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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 intensively 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.

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

36 **2. The physics of microemulsions**

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

47 *2.1. Bending properties*

48 Besides the volumes of the phases, microemulsion structure depends cru-
 49 cially on the quantity and properties of the surfactant. Indeed, the amount

50 of the latter defines the available specific surface S/V , as all oil-water in-
 51 terfaces need to be covered for energetical reasons: S/V is given by the
 52 product of surfactant concentration and head group area σ (σ contains not
 53 only steric interaction and might vary a bit with experimental conditions).
 54 Moreover, if we ignore solubility issues, the bending properties of the surfac-
 55 tant layer determine which type of morphology is accessible, and the strength
 56 of thermal fluctuation around these morphologies. The bending properties
 57 of surfactant monolayers depend on the molecular architecture and interac-
 58 tions, and may be tuned chemically [113]: e.g., by modifying the surfactant,
 59 or adding a co-surfactant [8], changing the temperature [9], adding salt [10],
 60 or more complex molecules like copolymers which can induce changes in the
 61 phase diagram, or contribute to changes in viscosity of the different phases
 62 [11, 12, 13, 14]; similar effects had already been reviewed by [15].

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

$$F = \int \left[\frac{1}{2} \kappa (c_1 + c_2 - 2c_0)^2 + \bar{\kappa} c_1 c_2 \right] dA \quad (1)$$

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

98 The roles of κ and $\bar{\kappa}$ are quite different. It can be shown with the Gauss-
 99 Bonnet theorem, that the second term in eq. 1, which is related to the Gaus-
 100 sian curvature, depends only on the topology of the surface, and in particular
 101 on the number of handles and independent pieces of membrane or monolayer
 102 [26]. This is particularly obvious in the phase sequence of non-ionic bilayer
 103 phases governed by the surfactant-co-surfactant ratio, where $\bar{\kappa}$ can be shown
 104 to trigger morphology changes from vesicular [27], to lamellar, and finally to
 105 sponge phases [28, 29]. Concerning this last and most intriguing phase, it
 106 should be noted that there is a close relationship between the sponge phase
 107 and bicontinuous microemulsions to be discussed below [30] Having under-
 108 stood the influence of $\bar{\kappa}$, it follows that for a fixed topology of any given
 109 structure, local topology-preserving bending fluctuations are entirely deter-
 110 mined by κ . Alternatively to eq. 1, the bending energy can also be expressed
 111 in terms of the deviation of the packing parameter $p = \frac{V}{l\sigma}$ [31, 32] of the
 112 molecules from their spontaneous value p_0 . Here, V is the molecular vol-
 113 ume, and l the extended chain length. σ indicates the area per headgroup of
 114 the surfactant. Indeed, if one integrates over the monolayer thickness λ , the
 115 packing parameter is found to be linked to the curvature in order to comply
 116 to complete surface coverage:

$$p = 1 + H\lambda + \frac{1}{3}K\lambda^2 \quad (2)$$

117 as long as the topology remains unchanged [33]. This covering relationship
 118 allows rewriting the Helfrich Hamiltonian as $\kappa \cdot (p - p_0)^2$, with $\kappa^* = 2\kappa + \bar{\kappa}$
 119 [34]. One sees that monolayers adopting configurations close to spontaneous
 120 packing can only be stable with respect to bending if κ^* is positive. Finally,
 121 the modulus κ can also be used to define a persistence length, exponentially

122 increasing with κ , as the characteristic length above which fluctuations are
 123 large enough to decorrelate the orientation of the layer [35]:

$$\xi_k = \xi_0 \exp \frac{4\pi\kappa}{3kT} \quad (3)$$

124 where ξ_0 is a molecular length. Choice of pre-factors and renormalization
 125 of the bending constant by fluctuations are discussed by Binks et al. [36].
 126 The concept of persistence allows understanding the formation of the sponge
 127 phase as a lamellar phase which loses its orientational order on scales of the
 128 persistence length and thus approaches a random surface. One may note
 129 that an alternative view of the sponge phase as a ‘molten’ periodic minimal
 130 surface favored by positive values of $\bar{\kappa}$ has been proposed [29]. Moreover,
 131 the bicontinuous microemulsion can be seen as an oil-swollen lamellar phase,
 132 and such pathways have been described in the literature [9].

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

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

160 Droplet phases were already used for enzymatically catalyzed reactions. Here,
 161 especially lipases are of relevance since they need the interface to be activated
 162 [50, 51, 52, 53, 54]. Also for other enzyme reactions microemulsions can be
 163 interesting media [55, 56, 57, 58]. In some cases the microemulsion is only
 164 used to solubilize the enzyme [59].

165 *2.2. Characterization of microemulsions by scattering*

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

171 surfactant layer. For simple geometries of domains, like droplets, including
 172 non-spherical or polydisperse droplets, analytical or quasi-analytical descrip-
 173 tions of the scattered intensity as a function of scattering vector q exist. An
 174 example has been provided by Arleth and Pedersen [63], who succeed in ex-
 175 tracting both κ and $\bar{\kappa}$ from a structural droplet model of an AOT-system
 176 using the formalism of Safran [64]. Here, a single size experiment would not
 177 be sufficient to obtain the two moduli. It is the description of both shape
 178 and polydispersity – in a manner analogous to fluctuations – which allow the
 179 determination of both constants. First experimental estimations of κ have
 180 been reported from observations of excess area due to membrane fluctuations,
 181 which result in small (logarithmic) corrections to the dilution laws of the peak
 182 position [65, 66, 67]. One may also note that a straightforward description
 183 of the high- q Porod scattering – if interfaces are well-defined – allows the
 184 determination of the specific surface S/V , which as already mentioned gives
 185 access to the head group area of the surfactant molecules. Finally, we would
 186 like to add that it is possible to describe fuzzy interfaces as discussed below
 187 [30, 68].

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

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

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

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

219 [78, 79]. The Debye model for the scattered intensity is simply the Fourier
 220 transform of a correlation function $\rho(r)$ with only one characteristic length
 221 scale, the domain size d : $\rho(r) \approx \exp(-r/d)$. There is thus no correlation
 222 between neighboring domains. In reciprocal space, the intensity reads:

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

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

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

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

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

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

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

244 Here, $\langle \eta^2 \rangle = \phi_w\phi_o(\Delta\rho)^2$ is the mean-squared fluctuation of the scatter-
245 ing length density of the polar and non polar domains in the microemulsions,
246 with volume fraction of ϕ_w and ϕ_o , respectively. The fit parameters a_2 , c_1 ,
247 c_2 of this peak shape function allow to compute the mean domain size d_{TS}
248 of the structure

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

249 and the correlation length ξ_{TS}

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

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

258 A word of caution should however be added: the presence of a peak is no
 259 guarantee of bicontinuity, and indeed it is impossible to prove bicontinuity
 260 by scattering only, as particulate models might very well work for bicon-
 261 tinuous systems [81]. A peak arising from, say, repelling droplets might be
 262 well described by the TS-formula over a limited q -range. It is recommended
 263 to always check Porod scattering and dilution lines in order to avoid these
 264 traps, and wherever possible combine with other techniques like e.g. NMR
 265 self-diffusion measurements [82, 83, 84, 85, 86, 87] or test of flow birefringence
 266 [88].

267 As a last approach to the structure of bicontinuous microemulsions, we
 268 would like to mention the description of the distribution of oil and wa-
 269 ter phases using random interfaces as proposed by Safran, Pieruschka, and
 270 Marcelja, based on ideas by Cahn and Berk [89, 81, 90]. The idea is to
 271 calculate the statistical properties of random distributions of matter, obey-
 272 ing a spectrum, with interfaces between domains identified by cut-off values
 273 set by volume conservation. One of the nice results of this rather involved
 274 method is that one can calculate the Helfrich bending energy of the resulting
 275 interfaces, and minimize it with respect to the spectrum used to construct
 276 the interfaces. As the spectrum is directly related to the scattered intensity,
 277 which picks up the relevant amplitudes of existing wavelengths in the sample,
 278 the outcome is rather astonishing: it is the Teubner-Strey formula, eq. (5)
 279 [91]. Finally, in more recent contributions, the random interface formalism
 280 based on two-level cut Gaussians has been used to study phase diagrams and
 281 in particular the swelling properties of microemulsions of various flexibilities
 282 $(\kappa, \bar{\kappa})$ of the surfactant layer [34].

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

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

(10)

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

305 form [96]

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

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

311 The index R denotes an average over the droplet size distribution. For a
 312 peanut-like shape deformation of a spherical shell ($l = 2$), e.g., the NSE
 313 relaxation time τ_2 can be related to κ and $\bar{\kappa}$:

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

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

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

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

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

320 with E being the ratio of the viscosities of the interior and the continuous
 321 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].

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

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 ϕ -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- ϕ 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

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

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

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

370 – with the technical difficulty of wavelength spread, partially circumvented
 371 by a low- q measurement – both constants can be extracted, as later done
 372 with higher precision by Arleth and Pedersen [63]. Ellipsometry being sen-
 373 sitive only to fluctuations around an on average flat macroscopic layer, a
 374 second, independent measurements of κ was obtained, comforting the more
 375 delicate measurement of the Gaussian bending modulus. Once the relation-
 376 ship between polydispersity measured by SANS and bending properties had
 377 been established, Sicoli and Langevin applied the approach to model surfac-
 378 tants of different chain length: C_8E_3 , $C_{10}E_4$, and $C_{12}E_5$. They concluded
 379 that the longer chains favored monodispersity and thus rigidity, while tem-
 380 perature and the length of the oil chain were only of secondary importance
 381 [106]. Similar results have been reported by Gradzielski and Langevin a year
 382 later[107].

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

395 by the new form factors than by the conventional one with sharp boundaries.
396 This allowed the precise extraction of droplet radii, shell thickness, and poly-
397 dispersity parameters, the latter also with the instrument resolution taken
398 into account.

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

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

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

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

445 accounted for by the continuum electrostatic theory.

446 We have tried to show in this section that during the late 80s up to the
447 end of 90s, the group of D. Langevin and others considerably improved our
448 understanding of microemulsion properties, in particular by identifying the
449 link between bending properties of the surfactant layer, microscopic struc-
450 ture and dynamics of aggregates, and macroscopic phase behavior. This
451 knowledge can be seen as the starting point of applications and more com-
452 plex systems, in particular those including polymer molecules. Still in the
453 90s, hydrophobically modified polymers and in particular triblock copoly-
454 mers with hydrophobic end groups became available, and several studies
455 were devoted to their synthesis and properties. The rheological properties
456 of aqueous solutions due to self-assembly of the ‘sticky’ ends leading to the
457 formation of volume-spanning, transient networks were rather astonishing
458 [115, 116, 117]. By offering a hydrophobic ‘harbour’ to the sticky ends [118],
459 droplet microemulsions of oil in water allowed the detailed control of the
460 number and properties of the transient crosslinks of these networks, and
461 thus of rheology [119, 85, 120]. By playing with the chemical nature of the
462 triblocks, including fluorination, additional triggers of structure and rheology
463 have been studied [121, 122, 123, 124]. Reviews on modification of interac-
464 tion between microemulsion droplets exist, see e.g. [125]. Once such model
465 transient networks of triblock copolymers connecting microemulsion droplets
466 had been understood and theoretically described [126, 127], they have been
467 used as matrix of model hydrogel nanocomposites. Indeed, the incorporation
468 of nanoparticles, in particular silica, into *hydrophobic* polymer matrices is a
469 popular method to improve the rheological properties of polymer materials,

470 be it model systems [128, 129, 130, 131], or more complex multi-scale filler
 471 materials for industrial applications [132, 133, 134]. The structure and rheo-
 472 logical properties of hydrogel nanocomposites has been studied by Puech et al
 473 [135, 136, 137]. Besides standard rheology characterizing the network perco-
 474 lation and its shift in the phase diagram with addition of nanoparticles, they
 475 have used small-angle neutron scattering with $\text{H}_2\text{O}/\text{D}_2\text{O}$ contrast-variation
 476 in order to characterize either the organic network, or the silica filler and its
 477 interactions, using a reverse Monte Carlo approach [138]. One of the surpris-
 478 ing findings was the peculiar interaction between the filler nanoparticles and
 479 the stabilizing surfactant layer of the microemulsion, which lead to a coverage
 480 of the particles by surfactant [139, 140], offering hydrophobic compartments
 481 to be connected to the transient network by the sticky endgroups.

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

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

505 **4. Microemulsions close to interfaces**

506 In applications often the behavior of microemulsions on a solid interface
 507 is of importance. This holds e.g. for tertiary oil recovery or for decontamina-
 508 tion [151, 152]. Early neutron work addressing this issue goes back to Chen,
 509 Strey and Lee [153]. In this work it was shown that the solid surface induces
 510 layer formation in bicontinuous microemulsions. A follow up of this study
 511 was published by Chen in 1995 [154]. Also in other related colloidal systems
 512 surface induced ordering was evidenced [155, 156].
 513 However, it was only recently that this topic was revisited and neutron reflec-
 514 tivity experiments were related to theoretical predictions of surface induced
 515 structuring of microemulsions[157, 158]. During the last five years researchers
 516 focused on the study of microemulsions close to interfaces [157, 159, 158].
 517 Especially, the mentioned work by Gompper et al. has revealed that the
 518 solid surface causes a structural transition in bicontinuous microemulsions

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

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

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

544 5. Dynamic properties of microemulsions

545 5.1. Droplet microemulsions

546 The theoretical basis of droplet dynamics and the determination of the
547 bending elasticity of the surfactant film at the droplet surface was already
548 described in section 2.2. In this subsection we will summarize the main re-
549 sults obtained. The first NSE work on droplet dynamics was published in
550 1987 by Huang and co-workers [161]. In this work $\bar{\kappa}$ was neglected and for
551 an D₂O/dioctyl sodium sulfosuccinate (AOT)/decane a value of $5kT$ for κ
552 was obtained. This work showed the valuable contribution of NSE for the
553 study of bending elasticity in microemulsions. However, $5kT$ was probably
554 an overestimation of κ . In a recent work by Stühn et al. [148] using a combi-
555 nation of small angle X-ray scattering and dielectric spectroscopy for a very
556 similar AOT based microemulsion only $\kappa = 1kT$ was found.

557 Besides AOT based microemulsions mainly droplet systems made using oligo-
558 ethyleneglycol alkylether surfactants (C_{*i*}E_{*j*}) were studied. In this context
559 major contributions came from Dominique Langevin and co-workers. For
560 droplet oil-in-water microemulsions made of deuterated *n*-octane, C₁₀E₅, and
561 heavy water $\kappa = 0.92kT$ was determined by Dominique Langevin and one
562 of us [95]. In the same work it was shown that by combining NSE with
563 DLS and SANS both κ and $\bar{\kappa}$ can be determined. $\bar{\kappa}$ was found to be about
564 $-0.4kT$ for the C₁₀E₅ based system. Changing the oil from *n*-octane to *n*-
565 dodecane lead to the following results for the same surfactant: $\kappa = 1.14kT$
566 and $\bar{\kappa} = -0.58kT$ [162]. Based on spinning drop measurements Strey and
567 Sottmann found $\kappa = 0.9kT$ and $\bar{\kappa} = -0.31kT$ [163]. All these values are in
568 good agreement within the experimental precision. The oil chain length has

569 nearly no influence on the bending elasticity of $C_{10}E_5$.
 570 Dominique Langevin et al. have also shown that NSE data can be com-
 571 bined with fluorescence recovery after photobleaching diffusion measurements
 572 (FRAP) to account for the center of mass diffusion of the droplets [164]. This
 573 approach was applied to C_8E_3 and $C_{10}E_4$ based microemulsions. Also in this
 574 case the found κ values are close to $1 kT$. The magnitude of the determined $\bar{\kappa}$
 575 values was also close to $1 kT$. In addition, the approach was used to analyze
 576 the shape fluctuation in an oil-continuous droplet microemulsion based on
 577 $C_{10}E_4$ by Sottmann and co-workers [165].
 578 Again in 2001, Farago and Gradzielski have used NSE to study the influence
 579 of subsequent increases in surface charge density of microemulsion droplets
 580 on κ [114].

581 5.2. Bicontinuous microemulsions

582 NSE is also a successful tool to study more complex surfactant and mi-
 583 croemulsion phases [166]. In the last 10 years, due to the fascinating struc-
 584 ture, several studies focused on the dynamics of bicontinuous structures.
 585 The bending moduli of bicontinuous microemulsions have been determined
 586 by combinations of SANS and neutron spin-echo techniques. In most of these
 587 works the Zilman-Granek description of membrane dynamics was employed
 588 to extract κ from the NSE data [167, 168, 169, 170].
 589 For the technical grade sugar surfactant SL55 Wellert et al. found κ in the
 590 range from $3.5 kT$ to about $4kT$ when the temperature is raised by about
 591 25 K [170]. This reveals that sugar surfactant based microemulsions are less
 592 temperature sensitive compared to other non-ionic systems. These values
 593 were obtained by fitting NSE data only with the Zilman-Granek prediction

594 of the intermediate scattering function. However, the fits are found to be im-
 595 perfect. Better description of the data can be achieved when an additional
 596 diffusional mode is taken into account in the analysis. Doing so, the κ values
 597 were found to be lower by a factor of three at least [170]. Another techni-
 598 cal grade sugar surfactant $C_{8/10}G_{1.3}$ (Glucopon 220; Cognis, Germany) was
 599 studied by neutron spin-echo and κ was found to be approximately $1.5 kT$
 600 [169]. Hence, it seems that sugar surfactants might exhibit slightly higher
 601 rigidities compared to the C_iE_j non-ionic surfactants. However, the data
 602 basis for sugar surfactants is still insufficient to make final conclusions about
 603 this point. Especially measurements on microemulsions based on purified
 604 sugar surfactants should be done in the future.
 605 In 2013 Holderer and co-workers have published a work giving a detailed
 606 analysis of the different values of κ which can be obtained from scattering
 607 experiments on bicontinuous phases [171].

608 6. Conclusions

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

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