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Abstract
The properties of bicontinuous microemulsions, consisting of water, oil and a surfactant, depend to a large extent on the bending moduli of the surfactant containing oil–water interface. In systems with C_iE_j as surfactant these moduli can be modified by the addition of diblock copolymers (boosting effect) and homopolymers (inverse boosting effect) or a combination of both. The influence of the addition of homopolymers (PEP_X and PEO_X, $X = 5$ or 10 kg/mol molecular weight) on the structure, bending modulus and dynamics of the surfactant layer is studied with small angle neutron scattering (SANS) and neutron spin-echo spectroscopy (NSE). Besides providing information on the microemulsion structure, neutron scattering is a microscopic probe that can be used to measure the local bending modulus κ. The polymer addition gives access to a homologous series of microemulsions with changing κ values. We relate the results obtained by analysis of SANS to those from NSE experiments. Comparison of the bending moduli obtained sheds light on the different renormalization length scales for NSE and SANS. Comparison of SANS and NSE derived κ values yields a consistent picture if renormalization properties are observed. Finally a ready to use method for converting NSE data into reliable values for κ is presented.

1. Introduction

Microemulsions are thermodynamically stable mixtures of water and oil mediated by a surfactant. Here, we focus on microemulsions with equal amounts of water and oil with different surfactant concentrations. The typical structural sizes d of oil/water domains are in

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the region of 20 nm. They directly depend on the surfactant content Ψ; $d \simeq 3.7\,\text{nm}/\Psi$ for the surfactant $C_{10}E_4$ in the bicontinuous phase [1]. Structures that can be obtained under these conditions are e.g. bicontinuous and lamellar microemulsions. Which structure is formed and how large the domains may become (i.e. the minimal amount of surfactant required to form a microemulsion) depend on the interface properties and eventually their interaction. It has been shown that added amphiphilic block copolymers stiffen the interface and thereby allow for the stable formation of larger domains. This means that less surfactant is needed to form the resulting homogeneous bicontinuous phase, a 'boosting' of the emulsification power [2–4]. Added homopolymers have the converse effect [1]. The combination of these effects allows for a systematic variation of the structural dimensions of homologous bicontinuous microemulsions. Here decane was used as the oil and $C_{10}E_4$ as the surfactant.

Different approaches have been developed for describing the physical properties of such microemulsions [5]. Ginzburg–Landau models lead to a fair description of the scattering properties of (bicontinuous) microemulsions [6, 7]:

$$S(q) \propto \frac{1}{q^4 - 2(q_0^2 - \xi^{-2})q^2 + (q_0^2 + \xi^{-2})^2} \tag{1}$$

with $q_0 = 2\pi/d$ and ξ a correlation length. Equation (1) matches the scattering from the scattering length contrast between oil and water in the wavevector region $q < \delta q_0$ ($\delta \simeq 2$–4). On the other hand a description of the free energy in terms of interface bending contributions is commonly used, where the Helfrich free energy is expressed as

$$F_{\text{el}} = \int dS \left[\frac{\kappa}{2}(c_1 + c_2 - 2c_0)^2 + \overline{\kappa}c_1 c_2 \right] \tag{2}$$

with $c_i = 1/R_i$ the local values of the principal curvatures, c_0 the spontaneous curvature (here $c_0 \simeq 0$) and $\kappa, \overline{\kappa}$ the bending modulus and the saddle splay modulus respectively. According to the Gauss–Bonnet theorem the latter term only contributes to the free energy changes when the surface topology changes.

By matching the Ginzburg–Landau free energy expression that underlies equation (1) to a Gaussian random field approach a relation between the parameters d and ξ of equation (1) and the (renormalized) bending modulus κ can be established [3, 4]:

$$q_0 \xi = \frac{64}{5\sqrt{3}} \frac{\kappa_R}{k_B T} \Theta \tag{3}$$

where Θ approaches 1 for large enough κ; here $\Theta = 1$ is assumed. The renormalized bending modulus κ_R is discussed in more detail below.

The elastic bending energy F_{el} of the surfactant membrane controls the phase behaviour. Much of the physics may be lumped into the physical parameters bending rigidity κ and the saddle splay modulus $\overline{\kappa}$. Specific theoretic predictions for the effect of homopolymer and block copolymer addition on κ are available [8, 9] and consistent with the observed qualitative trends (anti-boosting/boosting) in the phase diagram.

Experimentally, small angle neutron scattering (SANS) gives a deep insight into the structure of microemulsions. The characteristic distance d and correlation length ξ can be obtained by fitting equation (1) to SANS data from bulk (i.e. h-oil versus D_2O) contrast data, which then yield the renormalized bending rigidity κ_R via equation (3). Basically d determines the position of the maximum of $S(q)$ and ξ its width.

Complementarily, the membrane fluctuation dynamics as investigated with neutron spin-echo (NSE) spectroscopy also carries information on the interface bending modulus. The NSE allows one to analyse dynamic correlations in the neutron scattering intensity in the SANS regime which is relevant here. The accessible length (1–10 nm) and time ranges (0.1–20 ns)

allow for an analysis of the membrane motion on a local scale. The methodology for obtaining reliable κ values from NSE data is far from trivial. The commonly employed simple version of the theory for an ensemble of membrane patches of Zilman and Granek [10] leads to values for $\kappa \simeq 10\,k_B T$ that grossly deviate from expectation and values derived from SANS ($\kappa \simeq 1\,k_B T$). A description of an appropriate modification of this evaluation method is given below.

Finally the question of renormalization has to be addressed. The Helfrich free energy equation (2) is in principle scale invariant; i.e. enlarging of the interface structures proportionally reduces the curvatures, and the surface increases quadratically by the same factor and exactly compensates for the reduced curvature energy density. However, when the finite interface thickness, a, enters as an additional length scale and fluctuations are considered, extra contributions to the free energy violate the invariance. This may be fixed by lumping all these effects into a new, renormalized value of κ_R that is length scale dependent and 'hides' all fluctuation effects on smaller scales, $\kappa_R(d) = \kappa + \alpha/4\pi \ln \Psi$ with $\alpha \simeq 3$, where it should be noted that $\Psi \propto a/d$ contains the 'new' and the 'considered' length scales. Since the description of SANS data by equation (1) is based on the average structure around the peak length scale d, the SANS method yields renormalized bending moduli [4]. On the other hand the NSE evaluation explicitly integrates over the fluctuation spectrum and therefore should rather yield bare values of κ. This is corroborated by the experimental findings as explained below.

During our neutron scattering experiments the membrane properties were varied by the addition of homopolymers in the water and oil phases, which reduces the bending rigidity of the membrane, or amphiphilic diblock copolymers that arrange at the membrane and provoke a stiffening. Thereby ranges of $\Psi = 0.03–0.18$, $d \simeq 16–60$ nm, $\xi \simeq 10–30$ nm and finally $\kappa \simeq k_B T$ were accessible which allowed assessment of the methodology used and as a consequence more reliable conclusions on the polymer addition effects on κ.

2. Theory for $S(q, t)$

Neutron spin-echo spectroscopy measures the intermediate scattering function $S(q, t)$ usually given in normalized form as the relaxation function $S(q, t)/S(q)$. The NSE experiments on microemulsions are conducted using the so-called film contrast, i.e. deuterated oil and D_2O with only the protonated surfactant displaying contrast. The dynamics of fluctuating membranes in a microemulsion can be described by the model of fluctuating membranes in a viscous medium, as has been proposed by Zilman and Granek [10]. For small deformations of a nearly planar membrane (harmonic approximation), the free energy of deformation of an undulating patch of membrane can be described in terms of the Helfrich bending Hamiltonian [11]:

$$H = \tfrac{1}{2}\kappa \int \mathrm{d}^2 r \, [\nabla_r^2 h(\vec{r})]^2 = \tfrac{1}{2}\kappa \sum_{\vec{k}} k^4 h_{\vec{k}} h_{-\vec{k}} \tag{4}$$

where $h(\vec{r})$ denotes the amplitude of the undulation (the deviation of the membrane from a flat plane), and $h_{\vec{k}}$ its Fourier components. The wavevector of the undulation modes is $\vec{k}$ and must not be confused with the scattering wavevector $\vec{q}$.

The Helfrich Hamiltonian leads to the relaxation rate [12, 13] of $\langle h_{\vec{k}}(t) h_{-\vec{k}}(0) \rangle_{\mathrm{Helfrich}} = [k_B T/(\kappa k^4)] \exp[-\omega(k)t]$ with $\omega(k) = \kappa k^3/(4\eta)$. Besides the bending modulus also the average viscosity η of the surrounding medium determines the characteristic times.

Assuming an ensemble of independent, randomly oriented membrane patches that obey the above relation Zilman and Granek deduced an approximation for $S(q, t)$ in terms of a stretched exponential function, with a stretching exponent $\beta = 2/3$ [10]:
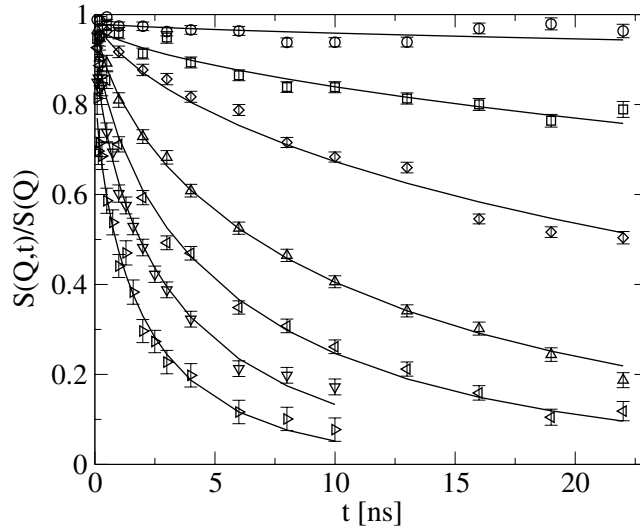
$$S(q, t) \simeq S(q) \exp[-(\Gamma_q t)^\beta] \tag{5}$$

Figure 1. NSE spectra ($q = 0.05$–0.24 Å^{-1}) from a bicontinuous microemulsion fitted with a stretched exponential function where Γ_q and β were separate fitted parameters for each curve. The β values approach 2/3 in the limit of high q and $\Gamma_q \propto q^3$; see also [14, 15].

where the q-dependent relaxation rate Γ_q can be written as

$$\Gamma_q = 0.025\gamma_\kappa \left(\frac{k_B T}{\kappa}\right)^{1/2} \frac{k_B T}{\eta} q^3 \tag{6}$$

where $\gamma_\kappa \simeq 1 - 3\frac{k_B T}{4\pi\kappa} \ln(q\xi) \longrightarrow 1$ for $\kappa \gg k_B T$ [13].

Whereas the functional form of equation (5) describes the NSE relaxation data (see figure 1) and the parameter β approaches 2/3 for large $q > 4q_0$ and $\Gamma_q \propto q^3$, the absolute value for κ inferred from equation (6) is grossly wrong. In addition variation of the structural length scale by change of surfactant volume fraction changes the reduced relaxation rate $\Gamma^* = (\Gamma_q/q^3)(\eta(T)/k_B T)$ significantly [14, 15]. For $\gamma_\kappa = 1$ this observation is completely incompatible with equation (5). It is clear that the length scale of the structure considered, that relates to the patch size of the model, has to enter the final result. To fix this and to avoid other approximations the Zilman–Granek model has been evaluated more directly, which, however, requires the numerical computation of nested integrals:

$$S(q, t) \propto \int_0^1 d\mu \int_0^{r_{max}} dr\, r\, J_0\left(qr\sqrt{1 - \mu^2}\right)$$
$$\times \exp\left(\frac{-k_B T}{(2\pi\kappa)} q^2 \mu^2 \int_{k_{min}}^{k_{max}} dk \frac{1 - J_0(kr)e^{-\omega(k)t}}{k^3}\right) \tag{7}$$

where J_0 is the Bessel function of order 0. The length scales of the problem enter in terms of the direct space value $r_{max} \propto \pi/k_{min}$ and the lowest mode wavevector k_{min}. The upper mode integration limit $k_{max} \propto \pi/a$. k_{min} relates to the correlation length ξ, which can be determined from SANS experiments in the case of bicontinuous microemulsions. It enters the equation as the lower integration cut-off $k_{min} = \pi\epsilon/\xi$ of the undulation mode spectrum, with a factor $\epsilon \simeq 1$. If ϵ is calibrated such that for a typical sample SANS and NSE results for κ match, a value of $\epsilon = 1.2$–1.3 is obtained. The dispersion relation of the undulation modes of a free planar membrane in a viscous liquid [12] is assumed to be $\omega(k) = (\kappa/4\eta)k^3$, with the average

solvent viscosity η. A similar expression can be found for lamellar microemulsions [16]. Using the same dispersion relation $\omega(k)$, a dynamic version of the Caillé theory [17] can be formulated. The first integral over μ in equation (7) accounts for the random distribution of orientations of membrane patches in a bicontinuous microemulsion. In the lamellar case, this integral is omitted, leading to

$$S(q,t) \propto \int_0^{r_{\max}} dr\, r J_0(qr) \exp\left(\frac{-k_B T}{(2\pi\kappa)} q^2 \mu^2 \int_{k_{\min}}^{k_{\max}} dk\, \frac{1 - J_0(kr)e^{-\omega(k)t}}{k^3}\right) \tag{8}$$

in the high q limit where independent local membrane fluctuations may be assumed. The determination of the lateral correlation length in lamellar microemulsions is not as easy to perform as in the case of bicontinuous microemulsions, whereas the determination of the lamellar spacing is straightforward from the peak position in SANS experiments. However, only for membrane stacks where the interaction is dominated by the steric repulsion may a direct proportionality between ξ and d be assumed, $\xi \simeq d\sqrt{\kappa/k_B T}$.

3. Experimental results and discussion

Microemulsions consisting of water, decane and the surfactant decyl polyglycol ether ($C_{10}E_4$) have been investigated with SANS and NSE. Two different contrasts have been considered. The structure of the microemulsion in SANS experiments is determined best in 'bulk' contrast with D_2O and protonated decane and $C_{10}E_4$, leading to a contrast between water and oil regions. In 'film' contrast, deuterated decane and D_2O were used, giving a scattering signal from the protonated surfactant membrane. This contrast has been used in NSE experiments, where the local dynamics of the membranes was studied. The membrane properties have been further modified by the addition of diblock copolymers polyethylenepropylene$_X$–polyethyleneoxide$_Y$ (PEP$_X$–PEO$_Y$) with X and Y being the molecular weight (5 or 10 kg/mol) or the corresponding homopolymers PEP$_X$ and PEO$_Y$. One way of evaluating NSE data is to fit the measured intermediate scattering function with a stretched exponential function, as described by Zilman and Granek [10]. This leads to a relaxation rate Γ_q as described in equation (6), which allows one in principle to deduce the bending rigidity κ. However, equation (6) seems not directly applicable for this purpose; only fitting with the integral form of the intermediate scattering function, equation (7) for bicontinuous microemulsions or equation (8) for lamellar ones, leads to a value of κ consistent with SANS results after correction for the renormalization effects by $\kappa = \kappa_{SANS} - 3/4\pi \ln \Psi$. In particular the SANS data from different length scale samples with the same type of membrane only yield the same value of κ after that correction [1], whereas the NSE evaluation yields constant values within error bars without 'derenormalization'—as expected [15]. The absolute values are still somewhat different (e.g. SANS: $\kappa = 1.1\ k_B T$, NSE: $\kappa = 1.4 \pm 0.15\ k_B T$). This has to be clarified by further refinement of the methods.

In the viable concentration range of about 1% added polymer the bending modulus determination yields increases of κ when block copolymers are added and a decrease for homopolymer addition. The order of magnitude of the effect is 0.1–0.2 $k_B T$. For more details we refer the reader to the papers [1] and [14, 15].

The evaluation of the integral in equation (7) in order to obtain κ is a rather complicated procedure. Here we also present a method which allows us to obtain reliable values of κ from a data evaluation with a stretched exponential function. $S(q,t)$ has been calculated using equation (7) for a set of κ and ξ values. It was then fitted with a stretched exponential function to provide Γ_q. Finally, $\Gamma^* = (\Gamma_q/q^3)(\eta(T)/k_B T)$ has been deduced which eliminates the q and η dependence from the relaxation rate and makes the result valid for a wide range of samples. Figures 2 and 3 show the map of $\Gamma^*(\kappa, \xi)$ for bicontinuous and lamellar microemulsions
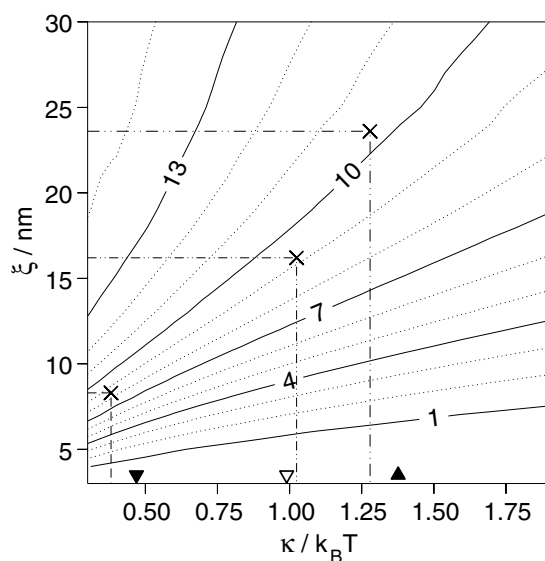
Figure 2. Representation of $\Gamma^*(\kappa, \xi)/10^{-3}$ for bicontinuous microemulsions. The procedure is illustrated with three examples: (a) a microemulsion with added homopolymers ($\xi = 8.3$ nm), (b) a pure microemulsion ($\xi = 16.2$ nm) and (c) one with added diblock copolymers ($\xi = 23.6$ nm). The crosses indicate the position of Γ^* at the correlation length ξ as determined from SANS for each sample, leading to the corresponding κ. The values of κ as determined by fitting the integral equation (7) to the experimental data are indicated ((a) triangle pointing down, (b) open triangle pointing down, (c) triangle pointing up) [15] for comparison.
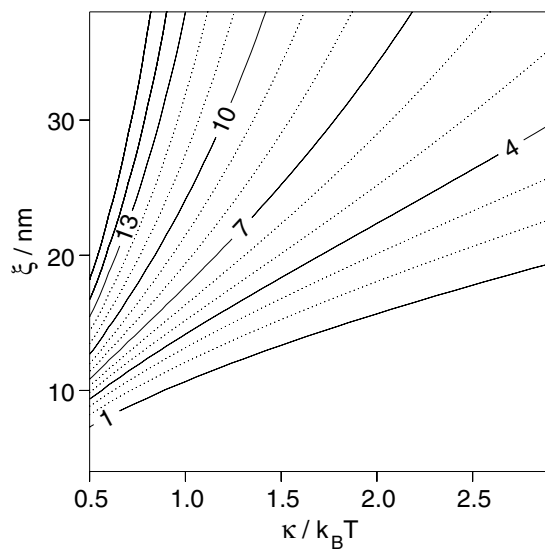

Figure 3. Representation of $\Gamma^*(\kappa, \xi)/10^{-3}$ for oriented lamellar microemulsions, under the assumption that $\vec{q}$ is perpendicular to the lamellar planes.

respectively. If ξ is known from SANS and Γ^* is deduced from NSE data, it is possible to get the corresponding κ from this plot. The procedure is illustrated in figure 2 for three bicontinuous microemulsions and compared to κ as obtained by fitting the experimental data

with equation (7). This procedure leads to κ values which are within $\pm 20\%$ of the fit results obtained using equations (7) and (8) directly for data for $q > 4q_0$. In any case, to obtain reliable results from dynamic NSE experiments it is necessary to know the effective viscosity including temperature, polymer and isotope effects and to have a good value for the correlation length ξ.

4. Conclusion

The determination of κ in microemulsions from NSE experiments by determining the relaxation rate of a stretched exponential function has its limitations when $\kappa \approx k_B T$. Avoiding part of the approximation in the Zilman–Granek theory leads to an integral expression, which allows one to determine κ also for these relatively small bending rigidities, but involves a large amount of computational effort. A simplified evaluation procedure, leading to a good approximation of κ_{NSE}, has been proposed in this work. It calibrates the reduced relaxation rate so that for known ξ and Γ^* the bending modulus can be determined. A combination of SANS experiments, which allow the determination of ξ and d, and NSE experiments, which give access to the relaxation rate, allows one then to obtain the bending rigidity from $S(q, t)$ in a reliable manner and can reveal effects of added polymers of the order of $\Delta\kappa \simeq 0.1\ k_B T$. Experiments corroborate that SANS data yield the renormalized and the NSE analysis the bare moduli as well as the prediction that diblock copolymers increase whereas added homopolymers decrease the bending modulus.

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