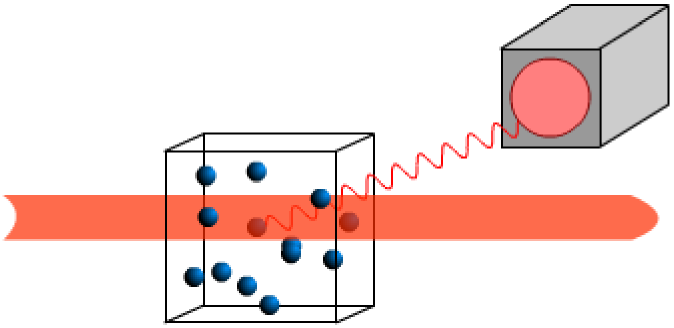
Scattering workshop (Cologne 2018):

Static light scattering + …

… Dynamic light scattering:

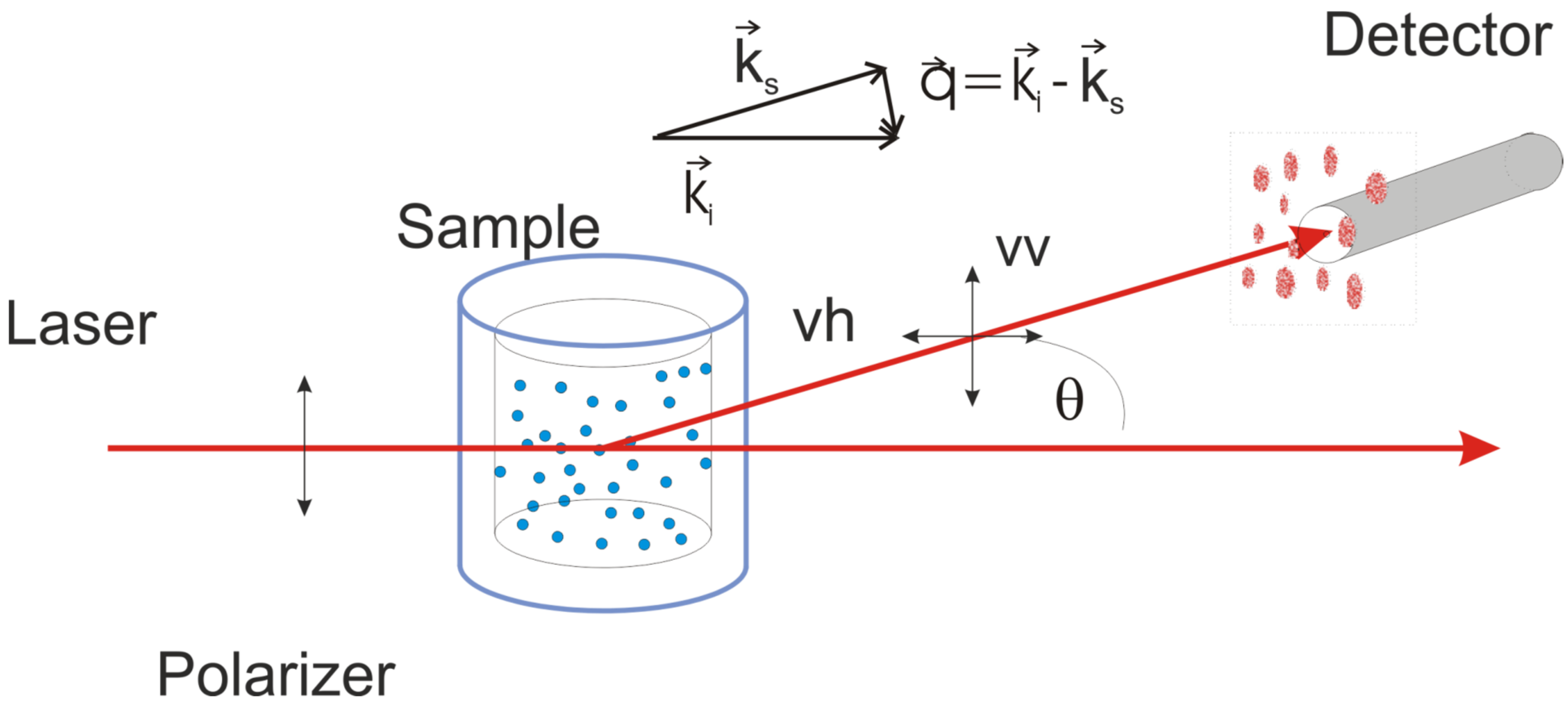
December, 5th 2018 | Simone Wiegand

Outline



- static light scattering:
  - Form factor (shape of the
  - Structure factor (structure in the fluid)
  - Absolute scattering (molar mass, radius of gyration and second virial coefficient)
- dynamic light scattering
  - Diffusion constant (⇒ hydrodynamic radius)
  - Distribution of diffusion constants (mass weighted!!!)
- Problems & examples

Setup: Static and dynamic light scattering

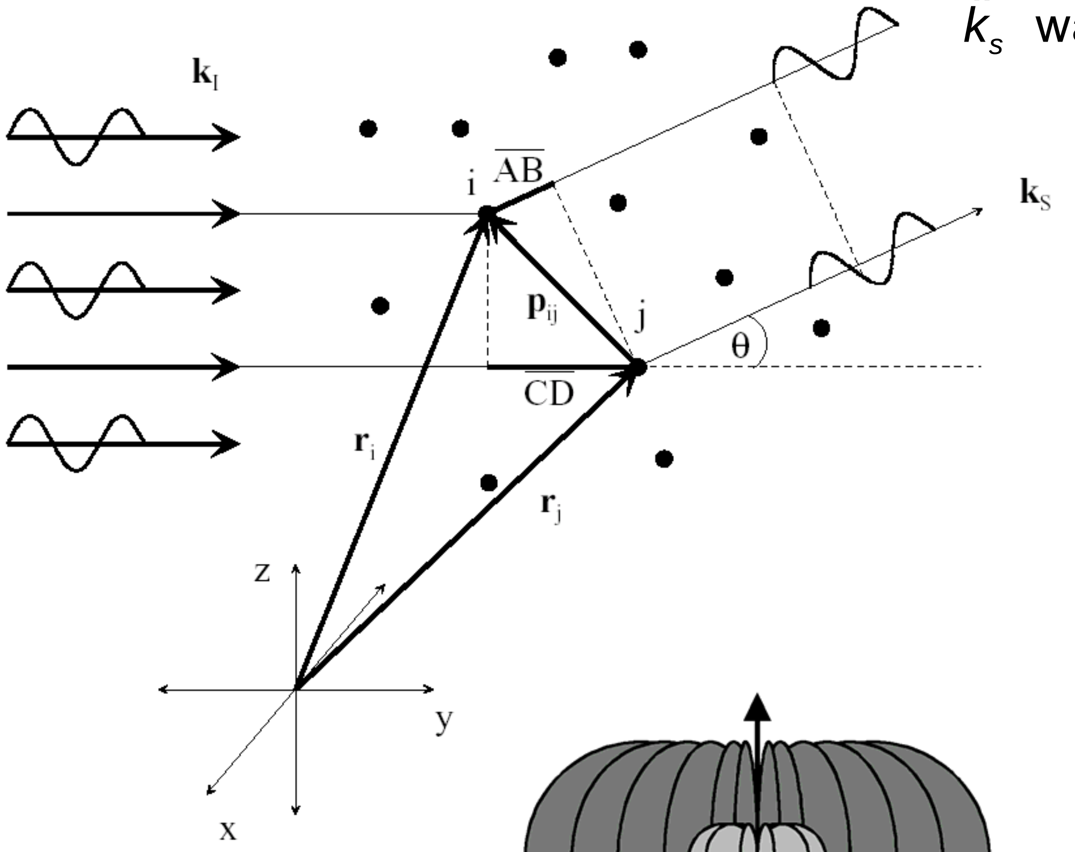


~~Depolarized scattering (anisotropic particles)~~

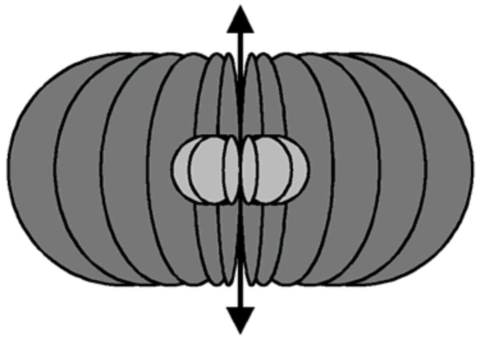
Scattering geometry: q-vector

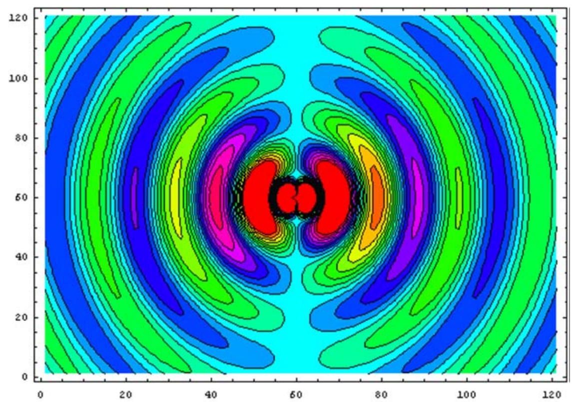
$\hat{k}_i$ wave vector of the incident field

$\hat{k}_s$ wave vector of the scattered field



- Each scatterer emitts a secondary wave
- no radiation in the direction of oscillation



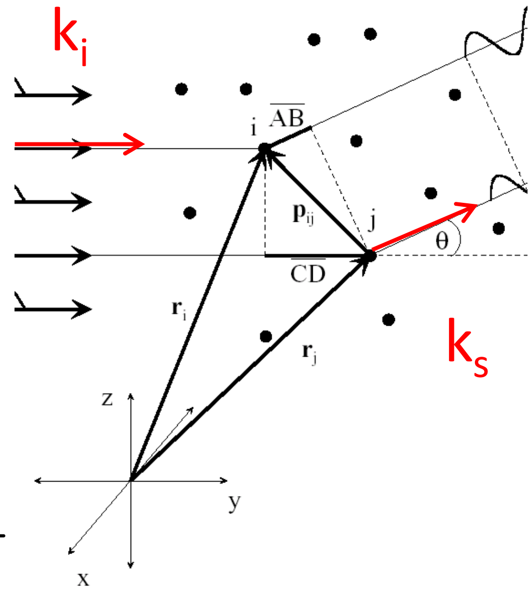


Scattering geometry: q-vector

Problem:

Calculate phase shift: $\phi_i - \phi_j = \Delta\phi$

path difference = $\overline{AB} - \overline{CD}$



$$\Rightarrow \Delta\phi = \text{path difference} \cdot \frac{2\pi}{\lambda} = \left(\overline{AB} - \overline{CD}\right) \cdot \frac{2\pi}{\lambda}$$

$$\overline{AB} = \hat{k}_s \cdot \vec{p}_{ij}$$

$$\overline{CD} = \hat{k}_i \cdot \vec{p}_{ij}$$

$\vec{p}_{ij} = \vec{r}_i - \vec{r}_j$ separation vector between space coordinates of particle *i* and *j*

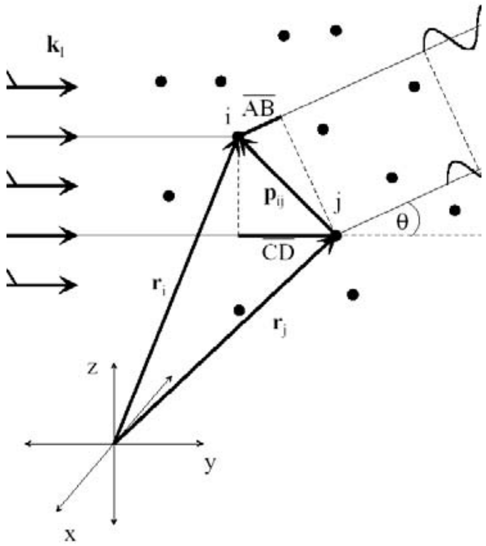
$\hat{k}_s$..unit vector

$\hat{k}_i$..unit vector

Scattering geometry: q-vector

$$\Delta\phi = \left(\hat{k}_s - \hat{k}_i\right)\left(\vec{r}_i - \vec{r}_j\right)\cdot\frac{2\pi}{\lambda} = \left(\hat{k}_s - \hat{k}_i\right)\left(\vec{r}_i - \vec{r}_j\right)\cdot k$$

$$= \underbrace{\vec{r}_i\left(\hat{k}_s - \hat{k}_i\right)k}_{\equiv\phi_i} - \underbrace{\vec{r}_j\left(\hat{k}_s - \hat{k}_i\right)k}_{\equiv\phi_j}$$



Each point scatterer can be assigned a phase !

General: $\phi(\vec{r}) = \vec{r}\,\vec{q}$

Scattering vector: $\vec{q} = \left(\hat{k}_s - \hat{k}_i\right)k$

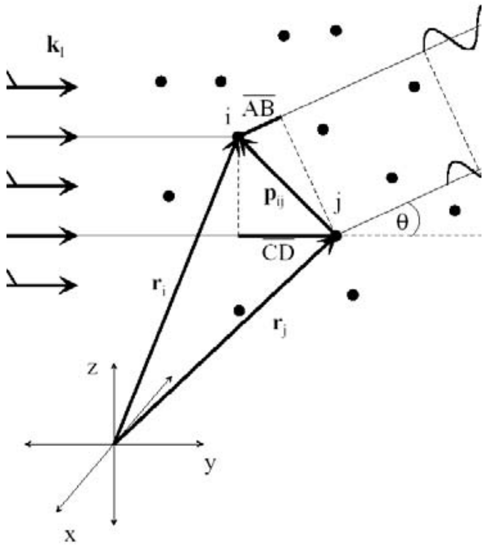
In general: in a medium

Norm of the scattering vector: $q = |\vec{q}| = \frac{4\pi n}{\lambda}\sin(\theta/2)$

Scattering geometry: q-vector

$$\Delta\phi = \left(\hat{k}_s - \hat{k}_i\right)\left(\vec{r}_i - \vec{r}_j\right)\cdot\frac{2\pi}{\lambda} = \left(\hat{k}_s - \hat{k}_i\right)\left(\vec{r}_i - \vec{r}_j\right)\cdot k$$

$$= \underbrace{\vec{r}_i\left(\hat{k}_s - \hat{k}_i\right)k}_{\equiv\phi_i} - \underbrace{\vec{r}_j\left(\hat{k}_s - \hat{k}_i\right)k}_{\equiv\phi_j}$$



Each point scatterer can be assigned a phase !

General: $\phi(\vec{r}) = \vec{r}\,\vec{q}$

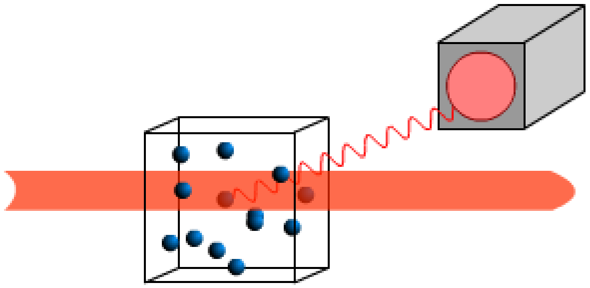
Scattering vector: $\vec{q} = \left(\hat{k}_s - \hat{k}_i\right)k$

Norm of the scattering vector: $q = \left|\vec{q}\right| = \frac{4\pi n}{\lambda}\sin(\theta/2)$

!

Mitglied in der Helmholtz-Gemeinschaft

Illustration



Time averaged scattering intensity:

static light scattering

Time resolved scattering intensity fluctuations:

dynamic light scattering

Mitglied in der Helmholtz-Gemeinschaft

Illustration

Scattered electric field from one volume element

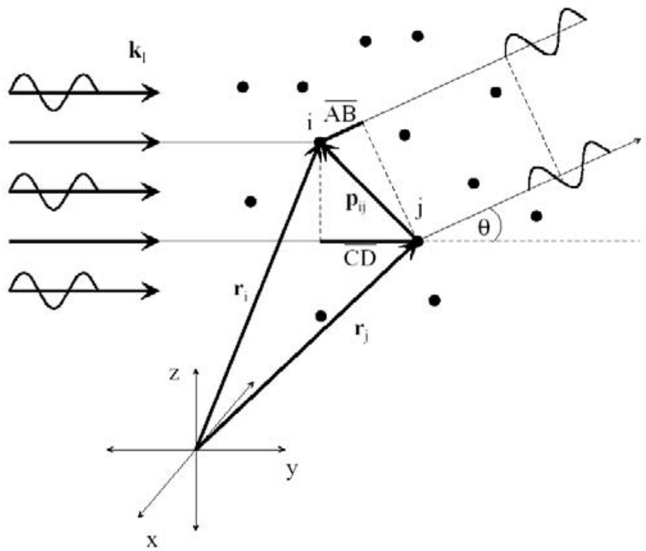
$$E_V(\vec{r},t) = f(\vec{r})E_I \exp\{i(\vec{q}\vec{r} - \omega t)\}$$

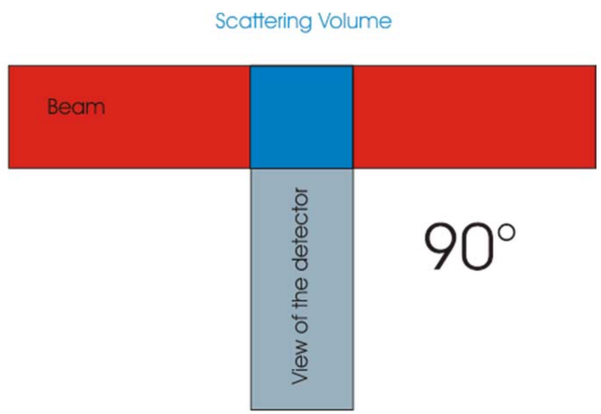
$f(\vec{r})$ scattering strength

E_I strength of the incoming field

Total electric field from the entire scattering volume

$$E_S \propto E_I \int_{\text{scattering volume}} f(\vec{r})\exp\{i\vec{q}\vec{r}\}d\vec{r}$$



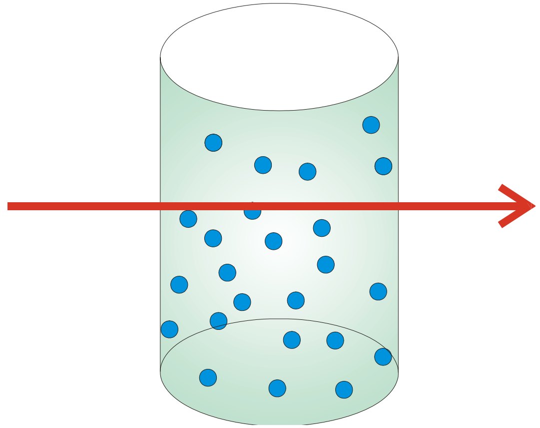


Illustration

$$E_S \propto E_{S,\text{solute}} + E_{S,\text{solvent}}$$

$$= E_I \int_{\text{scattering volume}} f_{\text{solute}}(\vec{r}) E_I \exp\{i\vec{q}\vec{r}\} d\vec{r}$$

$$+ E_I \int_{\text{scattering volume}} f_{\text{solvent}}(\vec{r}) E_I \exp\{i\vec{q}\vec{r}\} d\vec{r}$$



$f(\vec{r})$. scattering strength

$$E_S \propto E_{S,\text{solute}}$$

$$= E_I \underbrace{\sum_{j=1}^{N} \underbrace{\int_{V_j} f(\vec{r}) \exp\{i(\vec{q}\vec{r})\} d\vec{r}}_{\text{scattering contribution from volume element } V_j}}_{\text{sum over all volume elements}}$$

Illustration

$$E_S \propto E_{S,\text{solute}}$$

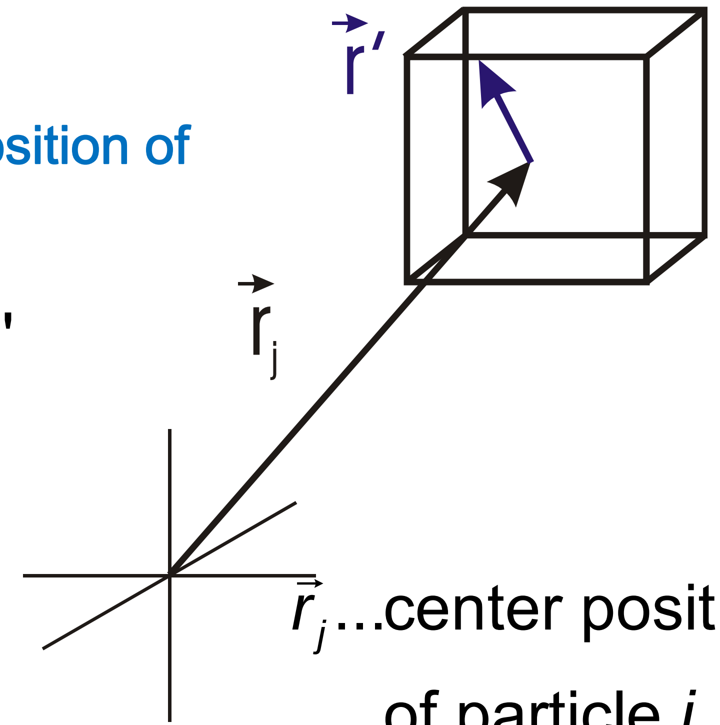
$$= E_I \sum_{j=1}^{N} \underbrace{\int_{V_j} f(\vec{r}) \exp\{i(\vec{q}\vec{r})\} d\vec{r}}_{\text{scattering contribution from volume element } V_j}$$

sum over all volume elements

Remark:
We omit the subscript solute.

Problem: Integration depends on the position of the particle

Variable substitution: $\vec{r} = \vec{r}_j + \vec{r}\,'$



$\vec{r}_j$...center position of particle j

Illustration

$$I(q) \propto E_S^2 = \underbrace{\left| \int_{V_j} g(\vec{r}\,') \exp\{i\vec{q}\vec{r}\,'\} d\vec{r}\,' \right|^2}_{\propto P(q)} \cdot \underbrace{\left| \sum_{j=1}^{N} \exp\{i q \vec{r}_j\} \right|^2}_{\equiv S(q)}$$

$$S(q) \equiv \left| \sum_{j=1}^{N} \exp\{i q \vec{r}_j\} \right|^2$$

Structure factor of the solution

$$P(q) \equiv \left| \frac{\int_{V_j} g(\vec{r}\,') \exp\{i\vec{q}\vec{r}\,'\} d\vec{r}\,'}{\int_{V_j} g(\vec{r}\,') d\vec{r}\,'} \right|^2$$

Normalized particle scattering factor or form factor

Normalization constant

$$\Rightarrow \quad I(q,N) \propto P(q) S(q)$$

Mitglied in der Helmholtz-Gemeinschaft

Illustration

$$I(q,N) \propto P(q)S(q)$$

- polydispersity
- micellar solutions
- conformational changes
- anisotropic particles
- Ergodicity of the system

Useful relation, but strictly correct only for a homogenous suspension of identical particles with a scattering power of spherical symmetry.

Illustration

$$I(q,N) \propto P(q)S(q)$$

N .. number of scatters

infinite dilution:

$$\lim_{N\to 0} I(q,N) \propto P(q)$$

limit of low scattering vector:

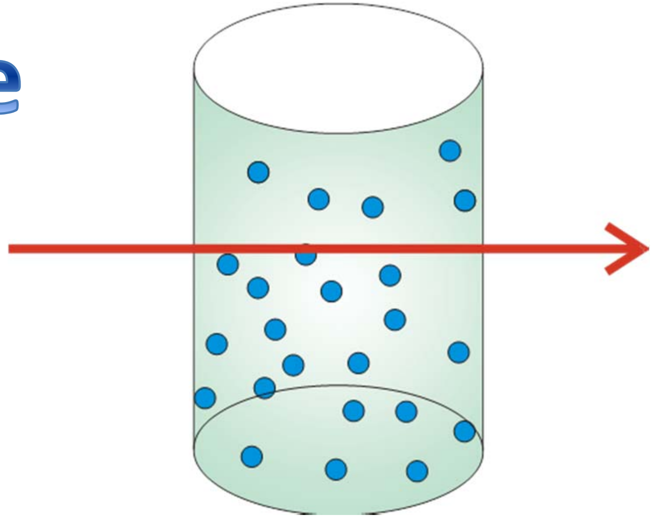
$$\lim_{q\to 0} I(q,N) \propto S(q=0)$$

Definitions:

$$S(q) \equiv \left| \sum_{j=1}^{N} \exp\left\{ iq\vec{r}_j \right\} \right|^2 \qquad P(q) \equiv \left| \frac{\int_{V_j} g(\vec{r}\,')\exp\left\{ i\vec{q}\vec{r}\,' \right\} d\vec{r}\,'}{\int_{V_j} g(\vec{r}\,') d\vec{r}\,'} \right|^2$$

Expressing the scattering intensity

Only the route



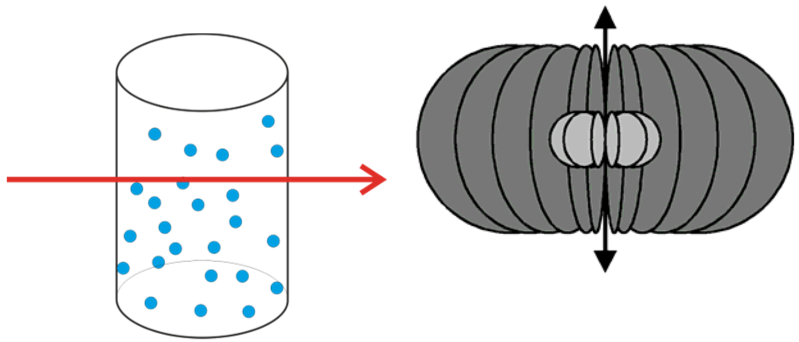
1) Rayleigh scattering equation
2) Infinitely dilution solution of small particles
3) Interparticle interference
4) Intraparticular interference

Details in the script of Peter Lang: http://www.fz-juelich.de/ics/ics-3/DE/UeberUns/Mitarbeiter/Lang_P/P_Lang_lec.html?nn=11606

1) Rayleigh scattering equation

Strength E_D of a single dipole in a distance R

$$E_D(t) = \frac{\omega^2 \vec{\mu}(t)}{4\pi\varepsilon_0 c^2} \frac{\sin\delta}{R}$$



$\vec{\mu}(t)$..time dependent moment of the dipole

δ…angle between dipole's oscillation direction and the observation direction

...after some calculation (time average, intensity...) ...

$$R_\theta = \frac{I_S}{I_I}\frac{R^2}{V} = \frac{k^4\left(n^2-1\right)^2}{16\pi^2 N_A \rho} M_r$$

n..refractive index $\qquad k = \frac{2\pi}{\lambda}$

I_s;I_I..scattered/irradiated intensity

V..scattering volume

2) Infinitely dilution solution of small particles

...with some calculation (Clausius-Mosotti, approximation...) ...

$$R_\theta = \frac{I_S}{I_I}\frac{R^2}{V} = \frac{k^4 (n^2 - 1)^2}{16\pi^2 N_A \rho} M_r$$

$$R_\theta = \frac{k^4 4 n^2_{\text{solvent}}}{16\pi^2 N_A} \left(\frac{\partial n}{\partial c}\right)^2 M_r c$$

$$k = 2\pi / \lambda$$

$$K \equiv \frac{4\pi n^2_{\text{solvent}}}{N_A \lambda_0^4} \left(\frac{\partial n}{\partial c}\right)^2$$

$$R_\theta = K c M_r$$

Mitglied in der Helmholtz-Gemeinschaft

3) Interparticle interference

$$\frac{Kc}{R_\theta(q,c)} = \frac{1}{M_r}$$ valid for infinitely diluted solutions

reasonable assumption for diluted solutions

$$\frac{Kc}{R_\theta(q,c)} = \frac{1}{M_r} + \mathcal{K}c$$

$$\Rightarrow \quad \frac{Kc}{R_\theta(q,c)} = \frac{1}{M_r} + 2A_2c$$

A_2 .. second virial coefficient

4) Intraparticle interference

$$\lim_{c\to 0, q\to 0} \frac{Kc}{R_\theta(q, c=0)} = \frac{1}{S(q=0, c)P(q)}$$

$$= \frac{1}{P(q)}\left(\frac{1}{M_r} + 2A_2 c\right)$$

Next step: Relate $P(q)$ with the dimensions of a polymer.

$$\frac{Kc}{R_\theta(q, c=0)} = \frac{1}{M_r}\left(1 + \frac{q^2 R_g^2}{3}\right) + 2A_2 c$$

Suggested by Zimm in 1949

Mitglied in der Helmholtz-Gemeinschaft

Zimm in practice

JÜLICH FORSCHUNGSZENTRUM

$$\frac{r_{\text{solute}}}{r_{\text{standard}}} = \frac{R_{\theta,\text{solute}}}{R_{\theta,\text{standard}}} \cdot \frac{n^2_{\text{standard}}}{n^2_{\text{solvent}}} \Rightarrow R_{\theta,\text{solute}} = R_{\theta,\text{standard}} \cdot \frac{r_{\text{standard}}}{r_{\text{solute}}} \cdot \frac{n^2_{\text{solvent}}}{n^2_{\text{standard}}}$$

$$\frac{r_{\text{solvent}}}{r_{\text{standard}}} = \frac{R_{\theta,\text{solvent}}}{R_{\theta,\text{standard}}} \cdot \frac{n^2_{\text{standard}}}{n^2_{\text{solvent}}} \Rightarrow R_{\theta,\text{solvent}} = R_{\theta,\text{standard}} \cdot \frac{r_{\text{solvent}}}{r_{\text{standard}}} \cdot \frac{n^2_{\text{solvent}}}{n^2_{\text{standard}}}$$

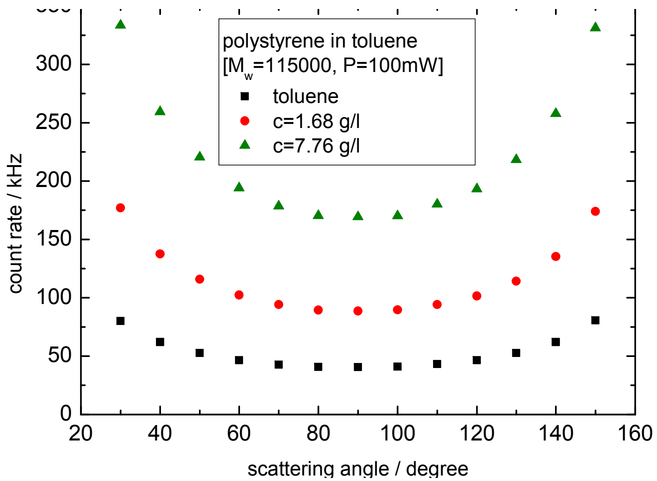
$$R_\theta = R_{\theta,\text{solute}} - R_{\theta,\text{solvent}} = \frac{R_{\theta,\text{standard}}}{r_{\text{standard}}}\left(r_{\text{solute}} - r_{\text{solvent}}\right)\frac{n^2_{\text{solvent}}}{n^2_{\text{standard}}}$$

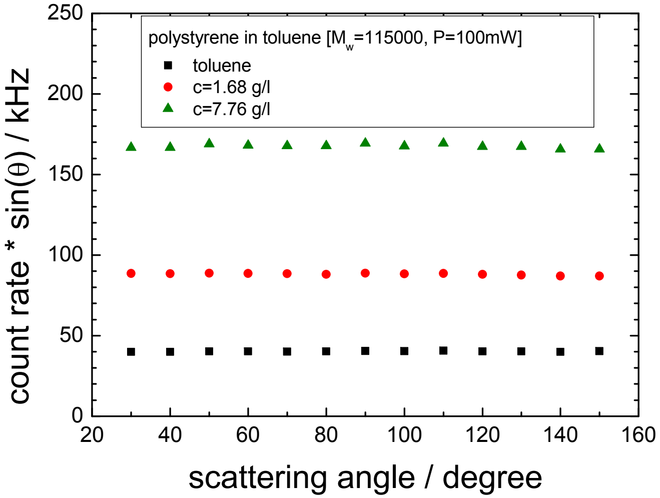
$r_{\text{solvent}}, r_{\text{solute}}, r_{\text{standard}}$ scattering intensities for solvent, solute and standard corrected for the size of the scattering volume

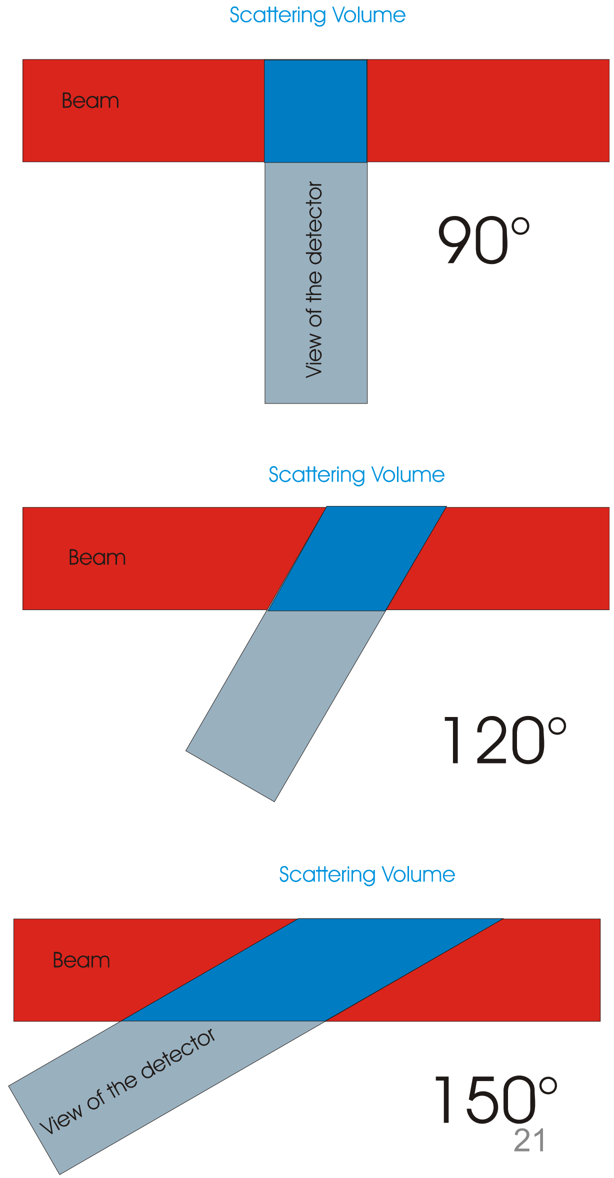
$n_{\text{standard}}, n_{\text{solvent}}$ refractive index for the standard and the solvent

e.g. toluene: $R_{\theta,\text{standard}} = 1.312\text{E}-5$ cm @ λ=632.8 nm

Size of the Scattering volume







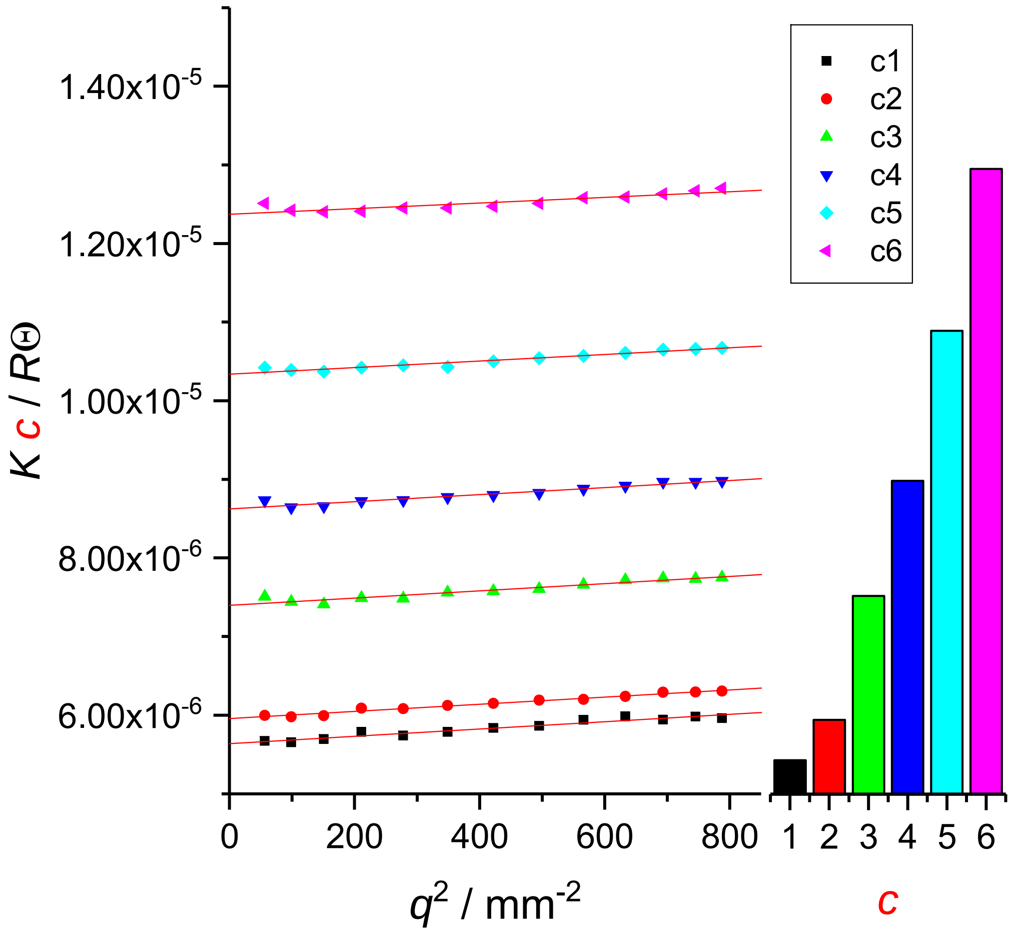
Countrate needs to be multiplied with sin(θ) !

Zimm in practice

PS 178100 Polystyrene/toluene
dn/dc=0.1069 ml/g
647.1nm / 100mW

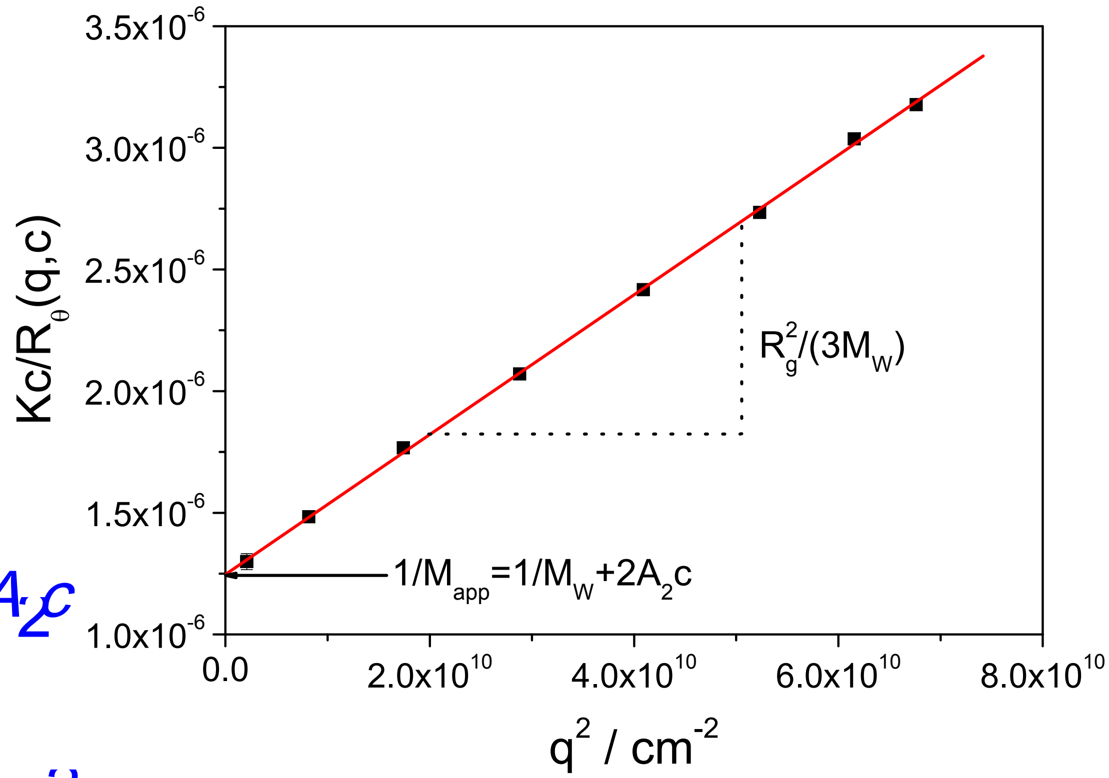
$$\frac{Kc}{R_\theta} = \frac{1}{M_w}\left(1 + \frac{q^2 R_g^2}{3}\right) + 2A_2 c$$

$$= \underbrace{\frac{1}{M_w} + 2A_2 c}_{\frac{1}{M_{app}}} + \underbrace{\frac{R_g^2}{3M_w}}_{slope} \cdot q^2$$



Zimm in practice

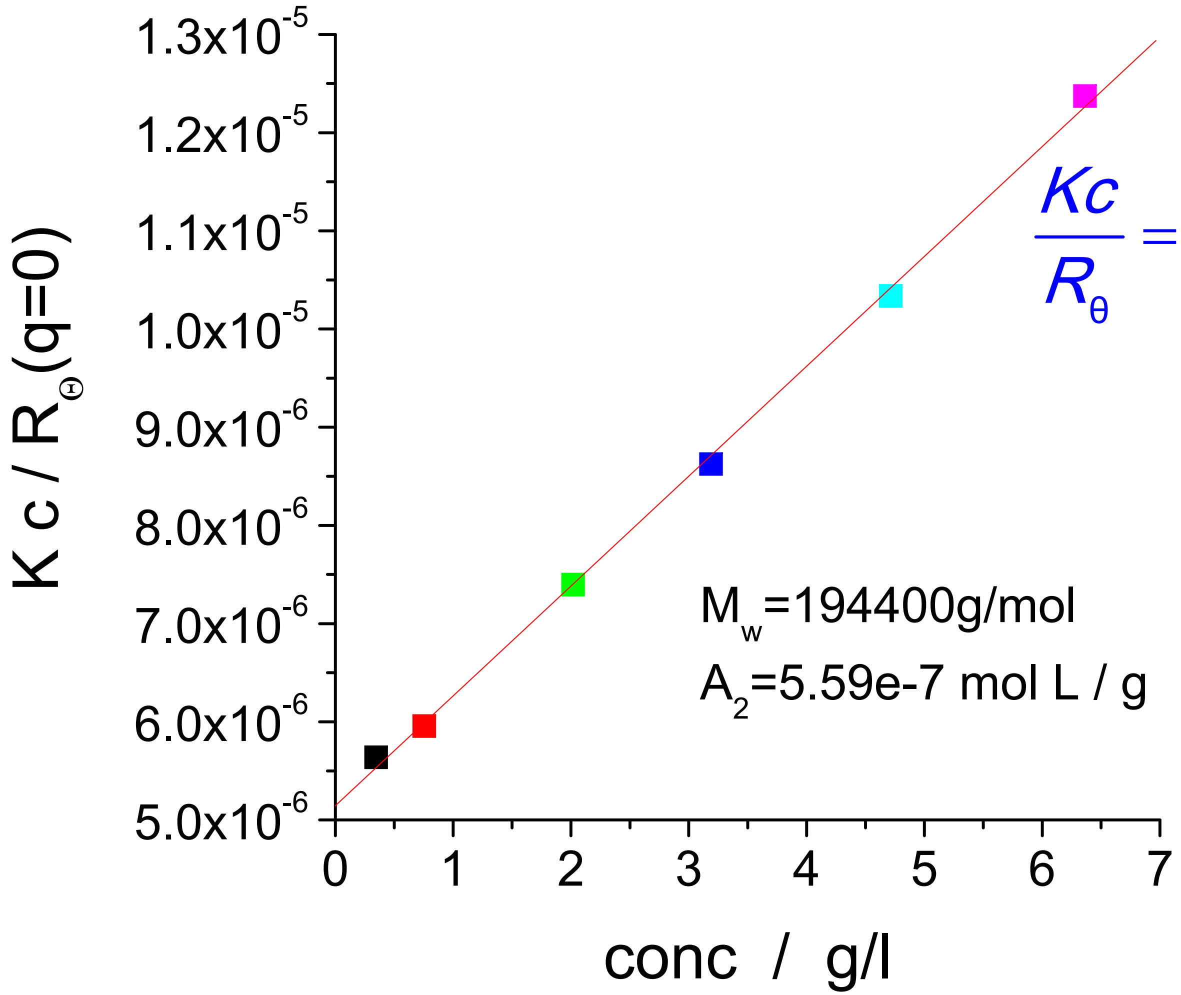
Linear interpolation of Kc/R_θ in dependence of q^2.



$$\frac{Kc}{R_\theta} = \frac{1}{M_W}\left(1+\frac{q^2R_g^2}{3}\right)+2A_2c$$

$$= \underbrace{\frac{1}{M_W}+2A_2c}_{\frac{1}{M_{app}}} + \underbrace{\frac{R_g^2}{3M_w}}_{slope}\cdot q^2$$

Zimm in practice

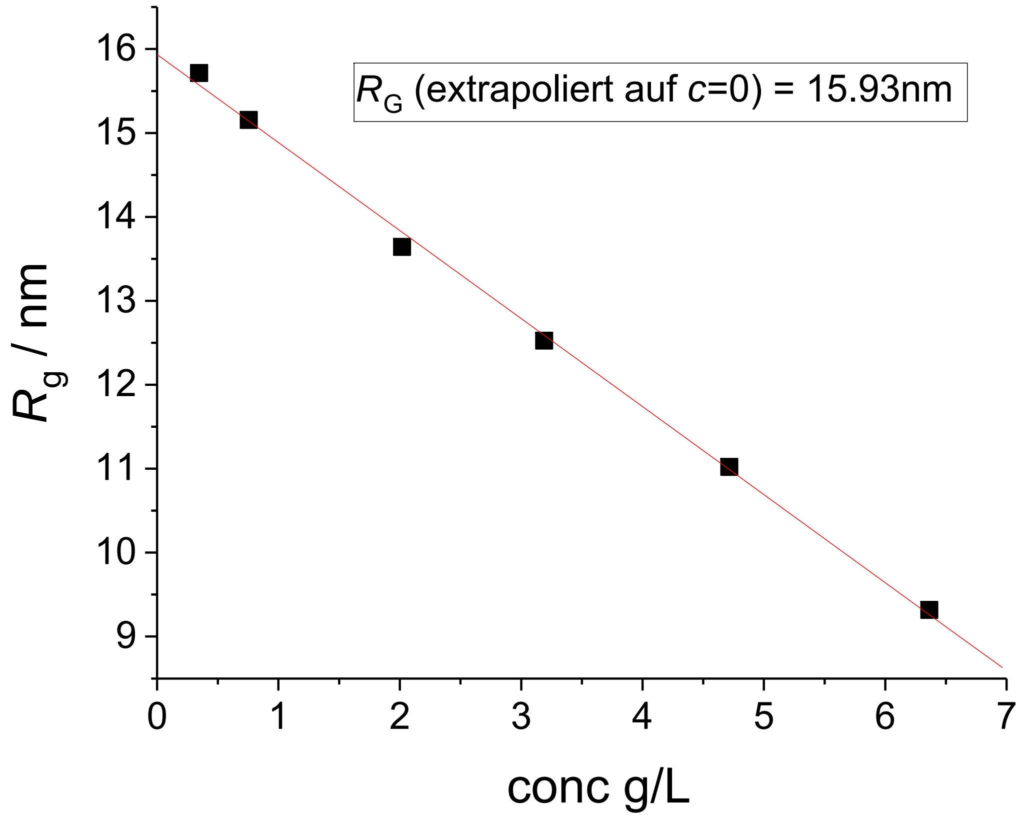


$$\frac{Kc}{R_\theta} = \underbrace{\frac{1}{M_w} + 2A_2c}_{\frac{1}{M_{app}}} + \underbrace{\frac{R_g^2}{3M_w}}_{slope} \cdot q^2$$

Zimm in practice

Für jede Konzentration ein R_g bestimmen

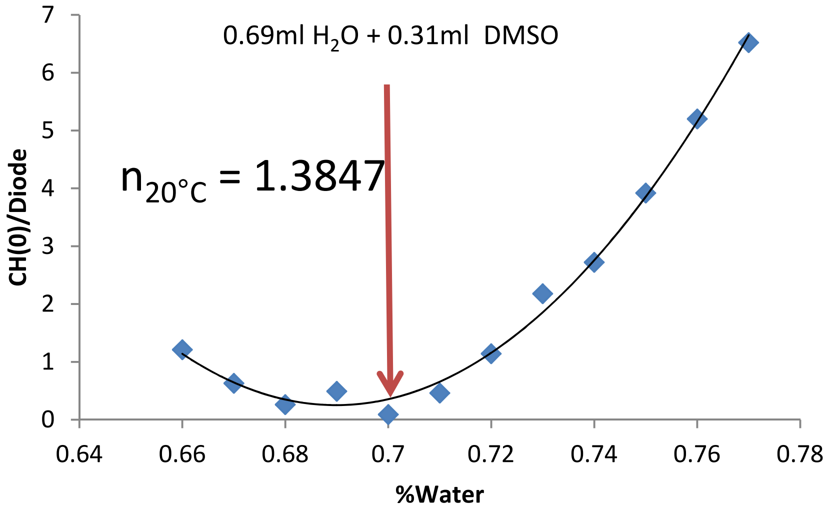
$$\frac{Kc}{R_\theta} = \underbrace{\frac{1}{M_w} + 2A_2c}_{\frac{1}{M_{app}}} + \underbrace{\frac{R_g^2}{3M_w}}_{slope} \cdot q^2$$

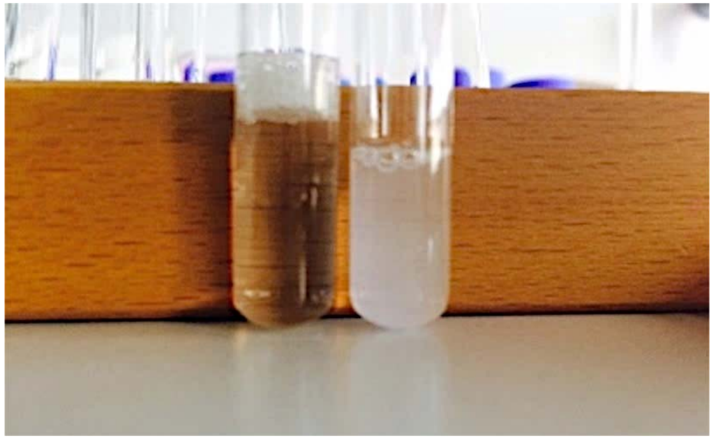


Zimm in practice

System: Partially fluorinated PMMA particles

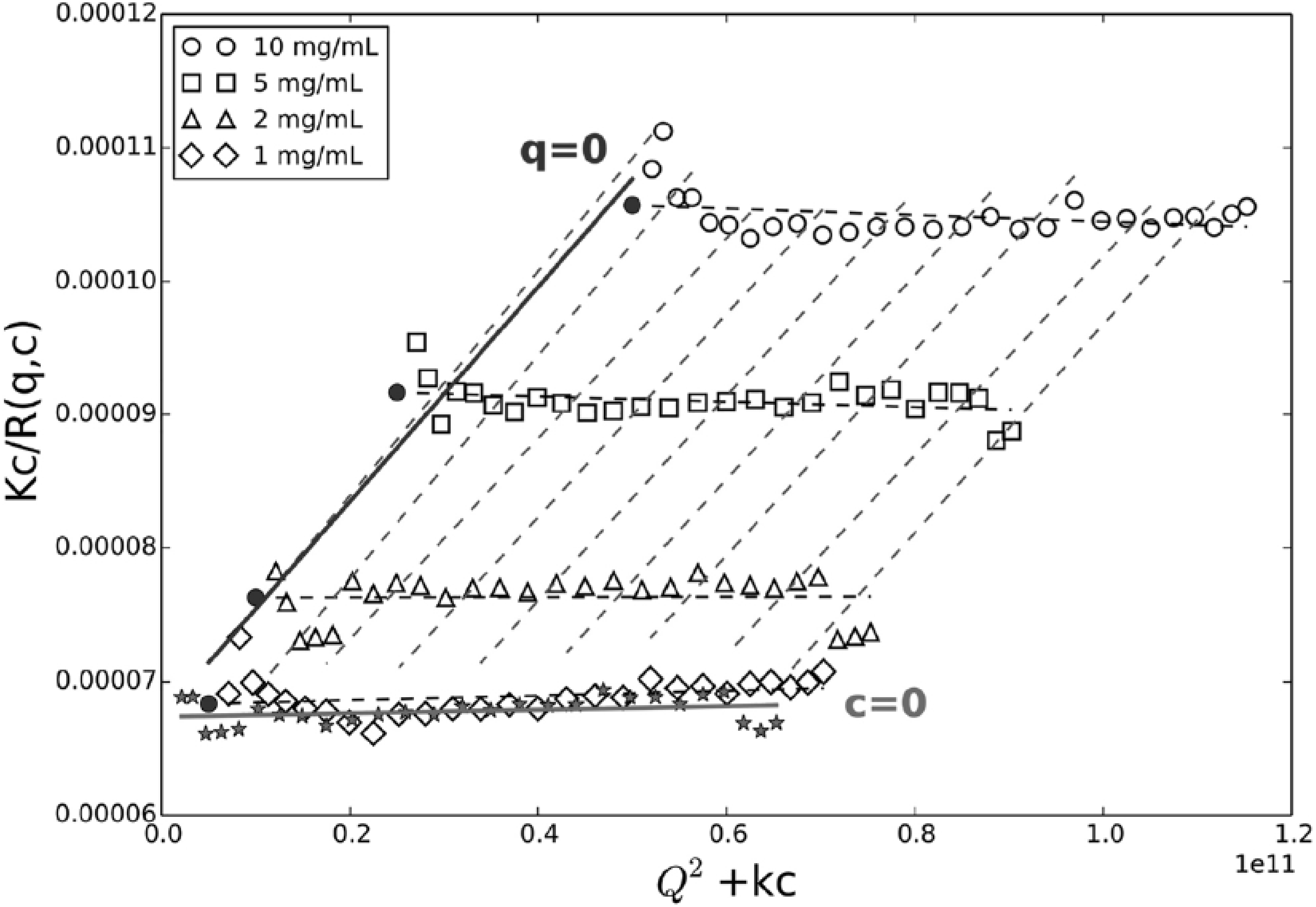
Index match H_2O/DMSO





System is described in: Y. Liu et al., Soft Matter, **12** (2016) 8485-8494.

Zimm in practice



Y. Liu at al., Colloids and Surfaces A, **544** (2018) 165-171.

Other particle scattering factors

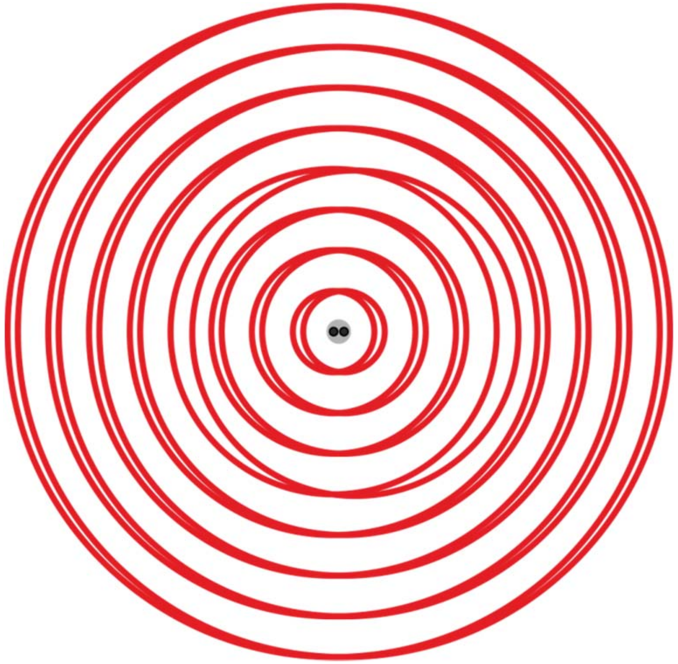
$$P_{sphere}(q) = \left\{ 3 \frac{\sin(qR) - qR\cos(qR)}{(qR)^3} \right\}^2 \quad \text{with } R_g = \sqrt{\frac{3}{5}} R$$

$$P_{coil}(q) = \frac{2}{qR_g} \left\{ \exp(-qR_g) + qR_g - 1 \right\}$$

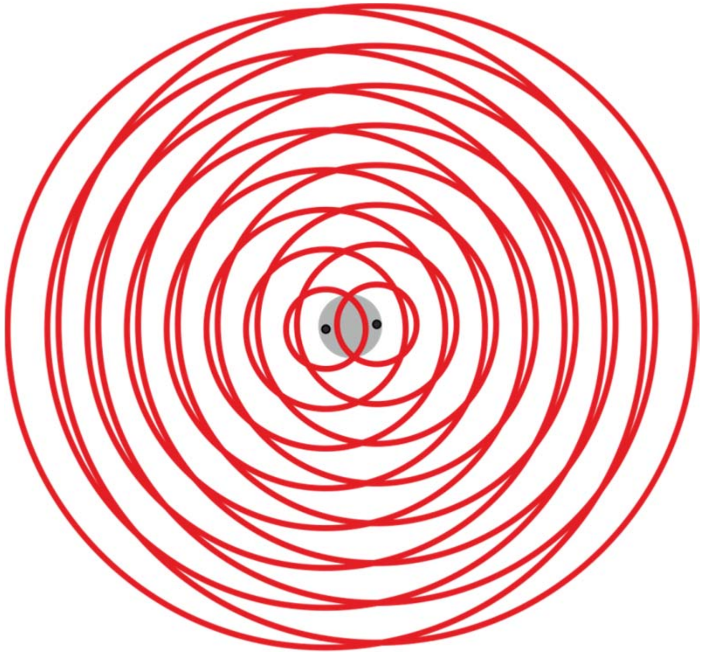
$$P_{rod}(q) = \frac{2}{qL} \int_0^{qL} \frac{\sin s}{s} ds - 4 \left(\frac{\sin(qL/2)}{qL} \right)^2 \quad \text{with } R_g = \sqrt{L^2/12}$$

Pedersen, J. S. Analysis of small-angle scattering data from colloids and polymer solutions: modeling and least-squares fitting. Adv Colloid Interfac 1997, 70, 171–210.

Angular dependence

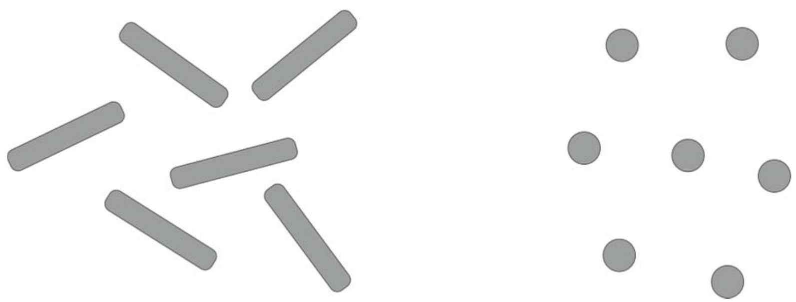


small particle do show a weak angular dependence



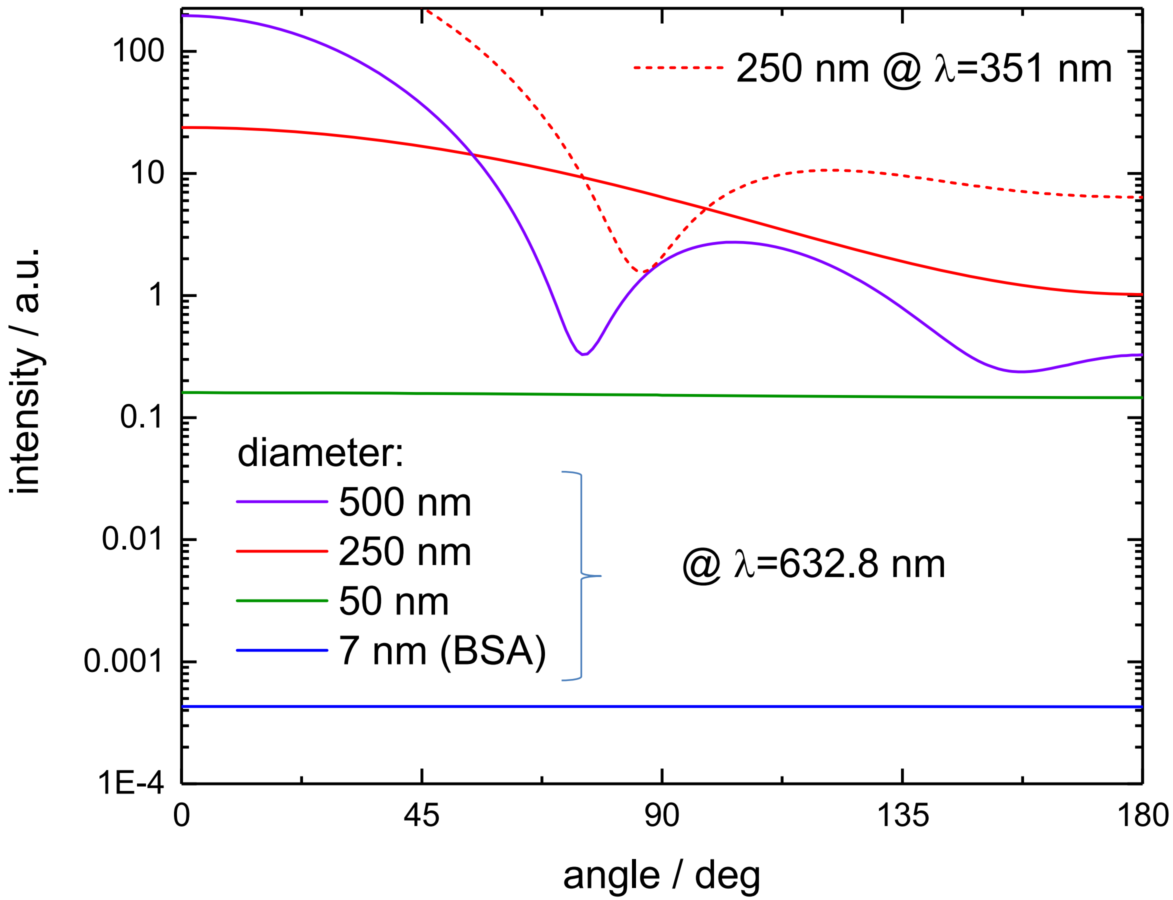
large particles show a strong angular dependence

Scattering of rods less coordinated.



scattering of spherical particles

diluted solutions:
scattering gives information about the form of the scatters



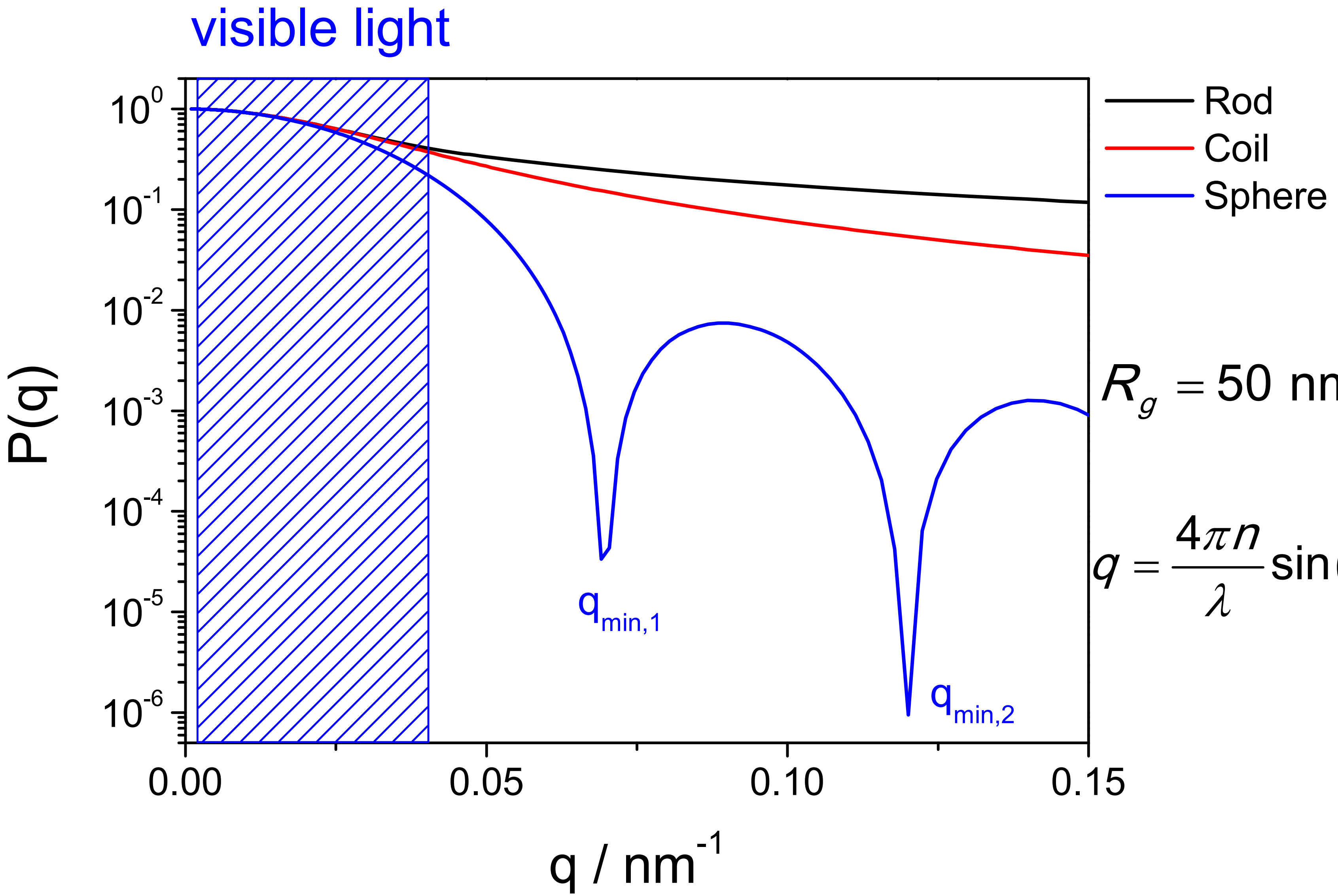
„formfactor“

remark

scattering vector:

$$q = |\vec{q}| = \frac{4\pi n}{\lambda}\sin(\theta/2)$$

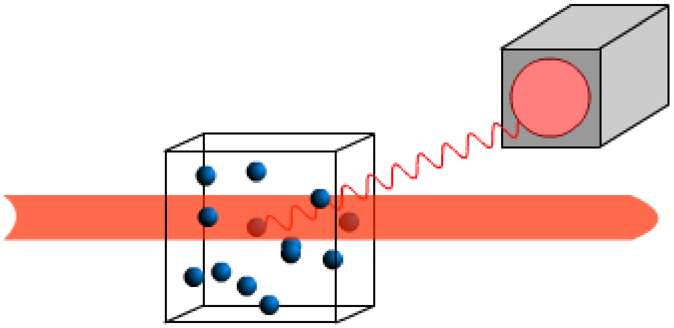
Other form factors



$$R_g = 50 \text{ nm}$$

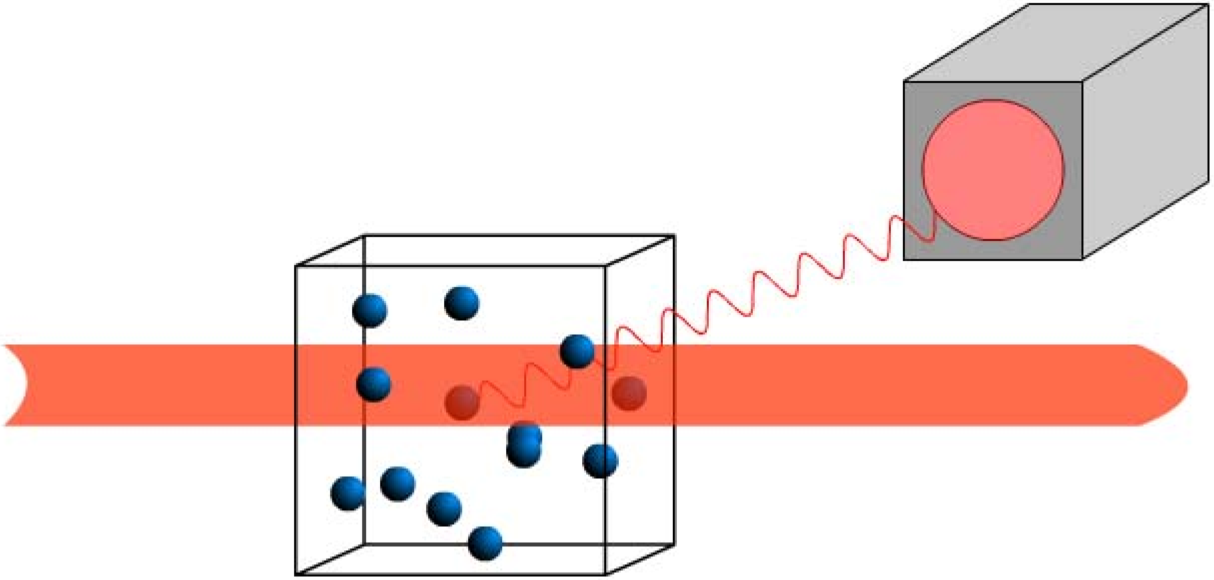
$$q = \frac{4\pi n}{\lambda}\sin(\theta/2)$$

Outline



- static light scattering:
  - Form factor (shape of the scatterer)
  - Structure factor (structure in the fluid)
  - Absolute scattering (molar mass, radius of gyration and second virial coefficient)
- **dynamic light scattering**
  - **Diffusion constant ($\Rightarrow$ hydrodynamic radius)**
  - **Distribution of diffusion constants**

DLS



1. Speckle pattern

2. Brownian motion

Time averaged scattering intensity:

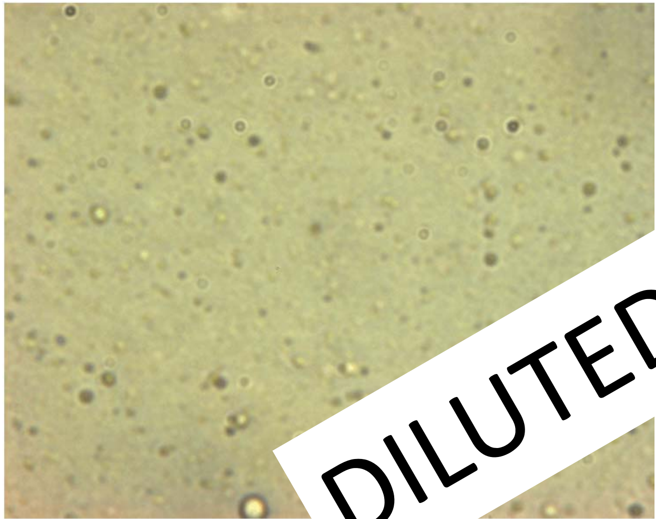
static light scattering

Time resolved scattering intensity fluctuations:

dynamic light scattering

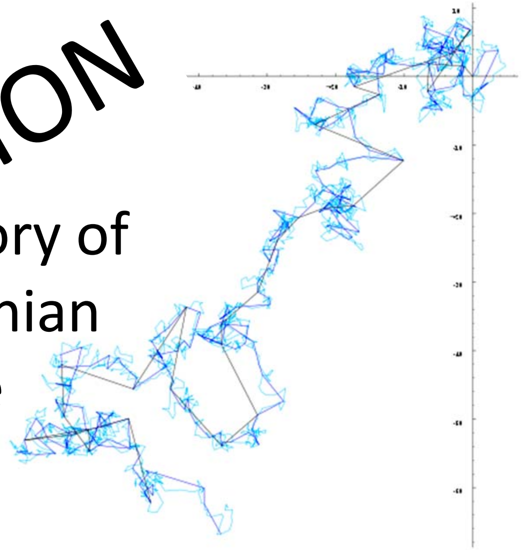
Mitglied in der Helmholtz-Gemeinschaft

Brownian motion



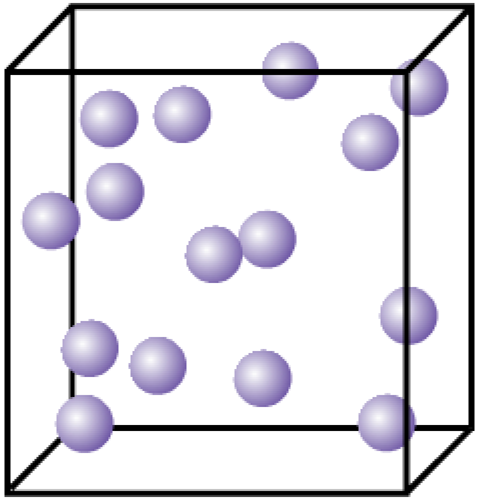
DILUTED SOLUTION

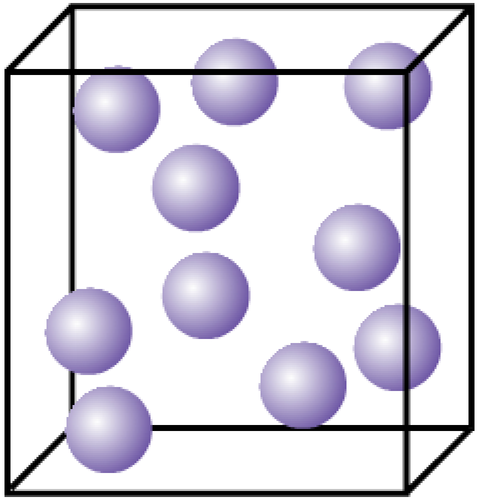
…tory of
… Brownian
particle



milk

small
fast

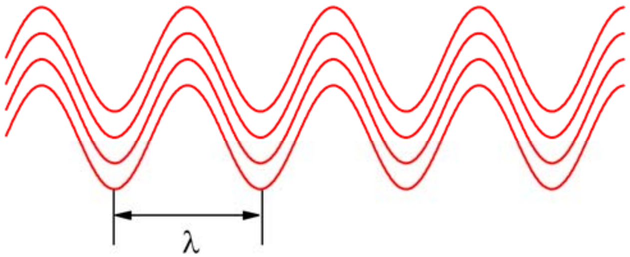


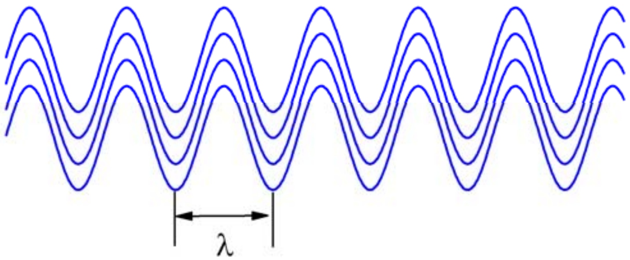


big
slow

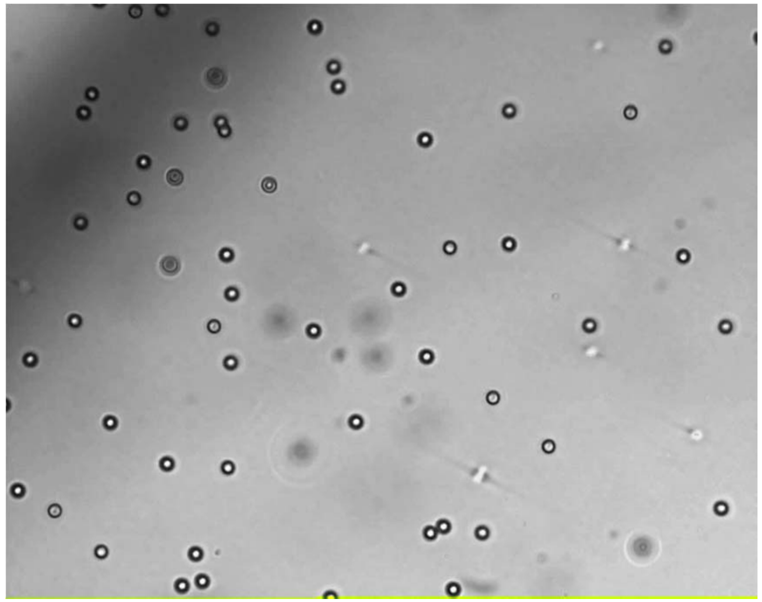
visualization and motivation

laser beam

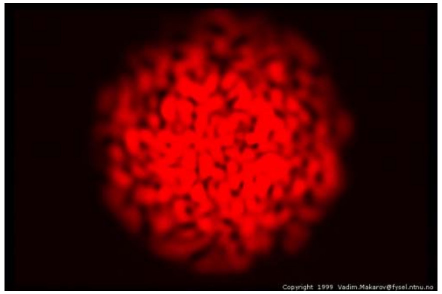




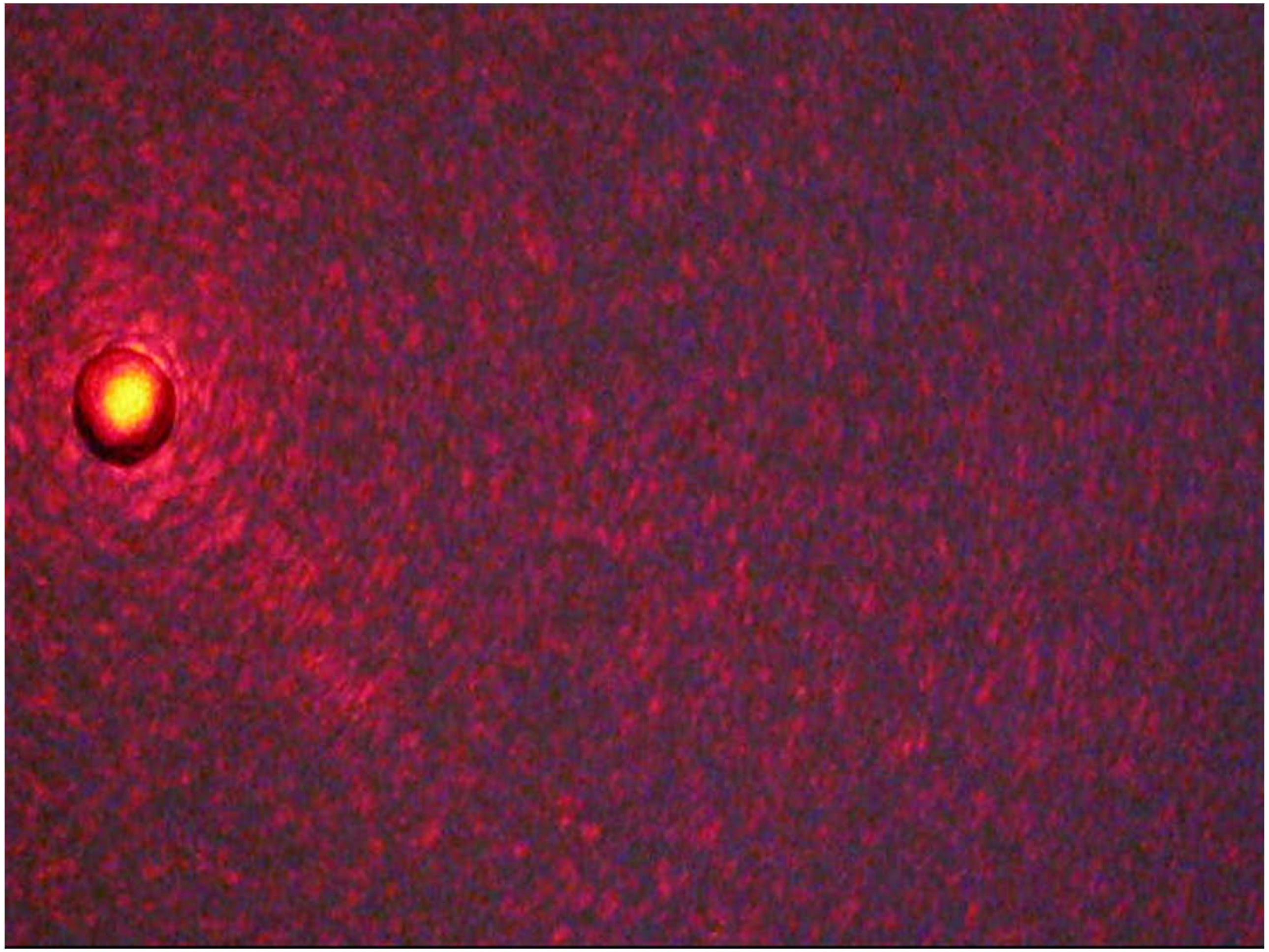
colloidal particles
(Brownian motion)



Speckle pattern

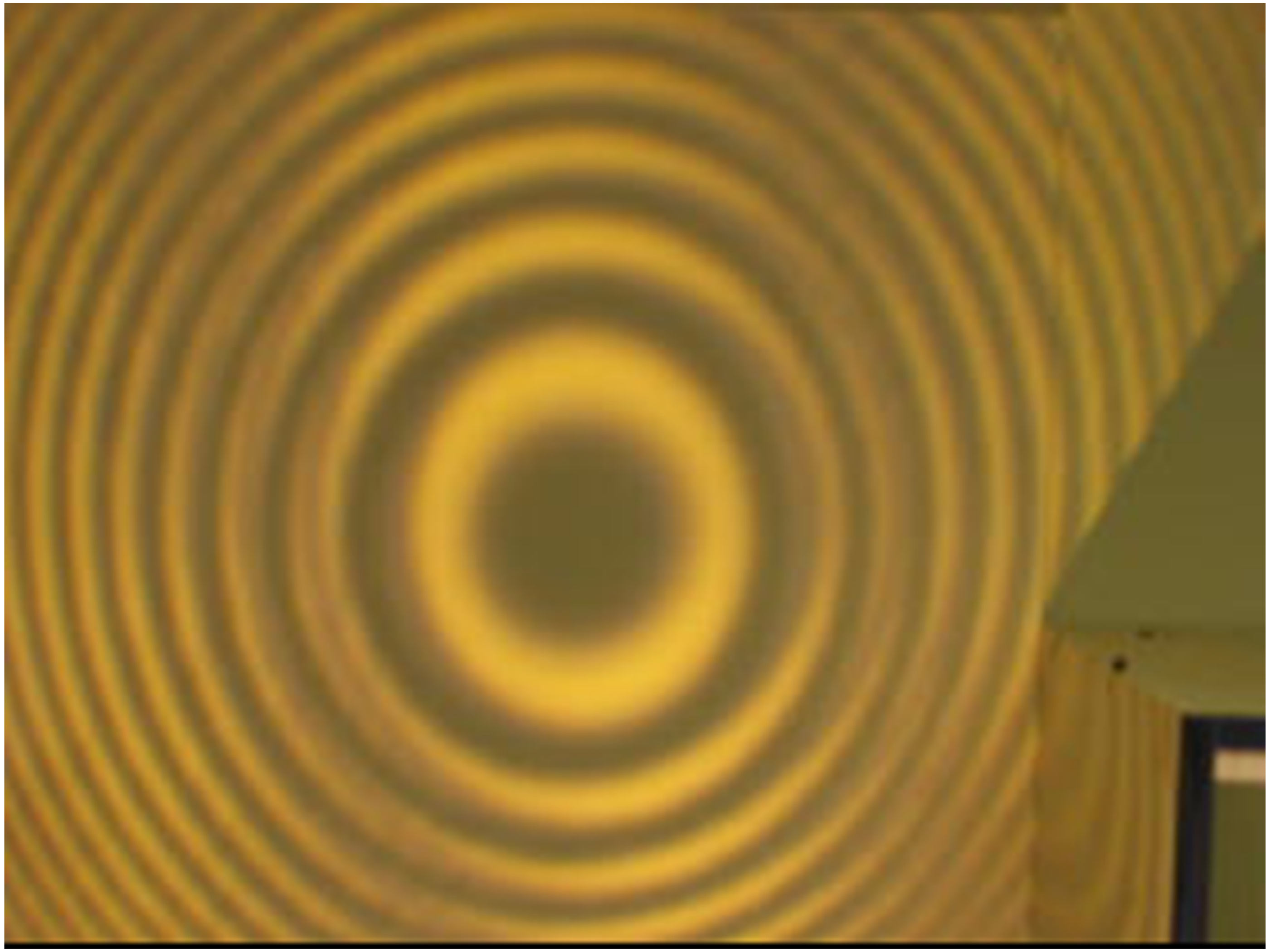


Large angle - faster motion

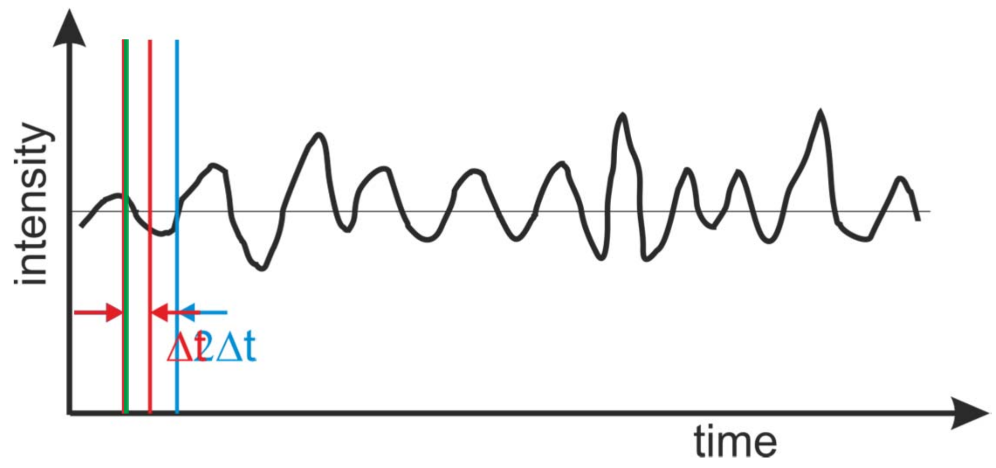


Low angle – slow motion

visualization and motivation



Intensity time correlation function



Dropping the subscript s

Auto correlation function (ACF) or
Time auto correlation function (TACF)

$$g_2(q,t) = g_I(q,t) \propto \langle I_S(q,0) I_S(q,t) \rangle$$

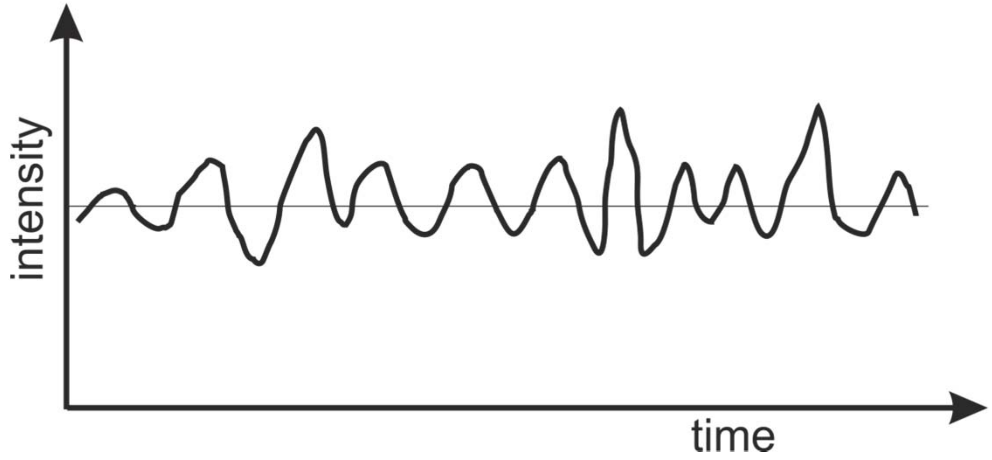
Experimental calculation of the ACF:

$$g_I(q, 0 \times \Delta t) = \frac{1}{M+1} \sum_{n=0}^{M} \langle I(q, n \times \Delta t) I(q, n \times \Delta t) \rangle$$

$$g_I(q, 1 \times \Delta t) = \frac{1}{M+1} \sum_{n=0}^{M} \langle I(q, n \times \Delta t) I(q, (n+1) \times \Delta t) \rangle$$

$$g_I(q, 2 \times \Delta t) = \frac{1}{M+1} \sum_{n=0}^{M} \langle I(q, n \times \Delta t) I(q, (n+2) \times \Delta t) \rangle$$

Intensity time correlation function



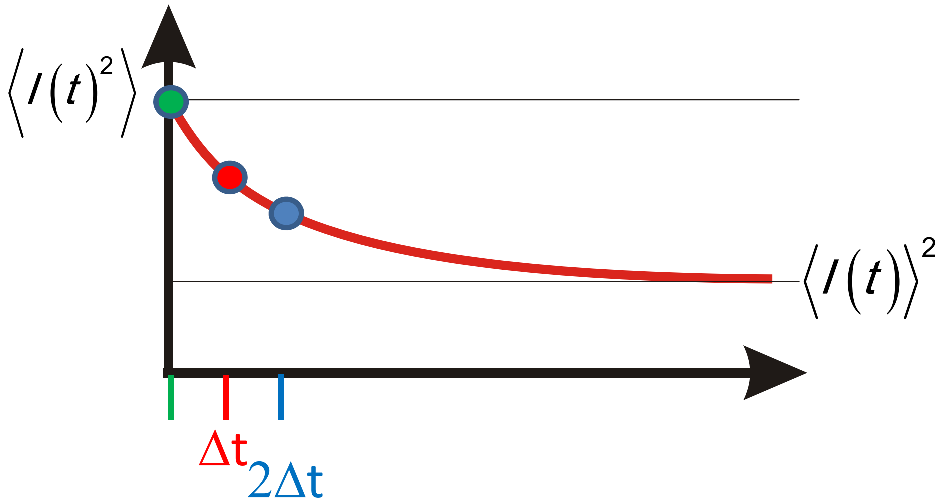
$$g_2(\Delta t) = \langle I(t) I(t+\Delta t) \rangle$$

For very short τ:

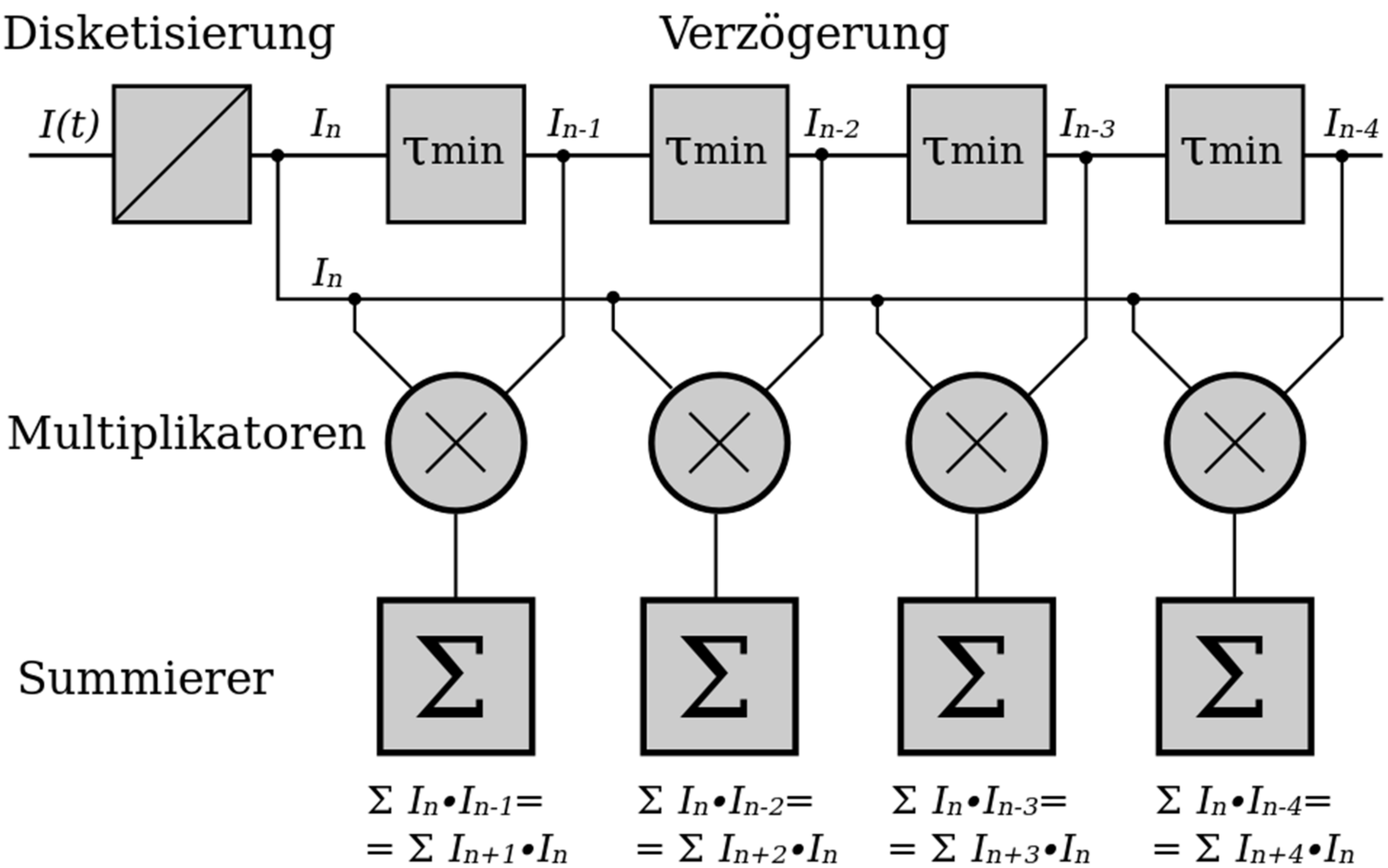
$$\lim_{\Delta t \to 0} g_2(\Delta t) = \langle I(t)^2 \rangle$$

For very long τ:

$$\lim_{\Delta t \to \infty} g_2(\Delta t) = \langle I(t) \rangle^2$$



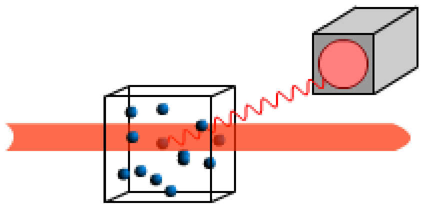
Principle correlator



Mitglied in der Helmholtz-Gemeinschaft

Field correlation function

$$E \propto \sum_{i=1}^{N} f(q)\exp\{\mathrm{i}qr_i\}$$



f(*q*) contains the scattering strength

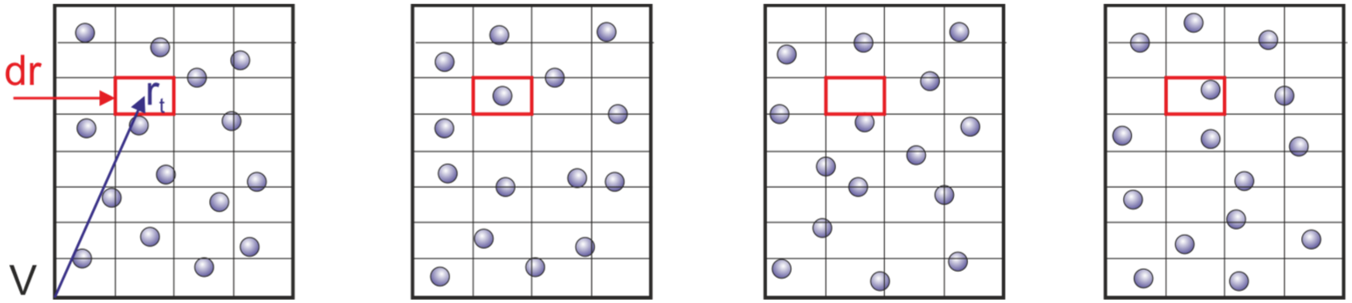
$$g_1(q,t) = g_E(q,t) \propto \langle E(q,0)E^*(q,t)\rangle$$
$$= \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\langle \exp\{\mathrm{i}qr_i(0)\}\exp\{-\mathrm{i}qr_j(t)\}\rangle$$

Field correlation function

non-interacting particles are statistically independent: i≠j vanishes

$$g_1(q,t) \propto \frac{1}{N}\sum_{i=1}^{N}\langle \exp\{\mathrm{i}qr_i(0)\}\exp\{-\mathrm{i}qr_i(t)\}\rangle$$
$$= \langle \exp\{\mathrm{i}qr_0\}\exp\{-\mathrm{i}qr_t\}\rangle$$
$$= \int dr_0 \int dr_t \exp\{\mathrm{i}q(r_0 - r_t)P(r_0, r_t, t)\}$$

Probability $P(r_t)$



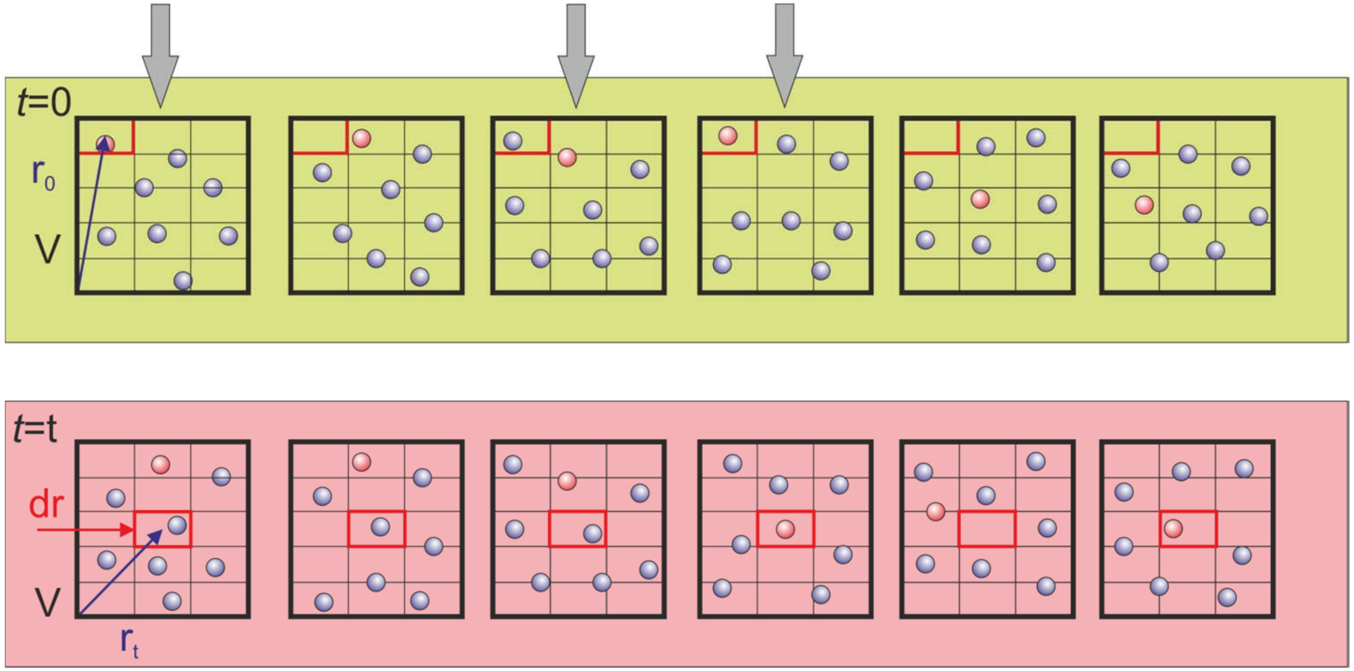
$P(r_t)\, dr$ = Probability that there are particles in the volume element dr around the position r_t

This function is normalized such that $$\int dr_t P(r_t) = 1$$

For homogenous non-interacting particles follows immediately

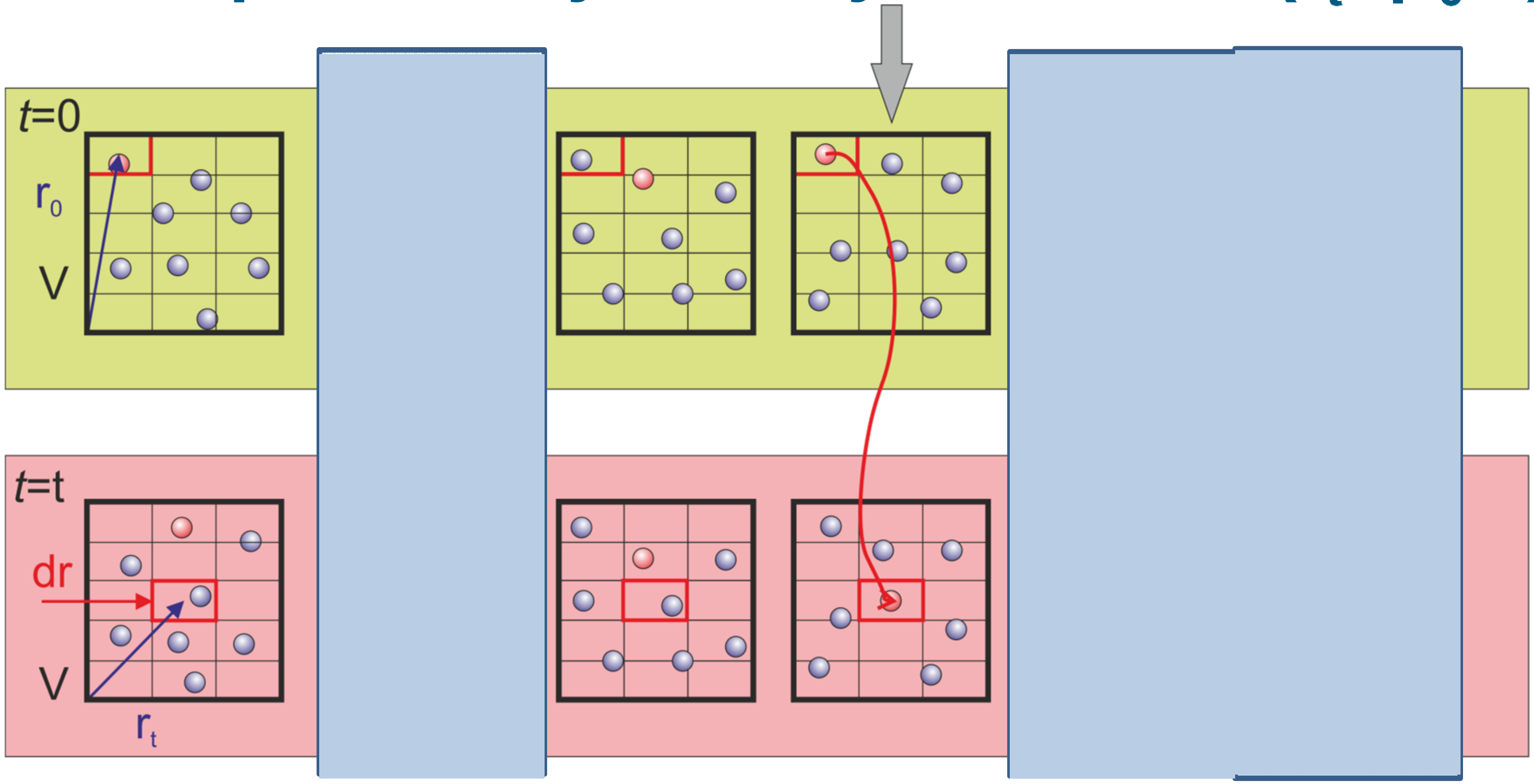
$$P(r_t) = \frac{1}{V}$$

Probability density function $P(r_0,r_t,t)$



$P(r_0,r_t,t)$ the probability density function that there are particles in dr around r_0 at t=0 AND in dr around r_t at t=t

Conditional probability density function $P(r_t,t|r_0,0)$

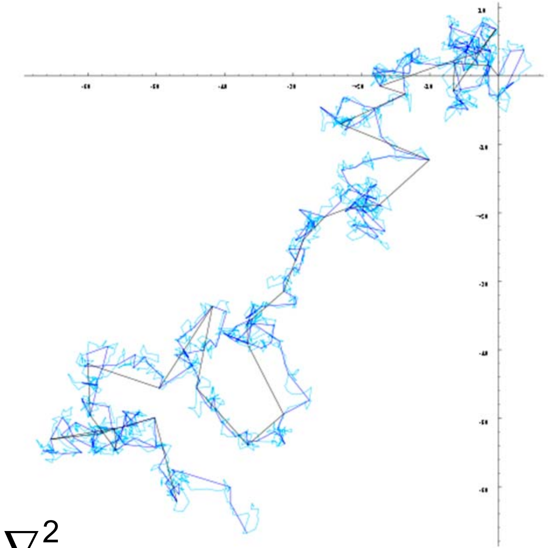


$P(r_t,t\,|\,r_0,0)$ the probability that there are particles in the volume element dr around r_t at t=t which had been at t=0 around r_0.

It holds: $$P(r_0,r_r,t) = P(r_0)\cdot\mathcal{P}(r_t,t\,|\,r_0,0)$$

Probability density function: 1-dim solution

Conditional probability $\mathcal{P}\left(\vec{r}_t,t\,|\,\vec{r}_0,0\right)$
to find the particle at r_t at time t,
which had been at r_0 at t=0.



Smoluchowsky equation:

$$\frac{\partial\mathcal{P}\left(\vec{r}_t,t\,|\,\vec{r}_0,0\right)}{\partial t}=\hat{\mathcal{L}}\mathcal{P}\left(\vec{r}_t,t\,|\,\vec{r}_0,0\right)$$

with $\hat{\mathcal{L}}=D_0\nabla^2$

… for dilute suspension of non-interacting spherical particles

with the initial condition at t=0: $\mathcal{P}\left(\vec{r}_t,t\,|\,\vec{r}_0,0\right)=\delta\left(\vec{r}_t-\vec{r}_0\right)$

formal solution $\mathcal{P}\left(\vec{r}_t,t\,|\,\vec{r}_0,0\right)=\exp\left(\hat{\mathcal{L}}t\right)\delta\left(\vec{r}_t-\vec{r}_0\right)$

Probability density function: 1-dim solution

We need to solve $g_1(q,t) = \int d\vec{r}_0 \int d\vec{r}_t \exp\{iq(\vec{r}_0 - \vec{r}_t)\} P(\vec{r}_0 \vec{r}_t, t)$

Rewrite the integral using:

$$P(\vec{r}_0, \vec{r}_r, t) = P(\vec{r}_0) \cdot \mathcal{P}(\vec{r}_t, t \,|\, \vec{r}_0, 0)$$

$$\mathcal{P}(\vec{r}_t, t \,|\, \vec{r}_0, 0) = \exp(\hat{\mathcal{L}} t)\, \delta(\vec{r}_t - \vec{r}_0)$$

$$\hat{g}_1 = \int d\vec{r}_0 \exp\{i\vec{q}\vec{r}_0\} P(\vec{r}_0) \int d\vec{r}_t \exp(\hat{\mathcal{L}} t)\, \delta(\vec{r}_t - \vec{r}_0) \exp\{-i\vec{q}\vec{r}_t\}$$

$$= \frac{1}{V} \int d\vec{r}_0 \exp\{i\vec{q}\vec{r}_0\} \exp(\hat{\mathcal{L}} t) \exp\{-i\vec{q}\vec{r}_0\}$$

using $P(\vec{r}) = 1/V$ for diluted solutions and the definition

$$\int dx' f'(x)\, \delta(x - x') = f(x)$$

Dropping the subscript 0 $\Rightarrow$ $\hat{g}_E = \hat{g}_1 = \frac{1}{V} \int d\vec{r} \exp\{i\vec{q}\vec{r}\} \exp(\hat{\mathcal{L}} t) \exp\{-i\vec{q}\vec{r}\}$

Probability density function: 1-dim solution

$$\hat{g}_1 = \hat{g}_E = \frac{1}{V}\int d\vec{r}\, \exp\{i\vec{q}\vec{r}\} \exp\left(\hat{\mathcal{L}}t\right) \exp\{-i\vec{q}\vec{r}\}$$

Taylor expansion: $\exp\left(\hat{\mathcal{L}}t\right) = \sum_{n=0}^{\infty} \frac{1}{n!} t^n \hat{\mathcal{L}}^n$

$$\hat{g}_1 = \hat{g}_E = \frac{1}{V}\int d\vec{r}\, \exp\{i\vec{q}\vec{r}\} \sum_{n=0}^{\infty} \frac{1}{n!} t^n \hat{\mathcal{L}}^n \exp\{-i\vec{q}\vec{r}\}$$

Auxiliary calculation:

$$\hat{\mathcal{L}}^n \exp\{i\vec{q}\vec{r}\} = (D_0 \nabla^2)^n \exp\{i\vec{q}\vec{r}\} = -\left(D_0 q^2\right)^n \exp\{-i\vec{q}\vec{r}\}$$

$$\frac{d^2}{dr^2} \exp\{-i\vec{q}\vec{r}\} = (-i)\frac{d}{dr} \exp\{-i\vec{q}\vec{r}\} = -\exp\{-i\vec{q}\vec{r}\}$$

$$\hat{g}_1 = \hat{g}_E = \frac{1}{V}\int d\vec{r}\, \exp\{i\vec{q}\vec{r}\} \sum_{n=0}^{\infty} \frac{1}{n!} t^n \left[-\left(D_0 q^2\right)^n\right] \exp\{-i\vec{q}\vec{r}\}$$

1-dim electric-field auto-correlation function

$$\hat{g}_1 = \hat{g}_E = \frac{1}{V}\int d\vec{r}\,\exp\{i\vec{q}\vec{r}\}\cdot \sum_{n=0}^{\infty}\frac{1}{n!}t^n\left[-\left(D_0 q^2\right)^n\right]\cdot \exp\{-i\vec{q}\vec{r}\}$$

Reversed Taylor expansion:

$$\hat{g}_1 = \hat{g}_E = \frac{1}{V}\int d\vec{r}\,\exp\{i\vec{q}\vec{r}\}\cdot \exp\left(-D_0 q^2 t\right)\cdot \exp\{-i\vec{q}\vec{r}\}$$

$$= \frac{1}{V}\int d\vec{r}\,\exp\left(-D_0 q^2 t\right)$$

$$= \frac{\exp\left(-D_0 q^2 t\right)}{V}\int d\vec{r}$$

$$\Rightarrow \quad \hat{g}_1 = \exp\left(-D_0 q^2 t\right)$$

... calculation in 3D- similiar ....

Field $\Rightarrow$ Intensity field correlation function

Field correlation function

$$g_1(q,t) = g_E(q,t) \propto \left\langle E(q,0)E^*(q,t)\right\rangle$$

Intensity correlation function

$$g_2(q,t) = g_I(q,t)$$

$$\propto \left\langle E(q,0)E^*(q,0)E(q,t)E^*(q,t)\right\rangle$$

$$\frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N}\sum_{l=1}^{N}\left\langle \exp\left\{\mathrm{i}q\left(r_i(0)-r_j(0)\right)\right\}\exp\left\{-\mathrm{i}q\left(r_k(t)-r_l(t)\right)\right\}\right\rangle$$

Statistical independence

all terms with *ijkl* will be zero if one index is different from the other three. At least pairs of equal indices are required to give a nonzero result

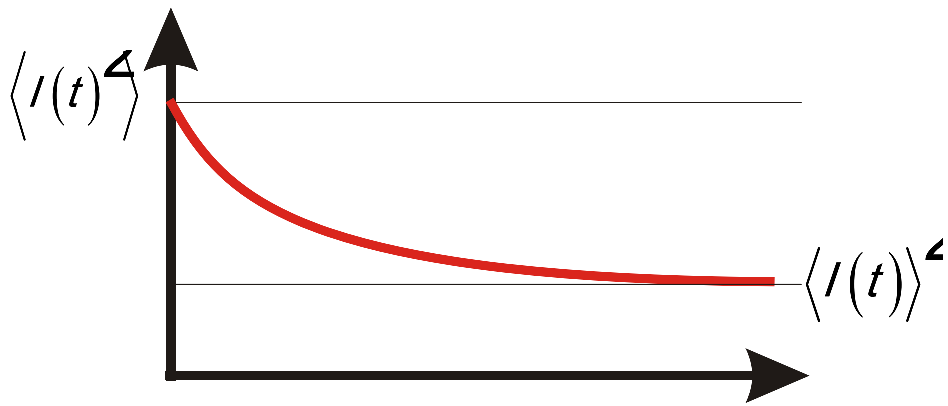
Siegert Relation

$$\hat{g}_2(q,t) = 1 + \left|\hat{g}_1(q,t)\right|^2$$

Intensity auto correlation function

Intensity auto correlation function

$$g_I(q,t) = g_2(q,t) = \langle I(q) \rangle^2 + |g_1(q,t)|^2$$



Normalized intensity auto correlation function

$$\hat{g}_2(q,t) = 1 + |\hat{g}_1(q,t)|^2$$

Field & intensity auto correlation function

Intensity correlation function

$$g_2(\tau) \propto \exp(-t/\tau)$$

$$\Gamma = \frac{1}{\tau} = 2Dq^2$$

Field correlation function

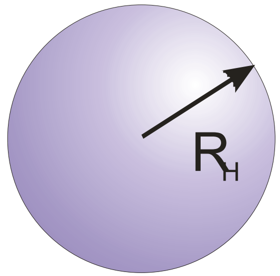
$$g_1(\tau') \propto \exp(-t/\tau')$$

$$\Gamma = \frac{1}{\tau'} = Dq^2$$

Collective diffusion and hydrodynamic radius

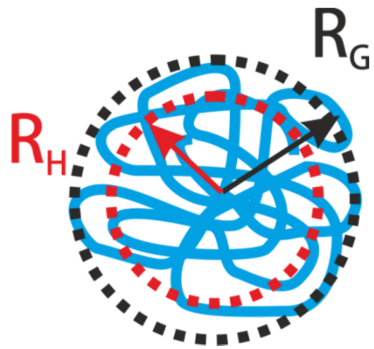
Stokes Einstein equation:

$$R_H = \frac{k_B T}{6\pi\eta_{solvent} D_0}$$



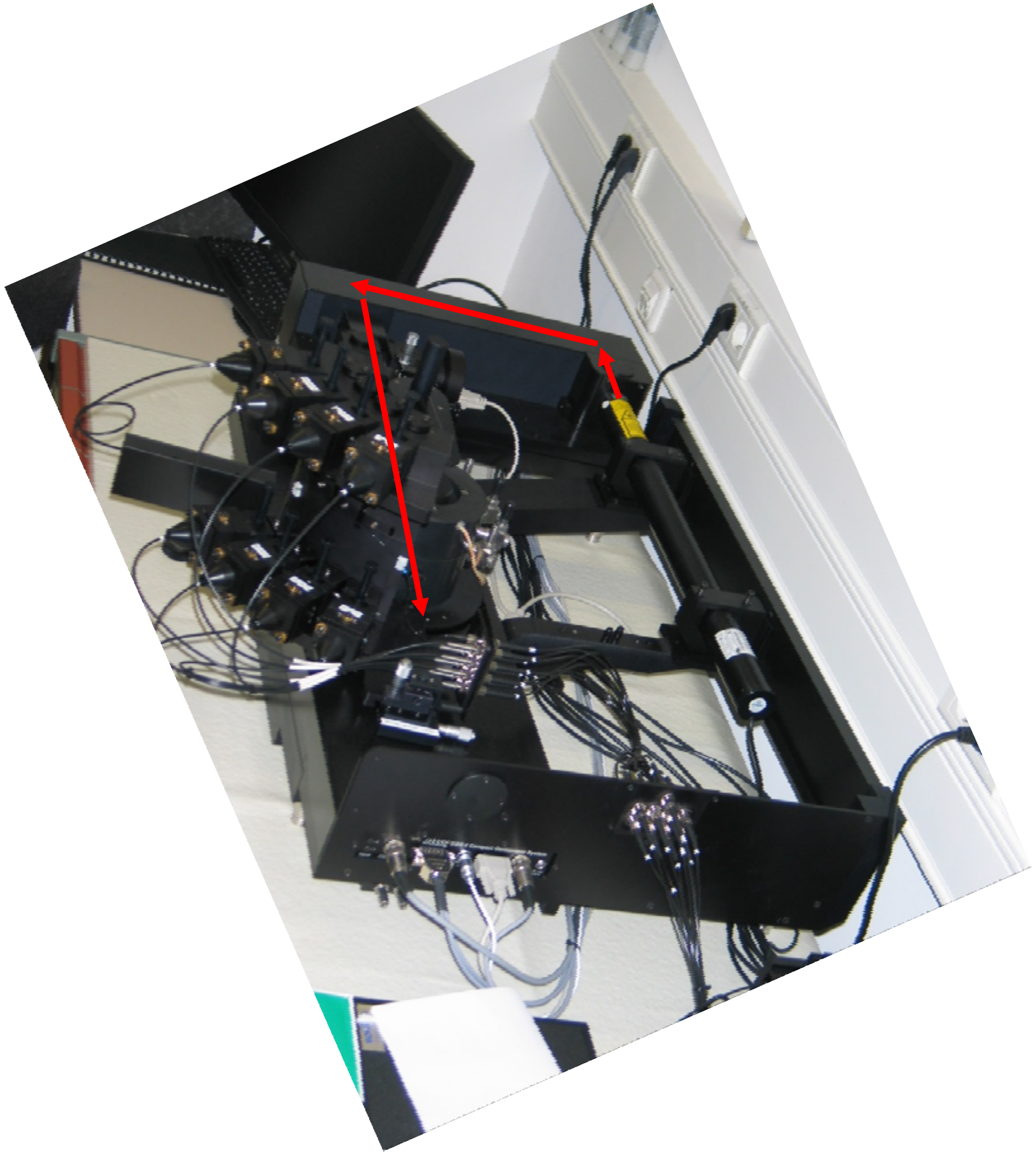
structure sensitive parameter $\rho = R_G / R_H$

- $\rho > 2$ cylinder
- $\rho = 1.5$ Θ - coil
- $\rho = 0.77$ sphere



Example:

Combined time-resolved SLS and DLS – wide angle set-up

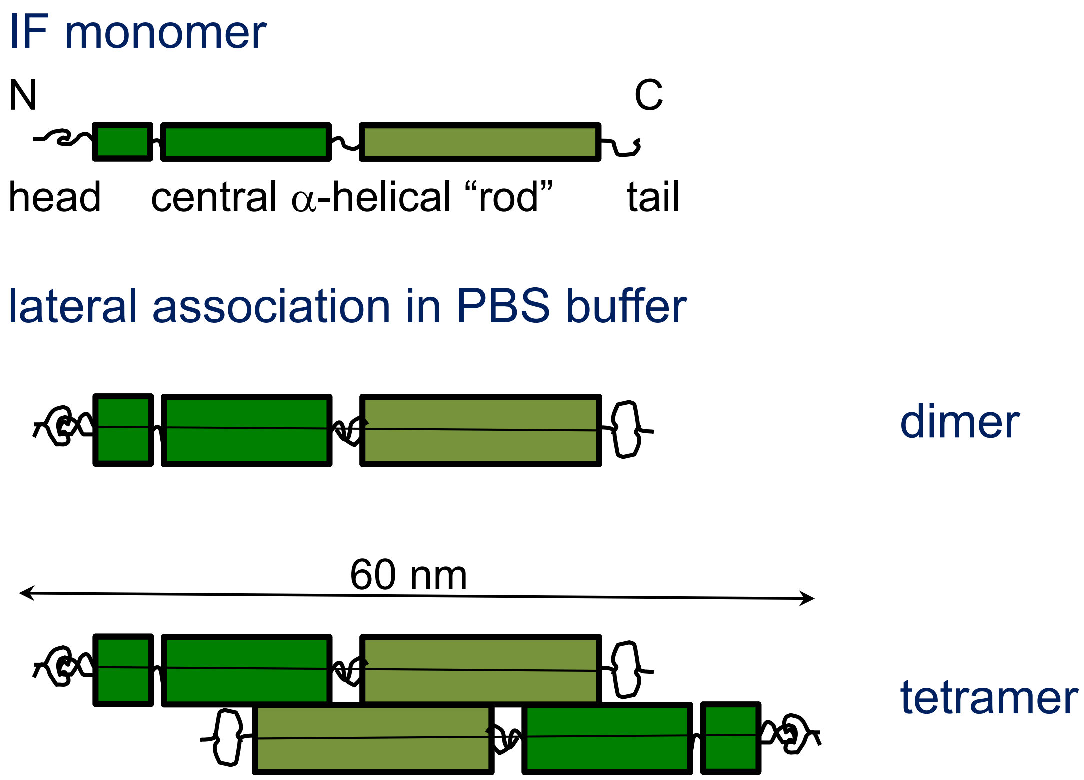


courtesy of Klaus Huber

Mitglied in der Helmholtz-Gemeinschaft

Self assembly of vimentin

human vimentin is an IF protein
expressed in
fibroblasts, the eye lens and cells of mesenchymal origin



courtesy of Klaus Huber

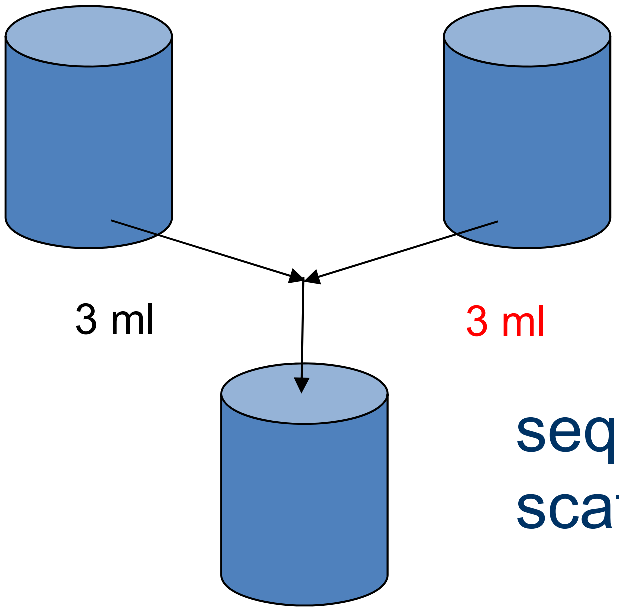
Lopez, C. G. et al. *PNAS* 2016 **113** 11152

Self assembly of vimentin

sodium phosphate buffer
2 mM

vimentin
0.14 g/L

KCl
0.1 M



sequential addition to scattering cell

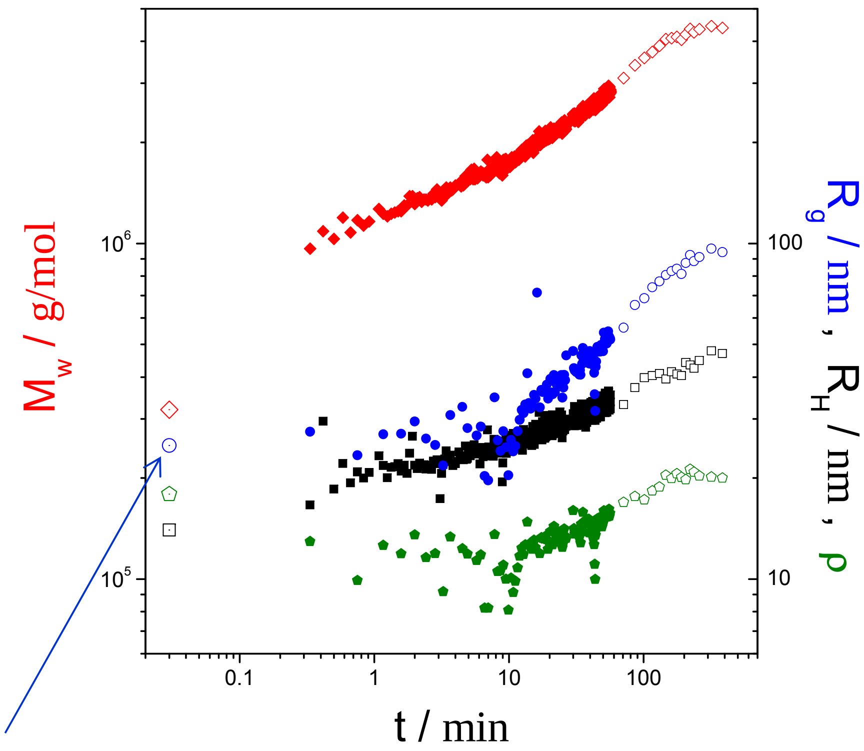
couresty of Klaus Huber

Lopez, C. G. et al. *PNAS* 2016 **113** 11152

Self assembly of vimentin

couresty of Klaus Huber

combined multi-angle SLS and DLS



state prior to addition of aq. KCl

lateral aggregation of tertamer

ρ exceeds the value of 2
-
highly anisometric structures

Lopez, C. G. et al. *PNAS* 2016 **113** 11152

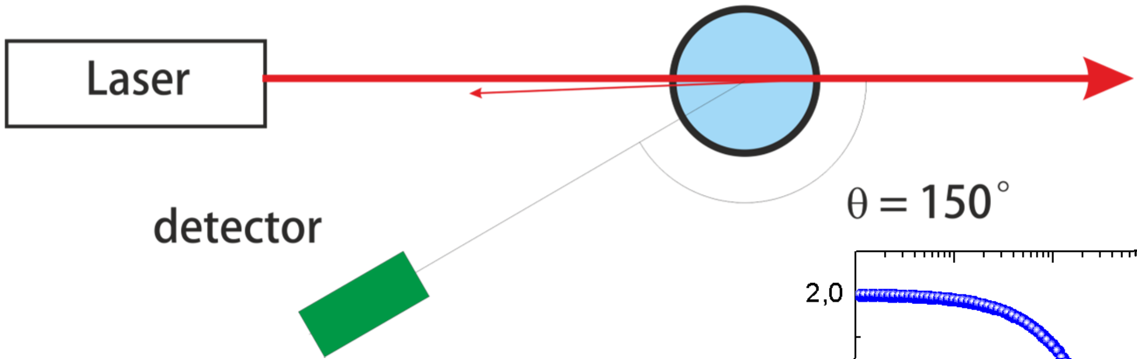
Problems

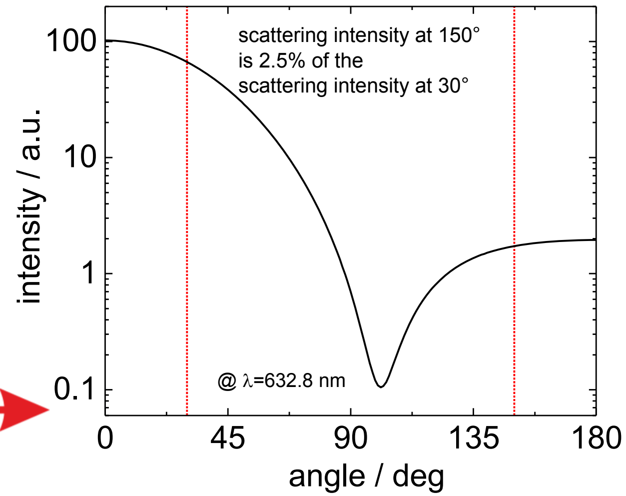
- backscattering of the light at surfaces
- multiple scattering

Problem: backscattering

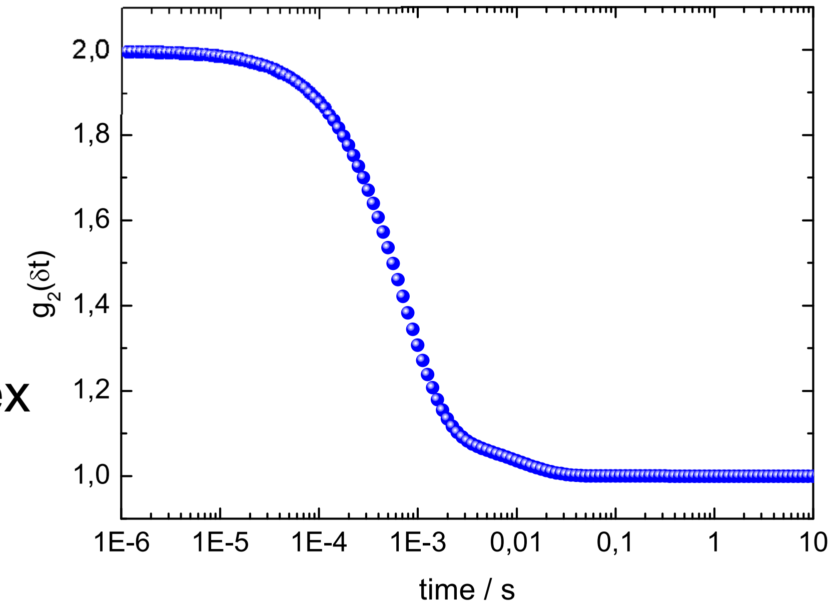
large particles with a diameter of 400 nm

without index bath



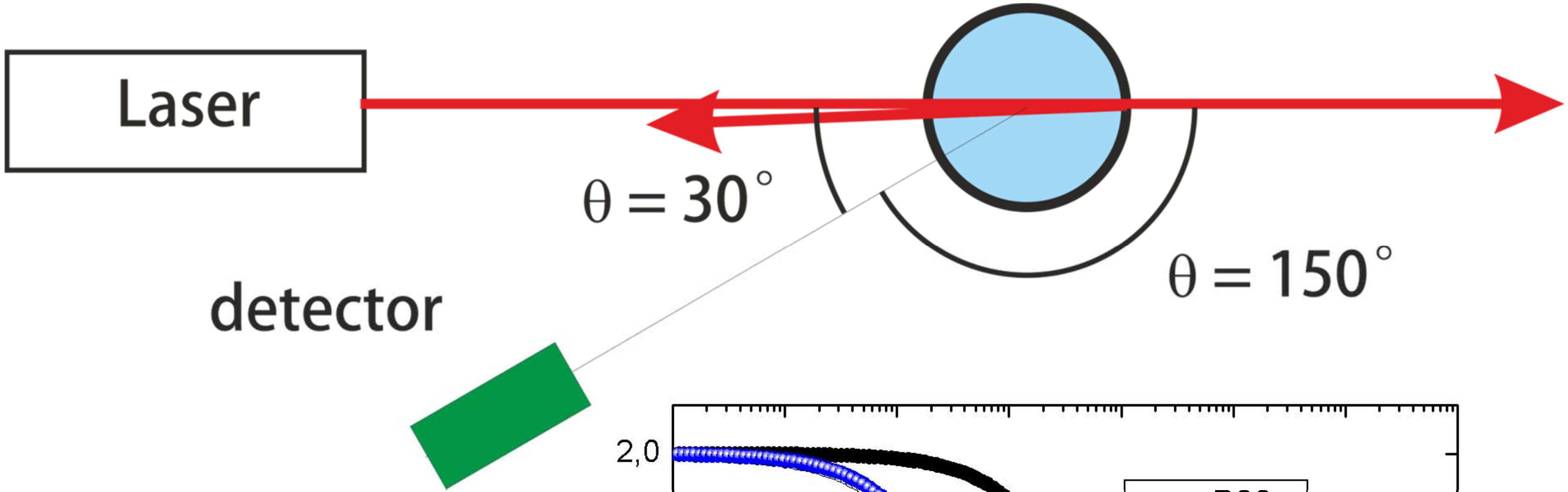


$\theta = 150^\circ$

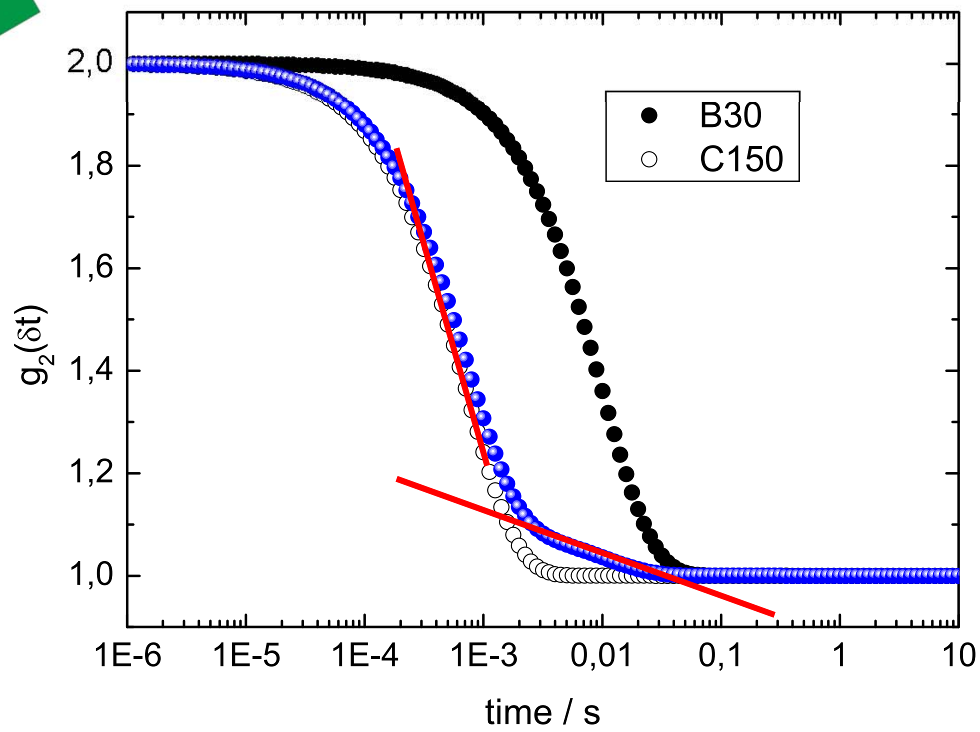


Measurement at θ=150° of Latex Particles with *R* = 200 nm

Problem: backscattering



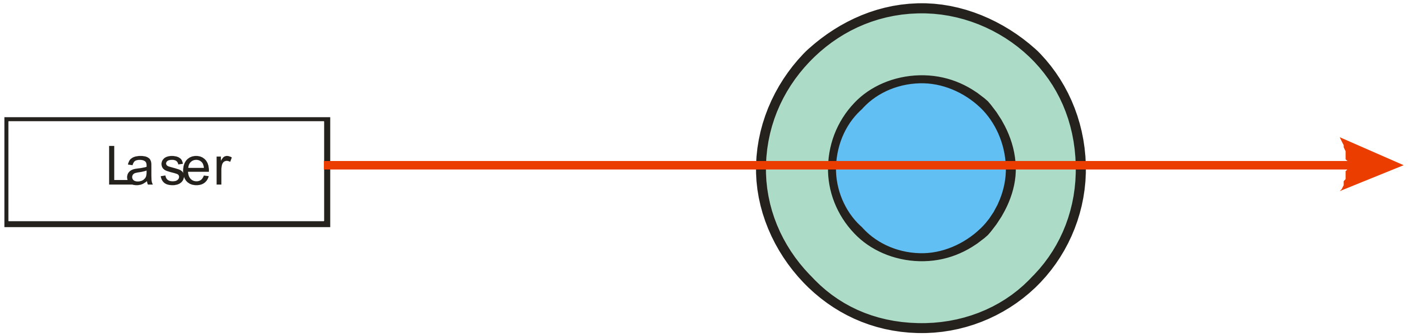
Measurement at θ=150° of Latex Particles with a *R* = 200 nm



Problem: backscattering

To avoid backscattering problems:

with index bath

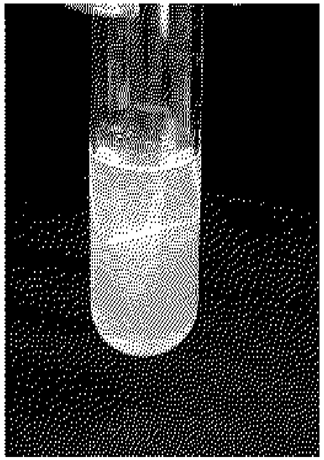


or/and

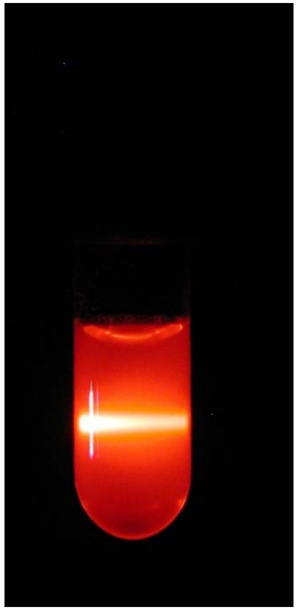
Rayleigh horn

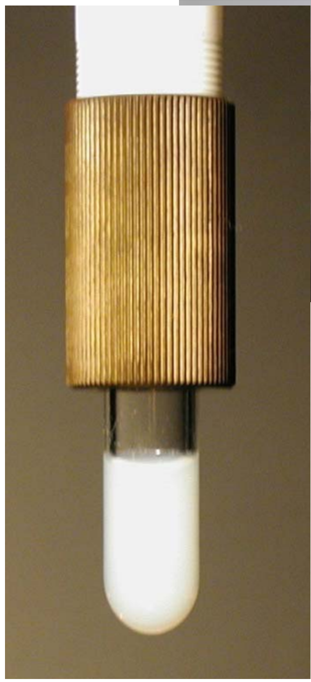
Problem:Multiple scattering

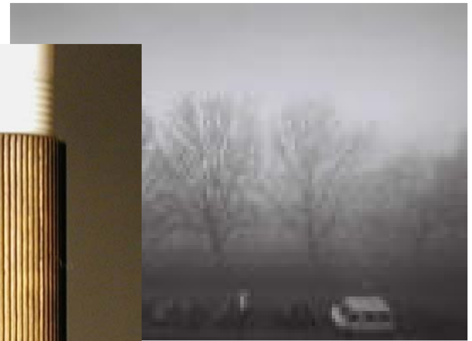
critical opalescence



KBr + $AgNO_3$



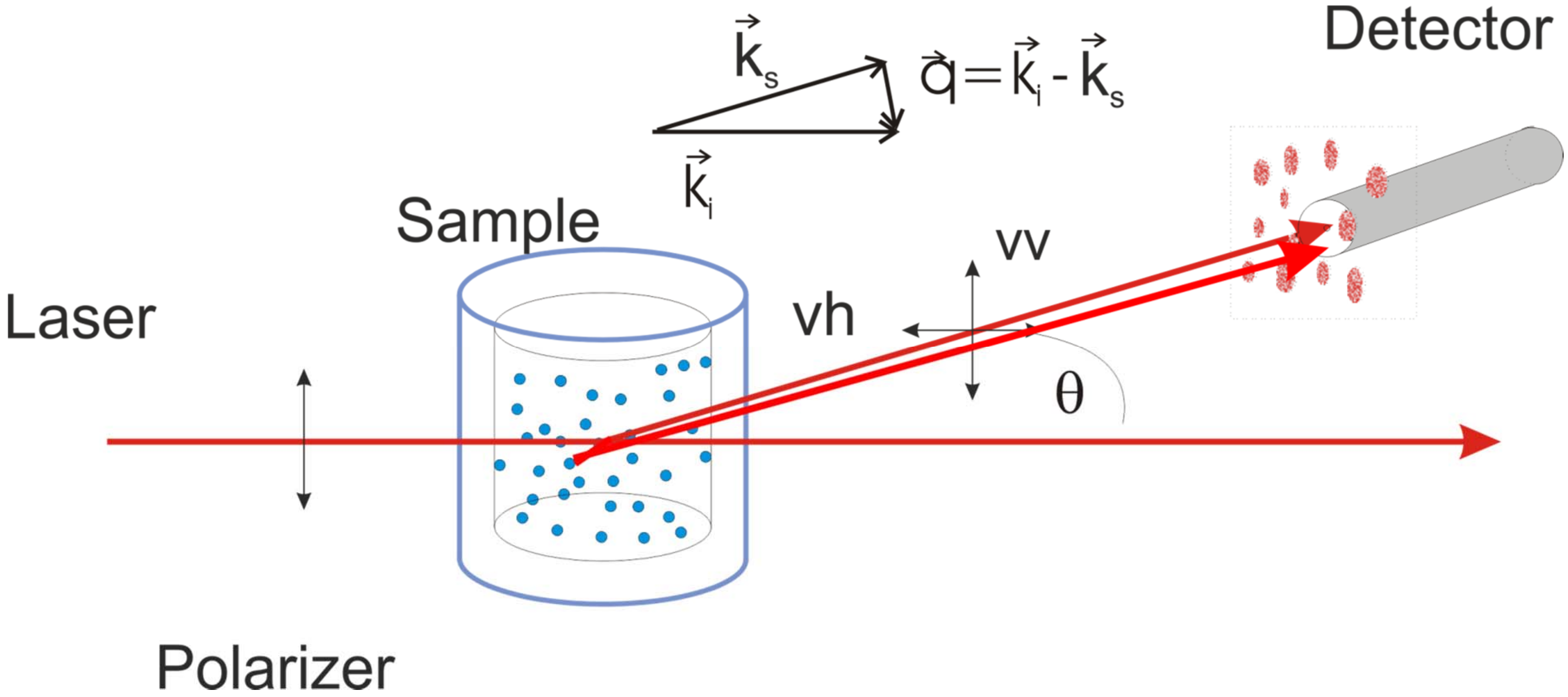




colloidal suspensions

Setup: Static and dynamic light scattering

JÜLICH
FORSCHUNGSZENTRUM



requirement: single scattering

- static $$\langle I_s \rangle = \frac{V_s I_0}{r^2} \frac{4\pi^2 n^2}{\lambda^4} \left(\frac{\partial n}{\partial c} \right)_T^2 \bar{\rho} (\hat{n}_s \cdot \hat{n}_0)^2 V_p^2 \; P(q) \; S(q)$$
- dynamic $$\langle I_S(q,0) I_S(q,t) \rangle \Rightarrow D(q), P(q), S(q)$$

Experimental solutions

2-beam-experiment, which fulfills the condition: $\vec{q}_1 = \vec{q}_2 = \vec{q}$

2-D
one wavelength
only θ = 90°

G.D.J. Phillies,
J. Chem. Phys., **74**,260
(1981)

2-D
two wavelengths
θ = variable

M. Drewel et al.,
J. opt.Soc. Am.A, **7**,206,
(1990)

3-D
one wavelength
θ = variable

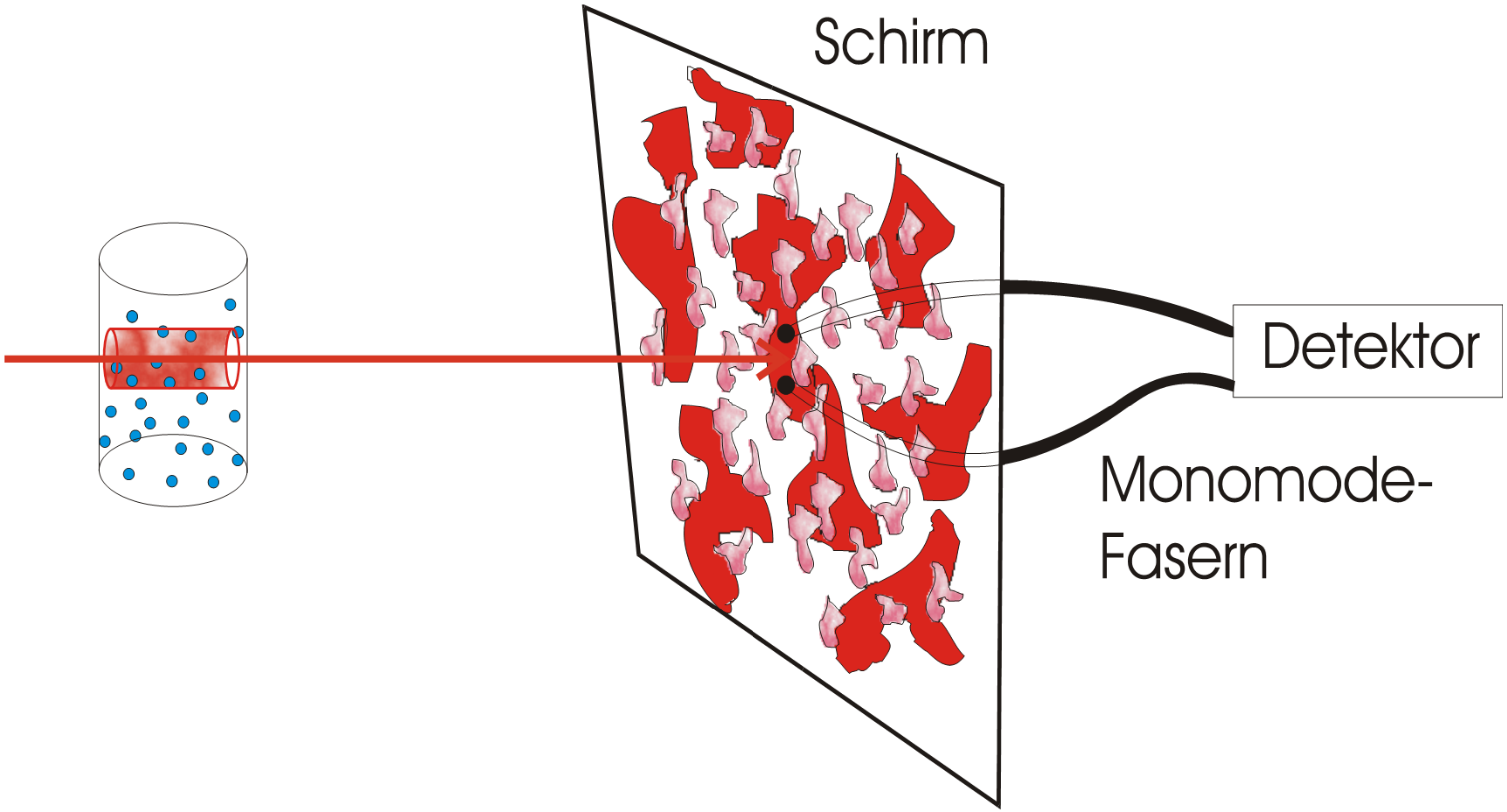
K. Schätzel,
J.Mod.Opt.,
38, 1849(1991)

1-beam-experiment :

2-D
θ = variable

W.V. Meyer et al.,Appl.Opt. **36**, 7551 (1997), J.-M Schröder & SW, PCCP, 2 (2000) 1493, J.-M Schröder & SW, Soft Materials, 1 (2003) 53

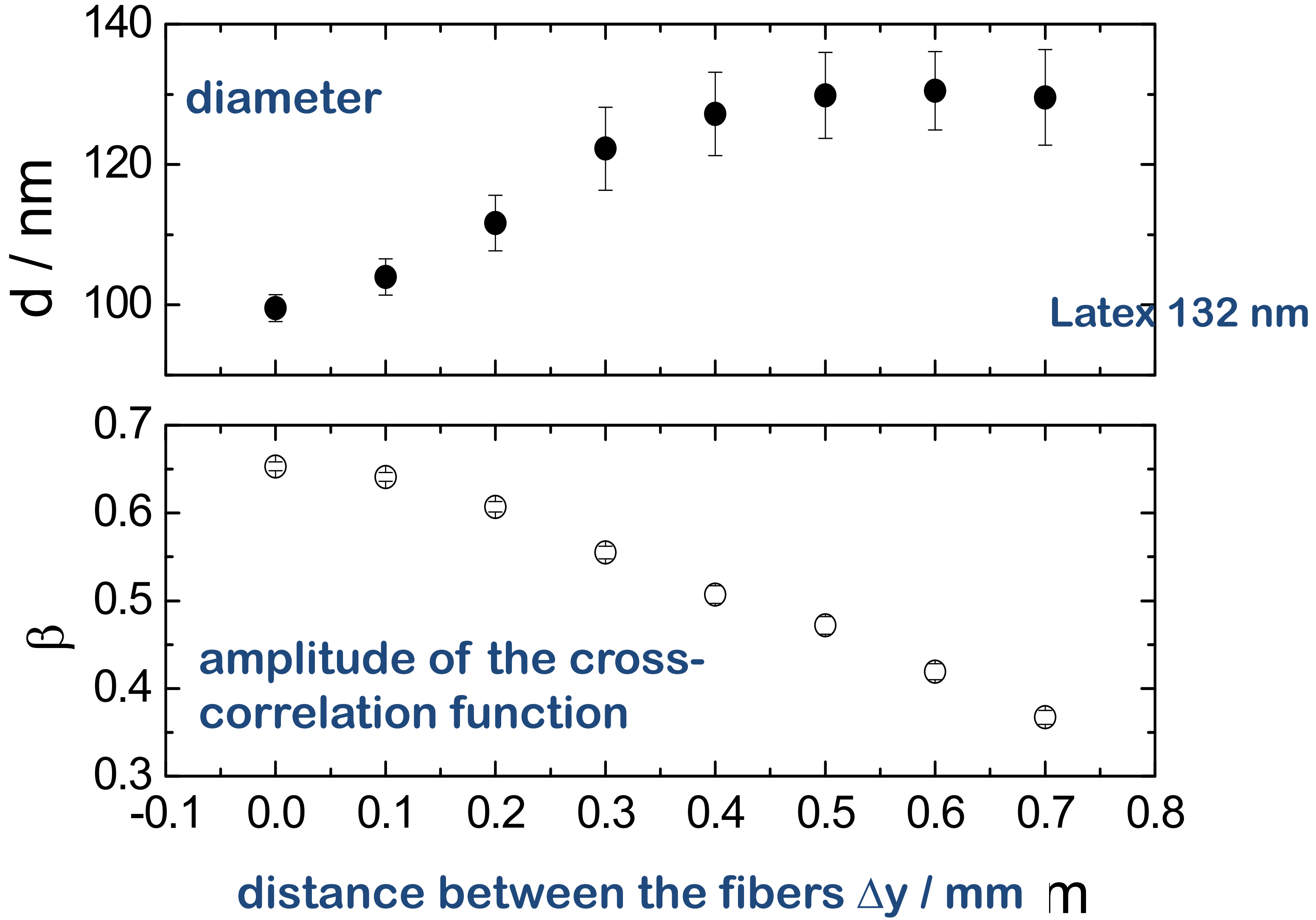
One-beam set-up: principle



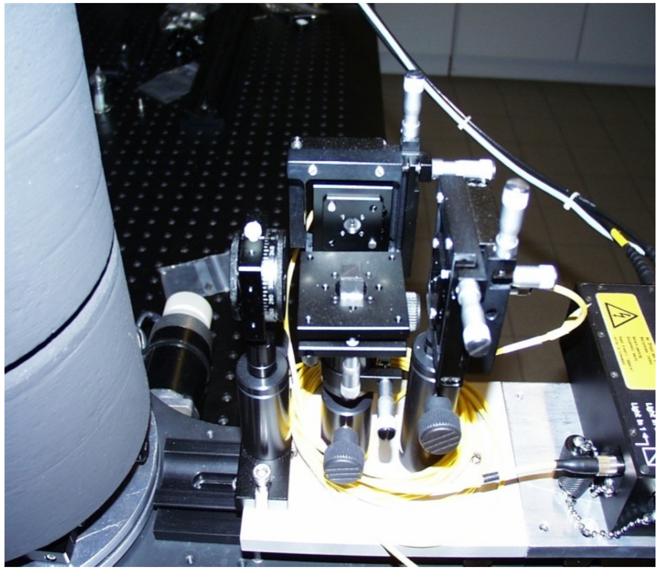
single scattered light ⇨ large coherence area

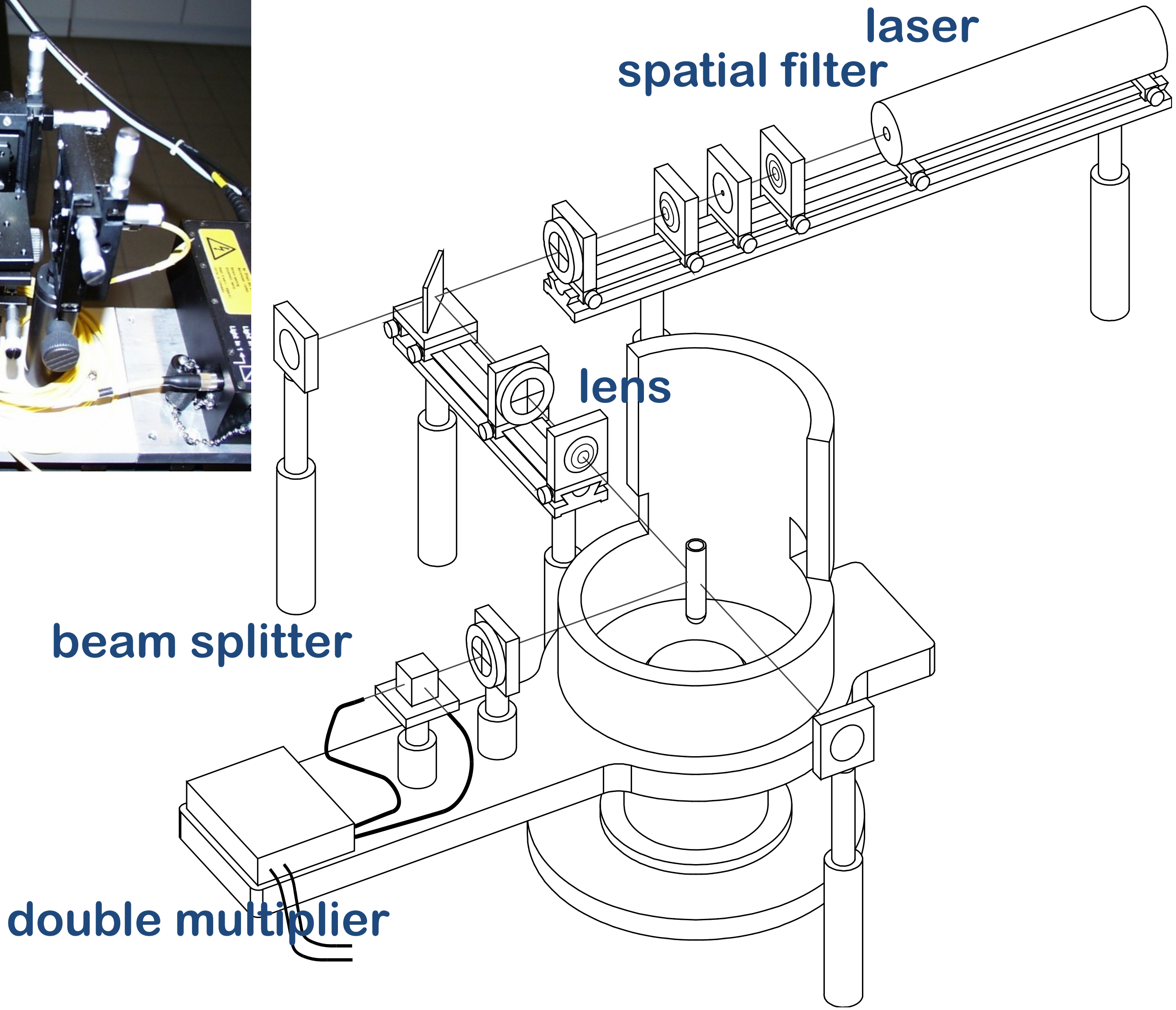
multiple scattered light ⇨ small coherence area

One-beam set-up: alignment



One-Beam set-up



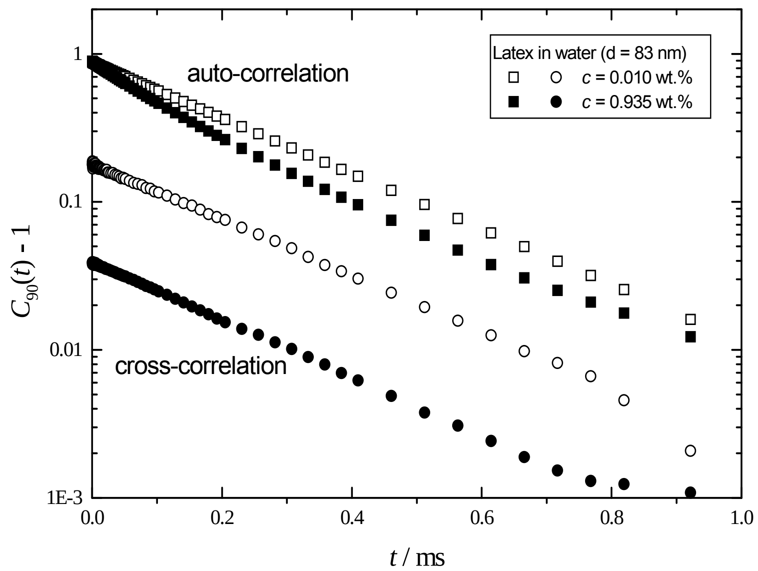


J.-M Schröder & SW, Soft Materials, 1 (2003) 53

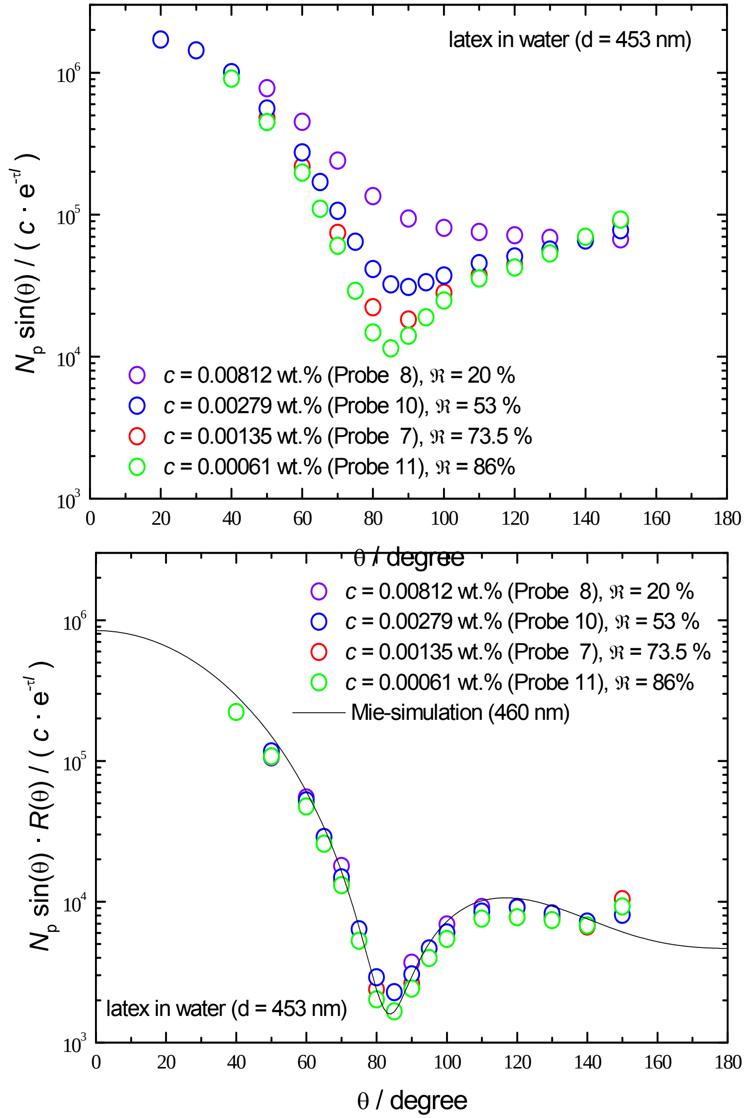
Works for dynamics and statics…

JÜLICH
FORSCHUNGSZENTRUM

dynamic



static

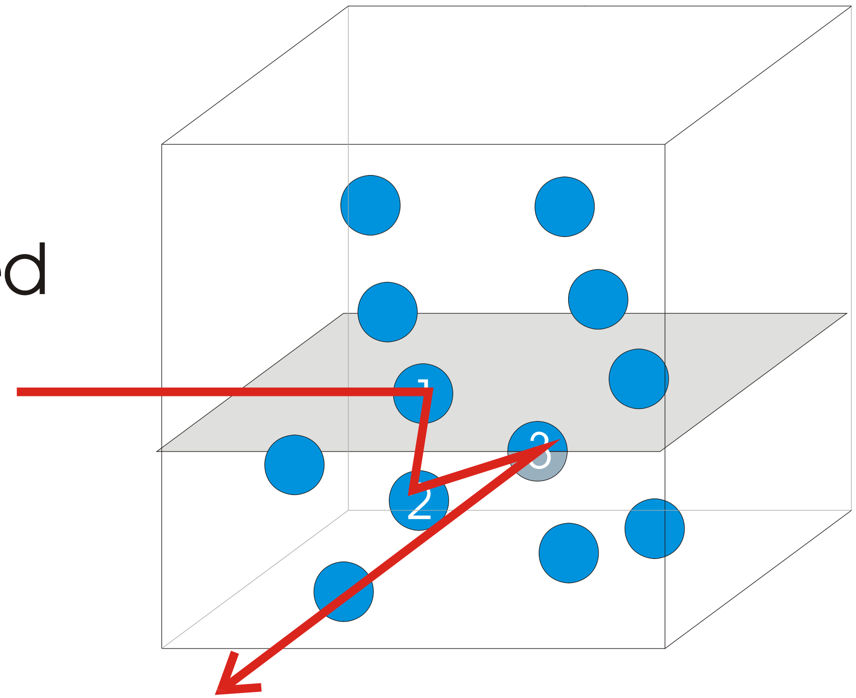


J.-M Schröder & SW, PCCP, 2 (2000) 1493

Depolarized light scattering

Depolarized scattering intensity often is very low and is easily disturbed by multiple scattering

vertikal
polarized

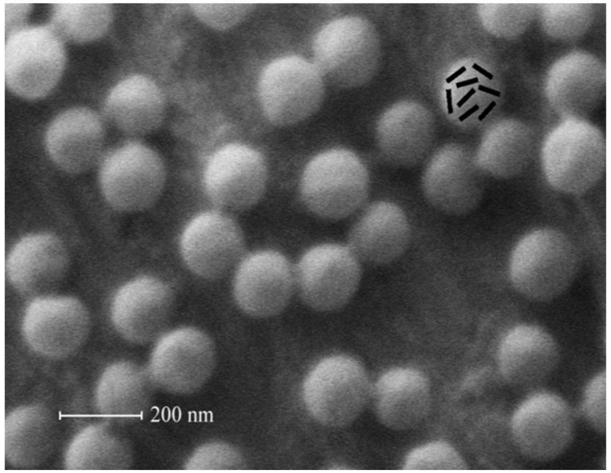


Plane of Polarisation
is rotated

Depolarized light scattering

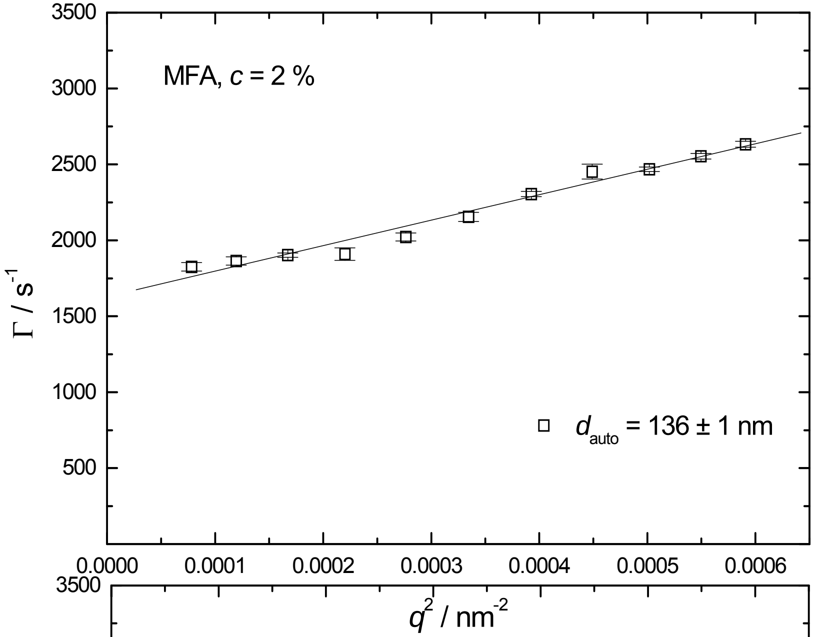
Colloid with a partially crystalline structure

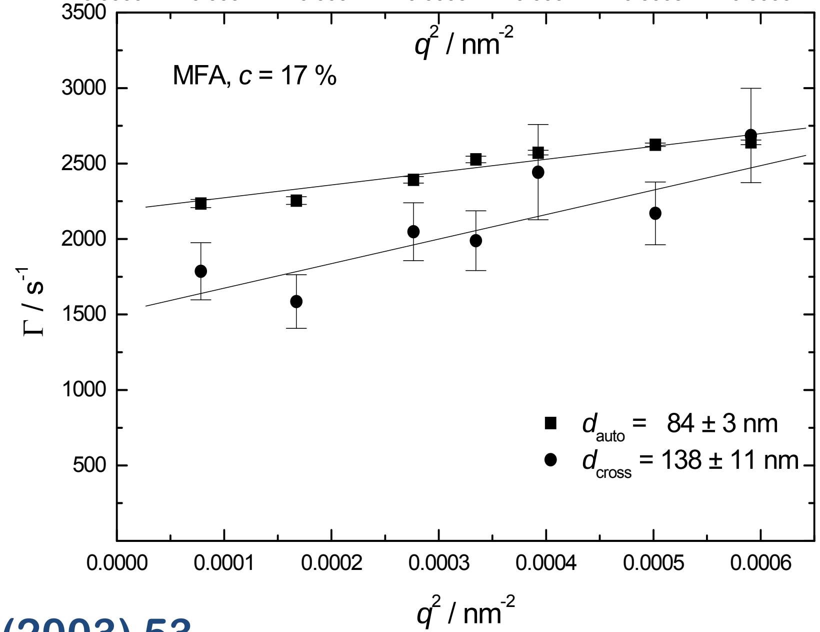
- Tetrafluorethylen copolymerised with perfluormethylvinylether (MFA)
- water soluble
- monodisperse



$$d = 146 \pm 10 \text{ nm}$$

J.-M Schröder & SW, Soft Materials, 1 (2003) 53

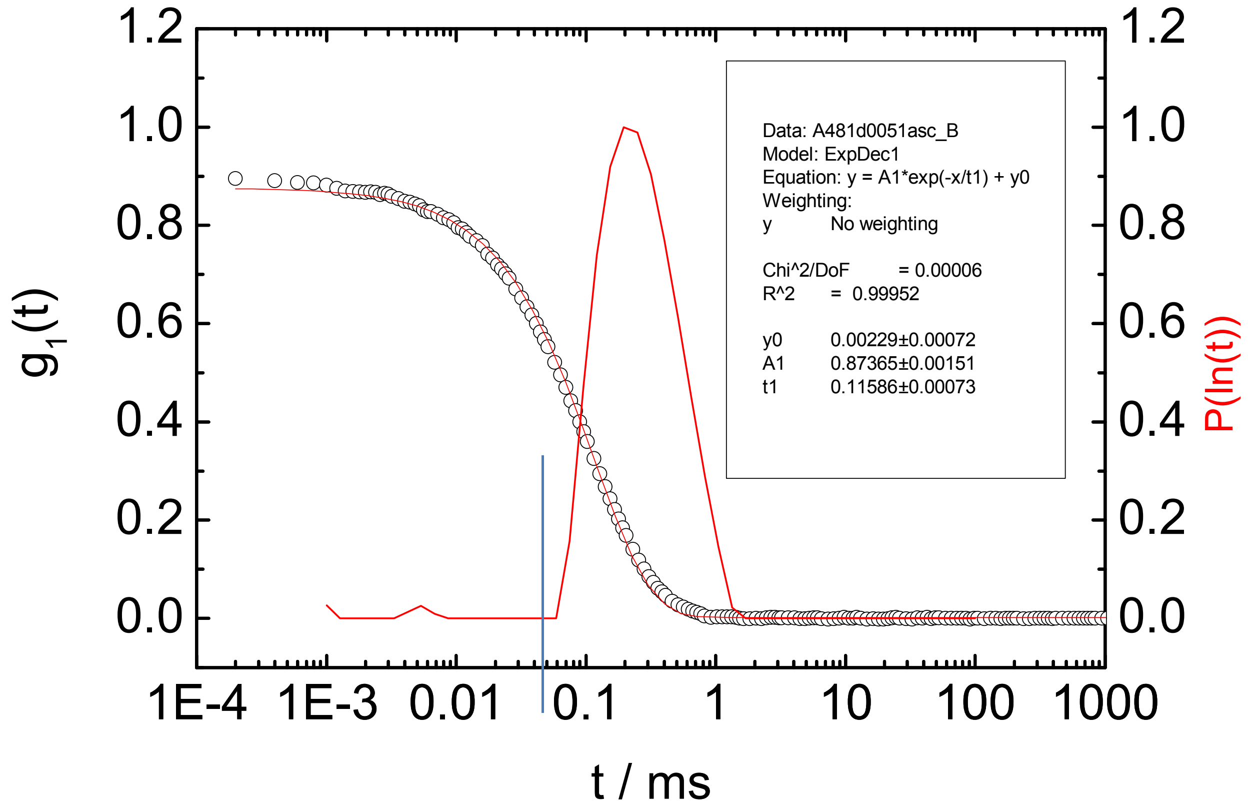




Data analysis

Data analysis – CONTIN analysis

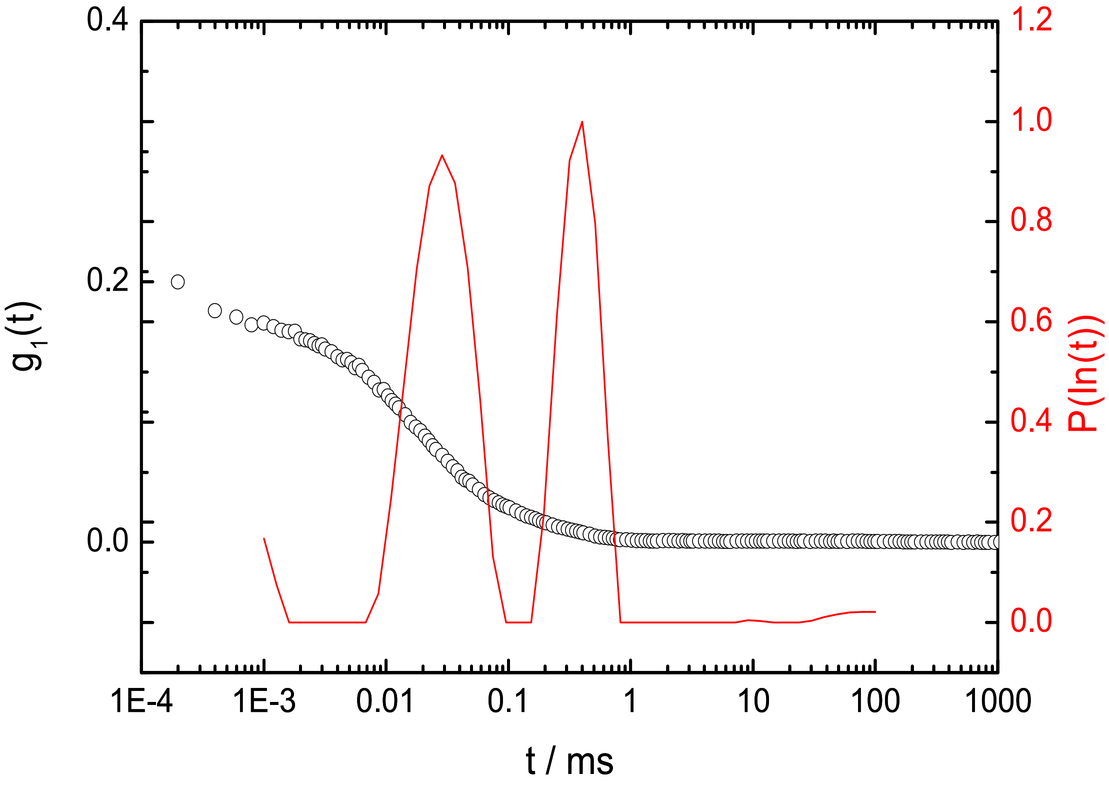
Fit one exponentiell decay: $g_1(t) = \text{base} + A\exp[-t/\tau]$



Contin Analysis

Data analysis – CONTIN analysis

Two or multi exponentiell decay:



Contin Analysis

Data analysis

Exponential decays:

$$g_2(t) = \text{base} + A\exp[-t/\tau]$$

$$g_2(t) = \text{base} + A_1\exp[-t/\tau_1] + A_2\exp[-t/\tau_2]$$

$$\vdots$$

Examples:

- diffusive processes
- two decay: diffusion and rotation
- ….

Data analysis

Stretched Exponential(s):

$$g_2(t) = \text{base} + A \exp\left[-(t/\tau)^{\beta}\right]$$

$$g_2(t) = \text{base} + A_1 \exp\left[-(t/\tau_1)^{\beta_1}\right] + A_2 \exp\left[-(t/\tau_2)^{\beta_2}\right]$$

$$\vdots$$

Examples:

- glass transition
- restricted movement of particles
- ….

Data analysis – CONTIN analysis

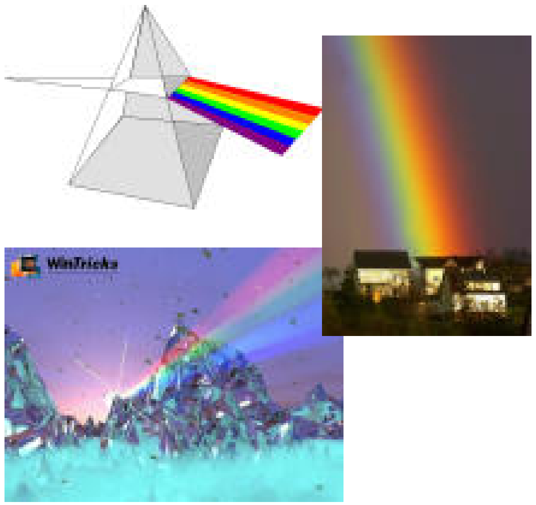
Regularization (CONTIN):

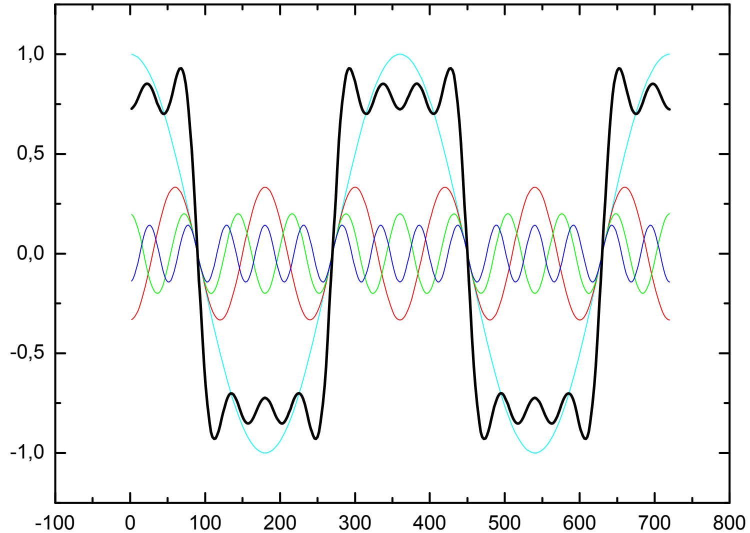
$$g_2(t) = \int_{\tau_{\min}}^{\tau_{\max}} P(\tau)\exp[-t/\tau]d\tau$$

Distribution of exponential functions

Analog to Fourier analysis:
Distribution of harmonic functions fairly easy

Square wave signal $f(x) = \frac{4a}{\pi}\left[\cos x - \frac{\cos 3x}{3} + \frac{\cos 5x}{5} + \cdots\right]$





The end

- **static light scattering:**
  - Form factor (shape of the scatterer)
  - Structure factor (structure in the fluid)
  - Absolute scattering (molar mass, radius of gyration and second virial coefficient)
- **dynamic light scattering**
  - Diffusion constant ($\Rightarrow$ hydrodynamic radius)
  - Distribution of diffusion constants (**mass weighted**!!!)
- **multiple scattering**
  - cross correlation techniques are required