Structure of Soft Matter: Small Angle Scattering

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1 Introduction

Soft Matter embraces many different substances which have to be described by manyfold concepts. These concepts are also taken from the neighboring material sciences. On the one hand the conventional solid state physics mainly focused on solid substances with many crystalline examples. On the other hand the simple liquids describe the other border. In this sense soft matter describes materials between the crystalline and the liquid state. This can be understood in terms of structure (long range order versus short range order), but also the dynamic responses of soft matter include elastic and viscous properties. Thus, viscoelastic materials and complex fluids are typical soft matter materials. In this sense the materials are soft. In the following, two examples should be discussed: Polymers are long chain molecules with interesting properties, and microemulsions are mixtures of oil and water mediated by a surfactant. Microscopically still domains of oil and water remain, but macroscopically these liquids appear homogenous and are thermodynamically stable.

The structural appearance of soft matter materials should be discussed on the basis of polymers. The smallest distance is represented by a chemical bond with the typical length scale of 1.5 Å. The repeat unit of a polymer, the monomer, embraces already several atoms. The connectivity of a chain becomes visible on the length scale of several monomers, i.e. around 10 Å. The chain-like molecules usually form coils resembling a random walk. Thus the whole chain is visible between approx. 30 Å and 500 Å. In polymeric blends consisting of several polymers demixing can occur. The typical domain size reaches from 300 Å to several 1000 Å. On even larger length scales, superstructures can appear with regular or fractal properties. The driving force for domain and larger structure formation is a reduced miscibility of at least two components. Especially when the structure is regular one speaks of self assembly. Many samples appear homogenous on much larger length scales (say at 1 to 10 µm) and can be even transparent for light. This is the reason why scattering experiments are considered for the structure determination.

A typical small angle scattering experiment with neutrons or x-rays detects structural sizes of 10 Å to several 1000 Å. Especially ultra small angle methods extend this range to several µm. The small angle light scattering method begins in the µm-range due to the larger wave length of the probe. Hierarchical structures often allow to separate the length scales in distinct ranges. So a single structural property becomes dominant for a certain length scale. For instance small angle scattering experiments do not detect the chemical structure of monomers anymore. Monomers appear as homogenous beads connected to a long chain molecule.

2 Small Angle Scattering

A typical small angle scattering experiment is schematically shown in Figure 1. The radiation of the source is prepared for the experiment by a monochromator and a collimation line. Neutrons are generated by a reactor or a spallation source. The monochromator is a rotating cylinder with tilted lamellae, and selects neutrons of a certain wave length. The collimation consists of two
Fig. 1: Scheme of a small angle scattering diffractometer. The neutrons pass from the left to the right. The incident beam is monochromated and collimated before it hits the sample. Non-scattered neutrons are absorbed by the beam stop in the center of the detector. The scattered neutron intensity is detected as a function of the scattering angle $\theta$.

Apertures, which define the maximum divergence of the incident beam. Right after the second aperture the sample is placed. Usually, many neutrons pass the sample unscattered. This high intensity has to be blocked by a beam stop close to the detector due to saturation problems of the detector. Only the scattered neutrons are detected by the detector. The scattered intensity is recorded as a function of the scattering angle $\theta$. The scattering vector $Q$ is related to $\theta$ by:

$$Q = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right) \approx \frac{2\pi}{\lambda} \theta$$

(1)

If a (quasi) Bragg peak is detected at a scattering vector $Q$ the underlying length scale $\ell$ of the structure is given by:

$$\ell = \frac{2\pi}{Q}$$

(2)

This concept is the reason why the $Q$-space is called reciprocal space. Large structures show scattering at small $Q$, while small structures appear at large scattering vectors. Hierarchical structures appear with different scattering laws for different $Q$-ranges. Often the scattering law appears to be a power law $Q^{-\alpha}$, indicating that the structure can be understood as a fractal. The transition points between the scattering laws indicate the structural size (as given by eq. 2) between the two conceptually different structures.
2.1 Scattering Length Density

With discussing the different length scales of a polymer we already mentioned that the detailed molecular structure of a monomer is not resolved by a typical small angle scattering experiment. For neutrons the typical wavelength is 7 Å. Thus, a single bond between carbon atoms cannot be resolved. The amplitude of the incident beam can be considered constant within 1 Å distant points. The second argument is the considered \( Q \)-range of a typical (neutron or x-ray) small angle scattering experiment. The maximal considered scattering vector often is 0.3 Å\(^{-1}\), and according to eq. 2 this translates to length scales of at least 20 Å. So a simple saturated carbon chain (also called polyethylene) appears as a homogenous worm without distinctions of hydrogen or carbon atoms.

When mixing two different substances, a scattering signal is only obtained for different scattering powers. The way of generating contrast for neutrons is the substitution of hydrogen by deuterium. Even the otherwise identical protonated and deuterated polymer can be studied by neutron scattering. Undisturbed chain conformations \cite{[1]} and chain dynamics \cite{[2]} were studied in this way. The scattering amplitude is proportional to the contrast, which is given by the scattering length density difference. For neutrons one obtains:

\[
\rho_A(\text{neutrons}) = \frac{1}{V_A} \sum_i b_i
\]

The scattering length density \( \rho_A \) is the sum of all scattering lengths \( b_i \) of all atoms of one monomer A divided by the monomer volume \( V_A \). Examples for scattering lengths are given in table 1 and can be found on a web page \cite{[4]}.

For x-rays the electron density difference describes the contrast. The scattering length density is calculated according to:

\[
\rho_A(\text{x-rays}) = \frac{r_e}{V_A} \sum_i Z_i
\]

The classical electron radius is \( r_e = e^2/(4\pi\varepsilon_0 m_e c^2) = 2.82 \text{ fm} \). The electron number of each atom \( i \) is \( Z_i \). Equation 4 means that chemically different substances do have a contrast, but it can be rather weak. Not only the sum of all electrons, but also the mass density finally plays a role for the x-ray contrast. The usually high intensity of the incident beam allows to collect scattered intensity even for low contrasts. The disadvantage of the high intensity is the potential radiation damage.

For the present discussion of small angle scattering it does not play a role that the electrons occupy a certain space around the nucleus, while for neutrons the scattering nucleus is a point-like particle. But when studying the crystalline structure of conventional salts for instance this difference has to be taken into account for the analysis of the scattering pattern and especially the intensities.
Table 1: *Scattering lengths and number of electrons for some elements.*

Another practical point is the transmission of the radiation. X-rays are rather strongly absorbed by usual samples. Thus, soft matter samples should have a thickness of 0.1 mm. For neutrons sample thicknesses of 1 mm to 5 mm or even more are possible. If multiple scattering (more scattering events) plays a role the measured intensity is smeared out, and is usually hard to be interpreted. The 1st Born Approximation is described in the following section and assumes single scattering processes only.

For light scattering experiments the polarizability plays an important role. Without going into details the final contrast is expressed by the refractive index increment $dn/dc$:

$$\rho_A(\text{light}) = \frac{2\pi n}{\lambda^2} \cdot \frac{dn}{dc} \quad (5)$$

The refractive index increment $dn/dc$ finally has to be determined separately when the absolute intensity is of interest. The concentration $c$ is given in units volume per volume. The used wavelength of light is $\lambda$.

### 2.2 First Born Approximation

The full presentation of the first Born approximation is quite lengthy. Thus, the essential points for small angle scattering experiments are presented here only. For further reading reference [3] is recommended. The assumptions of the Born approximation are the following: A monochromatic and non-divergent beam is assumed to irradiate (and pass) the sample. The sample potential is a small perturbation for the incident beam, and thus the scattered outgoing waves carry just a small fraction of the total radiation. Practically, as a rule of thumb, the total coherently scattered intensity should be less than 10% of the incoming intensity. The scattering occurs only once. That means that the outgoing waves arise from a single scattering process out of the incident wave. Multiple scattering would mean a redistribution of outgoing waves. The outgoing intensity is observed at large distances compared to the sample diameter. The mayor result of the first Born Approximation is that the amplitude of the outgoing waves is determined by the Fourier transform of the scattering length density:
\[ A(Q) = \int d^3 r \rho(r) \cdot \exp(i Q r) \] (6)

The imaginary unit is called \( i \) here. Please note that the argument carries the scalar product of the scattering vector \( Q \) and the spatial vector \( r \). The scattering intensity is proportional to the macroscopic cross section \( d\Sigma/d\Omega \):

\[ \frac{d\Sigma}{d\Omega}(Q) = \frac{1}{V_{\text{tot}}} |A|^2(Q) \] (7)

One important property of this equation is the absolute square of the amplitude. This means that the observed intensity does not contain any information about the phases anymore. So every scattering experiment interpretation has to be aware that the structure in real space cannot easily be reconstructed. Nonetheless most probable realizations can be calculated [5].

The macroscopic cross section is the instrument independent information about the sample, while a real measurement of the intensity carries also properties of the instrumental setup:

\[ \frac{d\Sigma}{d\Omega}(Q) = \frac{\Delta I}{\Delta \Omega} \cdot \frac{1}{I_0 d_S A_S T_S \epsilon} \] (8)

The intensity \( \Delta I \) is collected in a detector element covering the solid angle \( \Delta \Omega \). It has to be normalized to the incident intensity \( I_0 \), the sample thickness \( d_S \) and sample area \( A_S \), the sample transmission \( T_S \) and the detector efficiency \( \epsilon \). By the use of a calibration standard with known scattering power the geometrical and technical constants of the diffractometer machine can be removed and the unique information about the sample \( d\Sigma/d\Omega \) is obtained. This procedure is standard for neutron scattering, but also possible for x-ray and light scattering.

### 2.3 Independent Spheres

As a first example a collection of \( N \) independent homogenous spheres shall be considered. A realistic sample could contain spherical colloids with an extremely narrow size distribution. The scattering amplitude of a single sphere would be calculated as the following:

\[ A_1(Q) = \int_{r<R} d^3 r \rho_1 \cdot \exp(i \vec{Q} \cdot \vec{r}) \] (9)

The coordinate system should be oriented in this way that the \( Q \)-vector points along the z-axis. The vector \( \vec{r} \) is represented in spherical coordinates. Then one finds:

\[ A_1(Q) = \rho_1 \cdot \int_0^{2\pi} d\phi \int_0^\pi d\theta \int_0^R dr \exp(i r Q \cos \theta) r^2 \sin \theta \] (10)
Integration over the angles leads to:

\[
A_1(Q) = \rho_1 \cdot 2\pi \cdot 2 \cdot \int_0^R dr \frac{\sin(Qr)}{Qr} r^2
\]  

(11)

And finally one obtains:

\[
A_1(Q) = \rho_1 \frac{4\pi}{3} R^3 \cdot 3 \frac{\sin(QR) - QR \cos(QR)}{(QR)^3}
\]  

(12)

The considered integral was carried out just for the colloidal particle. In reality it is embedded in some environment with a scattering length density \(\rho_2\). The scattering amplitude would read then: \(A_1(Q) = (\rho_1 - \rho_2) \frac{4\pi}{3} R^3 \cdot 3 \frac{\sin(QR) - QR \cos(QR)}{(QR)^3} + \rho_2 \delta(Q)\). Now the scattering length density difference appears in the final expression as it is expected. Furthermore a Dirac delta function \(\delta\) describes the scattering from an infinitely large volume of the embedding environment. Mathematically, this term is correct, but physically it does not mean anything. This \(\delta\)-function describes some intensity at scattering vectors \(Q = 0\) where the transmitted, non-scattered beam is found anyways. So there is practically no distinction between the two intensities at \(Q = 0\). In the following, this \(\delta\)-function is simply neglected. For the final macroscopic cross section, the amplitudes are squared and normalized to the total volume:

\[
\frac{d\Sigma}{d\Omega}(Q) = \frac{N}{V_{tot}} A_1^2(Q) = \phi_1 \cdot V_1 \cdot (\Delta \rho)^2 \cdot \left( \frac{3 \sin(QR) - QR \cos(QR)}{(QR)^3} \right)^2
\]  

(13)

First of all, \(N\) scattered intensities of independent spheres were summed up independently. This means that the superposition was taken out incoherently. In reality many relative arrangements are realized within the experimental exposure time, and so special arrangements are averaged out. Another argument aims at the coherence volume of the incident beam. The full volume represents many realizations of such sub-volumes.

The final result of eq. 13 shows some important properties: The first three factors contain the concentration (volume fraction) \(\phi_1\), the individual volume \(V_1 = \frac{4\pi}{3} R^3\), and the contrast factor \((\Delta \rho)^2\). These factors describe the extrapolated intensity at small scattering angles (forward-scattering). Here, ‘extrapolated’ means a measurement close to the beam stop but neglecting the non-scattered neutrons. The last factor is the formfactor of the particle \(F(Q)\), and is depicted in Figure 2. The limit at low scattering angles is unity. At larger angles many oscillations occur due to the finite size of the particle. The first minimum occurs at \(Q_{\text{min}} = \frac{4.493}{R}\), which again shows the relation between real and reciprocal space: the larger the sphere the smaller \(Q_{\text{min}}\). The general structure of eq. 13 is kept for all dispersions and solutions with non-interacting particles: The forward-scattering tells about the concentration, the particle volume and the contrast. With knowing two of them, the third one is determined experimentally. The particle shape and size is determined by the \(Q\)-dependence of the intensity. Here, usually modelling helps to extract many details of the experiment.
A second effective formfactor is plotted in Figure 2. Here a distribution of spheres with different radii is assumed (polydispersity). The width of the $R$-distribution was assumed to be 10%. The minima are not as sharp as for the monodisperse spheres. Especially the oscillations of higher order are simply represented by a straight line. The straight line of this double logarithmic plot is connected with a $Q^{-4}$ power law. It can be shown that all compact volumes have such a scattering behaviour [6] (Porod scattering). Practically, all oscillations average out due to non-negligible polydispersities, and one observes:

$$d\Sigma d\Omega(Q) = P \cdot Q^{-4} \quad (14)$$

The amplitude of the Porod scattering $P$ tells about the surface per volume. The general appearance of the Porod constant is $P = 2\pi(\Delta\rho)^2 S_{tot}/V_{tot}$. So, apart from the contrast, it measures the total surface $S_{tot}$ per total volume $V_{tot}$. For our spheres the Porod constant becomes $P = 2\pi(\Delta\rho)^2 4\pi R^2/(4\pi R^3/(3\phi)) = 6\pi\phi_1(\Delta\rho)^2/R$. The surface to volume ratio is smaller the larger the individual radius $R$ is. The remaining scaling with the concentration $\phi_1$ and the contrast $(\Delta\rho)^2$ arises still from the prefactor which we discussed in context with eq. 13.
2.4 Spheres on a Lattice

Now the spheres shall be considered to have dependent positions. A typical soft matter example is a diblock copolymer. This is a linear polymer with two blocks consisting of different monomers. Once the two monomers become immiscible, a phase separation on macroscopic scales cannot take place, but small micro-domains can form consisting of (almost) one monomeric kind. This microphase separation can lead to spherical domains on a bcc (body centered cubic) lattice embedded in the other continuous domain.

If we calculate the amplitude now, the phases of all spheres have a relation. The integral over all spheres splits into a sum over all particles and an integral over the volume of one sphere:

\[ A(Q) = (\Delta \rho) \sum_{h,k,l} \exp(i a \left( \frac{h}{Q} \right)) \int_{\text{sphere}} \exp(i Q r) \]  

(15)

The length \( a \) marks the basic distance of the lattice. The indices \( h, k, l \) run over all positions, where a sphere is found. Now, the integral we have already solved (eq. 12), but the bcc lattice still needs to be Fourier transformed. From classical solid state physics we know, that a bcc lattice transforms in a fcc lattice and vice versa. When calculating the macroscopic cross section, we basically have to calculate the quadrature. So:

\[ \frac{d\Sigma}{d\Omega}(Q) = \frac{1}{V_{\text{tot}}} |A|^2(Q) = (\Delta \rho)^2 \cdot S(Q) \cdot F(Q) \]  

(16)

The form factor we already know \( F(Q) = \frac{3 \sin(QR)-Q^2 R \cos(QR)}{(QR)^3} \)^2, while the structure factor still is a sum over all points of the fcc lattice in reciprocal space \( S(Q) \propto N \sum_{h,k,l} \delta(Q_0 h - Q_x) \delta(Q_0 k - Q_y) \delta(Q_0 l - Q_z) \). The quadrature did not harm the peak shape, which appears infinitely sharp in this representation. In reality, the crystal has a finite size, and so the peak width is connected with its size. For polycrystals (powder samples) the average crystal domain size determines the peak width. This \( S(Q) \) has the property that it is proportional to the number of scatterers within a crystal domain, since all the waves of one crystal domain superimpose coherently.

An example of such a soft matter system is shown in Figure 3. The real system [7] consists of a polystyrene-polyisoprene block copolymer dissolved in squalane. The polystyrene block is immiscible neither in polyisoprene nor in squalane, and forms the spherical domains, while polyisoprene and squalane mix well and form the embedding matrix. This scattering experiment is conducted with x-rays since the resolution is much better than with usual small angle neutron scattering diffractometers. Improvements for neutron small angle scattering are about to come [8]. The left part of Figure 3 shows the theoretical expectations of \( S(Q) \), and \( F(Q) \) independently, and the product \( d\Sigma/d\Omega \). One directly finds the 6th maximum suppressed due to \( S(Q) \) and \( F(Q) \). This calculation is done for a powder sample with many orientations of the single crystal domains. Thus Debye-Scherrer rings are formed, the one-dimensional cut of which we see here. The indices of the first seven peaks read (1,1,0), (2,0,0), (2,1,1), (2,2,0),

...
Fig. 3: On the left the theoretical structure and form factor \( S(Q) \) and \( F(Q) \), and the product, the macroscopic cross section \( d\Sigma/d\Omega \) are shown. The calculations base on a lattice constant of 380 Å and a spherical radius of 80 Å. On the right hand side the x-ray experiment [7] shows peaks up to the 7th order. The real system consists of a polystyrene-polyisoprene diblock copolymer and squalane as a good solvent for the polyisoprene. Polystyrene spheres are formed in the matrix of the other two components.

\( (3,1,0), (2,2,2), \) and \( (3,2,1) \). The number of permutations and possible signs give rise to the intensity of a single peak. On the right hand side the experimental data are shown. The first four peaks are clearly indicated in a log-lin plot, while the 5th and 7th order peak are indicated in the inlay. The 5th order peak is really weak, but the 7th order peak is clearly visible.

To discuss the possible options of structure factors in soft matter science some examples are shown in Figure 4. The lowest one is the already discussed structure factor of a crystalline structure. It shows clearly developed peaks indicating the positions of the particles. The limit at small scattering angles is zero. This means the ideal crystal looks homogenous on large length scales, and no long range fluctuations can occur. This structure is formed due to the repulsive interaction of the particles (the polyisoprene corona looses entropy when two coronas intersect) and a particle conservation condition (no particles can leave the volume). A weaker case of repulsive interaction [9] is shown in the middle graph of Figure 4. Still some peaks occur due to neigboured particles, but all correlations are lost in the large \( Q \)-limit. On large length scales (low \( Q \)) the structure factor is suppressed (smaller 1), and the repulsive interaction becomes visible. The interactions make the sample look more homogenous than a sample with randomly distributed particles where the structure factor \( S(Q) = 1 \) is constant. The upper case of Figure 4 shows the influence of attractive interaction (in combination with repulsive short range interaction). Again some peaks are visible, indicating the correlations of neigboured particles, but now the attractive forces lead to an upturn of the structure factor at low scattering angles. The attraction can lead to cluster formation, and the larger entities appear less homogenous than randomly distributed spheres. Remember, the forward scattering can be interpreted by the prod-
Fig. 4: Structure factors of different soft matter examples. The lowest one is already discussed in Figure 3, and represents a bcc crystal structure. The middle case appears due to hard sphere interactions of colloidal particles (two particles cannot intersect) [9]. The hard core radius was assumed to be 266 Å, and the concentration was 20%. If some attractive forces come into play, such as depletion forces, the structure factor shows an upturn at low scattering angles. Depletion means, that small and large particles like to separate due to the larger entropy of more free small particles. The weaker form of depletion considered here is an effectively attractive interaction of the large particles.

\[ (\Delta \rho)^2 \phi V \]

while the first two factors remain constant, larger entities appear by a larger volume \( V \). The ultimate consequence of attraction are extremely large clusters [10], which can be formed by colloidal filler particles in rubbers. These particles lead to the strengthening of pure rubber. The formation of crystalline structures due to attractive interactions can be found in colloidal dispersions [11]. While the extreme cases of interactions can lead to crystalline structures, the weak cases of interaction lead to liquidlike structures. Now, we have seen structure factors for the crystalline, the liquid-like and the gas-like \((S(Q) = 1)\) states. Usually, phase transitions occur between these states.

### 2.5 Short Summary of Part One

Soft matter systems appear with many length scales, even hierarchical structures can form. The typical small angle scattering experiment smears the atomic structure out, and just an average chemical structure is seen. The important variable of a small angle scattering experiment is the scattering vector \( Q \), the variable of the reciprocal space. Large structures appear at small \( Q \)
and vice versa. The Fourier transformation of the scattering length density is connected with the observed intensity. Due to the quardature the information about the phases is lost. We have developed the concept of structure and form factors with some essential examples. The form factor can display the Porod law, which is typical for compact particles. Polydispersity smears the oscillations out. The structure factor is dependent on the interactions, which can be attractive or repulsive. The strength of interactions opens a large variety between crystalline [12] and liquidlike structures [9].

3 Further Examples of Soft Matter Research

The concept of structure and form factor is important for soft matter science, but finally does not cover all possible examples. In the following some other samples are shown which take us away from this simple picture. However, these examples have important applications and appear in our daily life.

3.1 Polymer Blend Phase Diagrams

Polymer blends contain at least two different monomeric units, and are heated to moderate temperatures where they are at least viscous. The simplest blend contains two homopolymers. Each of them contains just a single type of monomers. Just by mechanical mixing, homogenous blends may form. The mixing entropy is proportional to the reciprocal molar volume $V$, and thus relatively small. The entropy supports mixing and has to overcome the enthalpy for a homogenous blend. This is the explanation why many polymers do not mix, but of course, positive examples can be found. A phase diagram of a polybutadiene(1,4)/polystyrene blend is shown in Figure 5. At high temperatures the two polymers mix, while at low temperatures they do not. The immiscible region is separated from the miscible region by the binodal. The spinodal separates the metastable and the unstable region. In the metastable region the blend can be supercooled. At the highest temperature where binodal and spinodal meet the critical point is found.

While phase separation opens another interesting field of soft matter research [13], we focus on the one-phase region where the polymers do mix. As we have seen many times in the last section, the polymer blend looks homogenous by visual inspection but scattering experiments reveal more information. Close to the critical point the blend ‘feels’ the vicinity to the phase boundary. Energetically slightly demixed domains may occur due to fluctuations with the thermal energy. These thermal composition fluctuations are visible by scattering experiments. This scattering experiment is performed at several temperatures at the critical composition.

Before discussing further concepts, a similar phase diagram of a diblock copolymer is shown on the right side of Figure 5. This polymer is a linear chain with two blocks consisting of one monomer species. The chemistry does not allow the polymer to be phase separated on macro-
scopic length scales, but still microscopic domains of one species can be formed. The top line above the phase diagram shows possible structures: The bcc lattice of spheres we have already discussed. Important are also cylinders on a hexagonal lattice, the double diamond structure (Ia\̅3d) and the lamellar structure. The double diamond structure is also called bicontinuous structure since either domain forms a continuous structure in space. If one domain is etched away chemically still a spongelike structure remains and keeps its shape. The temperature axis ($\Gamma V \propto T^{-1}$) is reverted. Otherwise the general structure is similar to the phase diagram of homopolymers. At high temperatures the polymer is disordered, and at low temperatures the polymer is micro-phase separated (ordered). The in the following discussed experiment also changes the temperature in the disordered region until micro-phase separation occurs.

### 3.2 Lattice Theories

While the form factor usually describes whole domains, we look on the structure of a polymer blend with higher accuracy. The extreme microscopic viewpoint would include all positions of all atoms of the molecule. As we have discussed before, this viewpoint is too detailed in many cases. So we could embrace molecule parts as units, be it a CH$_2$ unit or a whole monomer (say a styrene monomer for polystyrene). Now we assume that these units are space filling, and even more crudely they fit on a cubic lattice [15, 16]. This modelling oversimplifies the real system, but many interesting questions can be addressed in a straight way. At each point we can define concentration variable $\phi(r)$, which turns to 1 or 0 if a monomer A or B is found. If the polymer placement is space filling (so we assume incompressibility), then we only need this variable $\phi(r)$. The scattering length density is directly connected to this variable:

$$\rho_A(r) = \rho_A \cdot \phi(r) \quad (17)$$

The scattering amplitude will be calculated on the basis of the Fourier transformation $A_A(Q) = \rho_A \int \phi(r) \exp(iQr)$, and the macroscopic cross section finally reads:

$$\frac{d\Sigma}{d\Omega}(Q) = (\Delta \rho)^2 \cdot S(Q) \quad (18)$$

The function $S(Q)$ is called scattering function from now on, and is related to the Fourier transformed concentration variable according to $S(Q) = \frac{1}{V_{tot}} |\tilde{\phi}(Q)|^2$.

These simple concepts allow to understand many properties of polymer blends, and are the basis for understanding an even more complex behaviour if some of the restrictions above are relaxed. The compressibility can be introduced by allowing for lattice voids. This concept is connected with the term free volume. Of course one has to introduce two concentrations for each of the polymer species $\phi_A$ and $\phi_B$, since $\phi_A + \phi_B < 1$.

However, the Random Phase Approximation (RPA) [17] deals with the scattering of such polymer blends, and bases on the local concentration $\phi$ of the polymer species. In a first step,
the scattering of a free polymer chain without interactions is determined [1] assuming simple properties of chainlike molecules. Then interactions are introduced, mainly represented by the exchange free energy $\Gamma$ (this energy is normalized to volume). The RPA describes then, how to combine the scattering of a free chain and the interaction parameter $\Gamma$ to obtain the scattering of an interacting chain. Some predictions of this theory we are going to discuss now.

### 3.3 Scattering Functions of Polymer Blends

Here we are discussing general properties of scattering functions of the considered polymer blends. The full $Q$-dependence gives us valuable details about the polymer kind. For the further analysis, the scattering patterns are reduced to two or three parameters.

In Figure 6 the characteristic scattering patterns of homopolymer blends and diblock copolymers are shown. The homopolymer has a continuously decreasing intensity with increasing scattering vector. This dependence can be described with a simple Ornstein-Zernicke formula according to $S(Q) = S(0)/(1 + \xi^2 Q^2)$. The forward scattering $S(0)$ describes the strength of the thermal fluctuations. Large intensities mean strong fluctuations which are excited by the thermal energy. This means that the free energy varies weakly as a function of the (local) composition. This relation is expressed by the Fluctuation-Dissipation theorem:

$$S^{-1}(0) = \frac{1}{k_B T} \cdot \frac{d^2(G/V)}{d\phi^2}$$  \hspace{1cm} (19)

The Gibb’s free energy appears here normalized to the Volume $V$. The first derivative of the Gibb’s free energy is connected with the osmotic pressure, while the second derivative is related to the osmotic compressibility. The inverse maximum intensity $S^{-1}(0)$ is also a susceptibility, describing the softness of the Gibb’s free energy with respect to external fields (while in the experiment the thermal energy excites the fluctuations). The correlation length $\xi$ is inversely proportional to the width of this curve. It describes over which distance the thermal fluctuations are correlated, i.e. over which distance enrichments of one species remain of similar strength. With weak interactions between the two polymer species the correlation length is tightly connected with the polymer size, since this size is the only length scale of the system. With interactions and temperatures a little closer to the critical point the fluctuations and the correlation length grow rapidly (as we will also see in Figure 7). The vicinity to the phase boundary induces this behaviour. As we will see below the fluctuations can grow so strongly that the fluctuations influence the Gibb’s free energy, and deviations from a simple model picture are visible.

The characteristic scattering pattern of a diblock copolymer shows a correlation peak at a finite $Q^*$. At large length scales (small $Q$) the chemical bond between the two blocks of the polymer inhibits fluctuations, and the ideal intensity grows like $S(Q) \propto Q^2$. Polydispersity of the block length ratio can lead to long range fluctuations, and finally the compressibility may allow for density fluctuations on large length scales. Practically the polydispersity is much more important. At small length scales far below the polymer size the chemical bond between the
blocks is not important anymore and only a mixture of chain parts is seen. Thus \( S(Q) \propto Q^{-2} \) which reflects the fractal property of the chains, i.e. on several length scales the chain keeps its chain properties. In this \( Q \)-range homopolymers and diblock copolymers cannot be distinguished. The maximum intensity \( S(Q^*) \) in between the two asymptotic scattering laws reflects the strong fluctuations with the by \( Q^* \) given periodicity. Again, this intensity is an inverse susceptibility. The periodicity is tightly connected with the polymer size [20]. The peak width \( \Delta Q \propto \xi^{-1} \) is connected with a correlation length. This \( \xi \) tells over which distance alternating enrichments can be expected. Again, with the vicinity of the phase boundary the fluctuations (and thus the intensity) and the correlation length grows. Strong fluctuations also have an influence on the Gibb’s free energy.

Now the temperature dependence of the susceptibilities shall be discussed (Figure 7). At high temperatures the homopolymer blends show a linear temperature dependence which is motivated by the mean field theory:

\[
\frac{1}{2} S^{-1}(Q = 0) = (\Gamma_S + \Gamma_\sigma) - \frac{\Gamma_H}{T} \tag{20}
\]

There are two entropic terms. The first term \( \Gamma_S \) arises from the mixing of two polymers with a given chain length; so this is an entropy of mixing of two particles with a given molecular size. The second term \( \Gamma_\sigma \) is a segmenal extropy of mixing, which considers the monomeric structure and the compressibility on the monomeric level. The enthalpic term \( \Gamma_H \) describes the enthalpy of mixing on the monomeric level. While we developed this general scheme about scattering and susceptibilities on the basis of the assumption of incompressability the generalization simply considers pressure dependent segmental terms \( \Gamma_\sigma \) and \( \Gamma_H \) [18]. These effective interaction terms can be compared with more enhanced theories [19].

Focussing on the temperature behaviour of the susceptibility again, the mean field behaviour can be extrapolated to a critical temperature \( T_{MF} \), where the susceptibility is infinitely small. This idealized critical behaviour of the susceptibility can be described by a power law according to \( S^{-1}(0) = C_{MF} \tau^{-1} \) where the reduced temperature is defined by \( \tau = (T - T_{MF})/T \). The mean field picture breaks down when the temperature is in the crossover region and deviations become visible. Another asymptotic power law is observed close to the real critical temperature according to \( S^{-1}(0) = C_+ \tau^{1.24} \) [21]. The underlying theory is the 3-dimensional Ising theory describing two-component critical systems. The whole temperature range is described well by a crossover function [22, 23, 24]. So the two univerality classes, i.e. the mean field and the 3d-Ising class, are connected by a single function.

The extrapolated mean field temperature \( T_{MF} \) indicates also the limit of the 3d-Ising region, which extends over the range between \( T_{MF} \) and \( T_C \), the real critical temperature. This temperature difference is connected to an important parameter the Ginzburg number \( Gi \propto (T_{MF} - T_C)/T_{MF} \). On the one hand this temperature difference is important for applications, because the real phase boundary has to be known well. On the other hand the Ginzburg number is important within the theoretical concept of homopolymer blends. The Ginzburg number is a measure
for the temperature range where thermal fluctuations influence the Gibb’s free energy and the 3d-Ising behaviour becomes visible. Within classical concepts the Ginzburg number $G_i \propto N^{-1}$ was estimated to be rather small due to the dependence on the degree of polymerization $N$. This term arises from the probability that two polymers meet in a given point (and interact). The probability to find one monomer of one species in a given point scales as $N/R_{ee}^2 \propto N^{-1/2}$. Here $R_{ee}$ is the typical polymer size [1]. The product of two probabilities for two species scales as $N^{-1}$. Thus, the scaling of the Ginzburg number is similar to the entropy of mixing $\Gamma_S$. It was an idea of Schwahn [22] that the segmental entropy $\Gamma_\sigma$ has also an influence on the Ginzburg number. As a consequence the Ginzburg number (a) is much larger than previously estimated, (b) depends on the monomeric structure and is not universal with respect to the degree of polymerisation $N$, and (c) depends on pressure [23].

For diblock copolymers one expects a similar temperature dependence at high temperatures according to eq. 20 (for $Q = Q^{*}$). When regarding the measurements one observes a more linear behaviour at high temperatures. At lower temperatures the behaviour is curved more and more. The applied theory [25] describes the whole disordered phase region. Only the extrapolated mean field behaviour is found to be much different from the measured curves. At lower temperatures $T_{ODT}$ the phase transition is indicated by a sudden increase of the measured intensity, while at even lower temperatures this intensity does not vary much anymore.

Again, the Ginzburg number can be related to the temperature difference of the mean field behaviour $T_{MF}$ and the real phase transition $T_{ODT}$. The Ginzburg number obviously is much larger than for homopolymer blends. The probability of interaction in a given point scales with $N^{1/2}$ since now both blocks are connected. Therefore, the Ginzburg number should scale as $G_i \propto N^{-1/2}$ according to this simple theory. The general trend is basically confirmed experimentally [26] but deviations are also visible. A theoretical concept for diblock copolymers including the segmental entropy is missing.

The whole understanding of phase boundaries and fluctuations is important for applications. Many daily life plastic products consist of polymer blends since the final product should have combined properties of two different polymers. Therefore, polymer granulates are mixed at high temperatures under shear in an extruder. The final shape is given by a metal form where the polymer also cools down. This process involves a certain temperature history which covers the one-phase and two-phase regions. Therefore, the final product consists of many domains with almost pure polymers. The domain size and shape are very important for the final product. So the process has to be tailored in the right way to yield the specified domain structure. This tailoring is supported by a detailed knowledge of the phase boundaries and fluctuation behaviour. Advanced polymer products also combine homopolymers and diblock copolymers for an even more precise and reproducible domain size/shape tailoring [27]. The diblock copolymer is mainly placed at the domain interfaces, and, therefore, influences the domain properties precisely.
3.4 Microemulsions

Microemulsions are another important example of soft matter research [28]. They consist of three components: Water and oil are immiscible; but a surfactant mediates between oil and water and macroscopically homogenous phases are formed. On a microscopic scale oil and water stay unmixed and form domains. The surfactant forms a film between oil and water and keeps the system thermodynamically stable.

A typical phase diagram is shown in Figure 8 [29]. For this purpose equal volumes of oil and water are mixed with a variable fraction of surfactant $\gamma = m_{\text{surf}}/(m_{\text{oil}} + m_{\text{water}} + m_{\text{surf}})$. At low surfactant concentration a three phase coexistence (3) is observed. Here a microemulsion phase coexists with excess oil and excess water. At high temperatures a two-phase coexistence occurs (2) with a microemulsion and an excess water phase. At low temperatures a two-phase coexistence occurs (2) with a microemulsion and an excess oil phase. At higher surfactant concentrations a one-phase microemulsion (1) is found. This microemulsion has a bicontinuous structure. That means that the oil and water domains are continuous by themselves and have a sponge-like structure which hosts the other domain. It is known that even higher surfactant concentrations lead to ordered structures. Again, lamellar structures, cylinders on a hexagonal lattice, and spheres on a cubic lattice appear [30]. Without these liquid crystalline phases the phase diagram has a simple appearance of a fish. It is mainly found for non-ionic surfactants, for instance for C$_i$E$_j$ surfactants.

When adding an amphiphilic polymer – a polymer which basically is a long surfactant molecule – new interesting effects are observed. Figure 8 also shows the one phase regions of microemulsions with a certain polymer content $\delta = m_{\text{pol}}/(m_{\text{pol}} + m_{\text{surf}})$. This content $\delta$ is given with respect to the total amphiphile, while the total content is less than 0.5%. One directly observes that much less surfactant is needed to form a single phase microemulsion. This dramatic increase of the efficiency is also called ‘polymer boosting effect’. In the following it is demonstrated that (a) the polymer decorates the surfactant membrane and (b) the polymer induces a larger rigidity of the membrane. This larger rigidity allows to form larger structures with a better surface to volume ratio.

3.5 Contrast Variation Experiments

Up to now, we discussed the scattering of materials with two components only. For a four component system (oil, water, surfactant, and polymer) this simple concept does not hold anymore. As we discussed already, single components can be made visible for neutron scattering experiments by the exchange of protons by deuterium (H-D-exchange). Thus, in principle every contrast can be rendered. Figure 9 shows the principle of making single components and therefore properties visible. The bulk contrast basically makes one domain visible against the other domain. Here, the film and the polymer play a minor role due to the much lower concentration. The film contrast makes the film visible against the two domains. Again, the polymer plays a minor role. The polymer contrast finally makes the polymer visible against all other compo-
Due to the decreasing concentration in this series the intensity for the three contrasts is decreasing by a factor of 100 with each step. This makes plausible why clean high intensity neutron scattering machines are desperately needed. In theory the macroscopic cross section of a four component system reads:

\[
\frac{d\Sigma}{d\Omega} = (\rho_O - \rho_W)^2 S_{OO} + (\rho_F - \rho_W)^2 S_{FF} + (\rho_P - \rho_W)^2 S_{PP} \\
+ (\rho_O - \rho_W)(\rho_F - \rho_W)S_{OF} + (\rho_F - \rho_W)(\rho_P - \rho_W)S_{FP} \\
+ (\rho_O - \rho_W)(\rho_P - \rho_W)S_{OP}
\]

(21)

Again, incompressibility is assumed for this expression. The equation 21 is expressed in this way that water is the matrix component; i.e. it is present at each position where no oil, no film and no polymer is found. The first three terms are already explained by the Figure 9. The bulk contrast scattering is expressed by \( S_{OO}(Q) = |\tilde{\phi}_O(Q)|^2 \), which is given by the Fourier transformation of the local oil concentration. The film contrast scattering is \( S_{FF} \), and the polymer contrast scattering is \( S_{PP} \). The three latter terms hardly can be depicted in a simple way. Since the scattering intensity is a quadrature of the scattering amplitude all cross terms between different components occur as well. In this manner the oil-film scattering is given by \( S_{OF}(Q) = 2\Re(\tilde{\phi}_O(Q)\tilde{\phi}_F(Q)) \). The product of the two Fourier transformations is a convolution in real space, i.e. \( S_{OF}(Q) = 2\Re(\int \phi_O(R-r)\phi_F(R+r) \exp(IQR)d^3Rd^3r) \). This means that the cross terms represent correlations between the components.

Practically, the six scattering functions are determined by measurements with many different contrasts. The three major contrasts (bulk, film and polymer) are selected plus a series of many contrasts around the polymer contrast. In this way, usually 15 to 20 scattering intensities are measured, which overdetermines the equation system and leads to a much higher accuracy for the six scattering functions. The equation system of eq. 21 can be understood as \( d\vec{\Sigma}/d\Omega = \Delta\rho \vec{S} \). The measured intensities are many more than the to be determined scattering functions, and so the matrix \( \Delta\rho \) is non-quadratic. When solving for the scattering functions this matrix \( \Delta\rho \) has to be inverted formally by the Singular Value Decomposition method and one obtains \( \vec{S} = \Delta\rho^{-1}d\vec{\Sigma}/d\Omega \).

An example for the polymer-film scattering function is shown in Figure 10. It describes the valuable information about the relative position of the polymer with respect to the film. So the pure polymer and the pure film scattering do not provide this information. As indicated by the solid line, this scattering can be described by a planar wall which is decorated by polymer in a mushroom conformation.

The bulk contrast scattering also reveals valuable information about the domain structure. An example for the scattering is shown in Figure 11. The macroscopic cross section can be described by the Teubner-Strey theory which bases on a Ginzburg-Landau approach. This approach considers long wavelength fluctuations of the oil and water domains. The final formula reads:
\[ \frac{d\Sigma}{d\Omega}(Q) = \frac{8\pi \phi_W (1 - \phi_W)/\xi}{((2\pi/d)^2 + \xi^{-2})^2 - 2((2\pi/d)^2 - \xi^{-2})Q^2 + Q^4} \]  

(22)

The denominator contains the total fraction of water \( \phi_W \). Much more interesting are the two structural parameters \( \xi \) and \( d \) which are obtained as fitting parameters from the measurement. The domain size \( d \) is to be understood as the average distance between two consecutive water parts. The correlation length \( \xi \) is a measure for the regularity of the alternating domains. As indicated in Figure 11 the peak position is mainly given by the domain size \( d \), and the peak width is mainly given by the correlation length \( \xi \). In comparison to diblock copolymers the forward scattering of microemulsions is clearly non-zero. Thermal fluctuations of oil and water can take place easily on large length scales while for the diblock copolymer the bond between the blocks makes sure that the polymer looks homogenous on large length scales.

The Gaussian random field theory allows for the calculation of the bending rigidity \( \kappa/(k_B T) = 0.85\xi/d \) from the structural parameters \( \xi \) and \( d \). This microscopic modulus depends linearly on the polymer content according to advanced theories \cite{31}. The other important modulus of the microscopic theory by Helfrich \cite{32} is the saddle splay modulus \( \Pi \) which has a very similar dependence on the polymer content. While the bending rigidity is measured quite directly, the saddle splay modulus is measured indirectly. At the minimum surfactant concentration \( \Psi \approx \gamma_{\text{min}} \) (fish tail point) the saddle splay modulus is a small constant. Relative changes of the surfactant concentration are related to changes of \( \Pi \) by the spatial renormalization (detailed information is discussed in reference \cite{32}). The bottom line is that the two functions \( \ln \Psi \) and \( \kappa \) vary in a similar manner as shown in Figure 12. Both variables are plotted as a function of the scaled polymer concentration \( \sigma R_{ee}^2 \) where \( \sigma \) is the polymer grafting density and \( R_{ee} \) is the typical polymer size. The minimum surfactant concentration \( \Psi \) decreases with the polymer amount which means that the amphiphile becomes more efficient. In a similar manner the bending rigidity \( \kappa \) increases. More rigid membranes allow to form larger structures with a better surface to volume ratio. Both experimental magnitudes are connected on the level of the Helfrich model by Lipowsky’s theory about polymers. The speciality of Figure 12 is that these variables were measured for sticker polymers which consist of a short hydrophobic sticker (C\(_{10}\)) and a long hydrophilic polymer chain (made of ethylene oxide). These stickers introduce some unsymmetry in comparison to diblock copolymers. On the one hand they change the preferred curvature of the membrane; on the other hand they work as well as efficiency boosters as diblock copolymers. The major advantage of sticker polymers is that they are cheaper to produce and they are well water soluble. Many applications need a quick solvation of powder components.

### 3.6 Summary on Polymers and Microemulsions

In summary we have learned about amphiphilic diblock copolymers that they enhance the efficiency of surfactants dramatically. The polymer decorates the membrane and makes the membrane more rigid. This rigidity allows to form larger structures with a better surface to volume ratio. The newly found sticker polymers have advantages in applications. The ongoing re-
search considers also a larger variety of polymer architectures which should allow for tailored properties of microemulsion.

In general we have learned about soft matter problems that they are close to applications. The major question is how to reach for tailor made properties. These questions can only be addressed by basic research knowledge. One important tool of basic research is the small angle scattering method. While x-rays are available by small machines in the basement and with large intensities by synchrotrons, neutrons are accessed through reactors and spallation sources. Reactors provide a continuously high intensity which is important for small angle neutron scattering diffractometers. Spallation sources work with extremely high intensity neutron pulses. These pulses can be used for SANS diffractometers in combination with a time of flight analysis. The major advantage of neutrons against x-rays is the free choice of contrasts which is important for multiple component systems. Especially in the near future basic research will be expanded to multiple component systems in order to mimick more complex functions of biological systems for instance. The common understanding of bio-physical principles is another major task for soft matter research which is about to expand strongly.
Fig. 5: On the left a typical phase diagram of homopolymer blends is found. Usually, the temperature is measured as a function of the composition. High temperatures lead to homogenous mixing. The binodal separates the mixing from the metastable region (upper curve), while the spinodal separates the metastable and the unstable region. The point where binodal and spinodal meet is called critical point. Close to the critical point thermal composition fluctuations are strong. The blue arrow indicates a temperature series of the considered experiment. On the right a typical phase diagram of diblock copolymers is shown [14]. On top, the different ordered structures are indicated. Below, the ordered structures are also marked in the phase diagram. The temperature axis ($\Gamma V \propto T^{-1}$) is reverted, while the x-axis shows the volume fraction of the polyisoprene block (chainlength ratio). The lower line is a theoretical spinodal line not supported by any phase transitions.
Fig. 6: The scattering function $S(Q)$ as a function of the scattering vector. On the left the typical scattering of a homopolymer is shown. The sample is a polybutadiene(1,4) / polystyrene blend at 104°C and 500 bar. The peak maximum intensity at $Q = 0$ is the inverse susceptibility. The peak width is inversely proportional to the correlation length $\xi$. On the right the typical scattering of a diblock polymer is shown which is a polyethylene-propylene–poly-dymethylsiloxane at 170°C and 1 bar. The peak maximum is the inverse susceptibility. The peak position is $Q^*$ and the peak width $\Delta Q$ is connected with the reciprocal correlation length $\xi$. 
Fig. 7: The susceptibility as a function of the inverse temperature. On the left the typical temperature dependence of a homopolymer is shown. At high temperatures a linear dependence is found which can be directly connected to mean field theories; at medium temperatures there is a crossover to the lower temperatures where the 3-dimensional Ising behaviour is found. The 3d-Ising critical behaviour is curved, and the critical exponent is 1.24. On the right the critical behaviour of a diblock copolymer is depicted. At higher temperatures the behaviour becomes quite linear, but the extrapolated mean field behaviour is different as shown by the lines in the lower left corner. The whole temperature range is fitted by a function which includes fluctuations [25]. At lower temperatures the phase transition is indicated by a sudden jump of the susceptibility. For different pressures the phase transition and the susceptibilities are different.
Fig. 8: The typical ‘fish’ phase diagram (red): temperature versus surfactant concentration $\gamma$. At low concentrations $\gamma$ there is a three phase coexistence (3) of two excess phases and a microemulsion. At high temperatures there is a two phase region (2) of an excess water phase and a microemulsion. At low temperatures (2) the excess phase is oil rich. At higher concentrations $\gamma$ there is a one phase microemulsion which is considered in this paper. There are also ‘fish tails’ (blue and green) shown with some polymer additive [29]. The polymer amount is measured relatively to the total amphiphile. The decreased need of surfactant is a measure for the dramatically increased efficiency (polymer boosting effect).
Fig. 9: The principal options of contrasts for a four component system, here water, oil, surfactant and polymer. In the bulk contrast the oil domains are mainly visible against water. In the film contrast the surfactant is mainly highlighted against the oil and water domains. The polymer contrast focuses on the polymer alone.
Fig. 10: The polymer-film scattering function as a function of the scattering vector \[Q\]. The fitted function describes a polymer in the presence of a planar wall. The polymer shows a mushroom conformation.

Fig. 11: A typical scattering pattern of a bicontinuous microemulsion. The peak position is connected to the domain spacing \(d\). The peak width is inversely proportional to the correlation length \(\xi\). This kind of data is usually well described by the Teubner-Strey fitting function given in eq. 22.
Fig. 12: The minimum surfactant amount \( \Psi \) as a function of the scaled polymer amount \( \sigma R^2_{cc} \) for microemulsions with increasing amount of a sticker polymer \( C_{12}E_{90} \). The decrease shows that the microemulsion becomes more and more efficient, i.e. the polymer boosting effect is successfully transferred to sticker polymers. On the right the bending rigidity \( \kappa \) is plotted as a function of the scaled polymer amount. The increased bending rigidity explains why larger domain structures with a better surface to volume ratio can be formed. On a microscopic scale both diagrams are related through the Helfrich [32] free energy. The general polymer effect was described by Lipowsky [31].
References


[8] Munich SANS


