Scattering Methods: Basic Principles and Application to Polymer and Colloidal Solutions

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Contents

1 Basic Principles

1.1 Mathematical description of wave motion

1.1.1 Propagation of waves

A wave is a perturbation, i.e. a deviation of a physical property Ψ from it's average value $\langle\Psi\rangle$,which propagates in space. For instance if you clap your hands you cause a local deviation of the air density $\rho/\langle\rho\rangle > 1$ at the spot where your hands meet. And a distant observer can hear the sound of your hands clapping, because the perturbation propagates all the way to the observer. In Fig. 1.1 the evolution of a Gaussian density perturbation is displayed at different times t. It is obvious from this figure that the value of the density, i. e. the perturbation is a function of the position variable x and the time t, that is $\Psi = f(x, t)$. To work out the proper expression for this dependencies, we consider first the perturbation at $t = 0$ which is $\Psi(x, t) \mid_{t=0} = f(x)$. After a finite time t we look at the perturbation in a new coordinate system which has traveled together with the perturbation with the common velocity v. In this coordinate system the perturbation is only a function of the position variable x', i. e. $\Psi = f(x')$. As can be seen from Fig. 1.2 the position of the maximum of the perturbation in the coordinate system at rest, x_c, and in the moving system, x'_c, are related by

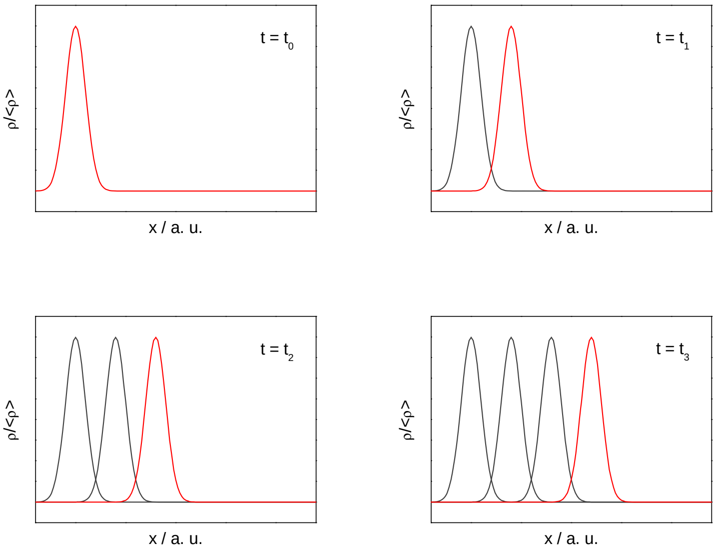

Figure 1.1: Propagation of a Gaussian perturbation in space and time

$$x_c = vt + x'_c. \tag{1.1}$$

This relation, of course, holds for all pairs of x and x', which gives

$$\Psi(x,t) = f(x') = f(x - vt) \tag{1.2}$$

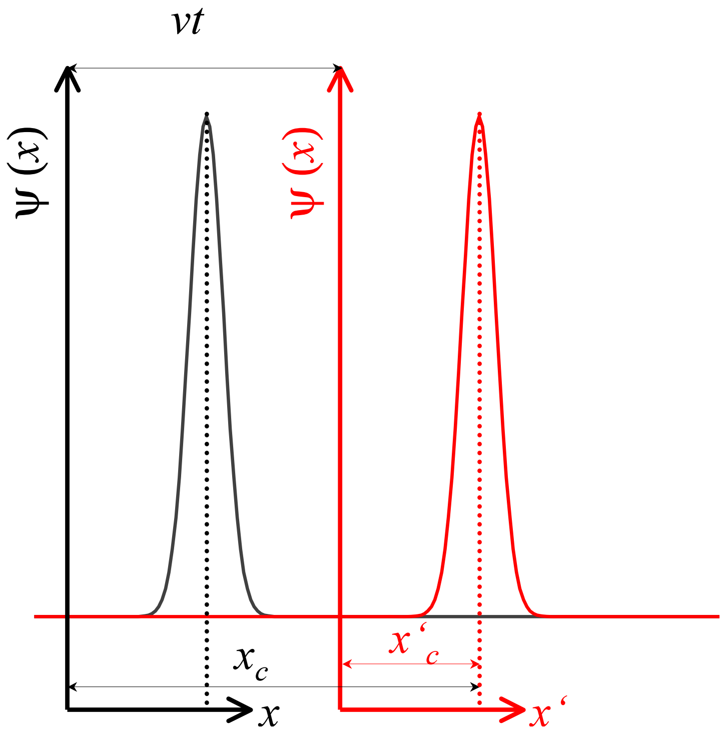

Figure 1.2: The propagation of a perturbation in a moving coordinate system

This means that we can describe a wave as the propagation of a perturbation in terms of a single variable of the form $(x - vt)$.

1.1.2 Harmonic waves

So far we have given our wave a rather unusual shape, commonly one associates with the term wave something which has a harmonic form. If we apply the above formalism to a harmonic perturbation we have to write

$$\Psi(x,t) \mid_{t=0} = A_0 \cos(kx) \tag{1.3}$$

where A_0 is the maximum value of the perturbation called its amplitude. The so called wavenumber k is a positive real number, which for the time being is only required to bring the dimensions of the argument of the cosine to unity (you can not calculate the cosine of a physical dimension). We could have taken a sin-function as well to describe a harmonic perturbation, but we thought it might be less tiring, if we write something else than you can read in every text book. To make the perturbation move we have to substitute x by $(x - vt)$ in eq. 1.3

$$\Psi(x,t) = A_0 \cos(k(x - vt)) \tag{1.4}$$

This function is periodic in space and time, i. e. there is a spatial period the wavelength λ, and a time period τ for which

$$\begin{aligned} \Psi(x,t) &= \Psi(x \pm \lambda, t) \\ &\text{and} \\ \Psi(x,t) &= \Psi(x, t \pm \tau) \end{aligned} \tag{1.5}$$

apply. On the other hand we know that the period of a cosine function is 2π, i. e. $\cos\alpha = \cos\alpha \pm (2\pi)$. Therefore

$$\begin{aligned} \cos(k(x - vt)) &= \cos(k(x - vt) \pm 2\pi) = \cos(k(x \pm \lambda - vt)) \\ &\text{and} \\ \cos(k(x - vt)) &= \cos(k(x - vt) \pm 2\pi) = \cos(k(x - v(t \pm \tau))). \end{aligned} \tag{1.6}$$

Rearranging the cosine arguments shows that $k = \pm 2\pi/\lambda$ and $k = \pm 2\pi/(v\tau)$, which is used to relate the wavelength and the time period

$$\lambda = v\tau \tag{1.7}$$

The wavelength is the number of length units per wave and the period is the number of time units per wave. Consequently we may define the number of waves per unit time, the frequency as $\nu = 1/\tau$. Multiplying the frequency with 2π we obtain the angular velocity $\omega = 2\pi\nu$, a quantity which is also used frequently to describe the time dependent part of a harmonic wave. Using the definitions of k, τ and ω we may rewrite eq. 1.4

$$\begin{aligned} \Psi(x,t) = A_0 \cos(k(x - vt)) &= A_0 \cos(\frac{2\pi}{\lambda}(x - vt)) \\ &= A_0 \cos(\frac{2\pi}{\lambda}x - \frac{2\pi}{\tau}t) \\ &= A_0 \cos(kx - \omega t). \end{aligned} \tag{1.8}$$

The argument of the cosine in eq. 1.8 is called the wave's phase angle or simply its phase $\phi(x,t)$. However, eq. 1.8 is certainly a special case of a more general description, since $\phi(x = 0, t = 0) = 0$ and therefore $\Psi(x = 0, t = 0) = A_0$. In general the wave will be different from it's amplitude at the origin, i. e.$\Psi(x = 0, t = 0) = A_0 \cos(\epsilon)$ and the initial phase is $\phi(x = 0, t = 0) = \epsilon$. Consequently the general expression for harmonic wave is

$$\begin{aligned}\Psi(x,t) &= A_0\cos(kx-\omega t+\epsilon) \qquad (1.9)\\ &\text{with}\\ \phi(x,t) &= kx-\omega t+\epsilon\end{aligned}$$

1.1.3 The complex representation

As we will see later it is often handy to describe waves in a complex representation. This becomes very useful if complicated operations have to be performed on the waves. According to Euler's theorem a cosine wave may be identified with the real part of a complex exponential and it's imaginary part is identified with sinusoidal waves.

$$\begin{aligned}\cos\alpha + i\sin\alpha &= \exp\{\imath\alpha\} \qquad (1.10)\\ \cos\alpha &= \Re\left[\exp\{\imath\alpha\}\right]\\ \sin\alpha &= \Im\left[\exp\{\imath\alpha\}\right]\end{aligned}$$

If we have to perform any arithmetic operation $\mathcal{O}$ on a cosine wave $\Psi(x,t)$we may use the following scheme:

- 1. identify $\Psi(x,t)$ as the real part of a complex expression $\mathcal{F}(x,t)$:
  $\Psi(x,t) = \Re[\mathcal{F}(x,t)]$
- 2. Perform the required operation on $\mathcal{F}(x,t)$ to get a new complex expression $\mathcal{G}(x,t)$:
  $\mathcal{O}\mathcal{F}(x,t) = \mathcal{G}(x,t)$
- 3. Identify the real part of $\mathcal{G}(x,t)$ with the result of the operation on $\Psi(x,t)$:
  $\Re[\mathcal{G}(x,t)] = \mathcal{O}\Psi(x,t)$

This formalism can also be applied to sinusoidal waves and the imaginary part of a complex expression. It seems to be a rather arbitrary and complicated procedure, but we will see in section 1.3 that it is often much easier to cope with the required arithmetic, if the complex representation is chosen.

1.1.4 Three dimensional waves

So far we have dealt with one dimensional waves only. For the practical purposes we will be discussing during this course, we will have to cope with three dimensional plane waves. At a given time t, the areas of equal phase of such a wave build a set of parallel planes which are oriented perpendicular to the direction of propagation. For a detailed mathematical description of these type of waves the reader is referred to the book by E. Hecht. Here we will stick to a very formalistic description.

Table 1.1: Formal changes which have to be made to get from the description of a one dimensional wave to a three dimensional wave

one dimensional wave	*three dimensional wave*
wave number k	wave vector $\mathbf{k}$
space coordinate x	position vector $\mathbf{r}$
Amplitude A_0	$\mathbf{A}_0$

Three dimensional plane waves can be treated with the same formalism as the one dimensional waves discussed so far. However, all position dependent scalar quantities have to be substituted by three dimensional vectors as outlined in table 1.1.4.

The wave vector $\mathbf{k} = \widehat{\mathbf{k}} 2\pi/\lambda$ has the magnitude $\mid \mathbf{k} \mid = k = 2\pi/\lambda$ and points into the direction of $\widehat{\mathbf{k}}$ which is the unit vector in the direction of the propagation of the wave. A three dimensional plane wave is therefore fully characterized by it's wave vector $\mathbf{k}$ and it's angular velocity ω. In the complex representation it reads

$$\mathbf{\Psi}(\mathbf{r}, t) = \mathbf{A}_0 \exp\{i(\mathbf{kr} - \omega t)\} \tag{1.11}$$

1.2 Light as electromagnetic wave

It is nowadays common understanding that light can be regarded as a transverse electromagnetic harmonic wave, i. e. an electric field $\mathbf{E}$ and a magnetic field $\mathbf{B}$ which both oscillate periodically in directions perpendicular to each other and perpendicular to their propagation direction. For our purposes we will have to deal mainly with the electric field, because generally the interaction of matter with magnetic fields is much weaker than the interaction with $\mathbf{E}$-fields (However, note that there is something like nuclear magnetic resonance spectroscopy, NMR).

1.2.1 The speed of light

We may thus describe light by a harmonicaly oscillating electric field

$$\begin{aligned} \mathbf{E}(x, t) &= \mathbf{E}_0 \cos(kx - \omega t + \epsilon) \qquad (1.12) \\ &= \mathbf{E}_0 \cos(k(x - vt) + \epsilon). \end{aligned}$$

We will now show that this equation fulfills the Maxwell-equation

$$\frac{\partial^2 \mathbf{E}}{\partial x^2} = \varepsilon_0 \mu_0 \frac{\partial^2 \mathbf{E}}{\partial t^2} \tag{1.13}$$

for the one dimensional case

$$\begin{aligned} \frac{\partial^2 \mathbf{E}}{\partial x^2} &= \frac{\partial - \mathbf{E}_0 k \sin(kx - \omega t + \epsilon)}{\partial x} = -\mathbf{E}_0 k^2 \cos(kx - \omega t + \epsilon) \qquad (1.14) \\ &\text{and} \\ \frac{\partial^2 \mathbf{E}}{\partial t^2} &= \frac{\partial \mathbf{E}_0 k v \sin(k(x - vt) + \epsilon)}{\partial t} = -\mathbf{E}_0 k^2 v^2 \cos(k(x - vt) + \epsilon) \end{aligned}$$

which reduces to

$$\frac{\partial^2 \mathbf{E}}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \mathbf{E}}{\partial t^2}. \qquad (1.15)$$

If we identify $1/v^2 = \varepsilon_0 \mu_0$ we see that eq. 1.12 fulfills the differential equation 1.13. we can therefore calculate the speed of light since we know the dielectric constant of vacuum $\varepsilon_0 = 8.85 \cdot 10^{-12}$ C^{2}J^{-1}m^{-1} and the magnetic permeability of free space $\mu_0 = 4\pi \cdot 10^{-7}$ Ns^{2}C^{-2}. Accordingly the speed of light is

$$v = \frac{1}{\sqrt{\varepsilon_0 \mu_0}} \approx 3 \cdot 10^8 \text{ms}^{-1} \equiv c \qquad (1.16)$$

1.2.2 The intensity of light

In experiments we are not able to measure the strength of the electric field of light, but we rather measure it's intensity, which is the energy flux

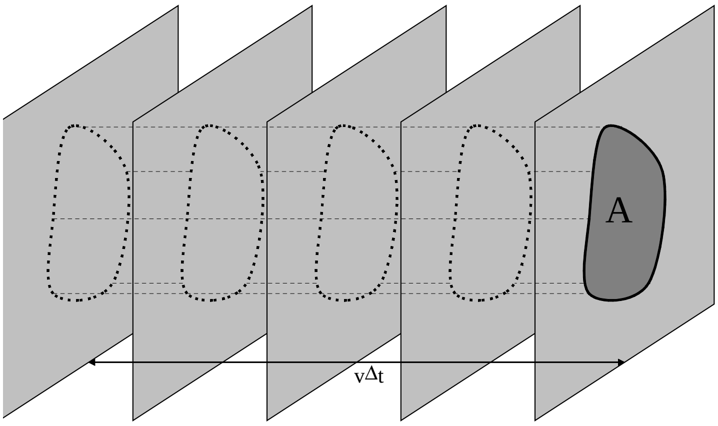

Figure 1.3: Energy flux through an aray A during timeΔt

$$S = \frac{U}{A \Delta t}. \qquad (1.17)$$

If we consider an area A through which light is transmitted as depicted in Fig. 1.3 , in the time interval Δt only the energy U which is in the volume $Av\Delta t$ is transmitted through A. Using the definition of an energy density $\rho_U = U/V$ the energy flux may be rewritten as

$$\begin{aligned} S &= \frac{\rho_U V}{A\Delta t} \\ &= \frac{\rho_U A v \Delta t}{A\Delta t} \\ &= v\rho_U \end{aligned} \tag{1.18}$$

To calculate the intensity of light, we need thus to know the energy density in an electric and a magnetic field. The energy density of an electric field $\rho_{U,E}$ and $\rho_{U,B}$ the energy density in magnetic field can be calculated for a condensator and a pair of coils respectively to be

$$\begin{aligned} \rho_{U,E} &= \frac{\varepsilon_0 E^2}{2} \\ \rho_{U,B} &= \frac{B^2}{2\mu_0} \end{aligned} \tag{1.19}$$

The two energy densities can be related to each other considering a further Maxwell-equation in it's one dimensional representation

$$\frac{\partial \mathbf{E}}{\partial x} = -\frac{\partial \mathbf{B}}{\partial t} \tag{1.20}$$

or in in its integral form

$$\mathbf{B} = -\int \frac{\partial \mathbf{E}}{\partial x} dt \tag{1.21}$$

which with eq. 1.12 gives

$$\begin{aligned} \mathbf{B} &= \mathbf{E}_0 k \int \sin(k(x-ct)+\epsilon)dt \\ &= \mathbf{E}_0 k \frac{1}{ck}\cos(k(x-ct)+\epsilon) \\ &= \frac{1}{c}\mathbf{E}. \end{aligned} \tag{1.22}$$

Introducing this relation into eq. 1.19 yields

$$\begin{aligned} \rho_{U,B} &= \frac{1}{2\mu_0 c^2}E^2 \\ &= \frac{\varepsilon_0\mu_0}{2\mu_0}E^2 \\ &= \rho_{U,E} \end{aligned} \tag{1.23}$$

Since the total energy density of an electromagnetic wave is $\rho_U = \rho_{U,E} + \rho_{U,B} = 2\rho_{U,E} = \varepsilon_0 E^2$, the energy flux S in eq. 1.18 can be rewritten

$$S = c\varepsilon_0 E^2 = c\varepsilon_0 E_0^2 \cos^2(kx - ct + \epsilon) \tag{1.24}$$

Since real detectors are not able to resolve the frequency of light which is typically of the order of $\nu \approx 5 \cdot 10^{14}$ Hz we will always measure average values of S such that the average value of the $\cos^2$-term reduces to 1/2 and the intensity is

$$I \equiv < S >= c\varepsilon_0 E_0^2 < \cos^2(kx - ct + \epsilon) >= \frac{c\varepsilon_0}{2} E_0^2 \tag{1.25}$$

1.3 Superposition of waves and interference

According to the superposition principle two harmonically oscillating electric fields add without disturbing each other at positions where they meet. For two one dimensional waves the total field strength is

$$\mathbf{E}_g = \mathbf{E}_1 + \mathbf{E}_1 = \mathbf{E}_{0,1} \cos\phi_1 + \mathbf{E}_{0,2} \cos\phi_2 \tag{1.26}$$

If we write for the phases $\phi_i = \alpha_i - \omega t$ with $\alpha_i(x, \epsilon_i) = k_i x + \epsilon_i$, we can rewrite eq. 1.26 to give

$$\mathbf{E}_g = \mathbf{E}_{0,1} \cos(\alpha_1 - \omega t) + \mathbf{E}_{0,2} \cos(\alpha_2 - \omega t) \tag{1.27}$$

where we have assumed for simplicity that $\omega_1 = \omega_2 = \omega$ which will be the case in any experiment that we will consider throughout this course. Applying $\cos(\alpha + \beta) = \cos\alpha\cos\beta - \sin\alpha\sin\beta$ we get

$$\begin{aligned} \mathbf{E}_g &= \mathbf{E}_{0,1} \{\cos\alpha_1 \cos(\omega t) + \sin\alpha_1 \sin(\omega t)\} \\ &+ \mathbf{E}_{0,2} \{\cos\alpha_2 \cos(\omega t) + \sin\alpha_2 \sin(\omega t)\} \end{aligned} \tag{1.28}$$

and if we factor out the time dependent terms we obtain

$$\begin{aligned} \mathbf{E}_g &= \cos(\omega t) \{\mathbf{E}_{0,1} \cos\alpha_1 + \mathbf{E}_{0,2} \cos\alpha_2\} \\ &+ \sin(\omega t) \{\mathbf{E}_{0,1} \sin\alpha_1 + \mathbf{E}_{0,2} \sin\alpha_2\}. \end{aligned} \tag{1.29}$$

To be further able to cope with this equation we make the Ansatz

$$\begin{aligned} \mathbf{E}_{0,1} \cos\alpha_1 + \mathbf{E}_{0,2} \cos\alpha_2 &= \mathbf{E}_0 \cos\alpha \\ \mathbf{E}_{0,1} \sin\alpha_1 + \mathbf{E}_{0,2} \sin\alpha_2 &= \mathbf{E}_0 \sin\alpha \end{aligned} \tag{1.30}$$

which is not a trivial substitution. However it will be justified, if we can find expressions which relate $\mathbf{E}_0$ to $\mathbf{E}_{0,1}, \mathbf{E_{0,2}}, \boldsymbol{\alpha_1}$ and α_2 independently of α and vice versa. To this end we simply divide the two expression in eq. 1.30 to get

$$\alpha = \arctan\left\{\frac{\mathbf{E}_{0,1} \sin\alpha_1 + \mathbf{E}_{0,2} \sin\alpha_2}{\mathbf{E}_{0,1} \cos\alpha_1 + \mathbf{E}_{0,2} \cos\alpha_2}\right\}. \tag{1.31}$$

An expression for $\mathbf{E}_0$ is derived by adding the squared terms of eq. 1.30 which is

$$\begin{aligned} E_0^2(\cos^2\alpha + sin^2\alpha) &= E_{0,1}^2\cos^2\alpha_1 + E_{0,2}^2\cos^2\alpha_2 + 2\mathbf{E}_{0,1}\mathbf{E}_{0,2}\cos\alpha_1\cos\alpha_2 \\ &+ E_{0,1}^2\sin^2\alpha_1 + E_{0,2}^2\sin^2\alpha_2 + 2\mathbf{E}_{0,1}\mathbf{E}_{0,2}\sin\alpha_1\sin\alpha_2 \\ E_0^2 &= E_{0,1}^2 + E_{0,2}^2 + 2\mathbf{E}_{0,1}\mathbf{E}_{0,2}\left\{\cos\alpha_1\cos\alpha_2 + \sin\alpha_1\sin\alpha_2\right\} \\ &= E_{0,1}^2 + E_{0,2}^2 + 2\mathbf{E}_{0,1}\mathbf{E}_{0,2}\cos(\alpha_1 - \alpha_2) \end{aligned} \tag{1.32}$$

For all pairs of $\mathbf{E}_0$ and α which satisfy eq. 1.32 and eq. 1.31 respectively, the Ansatz of eq. 1.30 is correct and we may rewrite eq. 1.29.

$$\begin{aligned} \mathbf{E}_g &= \mathbf{E}_0\cos\alpha\cos\omega t + \mathbf{E}_0\sin\alpha\sin\omega t \\ &= \mathbf{E}_0\cos(\alpha - \omega t) \end{aligned} \tag{1.33}$$

Equation 1.33 tells us that the superposition of two harmonic waves of equal frequency yields another harmonic wave with the same frequency however with a new amplitude $\mathbf{E}_0$ and a new phase. In Fig. 1.4 we display a numerical example for the above treatment. $\mathbf{E}_0$ is not simply the sum of the amplitudes, but it also depends on the phases of both constituting waves, as can be seen from eq. 1.32. If the constituting waves are in phase, $\alpha_1 = \alpha_2$, $\mathbf{E}_0$ is simply the sum of amplitudes, on the other hand if $\mathbf{E}_1$ and $\mathbf{E}_2$ have a phase difference of $\mid \alpha_1 - \alpha_2 \mid= \pi$ the minimum total amplitude $E_0 = \sqrt{E_{0,1}^2 + E_{0,2}^2}$ is obtained. A special case occurs when $\mathbf{E}_{0,1} = \mathbf{E}_{0,2}$ and $\mid \alpha_1 - \alpha_2 \mid= \pi$; then the total electric field would be zero, as can be seen from eq. 1.27.

This derivation has been rather tedious and things would become much worse, if we had to cope with many interfering waves. It is much more comfortable to use the complex representation in this case. Then the total electric field of N waves with equal frequency is written as

$$\mathbf{E}_g = \sum_{j=1}^{N}\mathbf{E}_{0j}\exp\{\imath(\alpha_j - \omega t)\} \tag{1.34}$$

We can now easily extract the time dependent part from the sum

$$\mathbf{E}_g = \exp\{-\imath\omega t\}\sum_{j=1}^{N}\mathbf{E}_{0j}\exp\{\imath\alpha_j\} \tag{1.35}$$

and define a complex amplitude and a phase of the total field

$$\sum_{j=1}^{N}\mathbf{E}_{0j}\exp\{\imath\alpha_j\} \equiv \mathbf{E}_0\exp\{\imath\alpha\} \tag{1.36}$$

to yield

$$\mathbf{E}_g = \mathbf{E}_0\exp\{\imath\alpha\}\exp\{-\imath\omega t\} \tag{1.37}$$

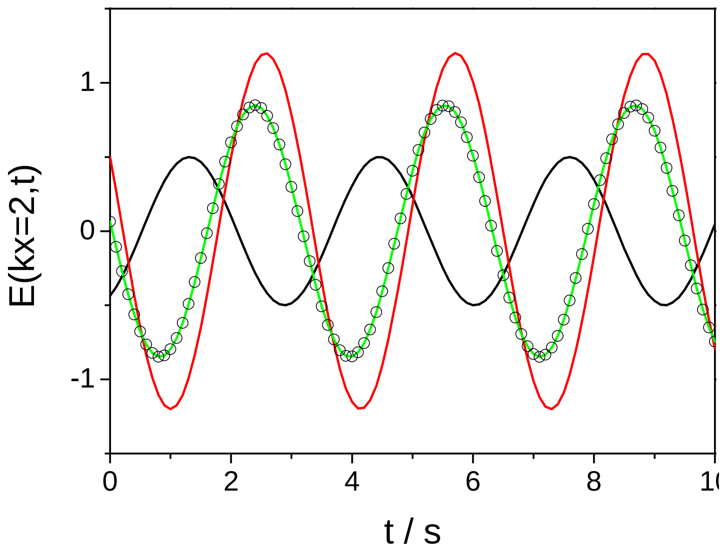

Figure 1.4: Superposition of two harmonic waves of equal frequency. The red ($\mathbf{E}_{0,1} = 1.2$, $\epsilon_1 = 0.2\pi$) and the black ($\mathbf{E}_{0,2} = 0.5$, $\epsilon_1 = \pi$) curve are the constituting waves, both with constant $kx = 2$ and $\omega = 2$. Open symbols are their sum at given times and the green curve is calculated using eq. 1.33 with $\alpha = -1.49549$ and $\mathbf{E}_0 = 0.84804$ according to eqs. 1.31 and 1.32 respectively

It is a simple task to show that for the case of two waves the real part of the right hand side of eq. 1.37 reproduces eq. 1.33

$$\Re[\mathbf{E}_0 \exp\{\imath(\alpha - \omega t)\}] = \mathbf{E}_0 \cos(\alpha - \omega t) \tag{1.38}$$

2 Static Light Scattering

2.1 The scattering equation: a heuristic derivation

We will now derive a heuristic relation which describes the scattered electric field from an ensemble of particles, as is sketched in Fig. 2.1 . For an exact derivation the interested reader is refered to the book of J. Dhont

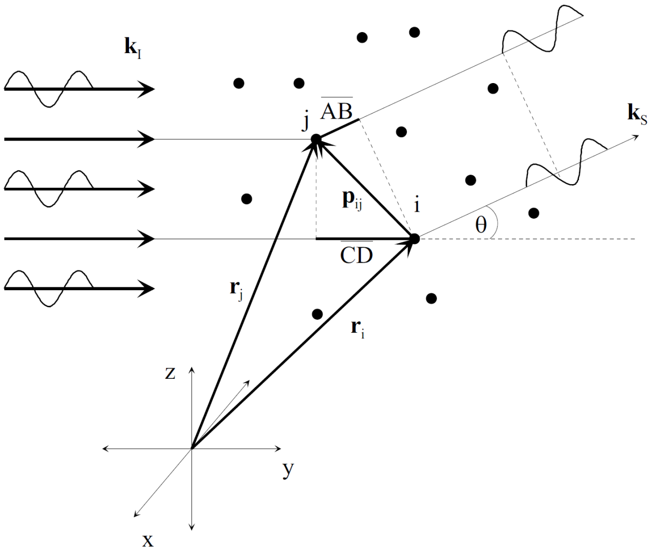

Figure 2.1: The electric fields scattered from different particles has different phases, depending on the location of the scattering particles in space.

Each dot in this figure is considered as an elastic dipole scatterer, i. e. when exited by an incident electric field with frequency ω, it will emit a secondary electric field with the same frequency without any phase delay. The spatial distribution of the field strength emitted by a single dipole is sketched in the Fig. 2.2 . If observed at quasi infinite distance the fields which are emitted from different scatterers into the direction defined by the observation angle θ propagate paralelly (Fraunhofer approximation). We may thus say that the scattered waves are characterized by a single wave vector $\mathbf{k}_S$, while the incident field has the wave vector $\mathbf{k}_I$. As we have seen in chapter 1.3 the total field strength of superimposed wave depends on their phases. We have therefore to calculate the phase of the scattered field from each point scatterer. From Fig. 2.1 it is obvious that the fields scattered from the particles i and j have traveled different distances. This results in a phase difference $\phi_i - \phi_j = \Delta\phi$ at the observer position, since the incoming field is a plane wave (i. e. it has constant phase in any plane perpendicular to it's propagation direction). This phase difference is given by $\Delta\phi = PD 2\pi/\lambda$ where the path difference is $PD = \overline{AB} - \overline{CD}$ according to Fig. 2.1 . The distances $\overline{AB}$ and $\overline{CD}$ are related to the wave vectors of the incident field and the scattered field by

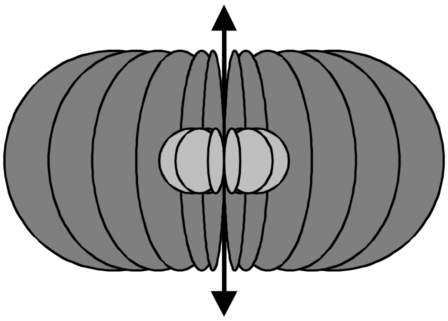

Figure 2.2: Spatial distribution of the electric field strength emitted by an oscillating dipole. The arrow indicates the direction of oscillation. Note that no field is emitted in the direction of oscillation.

$$\begin{aligned}\overline{AB} &= \widehat{\mathbf{k}}_S \cdot \mathbf{p}_{ij} \qquad (2.1)\\ \text{and} & \\ \overline{CD} &= \widehat{\mathbf{k}}_I \cdot \mathbf{p}_{ij}\end{aligned}$$

Where $\mathbf{p}_{ij}$ is the separation vector between the positions of point i and j, which may be written for any two point in space as the difference of their position vectors in an arbitrarily defined coordinate system $\mathbf{p}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. The phase difference is then

$$\begin{aligned} \Delta\phi &= (\mathbf{r}_i - \mathbf{r}_j)(\mathbf{k}_S - \mathbf{k}_I)k \\ &= \mathbf{r}_i(\mathbf{k}_S - \mathbf{k}_I)k - \mathbf{r}_j(\mathbf{k}_S - \mathbf{k}_I)k \end{aligned} \tag{2.2}$$

where $k = 2\pi/\lambda$. This relation allows to assign a phase to any of the point scatterers considered

$$\begin{aligned} \phi_i &= \mathbf{r}_i(\mathbf{k}_S - \mathbf{k}_I)k \\ \phi_j &= \mathbf{r}_j(\mathbf{k}_S - \mathbf{k}_I)k \end{aligned} \tag{2.3}$$

and so forth. Or more generally speaking, we can assign a phase to the field scattered from any volume element at the position $\mathbf{r}$

$$\phi(\mathbf{r}) = \mathbf{r}\mathbf{q} \tag{2.4}$$

where we have introduced the so–called scattering vector $\mathbf{q} \equiv \left(\widehat{\mathbf{k}}_S - \widehat{\mathbf{k}}_I\right) k = \mathbf{k_S} - \mathbf{k_I}$
The field strength of the scattered field further depends on the specific properties of the regarded volume element, which we summarize as the so–called scattering power $f(\mathbf{r})$. Further the scattered field strength is of course proportional to the strength of the incident field, such that the scattered electric field from one volume element is

$$\mathbf{E}_V(\mathbf{r}, t) = f(\mathbf{r})\mathbf{E}_I \exp\{\imath(\mathbf{q}\mathbf{r} - \omega t)\} \tag{2.5}$$

To get the total electric field $\mathbf{E}_S$ scattered from the entire scattering volume V_S we have to integrate over all volume elements

$$\mathbf{E}_S \propto \sum_{j=1}^{N} \langle \mathbf{E}_{V_j}(\mathbf{r}_j) \rangle = \mathbf{E}_I \int_{V_S} f(\mathbf{r}) \exp\{\imath\mathbf{q}\mathbf{r}\} d\mathbf{r}, \tag{2.6}$$

where we have performed the time average and put the resulting constant into the proportionality.

In most practical situations we are doing experiments on solutions of particles disperged in a solvent, such that we will observe scattered fields from volume elements, where particles are present and consequently the scattering power within a particle has to be applied. On the other hand, for dilute solutions the major part of volume elements contains solvent and there the scattering power of the solvent has to be inserted into eq. 2.6. Since we are usually interested only in the field scattered by the particle we separate expression 2.6 into a part originating from the particles, $\mathbf{E}_{S,solute}$, and one originating from the solvent, $\mathbf{E}_{S,solvent}$.

$$\mathbf{E}_S \propto \mathbf{E}_{S,solute} + \mathbf{E}_{S,solvent} = \mathbf{E}_I \int_{V_S} f_{solute}(\mathbf{r}) \exp\{\imath\mathbf{q}\mathbf{r}\} d\mathbf{r} + \mathbf{E}_I \int_{V_S} f_{solvent}(\mathbf{r}) \exp\{\imath\mathbf{q}\mathbf{r}\} d\mathbf{r} \tag{2.7}$$

Experimentally the two parts of the sum in eq. 2.7 are separated by measuring the scattered intensity from the solution and from the solvent independently. Subsequently the latter is subtracted from the former to give the contribution of the solute. For the further mathematical treatment, this is equivalent to the consideration of the solute particles in vacuum, if the solute scattering power is replaced by the difference between the scattering power of the solute and the solvent $f(\mathbf{r}) = f_{solute}(\mathbf{r}) - f_{solvent}(\mathbf{r})$. In what follows we will therefore drop the solvent contribution and the subscript $_{solute}$. We may than rewrite eq. 2.6 as

$$\mathbf{E}_S \propto \sum_{j=1}^{N} \mathbf{E}_I \int_{V_j} f(\mathbf{r}) \exp\{\imath \mathbf{q}\mathbf{r}\} d\mathbf{r} \tag{2.8}$$

where we have substituted the integration over the whole scattering volume by the sum of integrals over the volume of all individual particles in the scattering volume. We are allowed to do so, because the scattered field of the volume elements outside the particles is set to be zero according to the above consideration.

There is one major problem with eq. 2.8 to overcome. For each particle we have to integrate with respect to $\mathbf{r}$ which makes the integration limits for each particle depend on it's position. It is much more convenient to substitute $\mathbf{r}$ by the sum of two new position vectors $\mathbf{r} = \mathbf{r}_j + \mathbf{r}'$, where $\mathbf{r}_j$ points to the center position of the j^{th} particle and $\mathbf{r}'$ points from the center position to any arbitrary point within the particle. We may then rewrite eq. 2.8 to give

$$\begin{aligned} \mathbf{E}_S &\propto \sum_{j=1}^{N} \int_{V_j^0} \mathbf{E}_I g(\mathbf{r}') \exp\left\{\imath \mathbf{q}(\mathbf{r}_j + \mathbf{r}')\right\} d\mathbf{r}' \\ &= \mathbf{E}_I \sum_{j=1}^{N} \exp\left\{\imath \mathbf{q}\mathbf{r}_j\right\} \cdot \int_{V_j^0} g(\mathbf{r}') \exp\left\{\imath \mathbf{q}\mathbf{r}'\right\} d\mathbf{r}' \end{aligned} \tag{2.9}$$

where V_j^0 is the actual volume of the j^{th} particle. In deriving eq. 2.9 we have made use of the following simplifications. (i) The scattering power is described in terms of a function which depends only on $\mathbf{r}'$ and not on $\mathbf{r}$ anymore. This is justified since $\mathbf{r}'$ always points to a volume element within the particle. The scattering power outside the particle is zero. We therefore may write $f(\mathbf{r}) = g(\mathbf{r}')$. (ii) The substitution of the integration variable $d\mathbf{r} = d\mathbf{r}'$ seems to be arbitrary at first glance. However $\mathbf{r} = \mathbf{r}_j + \mathbf{r}'$ and therefore $d\mathbf{r} = d\mathbf{r}_j + d\mathbf{r}'$ and $\mathbf{r}_j$ was defined to direct to a fixed point in space, i. e. the center of particle j. Consequently $d\mathbf{r}_j = 0$ and $d\mathbf{r} = d\mathbf{r}'$

For a solution of identical particles the integrals in eq. 2.9 are equal for each particle and they can be factored out of the sum. For the scattered intensity from a solution of identical particles we may thus write

$$I(q) \propto \mathbf{E}_S^2 = \left| \int_{V_j^0} g(\mathbf{r}') exp\{\imath \mathbf{q}\mathbf{r}'\} d\mathbf{r}' \right|^2 \cdot \left| \sum_{j=1}^{N} exp\{\imath \mathbf{q}\mathbf{r}_j\} \right|^2 \tag{2.10}$$

We can see immediately that eq. 2.10 contains a factor which depends on the particle positions only while the other depends on the scattering power and the distances within a particle. The former

$$S(q) \equiv \frac{1}{N} \left\langle \left| \sum_{j=1}^{N} exp\{\imath \mathbf{q}\mathbf{r}_j\} \right|^2 \right\rangle \tag{2.11}$$

we call the structure factor of the solution, while the latter

$$P(q) \equiv \left\langle \left| \frac{\int_{V_j^0} g(\mathbf{r}')exp\{\imath \mathbf{q}\mathbf{r}'\}d\mathbf{r}'}{\int_{V_j^0} g(\mathbf{r}')d\mathbf{r}'} \right|^2 \right\rangle \tag{2.12}$$

is the so called particle scattering factor or form factor. Here the angular brackets indicate, that in a real experiment we will always probe time averaged quantities, which in turn means that we integrate over a large number of orientations. Mathematically spoken the numerator of eq. 2.12 is the Fourier–transform of the scattering power distribution within the particle. Note that the nominator in definition 2.12 is a normalization constant, which we may put into the proportionality of eq. 2.10 such that we finally may write

$$I(q,N) \propto \left(\int_{V_j^0} g(\mathbf{r}')d\mathbf{r}' \right)^2 P(q)NS(q) \tag{2.13}$$

where q is the magnitude of the scattering vector. Note that for particles with constant scattering power the integral in the proportionality becomes $g(r')V_{j^0}$, i. e. the scattered intensity is proportional to the particle volume squared.

We have to emphasize that this factorization of the scattered intensity is strictly correct only for a suspension of identical particles with a scattering power of spherical symmetry. However, it is a very useful and widely applied approximation in certain limiting cases for all kinds of particles. From the definitions 2.11 and 2.12 it can be seen that in the limit of $N \to 0$, that is infinite dilution in an experiment, the structure factor approaches unity and in the limit of $q \to 0$ the particle scattering factor approaches unity. The same argument holds for the factors constituing eq. 2.10 independent of the particles shape and scattering power. We may therefore safely apply the following approximations to experimental data

$$\begin{aligned} \lim_{N\to 0} I(q,N) \quad &\propto \quad P(q) \\ &\text{and} \\ \lim_{q\to 0} I(q,N) \quad &\propto \quad S(q=0) \end{aligned} \tag{2.14}$$

We shall now calculate the magnitude of the scattering vector as a function of the observation or scattering angle θ. We had defined the scattering vector as $\mathbf{q} = \mathbf{k}_S - \mathbf{k}_I$. From Fig. 2.3 it is obvious that the magnitude of $\mathbf{q}$ is related to $|\mathbf{k}_S| = 2\pi/\lambda$ by

$$\frac{|\mathbf{q}|}{2} = \sin\frac{\theta}{2}\,|\mathbf{k}_S| \tag{2.15}$$

which yields

$$|\mathbf{q}| \equiv q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2} \tag{2.16}$$

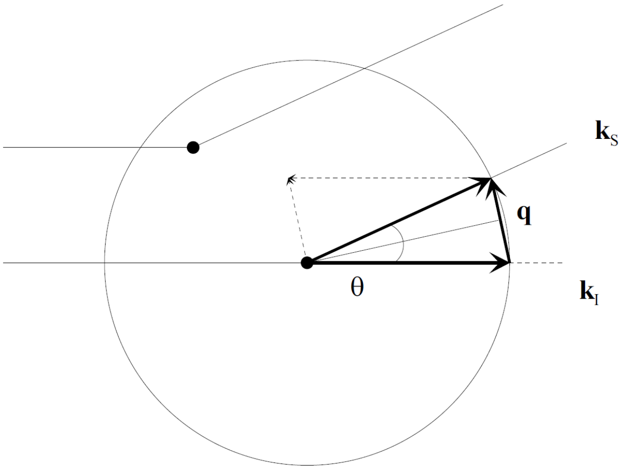

Figure 2.3: The magnitude of the scattering vector is calculated from $\frac{|\mathbf{q}|}{2} = \sin\frac{\theta}{2}\,|\mathbf{k}_S|$ Note that k_I and k_S have the same magnitude.

Here λ is the radiation wave length in the sample $\lambda = lambda_0/n$ with n being the index of refraction. In order to be able to cope with experimental scattering data on a quantitative level we will still have to calculate the proportionality constant in eq. 2.13, which will be done in the chapter 2.2.

In the above derivation of eq. 2.10 we have implicitly made several assumptions which shall be discussed now.

- First of all we assumed that the incident field is NOT attenuated, neither by absorption nor by scattering. This requires first that the solution does not have a resonance frequency in the vicinity of the frequency of the incident field. Secondly, only a very small portion of the incident field may be scattered.
- We further neglected multiple scattering, i. e. we assume that light scattered once is not scattered a second time. This assumption is also justified if only a small fraction of the incident light is scattered.
- Additionally we neglected the effect that a wave which travels through a particle has a wavelength different from the wavelength in the solvent because of the difference of refractive index $\Delta n = |n_{particle} - n_{solvent}|$. This may cause an additional

phase shift with respect to the incident wave, which we neglected. This approximation is justified when $2\pi\Delta n a/\lambda_0 < 0.1$, where a is the particle radius and λ_0 is the vacuum wave length of the incident field. In other words this approximation holds if the particle is significantly smaller than the wave length.

- Finally we assumed the the propagation direction of the incident field is the same throughout the sample. This condition ignores refraction at the particle solvent interface, which is justified if $\Delta n < 0.1$ roughly.

The scattering theory with the above approximations is called the *Rayleigh Gans Debye* scattering theory.

2.2 The Rayleigh scattering equation

2.2.1 Ideal gas

We shall consider the particles of an ideal gas as electric dipoles, which may be caused to oscillate by an incident electric field. The dipoles will then scatter, that is emit three dimensional secondary fields with the same frequency as the incident field and a spatial field strength characteristic as depicted in Fig. 2.2 . The strength of the field scattered from a single dipole $\mathbf{E}_D$ at a distance R from the dipole is

$$\mathbf{E}_D(t) = \frac{\omega^2 \boldsymbol{\mu}(t)}{4\pi\varepsilon_0 c^2}\frac{\sin\delta}{R} \tag{2.17}$$

where $\boldsymbol{\mu}(t)$ is the time dependent moment of the dipole and δ is the angle between the dipole's oscillation direction and the observation direction. In modern scattering experiments we usually use polarized laser light as the primary electric field, which allows to set $\delta = 90$ and consequently $\sin\delta = 1$. We will consider only this case in what follows. The time averaged intensity can be calculated according to eq. 1.25

$$I_D = \frac{k^4 < \mu^2(t) >}{16\pi^2\varepsilon_0^2 R^2} c\varepsilon_0 \tag{2.18}$$

where we made use of definition of the wave number $k = \omega/c$. The moment of an induced dipole is the product of it's polarizability, α and the exciting field strength, which in our case is a harmonic wave.

$$\boldsymbol{\mu}(t) = \alpha \mathbf{E}_{I,0}\cos(\omega t) \tag{2.19}$$

where $\mathbf{E}_{I,0}$ is the amplitude of the exciting field. Consequently the time averaged squared moment is

$$< \mu^2(t) >= \alpha^2 E_{I,0}^2 < \cos^2(\omega t) >= \frac{\alpha^2 E_{I,0}^2}{2} \tag{2.20}$$

Introducing eq. 2.20 into 2.18 yields

$$\frac{I_D}{I_I} R^2 = \frac{k^4 \alpha^2}{16\pi^2 \varepsilon_0^2} \tag{2.21}$$

where we used $c\varepsilon_0 E_{I,0}^2/2 = I_I$ for the intensity of the incident light. In the case of an ideal gas we may use the Clausius–Mosotti equation to write the polarizability

$$\begin{aligned} \alpha &= \frac{3\varepsilon_0}{\mathcal{N}} \left(\frac{\varepsilon_r - 1}{\varepsilon_r + 2} \right) \\ &\approx \frac{n^2 - 1}{\mathcal{N}} \varepsilon_0 . \end{aligned} \tag{2.22}$$

Here $\mathcal{N} = N/V$ is the particle number density and the refractive index for non–magnetic media is $n = \sqrt{\varepsilon_r}$, with ε_r the relative dielectricity constant of the gas. Since the refractive index of an ideal gas is not much different from unity we have approximated the denominator in the first part of eq. 2.22 by $\varepsilon_r + 2 \approx 3$. To obtain the scattered intensity I_S from an ensemble of N dipoles we multiply I_D by the number of particles and introduce eq. 2.22 into 2.21.

$$\frac{I_S}{I_I} R^2 = N \frac{k^4}{16\pi^2 \varepsilon_0^2} \frac{(n^2 - 1)^2}{\mathcal{N}^2} \varepsilon_0^2 \tag{2.23}$$

We will now substitute the particle number density in a convenient way, i. e.

$$\mathcal{N}^2 = N^2/V^2 = \frac{N}{V} \frac{N_A n}{V} = \frac{N}{V} \frac{N_A m}{M_r V} = \frac{N}{V} \frac{N_A}{M_r} \rho \tag{2.24}$$

where N_A is Avogadro's constant, n is the number of moles of particles (not to be mixed up with refractive index), m is their total mass, M_r is their molar mass and ρ is their mass density. Together with eq. 2.23 this gives.

$$\frac{I_S}{I_I} \frac{R^2}{V} = \frac{k^4 (n^2 - 1)^2}{N_A \rho 16\pi^2} M_r \tag{2.25}$$

The expression on the left hand side of this equation is usually referred to as the *Rayleigh–ratio* $\mathcal{R}$ to the honor of Lord Rayleigh who was the first to write down the scattering equation for an ideal Gas in 1871

$$\mathcal{R} = \frac{k^4 (n^2 - 1)^2}{16\pi^2 N_A \rho} M_r \tag{2.26}$$

Note that according to $k = 2\pi/\lambda$, the scattered intensity from an ideal gas depends on λ^{-4}, that is blue light is scattered much more strongly than red light. This is the reason why the sky above is blue. On the other hand sun downs are red because the blue part of the white sunlight is scattered off the observation direction most strongly, if you look directly into the sun.

2.2.2 Infinitely dilute solutions of small particles

The formalism for the calculation of the scattered intensity from an ideal gas can be easily adopted to dilute solutions of small particles. We have to perform three modifications to eq. 2.26.

- 1. We have to account for the dielectric properties of the solvent and the solution, when writing down the Clausius–Mosotti equation. Instead of eq. 2.22 we have to write

  $$\alpha = \frac{3\varepsilon_0}{\mathcal{N}} \left(\frac{\varepsilon_{r,solution} - \varepsilon_{r,solvent}}{\varepsilon_{r,solution} + 2\varepsilon_{r,solvent}} \right) \tag{2.27}$$

  The denominator of eq. 2.27 can be rewritten by factoring out the $\varepsilon_{r,solvent}$, which yields $\varepsilon_{r,solvent}\left(\varepsilon_{r,solution}/\varepsilon_{r,solvent} + 2\right)$, which may be approximated by $3\varepsilon_{r,solvent}$ if $\varepsilon_{r,solution} \approx \varepsilon_{r,solvent}$. With this approximation the Clausius–Mosotti equation reads

  $$\alpha = \frac{\varepsilon_0}{\mathcal{N}} \left(\frac{n^2_{solution} - n^2_{solvent}}{n^2_{solvent}} \right) \tag{2.28}$$

- 2. Also the relation for the moment of the induced dipole (eq. 2.19) has to be modified taking into account the relative dielectric constant of the solvent

  $$\boldsymbol{\mu}(t) = \alpha \varepsilon_{r,solvent} \mathbf{E}_{I,0} \cos(\omega t) \tag{2.29}$$

  This modification will cause an additional factor $n^4_{solvent}$ in the numerator of eq. 2.26.

- 3. The particle number density in a solution is $\mathcal{N} = c \cdot N_A/M_r$, where c is the solute mass per unit volume (not to be mixed up with the speed of light), which in light scattering is often called concentration.

Applying these modifications to eq. 2.26 leads to

$$\mathcal{R} = \frac{k^4 (n^2_{solution} - n^2_{solvent})^2}{16\pi^2 N_A c} M_r \tag{2.30}$$

The difference of squared refractive indexes may be approximated in the Rayleigh–Gans–Debye limit as

$$\begin{aligned} n^2_{solution} - n^2_{solvent} &= \left(n_{solution} - n_{solvent}\right)\left(n_{solution} + n_{solvent}\right) \\ &\approx \left(n_{solution} - n_{solvent}\right) \cdot 2n_{solvent} \\ &\equiv 2n_{solvent}\Delta n. \end{aligned} \tag{2.31}$$

The refractive index difference Δn can be written as $c\partial n/\partial c$, if the refractive index increment $\partial n/\partial c$ is a constant. Thus $n^2_{solution} - n^2_{solvent} \approx 2n_{solvent}c\partial n/\partial c$, which can be introduced into eq. 2.30 to yield

$$\mathcal{R} = \frac{k^4 4n^2_{solvent}}{16\pi^2 N_A}\left(\frac{\partial n}{\partial c}\right)^2 M_r c \tag{2.32}$$

If we substitute $k = 2\pi/\lambda_0$, were λ_0 is the vacuum wavelength of the incident light, and summarize all constants in $K = (2\pi n_{solvent}\partial n/\partial c)^2 / (N_A\lambda_0^4)$ we obtain the simple expression for the scattered intensity from a dilute solution, which you will find most frequently in text books on light scattering.

$$\mathcal{R} = KcM_r \tag{2.33}$$

It is thus possible to determine the molar mass M_r of solute particles by a light scattering experiment. It is important to notice that light scattering is one of the few experimental techniques to determine the molar mass of polymers in solution on absolute scale.

We have so far added up the scattering intensity of all dipoles in the solution to get the total scattered intensity. This simple procedure neglects any interference, which strictly speaking can only be correct for infinite dilution and zero scattering angle or scattering vector. In the next two sections we will introduce further improvements to eq. 2.33, which account for the effect of finite concentration and and finite scattering angle.

2.2.3 Interparticle interference

Because we have so far simply added the intensities stemming from single dipoles, any kind of interference has to reduce the total scattered intensity. In light scattering it is very common to express the scattered intensity in terms of the inverse Rayleigh–ratio, which depends on the scattering vector and the solute concentration.

$$\frac{Kc}{\mathcal{R}(q,c)} = \frac{1}{M_r} \tag{2.34}$$

This quantity has to increase with increasing concentration, and for moderate concentrations it is reasonable to assume that it will increase linearly with c, that is

$$\frac{Kc}{\mathcal{R}(q,c)} = \frac{1}{M_r} + \mathcal{K}c \tag{2.35}$$

This is an expansion in c, and a closer look reveals that the right hand side of the equation is related to the virial expansion of the osmotic pressure of a solution. For an ideal solution, i. e. a solution of particles which do not have any interactions, the osmotic pressure is

$$\Pi \;=\; \frac{n}{V}RT = \frac{m}{M_r V}RT \tag{2.36}$$

$$= \frac{1}{M_r} cRT$$

where R is the gas constant an T the temperature. For real solutions particle interaction has to be accounted for, which can be done to a first approximation by a virial expansion

$$\Pi \approx RT\left(\frac{1}{M_r}c + A_2c^2 + A_3c^3 + ...\right) \tag{2.37}$$

Truncating the expansion after the quadratic term and taking the derivative yields the osmotic compressibility as

$$\frac{d\Pi}{dc} \approx RT\left(\frac{1}{M_r} + 2A_2c\right). \tag{2.38}$$

If we identify $\mathcal{K}$ from eq. 2.35 with $2A_2$ we get

$$\frac{Kc}{\mathcal{R}(q,c)} = \frac{d\Pi}{dc}\frac{1}{RT} \tag{2.39}$$

From statistical thermodynamics it is known that the osmotic compressibility is related to $S(q=0)$ the zero scattering vector limit of the solution structure factor by

$$S(q=0) = \left(\frac{d\Pi}{dc}\right)^{-1} RT. \tag{2.40}$$

With this relation we have finally established the missing proportionality constant in eq. 2.13 for the zero q limit as

$$\begin{aligned} \frac{Kc}{\mathcal{R}(q=0,c)} &= \frac{1}{S(q=0,c)} \\ &= \frac{1}{M_r} + 2A_2c \end{aligned} \tag{2.41}$$

2.2.4 Intraparticular interference

In this section we will introduce a further improvement to eq. 2.41 to account for the angular dependence of the scattering. How we have to do that is immediately obvious from eq. 2.13. From the corresponding discussion in chapter 2.1 we now that

$$\lim_{c\to 0} I(q,c) \propto P(q) \tag{2.42}$$

In the preceding section we established the proportionality constant according to eq. 2.33. Thus we can write

$$\begin{aligned} \lim_{c\to 0} \mathcal{R}(q,c) &= KcM_rP(q) \\ &\text{or} \\ \frac{Kc}{\mathcal{R}(q,c=0)} &= \frac{1}{M_rP(q)} \end{aligned} \tag{2.43}$$

To account also for the concentration dependence we have to substitute M_r by $S(q=0)$ according to eq. 2.41, which gives

$$\begin{aligned} \lim_{c\to 0, q\to 0} \frac{Kc}{\mathcal{R}(q,c)} &= \frac{1}{S(q=0,c)P(q)} \\ &= \frac{1}{P(q)}\left(\frac{1}{M_r} + 2A_2c\right) \end{aligned} \tag{2.44}$$

This limiting relation is however often used to evaluate static light scattering data as will be discussed in chapter 2.3. For this purpose the particle scattering factor is written in the form derived by Debye

$$P(q) = \frac{1}{N^2}\sum_i^N\sum_j^N \frac{\sin qr_{ij}}{qr_{ij}}. \tag{2.45}$$

This expression can be related to the radius of gyration of the particle in the following way. Expanding the sin–term in $P(q)$ as a Taylor–series yields

$$P(q) = \frac{1}{N^2}\sum_i^N\sum_j^N \left\{1 - \frac{(qr_{ij})^2}{3!} + \frac{(qr_{ij})^4}{5!}\right\}. \tag{2.46}$$

If the sum is truncated after the square term it can be rewritten as

$$P(q) = 1 - \frac{q^2}{N^2}\sum_i^N\sum_j^N \frac{r_{ij}^2}{3!}. \tag{2.47}$$

As the radius of gyration R_g is defined as

$$< S^2 >= 1 - \frac{1}{2N^2}\sum_i^N\sum_j^N r_{ij}^2 \equiv R_g^2. \tag{2.48}$$

the form factor is approximately

$$P(q) \approx 1 - \frac{q^2R_g^2}{3}. \tag{2.49}$$

A further approximation can be applied for $\frac{q^2R_g^2}{3} << 1$, than

$$\frac{1}{P(q)} \approx 1 + \frac{q^2R_g^2}{3}, \tag{2.50}$$

which now can be introduced into eq. 2.44 and we obtain

$$\frac{Kc}{\mathcal{R}(q,c)} \approx \left(\frac{1}{M_r} + 2A_2c\right)\left(1 + \frac{q^2R_g^2}{3}\right) \tag{2.51}$$

According to Figs. 2.4 and 2.5 the above above approximations hold only for $(qR_g)^2 < 0.1$. Consequently eq. 2.51 can be further simplyfied to

$$\frac{Kc}{\mathcal{R}(q,c)} = \frac{1}{M_r}\left(1 + \frac{q^2R_g^2}{3}\right) + 2A_2c. \tag{2.52}$$

This is justified, because the second cross term $2A_2cq^2R_g^2/3$ is at least 30 times smaller than $2A_2c$, if $q^2R_g^2 < 0.1$. Eq. 2.52 is the so–called Zimm equation, which was suggested by B. Zimm in 1949, and is the most widely used formalism to evaluate static light scattering data.

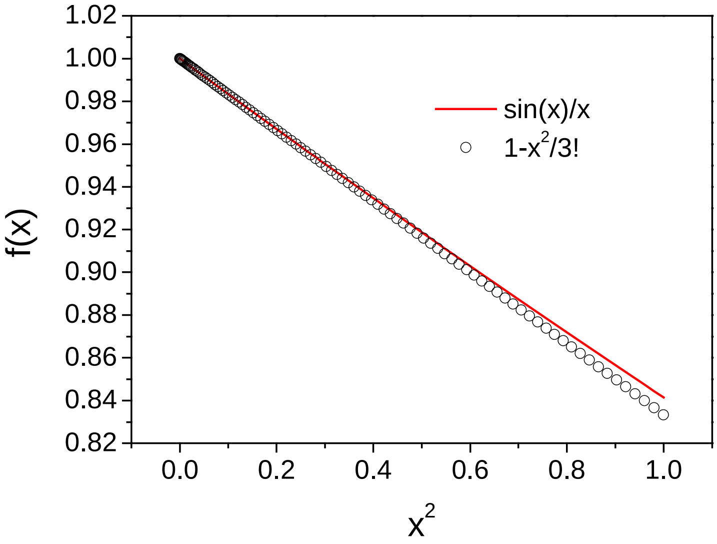

Figure 2.4: Comparison of $\sin x/x$ with the corresponding Taylor–expansion truncated at the quadratic term

2.3 Data evaluation

2.3.1 The Zimm plot

From eq. 2.52 it is evident that there are three basic parameters which can be determined by static light scattering (SLS) experiments, i. e. the particle molar mass, M_r, it's radius of gyration R_g and the second osmotic virial coefficient A_2 of the solution. In this section we will see how these parameters are extracted from experimental data, where we will neglect polydispersity effects except from stating that for polydisperse samples the molar

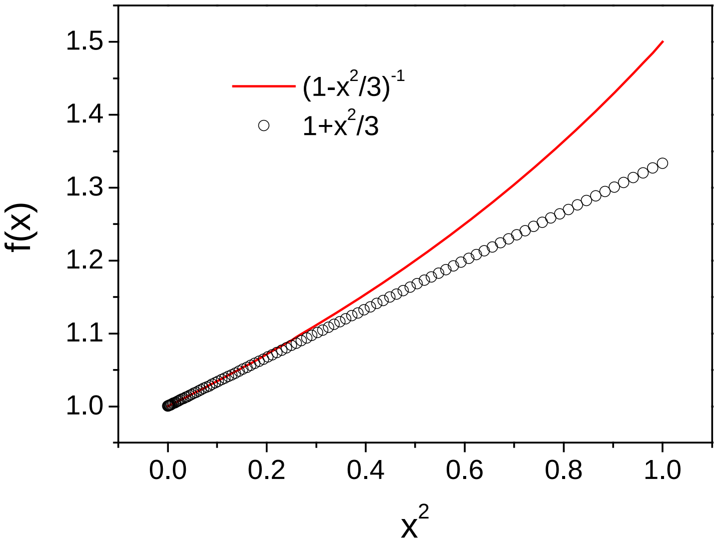

Figure 2.5: Comparison of $1/(1-x^2/3)$ with the approximation $1+x^2/3$. Note that the approximation deviates from the exact expression at $x^2 > 0.1$

mass determined by SLS is the mass average M_W and the radius of gyration is the z–average. For a thorough treatment of polydispersity effects the reader is referred to the book by J. Dhont. Before we start the detailed discussion please note that in light scattering almost all the time so–called cgs–units, i. e. centimeter, gram, seconds, are used instead of SI–units. That is the scattering vector is expressed in units of cm^{-1},the molar mass has the unit g/mol, the ragdius of gyration is expressed in nm and the virial coefficient has the unit $cm^3/(gmol)$.

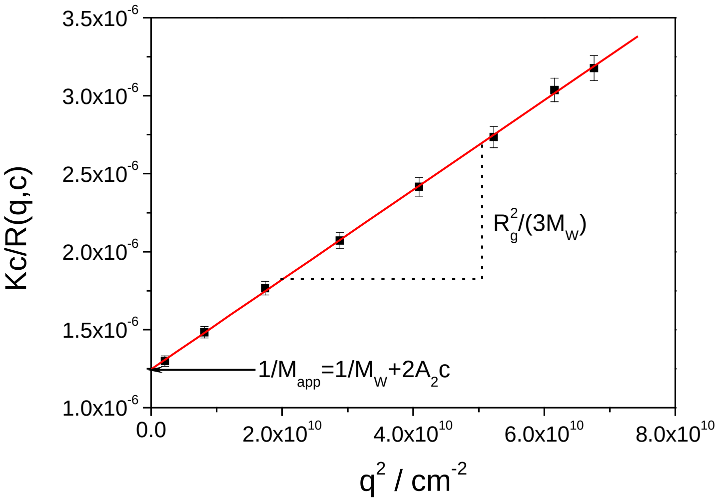

Figure 2.6: Scattering data from a hypothetic particle solution with molar mass $M_W = 9.5 \times 10^5$ g/mol, radius of gyration $R_g = 95$ nm and osmotic virial coefficient $A_2 = 10^{-4}$ cm^3/(g mol). The data were 'recorded' at a concentration of $c = 10^{-3}$ g/mL as a function of the scattering vector

Typically SLS measurements are performed on a dilution series of at minimum four concentrations. The q–dependence of the scattered intensity is detected for each solution and converted into values of $Kc/\mathcal{R}(q,c)$ at fixed c. These are plotted and approximated with a linear least squares fit, as is sketched in Fig. 2.6 . The linear extrapolation yields the so–called apparent molar mass M_{app} as the intercept

$$\begin{aligned} \frac{Kc}{\mathcal{R}(q=0,c)} &= \frac{1}{M_W}+2A_2c \\ &\equiv \frac{1}{M_{app}} \end{aligned} \tag{2.53}$$

and the slope is

$$slope = \frac{R_g^2}{3M_W}. \tag{2.54}$$

In a second step the obtained values of $1/M_{app}$ are plotted vs. concentration and again extrapolated linearly. According to eq. 2.53 this will yield $1/M_W$ as the intercept and $2A_2$ as the slope. Knowing the molar mass, it is also possible to calculate the radius of gyration according to eq. 2.54

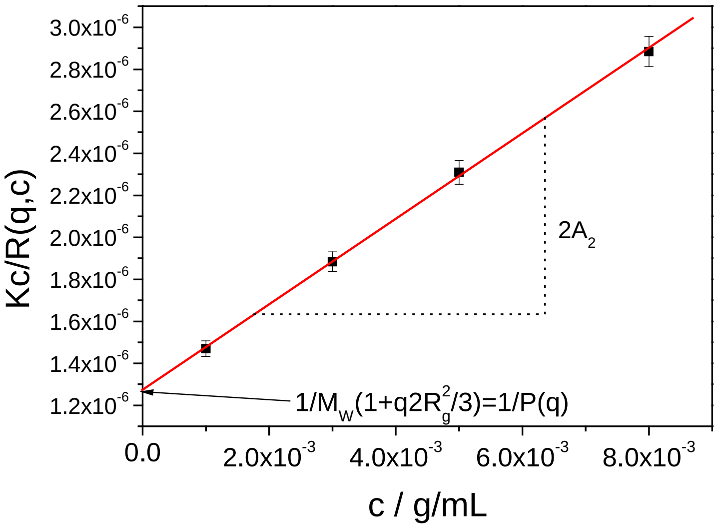

Figure 2.7: Scattering data from a hypothetic particle solution with molar mass $M_W = 9.5 \times 10^5$ g/mol, radius of gyration $R_g = 95$ nm and osmotic virial coefficient $A_2 = 10^{-4}$ cm^3/(g mol). The data were 'recorded' at a constant angle, i. e. scattering vector, as a function of the solute concentration.

Instead of first extrapolating the angular dependence at fixed c and subsequently extrapolating the zero–q results, the order of extrapolations can be inverted as well. The data obtained at a given scattering vector are than plotted versus concentration as shown in Fig. 2.7 and extrapolated linearly. This gives

$$\begin{aligned} \frac{Kc}{\mathcal{R}(q, c=0)} &= \frac{1}{M_W}\left(1+\frac{q^2R_g^2}{3}\right) \\ &\approx \frac{1}{P(q)} \end{aligned} \tag{2.55}$$

as the intercept and the slope is $2A_2$. In the second step the obtained values for $P(q)$ are plotted versus q^2 and extrapolated linearly to give again $1/M_W$ as the intercept while the slope is again given by eq. 2.54.

This procedure is rather tedious, but B. Zimm has suggested an elegant method to do all the necessary extrapolations in one graph, which is usually referred to as the *Zimm–plot*.

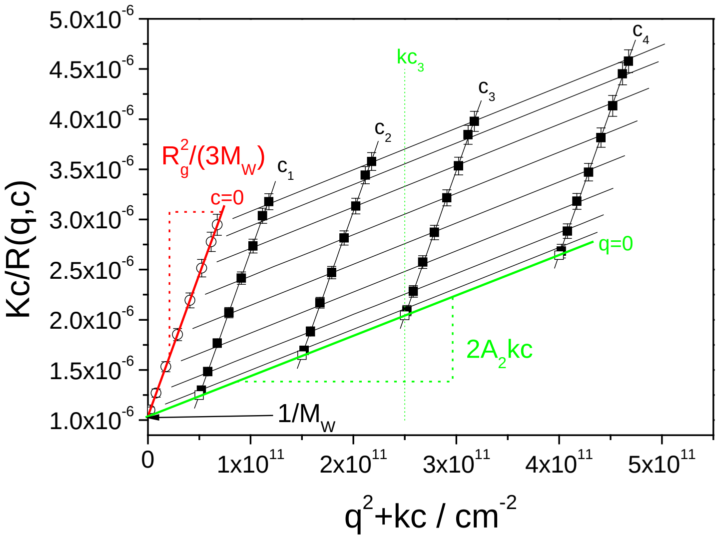

Figure 2.8: Zimm-plot of the scattering data from a hypothetic particle solution with molar mass $M_r = 9.5 \times 10^5$ g/mol, radius of gyration $R_g = 95$ nm and osmotic virial coefficient $A_2 = 10^{-4}$ cm^3/(g mol).

In this representation the data are plotted on an expanded x–axis which is $q^2 + kc$. The parameter k has no physical meaning and is chosen arbitrarily in order to get a convenient spacing between sets of data which belong to samples of different concentration. As to be seen from Fig. 2.8 , data points fall on an oblique grid. In the present case we have chosen k such that data at variable q and constant concentration lie at the lines with larger slope, while the data at variable c and constant q lie on the lines with smaller slopes. Now linear extrapolations can be performed both at constant concentration and at constant scattering vector. However there are some important details to be taken into account.

The data at variable scattering vector and constant c are NOT extrapolated to zero, but to $q^2 = 0$, which is a vertical line at kc. This sketched as an example for the concentration c_3 where the green dotted line corresponds to $q^2 = 0$. Accordingly the intercept of the angular dependence with this line is $1/M_{app}(c_3)$. The open squares in Fig. 2.8 are obtained in an analogue manner for the other concentrations. The slopes of these extrapolations is again related to the radius of gyration by eq. 2.54.

The data at variable concentration and constant q are also NOT extrapolated to zero, but to $c = 0$, which for every q is a vertical line at q^2. The intercept of the concentration dependence with this line is $1/P(q)$. The open circles in Fig. 2.8 were obtained in this manner. This is a very important feature since it is possible to get the complete angular dependence of the particle scattering factor by this procedure. We have now two new set of data, that is $1/M_{app}$ vs kc and $P(q)$ vs. q^2, which both can be again linearly extrapolated finally to zero. The slope of the former is $2A_2k$ and the slope of the latter is again given by eq. 2.54. Both regression lines should intersect the ordinate at $1/M_W$.

In many real cases however, $1/M_{app}$ vs kc and/or $1/P(q)$ vs. q^2 are not simple linear dependencies. In this cases the initial slopes for $c \to 0$ and $q^2 \to 0$ respectively have to be taken to determine A_2 and R_g.

We shall now discuss the limitations of determining particle parameters by SLS. We have already seen in chapter 2.1 that the Rayleigh–Gans–Debye scattering is only valid for particles which are significantly smaller than the wave length of the applied radiation source. As we have further seen, the approximation $P^{-1}(q) \approx 1 + q^2R_g^2/3$ holds only if $q^2R_g^2 < 0.3$. On the other hand the particles have to be large enough to produce a significant deviation of $P(q)$ from unity over the accessible range of scattering vectors. It is common understanding that a deviation from unity of five percent can be reliably detected. Thus

$$\begin{aligned} \frac{q^2R_g^2}{3} &> 0.05 \qquad (2.56)\\ R_g &> \frac{\sqrt{0.15}}{4\pi\sin(\theta/2)}\lambda \\ R_g &> 0.025\lambda, \end{aligned}$$

i. e. in a light scattering experiment, where the scattering angle is typically limited to 150 degree, the particles' radius of gyration should be larger than $\lambda/40$ to be detectable. Note that in most older monographs state a minimum value of $\lambda/20$.

2.3.2 Particle scattering factors

As we have seen in the preceding section, it is possible to determine the particle scattering factor from SLS experiments if the angular dependence of the scattered intensity is extrapolated to infinite dilution in a Zimm–plot. The most complete list of particle scattering factors is given by J. S. Pedersen *Adv. Coll. Interf. Sci.* **1997**, *70*, 171. Here we shall only discuss the properties of the three mostly used particle scattering factors, namely for a sphere, a random coil and a rigid infinitely thin rod.

$$P_{sphere}(q) = \left\{3\frac{\sin(qR) - qR\cos(qR)}{(qR)^3}\right\}^2 \qquad (2.57)$$

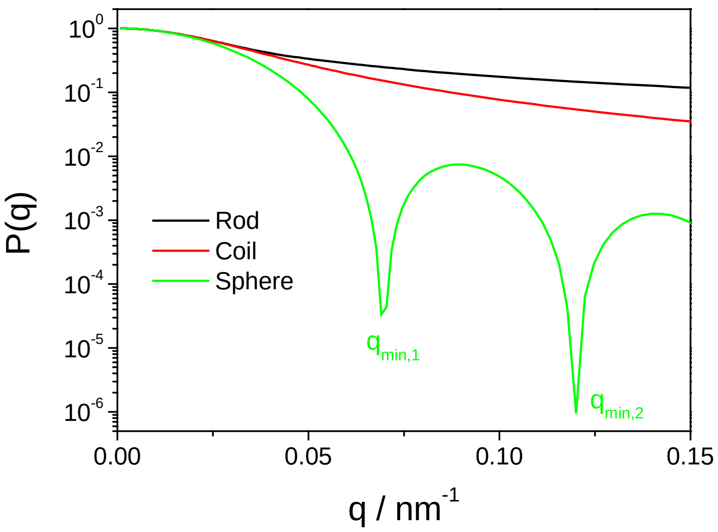

Figure 2.9: Particle scattering factors of a rod, a random polymer coil and a sphere with $R_g = 50$ nm.

where R is the sphere radius, which is related to the radius of gyration by $R_g = \sqrt{3/5}R$.

$$P_{coil}(q) = \frac{2}{u^2}\left(\exp\{-u\} + u - 1\right) \tag{2.58}$$

with $u = (qR_g)^2$.

$$P_{rod}(q) = \frac{2}{qL}\int_0^{qL}\frac{\sin s}{s}ds - 4\left(\frac{\sin(qL/2)}{qL}\right)^2 \tag{2.59}$$

where L is the rod length, which is related to the rod's radius of gyration by $R_g = \sqrt{L^2/12}$. Examples of these form factors for particles with $R_g = 50$ nm are displayed in Fig. 2.9 . Usually the experimental data are evaluated quantitatively by linear least squares fitting to an appropriate model form factor. Where the most difficult task is the proper choice of the model function. However, there is a large amount of information, which can be deduced very easily from the experimental form factors, without any sophisticated data fitting. The form factor of the rod decays slower than that of a coil with the same R_g, and the form factor of a sphere decays even faster than that of a coil. The latter has very characteristic pronounced minima, which are actually real zero, as can be seen from eq: 2.57. This zero positions can numerically be found to be $q_{min,1} = 4.49/R$ and $q_{min,2} = 7.73/R$ ... In other words, the radius of the sphere can be determined rather exactly from the position of the minima in the $P(q)$ vs $q-$ curve. Note that the radius of the sphere and the scattering vector at which the minimum occurs are related inversely. This is an important general feature of scattering experiments: *small distances will show up at large scattering vectors and vice versa.*

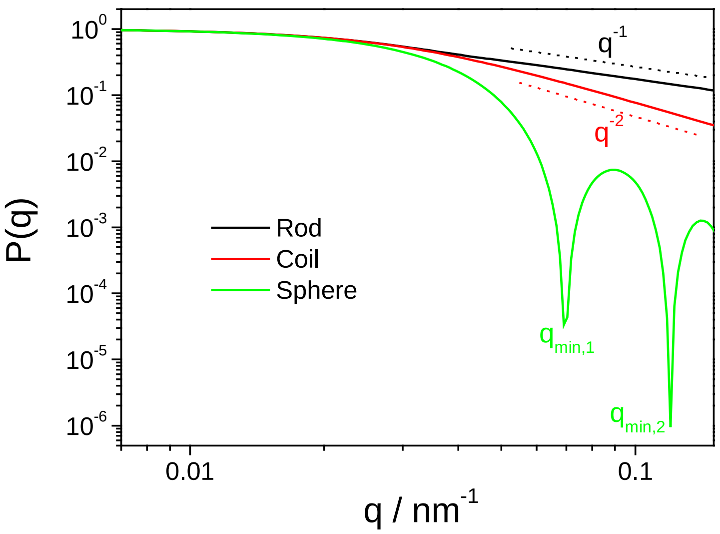

Figure 2.10: Particle scattering factors of a rod, a random polymer coil and a sphere with $R_g = 50$ nm.

Further information can be obtained if the data are plotted differently. In a log–log representation as depicted in Fig. 2.10 , the form factor of a rod has a final slope of -1, while that of a coil has a final slope of -2. Both values are highly characteristic for the respective shape of the scatterers as can be seen from eq. 2.59 and 2.58 respectively. In the high q–limit the form factor of a rod approaches

$$\lim_{q\to\infty} P_{rod} = \frac{\pi}{qL} \tag{2.60}$$

because the integral in eq. 2.59 approaches $\pi/2$ if q tends to infinity.

The high q–limit of the form factor of a coil is

$$\lim_{q\to\infty} P_{coil} = \frac{2}{q^2 R_g^2} \tag{2.61}$$

Eqs. 2.60 and 2.61 cause the observed values of the final slopes in the log–log representation of the form factor.

Further it is evident from eq. 2.60 that the length of a rod L can be determined from the high q–behavior of the form factor. If the particle scattering factor is plotted in a so–called Cassasa–Holtzer plot as $qP(q)$ vs q the curve will level off to a plateau at sufficiently high q, as is shown in Fig. 2.11 . The hight of this plateau is π/L.

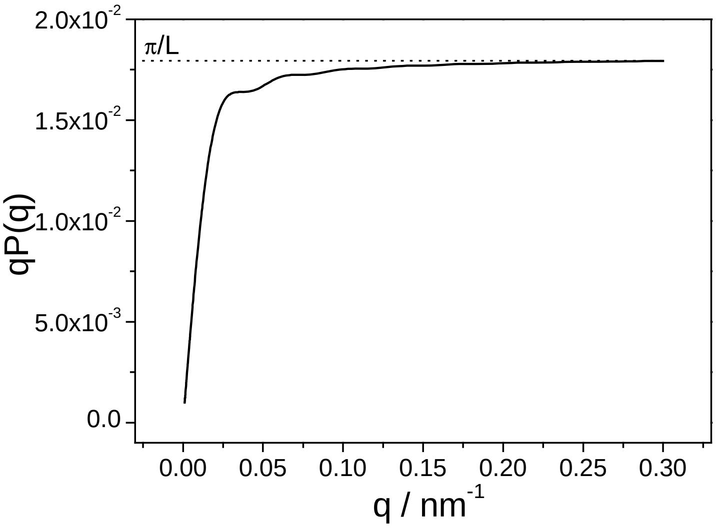

Figure 2.11: Cassasa–Holtzr plot of the particle scattering factor of a rod with $R_g = 50$ nm, corresponding to a length of $L = 173$ nm.

3 Dynamic Light Scattering

3.1 The effect of particle motion

Up to now we have treated our particle solution as if the particles were fixed in space, which is obviously not the case, but which is justified, if we measure the time average of the scattered intensity. In this case we measure besides the particle scattering factor, the time average of the structure factor which is determined by the average relative positions of particles with respect to each other.

This consideration does not hold anymore, if we measure the scattered intensity with a time resolution of milliseconds or even tenths of nanosecond, which is possible with modern instrumentation. In chapter 2.1 we have seen that the fields scattered from two particles in general have a phase shift due to the different paths the waves have to travel. Lets consider the field scattered from the green and the red particle in Fig. 3.1 . At $t = 0$ (top part) the two particles shall be located such that their separation vector is perpendicular to $\mathbf{k}_I$. In this case the scattered fields will have no phase shift. At some time $t > 0$ the red (and the green) particle shall have moved to a new position. Therefore the path difference of the two waves is now $\overline{AB} - \overline{CD}$, which causes a finite phase shift. The superposition of the two waves will now result in a total field strength which is smaller than at $t = 0$. The random movement of all particles in solution will thus cause a fluctuation of the scattered intensity as is sketched in Fig. 3.2.

3.2 Time–auto correlation functions (TACF)

The simplest method to analyze such fluctuations is tu use the time auto–correlation functions of the fluctuating quantity. For the scattered intensity this is defined as

$$g_I(q,t) \propto \langle I_S(q,0) I_S(q,t) \rangle \tag{3.1}$$

where the pointed brackets refer to an ensemble average an $I(q,0)$ is the observed scattered intensity at a given scattering vector and at time $t = 0$, while $I(q,t)$ is the scattered intensity at an later stage $t > 0$. At this point, it is important to note that, for ergodic systems, the correlation function will not depend on the state of the system at the starting time of the experiment. In other words, the time $t = 0$ can be chosen arbitrarily. This allows for a very efficient way to construct $g_I(q,t)$ experimentally, just by calculating the following sums at different times

$$g_I(q, 0 \times \Delta t) \;=\; \frac{1}{M+1} \sum_{n=0}^{M} \langle I(q, n \times \Delta t) I(q, n \times \Delta t) \rangle \tag{3.2}$$

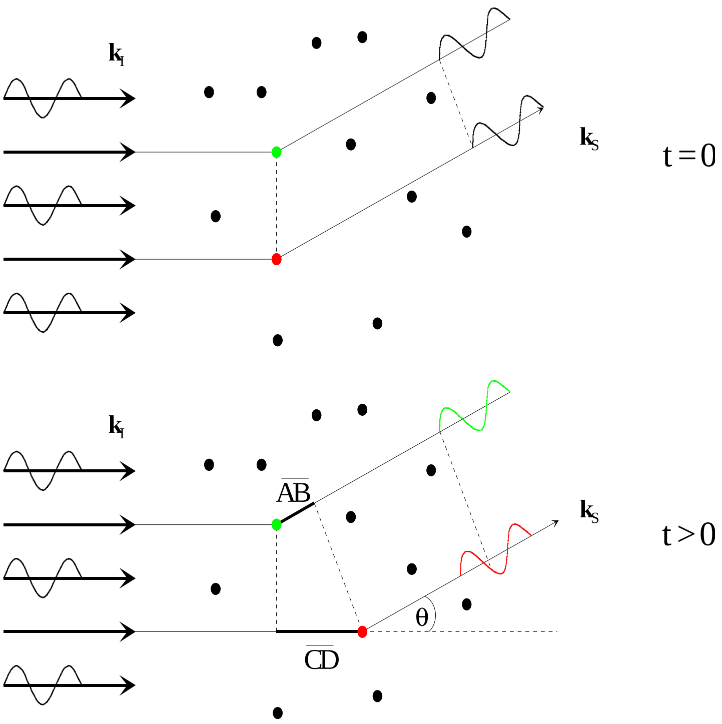

Figure 3.1: Variation of the phase shift of the fields scattered from two particles in dependence of the relative particle position.

$$
\begin{aligned}
g_I(q, 1\times\Delta t) &= \frac{1}{M+1}\sum_{n=0}^{M}\langle I(q, n\times\Delta t) I(q, (n+1)\times\Delta t)\rangle \\
g_I(q, 2\times\Delta t) &= \frac{1}{M+1}\sum_{n=0}^{M}\langle I(q, n\times\Delta t) I(q, (n+2)\times\Delta t)\rangle \\
g_I(q, 3\times\Delta t) &= \frac{1}{M+1}\sum_{n=0}^{M}\langle I(q, n\times\Delta t) I(q, (n+3)\times\Delta t)\rangle \\
&\vdots \\
g_I(q, M\times\Delta t) &= \frac{1}{M+1}\sum_{n=0}^{M}\langle I(q, n\times\Delta t) I(q, (n+M)\times\Delta t)\rangle
\end{aligned}
$$

where we have dropped the subscript S for convenience. Time is expressed in multi folds of Δt and $M\times\Delta t$ is some maximum time, which has to be significantly smaller than the total length of the intensity trace. According to eq. 3.2 the first value of the correlation function would be a summ of squared intensity values, which could become a very large number leading to numerical overflows in the case of a long time experiment. Therefore, a normalized time auto correlation function $\hat{g}_I(q,t) = g_I(q,t)/ < I >^2$ is calculated, where $< I >$ is the time-average of the scattered intensity, i. e. the static scattering intensity. To extract information on the dynamics of the scattering particles we have to calculate the $\hat{g}_I(q,t)$ explicitly. For this purpose, we first calculate the time auto

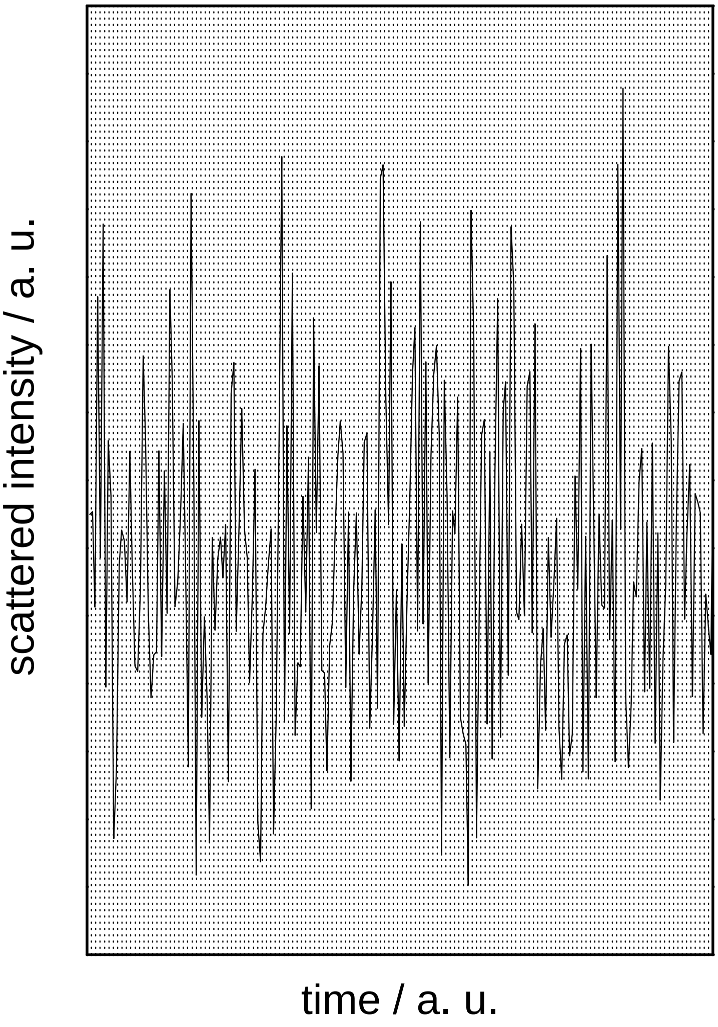

Figure 3.2: Intensity fluctuations caused by random particle motion.The verticals lines indicate time intervals of width Δt.

correlation function of the scattered field, which we will relate to the intensity TACF in a second step. The scattered field from an ensemble of particles can be written as

$$\mathbf{E}_S \propto \sum_{i=1}^{N} B(q) \exp\{\imath \mathbf{q}\mathbf{r}_i\} \tag{3.3}$$

where the proportionality constant contains the scattering power of the particles and the particle scattering amplitude is related to the form factor by $P(q) = |B(q)|^2$. If we define the time auto correlation function of the scattered field in the same way as that of the scattered intensity, i. e.

$$g_E(q,t) \propto \langle E_S(q,0) E_S^*(q,t) \rangle \tag{3.4}$$

where the asterisk refers to the complex conjugate, the normalized field TACF is

$$\hat{g}_E(q,t) = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\left\langle \exp\{\imath \mathbf{q}\mathbf{r}_i(0)\}\exp\left\{-\imath \mathbf{q}\mathbf{r}_j(t)\right\}\right\rangle \tag{3.5}$$

Here we made use of the fact that $S(q)N \propto \langle I(q)\rangle \propto \langle E_S(q,0)E_S^*(q,0)\rangle$ with $S(q) = 1$ for dilute suspensions and that the form amplitude as well as all proportionality constants cancel by normalization, if all particles are identical. The term on the r. h. s of eq. 3.5 is often referred to as the dynamic structure factor.

For the simple case of non–interacting particles $r_i(0)$ and $r_j(t)$ are statistically independent and the average over the product in eq. 3.5 may be replaced by the product of the averages $\langle \exp\{\imath \mathbf{q}\mathbf{r}_i(0)\}\rangle \left\langle \exp\left\{-\imath \mathbf{q}\mathbf{r}_j(t)\right\}\right\rangle$, which are both of the form $\int d\mathbf{r}P(\mathbf{r})\exp\{\imath \mathbf{q}\mathbf{r}\}$ in their integral representation. For dilute suspensions of particles the probability density $P(\mathbf{r})$ of finding a particle at position $\mathbf{r}$ is $P(\mathbf{r}) = 1/V$, where V is the system volume. It can be shown that these integrals tend to zero vor infinitely large V except for $q = 0$. We will not provide a rigorous proof for this statement but rather show graphically for the one dimensional case, that this is true. Consider the integral

$$f(q_x) = \int_{-L}^{L} dx \exp\{\imath q_x x\}. \tag{3.6}$$

the solution of which is

$$f(q_x) = \frac{\exp\{\imath q_x x\}}{\imath q_x} \Big|_{-L}^{L} = \frac{x\imath \sin q_x x}{\imath q_x x} \Big|_{-L}^{L} = 2L\frac{\sin q_x L}{q_x L} \tag{3.7}$$

It is evident that $f(q_x)$ has it's first zero at $q_x = \pi/L$ and the maximum value is $2L$ at $q_x = 0$. Consequently for infinite L, $f(q_x)$ becomes infinitely narrow and infinitely high at $q_x = 0$. Therefore we may safely assume that

$$\lim_{L\to\infty} f(q_x) = \int_{-\infty}^{\infty} dx \exp\{\imath q_x x\} \propto \delta(q_x), \tag{3.8}$$

which is zero everywhere except for $q_x = 0$ and therefore also $\langle \exp\{\imath \mathbf{q}\mathbf{r}_i(0)\}\rangle = 0$ for $q \neq 0$ q. e. d. In other word all terms with $i \neq j$ vanish in the average of eq. 3.5, and we remain with

$$\begin{aligned}\hat{g}_E(q,t) &= \frac{1}{N}\sum_{i=1}^{N}\langle \exp\{\imath \mathbf{q}\mathbf{r}_i(0)\}\exp\{-\imath \mathbf{q}\mathbf{r}_i(t)\}\rangle \\ &= \langle \exp\{\imath \mathbf{q}\mathbf{r}_0\}\exp\{-\imath \mathbf{q}\mathbf{r}_t\}\rangle \\ &= \int dr_0 \int dr_t \exp\{\imath \mathbf{q}(\mathbf{r}_0 - \mathbf{r}_t)P(\mathbf{r}_0, \mathbf{r}_t, t)\}.\end{aligned} \tag{3.9}$$

For convenience we have replaced the symbols $\mathbf{r}(0)$ by $\mathbf{r}_0$ and $\mathbf{r}(t)$ by $\mathbf{r}_t$.

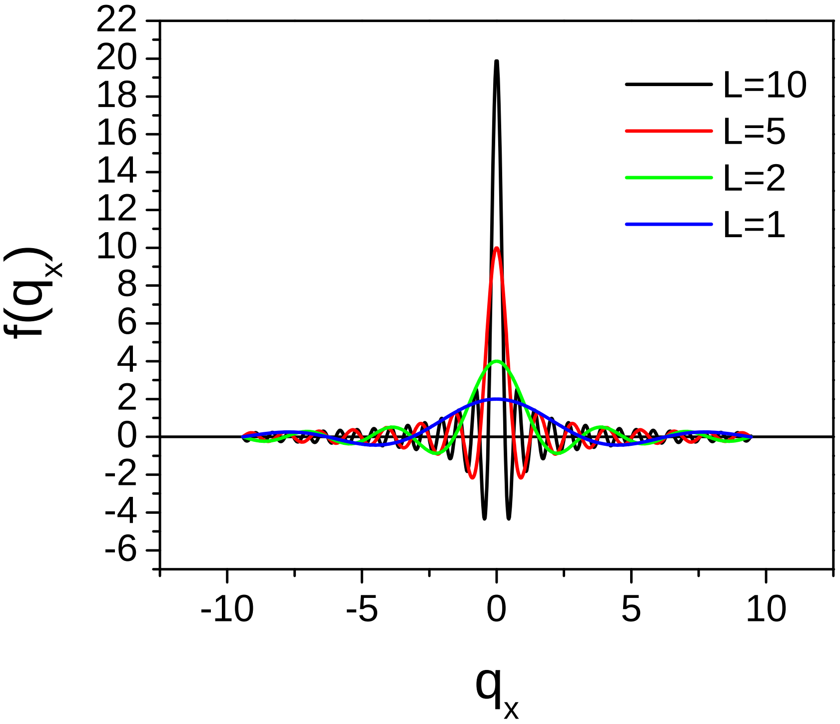

Figure 3.3: Approximation of a δ–distribution by a $\sin x/x$–function with $x = q_x L$

3.3 Brownian motion and the field TACF

To solve thew final integral in eq. 3.9 we use some properties of probability density functions (termed pdf hereafter) and and the Smoluchowsky–equation of motion for freely diffusing Brownian particles. To understand the properties of pdfs we have first to clarify what an ensemble is. Imagine a large number of systems consisting of colloidal particles suspended in a solvent, which are macroscopically identical in terms of there thermodynamic variables. However, the local arrangement of particles will be different in each system. Such a collection of systems is called an ensemble. Now the probability density function $P(\mathbf{r}_t)$ of $\mathbf{r}_t$ is defined by

$$\begin{aligned} P(\mathbf{r}_t)d\mathbf{r} \quad &= \quad \text{the probability that there are particles} \\ &\quad\ \text{in the volume element } d\mathbf{r} \text{ around the position defined by } \mathbf{r}_t \end{aligned}$$

This pdf is normalized such that $\int d\mathbf{r}_t P(\mathbf{r}_t) = 1$, wich leads immediately to $P(\mathbf{r}_t) = 1/V$ for dilute suspensions of noninteracting particles, where V is the system volume. An intuitive understanding of the pdf–concept can be gained by supposing to take a snapshot of the ensemble at two times $t = 0$ and $t > 0$. The probability $P(\mathbf{r}_0)d\mathbf{r}$ is given by the number of systems which show a particle in the volume $d\mathbf{r}$ (let's call these positive) divided by the total number of systems (see figure 3.3. The probability $P(\mathbf{r}_t)d\mathbf{r}$ can be visualized accordingly. To calculate the integrals in eq. 3.9 we use the pdf $P(\mathbf{r}_0, \mathbf{r}_t, t)$ which is defined by the probability that there are particles in $d\mathbf{r}$ around $\mathbf{r}_0$ at $t = 0$ *and* in

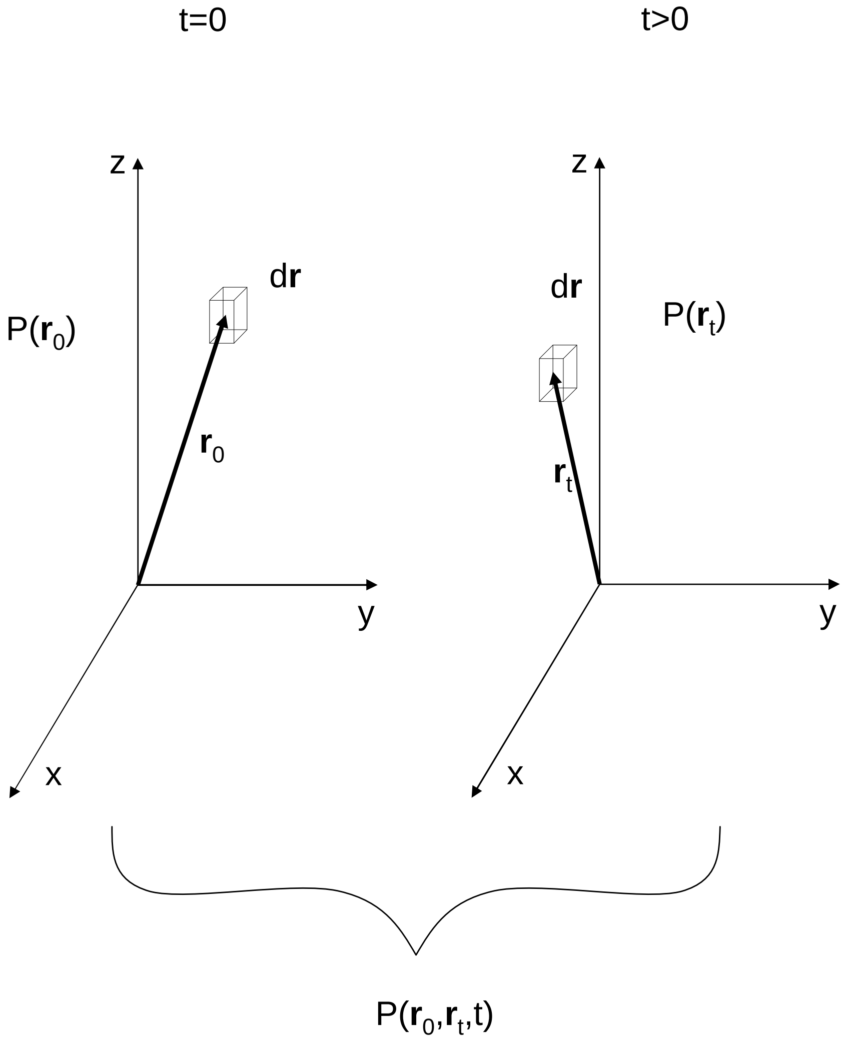

Figure 3.4: Illustration of probability density functions.

$d\mathbf{r}$ around $\mathbf{r}_t$ at a later time $t > 0$, i. e. $P(\mathbf{r}_0, \mathbf{r}_t, t)\, d\mathbf{r}_0 d\mathbf{r}$. In terms of the snapshot model this is the number of positive systems on the picture taken at $t = 0$ plus the number of positive systems on the photograph taken at $t > 0$ divided by the total number of systems.

The property of this pdf, which we are going to exploit, is that it can be related to $P(\mathbf{r}_0)$ by $P(\mathbf{r}_0, \mathbf{r}_t, t) = P(\mathbf{r}_0) P_c(\mathbf{r}_t, t|\mathbf{r}_0, 0)$ where the conditional pdf $P_c(\mathbf{r}_t, t|\mathbf{r}_0, 0)$ is defined by

$$\begin{aligned} P_c(\mathbf{r}_t, t|\mathbf{r}_0, 0) d\mathbf{r}_t \quad = \quad & \text{the probability that there are particles} \\ & \text{in the volume element } d\mathbf{r} \text{ around the position defined by } \mathbf{r}_t \text{ at time } t \\ & \text{provided that at } t = 0, \text{ there was a particle at } \mathbf{r}_0. \end{aligned}$$

The conditional pdf can formally be determined from the Smoluchowsky equation of motion

$$\frac{\partial P_c(\mathbf{r}_t, t|\mathbf{r}_0, 0)}{\partial t} = \hat{\mathcal{L}} P_c(\mathbf{r}_t, t|\mathbf{r}_0, 0) \tag{3.10}$$

where the operator working on the pdf $\hat{\mathcal{L}} = D_0 \nabla^2$ for a dilute suspension of non–interacting spherical particles with D_0 their Einstein diffusion coefficient. Under the initial condition that at time $t = 0$ $P_c(\mathbf{r}_t, t|\mathbf{r}_0, 0) = \delta(\mathbf{r}_t - \mathbf{r}_0)$ the differential eq. 3.10 has the formal solution

$$P_c(\mathbf{r}_t, t|\mathbf{r}_0, 0) = \exp\left\{\hat{\mathcal{L}} t\right\} \delta(\mathbf{r}_t - \mathbf{r}_0), \tag{3.11}$$

with which we can rewrite the integral of eq. 3.9 as

$$\begin{aligned} \hat{g}_E &= \int d\mathbf{r}_0 \exp\{\imath \mathbf{q}\mathbf{r}_0\} P(\mathbf{r}_0) \int d\mathbf{r}_t \exp\left\{\hat{\mathcal{L}} t\right\} \delta(\mathbf{r}_t - \mathbf{r}_0) \exp\{-\imath \mathbf{q}\mathbf{r}_t\} \qquad (3.12) \\ &= \int d\mathbf{r}_t \exp\left\{\hat{\mathcal{L}} t\right\} \exp\{-\imath \mathbf{q}\mathbf{r}_t\} \int d\mathbf{r}_0 \exp\{\imath \mathbf{q}\mathbf{r}_0\} P(\mathbf{r}_0) \delta(\mathbf{r}_t - \mathbf{r}_0) \\ &= \frac{1}{V} \int d\mathbf{r}_t \exp\{\imath \mathbf{q}\mathbf{r}_t\} \exp\left\{\hat{\mathcal{L}} t\right\} \exp\{-\imath \mathbf{q}\mathbf{r}_t\}. \end{aligned}$$

Here we used that $P(\mathbf{r}) = 1/V$ for dilute solutions and the definition of the δ–distribution $\int dx' f(x') \delta(x - x') = f(x)$. For convenience, we will drop the subscript $_t$ further on. To solve the remaining integral we replace the exponential operator by it's Taylor–expansion

$$\exp\left\{\hat{\mathcal{L}} t\right\} = \sum_{n=0}^{\infty} \frac{1}{n!} t^n \hat{\mathcal{L}}^n \tag{3.13}$$

where $\hat{\mathcal{L}}^n$ means the n-fold application of $\hat{\mathcal{L}}$, which gives

$$\hat{\mathcal{L}}^n \exp\{-\imath \mathbf{q}\mathbf{r}\} = -\left(D_0 q^2\right)^n \exp\{-\imath \mathbf{q}\mathbf{r}\}. \tag{3.14}$$

Reintroducing this result into the Taylor-Expansion results

$$\exp\left\{\hat{\mathcal{L}} t\right\} \exp\{-\imath \mathbf{q}\mathbf{r}\} = \exp\left\{-D_0 q^2 t\right\} \exp\{-i \mathbf{q}\mathbf{r}\} \tag{3.15}$$

and the field TACF attains it's final form

$$\begin{aligned} \hat{g}_E &= \frac{\exp\{-D_0 q^2 t\}}{V} \int d\mathbf{r} \qquad (3.16) \\ &= \exp\left\{-D_0 q^2 t\right\}. \end{aligned}$$

3.4 The Siegert–relation

In the previous section we derived an expression for the scattered field TACF from a dilute suspension of noninteracting identical spheres. This has now to be related to scattered intensity TACF which was introduced in section 3.2. In terms of the scattered field, $g_I(q,t)$ is an average of the product of four Gaussian variables

$$g_I(q,t) \propto \langle E_S(q,0)E_S^*(q,0)E_S(q,t)E_S^*(q,t)\rangle \, , \tag{3.17}$$

which according to Wick's theorem can be written in terms of averages of products of only two variable, i. e.

$$\begin{aligned} \langle E_S(q,0)E_S^*(q,0)E_S(q,t)E_S^*(q,t)\rangle &= \langle E_S(q,0)E_S^*(q,0)\rangle \langle E_S(q,t)E_S^*(q,t)\rangle \\ &+ \langle E_S(q,0)E_S(q,t)\rangle \langle E_S^*(q,0)E_S^*(q,t)\rangle \\ &+ \langle E_S(q,0)E_S^*(q,t)\rangle \langle E_S^*(q,0)E_S(q,t)\rangle \, . \end{aligned} \tag{3.18}$$

The first term of the r.h.s of eq. 3.18 is the square of the averaged scattered intensity $\langle I(q)\rangle^2$, while the third term is the absolute square of the field TACF as defined by eq. 3.4. The second term is the product of two averages of the form

$$\begin{aligned} \langle \exp\{\imath\mathbf{q}(\mathbf{r}_0+\mathbf{r}_t)\}\rangle &= \int d\mathbf{r}_0 \int d\mathbf{r}_t P(\mathbf{r}_0)P_c(\mathbf{r}_t,t|\mathbf{r}_0,0)\exp\{\imath\mathbf{q}(\mathbf{r}_0+\mathbf{r}_t)\} \\ &= \int d\mathbf{r}_0 \int d\mathbf{r}_t P(\mathbf{r}_0)P(\mathbf{r}_0-\mathbf{r}_t,t)\exp\{\imath\mathbf{q}(\mathbf{r}_0+\mathbf{r}_t)\} \end{aligned} \tag{3.19}$$

where we realized that the conditional pdf is only a function of the difference coordinate $\mathbf{r}_0 - \mathbf{r}_t$ for the case under consideration and thus $P_c(\mathbf{r}_t,t|\mathbf{r}_0,0) \equiv P(\mathbf{r}_0-\mathbf{r}_t,t)$. If we apply a coordinate transformation $(\mathbf{r}_0,\mathbf{r}_t) \rightarrow (\mathbf{r}_0+\mathbf{r}_t,\mathbf{r}_0-\mathbf{r}_t)$ which gives a Jacobian of 1/8 we can separated integration variables as

$$\langle \exp\{\imath\mathbf{q}(\mathbf{r}_0+\mathbf{r}_t)\}\rangle = \frac{1}{8}\frac{1}{V}\int d(\mathbf{r}_0+\mathbf{r}_t)\exp\{\imath\mathbf{q}(\mathbf{r}_0+\mathbf{r}_t)\}\int d(\mathbf{r}_0-\mathbf{r}_t)P(\mathbf{r}_0-\mathbf{r}_t,t). \tag{3.20}$$

The second integral is well behaved because the pdf is a normalized function, and the first integral is $\delta(q)$ for infinitely large scattering volumes which is zero everywhere except for $q = 0$ (see the arguments following eq. 3.6). Consequently we can establish a simple relation between the scattered field TACF and the scattered intensity TACF

$$g_I(q,t) = \langle I(q)\rangle^2 + |g_E(q,t)|^2 \, , \tag{3.21}$$

which is usually referred to as the Siegert–relation. In terms of the normalized TACFs this can be expressed as

$$\hat{g}_I(q,t) = 1 + |\hat{g}_E(q,t)|^2 \, , \tag{3.22}$$

According to the definition of the normalized field TACF it will approach unity at very short times (see eq. 3.5). At very large times the average of products

$$\left\langle \exp\{\imath\mathbf{q}\mathbf{r}_i(0)\}\exp\left\{-\imath\mathbf{q}\mathbf{r}_j(t)\right\}\right\rangle \;\rightarrow\; \langle \exp\{\imath\mathbf{q}\mathbf{r}_i(0)\}\rangle \left\langle \exp\left\{-\imath\mathbf{q}\mathbf{r}_j(t)\right\}\right\rangle$$

because the position of particles will be statistically independent at large times. The two averages on the r. h. s. are zero for $q \neq 0$. Thus we find that the normalized field TACF will start at unity and drop to zero with increasing time, while the normalized intensity TACF starts at two and decays to one with increasing time.

3.5 Diffusion coefficient and hydrodynamic radius

In a dynamic light scattering experiment we measure the intensity TACF and for simple case of a dilute suspension of non–interacting identical particles we observe a single exponential, the decay time of which is related to the Einstein–Diffusion coefficient of the particles according to eqs 3.16 and 3.22

$$\begin{aligned} g_I(g,t) &= \exp\{-t/\tau\} \\ &= \exp\left\{-2D_0q^2t\right\}. \end{aligned} \tag{3.23}$$

From the diffusion coefficient the so–called hydrodynamic radius, R_H, of the solute particles can be calculated using the Stokes–Einstein equation

$$R_H = \frac{k_BT}{6\pi\eta_0 D}. \tag{3.24}$$

Here k_B is the Boltzmann constant and η_0 is the viscosity of the solvent. In the cgs–system the diffusion coefficient has the unit cm^2/s. Consequently, $k_B = 1.38 \times 10^{-16}$ $\mathrm{cm}^2\mathrm{g}/(\mathrm{s}^2\mathrm{K})$ is often used to obtain the hydrodynamic radius in cm–units. We have to emphasize that R_H is a hypothetical radius and can be related to the geometric particle size only in the case of spherical bodies. However, according to eq. 3.23 particles with large diffusion coefficients cause correlation functions with small decay times. In combination with eq. 3.24, it follows that particles with large R_H cause slowly decaying TCFs.

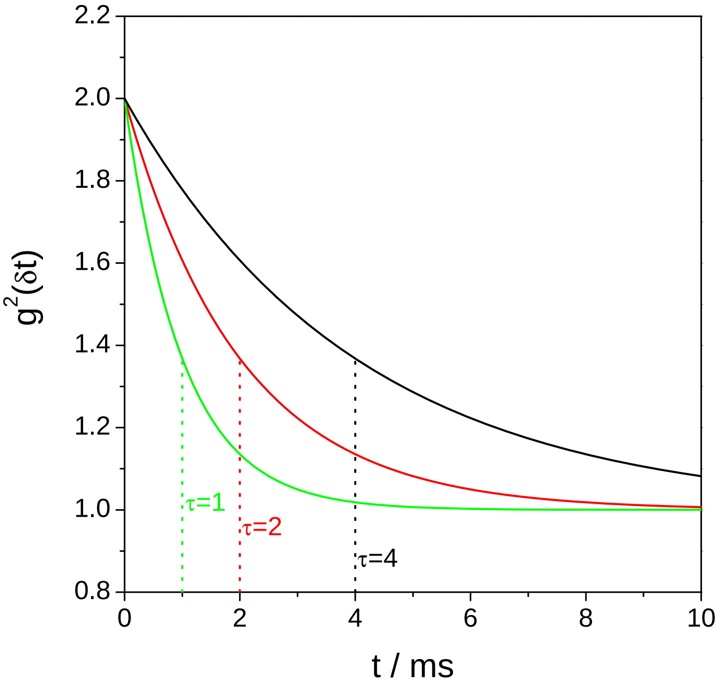

Figure 3.5: Intensity time auto correlation functions with different decay times.

3.6 Depolarized dynamic light scattering

If particles are anisotropic their random orientational motion will, like translation, contribute to the fluctuation of the scattered intensity. In the case of non–spherical particles, this effect can be due to their geometrical anisotropy and/or to an anisotropy of their dielectric properties. For spherical particles, evidently only optical anisotropy will contribute. This is the case we will discuss in the following. If a birefringent sphere is exposed to an oscillating incident electric field $\mathbf{E}_i$ the induced dipole μ will depend on the orientation of the sphere, characterized by the unit vector $\hat{\mathbf{u}}$ which points in the direction of the optical main axis of the particle. The dielectric constant along this direction ic called ε_p, while ε_n is the dielectric constant in the direction normal to $\hat{\mathbf{u}}$ (see Fig. 3.6). The induced dipole is proportional to the incident field strength where the proportionality constant is the dielectric tensor which depends on the particle orientation

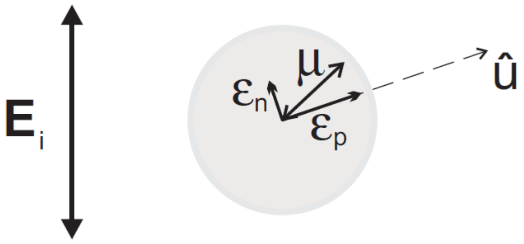

Figure 3.6: An optically anisotropic sphere in an oscillating electric field.

$$\begin{aligned} \mu &= \varepsilon(\hat{\mathbf{u}}) \cdot \mathbf{E}_i \\ &= \varepsilon_p \mathbf{E}_{i,p} + \varepsilon_n \mathbf{E}_{i,n} \end{aligned} \tag{3.25}$$

where the components of the incident electric field alon $\hat{\mathbf{u}}$ and normal to it are given by

$$\begin{aligned} \mathbf{E}_{i,p} &= \hat{\mathbf{u}}\hat{\mathbf{u}} \cdot \mathbf{E}_i \\ &\text{and} \\ \mathbf{E}_{i,n} &= \mathbf{E}_i - \mathbf{E}_{i,p} = \hat{\mathbf{I}} \cdot \mathbf{E}_i - \hat{\mathbf{u}}\hat{\mathbf{u}} \cdot \mathbf{E}_i \end{aligned} \tag{3.26}$$

with $\hat{\mathbf{I}}$ the identity matrix. Thus by comparison of coefficients we find

$$\varepsilon(\hat{\mathbf{u}}) = \varepsilon_p \hat{\mathbf{u}}\hat{\mathbf{u}} + \varepsilon_n \left(\hat{\mathbf{I}} - \hat{\mathbf{u}}\hat{\mathbf{u}}\right) \tag{3.27}$$

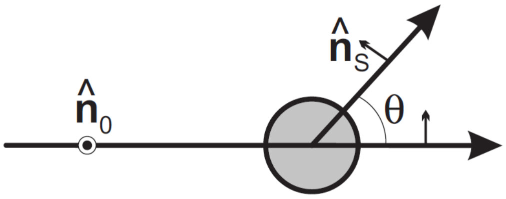

Figure 3.7: Illustration of the polarizer settings in a DDLS set up.

4 Scattering techniques using evanescent illumination

The techniques described in the preceding chapters are well suited to investigate static and dynamic properties of colloids or polymer in a bulk solution, far away from any bounding container wall. However, in the ultimate vicinity of solid surfaces the physical properties of suspension may differ largely from their bulk behavior. The near wall dynamics of colloids is slowed down and becomes anisotropic due to hydrodynamic interactions with the wall, while the static properties may be altered due to the additional interaction with the solid body. These effects can be quantitatively studied by scattering experiments with evanescent illumination.

4.1 Evanescent illumination

If a laser beam impinges on an interface between two dielectric media of different refractive index, the transmitted beam will be refracted according to Snell's law, as indicated in Figure 4.1. Here the wave vector of the transmitted light is given by $\mathbf{k}_2 = \mathbf{k}_{y,2} + \mathbf{k}_{z,2}$ with the corresponding vector amounts given by $k_2 = 2\pi n_2/\lambda_0 = \sqrt{k_{y,2}^2 + k_{z,2}^2}$. In particular the the

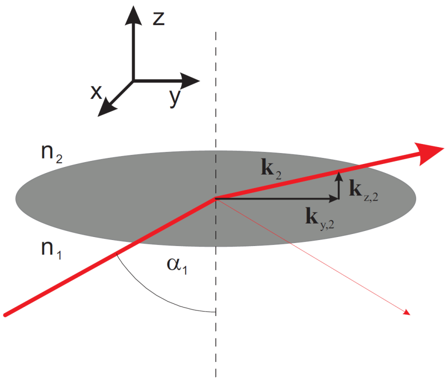

Figure 4.1: Transmission and reflection at a flat interface between two media of different refractive index.

5 Further Reading

- For the basics of optics and wave motion see:
  Eugene Hecht; Optics; Addison Wesley 1998.
- For a brief review on light scattering see:
  C. S. Johnson, Jr. and D. A. Gabriel; Laser Light Scattering; Dover Publications 1993.
- For a very thorough treatment of scattering theory see:
  J. K. G. Dhont; An introduction to the dynamics of colloids; Chapter III; Elsevier 1996.

6 Exercises

Exercise 1

Explain why it is not possible to determine a particle radius of gyration smaller than roughly 25 nm by static light scattering.

Excercise 2

In Fig. 5.1 the particle scattering factors of spheres with different radii are plotted. For clarity the the upper curve is displaced on the ordinate by a factor 100.

a) Judge from these curves, which corresponds to the spheres with smaller radius.

b) Determine the radii from the position of the minima.

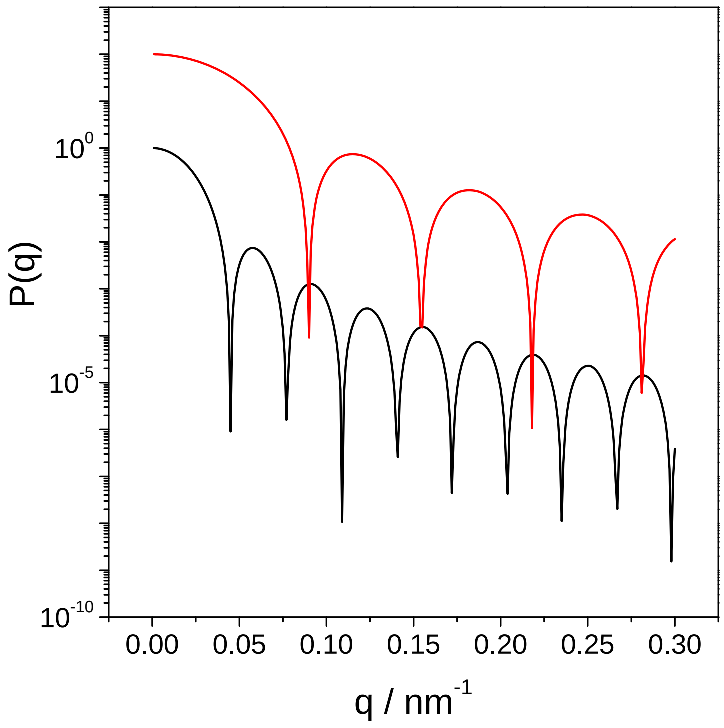

Figure 6.1: Particle scattering factor of spheres. The upper curve is shifted by factor of 100 on the ordinate.

Excercise 3

In Fig. 5.2 time auto–correlation functions of the scattered intensity of from two solutions spheres with different radii in water are plotted. The scattering angle is 90 degree the wave length of the incident light is 632 nm and the viscosity of water at 298 K is 0.089 cP.

a) Judge from these curves, which corresponds to the spheres with smaller radius.

b) Estimate the radii from the relaxation times.

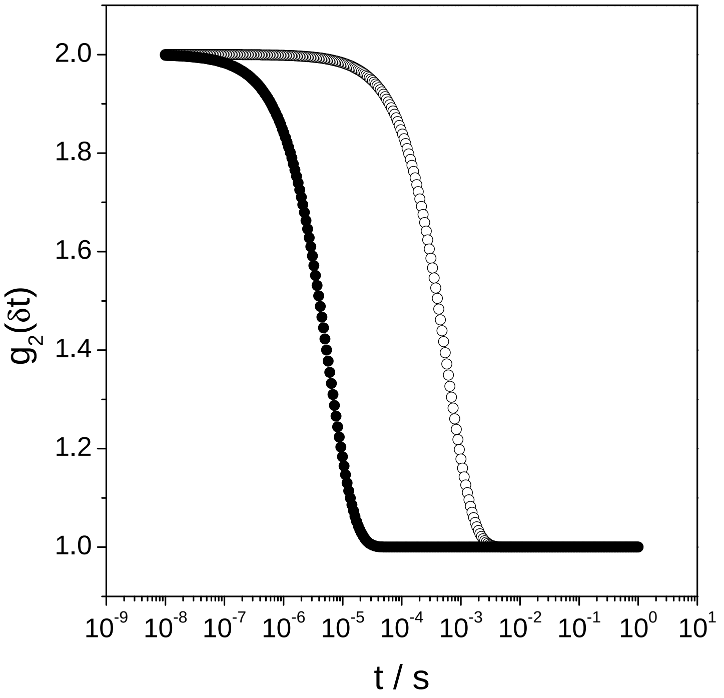

Figure 6.2: Time auto–correlation function of the scattered intensity of spheres of different size. The scattering angle is $\theta = 90$ degree.

Table 6.1: Scattering data from a polymer in water expressed as $Kc/\mathcal{R}(q,c) \times 10^6$.

Scattering angle degree	c_1 10^{-3} g/mL	c_2 2×10^{-3} g/mL	c_3 4×10^{-3} g/mL	c_4 8×10^{-3} g/mL
20	2,30	2,90	4,10	6,50
30	2,33	2,93	4,13	6,53
40	2,38	2,98	4,18	6,58
50	2,44	3,04	4,24	6,64
60	2,51	3,11	4,31	6,71
70	2,59	3,19	4,39	6,78
80	2,67	3,27	4,47	6,87
90	2,75	3,35	4,55	6,95
100	2,83	3,43	4,63	7,03
11ß	2,92	3,52	4,72	7,12
120	2,99	3,59	4,79	7,19
130	3,06	3,66	4,86	7,26
140	3,12	3,72	4,92	7,32
150	3,17	3,77	4,97	7,37

Excercise 4

In Table 5.1 scattering data from a polymer in aqueous solutions are listed. Determine the molar mass, M_W, the radius of gyration, R_g and the osmotic virial coefficient A_2 from these data. The wave length of the incident light is 632 nm and the refractive index of water is 1.33.