Characterization of Polymers and Particles by Analytical Ultracentrifugation

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Analytical Ultracentrifugation

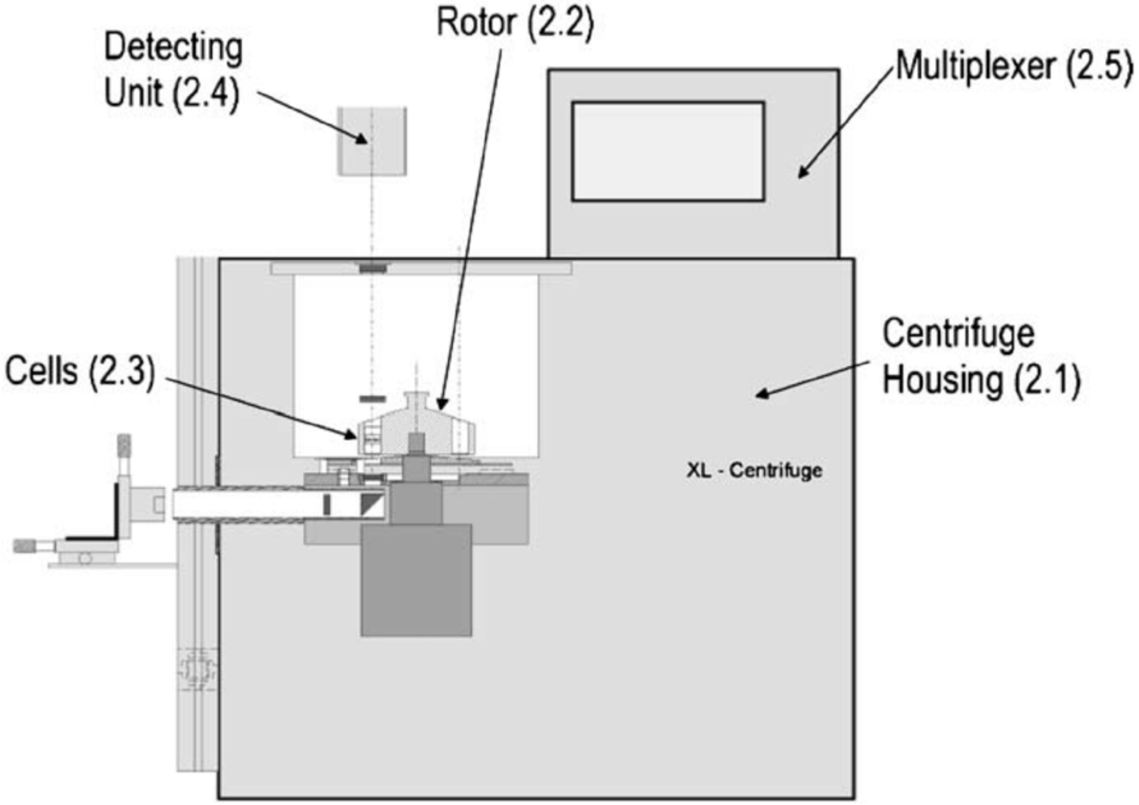
fractionation of particles and molecules by mass difference
(also possible on preparative scale)

accessible molar mass ranges:
about 10^3 to 10^{14} $g \cdot mol^{-1}$

accessible particle sizes:
about 1 nm to 1 µm

Analytical Ultracentrifuge

Beckman, Optima XL-I



rotor speeds: 1000 to 56000 rpm

g-forces 50 to $3 \cdot 10^5$ g

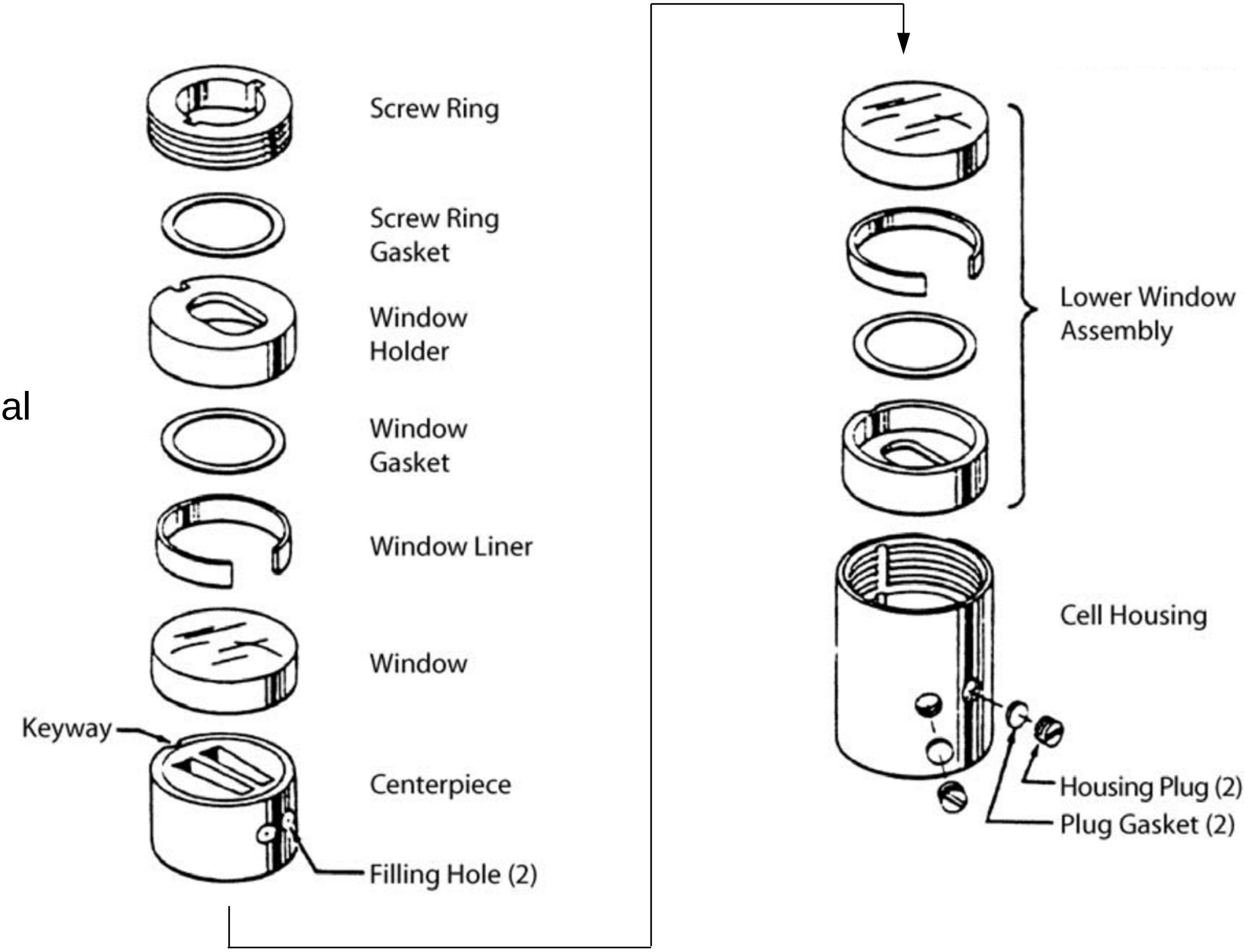
detection systems:

- UV/Vis absorption (200 nm - 800 nm)
- interference optics
- schlieren optics

AUC cell

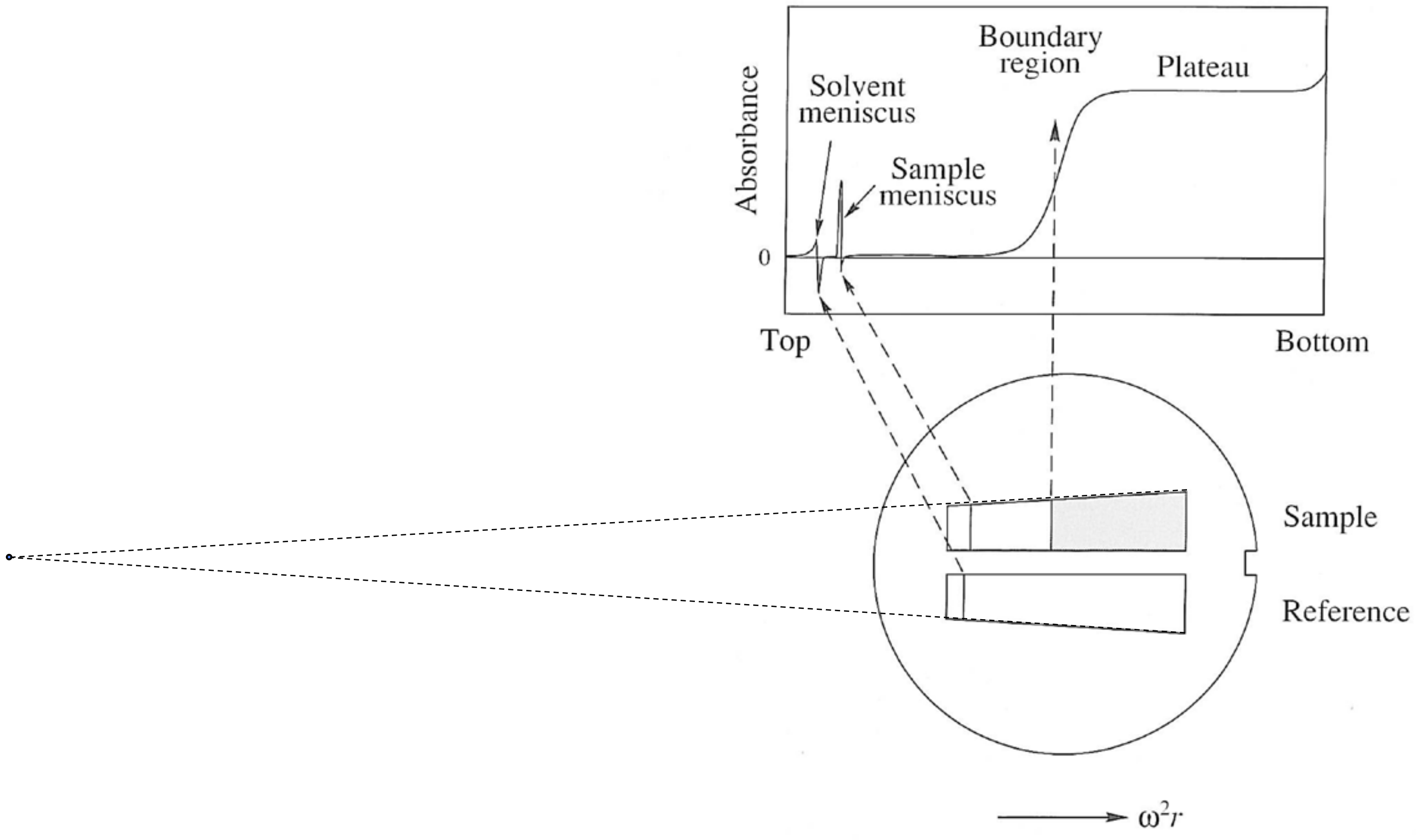
explosion drawing of an AUC cell

high requirements
regarding mechanical
stability and
leak tightness



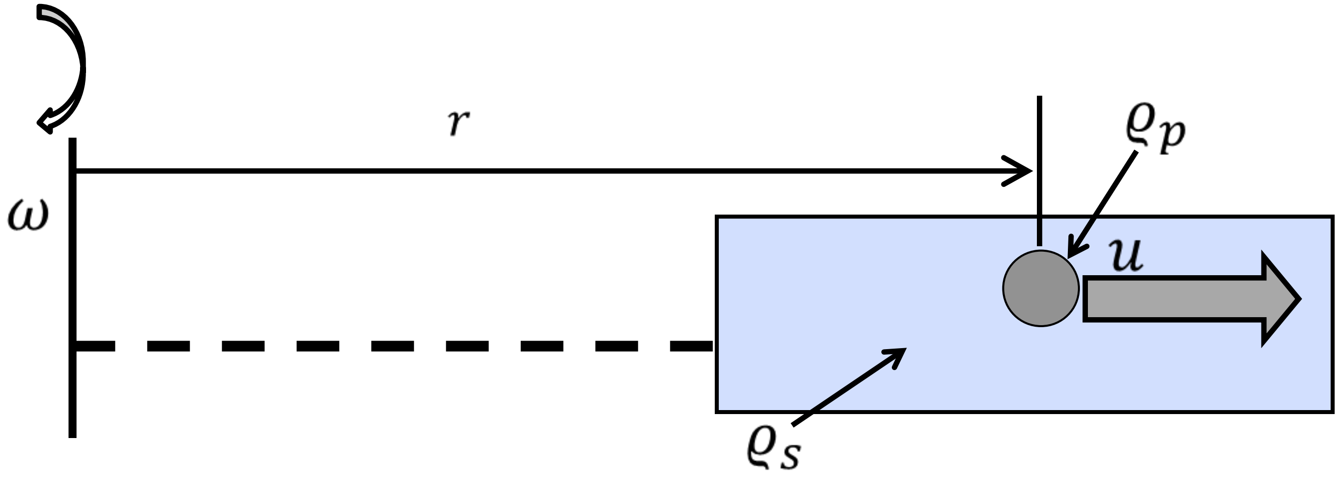
AUC cell

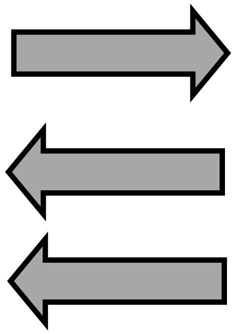
AUC cell in cross section



need for reduction of molecular impacts at the chamber wall
$\Rightarrow$ sample chambers have the form of a circle segment

Theory of Analytical Ultracentrifugation





centrifugal force: F_s

buoyancy: F_b

friction: F_f

molar mass: M
Avogadro no.: N
particle mass: m_p
particle diameter: d_p
friction coefficient: $f = 3\pi\eta_s d_p$
dynamic viscosity: η_s
sedimentation speed: u
density solvent/particle: ϱ_s/ϱ_p
partial specific volume: $\bar{v} = 1/\varrho_p$
diffusion coefficient: D

during centrifugation forces are balanced,
the sedimentation front moves at constant speed u

Theory of Analytical Ultracentrifugation

$$F_s = m_p\omega^2 r = \frac{M}{N}\omega^2 r \qquad F_b = -m_s\cdot\omega^2 r = -m_p\cdot\bar{v}\cdot\varrho_s\cdot\omega^2 r = -\frac{M}{N}\cdot\bar{v}\cdot\varrho_s\cdot\omega^2 r \qquad F_f = -f\cdot u$$

$$F_s + F_b + F_f = 0 = \frac{M}{N}\cdot\omega^2 r - \frac{M}{N}\cdot\bar{v}\cdot\varrho_s\cdot\omega^2 r - f\cdot u$$

$$\frac{M\left(1-\bar{v}\cdot\varrho_s\right)}{N\cdot f} = \frac{u}{\omega^2 r} \equiv s$$

insertion of $f = \frac{kT}{D} = \frac{RT}{ND}$ into $\frac{M\left(1-\bar{v}\cdot\varrho_s\right)}{N\cdot f} = \frac{u}{\omega^2 r} \equiv s$:

$$\boxed{M = \frac{s\cdot RT}{D\cdot\left(1-\bar{v}\cdot\varrho_s\right)}}$$

→ molar masses

insertion of $f = \frac{kT}{D} = \frac{RT}{ND}$ and $f = 3\pi\cdot\eta_s\cdot d_p$ into $\frac{M\left(1-\bar{v}\cdot\varrho_s\right)}{N\cdot f} = \frac{u}{\omega^2 r} \equiv s$:

$$\boxed{d_p = \sqrt{\frac{18\cdot\eta_s\cdot s}{\left(\varrho_p-\varrho_s\right)}}}$$

→ particle sizes

Theory of Analytical Ultracentrifugation

absolute method!

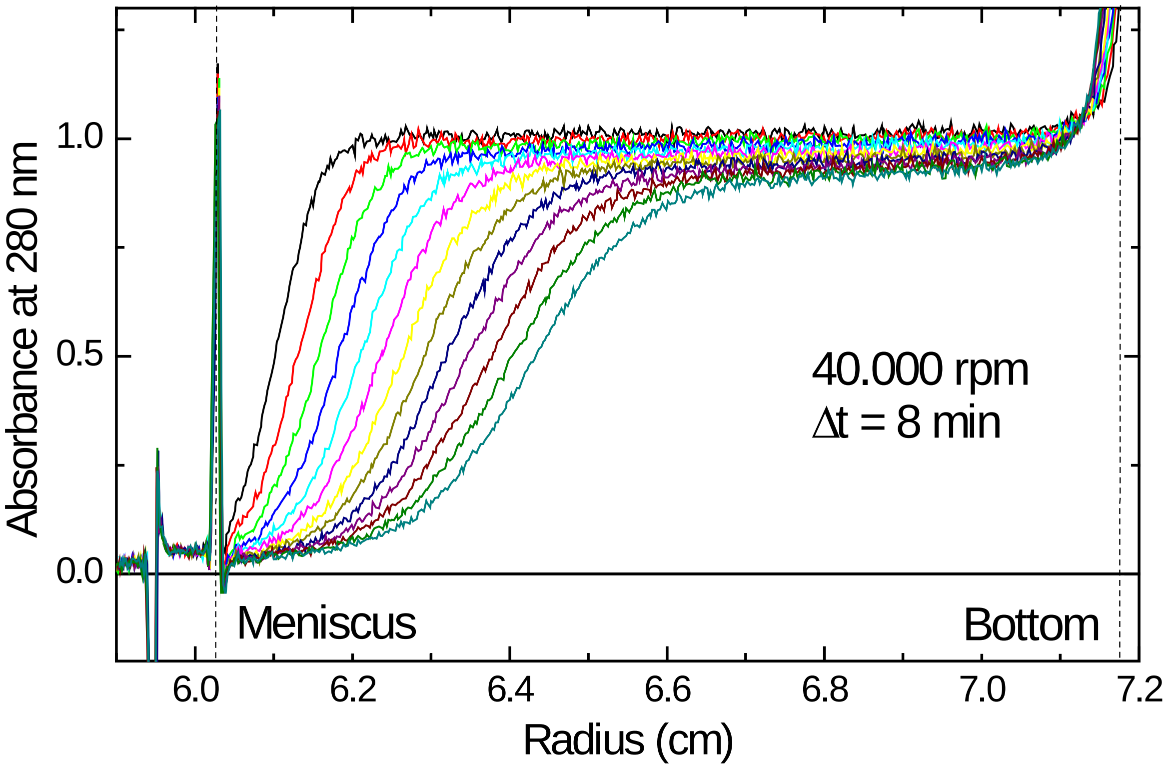
but: auxiliary measurements required!

$$M = \frac{s \cdot RT}{D \cdot \left(1 - \overline{v} \cdot \varrho_{\mathrm{s}}\right)}$$

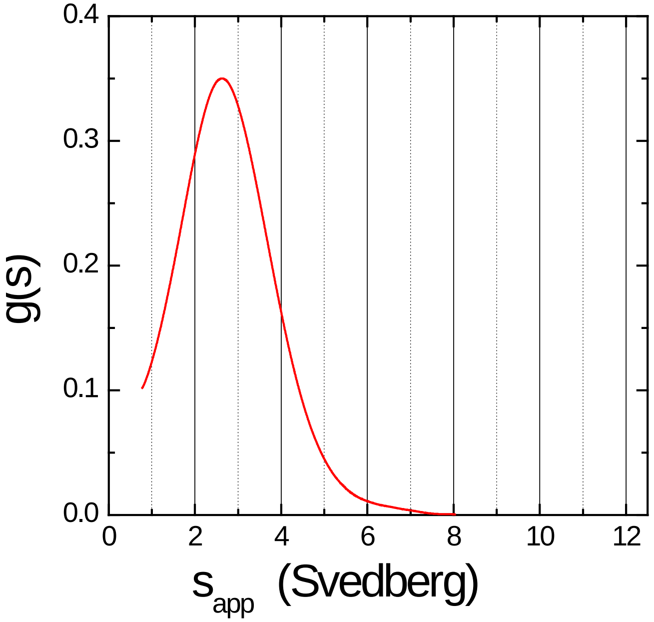
$$d_{\mathrm{p}} = \sqrt{\frac{18 \cdot \eta_{\mathrm{s}} \cdot s}{\left(\varrho_{\mathrm{p}} - \varrho_{\mathrm{s}}\right)}}$$

required: partial specific volume, density of solvent, viscosity

Analytical Ultracentrifugation



analysis of data,
z. B. with Sedfit*

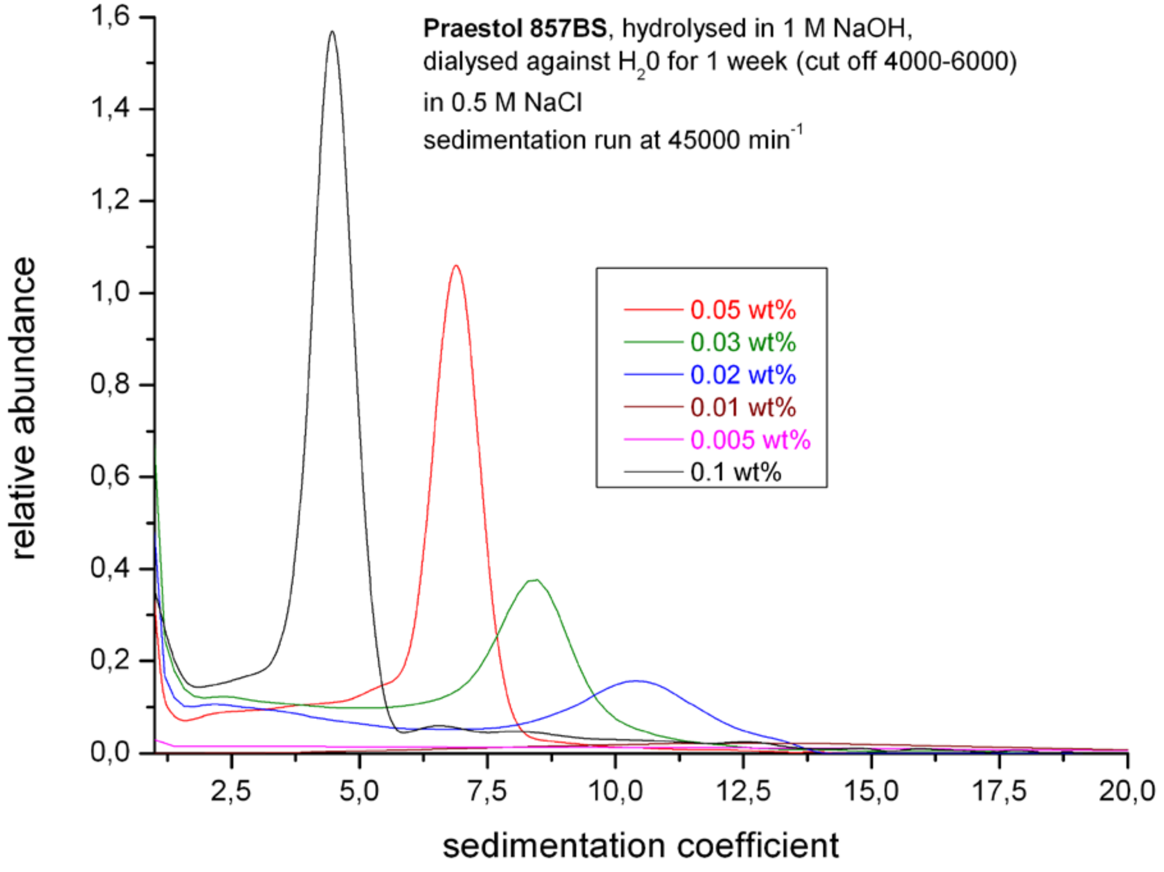


*https://sedfitsedphat.nibib.nih.gov/software/

www.analyticalultracentrifugation.com/download.htm

Molar Mass Calculation by Sedimentation Speed

suited for polymers with medium to very high molar masses



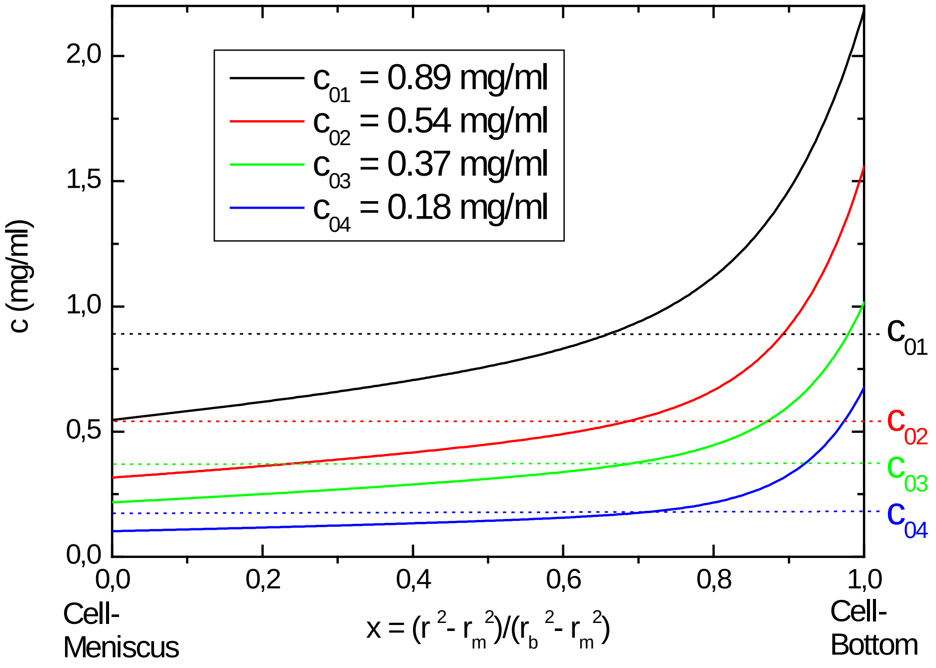
distribution of sedimentation coefficients (and thereby molar mass distribution) is (apparently) concentration dependent

cause:
entanglement of polymer chains

⇒ measurements at lowest possible polymer concentrations

Molar Mass Calculation by Sedimentation Equilibria

suited for polymers with low molar masses



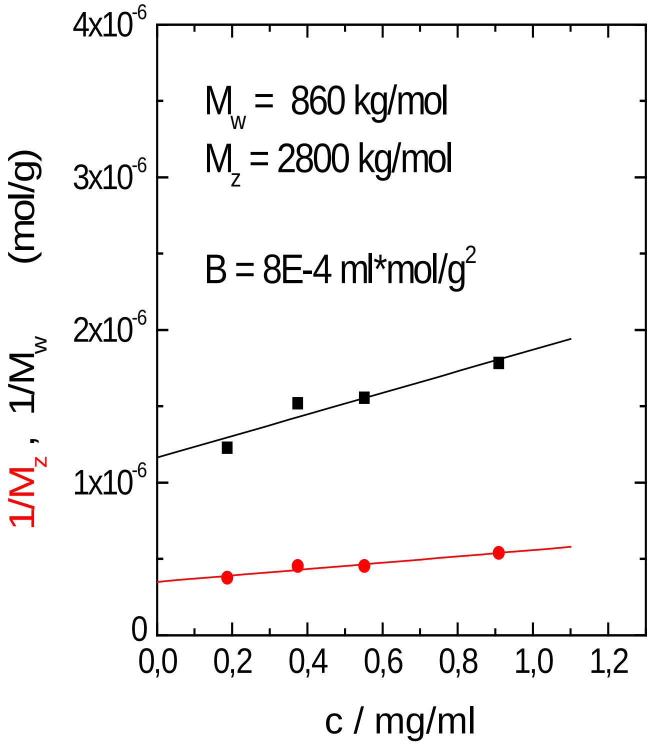
$$M_{w,app} = \frac{c_b - c_m}{\lambda c_o}$$

$$M_{z,app} = \frac{c_b (d\ln c/dx)_b - c_m (d\ln c/dx)_m}{\lambda (c_b - c_m)}$$

with $\lambda = (1-\bar{v}\rho_o)\cdot\omega^2\cdot(r_b^2 - r_m^2)/2RT$

and extrapolation to $c_0 \to 0$ acc. to

$$\frac{1}{M_{app}} = \frac{1}{M} + B\cdot c_o$$

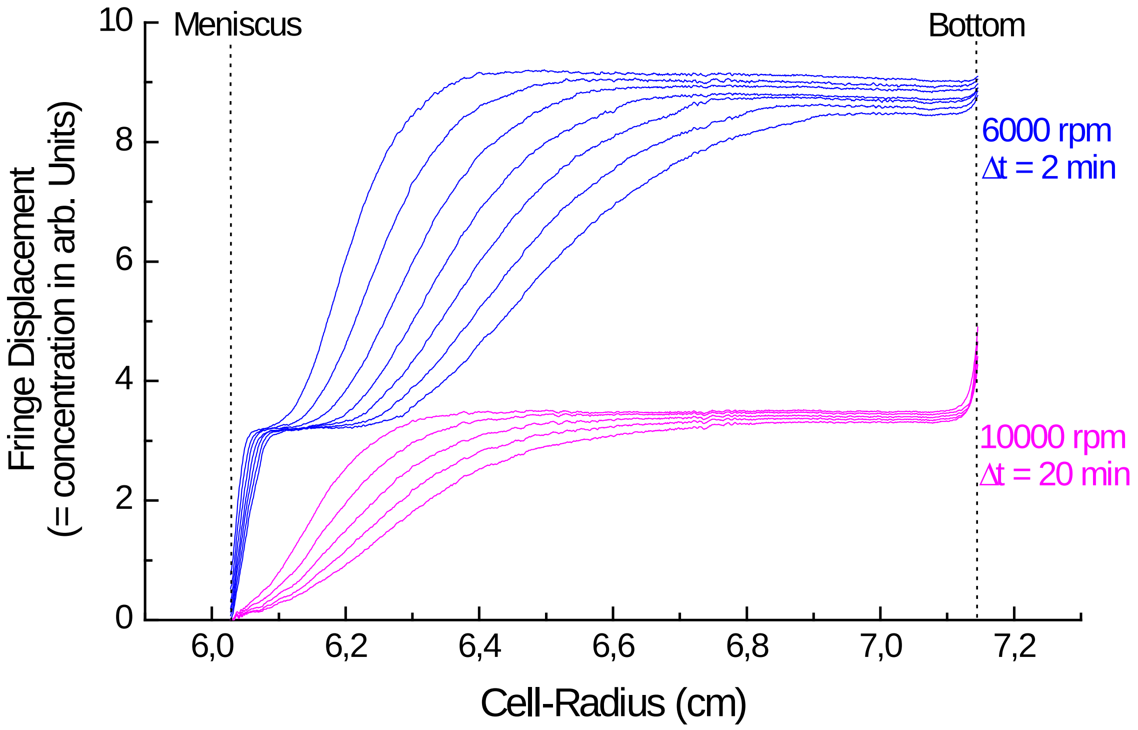


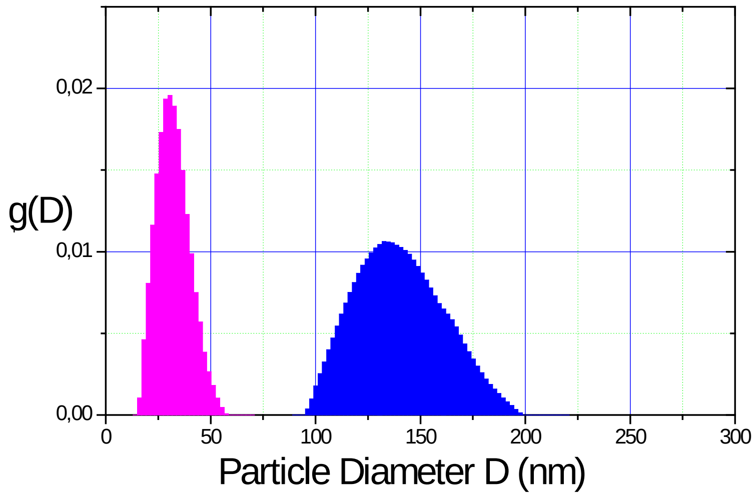
Particle Characterization by AUC

particle size calculation

$$D = \sqrt{\frac{18\eta s}{\rho_P - \rho_0}}$$

sample with complex composition





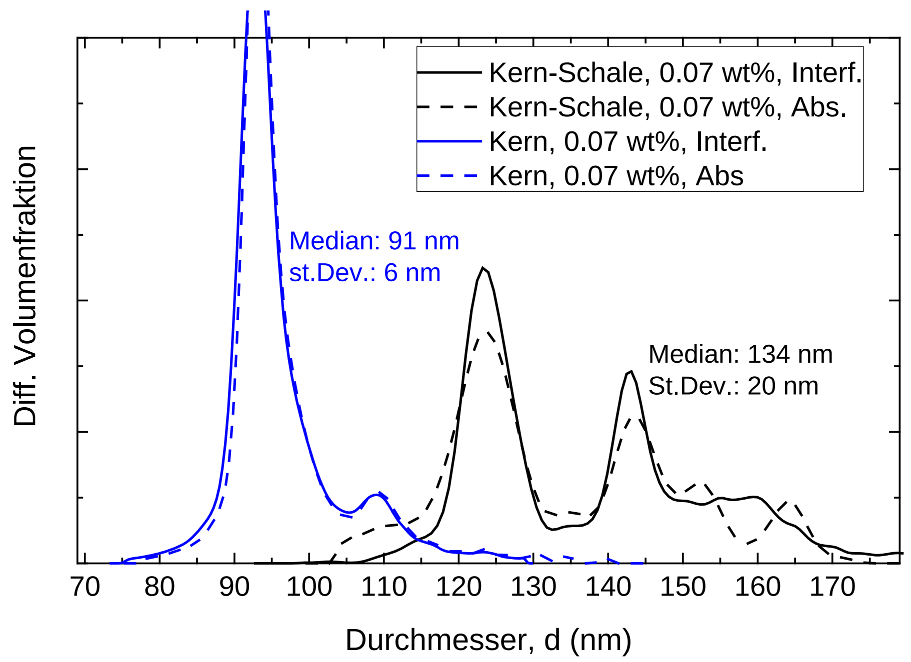
AUC – Practical Examples

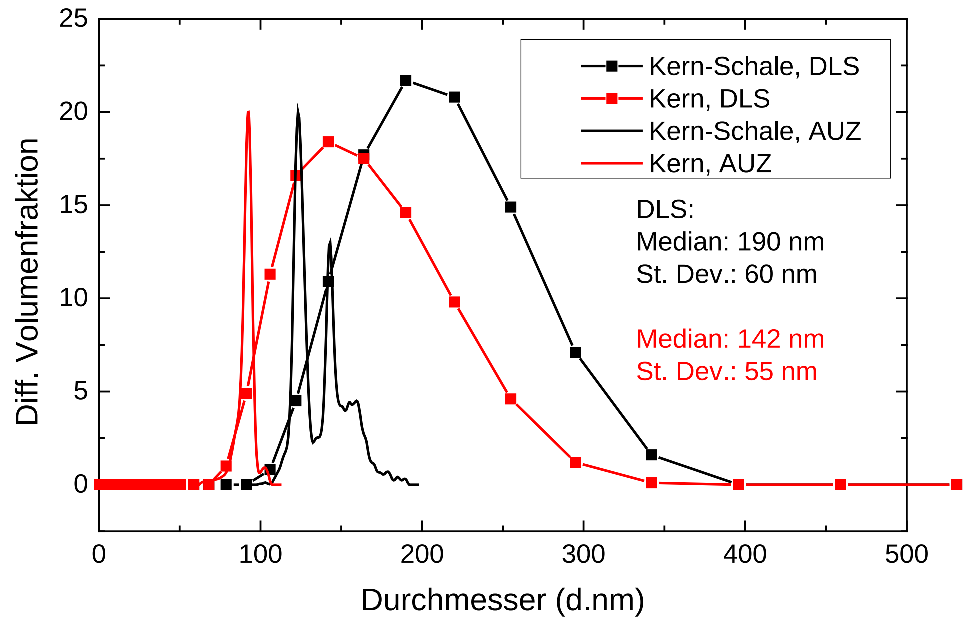
comparison of particle size distribution
by AUC and by dynamic light scattering (DLS):

core-shell particles:
- core polystyrene
- shell poly(butylcyanoacrylate)

provided by Dr. Bernd-Reiner Paulke (IAP)

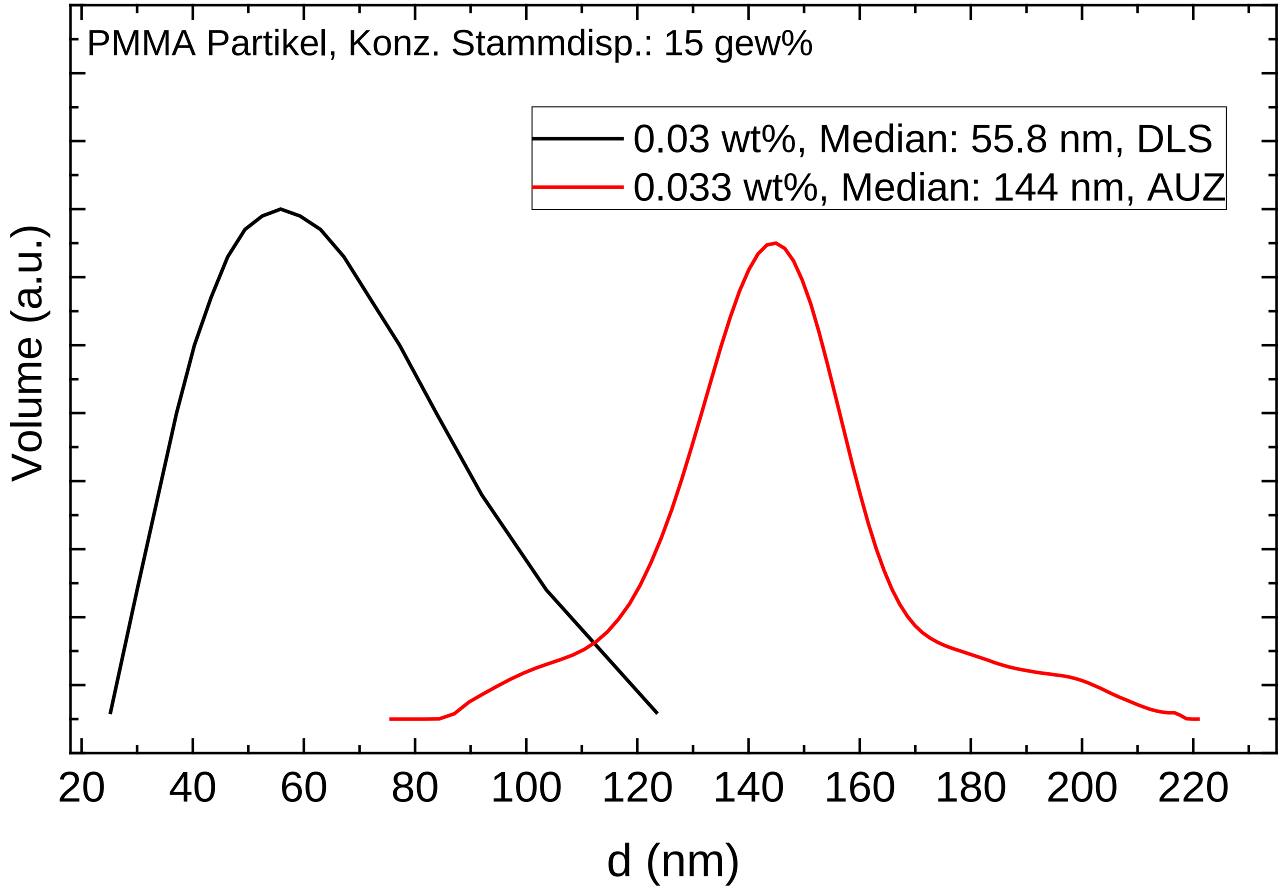
DLS gives by far too broad distributions
correct differentiation only possible by AUC





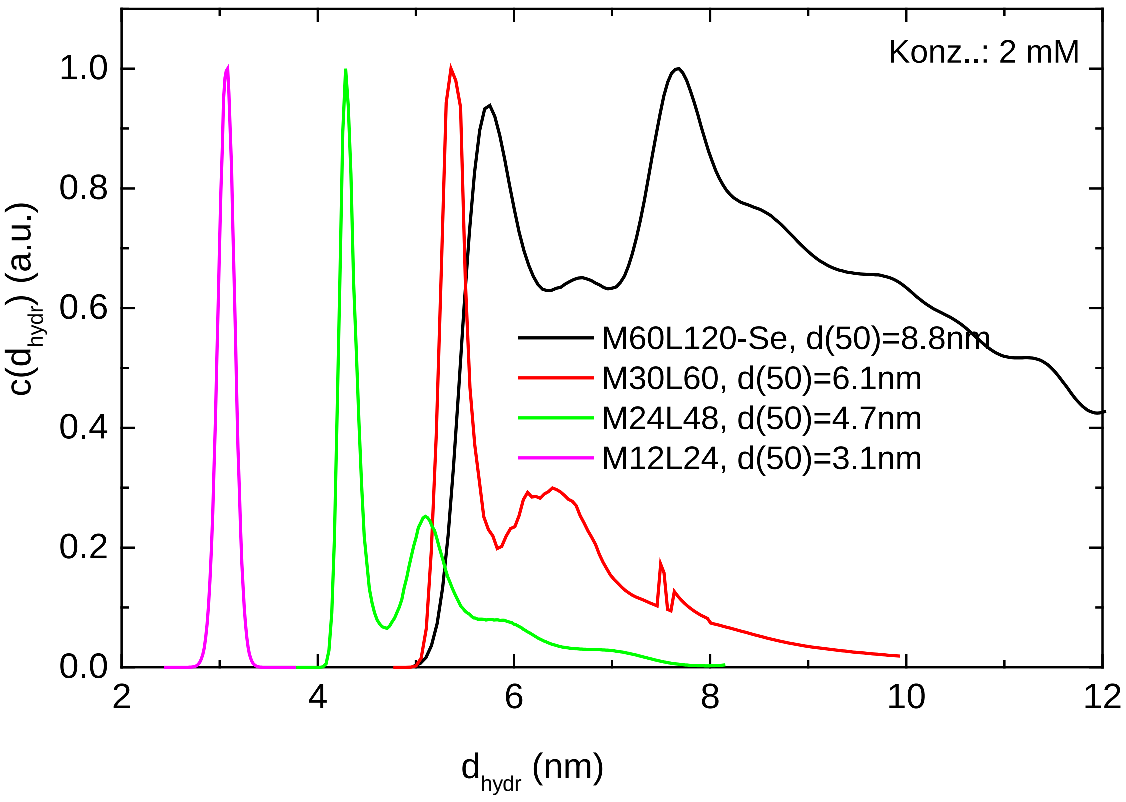
AUC – Practical Examples

DLS often overestimates particle diameters, *but not always*:

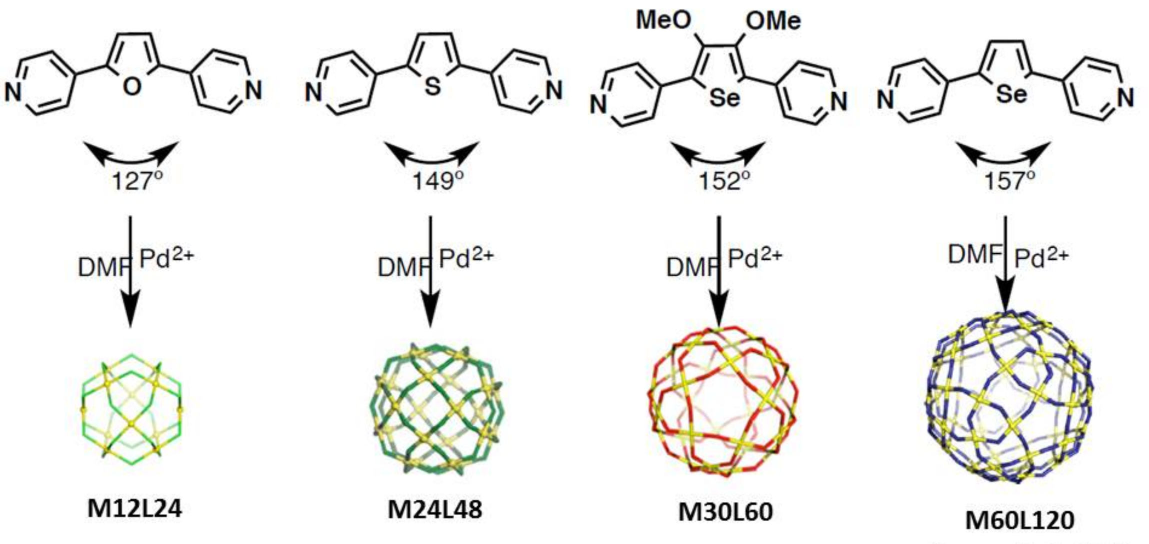


sample: PMMA-Partikel (090528-4L)
density: ρ=1.005 g/cm³
provided by Dr. Bernd-Reiner Paulke (IAP)

AUC – Practical Examples



M_nL_{2n} polyhedra with metal ions and ligands



Source: Daishi Fujita

provided by Dr. Daishi Fujita (Uni Tokio)

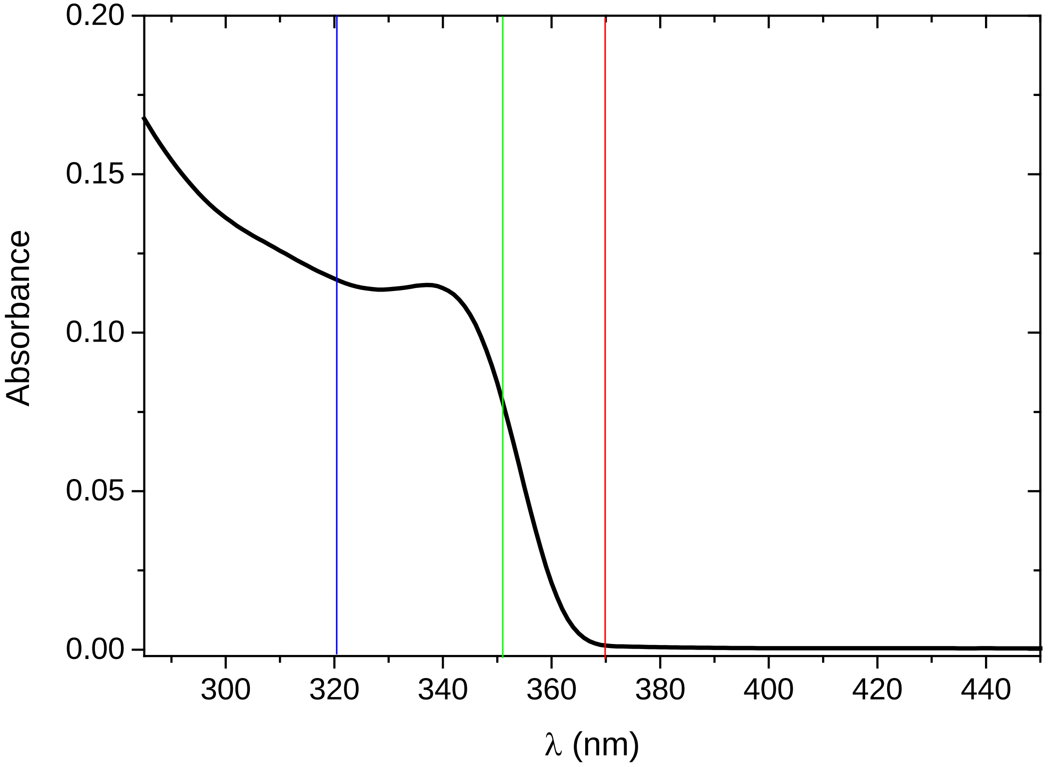
Ligand	d_0 [nm]	d_{peak} [Sved]	d_{th} [nm]
M12L24	3.1	3.1	3.5[a]
M24L48	5.0	4.4	4.5[a]
M30L60	6.6	5.3	5.0[a]
M60L120-Se	9.0	7.7	7.2[b]

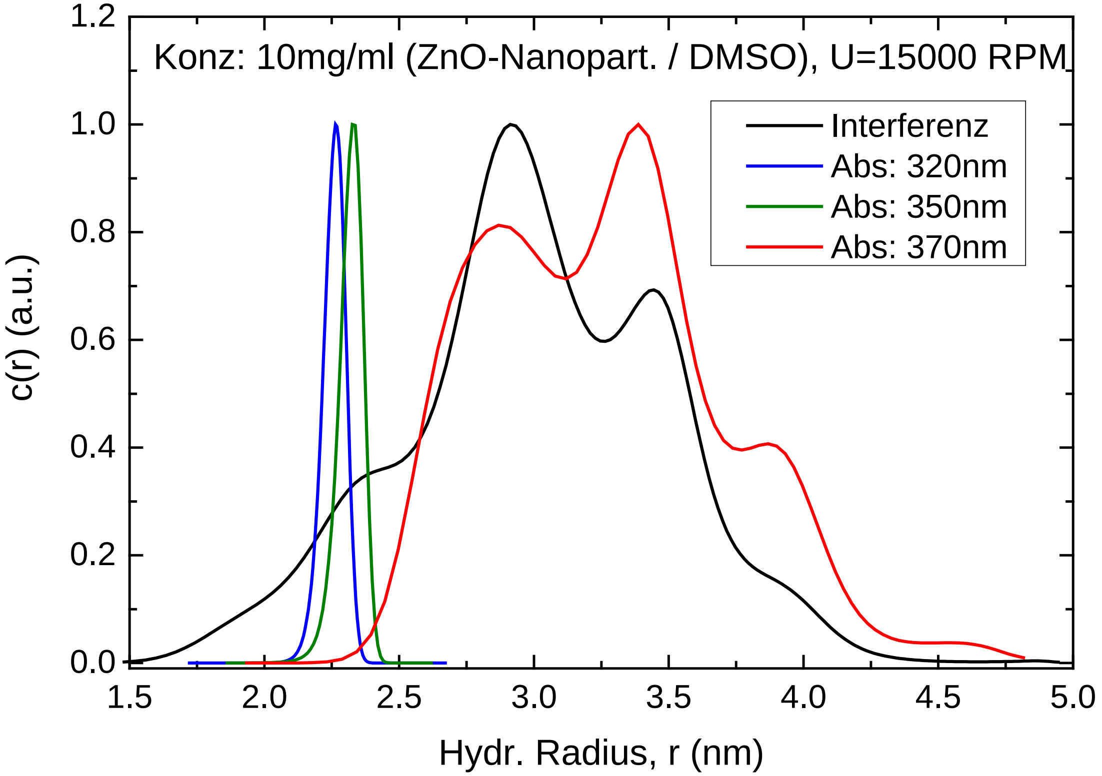
AUC – Practical Examples

analytical question: reason for diverging colors in nanoparticles

quantum confinement or *defects in crystal structure*

sample: ZnO nanoparticles with PEG shell
provided by Dr. Piotr Cywinski (IAP)





diverging colors stem from nanoparticles of different sizes

Summary

Analytical Ultracentrifugation (AUC)

- advantages
  - suitable for particles and dissolved macromolecules
  - extremly wide dynamic range for molar mass characterisation (11 orders of magnitude!)
  - absolute method (no need for calibration)
  - provides more realistic size distributions than other methods
  - potential to solve complex analytical problems

- disadvantages
  - laborious method
  - auxiliary measurements required
  - quality of results dependent on auxiliary measurements