No. 61: Dynamic Light Scattering

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Contents

Dynamic light scattering

Light scattering, like any scattering technique, is a non-destructive technique to observe the internal structure of a sample. Therefore light scattering offers a variety of ways to examine systems of soft matter (e.g. colloidal suspensions, polymer melts etc.). Dynamic processes, i.e. Brownian motion of mesoscopic particles (size range: from several nm to μm) in a carrier liquid, changes the internal structure with time. This process can then be characterized using the technique of *dynamic light scattering*.

This experiment is designed to examine the properties of highly diluted colloidal suspensions. The particles' diffusional motion causes fluctuation in the intensity of the scattered light. The diffusion coefficient and along with it the radius of the particles in solution can be determined from these fluctuations. The diffusion can also be examined as a function of solvent viscosity and particle concentration.

Required knowledge

- Colloids (properties, interactions (Van der Waals forces, electrostatics), phase behavior)

- Scattering theory (born approximation, scattering vector, structure factor, form factor)

- Correlation functions (autocorrelation, Siegert relation)

- Hydrodynamics (viscosity, stokes law, diffusion, Brownian motion)

- Laser (function, properties, focusing of laser beams)

- Photomultiplier (operating mode, signal resolution in time)

Experimental objectives

- measurement of autocorrelation function for colloidal samples at different scattering angles

- Determination of diffusion coefficients and hydrodynamic radii

- Observation of diffusion depending on particle concentration

Basic literature

1. Colloids:
    - H.-D. Dörfler: "Grenzflächen und kolloid-disperse Systeme", Springer Verlag, Berlin (2002), Kapitel 1
    - H. Löwen: "Weiche Materie: Vom hässlichen Entlein zum schönen Schwan", Jahrbuch der Heinrich-Heine-Universität Düsseldorf 2002 (2003), (http://www2.thphy.uni-duesseldorf.de/~hlowen/doc/ra/ra0016.pdf)

2. Scattering theory:

- H. Ibach, H. Lüth: "Festkörperphysik", Springer Verlag, Berlin (2009), Kapitel 3
- K. Schätzel: "Correlation Techniques in Dynamic light scattering", *Applied Physics B*, **42**, 193 (1987)
- K. Schätzel, Drewel: "Laser Light Scattering and Correlation Techniques for Characterization of Colloidal Suspensions", *Zeitschrift für Physik B*, **68**, 229 (1987)

Secondary literature

- B.-J. Berne, R. Pecora: "Dynamic Light Scattering", Dover Publications, Dover (2000)

- Hunter: "Foundations of colloid science", Oxford University Press, Oxford (2000)

1 Theory

1.1 Colloids

The field of colloidal research has grown more important over the last decades, which is partly due to its broad industrial applications (e.g. medicine and pharmacy, cosmetics, paints and varnish). In physics and chemistry, colloids are of particular interest because they can serve as model systems for crystals (fig. 1.1), metals and fluids.
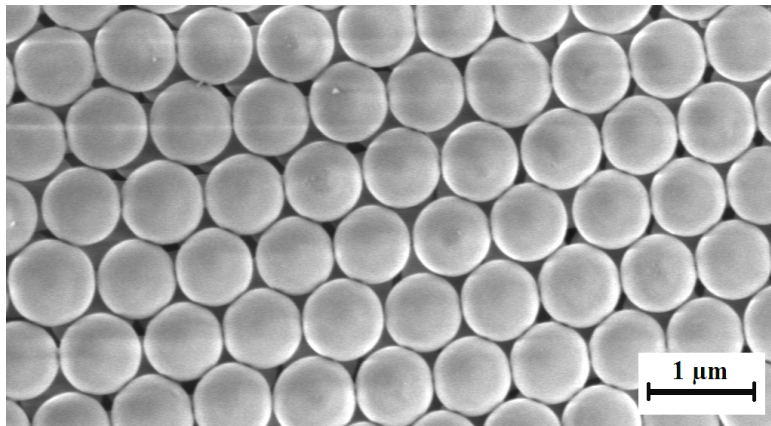

Figure 1.1: Silicon dioxide particles with a diameter of 850nm. Due to gravitation they are settled down and form a regular crystalline pattern.

A colloidal system consists of particles (dispersed phase) in a surrounding dispersion medium. As the particle size is typically 10^3 to 10^4 times the size of an atom, colloids can be examined using optical methods such as microscopy or scattering of visible light.
Additionally, the motion of colloids is much slower than that of atoms. Consequently, dynamic processes such as crystallization or Brownian motion are experimentally easily accessible. A big advantage of colloidal dispersions is the possibility of varying the particle interactions to realize different model systems.

1.1.1 Properties and applications

With sizes between roughly 10nm and 10μm, colloids are in an intermediate range, with microscopic systems of atomic and molecular dimensions on the one side and macroscopic dimension on the other side. Therefore colloidal dispersions are referred to as mesoscopic systems. Colloids are typically of spherical shape, although different shapes exist e.g. ellipsoids, plates or cylinders. The size does not have to be the same in all dimensions, there are particles with colloidal properties, who only fit into the size range in one or two dimensions. If all particles of a system are identical, it is called monodisperse. Polydisperse particles vary in size and shape

or have inhomogeneous optical properties such as a varying refractive index.

Colloids can be classified in three categories: association colloids, molecular colloids and dispersion colloids [1]. In this experiment we work with dispersion colloids. These systems are heterogeneous mixtures of two immiscible materials, namely (polydisperse) colloidal particles in a surrounding dispersion medium. These systems tend to aggregate, as they are thermodynamically unstable. Therefore stabilization techniques have to be used, to prevent coagulation. According to the state of aggregation (solid, liquid, gas) of the dispersed phase and dispersion medium, they are classified according to table (1.1.1):

| state | | | |
of the dispersed phase	of the continuous medium	class	example
solid	gas	solid aerosol	smoke
liquid	gas	liquid aerosol	mist
solid	liquid	suspension	paint
liquid	liquid	emulsion	milk
gas	liquid	foam	whipped cream
solid	solid	solid sol	colored glas
gas	solid	solid foam	styro foam

Table 1.1: Classification of colloidal systems according to the state of aggregation (solid, liquid, gas) of the dispersed and continuous phase.

1.1.2 Interactions between colloids

Structure and phase behavior of the colloidal system and diffusion of the suspended particles are determined by interactions between the colloids. The dominant interaction in these systems is the Van der Waals interaction. It origins from fluctuations of the electric charge in the atoms' electron cloud, which then creates dipoles with an attractive force. The potential describing this short-ranged attraction has a r^{-6}- dependence. With bigger objects, such as colloids, the range of the Van der Waals attraction is extended and can have a r^{-3}- or even r^{-2}- dependence. This yields then a Van der Waals energy superior to the thermal energy, a condition, which automatically results in coagulation of the particles. To prevent this, the particles have to be stabilized.

There are two main techniques to achieve this: Steric stabilization and electrostatic stabilization. In organic solvents normally the particles are sterically stabilized, while in water based systems electrostatic stabilization is preferred.

Steric stabilization

Steric stabilization is realized using fine hairy chains (e.g. polymers) on the particle surface (fig. 1.2). Upon approaching, these layers overlap and the single chains have less possibilities to move. The amount of entropic configurations of the chains is reduced and a repulsive force due to entropic pressure is created.

Under the precondition that the chain layer is significantly smaller than the particle diameter and else the repulsive interaction predominates the Van der Waals attraction. The colloidal system can then be describes as a hard sphere system. In a hard sphere system the potential is

$$\Psi_{HS} = \begin{cases} \infty, & r \leq 2a \\ 0, & r > 2a \end{cases} \tag{1.1}$$

Electrostatic stabilization

The electrostatic stabilization is based on Coulomb repulsion, which is a long range interaction. Chemical groups (e.g. $\tilde{}SO_3H$, $\tilde{}OH$) remain after the particle synthesis on the surface. When the particles are dispersed in a liquid solvent, these binded chemical groups can dissociate and the thermal motion removes the counterions from the surface. The amount of dissociated surface groups is dependent on the solvents' permittivity ε_r.
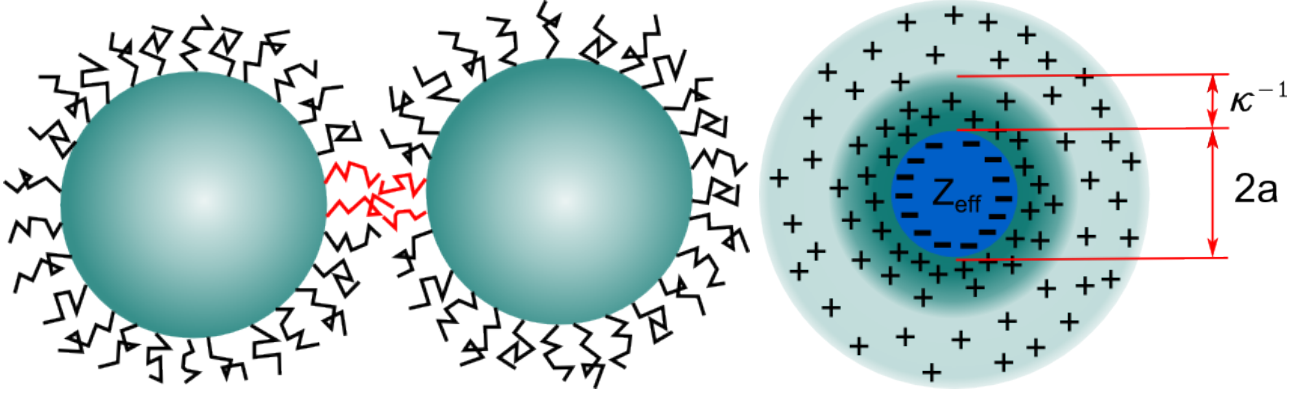

Figure 1.2: a) Colloidal particles with steric surface modification. The entropic pressure leads to a repulsion between the particles. b) charged colloid with effective charge Z_{eff} due to the screened coulomb potential. The counter ions are distributed around the colloid and form a diffusive charge cloud.

The surface is then charged and the counterions form a diffuse cloud around the particle (fig. 1.2). The counterions' charge distribution is described by the Boltzmann-statistics. Due to this diffuse charge cloud the coulomb interaction is screened. Hence the particles' charge is then not the sum over the charges of the surface groups but it can be described with a reduced effective charge Z_{eff}. Using the Poisson-Boltzmann-equation one can derive the so-called Debye-Hückel-potential $\Psi_{DH}(r)$ of a spherical charged colloid with radius a:

$$\Psi_{DH}(r) = \frac{Ze}{4\pi\varepsilon\varepsilon_0} \frac{e^{\kappa a}}{1 + \kappa a} \frac{e^{-\kappa r}}{r} \tag{1.2}$$

with the debye screening parameter (also called debye length)

$$\kappa = \sqrt{\frac{e^2}{\varepsilon\varepsilon_0 k_B T} \sum_i c_i Z_i^2} \tag{1.3}$$

This debye length describes the intensity of the interaction, which depends on the particle radius a and the effective charge Z_{eff}, but also on the solvents salt concentration c_s (fig. 1.3). If there are no salt or other molecules ($NaCl$, KCl, CO_2,...) in solution, the Coulomb repulsion is maximized and the electrostatic interaction between nearest neighbors is greater than the thermal energy $k_B T$. In water-based systems in this case c_s is determined only by the self-ionization of water and is equal to $c_s = 10^{-7} mM$. Increasing the solvent salt concentration c_s with additional ions or molecules decreases the Coulomb repulsion between nearest neighbors.
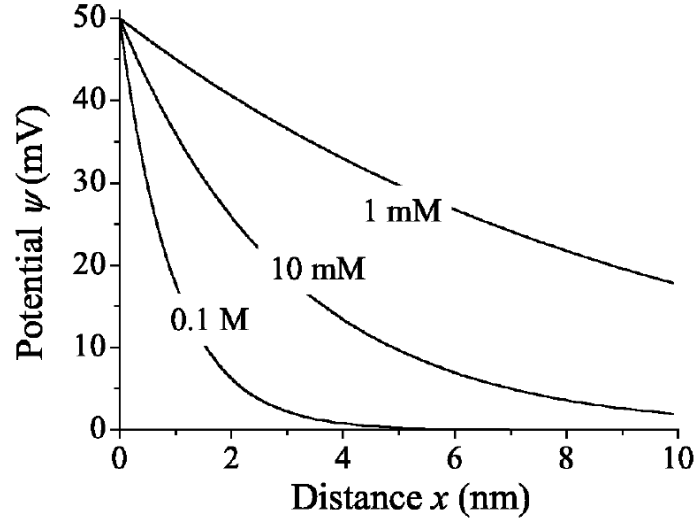

Figure 1.3: Schematic coulomb potential at different salt concentration. With additional salt ions the coulomb potential decreases, which leads to a reduced coulomb repulsion between the charged particles. [2]

1.1.3 Phase behavior

The potential between the particles determines the complex phase behavior of colloidal suspensions. In contrast to the case of atoms, there is no gas-liquid phase transition in stabilized systems due to the lack of an attractive force. Depending on the strength of the interaction, there is a fluid (gas or liquid), a crystalline or a glass-like particle order. We consider here systems consisting of colloids with a particle number density per volume unit n_p in a constant volume V. Often, the volume fraction $\Phi = \frac{N \cdot V_p}{V} = n_p \cdot V_p$ is used rather than n_p.

In systems consisting of hard spheres, the order only depends on the volume fraction Φ (fig. 1.4). At low volume fractions there is almost no interactions and the system is in a fluid phase. Once Φ reaches 0.494, the system starts to crystallize. At $\Phi = 0.545$ the system is finally in a crystalline phase. When the volume fraction is increased rapidly above a value of 0.58 the dynamics of the particles freeze in and the system is then in an unequilibrated state, the glass.
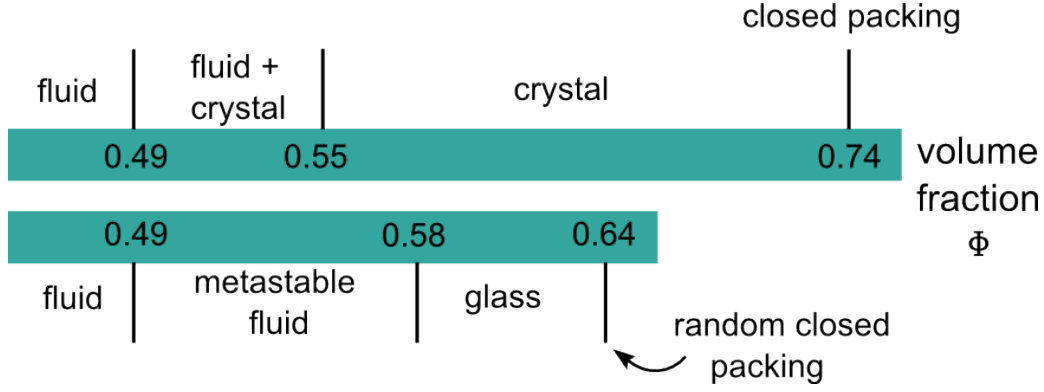
Figure 1.4: Phase diagram of hard spheres: The upper part describes the pase transition under equilibrium conditions. The crystallization starts at $\Phi = 0.494$ and ends at $\Phi = 0.545$, where the system is then fully crystallized. The lower part of the diagram shows the phase transition, when the volume fraction is increased rapidly and the glass phase occurs.

Charged colloids can already crystallize at much smaller volume fractions of about $\Phi = 0.1\%$. The phase diagram of charged colloids is not only dependent on the volume fraction but also on the salt concentration c_s. Increasing the volume fraction leads to a transition from the fluid to the crystalline state because of decreasing the next neighbor distance. In contrast the addition of salt ions leads to a shielding of the charge, and therefore to a reduced Coulomb potential. The repulsion between the particles decreases and the system changes from the crystalline to the fluid state.

1.2 Light scattering

The scattering of electromagnetic waves is an important way of examining objects in physics. For the scattering process wavelengths should be used, which are in the size dimension of the structures to investigate. For this purpose optical wavelengths (370nm -730nm) are suitable for examing colloids, as they are of sizes between roughly 10nm and 10μm. Electromagnetic waves are scattered at places of alternating refractive index between the colloids and the solvent. The refractive index n depends on the dielectric properties of the medium, particularly on the particles' polarizability α, which is described with the "Clausius-Mosotti-equation".
The incoming waves interact with the colloids and create an electric dipole moment $\vec{\mu}$, which depends on the particle properties like size or structure. The scattered light can thus give information about these properties. A distinction is to be made between static and dynamic light scattering, the former serving to characterize structures and phase transitions, whereas the latter can be used to determine dynamic properties such as the particles' Brownian motion and to draw conclusions on its diffusion coefficient and hydrodynamic radii.

1.2.1 Static light scattering

In order to achieve a relatively simple description of light scattering, we make the following assumptions: both the incoming and the scattered light is vertically polarized, there is no change in wavelength λ and phase φ and only one scattering process takes place. This caculation is

based on the assumption, that the particle radius a is small compared to λ (Rayleigh-scattering). The incoming wave $\vec{E}_{in} = \vec{E}_0 \cdot exp\left[-i\left(\omega t + \vec{k}_{in} \cdot \vec{r}_j\right)\right]$ then interacts with the scattering centers at $\vec{r}_j$ and creates a dipole moment $\vec{\mu}$.
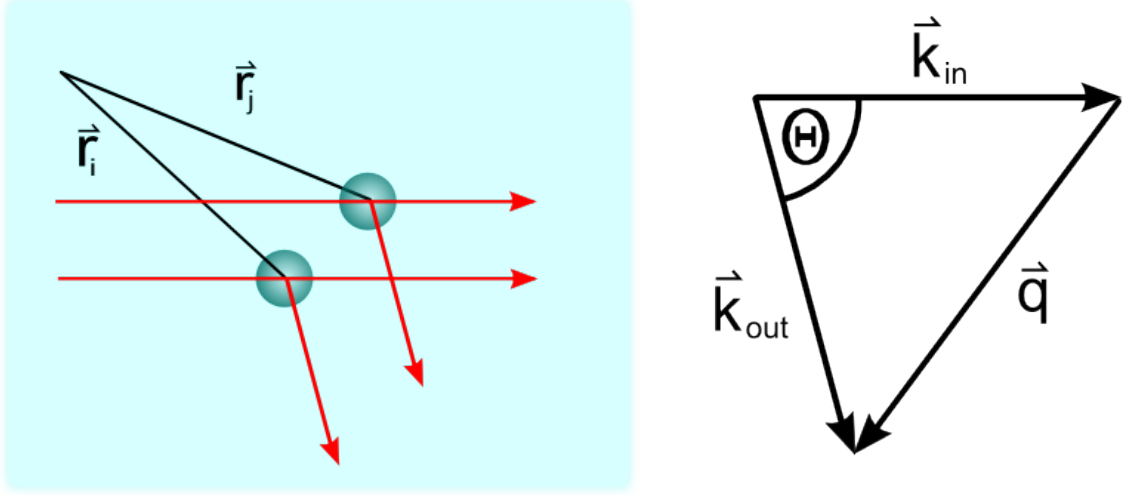

Figure 1.5: Scattering geometry. a The incoming wave interacts with the scattering centers at the positions $\vec{r}_i$ and $\vec{r}_j$. b The scattered light (with wave vector $\vec{k}_{out}$) can then be detected under an angle θ between the incoming and scattered beam. The scattering vector $\vec{q}$ describes the momentum transfer during the scattering process.

Under the precondition of quasi-elastic scattering $\left|\vec{k}_{in}\right| = \left|\vec{k}_{out}\right| = \frac{2\pi n}{\lambda}$ (n being the refractive index of the dispersing medium), the momentum transfer $\vec{q} = \vec{k}_{out} - \vec{k}_{in}$ to the scattering center becomes

$$\boxed{|\vec{q}| = q = \frac{4\pi n}{\lambda} \cdot sin\left(\frac{\theta}{2}\right)} \tag{1.4}$$

where θ is the angle under which the scattered light is detected (fig 1.5).
The interference between the different scattered waves depends only on the particle distances. Assuming that the detector is at a distance R superior to the dimensions of the scattering volume, the scattered wave can be described using the Born approximation, which yields

$$\vec{E}_{out} = \underbrace{-\frac{\vec{E}_0 k_{out}^2}{4\pi\varepsilon_0 R} \cdot e^{-i\left(\omega t + \vec{k}_{out}\vec{R}\right)}}_{\vec{E}_{0,out}} \cdot \underbrace{\int_V d\vec{r}\,\delta\vec{\varepsilon}(\vec{r},t)e^{(i\vec{q}\vec{r})}}_{\delta\vec{\varepsilon}(\vec{q},t)} \tag{1.5}$$

The meaning of this relatively long formula can be explained in a simple way: the first part, $\vec{E}_{0,out}$, only depends on the experiment's geometric dimensions and properties, not on the scatterers' properties, while the second part, $\delta\vec{\varepsilon}(\vec{q},t)$, represents the fourier transform of the spatial density fluctuations in the scattering volume, which means the distribution of the scatterers.

In this experiment, we are interested in colloids. As they are in the size range of the used

scattering wavelength, the assumption of Rayleigh-scattering cannot be held anymore. Therefore the colloids have to be split into different scattering centers. We introduce coordinates where $\vec{r}_j$ is the position vector of the colloids center of mass and $\vec{r}'$ the vector between the scattering center and the colloids center. Assuming that the colloids are spherical and identical, we can split the integration in $\delta\vec{\varepsilon}(\vec{q},t)$ into a summation over the particles centers and a $\vec{r}'$-integration over the particle volume V_j. The result of this integration is referred to as $b(\vec{q})$.

Light detectors such as photomultipliers do not measure the electric field vector, but only its intensity. In static light scattering, time averaging has to be performed and yields the following intensity:

$$I(q) = \langle \vec{E}_{0,out}\vec{E}^*_{0,out}\rangle \propto I_0(q)b(\vec{q}=0)^2 \cdot \underbrace{\left|\frac{b(\vec{q})}{b(\vec{q}=0)}\right|^2}_{P(q)} \cdot \underbrace{\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} e^{i\vec{q}(\vec{r}_j-\vec{r}_i)}\right\rangle}_{N\cdot S(q)}$$

$$= \boxed{I_0(q)b(\vec{q}=0)^2 \cdot P(q) \cdot NS(q)} \qquad (1.6)$$

$P(q)$ is called the particle form factor (fig. 1.7) and takes into account the shape and surface properties of a colloidal particle. $S(q)$ is the so-callled structure factor (fig. 1.6), which depends on the particle distribution in the scattering volume and gives therefore a hint on the local phase (e.g. fluid or crystalline) of the system.
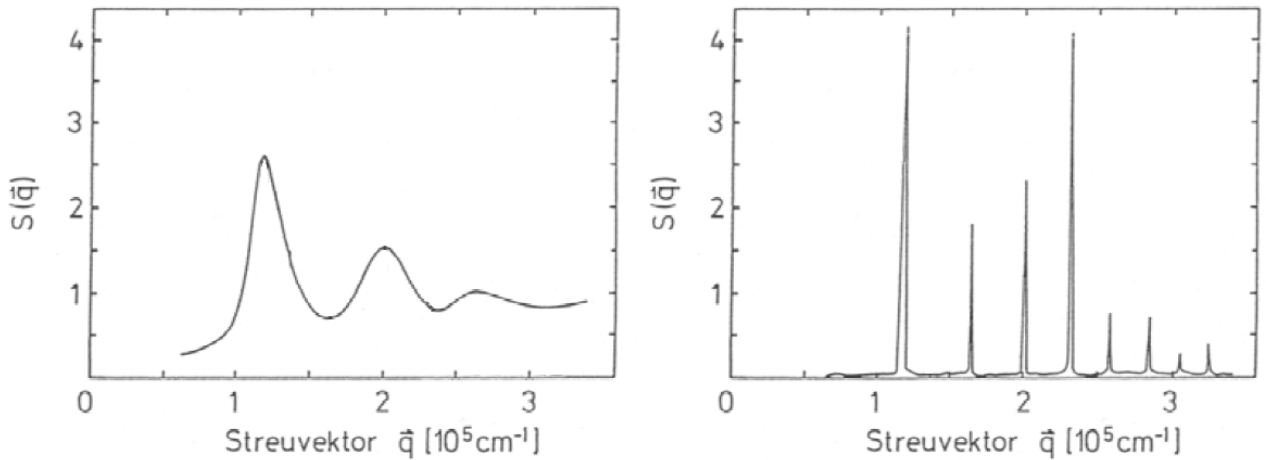

Figure 1.6: Structure factor of the same sample in the fluid (left) and crystalline (right) state [3]

For colloidal particles the form factor has to be calculated using the Rayleigh-Debye-Gans approximation, applying to cases in which the scatterers' size is of the same order of magnitude as the wavelength of the scattered light:

$$\boxed{P(q) = \frac{9}{(qa)^6}\left(sin(qa) - qa \cdot cos(qa)\right)^2} \qquad (1.7)$$

For polydisperse particles, there are deviations from this behavior and averaging over different radii becomes necessary.
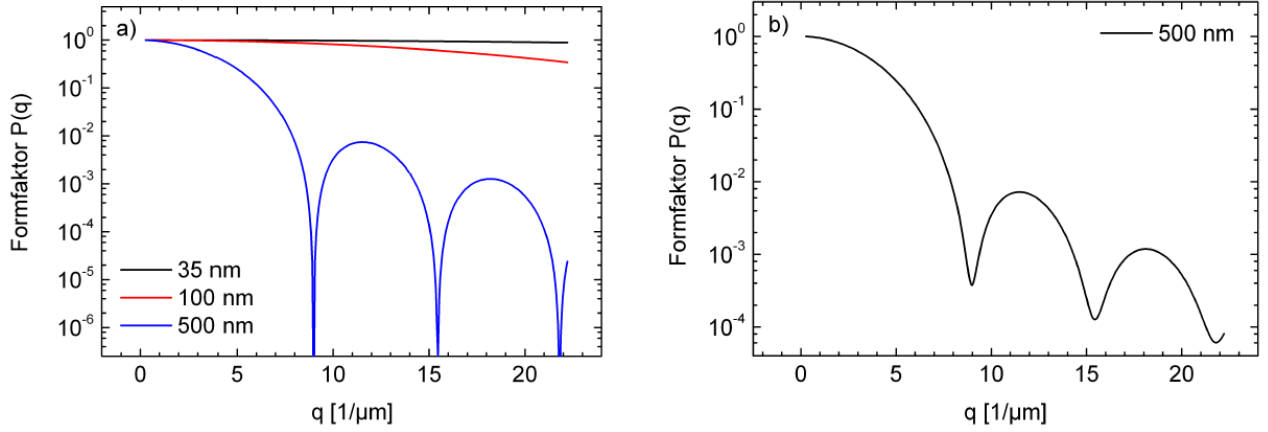
Figure 1.7: Form factor, derived with Rayleigh-Debye-Gans-approximation (eq. (1.7)), for different particle radii (aqueous solution, wavelength 532nm). a) For monodisperse and b) for polydisperse colloids with a size polydispersity of a few percent.

Therefore the formfactor has to be corrected with a distribution function $f(a)$, which takes the polydispersity into account:

$$\overline{P(q)} = \int_0^\infty da f(a) P(q, a) \tag{1.8}$$

1.2.2 Dynamic light scattering

Dynamic light scattering is based on the fact, that the Brownian motion of colloids leads to fluctuations in the particle density and therefore to variations in the scattered electric field. To examine this time-dependent behavior of the electric field the autocorrelation function of the signal is used and describes, how strong two signals at different times are correlated. In colloidal systems one can then determine the dynamics of the system, e.g. if the sample is in an arrested state or still fluid.

The field autocorrelation function $G^{(1)}(\vec{q}, \tau)$ is defined as the time average over the products of the scattered electric field strength at the time t and a later time $t + \tau$. This function describes how the field strengths at two different times are correlated to each other.

$$
\begin{aligned}
G^{(1)}(\vec{q}, \tau) &= \left\langle \vec{E}(\vec{q}, t), \vec{E}^*(\vec{q}, t + \tau) \right\rangle \\
&= \boxed{\lim_{T \to \infty} \frac{1}{T} \int_0^T dt \vec{E}(\vec{q}, t) \vec{E}^*(\vec{q}, t + \tau)}
\end{aligned} \tag{1.9}
$$

As the electric field is not accessible to the experiment, one has to consider the intensity autocorrelation function:

$$G^{(2)}(\vec{q}, \tau) = \langle I(\vec{q}, t), I(\vec{q}, t + \tau) \rangle \tag{1.10}$$

In the case of statistical fluctuations in the intensity or the amplitude of the electromagnetic field, a gaussian radiation field is created (fig. 1.8).
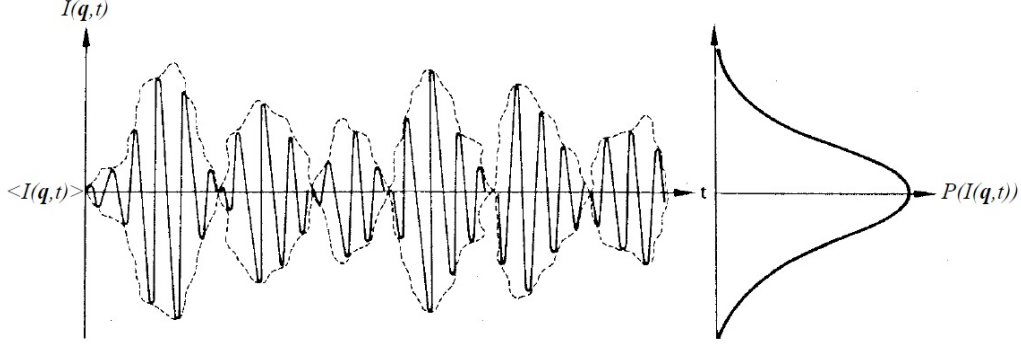
Figure 1.8: The scattered intensity changes statistically and forms a Gaussian distribution. [4]

Under this precondition, the field and the intensity autocorrelation functions are connected by the Siegert relation:

$$\boxed{G^{(2)}(\overrightarrow{q},\tau) = G^{(1)}(\overrightarrow{q},\tau)^2 + G^{(1)}(\overrightarrow{q},0)^2} \tag{1.11}$$

In literature, often a normalized expression of the autocorrelation function is used:

$$g^{(1)}(\overrightarrow{q},\tau) \;=\; \frac{G^{(1)}(\overrightarrow{q},\tau)}{G^{(1)}(\overrightarrow{q},0)} \tag{1.12}$$

$$g^{(2)}(\overrightarrow{q},\tau) \;=\; \frac{G^{(2)}(\overrightarrow{q},\tau)}{\langle I(\overrightarrow{q})\rangle_T} \tag{1.13}$$

the normalized field autocorrelation function can then be linked to the real space and the internal structure of the sample and therefore with the static structure factor S(q):

$$g^{(1)}(\overrightarrow{q},\tau) = \frac{1}{S(q)}\int_V d\overrightarrow{r}\, e^{i\overrightarrow{q}\overrightarrow{r}} H(\overrightarrow{r},\tau) \tag{1.14}$$

$H(\overrightarrow{r},t)$ is called the van Hove function. It gives the probability of finding a particle at $\overrightarrow{r}$ at time τ when at $t = 0$ a particle was at $\overrightarrow{r} = 0$. It can be split in two parts, one describing the correlation of a particle with itself and the second describing two-particle correlations.

$$H(\overrightarrow{r},\tau) = G_s(\overrightarrow{r},\tau) + G_d(\overrightarrow{r},\tau) \tag{1.15}$$

The self-term G_s describes the correlation between the positions of one particle at different times, while the distinct-term G_d describes the correlation of pairs of different particles. So G_d gives the probability to find a particle at time τ at $\overrightarrow{r}$, while another particle was located at $\tau = 0$ at the position $\overrightarrow{r} = 0$.
In highly diluted samples with negligible particle interactions, the second term does not contribute and $H(\overrightarrow{r},\tau)$ only contains the self-term G_s. A particle's self-diffusion is described by Fick's second law, a differential equation whose solution then can be identified with the self-term of the van Hove function:

$$\frac{\partial}{\partial \tau} G_s(\overrightarrow{r},\tau) = D_0 \overrightarrow{\nabla}^2 G_s(\overrightarrow{r},\tau) \tag{1.16}$$

A Fourier transformation yields

$$\frac{\partial}{\partial \tau} g_s^{(1)}(\overrightarrow{q},\tau) = D_0 \overrightarrow{\nabla}^2 g_s^{(1)}(\overrightarrow{q},\tau) \tag{1.17}$$

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with the solution

$$g^{(1)}(\vec{q}, \tau) = e^{-\vec{q}^2 D_0 \tau} \tag{1.18}$$

Applying the Siegert relation then gives the equation for the measurable intensity autocorrelation function:

$$\boxed{g^{(2)}(\vec{q}, \tau) = e^{-2\vec{q}^2 D_0 \tau} + 1} \tag{1.19}$$

Dynamic light scattering can thus be used to determine the Einstein coefficient of self-diffusion D_0 and, using the Stokes-Einstein relation, the particle's hydrodynamic radius.

1.3 Hydrodynamics

$D = \mu \cdot k_B T \qquad \mu = \frac{1}{\gamma} \qquad D = \frac{k_B T}{6\pi\eta r}$

Hydrodynamics is a sub-division of fluid dynamics and is the theory of fluids under motion, to wit flow. The fundamental equations, the Navie-Stokes-equations, describe the flow of simple liquids and gases, from which velocities, forces, etc. for certain applications can be derived.

1.3.1 Viscosity

$\gamma = 6\pi\eta d$

Viscosity is a measure of the drag force associated with motion in liquids. The higher the viscosity, the more force is needed to move an object through the liquid. To define viscosity, we consider two parallel plates at a distance x (small compared to the lateral size of the plates). The space between the plates is filled by a homogeneous liquid. We suppose that one of the plates is moved with a velocity v with respect to the other. The force needed to exercise this movement is proportional to the surface area A of the plate and to v, and inversely proportional to the plates' distance x:

$$\vec{F} = \eta A \frac{\partial \vec{v}}{\partial x} \tag{1.20}$$

The proportionality constant of this relation is called the viscosity η of the liquid between the plates. The viscosity depends on the molecular interactions in the liquid. Viscosity may vary strongly with temperature, this dependence can often be described by the Arrhenius relation (e.g. for water):

$$\eta(T) = \eta_0 e^{\frac{E_A}{RT}} \tag{1.21}$$

where E_A is the activation energy for diffusion, R is the gas constant and T is the absolute temperature in Kelvin.

1.3.2 Newtonian liquids

A further distinction has to be made between Newtonian and non-Newtonian liquids. The viscosity of Newtonian liquids is constant when a shear stress is applied. In this experiment we use a water-based system, while water is a good example for a Newtonian liquid. For non-Newtonian liquids the viscosity can increase (rheopecty) with increasing shear stress, for example in a system of starch in water. If the viscosity decreases with higher shear stress it is then called thixotropy, an example here is ketchup.

1.3.3 Stokes' law and Brownian motion

A simple method to determine the viscosity is to move a sphere of radius a through a quiescent liquid. The relation between the velocity of the sphere and the force needed is given by Stokes' law. For a slowly moving sphere, the frictional force is given by

$$\vec{F}_s = 6\pi\eta a \vec{v}_s \tag{1.22}$$

where a is the radius of the sphere and v_s is its velocity. In case the driving is due to gravity acting on the sphere, the settling velocity turns out to be

$$v_s = \frac{2}{9}\frac{(\varrho_p - \varrho_f)}{\eta}g \cdot a^2 \tag{1.23}$$

with the particle's and liquids's mass density ϱ_p and ϱ_l and the gravitational acceleration g.

As mentioned above, a particle's hydrodynamic radius can be calculated from diffusion coefficient D_0. A combination of the Einstein-Smoluchowski-equation with the Stokes force (eq. 1.22) leads to the the Stokes-Einstein relation:

$$\boxed{D_0 = \frac{k_B T}{6\pi\eta a_h}} \tag{1.24}$$

where k_B is Boltzmann's constant.

Stokes' law is used to define the hydrodynamic radius a_h (also termed Stokes radius) of a colloidal particle in a solvent. The particle is then hydrated, which means that there is a layer of solvent molecules around the particle, that has to be dragged along with it (fig 1.9).
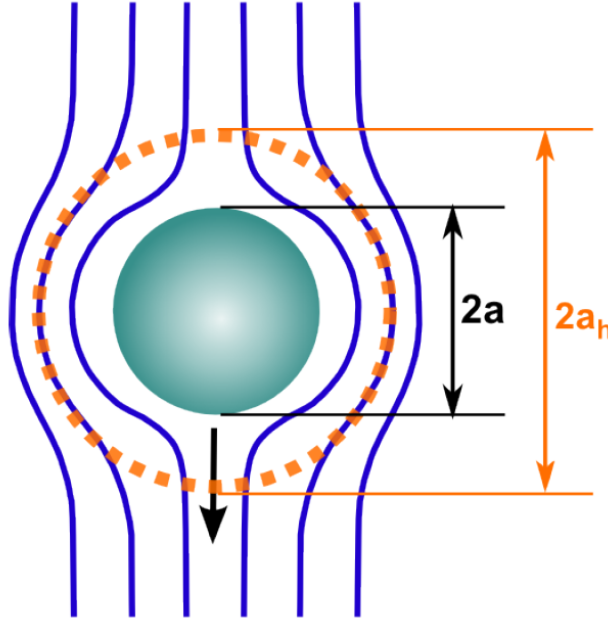

Figure 1.9: Colloid, which diffuses in a solvent. This solvent forms a layer arround the particle. The hydrodynamic radius takes this additional solvent layer into account.

The hydrodynamic radius takes this additional solvent layer into account. The thickness of this layer depends on the particle surface, shape and on the system temperature, while a different solvents leads to different layer characteristics. The hydrodynamic radius of a specific particle then depends on the surrounding liquid. So this radius is not the hard core radius of the particle, but the radius of an imaginary sphere that diffuses at the same rate as the particle in question.

2 Experimental setup

2.1 Setup

A dynamic light scattering setup consists of three main parts: an illumination source, a goniometer with sample holder and a detection part.
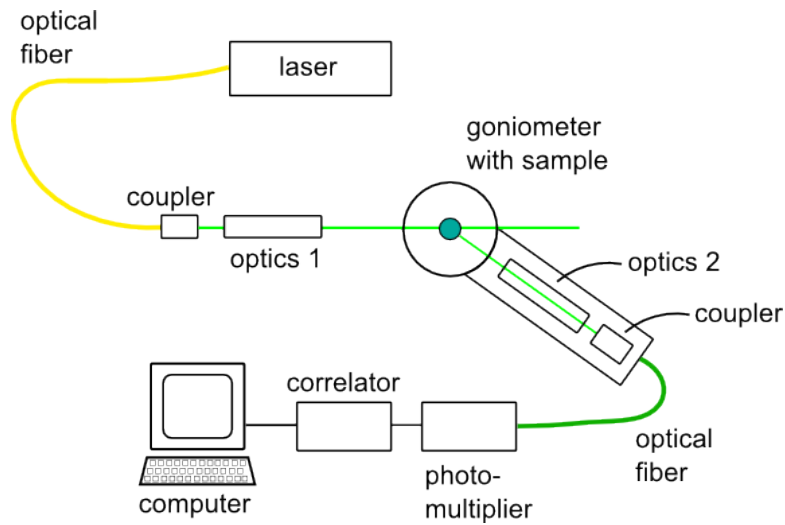

Figure 2.1: Dynamic light scattering setup

The illumination source is a diode pumped solid state laser with a wavelength of 532 nm. Over an optical fiber the laser beam is collimated onto the center of the goniometer, which includes the sample. Optical elements (e.g. lenses, pinholes and polarizer) generate a parallel and polarized laser beam. The scattered light is collected with a coupler and is then detected by a photomultiplier. Afterwards the signal is processed with a hard-ware correlator to calculate the autocorrelation function.

2.2 Measurement and analysis

Sample A (small particles, fluid phase)

- Measurement of autocorrelation function between 10° and 150°, in 10°-steps

- Determination of the hydrodynamic radius for each measurement and averaged hydrodynamic radius

- Plot of average of intensity for each measurement versus angle (angle correction, eqn. 2.2)

- Fit of P(q) (see eq. 1.7)

- Comparison of the hydrodynamic radius with form factor radius

Sample B (large particles, fluid)

- Same procedure as for sample A

- Comparison of P(q) of small and large particles, where are the differences?

- What were the difficulties when measuring at small angles (e.g. 20°)?

Wie bekomm wir P(q)?

Sample C (small particles, fluid, high concentrated)

- Measurement of high concentrated sample at 40°

- Comparison of diffusion coefficient of sample A and C, what are the differences and why?

Sample D (small particles, crystalline)

- Measurement of autocorrelation function (15min)

- Comparison of autocorrelation functions of fluid and crystalline phase, where are the differences and why?

2.3 Data analysis

2.3.1 DLS Data

The theory of dynamic light scattering is only valid for ideal and non-interacting particles. Size polydispersity and other irregularities change the autocorrelation function into a multiexponential decay, which can be described via a cumulant fit of the experimental data:

$$g^{(1)}(\vec{q}, \tau) = exp\left(K_1\tau + \frac{K_2\tau^2}{2} + ... \right) \tag{2.1}$$

while $K_1 = -D_0\vec{q}^2$ is directly related with the diffusion coefficient.
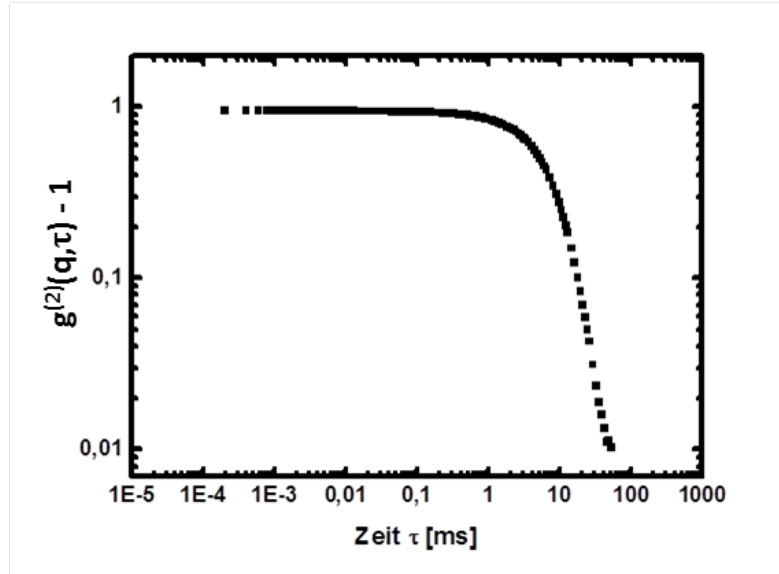In an experiment the measured autocorrelation function will then look like this:

Figure 2.2: Measured autocorrelation function of charged particles. As the colloids have a slight polydispersity the autocorrelation function gets a second slope, which describes a further diffusion behavior.

This curve contains more than one exponential decay due to non-identical particles and further diffusion behavior on different length and time scales.

2.3.2 SLS Data

In a static light scattering experiment one has to take into account, that the scattering volume (and therefore the number of scatterers in the illuminated volume) is angle-dependent.
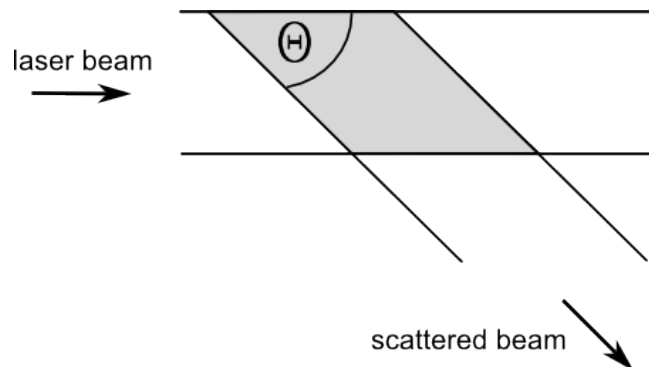

Figure 2.3: Angle dependence of the illuminated volume

The measured intensities have to be corrected, to get data, which are independent from the angle:

$$I_{corr} = I_{measured} \cdot sin(\theta) \tag{2.2}$$

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