# Structure, interfacial film properties, and thermal fluctuations of microemulsions as seen by scattering experiments

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**Abstract**

The physics of microemulsions and in particular Dominique Langevin's contributions to the understanding of microemulsion structure and bending properties using scattering techniques are reviewed. Among the many methods used by her and her co-workers, we particularly emphasize optical techniques and small angle neutron scattering, but also neutron spin echo spectroscopy. The review is then extended to more recent studies of properties of microemulsions close to surfaces, using reflectometry and grazing-incidence small angle neutron scattering (GISANS).

*Keywords:* SANS, neutron spin-echo, microemulsion, surfactant, bending elasticity, shape fluctuations, Helfrich Hamiltonian

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## 1. Introduction

Microemulsions are thermodynamically stable, isotropic, liquid mixtures of two immiscible fluids, typically oil and water, stabilized by surfactant and in some cases by an additional co-surfactant [1]. Such systems exhibit a low interfacial tension, combined with a high interfacial area between the immiscible fluids. Their phase diagrams and microstructures have been intensely studied over the past seventy years, both for fundamental reasons – understanding the structure and dynamics of a large variety of tunable, complex morphologies from a few simple principles – and industrial applications, namely enhanced oil recovery, further motivated by successive oil crises, extraction, decontamination and new fuels. The founding fathers of the discipline have proposed the name of 'microemulsion' when they realized the microstructure of these solutions, namely emulsified oil or water droplets in the appropriate continuous phase [2, 3, 4]. The adjective "isotropic" may be surprising, as some might still consider, e.g., a swollen lamellar phase a microemulsion [6, 7], which however may also be counted to the separate class of liquid crystals, depending on if you consider structure or oil solubilization the most remarkable property. Meanwhile microemulsion research is a mature field. This manifests in about 6000 publication since 2010 which are related to microemulsions. Most of these articles are dealing with applications of microemulsions in the mentioned areas.

This review aims at highlighting progress in fundamental understanding of microemulsion structure and properties since the 1980's, in particular using scattering techniques, as pioneered by the group of Dominique Langevin.

After a brief introduction to microemulsions in general, where we summarize our understanding of the bending properties of surfactant layers, early and dominantly optical bulk studies are discussed. In the following years, the experimental approach was considerably deepened: thanks to small-angle scattering and quasi-elastic neutron scattering (QENS, in particular neutron spin-echo spectroscopy (NSE)) combined with contrast variation, access to static and dynamic microemulsion properties on the molecular scale became available. The review is then extended to more recent results on microemulsions close to interfaces (see section 4). Finally, dynamics as seen by neutron spin-echo (NSE) are discussed in a separate section (see section 5).

## 2. The physics of microemulsions

Due to the strong molecular immiscibility of oil and water, domains of both solvents are usually formed, separated by a surfactant (mono-)layer. The size and shape of these domains depends on the relative amount of oil and water, and surfactant. The usually encountered morphology for minority compounds, like a little oil with much water, are (discontinuous) oil droplets suspended in a continuous water phase, or vice versa. In mixtures with approximately equal volumes, both phases may become continuous, and bicontinuity will be discussed below. For more detailed information, we refer the reader to a general introduction to both physics and characterization of microemulsions proposed by Chevalier and Zemb [5].

### *2.1. Bending properties*

Besides the volumes of the phases, microemulsion structure depends crucially on the quantity and properties of the surfactant. Indeed, the amount

of the latter defines the available specific surface $S/V$, as all oil-water interfaces need to be covered for energetical reasons: $S/V$ is given by the product of surfactant concentration and head group area $\sigma$ ($\sigma$ contains not only steric interaction and might vary a bit with experimental conditions). Moreover, if we ignore solubility issues, the bending properties of the surfactant layer determine which type of morphology is accessible, and the strength of thermal fluctuation around these morphologies. The bending properties of surfactant monolayers depend on the molecular architecture and interactions, and may be tuned chemically [113]: e.g., by modifying the surfactant, or adding a co-surfactant [8], changing the temperature [9], adding salt [10], or more complex molecules like copolymers which can induce changes in the phase diagram, or contribute to changes in viscosity of the different phases [11, 12, 13, 14]; similar effects had already been reviewed by [15].

The bending properties of surfactant layers were described in the 70s by Helfrich [16]. The Helfrich approach was originally developed for the description of lipid vesicles. However, it perfectly treats the bending properties of microemulsions of arbitrary morphology, including bicontinuous and in particular spherical microemulsion droplets [17, 18]. This is due to the fact that microemulsion droplets only comprise a surfactant monolayer which much better corresponds to the Helfrich bending free energy compared to vesicles. It is commonly expressed as a series expansion of the bending energy for the lowest curvatures. The free energy dF needed to bend a piece of monolayer of surface dA can then be expressed in terms of the two principal curvatures $c_1$ and $c_2$, which are related to the principal radii of curvature by $c_i = 1/R_i$. The so-called Helfrich Hamiltonian [16]of the bending free energy reads:

$$F = \int [\frac{1}{2}\kappa(c_1 + c_1 - 2c_0)^2 + \bar{\kappa}c_1c_2]dA \quad (1)$$

The spontaneous curvature, $c_0$, describes the state of lowest bending energy of the monolayer. Due to symmetry reasons, this term is zero for bilayers or balanced monolayers. Alternatively, the free energy can be formulated based on the total curvature $H = c_1 + c_2$, and the Gaussian curvature given by the product $K = c_1c_2$. Note that different notations exist in the literature, sometimes preferring the average curvature $(H/2)$, or the total spontaneous curvature $H_0 = 2c_0$, and similar variants. The above expression for the bending energy serves as definition of two material constants of the monolayer, the bending moduli, $\kappa$ and $\bar{\kappa}$, which are sometimes called bending rigidity and saddle-splay modulus, respectively. Following Helfrich's approach, they have been related by Safran and coworkers to the molecular conformation of the surfactant chains [19], and by Kabalnov et al. to ion concentrations [10]. Their magnitude may further depend on additional interactions, like added electrostatic terms [20, 21, 22] and studies of electrostatic effects in both microemulsion systems [23] and pure surfactant systems [8, 24, 25] exist. Both moduli are in units of energy, i.e. do not refer to any length scale, which has the surprising consequence that the bending energy of a spherical shell (with $c_0 = 0$) is independent of its radius: $8\pi(\kappa + \bar{\kappa}/2)$. A non-zero spontaneous bending, however, introduces a length-scale, and a preferred radius is selected. In a droplet microemulsion, e.g., the maximum droplet radius obtained at emulsification failure leading to an excess phase is given by the inverse of $c_0$, with corrections due to translational entropy and the bending moduli, see the discussion and references reported in section 3 .

The roles of $\kappa$ and $\bar{\kappa}$ are quite different. It can be shown with the Gauss-Bonnet theorem, that the second term in eq. 1, which is related to the Gaussian curvature, depends only on the topology of the surface, and in particular on the number of handles and independent pieces of membrane or monolayer [26]. This is particularly obvious in the phase sequence of non-ionic bilayer phases governed by the surfactant-co-surfactant ratio, where $\bar{\kappa}$ can be shown to trigger morphology changes from vesicular [27], to lamellar, and finally to sponge phases [28, 29]. Concerning this last and most intriguing phase, it should be noted that there is a close relationship between the sponge phase and bicontinuous microemulsions to be discussed below [30] Having understood the influence of $\bar{\kappa}$, it follows that for a fixed topology of any given structure, local topology-preserving bending fluctuations are entirely determined by $\kappa$. Alternatively to eq. 1, the bending energy can also be expressed in terms of the deviation of the packing parameter $p = \frac{V}{l\sigma}$ [31, 32] of the molecules from their spontaneous value $\mathrm{p}_0$. Here, $V$ is the molecular volume, and $l$ the extended chain length. $\sigma$ indicates the area per headgroup of the surfactant. Indeed, if one integrates over the monolayer thickness $\lambda$, the packing parameter is found to be linked to the curvature in order to comply to complete surface coverage:

$$p = 1 + H\lambda + \frac{1}{3}K\lambda^2 \tag{2}$$

as long as the topology remains unchanged [33]. This covering relationship allows rewriting the Helfrich Hamiltonian as $\kappa \cdot (p - p_0)^2$, with $\kappa^* = 2\kappa + \bar{\kappa}$ [34]. One sees that monolayers adopting configurations close to spontaneous packing can only be stable with respect to bending if $\kappa^*$ is positive. Finally, the modulus $\kappa$ can also be used to define a persistence length, exponentially

increasing with $\kappa$, as the characteristic length above which fluctuations are large enough to decorrelate the orientation of the layer [35]:

$$\xi_k = \xi_0 \exp \frac{4\pi\kappa}{3kT} \tag{3}$$

where $\xi_0$ is a molecular length. Choice of pre-factors and renormalization of the bending constant by fluctuations are discussed by Binks et al. [36]. The concept of persistence allows understanding the formation of the sponge phase as a lamellar phase which loses its orientational order on scales of the persistence length and thus approaches a random surface. One may note that an alternative view of the sponge phase as a 'molten' periodic minimal surface favored by positive values of $\bar{\kappa}$ has been proposed [29]. Moreover, the bicontinuous microemulsion can be seen as an oil-swollen lamellar phase, and such pathways have been described in the literature [9].

As indicated above, the relative amount of oil and water, and the amount and the bending properties of the surfactant determine the microstructure. Using our knowledge of the evolution of the spontaneous curvature of the monolayer, the complex phase diagrams of microemulsions, like e.g. the different Winsor-phases, can be understood [37, 38, 39]. A high curvature towards oil may set a typical droplet size, and the surfactant concentration the number of droplets. This defines how much oil can be solubilized, and emulsification failure with supernatant oil will in general be found for higher oil concentrations – forming what is called a Winsor I domain in the phase diagram. If the spontaneous curvature is of opposite sign, inverse systems with solubilized water in a continuous oil phase will be found – in case of emulsification failure as supernatant to an excess water phase, forming a Winsor II domain. Close to zero curvature, bicontinuous structures have

been conjectured [40] and been proven to exist by NMR self-diffusion and conductivity experiments [41, 42, 43, 44]. In these Winsor III domains, both excess oil and water exist. If one now increases the amount of surfactant, more and more oil and water can be solubilized, up to a point where the excess phases disappear forming a single bicontinuous microemulsion phase. The phase behavior described here in the curvature-surfactant phase plane for equal quantities of oil and water has the shape of a fish and is called the Kahlweit-Strey fish diagram [45, 38]. It gives a direct illustration of the fact that the topology of the phases can be tuned and even inverted [46, 47], opening the road to chemical reactions either in droplets of either type used as micro-reactors, or at the (giant) interface of bicontinuous microemulsions, making use of both available solubility channels in the samples. The last point is e.g. of paramount importance for the use of microemulsions in decontamination applications [48, 49].

Droplet phases were already used for enzymatically catalyzed reactions. Here, especially lipases are of relevance since they need the interface to be activated [50, 51, 52, 53, 54]. Also for other enzyme reactions microemulsions can be interesting media [55, 56, 57, 58]. In some cases the microemulsion is only used to solubilize the enzyme [59].

### *2.2. Characterization of microemulsions by scattering*

As reviews on the subject exist [60, 61], only the most useful concepts are summarized here. Small-angle scattering is a powerful tool for measurements of average nano-scale structures. It is based on differences in scattering length density [62], and with neutrons it is particularly suited for microemulsions if isotopic substitution can be used to highlight either the domains, or the

surfactant layer. For simple geometries of domains, like droplets, including non-spherical or polydisperse droplets, analytical or quasi-analytical descriptions of the scattered intensity as a function of scattering vector q exist. An example has been provided by Arleth and Pedersen [63], who succeed in extracting both $\kappa$ and $\bar{\kappa}$ from a structural droplet model of an AOT-system using the formalism of Safran [64]. Here, a single size experiment would not be sufficient to obtain the two moduli. It is the description of both shape and polydispersity – in a manner analogous to fluctuations – which allow the determination of both constants. First experimental estimations of $\kappa$ have been reported from observations of excess area due to membrane fluctuations, which result in small (logarithmic) corrections to the dilution laws of the peak position [65, 66, 67]. One may also note that a straightforward description of the high-$q$ Porod scattering – if interfaces are well-defined – allows the determination of the specific surface $S/V$, which as already mentioned gives access to the head group area of the surfactant molecules. Finally, we would like to add that it is possible to describe fuzzy interfaces as discussed below [30, 68].

Bicontinuous structures have been proven to be much harder to describe theoretically, although freeze-fracture electron microscopy gave a clear hint at the structure [69, 70]. Auvray et al. have shown early that bicontinuous phases may possess a surfactant layer of zero mean curvature. They have evidenced the absence of correlation between change in water volume and change in surfactant concentration, via the cross-correlation term measured by contrast-variation SANS [71]. The small-angle scattering of interconnected domains has been approached in different ways. First, it was

recognized that scattering often displays a peak characterizing a nanometric domain size. It is therefore tempting to divide space in squares (in 2D), or in cubes in 3D, and evaluate the amount of surface between (not-identically filled) neighboring cubes, as a function of the volume fraction $\Phi$ of for instance the water phase. This approach leads to the determination of a dimensionless number $a$, given by the product of the specific surface $S/V$ and the characteristic length $d$ determined from the peak position:

$$d\frac{S}{V} = a\Phi(1-\Phi) \tag{4}$$

In such models, the essential difference between different topologies amounts to different values of the dimensionless number $a$. For squares, $a$ equals 4, and for cubes $a = 6$. The statistical mechanics of more disordered systems are described by the Talmon-Prager model, which predicts $a = 5.82$ using a Voronoi tessellation of space [72, 73, 74]. To summarize, these types of models are based on a geometrical subdivision of space, which may also be more random, like Voronoi tessellation, or the family of DOC-models proposed by Zemb et al. [5, 33, 75, 76]. Obvious difficulties with all of these models are the non-physical description of highly bend states at the edges of the cubes, or at least the non-homogeneous distribution of curvature across the samples. Needless to say, fluctuations are entirely absent from such models. It may also be noted that random surface models for $L_3$-sponge phases have probably been inspired by such discretized systems, adding the contribution of the bending rigidity $\kappa$ to the statistical mechanics of random domains[77]. Secondly, analytical models of random mixtures with nanometric domain formation have been proposed, in particular by Debye for inhomogeneous solids

[78, 79]. The Debye model for the scattered intensity is simply the Fourier transform of a correlation function $\rho(r)$ with only one characteristic length scale, the domain size $d$: $\rho(r) \approx \exp(-r/d)$. There is thus no correlation between neighboring domains. In reciprocal space, the intensity reads:

$$I(q) = \frac{I_0}{(1 + q^2 d^2)^2} \tag{5}$$

If one multiplies out the square in eq. 5, one immediately sees that the dominant high-$q$ term obeys a Porod behavior. The prefactor $I_0$ is related to the product $8\pi d^3 \Delta\rho^2 \Phi_1 \Phi_2$, where $\Delta\rho$ is the scattering contrast, and $\Phi_i$ are the volume fractions. The surface-to-volume ratio is given by $\frac{4\Phi_1\Phi_2}{d}$. Due to the absence of inter-domain correlations, however, there is no peak predicted by eq. 5, which is linked to the fact that in the expansion of the square, the quadratic and the biquadratic term have prefactors based on one length only, $d$. One may note that a similar equation, called the Ornstein-Zernike equation, exists for the description of rapidly decaying thermal fluctuations. Then the correlation function has the Yukawa form $\rho(r) \approx 1/r \exp(-r/d)$, and the intensity is proportional to $1/(1 + q^2 d^2)$. In this case, there is no Porod scattering at high $q$, and no scattering peak indicative of domain size.

The extension of the Debye scattering law to correlated domains leads to the famous Teubner-Strey formula [80].

The Teubner-Strey approach originally was derived from an order parameter expansion of the free energy associating the water-to-oil ratio inside the microemulsion with the order parameter $\psi$. In [80] it was shown that a coefficient combination $a_i$=0 except $a_2 > 0$ and $c_i = 0$ except $c_1 < 0$ and $c_2 > 0$ results in a Landau free energy $F$ of the form

$$F = \int (a_2\psi^2 + c_1(\nabla\psi)^2 + c_2(\Delta\psi)^2)d^3r \tag{6}$$

with the stability condition $4a_2c_2 - c_1^2 > 0$.Based on this, the distribution of the scattered intensity $I(q)$ is found to be

$$I(q) = \frac{8\pi c_2 < \eta^2 > /\xi_{TS}}{a_2 + c_1q^2 + c_2q^4} \tag{7}$$

Here, $< \eta^2 >= \phi_w\phi_o(\Delta\rho)^2$ is the mean-squared fluctuation of the scattering length density of the polar and non polar domains in the microemulsions, with volume fraction of $\phi_w$ and $\phi_o$, respectively. The fit parameters $a_2$, $c_1$, $c_2$ of this peak shape function allow to compute the mean domain size $d_{TS}$ of the structure

$$d_{TS} = 2\pi \left( \frac{1}{2} \left( \frac{a_2}{c_2} \right)^{1/2} - \frac{c_1}{4c_2} \right)^{-1/2} , \tag{8}$$

and the correlation length $\xi_{TS}$

$$\xi_{TS} = \left( \frac{1}{2} \left( \frac{a_2}{c_2} \right)^{1/2} + \frac{c_1}{4c_2} \right)^{-1/2} \tag{9}$$

which describes the length scale of the intermediate range fluctuations. Hence, a fit of eq. 7 to experimental small angle data leads to the determination of $\xi_{TS}$ and $d_{TS}$. The position of the peak is related to domain size $d_{TS}$, whereas its width is related to the correlation length $\xi_{TS}$. The more ordered the microemulsion, the higher the correlation length, and thus the thinner the peak. The Teubner-Strey function is extremely successful in describing bicontinuous microemulsions with symmetric composition (equal volumes of oil and water).

A word of caution should however be added: the presence of a peak is no guarantee of bicontinuity, and indeed it is impossible to prove bicontinuity by scattering only, as particulate models might very well work for bicontinuous systems [81]. A peak arising from, say, repelling droplets might be well described by the TS-formula over a limited $q$-range. It is recommended to always check Porod scattering and dilution lines in order to avoid these traps, and wherever possible combine with other techniques like e.g. NMR self-diffusion measurements [82, 83, 84, 85, 86, 87] or test of flow birefringence [88].

As a last approach to the structure of bicontinuous microemulsions, we would like to mention the description of the distribution of oil and water phases using random interfaces as proposed by Safran, Pieruschka, and Marcelja, based on ideas by Cahn and Berk [89, 81, 90]. The idea is to calculate the statistical properties of random distributions of matter, obeying a spectrum, with interfaces between domains identified by cut-off values set by volume conservation. One of the nice results of this rather involved method is that one can calculate the Helfrich bending energy of the resulting interfaces, and minimize it with respect to the spectrum used to construct the interfaces. As the spectrum is directly related to the scattered intensity, which picks up the relevant amplitudes of existing wavelengths in the sample, the outcome is rather astonishing: it is the Teubner-Strey formula, eq. (5) [91]. Finally, in more recent contributions, the random interface formalism based on two-level cut Gaussians has been used to study phase diagrams and in particular the swelling properties of microemulsions of various flexibilities ($\kappa$, $\bar{\kappa}$) of the surfactant layer [34].

To round up this section on methodology, the dynamical properties of microemulsions have also been studied extensively by scattering methods. Strictly speaking, photon correlation spectroscopy (PCS, often also called DLS) should also be mentioned as a complementary technique, although it amounts to the determination of a hydrodynamic radius of droplets, which is closely related to the static droplet radius. Fluorescence correlation measuring the self-diffusion of a fluorophore is complementary to DLS accessing the auto-correlation of the total density fluctuations, and the former technique has been used for the detailed characterization of microemulsion droplets, recentlyy [92]. Neutron spin echo (NSE) allows to measure directly the correlation functions of Brownian motion in a sample, which includes self-diffusion of e.g., droplets, and fluctuations of interfaces. The theories of fluctuating surfaces are rather complex [64, 93, 94] and will not be outlined here. The main result is that depending on the geometry of the average surface, its undulations can be developed in a series expansion, like plane waves for flat surfaces, or spherical harmonics for spherical objects, described by an average mean square amplitude. At the lowest order, the autocorrelation function of the fluctuating surface is found to decay as the result of a competition between thermal motion expressed by $kT$, the local bending modulus $\kappa$, and dissipation related to viscosity. For spherical droplets, this leads to

$$S(q,t) = \langle \rho_q(t)\rho_{-q}(0)\rangle \exp(-D_0 q^2 t)\left[4\pi[j_0(qR)]^2 + \sum f_l(qR)\,\langle u_l(0)u_l(t)\rangle\right] \ . \tag{10}$$

Here, $l$ is the index of the spherical harmonics expansion, and $f_i$ are related to Bessel functions [95]. Therefore the time correlation function takes the

form [96]

$$I(q,t) = \left\langle \exp(-\Gamma_1 t) V_s^2 (\Delta\rho)^2 \left[ f_0(qR) + \sum_{l\geq 2} \frac{2l+1}{4\pi} f_l(qR) \left\langle |u_l|^2 \right\rangle \exp(-\Gamma_l t) \right] \right\rangle_R , \tag{11}$$

which at least is a sum of two exponential contributions if terms corresponding to $l > 2$ are omitted. The decay of the correlation of the droplet positions due to Fickian translational diffusion is represented by the first term in eq.11. The second term represents the shape fluctuations of the particles. $\Gamma_l$ is the relaxation rate of the corresponding mode.

The index $R$ denotes an average over the droplet size distribution. For a peanut-like shape deformation of a spherical shell ($l = 2$), e.g., the NSE relaxation time $\tau_2$ can be related to $\kappa$ and $\overline{\kappa}$:

$$\tau_2^{-1} = \frac{1}{\eta R^3} \left[ 4\kappa - \overline{\kappa} - \frac{kT(\ln\phi - 1)}{4\pi} \right] \frac{1}{Z(2)} \tag{12}$$

This expression was derived [64] at the emulsification failure boundary, where the microemulsion droplets are strictly spherical, since they are swollen to their maximum size. $Z(l)$ is given by

$$Z(l) = \frac{(2l+1)(2l^2+2l-1)}{l(l+1)(l+2)(l-1)} , \tag{13}$$

which leads for $l = 2$ to 55/24. In eq. 13, the oil and water viscosities were assumed to be equal. However, in real systems they differ and a generally improved description of $Z(l)$ has to be used [97].

$$Z(l) = \frac{\left[(2l^2+4l+3)\,E + 2l\,(l+2)\right]\left[2\,(l^2-1)\,E + 2l^2 + 1\right]}{(l-1)l(l+1)(l+2)(2l+1)(E+1)} , \tag{14}$$

with $E$ being the ratio of the viscosities of the interior and the continuous phase of the droplets. In the limit of equal viscosities and for $l = 2$ equation

14 leads to a ratio of 52.5/24, yielding only a minor difference compared to eq. 13. This theoretical description in terms of spherical harmonics also allows to relate the size polydispersity index $p$ of the microemulsion droplets and the bending elastic constants [94].

$$p^2 = \frac{kT}{8\pi(2\kappa + \overline{\kappa}) + 2kT(\ln\phi - 1)} \tag{15}$$

The quantity $p$ is accessible by neutron scattering - [98] or light scattering experiments [99]. In the literature different formulations of the entropy term in eq. 15 given by the $\phi$–dependent term in the denominator may be found. Eq. 15 is usually based on random mixing of droplets and the version given here is obtained as a low-$\phi$ limit.

## 3. Bulk structure and bending elasticity of microemulsions

Tremendous progress in understanding of the physics of microemulsions has been made in the 80s and 90s of the last century, due to continuous and combined efforts of a few research groups. Dominique Langevin has given an overview over the state of the art of the physics of microemulsions, from droplets to bicontinuous phases, using self-diffusion measurements, conductivity, as well as X-ray and dynamic light scattering, quite exactly thirty years ago [100]. She focused on the different Winsor phases in model microemulsions. The data analysis was based on the models outlined above, in particular the Talmon-Prager-de Gennes structural model, and the Helfrich free energy, and she reported on their attempts to correlate surface tension measured by surface light scattering to characteristic sizes, see also ref.[101]; a review article on the different aspects of optical methods has been published in 1996 [102]. Here and in the following articles the surface tension

characterized the planar interface between a microemulsion and its excess phase. The correlation was found to be delicate, in particular as the bending moduli and their evolutions were mostly unknown at that time. Moreover, through the relationship between moduli and persistence length given in eq. (2), the characteristic sizes were expected to be linked to $\kappa$.

Strong efforts were thus devoted by several groups to the determination of the bending moduli, and a major breakthrough for the bending rigidity and the spontaneous curvature was reported by Binks et al. in 1989 [36]. Using optical methods and in particular ellipsometry, they succeeded in first experimental estimations of $\kappa$. A year later, the Gaussian bending modulus was also deduced from ellipsometry [103], and in 1991 and 1992 D. Langevin published an overview [104, 37] where she summarized the physical properties of microemulsions, for droplets and bicontinuous phases, paying specifically attention to the Gaussian modulus. In particular, she linked recently acquired knowledge on bending moduli with structure formation: Too stiff monolayers leading to too high persistence lengths privilege the formation of lamellar (liquid crystalline) phases, whereas too floppy monolayers induce molecular mixtures. Only a careful choice of intermediate bending constants was recognized to favor proper microemulsions.

Once the importance of all bending parameters for the microstructure established, the group of D. Langevin made considerable progress by comparing SANS and ellipsometry data [105]. As outlined in section II, both bending moduli in the form of $8\pi(\kappa + \overline{\kappa}/2)$ enter the bending elasticity of spherical droplets, but a different combination enters droplet polydispersity, assimilated here to fluctuations. By describing both size and polydispersity

– with the technical difficulty of wavelength spread, partially circumvented by a low-$q$ measurement – both constants can be extracted, as later done with higher precision by Arleth and Pedersen [63]. Ellipsometry being sensitive only to fluctuations around an on average flat macroscopic layer, a second, independent measurements of $\kappa$ was obtained, comforting the more delicate measurement of the Gaussian bending modulus. Once the relationship between polydispersity measured by SANS and bending properties had been established, Sicoli and Langevin applied the approach to model surfactants of different chain length: $C_8E_3$, $C_{10}E_4$, and $C_{12}E_5$. They concluded that the longer chains favored monodispersity and thus rigidity, while temperature and the length of the oil chain were only of secondary importance [106]. Similar results have been reported by Gradzielski and Langevin a year later[107].

The pioneering paper by Sicoli, Langevin and Lee called for ever more sophisticated descriptions of neutron scattering experiments on microemulsions. In 1995, Gradzielski et al. reported on a core-shell description of microemulsion droplets, studying the increasing solubilization of oil with added co-surfactant [108]. They related structural information to macroscopic interfacial tension, and estimated the combination $\kappa + \overline{\kappa}/2$ to about $kT$. The same year, they reported on a fuzzy shell form factor well suited for microemulsion droplets [68]. This article was a follow-up of an earlier one by Strey studying microemulsion monolayers and $L_3$-bilayers by SANS, in both shell and bulk contrast [30], proposing a diffuse shell model hinting at penetration of water molecules. In 1995, they could show that scattering from common water/oil/$C_{10}E_4$ microemulsion droplets was better described

by the new form factors than by the conventional one with sharp boundaries. This allowed the precise extraction of droplet radii, shell thickness, and polydispersity parameters, the latter also with the instrument resolution taken into account.

In parallel with the work by the Langevin group, the group of Hoffmann contributed strongly to the field in the 1990s, before eventually combining their efforts in common publications, mainly following Michael Gradzielski's post-doctoral stay with Dominique Langevin. An early paper by Gradzielski and Hoffmann on charged microemulsion droplets may be cited [109]. They had the idea to mix surfactants in order to control the aggregate charge density, and used standard techniques including conductivity and viscosity measurements, but also light and small-angle neutron scattering, to characterize the system. As charged droplets interact over large distances given by the Debye length in water, the authors incorporated a description of the structure factor using the random phase approximation (RPA), while reviewing also other closure relations of the Ornstein-Zernike equation [110]. They succeeded in characterizing the repulsion between droplets, allowing for a precise determination of droplet geometry and charge. A more detailed analysis of the light scattering experiments was published a few years later by the same authors [23], see also [111].

The above-mentioned work by Sicoli et al. linking the droplet characteristics to the bending constants was further improved by Gradzielski and Langevin in 1996 [98], including contrast variation small-angle neutron scattering. Together with Sottmann and Strey, they then used the same methods to investigate the influence of the surfactant layer [112], with the main focus

on the combination of bending constants $\kappa + \bar{\kappa}/2$ relevant for spherical objects. These authors focused on oil droplets slightly above the emulsification failure, reaching a maximal droplet size. Under these conditions, any additional oil phase-separates as it cannot be accommodated in the droplets any more due to bending rigidity constraints. Characterization of these droplets thus offers access to bending properties of the monolayer. The authors then not only changed the chain length, but also studied systematically mixtures of molecules of different chain length, and different headgroups, non-ionic and zwitterionic. The following year, M. Gradzielski extended this approach to the study of the influence of linear and cyclic co-surfactants on microemulsion droplets stabilized with zwitterionic surfactants TDMAO [113]. He carefully characterized the droplets, and extracted the usual sum of the bending constants. He then correlated the observed weakening of the monolayer rigidity obtained with cyclic and short-chain alcohols with the phase behavior, where increasingly disordered phases were observed in these cases.

As discussed in section 2, electrostatic charges have been predicted to have a strong effect on the bending elasticity of monolayers. In 2001, Farago and Gradzielski investigated this effect by substituting some of the stabilizing TDMAO layer by ionic surfactants, TTABr [114]. They used a combination of SANS and NSE to separate the bending moduli, $\kappa$ and $\bar{\kappa}$, a method which has been used in the literature and which will be reviewed in section 5. Here, this work should be mentioned as it can be seen as a continuation of the systematic modification of the surfactant layer, now with charged molecules. These authors found surprisingly weak changes in the bending constants, conjecturing partial compensation by, e.g., changes in head group area not

accounted for by the continuum electrostatic theory.

We have tried to show in this section that during the late 80s up to the end of 90s, the group of D. Langevin and others considerably improved our understanding of microemulsion properties, in particular by identifying the link between bending properties of the surfactant layer, microscopic structure and dynamics of aggregates, and macroscopic phase behavior. This knowledge can be seen as the starting point of applications and more complex systems, in particular those including polymer molecules. Still in the 90s, hydrophobically modified polymers and in particular triblock copolymers with hydrophobic end groups became available, and several studies were devoted to their synthesis and properties. The rheological properties of aqueous solutions due to self-assembly of the 'sticky' ends leading to the formation of volume-spanning, transient networks were rather astonishing [115, 116, 117]. By offering a hydrophobic 'harbour' to the sticky ends [118], droplet microemulsions of oil in water allowed the detailed control of the number and properties of the transient crosslinks of these networks, and thus of rheology [119, 85, 120]. By playing with the chemical nature of the triblocks, including fluorination, additional triggers of structure and rheology have been studied [121, 122, 123, 124]. Reviews on modification of interaction between microemulsion droplets exist, see e.g. [125]. Once such model transient networks of triblock copolymers connecting microemulsion droplets had been understood and theoretically described [126, 127], they have been used as matrix of model hydrogel nanocomposites. Indeed, the incorporation of nanoparticles, in particular silica, into *hydrophobic* polymer matrices is a popular method to improve the rheological properties of polymer materials,

be it model systems [128, 129, 130, 131], or more complex multi-scale filler materials for industrial applications [132, 133, 134]. The structure and rheological properties of hydrogel nanocomposites has been studied by Puech et al [135, 136, 137]. Besides standard rheology characterizing the network percolation and its shift in the phase diagram with addition of nanoparticles, they have used small-angle neutron scattering with $H_2O/D_2O$ contrast-variation in order to characterize either the organic network, or the silica filler and its interactions, using a reverse Monte Carlo approach [138]. One of the surprising findings was the peculiar interaction between the filler nanoparticles and the stabilizing surfactant layer of the microemulsion, which lead to a coverage of the particles by surfactant [139, 140], offering hydrophobic compartments to be connected to the transient network by the sticky endgroups.

To finish this section with a completely different application of microemulsion droplets, showing the popularity and usefulness of this field, we come back to work of Dominique Langevin. In 2008, she co-authored an article on the structure of DNA molecules confined in microemulsion droplets, in an inverse system [141]. By increasing the concentration, and playing with the mass of the DNA molecules, the authors attempted to reach physiological concentrations, and study DNA under confinement. Studies of dynamics under confinement in water nanodroplets in microemulsions may also be mentioned in this context [142, 143, 144, 145], studies which recently led to investigations of synthetic macromolecules in microemulsion droplets, and their effect on the bending properties [146, 147, 148]. In all cases, microemulsions are used as nano-containers, which may or may not be deformed by the hosted molecules, inducing structural changes, in particular in droplet size,

as already observed by Swami et al. We would like to emphasize that none of these 'nano-engineering' approaches would have been feasible without the long term efforts undertaken from the 80s on in understanding the physical properties of microemulsions. In this context, one might follow a journey through the phase diagram of pharmaceutically relevant microemulsion systems published recently [149]. We have also chosen not to discuss any of the template applications of microemulsions – see [150] for a recent example – , which is an entire research field of its own, and would again not have been developed without the understanding of microemulsion physics obtained by a few excellent groups, among which D. Langevin's team.

## 4. Microemulsions close to interfaces

In applications often the behavior of microemulsions on a solid interface is of importance. This holds e.g. for tertiary oil recovery or for decontamination [151, 152]. Early neutron work addressing this issue goes back to Chen, Strey and Lee [153]. In this work it was shown that the solid surface induces layer formation in bicontinuous microemulsions. A follow up of this study was published by Chen in 1995 [154]. Also in other related colloidal systems surface induced ordering was evidenced [155, 156].

However, it was only recently that this topic was revisited and neutron reflectivity experiments were related to theoretical predictions of surface induced structuring of microemulsions[157, 158]. During the last five years researchers focused on the study of microemulsions close to interfaces [157, 159, 158]. Especially, the mentioned work by Gompper et al. has revealed that the solid surface causes a structural transition in bicontinuous microemulsions

towards lamellar ordering close to solid surfaces. Ordering was also found in microemulsion droplet phases close to the surface [159]. Stühn and co-workers have shown by X-ray reflectometry that droplets in a microemulsion start to arrange in an ordered way in the presence of an air-liquid interface. The droplet integrity is preserved but an interparticle structure factor appears and the found distances depend on the droplet volume fraction in the used microemulsion. The common point in all these investigations is the found structure formation induced by the partial confinement arising from the presence of an interface. However, in most of the works the chemical nature of the interfaces was ignored.

In a recent work by Vargas-Ruiz et al. different model surfaces were used to study the near surface structure formation in sugar surfactant based microemulsions [158]. As in the work by Gompper et al. also in this work layering close to the surfaces was evidenced. However, the range of the induced order was found to depend on the hydrophilicity of the surface and of the used solvents. Moreover, grazing incidence small angle neutron scattering was performed. In these experiments no indication for lateral order close to the surface could be observed.

In addition to static scattering experiments Frielinghaus et al. have shown recently how neutron spin-echo spectroscopy can be employed to study microemulsion dynamics near surfaces. This important work reveals an acceleration of the dynamics of the surfactant film at the surface by about a factor of three [160]. However, this so-called GINSE technique (grazing incidence neutron spin-echo) is still at the beginning and further advances can be expected with new high brilliance neutron sources.

## 5. Dynamic properties of microemulsions

### *5.1. Droplet microemulsions*

The theoretical basis of droplet dynamics and the determination of the bending elasticity of the surfactant film at the droplet surface was already described in section 2.2. In this subsection we will summarize the main results obtained. The first NSE work on droplet dynamics was published in 1987 by Huang and co-workers [161]. In this work $\overline{\kappa}$ was neglected and for an $D_2O$/dioctyl sodium sulfosuccinate (AOT)/decane a value of $5kT$ for $\kappa$ was obtained. This work showed the valuable contribution of NSE for the study of bending elasticity in microemulsions. However, $5kT$ was probably an overestimation of $\kappa$. In a recent work by Stühn et al. [148] using a combination of small angle X-ray scattering and dielectric spectroscopy for a very similar AOT based microemulsion only $\kappa = 1kT$ was found.

Besides AOT based microemulsions mainly droplet systems made using oligoethyleneglycol alkylether surfactants ($C_iE_j$) were studied. In this context major contributions came from Dominique Langevin and co-workers. For droplet oil-in-water microemulsions made of deuterated *n*-octane, $C_{10}E_5$, and heavy water $\kappa = 0.92kT$ was determined by Dominique Langevin and one of us [95]. In the same work it was shown that by combining NSE with DLS and SANS both $\kappa$ and $\overline{\kappa}$ can be determined. $\overline{\kappa}$ was found to be about $-0.4kT$ for the $C_{10}E_5$ based system. Changing the oil from *n*-octane to *n*-dodecane lead to the following results for the same surfactant: $\kappa = 1.14kT$ and $\overline{\kappa} = -0.58kT$ [162]. Based on spinning drop measurements Strey and Sottmann found $\kappa = 0.9kT$ and $\overline{\kappa} = -0.31kT$ [163]. All these values are in good agreement within the experimental precision. The oil chain length has

nearly no influence on the bending elasticity of $C_{10}E_5$.

Dominique Langevin et al. have also shown that NSE data can be combined with fluorescence recovery after photobleaching diffusion measurements (FRAP) to account for the center of mass diffusion of the droplets [164]. This approach was applied to $C_8E_3$ and $C_{10}E_4$ based microemulsions. Also in this case the found $\kappa$ values are close to 1 $kT$. The magnitude of the determined $\overline{\kappa}$ values was also close to 1 $kT$. In addition, the approach was used to analyze the shape fluctuation in an oil-continuous droplet microemulsion based on $C_{10}E_4$ by Sottmann and co-workers [165].

Again in 2001, Farago and Gradzielski have used NSE to study the influence of subsequent increases in surface charge density of microemulsion droplets on $\kappa$ [114].

### *5.2. Bicontinuous microemulsions*

NSE is also a successful tool to study more complex surfactant and microemulsion phases [166]. In the last 10 years, due to the fascinating structure, several studies focused on the dynamics of bicontinuous structures.

The bending moduli of bicontinuous microemulsions have been determined by combinations of SANS and neutron spin-echo techniques. In most of these works the Zilman-Granek description of membrane dynamics was employed to extract $\kappa$ from the NSE data [167, 168, 169, 170].

For the technical grade sugar surfactant SL55 Wellert et al. found $\kappa$ in the range from 3.5 $kT$ to about $4kT$ when the temperature is raised by about 25 K[170]. This reveals that sugar surfactant based microemulsions are less temperature sensitive compared to other non-ionic systems. These values were obtained by fitting NSE data only with the Zilman-Granek prediction

of the intermediate scattering function. However, the fits are found to be imperfect. Better description of the data can be achieved when an additional diffusional mode is taken into account in the analysis. Doing so, the $\kappa$ values were found to be lower by a factor of three at least [170]. Another technical grade sugar surfactant $C_{8/10}G_{1.3}$ (Glucopon 220; Cognis, Germany) was studied by neutron spin-echo and $\kappa$ was found to be approximately 1.5 $kT$ [169]. Hence, it seems that sugar surfactants might exhibit slightly higher rigidities compared to the $C_iE_j$ non-ionic surfactants. However, the data basis for sugar surfactants is still insufficient to make final conclusions about this point. Especially measurements on microemulsions based on purified sugar surfactants should be done in the future.

In 2013 Holderer and co-workers have published a work giving a detailed analysis of the different values of $\kappa$ which can be obtained from scattering experiments on bicontinuous phases [171].

## 6. Conclusions

After a short introduction to the physics of microemulsions, we have reviewed the contributions of several groups and in particular those of Dominique Langevin and coworkers aiming at a microscopic understanding of microemulsions, using mainly optical and scattering techniques. These investigations focused on the bending properties of the surfactant monolayers, which are the basis of the physics of microemulsions, and which became quantitatively accessible only with the use of sophisticated scattering techniques like e.g. neutron spin-echo experiments combined with dynamic light scattering. We have also reviewed a few more recent applications of mi-

croemulsion science, like droplets playing the role of nodes in the formation of hydrogels with hydrophobically modified polymer. Microemulsion droplets have also been used as microreactors, and examples of their use to confine synthetic and natural polymers have been discussed. Finally, we have reviewed the structure and dynamics of microemulsions close to macroscopic interfaces, which has attracted interest in the scattering community over the past decade. At the end of the review we report on the dynamic behavior of the interfacial film in bulk microemulsion phases. As a general conclusion of this necessarily partial review of the many contributions on the structure and dynamics of microemulsion droplets over the past decades, one may observe that there is nowadays a tendency to address ever more complex systems, where microemulsions are used as components e.g. to generate soft confinement or to create hierarchical structures. Needless to say, the rational design of such systems would not be possible without the detailed microscopic understanding obtained by careful experimental observations, and in particular scattering.

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