
Dynamic Light Scattering in Microgels

Advanced physical lab exercises

Lab course, Working Group "Soft Matter at Interfaces "

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1 Introduction

The method of dynamic light scattering (DLS) is one of the most often applied technique to analyse particle in the nanometer range. The following passages are a brief introduction into colloidal particles, zeta potential measurements and dynamic light scattering. Nowadays, nanoparticles are used in a wide range of applications. Nanoparticles can be used in the chemical, medical, pharmaceutical, or industries. Compared to bulk materials, the properties of nanoparticles can be adjusted by size (size-induced functionality). For small particles, quantum mechanical effects are dominating, while for larger particles the gravitational force plays the dominating role. A system of nanoparticles that are finely distributed in a solution is called colloid or (colloidal) dispersion.

Dispersion is derived from the Latin word *dispergere*, which means *spreading* or *dispersing*. A dispersion is thus a mixture of at least two substances that are not soluble in each other. In this process, one substance is finely dispersed (disperse phase) in the other phase (continuous phase or dispersant). The particle size cut off from suspensions to solutions is 1 nm (Figure 1). Dispersions can be classified as colloidal or coarsely dispersed systems, depending on particle size. *Colloid* derives from *Colla*, meaning *glue*, and *Eidos*, meaning *shape* or *appearance*. Colloids or colloidal dispersion (e.g., suspensions) exist when the particle diameter is between 1 nm (10^{-9} m) and $1\ \mu\text{m}$ (10^{-6} m). Colloidal dispersed particles are thus approximately not subject to gravitational force, but to Brownian molecular motion. This leads to a constant fluctuation in the distance between the particles. Since the system always strives for a state of minimum surface (minimization of surface energy), non-stabilized particles tend to coagulate. This is counteracted by various stabilization mechanisms, which will be briefly explained below.

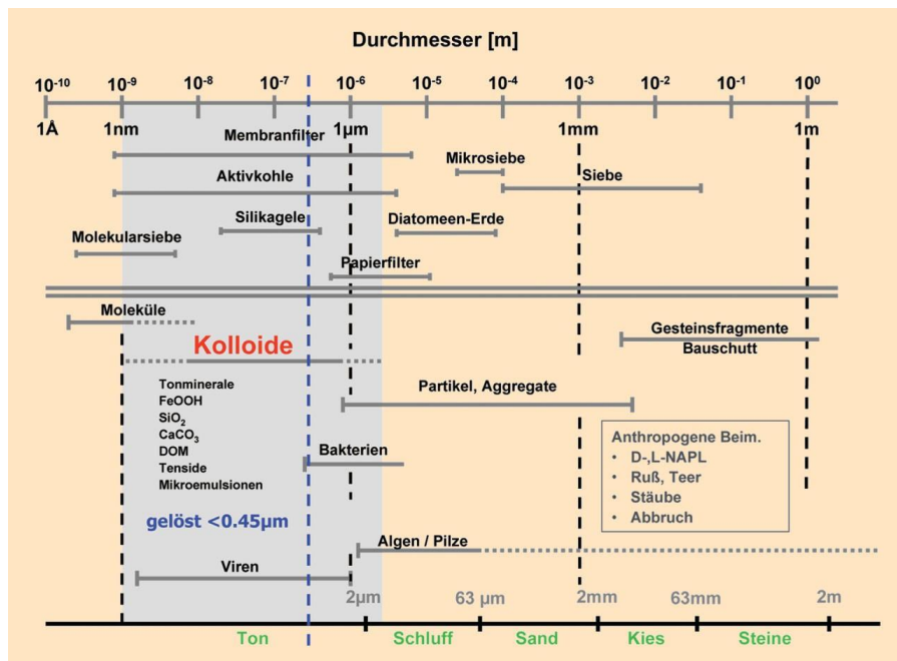


Figure 1: Classification of different sized materials according to their size [1].

1.1 Nanoparticle Stabilization

The most common stabilization mechanisms are as follows: If the nanoparticles possess a surface charge (due to certain groups on the surface, e.g., Si-OH), they can be stabilized via *Electrostatic Repulsion*. Another mechanism is *Steric Stabilization*. This occurs when the surface of the nanoparticles is decorated with fuzzy longer molecular chains, which also can prevent coagulation. These stabilization mechanisms may be present alone or in combination.

1.1.1 Electrostatic Stabilization

The charge of a charged interface in a liquid is compensated by counterions in its environment. The first model to describe the potential profile on the surface was described by Helmholtz. It assumes that all counterions are adsorbed and equally distributed on the particle surface as a rigid layer. Thus, this situation is similar to the charge separation in a plate capacitor. The potential decreases

linearly with distance (Figure 2 (A)). The drawback to the Helmholtz model is that the entropy of the ions is not considered. The model of Gouy and Chapman considers the enthalpy and the entropy (in "competition" with each other) of the counterions. The ions thereby form a so-called *diffuse double layer*. The potential then decreases exponentially with distance (Figure 2 (B)). The relation between the potential and the charge density of the free ions is thereby expressed by the Poisson-Boltzmann equation. The nonlinear Poisson-Boltzmann equation is solved with the Debye-Hückel approximation. Stern developed a third model to include both, the strongly bonded ions in proximity to the interface and the diffuse double layer for larger distances. This model combines the two upper models.

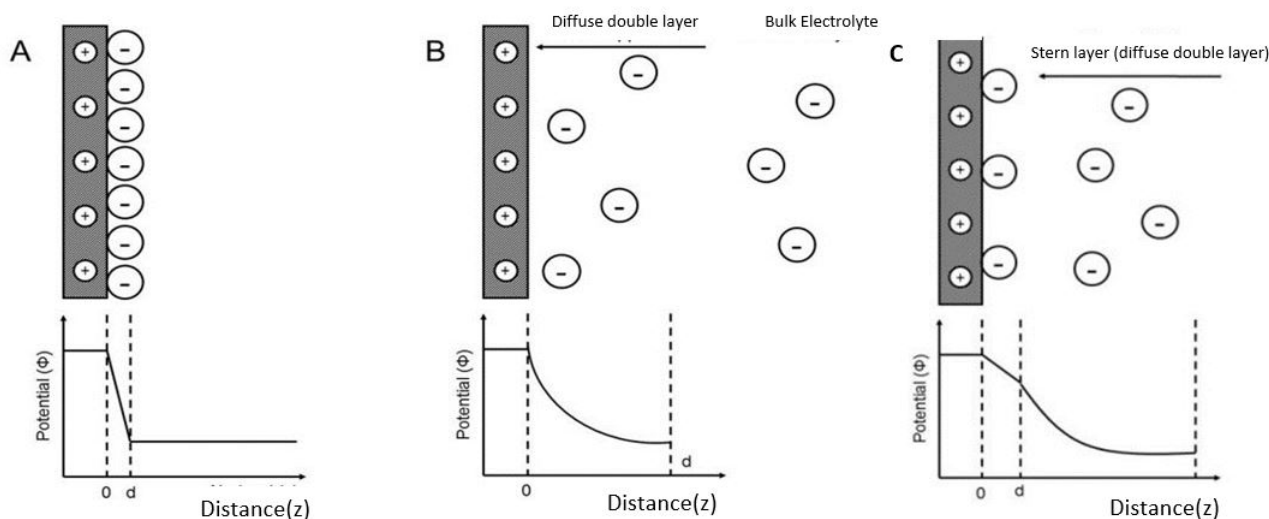


Figure 2: Comparison between Helmholtz (A) Gouy and Chapman model (B) and Stern Model

The Stern model states that on the direct particle surface, the counterions are rigidly adsorbed. In further distance, the so-called stern layer follows (diffuse layer). This means that, on the surface, the potential first decreases linearly and then decreases exponentially from the stern layer (Figure 2 (C)).

1.1.2 DLVO Theory

The DLVO theory is named after Derjaguin, Landau, Verwey, and Overbeek. It is the explanation of the stability of colloidal suspension. It describes the balance between two forces, electrostatic repulsion and van der Waals attraction. Electrostatic repulsion becomes significant when two colloids approach each other and their electrical double layers begin to interfere. Some energy is required to overcome this repulsive force, so that the repulsion curve in the figure indicates the energy that must overcome if the particles are forced together. It has a maximum value which is related to the surface potential when they almost touch and decrease to zero outside the double layer. Van der Waals attraction is the results of forces between molecules in each colloidal particle. One molecule of the colloid has a van der Waals attraction to each molecule in the other colloid, which means additive force. The curve which represents an attractive energy indicates the variation in van der Waals force between colloidal particles. The DLVO theory explains the tendency of colloids to agglomerate or separate by combining two curves of electrostatic repulsion and van der Waals attraction. At each distance, the smaller value is subtracted from the larger value to obtain the net energy. In the regime where there is repulsion, energy can be thought to be an energy barrier. We can increase or decrease the energy barrier by changing the ionic or pH environment or adding surfactants to affect the surface charge of the colloid. In this case, zeta potential can be measured to know the stability of dispersion. There are many other effects we should consider, for sure, but steric stabilization is the most important thing. An adsorbed layer on each particle prevent the particles from coming close enough for van der Waals attraction to cause flocculation.[7] In the case that at large distances the Van der Waals attraction outweighs the electrostatic repulsion, a secondary minimum is formed (Figure 3). In this minimum, the particles can form "loose" agglomerates. This process is called *flocculation*. These flocculated agglomerates are reversible, and the particles can be redispersed, for example, by gentle shaking. When the particle spacing is reduced, electrostatic repulsion takes effect. This means that V_M reflects the stability of the dispersion. The higher the energy barrier V_M , the more stable the dispersion. If the particles overcome the energy barrier, the potential of the particles reaches the *primary minimum*. At the *primary minimum*, the particles coagulate and the agglomerates are not redispersible.

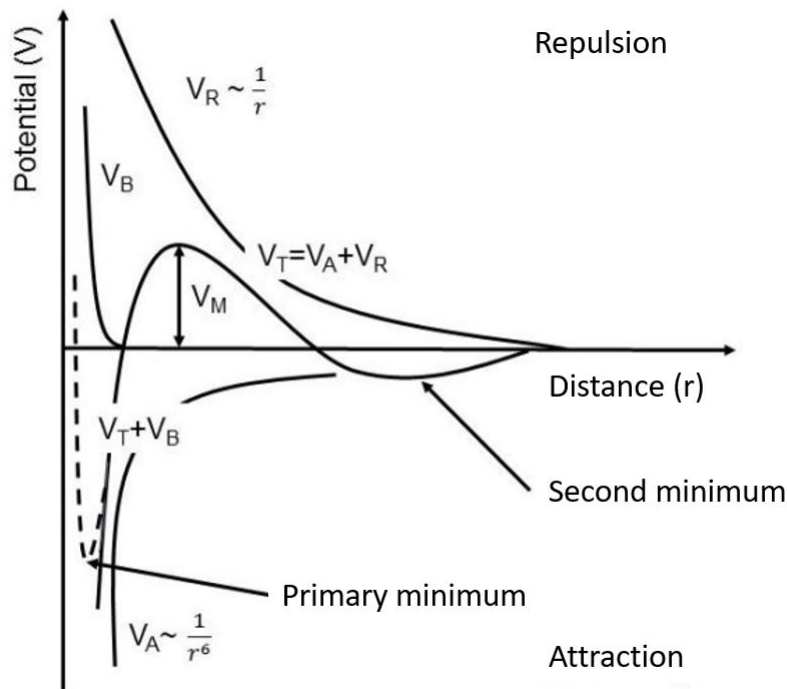


Figure 3: Potential curve between two particles depending on the particle distance

1.1.3 Steric Stabilization

Steric stabilization results from possible longer chain molecules or even polymer chains at the interface. Polymers are particularly effective, which have a stronger attraction to the dispersing agent than to each other (so-called good solvent for polymers). In this state, the chains are solvated and maximally stretched (Figure 4).

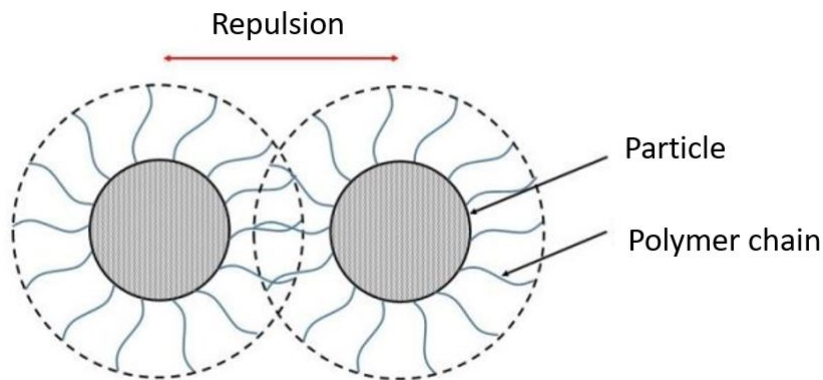


Figure 4: An overlap in the residence areas of the polymers results in a repulsion of the particles

If these particles now approach each other, the residence areas of the polymer chains overlap. Due to the overlap, the concentration of dispersant in the overlapping volume decreases. This increases the osmotic pressure in the overlapping volume, which causes the particles to be repelled and stabilized. The reason for this is entropy: the number of degrees of freedom of the polymer chains

decreases in the overlap volume.

1.2 PNIPAM Microgels and Polystyrene Nanospheres

PolyNIPAM and polystyrene particles are to be used as samples. PolyNIPAM particles are prepared from the monomer NIPAM (N-isopropylacrylamide, Figure 5, left) by free radical precipitation polymerization. PolyNIPAM is a hydrogel and has a VPTT (Volume phase transition temperature) at about 32 ° C, and thus belongs to thermo responsive microgels. The reason for this is the monomer (the building block) of the gel. The NIPAM monomer has a LCST (lower critical solution temperature). Depending on the temperature, NIPAM is very well (<32 ° C) or very poorly to not at all (>32 ° C)) soluble in water. When polymerized to polyNIPAM, this property is retained. It results in PolyNIPAM being in a swollen state below 32 ° C and in a shrunken state above 32 ° C (Figure 6)

At low temperatures, water bonds can be formed at the secondary amine group and at the oxygen atom. Water bonds can be formed with the surrounding water, and the PolyNIPAM is present in the swollen state. If the temperature is now increased above the VPTT, the water bridge bonds dissolve, the water is pressed out of the gel, and the microgel gel and the microgel shrinks. The release of the water increases the entropy in the system, which also promotes the shrinkage process. This process is reversible: If the temperature is lowered, the microgel swells up again.

PolyNIPAM microgels have a surface charge and polymer chains on the particle surface. Thus, they are sterically as well as electrostatically stabilized. Polystyrene particles are prepared from the monomer styrene (Figure 5, right). Compared to PolyNIPAM, the monomer does not exhibit LCST. Thus, the polymer particles do not have VPTT. Although the monomer styrene has no charged groups, a surface charge is introduced during the production process. Polystyrene particles are to be used as reference particles in comparison with PolyNIPAM, in order to distinguish VPTT effects from other effects associated with the temperature.

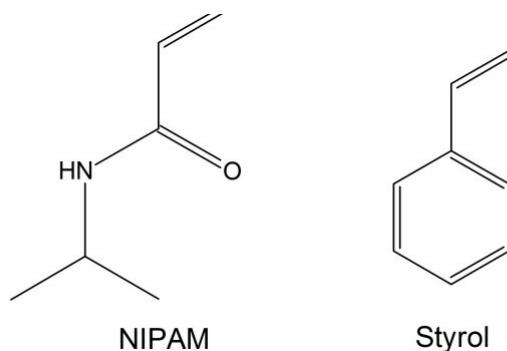


Figure 5: Structural formula of the monomers NIPAM and styrene

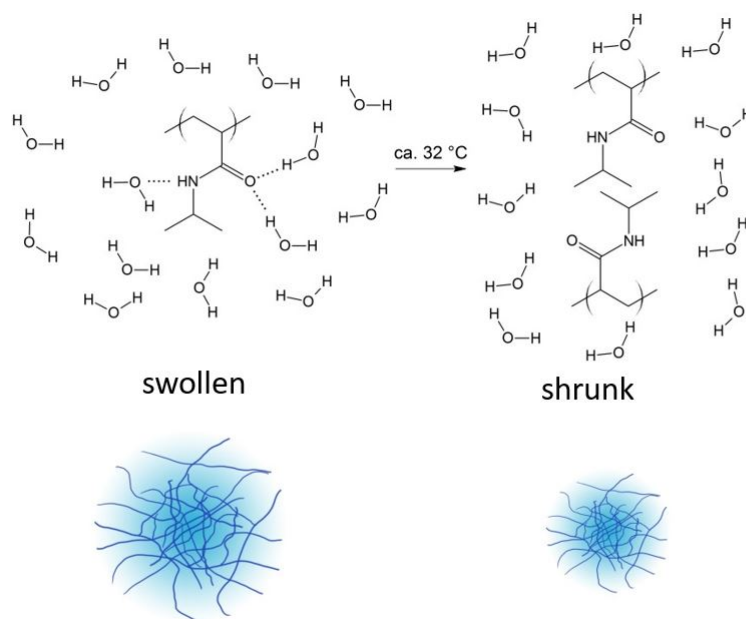


Figure 6: Change in the volume of PolyNIPAM. If the temperature is increased above the VPTT (approx.32 ° C), the H- bonds dissolve and the water molecules are released (top)

1.3 Scattering

The scattering modes of interest for this experiment are Rayleigh and Mie scattering. The phenomenon of Rayleigh scattering occurs with particles that are much smaller than the wavelength of light. It is responsible, for example, for the sky being blue. The scattering intensity is isotropic. Mie scattering is prominent as the particle size corresponds approximately to the wavelength of the light. The scattering intensity depends on the angle. The scattering is no longer isotropic.

1.3.1 Dynamic Light Scattering (DLS)

Mie scattering is important in dynamic light scattering (DLS). the principal setup of which is sketched in Figure 7. The setup consists of five main elements: a laser (here with $\lambda = 660 \text{ nm}$), a sample chamber (here a Decalin bath with temperature control), a detector (here two avalanche photodetectors) mounted on a goniometer, a correlator (here a hardware correlator from the company LS-Instruments) and a PC for control.

The laser beam passes an attenuator (gray filter) and the adjusted laser intensity is measured. The beam is then focused into the sample chamber. The scattered light is now anisotropically distributed over the solid angles. An example scattering pattern is shown in Figure 8.

The scattered light is coupled into one or two detectors using fiber optics. In principle, it is possible to operate a DLS with one detector. By using two detectors, a possible detector error is detectable. The particle dynamics is calculated with the help of the autocorrelation function (one detector) equation 1 or the pseudo-cross correlation (two detectors behind a beam splitter). The results of the correlation function $\langle I(t)I(t + \tau) \rangle$ are transmitted to the PC. In addition, the measured intensities are transmitted randomly (about one in a million intensity measurements).

$$g^2(q, \tau) = \frac{\langle I(t)I(t + \tau) \rangle}{\langle I(t) \rangle^2} \quad (1)$$

I is the measured scattering intensity, q the scattering vector, τ the time interval between two measurements (*lag time*). The scattering vector is given by equation 2, where n_0 is the refractive index, λ , is the laser wavelength and θ is the measurement angle.

$$q = \frac{4\pi n_0}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (2)$$

A distinction is made between the first and second order correlation. The correlation of the intensity is the second order correlation. Now, in order to determine the diffusion coefficient, one must determine the first order correlation function. This corresponds to the electric field strength of the photons. The correlation of both correlation functions is given by the Siegert function:

$$g^2(q, \tau) = 1 + \beta[g^1(q, \tau)]^2 \quad (3)$$

β is a correction factor, which is mainly determined by the measurement geometry and the number of the measured speckles. For the evaluation of the correlation function, different functions are available. The most prominent are the Cumulant fit and the Contin fit. The Contin evaluation is an inverse Laplace Transform [2]. In the cumulant analysis, the data is got with an exponential function. For a monodisperse sample applies:

$$g^1(q, \tau) = \exp(-\Gamma\tau) \quad (4)$$

For polydisperse samples the function is extended by the moments of the size distribution, and it holds:

$$g^1(q, \tau) = \exp\left(-\Gamma\left(\tau - \frac{\mu_2\tau^2}{2!} + \frac{\mu_3\tau^3}{3!}\right)\right) \quad (5)$$

Γ is the 1st order moment, μ_2 and μ_3 are the second and third order moments. The diffusion coefficient and the square of the scattering vector are reciprocally proportional with: $\Gamma = Dq^2$. Thus, the diffusion coefficient can be determined from the slope of a plot Γ versus q^2 . The motion of the particles is driven by Brownian motion and the frictional force. The Stokes-Einstein equation (6) is obtained.

$$D = \frac{k_B T}{6\pi\eta r_H} \quad (6)$$

k_B is the Boltzmann constant, T is the temperature, η is the kinematic viscosity of the solvent, and r_H is the hydrodynamic radius. For more detailed theory, see the paper by Barbara J. Frisken [3] and the book Dynamic Light Scattering, with Applications to Chemistry, Biology, and Physics by Bruce J. Berne and Robert Pecora [4].

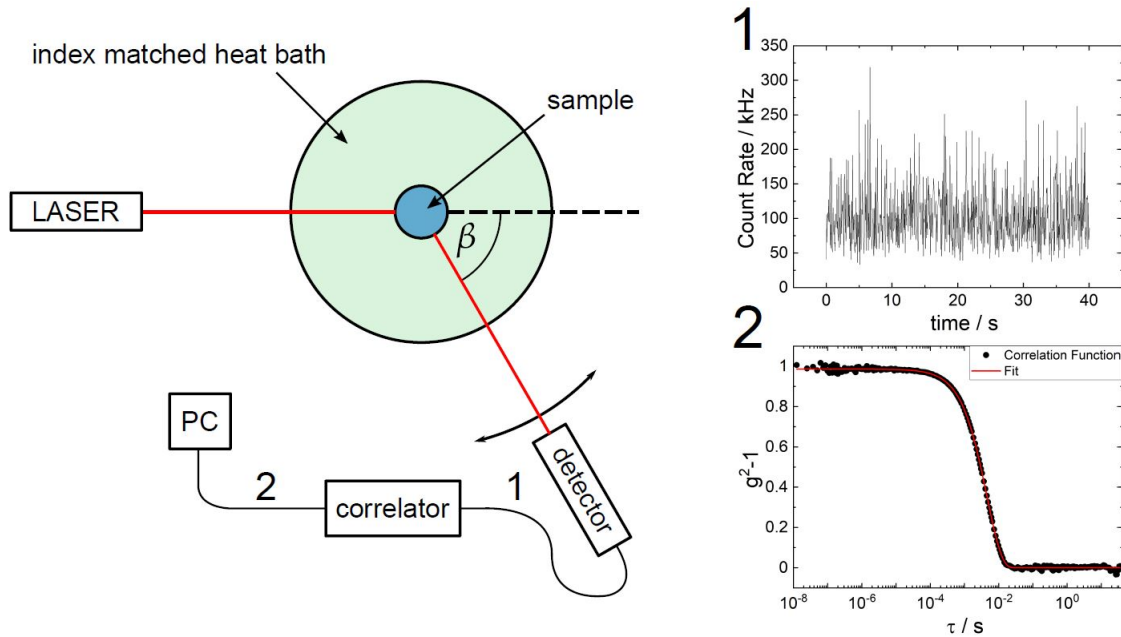


Figure 7: Schematic representation of a DLS setup. The laser is directed into the sample chamber via two deflection mirrors. The detector is mounted on a goniometer.

1.3.2 Zeta potential

The zeta potential ζ is a measure of the charge of the particles. The higher the zeta potential, the higher the electrostatic repulsion. The zeta potential is not the surface charge of the particle. This can be seen from the potential curve of the Stern model (Figure 9). As the particle moves in the solvent, the diffuse ion layer is subjected to shear forces. It is at this shear plane (*slipping plane*) that the zeta potential is measured. As a rule of thumb, a zeta potential below 25 mV is too low to stabilize a dispersion. Another important

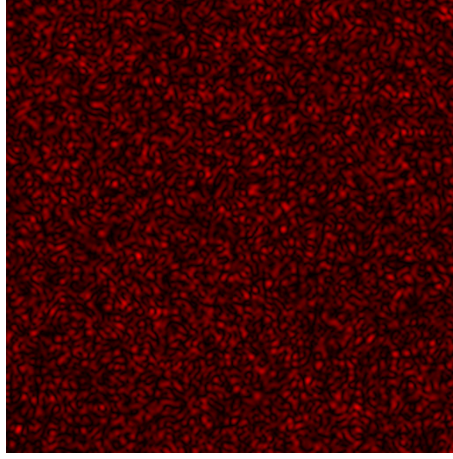


Figure 8: Scattered light distribution after the sample chamber

quantity is the so-called Debye length κ^{-1} . It is also called the shielding length. The Debye length is the distance from the particle at which the potential has dropped to $\frac{1}{e}$. The Debye length is expressed as follows:

$$\kappa^{-1} = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{2 N_A e^2 I}} \quad (7)$$

Where ϵ_0 is the electric field constant, ϵ_r is the relative permittivity, k_B is the Boltzmann constant, T is the temperature, N_A is the Avogadro constant, e is the elementary charge, and I is the ionic strength with:

$$I = \frac{1}{2} \sum_i z_i^2 c_{i0} \quad (8)$$

Here z_i is the valence of the ions and c_{i0} is the concentration of ions of variety i . Thus, it is evident from equation 7 that as the ion concentration in a suspension increases, the Debye length of the charged particles decreases. Thus, addition of salt (e.g., NaCl) increases the ionic strength. For 10^{-3} mol/L, the Debye length is about 10 nm. In contrast, for 10^{-5} mol/L, the Debye length is about 100 nm. This leads to the fact that with increasing ionic strength, the distance between two particles decreases and the electrostatic stabilization is reduced. The mobility of particles in the electric field can be measured using laser Doppler electrophoresis (Fig.11) A laser beam of a specific wavelength λ is directed onto the sample. If the particle now moves in the direction of the oppositely charged electrode due to an applied electric field E , there is a shift in the frequency of the scattered laser beam (Doppler shift, Δv). This frequency shift is proportional to the phoretic velocity v . If the refractive index n of the dispersion medium and the scattering angle θ are known, the following relationship arises:

$$\Delta v = \frac{2v \cdot n \cdot \sin(\frac{\theta}{2})}{\lambda} \quad (9)$$

The electrophoretic mobility μ_e can then be calculated using equation 10.

$$\mu_e = \frac{v}{E} \quad (10)$$

The zeta potential can then be determined via the Henry relation (equation 11).

$$\zeta = \frac{3\eta\mu_e}{2\epsilon_0\epsilon_r f(\kappa R)} \quad (11)$$

Here R is the particle radius, η the viscosity of the dispersant and the Henry function $f(\kappa R)$. The Henry function is a function of the Debye length and the particle radius. If large particles with a high ionic strength are present in the sample ($\kappa R \gg 1$), the Henry function converges to 3/2 and the zeta potential can be expressed using the Smoluchowski approximation.

$$\zeta = \frac{\eta\mu_e}{2\epsilon_0\epsilon_r} \quad (12)$$

On the other hand, if a very small particle is present in a dispersant with small ionic strength ($\kappa R \ll 1$), the Henry function converges to 1 and the Hückel approximation can be used.

$$\zeta = \frac{3\eta\mu_e}{2\epsilon_0\epsilon_r} \quad (13)$$

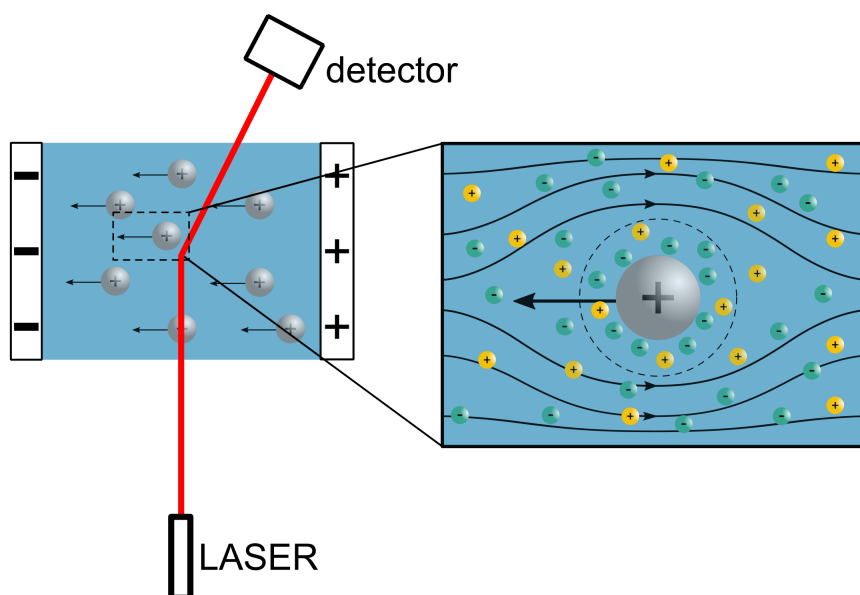


Figure 9: Schematic representation of the zeta potential in the potential curve according to the Stern model.

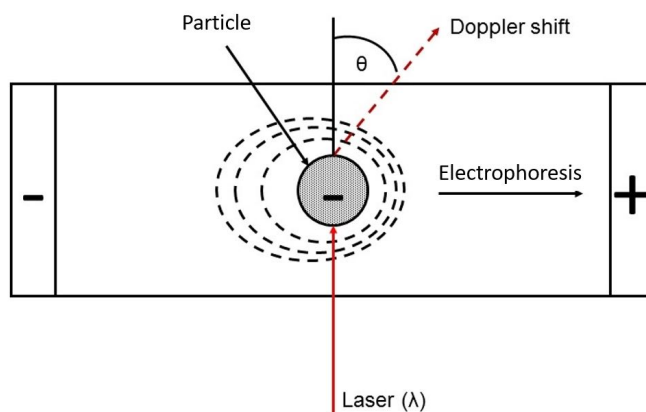


Figure 10: Schematic representation of a laser Doppler electrophoresis measurement to determine the zeta potential.

2 Implementation

The hydrodynamic diameter of PolyNIPAM and Polystyrene at two different temperatures will be determined. Then, using the hydrodynamic diameter and the phase transition of PolyNIPAM will be shown and compared with polystyrene particles. A lab coat and protective goggles are compulsory for all work.

2.1 Measurement of the hydrodynamic diameter using DLS

The DLS consists of many optical components which are very sensitive. In addition, a laser with a power of 100 mW is operated. Therefore, it is urgent to pay attention to clean and attentive work on the DLS.

Dilute the suspensions until they are clear before measurement. Now fill the respective suspension into a DLS cuvette to a level of 2-3 cm. The cuvette is tightly closed with a plastic lid. The cuvette is spotless of contamination (e.g., finger grease) using very pure acetone (spray bottle) and a dust-free cloth. The remaining acetone on the cuvette and any dust particles or lint are blown off with a nitrogen gun (caution: hold the cuvette firmly). Carefully insert the clean cuvette into the sample holder of the DSL. If necessary, the holder must be lifted out slightly with the appropriate tool. The sample holder is then closed. The measurement script can now be

started. The measurement protocol is created with the help of the wizard before the measurement. The following samples are to be measured:

Table 1: Samples to be measured with the DLS at different temperatures

Sample	Temperature
PolyNIPAM(2.5% <i>cross-linker content</i>)	20 °C
PolyNIPAM (2.5% <i>cross-linker content</i>)	50 °C
PolyNIPAM(5% <i>cross-linker content</i>)	20 °C
PolyNIPAM(5% <i>cross-linker content</i>)	50 °C
Polystyrol	20 °C
Polystyrol	50 °C

2.2 Zetapotential

Before measuring the samples, a standard must be measured. For this purpose, the standard provided by the assistant is carefully added to the cuvette using a glass pipette. The cuvette is closed accordingly and inserted into the zetasizer. The measurement protocol is created with the help of the assistant before the measurement. The effects of the volume phase transition of the pNIPAM particles on their zeta potential will be investigated. For this purpose, the zeta potential sample will be measured with the microgel at 20 °C, 30 °C, 35 °C, 40 °, 50 °C. Be sure to allow sufficient equilibrating time to allow the sample to adjust to the respective temperatures. For the polystyrene samples, it is sufficient to measure at 20 °C and 50 °C.

3 Preparation for Colloquium

Preparation

1. Which forces and interactions are important in colloidal systems, and which are negligible? How do van der Waals interactions arise?
2. Learn about the basics of dynamic light scattering (DLS) for determining hydrodynamic radius. How are measured intensity curves related to particle motions and the hydrodynamic radius? How does the typical curve shape of the correlation function emerge?
3. Learn about the basics of laser Doppler electrophoresis for the determination of the zeta potential.
4. Practical questions: Why does the solution have to be diluted like this for the DLS measurement? Is this also necessary in the Malvern zetasizer? In what order should they mix water particles and why?

4 Working in the laboratory

- Eating, drinking, chewing gum and smoking are strictly prohibited in all laboratories!
- Attention must be paid to appropriate clothing (in particular: closed shoes and long leg clothing, no shorts!). Protective goggles and gowns will be provided.
- Inform yourself independently about the dangers of the chemicals used (here: acetone, decalin).
- In the laser laboratory, the following must also be observed:
 - Wear laser safety goggles adapted to the laser.
 - Do not wear jewelry (earrings, watches, necklaces, etc.) or reflective objects openly.
 - Do not look directly into the laser or into the laser beam.
 - Do not touch any optical components or the goniometer!
 - Do not place any documents/objects (laptops, cell phone, etc.) on the optical table.
 - Always wear gloves when handling the specimens.

5 Evaluation

A mathematical program is needed to evaluate the DLS data. For example, the following programs can be used: Mathematica, Origin, (Excel). All equations and fits used should be available from the protocol.

1. Load the raw data into the analysis software. The intensity fluctuations as well as the autocorrelation curves for the different measurement angles should be plotted.
2. Consider what quality statement you get from the plots for intensity versus time.
3. The autocorrelation curves are now to be fitted with eq.3 and eq.4.
4. Γ is to be determined for each measurement angle from the fits.
5. Γ is plotted over q^2 .
6. The diffusion coefficient D is now calculated from the slope and the hydrodynamic radius r_H is calculated from this.
7. Calculate the swelling factor (volume swollen state by volume shrunk state) for the PolyNIPAM microgel.
8. Compare swollen ratio in microgels and explain how it changes by increasing amount of cross linker in microgels. Why?

Compare and discuss both the results of the DLS measurement and the zeta potential measurements. What is the effect of temperature on the zeta potential and hydrodynamic radius of each type of particle? Plot zeta potential of each particle vs temperature and compare them. Does this correspond to the expectations?

6 Litterateur

- [1] Thilo Hofmann. Die Welt der vernachlässigten Dimensionen: Kolloide. Chemie in Unserer Zeit, 38(1):24-35, 2004
- [2] Stephen W. Provencher and Petr tĕpánek. Global Analysis of Dynamic Light Scattering Autocorrelation Functions. Particle and Particle Systems Characterization, 13(5):291-294, 1996.
- [3] Barbara J Frisken. Revisiting the method of cumulants for the analysis of dynamic light-scattering data. 40(24):4087-4091, 2001
- [4] Bruce J. Berne and Robert Pecora. Dynamic light scattering: With applications to chemistry, biology, and physics. Dover Publications, Mineola, NY, dover ed. edition, 2000.
- [5] ISO 22412:2017. Particle Size Analysis – Dynamic Light Scattering (DLS). International Organization for Standardization.
- [6] Lauth, Günter Jakob, and Jürgen Kowalczyk. Einführung in die Physik und Chemie der Grenzflächen und Kolloide. Berlin: Springer Spektrum, 2016.
- [7] Israelachvili, Jacob N. (2011). Intermolecular and Surface Forces. Academic Press. ISBN 9780123919274.