Workshop
HDR-MULTIFIT
Analysis of Turbidity Data and Determination of Particle Size Distributions

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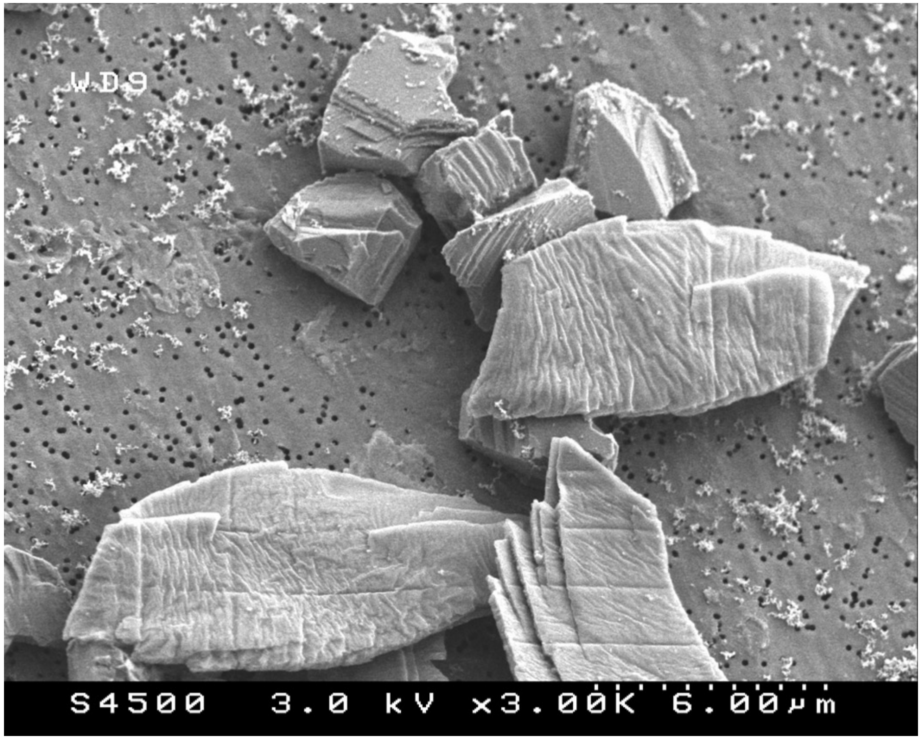
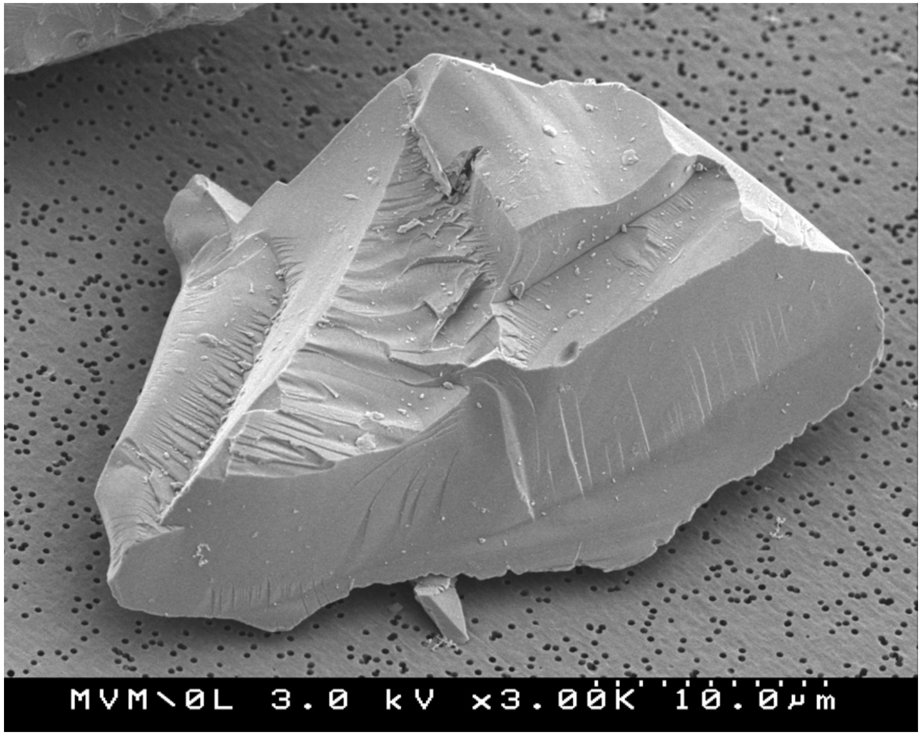
Quartz Particles





What is the size of these particles?

Geometrical particle features - Length

Main dimensions are

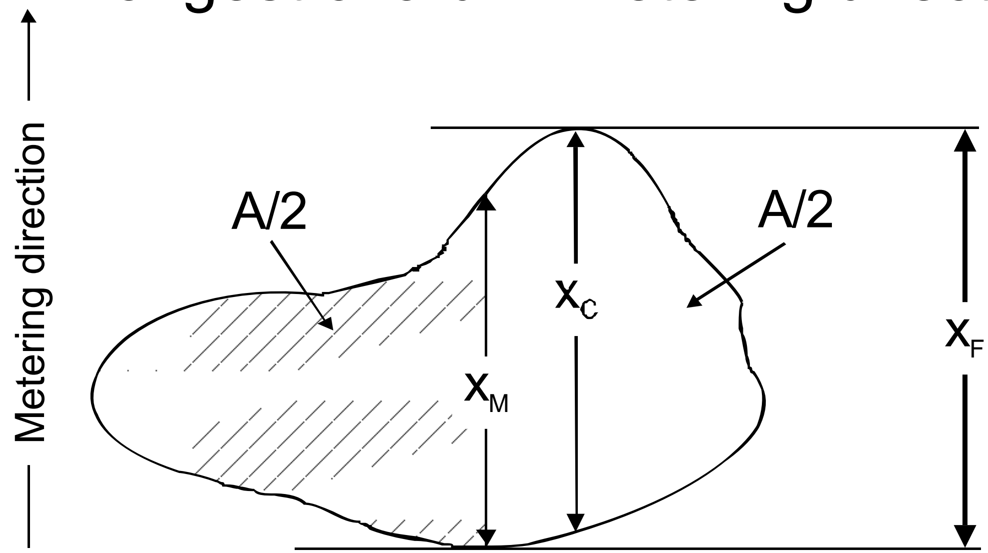
- Feret diameter x_F

  (distance between to parallel tangents)

- Martin diameter x_M

  (length of the chord which bisects the projected area of the particle)

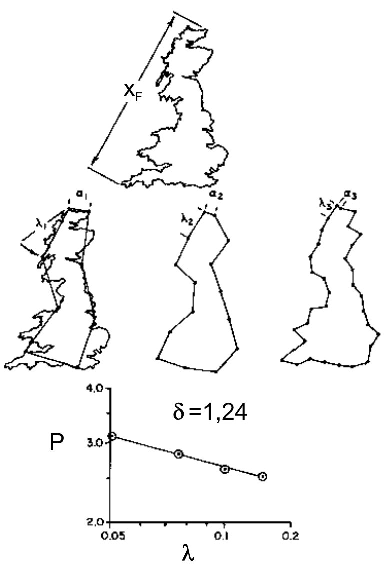
- Longest chord in metering direction x_c



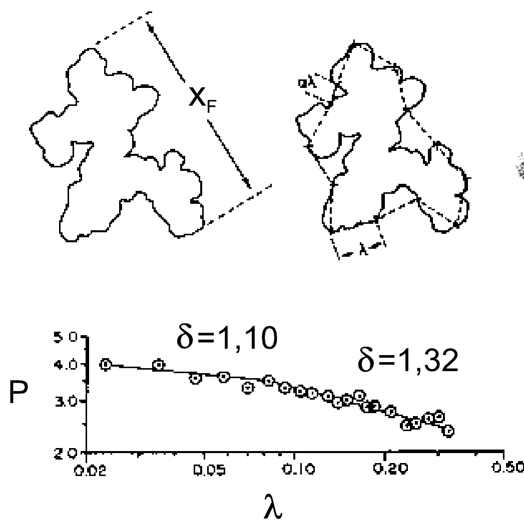
Fractal analysis (Mandelbrot)

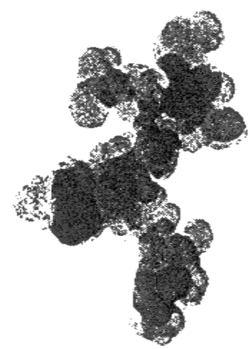
- Perimeter P of an object is measured with a measuring stick with length λ (both normalised with x_F).
- The smaller λ, the more precisely the contour can be represented.
- The non-linear correlation between perimeter and measuring stick is characterized with the fractal dimension $\delta = 1 - m$.

England's Coastline

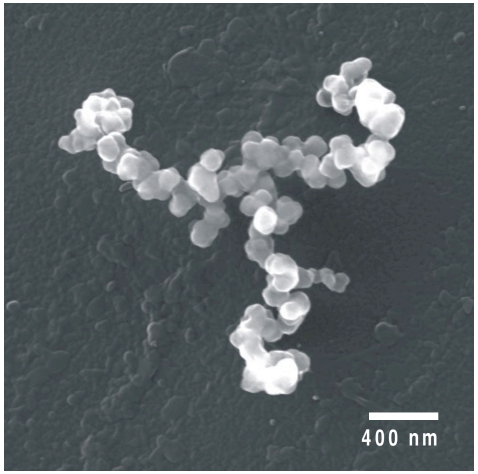


Carbon Black Particle





Nanoparticles after gasphase synthesis



$$\lambda = \frac{\text{Measuring Stick}}{x_F} \qquad P = \frac{\text{Perimeter}}{x_F} \qquad P = \text{const} \cdot \lambda^{1-m} + \alpha$$

Shape transformation by sintering

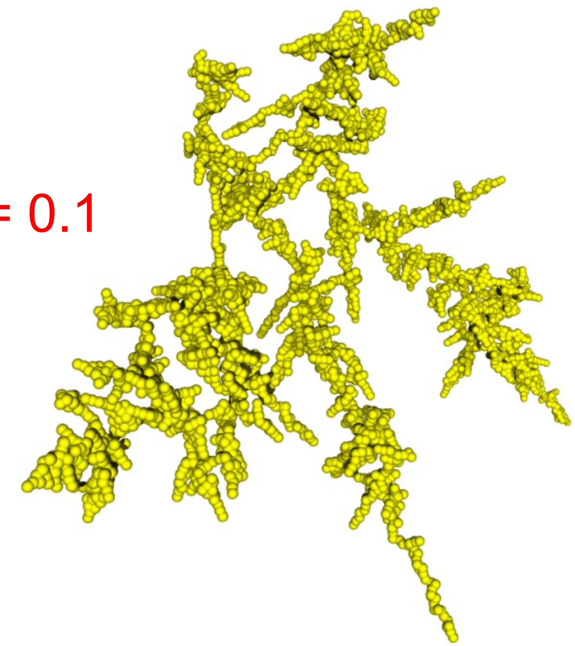
Aggregate formation by coagulation of particles in the gas phase

τ_f = dimensionless time for sintering

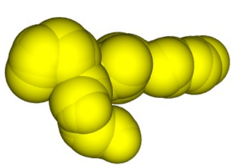
τ_f = 0: no sintering; $\tau_f = \infty$ immediate sintering

$\tau_f = 0$
$\delta = 1.8$

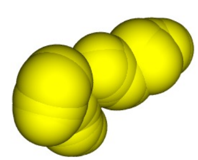
$\tau_f = 0.1$



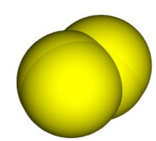
Schmid H., J. Nanoparticle Technology 2004



$\tau_f = 0.75$

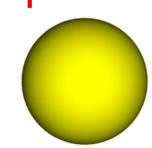


$\tau_f = 1.0$



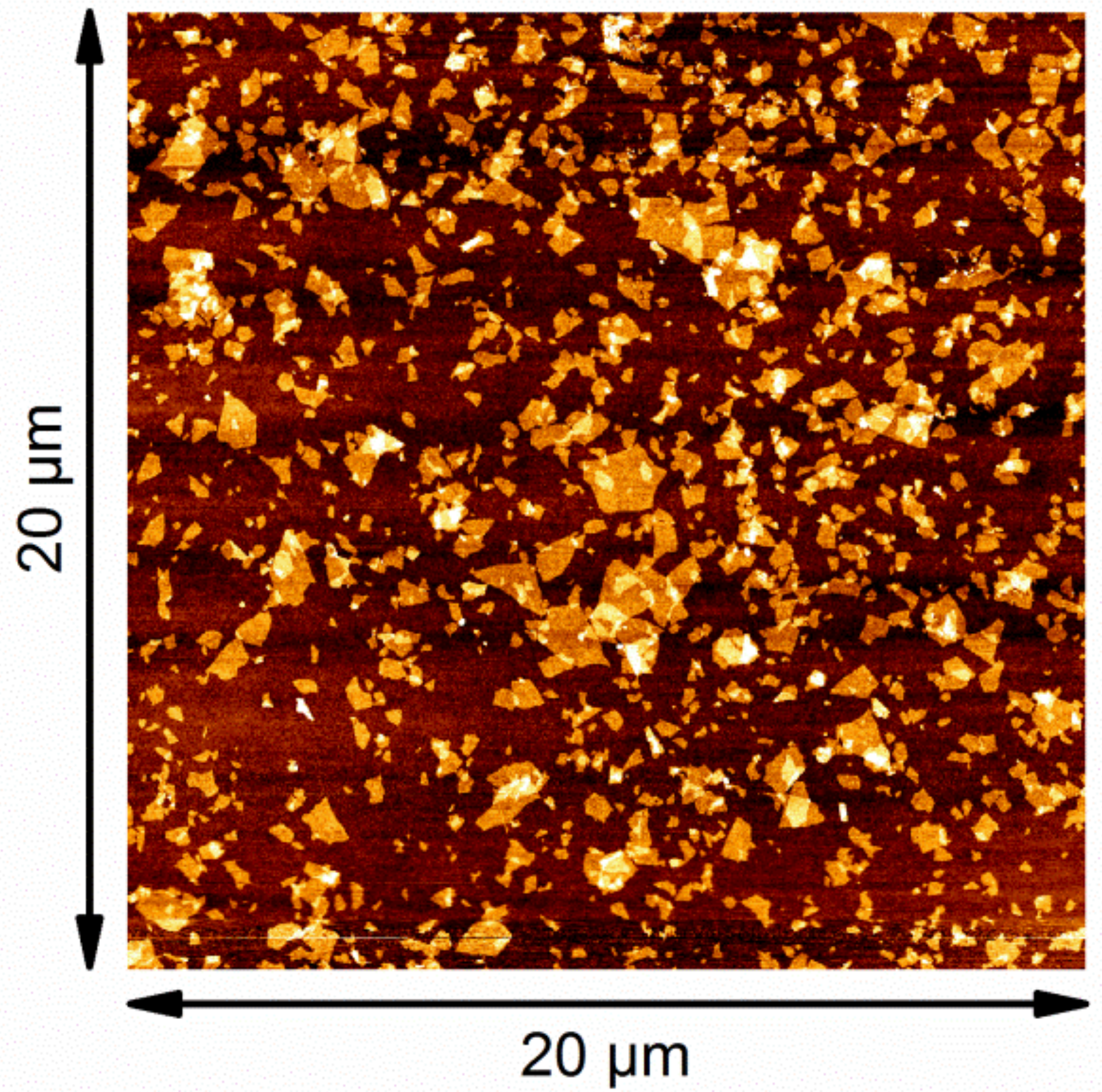
$\tau_f = 4.0$

Volume equivalent sphere



$\tau_f = \infty$
$\delta = 3.0$

AFM image of graphene oxide platelets



Categories of Measurements

Equivalent Size & Distribution

Measurement Techniques

Equivalent size = disperse property:

Measured size: use physical effects

 Sphere with equal behavior

‚size' with respect to a __single__ property

Measurement duration

Measurement point

Equivalent diameter

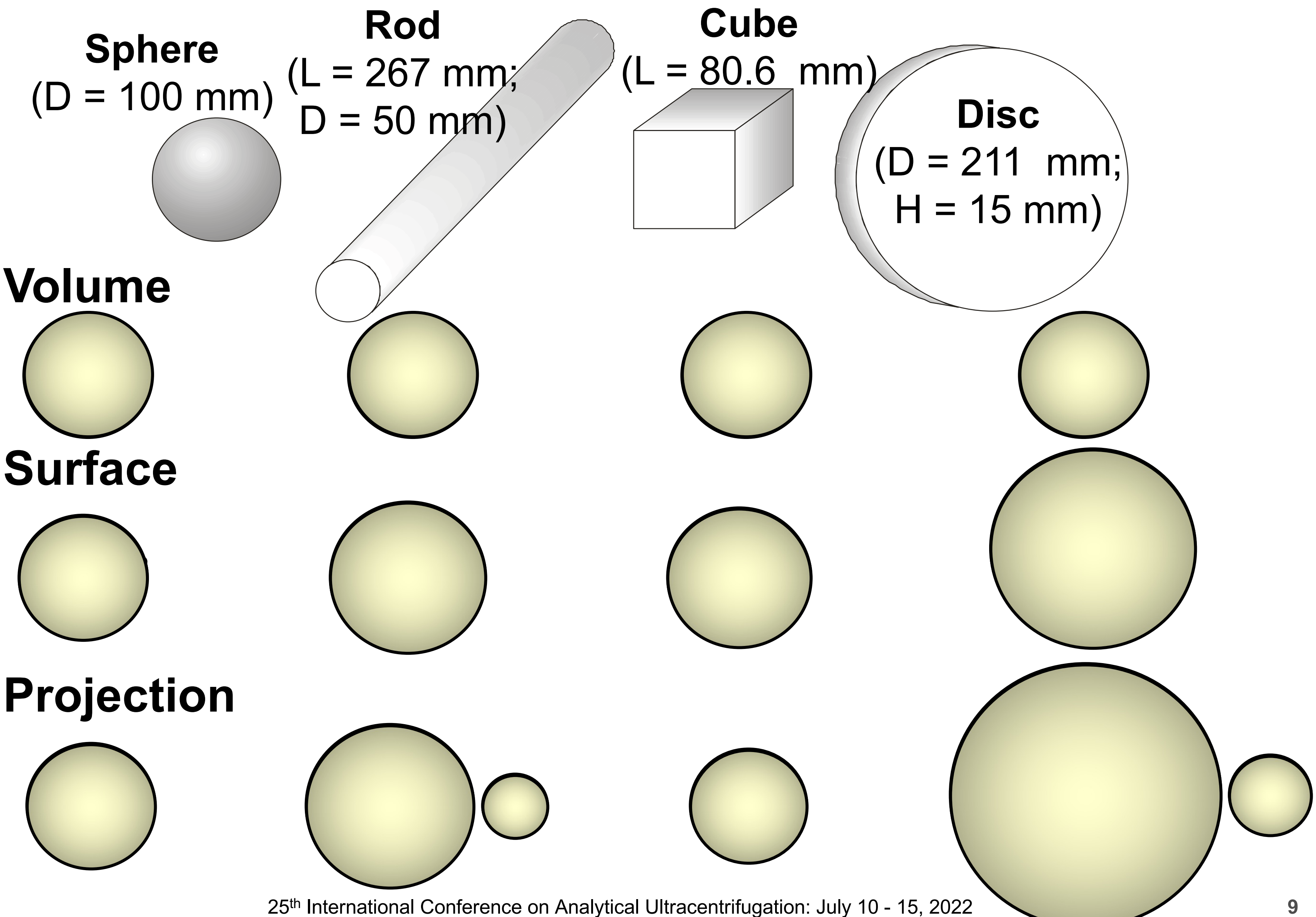
...is the diameter of a sphere with the same physical properties as the irregular particle.

Different physical measuring techniques → Different values of equivalent diameter

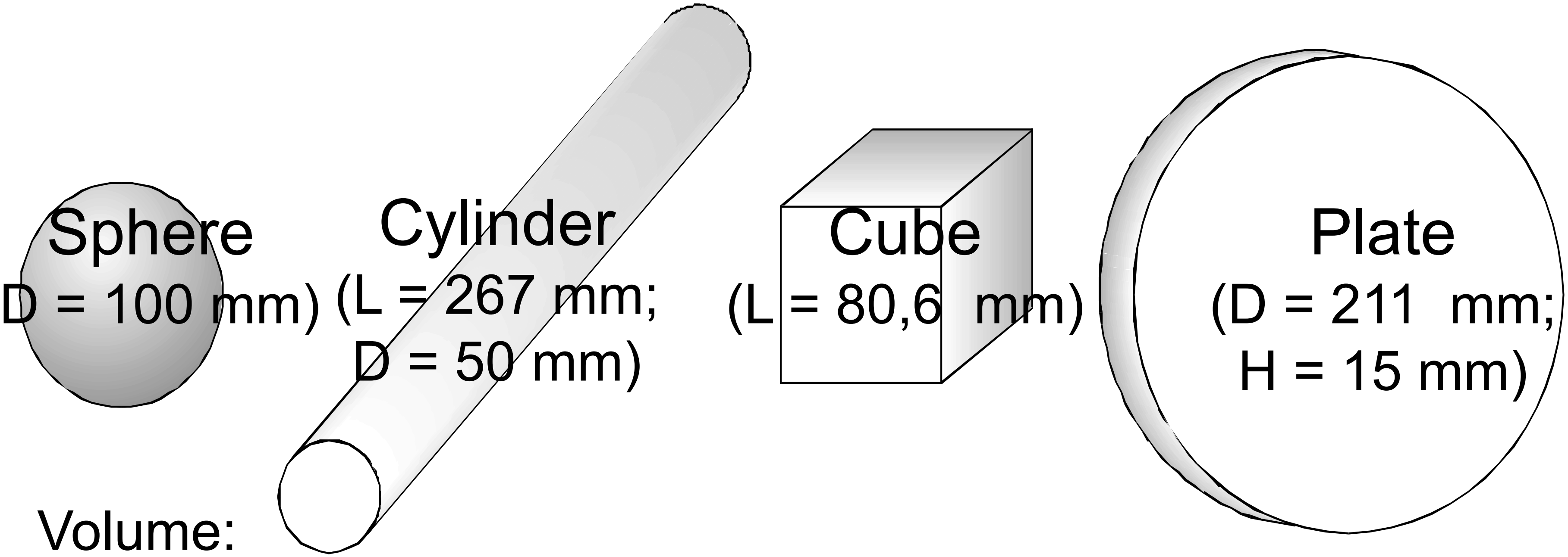
➢ Some important equivalent diameters are:

- Diameter x_S of a sphere with the same **surface area**
- Diameter x_A of a sphere with the same **projection area** (in a fixed position)
- Diameter x_V of a sphere with the same **volume**
- Diameter x_w of a sphere with the same **settling velocity**
- Diameter x_H of a sphere with the same **diffusion coefficient**
- Diameter x_{SL} of a sphere with the same **light scattering intensity**

Equivalent Sizes (e.g. geometric)



Examples of equivalent volume diameter



Sphere	Cylinder	Cube	Plate
(D = 100 mm)	(L = 267 mm; D = 50 mm)	(L = 80,6 mm)	(D = 211 mm; H = 15 mm)

Volume:

523,6 cm^3	523,6 cm^3	523,6 cm^3	523,6 cm^3

Surface area:

314,2 cm^2	458,7 cm^2	389,8 cm^2	798,8 cm^2

Projection surface area:

78,5 cm^2	133,5 cm^2 (19,5 cm^2)	65,0 cm^2	346,7 cm^2 (31,7 cm^2)

Concept of equivalent diameters

Goal:

Reduce complex description particle geometry to a single number!

Definition:

Determination of a unique and single particle ***property***

Equivalent diameter = diameter of a sphere that matches this ***property***

Background:

For spheres theoretical models and simulations are available.

⇨ Calculate particle behavior on the basis of the predetermined property

Equivalent Sizes

- **Geometric particle characteristics**
  - one dimensional
  - two dimensional
  - three dimensional (volume, mass)

- **Particle characteristics ‘translation/velocity’**
  - sedimentation velocity (‘Sinkgeschwindigkeit‘)
  - Inertia (‘Trägheit‘)
  - (electric.) mobility
  - diffusion

- **Particle characteristics ‘Interactions‘ with fields/waves**
  - Electric field disturbances
  - Light scattering / diffraction / extinction
  - Ultra-sound extinction

Shape factor

… is the ratio between two equivalent diameters of the same particle x_A and x_B.

$$\Psi_{A,B} = x_A / x_B$$

“Sphericity” $\Psi_{V,S}^2 = x_V^2 / x_S^2 \leq 1$

(Wadell, 1932):

The value of 1 corresponds to a sphere. Smaller values denote an increasing deviation from the sphere.

Surface

Cauchy-Theorem: $S = 4\,A$

with Projection Area: $A = \frac{\pi}{4} x^2$

Surface: $S = \pi\, x^2$

Specific surface area

Specific surface by volume: $$S_V = \frac{\text{Surface}}{\text{Volume}} = \frac{\pi \cdot x_S^2}{\pi/6 \cdot x_V^3}$$

Specific surface by mass: $$S_M = \frac{\text{Surface}}{\text{Mass}} = \frac{S}{\rho \cdot V} = \frac{S_V}{\rho}$$

For spheres: $S_V = 6 / x$, where $x_S = x_V = x$

For any particle feature M is: $x_V = \Psi_{V,M} \cdot x_M$ $x_S = \Psi_{S,M} \cdot x_M$

It follows : $$S_V = 6 \frac{\Psi_{S,M}^2}{\Psi_{V,M}^3} \frac{1}{x_M}$$

Categories of Measurements

Equivalent Size & Distribution

Measurement Techniques

Distribution:

- Kind of quantity which is detected
- Type of distribution
  * Approximating function (➠ parameter)
  * Complete distribution (➠ resolution)

Measurement duration

Measurement point

Cumulative distribution and density distribution

Cumulative distribution:

Number of particles which are equal to or smaller than a certain particle size

$$Q_r(x) = \frac{\text{Sum of all particles with size } x \leq x_i}{\text{Total quantity}}$$

Density distribution:

Number of particles, whose size lies within a certain particle size interval

$$q_r(\bar{x}_i) = \frac{\text{Amount in interval between } x_i \text{ and } x_{i+1}}{\text{Interval length } (x_{i+1} - x_i) \cdot \text{Total quantity}}$$

Notice the dimensions: $Q_r(x)$: [-] ,$q_r(x)$: $[L^{-1}]$

Resulting in:

$$Q_r(x_{min}) = 0 \text{ and } Q_r(x_{max}) = 1 \qquad q_r(\bar{x}_i) = \frac{Q_r(x_{i+1}) - Q_r(x_i)}{x_{i+1} - x_i} = \frac{\Delta Q_r(x_i)}{\Delta x_i}$$

Particle ensembles are characterized by their **physical features**:

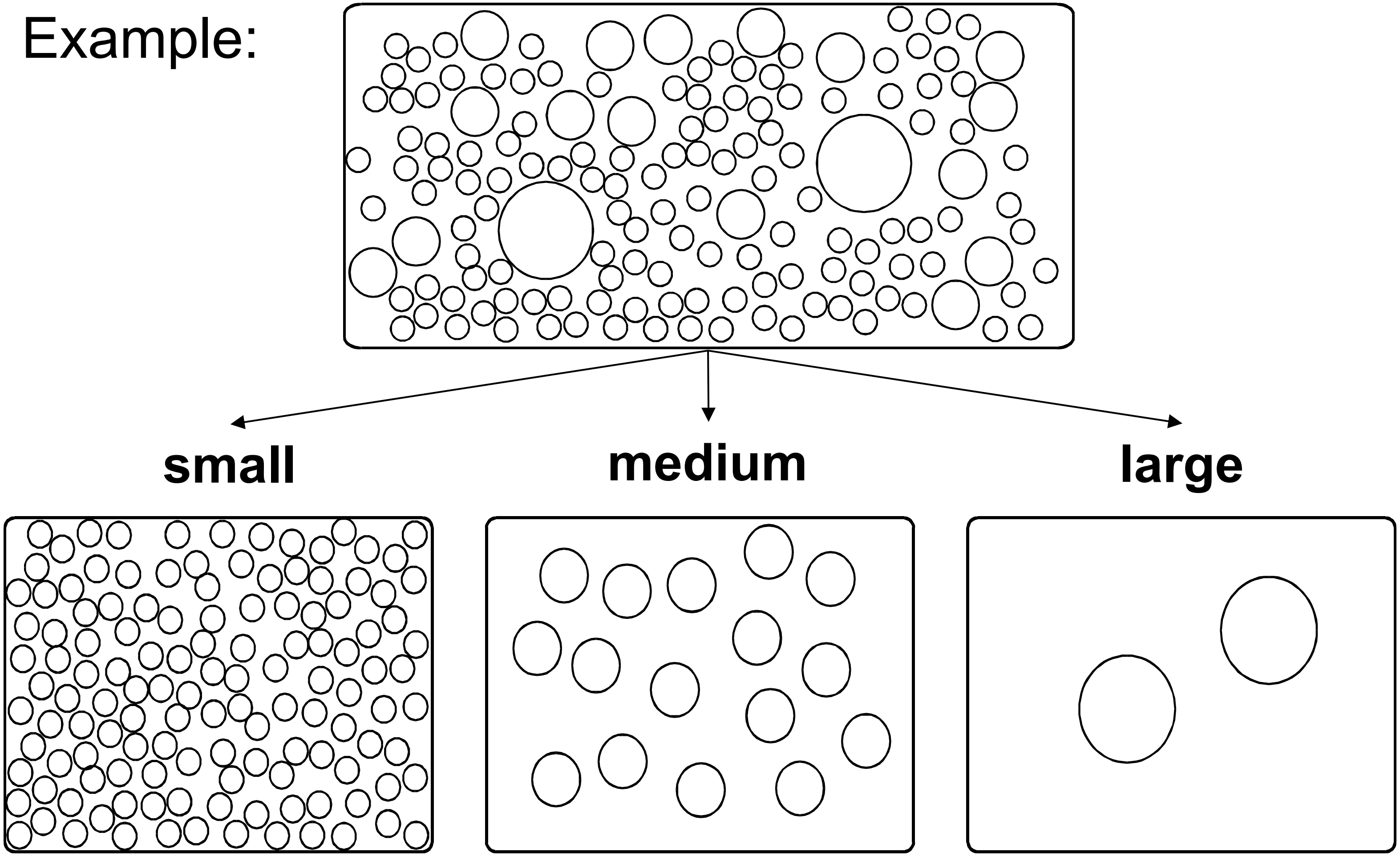
Kind of quantity	Dimensions	Index	Measuring process
Number	L^0	r = 0	counting
Length	L^1	r = 1	
Surface	L^2	r = 2	extinction
Mass/volume	L^3	r = 3	weighing

Note:

- One particle of 1 mm has the same mass as 1000 particles of 0,1 mm.
- Attention must be paid to the statistical data of the measuring procedure.

Particle size distributions: number count

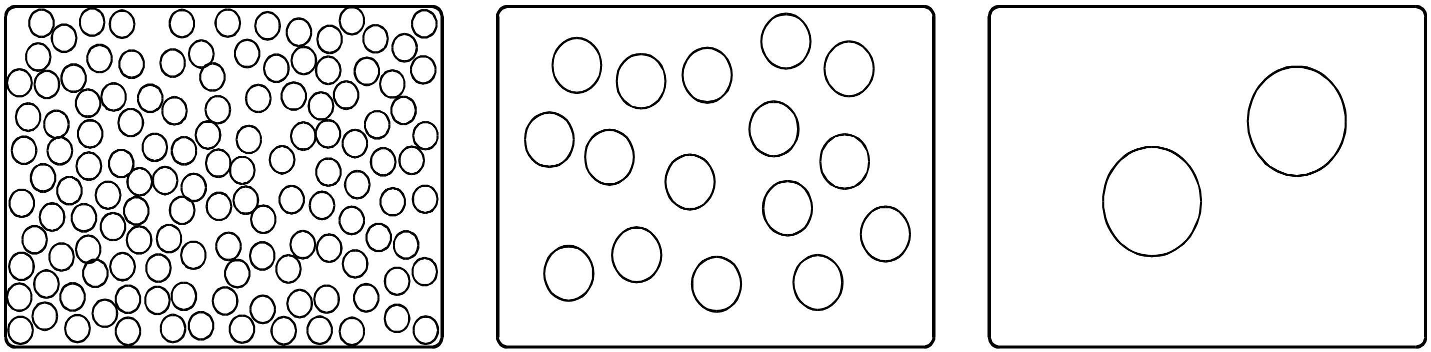
Example:



	small		medium		large
Particle size	**1**	**:**	**2**	**:**	**4**
Number	**128**		**16**		**2**

Particle size distributions: number count

	small		medium		large



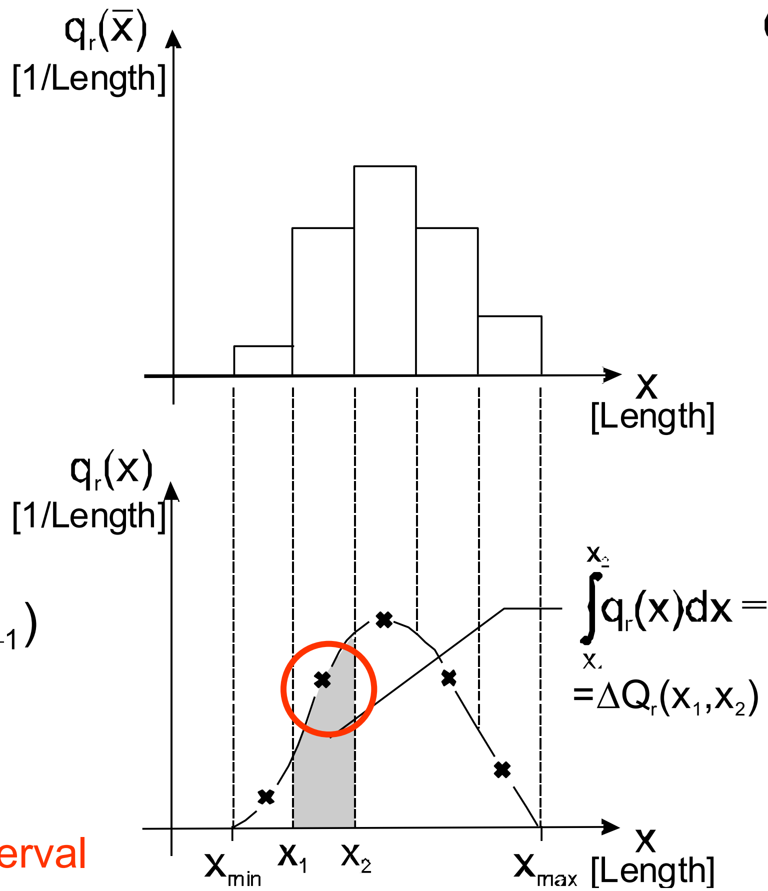
Size	1	:	2	:	4
Mass	1	:	1	:	1
$Q_3 =$	0,33		0,67		1,0
Number	64	:	8	:	1
$Q_0 =$	0,88		0,99		1,0

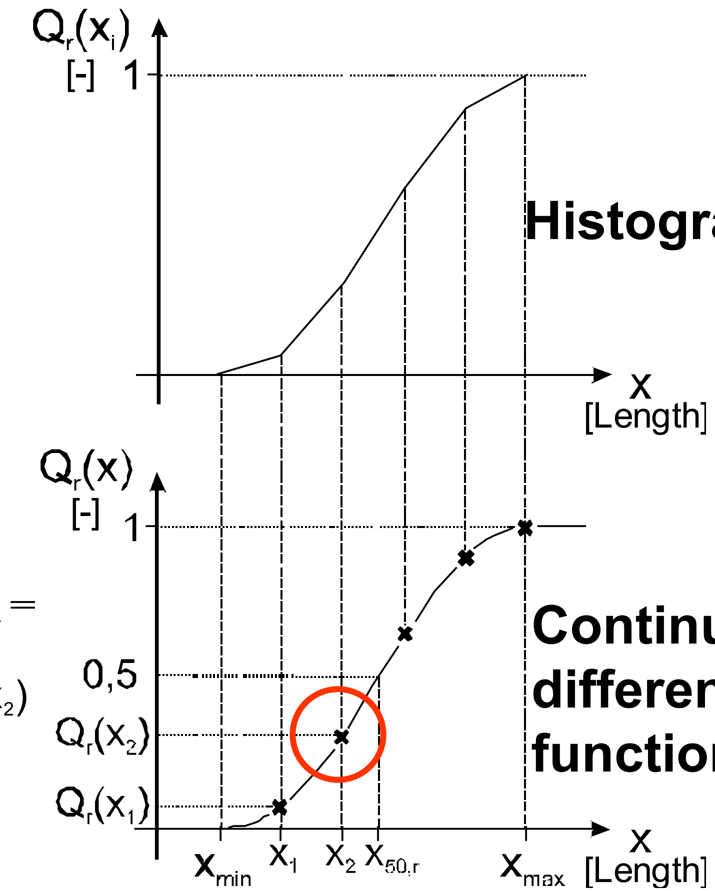
Representation of distribution functions

Distribution densities are plotted over the mean of the interval

$$\bar{x}_i = \frac{1}{2}(x_i + x_{i+1})$$

Plot over midst of interval





$$q_r(x) = \frac{dQ_r(x)}{dx}$$

resp.

$$Q_r(x) = \int_{x_{min}}^{x} q_r(x)dx$$

Plot over end of interval

with $\int_{x_1}^{x_2} q_r(x)dx = Q_r(x_2) - Q_r(x_1)$ and $\int_{x_{min}}^{x_{max}} q_r(x)dx = 1$

Incomplete moments and abscissa substitution

Abscissa substitution $dQ(x) \rightarrow dQ(\xi),\ \xi = f(x)$

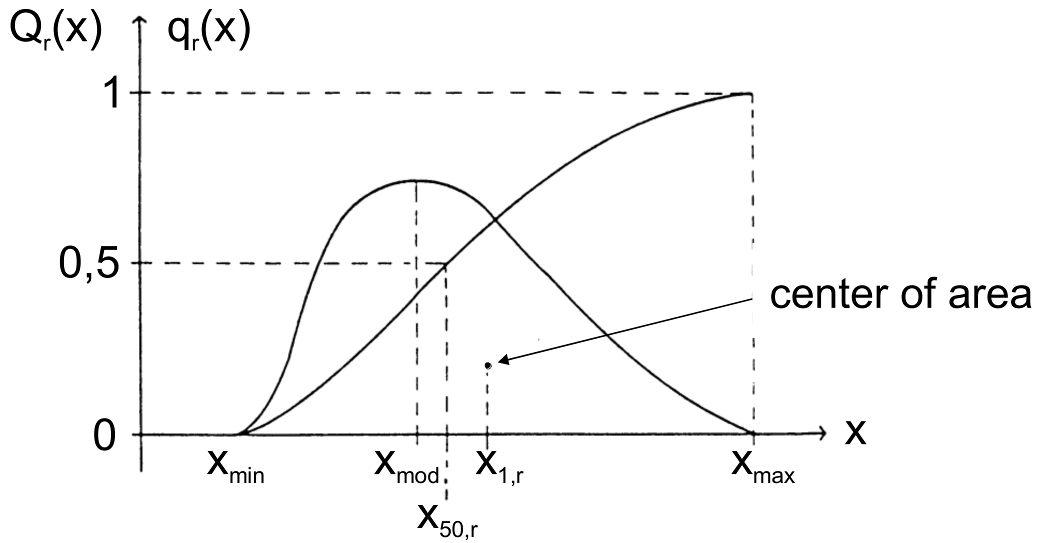
$dQ_r(x_1, x_2) = dQ_r(\xi_1, \xi_2)$, resp. $dQ_r(x) = q_r(x)dx = q_r(\xi)d\xi = dQ_r(\xi)$

$$\Rightarrow \quad q_r(\xi) = \frac{dx}{d\xi} q_r(x)$$

Applications:

- Linearly plotted distribution often asymmetric
  => Use of log units - representation
- Measuring of Q_2 (constant $\cdot$ x^2) ,
  e.g. cross sectional area of the particles (extinction)
  => Plot over particle size

Distribution parameters



- Median value $x_{50,r}$: $Q_r(x_{50,r}) = 0{,}5$, i.e. 50 % of the total amount is smaller than $x_{50,r}$
- Modal value $x_{mod,r}$: maximum of the density distribution at this particle size (bimodal resp. polymodal distributions have 2 resp. several maxima)
- Balanced mean $x_{1,r}$: abscissa of the center of area of the distribution density $q_r(x)$

$$x_{1,r} = M_{1,r} = \int_{x_{min}}^{x_{max}} x q_r(x) dx$$

- Arithmetical mean value $\overline{x^k}$: $\overline{x^k} = M_{k,0}$

Note: $\overline{x^k} \neq \overline{x}^k$

Width of the PSD

Width of the PSD is characterized by:

- Upper and lower limits of the particle size range: due to practical reasons (e.g. measuring precision) $x_{0,05}$, $x_{0,95}$ is used

- Variance of distribution:

$$s_r^2 = \int_{x_{min}}^{x_{max}} (x - x_{1,r})^2 q_r(x) dx$$

after multiplying

The square root of the variance is standard deviation.

Particle size distributions

- Cumulative distribution:

$$Q_r(x) = \frac{\text{Quantity of all particles with } x \le x_i}{\text{Total quantity}} = \int_{x_{min}}^{x} q_r(x)dx$$

- Density distribution:

$$q_r(\bar{x}_i) = \frac{\text{Amount in interval between } x_i \text{ and } x_{i+1}}{\text{Interval length } (x_{i+1} - x_i) \cdot \text{Total quantity}} = \frac{dQ_r(x)}{dx}$$

- Moment as integral mean value:

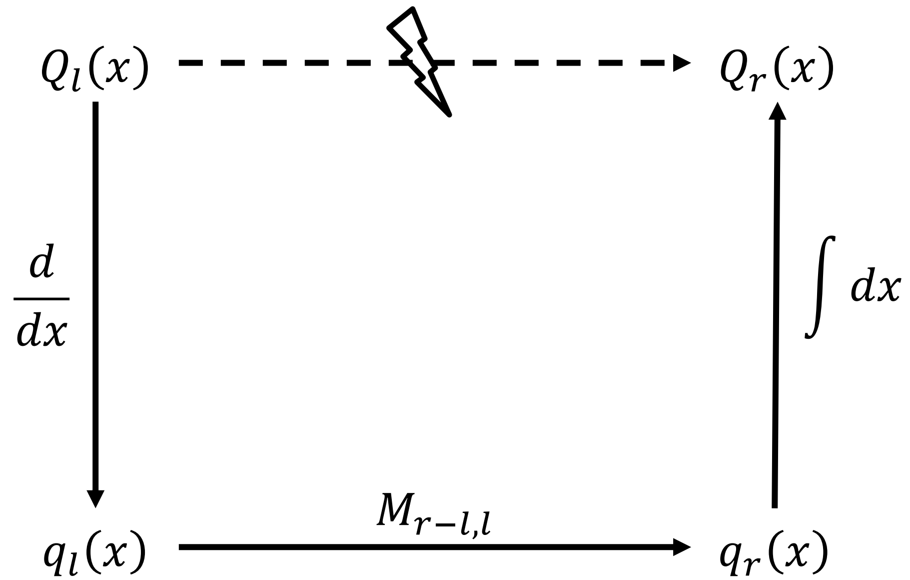
$$M_{k,r} = \int_{x_{min}}^{x_{max}} x^k q_r(x)dx = \frac{M_{k+r\text{-}l,l}}{M_{r\text{-}l,l}} \qquad q_r(x) = \frac{x^{r-l} q_l(x)}{M_{r-l,l}}$$

- Specific surface area:

$$S_V = 6 \cdot \Psi_{S,V}^2 \cdot \frac{M_{2,0}}{M_{3,0}} = \frac{6 \cdot \Psi_{S,V}^2}{M_{1,2}} = 6 \cdot \Psi_{S,V}^2 \cdot M_{-1,3}$$

Summary
Particle size distributions

Conversions and moments



$$q_r(x) = \frac{q_l(x)x^{r-l}}{M_{r-l,l}}$$

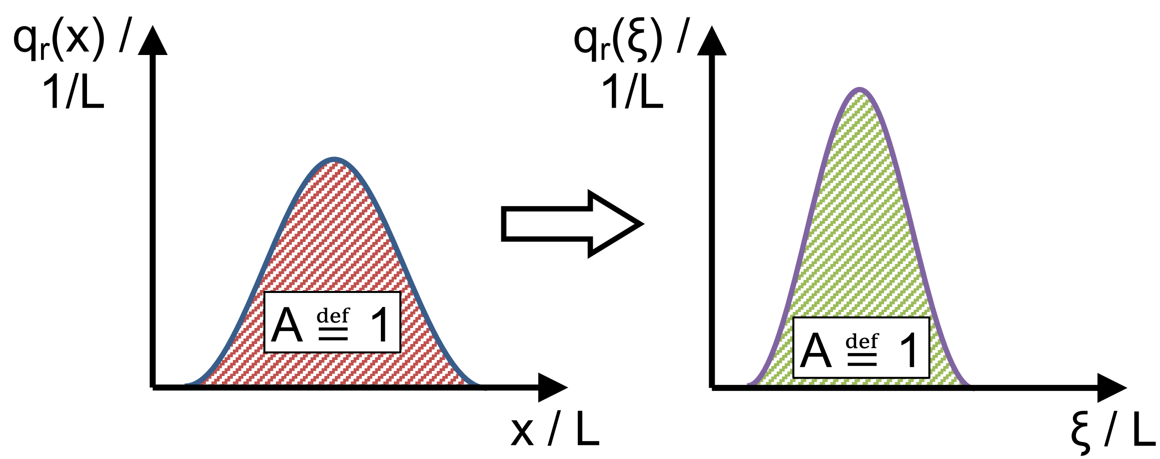
$$M_{r-l,l} = \int_{x_{min}}^{x_{max}} x^{r-l} q_l(x)dx$$

Abscissa substitution:

$$q_r(\xi) = q_r(x)\frac{\partial x}{\partial \xi}$$

Normalization:

$$\int_{x_{min}}^{x_{max}} q_r(x)dx \stackrel{\text{def}}{=} 1$$

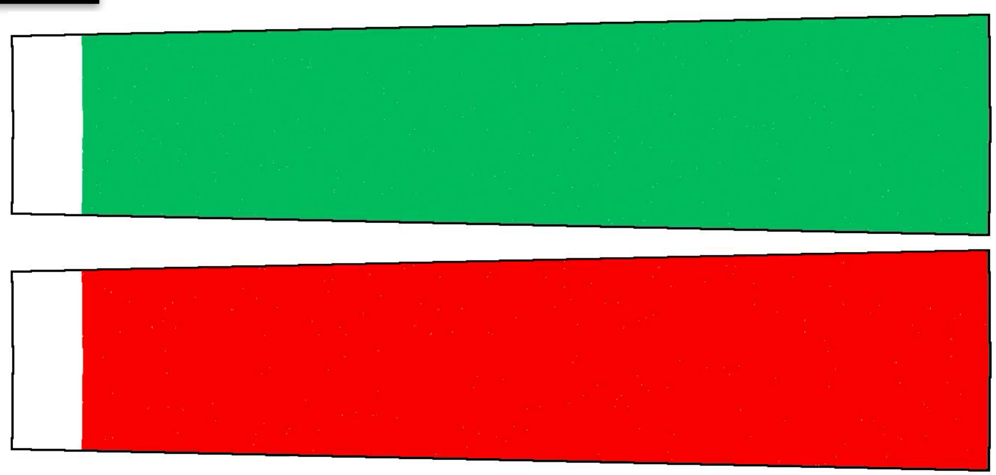


Analytical Ultracentrifugation
Basic Working Principle

➢ Ultracentrifuge equipped with multiwavelength extinction detector

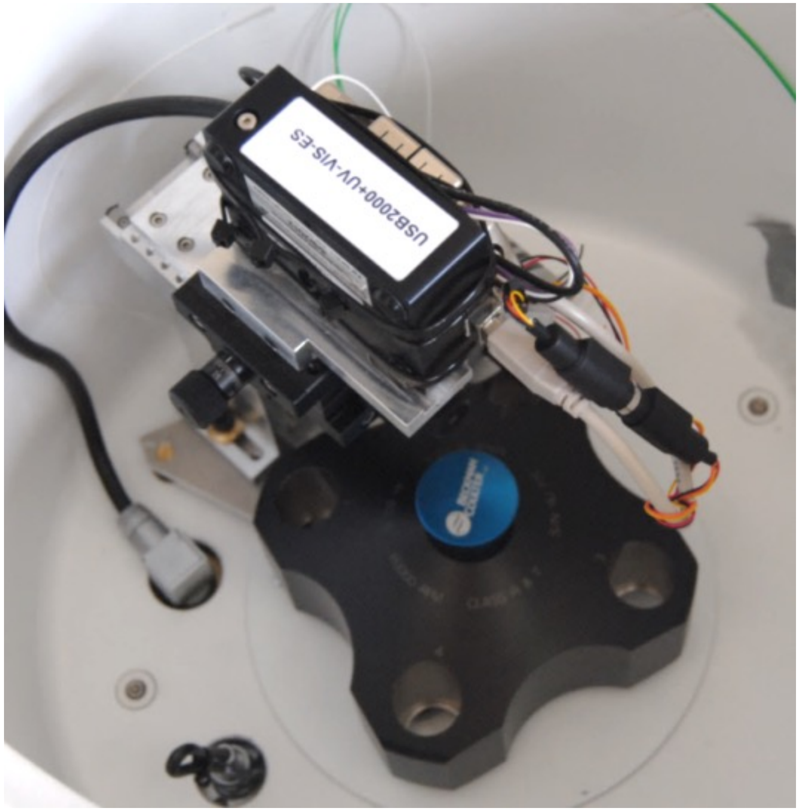
Sedimentation:

Flotation:



➡ Particles sediment/float according to **mass/size, density** and **shape**

- Hardware
  - Beckman Coulter Optima L/XL as platform
  - Operation in vacuum
  - Fiber-coupled xenon flash-lamp
  - Inline detection with modular CCD-spectrometer (UV-VIS & VIS-NIR)
  - Light barrier measures rotor speed (up to 60 000 rpm)
  - Step motor scanning in radial dimension



Hardware

- Beckman Coulter Optima L/XL as platform
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- Light barrier measures rotor speed (up to 60 000 rpm)
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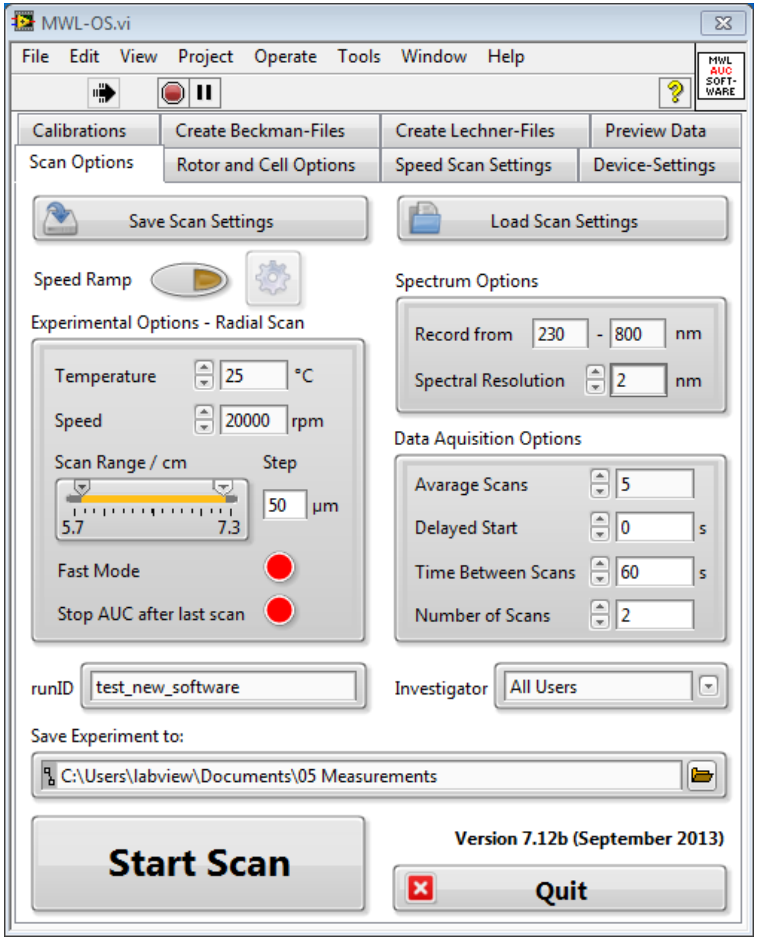
Software

- Acquisition software based on LabVIEW
- Highly accurate data acquisition (rotor speed, triggering, etc.)
- Techniques to improve signal-to-noise ratio



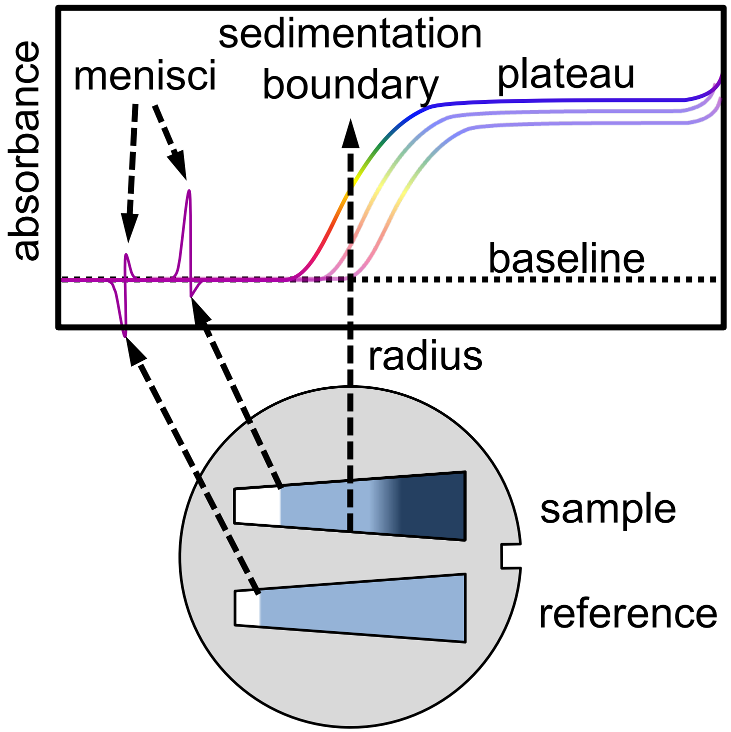
What about the costs?

- Custom design ~ 120 k€
- Commercial AUC ~ 450 k€

Operation Principles

I. Sedimentation velocity

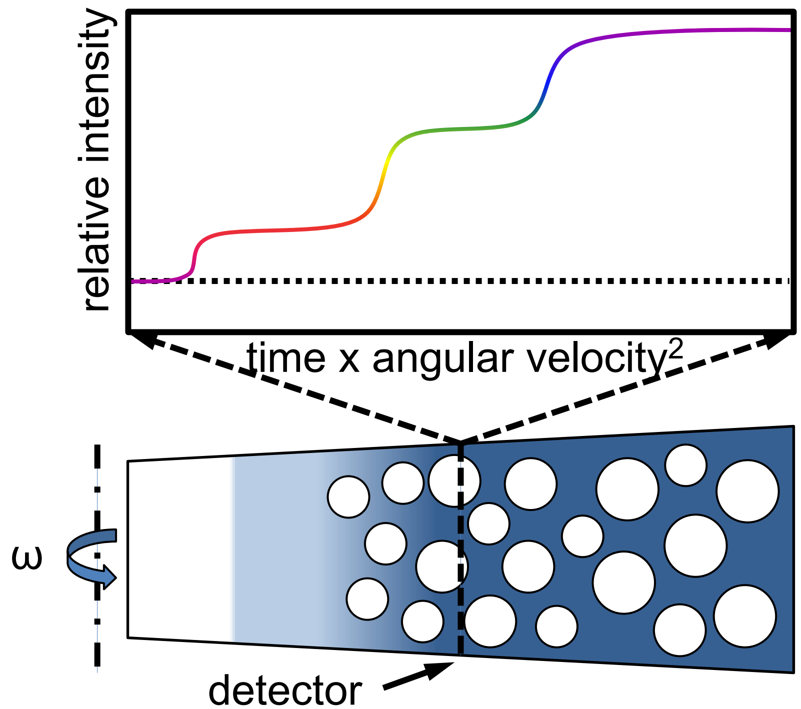
> 1 h



- Mostly for narrow distributions
- Highly accurate
- Diffusion analysis possible

II. Gravitation sweep

typ. < 1 h



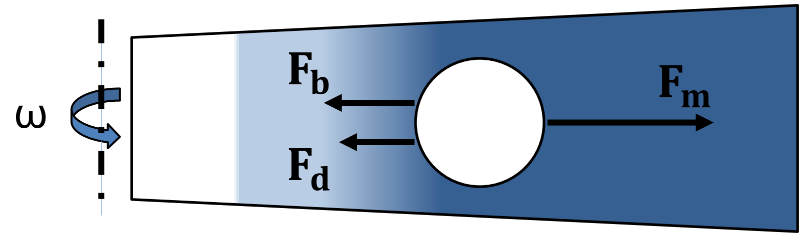
- Detection of large particles
- Very broad distributions
- Very fast experiments

➡ Particles sediment according to **mass/size, density** and **shape**

Basics of Sedimentation Theory

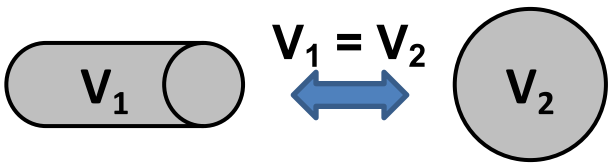
- Force balance of sedimenting particle

$$F_m + F_b + F_d = \omega^2 r (m_p - m_s) - fu = 0$$



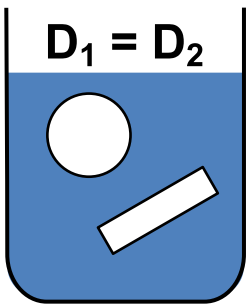
- Concept of equivalent diameters

A)



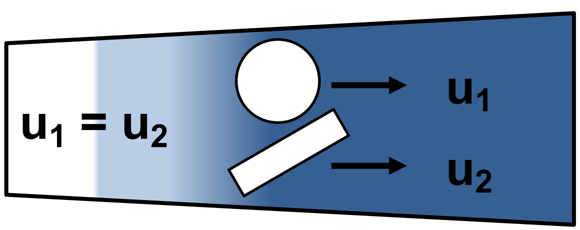
x_V
Diameter of sphere with equal volume

B)



x_H
Diameter of sphere with equal diffusion

C)



x_{Stokes}
Diameter of sphere with equal sedimentation

Sedimentation coefficient: $s = \frac{u}{\omega^2 r}$ ⇒ $\frac{\pi}{6s} x_V^3 (\rho_p - \rho_s) - f = 0$ (1)

Unit is in Svedberg (≙ 10^{-13} s)

Basics of Sedimentation Theory

- Important correlations

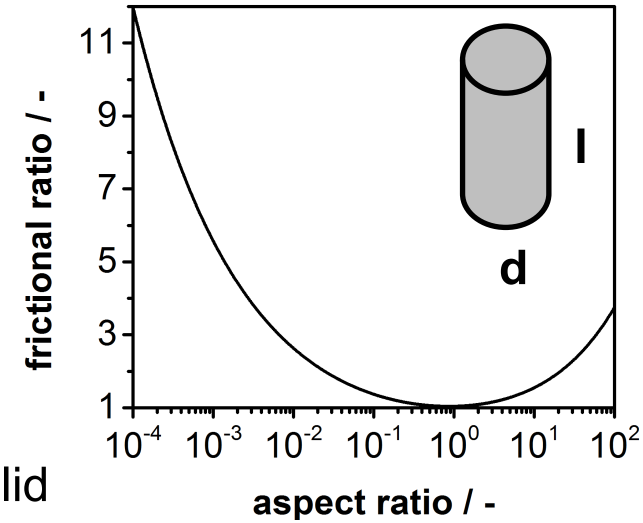
  Translational frictional coefficient: $f = 3\pi\eta x_H$ (2a) and $f = \frac{RT}{N_A D}$ (2b)

  Svedberg equation: $\frac{s}{D} = \frac{M(1-\rho_s\rho_p^{-1})}{RT}$

  Frictional ratio: $f/f_0 = \frac{x_H}{x_V} = \text{fct(shape)}$ → $x_V = \frac{x_H}{f/f_0}$ (3)

- Shape dependencies of cylindrical particles

  Aspect ratio: $q = \frac{l}{d}$ with
  $q > 1$ rod / tube
  $q \approx 1$ sphere (4)
  $q < 1$ disc



- Determination of particle diameters from hydrodynamic properties

  → $x_{Stokes} = \left(\frac{18\eta s}{\rho_p - \rho_s}\right)^{1/2}$

  Stokes–Equation

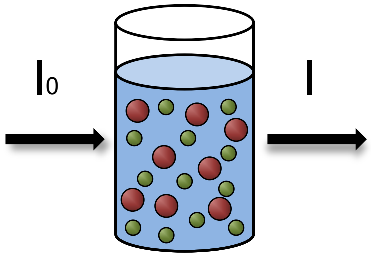
  $x_{Stokes} = x_H = x_V$ only valid for spheres ($f/f_0 = 1$)!

- Correlation of size, shape and particle density

  (2) + (3) in (1) → $D(s, f/f_0) = RT[2(\rho_p - \rho_s)]^{1/2}\left[18 s^{1/2} N_A \pi (f/f_0 \eta)^{\frac{3}{2}}\right]^{-1}$

Optical Properties

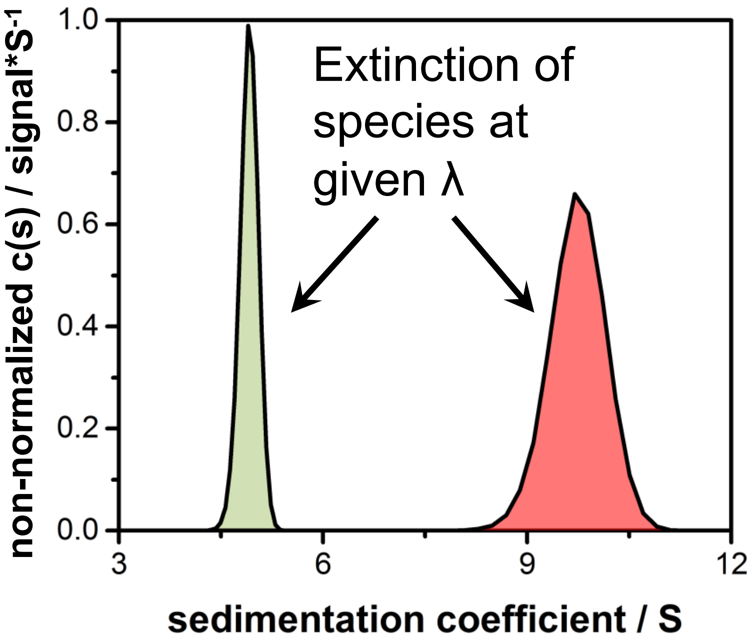
- Many applications dependent upon the optical properties of particles
- Differentiation of individual optical properties difficult because most techniques offer only integral information on the mixture
- MWL-AUC based on absorption spectroscopy



Lambert-Beer's-Law: $\log_{10}\frac{I}{I_0} = -\varepsilon c l = -\tau c$

- Path length and loading concentration is constant and independent of wavelength throughout AUC experiment
- AUC-signal (area of distribution) is proportional to extinction coefficient
- Extinction spectra can be easily derived by:

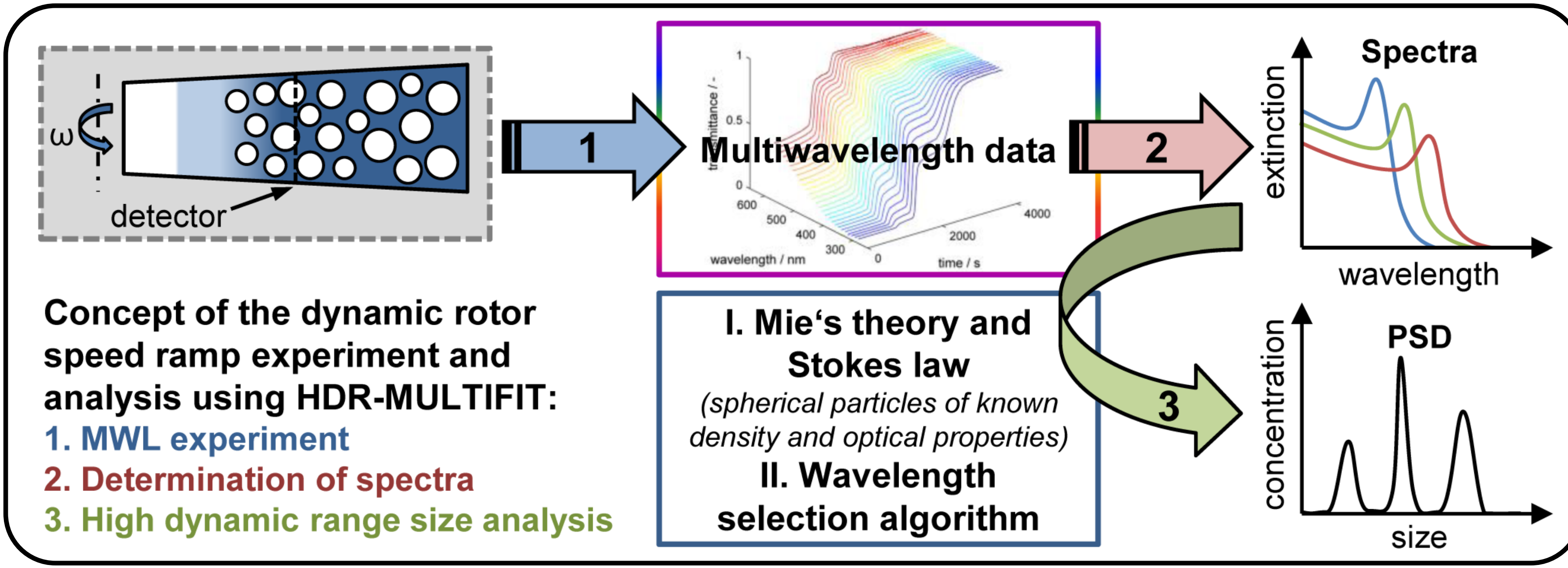
$$a(\lambda) = \int_{s_1}^{s_2} \left(\frac{\partial a}{\partial s^*}\right)_\lambda ds^*$$



➡ AUC allows for the simultaneous analysis of size and optical properties

Analysis of Broad PSDs Dynamic Rotor Speed Gradient

- Dynamic increase of rotor speed at fixed radial position for broad particle size distributions
  - Dynamic range limited due to size dependent scattering of particles
  - Development of data evaluation software capable of MWL evaluation



➡ Determination of size dependent extinction spectra

➡ High dynamic range detection for broad PSDs using Mie's theory

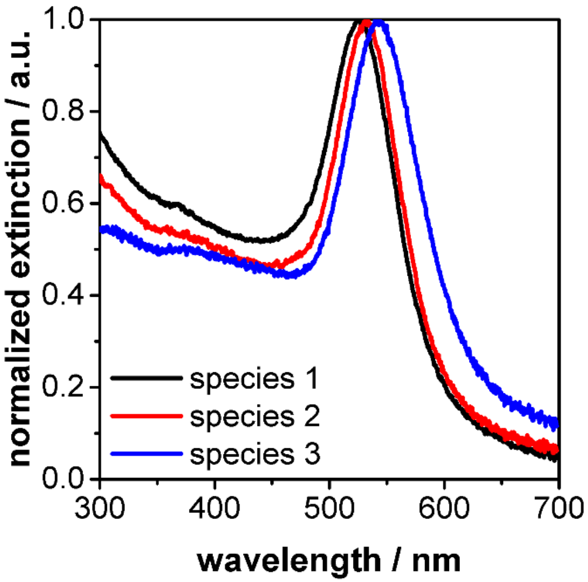
J. Walter et al., ACS Nano **2014**
J. Walter and W. Peukert, Nanoscale

Analysis of Broad PSDs
High Dynamic Range Detection

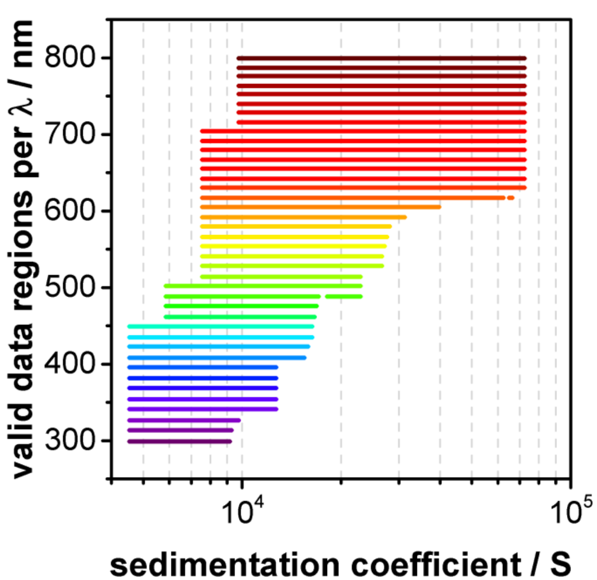
- Combined data evaluation at several wavelengths (“HDR detection”)
  - Determination of extinction spectra
  - Generate grid for dimension of sedimentation coefficient
  - Determine reasonable wavelengths for each interval i (*e.g.* $OD_{max,i} = 1$, $\Delta OD_{min,i} = 0.1\ \Delta OD_{max,i}$)
  - Evaluate data for all selected wavelengths and combine distributions

$$I_{scattering,rayleigh} \sim \frac{x^6}{\lambda^4}$$

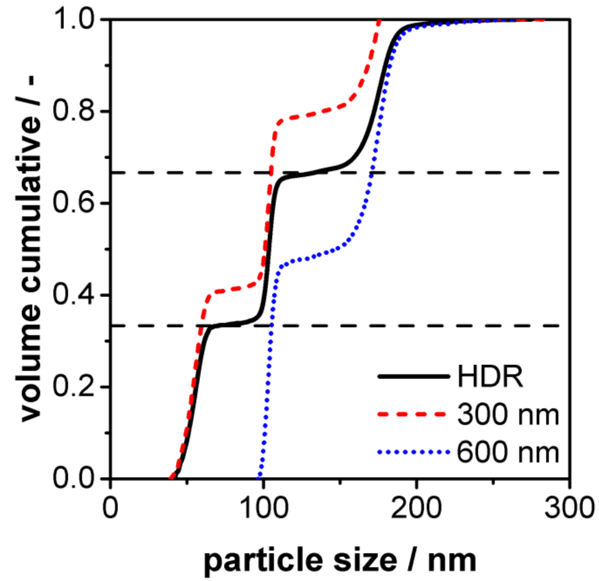
1. *3-modal gold mix*



2. *Exemplary grid*



3. *3-modal polystyrene mix*



… and now a lot of formula

$C_{ext} = C_{sca} + C_{abs}$ extinction cross-section

$\tilde{n} = n - ik$ complex refractive index

$\tau_\lambda = N_P C_{ext} = \frac{\varphi}{V_P} C_{ext}$ turbidity

$Q_{ext} = \frac{C_{ext}}{A_P} = \frac{4C_{ext}}{\pi x_P^2}$ extinction efficiency

$$\tau = \frac{3\varphi Q_{ext}}{2x_P}$$

$\varphi = \frac{V_P}{V_{total}} = \frac{V_P}{V_F + V_P} \approx \frac{V_P}{V_F} = \frac{m_P}{\rho_P V_F} = \frac{c}{\rho_P}$ volume fraction

$$\frac{\tau}{c} = \varepsilon_\lambda = \frac{3Q_{ext}}{2x\rho_P}$$

$n^2(\lambda) = A + \sum_j \frac{B_j \lambda^2}{\lambda^2 - C_j}$ Sellmeier approach

$$k(\lambda) = \left[n(\lambda)\left(D_1\lambda + \frac{D_2}{\lambda} + \frac{D_3}{\lambda^3}\right)\right]^{-1}$$