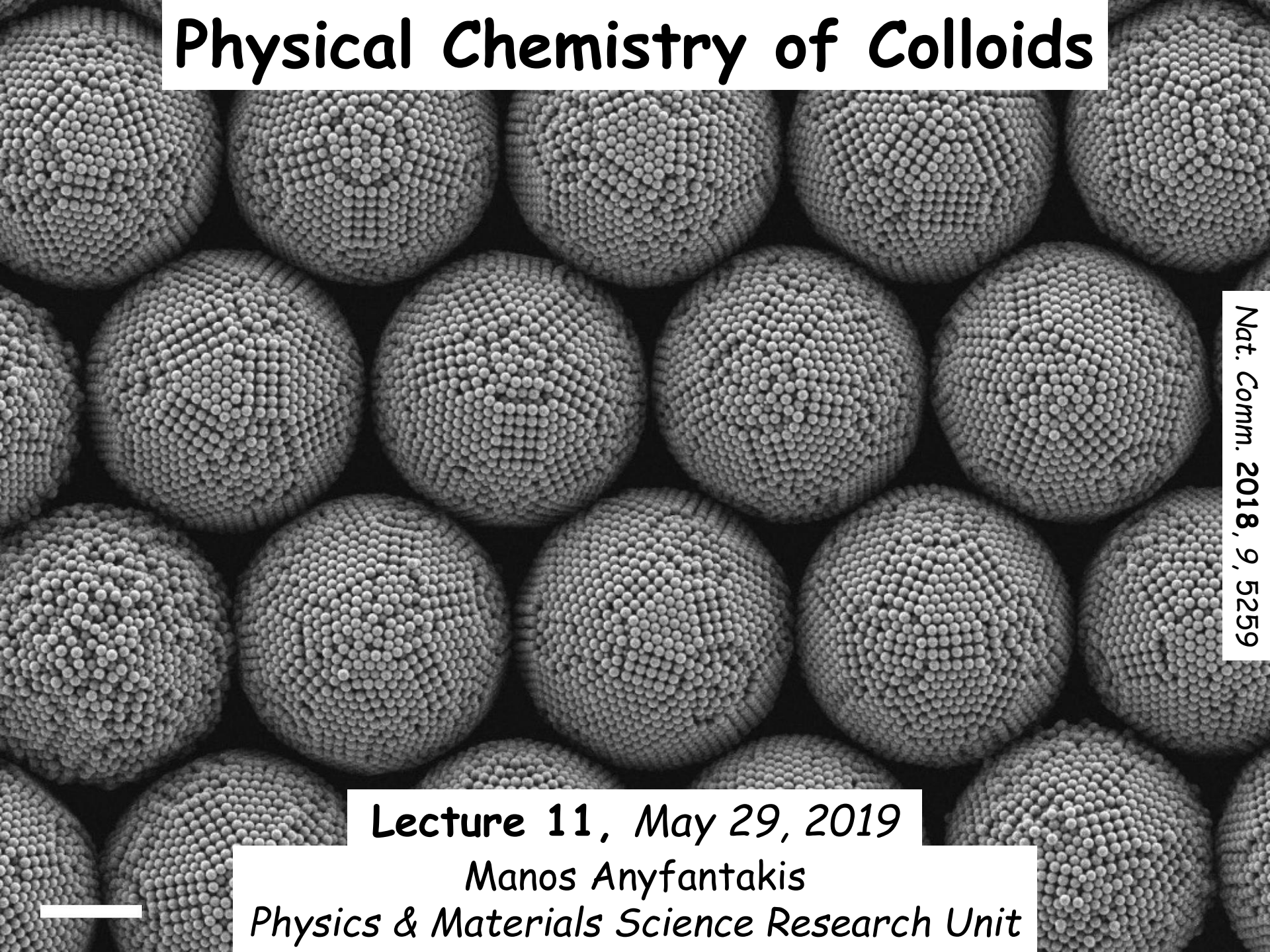
Physical Chemistry of Colloids



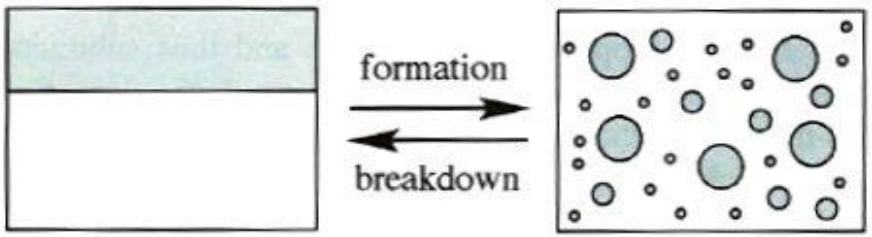
Nat. Comm. **2018**, *9*, 5259

Lecture 11, *May 29, 2019*

Manos Anyfantakis
Physics & Materials Science Research Unit

Previously in ColloidsPhysChem…(I)

emulsion (general)
two-phase system where droplets of one liquid are dispersed in another immiscible liquid (continuous phase)

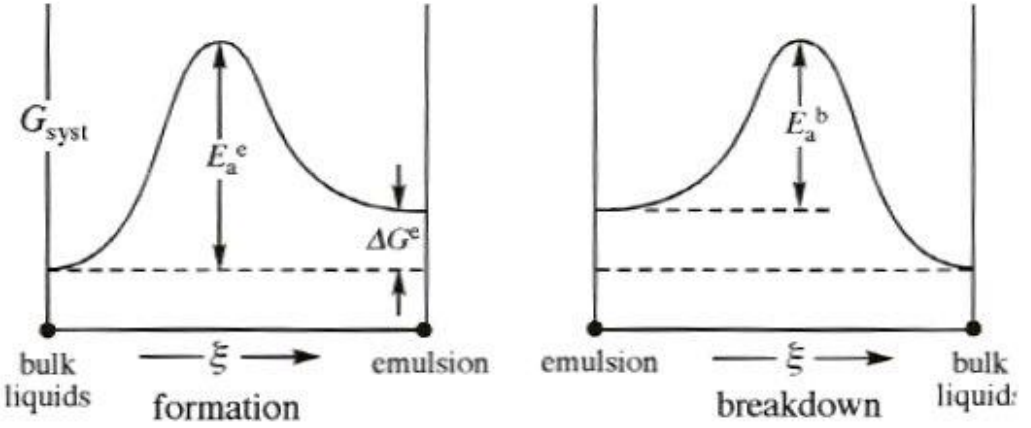


microemulsions

- thermodynamically stable dispersions made of water, oil & surfactant(s) with droplets of ~ 1 to 100 nm

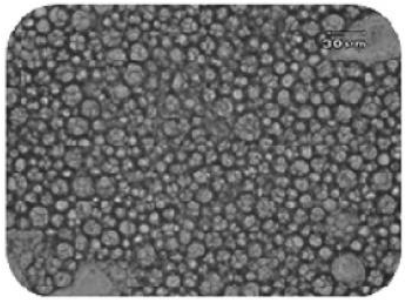
macroemulsions

- order of magnitude larger drops than in μemulsions, large dispersity
- lyophobic colloids, thermodynamically unstable



oil-in-water (O/W) emulsions
(water-insoluble) organic droplets dispersed in water

Food Hydrocolloid **2012**, *28*, 344

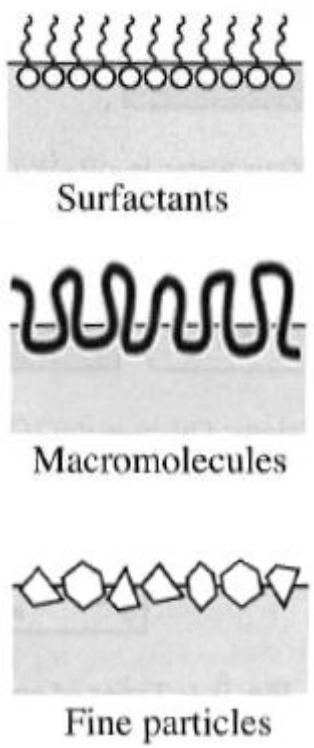


water-in-oil (W/O) emulsions
aqueous phase dispersed in organic liquid

wikipedia

Previously in ColloidsPhysChem…(II)

emulsions are kinetically stable due to the presence of an emulsifier @ the interface between the two liquids



emulsifier

- a substance that adsorbs @ the fluid interface & stabilizes the dispersed liquid within the continuous phase
- different types: surfactants, polymers (proteins, starches, cellulose-based, polyelectrolytes), particles, inorganic anions
- assist in emulsion formation by reducing interfacial tension
- ***mainly:*** preserve drops from coalescence by forming a mechanical & interaction barrier between the two phases
- better solvent for emulsifier → continuous phase (Bancroft rule)

interactions

- electrostatic repulsion (e.g. ionic surfactant)
- steric repulsion (e.g. non-ionic surfactant or polymer)

mechanical stability

- stabilization of thin film between adjacent droplets that can otherwise become unstable & rupture (Gibbs elasticity)
- polymer or particle stabilizers form interfacial gels that stop drainage

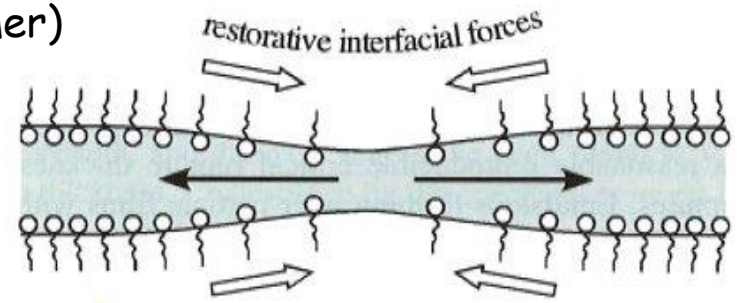
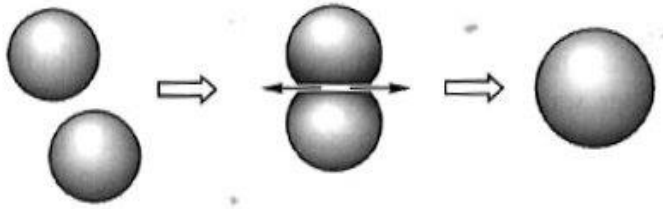


Fig. 9-4: The mechanism of Gibbs elasticity stabilizing the film between emulsion droplets.

Previously in ColloidsPhysChem…(III)

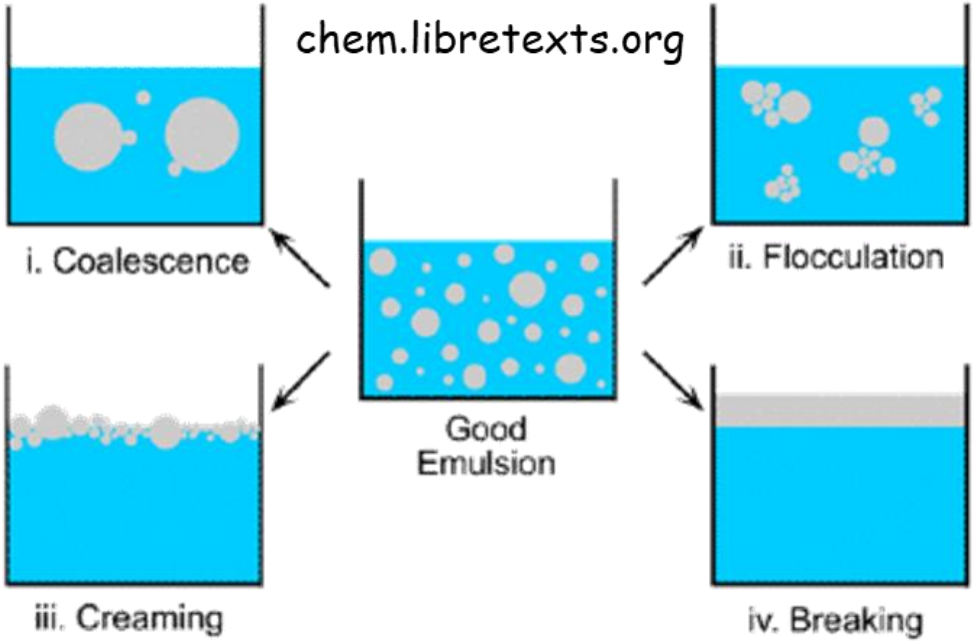
thermodynamic instability → emulsions tend to reduce free energy by reducing total interfacial area (increase in drop diameter)



Fig, 9-2: The breakdown of emulsions through flocculation and coalescence.

destabilization mechanisms

- same as for other lyophobic colloids
- flocculation: reversible clustering of droplets
- coalescence: merging of droplets into larger droplets (irreversible)
- macroscopic phase separation: gravity-induced sedimentation or creaming
- Ostwald ripening



Ostwald ripening

- droplet proximity is not required
- mass transfer between drops of different curvature through the surrounding solvent
- mass transfer from small to large drops → latter grow @ the expense of former

Previously in ColloidsPhysChem…(IV)

foam (IUPAC)

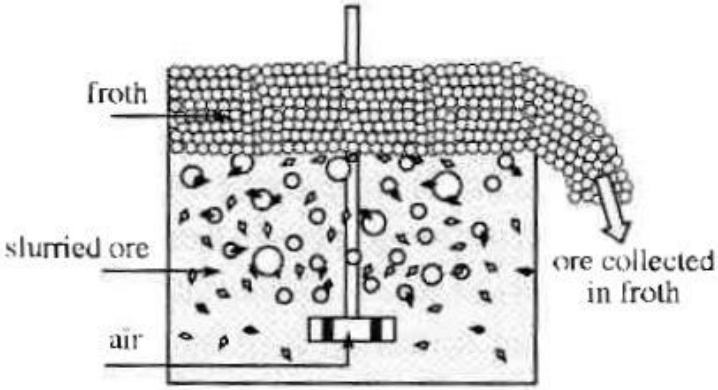
- dispersion in which a large proportion of gas (by volume) in form of bubbles, is dispersed in a liquid, solid or gel
- bubble diameter usually > 1 μm, but thickness of lamellae between bubbles often in colloidal range

similarities to emulsions

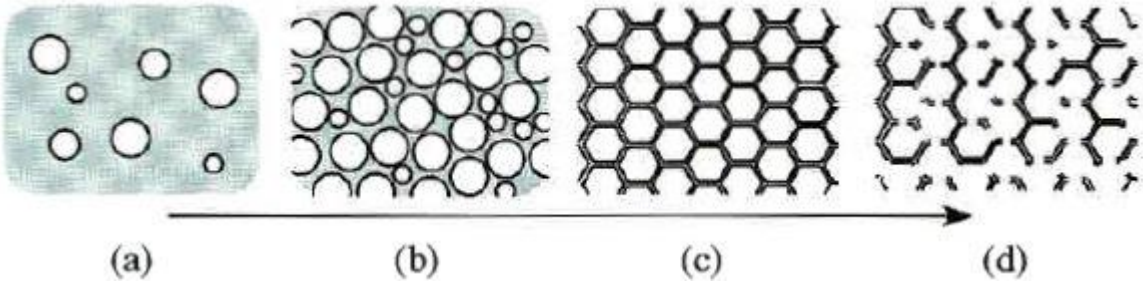
- foam breakdown depends on bubble approaching followed by drainage of continuous phase from the film between them & its rupture (→ coalescence)
- **foaming agent:** required for a reasonable lifetime

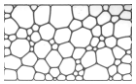
differences with emulsions

- large bubble-solvent Δρ → segregation by gravity → pressed bubbles form polyhedral structure
- larger drainingg films → complex hydrodynamics
- bubble gases diffuse rapidly across thin films → disproportionation important (larger P in small bubbles)



stages in a foam lifetime





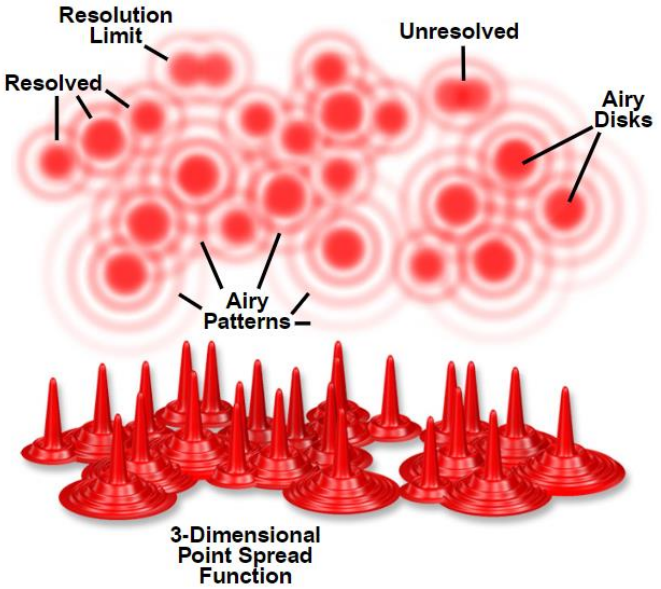
youtube.com/watch?v=HPRGa3_On6s

Optical microscopy

Optical microscopy (in its various forms) is a direct method for examining interfaces & colloids

- morphology of surfaces
- information about size & shape of individual particles & structures of their assemblies

point sources of light from points in object appear as diffraction patterns: bright central region & concentric rings of decreasing intensity (Airy disk)

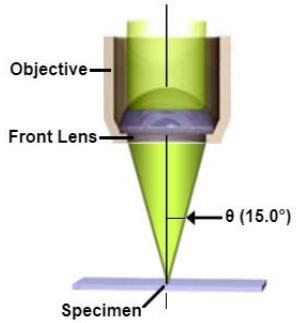


resolution

- shortest distance (***d***) between two points that can be distinguished by imaging system as separate entities
- lower ***d*** → higher resolution

λ: light wavelength

$$d = \frac{0.61\lambda}{2n\sin\theta} = \frac{0.61\lambda}{NA}$$



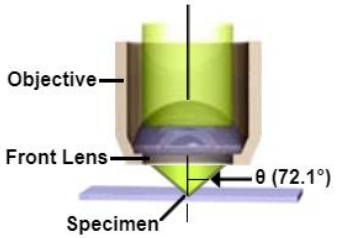
NA = n sin(θ)
0.25 = 1.0 sin 15.0°

NA = Numerical Aperture
n = Refractive Index
= 1.00 (Air)
θ = 1/2 Angular Aperture

Approximate Magnification
10

numerical aperture *NA*

- key parameter for all imaging systems
- larger NA → better resolution (objective should have large max. entry angle)
- immersion oil ($n_{oil} > n_{air}$) for increasing NA



NA = n sin(θ)
0.95 = 1.0 sin 72.1°

NA = Numerical Aperture
n = Refractive Index
= 1.00 (Air)
θ = 1/2 Angular Aperture

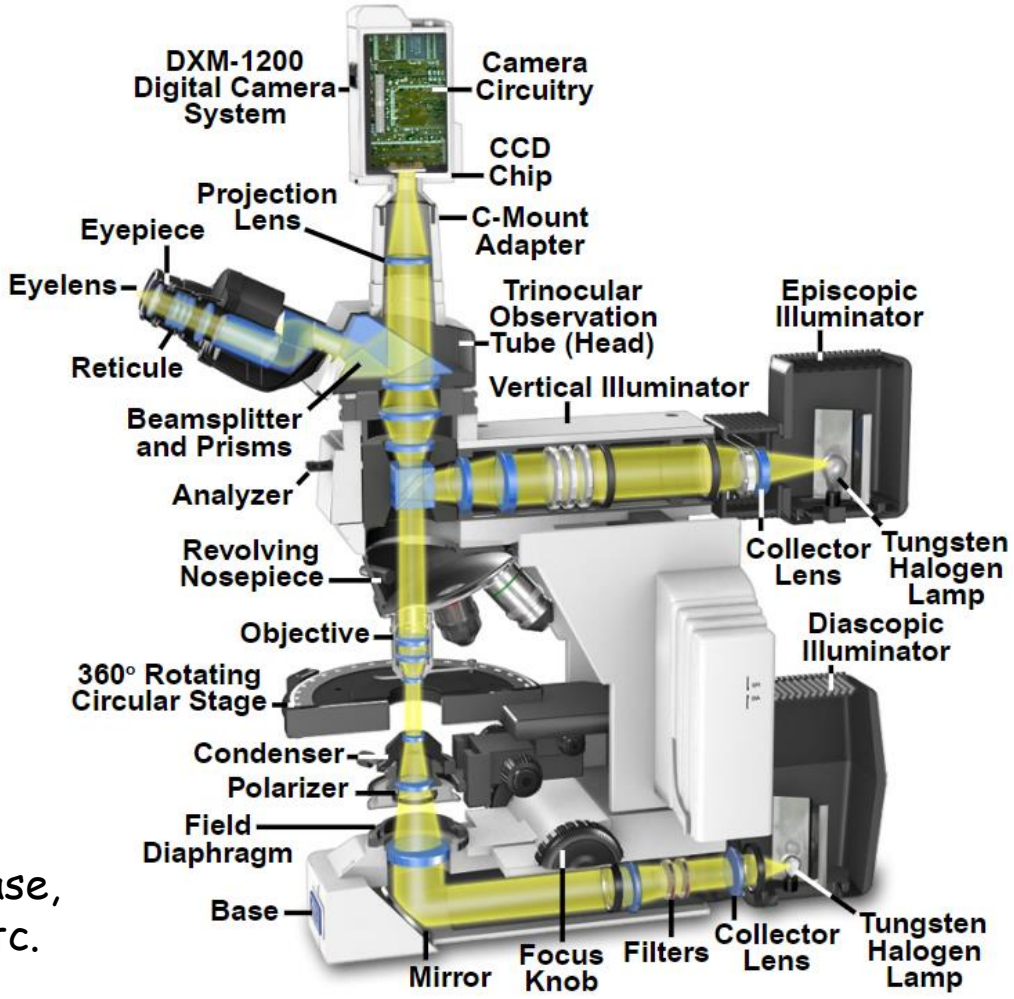
Approximate Magnification
100

optical microscopy limit (air): λ ≈ 0.5 μm, NA ≈ 1 → d_{min} ≈ 0.5 μm

Light path in an optical microscope

- microscope → 2D magnified image that can be focused axially in successive focal planes (z) & can be moved laterally (x,y)
- optical train: optical + mechanical components of the microscope
- light from a source driven onto sample & after interacting with it, collected by detector
  - *reflection microscopy*
  - *transmission microscopy*
  - *fluorescent microscopy*
  - *dark-field (scattering)*
- light intensity & orientation controlled with optical elements (diaphragms, mirrors, prisms, beam splitters)
- light-conditioning devices modify image contrast as a function of frequency, phase, polarization, absorption, fluorescence etc.
- optical components (condenser, objective, eypiece & camera elements) involved in image formation → define quality

Figure 1 - The Microscope Optical Train



images from: **www.microscopyu.com**
(great website for learning)

Bright-field microscopy

Reflected light microscopy

- method of choice for imaging specimens that remain opaque even when ground to a thickness of 30 µm
- light from source directed onto sample surface & returned to the objective by specular or diffuse reflection
- useful for examining surfaces of metals, ceramics, semidconductors, wood, plastics

Transmitted bright-field microscopy

- illumination is transmitted white light, contrast caused by light attenuation in sample areas → dark sample on bright background
- **contrast:** ability of an individual specimen detail to be distinguished when compared to the background or other adjacent features
- properties producing changes in brightness or color differ. arise from absorption, reflection, refr. index variation, scattering, diffraction
- out-of-focus light originating from planes above & below the focal plane obscure the image

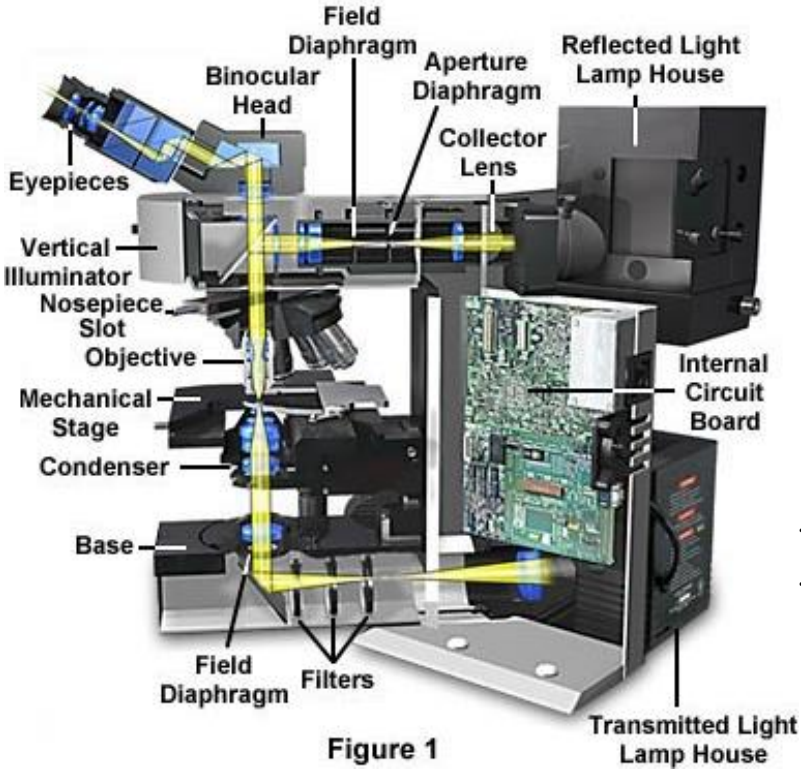


Figure 1

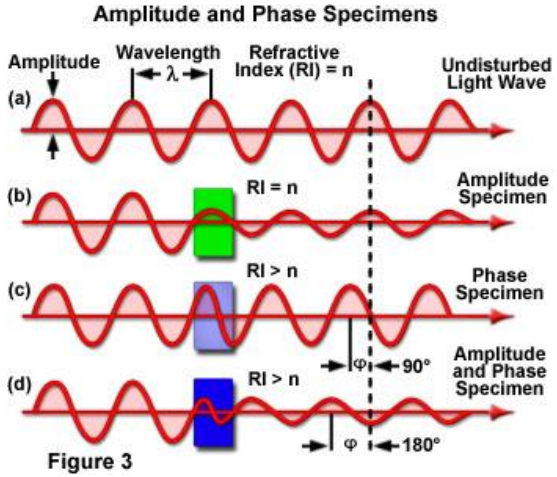


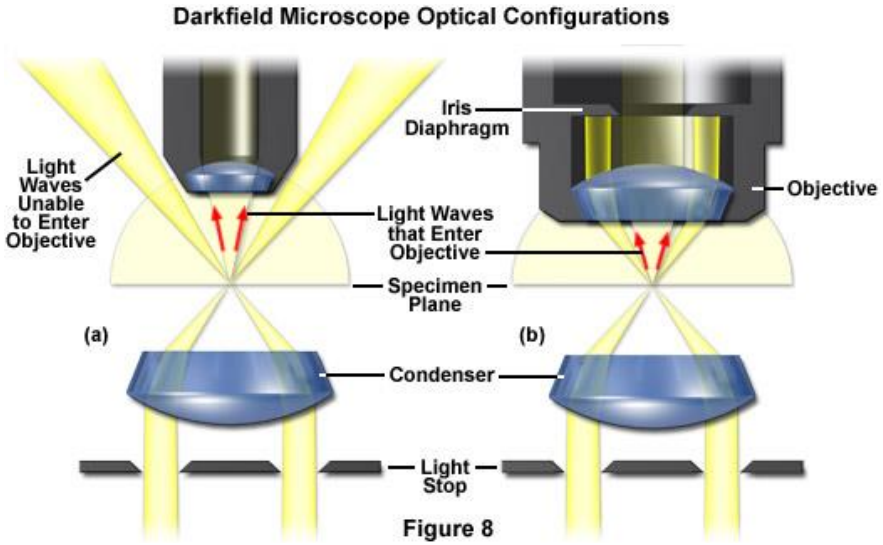
Figure 3

Dark-field microscopy

- popular method for rendering unstained & transparent specimens visible
- invented by Richard A. Zsigmondy (Nobel in Chemistry 1925)
- no direct observation, based light scattering from particles

dark-field illumination

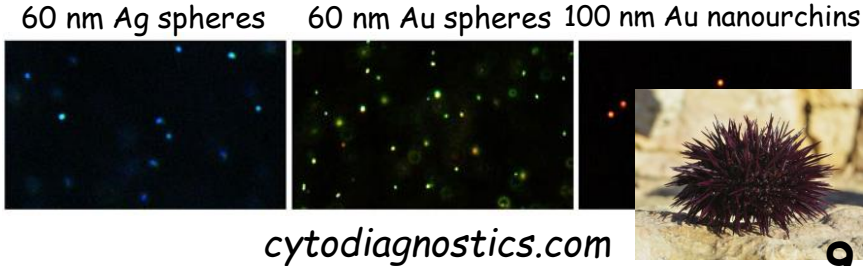
- req. blocking out of central rays along optical axis (norm. passing through sample)
- doing so, allows only oblique rays from large angles to strike the specimen
- achieved using annular stop in condenser
- *result:* particles scatter light to the objective & thus appear bright, background appears dark



http://zeiss-campus.magnet.fsu.edu

advantages & drawbacks

- can be implemented in ordinary μscopes using an appropriate condenser
- specimens with very low contrast & outlines & boundaries readily observable
- particles down to 5 nm can be detected!
- less useful for revealing internal details

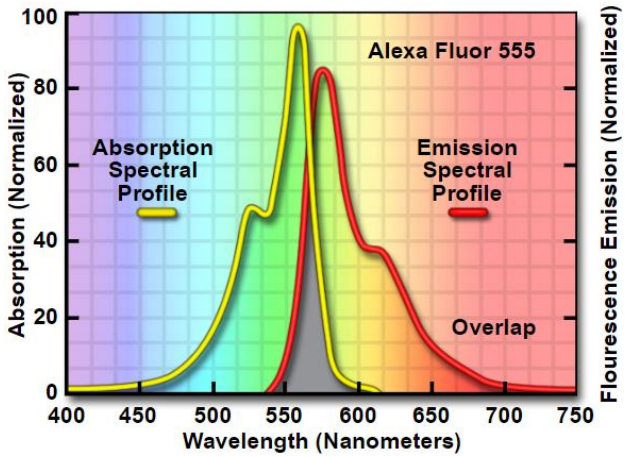


cytodiagnostics.com

Fluorescence microscopy

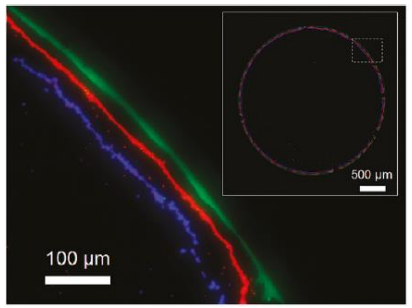
fluorescence

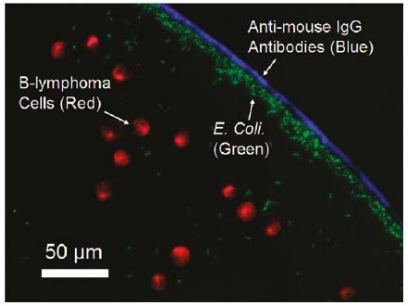
- nearly simultaneous light absorption by specimen & subsequent re-radiation (delay < μs)
- fluorescence emission always occurs @ longer **λ** than that of excitation light



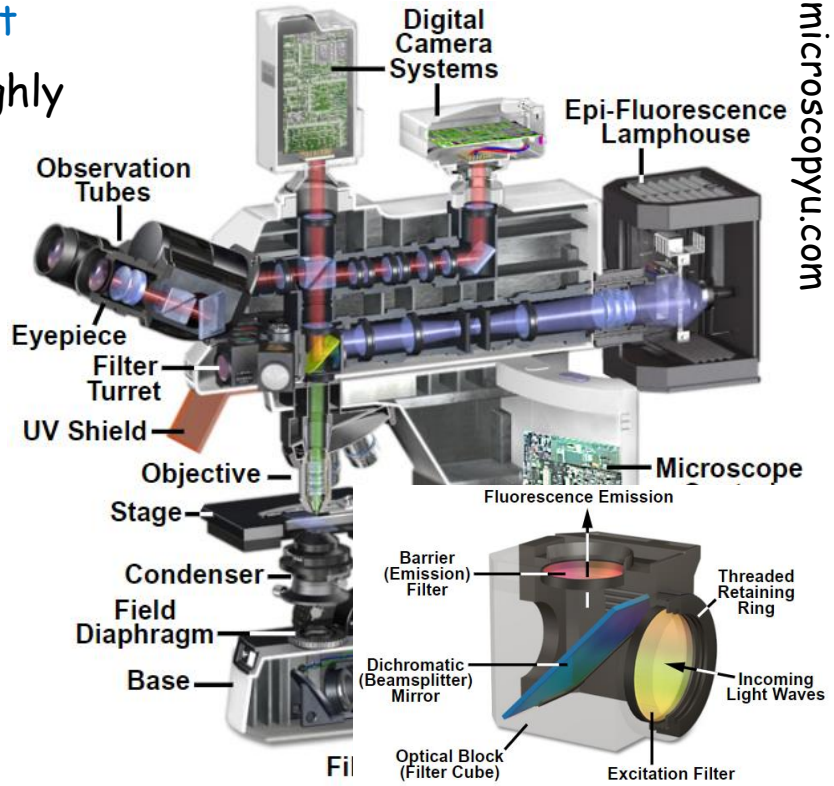
fluorescence microscopy

- sample irradiation with specific **λ** band & then separate & detect only emmited fluorescent light
- ***fluorophores:*** stains attaching to structures; highly specific in their targeting, good quantum yield
- although it cannot provide resolution below diffraction limit, detection of fluorescing molecules below such limit readily achieved
- multiple fluorescence labelling → several target molecules simultaneously identified





Anal. Chem. **2011**, *83*, 6136–6142



microscopyu.com

Confocal microscopy

- widefield fluorescence µscopy suffers from light emitted from out of focus regions
  → resolution problems (esp. for thickness > 2 µm)

confocal microscopy

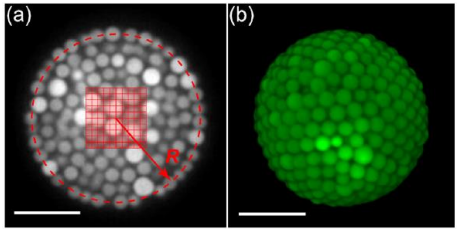
- slight improvem. in axial & radial resolution
- ***main advantage:*** elimination of image degradation by out of focus information
- ***widefield µscopy:*** entire sample (or large part) illuminated by light from a source (lamp)
- ***confocal µscopy:*** a sharply focused laser beam is scanned (point by point) laterally across the sample → optical section

confocal principle

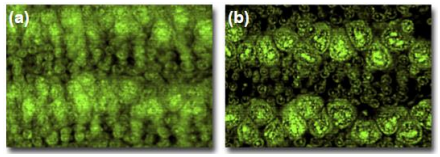
- *laser passes through a 1st pinhole situated in a conjugate plane (confocal) with scanning point on sample & a 2nd pinhole positioned in front of detector*
- *fluorescence from above & below focal plane not confocal with pinhole → most of extraneous light not detected*

Marvin Minsky

microscopyu.com



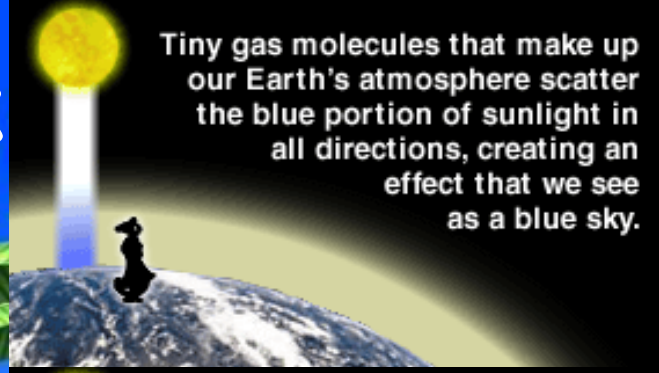
Phys. Rev. Lett. **2016**, *116*, 098302



butterfly pupal wing epithelium

Coffee break

Mario is looking at the sky, wondering:
"Why is it blue and why it turns red during sunset?"



Atomic Force Microscopy (AFM)

Scanning Probe Microscopy (SPM)

"family" techniques in which a sharp tipped probe is moved with atomic precision over/near surface → topography &/or surface forces

Atomic Force Microscopy (AFM)

- very-high-resolution type of SPM, with resolution ~ fractions of a nm
- information by "feeling" or "touching" the sample surface with a sharp tip attached to a flexible cantilever → force measurement
- precise scanning achieved by piezoelectric elements capable of accurate movements

three types of measurements

- ***measurement of tip-sample forces*** *vs.* separation → mechanical properties
- ***imaging:*** 3D topography of surface @ high resolution; scanning & recording tip height corresp. to constant tip-sample interaction
- ***micromanipulation:*** forces used to change sample properties controllably (lithography, local stimulation)

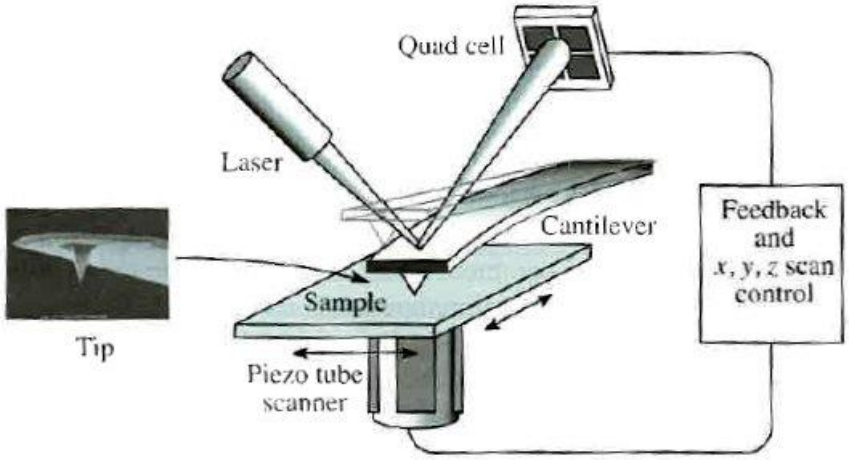
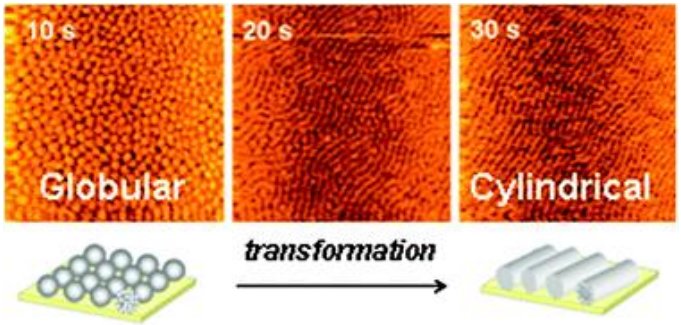
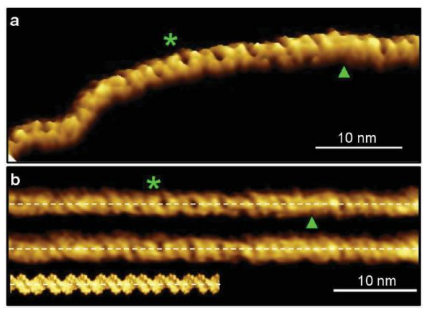


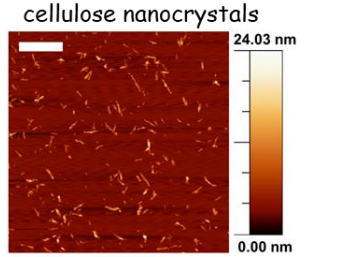
Fig. 4-93: Schematic of Atomic Force Microscopy (AFM), showing the beam deflection system used for vertical motion detection.

Chem. Commun. **2011**, *47*, 4974



Small **2014**, *10*, 3257





Electron microscopy basics

- electrons have wave-like properties (de Broglie)
  → a beam of accelerated electrons can be used for imaging
- resolution of e^- μscopy techniques → full range of interest for colloids & interfaces

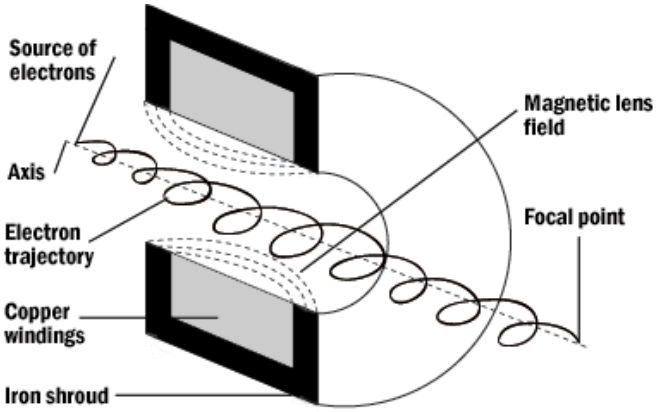
$$\lambda = \frac{h}{\sqrt{2meV}}$$

h: Planck's constant m: electron mass

e: electron charge V: accelerating voltage

- (relativistic effects) ***V*** = 200 keV → **λ** = 2.51 pm
- electron microscopy resolution ~ 0.1 nm
- e^- microscopes use electromagnetic lens systems; analogous to glass lenses of light microscopes

cmrf.research.uiowa.edu

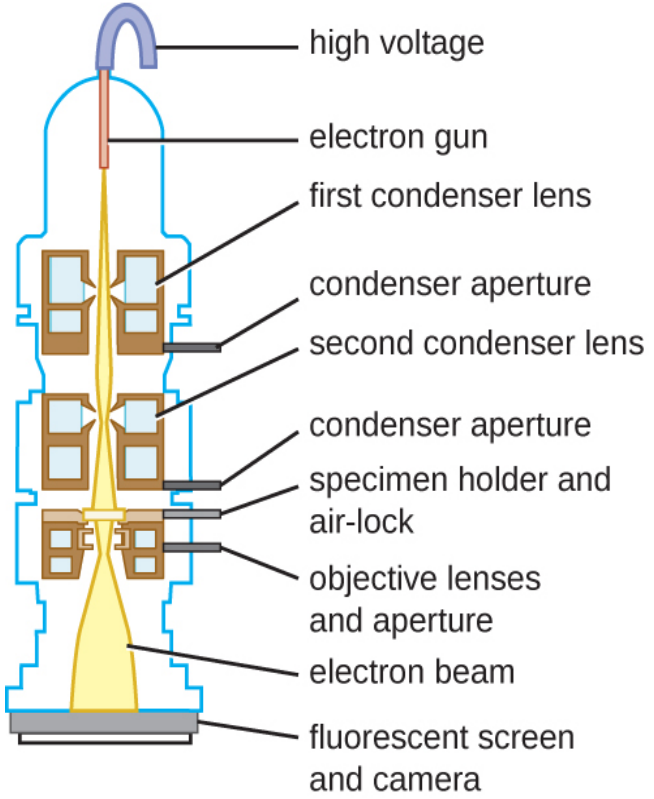


disadvantages

- expensive to build & maintain; high resol. require stability & magnetic field cancelling
- usually samples must be kept in vacuum because air molecules scatter e^- (exceptions: liquid-phase EM, environmental SEM)
- usually samples must be conductive → non-conductive materials require conductive coating (Au/Pd alloy, Os); imaging of non-conductive specimen is improving
- hydrated materials (e.g. biological samples) require stabilization, cutting & staining

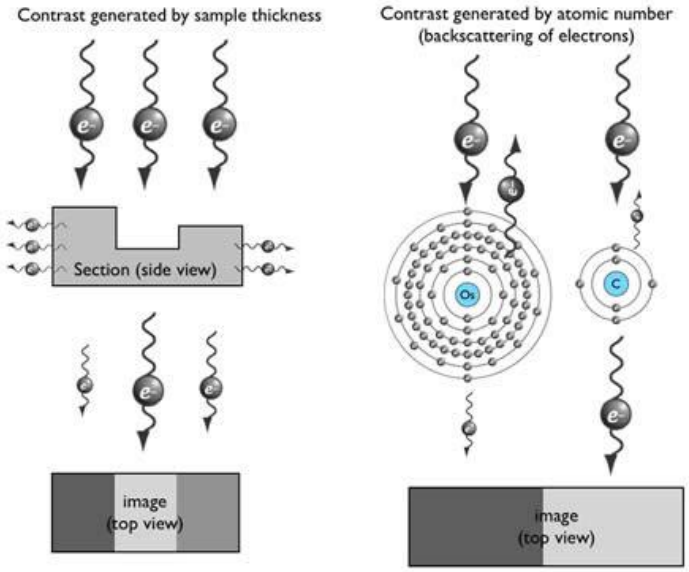
Transmission electron microscopy (TEM)

- demonstrated in 1931 by Max Knoll & Ernst Ruska (Nobel in Physics 1986)
- an e^- beam is transmitted through an ultrathin sample to form an image which is then magnified & focused onto a detector

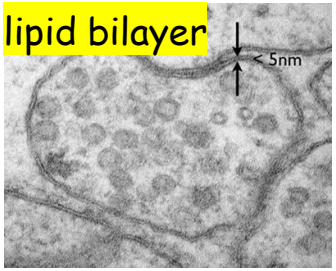


commons.wikimedia.org

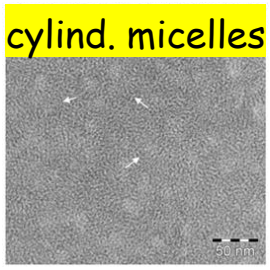
- beam e^- scattered by e^- surrounding the nucleus of atoms → e^- density important
- sample thickness & atomic number define contrast



- samples must be fixed either by chemical x-linking (→ shrinkage, distortion, aggregation…) or rapid freezing under high P
- after fixation → embedding in plastic & cut with diamond knife (thickness < 100 nm)



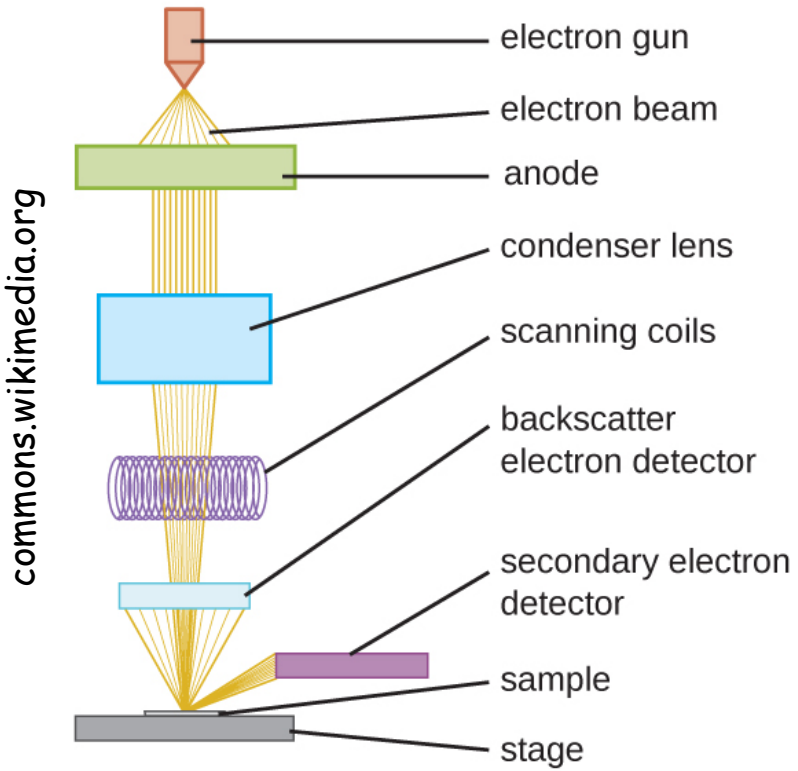
advanced-microscopy.utah.edu



Polymers **2017**, *9*(10), 521

Scanning Electron Microscopy (SEM)

- a focused e^- beam is scanned across a solid surface to generate a variety of signals due to e^- - sample interactions @ various depths
- *various signals:* secondary e^-, back-scattered e^-, X-rays, transmitted e^-, luminescent light
- information about external morphology, chemical composition, & crystalline structure & orientation
- areas ~ 5 μm – 1 cm can be scanned
- *usual* resolution ~ 50 – 100 nm
- *most often:* secondary e^- emitted from near the surface are detected → information about surface features with resolution ~ 1 nm
- back-scattered e^- come from deeper → lower resolution; useful in analytical SEM (+ X-rays)



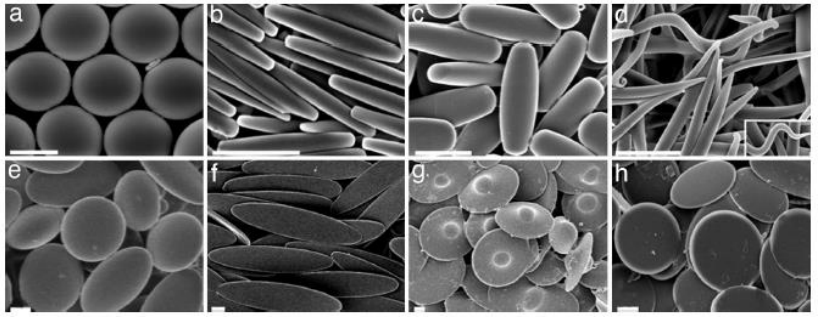
advantages

- versatile imaging technique, easy to use

limitations

- vacuum required (environmental SEM ☺)
- usually conductive coating is required

PNAS **2007**, *104*, 11901



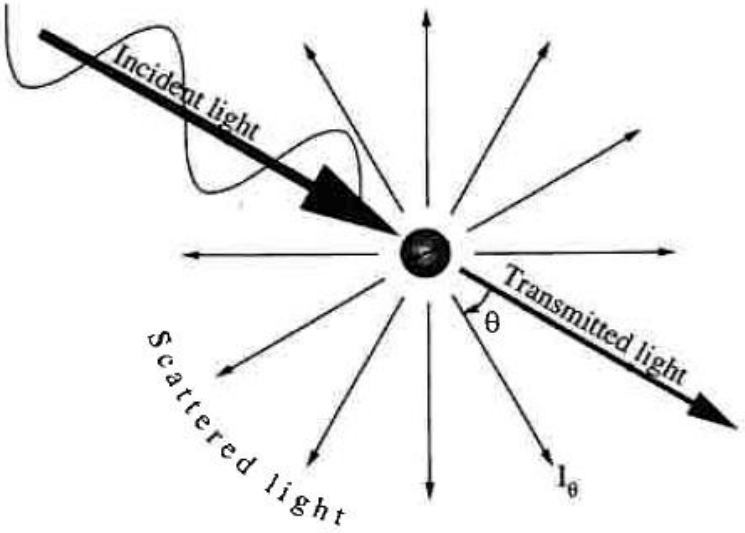
Light scattering basics

scattering from particles (general)

- particles of radius **α** are illuminated with electromagnetic radiation of **λ** comparable or larger than **α** → portion of incident photons are re-radiated (scattered) in all directions
- radiation may be light (**λ** ~ 400 – 700 nm), X-rays or neutrons (**λ** ~ Å)

light scattering from particles

- when light passes through a transparent medium, its oscillating electric field induces synchronous oscillating dipoles in the molecules → re-emission of radiation
- homogeneous medium → light refraction
- inhomogeneous medium due to refractive index variations → light scattering from inhomogeneities
- colloidal dispersions show significant light scattering (Tyndall effect)
- light scattering from colloids depends on particle size, shape, concentrations, refractive indices & spatial arrangement



Ouzo effect

- emulsification & light scattering

youtube.com/watch?v=mkhxY0IGJN4

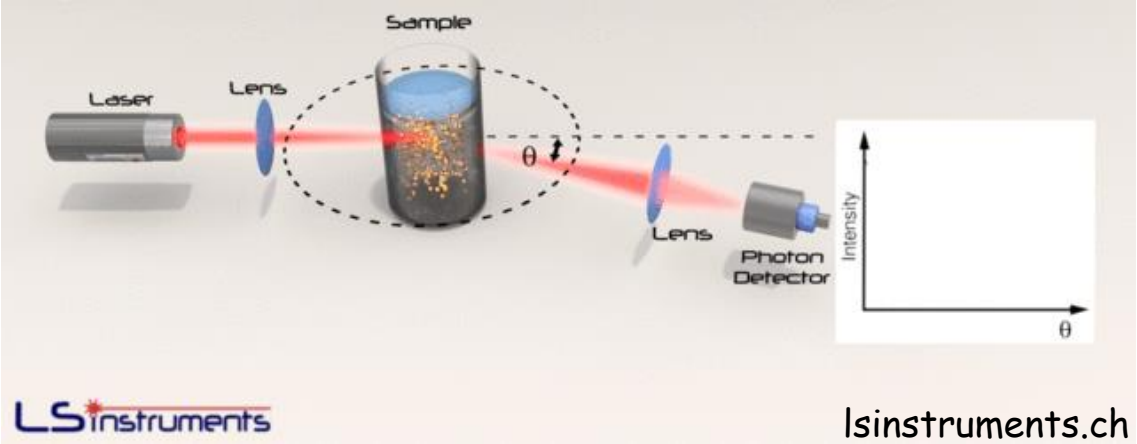
Static Light Scattering

Rayleigh scattering

- scattering from objects (e.g. nanoparticles) with radius α << than the wavelength λ
- scatterers treated as small dipoles oscillating in uniform electric field → radiation

Static Light Scattering

- a laser beam illuminates the colloidal dispersion & detector used to measure the scattering intensity I_θ @ different scattering angles θ
- dipole (& field) induced in particle by laser electric field ∝ particle polarizability
- intensity of scattered light ∝ (induced field)^2
- basic info: v_p if ρ_N is known & vice-versa
- in-situ technique contrarily to direct imaging (SEM, TEM) → sample measured in its natural state (low concentrations)



Rayleigh ratio

$$R_\Theta = \left(\frac{I_\Theta}{I_0}\right)\frac{r^2}{V_s} = \frac{9\pi^2\rho_N v_p^2}{2\lambda^4}\left(\frac{m^2-1}{m^2+2}\right)^2(1+\cos^2\theta)$$

I_0: incident intensity r: detector − scatterer distance

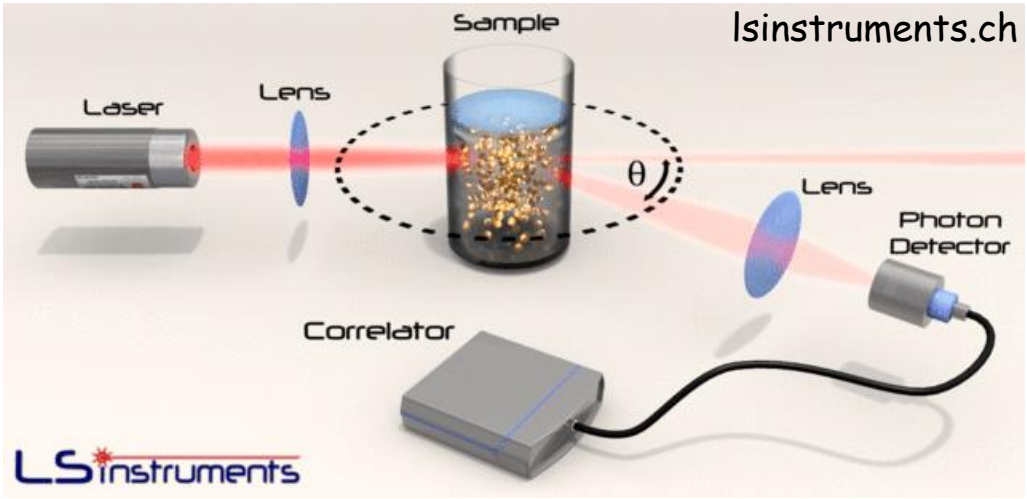
V_s: sample volume ρ_N: particle number density v_p: particle volume

$m = \frac{n_p}{n_m}$ n_p: particle refr. index n_m: medium refr. index

Dynamic Light Scattering

Dynamic Light Scattering

- spectroscopy method to determine size distribution of various objects (polymers, micelles,proteins, particles, emulsions…) in solution/suspension down to 1 nm
- similar setup as in DLS used
- particles move randomly due to Brownian motion; interparticle distance affects interference of scattered waves → scattering intensity fluctuations *vs.* time
- time scale of fluctuations related to particle diffusion rate



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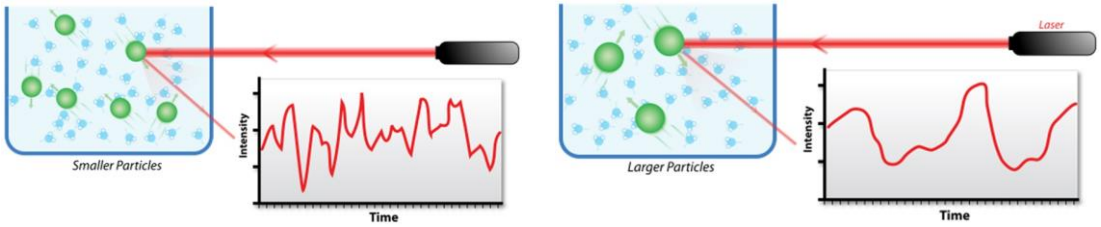


autocorrelation function of scattered intensity

$$G(\tau) = \lim_{T\to\infty} \frac{1}{T}\int_0^T I(t)I(t+\tau)dt = \langle I_S(t)I_S(t+\tau)\rangle$$

τ: time shift T: integration time

$$G(\tau) = A_0 + A\exp(-\Gamma\tau) \qquad \Gamma = Dq^2 \qquad q = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

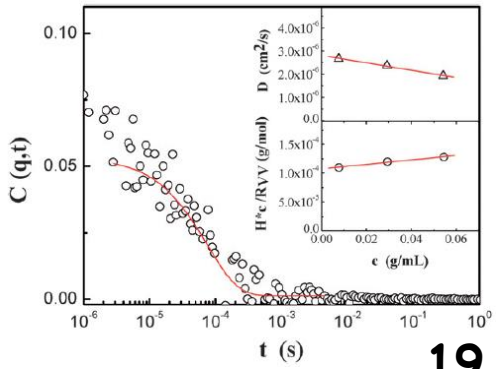
Stokes-Einstein-Sutherland

$$D = \frac{k_B T}{6\pi\eta R_h}$$

η: viscosity of sample

R_h: particle hydrodynamic radius

Soft Matter **2009**, *5*, 4256



THANKS FOR PLAYING!

GAME OVER