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► **To cite this version:**

Julian Oberdisse, Thomas Hellweg. Structure, interfacial film properties, and thermal fluctuations of microemulsions as seen by scattering experiments. *Advances in Colloid and Interface Science*, 2017, 247, pp.354-362. 10.1016/j.cis.2017.07.011 . hal-03013763

**HAL Id: hal-03013763**

**<https://hal.science/hal-03013763v1>**

Submitted on 19 Nov 2020

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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 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 publications 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  $\sigma$  ( $\sigma$  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,  $\kappa$  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  $\kappa$  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  $\kappa$ . 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.  $\sigma$  indicates the area per headgroup of  
 114 the surfactant. Indeed, if one integrates over the monolayer thickness  $\lambda$ , 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  $\kappa^*$  is positive. Finally,  
 121 the modulus  $\kappa$  can also be used to define a persistence length, exponentially

122 increasing with  $\kappa$ , 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  $\xi_0$  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  $\kappa$  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  $\kappa$  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  $\Phi$  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  $\kappa$  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  $\Phi_i$  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 parame-  
 238 ter expansion of the free energy associating the water-to-oil ratio inside the  
 239 microemulsion with the order parameter  $\psi$ . 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  $\phi_w$  and  $\phi_o$ , 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  $\xi_{TS}$

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

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  $\xi_{TS}$  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  $\xi_{TS}$ . 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  $\kappa$ , 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.  $\Gamma_l$  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  $\tau_2$  can be related to  $\kappa$  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



322 14 leads to a ratio of 52.5/24, yielding only a minor difference compared to  
 323 eq. 13. This theoretical description in terms of spherical harmonics also  
 324 allows to relate the size polydispersity index  $p$  of the microemulsion droplets  
 325 and the bending elastic constants [94].

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

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

### 331 **3. Bulk structure and bending elasticity of microemulsions**

332 Tremendous progress in understanding of the physics of microemulsions  
 333 has been made in the 80s and 90s of the last century, due to continuous and  
 334 combined efforts of a few research groups. Dominique Langevin has given  
 335 an overview over the state of the art of the physics of microemulsions, from  
 336 droplets to bicontinuous phases, using self-diffusion measurements, conduc-  
 337 tivity, as well as X-ray and dynamic light scattering, quite exactly thirty  
 338 years ago [100]. She focused on the different Winsor phases in model mi-  
 339 croemulsions. The data analysis was based on the models outlined above, in  
 340 particular the Talmon-Prager-de Gennes structural model, and the Helfrich  
 341 free energy, and she reported on their attempts to correlate surface tension  
 342 measured by surface light scattering to characteristic sizes, see also ref.[101];  
 343 a review article on the different aspects of optical methods has been pub-  
 344 lished 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  $\kappa$ .

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  $\kappa$ . 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  $\kappa$  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<sub>8</sub>E<sub>3</sub>, C<sub>10</sub>E<sub>4</sub>, and C<sub>12</sub>E<sub>5</sub>. 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<sub>3</sub>-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<sub>10</sub>E<sub>4</sub> 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,  $\kappa$  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 H<sub>2</sub>O/D<sub>2</sub>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 D<sub>2</sub>O/dioctyl sodium sulfosuccinate (AOT)/decane a value of  $5kT$  for  $\kappa$   
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  $\kappa$ . 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 ( $C_iE_j$ ) 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,  $C_{10}E_5$ , 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  $\kappa$  and  $\bar{\kappa}$  can be determined.  $\bar{\kappa}$  was found to be about  
564  $-0.4kT$  for the  $C_{10}E_5$  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  $\kappa$  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  $\kappa$  [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  $\kappa$  from the NSE data [167, 168, 169, 170].  
589 For the technical grade sugar surfactant SL55 Wellert et al. found  $\kappa$  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  $\kappa$  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  $\kappa$  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  $\kappa$  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  
633 scattering.

- 634 [1] I. Danielsson, B. Lindman, The definition of microemulsion, *Colloids*  
635 *and Surfaces* 3 (1981) 391–392.
- 636 [2] T. P. Hoar, J. H. Schulman, Transparent water-in-oil dispersions: the  
637 oleopathic hydro-micelle, *Nature (London)* 102 (1943) 152.
- 638 [3] J. H. Schulman, W. Stoeckenius, L. M. Prince, Mechanism of forma-  
639 tion and structure of micro emulsions by electron microscopy, *J. Phys.*  
640 *Chem.* 63 (1959) 1677–1680.

- 641 [4] P. A. Winsor, Solvent properties of amphiphilic compounds., Butter-  
642 worths, London, 1954.
- 643 [5] Y. Chevalier, T. Zemb, The structure of micelles and microemulsions,  
644 Rep. Prog. Phys. 53 (1990) 279–371, review.
- 645 [6] J. M. di Meglio, M. Dvolaitzky, R. Ober, C. Taupin, Defects and cur-  
646 vatures of the interfaces in a birefringent microemulsion, J. Physique  
647 Lettres 44 (6) (1983) L229–L234.
- 648 [7] J.-M. di Meglio, M. Dvolaitzky, L. Leger, C. Taupin, First observation  
649 of the undulation mode in birefringent microemulsions by quasielastic  
650 light scattering, Phys. Rev. Lett. 54 (15) (1985) 1686–1689.
- 651 [8] J. Oberdisse, C. Couve, J. Appell, J. F. Berret, C. Ligoure, G. Porte,  
652 Vesicles and onions from charged surfactant bilayers: A neutron scat-  
653 tering study, Langmuir 12 (1996) 1212–1218.
- 654 [9] U. Olsson, H. Wennerström, Globular and bicontinuous phases of non-  
655 ionic surfactant films, Adv. Coll. Interf. Sci. 49 (1994) 113–146.
- 656 [10] A. Kabalnov, U. Olsson, H. Wennerström, Salt effects on nonionic  
657 microemulsions are driven by adsorption/depletion at the surfactant  
658 monolayer, J. Phys. Chem. 99 (16) (1995) 6220–6230.
- 659 [11] B. Jakobs, T. Sottmann, R. Strey, J. Allgaier, L. Willner, D. Richter,  
660 Amphiphilic block copolymers as efficiency boosters for microemul-  
661 sions, Langmuir 15 (1999) 6707–6711.

- 662 [12] H. Frielinghaus, D. Byelov, J. Allgaier, G. Gompper, D. Richter., Effi-  
663 ciency boosting ad optional viscosity tuning in microemulsions studied  
664 by SANS, *Physica B* 350 (2004) 186–192.
- 665 [13] D. Byelov, H. Frielinghaus, O. Holderer, J. Allgaier, D. Richter, Mi-  
666 croemulsion efficiency boosting and the complementary effect. 1. Struc-  
667 tural properties, *Langmuir* 20 (2004) 10433–10443.
- 668 [14] M. Brodeck, S. Maccarone, D. Saha, L. Willner, J. Allgaier, G. Man-  
669 giapia, H. Frielinghaus, O. Holderer, A. Faraone, D. Richter, Asymmet-  
670 ric polymers in bicontinuous microemulsions and their accretion to the  
671 bending of the membrane, *Colloid Polym. Sci.* 293 (2015) 1253–1265.
- 672 [15] T. Sottmann, K. Kluge, R. Strey, J. Reimer, O. Söderman, General  
673 patterns of the phase behavior of mixtures of H<sub>2</sub>O, alkyl glucosides,  
674 and cosurfactants, *Langmuir* 18 (2002) 3058–3067.
- 675 [16] W. Helfrich, Elastic properties of lipid bilayers: Theory and possible  
676 experiments, *Z. Naturforschung* 28c (1973) 693–703.
- 677 [17] L. R. Arriaga, I. Lopez-Montero, F. Monroy, G. O. Gil, B. Farago,  
678 T. Hellweg, Stiffening effect of cholesterol on disordered lipid phases:  
679 a combined NSE + DLS analysis of the bending elasticity of large  
680 unilamellar vesicles based on popc, *Biophys. J.* 96 (2009) 3629–3637.
- 681 [18] M. Mell, L. H. Moleiro, Y. Hertle, P. Fouquet, R. Schweins, I. Lopez-  
682 Montero, T. Hellweg, F. Monroy, Bending stiffness of biological mem-  
683 branes: What can be measured by neutron spin echo?, *Eur. Phys. J. E*  
684 36 (7) (2013) 75(1–13).

- 685 [19] I. Szleifer, D. Kramer, A. Ben-Shaul, W. M. Gelbart, S. A. Safran,  
686 Molecular theory of curvature elasticity in surfactant films, *J. Chem.*  
687 *Phys.* 92 (1990) 6800–6817.
- 688 [20] M. Winterhalter, W. Helfrich, Effect of surface-charge on the curvature  
689 elasticity of membranes, *J. Phys. Chem* 92 (24) (1988) 6865–6867.
- 690 [21] R. Schomäcker, R. Strey, Effect of ionic surfactants on nonionic bilay-  
691 ers - bending elasticity of weakly charged membranes, *J. Phys. Chem.*  
692 98 (14) (1994) 3908–3912.
- 693 [22] P. G. Higgs, J. F. Joanny, Enhanced membrane rigidity in charged  
694 lamellar phases, *J. Physique* 51 (20) (1990) 2307–2320.
- 695 [23] M. Gradzielski, H. Hoffmann, Influence of charges on the structure and  
696 dynamics of an *o/w* microemulsion. effect of admixing ionic surfactants,  
697 *J. Phys. Chem.* 98 (1994) 2613–2623.
- 698 [24] J. Oberdisse, G. Porte, Size of microvesicles from charged surfactant  
699 bilayers: Neutron scattering data compared to an electrostatic model,  
700 *Phys. Rev. E* 56 (2) (1997) 1965–1975.
- 701 [25] J. Oberdisse, Transition from small to big charged unilamellar vesicles,  
702 *Euro. Phys. J. B* 3 (4) (1998) 463–469.
- 703 [26] G. Porte, Isotropic phases of bilayers, *Current Opinion in Coll. Interf.*  
704 *Sci.* 1 (3) (1996) 345–349.
- 705 [27] P. Herve, D. Roux, A.-M. Bellocq, F. Nallet, T. Gulik-Krzywicki, Di-



- 706 lute and concentrated phases of vesicles at thermal equilibrium, *J. de*  
707 *Physique II* 3 (8) (1993) 1255–1270.
- 708 [28] G. J. Porte, Lamellar phases and disordered phases of fluid bilayer-  
709 membranes, *J. Phys.: Condens. Matter* 4 (1992) 8649.
- 710 [29] G. Porte, J. Appell, P. Bassereau, J. Marignan,  $L_\alpha$  to  $L_3$  - a topology  
711 driven transition in phases of infinite fluid membranes, *J. de Physique*  
712 50 (11) (1989) 1335–1347.
- 713 [30] R. Strey, J. Winkler, L. Magid, Small-angle neutron scattering from  
714 diffuse interfaces. 1. Mono- and bilayers in the water-octane- $C_{12}E_5$  sys-  
715 tem, *J. Phys. Chem.* 95 (1991) 7502–7507.
- 716 [31] J. Israelachvili, D. J. Mitchell, B. W. Ninham, Theory of self-assembly  
717 of hydrocarbon and amphiphiles into micelles and nilayers, *J. Chem.*  
718 *Soc. Faraday Trans. II* 72 (1976) 1525–1568.
- 719 [32] D. J. Mitchell, B. W. Ninham, Micelles, vesicles and microemulsions,  
720 *J. Chem. Soc. Faraday Trans. II* 77 (1981) 601–629.
- 721 [33] T. Zemb, S. T. Hyde, P. J. Derian, I. S. Barnes, B. W. Ninham,  
722 Microstructure from x-ray-scattering - the disordered open connected  
723 model of microemulsion, *J. Phys. Chem.* 91 (14) (1987) 3814–3820.
- 724 [34] M. Duvail, J. F. Dufreche, L. Arleth, T. Zemb, Mesoscopic modelling  
725 of frustration in microemulsions, *Phys. Chem. Chem. Phys.* 15 (19)  
726 (2013) 7133–7141.

- 727 [35] P. G. de Gennes, C. Taupin, Microemulsions and the flexibility of  
728 oil/water interfaces, *J. Phys. Chem.* 86 (1982) 2294–2304.
- 729 [36] B. P. Binks, J. Meunier, O. Abillon, D. Langevin, Measurement of  
730 film rigidity and interfacial tensions in several ionic surfactant-oil-water  
731 microemulsion systems, *Langmuir* 5 (1989) 415–421.
- 732 [37] D. Langevin, Micelles and microemulsions, *Annu. Rev. Phys. Chem* 43  
733 (1992) 341–369.
- 734 [38] R. Strey, Microemulsion microstructure and interfacial curvature, *Col-  
735 loid & Polymer Science* 272 (1994) 1005–1019.
- 736 [39] R. Strey, Phase behavior and interfacial curvature in water-oil-  
737 surfactant systems, *Current Opinion in Colloid & Interface Science*  
738 1 (1996) 402–410.
- 739 [40] L. E. Scriven, Equilibrium bicontinuous structure, *Nature* 263 (1976)  
740 123–125.
- 741 [41] F. Larche, J. Rouviere, P. Delord, B. Brun, J. L. Dussossoy, Existence  
742 of a bicontinuous zone in microemulsion systems, *J. Physique Lett.*  
743 41 (18) (1980) L437–L440.
- 744 [42] M. Kahlweit, et al., How to study microemulsions, *J. of Colloid and  
745 Interface Science* 118 (2) (1987) 436–453.
- 746 [43] B. Lindman, K. Shinoda, U. Olsson, D. Anderson, G. Karlström,  
747 H. Wennerström, On the demonstration of bicontinuous structures in  
748 microemulsions, *Coll. Surf.* 38 (1-3) (1989) 205–224.

- 749 [44] U. Olsson, K. Shinoda, B. Lindman, Change of the structure of mi-  
750 croemulsions with the hydrophile lipophile balance of nonionic surfac-  
751 tant as revealed by NMR self-diffusion studies, *J. Phys. Chem.* 90 (17)  
752 (1986) 4083–4088.
- 753 [45] M. Kahlweit, R. Strey, G. Busse, Weakly to strongly structured mix-  
754 tures, *Phys. Rev. A* 47 (6) (1993) 4197–4209.
- 755 [46] K. Shinoda, Solvent properties of surfactant solutions, Vol. 2 of surfac-  
756 tant science series, M. Dekker, 1967.
- 757 [47] K. Shinoda, S. Friberg, Emulsions and Solubilization, John Wiley &  
758 Sons Inc., 1986.
- 759 [48] J. Gäb, M. Melzer, K. Kehe, S. Wellert, T. Hellweg, M.-M. Blum,  
760 Monitoring the hydrolysis of toxic organophosphonate nerve agents by  
761 diisopropyl fluorophosphatase (dfpase) in aqueous buffer and bicon-  
762 tinuous microemulsions with  $^1\text{H}$ - $^{31}\text{P}$ -HSQC NMR spectroscopy, *Anal.*  
763 *Bioanal. Chem.* 396 (2010) 1213–1221.
- 764 [49] R. Stehle, C. Schulreich, S. Wellert, J. Gäb, M.-M. Blum, K. Kehe,  
765 A. Richardt, T. Hellweg, An enzyme containing microemulsion based  
766 on skin friendly oil and surfactant as decontamination medium for  
767 organo phosphates: phase behavior, structure, and enzyme activity,  
768 *J. Coll. Interf. Sci.* 413 (2014) 127–132.
- 769 [50] H. Stamatia, A. Xenakis, M. Provelegiou, F. N. Kolisis, Esterification  
770 reactions catalyzed by lipases in microemulsions: The role of the en-

- 771 zyme localisation in relation to its selectivity, *Biotechnology and Bio-*  
772 *engineering* 42 (1993) 103–110.
- 773 [51] B. Orlich, R. Schomäcker, *Candida rugosa* lipase reactions in nonionic  
774 w/o-microemulsion with a technical surfactant, *Enzyme and Microbial*  
775 *Technology* 28 (2001) 42–48.
- 776 [52] D. Das, S. Roy, R. N. Mitra, A. Dasgupta, P. K. Das, Head-group size of  
777 hydrophilicity of surfactants: The major regulator of lipase activity in  
778 cationic water-in-oil microemulsions, *Chemistry – A European Journal*  
779 11 (2005) 4881–4889.
- 780 [53] M. Sathishkumar, E. S. Jeong, S. E. Yun, S. P. Mun, J. F. Rusling,  
781 Bicontinuous microemulsion as reaction medium for the  $\beta$ -glucosidase-  
782 catalyzed synthesis of n-hexyl- $\beta$ -d-glucopyranoside, *Enzyme and Mi-*  
783 *crobial Technology* 42 (2008) 252–258.
- 784 [54] M. Sathishkumar, R. Jayabalan, S. P. Mun, S. E. Yun, Role of bi-  
785 continuous microemulsion in the rapid enzymatic hydrolysis of (r,s)-  
786 ketoprofen ethyl ester in a micro-reactor, *Bioresource Technology* 101  
787 (2010) 7834–7840.
- 788 [55] B. Orlich, H. Berger, R. Schomäcker, Stability and activity of alcohol  
789 dehydrogenase in w/o-microemulsions: Enantioselective reduction in-  
790 cluding cofactor regeneration, *Biotch. and Bioeng.* 70 (6) (2000) 638–  
791 646.
- 792 [56] C. Oldfield, R. B. Freedman, B. H. Robinson, Enzyme hyperactivity in

- 793 aot water-in-oil micromulsions is induced by lone sodium counterions  
794 in the water pool, *Faraday Discuss.* 129 (2005) 247–263.
- 795 [57] E. D. Tzika, M. Christoforou, S. Pispas, M. Zervou, V. Papadimitriou,  
796 T. G. Sotiroudis, E. Leontidis, A. Xenakis, Influence of nanoreactor  
797 environment and substrate location on the activity of horseradish perox-  
798 idase in olive oil based water-in-oil microemulsions, *Langmuir* 27 (2011)  
799 2692–2700.
- 800 [58] M. Laupheimer, S. Engelskirchen, K. Tauber, W. Kroutil, C. Stuben-  
801 rauch, Bicontinuous microemulsion as reaction medium for  $\omega$ -  
802 transaminase catalysed biotransformations, *Tenside Surf. Det.* 48  
803 (2011) 28–33.
- 804 [59] M.-B. Cheng, J.-C. Wang, Y.-H. Li, X.-Y. Liu, X. Zhang, D.-W. Chen,  
805 S.-F. Zhou, Q. Zhang, Characterization of water-in-oil microemulsions  
806 for oral delivery of earthworm fibrinolytic enzyme, *J. Controlled Re-  
807 lease* 129 (2008) 41–48.
- 808 [60] T. Hellweg, in: *Microemulsions – Background, New Concepts and Ap-  
809 plications, Perspectives*, ed.: C. Stubenrauch, 1st Edition, Blackwell  
810 Publishing Ltd., Oxford, 2009, Ch. Scattering techniques to study the  
811 microstructure of microemulsions, pp. 48–83.
- 812 [61] P. Lindner, T. Zemb, *Neutron, X-rays and Light. Scattering Methods  
813 Applied to Soft Condensed Matter*, North Holland, Amsterdam, 2004.
- 814 [62] P. Pusey, in: *Neutron, X-rays and Light. Scattering Methods Applied*

- 815 to Soft Condensed Matter, ed.: P. Lindner, T. Zemb, North Holland,  
816 Amsterdam, 2002.
- 817 [63] L. Arleth, J. S. Pedersen, Droplet polydispersity and shape fluctu-  
818 ations in aot [bis(2-ethylhexyl)sulfosuccinate sodium salt] microemul-  
819 sions studied by contrast variation small-angle neutron scattering, Phys.  
820 Rev E 63 (6) (2001) 61406–61423.
- 821 [64] S. A. Safran, Saddle-splay modulus and the stability of spherical mi-  
822 croemulsions, Phys. Rev. A 43 (6) (1991) 2903–2904.
- 823 [65] R. Strey, R. Schomäcker, D. Roux, F. Nallet, U. Olsson, Dilute lamel-  
824 lar and  $L_3$  phases in the binary water- $C_{12}E_5$  system, J. Chem. Soc.  
825 Faraday Trans. 86 (12) (1990) 2253–2261.
- 826 [66] P. Bassereau, J. Appell, J. Marignan, Flexibility of lyotropic mem-  
827 branes: a comparative study between static and hydrodynamic mea-  
828 surements, J. Phys. II France 2 (1992) 1257–1271.
- 829 [67] E. Freyssingeas, F. Nallet, D. Roux, Measurement of the membrane  
830 flexibility in lamellar and "sponge" phases of the  $C_{12}E_5$ /hexanol/water  
831 system, Langmuir 12 (1996) 6028–6035.
- 832 [68] M. Gradzielski, D. Langevin, L. Magid, R. Strey, Small-angle neu-  
833 tron scattering from diffuse interfaces. 2. polydisperse shells in water-n-  
834 alkane- $C_{10}E_4$  microemulsions, J. Phys. Chem. 99 (1995) 13232–13238.
- 835 [69] W. Jahn, R. Strey, Microstructure of microemulsions by freeze-fracture  
836 electron-microscopy, J. Phys. Chem. 92 (1988) 2294–2301.

- 837 [70] I. Davidovich, L. Issman, C. de Paula, I. Ben-Barak, Y. Talmon, A  
838 cryogenic-electron microscopy study of the one-phase corridor in the  
839 phase diagram of a nonionic surfactant-based microemulsion system,  
840 *Coll. Polym. Sci.* 293 (11) (2015) 3189–3197.
- 841 [71] L. Auvray, J. P. Cotton, R. Ober, C. Taupin, Evidence for zero mean  
842 curvature microemulsions, *J. Phys. Chem.* 88 (1984) 4586–4589.
- 843 [72] Y. Talmon, S. Prager, Statistical mechanics of microemulsions, *Nature*  
844 267 (1977) 333–335.
- 845 [73] Y. Talmon, S. Prager, Statistical thermodynamics of phase equilibria  
846 in microemulsions, *J. Chem. Phys.* 69 (7) (1978) 2984–2991.
- 847 [74] Y. Talmon, S. Prager, The statistical thermodynamics of microemul-  
848 sions. 2. The interfacial region, *J. Chem. Phys.* 76 (3) (1982) 1535–1538.
- 849 [75] B. W. Ninham, I. S. Barnes, S. T. Hyde, P. J. Derian, T. N. Zemb,  
850 Random connected cylinders - a new structure in 3-component mi-  
851 croemulsions, *Europhys. Lett.* 4 (1987) 561–568.
- 852 [76] T. N. Zemb, The doc model of microemulsions: microstructure, scat-  
853 tering, conductivity and phase limits imposed by sterical constraints,  
854 *Coll. Surf. A* 129 (1997) 435–454.
- 855 [77] M. E. Cates, D. Roux, D. Andelman, S. T. Milner, S. A. Safran, Ran-  
856 dom surface model for the  $L_3$ -phase of dilute surfactant solutions, *Eu-  
857 rophys. Lett.* 5 (8) (1988) 733–739.

- 858 [78] P. Debye, A. M. Bueche, Scattering by an inhomogeneous solid, J.  
859 Appl. Phys. 20 (6) (1949) 518–525.
- 860 [79] P. Debye, H. R. A. jr., H. Brumberger, Scattering by an inhomogeneous  
861 solid. ii. the correlation function and its application, J. Appl. Phys.  
862 28 (6) (1957) 679–683.
- 863 [80] M. Teubner, R. Strey, Origin of the scattering peak in microemulsions,  
864 J. Chem. Phys. 87 (5) (1987) 3195–3200.
- 865 [81] N. Freiburger, C. Moitzi, L. de Campo, O. Glatter, An attempt to  
866 detect bicontinuity from SANS data, J. Colloid Interf. Sci. 312 (1)  
867 (2007) 59–67.
- 868 [82] P. T. Callaghan, Pulsed field gradient nuclear magnetic resonance as a  
869 probe of liquid state molecular organization, Aust. J. Phys. 37 (1984)  
870 359–87.
- 871 [83] U. Olsson, P. Ström, O. Söderman, H. Wennerström, Phase behavior,  
872 self-diffusion, and  $^2\text{H}$  NMR relaxation studies in an ionic surfactant  
873 system containing cosurfactant and salt. a comparison with nonionic  
874 surfactant systems, J. Phys. Chem. 93 (1989) 4572–4580.
- 875 [84] H. Wennerström, O. Söderman, U. Olsson, B. Lindman, Macroemul-  
876 sions versus microemulsions, Colloids and Surfaces A 123-124 (1997)  
877 13–26.
- 878 [85] H. Bagger-Jørgensen, L. Coppola, K. Thuresson, U. Olsson,  
879 K. Mortensen, Phase behavior, microstructure, and dynamics in a



- 880 nonionic microemulsion on addition of hydrophobically end-capped  
881 poly(ethylene oxide), *Langmuir* 13 (1997) 4204–4218.
- 882 [86] C. Stubenrauch, G. H. Findenegg, Microemulsions supported by octyl  
883 monoglucoside and geraniol. 2. An NMR self-diffusion study of the  
884 microstructure, *Langmuir* 14 (21) (1998) 6005–6012.
- 885 [87] F. Nilsson, O. Söderman, I. Johansson, Four different  $C_8G_1$  alkylglu-  
886 cosides. anomeric effects and the influence of straight vs branched hy-  
887 drocarbon chain, *J. Coll. Inter. Sci.* 203 (1998) 131–139.
- 888 [88] E. Hecht, K. Mortensen, H. Hoffmann,  $L_3$  phase in a binary block  
889 copolymer/water system, *Macromolecules* 28 (1995) 5465–5476.
- 890 [89] P. Pieruschka, S. Safran, Random interfaces and the physics of mi-  
891 croemulsions, *Europhys. Lett.* 22 (1993) 625–630.
- 892 [90] Pieruschka, S. A. Safran, A random interface model of microemulsions,  
893 *Journal of Physics-Condensed Matter* 6 (1994) A357–A362.
- 894 [91] L. Arleth, S. Marcelja, T. Zemb, Gaussian random fields with two level-  
895 cuts-model for asymmetric microemulsions with nonzero spontaneous  
896 curvature?, *J. Chem. Phys.* 115 (8) (2001) 3923–3936.
- 897 [92] M. F. Khan, M. K. Singh, S. Sen, Measuring size, size distribution, and  
898 polydispersity of water-in-oil microemulsion droplets using fluorescence  
899 correlation spectroscopy: Comparison to dynamic light scattering, *J.*  
900 *Phys. Chem. B* 120 (2016) 1008–1020.

- 901 [93] S. A. Safran, Fluctuations of spherical microemulsions, *J. Chem. Phys.*  
902 78 (4) (1983) 2073–2076.
- 903 [94] S. T. Milner, S. A. Safran, Dynamical fluctuations of droplet mi-  
904 croemulsions and vesicles, *Phys. Rev. A* 36 (9) (1987) 4371–4379.
- 905 [95] T. Hellweg, D. Langevin, Bending elasticity of the surfactant film in  
906 droplet microemulsions: Determination by a combination of dynamic  
907 light scattering and neutron spin-echo spectroscopy, *Phys. Rev. E* 57 (6)  
908 (1998) 6825–6834.
- 909 [96] B. Farago, M. Monkenbusch, K. D. Goecking, D. Richter, J. S. Huang,  
910 Dynamics of microemulsions as seen by neutron spin echo, *Physica B*  
911 213 & 214 (1995) 712–717.
- 912 [97] S. Komura, K. Seki, Dynamical fluctuations of spherically closed fluid  
913 membranes, *Physica A* 192 (1993) 27–46.
- 914 [98] M. Gradzielski, D. Langevin, B. Farago, Experimental investigation  
915 of the structure of nonionic microemulsions and their relation to the  
916 bending elasticity of the amphiphilic film, *Phys. Rev. E* 53 (4) (1996)  
917 3900–3919.
- 918 [99] T. Hellweg, D. Langevin, Droplet microemulsions: Determination  
919 of the bending elastic constants by photon correlation spectroscopy,  
920 *Progr. Colloid Polym. Sci.* 104 (1997) 155–156.
- 921 [100] D. Langevin, Recent advances in the physics of microemulsions, *Phys-*  
922 *ica Scripta* T13 (1986) 252–258.

- 923 [101] D. Guest, D. Langevin, Light scattering study of a multiphase mi-  
924 croemulsion system, *J. Coll. Inter. Sc.* 112 (1) (1986) 208–220.
- 925 [102] D. Langevin, Optical methods for studying microemulsions and mi-  
926 croemulsion interfaces, *Berichte d. Bunsenges. - Physical Chem. Chem.*  
927 *Phys.* 100 (1996) 336–343.
- 928 [103] L. T. Lee, D. Langevin, R. Strey, Relationship between microemulsion  
929 structure and surfactant layer bending elasticity, *Physica A* 168 (1990)  
930 210–219.
- 931 [104] D. Langevin, Microemulsions - interfacial aspects, *Adv. Colloid Interf.*  
932 *Sci.* 34 (1991) 583–595.
- 933 [105] F. Sicoli, D. Langevin, L. T. Lee, Surfactant film bending elasticity in  
934 microemulsions: Structure and droplet polydispersity, *J. Chem. Phys.*  
935 99 (6) (1993) 4759–4765.
- 936 [106] F. Sicoli, D. Langevin, Shape fluctuations of microemulsion droplets,  
937 *J. Phys. Chem.* 99 (40) (1995) 14819–14823.
- 938 [107] M. Gradzielski, D. Langevin, Small-angle neutron scattering experi-  
939 ments on microemulsion droplets: Relation to the bending elasticity of  
940 the amphiphilic film, *J. Molecular Struct.* 383 (1996) 145–156.
- 941 [108] M. Gradzielski, H. Hoffmann, D. Langevin, Solubilization of decane  
942 into the ternary system TDMAO/1-hexanol/water, *J. Chem. Phys.* 99  
943 (1995) 12612–12623.

- 944 [109] M. Gradzielski, H. Hoffmann, Structural investigations of charged o/w  
945 microemulsion droplets, *Adv. Coll. Interf. Sci.* 42 (1992) 149–173.
- 946 [110] R. Klein, in: *Neutrons, X-ray and Light Scattering*, ed.: P. Lindner,  
947 T. Zemb, North Holland, 2002, Ch. Interacting colloidal suspensions,  
948 pp. 351–380.
- 949 [111] N. Gorski, M. Gradzielski, H. Hoffmann, Mixture of nonionic and ionic  
950 surfactants - the effect of counterion binding in mixtures of tetradecyl-  
951 cyldimethylamine oxide and tetradecyltrimethylammonium bromide,  
952 *Langmuir* 10 (8) (1994) 2594–2603.
- 953 [112] M. Gradzielski, D. Langevin, T. Sottmann, R. Strey, Droplet mi-  
954 croemulsions at the emulsification boundary: The influence of the sur-  
955 factant structure on the elastic constants of the amphiphilic film, *J.*  
956 *Chem. Phys.* 106 (19) (1997) 8232–8238.
- 957 [113] M. Gradzielski, Effect of the cosurfactant structure on the bending  
958 elasticity in nonionic oil-in-water microemulsions, *Langmuir* 14 (1998)  
959 6037–6044.
- 960 [114] B. Farago, M. Gradzielski, The effect of the charge density of mi-  
961 croemulsion droplets on the bending elasticity of their amphiphilic film,  
962 *J. Chem. Phys.* 114 (22) (2001) 10105–10122.
- 963 [115] T. Annable, R. Buscall, R. Ettelaie, D. Whittlestone, The rheology of  
964 solutions of associating polymers - comparison of experimental behavior  
965 with transient network theory, *J. Rheology* 37 (4) (1993) 695–726.

- 966 [116] Y. Serero, R. Aznar, G. Porte, J. F. Berret, D. Calvet, A. Collet,  
967 M. Viguier, Associating polymers: From "flowers" to transient net-  
968 works, *Phys. Rev. Lett.* 81 (25) (1998) 5584–5587.
- 969 [117] J. F. Berret, Y. Serero, Evidence of shear-induced fluid fracture in  
970 telechelic polymer networks, *Phys. Rev. Lett.* 87 (4) (2001) 048303.
- 971 [118] T. Annable, R. Buscal, R. Ettelaie, P. Shepherd, D. Whittlestone, Influ-  
972 ence of surfactants on the rheology of associating polymers in solution,  
973 *Langmuir* 10 (1994) 1060–1070.
- 974 [119] H. Bagger-Jørgensen, U. Olsson, K. Mortensen, Microstructure in a  
975 ternary microemulsion studied by small angle neutron scattering, *Lang-*  
976 *muir* 13 (1997) 1413–1421.
- 977 [120] F. Molino, J. Appell, M. Filali, E. Michel, G. Porte, S. Mora, E. Sunyer,  
978 A transient network of telechelic polymers and microspheres: structure  
979 and rheology, *J. Phys. - Condensed Matt.* 12 (8A) (2000) A491–A498.
- 980 [121] D. Calvet, A. Collet, M. Viguier, J. F. Berret, Y. Serero, Perfluoroalkyl  
981 end-capped poly(ethylene oxide). synthesis, characterization, and rhe-  
982 ological behavior in aqueous solution, *Macromolecules* 36 (2) (2003)  
983 449–457.
- 984 [122] C. Rufier, A. Collet, M. Viguier, J. O. S. Mora, Asymmetric end-capped  
985 poly(ethylene oxide). Synthesis and rheological behavior in aqueous  
986 solution, *Macromolecules* 41 (15) (2008) 5854–5862.
- 987 [123] C. Rufier, A. Collet, M. Viguier, J. O. S. Mora, SDS interactions

- 988 with hydrophobically end-capped poly(ethylene oxide) studied by C-13  
989 NMR and SANS, *Macromolecules* 42 (14) (2009) 5226–5235.
- 990 [124] P. M. de Molina, F. S. Ihlefeldt, S. Prevost, C. Herfurth, M. S. Ap-  
991 pavou, A. Laschewsky, M. Gradzielski, Phase behavior of nonionic mi-  
992 croemulsions with multi-end-capped polymers and its relation to the  
993 mesoscopic structure, *Langmuir* 31 (18) (2015) 5198–5209.
- 994 [125] S. Kosmella, J. Koetz, Polymer-modified w/o microemulsions - with  
995 tunable droplet-droplet interactions, *Current Opin. Coll. Interf. Sci.*  
996 17 (5) (2012) 261–265.
- 997 [126] V. Testard, J. Oberdisse, C. Ligoure, Monte carlo simulations of col-  
998 loidal pair potential induced by telechelic polymers: Statistics of loops  
999 and bridges, *Macromolecules* 41 (19) (2008) 7219–7226.
- 1000 [127] P. I. Hurtado, L. Berthier, W. Kob, Heterogeneous diffusion in a re-  
1001 versible gel, *Phys. Rev. Lett.* 98 (13) (2007) 135503.
- 1002 [128] J. Oberdisse, Aggregation of colloidal nanoparticles in polymer matri-  
1003 ces, *Soft Matter* 2 (1) (2006) 29–36.
- 1004 [129] A.-C. Genix, J. Oberdisse, Structure and dynamics of polymer  
1005 nanocomposites studied by X-ray and neutron scattering techniques,  
1006 *Current Opin. Coll. Interf. Sci.* 20 (4) (2015) 293–303.
- 1007 [130] J. Oberdisse, Structure and rheological properties of latex-silica  
1008 nanocomposite films: Stress-strain isotherms, *Macromolecules* 35 (25)  
1009 (2002) 9441–9450.

- 1010 [131] C. S. Pauly, A.-C. Genix, J. G. Alauzun, J. Jestin, M. Sztucki,  
1011 P. H. Mutin, J. Oberdisse, Structure of alumina-silica nanoparticles  
1012 grafted with alkylphosphonic acids in poly(ethylacrylate) nanocompos-  
1013 ites, *Polymer* 97 (2016) 138–146.
- 1014 [132] G. P. Baeza, A. C. Genix, C. Degrandcourt, L. Petitjean, J. Gum-  
1015 mel, M. Couty, J. Oberdisse, Multiscale filler structure in simplified  
1016 industrial nanocomposite silica/SBR systems studied by saxs and tem,  
1017 *Macromolecules* 46 (16) (2013) 317.
- 1018 [133] G. P. Baeza, A. C. Genix, C. Degrandcourt, L. Petitjean, J. Gummel,  
1019 R. Schweins, M. Couty, J. Oberdisse, Effect of grafting on rheology and  
1020 structure of a simplified industrial nanocomposite silica/SBR, *Macro-*  
1021 *molecules* 46 (16) (2013) 6621–6633.
- 1022 [134] G. P. Baeza, A. C. Genix, C. Degrandcourt, L. Petitjean, J. Gummel,  
1023 M. Couty, J. Oberdisse, Mechanism of aggregate formation in simplified  
1024 industrial silica styrene-butadiene nanocomposites: effect of chain mass  
1025 and grafting on rheology and structure, *Soft Matter* 10 (35) (2014)  
1026 6686–6695.
- 1027 [135] N. Puech, S. Mora, V. Testard, G. Porte, C. Ligoure, I. Grillo, T. Phou,  
1028 J. Oberdisse, Structure and rheological properties of model microemul-  
1029 sion networks filled with nanoparticles, *Eur. Phys. J. E* 26 (1-2) (2008)  
1030 13–24.
- 1031 [136] N. Puech, S. Mora, G. Porte, T. Phou, I. Grillo, J. Oberdisse, Silica  
1032 nanoparticles dispersed in a self-assembled viscoelastic matrix: Struc-

- 1033            ture, rheology, and comparison to reinforced elastomers, *Brazilian Jour-*  
1034            nal of Physics 39 (2009) 198–204.
- 1035 [137] N. Puech, S. Mora, T. Phou, G. Porte, J. Jestin, J. Oberdisse, Mi-  
1036            croemulsion nanocomposites: phase diagram, rheology and structure  
1037            using a combined small angle neutron scattering and reverse Monte  
1038            Carlo approach, *Soft Matter* 6 (21) (2010) 5605–5614.
- 1039 [138] J. Oberdisse, P. Hine, W. Pyckhout-Hintzen, Structure of interacting  
1040            aggregates of silica nanoparticles in a polymer matrix: small-angle scat-  
1041            tering and reverse Monte Carlo simulations, *Soft Matter* 3 (4) (2007)  
1042            476–485.
- 1043 [139] G. Despert, J. Oberdisse, Formation of micelle-decorated colloidal silica  
1044            by adsorption of nonionic surfactant, *Langmuir* 19 (2003) 7604–7610.
- 1045 [140] D. Lugo, J. Oberdisse, M. Karg, R. Schweins, G. Findenegg, Surface  
1046            aggregate structure of nonionic surfactants on silica nanoparticles, *Soft*  
1047            *Matter* 5 (15) (2009) 2928–2936.
- 1048 [141] A. Swami, G. Espinosa, S. Guillot, E. Raspaud, F. Boue, D. Langevin,  
1049            Confinement of dna in water-in-oil microemulsions, *Langmuir* 24 (2008)  
1050            11828–11833.
- 1051 [142] T. Spehr, B. Frick, I. Grillo, B. Stühn, Supercooling of water confined  
1052            in reverse micelles, *J. Phys.: Condensed Matter* 20 (2008) 104204(1–6).
- 1053 [143] T. Blochowicz, E. Gouirand, A. Fricke, T. Spehr, B. Stühn, B. Frick,  
1054            Accelerated dynamics of supercooled glycerol in soft confinement,  
1055            *Chem. Phys. Lett.* 475 (2009) 171–174.



- 1056 [144] T. Spehr, B. Frick, I. Grillo, P. Falus, M. Müller, B. Stühn, Structure  
1057 and dynamics of reverse micelles containing supercooled water investi-  
1058 gated by neutron scattering, *Phys. Rev. E* 79 (3) (2009) 031404.
- 1059 [145] T. L. Spehr, B. Frick, M. Zamponi, B. Stühn, Dynamics of water con-  
1060 fined to reverse aot micelles, *Soft Matter* 7 (12) (2011) 5745–5755.
- 1061 [146] B. Kuttich, O. Ivanova, I. Grillo, B. Stühn, Polymer loaded microemul-  
1062 sions: Changeover from finite size effects to interfacial interactions, *J.*  
1063 *Chem. Phys.* 145 (16) (2016) 164904.
- 1064 [147] A. Weber, B. Stuhn, Structure and phase behavior of polymer loaded  
1065 non-ionic and anionic microemulsions, *J. Chem. Phys.* 144 (14) (2016)  
1066 144903.
- 1067 [148] B. Kuttich, A. K. Grefe, B. Stuhn, Changes in the bending modulus  
1068 of aot based microemulsions induced by the incorporation of polymers  
1069 in the water core, *Soft Matter* 12 (30) (2016) 6400–6411.
- 1070 [149] L. Chiappisi, L. Noirez, M. Gradzielski, A journey through the phase  
1071 diagram of a pharmaceutically relevant microemulsion system, *J. Coll.*  
1072 *Interf. Sci.* 473 (2016) 52–59.
- 1073 [150] S. Sharma, N. Yadav, P. K. Chowdhury, A. K. Ganguli, Controlling the  
1074 microstructure of reverse micelles and their templating effect on shap-  
1075 ing nanostructures, *J. Phys. Chem. B* 119 (34) (2015) 11295–11306.
- 1076 [151] S. Wellert, H. Imhof, M.-J. Altmann, M. Dolle, A. Richardt, T. Hell-  
1077 weg, Decontamination of chemical warfare agents using perchloroethy-

- 1078 lene/Marlowet IHF/H<sub>2</sub>O based microemulsions: Wetting and extrac-  
1079 tion properties on realistic surfaces, *Colloid Polym. Sci.* 285 (2008)  
1080 417–426.
- 1081 [152] S. Wellert, M. Karg, H. Imhof, A. Steppin, H.-J. Altmann, M. Dolle,  
1082 A. Richardt, B. Tiersch, J. Koetz, A. Lapp, T. Hellweg, Structure of  
1083 biodiesel based bicontinuous microemulsions for environmentally com-  
1084 patible decontamination as seen by small angle neutron scattering and  
1085 freeze fracture electron microscopy, *J. Colloid Interf. Sci.* 325 (2008)  
1086 250–258.
- 1087 [153] X.-L. Zhou, L.-T. Lee, S.-H. Chen, R. Strey, Observation of surface-  
1088 induced layering in bicontinuous microemulsions, *Phys. Rev. A* 46  
1089 (1992) 6479–6489.
- 1090 [154] D. D. Lee, S.-H. Chen, C. F. Majkrzak, S. K. Satija, Bulk and surface  
1091 correlations in a microemulsion, *Phys. Rev. E* 52 (1) (1995) R29–R32.
- 1092 [155] J. Bowers, M. C. Vergara-Gutierrez, J. R. P. Webster, Surface ordering  
1093 of amphiphilic ionic liquids, *Langmuir* 20 (2004) 309–312.
- 1094 [156] W. A. Hamilton, L. Porcar, P. D. Butler, G. G. Warr, Local membrane  
1095 ordering of sponge phases at a solid-solution interface, *J. Chem. Phys.*  
1096 116 (19) (2002) 8533–8546.
- 1097 [157] M. Kerscher, P. Busch, S. Mattauch, H. Frielinghaus, D. Richter,  
1098 M. Belushkin, G. Gompper, Near-surface structure of a bicontinuous  
1099 microemulsion with a transition region, *Phys. Rev. E* 83 (3) (2011)  
1100 030401/1–4.

- 1101 [158] S. Vargas-Ruiz, O. Soltwedel, S. Micciulla, R. Sreij, A. Feoktystov,  
1102 R. von Klitzing, T. Hellweg, S. Wellert, Sugar surfactant based mi-  
1103 croemulsions at solid surfaces: Influence of the oil type and surface  
1104 polarity, *Langmuir* 32 (2016) 11928–11938.
- 1105 [159] M. Kraska, M. Domschke, B. Stühn, Concentration induced ordering  
1106 of microemulsion droplets in bulk and near the liquid-air interface, *Soft*  
1107 *Matter* 9 (2013) 3488–3496.
- 1108 [160] H. Frielinghaus, M. Kerscher, O. Holderer, M. Monkenbusch,  
1109 D. Richter, Acceleration of membrane dynamics adjacent to a wall,  
1110 *Phys. Rev. E* 85 (2012) 041408.
- 1111 [161] J. S. Huang, S. T. Milner, B. Farago, D. Richter, Study of dynamics of  
1112 microemulsion droplets by neutron spin-echo spectroscopy, *Phys. Rev.*  
1113 *Lett.* 59 (22) (1987) 2600–2603.
- 1114 [162] T. Hellweg, D. Langevin, The dynamics in dodecane/ $C_{10}E_5$ /water mi-  
1115 croemulsions determined by time resolved scattering techniques, *Phys-*  
1116 *ica A* 264 (1999) 370–387.
- 1117 [163] T. Sottmann, R. Strey, Ultralow interfacial tensions in water-n-alkane-  
1118 surfactant systems, *J. Chem. Phys.* 106 (20) (1997) 8606–8615.
- 1119 [164] T. Hellweg, M. Gradzielski, B. Farago, D. Langevin, Shape fluctua-  
1120 tion of microemulsion droplets: A neutron spin-echo study, *Colloids &*  
1121 *Surfaces A* 183-185 (2001) 159–169.
- 1122 [165] T. Hellweg, A. Brûlet, T. Sottmann, Dynamics in an oil-continuous

- 1123 droplet microemulsions as seen by quasielastic scattering techniques,  
1124 Phys. Chem. Chem. Phys. 2 (22) (2000) 5168–5174.
- 1125 [166] B. Farago, Recent results from the ILL NSEs, Physica B 397 (1-2)  
1126 (2007) 91–94.
- 1127 [167] O. Holderer, H. Frielinghaus, M. Monkenbusch, J. Allgaier, D. Richter,  
1128 B. Farago, Hydrodynamic effects in bicontinuous microemulsions mea-  
1129 sured by inelastic neutron scattering, Eur. Phys. J. E 22 (2007) 157–  
1130 161.
- 1131 [168] S. Wellert, H.-J. Altmann, A. Richardt, A. Lapp, P. Falus, B. Farago,  
1132 T. Hellweg, Dynamics of the interfacial film in bicontinuous microemul-  
1133 sions based on a partly ionic surfactant mixture: A neutron spin-echo  
1134 study, Eur. Phys. J. E 33 (2010) 243–250.
- 1135 [169] S. Wellert, B. Tiersch, J. Koetz, A. Richardt, A. Lapp, O. Holderer,  
1136 J. Gäb, M.-M. Blum, C. Schulreich, R. Stehle, T. Hellweg, The DFPase  
1137 from *loligo vulgaris* in sugar surfactant based bicontinuous microemul-  
1138 sions, Euro. Biophysics J. 40 (2011) 761–774.
- 1139 [170] S. Wellert, M. Karg, O. Holderer, A. Richardt, T. Hellweg, Tempera-  
1140 ture dependence of the surfactant film bending elasticity in a bicontin-  
1141 uous sugar surfactant based microemulsion: a quasielastic scattering  
1142 study, Phys. Chem. Chem. Phys. 13 (2011) 3092–3099.
- 1143 [171] O. Holderer, H. Frielinghaus, M. Monkenbusch, M. Klostermann,  
1144 T. Sottmann, D. Richter, Experimental determination of bending rigid-

1145      ity and saddle splay modulus in bicontinuous microemulsions, *Soft*  
1146      *Matter* 9 (2013) 2308–2313.