Characterization of nanomaterials

CHEM-E5120 INTERFACES AND NANOMATERIALS

MASTER PROGRAMME OF FUNCTIONAL MATERIALS

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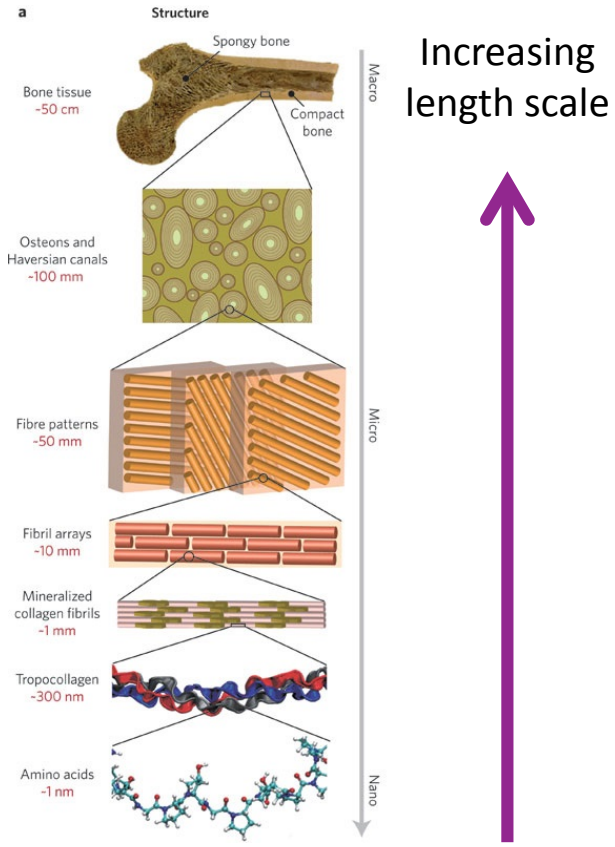
On this lecture

- General remarks about nanomaterials characterization
- Characterization of particles
  - UV-vis spectroscopy, Transmission electron microscopy, Dynamic light scattering
- Characterization of thin films
  - Quartz crystal microbalance
  - Ellipsometry

How to characterize nanomaterials?

- Particles in a matrix
  - macroscale materials
- Population of nanoparticles
  - Collective behavior
- Monolayer of nanoparticles
  - interaction at the interface
- Single nanoparticles/molecules



Sample preparation – liquid environment

- Nanomaterials, especially nanoparticles (dots, rodlets, wires etc.) may be dispersed in liquids
- Choice of solvent and liquid environment affects the colloidal stability
  - Stability critical for certain properties ➔ aggregation may lead to false result
  - Stabilizing may be needed
- Also concentration-related artefacts
  - Too high ➔ collective behavior
  - Too low, problems with detection
- Fibrillar nanomaterials may form gels
  - for instance hydrogel from nanofibrillated cellulose

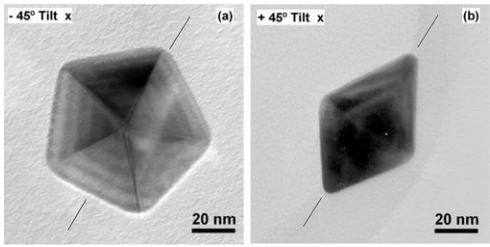
Sample preparation - solids

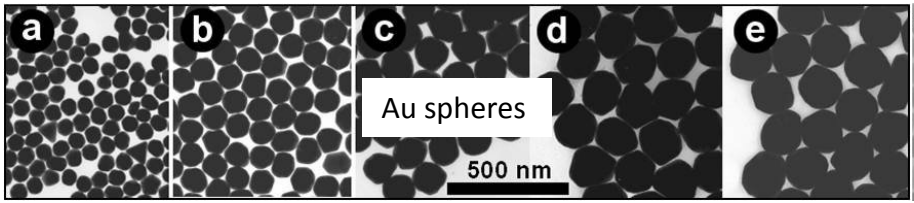
- Powder
  - Aggregation through electrostatic forces
  - Typically quite large amounts needed for analysis
- In matrix (nanocomposite)
  - Choice of methods and the preparation critical
  - Surface vs. bulk
- Immobilized on a substrate
  - Substrate: see-through, metallic etc.
  - Layer thickness, assembly, aggregation, stability
- Biological samples (tissues, cell cultures)
  - Need to be fixed in epoxy matrix ➔ cut to thin slices for microscopy

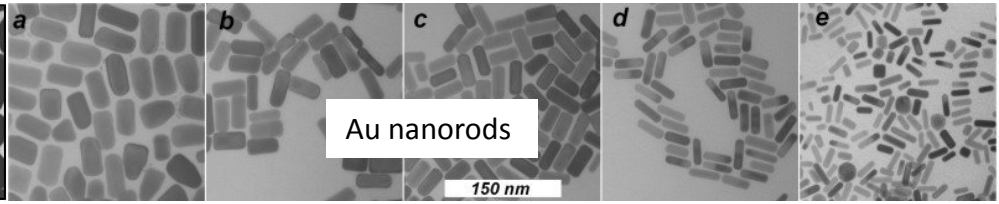
Characterization of particles

Characterization of size and shape

- Often colloidal nanoparticle synthesis results in particles with various sizes
  - The size dispersion may be affected by the synthesis properties (rates of nucleation vs. growth etc.) but only to certain limit
  - The size distribution may be manipulated by post-synthesis treatments
  - Morphology may be controlled by the growth conditions but there are no general rules for the shape control
- Size and shape have major role in the optic, magnetic and electronic properties of the nanoparticles
- Characterization of the nanoparticle size and shape is typically carried out by electron microscopy, atomic force microscopy (AFM), light scattering or spectroscopic methods







http://coloides.webs.uvigo.es/nano/gallery/TEM%20pictures/index.html

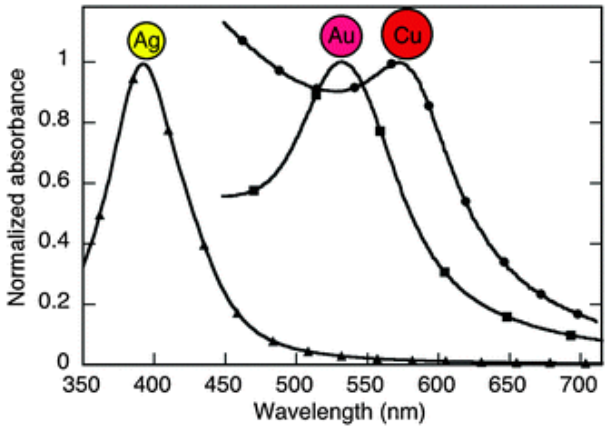
UV vis spectroscopy of metal nanoparticles

- In metallic nanoparticles, the electrons are delocalized on the whole nanoparticle as an oscillating electron cloud (surface plasmon), which causes polarizability for the whole nanoparticle
- When the plasmon is excited with light that has longer wavelength compared to the size of the nanoparticle, a localized surface plasmon appears
- The resonance frequency of the localized surface plasmon noble metals (for instance Au, Ag, Cu) is in the range of visible light and is observed as strong absorbance of light

Localized surface plasmon resonance

- The position of the plasmon resonance strongly depends on the surrounding electric field
  - Sensitive for size and shape of the particle, changes in the surface of the nanoparticle
  - Dielectricity of the solvent
  - Vicinity of other nanoparticles

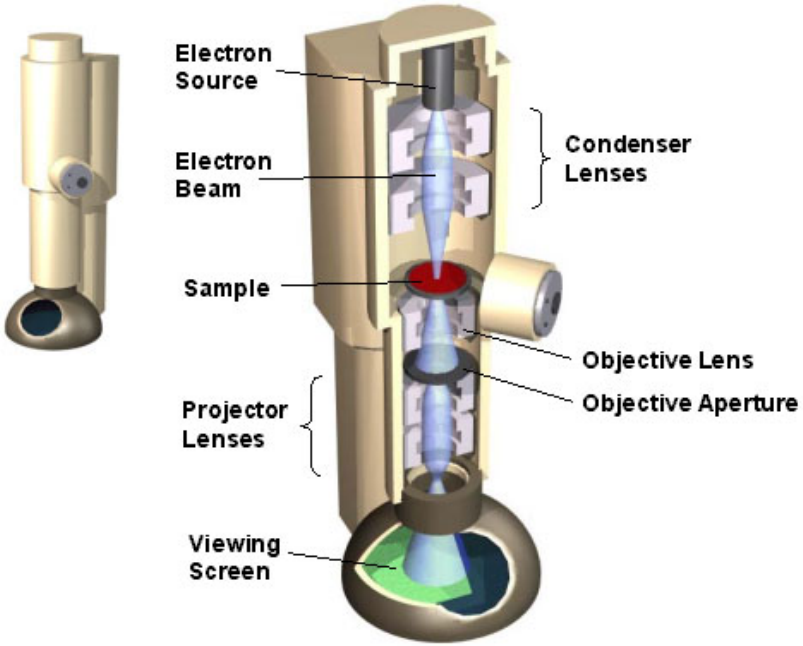
  ➔ Sensitive colorimetric characteristics



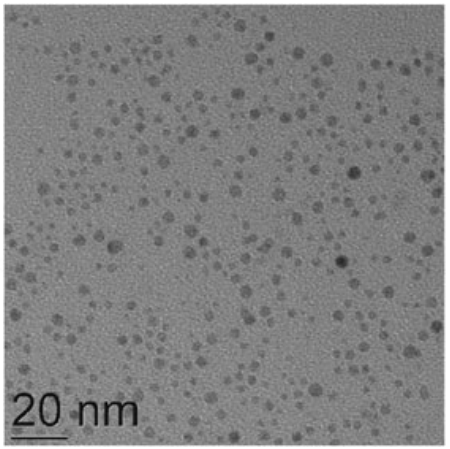
J. C. Scaiano *et al.* Pure Appl. Chem., 2011, 83, 913

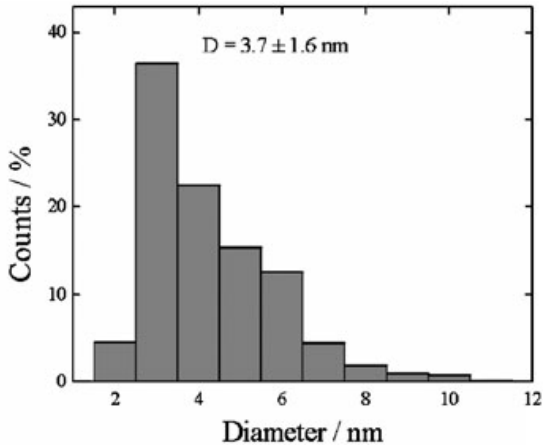
Transmission electron microscopy

- Image is formed of intensities of electrons scattered by the sample
  - Projection of 3D sample on 2D detector
- Allows high resolution imaging even on sub-nanoscale



TEM micrograph of silver nanoparticles
Sample preparation: droplet of nanoparticle solution dried on a thin polymer film
Particle size measured from image ➔ distribution of sizes





Ahonen et al. Phys. Chem. Chem. Phys., 2007, 9, 651

Resolution of TEM

The image resolution depends on the wavelength of electrons

De Broglie relationship:

$$\lambda = \frac{h}{(2mqV)^{1/2}}$$

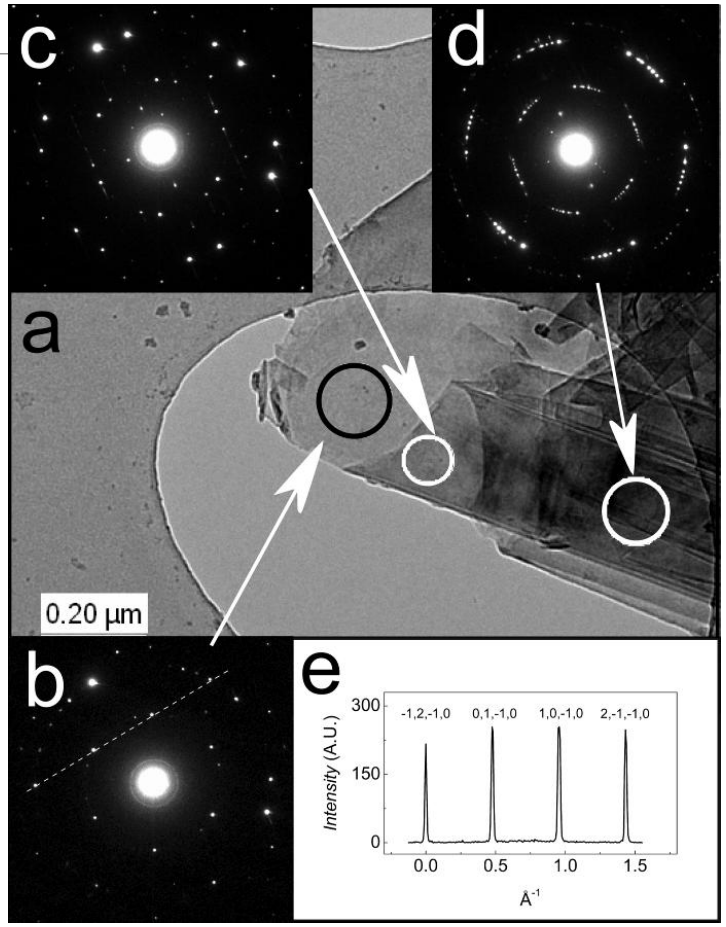
m and *q* are the mass and charge, h is Planck's constant and V is the acceleration potential

Theoretical point-to-point resolution $\propto \lambda^{3/4}$

High energy electrons interact less with the matter ➔ higher spatial resolution

TEM – selected area electron diffraction (SAED)

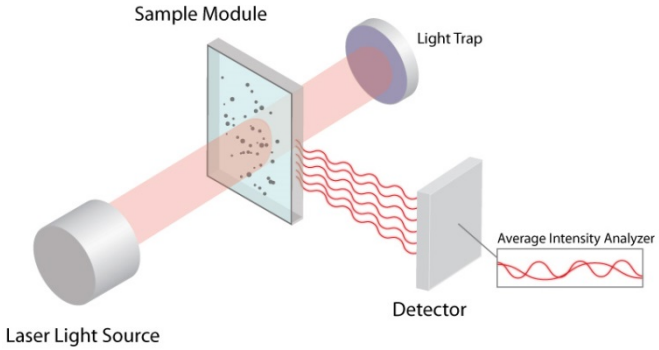
- Measurement of electron diffraction at a chosen area
- Each intensity peak represents periodicity in the electron structure ➔ crystal structure
  - Reciprocal lattice i.e. Fourier transform of the crystal lattice
- Example: layers of graphene



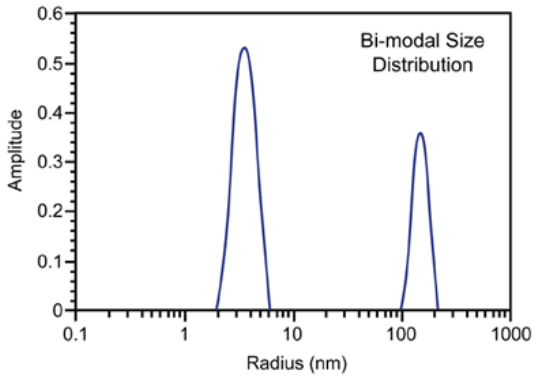
P. Laaksonen, M. Kainlauri, T. Laaksonen, A. Shchepetov, H. Jiang, J. Ahopelto, M. B. Linder, Angew. Chem. Int. Ed. 2010, 49, 4946.

Dynamic light scattering for size measurement

- Laser light is shone at a solution containing particles in Brownian motion
- Light scattered from the particles is detected (intensity $I \propto r^3$)
- Because the particles move, the scattered light is distributed
- The intensity of the scattered light fluctuates depending on the diffusion of the particles
- Based on the correlation of consecutive measurements, the rate of diffusion *D* of the particles is determined ➔ particle size



chemwiki.ucdavis.edu



http://www.azonano.com/article.aspx?ArticleID=1240

Dynamic light scattering

The sample is illuminated by a laser ➔ the fluctuation of the scattered light in the illuminated volume is analyzed

The rate of fluctuations depend on the diffusion constant of the species

Fluctuations from the mean intensity are analyzed from the correlation function

$$C(\tau) = \langle [\Delta I(t)][\Delta I(t+\tau)] \rangle$$

The correlation function decays exponentially as a function of time ➔ the time constant is proportional to the diffusion constant

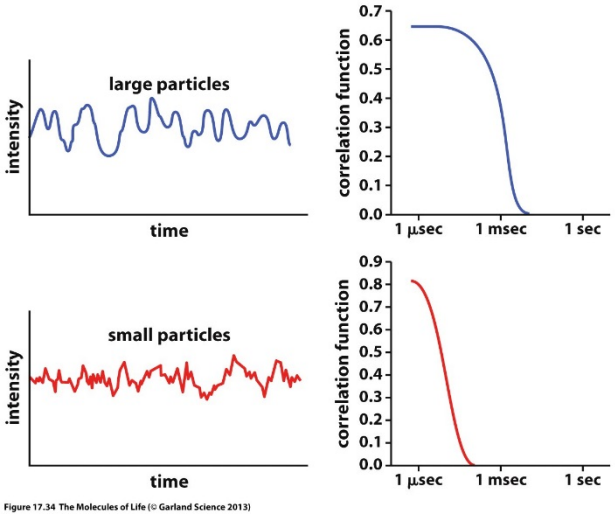


Figure 17.34 The Molecules of Life (© Garland Science 2013)

Diffusion - friction factor

Fluid resists the motion of particles/molecules

The resistance causes a friction force that acts against the movement

Friction force depends on the size and shape of the particle and the solvent properties

$$F_{friction} = -fv$$

where f is the friction factor and v is the velocity of the particle

Terminal velocity

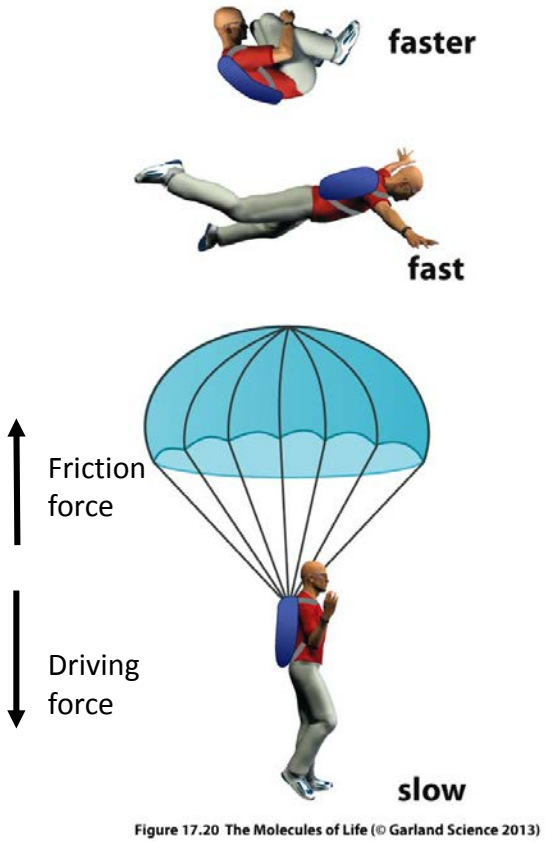


Figure 17.20 The Molecules of Life (© Garland Science 2013)

Under an applied force (gravity, centrifugal or electrophoretic force), the particle will reach a constant velocity depending to the balance of the forces

$$F_{friction} = -v_{terminal} f = -F_{drive}$$

	$V_{terminal}$ (m/s)	f (kg/s)
Free fall	56	12
Parachute open	8	86

Diffusion constant vs. friction factor 1/2

Random movement can be understood as frictionally dampedmotion

The flux of particles in one dimension: $J(x) = v \cdot c(x)$

The driving force for diffusion arises from the chemical potential difference:

$$\mu = \mu^0 + k_B T ln(c)$$

The gradient along the x axis:

$$F_{drive} = -\frac{\mathrm{d}\mu}{\mathrm{d}x} = -k_B T \frac{\mathrm{d}}{\mathrm{d}x} \ln\big(c(x)\big) = -k_B T \frac{1}{c(x)} \frac{\mathrm{d}c(x)}{\mathrm{d}x}$$

Where k_B is the Boltzmann constant $k_B = 1.381 \cdot 10^{-23} \frac{J}{K} = 1.381 \cdot 10^{-16} \frac{cm^2 g}{s^2 K}$

Diffusion constant vs. friction factor 2/2

Now, combining this, to Fick's first law and the equation of the friction factor

$$J = -D\nabla c$$

Where *J* is flux and *D* is diffusion constant

$$J(x) = -D\frac{\mathrm{d}c(x)}{\mathrm{d}x}$$

$$J(x) = c(x)\cdot v = c(x)\cdot\frac{F_{drive}}{f} = c(x)\left(-k_B T\frac{1}{c(x)}\frac{\mathrm{d}c(x)}{\mathrm{d}x}\right)\frac{1}{f}$$

$$\Rightarrow D = \frac{k_B T}{f}$$

Einstein's equation

Diffusion constant of a spherical particle

For particles with low mass, the flow around them is dominated by viscosity, which simplifies the fluid dynamics

For a small sphere having *r* radius in a system with low Reynolds number (laminar flow), the friction factor is defined by the Stokes law:

$$f_{sphere} = 6\pi\eta r$$

Where η is viscosity

Combining with $D = \frac{k_B T}{f}$

We get the Stokes-Einstein equation:

$$D_{sphere} = \frac{k_B T}{6\pi\eta r}$$

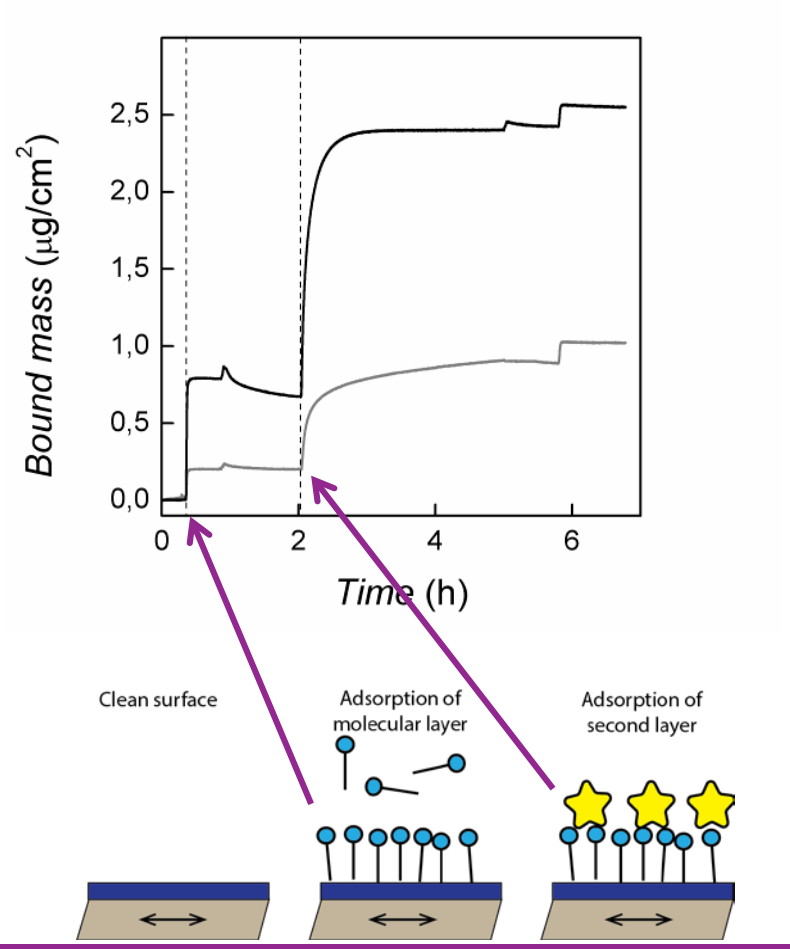
Characterization of thin films

Characterization of thin films

- Thin, monomolecular layers are a typical form of 2D nanomaterials
- Often require special characterization techniques due to the low thickness and mass
- Thickness, surface coverage, morphology, density, stability, electric properties are typically investigated
- Non-destructive methods are preferred
  - Optical methods where light interacts with the material of interest: ellipsometry, surface plasmon resonance (SPR)
  - Mass-detection by quartz crystal microbalance (QCM)
- Some more classical methods (with certain limitations) are also suitable for analysis of thin layers
  - Surface tension measurements

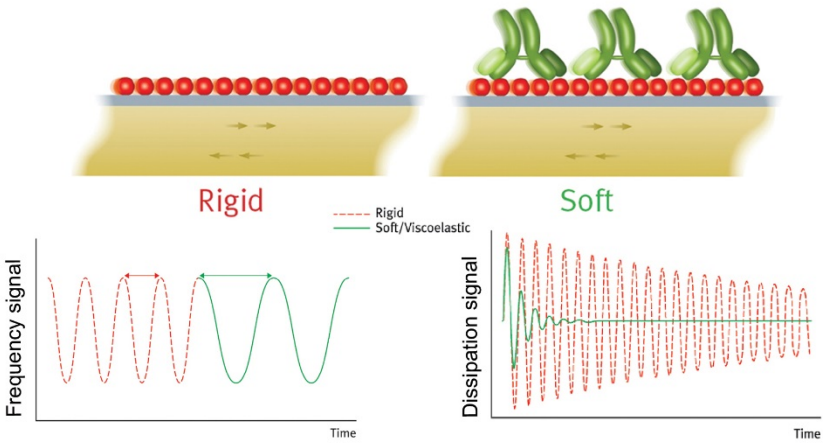
Detection of molecular layers by Quartz Crystal Microbalance QCM-D

- Detection of low masses adsorbed on a coated piezoelectric quartz crystal
  - Based on the change in the resonance frequency of the oscillating crystal
  - Increase in the resonance frequency as more mass is adsorbed
- Allows precise detection of the layer adsorbed from gas or liquid
  - Also in-situ measurement of binding
  - Changes in the viscoelasticity of the layer are observed
- D stands for dissipation of the oscillations
- The mass measured by QCM-D includes also the solvent associated with the molecules and the layer structure



Principles of QCM-D

- Frequency change of the oscillations indicate mass change at the surface
- Dampening of the oscillations are the measure of the film viscosity



http://www.biolinscientific.com/q-sense/technologies/?card=QT1

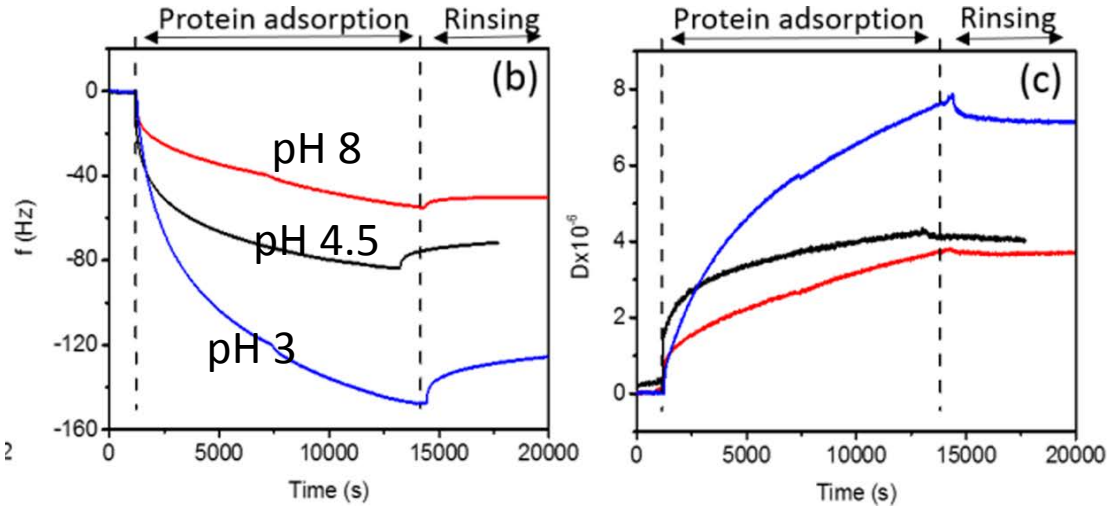
- The mass change of a rigid film can be estimated from the Sauerbrey equation:

$$\Delta m = -\frac{C\Delta f}{n}$$

- Where *C* is a constant depending on the properties of the quartz crystal, typically 17.7 ng Hz^{-1} cm^{-2}
- Δf is the observed frequency change
- *n* is the overtone of the oscillations

Example: Adsorption of protein at different conditions

- In situ monitoring of a cellulose binding protein on a thin cellulose film
- pH is controlled by buffer solutions, protein concentration is constant
- Below pH 4, there is electrostatic attraction between the protein and the surface➔ increases the adsorbed amount (also non-specific binding)
- At pH 4.5, the protein has random coil conformation, in other pHs swollen conformation



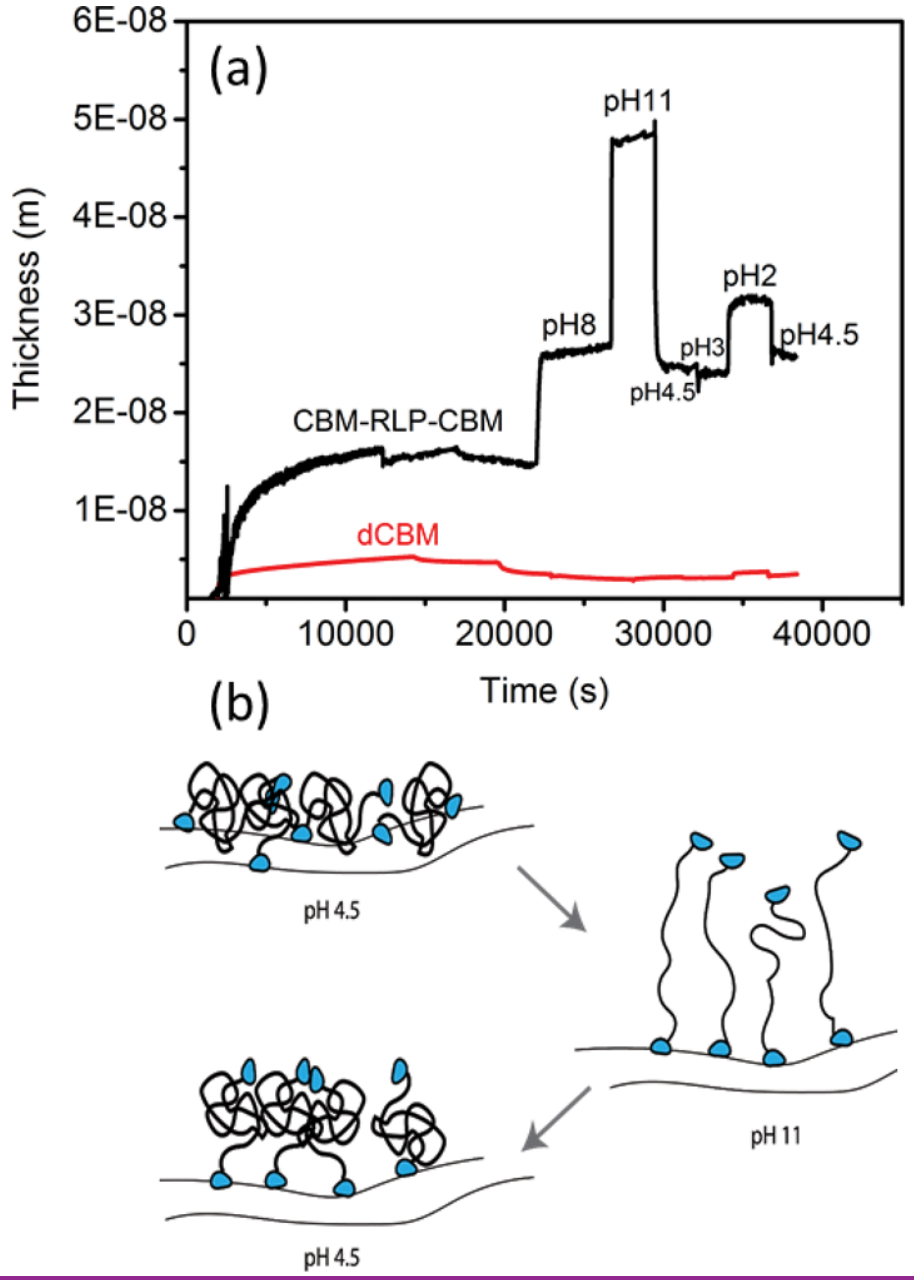
D is not straight-forward, but depends on protein density and conformation

- We need to choose what to monitor

➔For studying conformation, constant adsorption density is needed

1. Adsorption at chosen conditions
2. Stabilization
3. Changing the pH by buffers

- Density and viscosity of the solutions need to remain constant (dilute enough, similar concentrations)



Sensitivity of QCM-D

If the QCM-D instrument is able to measure a frequency change of 0.1 Hz, what is the smallest mass change that can be observed at the fundamental resonance frequency?

- Sauerbrey equation: $\Delta m = -\frac{C\Delta f}{n}$

$n = 1$

$C = 17.7$ ng Hz^{-1} cm^{-2}

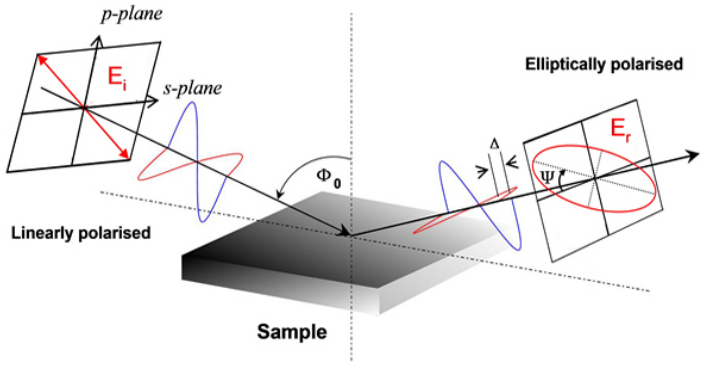
$\Delta f = 0.1$ Hz

➔ $\Delta m = \pm 2$ ng cm^{-2}

Ellipsometry

- A non-invasive method for measuring a film thickness from Ångström level up to ~ 1 µm
- Analysis of polarization of light that is reflecting from a surface

➔ resolving thickness and refractive index based on laws of electromagnetism



https://www.tcd.ie/Physics/Surfaces/ellipsometry2.php

Polarization of light

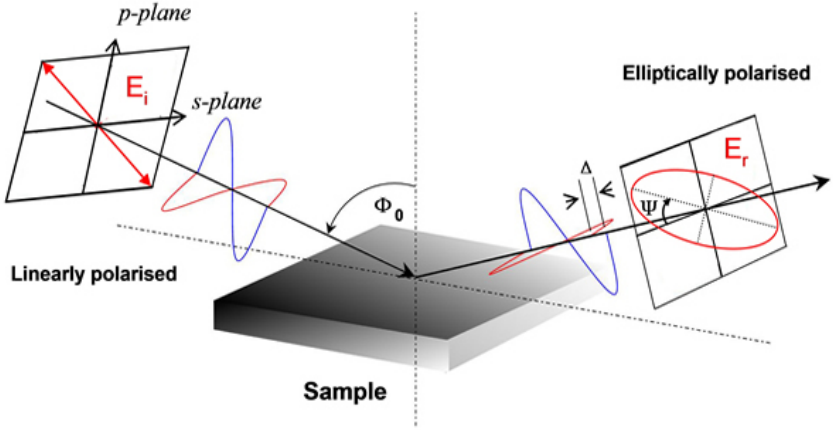
Polarized along the plane of incidence : p-polarized

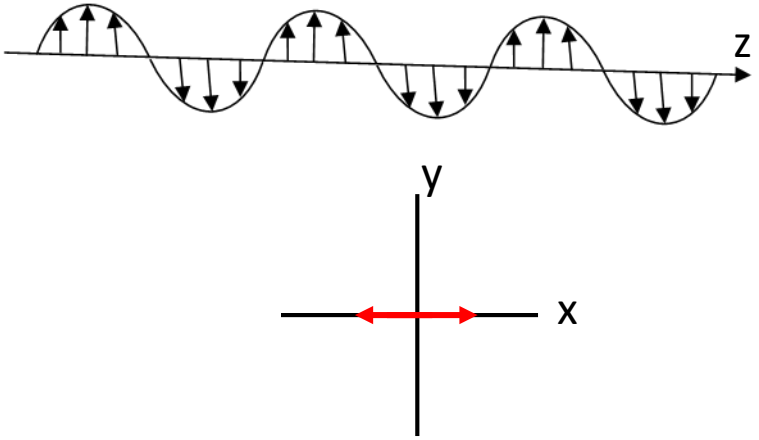
Polarized along the plane perpendicular to plane of incidence: s-polarized

When the phase difference is 0 ➔ linearly polarized light

Here we assume that the amplitudes of the electromagnetic vectors are equal

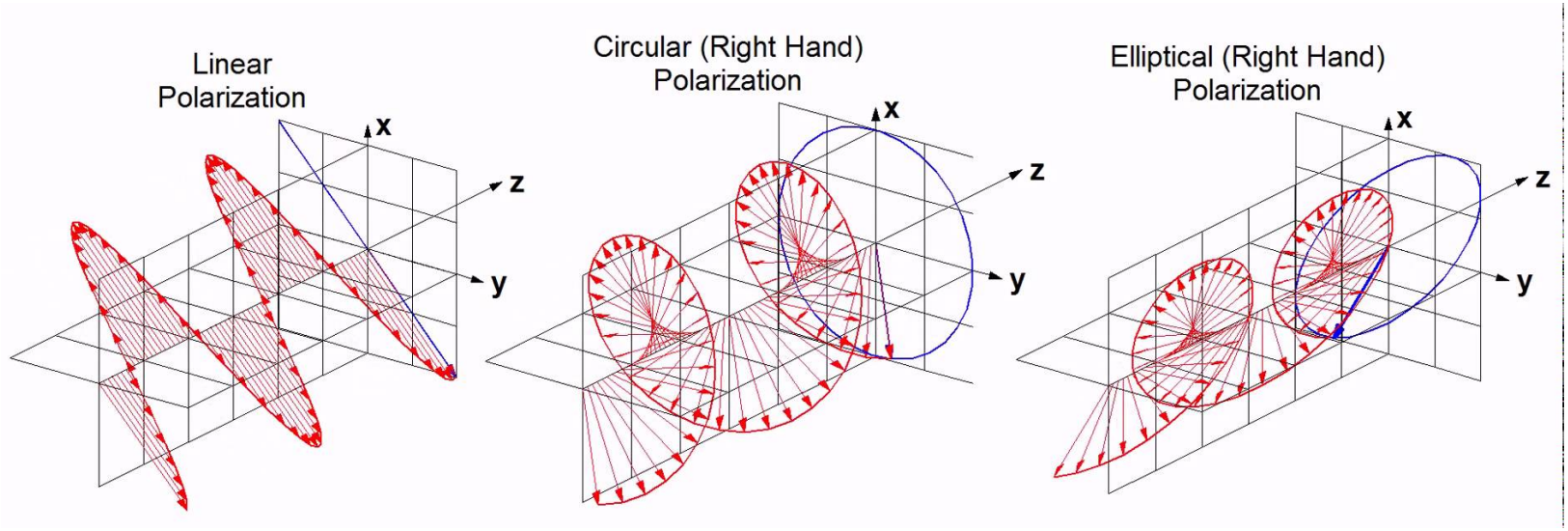
We only consider the electric field





Cases of polarization

- 0 ° out of phase: linearly polarized light
- 90° out of phase: circularly polarized light
- Other phase difference : elliptically polarized light



The fundamental ellipsometric optical parameters

- Polarisation of light changes upon reflection from a surface
- Interaction of the incident light with the matter cause phase shift and amplitude changes,
  - Include important information on the optical properties of the sample
- Both p and s components phase and intensity may change

- Phase angles of coming and reflecting waves: $\Delta = \delta_1 - \delta_2$
- The amplitude change: $tan\Psi = \left|\frac{R^p}{R^s}\right|$

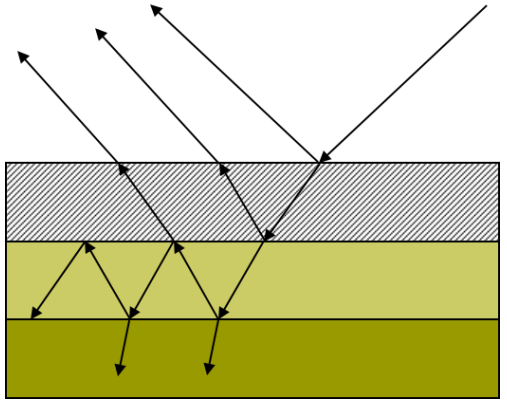
  - Where R is the total reflection coefficient

Extracting the result

- The reflected light is a sum of all the interactions
- The refractive index and film thickness are extracted from the measured data by using an appropriate model
- A proper model to fit Ψ, Δ need to be found to make the data relevant
- The refractive index is complex $\tilde{N} = n - ik$
  - *n* denotes refraction, *k* describes absorption

The complex dielectric constant $\tilde{\varepsilon} = \tilde{N}^2 = (n - ik)^2$

- For dielectric materials *k* = 0



Typical models

Cauchy relation for transparent materials:

$$n(\lambda) = N_0 + \frac{N_2}{\lambda^2} + \frac{N_4}{\lambda^4}$$

Cauchy relation for absorbing materials

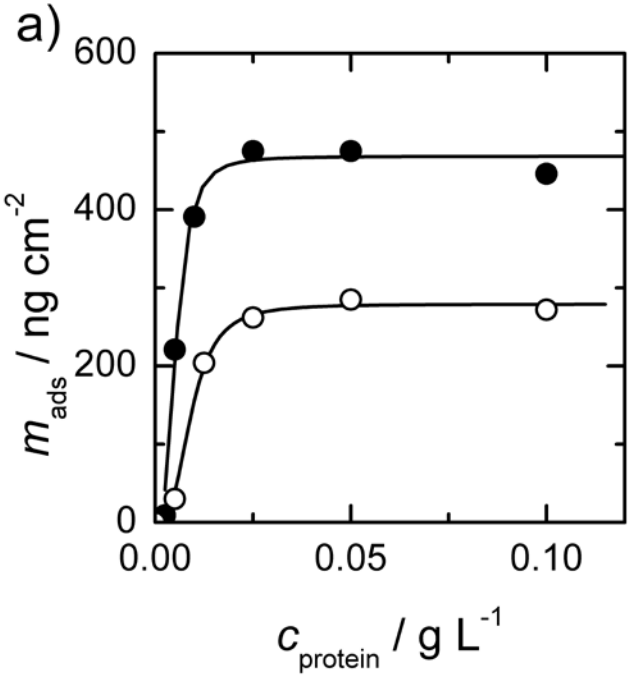
$$k(\lambda) = K_0 + \frac{K_2}{\lambda^2} + \frac{K_4}{\lambda^4}$$

Lorenz oscillator (describes absorbance peak)

$$\varepsilon(E) = 2nk = \frac{A_L E_0 C E}{\left(E^2 - E_0^2\right)^2 - C^2 E^2}$$

λ is wavelenght of light, E is energy of light

Example - Combining QCM-D and ellipsometry



- Adsorption of a molecule was monitored by QCM-D and ellipsometry
- Mass of the bound layer was recorded
- QCM-D: Black dots
- Ellipsometry: Open dots

- Why is the result so different?

Hakala t. *et al. RSC Advances*, **2012**, *2*

Summary of imaging methods

METHOD	PRINCIPLE	SPECIAL	RESOLUTION	SOURCE
Transmission electron microscopy (TEM)	Interaction of the sample with the electron beam ➔ image based on electron density	Transmission through the sample (projection)	Atoms, molecules ➔ micrometers	Nanotechnology in a nutshell 9-13, **Lecture 8**
Scanning electron microscopy (SEM)	Interaction of the sample with the electron beam ➔ image based on electron density	Surface of the sample	Nano-sized objects ➔ micrometers	Nanotechnology in a nutshell 9-13
Atomic force microscopy (AFM)	Scanning the sample surface with small needle (in contact or non-contact) ➔ image of the topography	Surface of the sample	Molecules ➔ micrometers	Understanding Nanomaterials 176-179, **Lecture 9**
Scanning tunneling microscopy (STM)	Scanning the sample with small electrode while measuring the tunneling current ➔ image of electrical conductivity	Surface of the sample	Atoms, molecules ➔ micrometers	Understanding Nanomaterials 172-176, **Lecture 9**
Imaging ellipsometry	Interaction of the sample with light ➔ thickness and refractive index of the sample	Surface of the sample, also interfaces	Micrometers	Understanding Nanomaterials 108-117, 169-171, **Lecture 8**

Summary of spectroscopic methods

METHOD	PRINCIPLE	SPECIAL	RESOLUTION	Source
UV vis spectroscopy	Absorption of light (~ 200 - 700 nm) with the sample, transmittance or reflectance	Excitation of electrons between HOMO and LUMO states, also localized surface plasmons	Macroscopic	Understanding Nanomaterials 135-140
Fluorescence spectroscopy	Excitation of the electrons causes light emission from the sample	Excitation typically UV, emission visible	Macroscopic	Understanding Nanomaterials 141-143
FTIR spectroscopy	Absorption of infrared radiation (700 nm - 1 mm) by molecules	Detection of bonds, identification of chemical groups	Macroscopic – mesoscopic	Understanding Nanomaterials 144-149
Raman spectroscopy	Scattering of infrared radiation (700 nm - 1 mm) by molecules	Detection of bonds, identification of different crystal structures	Macroscopic-mesoscopic	Understanding Nanomaterials 150-154.
X-Ray spectroscopy	Interaction of X-Rays (0.001 - 2.5 nm) with the sample ➔ Absorption, fluorescence, diffraction	Electronic structure of the molecules, elemental analysis, crystal structures Also large-scale facilities	Macroscopic-atoms	Understanding Nanomaterials 167-168

Summary of surface sensitive methods

METHOD	PRINCIPLE	SPECIAL	SOURCES
QCM-D	Added mass is detected on a resonating quartz crystal, changes in viscoelasticity observed by dissipation monitoring.	Sensitive to very small masses ~ ng/cm^2 Limited thickness (mass)	Understanding Nanomaterials 101-107, **Lecture 8**
Tensiometry	Surface tension is recorded by Wilhelmy plate, capillary rise, sessile drop, hanging drop	Also for oil/water interface	Understanding Nanomaterials 97-100, **Lecture 8**
Surface Plasmon Resonance (SPR)	Detection of change in refractive index and film thickness from change in the surface plasmon resonance of the sensor surface	Needs a thin metal layer underneath the sample, limited thickness of the sample	Understanding Nanomaterials 119-123

Concept check

True or false?

A) Nanomaterials have special features that set challenges for the characterization

B) Sample preparation may be critical for successful characterization

C) One method is enough to fully characterize the materials

D) Diffusion depends only on the particle shape

E) Ellipsometry is based on the magnetic properties of the material

Literature

TEM: Cao G. *et al*. Nanostructures and Nanomaterials, Chapter 8.2.4

Johal M. S. Understanding nanomaterials:

QCM-D: 4.2,

Ellipsometry: 4.3,

UV-vis spectroscopy 4.6.2

Next week: elevator pitch

Why?

- To learn to present your ideas in compact informative way
- To help you analyze and develop you skills for efficient communication

How?

- Prepare your 30 seconds pitch and charm the audience
- Help from the instructions in MyCourses