomic level characterization *Visiting Lecturer: Prof. Peter Liljeroth*	**5.10.** Exercises
Nanotoxicity	**9.10.** Nanotoxicity and nanosafety	**11.10.** Pitching **Compulsory attendance**	**12.10.** Exercises
OUTCOME OF THE GROUP WORK	**16.10.** Course Review	**18.10.** (12-16) COSIO: Poster session **Compulsory attendance**	**N/A**

Course Material

The lecture slides are NOT enough as a reading material for the exam

- **Read the course books (available as e-books via library, links in MyCourses):**
  1. M.F. Ashby, P.J. Ferreira, D.L. Schodek: *Nanomaterials, Nanotechnologies and Design*
  2. G. Cao, Y. Wang: *Nanostructures and Nanomaterials - Synthesis, Properties, and Applications*
  3. *A.Y. Grosberg, A. R. Khokhlov, Giant Molecules – Here, There and Everywhere*

Course assessment: Max. Points from Different Tasks

Exercises	Abstract	Elevator pitch	Poster presentation	Exam	Total
15	**5**	**-**	**10**	**20**	**50**
	Compulsory	***Compulsory***	***Compulsory***	***Min. 7***	***Pass 50 % of total***

Lectures

- A/B/C voting via smart phones etc. ≈ **most important concepts**

Tight timetable: the home-exercises are discussed only in the exercise sessions

Lectures are NOT compulsory but recommended

Exercises

All exercises are available now in MyCourses

- **PART I questions: return latest on the 1st October**
  - **Total: 9 points (3 weeks)**
- **PART II questions: return latest on the 15th October**
  - **Total: 6 points (2 weeks)**

Exercises and Exercise Sessions are NOT compulsory

Exercises

1. **Calculate in your own time**
2. **Exercise sessions**

A place where you can ask help & get hints

Each week we'll concentrate on the exercises related to that week's topics

3. **Only the questions marked with asterisk (*) give points**

The other questions are for you own practice:

similar questions to non-graded questions might come to the exam, though

The correct answers of ALL PART I/PART II questions will be available in MyCourses after submission dates

Exercises

Submission of answers*

1. Take a photo from each, **hand-written** answer
2. Combine to ***a pdf file***
   - *One pdf file of Part I answers*
   - *Another pdf file of Part II answers*
     - *WEEK 5 (Nanotoxicity) – submit your answers to Nanotoxicity Quiz (in MyCourses)*
3. Submit to MyCourses
   - Submission boxes: PART I and PART II

* ***The answers must be clearly visible (easy to read) in the pdf files***

Written Exam

You are allowed to bring with you

- Pens / pencils, eraser, ruler etc.
- Calculator
- **One A4, hand-written of your own notes**
  - All constants (F, R, k_B, etc.) and necessary equations are provided in the exam paper though
  - Equations or used symbols are **NOT** named or explained, you need to recognise the important equations from the long list of equations

Exam has 4 questions (á 5 points) → 20 points

Questions can be:

- Calculations
- Essays
- Explanations from schematics, concepts
- Combination of all the above

Remember these!

Course registration automatically includes registration for the course examination.

For other examinations, including make-up examinations or examinations for self-study courses, students must register no later than 7 days beforehand.

Only examination registrants may enter the examination hall.

Once 30 minutes have elapsed since the official commencement of the examination, no students will be let in the hall.

At the end of the examination, turn in all answer sheets, including empty ones, and question sheets.

Pair Work =
Poster Project

More instructions for abstracts, posters and pitching on MyCourses

PAIR WORK: Poster

- ❑ Choose the theme, **read literature. Write** on the theme: *mind map, bullet points etc. (no submission, just for you)*
- ❑ Choose **a specific topic** within the theme (1-2 papers, from 2016-2017)
- ❑ **Write the abstract, max 1 A4 (DL: 28th September)**
- ❑ **Keep the elevator pitch (individual task)** on the topic (**11th October**)
  - 30 s talk
  - *best pitch gets awarded!*
- ❑ **Design** and make the poster
  - ❑ Make it in PowerPoint, submit as **pdf, DL: 15th October**
- ❑ **Present** the poster in the COSIO event (**18th October**)
  - Each group member presents separately

Themes

- **Super-repellent coatings**
- **Clean energy conversion and storage**
- **Nanosensors**
- **Nanotechnology for analytics**
- **Thin films: nanocarbons or ALD**

Read about themes in general.
Choose **one specific topic** related to one of the themes.
Find **1-2** interesting scientific publications from years **2016-2017**.
Make your poster about them.

Poster Content

Choose **one specific topic** (related to themes).

Find **1-2 interesting scientific publications from years 2016-2017**.

Each poster must contain also measurement data (not just schematics).

More figures, less text → better poster!

Poster Content

In order to be able to really explain your poster in a poster session:

- You need to study much more than those 1-2 papers about the theme

➢ We may ask also general, theoretical questions related to your poster's theme.

PAIR WORK: Deadlines and Assessment

TASK	Deadline	Other Info	Assessment
Abstract Submission	**28th September**	*One A4*	Max. 6 p
Elevator Pitch	**11th October**	*30 s, **everyone** keeps*	N/A
Poster Submission	**15th October**	*One A0, submission as pdf*	Visuality: max. 5 p
Poster sessions	**18th October**	*COSIO Event (companies present)*	Presentation: max. 5p

More detailed instructions for abstracts, posters and pitching on MyCourses

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

Justyna Jedraszko[1], Wojciech Adamiak[1]*, Wojciech Nogala[1], Hubert H. Girault[2], and Marcin Opallo[1]

[1] Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-228 Warsaw, Poland
[2] EPFL Valais Wallis, EPFL SB ISIC LEPA, Rue de l'Industrie 17, P.O. Box 440, CH-1951 Sion, Switzerland
* Presenting Author: wadamiak@ichf.edu.pl

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 amperommetric 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 amperommetric 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.

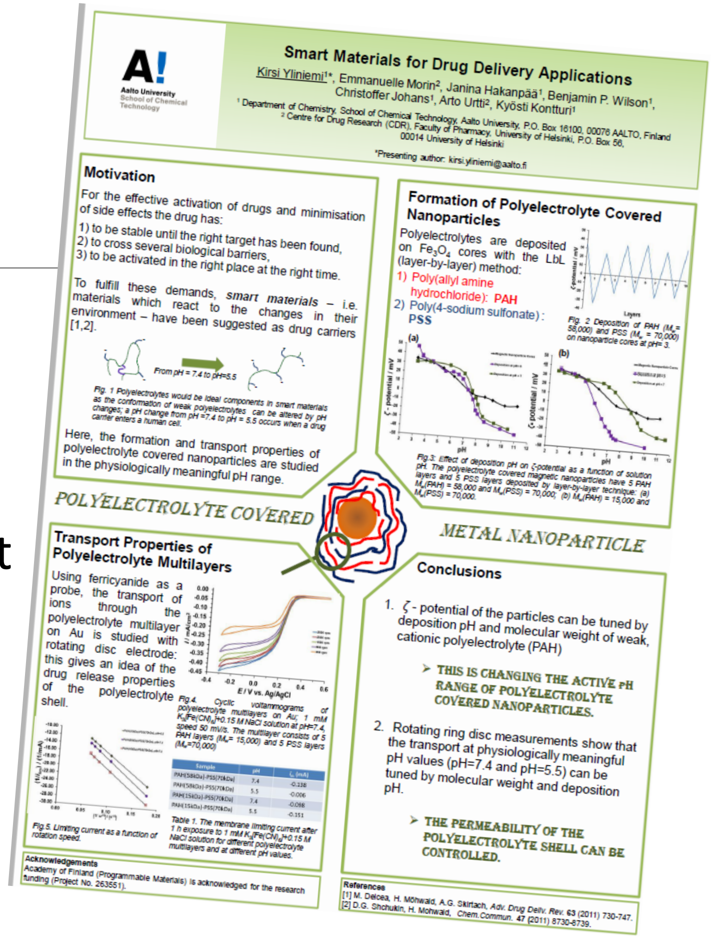
REFERENCES

[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.

Conference Poster

***A0, portrait* (≈84 cm x 118 cm):**
Make in PowerPoint, submit as pdf

- **Use large fonts**
  - main title>60 pt; sub-titles>55 pt; body text>40 pt
- **Hardly no text, more images (and data)**
  - You will explain your poster
  - Still, must have real content in writing too
  - Choose results **from 1-2 publication**



➢ **Difficult balance**

VISUALITY: colours, images AND

SCIENCE: content, references, story

COSIO

MEET THE STUDENTS OF AALTO FUNCTIONAL MATERIALS MASTER PROGRAMME

WHEN

Oct 18TH. 2017

12-16 pm

WHERE

Aalto University,
School of Chemical Engineering,
Kemistintie 1

Main lobby / Lecture hall Ke2

Poster presentations 18th October

12-14 Grading by teachers

- 1h / presenter
- When you are not presented, circulate and ask questions from the other students
- Compulsory attendance

15-16 Companies present

- **Visit company stands**
- **Present your poster for company people**
- **free “mingling” but hopefully at least one of you by the poster most of the time**

Presenting a Poster

POSTER SESSION = DISCUSSION about science presented in the posters

- **One of you stands by the poster = presenter; others go from poster to poster to see and discuss about them = visitors**

- **Plan short "walk through talk" of your poster**
  - 90 seconds or so: *What is the point of the poster? Explain main results and conclusions.*

→ DISCUSSION

- **Be ready to answer to questions and discuss about the topic more**

Questions may come already through your "walk through talk"

→ DISCUSSION

If no questions, be prepared to explain then some interesting part of the poster deeper

→DISCUSSION

DO NOT READ YOUR POSTER TO THE AUDIENCE/VISITORS (explain it)

YOU MAY HAVE NOTES WITH YOU BUT DO NOT READ THROUGH THEM EITHER

(notes should be just something you check if you have forgotten some small detail)

Basic Principles in Nanoscale: Surface Energy and Surface Curvature

CHEM-E120 INTERFACES AND NANOMATERIALS

DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

UNIVERSITY TEACHER KIRSI YLINIEMI

KIRSI.YLINIEMI@AALTO.FI

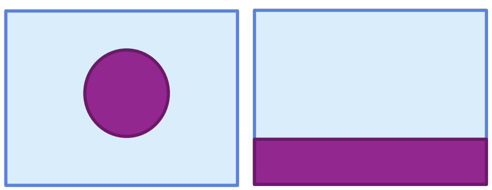
After This Lecture You Can

Explain the concept surface energy

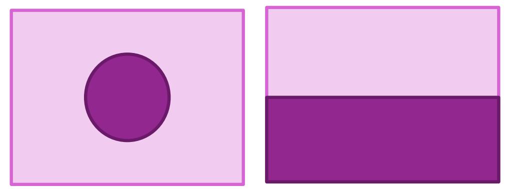
Connect chemical potential to surface curvature

Understand why surface atoms play a critical role in nanomaterials

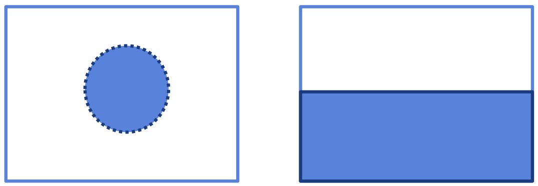
Interfaces



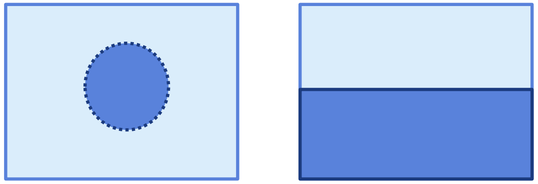
Solid|Liquid



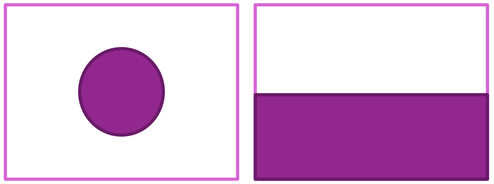
Solid|Solid



Liquid|Gas



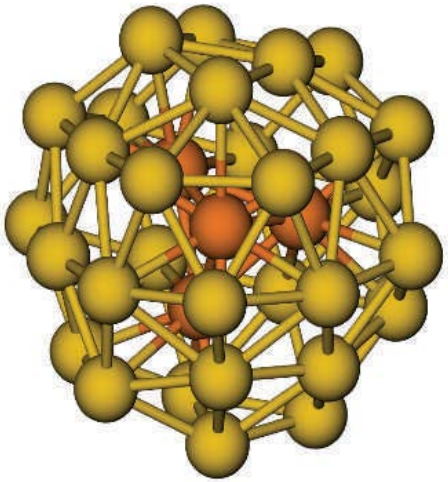
Liquid|Liquid



Solid|Gas

Nano is curious….

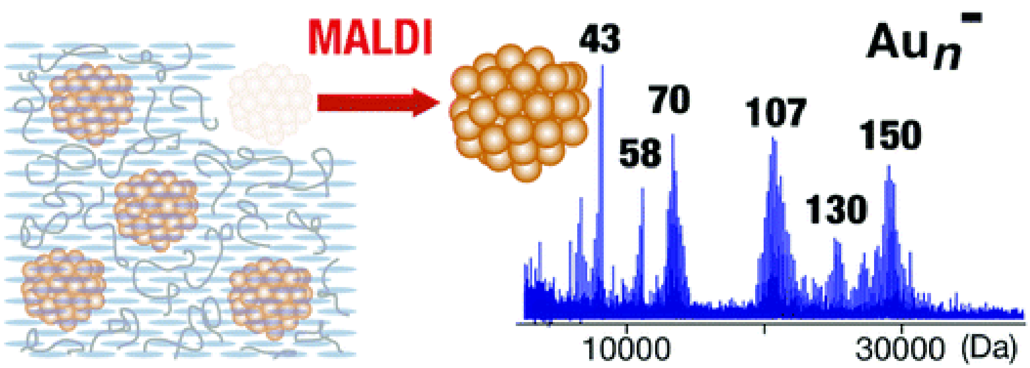
Magic Numbers



P. Pyykkö, *Nature Nanotechnology* **2** (2007) 273-274.

Structural

Number of atoms in the core



H. Tsunoyama, T. Tsukuda, *JACS* **131** (2009) 18216-18217.

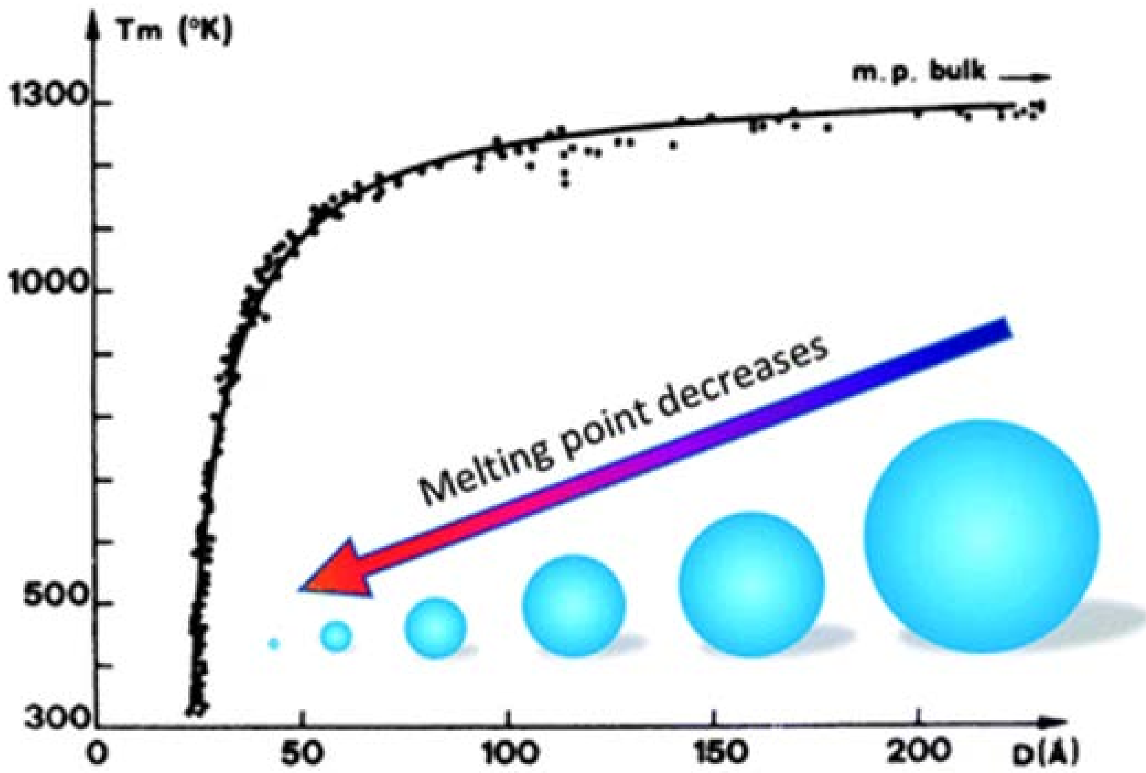
Electronic

Number of valence electrons:

2, 8, 18, 32, 50, 72, …

$2(L+1)^2$

Melting Point

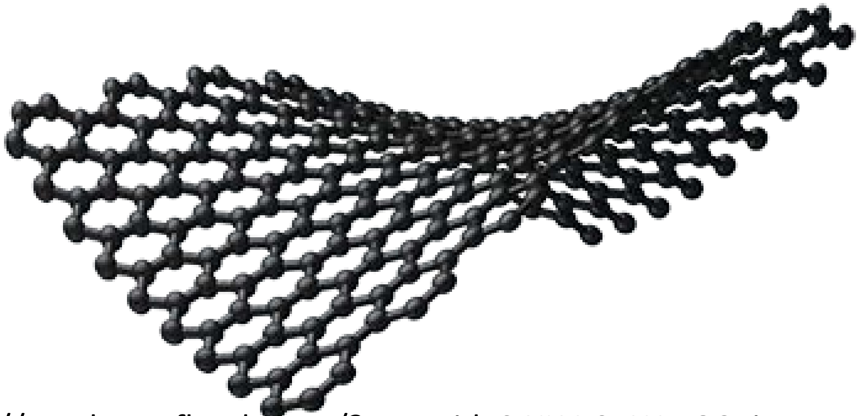


Controlled drug release with local heating?

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

More in Lecture 5

Graphene

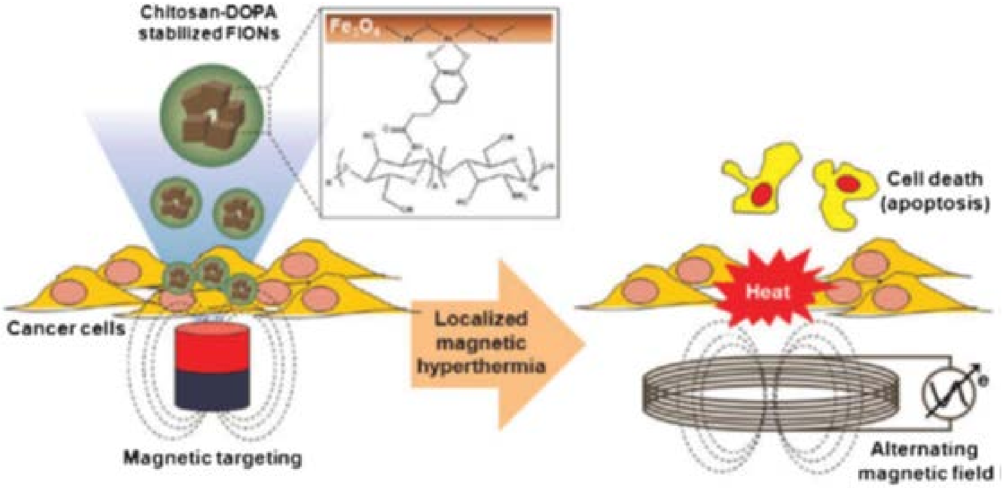


http://graphene-flagship.eu/?page_id=34#.Vc3BWmO8pio

- Electron mobility: 200 000 cm^2V/s
- Transparent
- Young’s modulus: 1 100 GPa

More in Lecture 4

Superparamagnetism

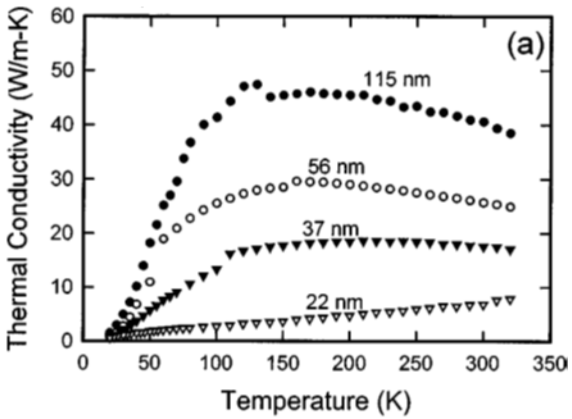


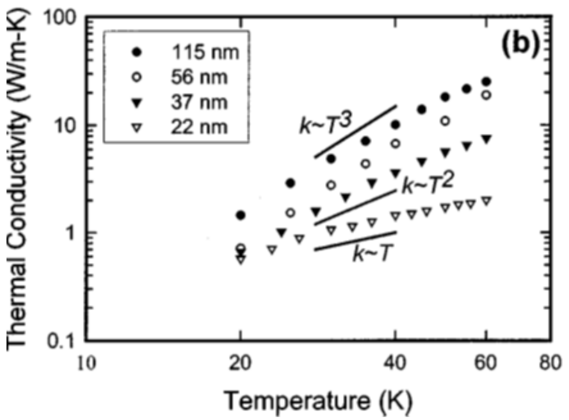
Killing cancer cells with superparamagnetism?

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.

More in Lecture 6

Thermal Conductivity



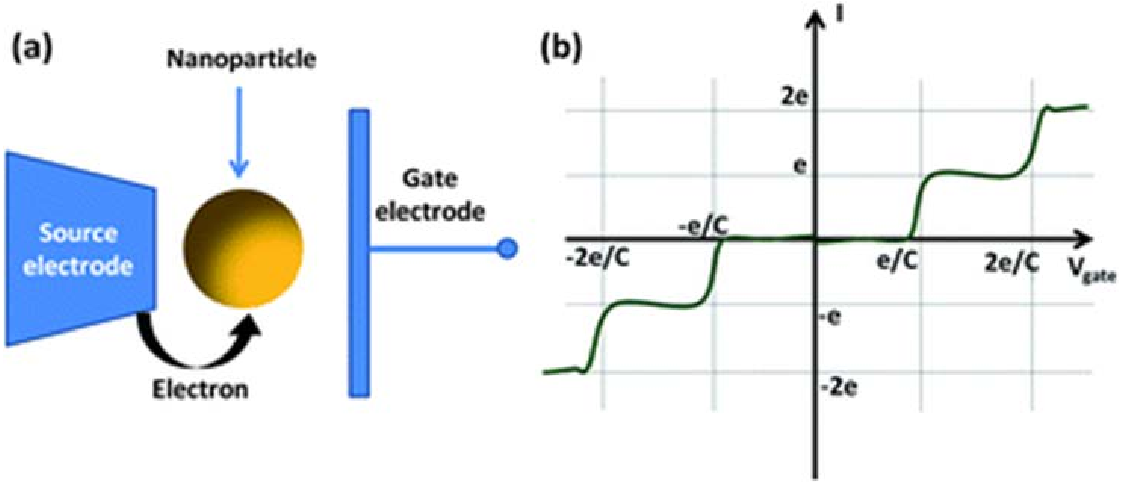


Thermo-electric materials?

More in Lecture 5

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

Current is not continuous



Single-electron devices?

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

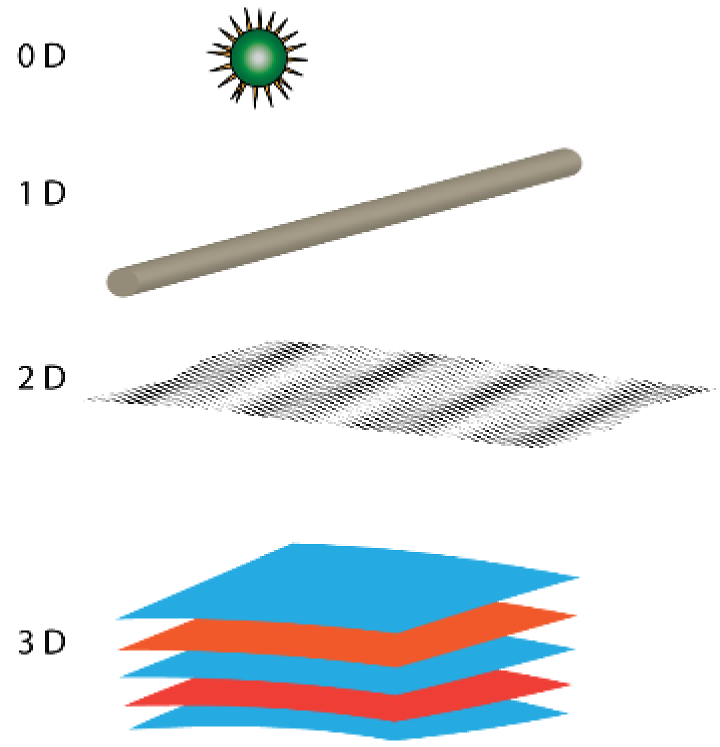
Examples of nanomaterials– different geometries

0 dimensions: all dimensions on nanoscale (a dot)
- Quantum dots (semiconductor nanoparticles)
- Monolayer protected clusters (metallic nanoparticles with a capping layer)

1 dimension: two dimensions on nanoscale (a line)
- Metal nanowires
- Carbon nanotubes
- Cellulose nanofibrils

2 dimensions: one dimension on nanoscale (a plane)
- Graphene
- Nanoclay platelets
- Self-assembled monolayers

3 dimensions:
- Layer-by-layer polyelectrolyte structures
- Viral capsides
- Nanocomposites



Nano is curious….

… but it can be also quite a challenging friend

Stability?

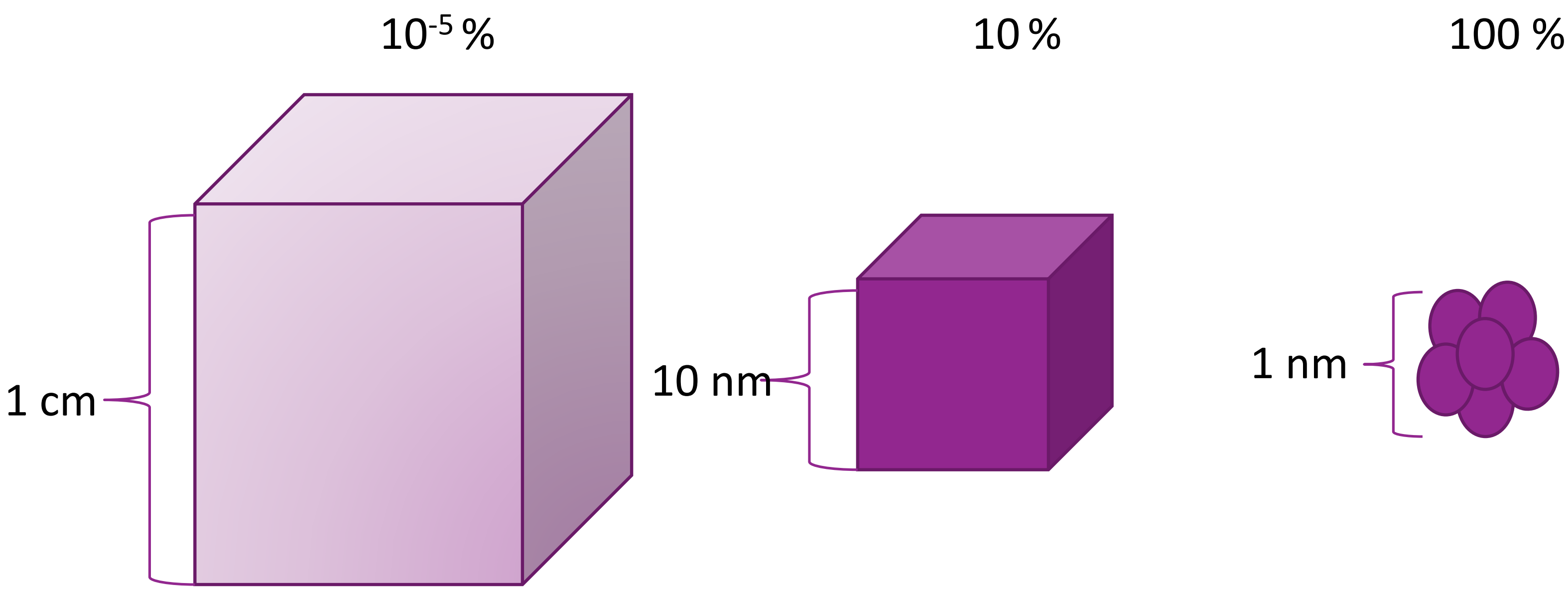
Between bulk and atom scale

Toxicity?

Characterization?

Surface Atoms and Surface Energy

Size vs. Surface

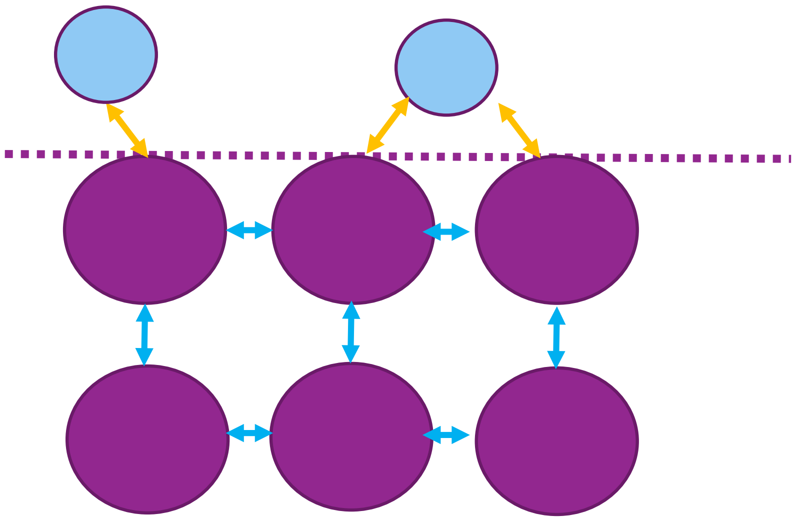


For nanomaterials, more atoms are at the surface!

Surface atom vs. bulk atom

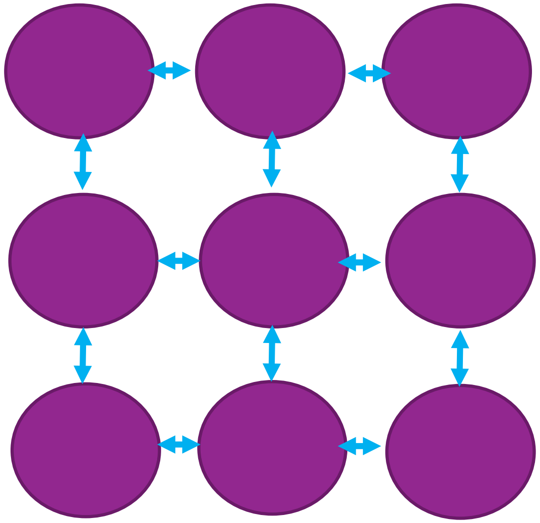
SURFACE

- Forces to bulk atoms and atoms on the other side of the interface
- Fewer nearest neighbours
- Unused "electrons/bonds"



BULK

- Forces to other atoms within the phase



Surface energy

= Extra energy possessed by the surface atoms

$$\boldsymbol{\gamma = \left(\frac{\partial G}{\partial A}\right)_{n,T,P}} \qquad [\gamma] = \frac{J}{m^2} = \frac{N}{m}$$

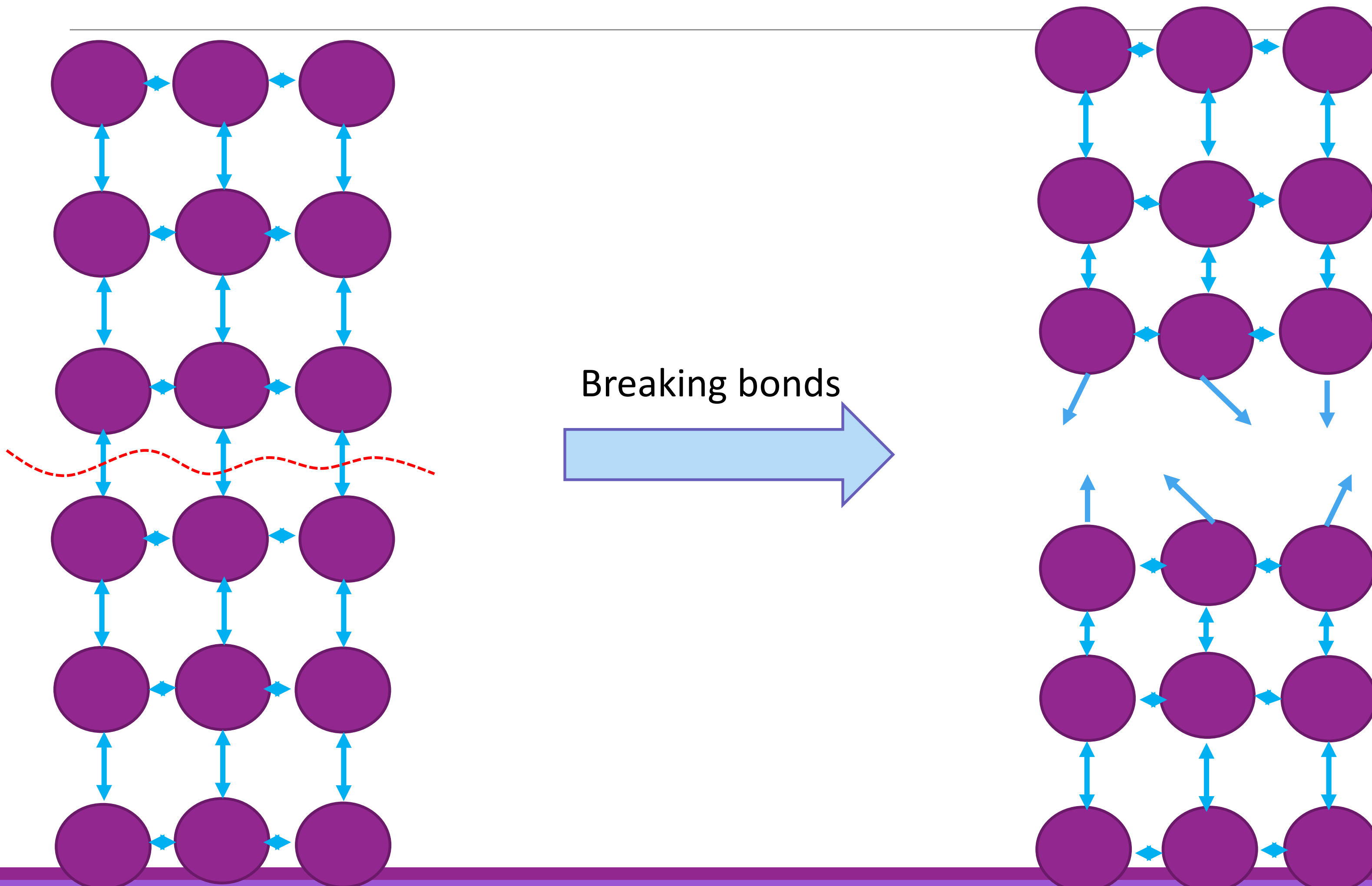
G = Gibb's free energy
A= surface area
n = number of moles
T= temperature
P = pressure

Example: 1 g of NaCl

Size (cm)	Total Surface Area (cm^2)	Surface Energy (J/g)
0.77	3.6	$7.2 \cdot 10^{-5}$
0.1	28	$5.6 \cdot 10^{-4}$
0.01	280	$5.6 \cdot 10^{-3}$
0.001	$2.8 \cdot 10^{3}$	$5.6 \cdot 10^{-2}$
10^{-4} (µm)	$2.8 \cdot 10^{4}$	0.56
10^{-7} (nm)	$2.8 \cdot 10^{7}$	560

Data from Guozhong Cao, Ying Lwang, Nanostructurews and Nanomaterials – Synthesis, Properties and Applications, World Scientific, 2nd Ed. pp. 19-20.

Surface Energy vs. Broken Bonds



Surface Energy vs. Broken Bonds

$$\boldsymbol{\gamma = \left(\frac{1}{2}\right) N_b \varepsilon \rho_a}$$

N_b = Number of broken bonds
ε = Bond strength
ρ_a = Surface atom density ($1/cm^2$)

Surface Energy vs. Broken Bonds

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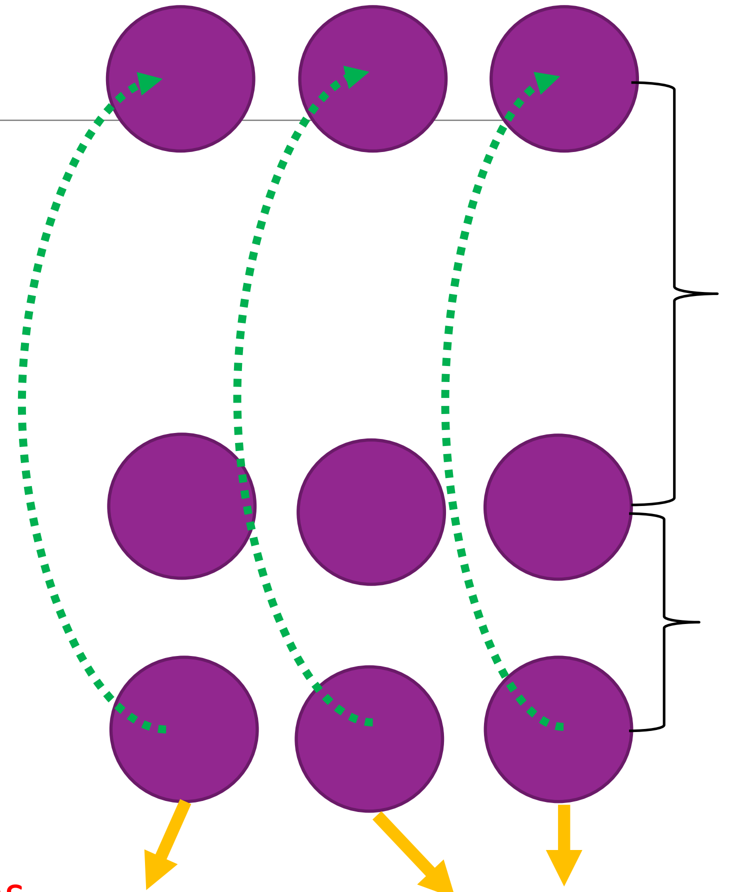


Simplification!
- No inward motion taken into account
- Bond strength same for the bulk and surface atoms
- Only nearest neighbour forces

Example: Surface Energy of FCC Material

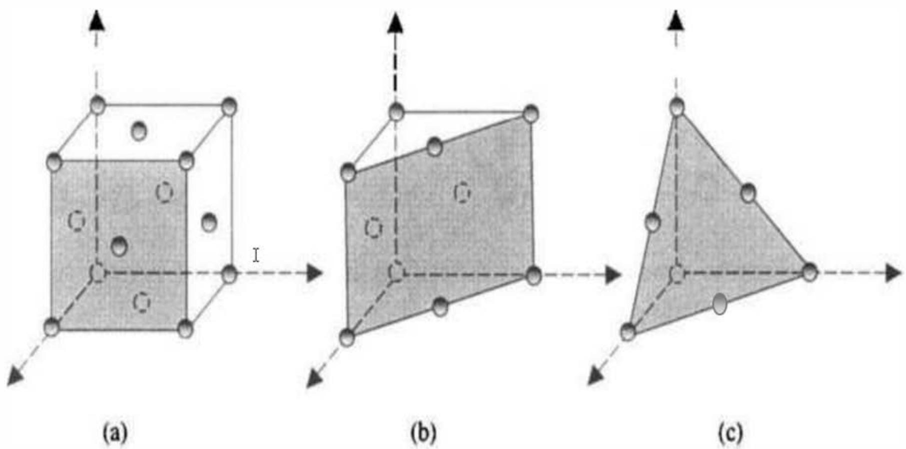


Fig. 2.3. Schematic representing low index faces of a face-centered cubic (fcc) crystal structure: (a) {100}, (b) {110} and (c) {111}.

$$\gamma_{\{100\}} = \frac{4\varepsilon}{a^2}$$

$$\gamma_{\{110\}} = \frac{5\varepsilon}{\sqrt{2}a^2}$$

$$\gamma_{\{111\}} = \frac{6\varepsilon}{\sqrt{3}a^2}$$

G. Cao, Y. Wang, Nanostructures and Nanomaterials – Synthesis, Properties and Applications: 1st Ed. p. 18 or 2nd Ed. p. 20.

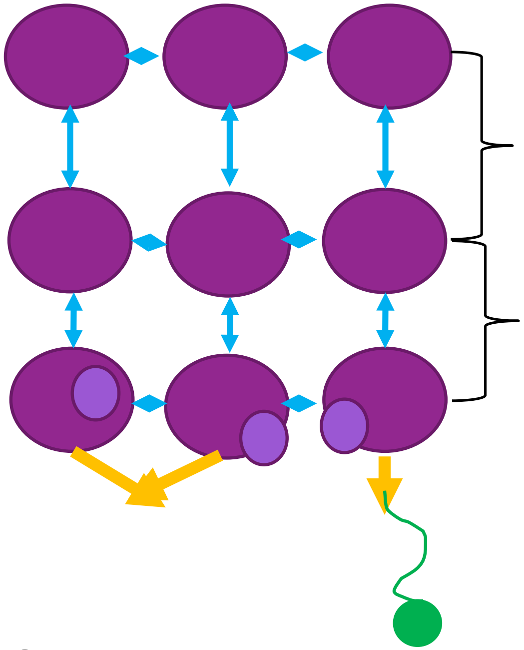
Note! Mistake in {111} (Fig. 2.3. c) in the 1st edition + mistake in Eq. 2.5 ($\gamma\{111\}$) in both editions.

Reducing Surface Energy

1. Surface Relaxation
2. Surface Restructuring
3. Surface Adsorption
4. Composition Segregation / Impurity Enrichment
5. Reducing Surface Area

Reducing Surface Energy

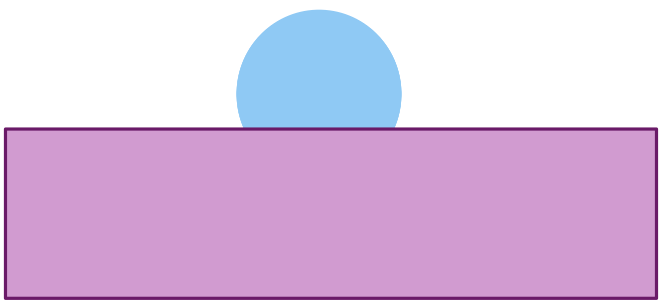
1. **Surface Relaxation**
   - Surface atoms moving inwardly
2. **Surface Restructuring**
   - Combination of dangling bonds
3. **Surface Adsorption**
   - Adsorption to dangling bonds and modifying electrostatic and/or VdW forces
4. **Composition Segregation / Impurity Enrichment**
   - Solid-state diffusion



Reducing Surface Area

LIQUID

- "Softening the corners"
- Spherical shape

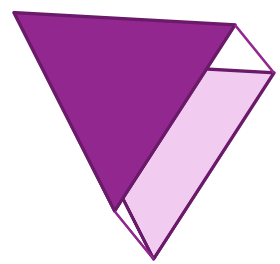


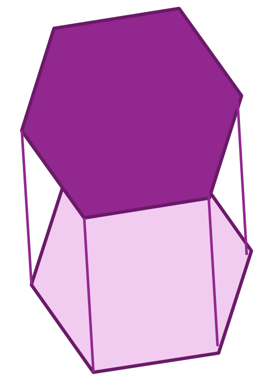
- Hydrophobicity

$$\gamma_{\mathrm{SV}} = \gamma_{\mathrm{SL}} + \gamma_{\mathrm{LV}} \cos\theta$$

SOLID

- Facets



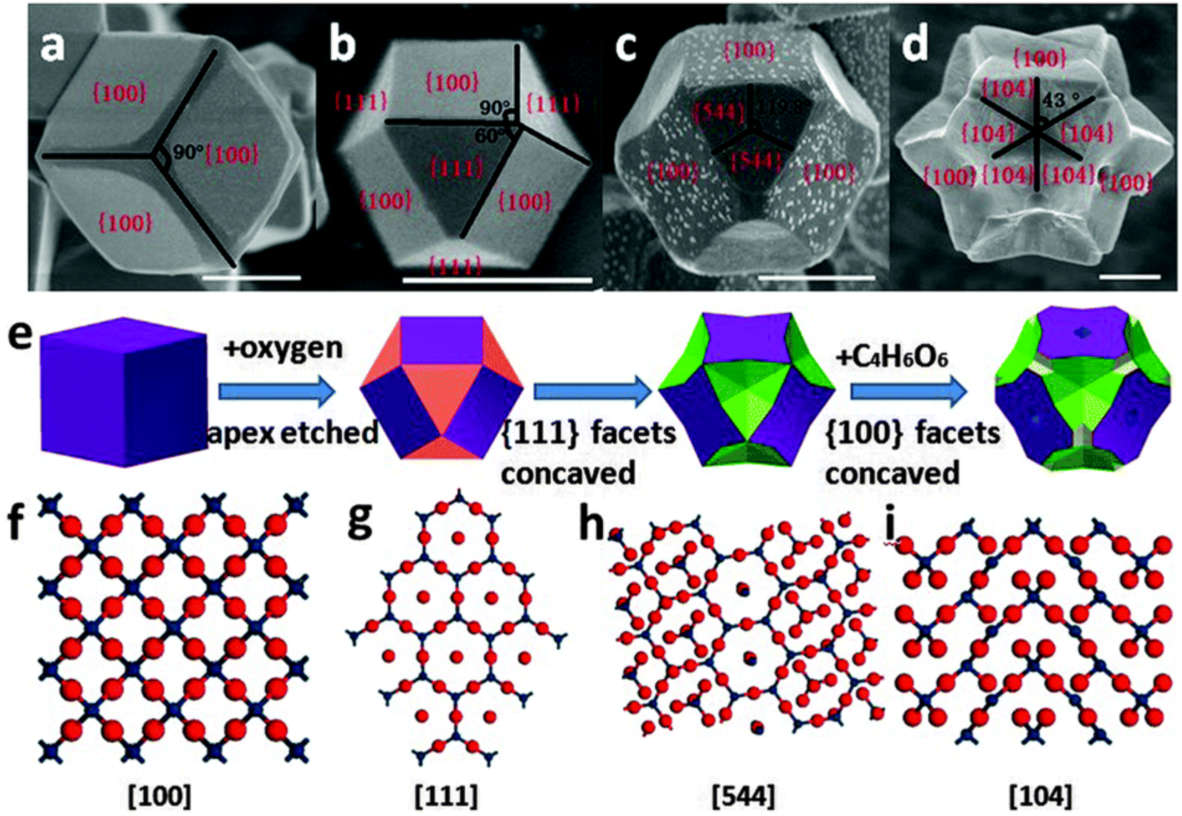


- Wulff's plot

$$\gamma_i = Ch_i$$

This also leads to structural magic numbers!

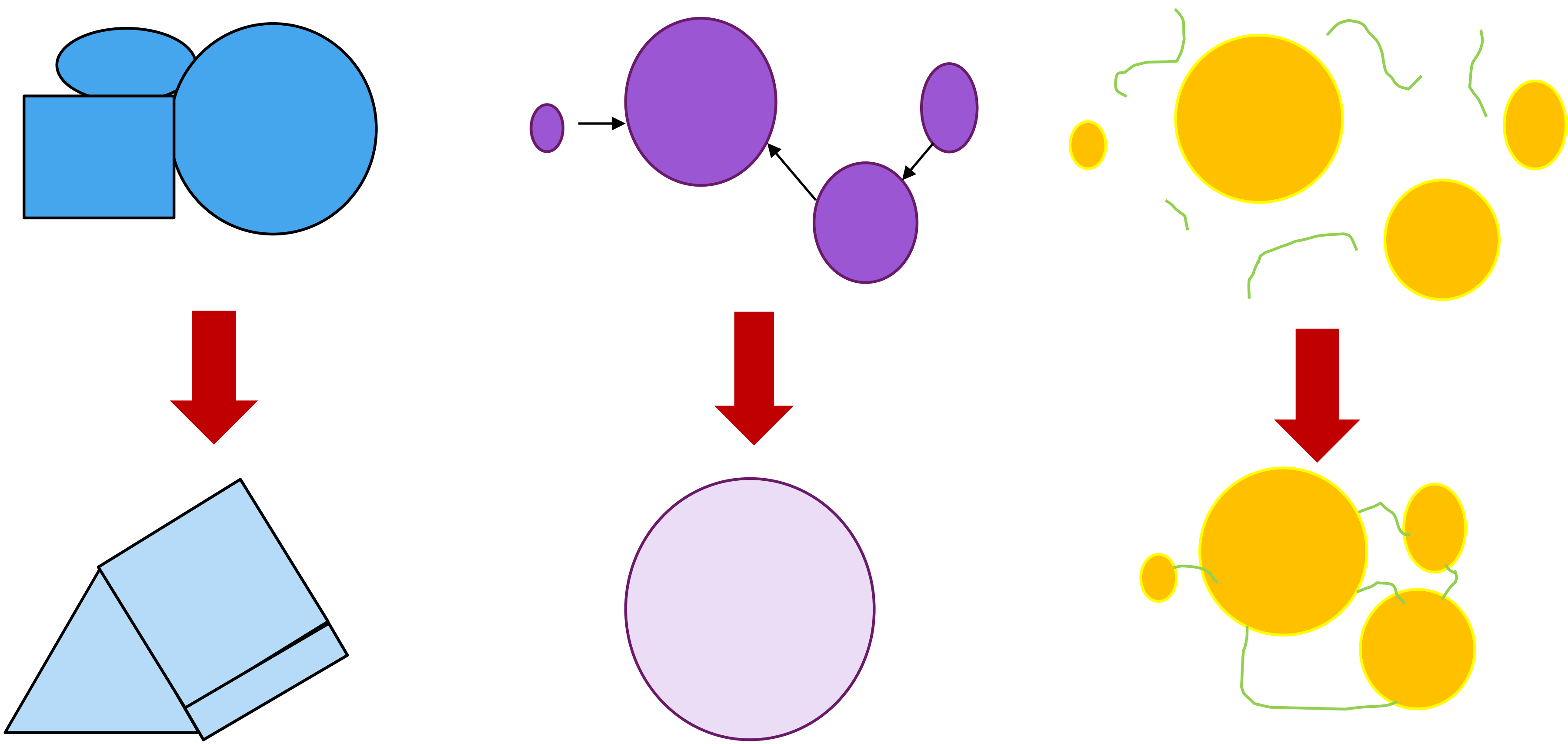
Cu_2O Polyhedrons



Morphological evolution of Cu_2O prepared at different reaction times, (a) 30 min, (b) 60 min, (c) 90 min and (d) 120 min. All scale bars are 1 μm.

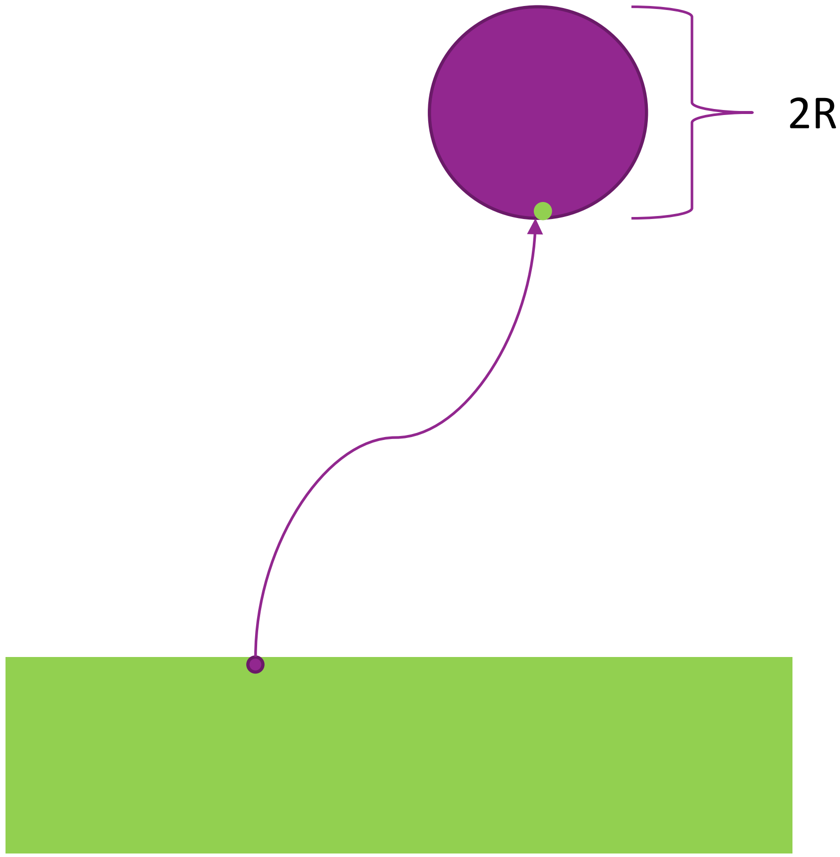
L. Zhang , J. Shi , M. Liu , D. Jing, L. Guo, *Chem. Commun.* **50** (2014) 192-194.

Reducing Surface Area



Sintering **Ostwald Ripening** **Agglomeration**

Surface Curvature and Chemical Potential



Transporting **n** atoms from a flat surface (of an infinite solid) to a curved surface (of a spherical particle):

How much "chemical work" this will take? = What is the chemical potential difference

$$\Delta\boldsymbol{\mu} = \boldsymbol{\mu}_c - \boldsymbol{\mu}_\infty ?$$

Young-Laplace Equation

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

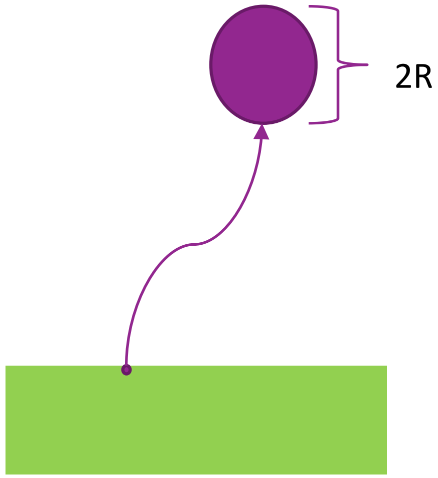
where

$\Delta\mu$=chemical potential difference between flat and curved surface

γ=surface energy of curved surface

Ω = atomic volume (of atom types transferring)

R= radius of the spherical particle

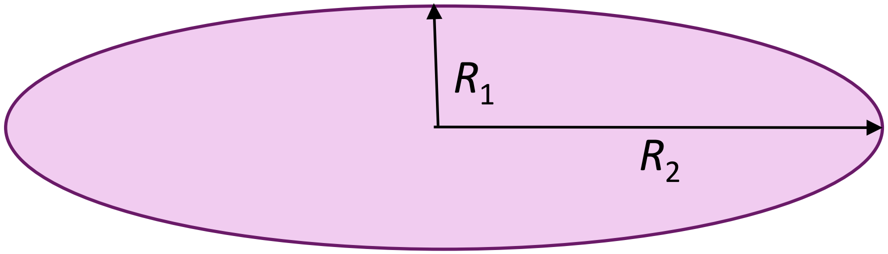


Note! Derivation of this equation is left as a homework.

Generalization: Young-Laplace of Any Curved Surface

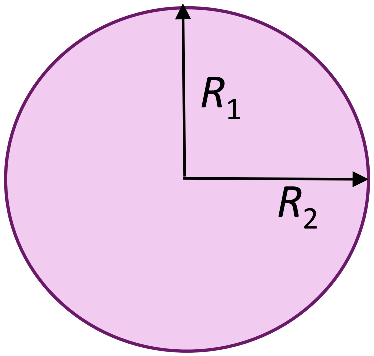
$$\Delta\mu = \gamma\Omega\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

where R_1 and R_2 define the curvature



Generalization: Young-Laplace of Any Curved Surface

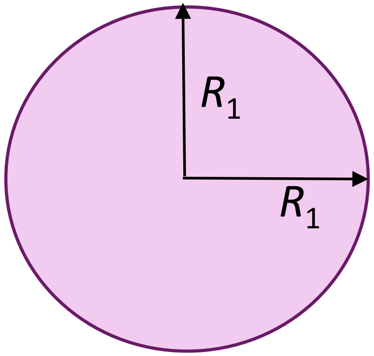
$$\Delta\mu = \gamma\Omega\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$



What happens when R_1=R_2?

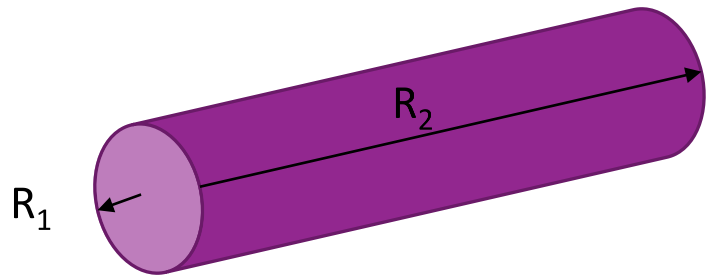
Generalization: Young-Laplace of Any Curved Surface

$$\Delta\mu = \gamma\Omega\left(\frac{1}{R_1} + \frac{1}{R_1}\right) = \frac{2\gamma\Omega}{R_1}$$



Generalization: Young-Laplace of Any Curved Surface

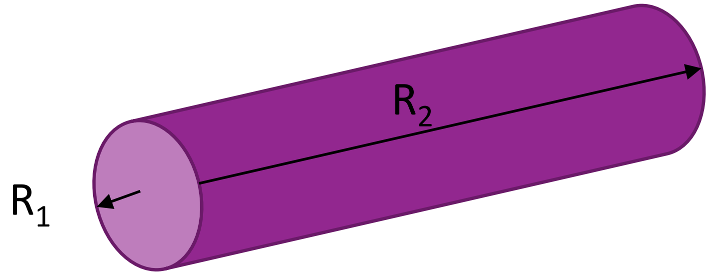
$$\Delta\mu = \gamma\Omega\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$



What happens now?

Generalization: Young-Laplace of Any Curved Surface

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

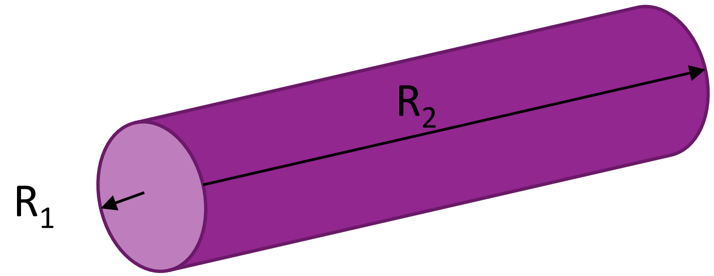


What happens now?

$$R_2 \to \infty$$

Generalization: Young-Laplace of Any Curved Surface

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



What happens now?

Generalization: Young-Laplace of Any Curved Surface

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

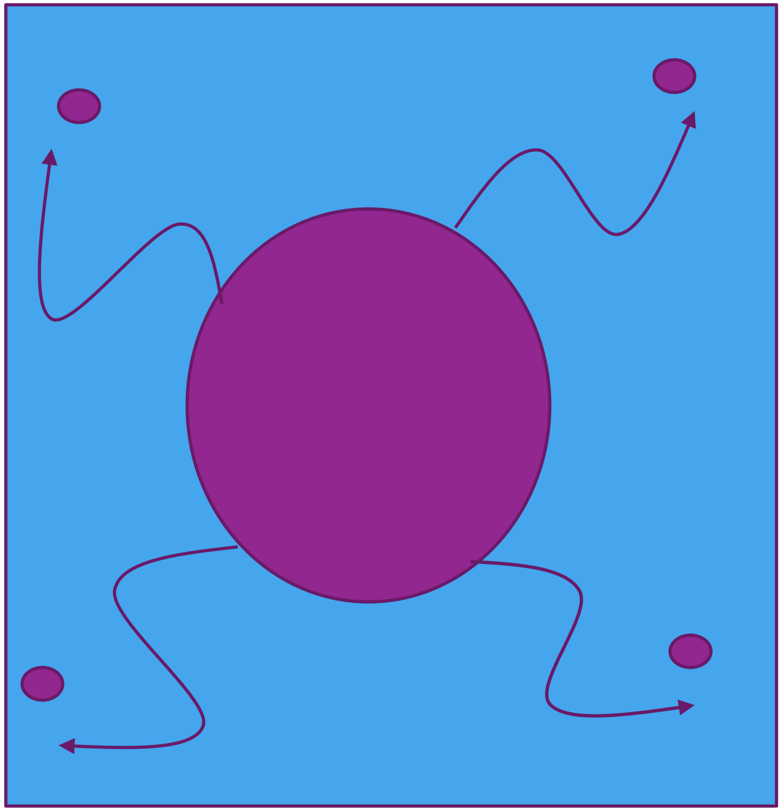
What happens when R_1 and R_2 become smaller?

Generalization: Young-Laplace of Any Curved Surface

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

→ Δμ increases →Smaller particles are thermodynamically less stable

Particles want to "dissolve"



Solid | liquid interface

Solid | vapour interface

And what does this all mean for nanomaterials?

Answer: Stability (next lecture!)

Concept checks

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Concept Check #1

Surface energy

(a) decreases with increasing surface area

(b) **causes inward motion of surface atoms**

(c) cannot be altered by adsorption

Concept Check #2

Which one of the following statements is correct?

(a) Smaller the particle radius, less reactive the particle is.

(b) **Smaller the particle radius, more likely the particle is dissolved.**

(c) Smaller the particle radius, more stable the particle is.

Concept Check #3

Young-Laplace $\Delta\mu = \frac{2\gamma\Omega}{R}$ equation…

(a) shows the chemical work done to remove an atom from a bulk.

(b) **shows the chemical work done to remove atoms from flat surface to curved surface .**

(c) shows the chemical work done to break the bonds between atoms.

Read (for learning, exercises and exam)

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

- 1st Ed. p. 1-31 (2004)

- 2nd Ed. Pp. 1-38 (2013)

Before the next lecture, remind yourself from previous courses about

Nucleation and critical radius

Cao, Wang: Nanostructures and Nanomatertials

p. 53 -> (electronic version)

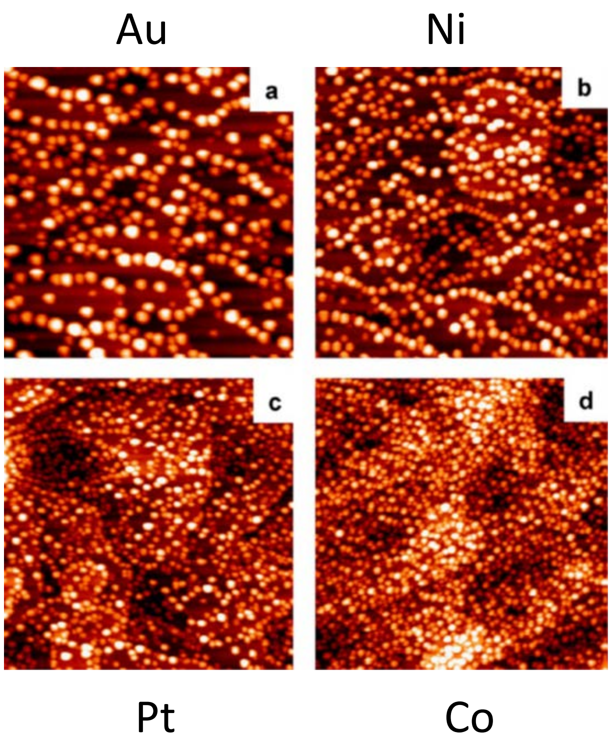
Nucleation vs. Growth

Nucleation = Stotastic process in which a new phase is formed

1. Homogenous nucleation
2. Heterogenous nucleation

Growth = “Phase expansion”

- depends on the binding energy between the surface site/cluster and the material which is growing

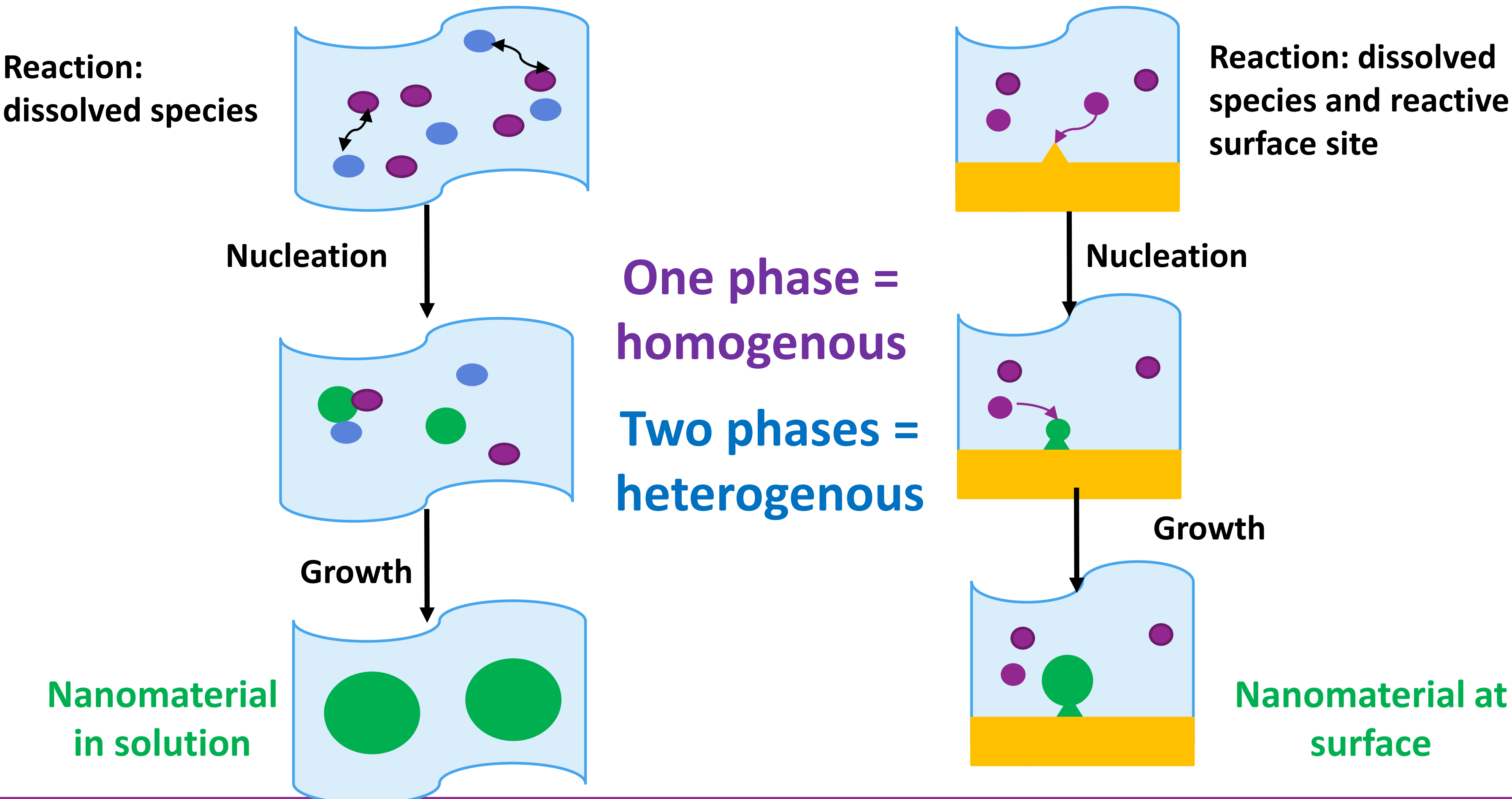


TiO_2 surface

Au < Ni < Pt < Co

R. P. Galhenage, H. Yan,S. A. Tenney, N. Park, G. Henkelman, P. Albrecht, D. R. Mullins, D. A. Chen, *J. Phys. Chem. C* **117** (2013)7191–7201.

Nucleation


Reaction:
dissolved species
Nucleation
Growth
Nanomaterial
in solution
One phase =
homogenous
Two phases =
heterogenous
Reaction: dissolved
species and reactive
surface site
Nucleation
Growth
Nanomaterial at
surface

Homogenous Nucleation

Intuitive test

Imagine KCl solution which is near the saturation point

1. What happens when we add more KCl?
2. What happens when we cool down the KCl solution?

Homogenous Nucleation

Intuitive test

Imagine KCl solution which is near the saturation point

1. What happens when we add more KCl?

➢ The concentration of species exceeds saturation point

→ **Homogenous Nucleation**

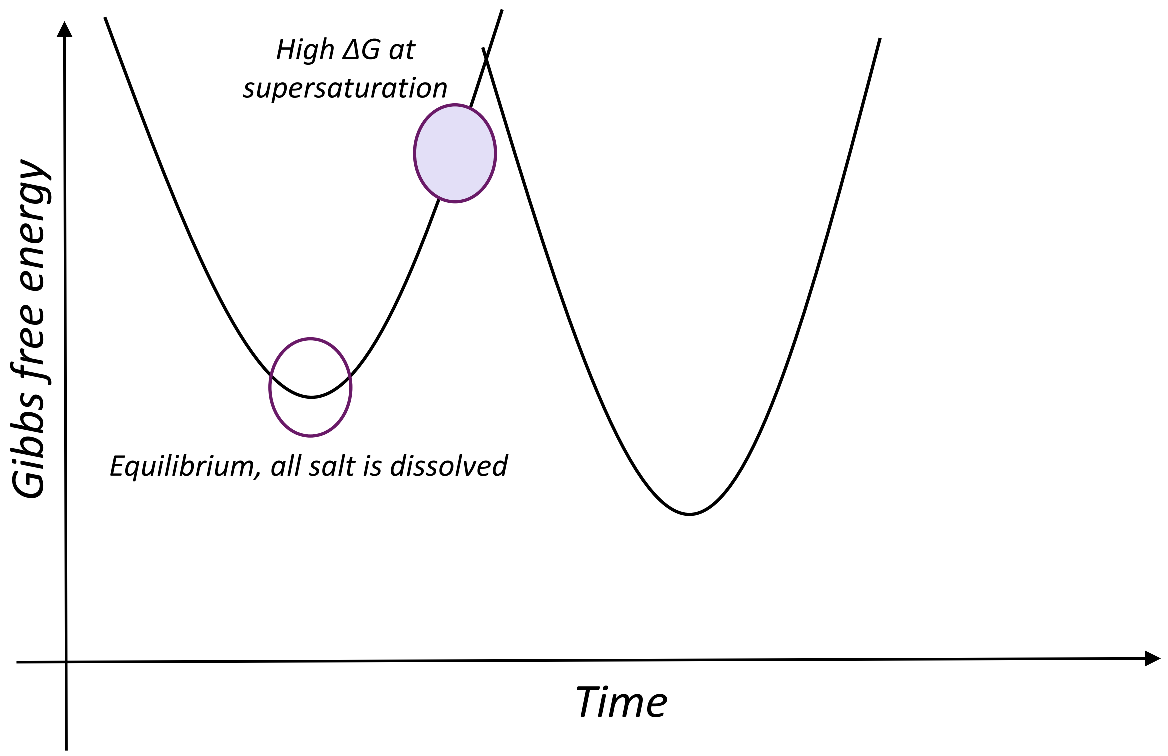
2. What happens when we cool down the KCl solution?

➢ When temperature is lower, also saturation point is lower, i.e. we exceed the saturation point

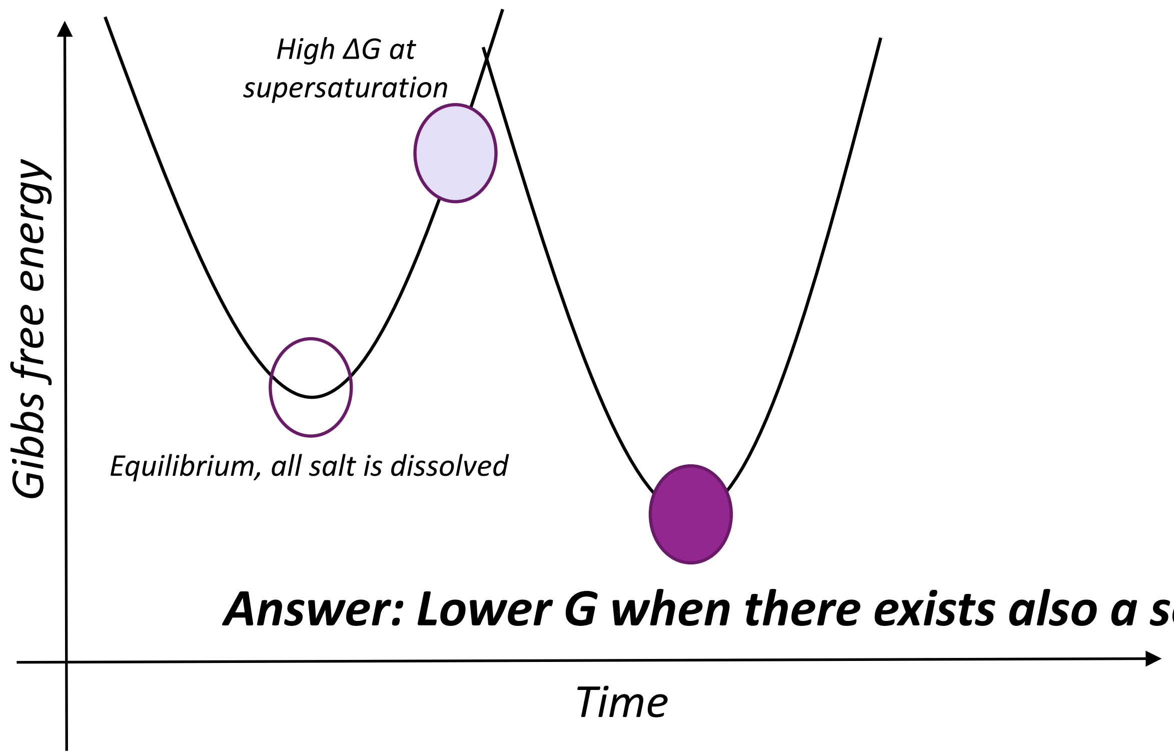
→ **Homogenous Nucleation**

What happens if we have supersaturated KCl and we shake it?

Saturated solution → changing the conditions quicker than nucleation → supersaturation



Saturated solution → changing the conditions quicker than nucleation → supersaturation → **adding a bit of energy → over the hill → precipitation**



Answer: Lower G when there exists also a solid phase

Where Δ*G* Comes From?

1. Gibbs free energy change (ΔG_v) between solid phase and liquid phase

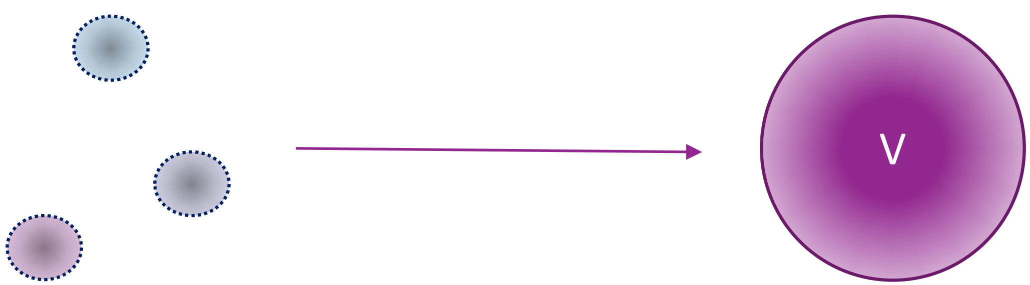
Energy change associated to volume of nucleus (volume free energy μ_v):

$$\boldsymbol{\mu_v = \frac{4}{3}\pi r^3 \boxed{\Delta G_v}}$$

where ΔG_v = Gibbs free energy / unit volume (negative)

r = radius of the nucleus

Decreases the system's energy



Homogenous Nucleation: Where ΔG Comes From?

2. Formation of new (solid) phase = new interface = more surface energy μ_s

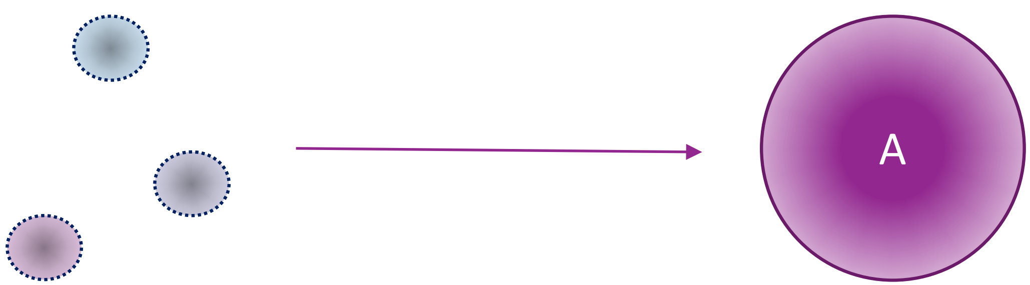
➢ Surface energy related to surface area of nucleus:

$$\mu_s = 4\pi r^2 \boxed{\gamma}$$

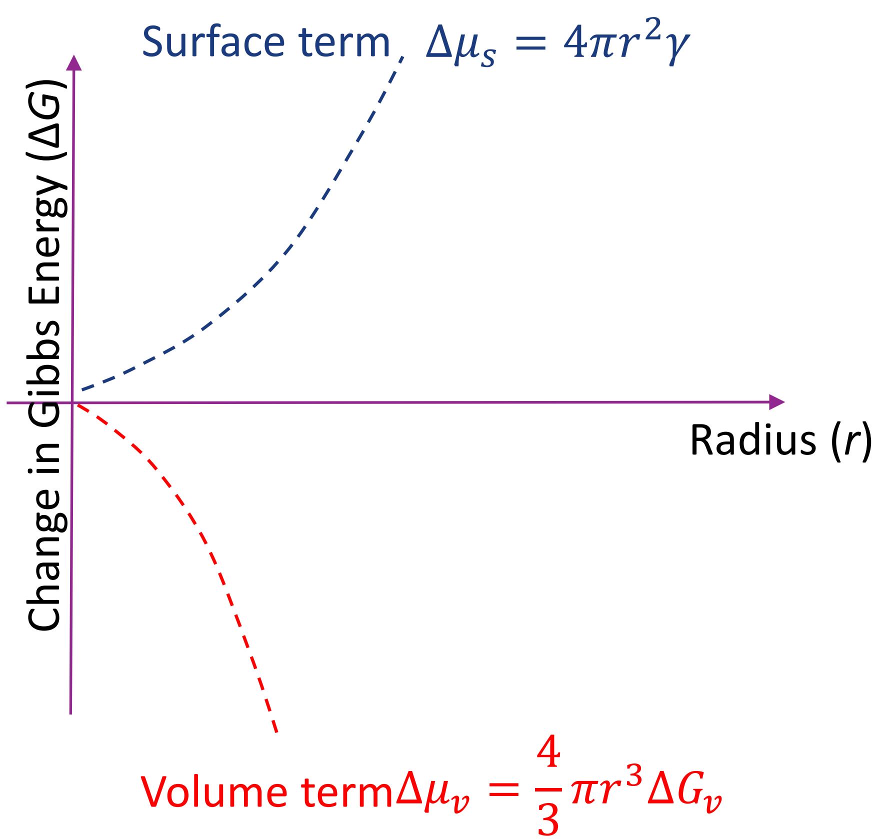
where γ= surface free energy / unit area (positive)

r = radius of the nucleus

Increases the system's energy

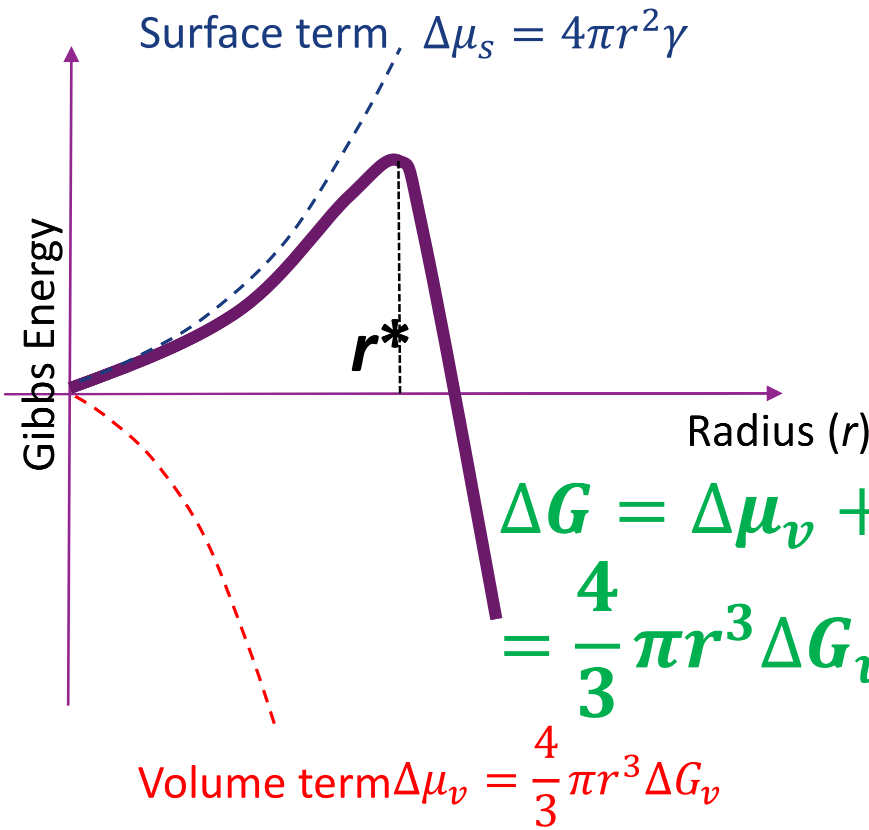


Homogenous Nucleation



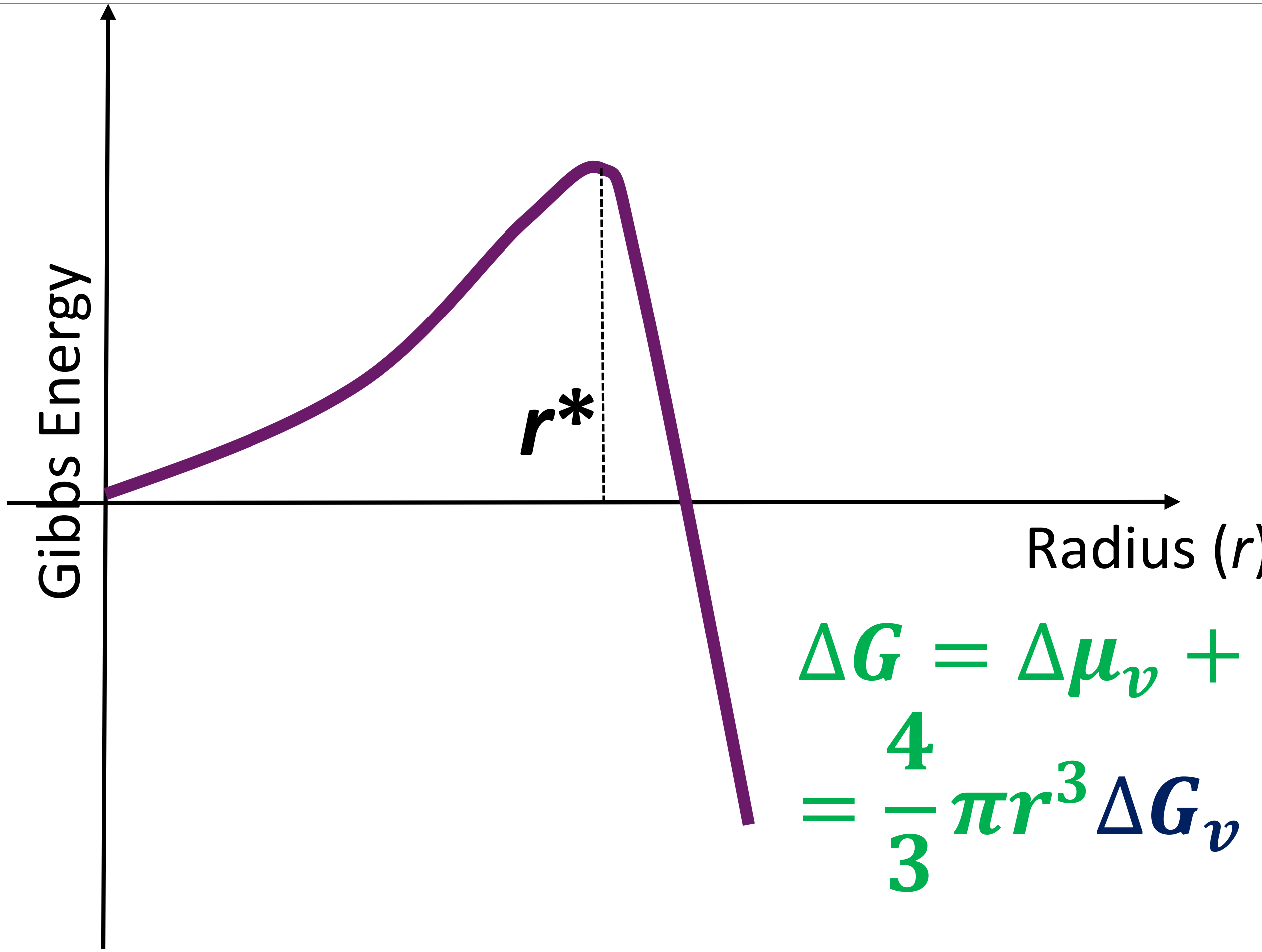
1. Volume term
   - *Related to the radius of nucleus*
   - **Energy decreases by $\Delta\mu_v$**
2. Surface term
   - *Related to the radius of nucleus*
   - **Energy increases by $\Delta\mu_s$**

Homogenous Nucleation



$$\boldsymbol{\Delta G = \Delta\mu_v + \Delta\mu_s}$$
$$\boldsymbol{= \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma}$$

Homogenous Nucleation



$$\Delta G = \Delta\mu_v + \Delta\mu_s$$

$$= \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

Heterogenous Nucleation

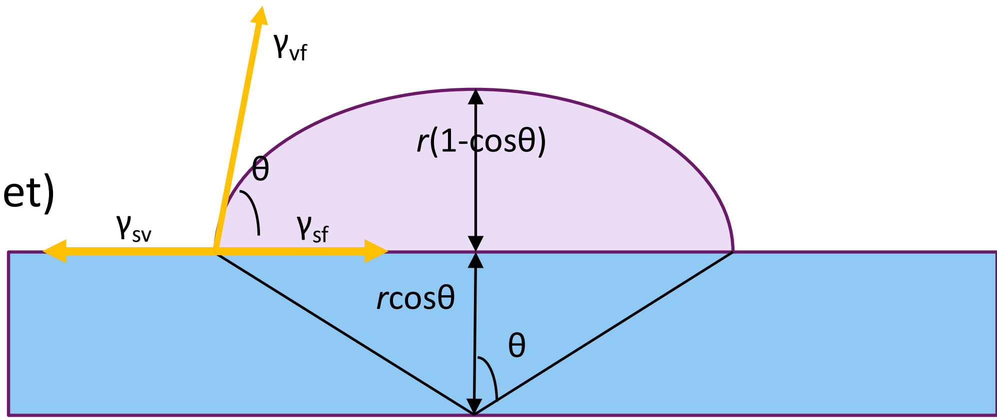
- Similar to homogenous nucleation
  - Decrease volume free energy and increase of surface (interfacial) energy
- Nucleus is stable only when *r*=*r**

$$r* = \frac{-2(a_1\gamma_{vf} + a_2\gamma_{fs} + a_3\gamma_{sv})}{3a_3\Delta G_v}$$

γ_{sv} = surface energy (solid vapour)
γ_{vf} = surface energy (solution vapour)
γ_{sv} = surface energy (solution solid)

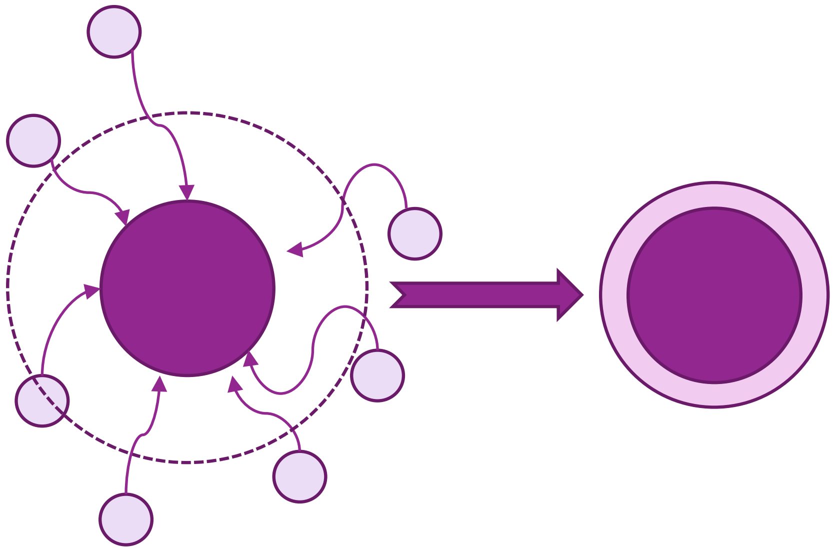
Interfacial areas (*r* = curvature of the droplet)

$a_1 = 2\pi(1 - \cos\theta)$
$a_2 = \pi\sin^2\theta$
$a_3 = 3\pi(2 - 3\cos\theta - \cos^2\theta)$



Diffusion Controlled Growth

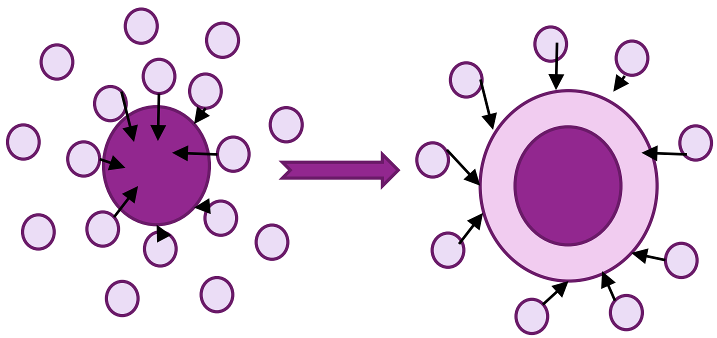
- The controlling factor is diffusion of species to the surface
  - Dilute solution
- Uniformly sized particles



Surface Controlled Growth

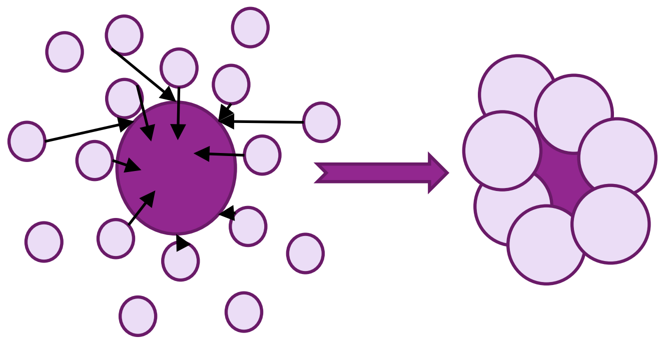
- Enough species & rapid surface reactions
  - reaction rate (*k*) at the surface vs. diffusion (*D*)

1. Mononuclear growth



- Layer-type growth
- Rapid surface reaction and semi-dilute
- ➢ Diffusion

2. Polynuclear growth



- Fast surface reaction and concentrated:
- ➢ 2[nd] layer starts growing before the first one is finished