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Measuring bending rigidity and spatial renormalization in bicontinuous microemulsions

G. Gompper[1], H. Endo[1], M. Mihailescu[1], J. Allgaier[1], M. Monkenbusch[1],
D. Richter[1], B. Jakobs[2], T. Sottmann[2] and R. Strey[2]

[1] *Institut für Festkörperforschung, Forschungszentrum Jülich*
D-52425 Jülich, Germany
[2] *Institut für Physikalische Chemie, Universität zu Köln*
Luxemburger Str. 116, D-50939 Köln, Germany

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Abstract. – We demonstrate a new approach to determine the bending rigidity of the amphiphile film in microemulsions and sponge phases from neutron scattering data. This method is precise enough to measure the logarithmic scale dependence of the bending rigidity and its universal prefactor for the first time. Furthermore, we show that in the mushroom regime the bending rigidity of a membrane decorated by amphiphilic block copolymers increases linearly with the polymer concentration on the membrane; the amplitude is found to be about a factor 1.5 larger than theoretical results for ideal chains.

Our understanding of the structure and phase behavior of binary and ternary amphiphilic systems is based to a large extent on the description of the surfactant layers, which divide oil and water on a mesoscopic scale, in terms of their curvature elasticity [1–3]. The shapes and fluctations of these membranes are controlled in the curvature model by two elastic moduli, the bending rigidity κ and the saddle-splay modulus $\bar{\kappa}$, and the preferred (or spontaneous) curvature c_0. Though this has been questioned recently [4], both moduli are considered to be spatially renormalized [5–11] by thermal fluctuations for small surfactant volume fractions. Neither the logarithmic spatial renormalization of the bending rigidity as such, nor its strength, and not even κ itself have ever been measured in bicontinuous microemulsions.

This lack of accessibility can be traced back to the fact that up to now it was impossible to vary systematically both the length scales and the elastic properties of the surfactant films in a controlled way over a wide range. Furthermore, the standard techniques to measure κ for low-bending-rigidity membranes (with $\kappa \sim k_\mathrm{B}T$) —which analyze the shape fluctuations of microemulsion droplets [12], the membrane fluctuations in the lamellar phase [13], or the surface tension of the interface between a droplet microemulsion and the water-rich phase [14]— are not applicable to bicontinuous systems.

In this letter, we use ternary bicontinuous microemulsion, where by minute additions of amphiphilic diblock copolymers the membrane properties can be tuned continuously [15, 16], to demonstrate that the relations between scattering and curvature elasticity originating from the Gaussian-random-field model [17] can be used quantitatively to evaluate the bending rigidity. With this approach, we are able to show directly the existence of the logarithmic scale dependence of the bending rigidity for the first time. Furthermore, we are able to determine its universal prefactor, which has been under debate for more than a decade [5,6,18–20]! Finally, we are able to extract the universal amplitude of the dependence of the bending rigidity on the dimensionless polymer grafting density in the mushroom regime, which is found to be somewhat larger than predicted theoretically [21] for ideal chains.

The background of our approach is the use of the Gaussian-random-field model (GRFM) for a variational calculation [17] of the free energy of an ensemble of membranes described by the curvature elasticity [1]

$$\mathcal{H} = \int \mathrm{d}S \left[\frac{\kappa}{2}(c_1 + c_2)^2 + \bar{\kappa} c_1 c_2 \right], \tag{1}$$

where c_1 and c_2 are the principal curvatures at each point of the membrane, and the integral extends over the whole membrane area. The membrane configurations in the microemulsion phase are described by the $\Phi(\boldsymbol{r}) = 0$ level surfaces of the Gaussian random field, which is controlled by the free-energy functional

$$\mathcal{H}_0[\Phi] = \frac{1}{2} \int \mathrm{d}^3 q \; \nu(\boldsymbol{q})^{-1} \Phi(\boldsymbol{q}) \Phi(-\boldsymbol{q}) \tag{2}$$

with the constraint $\langle \Phi(\boldsymbol{r})^2 \rangle = 1$. The scalar field $\Phi(\boldsymbol{r})$ can be understood as a local concentration difference between oil and water, which disappears at the interface. The result of this variational approach is the optimal spectral density [17]

$$\nu(q) = \frac{a}{q^4 - bq^2 + c}, \tag{3}$$

where a, b and c are *independent of* $\bar{\kappa}$, and $a = (15\pi^2/16)(k_\mathrm{B}T/\kappa)(S/V)$ with membrane area S and sample volume V.

The coefficients b and c in eq. (3) can easily be calculated exactly in this model; they are not too complicated functions of the bending rigidity κ and the membrane concentration S/V. For large κ, these expressions simplify [17] to $b = (3\pi^2/2)(S/V)^2$ and $c = b^2/4$. The spectral density of eq. (3) is equivalent to a bulk correlation function of exponentially damped sinusoidal waves with a correlation length ξ and a propagation vector $k = 2\pi/d$, where d is the characteristic domain size. The results for a, b and c imply, in particular, that

$$k\xi = \frac{64}{5\sqrt{3}} \, \frac{\kappa}{k_\mathrm{B}T} \, \Theta\left(\frac{\kappa}{k_\mathrm{B}T}, \delta \frac{S}{V} \right) \tag{4}$$

with an algebraic function $\Theta(x, y)$, which approaches unity for large κ. Here, $\delta\, S/V \equiv \phi_\mathrm{s}$ is the membrane volume fraction, where δ is the membrane thickness. With decreasing values of κ and/or S/V, the structure factor in the GRFM develops a singularity at $q = 0$, which indicates an instability towards a macroscopic phase separation of oil and water [17].

In a second step, we note that recent results from experiments [8,15] and computer simulations of randomly triangulated surfaces [19,22] provide strong evidence that the GRFM does *not* capture all essential aspects of an ensemble of thermally fluctuating membranes. In particular, it does not contain the effect of the scale-dependence of the renormalized elastic moduli [5–7]

$$\kappa_\mathrm{R}(\ell) = \kappa - \alpha \frac{k_\mathrm{B}T}{4\pi} \ln(\ell/\delta) \tag{5}$$

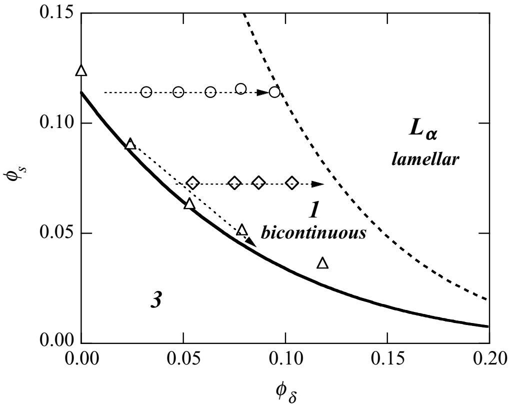

Fig. 1 – Experimental paths in the phase diagram (at equal volume fractions of oil and water) of a balanced microemulsion containing small amounts of amphiphilic PEP-PEO diblock copolymer, as a function of surfactant volume fraction ϕ_{s} and polymer volume fraction ϕ_δ in the mixture of both amphiphiles. The different symbols indicate the experimental compositions for PEP5-PEO5 (○, ◇) and PEP10-PEO10 (△).

—and, similarly, $\bar{\kappa}_{\mathrm{R}}(\ell)$ with prefactor $\bar{\alpha}$— on the length scale ℓ, where δ is the size of the surfactant molecules. Therefore, the location of the emulsification phase boundary predicted from the GRFM —indicated by the approach of the coefficient $c(\kappa, \phi_{\mathrm{s}})$ in eq. (3) to zero— does not agree with the predictions based on the renormalization of κ and $\bar{\kappa}$, where this phase boundary is determined by the relation $\bar{\kappa}_{\mathrm{R}}(\ell) = 0$, with $\ell \sim V/S$ [9,10]. It has been argued in ref. [23] that the failure of the GRFM may be traced back to an overestimate of the entropy due to bulk fluctuations in the oil- and water-regions.

Thus, we propose in a third step to discard the singularities of the dimensionless ratio $k\xi$ as predicted by the Gaussian-random-field model for small κ or small surfactant volume fraction ϕ_{s}, but assume that the result for large κ gives the correct behavior. As indirect evidence that the GRFM does indeed predict some aspects of the leading behavior in $k_{\mathrm{B}}T/\kappa$ and $k_{\mathrm{B}}T/\bar{\kappa}$ correctly, we consider the dependence of the free-energy density of a balanced microemulsion on the saddle-splay modulus $\bar{\kappa}$. The GRFM predicts a contribution $-\mu\bar{\kappa}\phi_{\mathrm{s}}^3$ with $\mu = 5\pi^2/40 = 1.234$ [17], while Monte Carlo simulations give $\mu = 1.26 \pm 0.12$ [22] —obviously in very good agreement.

Therefore, we conjecture to replace the Gaussian-random-field result for the κ- and ϕ_{s}-dependence of $k\xi$ by

$$k\xi = \frac{64}{5\sqrt{3}} \frac{\kappa_{\mathrm{R}}(\phi_{\mathrm{s}})}{k_{\mathrm{B}}T}\,, \tag{6}$$

where κ_{R} is given by eq. (5), *i.e.* we propose to replace the function Θ in eq. (4) by $\kappa_{\mathrm{R}}(\phi_{\mathrm{s}})/\kappa$ for *all* κ and ϕ_{s}. The relation (6) and its experimental verification, discussed below, are the main results of this letter.

It is important to realize that the values of the universal prefactors α and $\bar{\alpha}$ are still under debate. Most calculations [5,7,18] arrive at the values

$$\alpha = 3, \qquad \bar{\alpha} = -10/3, \tag{7}$$

which imply a softening of the membrane with increasing membrane size. These values are also consistent with recent Monte Carlo simulations of triangulated surfaces [19,22]. Helfrich [20],

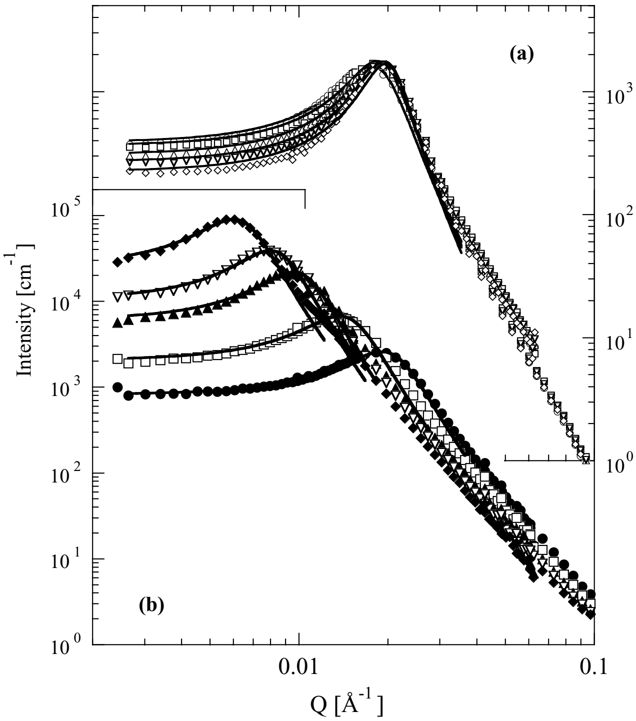

Fig. 2 – Small-angle neutron scattering intensities $I(Q)$ for two paths in the phase diagram. (a) Along the constant surface line $\phi_\mathrm{s} = 0.12$, with $\phi_\delta = 0.03$ (○), $\phi_\delta = 0.045$ (□), $\phi_\delta = 0.06$ (△), $\phi_\delta = 0.074$ (▽), and $\phi_\delta = 0.09$) (◇). (b) Along the three-phase coexistence line, with $\phi_\mathrm{s} = 0.131$, $\phi_\delta = 0.0$ (●); $\phi_\mathrm{s} = 0.098$, $\phi_\delta = 0.022$ (□); $\phi_\mathrm{s} = 0.071$, $\phi_\delta = 0.048$ (▲); $\phi_\mathrm{s} = 0.059$, $\phi_\delta = 0.070$ (▽); and $\phi_\mathrm{s} = 0.044$, $\phi_\delta = 0.101$ (◆). The solid lines represent fits with eq. (3).

on the other hand, has argued recently that $\alpha = -1$ and $\bar{\alpha} = 0$, which indicates a stiffening of the membrane at large length scales.

Finally, we have to consider a surfactant membrane which is decorated by amphiphilic block copolymers. For ideal polymer chains (without self-avoidance), it has been shown in ref. [21] that in the mushroom regime

$$\kappa_\mathrm{eff} = \kappa_0 + \frac{k_\mathrm{B}T}{12}\left(1 + \frac{\pi}{2}\right)\sigma(\mathcal{R}_\mathrm{w}^2 + \mathcal{R}_\mathrm{o}^2)\,, \tag{8}$$

where σ is the number density of block copolymer on the membrane and $\mathcal{R}_\mathrm{w/o}$ is the end-to-end distance of hydrophilic/hydrophobic polymer block. For a polymer-decorated membrane, we have to replace κ by κ_eff in eq. (5).

In our experiments, balanced oil-water microemulsions based on the non-ionic surfactant $C_{10}E_4$ and containing various amounts of amphiphilic block-copolymers of PEPx-PEOy (polyethylenepropylene/polyethyleneoxide with $x = y = 5$, 10 kg/mol) were investigated. Experiments were performed at constant membrane area ($\phi_\mathrm{s} = 0.12$ and $\phi_\mathrm{s} = 0.08$) by varying the relative polymer volume fraction, ϕ_δ, in the mixture of amphiphiles, and along the three-phase coexistence line, see fig. 1.

The small-angle neutron scattering (SANS) experiments were performed at the KWS1 instrument at the FRJ-2 reactor in Jülich. We are interested here in bulk contrast, which is

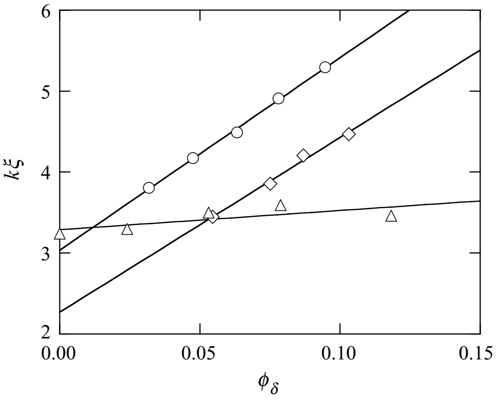

Fig. 3

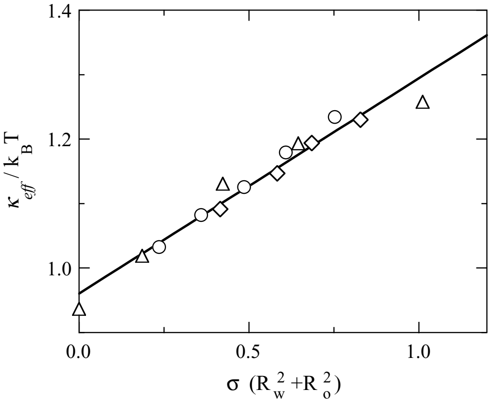

Fig. 4

Fig. 3 – Dimensionless ratio $k\xi$ of the two lengths scales characterizing the structure of a bicontinuous microemulsion. Data are shown for PEP5-PEO5 with membrane volume fraction $\phi_s = 0.12$ (○) and $\phi_s = 0.08$ (◇), and for PEP10-PEO10 along the three-phase coexistence line (△), in all cases as a function of the polymer volume fraction ϕ_δ in the mixture of both amphiphiles.

Fig. 4 – The effective bending rigidity κ_{eff} of a membrane decorated by amphiphilic block copolymers, as a function of the dimensionless density $\sigma(R_o^2+R_w^2)$ of polymers on the membrane. Data are shown for membrane volume fraction $\phi_s = 0.12$ (○), $\phi_s = 0.08$ (◇), and along the three-phase coexistence line (△); compare fig. 3.

conveniently measured with deuterated water and protonated oil. Figure 2a presents SANS results for $\phi_s = 0.121$ and varying polymer content ϕ_δ. Since the membrane area is constant, the position of the scattering peak determined by the domain size remains unchanged. The addition of polymer sharpens the peak, indicating an increase of the correlation length ξ and via eq. (6) an increase of κ. Figure 2b presents data taken along the coexistence line. Since ϕ_s is reduced with increasing ϕ_δ in this case, the domain size increases and the scattering peak shifts to smaller q. Its shape remains nearly unchanged.

In the region around the scattering peak, the data were fitted with eq. (3), which reveals k and ξ. Our results for $k\xi$ are displayed in fig. 3. The data provide strong evidence that several of the assumptions in our derivation of eq. (6) are indeed correct. First, the results for fixed surfactant volume fraction are linear in ϕ_δ (or σ) with a slope independent of ϕ_s. This indicates that —for fixed ϕ_s— the dimensionless product $k\xi$ is indeed a *linear* function of the bending rigidity. Second, the data for smaller surfactant concentration appear at smaller values of $k\xi$, which is consistent with $\alpha > 0$, *i.e.* a softening of the membrane due to thermal fluctuations on smaller scales. Finally, the slope of the data along the phase boundary is much smaller than for fixed surfactant concentration. This is again consistent with eqs. (5) and (8), since the emulsification failure phase boundary is very well described by $\ln(\phi_s/\phi^*) = -4\pi\bar{\kappa}_{\text{eff}}/(\bar{\alpha}k_BT)$, with $\bar{\kappa}_{\text{eff}} = \bar{\kappa}_0 - (k_BT/6)\sigma(R_o^2+R_w^2)$ and a constant ϕ^* of order unity [15], so that

$$\kappa_R(\sigma) = \left(\kappa_0 - \frac{\alpha}{\bar{\alpha}}\bar{\kappa}_0\right) + \frac{k_BT}{12}\left[1 + \frac{\pi}{2} + 2\frac{\alpha}{\bar{\alpha}}\right]\sigma\left(R_w^2 + R_o^2\right) \tag{9}$$

along this line. For $\alpha = 3$ and $\bar{\alpha} = -10/3$ of eq. (7), we thus expect a slope of the dependence of $\kappa_R(\sigma)$ on the dimensionless polymer grafting density of $[\pi/2-4/5]/12 = 0.0642$ which is much smaller (more than a factor 3) than the polymer effect at fixed membrane volume fraction, where the slope is given by $(1+\pi/2)/12 = 0.214$. We want to point out parenthetically that Helfrich's values of $\alpha = -1$ and $\bar{\alpha} = 0$ would imply an infinite slope in eq. (9); higher-order terms in the renormalization of $\bar{\kappa}$ have to be taken into account in this case. Thus, along the phase boundary, the two contributions to the bending rigidity —of the stiffening of the membrane due to the presence of the polymer, and the additional fluctuation modes due to the decreased membrane volume fraction— cancel each other to a large extent.

A more stringent comparison can be made by using eqs. (6) and (5) to extract κ_{eff}. All the data shown in fig. 3 are indeed found to collapse very nicely onto a single curve, when the values $64/(5\sqrt{3})$ *and* $\alpha = 3$ are used in eqs. (6) and (5), respectively, as demonstrated in fig. 4. A fit of α in eq. (5) yields $\alpha = 2.96 \pm 0.2$. Thus, Helfrich's value of $\alpha = -1$ [20] can now clearly be ruled out. Finally, the slope of κ_{eff} as a function of the dimensionless polymer grafting density can be compared with the theoretical result [21] for ideal polymer chains. We find a slope $\Xi = 0.334$, which is about a factor 1.5 larger than the slope $(1+\pi/2)/12 = 0.214$ expected from eq. (8). This is entirely consistent with a similar increase of the magnitude of the polymer effect observed in ref. [15] for the effective saddle-splay modulus $\bar{\kappa}$. We believe that the different values of Ξ reflect the different properties of polymers in good and in theta solvents. A previous measurement [24] of the effect of anchored polymers on the bending rigidity of lipid bilayer vesicles gave a considerably larger discrepancy of a factor 4 to 5, with a linear dependence on the grafting density *above* the overlap concentration.

In summary, we have shown that the dimensionless ratio of the two characteristic lengths in bicontinuous microemulsions provides a straightforward and very precise way of measuring the bending rigidity of membranes. We have applied this approach to the investigation of the effect of amphiphilic block copolymers on the curvature elasticity of membranes. At the same time, this system provides the necessary test to validate some of the assumptions in our theoretical derivation, and thus is a crucial element in establishing the approach. This method can now be applied to many other systems. Two obvious candidates are polymeric microemulsions [25], and ternary amphiphilic systems with the additive of non-adsorbing polymers in one or both solvents [26].

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