

Internal structure of aqueous foams stabilised by surfactants or microgels

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Abstract

Foams are abundant in everyday life in the form of cleaning agents or personal care products. In addition, they play an important role in certain industrial processes like flotation in the mining industry or textile manufacturing. Many foam properties like stability or rheology are governed by their structure. However, the internal structure of foams is difficult to determine experimentally. Optical methods are only able to probe the first few layers of bubbles, because of the large difference in refractive indices of gas and (mostly aqueous) liquid phase. This thesis aims to extend the experimental accessibility of the foam structure.

For this purpose a sample environment enabling small-angle neutron scattering (SANS) experiments with macroscopic foams is designed and constructed. This sample environment allows measuring foams at different drainage stages, controlling the rate of foam formation, temperature and measurement position. In addition, a sample changer for up to three foam cells is included to utilise the full potential of future high brilliance neutron sources like the European Spallation Source (ESS).

In order to extract structural information about the foam from the data, a new model for the description of SANS data from foams is presented. This model is based on an incoherent superposition of reflectivity curves, arising from the foam films, and a small-angle scattering (SAS) contribution arising mainly from the Plateau borders. In addition, a correction factor accounting for the spherical geometry of the foam bubble is introduced. The model is capable of describing the complete scattering curves of a foam stabilised by the standard cationic surfactant tetradecyltrimethylammonium bromide (C_{14} TAB) with different water contents, i.e. drainage states, and provides information about the thickness distribution of liquid films inside the foam.

The validity of the model is tested further by studying foams stabilised by poly(*N*-isopropylacrylamide) (PNIPAM) microgels (MGs). The macroscopic foam properties in dependence of the cross-linker concentration of the MGs and temperature are investigated as well as the corresponding structuring in single foam films and macroscopic foams. Furthermore, the deformation of MGs inside the foam films is correlated with their elasticity as predicted by the affine network model.

Kurzzusammenfassug

Schäume gibt es im Alltag in Form von Reinigungs- oder Körperpflegeprodukten. Darüber hinaus spielen sie eine wichtige Rolle in industriellen Anwendungen wie der Flotation in der Bergbauindustrie oder in der Textilverarbeitung. Viele Schaumeigenschaften wie ihre Stabilität oder Fließfähigkeit werden von der Schaumstruktur bestimmt. Allerdings ist die innere Struktur von Schäumen ist experimentell schwer zu bestimmen. Aufgrund der stark verschiedenen Brechungsindices der gasförmigen und (meist wässrigen) flüssigen Phase, sind optische Methoden nur dazu geeignet die ersten wenigen Blasenschichten eines makroskopischen Schaumes zu untersuchen. Das Ziel dieser Arbeit ist es die experimentelle Zugänglichkeit zur inneren Struktur von Schäumen zu verbessern.

Zu diesem Zweck wird eine Probenumgebung für die Untersuchung von Schäumen mittels Neutronenkleinwinkelstreuung (SANS) entwickelt und konstruiert. Diese Probenumgebung ermöglicht es Schäume in unterschiedlichen Drainagestadien zu untersuchen und erlaubt die Kontrolle der Schaumbildungsrate, Temperatur und Messposition. Um das volle Potential zukünftiger Neutronenquellen mit hoher Brillanz wie der Europäischen Spallationsquelle (ESS) ausschöpfen zu können, wird außerdem ein Probenwechsler für bis zu drei Schaumzellen implementiert.

Um strukturelle Informationen aus den Daten zu gewinnen, wird ein neues Modell für die Auswertung von SANS Daten von Schäumen entwickelt und vorgestellt. Das Modell beruht auf der inkohärenten Überlagerung von Reflektivitätskurven einzelner Schaumfilme und einem Kleinwinkelstreuanteil, der hauptsächlich von den Plateau-Kanten herrührt. Um die kugelförmigen Schaumblasen korrekt zu beschreiben, wird ein geometrischer Korrekturterm eingeführt. Das Modell ist in der Lage die kompletten Streukurven eines Schaumes, welcher mit dem kationischen Standardtensid Tetradecyltrimethylammoniumbromid (C_{14} TAB) stabilisiert ist, mit verschiedenen Wassergehalten, das heißt Drainagestadien, zu beschreiben und liefert Informationen über die Dickenverteilung der Schaumfilme.

Die Validität des Models wird außerdem an Schäumen, welche von poly(*N*-isopropylacrylamid) (PNIPAM) Mikrogelen (MGs) stabilisiert sind, getestet. Die makroskopischen Schaumeigenschaften in Abhängigkeit des Quervernetzergehalts und der Temperatur werden studiert und die Strukturierung der MGs in einzelnen Schaumfilmen und in makroskopischen Schäumen untersucht. Schließlich wird die Verformbarkeit der MGs in den Schaumfilmen mit dem affinen Netzwerkmodell korreliert.

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List of abbreviations

AFM	Atomic force microscopy
BIS	N, N'-methylenebisacrylamide
C ₁₄ TAB	Tetradecyltrimethylammonium bromide
CBF	Common black film
cmc	critical micelle concentration
DLS	Dynamic light scattering
ESS	European spallation source
LCST	Lower critical solution temperature
MG	Microgel
NBF	Newton black film
PB	Plateau Border
PNIPAM	poly(N-isopropylacrylamide)
SANS	Small-angle neutron scattering
SDS	Sodium dodecyl sulfate
SE	Sample environment
SLD	Scattering length density
TFPB	Thin film pressure balance
vdW	van der Waals
VPTT	Volume phase transition temperature

List of symbols

а	Area
Α	Reflectivity scaling factor
В	SAS scaling factor
С	Background
С	Concentration
d	Foam film thickness
Ε	Elastic modulus
8	Gravitational acceleration
h	Foam height
Ι	Scattered intensity
\vec{k}	Wave vector
N _{chain}	Number of polymer chains
Р	Pressure
9	Wave vector transfer
r _B	Bubble radius
R	Reflected intensity
R_h	Hydrodynamic radius

Т	Temperature		
t	Time		
<i>t</i> _{1/2}	Foam half life time		
V	Volume		
w	Mass fraction		
β	Small-angle scattering exponent		
γ	Surface tension		
δ	Interfacial roughness		
κ^{-1}	Debye length		
λ	Wavelength		
ν	Poisson ratio		
П	Disjoining pressure		
$\Pi_{\rm el}$	Elastic contribution to the osmotic pressure according to the Flory-		
	Rehner theory		
$\Phi_{\rm s}$	Solid volume fraction		
Φ_1	Liquid volume fraction		
$\Phi_{\rm g}$	Gas volume fraction		
$\Phi_{g,crit}$	Critical gas volume fraction		
ρ	Scattering length density		
σ	Film thickness standard deviation		
θ	Scattering angle		
ζ	Zeta-potential		

List of physical constants

π	$= 3.14159265359\dots$
N_A	$= 6.02214 \times 10^{23}\mathrm{mol}^{-1}$
k_B	$= 1.38065 \times 10^{-23}\mathrm{J}\mathrm{K}^{-1}$
е	$= 1.602176 \times 10^{-19}\mathrm{C}$
ϵ_0	$= 8.85419 \times 10^{-12} \text{ CV}^{-1} \text{ m}^{-1}$
	π N_A k_B e ϵ_0

Non-essential and empirical parameters are not included

1 Introduction

Foams fascinate humans since centuries. According to the ancient Greek poet Hesiod, the name of the Greek goddess Aphrodite originates from $d\phi\rho\phi\varsigma$ ("aphrós"), which means sea-foam and implies that the Greek goddess of beauty is born from foam [1]. The fundamental building blocks of foams, namely soap bubbles, are also a popular theme in art. Originally, soap bubbles were used in baroque paintings, mainly by Dutch artists, as a metaphor for the human life's beautiful but fleeting nature. Over the course of time the interpretation moved from a metaphor for perishability towards the representation of joy and curiosity [2].



Figure 1.1: (a) Cupid Blowing Soap Bubbles by Rembrandt van Rijn, 1634, via Wikimedia Commons. (b) Soap Bubbles by Jean Siméon Chardin, 1733-34, via Wikimedia Commons.

Figure 1.1 shows paintings representing the different symbolisms of soap bubbles. *Cupid Blowing Soap Bubbles* by Rembrandt van Rijn from 1634 (Figure 1.1 (**a**)) is an example for the baroque symbol laden style, while *Soap Bubbles* by Jean Siméon Chardin from 1733-34 (Figure 1.1 (**b**)) focuses more on the act of blowing foam bubbles, the bubble itself and the joy associated with its observation. The scientific interest in soap bubbles grew at a similar time as their emergence in paintings. It is even hypothesised that the popularity of soap bubbles in art stimulated scientists to study the phenomena associated with them [3]. Robert Hooke and Isaac Newton were fascinated by soap bubbles and the colours of refracted light. Newton wrote in his Opticks in 1704:

"If a Bubble be blown with Water first made tenacious by dissolving a little Soap in it, 'tis a common Observation, that after a while it will appear tinged with a great variety of Colours. [...] Because the Colours of these Bubbles were more extended and lively than those of the Air thinn'd between two Glasses, and so more easy to be distinguish'd, I shall here give you a farther description of their order, as they were observ'd in viewing them by Reflexion of the Skies when of a white Colour, whilst a black substance was placed behind the Bubble. And they were these, red, blue; red, blue; red, blue; red, green; red, yellow, green, blue, purple; red, yellow, green, blue, violet; red, yellow, white, blue, black." [4]

A full circle of mutual inspiration between art and science can be drawn, considering the painting *Newton's Discovery of the Refraction of Light* by Pelagio Palagi from 1827 (see Figure 1.2).



Figure 1.2: *Newton's Discovery of the Refraction of Light* by Pelagio Palagi, 1827, via Wikimedia Commons.

Over the years several more scientists made notable contributions to the understanding of foams. Joseph Plateau studied the structure of polyhedral foams in great detail and derived physical principles governing the foam's geometry [5]. On a similar note around 1887, William Thomson, Lord Kelvin was interested in the problem of the division of space into equal polyhedral foam bubbles or cells with minimal overall surface area [6, 7]. The structure he found, the so-called "Kelvin cell", was a tetradecahedron, which can be packed into a body-centred cubic structure to fill all space [8]. Investigating the structure of foams from a fundamental perspective remains an active research field even today. For more than 100 years, the Kelvin cell remained the best solution to the Kelvin problem, until Weaire and Phelan found a structure with a 0.3 % lower surface area than Kelvin's structure in 1994 [9]. The experimental realisation of a liquid foam adopting the Kelvin structure even took until the early 2000s [10–12] and the Weaire-Phelan structure was experimentally observed for the first time only in 2012 [13]. In addition to these and many other fundamental studies, foams are also abundant in every day life in the form of food, personal care products or household cleaning agents [14, 15]. Furthermore, foams are also important for industrial processes like flotation in the mining industry or textile manufacturing [16, 17].

This thesis aims to contribute to the field of experimental determination of the structure of macroscopic aqueous foams. Specifically, by using small-angle neutron scattering (SANS).

Chapter 2 provides a brief scientific background. Here, foams are introduced in detail by discussing the different types of structures they adopt and their (in-)stability. In addition, an introduction to microgels (MGs), which serve as stabilisers for some of the studied foams, is provided. After covering the theoretical concepts like the affine network model and the Flory-Rehner theory, poly(*N*-isopropylacrylamide) (PNIPAM) based MGs are introduced, which is the specific type of MGs used in this thesis.

The experiments conducted in this thesis are described in detail in Chapter 3 together with a short introduction to the measurement principles of each method.

In Chapter 4 the design and construction of a sample environment (SE) for the investigation of macroscopic aqueous foams by SANS for future implementation at the European spallation source (ESS) is described. The SE allows measuring foams at different drainage states and the control of the rate of foam formation, temperature and measurement position. The compatibility with ESS standards is tested and SANS test measurements with a reference system are performed. Because of the complex foam structure, the analysis of SANS data from foams was for a long time limited to fitting of single peak positions or feature mimicking. In Chapter 5 a new model for the description of SANS from foams is presented. The model takes into account the geometry of the foam bubbles and is based on an incoherent superposition of reflectivity curves, arising from the foam films, and a small-angle scattering (SAS) contribution from the Plateau borders. The model is capable of describing the complete scattering curves of a foam stabilised by the standard cationic surfactant tetradecyltrimethylammonium bromide (C₁₄TAB) with different water contents, i.e. drainage states, and provides information about the thickness distribution of liquid films inside the foam.

In Chapter 6 thermoresponsive, aqueous foams stabilised by poly(*N*-isopropylacrylamide) (PNIPAM) microgels (MGs) with varying cross-linker content are studied. The structure of these foams is elucidated by a combination of SANS and measurements of individual foam films in a thin film pressure balance (TFPB). The inhomogeneous foam films consist of thin, MG depleted zones interspersed in a network-like structure of thicker, MG-laden areas. The thickness of the MG-laden areas and the elastic modulus, measured by atomic force microscopy (AFM), both are correlated with the network elasticity of the MGs, predicted by the affine network model.

Chapter 7 concludes the thesis by summarising all relevant results and discussing potential future perspectives in the research field.

2 Scientific background

2.1 Foams

This section provides a general overview of foams. First the different types of foams, categorised by their continuous phase and stabiliser, are discussed. After that, the hierarchical structure of foams is introduced and experimental approaches to access this structure are presented. The main mechanisms involved in foam decay are explained.

2.1.1 Types of foams

The term "foam" refers to a colloidal dispersion in which the dispersed phase is gaseous. In contrast to solutions, in which a solute is distributed in a solvent on a molecular level, colloidal dispersions consist of small entities with sizes in the range of 1 nm to several µm (dispersed phase) in a continuous phase [18–20]. The scale of the dispersed phase is also referred to as the mesoscopic scale, as it's dimensions lie between the atomic and macroscopic worlds. For simplicity colloidal dispersions are called dispersions in this thesis. The terminology of dispersions depends on the state of matter of the dispersed and continuous phase. Table 2.1 summarises the different types of dispersions and the corresponding terminology.

As the name suggests, solid foams are characterised by a solid continuous phase, which can be made from polymers (e.g. styrofoam), metals or complex mixtures in the case of soufflé, angel cake or bread. Solid foams are used in many practical applications like light weight construction or insulation, because of their extremely low density and their low thermal conductivity. Since the continuous phase is solid and provides structural integrity, these foams generally behave like solids on a macroscopic scale. Their

Dispersed	Continuous	Terminology	Examples
phase	phase		
Gas	Liquid	Foam	Foam on drinks, shaving foam
	Solid	Solid foam	Styrofoam, soufflé
Liquid	Gas	Aerosol	Clouds, fog, hairspray
	Liquid	Emulsion	Milk, mayonnaise, skin creams
	Solid	Solid emulsion	Butter, bituminous road paving
Solid	Gas	Aerosol	Smoke, dust
	Liquid	Sol	Ink, dispersion paint
	Solid	Solid suspension	Concrete, ruby glass

Table 2.1: Different types of colloidal dispersions with the corresponding terminology and examples. Adapted from [19, 20].

elastic modulus roughly scales as $\Phi_s^{3/2}$ with the volume fraction of the solid phase Φ_s . Since Φ_s is typically in the range of a few percent, the elastic moduli of solid foams are around two orders of magnitude lower then the ones of the corresponding homogeneous solid [21]. Liquid foams, which have a liquid continuous phase are commonly also simply called foams. They are the kind of material which typically comes to mind when hearing the term "foam". Liquid foams can display properties of solids, liquids and gases, depending on parameters like the liquid volume fraction, the viscosity of the liquid phase and the bubble size distribution [21, 22]. There are examples of liquid foams with a non-aqueous continuous phase, but up to now they are scarcely studied [23]. The vast majority of liquid foams consist of an aqueous continuous phase. As already observed by Newton in the quote given in Chapter 1, bubbles purely made from water are not stable and the same principle applies for foams with a neat aqueous phase. Consequently, aqueous foams can be subdivided further by the stabilising or foaming agent used. Foams are most commonly stabilised by surfactants but can also be stabilised by solid particles [24, 25], proteins [26-28] or polymer/surfactant mixtures [29, 30].

2.1.2 The structure of foams

Being a dispersion, the properties and structure of a foam depend on its liquid volume fraction Φ_1 . Since foams consist of two phases, Φ_1 is linked to the gas volume fraction

 Φ_{g} by:

$$\Phi_{\rm l} = 1 - \Phi_{\rm g} \tag{2.1}$$

The critical gas volume fraction $\Phi_{g,crit}$ is defined as the maximum Φ_g where the foam bubbles are still spherical. Further increasing Φ_g requires the foam bubbles to deform into polyhedral shapes [21]. In the ideal case of perfectly ordered monodisperse bubbles, $\Phi_{g,crit}$ is the packing efficiency of a close-packing of equally sized spheres and therefore \approx 74%. For the more practical case of polydisperse bubbles, $\Phi_{g,crit}$ is higher, but since in this case the bubble size distribution has a large impact, no exact value can be given for $\Phi_{g,crit}$.

The liquid volume fraction Φ_l can vary from below 1%, where the foam is then called a dry foam to around 35% for wet foams [22]. The exact transition point from a wet to a dry foam is hard to quantify. Some authors define dry foams having $\Phi_l < 5\%$ and wet foams having $\Phi_l > 15\%$ [31]. Sometimes $\Phi_{g,crit}$ is used as the transition point between wet and dry foams, but since its value is hard to quantify for most foams, the terminology of "wet" and "dry" foams is mostly used by experimenters to communicate the assumed shape of the foam bubbles.



Figure 2.1: Illustration of the structural motifs in foams on different length scales.

The structure of the liquid phase of foams is hierarchical with several structural motifs

on different length scales. The smallest building blocks of this network are foam films, which typically have a thickness of several 10 nm. These are the liquid films which separate two bubbles. The connections between three foam films are called Plateau Borders (PBs). Typically, PBs have thicknesses of several 10 μ m [32, 33]. Their length is coupled to the foam bubble diameter, which ranges from several μ m to cm depending on the drainage state and foaming technique [34]. The intersection of PBs is called a node [35].

Figure 2.1 illustrates the structural motifs of foams on different length scales. For dry foams ($\Phi_l < 5$ %) the geometry of the foam structure is very well described by Plateau's laws, first formulated by Plateau in 1873 [5, 21, 31]:

- Only three foam films can intersect at a time and must do so symmetrically under an angle of 120°. The channel they form is called a PB.
- Four such PBs intersect symmetrically under the tetrahedral angle $\approx 109.5^\circ$ and form a node.

2.1.3 Foamability and (in-)stability of foams

The fundamental process in foam production is the formation of gas bubbles within the foaming liquid. Depending on the nature of this bubble formation, foaming techniques can be divided into physical and chemical foaming. Physical foaming includes bubbling or sparging gas through a nozzle or a porous plug, shaking, stirring or the nucleation of bubbles in a supersaturated solution. In the case of chemical foaming, gas is formed via an (electro-)chemical reaction and includes foaming using fizzy drink tablets, baking powder or electrolysis [22, 34].

The tendency of a liquid to form a foam is called "foamability" and is measured as the foam volume or height (in a container with defined geometry) immediately after a specific foaming procedure [21]. Since the foamability depends on the foaming procedure, various standardised foam tests are defined. Examples for these tests are:

• The "Bikerman test", in which a fixed volume of gas is sparged into the foaming solution [21].

- The "Ross-Miles test", which involves pouring a certain amount of foaming solution from a defined height into a reservoir containing a defined volume of the foaming solution [22].
- The "Bartsch test", in which the foaming solution is shaken for a certain amount of time in a container of defined geometry [36].

Because of its large surface area and the resulting large surface energy, a liquid foam is an intrinsically unstable system [31]. This highly energetic state can relax via various paths. The main mechanisms are coarsening (diffusion of gas between bubbles) [37], gravitational drainage [38] and coalescence (merging of bubbles or breakage by rupturing films) [39]. The origin of coarsening lies in the pressure difference between the foam bubbles [21, 40]. The pressure difference ΔP between a foam bubble and it's surrounding is given by the Laplace pressure [21]

$$\Delta P = \frac{2\gamma}{r_B}.\tag{2.2}$$

Here, γ is the surface tension of the liquid surrounding a bubble with radius r_B . Equation 2.2 indicates that the pressure inside smaller bubbles is higher than in larger bubbles, which results in a gas diffusion from smaller to larger bubbles. A similar phenomenon is observed in materials with well separated bubbles or droplets. In these cases this process is called Ostwald ripening, while in cellular materials like foams, the term coarsening is more common [40]. Coarsening is influenced by a multitude of parameters like the bubble geometry, the inter-bubble contact area, the composition of the foaming liquid and the type of gas used. Regarding the gas type, coarsening is mainly controlled by the solubility of the gas in the liquid phase. For two otherwise identical foams made with N_2 and C_2F_6 gas, respectively, the difference in coarsening speed was found to be equal to the difference in gas solubility [40]. This behaviour has some interesting implications for the use of gas mixtures in foams, as the solubility of a gas in a liquid given by Henry's law is governed by its partial pressure in the gas phase. When mixing a gas with high solubility with a gas with low solubility, the coalescence is initially governed by a fast equilibration of the partial pressures of the highly soluble gas. In the following the coalescence slows down considerably and is nearly the same as for a foam with a pure gas phase of the low solubility gas [41, 42].

The drainage in liquid foams is governed by gravity. There are a few experimental studies of foam drainage in microgravity environments like the International Space

Station (ISS) or on parabolic flights. These experiments showed a drastic increase in foam stability under these conditions and even the existence of stable foams, which are extremely unstable under normal earth gravity conditions [43, 44]. Since most of the liquid in a foam is located in the PBs, drainage is typically seen and modelled as the flow of liquid through the network formed by the PBs [21, 40]. This flow is driven by capillarity and gravity and is counteracted by viscous damping [35]. Considering a foam column, these contributions lead to the development of a vertical liquid volume fraction profile over time. With zones of lower Φ_1 (driver foams) at the top and zones of higher Φ_1 (wetter foams) at the bottom of the column.

The ultimate fate of a soap bubble or a foam bubble is to rupture. This process is called coalescence. Before coalescence can happen in a foam, the foam film thickness needs to be reduced to a certain threshold value by drainage [39]. Once this threshold thickness is reached, the foam film is governed by forces between its two air/water interfaces, which give rise to the so-called disjoining pressure II. A detailed description of these forces is provided in Chapter 2.1.4. In order for the foam film to rupture, this stabilising pressure needs to be overcome. This can either happen by further drainage and reduction of the film thickness below a critical value or by local fluctuations of the film thickness due to impurities or local perturbations, which puncture the film [21]. In this context a higher surface elasticity of the foam film was found to increase the stability, as a higher film elasticity increases the stability against local perturbations and puncture processes [22]. In general, coalescence is rather poorly understood, as it is always related to other processes like drainage, heavily depends on the composition of the system and cannot be studied isolated in a real foam [21, 45].

2.1.4 Foam films

In order to improve the understanding of coalescence, the stability of the liquid foam films separating two bubbles must be considered in greater detail. After foam formation and an initial drainage stage, the forces between the two air/water interfaces of the foam film come into play [46]. These interfacial forces include van der Waals, electrostatic, and steric forces and give rise to the so-called disjoining pressure Π , which is expressed as the sum of these contributions [16, 47]

$$\Pi = \Pi_{\text{elec}} + \Pi_{\text{vdW}} + \Pi_{\text{steric}}.$$
(2.3)

Figure 2.2 shows an illustration of a typical curve of Π in dependence of the film thickness *d*, resulting from these contributions. In general two types of foam films are distinguished. On the one hand, the thicker common black film (CBF, $d \approx 10-100$ nm), which is mainly stabilised by electrostatic interactions. And on the other hand the thinner Newton black film (NBF, $d \leq 10$ nm), which is governed by steric forces [47].



Figure 2.2: Schematic representation of the disjoining pressure Π as a function of the film thickness *d* (solid line). The main contributions to Π are displayed as dashed lines and consist of electrostatic (Π_{elec} , red), steric (Π_{steric} , blue) and van der Waals (Π_{vdW} , green) contributions. Common black films (CBFs) with a thickness of $d \approx 10-100$ nm are mainly stabilised by electrostatic forces. Newton black films (NBFs) have a thickness of $d \leq 10$ nm and are stabilised by steric interactions. Figure adapted from [46].

After the initial drainage stage, Π is counteracting the pressure difference between the gas and liquid phase arising from the bubble curvature and the resulting Laplace pressure ΔP (see Equation 2.2). When Π and ΔP are equal, a quasi-static situation is reached [46]. This allows to determine Π when the pressure around the foam film is known.

As real foam bubbles have irregular shapes and are constantly evolving, ΔP is very difficult to determine in a real foam. Disjoining pressure isotherms $\Pi(d)$ are therefore

typically measured using a thin film pressure balance (TFPB). Here, a single foam film in an appropriate holder is placed in a pressurised chamber and the film thickness is measured by light interferometry. A detailed description of this method is given in Chapter 3.5.

2.1.5 Probing the structure of foams

The complex and evolving structure of foams and the large difference in refractive indices of gas and (aqueous) liquid phases limits usage of light microscopy to very dry foams with large bubbles [48, 49]. A more powerful technique for the investigation of the 3-dimensional structure of foams is X-ray tomography, which allows a detailed analysis of bubble size and shape inside the foam [50, 51]. However, a determination of film thicknesses inside the foam is not possible with this method. Moreover, the time required to record such a tomographic image ranged from a few minutes to a few hours, which limits this technique to rather stable foams, which don't change their structure during this time frame. The dynamics inside of nanoparticle stabilised foams can be studied by diffusing wave spectroscopy [52, 53]. Here, two dynamic processes were observed: a fast one caused by the nanoparticle diffusion and a slow one reflecting the foam dynamics.

Investigations regarding foam films were for a long time limited to experiments with single, horizontal foam films in a pressurized chamber and interferometric analysis of the thickness. The initial experiments performed by Scheludko and Exerowa with the so-called Scheludko-cell, which consists of a glass ring in which a liquid film is generated [54–56]. Numerous studies were performed with similar experimental setups, referred to as thin film pressure balances (TFPBs), with a variety of systems [46, 57–63]. A detailed description of this experiment is provided in Chapter 3.5. Despite the valuable insight these studies provided regarding the forces in liquid films, the results often are not consistent with macroscopic foam properties like foam stability. Probably because a single horizontal liquid film is an oversimplification of the complex structure of foams [64].

In this thesis small-angle neutron scattering (SANS) is used to elucidate the internal structure of foams, the literature regarding this characterisation approach is discussed in greater detail. In principle SANS has a similar drawback as X-ray tomography, as the acquisition time for a SANS curve from foams is typically in the range of 5 - 15 min. However, this time will be drastically reduced with new highly brilliant neutron sources like the European Spallation Source (ESS), which is currently under construction in Lund, Sweden.

Axelos and Boué were the first to use SANS to study liquid foams [65]. In general, the foam film thickness inside macroscopic foams can be measured by SANS. There is however, no unified approach to extract structural information about foams from SANS data, mainly because of the complex foam structure [66]. The state of the art of SANS from foams and the corresponding data analysis is discussed in detail in Chapter 5.1.

2.2 Microgels

This section introduces polymer gels, especially microgels (MGs) and fundamental theoretical approaches to quantify their elasticities and swelling behaviour. In addition, the extensively studied system of MGs made from poly(*N*-isopropylacrylamide) (PNIPAM) is discussed in detail and an overview about PNIPAM MGs adsorbed at the air/water interface and in foams is provided.



Figure 2.3: 2D illustration of a polymer network.

The term "gel" refers to a three-dimensional polymer network containing a solvent. If

the solvent is water the term "hydrogel" is used [67]. As the term indicates, a MG is a micron-sized gel particle. Most MGs are synthesised by radical precipitation polymerisation of monomer and cross-linker molecules bearing one (monomer) or multiple (cross-linker) vinyl groups [68, 69]. Through controlling the ratio between monomer and cross-linker during the synthesis, the density of the polymer network and consequently the stiffness of MGs can be tuned. MGs combine properties of rigid colloids (e.g. nanoparticles, globular proteins) and regular polymers [70, 71]. Depending on the monomer, MGs can also be surface active (meaning that it is energetically favourable for them to adsorb at an interface), which also makes them similar to surfactants.



Figure 2.4: Microgels combine properties of different systems studied in colloidal science. Figure adapted from [71].

Given their small size, MGs were shown to react very fast to external stimuli like changes in the solvent composition [72] or pressure [73]. By using different monomers, introducing co-monomers, or incorporating nanoparticles, a broad range of stimuli responsive MGs can be obtained. These external stimuli include temperature [74–77],

pH [78–80], ionic strength [81–83], light [84, 85], electrochemical potentials [86] and magnetic fields [87].

This variety of MGs with various properties inspired the investigation of several practical applications of MGs in biocatalysis [88, 89], biosensors [90, 91], drug delivery [92, 93], tissue engineering [94, 95] or as nano-actuators [96–100].

2.2.1 Elasticity of gels

One of the most interesting properties of gels is their large elastic deformability. When applying a force, some polymer gels can be stretched to increase their length by a factor of 10 and recover their original shape once the force is nullified [67]. As gels only consist of solvent molecules and the polymer network, it is natural to assume that the elasticity of gels is reflected in the structure of the polymer network [67, 101]. The first model to describe the elasticity of polymer networks is the affine network model proposed by Kuhn [102]. The main assumption of this model is that the relative deformation of the whole gel is the same as the relative deformation of the individual polymer chains in the network.



Figure 2.5: Illustration of the deformation of an affine polymer network. Figure adapted from [67, 101].

Assuming a cuboid polymer network particle with the initial side lengths $L_{x,0}$, $L_{y,0}$ and $L_{z,0}$ is deformed by the factors λ_x , λ_y and λ_z in the directions x, y and z, the final side lengths then are

$$L_x = \lambda_x L_{x,0}, \quad L_y = \lambda_y L_{y,0} \quad \text{and} \quad L_z = \lambda_z L_{z,0}.$$
 (2.4)

Considering an individual polymer chain inside this gel with an initial end-to-end vector $\vec{r_0} = (r_{x,0}, r_{y,0}, r_{z,0})$, the affine deformation results in a final end-to-end vector \vec{r} of

$$\vec{r} = \begin{pmatrix} \lambda_x r_{x,0} \\ \lambda_y r_{y,0} \\ \lambda_z r_{z,0} \end{pmatrix}.$$
(2.5)

The affine deformation is also illustrated in Figure 2.5.

The entropy of an ideal polymer chain with *N* monomers of length *a* and an end-to-end vector \vec{r} is given by

$$S(N,\vec{r}) = -\frac{3k_B\vec{r}^2}{2Na^2} + S(N,0).$$
(2.6)

The change in entropy ΔS upon deformation of this chain is given by the difference between the final $(S(N, \vec{r}))$ and initial $(S(N, \vec{r_0}))$ state

$$\begin{split} \Delta S &= S(N, \vec{r}) - S(N, \vec{r_0}) \\ &= -\frac{3k_B(\vec{r}^2 - \vec{r_0}^2)}{2Na^2} \\ &= -\frac{3k_B}{2Na^2} \left(\left((\lambda_x r_{x,0})^2 + (\lambda_y r_{y,0})^2 + (\lambda_z r_{z,0})^2 \right) - (r_{x,0}^2 + r_{y,0}^2 + r_{z,0}^2) \right) \\ &= -\frac{3k_B}{2Na^2} \left((\lambda_x^2 - 1)r_{x,0}^2 + (\lambda_y^2 - 1)r_{y,0}^2 + (\lambda_z^2 - 1)r_{z,0}^2 \right). \end{split}$$
(2.7)

Since an ideal and therefore isotropic chain is considered, $r_0^2 = Na^2$. The individual parts of r_0^2 are

$$r_{x,0}^2 = r_{y,0}^2 = r_{z,0}^2 = \frac{Na^2}{3}.$$
(2.8)

This relation simplifies Equation 2.7 to

$$\Delta S = -\frac{k_B}{2} \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 \right).$$
(2.9)

The change in free energy upon deformation is dominated by the entropic term [101]. Neglecting enthalpic contributions, the change in free energy ΔF of a polymer network with a number of individual polymer chains N_{chain} is given by

$$\Delta F = -N_{\text{chain}}T\Delta S = \frac{N_{\text{chain}}k_BT}{2} \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right).$$
(2.10)

The affine network model is an idealised model, based on the assumption of affine deformation of ideal polymer chains in a homogeneous network (i.e. with constant mesh size) without defects. In order to get a more general description of polymer network elasticity, several other models were developed. These include the phantom network [103], the constraint-junction [104–106], Edwards tube [107] or slip-tube [108] model to name a few. The prerequisites for the applicability of each model are still debated, but the polymer volume fraction and heterogeneity of the polymer network were shown to have an influence on which model describes experimental observations best [109, 110].

2.2.2 Flory-Rehner theory

The Flory-Rehner theory is used to describe the equilibrium swelling of polymer networks [111, 112]. In the case of an uncharged gel in a solvent *S*, the overall osmotic pressure Π_o is split up into a mixing contribution Π_{mix} and an elastic contribution Π_{el} . In equilibrium these contribution are balanced, resulting in

$$\Pi_o = \Pi_{\rm mix} + \Pi_{\rm el} = 0. \tag{2.11}$$

The mixing contribution is given by

$$\Pi_{\rm mix} = -\frac{N_{\rm A}k_BT}{v_S} \left(\phi + \ln(1-\phi) + \chi\phi^2\right). \tag{2.12}$$

Here, N_A is Avogadro's constant, v_S is the molar volume of a solvent molecule, ϕ is the polymer volume fraction in the gel and χ is the Flory-Huggins interaction parameter for the interaction between solvent and polymer.

The elastic contribution to swelling is defined as the change in elastic energy upon incorporation of a solvent molecule and defined as

$$\Pi_{\rm el} = -\frac{N_{\rm A}}{v_{\rm S}} \left(\frac{\partial \Delta F_{\rm el}}{\partial n_{\rm S}}\right). \tag{2.13}$$

 $\Delta F_{\rm el}$ is calculated from the affine network model described before.

$$\Delta F_{\rm el} = \frac{N_{\rm chain} k_B T}{2} \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 - \ln(\lambda_x \lambda_y \lambda_z) \right) \tag{2.14}$$

This equation resembles Equation 2.10 with an additional term $(\ln(\lambda_x \lambda_y \lambda_z))$. The origin of this term is the change in entropy due to the rearrangement of polymer chains within the network and was a modification to the affine network model made by Flory [112]. Note that in the original affine network model only the overall entropy change of isolated polymer chains is considered, while inter-chain relations are neglected.

Since the Flory-Rehner theory describes swelling, which is isotropic, the relative deformations in all directions are equal and related to the volume change due to swelling:

$$\lambda_x = \lambda_y = \lambda_z = \lambda = \left(\frac{V}{V_0}\right)^{1/3}$$
(2.15)

Here, V_0 and V are the volume of the unswollen and swollen gel, respectively. In this case Equation 2.14 simplifies to:

$$\Delta F_{\rm el} = \frac{3N_{\rm chain}k_BT}{2} \left(\lambda^2 - 1 - \ln(\lambda)\right) \tag{2.16}$$

Finally, the elastic contribution to the osmotic pressure is given by:

$$\Pi_{\rm el} = \frac{N_{\rm chain} k_B T}{V_0} \left(0.5\lambda^{-3} - \lambda^{-1} \right) \tag{2.17}$$

Using Equation 2.15, Π_{el} can be expressed in terms of the swollen and unswollen size of the gel:

$$\Pi_{\rm el} = \frac{N_{\rm chain} k_B T}{V_0} \left(0.5 \left(\frac{V_0}{V} \right)^3 - \frac{V_0}{V} \right)$$
(2.18)

The Flory-Rehner theory was not only used to describe large polymeric networks but also for the description of the swelling of MGs [113–116].
2.2.3 PNIPAM microgels



Figure 2.6: Illustration of the stimuli-responsive collapse of MGs.

One of the most extensively studied MGs are poly(*N*-isopropylacrylamide) (PNIPAM) MGs, with *N*-isopropylacrylamide (NIPAM) as the monomer and the typical crosslinker *N*,*N*'-methylenebisacrylamide (BIS). PNIPAM MGs are thermoresponsive, as linear PNIPAM has a lower critical solution temperature (LCST) of approximately 32 °C in water [117, 118]. This means that upon increasing the temperature, the completely miscible PNIPAM/water system separates into two phases, a PNIPAM-rich phase and a water phase. An illustration of a phase diagram of a system with a LCST in shown in Figure 2.7.



composition

Figure 2.7: Illustration of a system with a LCST.

The origin of the LCST behaviour of aqueous PNIPAM solutions is a relative weaken-

ing of hydrogen bonds between the polymer and water upon heating [119]. At temperatures below the LCST, a hydration shell of water molecules around the polymer is formed and the polymer is solubilised. The binding of water molecules to the polymer via hydrogen bonds increases the enthalpy of mixing. At the same time, this is entropically unfavourable as the degrees of freedom of bound water molecules are reduced. Upon increasing the temperature, the entropic contribution $T\Delta S$ to the overall free energy dominates, which leads to a breaking of the hydrogen bonds, demixing and ultimately macroscopic phase separation.

PNIPAM MGs collapse when the temperature is increased above the volume phase transition temperature (VPTT) [77]. The mechanism is the same as the one of the LCST behaviour of linear PNIPAM described above. The difference in terminology is due to the fact that the temperature increase does not necessitate a macroscopic phase separation. PNIPAM MGs synthesised using the well-established precipitation polymerisation method [120] have a heterogeneous structure with a densely cross-linked core and a loosely cross-linked shell with dangling polymer strands [76, 121]. This is due to the faster reaction kinetics of BIS in comparison to NIPAM in the reaction mixture [122]. PNIPAM MGs are surface active and spontaneously adsorb to air/water or oil/water interfaces [123–125]. This inspired the fabrication of a range of stimuli-responsive emulsions which can be broken by changing the pH or the temperature [126–130].

2.2.4 PNIPAM microgels at air/water interfaces and in foams

Parts of this section are published in "Stability of aqueous foam films and foams containing polymers: Discrepancies between different length scales" L. Braun, M. Kühnhammer, R. von Klitzing, *Curr. Opin. Colloid Interface Sci.*, **2020**, 50, 101379. doi: 10.1016/j.cocis.2020.08.004 [64].

In Chapter 6 PNIPAM MGs are investigated as foam stabilisers. Therefore, the literature regarding their adsorption at air/water interfaces, their behaviour in foam films and foams is reviewed in greater detail.

Macroscopic air/water interfaces As shown by Zhang and Pelton in a pendent drop experiment, PNIPAM MGs adsorb at the air/water interface and lower the surface

tension of water. The equilibrium surface tension is nearly not affected by the crosslinker concentration or temperature and is 41-48 mN m⁻¹ [123].

Because of their softness, MGs adsorbed at the air/water interface are flattened, adopting a "fried-egg" structure as a consequence of their core-shell morphology [131–133]. The arrangement of MGs on liquid interfaces is mostly studied by lateral pressure isotherms in a Langmuir trough. The lateral pattern formation of the MGs was can be assessed by transferring the layer to a solid substrate via Langmuir-Schäfer deposition and subsequent analysis by atomic force microscopy (AFM) or electron microscopy.

Picard et al. found that MG films at an air/water interface give rise to a lateral pressure at interparticle distances much larger than the bulk diameter [131]. This is a direct proof for the stretching of the MGs after adsorption at a fluid interface. Furthermore, the extent of this deformation is linked to the cross-linker concentration of the MG, where a higher degree of cross-linking leads to less deformation. This can be understood as a balance between the energetically favorable adsorption of the surface active NIPAM chains and the cross-links restricting the degree of deformation of the gel particle. Upon compression on the Langmuir trough the lateral pressure increases, indicating that the MGs interact with each other and don't desorb from the interface. Consequently, the interparticle distance is reduced, the MGs become thicker and form a regular hexagonal lattice, with the lattice spacing being tunable by the compression. In addition, the authors observed that Langmuir films prepared from MGs with a rather high cross-linker content (5 mol% BIS) show a phase transition at quasi-constant lateral pressure between two hexagonal structures with different lattice parameters (see Figure 2.8). This was attributed to the transition from a shell-shell to a core-core contact of the MGs. The fact that this transition was not visible for less cross-linked gels, was explained by the occurrence of capillary forces between the stiff cores, which are weaker for less cross-linked MGs [131].

Rey et al. studied this phase transition in greater detail by varying the MG softness to a larger extent and obtained similar results. In addition, they could show that the onset of this transition is governed by the cross-linker concentration. Stiffer gels adopt a corecore structure at lower surface pressures [132]. This again reflects that the softness of MGs is a crucial parameter for their interfacial ordering and supports the idea of Picard et al. that the formation of the core-core structure is driven by capillary forces, which increase with the core stiffness.



Figure 2.8: AFM images of PNIPAM microgels with 1 mol% (a - d) and 5 mol% BIS (e - h), after transfer on silicon substrate at different surface pressures. (a, e) 0.5 mN m⁻¹, (b, f) 23 mN m⁻¹, (c, g) 27 mN m⁻¹, (d, h) 30 mN m⁻¹. The images are 10 x 10 μm², except image a, which is 20 × 20 μm². Reprinted with permission from [131]. Copyright 2017 American Chemical Society.

Regarding the effect of temperature on adsorbed PNIPAM MGs, Harrer et al. could show by phase contrast AFM of MG films transferred to a solid substrate that the core-shell structure is preserved, even at temperatures above the VPTT [133]. The size of the shell is nearly unaffected at temperatures between 23°C and 57°C, preserving the hexagonal structure. The diameter of the core however decreases by roughly 10% upon heating. This interfacial collapse is much less pronounced than in bulk. This is attributed to the energetically favourable reduction of the surface tension, achieved by increasing the contact area between core and interface and thus preventing complete deswelling of the core. With the area of the shell projected onto the interface being unaffected by temperature, the authors concluded that the MGs rather collapse in the direction normal than parallel to the interface. These findings were confirmed by coarse-grained molecular dynamics simulations [133]. *In situ* ellipsometry also confirmed the collapse normal to the interface and the reduced shrinkage compared to the bulk behaviour [134].

Foam films So far there have only been two studies investigating MG stabilised foam films, both of which investigated the drainage of foam films at a constant pressure [135, 136]. Cohin et al. showed that right after the film formation a dimple is formed.

This dimple has a thickness of least 1.8 µm and drains in a symmetric fashion, which is a characteristic of films with a high surface viscosity. During the drainage process a thinner film nucleates, which has a thickness of 250 nm or 445 nm, depending on whether the reflected light is assigned to the first or second Newton fringe [135]. Keal et al. performed a detailed study on the drainage of MG-laden foam films and investigated the influence of particle concentration and cross-linking density on the film properties. They found that at a particle concentration of 1 wt% the initially formed dimple drains slowly and a film with a thickness of around 1 µm is formed. This thickness was attributed to a bilayer of MG particles inside the foam film. At a MG concentration of 0.1 wt%, film thicknesses were determined to be 340 nm for the particles with 1.5% BIS and 400 nm for the gels with 5% BIS, corresponding to a bridged monolayer of MG particles in the film. The formation of bridges, meaning that a single particle spans across the liquid film and is adsorbed at both air/water interfaces, is heavily influencing the life time of the films, since bridged films are less stable against mechanical disturbances. Another indirect proof for this bi- to monolayer transition is the adhesion between the two interfaces. Adhesion can be studied by reducing the hydrostatic pressure acting on the film to zero and monitoring the re-swelling of the film. At a MG concentration of 1 wt%, the films were not adhesive, whereas considerable adhesion was observed at 0.1 wt%. This, together with the differences in thickness, supports the picture of a bridged monolayer at low concentrations and a multi- or bilayer at high concentrations.

Again, the cross-linking density was identified as a crucial parameter in this system. Films prepared with 5% BIS MGs drained faster and are more likely to form bridges, which in turn led to less stable films overall, compared to the films formed with 1.5% BIS MGs [136].

Foams So far, the properties of macroscopic PNIPAM MG stabilised foams were studied by Maestro et al. and Horiguchi et al. [137, 138]. The latter publication found that foams can be produced from MG dispersions at temperatures below the VPTT, namely 25°C, whereas nearly no foam formation was observed at 60 °C. In addition, a foam produced at temperatures below the VPTT could be rapidly destabilised by exposing the foam to higher temperatures. Furthermore, the authors found that the MG stabilised foams are more stable than foams stabilised by linear PNIPAM polymers, reflecting the effect of the particle architecture on the foam properties [138]. Maestro and

coworkers found similar results, with the foamability and foam stability decreasing at temperatures above the VPTT. In addition, passive microrheology measurements at the single air/water interface were performed, which showed a transition from a solid-like film below to a liquid-like behaviour above the VPTT. This transition was attributed to the collapse of the MGs. The authors suggested that the liquid-like films at higher temperatures should have an increased permeability, due to a lateral collapse of the MGs, which in turn leads to dramatic changes regarding the properties of the macroscopic foam [137]. This interpretation is not consistent with the results obtained for macroscopic air/water interfaces described before, where no lateral collapse of the MGs was observed. Thus, the exact origin of the thermoresponsiveness of PNIPAM MG stabilised foams remains unclear.

3 Experimental section

3.1 Materials

Tetradecyltrimethylammonium bromide (C₁₄TAB, \geq 98%), *N*-isopropylacrylamide (NIPAM, \geq 99%) and *N*,*N'*-methylenebisacrylamide (BIS, \geq 99.5%) were purchased from Sigma-Aldrich (USA). 2,2'-azobis(2-methyl-propanimidamide) dihydrochloride (AAPH, \geq 98%) was purchased from Cayman Chemical Company (USA). D₂O (99.9% D) was purchased from Eurisotop (France). C₁₄TAB was recrystallized three times in acetone with traces of ethanol. All other chemicals were used as received. Deionised H₂O from a MilliQ water purification system (Merck KGaA, Germany) with a specific resistance of 18.2 MΩ cm was used.

3.2 Microgel synthesis



Microgels (MGs) were synthesized by surfactant-free precipitation polymerization (see Figure 3.1) [120]. In a custom-built, double walled reaction vessel equipped with a reflux condenser and stirrer, NIPAM and BIS (total amount 20 mmol with varying NIPAM/BIS ratios, see Table 3.1) were dissolved in 120 mL water. The solution was heated to 80 °C and sparged with nitrogen gas for 1 h. Under constant stirring (1000 rpm) the reaction was initiated by injecting AAPH (33.9 mg, 0.125 mmol) dissolved in 1 mL water into the reaction mixture. After 1.5 h the turbid suspension was cooled down to room temperature and dialysed for 10 days against water with daily water exchange. The cleaned MG suspension was lyophilised for storage.

Name	Cross-linker content	m(NIPAM)	n(NIPAM)	m(BIS)	n(BIS)
	mol%	g	mmol	g	mmol
MG2	2.0	2.218	19.60	0.062	0.40
MG3.5	3.5	2.191	19.36	0.108	0.70
MG5	5.0	2.151	19.01	0.154	1.00
MG7.5	7.5	2.100	18.56	0.232	1.50
MG10	10.0	2.040	18.03	0.309	2.00

Table 3.1: Amounts of NIPAM and BIS used for the synthesis of MGs with varying cross-linker content.

3.3 Small-angle neutron scattering



Figure 3.2: Schematic representation of a SANS experiment. Figure adapted from [139].

Principle Figure 3.2 shows the setup of a typical small-angle neutron scattering (SANS) experiment. An incoming neutron with wave vector $\vec{k_i}$ is scattered by the sample under an angle θ . The scattered wave vector is $\vec{k_s}$. The difference between $\vec{k_s}$ and $\vec{k_i}$

is defined as the momentum transfer q [140]

$$q = |\vec{k_s} - \vec{k_i}|. \tag{3.1}$$

In the case of purely elastic scattering there is no energy transfer between the neutron and the sample, which means that

$$|\vec{k_s}| = |\vec{k_i}| = \frac{2\pi}{\lambda} \tag{3.2}$$

and *q* is defined by the scattering angle θ as

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \tag{3.3}$$

with the neutron wavelength λ .

Neglecting multiple scattering, the scattered intensity I(q) of a single, isolated particle is given by [141, 142]:

$$I(q) = \left| \iint_{\text{particle}} e^{iqr} \rho dx \, dy \, dz \right|^2 \tag{3.4}$$

 ρ is the scattering length density, which is a measure for the interaction of the neutrons with the nuclei of the sample and is defined as

$$\rho = \frac{1}{V} \sum_{i} b_i. \tag{3.5}$$

Here, b_i is the coherent scattering length of an individual atom in the volume *V*.

This allows for powerful contrast variation experiments in SANS by changing the isotopes in the sample. In soft matter research contrasts in aqueous samples are often tuned by mixing H₂O and D₂O, as they have very different scattering length densities $(\rho_{\rm H_2O} = -0.56 \times 10^{-6} \text{ Å}^{-2}, \rho_{\rm D_2O} = 6.34 \times 10^{-6} \text{ Å}^{-2})$ [143].

Solutions of Equation 3.4 depend on the shape of the particle and are called form factors P(q). Usually the constant scattering length density ρ and the particle volume V are factored out, which leads to the expression

$$I(q) = \rho^2 V^2 P(q).$$
(3.6)

Form factors were calculated for a wide variety of particle shapes. A good overview is provided by Pedersen [144]. Exemplary the form factor of a sphere with radius *R* is

$$P(q) = \left(3\frac{\sin(qR) - qR\cos(qR)}{(qR)^3}\right)^2.$$
 (3.7)

The overall decay of scattered intensity over *q*, excluding interference phenomena, depends on the particle shape and is expressed as

$$I(q) \propto q^{\beta}. \tag{3.8}$$

This allows for a pre-determination of the particle shape by analysing the slope of I(q) vs. q in a double logarithmic plot. Although the scattering exponent β is not unambiguous for a specific particle shape, this is a powerful tool in the analysis of SANS data. An overview of some common scattering exponents and the associated structures are given in Table 3.2.

Table 3.2: Scattering exponent β and associated structures, adapted from [142].

β	Associated structure	
-1	Elongated objects (rods, needles, etc.) with random orientation	
-1.7	Self-avoiding polymer coil	
-2	Flat objects (discs, platelets, etc.) with random orientation,	
	ideal polymer chain following random walk	
$-3 \le \beta \le -1$	Volume fractals with fractal dimension $D = -\beta$	
$-4 \leq eta \leq -3$	Surface fractals with fractal dimension $D_S = 6 + \beta$	
-4	Sharply contrasted interfaces (Porod's law)	
$eta \leq -4$	Smooth transition between contrasted domains	

In more concentrated solutions, multiple particles might be in the coherence volume of the neutron beam. This then leads to additional interference phenomena depending on the interparticle structuring and gives rise to an additional scattering contribution, namely the structure factor S(q). The overall scattered intensity then reads

$$I(q) = \rho^2 V^2 P(q) S(q) + C.$$
 (3.9)

Here, *C* is the background of the measurement due to incoherent scattering of the sample.

Measurements The SANS data presented in Chapter 4 and 6 were recorded at the KWS-1 instrument at the Heinz Maier-Leibnitz Zentrum (MLZ, Garching, Germany) [145, 146]. All measurements were performed with a $10 \times 10 \text{ mm}^2$ neutron beam and a wavelength of 0.49 nm with a 10% wavelength resolution (FWHM). Scattering patterns were recorded with a ⁶Li-scintillation detector with photomultiplier tubes and a spatial resolution of $5.3 \times 5.3 \text{ mm}^2$ at sample–detector distances of 7.615 m (collimation length 8 m, data acquisition time 5 min) and 19.615 m (collimation length 20 m, data acquisition time 15 min), covering a *q*-range of $\approx 0.04 - 1.1 \text{ nm}^{-1}$. Radial averaging of the 2D detector images, processing and merging of the data was done with the QtiSAS software [147].

The SANS data presented in Chapter 5 were recorded at the D33 instrument at the Institut Laue-Langevin (ILL, Grenoble, France) [148, 149]. SANS measurements were performed with a circular neutron beam (diameter 15 mm) and a data acquisition time of 15 min at sample–detector distances of 1.7 m (front detector) and 10 m (rear detector) and a neutron wavelength of 0.46 nm, covering a *q*-range of $\approx 0.05 - 4 \text{ nm}^{-1}$. The collimation was set to 10.3 m. Processing and radial averaging of the 2D detector images were done with the GRASP software [150]. Absolute units were obtained by normalising for the direct beam.

A custom-built sample cell, specifically designed for studying macroscopic foams with SANS, was used in both cases [151]. A detailed description of this sample environment is presented in Chapter 4. Foams were produced from the desired foaming sample 86.7 mM SDS solution (Chapter 4), 3.5 mM C_{14} TAB solution (Chapter 5) or 0.3 wt% MG dispersion (Chapter 6) in D₂O by bubbling nitrogen gas at a rate of 10 mL min⁻¹ through a porous glass plate (pore size $10 - 16 \mu$ m, porosity P16 (ISO 4793)) at the bottom of the cell. Once the foam level reached the top of the column, the flow rate was reduced to a value that ensures a constant foam height over time. The flow rates were in a range of $1 - 3 \text{ mL min}^{-1}$ with the exact value depending on the sample studied. Once this steady-state was reached, measurements at three different foam heights (KWS-1: h = 2 cm, 9.5 cm and 16 cm, D33: h = 7 cm, 12 cm and 16.5 cm above the foaming solution) were performed.

The Institut Laue-Langevin is acknowledged for the provision of beam time, data from these experiments is available at doi:10.5291/ILL-DATA.9-12-600 [149].

Parts of this work is based upon experiments performed at the KWS-1 instrument operated by JCNS at the Heinz Maier-Leibnitz Zentrum (MLZ), Garching, Germany.

3.4 Reflectometry

In the framework of this thesis no dedicated reflectometry experiments were performed, but since a combination of SANS and reflectivity contributions is used to model the SANS curves of foams in Chapter 5 and 6, a brief introduction to the principles of reflectometry is given.



Figure 3.3: Schematic representation of a reflectometry experiment and resulting reflectivity curves for a flat substrate (top) and a thin layer on a substrate (bottom).

In specular neutron reflectometry, the momentum transfer between an incoming $(\vec{k_i})$ and a reflected $(\vec{k_f})$ neutron beam in the direction normal to the sample's surface is of interest. This quantity q_z is defined as [152, 153]

$$q_z = |\vec{k_f} - \vec{k_i}| = \frac{4\pi}{\lambda} \sin \theta_i \tag{3.10}$$

with the angle of incidence θ_i and the neutron wavelength λ . Considering the reflection of a neutron beam at the surface of an ideally flat substrate with infinite thickness, the reflectivity coefficient *r* is

$$r = \frac{k_i - k_f}{k_i + k_f} \tag{3.11}$$

and the reflected intensity R as

$$R = rr^* \tag{3.12}$$

with r^* being the complex conjugate of r.

In the case of a thin layer (medium 1, ρ_1) on a substrate (medium 2, ρ_2 , see Figure 3.3 bottom), the reflectivity coefficients for both interfaces have to be calculated [152]:

$$r_{0,1} = \frac{k_{0,z} - k_{1,z}}{k_{0,z} + k_{1,z}} \cdot e^{-2k_{0,z}k_{1,z}\delta_1^2}$$
(3.13)

$$r_{1,2} = \frac{k_{1,z} - k_{2,z}}{k_{1,z} + k_{2,z}} \cdot e^{-2k_{1,z}k_{2,z}\delta_2^2}.$$
(3.14)

Here, $k_{j,z}$ is the *z*-component of the wave vector in medium *j* and δ_j the roughness of the interface. Neglecting absorption effects, $k_{j,z}$ can be calculated from:

$$k_{j,z} = -\sqrt{k_i^2 \left(\frac{1-\lambda^2}{2\pi}\rho_j\right)^2 - k_i^2 \cos^2(\theta_i)}$$
(3.15)

with the scattering length density ρ_j of medium *j* and the initial wave vector $k_i = 2\pi/\lambda$. The overall reflectivity coefficient in this case is

$$r = \frac{r_{0,1} + r_{1,2} \cdot e^{-2ik_{1,z}d}}{1 + r_{0,1}r_{1,2} \cdot e^{-2ik_{1,z}d}}$$
(3.16)

with the thickness of the film d.

The cases of an ideally flat substrate and a thin film on a substrate with the corresponding reflectivity curves are illustrated in Figure 3.3.



3.5 Thin film pressure balance

Figure 3.4: Illustration of a TFPB experiment.

Principle In foam films a disjoining pressure Π arises due to the close proximity of the two air/water interfaces. Π can have a variety of different origins like electrostatic, van der Waals or steric interactions and is expressed as the sum of these [16, 46]

$$\Pi = \Pi_{\text{elec}} + \Pi_{\text{vdW}} + \Pi_{\text{steric}}.$$
(3.17)

Experimentally, Π can be determined with a thin film pressure balance (TFPB) using the porous plate technique (shown in Figure 3.4) [56, 154]. Here, a foam film is formed in a hole drilled into a plate of a porous material like sintered glass beads, which is connected to a glass tube filled with the studied solution, acting as a reservoir. The film holder is located in a pressure chamber and Π can be calculated from

$$\Pi = P_g - P_0 + \frac{2\gamma}{r_{\text{tube}}} - \Delta \rho_l g h_l.$$
(3.18)

With the pressure inside the measurement chamber P_g , the pressure outside the chamber P_0 , the surface tension of the studied solution γ , the radius of the glass tube r_{tube} , the density difference between air and the studied solution $\Delta \rho_l$, the height of the sample solution in the glass tube above the foam film h_l and the gravitational acceleration g.

In order to obtain disjoining pressure isotherms $\Pi(d)$, the thickness *d* of the foam film is measured as a function of Π . This is typically done by light interferometry. Figure 3.4 illustrates a typical TFPB experiment.

Measurements In this thesis, a custom-built TFPB setup is used. Foam films are formed in a 1 mm hole drilled into a porous glass disc (pore size 10-16 µm, porosity P16 (ISO 4793)). The film holder is placed in a sealed stainless steel chamber, which also contains a reservoir of the studied sample solution to ensure a saturated atmosphere and prevent film drainage. Before each measurement, the film holder was immersed in the sample solution for at least 2 h to equilibrate the porous glass disc with the solution. In the experiments described in Chapter 5 with a C₁₄TAB solution, the foam film thickness was determined by regular white light interferometry. Disjoining pressure isotherms $\Pi(d)$ were recorded by interferometrically measuring the equilibrium film thickness was assumed to be reached after the intensity of the reflected light was constant for 20 min. The disjoining pressure isotherm presented in Chapter 5 is an average from five individual measurements.

As the foam films stabilised by MGs, discussed in Chapter 6, were inhomogeneous in thickness, a different approach developed by Kevin Gräff, was used to measure their thickness. The whole film area is illuminated by a halogen lamp and imaged by a colour CMOS camera (JAI Go-2400-USB, pixel size: 5.86 µm x 5.86 µm, Stemmer Imaging, Germany). In combination with the optics (reflected light microscope, focal reducer, extension tube) the resolution of the camera system is $1.07 \text{ pixel} \cdot \mu \text{m}^{-2}$. Since the films are colourful (thickness > 100 nm) a purely intensity based thickness calculation approach cannot be used. Instead, a colour comparing algorithm was used to determine the film thickness. The algorithm is based on a theoretical spectrum of a free standing water slab surrounded by air [156]. The spectrum is represented in the HSV colour space (hue, saturation, value) and is stored in a lookup table with the regarding thickness values in 1 nm steps. For each film thickness in the range from 100 nm to 800 nm there is a corresponding set of unique HSV values. Single spots with distinguishable features were selected for every measurement and spatially tracked over the whole pressure ramp. The film thickness was determined by an automated comparison between the experimental and theoretical hue values from the lookup table. Being grey, the thickness of the interspersed film areas can be assumed to be below 100 nm and therefore within the first interference order. The disjoining pressure isotherms

presented in Chapter 6 are an average from at least three individual measurements.



3.6 Atomic force microscopy

Figure 3.5: Illustration of the two types of AFM experiments conducted in this thesis.(a) Indentation experiment for the determination of the elastic modulus. (b)Scanning experiment for topographic imaging.

Principle Atomic force microscopy (AFM) was invented as a topographic imaging technique and is based on the interaction of a sharp tip mounted on a bendable cantilever with the surface of the sample [157]. There is a wide variety of forces relevant for AFM experiments, depending on the exact nature of the system studied. These



Figure 3.6: Examples of force vs. indentation curves recorded by AFM on a PNIPAM MG at 20 °C (blue curve) and 50 °C (red curve). The black dashed line corresponds to fits to the data using the Hertz model described in Equation 3.20.

forces include van der Waals, electrostatic, steric, capillary and oscillatory structural forces [20, 158]. When the AFM tip experiences a force from the interaction with the sample surface, the attached cantilever is bent. The bending is measured by the deflection of a laser reflected from the backside of the cantilever. The interaction force can be determined using Hooke's law

$$\Delta F = -k\Delta z. \tag{3.19}$$

Here, Δz is the deflection and *k* the spring constant of the cantilever. This allows the determination of the interaction forces between sample and tip. The elastic properties of a sample can be measured by indenting the AFM tip into the sample and measure the deflection of the cantilever as a function of the indentation depth (see Figure 3.5(**a**)). Using the Hertz model for contact mechanics, the Young's modulus of the sample can be calculated by [159]

$$F = \frac{4E\sqrt{R}}{3(1-\nu^2)} \cdot \delta^{3/2}.$$
 (3.20)

Here, *F* is the force exerted by a spherical indenter with radius *R*, *E* is the Young's modulus, ν the Poisson ratio and δ the indentation depth. Experimentally, *E* can be determined by fitting a force vs. indentation curve with Equation 3.20.

As mentioned above, AFM was originally invented as a topographic imaging technique. The two most common imaging modes are the contact and the intermittent contact also called tapping mode. In contact mode the AFM tip is in physical contact with the sample, which results in a deflection of the cantilever. The surface is scanned either by moving the sample under the tip or the tip itself. During scanning the tip is lifted or lowered by the *z*-piezo to maintain constant cantilever deflection by a software feedback loop. This way, the vertical displacement of the *z*-piezo correlates to the topography of the sample. In intermittent contact or tapping mode, the cantilever is excited to oscillate at its resonance frequency. Upon approaching the sample, the amplitude of this oscillation is damped by the tip-sample interaction. In order to image the topography of the sample, the surface is scanned by keeping the oscillation amplitude constant. This is achieved by adjusting the cantilever's height with the *z*-piezo and the feedback loop. An illustration of the tapping mode is shown in Figure 3.5 (b) In general, the contact mode has a higher resolution, but since the AFM tip is "scratched" over the surface, this increases wear of the tip and might also damage soft samples. For these reasons the tapping mode is the most widely used imaging technique in soft matter science.

Measurements Microgel (MG) samples for atomic force microscopy (AFM) measurements were prepared by spin coating 0.5 mL of 0.05 wt% MG dispersion at 1000 rpm for 90 s and 2000 rpm for 30 s onto $10 \times 10 \text{ mm}^2$ silicon wafers (Soitec, France). Immediately before the spin coating procedure, the silicon wafers were cleaned by exposure to oxygen plasma (Diener Femto, Germany). Two types of AFM experiments were performed with the MG samples: Imaging of MGs on a substrate in tapping mode in air to study the MGs' shape and indentation measurements in water to study their elastic properties.

AFM scans in air were performed with an MFP-3D AFM (Oxford Instrument, UK) situated in an acoustic enclosure using AC160TS cantilevers (Olympus, Japan) with a typical spring constant of $k = 26 \text{ N m}^{-1}$ and resonance frequency of $f_{\text{res}} = 300 \text{ kHz}$. in tapping mode.

The indentation measurements were performed with a Cypher AFM (Oxford Instruments, UK) equipped with BL-AC40TS cantilevers (Oxford Instruments, UK) with a typical spring constant of $k = 0.09 \text{ Nm}^{-1}$, resonance frequency of $f_{\text{res}} = 110 \text{ kHz}$ and a typical tip radius of R = 8 nm. Before each measurement the exact spring constants of the cantilevers were determined by the method described by Sader et al. to be $0.076 - 0.112 \text{ Nm}^{-1}$ [160]. The MG sample and the cantilever were submerged in water and the temperature was set to 20.0 °C. After equilibration for at least 30 min, force curves were recorded by indenting the tip of the cantilever into the center of the adsorbed MGs. At least 8 force curves from different MG particles were recorded for each sample. Elastic properties of the MGs were extracted by fitting the force curves with the Hertz model. The fit region was set to 0-40% of the maximal indentation depth (dashed line in Figure 3.6). The Poisson ratio ν of the PNIPIAM MGs was assumed to be 0.5.

3.7 Foaming experiments

Foams were generated using the so-called Bartsch method [36] in which a defined amount of liquid is shaken for a defined amount of time in a container of defined geometry. In the experiments presented in Chapter 6, foams were generated by vigorously shaking 8 mL of microgel (MG) dispersion in a 40 mL glass vial (inner diameter: 27.5 mm, height: 95 mm) by hand for 30 s. The foam decay was monitored by taking photos in regular time intervals and subsequent image analysis. Image analysis was performed using the Fiji distribution of the open-source image analysis software ImageJ [161]. Pixel sizes were converted into real-space lengths by using the height of the foaming vial as a reference. The foam height was measured as the distance between the upper edge of the foaming solution and the upper edge of the foam. The foamability is the initial foam height immediately after the foaming procedure. The foam stability is judged by the half life time $t_{1/2}$, which is the time it took for the initial foam height to be cut in half. Dispersions in water of all MGs mentioned in Table 3.1 were studied at three different concentrations (w = 0.3, 0.5 and 1.0 wt%). In order to investigate the influence of temperature on the foamability, the MG dispersions were preheated for 30 min in a 50 °C water bath and shaken according to the procedure described above. The temperature dependent foam stability was studied by placing MG dispersions, which were foamed at 22 °C, into a 50 °C water bath and subsequent photo monitoring. Every foaming experiment was repeated at least three times. Prior to use, the glass vials were soaked in diluted alkaline Q9 cleaning solution (Bernd Kraft, Germany) overnight and thoroughly rinsed with water.

3.8 Additional methods

Dynamic light scattering Dynamic light scattering (DLS) was used to measure the hydrodynamic radius R_h of particles in a dispersion. The sample is probed with a laser beam and because of the Brownian motion of the particles, the intensity of the scattered light fluctuates over time. These fluctuations are analysed using the field auto correlation function $g^1(\tau)$. In the ideal case of purely diffusive motion of monodisperse particles, $g^1(\tau)$ follows a simple exponential decay:

$$g^1(\tau) = e^{-\Gamma\tau}.\tag{3.21}$$

With the decay rate Γ and the lag time τ . Γ is related to the diffusion coefficient *D* by:

$$\Gamma = Dq^2 \tag{3.22}$$

with the angle dependent momentum transfer of the scattered light q. The hydrodynamic radius R_h of the particle can be calculated using the Stokes-Einstein equation

$$D = \frac{k_{\rm B}T}{6\pi\eta R_h} \tag{3.23}$$

with the dynamic viscosity of the sample η . In this thesis, the hydrodynamic radii R_h of all microgels (MGs) at 20 °C and 50 °C were determined using a multi-angle DLS setup (LS Instruments, Switzerland). Data analysis was performed using a Mathematica script written by Marcus U. Witt.

Electrophoretic mobility The electrophoretic mobility μ_e relates the velocity of a particle v in an electric field, to its field strength *E*

$$\mu_e = \frac{v}{E}.\tag{3.24}$$

The ζ potential can be calculated from μ_e , using the Henry equation [162]

$$\mu_e = \frac{2\epsilon_o \epsilon \zeta}{3\eta} f(\kappa r) \tag{3.25}$$

with the dielectric permittivity in vacuum ϵ_0 , the dielectric constant of the sample ϵ , the dynamic viscosity of the sample η and the Henry function $f(\kappa r)$. The Henry function is a measure for the relative thickness of the ion double layer around the particle, expressed by the Debye length κ^{-1} , relative to the particle radius r.

For small particles in solutions with low ionic strength ($r \ll \kappa^{-1}$), $f(\kappa r)$ approaches 1. This is also known as the Hückel approximation. For large colloidal particles in polar solvents ($r \gg \kappa^{-1}$), $f(\kappa r)$ approaches 1.5, which is known as the Smoluchowski approximation [19, 163].

The electrophoretic mobility μ_e of all MGs at 20 °C and 50 °C in water was determined with a Zetasizer Nano (Malvern Panalytical, UK). Before the measurement, the measurement cell was thoroughly rinsed with water and the sample solution. The sample solutions had a MG concentration of approximately 0.005 wt%. For every sample, 6 individual measurements were performed for both temperatures. The ζ potentials presented in Chapter 6 were calculated with the Henry equation (Equation 3.25) under the Smoluchowski approximation.

4 Construction of a sample environment for neuron scattering experiments with foams for future implementation at the European Spallation Source

Similar content is published in "Flexible Sample Environments for the Investigation of Soft Matter at the European Spallation Source: Part III — The Macroscopic Foam Cell" Matthias Kühnhammer et al., *Appl. Sci.*, **2021**, *11*, 5116. [151] doi: 10.3390/app11094089.



Abstract

The European Spallation Source (ESS), which is under construction in Lund (Sweden), will be the leading and most brilliant neutron source and aims at starting user operation at the end of 2023. Among others, two small-angle neutron scattering (SANS) machines will be operated. Due to the high brilliance of the source, it is important to minimise the downtime of the instruments. For this, a collaboration between three German universities and the ESS was initialized to develop and construct a unified sample environment (SE) system. The main focus was set on the use of a robust carrier system for the different SEs, which allows setting up experiments and first prealignment outside the SANS instruments. This chapter covers the development and construction of a SE for SANS experiments with foams, which allows measuring foams at different drainage states and the control of the rate of foam formation, temperature, and measurement position. The functionality under ESS conditions was tested and neutron test measurement were carried out.

4.1 Introduction

Neutrons play an important role for current fundamental science. Investigation of soft matter in the submicrometer range relies on neutron science due to the possibility of an unique contrast variation based on hydrogen–deuterium exchange. The European Spallation Source (ESS), which is under construction in Lund (Sweden), will be the leading neutron source in terms of flux and brilliance in the future [164, 165]. This high flux will lead to decreasing measurement times and, therefore, will reduce the amount of beam time allocated to the individual users. This benefit also comes with a challenge, since the installation of sample environments (SEs) and the time required for preparation of the experiment will become a crucial factor for an efficient use of the beamtime. Consequently, the design of SEs should have a strong emphasis on the reduction of down time during sample and SE changes. The FlexiProb project (funded by the Federal Ministry of Education and Research of Germany, BMBF) is a collaborative effort of three research groups to design and construct three SEs in the field of soft matter research for implementation at the two small-angle neutron scattering (SANS) instruments at the ESS, namely LoKI [166] and SKADI [167, 168]. The SEs include

an in situ SANS/DLS setup [169], a GISANS setup [170], and a SE for SANS experiments on aqueous foams, which is presented in this chapter. In principle, the SEs are also compatible with beamlines at other neutron sources. However, the carrier system was designed to specifically fit into the sample areas of the instruments mentioned above. Every SE is assembled on an optical breadboard, which will be mounted on the kinematic mounting system, which is currently developed by the ESS. The whole setup is then transferred to the sample area of SANS instrument with a pallet truck. This approach allows preparing the experimental setup outside the instrument before the actual experiment. In addition, the ESS is planning offline alignment stations at which prealignment can be done within the ESS Universal Sample Coordinate System (USCS) [171]. All of this will allow for an exchange of the whole SE in a single step. This should enable fast and easy exchanges between different SEs and, therefore, should reduce down time between different experiments and users.

As discussed in Chapter 2.1.5 the internal structure of macroscopic foams is difficult to probe. SANS was identified as a promising technique to tackle this problem and is until now the only technique, which allows the determination of foam film thicknesses inside a macroscopic foam [65, 66, 172–175]. Since individual foam bubbles can have diameters of several mm and standard SANS cuvettes have neutron path lengths in the same range, special foam cells are required.

Different cell designs for SANS on foams were reported in literature [65, 173–175]. In all of these cells, foam formation is realized by bubbling gas through a porous plate either made of steel or sintered glass. The first cell of this type was designed by Axelos et al. and consists of a Plexiglas cylinder with a single quartz window for the neutron beam [65]. Taking into account the changing liquid volume fraction along the height of a foam column, Micheau et al. used a cell with three plane parallel windows at different positions along the foam cylinder [174]. This made it possible to probe the foam at different (gravitational) drainage stages. Following this approach, a foam cell that allows SANS measurements at any desired height along the foam cylinder is designed. Since the foam formation before each SANS experiment takes several minutes, the presented SE includes a sample changer for up to three foam cells, allowing foaming the next sample during the measurement of the previous one. As stated above, this is especially important for highly brilliant neutron sources such as the ESS in order to reduce the downtime between sample changes. The high flux and reduced measurement time at the ESS will also enable measurements with more dynamic and less stable foams and will allow studies with high time resolution, which is especially appealing for highly dynamic foams. In order to use the full potential of the ESS from day one, it is crucial to design and test SEs for various experiments before the start of operation.

In this chapter, the design and construction of the FlexiProb SE for SANS experiments on foams is presented. Detailed technical aspects of the measurement cell itself and the peripheral components such as temperature control, gas flow control, and sample positioning, as well as first benchmarks for measurements with neutrons, are shown.

4.2 Instrumental concept and performance

4.2.1 General construction

The main parts of the sample environment are three foam cells, in which the foam will be formed. Figure 4.1 (**a**, **b**) show an engineering drawing and a photograph of a single foam cell. Each cell consists of a 250 mm long quartz glass cylinder with an inner diameter of 30 mm and a wall thickness of 2 mm. Quartz is almost transparent to neutrons and the circular design avoids the rupture of lamellae at edges. A porous quartz glass plate (pore size 10-16 µm, porosity P16 (ISO 4793)) is fused to the bottom of the cylinder. The whole cylinder is mounted to a gas-inlet socket via an O-ring in a crimp connection. From below, a gas (e.g., air or nitrogen) is pressed through the porous plate, which breaks the continuous gas flow into small bubbles. This results in the formation of foam, when an appropriate foaming solution is poured into the cylinder. Finally, the gas exits the cylinder at the open top, which ensures pressure equilibrium. For temperature control, two thermostating jackets are fitted to each foam cylinder, using titanium screws from the bottom of the gas-inlet socket. One of the main features and advantages of this foam cell is the possibility to measure at any position along the height of the foam cylinder. Therefore, the thermojackets are designed in a way to leave a slit-shaped gap between them. The width of this gap governs the maximum scattering angle accessible. Figure 4.1 (c) shows a sketch in top view for the estimation of the maximum scattering angle at the geometrically least favourable position. For a scattering event occurring at the edge of a 10 mm wide primary neutron beam (highlighted in orange) at the side facing the primary beam, the scattering angle limit $2\theta_{\text{lim}}$ is 13.8°. Assuming a neutron wavelength of $\lambda = 0.5$ nm, the maximum scattering vector q_{max} is calculated by

$$q_{\rm max} = \frac{4\pi}{\lambda} \sin(\theta_{\rm lim}) \approx 0.3 \,\rm nm^{-1} \tag{4.1}$$

This corresponds to a minimum measurable size of 2 nm in real space, which is sufficient to resolve structures such as foam films or incorporated objects such as micelles or nanoparticles. It is worth noting that the SANS instruments LoKI and SKADI at the ESS will be operated with a predicted neutron wavelength band of 0.2 nm to 2.2 nm and 0.3 nm to 2.1 nm, respectively [165]. An accessible *q* range of 0.05–6 nm⁻¹ for the foam cell at these ESS instruments can be expected. The lower limit is governed by the instrument's design and the upper limit by the cell geometry. This will lead to a range of measurable sizes of ca. 1–125 nm. The gas-inlet socket and thermostating cylinder are made of AlMg_{4.5}Mn_{0.7}, a special aluminum alloy that is easy to process and not activated by neutrons. All three foam cells are placed in a folded AlMg_{4.5} socket.



Figure 4.1: Individual foam cell. (a) Explosion-view drawing and (b) photograph in front view. (c) Schematic top view. The individual foam cells consist of a quartz glass cylinder, thermojackets, and a gas-inlet socket. The neutron beam (highlighted in orange) passes the cell perpendicular to the thermojackets in variable height. For the estimation of the minimal range of scattering angles accessible, a scattering event at the (geometrically) least favorable position is considered (green arrow).

The side facing the primary neutron beam is protected by an aluminum plate covered with 1 mm B₄C including rectangular slits at the respective positions of the foam cells. Since the cells are open to the top, an aluminum cover was placed above the cells to avoid dust incorporation. A backview of the mounted cells is shown in Figure 4.2 (a). The setup is placed on a translation stage (travel range 508 mm), which allows remote controlled sample changes between the different foam cells as shown in Figure 4.2 (b, c). The entire setup is mounted on a breadboard (900 × 1200 mm², Newport Spectra-Physics GmbH, Germany). Later on at the ESS, the entire setup will be mounted on a lifting table, which is also part of the unified carrier system used by all FlexiProb SEs. This will ensure fast setup changes by removing the entire setup including the board. The lifting table installed at LoKI and SKADI will have a vertical displacement range of >300 mm with a 0.1 mm positional accuracy, which is sufficient for the foam cell SE.



Figure 4.2: Overview of the sample environment (SE). (a) Backview of three foam cells on folded aluminum construction. (b) Technical drawing of the complete SE mounted on the breadboard. (c) Front view of the SE (technical drawing) without shielding.

4.2.2 Gas flow control

The flow of the foaming gas is controlled by a FG-201CV mass flow controller (Bronkhorst, Netherlands) operating at an upstream pressure of 3 bar. The gas flow rate can be adjusted between 0–30 mL min⁻¹. The three foam cells have separate gas circuits with individual mass flow controllers. This opens the possibility to prepare foams while another is measured or to define different foam states with a fast shift between different columns. The devices are connected via RS232 connections to a serial device server (NPort 5450, Moxa, Taiwan). Here, the RS232 signal is converted into an Ethernet signal, which is transmitted via LAN to the instrument control. Communication is realized on a dynamic data exchange (DDE) server implemented in the supplier's FlowDDE software (Version 4.81). With this connection established, the devices are controlled using the DDE client program FlowView (Version 1.23) also distributed by the supplier.

Figure 4.3 shows the results of a foaming experiment in which 12 mL of tetradecyltrimethylammonium bromide (C₁₄TAB) (c = 3.5 mM) surfactant solution were foamed with synthetic air at a flow rate of $\dot{V} = 30$ mL min⁻¹. Pictures of the foam column were taken in a time interval of 80 s and the respective foam heights extracted by image analysis. Neglecting foam decay, a theoretical foam height $h_{th}(t)$ was calculated using Equation 4.2 for comparison, which is based on the volumetric gas flow rate and the cross-sectional area of the foam cell.



Figure 4.3: Test of the foaming procedure and tightness of the gas flow system. (a) Three pictures of a foaming $C_{14}TAB$ (c = 3.5 mM) solution at different times. (b) Foam height as a function of time (black squares) and the theoretical height (red line) according to Equation 4.2.

$$h_{th}(t) = \frac{\dot{V} \cdot t}{a} \tag{4.2}$$

Here, \dot{V} is the volumetric gas flow rate, *t* is the foaming time, and *a* is the cross-sectional area of the foaming cylinder.

The measured values are in good agreement with the theoretical foam height as shown in Figure 4.3 (b). This shows that the gas flow system works and the foam is formed as intended.

4.2.3 Temperature control

Temperature change of the foams is achieved by two $AlMg_{4.5}Mn_{0.7}$ thermostating jackets at both sides of each foam cylinder. The thermostating jackets of all three sample cells are connected via appropriate distributors to a Julabo FP50-HL circulating thermostat (Julabo GmbH, Germany) with a temperature range of -50 °C to 200 °C when the appropriate thermofluid is used. For studying aqueous foams, however, an achievable temperature range of 10 °C to 80 °C is typically sufficient, allowing the use of water as thermofluid. To validate the performance of the heat input by the thermostating

jackets, tests with a foam stabilised by C_{14} TAB at its critical micelle concentration of c = 3.5 mM were performed [176]. Therefore, 12 mL of the surfactant solution were foamed at ambient temperature with a synthetic air flow of 15 mL min⁻¹. After the foam reached the top of the quartz cylinder, the gas flow was stopped and the setpoint of the water bath thermostat was adjusted to 50 °C. The evolution of the temperature was monitored by three Pt-100 temperature sensors (model PT-102-3S-QT, Lake Shore Cryotronics, Inc., USA) at different positions at a height of 11.5 cm inside of the foam cylinder. The positions were chosen in a way to reflect the asymmetric shape of the thermostating jacket around the foam cylinder as indicated by A, B, and C in Figure 4.4. One sensor was put in the center of the cylinder (C), while the remaining two sensors were placed on the rim of the foam column, one in close proximity to the thermostating jacket (A) and one right behind the neutron window slit (B). The evolution of the temperature and a schematic sketch of the different positions are shown in Figure 4.4 (a).

Following an initial increase, the temperature reaches a plateau at all three positions after around 20 min. The final temperatures were 48 °C at position A (close to thermostating jacket), 42 °C at position B (behind neutron window slit), and 45 °C at position C (center). This temperature gradient is explained by the asymmetric shape of the thermostating jacket around the foam cell and the low heat conductivity of foams. As explained in Section 4.2.1, this asymmetric shape was chosen to allow SANS measurements at any height along the foam cylinder, accepting the drawback of a potential temperature gradient. The temperature jumps observed at every position are most likely due to air bubbles passing by the sensors, changing the heat conductivity next to them.

In order to reduce this temperature gradient, the experiment was repeated with the foam cylinder wrapped in aluminum foil (see Figure 4.4 (b)). Again, the temperature reaches a plateau after around 20 min with final temperatures of 49 °C at position A, 47 °C at position B, and 48 °C at position C. Wrapping the cylinder in aluminum foil decreases the temperature gradient inside the foam because of the improved thermal contact between the quartz cylinder and the thermostating jackets. In addition, aluminum is almost transparent to neutrons and is also often used as a material for neutron windows. A drawback of this approach is that it is no longer possible to observe the foam during a SANS experiment with a camera. Detecting the formation of holes at the measuring position is sometimes beneficial, especially when dealing with rather

unstable foams where holes may form randomly. Depending on the requirements regarding the accuracy of temperature control, one of the two methods described can be used.



Figure 4.4: Evolution of the temperature of a tetradecyltrimethylammonium bromide $(C_{14}TAB, c = 3.5 \text{ mM})$ foam in the foam cylinder without (**a**) and with (**b**) aluminum foil cover. The temperature was monitored using three Pt-100 temperature sensors at positions depicted by the inset. The setpoint of the water bath thermostat was adjusted to 50 °C at the beginning of the experiment and was reached after ca. 8 min.

4.2.4 Sample positioning

Horizontal sample alignment is achieved with a linear translation stage (LS-180, Physik Instrumente GmbH & Co. KG, Germany) with a maximum load of 100 kg, an operating displacement of 508 mm at a maximum speed of 150 mm s⁻¹, and a bidirectional repetition accuracy of $\pm 0.1 \,\mu$ m. The linear stage is driven by a two-phase bipolar half-coil stepper motor (model PK-258-02B, Oriental Motor, Japan). The position is monitored with a linear optical encoder with RS-422 quadrature signal transmission (LIA-20, Numerik Jena, Germany). The entire setup will be placed on an optical breadboard based on a lifting table, which ensures the vertical sample alignment. The control unit was built according to ESS specifications ensuring compatibility with ESS control standards. Figure 4.5 shows the corresponding circuit diagram for the custom built crate. The translation stage is labeled with "AXIS 1". For testing purposes, a two-axis goniometer was also integrated (motor top, motor bottom, encoder top, and encoder bottom). However, in the framework of the foam cell SE, this goniometer is not used.



Figure 4.5: Circiut diagram of the motion control crate. Beside the translation stage, a two-axis goniometer is also controlled by this crate.

The custom built 19-inch crate is equipped with 24 V (BLOCK Transformatoren-Elektronik GmbH, Germany) and 48 V (Mean Well Enterprises, New Taipei City, Taiwan) power supplies. The latter one provides power for the motors while the first one provides
the power for the control unit. The control unit is based on an Ethernet fieldbus system (EtherCAT, Beckhoff Automation GmbH & Co. KG, Germany). An embedded PC (CX5130) is connected to a potential distribution terminal (EL 9189) and a stepper motor terminal (EL7041), which ensure the motor movement. A digital input terminal (EL1808) and a digital output terminal (EL2819) are connected, sending and reading the motor positions. Additionally, an incremental encoder interface terminal (EL5101) is added to read the encoder signal out.

The embedded PC communicates with the hardware of the linear stage via the Twin-CAT 3 software. This signal is forwarded to the Experimental Physics and Industrial Control System (EPICS) [177], which will be the unified control software for beamline devices at the ESS and is able to control the devices and monitor their state. The EPICS is used by the Networked Instrument Control System (NICOS) [178], which offers a graphical interface for users and is the outermost layer of the instrument control structure at the ESS. Further details regarding instrument control and data streaming are described elsewhere [179].

From 2015 until 2019, the ESS operated a dedicated testbeamline at the Helmholtz-Zentrum Berlin, also known as V20 [180, 181]. Here, a fully workable environment, mimicking a future ESS instrument, was built up for testing and development. The linear stage was successfully tested at this instrument, proving the compatibility with the ESS standards in terms of control, interaction with other devices, and data log-ging.

The integration of the peripheral SE components into NICOS also allows programmable measurements with automated changes between the three foam cells and the measurement height along each cell, varying temperature, and gas flows.

4.3 Neutron test measurements

Figure 4.6 (b) shows the 2D detector image of the empty foam cell recorded at a sampledetector distance of 7.615 m. As expected, the empty quartz cylinder provides a low background with no significant secondary scattering.



Figure 4.6: (a) Single foam cell installed at the KWS-1 beamline at the MLZ. (b) 2D SANS data of an empty quartz foam cylinder. (c-e) 2D SANS data of a steady-state foam produced from a 25 g L⁻¹ SDS solution at 16 cm (c), 9.5 cm (d), and 2 cm (e) foam height above the foaming solution. All experiments were carried out at a sample–detector distance of 7.615 m. Data acquisition time was 5 min.

Test measurements were conducted with a foam stabilised by 25 g L^{-1} (86.7 mM) sodium dodecyl sulfate (SDS), which is well above the critical micelle concentration of 8 mM [182], at different foam heights. This system was chosen because of the high foam stability and the fact that the first study ever performed on SANS on foams also used a SDS foam at this concentration, making it a reference system [65]. 12 mL of the surfactant solution were initially foamed with a nitrogen gas flow rate of 10 mL min⁻¹. After the foam level reached a height of around 18 cm, the gas flow was reduced to 1 mL min⁻¹. At this flow rate the foam height does not change anymore, meaning that the foam formation at the bottom and the foam decay at the top of the column are more or less balanced. This results in a steady-state foam, in which the foam height corresponds to the age of the foam (i.e., the time passed after its formation at the bottom of the cylinder) and therefore its drainage state.

Figure 4.6 (c-e) shows the corresponding 2D detector images recorded at 16 cm, 9.5 cm

and 2 cm above the foaming solution. All images exhibit an isotropic scattering signal around the primary beam. This reveals that the neutron path length through the cell is long enough to average over all orientations of the foam structure, namely the liquid films, within the measuring window. The scattered intensity decreases with increasing measurement height. This is explained by the decreasing liquid volume fraction of the foam with increasing foam age (or height) and proves that different states of the foam can be accessed with a steady-state foam in one experiment.

Axelos et al. studied the same system using a similar foam cell with a single quartz window for the neutron beam in the lower third of the cylinder and the reported values are shown for comparison (closed squares in Figure 4.7) [65]. They performed two types of measurements. The first type of measurement was a continuous foaming experiment, in which the SANS data were recorded while nitrogen was continuously bubbled through the foaming solution. This resulted in a wet foam at the measuring position. The second type of measurement was a drainage experiment, in which the gas flow was stopped after foam formation. After some time, this led to a dry foam at the measuring position at the bottom of the foam column. These two types of foams are related to different foam heights in a steady-state foam. Here, a wet and fresh foam is observed at the bottom while a dry and aged foam is observed at the top of the steady-state foam.



Figure 4.7: Radial averaged scattering data from a 25 g L⁻¹ SDS foam (86.7 mM) at three different foam heights in a steady-state foam (open symbols) and comparison with reference data of a wet foam with continuous gas flow (black squares) and a foam after drainage due to stopped flow (blue squares) [65].

The measured radial averaged scattering curves are plotted in Figure 4.7 (open squares). The data were shifted in intensity for better comparison. Normalization of SANS data of foams is still challenging and was not an aim of this experiment. The determination of the foam's liquid volume fraction based on the neutron transmission is prone to errors, since most foams show a high transmission close to 1 [65, 174]. In general, the trends of measured scattering curves are in good agreement with the literature data, showing that there are no intrinsic artefacts caused by the foam cell. Data recorded at a height of 2 cm are similar to the one of a wet foam reported in literature and the data recorded at a height of 9.5 cm are in good agreement with the one of a drained foam. The data measured at a height of 16 cm correspond to a foam in an even more drained state. The shoulder at $q \approx 0.8 \,\mathrm{nm^{-1}}$ is attributed to surfact the micelles present in the liquid foam films. Consequently, the intensity of this shoulder decreases with increasing foam height, as the liquid drains out of the foam films over time. The shoulder at $q \approx 0.2 \,\mathrm{nm^{-1}}$ occurs due to scattering at the liquid foam films and is related to their thickness [65]. The fact that this shoulder was not observed by Axelos et al. in their wet foam with continuous gas flow could be explained by an even lower measuring position or higher gas flow rate in the steady-state in their experiment. Both factors would result in a wetter foam, leading to a less ordered foam structure with a higher polydispersity regarding the film thickness and, therefore, in a smearing out of the corresponding scattering feature. Unfortunately, no information regarding the measurement position and flow rate are given in the publication, which makes an exact comparison difficult. Nonetheless, it was possible to reproduce two different experiments reported in the literature by scanning along the foam height of a steady-state foam, which makes the presented approach valid for accessing the foam in different drainage stages with varying liquid volume fractions in one experiment.

4.4 Conclusions

A sample environment (SE) for SANS measurements on liquid foams is successfully designed, constructed, and tested. The SE allows the control of the gas flow rate used for foam formation and offers the possibility to control the temperature. The complete foam cylinder is made from neutron-transparent quartz glass, which enables SANS measurements at any position along the foam height and the possibility to study different drainage stages in a single experiment. Additionally, a sample changer on the

basis of a linear stage was constructed and completely integrated into the foreseen ESS control structure at the ESS test beamline V20 at the HZB. Finally, SANS test measurements were successfully performed at the KWS-1 beamline at the MLZ with a model foam already reported in literature.

The presented SE is well-suited for studying liquid foams with SANS and should meet the special requirements of neutron sources with high brilliance such as the ESS, where an efficient use of the allocated beamtime becomes more important and the time required for sample changes should be reduced to an absolute minimum. This is accounted for by the sample changer for up to three foam cells and the possibility to access different states of the same foam in a single measurement cell. In return, a neutron source such as the ESS will allow new and/or more detailed SANS experiments using foams. The high neutron flux at the ESS will reduce the data acquisition time for a similar experiment as presented above at least by one order of magnitude to below 1 min. This will enable experiments with less stable foams or studies investigating structural changes in foams caused by external stimuli.

5 A new model to describe small-angle neutron scattering from foams

Similar content is published in "A new model to describe small-angle neutron scattering from foams" Matthias Kühnhammer et al., *J. Appl. Crystallogr.*, **2022**, *55*, 758. [183] doi: 10.1107/S1600576722004691.

TFPB measurements presented in this chapter were performed by Larissa Braun.



Abstract

The modelling of scattering data of foams is very challenging due to the complex structure of foams and therefore often reduced to fitting of single peak positions or feature mimicking. In this chapter, a more elaborated model, describing small-angle neutron scattering (SANS) data of foams, is presented. The model takes into account the geometry of the foam bubbles and is based on an incoherent superposition of reflectivity curves, arising from the foam films, and a small-angle scattering (SAS) contribution from the Plateau borders. The model is capable of describing the complete scattering curves of a foam stabilised by the standard cationic surfactant tetradecyltrimethylammonium bromide (C_{14} TAB) with different water contents, i.e. drainage states and provides information about the thickness distribution of liquid films inside the foam. The mean film thickness decreases with decreasing water content because of drainage from 28 nm to 22 nm, while the polydispersity increases. These results are in good agreement with film thicknesses of individual, horizontal foam films studied with a thin film pressure balance (TFPB).

5.1 Introduction

Axelos and Boué were the first to use small-angle neutron scattering (SANS) to study liquid foams in 2003 [65]. SANS allows to excellently probe liquid foams. On the one hand, air and D₂O provide excellent contrast conditions, with the possibility to match the stabilising agent. On the other hand, the large neutron beam (tens of millimetres) allow to probe simultaneously a large number of bubbles, providing a representative ensemble equivalent. Moreover, the probed *q*-range also allows to access structural features in the range 1-100 nm, hardly accessible by other techniques. Axelos and Boué investigated foams stabilised by sodium dodecyl sulfate (SDS) at various concentrations above its critical micelle concentration (cmc). In wet foams they observed similar scattering features as in the corresponding micellar bulk solution and concluded the presence of micelles inside the foam. Upon drainage another peak was observed in the scattering curves, which they interpreted as interference between the two gas/liquid interfaces of a foam film and hence allowed the determination of the film thickness inside the foam, which was 16 - 18 nm depending on the SDS concentration. Subsequent publications interpreted the oscillations in the scattering signal attributed to the film thickness in terms of reflectometry from randomly oriented mirrors [184, 185]. One of the justifications for this interpretation was that the first maximum of these oscillations appeared at a value of the scattering vector q close the one of the critical edge q_c of a hypothetical reflectivity experiment with a single liquid layer in air and did not change during drainage. Following this interpretation the film thickness d can be extracted from the period of the oscillations Δq via $d = 2\pi/\Delta q$. This interpretation was also used by Micheau et al. studying foams stabilised by nonaoxyethylene oleylether carboxylic acid [174]. Yada et al. followed the interpretation by Axelos et al. and extracted foam film thicknesses from a single peak position [175]. Recently, Perticaroli et al. and Hohenschutz et al. used the reflectivity-based interpretation and modelled a reflectivity curve of a single liquid layer with thickness *d* to match the oscillations observed in their data [186, 187]. Hurcom et al. and Mansour et al. followed a different interpretation and were the first to model the full scattering curves of foams [173, 188, 189]. They studied foams stabilised by polymeric and small molecule surfactants and polymer/surfactant mixtures. They attributed the oscillations to (surface-induced) lamellar structures inside the foam films and fitted the data with a paracrystalline model, which yielded micron-sized film thicknesses in wet foams.

Given the complex structure of foams several scattering and reflectivity processes might occur as pointed out by Mikhailovskaya et al [66]. Depending on the drainage state of the foam and the stabiliser used, different processes might dominate, which makes a unified description of these scattering curves very challenging. Most articles following the reflectivity-based interpretation mentioning that the complete scattering curve is a combination of Porod scattering ($I \propto B \cdot q^{-4}$) and a reflectivity contribution [174, 184, 186, 187]. However, in these articles no attempt at modelling the full scattering curve was made.

Here, a new approach to model SANS curves of foams is presented. The model uses an incoherent superposition of a multitude of individual reflectivity curves and therefore explicitly accounts for the polydispersity in film thickness in the foam and a small-angle scattering (SAS) contribution. Furthermore, the model takes into account the spherical shape of foam bubbles in wet foams. In this way the complete scattering curves of a foam stabilised by the standard surfactant tetradecyltrimethylammonium bromide (C_{14} TAB) can be described. This specific surfactant system was used, because it is a well-studied model system and very stable in aqueous solution. The model allows extracting detailed information about the evolution and distribution of film thicknesses and thus improves the understanding of the internal structure of foams.

5.2 Model for the description of SANS curves

SANS curves are modelled with a self-written program using the Python programming language [190] with the SciPy [191], NumPy [192] and pandas [193, 194] packages. The model employs an incoherent superposition of a small-angle scattering (SAS) decay and a reflectivity term. Incoherent superposition results in an additive description of the total scattering signal. It is justified, because the size of foam bubbles $(r_B \approx 0.1 - 1 \text{ mm})$ and therefore the distance between two foam films is larger then the coherence length of the neutrons.

The coherence length l_{coh} in a pinhole setup is estimated as follows:

$$l_{\rm coh} = \frac{\lambda}{\frac{a}{c}} \approx 315\,{\rm nm}$$
 (5.1)

With the neutron wavelength $\lambda = 0.46$ nm, the aperture opening a = 15 mm and the collimation length c = 10.3 m.

The angular divergence $\Delta \theta$ in the SANS experiment is given by:

$$\Delta\theta = \tan^{-1}\left(\frac{a}{c}\right) \approx 1.5 \,\mathrm{mrad} \tag{5.2}$$

The maximal relative divergence of the scattering vector $\Delta q/q$ is:

$$\frac{\Delta q}{q} = \sqrt{\left(\frac{\Delta\lambda}{\lambda}\right)^2 + \left(\frac{\Delta\theta}{\theta}\right)^2} \tag{5.3}$$

In monochromatic mode the D33 instrument has a wavelength spread of $\Delta\lambda/\lambda = 0.1$ [148]. At the position of the first feature in the scattering data ($q \approx 0.2 \text{ nm}^{-1}$), $\Delta q/q$ is approximately 0.23, which is sufficient to resolve the feature.

The reflectivity term is a weighted sum of individual reflectivity curves of D_2O layers in air with normal distributed thicknesses d_i . This reflects the polydispersity of foam films in the macroscopic foam. This polydispersity can either be interpreted as the varying film thickness of a single foam film due to the curved bubble interface or as the thickness variation of all films in the foam. Since a single foam bubble is much larger than the coherence volume, the films (or film segments) within the coherence volume are approximated to have a monodisperse thickness. Using a normal distribution, a weighting factor accounting for the polydispersity in film thickness w_i is introduced:

$$w_i = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(d_i - d_0)^2}{2\sigma^2}}$$
(5.4)

Here, d_0 and σ are the mean and standard deviation of the normally distributed film thicknesses and d_i is the specific, monodisperse film thickness weighted by w_i . The region of interest of this distribution was set to be $d_0 \pm 20$ nm and the increment $\Delta d_i = 0.1$ nm. This results in 400 simulated reflectivity curves, which are summed up to the reflectivity contribution of the model.

In classic reflectometry experiments at flat substrates the angle of incidence is only governed by the experimental setup and does not change over the length of the sample. This is not the case for curved interfaces or many randomly oriented interfaces as in foams. In this case the projection of the incident beam on the surface of the scattering object has to be taken into account. This effect is similar to the footprint effect in reflectometry, where the projection of the incident beam under small angles becomes larger than the sample, leading to a reduction of the measured reflectivity. In the case of foams this means that foam films which are (nearly) parallel to the incident beam interact with less neutrons than foam films which enclose a larger angle with the incident beam. Therefore, the reflectivity contribution is modified by an angle correction $P(\theta)$. Considering the many randomly oriented foam films probed by the neutron beam, $P(\theta)$ is estimated by the projection of a parallel beam onto the surface of a sphere. The small plane-parallel foam films can also be considered as tangent planes to this sphere. Note that this sphere is only a theoretical construct and should not be interpreted as a foam bubble. For the calculation of $P(\theta)$ two factors have to be considered: 1. The fraction of a sphere's surface resulting in an angle of incidence θ_i when illuminated with a parallel beam. 2. The probability for an angle of incidence θ_i given by the projection of a parallel beam onto a circle.

The normalized fraction of a sphere's surface resulting in a certain angle of incidence θ_i is given by:

$$U(\theta_i) = \frac{2\pi h_i}{2\pi r} \tag{5.5}$$

Here, h_i is the height corresponding to the surface section *i* and *r* is the radius of the sphere. Figure 5.1 (a) illustrates this for one specific value of θ_i . Note that $\theta_i = \theta_p = \theta$.



Figure 5.1: (**a**, **b**) Illustration of the angle correction. (**c**) Comparison between an uncorrected reflectivity curve *R* of a planar layer (30 nm D₂O layer in air, interfacial roughness $\delta = 0.3$ nm, black) and the same curve of a spherical cap taking the angle correction $R \cdot P(\theta)$ (red) into account. For better comparability with the uncorrected reflectivity curve, the maximum of the angle corrected reflectivity curve is rescaled to 1.

With the relation $h = r \cos(\theta_p)$ with the polar angle θ_p , $U(\theta_i)$ is:

$$U(\theta_i) = \frac{2\pi r \cos(\theta_p)}{2\pi r} = \cos(\theta_p)$$
(5.6)

The probability for an angle of incidence θ_i is given by the projection of a parallel beam onto a circle. This projection is illustrated in Figure 5.1 (b).

$$x(\theta_i) = \frac{H}{K} = \sin(\theta_i) \tag{5.7}$$

The combination of Equations 5.6 and 5.7 yields the correction term $P(\theta)$, which describes the distribution of angles of incidence for the reflection of a parallel beam from a sphere.

$$P(\theta) = x(\theta) \cdot U(\theta) = \sin(\theta)\cos(\theta) = 0.5\sin(2\theta)$$
(5.8)

With the relation $\theta = \arcsin(q\lambda/4\pi)$, $P(\theta)$ is:

$$P(\theta) = 0.5 \sin\left(2 \arcsin\left(\frac{q\lambda}{4\pi}\right)\right)$$
(5.9)

Including both correction factors w_i and $P(\theta)$ the scattered intensity *I* reads:

$$I = A \cdot P(\theta) \sum_{d_i} w_i \cdot R(d_i) + B \cdot q^{\beta} + C$$
(5.10)

Here *A* and *B* are scaling factors for the reflectivity and SAS contribution, respectively. $R(d_i)$ is an individual reflectivity curve for a D₂O layer in air with thickness d_i . β is the exponent of the SAS decay and *C* is the constant, incoherent background.

It is worth noting that the model in the form given in Equation 5.10 is not capable of describing additional scattering features arising from aggregates or structures inside the foam films or Plateau borders like micelles as was already reported in literature [65, 172]. It was possible to neglect the presence of micelles inside the foam films, because the surfactant concentration was set to its critical micelle concentration (cmc). Depending on the study and technique used the cmc of C_{14} TAB is reported to be between 3.4 mM and 3.6 mM [195–197]. Upon foaming, the surfactant molecules are gradually extracted from the foaming solution, leading to a reduced C_{14} TAB concentration in the foam and consequently to the absence of micelles in the foam. This is beneficial for the development of a model for SANS at foams as it allows to focus on

the scattering features arising from the foam structure rather then the scattering from objects inside the foam films.

The fitting routine first determines *C* by averaging the 15 data points with the highest *q* values. Afterwards, *A*, *B*, β , d_0 and σ are fitted to the data using the Nelder-Mead algorithm [198]. The individual reflectivity curves are calculated for a free standing D₂O layer in air with the matrix method [152]. The roughness of all air/water interfaces was fixed to the literature value of 0.3 nm [199].

The model used here employs several assumptions that were not made in models describing SANS data from foams so far: The introduction of polydispersity in the foam film thickness, the angle correction for the reflectivity term and the deviation from a strict Porod-type SAS contribution. The validity of the latter two was checked by performing model fits without them. Figure 5.2 shows the best model fits for the lowest foam height (h = 7 cm) for a series of models with different assumptions and the corresponding values of χ^2 . The experimental data (black squares) are shown together with the (angle-corrected) reflectivity (dotted blue line), the Porod/SAS contribution (dashed green line) and the total model fit curve (solid red line). In Figure 5.2 (a) and (**b**) a strict Porod-type SAS contribution $(B \cdot q^{-4})$ was used without and with the angle-corrected reflectivity term, respectively. In Figure 5.2 (c) and (d) a flexible SAS contribution $(B \cdot q^{\beta})$ was used without and with the angle-corrected reflectivity term, respectively. Both, the angle correction and the use of a flexible SAS decay decrease χ^2 by nearly one order of magnitude compared to the combination of a strict Porod decay and an uncorrected reflectivity term. Combining both assumptions further reduces χ^2 by a factor of 1.25 and 1.65, respectively, which suggests a certain validity and necessity of the assumptions to describe the presented scattering curve.

5.3 Results and Discussion

5.3.1 SANS experiments and model fits

Figure 5.3 shows SANS data of a foam prepared from a C₁₄TAB solution (c = 3.5 mM in D₂O), measured at different foam heights *h* together with the model fits obtained using Equation 5.10. In Figure 5.3 (**a-c**) the angle-corrected reflectivity $R \cdot P(\theta)$ was used to model the data. Figure 5.3 (**d**) was modelled without the angle correction. For the



Figure 5.2: Comparison of the best model fits with different assumptions ((**a**) strict Porod decay without angle correction, (**b**) strict Porod decay with angle correction, (**c**) SAS decay without angle correction, (**d**) SAS decay with angle correction). Experimental scattering data recorded at the lowest foam height (h = 7 cm, black squares) is shown together with the (angle-corrected) reflectivity (dotted blue line), the Porod/SAS contribution (dashed green line) and the total model fit curve (solid red line). The quality of the fit is judged by the value of χ^2 .

Table 5.1	Fit parameters of t	he model fits emplo	ying Equation 5.	10 for the thre	e differ-
	ent foam heights.	The corresponding	curves are show	vn in Figure 5	5.3 (a , b ,
	d).				

h	А	d_0	σ	$B\cdot 10^{-8}$	β	$C \cdot 10^{-4}$
cm	cm^{-1}	nm	nm			cm^{-1}
7	0.18	28.2	2.7	15.49	-3.45	3.43
12	0.17	24.7	3.6	4.09	-3.45	2.30
16.5	0.06	22.4	5.2	5.09	-3.12	2.22

two lower foam heights h = 7 cm and h = 12 cm (Figure 5.3 **a**, **b**) the angle-corrected model fits are in good agreement with the experimental data. For h = 16.5 cm the angle-corrected model deviates significantly from the data at $q \approx 0.13 \text{ nm}^{-1}$ (Figure 5.3 (c)). Here, a description of the data with a reflectivity term without angle correction reduces χ^2 nearly by a factor of 2 (Figure 5.3 (d)).

Since the overall decay in intensity is close to $I \propto q^{-4}$, the data and model fits from Figure 5.3 are presented in Figure 5.4 in the so called Porod representation $I \cdot q^4(q)$, which highlights the reflectivity features.

The fit parameters of the best model fits for the different foam heights are summarised in Table 5.1. The fit parameters are: reflectivity scale factor *A*, mean foam film thickness d_0 , standard deviation of the foam film thickness σ , SAS scale factor *B*, power of the SAS decay β and incoherent background *C*.

With increasing foam height the overall scattered intensity decreases. This was also observed in various other publications investigating foams with SANS and is explained by drainage of the foam [65, 174, 175, 184]. During drainage the liquid films inside the foam become thinner and eventually rupture [21, 38, 200]. Consequently, the number of contrast-bearing objects in the foam decreases, which leads to a decrease in scattered intensity.

This drainage process also explains the evolution of some of the SANS model fit parameters with increasing foam height. The mean film thickness d_0 decreases, because of drainage. The reflectivity scale factor *A* decreases, because of film rupturing. This



Figure 5.3: SANS data of a foam prepared from a C₁₄TAB solution (c = 3.5 mM in D₂O), measured at different foam heights. (**a**) h = 7 cm, (**b**) h = 12 cm, (**c**, **d**) h =16.5 cm. Black squares are experimental data. Lines are model fits according to Equation 5.10. For clarity the full curve (solid red line) is shown together with the SAS decay (dashed green line) and the reflectivity contribution (dotted blue line). In (**a-c**) the angle-corrected reflectivity $R \cdot P(\theta)$ is applied. (**d**) was modelled without the angle correction.



Figure 5.4: $I \cdot q^4$ plots of the data and model fits presented in Figure 5.3. (a) h = 7 cm, (b) h = 12 cm, (c, d) h = 16.5 cm. Black squares are experimental data. Lines are model fits according to Equation 5.10. For clarity the full curve (solid red line) is shown together with the SAS decay (dashed green line) and the reflectivity contribution (dotted blue line). In (**a**-c) the angle-corrected reflectivity $R \cdot P(\theta)$ is applied. (d) was modelled without the angle correction.

process reduces the number of foam films in the sample cell and consequently the probability of a reflectivity event to occur decreases. Both, drainage and rupturing of foam films lead to a reduction of scattering volume inside the sample, hence the incoherent background *C* decreases with increasing foam height.

The standard deviation of the foam film thickness σ increases with increasing foam height. This means, that the thickness distribution of liquid films used in the model fit is broader, i.e. the film thickness becomes more polydisperse. Considering again the aging processes described above, the increase of σ could be rationalized as follows: With proceeding rupturing of the foam films, the statistics of the film thickness distribution becomes worse and more susceptible to local thickness deviations. These thickness deviations might become more likely with increasing foam age as the liquid released during film breakups is incorporated by the remaining films, leading to a broader thickness distribution.

The SAS contribution to the overall signal can be interpreted as scattering from foam films under angles where reflection can be neglected and from other structural motifs of the foam such as Plateau Borders and objects inside the foam (e.g. micelles, polymer chains) [66]. Previous publications on this topic mostly interpreted this contribution in terms of Porod's law [65, 173-175, 185-189], which describes the scattering from randomly oriented, sharp interfaces and is characterized by a q^{-4} power law regarding the decrease of scattered intensity [201]. However, in most of the studies cited above the decrease in scattered intensity over *q* was weaker than q^{-4} [65, 173–175, 186, 187]. Therefore, the model used here also included β as a free parameter. β changes from -3.45 for both h = 7 cm and h = 12 cm to -3.12 for h = 16.5 cm (see Table 5.1). Scattering exponents between -3 and -4 can either be interpreted as scattering from surface fractals with a fractal dimension of $D_S = 6 + \beta$ [142, 202] or as a combination of multiple scattering power laws. An interpretation in terms of surface fractals would mean that the fractal dimension of the internal foam surface increases with increasing foam height. This would mean that the air/liquid interfaces inside the foam are not perfectly flat ($D_S = 2$), but have features normal to the interface, which can be interpreted as some type of roughness. The fact that this power law is present in the data even at very low *q* values would however imply a roughness in the order of several 10 nm, which is much too high for an air/liquid interface and therefore makes this interpretation not applicable. It is worth noting that the radius of curvature of foam bubbles in wet foams ($r_B \approx 0.1 - 1 \text{ mm}$) is too large to be detected by SANS measurements. An-



Figure 5.5: 2D detector images of the SANS data measured at different foam heights. (a) h = 7 cm, (b) h = 12 cm, (c) h = 16.5 cm.

other interpretation is the combination of different SAS power laws. Here, the nodes and Plateau Borders would yield classic Porod scattering with $\beta = -4$ and the thinner plane-parallel portions of the films might be considered as randomly oriented flat objects resulting in a SAS exponent of $\beta = -2$ [142]. Upon drainage the distribution of these scattering objects shifts towards the thin, plane-parallel films and β increases. This argumentation is in line with the well-known transition from spherical bubbles in wet foams with a higher liquid volume fraction to polyhedral shaped bubbles in dry foams with very low liquid volume fractions [31, 200]. This transition was already observed in SANS experiments and associated with the appearance of "spikes" in the 2D detector images [65, 174]. This trend is also visible in the SANS data presented here. Figure 5.5 shows the 2D detector images of the SANS measurements at the three different foam heights. With increasing foam height the degree of radial symmetry in the scattering data decreases. At the highest measurement position several "spikes" are visible, which are due to the decreased statistics regarding the orientation of the foam films because of coalescence.

Despite the fact that considering a transition from spherical to polyhedral bubbles can be explained by drainage and partly reflects the different structures inside a foam, the limited amount of data presented here does not suffice to give a definite explanation for the observed change in β and therefore the nature of the SAS contribution to the overall scattering. Consequently, the SAS scaling factor *B* is not further discussed here. In order to improve the understanding of this contribution to the overall scattering signal more detailed investigations for example with an improved height resolution along the foam are required. The transition towards large, polyhedral shaped bubbles also explains the improved description of the SANS data without the angle correction term at the highest measurement position in the foam. It can be assumed that here the foam bubbles are larger than at the lower measurement positions, which leads to a reduced number of foam films in the neutron beam. It appears that in this situation the number of foam films inside the beam is too small to justify the assumption that their orientation can be approximated by the projection of the incident beam onto a sphere. Here, the experimental data are better described with an even distribution of the angles of incidence. This finding supports the initial assumption that the bubble shape and the resulting orientational distribution of the foam films is relevant for the profile of the scattering curves. In addition, a rough estimation about the bubble shape can be made based on the SANS data of a foam.

All model fits used a constant SLD contrast between air ($\rho_{air} = 0$) and D₂O ($\rho_{D_2O} = 6.34 \times 10^{-6} \text{ Å}^{-2}$). This can be rationalized as follows: As stated above, there are no micelles present in the foam films, because the concentration of C₁₄TAB was set to its cmc. Considering this, the C₁₄TAB molecules should mainly be located at the air/D₂O interface, which results in D₂O films with a very low concentration of surfactant molecules inside. Consequently, scattering from micelles in the foam was neglected. At concentrations above the cmc this assumption might not be valid anymore and scattering from micelles as well as a changing SLD will have to be considered.

The same approximation of only considering the air/D₂O contrast was also made by previous studies investigating surfactant stabilised foams by SANS [173, 174, 184, 187]. In the model presented in this chapter the reflectivity contribution (dotted blue lines in Figure 5.3) solely governs the oscillations in the scattering curves. Following this reflectivity-based interpretation, the first maximum in the scattering curves can be interpreted as a "pseudo-critical edge" and its position is therefore only governed by the neutron contrast between the liquid films and the gas bubbles and not by the film thickness as already stated by Ropers et al. and Schmidt et al. [184, 185]. All first maxima can be described by using a air/D₂O contrast, which further supports the assumption that this contrast suffices to describe the scattering curves.



Figure 5.6: Comparison between foam film thicknesses extracted from SANS (h = 7 cm (orange), h = 12 cm (blue), h = 16.5 cm (magenta), right ordinate) and TFPB measurements (black squares, left ordinate) with a 3.5 mM C₁₄TAB solution.

5.3.2 Comparison of SANS results with TFPB experiments

In order to verify that the oscillations in the SANS curves can be attributed to the thickness of individual foam films, the disjoining pressure isotherm of an individual foam film was recorded with a thin Film Pressure Balance (TFPB). Figure 5.6 shows a comparison between the $\Pi(d)$ curve of an individual, horizontal foam film, measured with a TFPB and the film thickness distributions extracted from the model fit parameters d_0 and σ for the three different foam heights.

The disjoining pressure Π is the pressure inside the foam film required to balance the external pressure in the measurement cell [46]. Upon increasing the external pressure the foam film becomes thinner and water is pushed back into the porous glass disc, holding the film. The thickness of the individual foam film decreases from d = 46 nmat $\Pi = 70$ Pa to d = 19 nm at $\Pi = 11000$ Pa. This is in good agreement with previous studies investigating the same system [57, 60]. Note that the foam film inside the TFPB did not rupture at the highest pressure. Here, the upper limit of the instrumental accessible pressure range was reached. The film thickness distributions extracted from the model fits lie mostly within the film thickness range measured with the TFPB and indicate that the disjoining pressure Π in films inside the foam ranges from $\approx 800 \, \text{Pa}$ to more than 11000 Pa. The foam film thicknesses extracted from the model fits are in agreement with the results of the TFPB experiment (see Figure 5.6), which validates the interpretation of the oscillations in the SANS curves in terms of foam film thicknesses. However, the film thickness distributions for h = 12 cm and h = 16.5 cm include film thicknesses thinner than the range covered by the TFPB measurement. This can be explained by the fact that the maximum experimentally accessible pressure was reached before the films ruptured. In addition the films in a foam are more dynamic and do not adopt an equilibrium thickness as in a TFPB experiment. The thinnest films observed by SANS might also undergo a final non-equilibrium thinning step before rupturing that is not resolvable in a TFPB. A critical point in this context might also be an oversimplification of the thickness distribution of the foam films. This possibility was further investigated by changing the film thickness distribution in the model fit from a normal to a log-normal distribution. A comparison of the resulting model fits and the film thickness distributions for the lowest foam height (h = 7 cm) is shown in Figure 5.7.

The final model fits and the resulting film thickness distributions are virtually identical. The mean thickness d_0 is 28.26 nm and 28.24 nm for the fits with log-normal and normal



Figure 5.7: Comparison between normal and log-normal distribution of the foam film thicknesses in the fitting model. (a) Experimental scattering curve (black squares) and final model fits with normal (solid red line) and log-normal (dashed blue line) distribution, respectively. (b) Foam film thickness distributions of the model fits in (a).

distribution, respectively. The standard deviation of the thickness distribution σ is = 2.68 nm and 2.67 nm. This means that an asymmetric distribution of the foam film thickness does not improve the agreement between experimental data and theoretical scattering curve and underlines that a normal distribution of the foam film thicknesses is a reasonable assumption.

5.4 Conclusion

Aqueous foams stabilised by the standard cationic surfactant tetradecyltrimethylammonium bromide (C_{14} TAB) were studied using SANS and complementary TFPB experiments. A new model for the interpretation of SANS experiments on foams is developed, which employs an incoherent superposition of weighted reflectivity curves and a small-angle scattering (SAS) contribution. The reflectivity contribution is modified by an angle-correction, which takes the distribution of angles of incidence on a spherical bubble into account. This model fully describes scattering curves of surfactant stabilised foams, yielding information about the thickness distribution of films inside the foam. With increasing foam height (corresponding to the time passed after foam formation) the mean film thickness decreases from 28 nm to 22 nm, because of drainage. Simultaneously, the film thickness becomes more polydisperse. This is probably caused by film rupturing during coalescence and subsequent uptake of the released liquid by the remaining films. The angle-corrected reflectivity contribution is not suitable for the description of the scattering curve of the driest foam (highest measurement position). Here, an uncorrected reflectivity term was sufficient to describe the experimental data, which is attributed to the transition from curved to faceted interfaces between bubbles in a polyhedral foam. In addition, the power law of the SAS contribution changes from $\beta = -3.45$ for wet foams to $\beta = -3.12$ for the driest foam. This is attributed to the progressive drainage and decomposition of larger structures in the foam like Plateau borders ($\beta = -4$) and the continuous emergence of plane-parallel films ($\beta = -2$) during foam ageing and is again a hint towards a more

plane-parallel films ($\beta = -2$) during foam ageing and is again a hint towards a more polyhedral-like foam structure. The film thicknesses extracted from the model fits are comparable to thicknesses of individual foam films in a TFPB experiment, further validating our model. In summary, this chapter presents a new model for the description of scattering data from foams, which takes into account reflectivity and small-angle scattering as well as the polydispersity of the foam films. Since the angle-corrected reflectivity term proposed here is only suitable for the description of wet foams with curved bubble interfaces, a future challenge in this field will be a more realistic model for the reflectivity contribution in dry, polyhedral foams.

6 Foams stabilised by PNIPAM microgels

Similar content is published in "Structure formation of PNIPAM microgels in foams and foam films" Matthias Kühnhammer et al., *Soft Matter*, **2022**. [203] doi: 10.1039/D2SM01021F. TFPB measurements and subsequent thickness analysis presented in this chapter were performed by Kevin Gräff.



Abstract

Responsive aqueous foams are very interesting from a fundamental point of view and for various applications. Here, thermoresponsive MGs made from poly(*N*-isopropyl-acrylamide) (PNIPAM) microgels (MGs) with varying cross-linker content, are used as foam stabilisers. The foams obtained are thermoresponsive and can be destabilised by increasing the temperature. The structuring of MGs inside the foam films is investigated with small-angle neutron scattering and in a thin film pressure balance. The

foam films are inhomogeneous and form a network-like structure, in which thin and MG depleted zones with a thickness of ca. 30 nm are interspersed in a continuous network of thick MG containing areas with a thickness of several 100 nm. The thickness of this continuous network is related to the elastic modulus of the individual MGs, which was determined by atomic force microscopy indentation experiments. Both the elastic moduli and foam film thicknesses indicate a correlation to the network elasticity of the MGs predicted by the affine network model.

6.1 Introduction

Stimuli-responsive foams can be obtained by using stimuli-responsive foam stabilisers. Following this approach, foams responsive to temperature, pH, magnetic fields or light irradiation were reported [204-207]. As discussed in Chapter 2.2.3 PNIPAM MGs are a well-established temperature-responsive material. PNIPAM MGs are surface active and spontaneously adsorb at the air/water or oil/water interfaces [123–125]. This inspired the fabrication of a range of stimuli-responsive emulsions which can be broken by changing the pH or the temperature [126–130]. Originally the responsivity of these emulsions to external stimuli was hypothesised to be related to a lateral collapse of the MGs at the interface, which would reduce the surface coverage and facilitate the coalescence of emulsion droplets [125, 130]. Recent studies by Harrer et al. and Bochenek et al. investigating the temperature response of MG monolayers adsorbed at the air (oil)/water interface rebutted this interpretation as they found that adsorbed MGs only show a size reduction in the direction normal to the interface when heated above the VPTT [133, 134]. More precisely, the size of the flat shell adsorbed at the interface is not affected by temperature, whereas the core shrinks when the system is heated above the VPTT [134, 208]. The structure of PNIPAM MGs adsorbed at interfaces was also studied thoroughly. Given their soft nature, MGs deform upon adsorption at an interface [131, 132, 209-211]. Picard et al. and Rey et al. studied the lateral ordering of MGs at the air/water interface by analysing monolayers transferred to a solid substrate along the compression isotherm in a Langmuir trough [131, 132]. In both studies very long ranged hexagonal ordering of the MGs even at very low surface pressures was observed. Upon compression, the inter-particle distance decreases gradually and eventually a phase transition characterised by an abrupt change in inter-particle distance is observed. In both studies this phase transition is explained by a change from

shell-shell to core-core contact of the MGs. The phase transition seems to be facilitated by a higher amount of cross-linker used in the MG synthesis. Rey et al. observed the phase transition at lower surface pressures for higher cross-linker concentrations [132]. Considering the large amount of publications dealing with PNIPAM MG stabilised emulsions, there are only very few publications investigating foams stabilised by PNI-PAM MGs. Horiguchi et al. demonstrated that MG stabilised foams can be obtained at temperatures below the VPTT, whereas no foam formation is observed at temperatures above the VPTT [138]. In addition the foams are temperature responsive as they rapidly collapse when the temperature is increased above the VPTT. Maestro et al. reported similar results and were able to detect a transition from a solid-like (T < VPTT) to a liquid-like (T > VPTT) behaviour of the interfacial MG films by passive interface rheology [137]. According to the authors the liquid-like film should have a higher permeability, which could explain the decrease in foam stability at temperatures above the VPTT.

This chapter aims to deepen the understanding of aqueous foams stabilised by PNI-PAM MGs. A series of MGs with varying cross-linker content is used to study macroscopic foam properties and the influence of temperature on them. Furthermore, the structure of MG stabilised foams is investigated by analysing single horizontal foam films in a thin film pressure balance (TFPB) and macroscopic foams by small-angle neutron scattering (SANS). In addition, the deformation of MGs inside foam films is correlated with the elastic properties measured with atomic force microscopy (AFM).

The SANS data presented here were analysed using a slightly adapted version of the model described in Chapter 5.

$$I = A \cdot \sum_{d_i} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(d_i - d_0)^2}{2\sigma^2}} \cdot R(d_i) + B \cdot q^{-4} + C$$
(6.1)

In contrast to the SAS decay used in Chapter 5, a strict Porod term is sufficient for the description of SANS curves from MG foams. The reason behind this is further discussed in Chapter 6.3.

6.2 Results

6.2.1 Microgel characterization

MG10.0

 419 ± 17

The hydrodynamic radii and ζ potentials of all microgels (MGs) are summarised in Table 6.1. A temperature-induced collapse of all MGs is observed. This volume phase transition is well-known for NIPAM MGs [77] and is linked to the lower critical solution temperature (LCST) of linear PNIPAM, which is approximately 32 °C [117, 118]. All MGs have a small, positive ζ potential in the swollen state at 20 °C, which is due to the positively charged initiator fragments incorporated during the MG synthesis. In the collapsed state at 50 °C the ζ potential increases notably, which is attributed to the reduced surface area of the collapsed particles.

50 °C.					
	MG	<i>R_h</i> (20 °C)	<i>R_h</i> (50 °C)	ζ(20 °C)	ζ(50 °C)
		nm	nm	mV	mV
	MG2.0	393 ± 8	133 ± 4	13 ± 4	44 ± 6
	MG3.5	319 ± 5	128 ± 2	7 ± 4	34 ± 5
	MG5.0	320 ± 11	142 ± 2	6 ± 4	35 ± 5
	MG7.5	348 ± 7	189 ± 8	10 ± 4	31 ± 6

Table 6.1: Hydrodynamic radii R_h and ζ potentials of all microgels studied at 20 °C and 50 °C.

Figure 6.1 shows the swelling ratio of the MGs studied as a function of the cross-linker concentration c(BIS). The swelling ratio is calculated as the hydrodynamic volume increase upon swelling $(R_{20}/R_{50})^3$. The swelling ratio decreases with increasing cross-linker concentration, which is an indirect indication for decreasing deformability and consequently decreasing mesh size with increasing cross-linker concentration.

 246 ± 7

 11 ± 4

 36 ± 5

Figure 6.2 shows AFM scans of spin-coated MG samples under ambient conditions in air. All MGs have a spherical shape and a low polydispersity.



Figure 6.1: Temperature induced swelling ratio of the MGs as a function of cross-linker concentration.



Figure 6.2: AFM scans of the MG substrates in air. (**a**) MG2, (**b**) MG3.5, (**c**) MG5, (**d**) MG7.5, (**e**) MG10.0.



Figure 6.3: Foamability of the MG dispersions at $T = 22 \degree C$ (**a**) as a function of MG concentration *w* and (**b**) as a function of cross-linker concentration *c*(BIS).

6.2.2 Foaming experiments

The foamability, which is the initial foam height immediately after foam formation, of the different MG dispersions at 22 °C is summarised in Figure 6.3. The foamability of all MG dispersion increases approximately linear with the MG concentration w (see Figure 6.3 (a)). This observation indicates the absence of any aggregation processes in the studied concentration range and can be rationalised by the consideration that a larger number of MGs are capable of stabilising a larger interfacial area. Assuming a constant bubble size for the different MG concentrations leads to a linear relation between w(MG) and the foamability. Despite the seemingly imprecise foaming procedure, all foamability values are well reproducible. This suggests that during the foaming procedure some type of steady-state regarding the foamability is reached, which is not influenced by further shaking cycles. The existence of this steady-state in foamability was also reported in literature and is explained by an equilibrium between bubble formation and coalescence during the foaming procedure [31, 212]. When plotted against the cross-linker concentration c(BIS) (see Figure 6.3 (**b**)), a non-monotonous trend is observable at all three MG concentrations studied. The foamability is maximal for c(BIS) = 2.0 mol%, decreases to its minimum around 5.0 mol% and increases slightly again for higher cross-linker concentrations.

Figure 6.4 shows a selection of photographs used to determine the half life time $t_{1/2}$ at $T = 22 \degree C$ of MG dispersions with w = 1.0 wt%. Figure 6.4 (a), (b) and (c) show



Figure 6.4: Exemplary foam decay at $T = 22 \degree C$ for the different MGs studied at a concentration of w = 1.0 wt%. (a) Immediately after foam formation, (b) after 5 h and (c) after 30 h. Samples are MG2.0, MG3.5, MG5.0, MG7.5 and MG10.0 from left to right.



Figure 6.5: Half life time $t_{1/2}$ at $T = 22 \,^{\circ}$ C of foams produced from MG dispersions at three different concentrations (black squares: $w = 0.3 \,\text{wt\%}$, red circles: $w = 0.5 \,\text{wt\%}$ and blue triangles: $w = 1.0 \,\text{wt\%}$) as a function of cross-linker concentration c(BIS).

photographs of the foamed dispersions directly after foam formation (t = 0), after t = 5 h and t = 30 h, respectively. Figure 6.5 shows the half life times at T = 22 °C of all MG dispersions studied.

There is no clear trend observable for $t_{1/2}$, neither as a function of MG concentration, nor as a function of cross-linker concentration. Most of the studied foams have half life times in the range of 10 ± 5 h with standard deviations of several h. These large standard deviations and the absence of a clear trend in $t_{1/2}$ is a reflection of the stochastic nature of foam decay and should therefore not be over interpreted. Nevertheless, there appears to be a slight increase of $t_{1/2}$ for the two MGs with the highest cross-linker concentration (MG7.5 and MG10.0) at high MG concentrations (w = 0.5 and 1.0 wt%).

Effect of temperature



Figure 6.6: Foamability of a 1.0 wt% dispersion of MG2.0 (**a**) at $T = 22 \degree \text{C}$ and (**b**) at $T = 50 \degree \text{C}$. Red, dotted lines highlight the foam height, i.e. foamability.

Figure 6.6 illustrates the effect of temperature on the foamability. Photographs of 1.0 wt% dispersions of MG2.0 taken immediately after the foaming procedure are shown. The dispersion in Figure 6.6 (**a**) was equilibrated at room temperature (T = 22 °C). The dispersion shown in Figure 6.6 (**b**) was equilibrated in a water bath (T = 50 °C) before the foam formation. Red, dotted lines highlight the foam height, i.e. foamability. The foamability of the heated dispersion is drastically decreased, indicating a temperature dependent foam formation.



Figure 6.7: Exemplary foam decay of a foam formed from a w = 1.0 wt% dispersion of MG2.0 subjected to a T = 50 °C water bath at t = 0. (a) Immediately after foam formation, (b) after 5 min and (c) after 12 min. Red, dotted lines highlight the foam height.

Figure 6.7 shows a series of photographs used to determine the half life time $t_{1/2}$ at $T = 50 \,^{\circ}\text{C}$ of a 1.0 wt% dispersion of MG2.0. Figure 6.7 (**a**), (**b**) and (**c**) show photographs of the foamed dispersions directly after foam formation (t = 0), after $t = 5 \,\text{min}$ and $t = 12 \,\text{min}$, respectively. Figure 6.8 summarises the half life times at $T = 22 \,^{\circ}\text{C}$ (closed symbols) and at $T = 50 \,^{\circ}\text{C}$ (open symbols) of all MG dispersions studied.

 $t_{1/2}$ at $T = 50 \,^{\circ}\text{C}$ is independent of MG and cross-linker concentration and is approximately $15 \pm 5 \,\text{min}$ for every foam studied, meaning that $t_{1/2}$ at $50 \,^{\circ}\text{C}$ is around two orders of magnitude lower than $t_{1/2}$ at $22 \,^{\circ}\text{C}$.

6.2.3 SANS measurements

Figure 6.9 shows SANS data of a foam prepared from a 0.3 wt% dispersion of MG2.0 recorded at different foam heights ((**a**) h = 2 cm, (**b**) h = 9.5 cm, (**c**) h = 16 cm) together with the model fits obtained using Equation 6.1 with a scattering length density (SLD) contrast of $\rho_{\text{film}} = 4.5 \times 10^{-6} \text{ Å}^{-2}$ for the foam films in the reflectivity contribution. For all foam heights the overall scattered intensity is dominated by the Porod contribution ($I \propto q^{-4}$) at low q. At $q \approx 0.1 \cdot 0.2 \text{ nm}^{-1}$ the scattered intensity is set off from the strict Porod behaviour (dashed green line) to higher intensities by the reflectivity contribution (dotted blue line). The magnitude of this intensity offset is increased for


Figure 6.8: Half life time $t_{1/2}$ at $T = 22 \,^{\circ}\text{C}$ (closed symbols) and $T = 50 \,^{\circ}\text{C}$ (open symbols) of foams produced from MG dispersions at three different concentrations as a function of cross-linker concentration c(BIS).



Figure 6.9: SANS data of a foam prepared from a 0.3 wt% dispersion of MG2.0, measured at different foam heights. (a) h = 2 cm, (b) h = 9.5 cm, (c) h = 16 cm. Black squares are experimental data. Lines are model fits according to Equation 6.1. For clarity the full curve (solid red line) is shown together with the Porod (dashed green line) and the reflectivity (dotted blue line) contribution.

Table 6.2: Fit parameters of the model fits employing Equation 6.1 for the three different foam heights. The corresponding curves are shown in Figure 6.9 (**a**, **b**, **c**).

	h	A	d_0	σ	$B\cdot 10^{-8}$	$C \cdot 10^{-3}$
	cm	cm^{-1}	nm	nm	$nm^4 \cdot cm^{-1}$	cm^{-1}
-	2	5.89	24.7	291	3.15	1.77
	9.5	8.48	24.5	225	1.90	1.03
	16	6.53	23.2	199	1.30	0.60

the two higher measurement positions (h = 9.5 cm and h = 16 cm). The fit parameters used for the model fits in Figure 6.9 are summarised in Table 6.2. The fit parameters are: reflectivity scale factor A, mean foam film thickness d_0 , standard deviation of the foam film thickness σ , Porod scale factor B and incoherent background C.

With increasing foam height both the Porod scale factor *B* and the incoherent background *C* decrease. The reflectivity scale factor *A* first increases from 5.89 cm^{-1} to 8.48 cm^{-1} when the foam height is increased from 2.0 cm to 9.5 cm and then decreases again to 6.53 cm^{-1} for the highest foam height measured (h = 16.0 cm). The mean foam film thickness d_0 is around 23 nm to 25 nm for all foam heights. The standard deviation decreases from 291 nm to 199 nm with increasing foam height. This large standard deviation is further discussed in Section 6.3.

Since all scattering curves are dominated by the Porod contribution and the features arising from the reflectivity contribution are barely visible in Figure 6.9, the SANS data of foams prepared from 0.3 wt% dispersions of four different MGs ((**a**) MG2.0, (**b**) MG3.5, (**c**) MG5.0, (**d**) MG7.5) are presented in so-called Porod plots ($I \cdot q^4 \text{ vs } q$) in Figure 6.10. Again, every foam was studied at three different heights (red squares h = 2 cm, blue circles h = 9.5 cm and green triangles h = 16 cm). For comparison a theoretical reflectivity curve of a free-standing 30 nm thick film in air with a SLD contrast of $\rho_{\text{film}} = 4.5 \times 10^{-6} \text{ Å}^{-2}$ is shown (black line). Here, the q^{-4} decay corresponds to the Fresnel reflectivity of a bare interface. The Porod plots of foams prepared from 0.5 wt% and 1.0 wt% MG dispersions, are shown in Figure 6.17 and Figure 6.18 in the appendix.

All scattering curves display a first maximum at $q \approx 0.15 \,\mathrm{nm^{-1}}$ and a very weak,



Figure 6.10: Porod plots of SANS data of foams prepared from 0.3 wt% dispersions of (a) MG2.0, (b) MG3.5, (c) MG5.0, (d) MG7.5, measured at different foam heights (red squares (h = 2 cm), blue circles (h = 9.5 cm) and green triangles (h = 16 cm)). The curves are shifted in intensity for clarity. For comparison a theoretical reflectivity curve of a 30 nm film in air with a SLD contrast of $\rho_{\text{film}} = 4.5 \times 10^{-6} \text{ Å}^{-2}$ is shown (black line).

in some cases barely visible, second maximum at $q \approx 0.33 \,\mathrm{nm^{-1}}$. Albeit much less pronounced, both maxima and the intermediate minimum in the experimental SANS curves are roughly at the same positions as the corresponding extrema of the theoretical reflectivity curve. It is important to note that for sufficiently thick films ($d > 20 \,\mathrm{nm}$) the position of the first maximum of the theoretical reflectivity curve in the Porod plot corresponds to its critical edge and its *q*-position is therefore only governed by the SLD contrast between the film (ρ_{film}) and the surrounding medium (air, ρ_{air}) via the following relation:

$$q_c = \sqrt{16\pi(\rho_{\rm film} - \rho_{\rm air})} \tag{6.2}$$

Assuming that $\rho_{air} = 0$, the position of q_c (i.e. the first maximum in the SANS curves) allows to calculate ρ_{film} . The first maximum in the SANS curves of the MG foams appears at $q_c \approx 0.15 \, \text{nm}^{-1}$, which means that the foam films consisting of MGs and D₂O have a SLD ρ_{film} of approximately $4.5 \times 10^{-6} \text{ Å}^{-2}$. An estimation of the foam films' expected SLD is not possible, because their composition (MG concentration inside the foam film) and the composition of the individual D₂O swollen MGs is unknown. There are however reference values in literature which were determined using neutron reflectometry. Widmann et al. reported a SLD of a thin film of PNIPAM MGs on a solid substrate in a saturated D₂O atmosphere of around $3 \times 10^{-6} \, \text{\AA}^{-2}$ [213]. Assuming that the MGs swell more in pure D₂O than in a D₂O vapour and taking into account the increased D₂O concentration ($\rho_{D_2O} = 6.34 \times 10^{-6} \, \text{\AA}^{-2}$) in the foam films, a SLD of $4.5 \times 10^{-6} \, \text{\AA}^{-2}$ for the MG stabilised foam films is realistic.

6.2.4 TFPB measurements

Figure 6.11 shows photographs of individual foam films formed in the TFPB using (**a**) MG2.0, (**b**) MG3.5, (**c**) MG5.0, (**d**) MG7.5, (**e**) MG10.0 at a concentration of w = 0.3 wt% at intermediate pressures of the isotherms shown in Figure 6.12. In all cases the films consist of a coloured area which is interspersed with small, grey spots with varying brightness. It is worth noting that the colours of the films do not originate from the usage of a filter or image post processing, they originate from interference of white light. Consequently, the thickness of the colourful areas is in the range of several 100 nm and



Figure 6.11: Photographs of foam films inside the TFPB stabilised by different MG dispersions at a concentration of w = 0.3 wt% (a) MG2.0, (b) MG3.5, (c) MG5.0, (d) MG7.5, (e) MG10.0. Pictures are taken at intermediate pressures of the isotherms shown in Figure 6.12, which are $\approx 500 \text{ Pa}$ for MG2.0, MG3.5, MG5.0 and MG7.5 and $\approx 150 \text{ Pa}$ for MG10.0. Scale bars are 200 µm.

can be analysed using the colour comparing algorithm described in Chapter 3. The exact thickness of the grey areas is more difficult to determine because this would require an intensity calibration, which is very challenging in the case of inhomogeneous films. However, as they appear to be colourless their thickness should be less then 100 nm.

The disjoining pressure isotherms of the colourful areas of the foam films stabilised by the different MGs are summarised in Figure 6.12. In the case of MG2.0 the foam film thickness *d* decreases notably with increasing disjoining pressure Π . The foam film thicknesses in the case of the other MGs don't decrease significantly with increasing Π . The foam films with MG10.0 were only stable until $\Pi \approx 200$ Pa, whereas all other foam films were stable up to $\Pi > 1000$ Pa. The initial foam film thickness *d* increases with the cross-linker concentration *c*(BIS) from $d \approx 300$ nm for MG2.0 to $d \approx 540$ nm



Figure 6.12: Disjoining pressure isotherms of coloured area of foam films stabilised by different MG dispersions (w = 0.3 wt%).

for MG10.0.

6.2.5 AFM indentation measurements

In Figure 6.13 (**a**) exemplary force curves (open symbols) are shown together with the corresponding fits using the Hertz model (solid lines, Equation. 3.20). The slope of the force increase upon indentation increases with the cross-linker concentration. This shows the influence of the cross-linker concentration on the mechanical properties of the MGs. The elastic moduli *E* of the different MGs (given in Figure 6.13 (**b**)) increase from 100 kPa for MG2.0 to 400 kPa for MG10.0. All force curves used for the determination of *E* for every MG are summarised in Figure 6.19 in the appendix. Every force curve was recorded at the apex, i.e. height maximum, of a individual MG, because of the radial inhomogeneity of the elastic properties of MGs synthesised with the so-called batch method used here [214–217].

Similar experiments were reported in literature, which yielded elastic moduli in the range from 5 kPa to 550 kPa for PNIPAM MGs prepared with varying amounts of cross-linker and synthesis conditions [185, 214, 218–221].



Figure 6.13: (a) Exemplary force curves for all MGs studied (open symbols) with corresponding fits using the Hertz model (solid lines, Eq. 3.20). (b) Elastic moduli as a function of cross-linker concentration extracted from Hertz model fits to the force curves shown in Figure 6.19.

6.3 Discussion

6.3.1 Macroscopic foam properties

A possible explanation for the non-monotonous trend in foamability described in Section 6.2 is the difference in size of the MGs. This possible correlation is investigated in Figure 6.14. Here, the foamability at different concentrations (black squares: w = 0.3 wt%, red circles: w = 0.5 wt% and blue triangles: w = 1.0 wt%, left ordinate) is plotted together with the hydrodynamic radius $R_h(20 \text{ °C})$ (connected green diamonds, right ordinate) as a function of the cross-linker concentration c(BIS).

 $R_h(20 \,^{\circ}\text{C})$ also shows a non-monotonous trend with respect to c(BIS), displaying a minimum between $c(\text{BIS}) = 3.5 \,\text{mol}\%$ and 5.0 mol%. Although the trend is similar for R_h and foamability, a direct correlation is not obvious. In this context it is important to keep in mind that the concentrations of the MG dispersions are given in wt%. Assuming that all MGs have a similar density, the absolute amount of MG particles present in a dispersion with a certain mass concentration w should be inversely proportional to the size of the MGs. This relation would suggest that the foamability of the resulting dispersions also should be inversely proportional to the size of the MGs, as the MGs' total surface area is higher at a given mass concentration. Even if there are differences



Figure 6.14: Foamability of the MG dispersions at different concentrations (black squares: w = 0.3 wt%, red circles: w = 0.5 wt% and blue triangles: w = 1.0 wt%, left ordinate) and hydrodynamic radius $R_h(20 \,^\circ\text{C})$ (connected green diamonds, right ordinate) as a function of cross-linker concentration c(BIS).

in the density of the MGs with varying cross-linker concentration, this effect should not suffice to invert the expected trend described above, which leads to the conclusion that the MG size is not the reason for the non-monotonous foamability. The exact origin of the observed trend in foamability remains unclear. There are several parameters governing foamability discussed in literature like viscosity of the bulk solution [222, 223], dynamic surface tension [224–227] or dilatational surface viscosity [228–231]. However, there is no unifying general theory for foam formation as the relevant factors depend on the system and even the foaming procedure used [31, 232, 233].

The increase of $t_{1/2}$ observed for the MG7.5 and MG10.0 at high MG concentrations could be related to the formation of MG aggregates inside the foam films or Plateau borders and subsequent slowdown or blockage of drainage. The overall stabilising effect of aggregate formation or "jamming" inside the liquid phase of foams is well documented [172, 234–236]. In addition, MGs with higher cross-linker concentration were reported to form aggregates with close core-core contacts more readily than MGs with lower cross-linker concentrations [131, 132]. Following this argumentation, the increased foam stability at high cross-linker contents and MG concentrations could be rationalised by the presence of MG aggregates in the Plateau borders. However, since there is no direct proof for the existence of these MG aggregates in the Plateau borders, this explanation should not be over interpreted. Another noteworthy observation regarding the foam stability is the fact that the maximum disjoining pressure before film rupture Π_{max} is not related to the macroscopic foam stability. Π_{max} is minimal for MG10.0 (see Figure 6.12), whereas $t_{1/2}$ is maximal (see Figure 6.5). A discrepancy between stability of individual foam films and macroscopic foam stability is regularly observed [64]. The main reason for this is most likely the difference in experimental conditions between comparably large single foam films under static and isolated conditions and a multitude of small foam films in the highly dynamic setting inside a foam [237, 238].

The temperature responsiveness of PNIPAM MG stabilised foams was already reported in literature [137, 138] and suggests a link between the collapse of individual MG particles when heated above the VPTT and the macroscopic foam properties. The foam half life time at 50 °C is not influenced by the MG or cross-linker concentration and approximately 15 ± 5 min for every foam. This finding suggests that the dominant mechanism for foam destabilisation at 50 °C is the time it takes for the temperature to equilibrate inside the foam. This is also underlined by the photograph in Figure 6.7 (c), in which the foam decay is progressed further at the edge of the foaming vial, which is in contact with the heated water bath, then in the center. Temperature responsiveness was also reported for MG stabilised oil-in-water emulsions, which are stable at temperatures below and rapidly break at temperatures above the VPTT [128–130, 239]. As stated in the introduction, MGs adsorbed at interfaces do not collapse in the lateral direction when the temperature is increased above the VPTT, which suggests a different destabilisation mechanism than the reduction of surface coverage [133, 134]. Another explanation for the temperature responsiveness of MG stabilised emulsions is the temperature induced change in interfacial viscoelasticity of MG laden interfaces [240–242]. In our opinion, this explanation also appears to be the best candidate for the rationalization of the temperature responsiveness of MG foams, as the interfacial viscoelasticity is also very often related to macroscopic foam stability [243–246].

6.3.2 Foam structure

In the SANS experiments with MG foams the overall scattered intensity decreases slightly with increasing foam height. This was also observed in various other publications investigating foams with SANS and is explained by drainage of the foam [65, 174, 175, 184]. During drainage the liquid films inside the foam become thinner and eventually rupture [21, 38, 200]. As a result of this, the amount of contrasted structures in the foam decreases, which leads to a decrease in scattered intensity as already described in Chapter 5. This trend is also visible in the fit parameters *B* and *C* (Table 6.2), which decrease monotonously with increasing foam height.

The fact that the theoretical reflectivity curve displays extrema at the same q values as the experimental SANS curves of the MGs, suggests the presence of a slightly preferential film thickness of around 30 nm with a pronounced polydispersity. The large polydispersity of the film thickness is reflected by the very high value of the standard deviation of the foam film thickness σ (Table 6.2), which is one order of magnitude higher than the mean film thickness d_0 .

In combination with the results obtained for individual foam films in a TFPB the following picture arises: Foam films in MG stabilised foams are inhomogeneous in thickness. Only the thinner parts of the foam films (grey areas in Figure 6.11, thickness of around 30 nm) are detectable by SANS (detection limit ≈ 200 nm in the setup used) but the corresponding scattering features are not very well defined as the thin films have a very high polydispersity and only represent a small portion of the total foam film. The foam film's inhomogeneity is also the reason for the rather exact Porod decay of the scattered intensity ($I \propto q^{-4}$) as the thicker parts of the foam films are too large to display a distinct form factor and are only detectable as single interfaces by the neutrons [142]. In agreement, deviations from strict Porod behaviour was reported for SANS curves from surfactant stabilised foams, which should have thinner foam films with a more homogeneous thickness profile [65, 173–175, 183, 186, 187].

As stated in the introduction it is well established that MGs, adsorbed at a single air/water interface, adopt very well defined long-ranged hexagonal structures even at low surface pressures [131, 132, 211]. The behaviour in foam films however, can be different as the presence of a second air/water interface in close proximity can add further geometrical constraints. Keal et al. were the first to report the inhomogeneous structure of foam films stabilised by PNIPAM MGs [136]. This observation is further corroborated in this chapter, which suggests that the presence of a second air/water interface changes the interfacial arrangement of MGs as they are gradually confined inside the foam film. Keal et al. were able to verify the depletion of MGs from the thinner regions of the foam film via fluorescence microscopy. The absence of MGs in the

thinner and by SANS detectable regions of the foam films also explains the very similar scattering curves irrespective of MG concentration or cross-linker content. The stabilisation mechanism of these thinner regions is still unclear. The dangling ends of MGs might extend into the depleted zones, but since these zones can be $10 \,\mu\text{m}$ and even more in diameter this cannot be the sole explanation. Another possibility is that the MGs around the depleted areas are heavily jammed and form a sort of corset structure which stabilises the depleted zones. Finally, small surface active components like PNI-PAM oligomers might still be present in small quantities after the dialysis and could stabilise the MG depleted zones.

6.3.3 Elastic properties of microgels govern the foam film thickness

Since the thickness of the colourful areas of the foam films increases with the cross linker concentration of the MGs used for stabilising them (see Figure 6.12), a relation between the stiffness or deformability of the individual MGs and this thickness is observed. This correlation is explored in Figure 6.15, in which the foam film thickness at the lowest disjoining pressure, where the foam film forms $d(\Pi_{\min})$ (black squares, left ordinate) and the elastic modulus extracted from AFM indentation experiments E (red circles, right ordinate) are plotted together as a function of the cross-linker concentration c(BIS). There is a linear relation between these two quantities, which is further highlighted in the inset of this figure, in which *E* is plotted against $d(\Pi_{\min})$. The thickness at the lowest disjoining pressure was used in this evaluation, since the elastic moduli were extracted from the force curves by fitting the first few 10 nm of indentation, which should probe the elastic properties at low compression. The absolute values of *E* might differ from the values reported here, as the Poisson ratio ν of PNI-PAM MGs is still not known exactly. The values reported in literature range from 0.25 to 0.5 for temperatures below the VPTT [121, 185, 218, 247]. However, assuming that the Poisson ratio is not strongly influenced by the cross-linker concentration the trend of *E* is maintained.

The observed relation suggests that the MGs' resistance to indentation of an AFM tip and to deformation inside a foam film probe the same overall elastic properties. One of the first models for the description of elastic properties of polymer networks is the affine network model [101, 102, 112]. The main assumption of this model is that the relative macroscopic deformation of a polymer network is the same as the relative



Figure 6.15: Foam film thickness at the lowest disjoining pressure $d(\Pi_{\min})$ (black squares, left ordinate) and elastic modulus *E* (red circles, right ordinate) as a function the cross-linker concentration *c*(BIS). The linear correlation between the to parameters is shown in the inset.

deformation of the individual polymer chains. The expression for the osmotic pressure arising from the isotropic elastic deformation of such a network is:

$$\frac{\Pi_{\rm el}}{k_B T} = \frac{N_{\rm chain}}{V_0} \left(0.5 \frac{\phi}{\phi_0} - \left(\frac{\phi}{\phi_0}\right)^{1/3} \right) \tag{6.3}$$

Here, N_{chain} is the number of polymer chains in each MG particle and V_0 represents the volume of a MG particle in the reference state. This reference state is typically interpreted as the state the MGs were during synthesis, which would mean in the collapsed state in this case. However, there is an ongoing debate about whether this reference state is well-defined when solvent molecules are already present during synthesis [248]. For simplicity the reference state here is defined as the state at T = 50 °C. This implies that ϕ and ϕ_0 are the polymer volume fractions in the MG particles under experimental conditions and the reference state, respectively. Note that the osmotic pressure Π_{el} given in Equation 6.3 is also used as the elastic contribution in the Flory-Rehner theory used for the description of gel swelling [112].

The polymer volume fraction can be estimated by the relation

$$\phi = \phi_0 \left(\frac{R_0}{R}\right)^3 \tag{6.4}$$



Figure 6.16: (a) Elastic modulus *E* (black squares, left ordinate) and affine network factor α (red circles, right ordinate) as a function the cross-linker concentration *c*(BIS). (b) Foam film thickness at the lowest disjoining pressure $d(\Pi_{\min})$ (black squares, left ordinate) and affine network factor α (red circles, right ordinate) as a function the cross-linker concentration *c*(BIS). The linear correlations between the respective parameters is shown in the insets.

with the polymer volume fraction under experimental conditions ϕ and the hydrodynamic radii R_0 and R in the reference state and under experimental conditions.

Using this relation and the hydrodynamic radii at 50 °C and 20 °C as reference and experimental state, Equation 6.3 can be rewritten as:

$$\frac{\Pi_{\rm el}}{k_B T} = \frac{N_{\rm chain}}{V_0} \left(0.5 \left(\frac{R_{50}}{R_{20}} \right)^3 - \frac{R_{50}}{R_{20}} \right)$$
(6.5)

Combining the experimental accessible parameters of the MGs, an affine network factor $\alpha = -\left(0.5\left(\frac{R_{50}}{R_{20}}\right)^3 - \frac{R_{50}}{R_{20}}\right)$ is defined. Possible correlations between α and the elastic moduli *E* and foam film thicknesses at the lowest disjoining pressure $d(\Pi_{\min})$ are explored in Figure 6.16.

Both *E* and $d(\Pi_{\min})$ seem to be strongly correlated with α . This correlation suggests that the deformation of MGs inside a foam and the elastic modulus extracted from AFM indentation measurements can both be described by applying the affine network model to MGs. However, some assumptions were made, which have to be kept in mind. The affine network model formalism for isotropic deformation was used, while

the deformation of MGs in a foam film is uniaxial and the indentation of a AFM tip into a MG is an even more local deformation. The model for isotropic deformation was used, because the isotropic deformation of MGs upon changing from the reference state (collapsed, $T = 50 \,^{\circ}$ C) to the experimental state of interest (here $T = 20 \,^{\circ}$ C) can easily be determined using DLS. Despite the difference in deformation symmetry this allows the determination of α with a completely different experimental technique and omits the danger of circular reasoning when correlating α with other parameters. Another point is the question of validity of the affine network model for MGs. Affine swelling was reported for PNIPAM MGs [249], but the exact requirements for the affine network model to be applicable are still unclear [250]. In general there is a variety of models, which try to describe the elastic properties of polymer networks, including the phantom network [103], the constraint-junction [104–106], Edwards tube [107] or slip-tube [108] model to name a few. The prerequisites for the applicability of each model are still debated, but the polymer concentration and heterogeneity of the polymer network were shown to have an influence on which model describes experimental observations best [109, 110]. A more detailed understanding of the elastic properties of MGs would be beneficial, especially regarding their possible application as nanoactuators [96-100].

6.4 Conclusion

Aqueous foams stabilised by PNIPAM MGs with varying cross-linker content were studied regarding their macroscopic foam properties and their structure. These foams are thermoresponsive, as they are stable for several hours at temperatures below the VPTT and rapidly collapse when heated above the VPTT. Below the VPTT an increase in foam stability was observed for high cross-linker contents and high MG concentrations, which might be due to the formation of MG aggregates inside the foam and subsequent blockage of drainage. All MGs form heterogeneous foam films inside a TFPB, with small areas (thickness around 30 nm) interspersed in a network structure with a thickness of several 100 nm. This heterogeneity also explains the scattering curves of MG stabilised foams. These SANS curves show a strict Porod behaviour ($I \propto q^{-4}$) over a large *q*-range, which can be attributed to structures larger than 200 nm and therefore includes Plateau borders, nodes and the thicker parts of the foam films. In addition,

a strongly damped reflectivity term was used to model the scattering curves. The reflectivity contribution in SANS from foams is typically attributed to foam films with a thickness below 100 nm and was consequently attributed to the thinner regions of the foam films. As these thinner regions only represent a fraction of the complete foam film, the reflectivity contribution to the scattering signal is rather small. A theoretical reflectivity curve of a 30 nm thick D₂O layer in air reproduces the position of the extrema in all scattering curves, which leads to the conclusion that the thinner regions of the foam films are around 30 nm thick. The fact that this thickness is comparable for all MGs and much smaller then their hydrodynamic sizes suggests that the MGs are depleted from the thinner areas of the foam film, which might be stabilised by the formation of a corset-like structure around them. The model used for the description of the SANS curves is a restricted version of the model described in Chapter 5, as the power of the SAS decay was fixed to $\beta = -4$ (Porod behaviour). The model seems to be on the verge of over describing the SANS data of MG foams as the foam film polydispersity has to be very high to attenuate the features of the reflectivity contribution. However, the fact that the model is capable of describing two very different types of foams further corroborates its validity. Finally, a correlation between the thickness of the thicker areas of the foam films and the elastic moduli determined by AFM indentation experiments of the individual MGs is observed. This correlation implies that both parameters are governed by the overall elastic properties of the MGs. In fact, both properties also show a strong correlation with the elastic osmotic pressure according to the affine network model describing the elasticity of polymer networks.



6.5 Appendix

Figure 6.17: Porod plots of SANS data of foams prepared from 0.5 wt% dispersions of (a) MG2.0, (b) MG3.5, (c) MG5.0, (d) MG7.5, measured at different foam heights (red squares (h = 2 cm), blue circles (h = 9.5 cm) and green triangles (h = 16 cm)). The curves are shifted in intensity for clarity. For comparison a theoretical reflectivity curve of a 30 nm film in air with a SLD contrast of $\rho_{\text{film}} = 4.5 \times 10^{-6} \text{ Å}^{-2}$ is shown (black line).



Figure 6.18: Porod plots of SANS data of foams prepared from 1.0 wt% dispersions of (a) MG2.0, (b) MG3.5, (c) MG5.0, (d) MG7.5, measured at different foam heights (red squares (h = 2 cm), blue circles (h = 9.5 cm) and green triangles (h = 16 cm)). The curves are shifted in intensity for clarity. For comparison a theoretical reflectivity curve of a 30 nm film in air with a SLD contrast of $\rho_{\text{film}} = 4.5 \times 10^{-6} \text{ Å}^{-2}$ is shown (black line).



Figure 6.19: All force curves used for the determination of the elastic molduli given in Figure 6.13.

7 Conclusions, open questions and future perspectives

7.1 Conclusions

In this thesis the internal structure of foams is studied by small-angle neutron scattering (SANS). For this purpose a designated sample environment (SE) with future compatibility with the European Spallation Source (ESS) is designed and constructed. The SE allows studying foams with SANS at different drainage stages, i.e. water contents and allows controlling experimental parameters like temperature and the foam formation rate. This SE was used to study two different types of foams by SANS. Firstly, a foam stabilised by the standard cationic surfactant tetradecyltrimethylammonium bromide (C_{14} TAB) is investigated. This foam is a well-studied reference system and is used to develop a model for the description of SANS curves from foams. Secondly, foams stabilised by thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM) microgels (MGs) are investigated. Within the last decades PNIPAM MGs received considerable scientific attention, but their role as foam stabilisers was scarcely studied. The thermoresponsiveness of the individual MGs is reflected in the macroscopic foam properties as the foams rapidly decays when the temperature is increased above the volume phase transition temperature (VPTT) of the MGs. A combination of SANS and thin film pressure balance (TFPB) experiments is used to elucidate the internal structure of MG stabilised foams. Finally, the elastic properties of MGs is correlated with the network elasticity as predicted by the affine network model. The main results of this thesis are highlighted in the following:

Modelling SANS curves of foams

A new model for the description of SANS from foams is presented. The model is

based on the incoherent superposition of reflectivity curves and a small-angle scattering (SAS) contribution. Using a self-written fitting routine, the complete scattering curves of a C_{14} TAB foam at three different drainage stages can be modelled. The foam film thicknesses extracted from the model fits are in good agreement with film thicknesses obtained with a TFPB for single films. During drainage the film thickness decreases from 28.2 nm to 22.4 nm. Simultaneously, the SAS scaling factor β increases from -3.45 to -3.12. This is interpreted as a decreasing number of larger structural motifs in the foam (e.g. Plateau Borders), which would yield Porod scattering ($\beta = -4$) and an increasing number of thin foam films, which give a $\beta = -2$ contribution. The model is also able to describe the SANS curves of MG stabilised foams, which supports the general validity of the model as it is able to describe the scattering from two very different foam systems. In the case of MG foams however, the SANS data show very few distinct features and the model is on the verge of over describing the data. The film thickness extracted from the model fits is around 30 nm and $\beta = -4$, irrespective of the cross-linker concentration of the MG used or the drainage state of the foam. The reason for this invariance in the fit parameters can be found in the special structure of MG stabilised foam films.

Structure of MG stabilised foams

The foam films in MG stabilised foams are very heterogeneous in thickness. TFPB experiments reveal thin and MG depleted areas interspersed in a network-like structure of thicker MG-laden areas. The thickness of the MG-laden network depends on the cross-linker concentration of the MG and ranges from 300 nm (2 mol% BIS) to 540 nm (10 mol% BIS). These areas are too thick to be measured in the SANS setup used in this thesis and consequently they appear as sharp interfaces, yielding Porod scattering ($\beta = -4$). This is the reason why the SANS curves of MG foams exhibit a strict Porod decay whereas this is not the case for SANS curves of C₁₄TAB foams, which have thin and homogeneous foam films. The thickness of the thin, MG depleted areas appears to be independent of the MG used to stabilise the foam and around 30 nm as determined by SANS.

Elastic properties of MGs

The elastic properties of MGs as probed by the deformation in a foam film or the indentation with an atomic force microscopy (AFM) tip are shown to be correlated with the elastic properties as predicted by the affine network model. Even though this is only a qualitative correlation and a different model of network elasticity might improve the description of the experimentally observed trends, this opens the door to a better-founded understanding and theoretical prediction of MG elasticity.

7.2 Open questions and future perspectives

This thesis was able to advance the experimental accessibility of the internal structure of foams in general by the use of SANS, elucidate the special structure of MG stabilised foam films and improve the understanding of the elastic properties of MGs. While some questions could be answered in this thesis, some remain open and a few new ones emerged. In the following some of these open questions are discussed and a personal opinion about possible solutions and further experiments is presented.

The foam cell presented in Chapter 4 could be further improved. For example by implementing a camera to determine the bubble size distribution of the first layer of bubbles and to observe their shape. Furthermore, electrodes could be added to measure the liquid volume fraction of the foam by electrical conductivity. This additional experimental data might then be used to improve the fitting model or at least cross-check the fitting results. For instance, the necessity of the angle-correction for a description of the SANS data could be correlated with the bubble size and shape.

As discussed in Chapter 5, an increase of the standard deviation of the foam film thickness σ is observed with proceeding foam ageing in the C₁₄TAB foam. This is rationalised by the reduced number of foam films in the neutron beam and the resulting reduced statistics and by local incorporation of liquid released during film breakups. As this is the very first attempt at the determination of the foam film thickness distribution inside a macroscopic aqueous foam, these interpretations are only speculative. Ideally, this result should be verified by a different experimental approach. A potential candidate for this is high-resolution X-ray tomography, as the 3D resolution of this technique can be as low as 16 nm [251]. The imaged area in these experiments is typically only a few µm, which is not sufficient for foams. This might change however, with the increasing performance of synchrotron radiation facilities.

The inhomogeneous structure of MG stabilised foam films as described in Chapter 6 leads to several interesting questions. The exact stabilisation mechanism of the MG depleted thin film areas remains unclear. It might be due to a jamming of MGs and the formation of a corset-like structure, the strong deformation of the weakly cross-linked MG shell and subsequent extension into the thin areas or even due to impurities of very weakly branched PNIPAM polymers. Another open question is the structuring of the MGs in the thicker MG laden areas of the films. Do they form mono- or multilayer? Do the MGs at the two opposing interfaces adopt a zip-like structure as proposed by Cohin et al. [135]? Do the MGs still adopt a long ranged hexagonal order as observed at single air/water interfaces? A possible way to study some of these questions could be a reflectometry experiment with a single horizontal foam film. Albeit experimentally very challenging, such an experiment was already performed by Ederth and Thomas, who studied the drainage and stratification of a single foam by neutron reflectometry [252].

Lastly, the connection made in Chapter 6 between the affine network model and the elastic modulus of the MGs and their deformation inside a foam film is only qualitative. In order to potentially establish a quantitative link between the model and the experimental results, more detailed information about the exact architecture of the MG's polymer network is required, like the mesh size distribution and the length and number of polymer chains. These parameters are nearly impossible to determine experimentally, but are readily accessible in computer simulations [253]. Consequently, computer simulations might be used to elucidate the mechanical properties of MGs and maybe even establish a quantitative link to experimental results.

In summary, the results presented in this thesis improve the experimental accessibility of the internal structure of foams. This might contribute to deepen the understanding of structure-property relations in all kinds of different aqueous foams, which could help choosing the optimal foam for a certain application. Especially the thermoresponsiveness of foams stabilised by PNIPAM MGs might be interesting for applications like floatation or other extraction processes, as the foam can be selectively destroyed after the extraction simply by increasing the temperature.

Bibliography

- [1] Cyrino, M. Aphrodite; Gods and heroes of the ancient world; Routledge, 2010.
- [2] Behroozi, F. Soap bubbles in paintings: Art and science. *American Journal of Physics* **2008**, *76*, 1087–1091.
- [3] Emmer, M. Soap Bubbles in Art and Science: From the Past to the Future of Math Art. *Leonardo* **1987**, *20*, 327.
- [4] Newton, I. Opticks: Or, a Treatise of the Reflexitons, Refractions, Inflexions and Colours of Light; London, 1704.
- [5] Plateau, J. A. F. Statique expérimentale et théorique des liquides soumis aux seules forces moléculaires; Gauthier-Villars: Paris, 1873.
- [6] Thomson, W. On the division of space with minimum partitional area. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **1887**, 24, 503–514.
- [7] Weaire, D. Kelvin's foam structure: A commentary. *Philosophical Magazine Letters* 2008, *88*, 91–102.
- [8] Weaire, D. Kelvin's ideal foam structure. *Journal of Physics: Conference Series* **2009**, 158.
- [9] Weaire, D.; Phelan, R. A counter-example to kelvin's conjecture on minimal surfaces. *Philosophical Magazine Letters* **1994**, *69*, 107–110.
- [10] Rosa, M.; Fortes, M.; Vaz, M. Deformation of three-dimensional monodisperse liquid foams. *The European Physical Journal E* 2002, 7, 129–140.
- [11] Van Der Net, A.; Drenckhan, W.; Weaire, D.; Hutzler, S. The crystal structure of bubbles in the wet foam limit. *Soft Matter* 2006, 2, 129–134.

- [12] van der Net, A.; Delaney, G. W.; Drenckhan, W.; Weaire, D.; Hutzler, S. Crystalline arrangements of microbubbles in monodisperse foams. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2007, 309, 117–124.
- [13] Gabbrielli, R.; Meagher, A. J.; Weaire, D.; Brakke, K. A.; Hutzler, S. An experimental realization of the Weaire-Phelan structure in monodisperse liquid foam. *Philosophical Magazine Letters* 2012, 92, 1–6.
- [14] Prud'homme, R. K.; Khan, S. A. Foams Theory, Measurements, and Applications; Marcel Dekker: New York, 1995.
- [15] Schramm, L. L. Emulsions, Foams, and Suspensions Fundamentals and Applications; Wiley-VCH: Weinheim, 2005.
- [16] Exerowa, D. R.; Gochev, G.; Platikanov, D.; Liggieri, L.; Miller, R. Foam Films and Foams - Fundamentals and Applications; CRC Press: Boca Raton, FL, 2019.
- [17] Dickinson, E. Food emulsions and foams; Elsevier, 1987.
- [18] Evans, D. F.; Wennerström, H. The colloidal domain: Where physics, chemistry, biology, and technology meet, 2nd ed.; Wiley-VCH: New York, NY, 1999.
- [19] Hunter, R. J. Foundations of Colloid Science, second ed ed.; Oxford University Press: Oxford, New York, 2001.
- [20] Butt, H.-J.; Kappl, M. Surface and Interfacial Forces, 2nd ed.; Wiley-VCH: Weinheim, 2018.
- [21] Weaire, D.; Hutzler, S. *The Physics of Foams*; Oxford University Press: Oxford, New York, 1999.
- [22] Pugh, R. J. Bubble and Foam Chemistry; Cambridge University Press: Cambridge, 2016.
- [23] Fameau, A.-L.; Saint-Jalmes, A. Non-aqueous foams: Current understanding on the formation and stability mechanisms. *Advances in Colloid and Interface Science* 2017,
- [24] Binks, B. P. Particles as surfactants similarities and differences. *Current Opinion in Colloid and Interface Science* 2002, 7, 21–41.
- [25] Horozov, T. S. Foams and foam films stabilised by solid particles. *Current Opinion in Colloid and Interface Science* 2008, 13, 134–140.

- [26] Murray, B. S.; Ettelaie, R. Foam stability: Proteins and nanoparticles. *Current Opinion in Colloid and Interface Science* **2004**, *9*, 314–320.
- [27] Engelhardt, K.; Lexis, M.; Gochev, G.; Konnerth, C.; Miller, R.; Willenbacher, N.; Peukert, W.; Braunschweig, B. pH effects on the molecular structure of βlactoglobulin modified air-water interfaces and its impact on foam rheology. *Langmuir* 2013, 29, 11646–11655.
- [28] Wilde, P.; Mackie, A.; Husband, F.; Gunning, P.; Morris, V. Proteins and emulsifiers at liquid interfaces. *Advances in Colloid and Interface Science* 2004, 108, 63–71.
- [29] Bureiko, A.; Trybala, A.; Kovalchuk, N.; Starov, V. Current applications of foams formed from mixed surfactant-polymer solutions. *Advances in Colloid and Interface Science* 2015, 222, 670–677.
- [30] Guzmán, E.; Llamas, S.; Maestro, A.; Fernández-Peña, L.; Akanno, A.; Miller, R.; Ortega, F.; Rubio, R. G. Polymer-surfactant systems in bulk and at fluid interfaces. *Advances in Colloid and Interface Science* 2016, 233, 38–64.
- [31] Drenckhan, W.; Hutzler, S. Structure and energy of liquid foams. *Advances in Colloid and Interface Science* **2015**, 224, 1–16.
- [32] Koehler, S. A.; Hilgenfeldt, S.; Weeks, E. R.; Stone, H. A. Drainage of single Plateau borders: Direct observation of rigid and mobile interfaces. *Physical Review E - Statistical Physics, Plasmas, Fluids, and Related Interdisciplinary Topics* 2002, 66, 4.
- [33] Koehler, S. A.; Hilgenfeldt, S.; Weeks, E. R.; Stone, H. A. Foam drainage on the microscale II. Imaging flow through single Plateau borders. *Journal of Colloid and Interface Science* 2004, 276, 439–449.
- [34] Drenckhan, W.; Saint-Jalmes, A. The science of foaming. *Advances in Colloid and Interface Science* **2015**, 222, 228–259.
- [35] Koehler, S. A.; Hilgenfeldt, S.; Stone, H. A. Generalized view of foam drainage: Experiment and theory. *Langmuir* **2000**, *16*, 6327–6341.
- [36] Bartsch, O. Über Schaumsysteme. Kolloidchemische Beihefte 1924, 20, 1–49.
- [37] Briceño-Ahumada, Z.; Langevin, D. On the influence of surfactant on the coarsening of aqueous foams. *Advances in Colloid and Interface Science* 2017, 244, 124– 131.

- [38] Kruglyakov, P. M.; Karakashev, S. I.; Nguyen, A. V.; Vilkova, N. G. Foam drainage. *Current Opinion in Colloid and Interface Science* **2008**, *13*, 163–170.
- [39] Rio, E.; Biance, A. L. Thermodynamic and mechanical timescales involved in foam film rupture and liquid foam coalescence. *ChemPhysChem* 2014, 15, 3692– 3707.
- [40] Saint-Jalmes, A. Physical chemistry in foam drainage and coarsening. Soft Matter 2006, 2, 836–849.
- [41] Weaire, D.; Pageron, V. Frustrated froth: Evolution of foam inhibited by an insoluble gaseous component. *Philosophical Magazine Letters* **1990**, *62*, 417–421.
- [42] Gandolfo, F. G.; Rosano, H. L. Interbubble gas diffusion and the stability of foams. *Journal of Colloid and Interface Science* 1997, 194, 31–36.
- [43] Langevin, D.; Vignes-Adler, M. Microgravity studies of aqueous wet foams. *European Physical Journal E* 2014, 37, 1–8.
- [44] Langevin, D. Aqueous foams and foam films stabilised by surfactants. Gravityfree studies. *Comptes Rendus - Mecanique* 2017, 345, 47–55.
- [45] Langevin, D. Bubble coalescence in pure liquids and in surfactant solutions. *Current Opinion in Colloid and Interface Science* 2015, 20, 92–97.
- [46] Stubenrauch, C.; von Klitzing, R. Forces and structure in thin liquid soap films Disjoining pressure in thin liquid foam and emulsion films — new concepts and perspectives. J. Phys.: Condens. Matter 2003, 15, R1197–R1232.
- [47] Bergeron, V. Forces and structure in thin liquid soap films. *J. Phys. Condens. Matter* **1999**, *11*, R215–R238.
- [48] Monnereau, C.; Vignes-Adler, M. Dynamics of 3D real foam coarsening. *Physical Review Letters* 1998, 80, 5228–5231.
- [49] Fetterman, M.; Tan, E.; Ying, L.; Stack, R.; Marks, D.; Feller, S.; Cull, E.; Sullivan, J.; Munson, D.; Thoroddsen, S.; Brady, D. Tomographic imaging of foam. *Optics Express* 2000, 7, 186.
- [50] Lambert, J.; Cantat, I.; Delannay, R.; Renault, A.; Graner, F.; Glazier, J. A.; Veretennikov, I.; Cloetens, P. Extraction of relevant physical parameters from 3D images

of foams obtained by X-ray tomography. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2005**, *263*, 295–302.

- [51] Meagher, A. J.; Mukherjee, M.; Weaire, D.; Hutzler, S.; Banhart, J.; Garcia-Moreno, F. Analysis of the internal structure of monodisperse liquid foams by X-ray tomography. *Soft Matter* 2011, 7, 9881–9885.
- [52] Crassous, J.; Saint-Jalmes, A. Probing the dynamics of particles in an aging dispersion using diffusing wave spectroscopy. *Soft Matter* 2012, *8*, 7683–7689.
- [53] Carl, A.; Witte, J.; von Klitzing, R. A look inside particle stabilized foams—particle structure and dynamics. *Journal of Physics D: Applied Physics* 2015, 48, 434003.
- [54] Scheludko, A. über das Ausfließen der Lösung aus Schaumfilmen. *Kolloid-Zeitschrift* **1957**, 155, 39–44.
- [55] Scheludko, A.; Exerowa, D. Über den elektrostatischen Druck in Schaumfilmen aus wässerigen Elektrolytlösungen. *Kolloid-Zeitschrift* **1959**, *165*, 148–151.
- [56] Scheludko, A.; Exerowa, D. Über den elektrostatischen und van der Waalsschen zusätzlichen Druck in wässerigen Schaumfilmen. *Kolloid-Z.* **1960**, *168*, 24–28.
- [57] Bergeron, V. Disjoining Pressures and Film Stability of Alkyltrimethylammonium Bromide Foam Films. *Langmuir* **1997**, *13*, 3474–3482.
- [58] Bergeron, V. Measurement of forces and structure between fluid interfaces. *Current Opinion in Colloid and Interface Science* **1999**, *4*, 249–255.
- [59] Stubenrauch, C.; Schlarmann, J.; Strey, R. A disjoining pressure study of ndodecyl-beta-D-maltoside foam films. *Physical Chemistry Chemical Physics* 2002, 4, 4504–4513.
- [60] Schulze-Schlarmann, J.; Buchavzov, N.; Stubenrauch, C. A disjoining pressure study of foam films stabilized by tetradecyl trimethyl ammonium bromide C14TAB. *Soft Matter* 2006, 2, 584–594.
- [61] Schelero, N.; Miller, R.; von Klitzing, R. Effect of oppositely charged hydrophobic additives (alkanoates) on the stability of C14TAB foam films. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2014, 460, 158–167.

- [62] Uhlig, M.; Miller, R.; von Klitzing, R. Surface adsorption of sulfonated poly(phenylene sulfone)/C14TAB mixtures and its correlation with foam film stability. *Phys. Chem. Chem. Phys.* 2016, 18, 18414–18423.
- [63] Uhlig, M.; Löhmann, O.; Vargas Ruiz, S.; Varga, I.; von Klitzing, R.; Campbell, R. A. New structural approach to rationalize the foam film stability of oppositely charged polyelectrolyte/surfactant mixtures. *Chemical Communications* 2020, 56, 952–955.
- [64] Braun, L.; Kühnhammer, M.; von Klitzing, R. Stability of aqueous foam films and foams containing polymers: Discrepancies between different length scales. *Current Opinion in Colloid and Interface Science* 2020, 50, 101379.
- [65] Axelos, M. A. V.; Boué, F. Foams as viewed by small-angle neutron scattering. Langmuir 2003, 19, 6598–6604.
- [66] Mikhailovskaya, A.; Zhang, L.; Cousin, F.; Boué, F.; Yazhgur, P.; Muller, F.; Gay, C.; Salonen, A. Probing foam with neutrons. *Advances in Colloid and Interface Science* 2017, 247, 444–453.
- [67] Sakai, T. In *Physics of Polymer Gels*; Sakai, T., Ed.; Wiley-VCH: Weinheim, 2020.
- [68] Fernandez-Nieves, A., Wyss, H. M., Mattsson, J., Weitz, D. A., Eds. Microgel Suspensions; Wiley-VCH: Weinheim, 2011.
- [69] Suzuki, D.; Horigome, K.; Kureha, T.; Matsui, S.; Watanabe, T. Polymeric hydrogel microspheres: Design, synthesis, characterization, assembly and applications. *Polymer Journal* 2017, 49, 695–702.
- [70] Lyon, L. A.; Fernandez-Nieves, A. The polymer/colloid duality of microgel suspensions. *Annual Review of Physical Chemistry* 2012, 63, 25–43.
- [71] Plamper, F. A.; Richtering, W. Functional Microgels and Microgel Systems. Accounts of Chemical Research 2017, 50, 131–140.
- [72] Keidel, R.; Ghavami, A.; Lugo, D. M.; Lotze, G.; Virtanen, O.; Beumers, P.; Pedersen, J. S.; Bardow, A.; Winkler, R. G.; Richtering, W. Time-resolved structural evolution during the collapse of responsive hydrogels: The microgel-to-particle transition. *Science Advances* 2018, 4, 1–9.

- [73] Wrede, O.; Reimann, Y.; Lülsdorf, S.; Emmrich, D.; Schneider, K.; Schmid, A. J.; Zauser, D.; Hannappel, Y.; Beyer, A.; Schweins, R.; Gölzhäuser, A.; Hellweg, T.; Sottmann, T. Volume phase transition kinetics of smart N-n-propylacrylamide microgels studied by time-resolved pressure jump small angle neutron scattering. *Scientific Reports* 2018, *8*, 1–13.
- [74] Senff, H.; Richtering, W. Temperature sensitive microgel suspensions: Colloidal phase behavior and rheology of soft spheres. *The Journal of Chemical Physics* 1999, 111, 1705–1711.
- [75] Kratz, K.; Hellweg, T.; Eimer, W. Structural changes in PNIPAM microgel particles as seen by SANS, DLS, and EM techniques. *Polymer* 2001, 42, 6631–6639.
- [76] Stieger, M.; Richtering, W.; Pedersen, J. S.; Lindner, P. Small-angle neutron scattering study of structural changes in temperature sensitive microgel colloids. *Journal of Chemical Physics* 2004, 120, 6197–6206.
- [77] Pelton, R. Temperature-sensitive aqueous microgels. *Advances in Colloid and Interface Science* **2000**, *85*, 1–33.
- [78] Fernández-Nieves, A.; Fernández-Barbero, A.; Vincent, B.; De Las Nieves, F. J. Charge controlled swelling of microgel particles. *Macromolecules* 2000, 33, 2114– 2118.
- [79] Kratz, K.; Hellweg, T.; Eimer, W. Influence of charge density on the swelling of colloidal poly(N-isopropylacrylamide-co-acrylic acid) microgels. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2000, 170, 137–149.
- [80] Hoare, T.; Pelton, R. Highly pH and Temperature Responsive Microgels Functionalized with Vinylacetic Acid. *Macromolecules* 2004, 37, 2544–2550.
- [81] Snowden, M. J.; Chowdhry, B. Z.; Vincent, B.; Morris, G. Colloidal copolymer microgels of N-isopropylacrylamide and acrylic acid: pH, ionic strength and temperature effects. *Journal of the Chemical Society, Faraday Transactions* 1996, 92, 5013–5016.
- [82] Shibayama, M.; Ikkai, F.; Inamoto, S.; Nomura, S.; Han, C. C. PH and salt concentration dependence of the microstructure of poly(N-isopropylacrylamide-coacrylic acid) gels. *Journal of Chemical Physics* **1996**, 105, 4358–4366.

- [83] Karg, M.; Pastoriza-Santos, I.; Rodriguez-González, B.; von Klitzing, R.; Wellert, S.; Hellweg, T. Temperature, pH, and ionic strength induced changes of the swelling behavior of PNIPAM-poly(allylacetic acid) copolymer microgels. *Langmuir* 2008, 24, 6300–6306.
- [84] Das, M.; Sanson, N.; Fava, D.; Kumacheva, E. Microgels loaded with gold nanorods: Photothermally triggered volume transitions under physiological conditions. *Langmuir* 2007, 23, 196–201.
- [85] Lehmann, M.; Tabaka, W.; Möller, T.; Oppermann, A.; Wöll, D.; Volodkin, D.; Wellert, S.; von Klitzing, R. DLS Setup for in Situ Measurements of Photoinduced Size Changes of Microgel-Based Hybrid Particles. *Langmuir* 2018, 34, 3597–3603.
- [86] Mergel, O.; Wünnemann, P.; Simon, U.; Böker, A.; Plamper, F. A. Microgel Size Modulation by Electrochemical Switching. *Chemistry of Materials* 2015, 27, 7306– 7312.
- [87] Witt, M. U.; Landers, J.; Hinrichs, S.; Salamon, S.; Kopp, J.; Hankiewicz, B.; Wende, H.; von Klitzing, R. Magnetic response of CoFe2O4nanoparticles confined in a PNIPAM microgel network. *Soft Matter* 2022, *18*, 1089–1099.
- [88] Zhou, X. M.; Shimanovich, U.; Herling, T. W.; Wu, S.; Dobson, C. M.; Knowles, T. P.; Perrett, S. Enzymatically Active Microgels from Self-Assembling Protein Nanofibrils for Microflow Chemistry. ACS Nano 2015, 9, 5772–5781.
- [89] Peng, H.; Rübsam, K.; Jakob, F.; Schwaneberg, U.; Pich, A. Tunable Enzymatic Activity and Enhanced Stability of Cellulase Immobilized in Biohybrid Nanogels. *Biomacromolecules* 2016, 17, 3619–3631.
- [90] Gu, Z.; Dang, T. T.; Ma, M.; Tang, B. C.; Cheng, H.; Jiang, S.; Dong, Y.; Zhang, Y.; Anderson, D. G. Glucose-responsive microgels integrated with enzyme nanocapsules for closed-loop insulin delivery. ACS Nano 2013, 7, 6758– 6766.
- [91] Ye, T.; Bai, X.; Jiang, X.; Wu, Q.; Chen, S.; Qu, A.; Huang, J.; Shen, J.; Wu, W. Glucose-responsive microgels based on apo-enzyme recognition. *Polymer Chemistry* 2016, 7, 2847–2857.
- [92] Smeets, N. M.; Hoare, T. Designing responsive microgels for drug delivery applications. *Journal of Polymer Science, Part A: Polymer Chemistry* 2013, 51, 3027–3043.

- [93] Richtering, W.; Potemkin, I. I.; Rudov, A. A.; Sellge, G.; Trautwein, C. Could multiresponsive hollow shell-shell nanocontainers offer an improved strategy for drug delivery? *Nanomedicine* 2016, 11, 2879–2883.
- [94] Zhou, W.; Stukel, J. M.; Cebull, H. L.; Kuntz Willits, R. Tuning the Mechanical Properties of Poly(Ethylene Glycol) Microgel-Based Scaffolds to Increase 3D Schwann Cell Proliferation. *Macromolecular Bioscience* 2016, 16, 535–544.
- [95] Mealy, J. E.; Chung, J. J.; Jeong, H. H.; Issadore, D.; Lee, D.; Atluri, P.; Burdick, J. A. Injectable Granular Hydrogels with Multifunctional Properties for Biomedical Applications. *Advanced Materials* 2018, 30.
- [96] Suzuki, D.; Kobayashi, T.; Yoshida, R.; Hirai, T. Soft actuators of organized selfoscillating microgels. *Soft Matter* 2012, *8*, 11447–11449.
- [97] Fernández-Barbero, A.; Suárez, I. J.; Sierra-Martín, B.; Fernández-Nieves, A.; de las Nieves, F. J.; Marquez, M.; Rubio-Retama, J.; López-Cabarcos, E. Gels and microgels for nanotechnological applications. *Advances in Colloid and Interface Science* 2009, 147-148, 88–108.
- [98] Zeiser, M.; Freudensprung, I.; Hellweg, T. Linearly thermoresponsive core-shell microgels: Towards a new class of nanoactuators. *Polymer* 2012, 53, 6096–6101.
- [99] Özkale, B.; Lou, J.; Ozelci, E.; Elosegui-Artola, A.; Tringides, C. M.; Mao, A.; Sakar, M. S.; Mooney, D. J. Actuated 3D microgels for single cell mechanobiology. *Lab on a Chip* 2022,
- [100] Bowen, J. J.; Rose, M. A.; Morin, S. A. Surface molding of multi-stimuliresponsive microgel actuators. *MRS Bulletin* **2021**, *46*, 337–344.
- [101] M. Rubinstein, R. H. C. Polymer Physics; Oxford University Press, 2003.
- [102] Kuhn, W. Dependence of the Average Transversal on the Longitudinal Dimensions of Statistical Coils Formed by Chain Molecules. *Journal of Polymer Science* 1946, 1, 380–388.
- [103] James, H. M.; Guth, E. Statistical thermodynamics of rubber elasticity. *The Journal* of *Chemical Physics* **1953**, *21*, 1039–1049.
- [104] Flory, P. J. Theory of elasticity of polymer networks. The effect of local constraints on junctions. *The Journal of Chemical Physics* 1977, 66, 5720–5729.

- [105] Erman, B.; Flory, P. J. Theory of elasticity of polymer networks. II. The effect of geometric constraints on junctions. *The Journal of Chemical Physics* 1977, 68, 5363– 5369.
- [106] Flory, P. J.; Erman, B. Theory of Elasticity of Polymer Networks. *Macromolecules* 1982, 15, 800–806.
- [107] Edwards, S. F. The statistical mechanics of polymerized material. *Proceedings of the Physical Society* **1967**, *92*, 9–16.
- [108] Rubinstein, M.; Panyukov, S. Elasticity of polymer networks. *Macromolecules* **2002**, *35*, 6670–6686.
- [109] Akagi, Y.; Gong, J. P.; Chung, U. I.; Sakai, T. Transition between phantom and affine network model observed in polymer gels with controlled network structure. *Macromolecules* 2013, 46, 1035–1040.
- [110] Panyukov, S. Theory of flexible polymer networks: Elasticity and heterogeneities. *Polymers* **2020**, 12.
- [111] Flory, P. J.; Rehner, J. Statistical mechanics of cross-linked polymer networks I. Rubberlike elasticity. *The Journal of Chemical Physics* **1943**, *11*, 512–520.
- [112] Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, and London, 1953.
- [113] Lopez, C. G.; Richtering, W. Does Flory-Rehner theory quantitatively describe the swelling of thermoresponsive microgels? *Soft Matter* **2017**, *13*, 8271–8280.
- [114] Leite, D. C.; Kakorin, S.; Hertle, Y.; Hellweg, T.; da Silveira, N. P. Smart Starch-Poly(N-isopropylacrylamide) Hybrid Microgels: Synthesis, Structure, and Swelling Behavior. *Langmuir : the ACS journal of surfaces and colloids* 2018, 34, 10943–10954.
- [115] Friesen, S.; Hannappel, Y.; Kakorin, S.; Hellweg, T. Comparison of different approaches to describe the thermotropic volume phase transition of smart microgels. *Colloid and Polymer Science* 2022,
- [116] Friesen, S.; Kakorin, S. Modified Flory Rehner Theory Describes Thermotropic Swelling Transition of Smart Copolymer Microgels. *Polymers* 2022, 14, 1999.

- [117] Heskins, M.; Guillet, J. E. Solution Properties of Poly(N-isopropylacrylamide). *Journal of Macromolecular Science: Part A - Chemistry* **1968**, 2, 1441–1455.
- [118] Schild, H. G. Poly(N-isopropylacrylamide): experiment, theory and application. *Progress in Polymer Science* **1992**, *17*, 163–249.
- [119] Zhang, Q.; Weber, C.; Schubert, U. S.; Hoogenboom, R. Thermoresponsive polymers with lower critical solution temperature: From fundamental aspects and measuring techniques to recommended turbidimetry conditions. *Materials Horizons* 2017, *4*, 109–116.
- [120] Pelton, R.; Chibante, P. Preparation of aqueous latices with Nisopropylacrylamide. *Colloids and Surfaces* **1986**, 20, 247–256.
- [121] Boon, N.; Schurtenberger, P. Swelling of micro-hydrogels with a crosslinker gradient. *Physical Chemistry Chemical Physics* 2017, 19, 23740–23746.
- [122] Kröger, L. C.; Kopp, W. A.; Leonhard, K. Prediction of Chain Propagation Rate Constants of Polymerization Reactions in Aqueous NIPAM/BIS and VCL/BIS Systems. *Journal of Physical Chemistry B* 2017, 121, 2887–2895.
- [123] Zhang, J.; Pelton, R. Poly(N-isopropylacrylamide) microgels at the air-water interface. *Langmuir* 1999, 15, 8032–8036.
- [124] Monteux, C.; Marliére, C.; Paris, P.; Pantoustier, N.; Sanson, N.; Perrin, P. Poly(Nisopropylacrylamide) microgels at the oil-water interface: Interfacial properties as a function of temperature. *Langmuir* 2010, 26, 13839–13846.
- [125] Li, Z.; Richtering, W.; Ngai, T. Poly(N-isopropylacrylamide) microgels at the oilwater interface: Temperature effect. *Soft Matter* 2014, 10, 6182–6191.
- [126] Ngai, T.; Behrens, S. H.; Auweter, H. Novel emulsions stabilized by pH and temperature sensitive microgels. *Chemical Communications* 2005, 331–333.
- [127] Ngai, T.; Auweter, H.; Behrens, S. H. Environmental responsiveness of microgel particles and particle-stabilized emulsions. *Macromolecules* 2006, *39*, 8171–8177.
- [128] Brugger, B.; Rosen, B. A.; Richtering, W. Microgels as stimuli-responsive stabilizers for emulsions. *Langmuir* **2008**, *24*, 12202–12208.

- [129] Richtering, W. Responsive emulsions stabilized by stimuli-sensitive microgels: Emulsions with special non-pickering properties. *Langmuir* 2012, 28, 17218– 17229.
- [130] Schmitt, V.; Ravaine, V. Surface compaction versus stretching in Pickering emulsions stabilised by microgels. *Current Opinion in Colloid and Interface Science* 2013, 18, 532–541.
- [131] Picard, C.; Garrigue, P.; Tatry, M.-C.; Lapeyre, V.; Ravaine, S.; Schmitt, V.; Ravaine, V. Organization of microgels at the air-water interface under compression: role of electrostatics and cross-linking density. *Langmuir* 2017, 33, 7968–7981.
- [132] Rey, M.; Hou, X.; Tang, J. S. J.; Vogel, N. Interfacial arrangement and phase transitions of PNiPAm microgels with different crosslinking densities. *Soft Matter* 2017, 13, 8717–8727.
- [133] Harrer, J.; Rey, M.; Ciarella, S.; Janssen, L. M. C.; Vogel, N. Stimuli-responsive behavior of poly (N- isopropylacrylamide) microgels under interfacial confinement. *Langmuir* 2019, 10512–10521.
- [134] Bochenek, S.; Scotti, A.; Ogieglo, W.; Fernández-Rodríguez, M. Á.; Schulte, M. F.; Gumerov, R. A.; Bushuev, N. V.; Potemkin, I. I.; Wessling, M.; Isa, L.; Richtering, W. Effect of the 3D Swelling of Microgels on Their 2D Phase Behavior at the Liquid-Liquid Interface. *Langmuir* 2019, 16780–16792.
- [135] Cohin, Y.; Fisson, M.; Jourde, K.; Fuller, G. G.; Sanson, N.; Talini, L.; Monteux, C. Tracking the interfacial dynamics of PNiPAM soft microgels particles adsorbed at the air-water interface and in thin liquid films. *Rheologica Acta* 2013, 52, 445– 454.
- [136] Keal, L.; Lapeyre, V.; Ravaine, V.; Schmitt, V.; Monteux, C. Drainage dynamics of thin liquid foam films containing soft PNiPAM microgels: influence of the cross-linking density and concentration. *Soft Matter* 2016, 13, 170–180.
- [137] Maestro, A.; Jones, D.; Sánchez De Rojas Candela, C.; Guzman, E.; Duits, M. H.; Cicuta, P. Tuning Interfacial Properties and Processes by Controlling the Rheology and Structure of Poly(N-isopropylacrylamide) Particles at Air/Water Interfaces. *Langmuir* 2018, 34, 7067–7076.

- [138] Horiguchi, Y.; Kawakita, H.; Ohto, K.; Morisada, S. Temperature-responsive Pickering foams stabilized by poly(N-isopropylacrylamide) nanogels. *Advanced Powder Technology* 2018, 29, 266–272.
- [139] Kumar, C. S. S. R. X-ray and Neutron Techniques for Nanomaterials Characterization; Springer Berlin Heidelberg, 2016; pp 507–544.
- [140] Sivia, D. S. Elementary Scattering Theory; Oxford University Press, 2011.
- [141] Guinier, A.; Fournet, G. Small-angle scattering of X-rays; Wiley: New York, 1955.
- [142] Gommes, C. J.; Jaksch, S.; Frielinghaus, H. Small-angle scattering for beginners. *Journal of Applied Crystallography* **2021**, *54*, 1–12.
- [143] NIST SLD calculator, https://www.ncnr.nist.gov/resources/activation/. accessed on 14th Jun 2022.
- [144] Pedersen, J. S. Analysis of small-angle scattering data from colloids and polymer solutions: Modeling and least-squares fitting. *Advances in Colloid and Interface Science* 1997, 70, 171–210.
- [145] Frielinghaus, H.; Feoktystov, A.; Berts, I.; Mangiapia, G. KWS-1: Small-angle scattering diffractometer. *Journal of large-scale research facilities JLSRF* 2015, 1, 26–29.
- [146] Feoktystov, A. V.; Frielinghaus, H.; Di, Z.; Jaksch, S.; Pipich, V.; Appavou, M. S.; Babcock, E.; Hanslik, R.; Engels, R.; Kemmerling, G.; Kleines, H.; Ioffe, A.; Richter, D.; Brückel, T. KWS-1 high-resolution small-angle neutron scattering instrument at JCNS: Current state. *Journal of Applied Crystallography* 2015, 48, 61–70.
- [147] Vitaliy Pipich, "QtiSAS: user-friendly program for reduction, visualization, analysis and fit of SA(N)S data" (2020), https://www.qtisas.com. accessed on 14th Jun 2022.
- [148] Dewhurst, C. D.; Grillo, I.; Honecker, D.; Bonnaud, M.; Jacques, M.; Amrouni, C.; Perillo-Marcone, A.; Manzin, G.; Cubitt, R. The small-angle neutron scattering instrument D33 at the Institut Laue-Langevin. *Journal of Applied Crystallography* 2016, 49, 1–14.

- [149] Kühnhammer, M.; Chiappisi, L.; Ludwig, M.; Soltwedel, O.; von Klitzing, R. PNIPAM microgel stabilised foams - Effect of particle concentration and stiffness on structuring inside of foam lamellae. Institut Laue-Langevin (ILL) doi:10.5291/ILL-DATA.9-12-600. 2020.
- [150] https://www.ill.eu/users/support-labs-infrastructure/software-scientifictools/grasp. accessed on 14th Jun 2022.
- [151] Kühnhammer, M.; Widmann, T.; Kreuzer, L. P.; Schmid, A. J.; Wiehemeier, L.; Frielinghaus, H.; Jaksch, S.; Bögershausen, T.; Barron, P.; Schneider, H.; Hiess, A.; Müller-Buschbaum, P.; Hellweg, T.; von Klitzing, R.; Löhmann, O. Flexible Sample Environments for the Investigation of Soft Matter at the European Spallation Source: Part III—The Macroscopic Foam Cell. *Applied Sciences* 2021, *11*, 5116.
- [152] Daillant, J., Gibaud, A., Eds. X-ray and Neutron Reflectivity. Principles and Applications; Springer: Berlin, Heidelberg, 2009.
- [153] Tolan, M. X-Ray Scattering from Soft-Matter Thin Films; Springer: Berlin, Heidelberg, 1999.
- [154] Mysels, K. J.; Jones, M. N. Direct Measurement of the Variation of Double-Layer Repulsion with Distance. *Discuss. Faraday Soc.* **1966**, 42, 42–50.
- [155] Scheludko, A. Thin liquid films. Advances in Colloid and Interface Science 1967, 1, 391–464.
- [156] Basheva, E. S.; Kralchevsky, P. A.; Danov, K. D.; Stanimirova, R. D.; Shaw, N.; Petkov, J. T. Vortex in liquid films from concentrated surfactant solutions containing micelles and colloidal particles. *Journal of Colloid and Interface Science* 2020, 576, 345–355.
- [157] Binnig, G.; Quate, C. F.; Gerber, C. Atomic Forve Microscopy. *Physical Review Letters* **1986**, *56*, 930–933.
- [158] Israelachvili, J. N. Intermolecular and Surface Forces, 3rd ed.; Elsevier, 2011.
- [159] Hertz, H. Über die Berührung fester elastischer Körper. *Journal für die reine und angewandte Mathematik* **1881**, 92, 156–171.
- [160] Sader, J. E.; Chon, J. W.; Mulvaney, P. Calibration of rectangular atomic force microscope cantilevers. *Review of Scientific Instruments* 1999, 70, 3967–3969.
- [161] Schindelin, J. et al. Fiji: An open-source platform for biological-image analysis. *Nature Methods* **2012**, *9*, 676–682.
- [162] Delgado, A. V.; González-Caballero, F.; Hunter, R. J.; Koopal, L. K.; Lyklema, J. Measurement and interpretation of electrokinetic phenomena: (IUPAC technical report). *Pure and Applied Chemistry* 2005, 77, 1753–1805.
- [163] von Smoluchowski, M. In *Handbuch der Electrizität und des Magnetismus*; Barth, J. A., Ed.; 1921.
- [164] Garoby, R. et al. The European Spallation Source Design. *Physica Scripta* **2017**, *93*, 014001.
- [165] Andersen, K. et al. The instrument suite of the European Spallation Source. Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment 2020, 957, 163402.
- [166] Jackson, A. J.; Kanaki, K. ESS Construction Proposal LoKI A broad-band SANS instrument. 2013.
- [167] Jaksch, S.; Martin-Rodriguez, D.; Ostermann, A.; Jestin, J.; Duarte Pinto, S.; Bouwman, W. G.; Uher, J.; Engels, R.; Frielinghaus, H. Concept for a time-offlight Small Angle Neutron Scattering instrument at the European Spallation Source. Nuclear Instruments and Methods in Physics Research, Section A: Accelerators, Spectrometers, Detectors and Associated Equipment 2014, 762, 22–30.
- [168] Jaksch, S.; Chennevière, A.; Désert, S.; Kozielewski, T.; Feilbach, H.; Lavie, P.; Hanslik, R.; Gussen, A.; Butterweck, S.; Engels, R.; Frielinghaus, H.; Förster, S.; Müller-Buschbaum, P. Technical Specification of the Small-Angle Neutron Scattering Instrument SKADI at the European Spallation Source. *applied sciences* 2021, 11, 3620.
- [169] Schmid, A. J. et al. Flexible Sample Environments for the Investigation of Soft Matter at the European Spallation Source : Part I — The In Situ SANS / DLS Setup. *applied sciences* 2021, 11, 4089.
- [170] Widmann, T.; Kreuzer, L. P.; Kühnhammer, M.; Schmid, A. J.; Wiehemeier, L.; Jaksch, S.; Frielinghaus, H.; Löhmann, O.; Schneider, H.; Hiess, A.; von Klitzing, R.; Hellweg, T.; Müller-Buschbaum, P. Flexible Sample Environment for the Investigation of Soft Matter at the European Spallation Source : Part II — The GISANS Setup. *applied sciences* 2021, *11*, 4036.

- [171] Guthrie, M.; Perez, B. ESS Sample Environment Mechanical Interfaces for Instruments. 2015.
- [172] Fameau, A.-L.; Saint-Jalmes, A.; Cousin, F.; Houinsou Houssou, B.; Novales, B.; Navailles, L.; Nallet, F.; Gaillard, C.; Boué, F.; Douliez, J.-P. Smart Foams: Switching Reversibly between Ultrastable and Unstable Foams. *Angewandte Chemie International Edition* 2011, 50, 8264–8269.
- [173] Hurcom, J.; Paul, A.; Heenan, R. K.; Davies, A.; Woodman, N.; Schweins, R.; Griffiths, P. C. The interfacial structure of polymeric surfactant stabilised air-inwater foams. *Soft matter* 2014, 10, 3003–8.
- [174] Micheau, C.; Bauduin, P.; Diat, O.; Faure, S. Specific Salt and pH Effects on Foam Film of a pH Sensitive Surfactant. *Langmuir* 2013, 29, 8472–8481.
- [175] Yada, S.; Shimosegawa, H.; Fujita, H.; Yamada, M.; Matsue, Y.; Yoshimura, T. Microstructural Characterization of Foam Formed by a Hydroxy Group-Containing Amino Acid Surfactant Using Small-Angle Neutron Scattering. *Langmuir* 2020, 36, 7808–7813.
- [176] Domínguez, A.; Fernández, A.; Gonzalez, N.; Iglesias, E.; Montenegro, L. Determination of critical micelle concentration of some surfactants by three techniques. *Journal of Chemical Education* **1997**, 74, 1227–1231.
- [177] https://epics-controls.org/. access on 14th Jun 2022.
- [178] https://nicos-controls.org/. access on 114th Jun 2022.
- [179] Löhmann, O.; Silvi, L.; Kadletz, P. M.; Vaytet, N.; Arnold, O.; Jones, M. D.; Nilsson, J.; Hart, M.; Richter, T.; von Klitzing, R.; Jackson, A. J.; Arnold, T.; Woracek, R. Wavelength frame multiplication for reflectometry at long-pulse neutron sources. *Review of Scientific Instruments* **2020**, *91*, 125111.
- [180] Strobl, M.; Bulat, M.; Habicht, K. The wavelength frame multiplication chopper system for the ESS test beamline at the BER II reactor - A concept study of a fundamental ESS instrument principle. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* 2013, 705, 74–84.

- [181] Woracek, R.; Hofmann, T.; Bulat, M.; Sales, M.; Habicht, K.; Andersen, K.; Strobl, M. The test beamline of the European Spallation Source – Instrumentation development and wavelength frame multiplication. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* 2016, 839, 102–116.
- [182] Danov, K. D.; Kralchevsky, P. A.; Ananthapadmanabhan, K. P. Micelle-monomer equilibria in solutions of ionic surfactants and in ionic-nonionic mixtures: A generalized phase separation model. *Advances in Colloid and Interface Science* 2014, 206, 17–45.
- [183] Kühnhammer, M.; Braun, L.; Ludwig, M.; Soltwedel, O.; Chiappisi, L.; von Klitzing, R. A new model to describe small-angle neutron scattering from foams. *Journal of Applied Crystallography* 2022, 55, 758–768.
- [184] Ropers, M. H.; Novales, B.; Boué, F.; Axelos, M. A. V. Polysaccharide/surfactant complexes at the air-water interface - Effect of the charge density on interfacial and foaming behaviors. *Langmuir* 2008, 24, 12849–12857.
- [185] Schmidt, S.; Zeiser, M.; Hellweg, T.; Duschl, C.; Fery, A.; Möhwald, H. Adhesion and mechanical properties of PNIPAM microgel films and their potential use as switchable cell culture substrates. *Advanced Functional Materials* 2010, 20, 3235– 3243.
- [186] Perticaroli, S.; Herzberger, J.; Sun, Y.; Nickels, J. D.; Murphy, R. P.; Weigandt, K.; Ray, P. J. Multiscale Microstructure, Composition, and Stability of Surfactant/Polymer Foams. *Langmuir* 2020, *36*, 14763–14771.
- [187] Hohenschutz, M.; Grillo, I.; Dewhurst, C.; Schmid, P.; Girard, L.; Jonchère, A.; Diat, O.; Bauduin, P. Superchaotropic nano-ions as foam stabilizers. *Journal of Colloid and Interface Science* 2021, 603, 141–147.
- [188] Mansour, O. T.; Cattoz, B.; Beaube, M.; Montagnon, M.; Heenan, R. K.; Schweins, R.; Appavou, M. S.; Griffiths, P. C. Assembly of small molecule surfactants at highly dynamic air-water interfaces. *Soft Matter* 2017, *13*, 8807–8815.
- [189] Mansour, O. T.; Cattoz, B.; Beaube, M.; Heenan, R. K.; Schweins, R.; Hurcom, J.; Griffiths, P. C. Segregation versus interdigitation in highly dynamic polymer/surfactant layers. *Polymers* 2019, *11*, 109.

- [190] Van Rossum, G.; Drake, F. L. Python 3 Reference Manual; CreateSpace: Scotts Valley, CA, 2009.
- [191] Virtanen, P. et al. SciPy 1.0: Fundamental Algorithms for Scientific Computing in Python. *Nature Methods* **2020**, *17*, 261–272.
- [192] Harris, C. R. et al. Array programming with NumPy. *Nature* 2020, 585, 357–362.
- [193] McKinney, W. Data Structures for Statistical Computing in Python. *Proceedings of the 9th Python in Science Conference* **2010**, 445, 56–61.
- [194] Pandas development team, The pandas development team, pandasdev/pandas: Pandas. 2020.
- [195] Mysels, K. J. Charge effects in light scattering by association colloidal electrolytes. *Journal of Colloid Science* **1955**, *10*, 507–522.
- [196] Venable, R. L.; Nauman, R. V. Micellar weights of and solubilization of benzene by a series of tetradecylammonium bromides. The effect of the size of the charged head. *Journal of Physical Chemistry* **1964**, *68*, 3498–3503.
- [197] Simister, E. A.; Thomas, R. K.; Penfold, J.; Aveyard, R.; Binks, B. P.; Cooper, P.; Fletcher, P. D.; Lu, J. R.; Sokolowski, A. Comparison of neutron reflection and surface tension measurements of the surface excess of tetradecyltrimethylammonium bromide layers at the air/water interface. *Journal of Physical Chemistry* 1992, 96, 1383–1388.
- [198] Nelder, J. A.; Mead, R. A Simplex Method for Function Minimization. *The Computer Journal* **1965**, *7*, 308–313.
- [199] Braslau, A.; Deutsch, M.; Pershan, P. S.; Weiss, A. H.; Als-Nielsen, J.; Bohr, J. Surface roughness of water measured by x-ray reflectivity. *Physical Review Letters* 1985, 54, 114–117.
- [200] Rio, E.; Drenckhan, W.; Salonen, A.; Langevin, D. Unusually stable liquid foams. *Advances in Colloid and Interface Science* **2014**, 205, 74–86.
- [201] Porod, G. Die Röntgenkleinwinkelstreuung von dichtgepackten kolloiden Systemen - I. Teil. Kolloid-Zeitschrift 1951, 124, 83–114.
- [202] Teixeira, J. Small-angle scattering by fractal systems. *Journal of Applied Crystallography* **1988**, *21*, 781–785.

- [203] Kühnhammer, M.; Gräff, K.; Loran, E.; Soltwedel, O.; Löhmann, O.; Frielinghaus, H.; von Klitzing, R. Soft Matter. *Soft Matter* **2022**,
- [204] Fujii, S.; Nakamura, Y. Stimuli-Responsive Bubbles and Foams Stabilized with Solid Particles. *Langmuir* **2017**, *33*, 7365–7379.
- [205] Fameau, A. L.; Carl, A.; Saint-Jalmes, A.; von Klitzing, R. Responsive aqueous foams. *ChemPhysChem* 2015, 16, 66–75.
- [206] Fameau, A. L.; Fujii, S. Stimuli-responsive liquid foams: From design to applications. *Current Opinion in Colloid and Interface Science* 2020, 50, 101380.
- [207] Schnurbus, M.; Hardt, M.; Steinforth, P.; Carrascosa-Tejedor, J.; Winnall, S.; Gutfreund, P.; Schönhoff, M.; Campbell, R. A.; Braunschweig, B. Responsive Material and Interfacial Properties through Remote Control of Polyelectrolyte–Surfactant Mixtures. ACS Applied Materials and Interfaces 2022, 14, 4656–4667.
- [208] Bochenek, S.; Scotti, A.; Richtering, W. Temperature-sensitive soft microgels at interfaces: air-water versus oil-water. *Soft Matter* **2021**, *17*, 976–988.
- [209] Geisel, K.; Isa, L.; Richtering, W. Unraveling the 3D localization and deformation of responsive microgels at oil/water interfaces: A step forward in understanding soft emulsion stabilizers. *Langmuir* 2012, 28, 15770–15776.
- [210] Geisel, K.; Isa, L.; Richtering, W. The compressibility of ph-sensitive microgels at the oil-water interface: Higher charge leads to less repulsion. *Angewandte Chemie* - *International Edition* 2014, 53, 4905–4909.
- [211] Rey, M.; Fernandez-Rodriguez, M. A.; Karg, M.; Isa, L.; Vogel, N. Poly- Nisopropylacrylamide Nanogels and Microgels at Fluid Interfaces. *Accounts of Chemical Research* 2020,
- [212] Petkova, B.; Tcholakova, S.; Chenkova, M.; Golemanov, K.; Denkov, N.; Thorley, D.; Stoyanov, S. Foamability of aqueous solutions: Role of surfactant type and concentration. *Advances in Colloid and Interface Science* **2020**, 276, 102084.
- [213] Widmann, T.; Kreuzer, L. P.; Hohn, N.; Bießmann, L.; Wang, K.; Rinner, S.; Moulin, J. F.; Schmid, A. J.; Hannappel, Y.; Wrede, O.; Kühnhammer, M.; Hellweg, T.; von Klitzing, R.; Müller-Buschbaum, P. Hydration and Solvent Exchange Induced Swelling and Deswelling of Homogeneous Poly(Nisopropylacrylamide) Microgel Thin Films. *Langmuir* 2019, 35, 16341–16352.

- [214] Burmistrova, A.; Richter, M.; Uzum, C.; von Klitzing, R. Effect of crosslinker density of P(NIPAM-co-AAc) microgels at solid surfaces on the swelling/shrinking behaviour and the Young's modulus. *Colloid and Polymer Science* 2011, 289, 613–624.
- [215] Burmistrova, A.; Richter, M.; Eisele, M.; Üzüm, C.; von Klitzing, R. The effect of co-monomer content on the swelling/shrinking and mechanical behaviour of individually adsorbed PNIPAM microgel particles. *Polymers* 2011, 3, 1575–1590.
- [216] Witt, M. U.; Hinrichs, S.; Möller, N.; Backes, S.; Fischer, B.; von Klitzing, R. Distribution of CoFe₂O₄ Nanoparticles Inside PNIPAM-Based Microgels of Different Cross-linker Distributions. *Journal of Physical Chemistry B* 2019, 123, 2405–2413.
- [217] Witte, J.; Kyrey, T.; Lutzki, J.; Dahl, A. M.; Kühnhammer, M.; von Klitzing, R.; Holderer, O.; Wellert, S. Looking inside Poly(N-isopropylacrylamide) Microgels: Nanomechanics and Dynamics at Solid-Liquid Interfaces. ACS Applied Polymer Materials 2021, 3, 976–985.
- [218] Hashmi, S. M.; Dufresne, E. R. Mechanical properties of individual microgel particles through the deswelling transition. *Soft Matter* **2009**, *5*, 3682–3688.
- [219] Backes, S.; von Klitzing, R. Nanomechanics and nanorheology of microgels at interfaces. *Polymers* **2018**, *10*, 1–23.
- [220] Witte, J.; Kyrey, T.; Lutzki, J.; Dahl, A. M.; Houston, J.; Radulescu, A.; Pipich, V.; Stingaciu, L.; Kühnhammer, M.; Witt, M. U.; von Klitzing, R.; Holderer, O.; Wellert, S. A comparison of the network structure and inner dynamics of homogeneously and heterogeneously crosslinked PNIPAM microgels with high crosslinker content. *Soft Matter* **2019**, *15*, 1053–1064.
- [221] Aufderhorst-Roberts, A.; Baker, D.; Foster, R. J.; Cayre, O.; Mattsson, J.; Connell, S. D. Nanoscale mechanics of microgel particles. *Nanoscale* 2018, 10, 16050– 16061.
- [222] Lesov, I.; Tcholakova, S.; Denkov, N. Factors controlling the formation and stability of foams used as precursors of porous materials. *Journal of Colloid and Interface Science* **2014**, 426, 9–21.
- [223] Politova, N.; Tcholakova, S.; Valkova, Z.; Golemanov, K.; Denkov, N. D. Selfregulation of foam volume and bubble size during foaming via shear mixing. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2018, 539, 18–28.

- [224] Varadaraj, R.; Bock, J.; Valint, P.; Zushma, S.; Brons, N. Relationship between fundamental interfacial properties and foaming in linear and branched sulfate, ethoxysulfate, and ethoxylate surfactants. *Journal of Colloid And Interface Science* 1990, 140, 31–34.
- [225] Tamura, T.; Kaneko, Y.; Ohyama, M. Dynamic Surface Tension and Foaming Properties of Aqueous Polyoxyethylene n-Dodecyl Ether Solutions. 1995.
- [226] Buzzacchi, M.; Schmiedel, P.; Von Rybinski, W. Dynamic surface tension of surfactant systems and its relation to foam formation and liquid film drainage on solid surfaces. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2006, 273, 47–54.
- [227] Kawale, D.; van Nimwegen, A. T.; Portela, L. M.; van Dijk, M. A.; Henkes, R. A. The relation between the dynamic surface tension and the foaming behaviour in a sparger setup. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2015, 481, 328–336.
- [228] Gupta, L.; Wasan, D. T. Surface Shear Viscosity and Related Properties of Adsorbed Surfactant Films. *Industrial and Engineering Chemistry Fundamentals* 1974, 13, 26–33.
- [229] Miller, R.; Wüstneck, R.; Krägel, J.; Kretzschmar, G. Dilational and shear rheology of adsorption layers at liquid interfaces. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 1996, 111, 75–118.
- [230] Bos, M.; van Vliet, T. Interfacial rheological properties of adsorbed protein layers and surfactants: a review. *Advances in Colloid and Interface Science* 2001, 91, 437– 471.
- [231] Miller, R.; Liggieri, L. Interfacial rheology; CRC Press, 2009; Vol. 1.
- [232] Malysa, K.; Lunkenheimer, K. Foams under dynamic conditions. *Current Opinion in Colloid and Interface Science* **2008**, *13*, 150–162.
- [233] Wang, J.; Nguyen, A. V.; Farrokhpay, S. A critical review of the growth, drainage and collapse of foams. *Advances in Colloid and Interface Science* 2016, 228, 55–70.
- [234] Varade, D.; Carriere, D.; Arriaga, L. R.; Fameau, A. L.; Rio, E.; Langevin, D.; Drenckhan, W. On the origin of the stability of foams made from catanionic surfactant mixtures. *Soft Matter* 2011, 7, 6557–6570.

- [235] Fameau, A. L.; Salonen, A. Effect of particles and aggregated structures on the foam stability and aging. *Comptes Rendus Physique* **2014**, *15*, 748–760.
- [236] Haffner, B.; Khidas, Y.; Pitois, O. Flow and jamming of granular suspensions in foams. *Soft Matter* **2014**, *10*, 3277–3283.
- [237] Khristov, K.; Jachimska, B.; Malysa, K.; Exerowa, D. 'Static' and steady-state foams from ABA triblock copolymers: Influence of the type of foam films. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2001, 186, 93–101.
- [238] Stubenrauch, C.; Khristov, K. Foams and foam films stabilized by CnTAB: Influence of the chain length and of impurities. *Journal of Colloid and Interface Science* 2005, 286, 710–718.
- [239] Destribats, M.; Lapeyre, V.; Sellier, E.; Leal-Calderon, F.; Ravaine, V.; Schmitt, V. Origin and control of adhesion between emulsion drops stabilized by thermally sensitive soft colloidal particles. *Langmuir* 2012, 28, 3744–3755.
- [240] Brugger, B.; Rütten, S.; Phan, K. H.; Moller, M.; Richtering, W. The colloidal suprastructure of smart microgels at oil- Water interfaces. *Angewandte Chemie -International Edition* 2009, 48, 3978–3981.
- [241] Brugger, B.; Vermant, J.; Richtering, W. Interfacial layers of stimuli-responsive poly-(N-isopropylacrylamide-co- methacrylicacid) (PNIPAM-co-MAA) microgels characterized by interfacial rheology and compression isotherms. *Physical Chemistry Chemical Physics* 2010, 12, 14573–14578.
- [242] Destribats, M.; Lapeyre, V.; Wolfs, M.; Sellier, E.; Leal-Calderon, F.; Ravaine, V.; Schmitt, V. Soft microgels as Pickering emulsion stabilisers: role of particle deformability. *Soft Matter* 2011, 7, 7689.
- [243] Małysa, K.; Lunkenheimer, K.; Miller, R.; Hempt, C. Surface elasticity and dynamic stability of wet foams. *Colloids and Surfaces* **1985**, *16*, 9–20.
- [244] Fruhner, H.; Wantke, K. D.; Lunkenheimer, K. Relationship between surface dilational properties and foam stability. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2000, 162, 193–202.
- [245] Langevin, D. Influence of interfacial rheology on foam and emulsion properties. *Advances in Colloid and Interface Science* **2000**, *88*, 209–222.

- [246] Wantke, K. D.; Örtegren, J.; Fruhner, H.; Andersen, A.; Motschmann, H. The influence of the sublayer on the surface dilatational modulus. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2005, 261, 75–83.
- [247] Voudouris, P.; Florea, D.; Van Der Schoot, P.; Wyss, H. M. Micromechanics of temperature sensitive microgels: Dip in the Poisson ratio near the LCST. *Soft Matter* 2013, 9, 7158–7166.
- [248] Quesada-Pérez, M.; Maroto-Centeno, J. A.; Forcada, J.; Hidalgo-Alvarez, R. Gel swelling theories: The classical formalism and recent approaches. *Soft Matter* 2011, 7, 10536–10547.
- [249] Saunders, B. R. On the structure of poly(N-isopropylacrylamide) microgel particles. *Langmuir* **2004**, *20*, 3925–3932.
- [250] Hild, G. Model networks based on 'endlinking' processes: Synthesis, structure and properties. *Progress in Polymer Science (Oxford)* **1998**, 23, 1019–1149.
- [251] Holler, M.; Diaz, A.; Guizar-Sicairos, M.; Karvinen, P.; Färm, E.; Härkönen, E.; Ritala, M.; Menzel, A.; Raabe, J.; Bunk, O. X-ray ptychographic computed tomography at 16 nm isotropic 3D resolution. *Scientific Reports* 2014, *4*, 1–5.
- [252] Ederth, T.; Thomas, R. K. A neutron reflectivity study of drainage and stratification of AOT foam films. *Langmuir* **2003**, *19*, 7727–7733.
- [253] Martín-Molina, A.; Quesada-Pérez, M. A review of coarse-grained simulations of nanogel and microgel particles. *Journal of Molecular Liquids* 2019, 280, 374–381.

Appendix

Curriculum vitae

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