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ON SMALL-ANGLE NEUTRON SCATTERING
FROM MICROEMULSION DROPLETS:
THE ROLE OF SHAPE FLUCTUATIONS

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I. Introduction

Microemulsions are thermodynamically stable homogeneous mixtures of two immiscible liquids (oil and water), stabilized by surfactants and in some cases additionally by cosurfactants.[1] The surface-active molecules form a layer that covers the microemulsion droplets dispersed in the continuous phase. By now it is widely agreed upon that the characteristics of the layer determine to a large degree the properties of the microemulsion. Within the Helfrich concept of the interfacial elasticity,[2,3] the interface is characterized by a few parameters (the bending modulus κ, the saddle-splay or Gaussian modulus $\overline{\kappa}$, and the spontaneous curvature) that are together with the surface tension coefficient needed to describe the elastic properties of the layer. Much effort has been devoted to determine these parameters using different approaches.[4-7] Among the experimental techniques, small-angle neutron scattering (SANS) is a powerful tool for studying microemulsion structure and properties because different regions can be contrasted by selectively deuterating the components.[6-11] Furthermore, the interpretation of SANS results is less model-dependent than the interpretation of dynamic scattering experiments since it does not require a knowledge of the frequency spectra (or relaxation rates) of the microemulsion system. A typical model used to fit the SANS intensity $I(Q)$ (where Q is the wave-vector transfer) to experimental data describes the microemulsion as a system of polydisperse double-layered spheres.[12] The aim is to extract from the fit the above mentioned most representative parameters of the surface layer, and the mean radius of the droplets, R_m. Typically, $I(Q)$ measured in the shell contrast displays a minimum which is thought to be located at $QR_m \approx \pi$.[6,7,11] As to the elasticity parameters κ and $\overline{\kappa}$, the reported values for them differ notably from work to work. For example, a combined fit on the static and dynamic data with the AOT (sodium di-ethylhexyl sulfosuccinate)-decane-water system led to $\kappa \approx 3.5 \ k_B T$,[5] the value about a factor two higher

than measured with indirect macroscopical or optical methods.[4] Relatively small values of κ ($0.5 \div 1$ k_BT) were also found for other surfactant systems.[7,13] The frequently determined value of the combination $2\kappa + \bar{\kappa}$ for various systems changes usually from about 1 to 6 k_BT;[6-11] smaller values up to 0.2 k_BT were also found.[14] Interfacial tension measurements give values of $2\kappa + \bar{\kappa}$ which can differ by 25 per cent or so from the results of SANS.[6,11]

The present study comes from the fact that for a wide range of the reported elasticity parameters, the microemulsion systems would be in conditions when the droplets relatively freely fluctuate in the shape. Indeed, consider e.g. a dilute microemulsion[3] with $\kappa \approx 0.5$ k_BT and a typical polydispersity $\varepsilon \approx 0.04$ (when $2\kappa + \bar{\kappa} \approx k_BT$) defined by $\langle (R_0-R_m)^2 \rangle \approx \varepsilon R_m^2$, where R_0 and R_m are the radius of the nondeformed shell and its mean radius, respectively, and the average is over the radii R_0. The role of fluctuations can be illustrated showing that in this case the total polydispersity $\varepsilon_{tot} = \langle (R-\langle R \rangle)^2 \rangle \langle R \rangle^{-2}$, where R is now the fluctuating droplet radius (and the averages are over the radii and the fluctuations), is according to Ref.[6], eq.20, $\varepsilon_{tot} \approx 2.75$ ε. One can expect that other quantities relevant for the description of SANS could be influenced by the fluctuations as well. Although such fluctuations are intensively studied in the literature for years,[15] surprisingly, in the interpretation of SANS measurements these fluctuations are not considered at all[6-11] or the account for them[14] should be corrected.

The aim of this work is to calculate the intensity of SANS on microemulsions taking into account the droplet thermal fluctuations in the shape. The microemulsion droplet is modeled by a double-layered sphere consisting of a fluid core and a surfactant layer, immersed in another fluid. The three components are, in general, characterized by different scattering length densities which makes the theory appropriate for experimental situations other than corresponding to the shell contrast.[16] The form factor of the scattering is calculated up to the second order in the fluctuations of the droplet radius.

II. Form factor of the static scattering and the SANS intensity

Consider first an individual droplet. Let the scattering length density of our three component system is ρ_1 in the droplet interior, ρ_2 in its exterior, and the surface layer is characterized by the constant ρ_0. The thickness of the layer is d, and $u=R-R_0$ describes the deviation from the mean of the inner and outer radii of the nondeformed shell, R_0. The small fluctuating quantity u can be expressed as an expansion in spherical harmonics $Y_{lm}(\vartheta,\varphi)$,[15]

$$u(\vartheta,\varphi) = R_0 \sum_{l,m} u_{lm} Y_{lm}(\vartheta,\varphi) , \qquad (1)$$

where $m=-l, -l+1, ..., l$, and $l=0, 1, 2, ...$, is smaller than some $l_{max} \sim R_0/a$, a being a typical molecular diameter. The fluctuations of the molecules in the layer are neglected, that is, in agreement with the common opinion, the layer is incompressible.[15] To find the form factor of the scattering,[12] we calculate the correlator $\langle \rho(Q)\rho^*(Q)\rangle$, where Q is the wave-vector transfer and $\rho(Q)$ is the Fourier transform of the scattering length density

$$\rho(r) = \rho_1 \Theta(R_1 + u - r) + \rho_2(r - R_2 - u) + \rho_0 \{\Theta(r - R_1 - u) + \Theta(R_2 - r + u) - 1\} . \qquad (2)$$

Here $\Theta(...)$ is the Heaviside function, $R_1=R_0-d/2$, and $R_2=R_0+d/2$. In the calculations of the form factor, $\rho(r)$ is expanded to the second order in the small quantity u. To find the necessary density-density correlator, we use that the fluctuations with different numbers l and m are uncorrelated, and $\langle u_{lm}\rangle=0$ for $l>1$.[15] The mean quadrate of the fluctuations and the quantity u_{00} are

$$\langle u_{10}^2 \rangle \approx \frac{k_B T}{\alpha_1 R_0^2 (l+2)(l-1)}, \quad \sum_{lm}\langle |u_{lm}|^2 \rangle = \sum_{l>1}(2l+1)\langle |u_{10}|^2 \rangle, \quad u_{00} = -\frac{1}{\sqrt{4\pi}} \sum_{l>1,m} |u_{lm}|^2 . \qquad (3)$$

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The last condition is due to the conservation of the droplet volume.[15] Here $\alpha_l = \alpha - 2\kappa C_s R_0^{-1} + \kappa l(l+1)R_0^{-2}$ is determined by the bending elasticity of the layer, κ, the surface tension coefficient for the plane interface, $\alpha = \sigma + C_s^2 \kappa/2$ (σ is the microscopic interfacial tension[3]), and the spontaneous curvature C_s. The above formulae can be applied to independent, noninteracting droplets in an infinitely diluted monodisperse solution. In dense microemulsions the droplets interact, they may collide and exchange surfactants and fluid; only the total amounts of fluid and surfactant are conserved.[15] Taking into consideration the entropy of the dispersion, the dependence of $\langle u_{l0}^2 \rangle$ (as well as the polydispersity) on the dispersed phase volume fraction ϕ should be included.[7,15] This will be done below when the scattering intensity will be calculated and compared with experimental results from literature.

Using the properties of spherical harmonics and Bessel functions,[17,18] the final result for the form factor reads ($Q \neq 0$, $x_i = QR_i$):

$$P(Q) = \left\langle |\rho(Q)|^2 \right\rangle \approx \left(4\pi R_0^2 d\Delta\right)^2 \left\{ \Phi^2 + \sum_{l>1}^{l_{max}} \frac{2l+1}{4\pi}\left[\Phi(\Psi - 2\Phi_0) + \Phi_l^2(x)\right]\langle u_{l0}^2 \rangle \right\}, \quad (4)$$

$$\Phi(Q) = \frac{1}{R_0^2 d\Delta}\left\{(\rho_1 - \rho_0)R_1^3\frac{j_1(x_1)}{x_1} + (\rho_0 - \rho_2)R_2^3\frac{j_1(x_2)}{x_2}\right\},$$

$$\Phi_l(Q) = \frac{1}{R_0 d\Delta}\left[(\rho_1 - \rho_0)R_1^2 j_l(x_1) + (\rho_0 - \rho_2)R_2^2 j_l(x_2)\right],$$

$$\Psi(Q) = \frac{1}{d\Delta}\left[(\rho_1 - \rho_0)R_1\varphi(x_1) + (\rho_0 - \rho_2)R_2\varphi(x_2)\right], \quad \varphi(x) = 2j_0(x) - xj_1(x).$$

Here $\Delta = -\rho_0 + (\rho_1 + \rho_2)/2$. The first term in the brackets of eq 4 corresponds to the well-known form factor of a double-layered sphere.[12] The second term, reflecting the shape fluctuations of the droplet, differs significantly from the corresponding contributions that can be found in the

literature.[5-7,14,15] First, all such expressions assume the perfect shell contrast ($\rho_1=\rho_2>>\rho_0$) and $d<<R_0$, but the main difference is in the term $\sim\Phi(\Psi-2\Phi_0)$,[5,6,14] (or in its full absence[7,15]). The appearance of this term is due to the account for all second-order corrections in the fluctuating density expansion of eq.2 and the constraint on the droplet volume.[15] As a concequence of this constraint, $\langle u_{00}\rangle\neq0$, as reflected in eq 3. The mode l=1 does not contribute to the final result that is in agreement with the known fact that this mode corresponds to the translational motion of the droplet.[15]

The effects of the fluctuations on the form factor cannot be *a priori* neglected. It can be shown by the following consideration of $P(Q)$ approximated to small d/R_0. If the fluctuations were negligible, the minimum of $P(Q)$ would correspond to the first zero of the function $\Phi(x)$, i.e. $x_0\approx\pi$ in conditions close to the shell contrast. Since the l=2 mode of the fluctuations is dominant, $P(Q)$ for a droplet with a mean radius R_m can be approximated by $P(Q)\sim j_0^2(x)+\chi\{-j_0^2(x)(2+x^2)+[xj_3(x)-4j_2(x)]^2\}$, where $\chi=5/[96\pi\kappa/k_BT-2/\varepsilon]$. The droplet distribution in radii follows from the phenomenological theory of the droplet formation,[3]

$$f(R_0)\propto\exp\left[-\frac{1}{2\varepsilon}\left(1-\frac{R_0}{R_m}\right)^2\right], \qquad \varepsilon=\frac{k_BT}{8\pi\left(2\kappa C_sR_m-\alpha R_m^2\right)} \; . \tag{5}$$

For very small χ, $P(Q)$ is determined mainly by the function $j_0^2(x)$, its minima are close to $x\approx\pi$, 2π, ..., and at $x\approx4.5$ (the root of $j_1(x)$) there is a local maximum. With growing χ the fluctuation terms change the character of $P(Q)$: the second minimum disappears and turns into a maximum. A new minimum arises between this maximum and the former maximum at $x\approx4.5$. This takes place for $\chi\approx0.025$. With a further growth of χ the location of this new minimum moves towards $x\approx4.5$, its depth becomes larger, and the height of the original maximum in this region decreases together with the depth of the minimum at $x\approx\pi$. Finally (at $\chi\approx0.035$), the

original minimum (at $x \approx \pi$) and maximum (at $x \approx 4.5$) both disappear and the new minimum is shifted to $x \approx 4.5$. For very large fluctuations ($\chi \approx 0.05$), the approximation no longer holds since $P(Q)$ takes unphysical negative values near its minimum. Unphysical values of the form factor appear also for large $x \gg 1$; this is however just a property of the approximation $d/R_0 \ll 1$ (the form factor (4) has the correct limit correct limit $P \to 0$ as $x \to \infty$).

In Figure 1 the normalized form factor from eq.4 is shown for the octane-d_{18}-surfactant ($C_{10}E_5$)-water microemulsion system.[7] The scattering length densities of the deuterated bulk fluids are close,[6] $\rho_1 = 6.35 \times 10^{10}$ and $\rho_2 = 6.36 \times 10^{10}$ cm^{-2}, and the hydrogenated surfactant is characterized by the density $\rho_0 = 1.65 \times 10^9$ cm^{-2}.[19] The system was in conditions of the so-called two-phase coexistence[3] when the surface tension is $\alpha = (2\kappa + \bar{\kappa})/R_m^2 = 4C_s\kappa/R_m$,[6,20] so that the polydispersity from eq 5 is $\varepsilon = k_B T/8\pi(2\kappa + \bar{\kappa})$. The thickness of the surface layer is $d = 4.3$ $(2\pi)^{1/2}$ Å,[21,7] and the mean radius $R_m = 48$ Å and the polydispersity $\varepsilon \approx 0.04$ were determined in the SANS study[7] using the polydisperse shell model without fluctuations. Figure 1 shows the form factor for several bending elasticities κ including $\kappa \approx 0.92$ $k_B T$ (when $\chi \approx 0.025$) found in Ref.[7] by a combination of neutron spin-echo spectroscopy and SANS. In the calculations we account for the modes up to $l_{max} = 20$. The behavior of the form factor with κ is in agreement with the above qualitative discussion. For real polydisperse systems the form factor (4) has to be averaged over the droplet radii. For small polydispersities (when the distribution (5) has a sharp peak around R_m, $\langle R_0 \rangle \approx R_m$, and $\langle (R_0 - R_m)^2 \rangle \approx \varepsilon R_m^2$, neglecting exponentially small terms $\sim \exp[-1/2\varepsilon]$) this leads, in particular, to a shift of the minima in $P(Q)$ to smaller wave-vectors: a minimum located at some Q_0 will be in $\langle P(Q) \rangle$ shifted to $Q_{min} \approx Q_0/(1+\varepsilon)$. Depending on the value of ε, the average somewhat smooths out the details of the Q-dependence of the form factor; for example, having originally the two above discussed minima in $P(Q)$, we can have in $\langle P(Q) \rangle$ one broader minimum located between the positions of the original minima. This

consideration indicates that the account for the fluctuations can be important for the determination of the parameters of microemulsion systems from SANS. Particularly, in our example the position of the minimum (observed in the experiment at $Q \approx 0.06$ Å^{-1})[7] does not satisfy the condition $x \approx \pi$ as assumed in Ref.[7]; if $\kappa = 0.92 \, k_B T$,[7] the mean radius should be notably larger.

Using the form factor (4), the SANS intensity is calculated according to the formula[6,7,11]

$$I(Q) = N \langle P(Q) S(Q) \rangle .$$
(6)

Here N is the number density of the scattering microemulsion droplets and $S(Q)$ is an interference function (the static structure factor) describing the interactions between the droplets. For dilute nonionic microemulsions a hard sphere structure factor[22] is usually employed.[6,7,11,23] For larger Q (but smaller than the minimum of $I(Q)$), $S(Q)$ approaches unity.[7,23] Since the value of the droplet radius is fixed by the position of the minimum of $I(Q)$, $S(Q) \approx 1$ is considered as a good approximation in the determination of R_m, if the low-Q data are omitted in the fitting procedure.[7]

The influence of the entropy of dispersion can be accounted for as follows. In conditions of the two-phase coexistence and within the random mixing approximation,[15,6] the quantity α_l (defined after eq.3) becomes

$$R_0^2 \alpha_l = \kappa (l-1)(l+2) - \bar{\kappa} - (k_B T / 4\pi) F(\Phi),$$
(7)

and the polydispersity from eq.5 is now

$$\varepsilon = \frac{k_B T}{8\pi (2\kappa + \bar{\kappa}) + 2k_B T F(\Phi)},$$
(8)

with

$$F(\Phi) = \ln\Phi + \frac{1-\Phi}{\Phi}\ln(1-\Phi) \approx \ln\Phi - 1, \tag{9}$$

where the approximation is for small volume fractions of the droplets, Φ. Equations (7) - (9) allow one to rewrite the mean quadrate of the fluctuation amplitudes from eq.3 in the form

$$\left\langle u_{l0}^2 \right\rangle = \left\{ (l-1)(l+2)\left[\frac{\kappa}{k_B T} l(l+1) - \frac{1}{8\pi\varepsilon} \right] \right\}^{-1}, \tag{10}$$

that is particularly useful for the fits to experimental data since it does not explicitly depend on the function $F(\Phi)$.

We used eqs. 4,6,8-10 to calculate the SANS intensity as shown on Figure 2. The microemulsion parameters are taken from the work[7] (κ=0.92 $k_B T$ at T=305.2 K, ε=0.0356, R_m=48 Å, d=10.8 Å,[7,21] ϕ_{hs}=0.049 (the hard-sphere volume fraction), and the scattering length densities are the same as in the calculations to Figure 1). The result is compared with the intensity that does not include fluctuations. It is seen that due to the fluctuations the minimum in $I(Q)$ is shifted to higher Qs so that, for given ε and d, the used mean radius or κ are smaller than their values needed to describe the experiment. It is thus seen that if the droplet fluctuations are taken into account, the set of the parameters κ, ε, R_m, and d, as they were determined in Ref[7]., cannot describe the experiment. The result of our own fit of eq 6 to the experimental SANS data[7] are shown on Figure 3. In the fitting the volume fraction of the droplets was the same as in Ref[7] and following that work the region Q>0.03 Å^{-1} was considered to have $S(Q)\approx 1$. The best fit to the experiment was achieved for the values κ=1.93 $k_B T$, ε=0.0463, R_m=47.7 Å, and d=6.44 Å. The difference from the parameters found in Ref[7]. is reflected mainly in the elasticity coefficients: together with a larger κ we have now $\bar{\kappa}$ =-2.68 $k_B T$ instead of $\bar{\kappa}$ =-0.38 $k_B T$.[7] If the entropy-of-mixing contributions are not taken into

account in eqs. 9 and 10, the fit yields $|\bar{\kappa}|$ slightly larger ($\approx$-3 k_BT) while κ and ε remain unchanged. One more example of the fit shown by Figure 3 is for a different D_{22}-decane-surfactant($C_{12}E_5$)-D_2O microemulsion system at 10 °C,[6] described by the parameters ρ_1=6.54×10^{10}, ρ_2=6.36 ×10^{10} and ρ_0=2.76×10^9 cm^{-2}, and the volume fraction ϕ_{hs}=0.0765. Instead of the parameters determined in the original work,[6] $2\kappa+\bar{\kappa}$ =3.42 k_BT, ε=0.0127, R_m=49.1 Å, and d=15.2 Å (the elasticity κ was not found), our fit yielded the values $2\kappa+\bar{\kappa}$ =1.97 k_BT, (κ=4.05 and $\bar{\kappa}$ =-6.13 k_BT), ε=0.0236, R_m=49.1 Å, and d=14.6 Å. The presented values should be considered just as estimations of the system parameters within the used approximations since we do not use the original experimental data and do not take into account the smearing of the data points. Despite this it allows us to make some conclusions about the studied systems. In both the examples the fluctuations are relatively small that agrees with our assumption. This is reflected by rather large bending elasticities (note that the further increase of κ weakly affects the quality of our fits), especially in the second case. In the first example the bending elasticity is smaller but evidently underestimated in the original work.[7] The difference between the experiment[7] and the theoretical curve for larger Q seen on Figure 3 can be attributed to the increasing role of the fluctuations with growing Qs; probably, in the high-Q region the higher-order terms due to fluctuations cannot be neglected. It is also possible that the model should be improved by taking into account the diffuseness of the scattering length distribution at the droplet boundaries - it has been shown in Ref.[21] that the model with diffuse boundaries possesses a better behavior of the scattering curve at large Qs than the conventional model with sharp boundaries considered here. Finally, add that the thickness of the layer is relatively large compared with R_m so that a theory not limited to small values of d, seems to be needed.

Note that on the basis of our qualitative consideration of the behavior of SANS intensity we expected to obtain a good fit to the experiment for smaller κ and larger R_m. However, such attempts gave somewhat worse results than those presented on Figure 3 and are not shown here.

Except the region of high wave vectors our calculations give a good quantitative description of the SANS experiments. Moreover, a decision about the role of the fluctuations can be made that was not possible in previous theories. The inclusion of the droplet fluctuations into the consideration allowed us to obtain the mean radius of the droplets, their shell thickness, the polydispersity, and the bending elasticity. As a result (since in the case of two-phase coexistence ε is functionally connected with $2\kappa + \bar{\kappa}$)[3-6], both the elasticity coefficients κ and $\bar{\kappa}$ can be in principle determined. In the case of one-phase coexistence there is one more parameter to be determined: the set of the parameters describing the properties of the droplet is R_m, C_s, κ, α, d, and ε is connected with the first three parameters by eq.3. Due to a large number of the parameters it is desirable to combine the information from SANS with data obtained from other sources, like dynamical experiments.[7] The coefficient α can also be found from surface tension measurements,[11] that are however not entirely independent from SANS since one of the parameters needed to determine α (the maximum length scale) is measured by SANS.[24]

We add that in previous interpretations the SANS results were connected with the fluctuations only through the polydispersity formally determined by $\varepsilon = \langle u_{00}^2 \rangle / 4\pi$,[6] with $\langle u_{00}^2 \rangle = k_B T / (-2R_0^2 \alpha_{l=0})$. Due to the conservation of the droplet volume, a very different expression follows for the quantity $\langle u_{00}^2 \rangle$. The free energy of the droplet fluctuations in harmonic approximation,[3] which is a sum of the terms $k_B T |u_{lm}|^2 / 2 \langle |u_{lm}|^2 \rangle$, does not contain the $l=0$ mode contribution. With the use of eq 3 one obtains

$$4\pi\langle u_{00}^2\rangle = \left(\sum_{l>1}(2l+1)\langle u_{l0}^2\rangle\right)^2 + 2\sum_{l>1}(2l+1)\langle u_{l0}^2\rangle^2 .$$ (11)

III. Conclusions and discussion

We have calculated the form factor and intensity of the static neutron scattering from droplet microemulsions considering the role of the droplet fluctuations in the shape. To our knowledge, for the first time we have consistently accounted for all the contributions to the scattering up to the second order of the fluctuations. The results are appropriate for the description of SANS on dilute microemulsions containing droplets with a surface layer of relatively small thickness: this restriction is due to the fact that while the form factor was calculated without an explicit limitation on the thickness d, the correlators of the fluctuating radius, eq.3, follow from the theory limited to small d/R_0.[15,2] From SANS experiments crucial parameters determining the properties of microemulsions are often extracted, like the mean radius R_m of the droplets, polydispersity and, in favorable conditions (two-phase coexistence), the combination $2\kappa + \bar{\kappa}$ of the elasticity coefficients of the surfactant film. So far these characteristics were obtained fitting the experimental SANS data with the model of double-layered, nonfluctuating spheres. Using our approach, both the bending elasticity κ and the saddle-splay modulus $\bar{\kappa}$ can be determined simultaneously. We have also demonstrated that the effect of the fluctuations on SANS spectra cannot be *a priori* neglected. The bending elasticities κ are often thought to be of the order of $k_B T$ or smaller. For such values of κ and usual polydispersities the role of the fluctuations is important. In particular, when the experimental conditions are close to the shell contrast, the account for the fluctuations leads to a notable shift of the observed minimum in the SANS intensity to higher wave-vector transfers of the scattering than it follows from the theory without fluctuations. As a result, an

agreement with the experiment requires larger κ and/or R_m. Describing two recent experiments,[6,7] we found for κ significantly larger values than in the original works while the radii R_m did not change notably. In spite of this we do not exclude the alternative that the radius of the droplets was underestimated in the interpretations of the SANS experiments. Such a possibility can be supported by the results of dynamic neutron scattering experiments. These experiments[5,7,14] yield an effective diffusion coefficient of the microemulsion droplets, $D_{eff}(Q)$. The observed peak in $D_{eff}(Q)$ (attributed to the shape fluctuations of the droplets)[15] cannot be quantitatively described using the parameters as determined from SANS: in particular, its experimentally observed height is several times smaller than it follows from the theory.[5] While the increase of κ increases the peak height, it can be lowered by increasing R_m since the maximum of $D_{eff}(Q)$ scales proportionally to R_m^{-3}.[25-27] Finally, the dynamic light scattering experiments[7] yield small self-diffusion coefficients of microemulsion droplets that are difficult to explain using R_m determined from the polydisperse (nonfluctuating) shell model[12] fitted to SANS data, unless the shell is surrounded by several hydration layers.

We conclude that the inclusion of the shape fluctuations of the droplets into the consideration essentially affects the interpretation of SANS experiments on microemulsions. More information can be now obtained about important phenomenological parameters of microemulsion systems. However, the problem of the extraction of these characteristics from SANS still remains far from a satisfactory solution. We suppose that a number of improvements to the presented theory should be done, e.g., in a more exact approach the model should be generalized to surface layers of arbitrary thickness. In our analysis, valid to the second order in (presumably) small fluctuations, unphysical scattering intensities appear for small values of κ ($\sim 0.5\ k_B T$ or smaller). This means that in this case (within our approach)

the fluctuations are large. We cannot exclude such a possibility until a more exact theory, taking into account higher order terms in the fluctuations, will be developed.
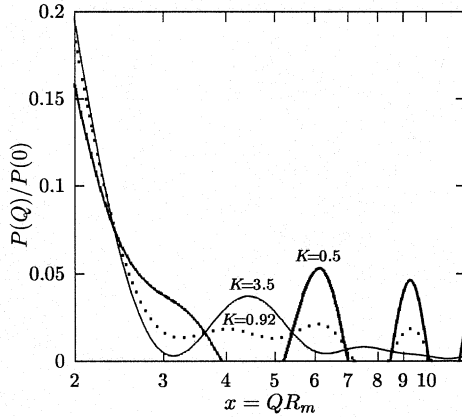
Figure 1. The normalized form factor from eqs.4, 10 as a function of $x=QR_m$ for several bending elasticities κ. The octane-d_{18}-surfactant ($C_{10}E_5$)-water microemulsion system[7] is characterized by the neutron scattering length densities $\rho_1=6.35\times10^{10}$ and $\rho_2=6.36\times10^{10}$ cm^{-2} for the bulk fluids, and $\rho_0=1.65\times10^9$ cm^{-2} for the surfactant layer.[19] The thickness of the layer is $d=10.8$ Å,[21,7] the droplet radius $R_m=48$ Å, and the polydispersity $\varepsilon=0.0356$.[7] The figure illustrates how the form factor is influenced by the droplet fluctuations in the shape (when κ decreases, the amplitudes of the fluctuations increase).
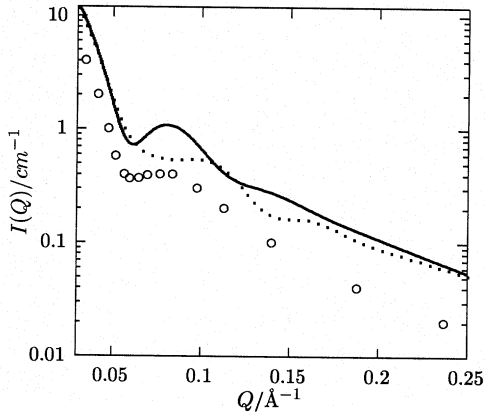
Figure 2. SANS intensity from eqs 4,6,8-10 with (dashed line) and without (full line) the droplet fluctuations. The experimental data (points) are taken from Ref[7]. The bending elasticity is κ=0.92 k_BT at T=305.2 K, the volume fraction of the droplets is ϕ_{hs}=0.049, and other parameters of the microemulsion are as in Figure 1. It is seen that the set of the parameters κ, ε, R_m, and d, as they were determined in Ref[7] using the nonfluctuating shell model, cannot describe the experiment. The necessary changes of the parameters are discussed in the text (see also Figure 3).
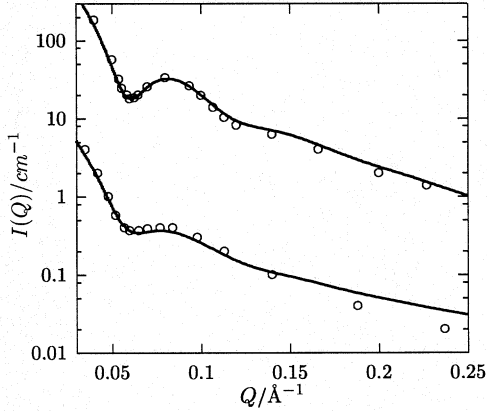
Figure 3. Scattering intensity from eq 6 fitted to SANS data represented by points.[6,7] In the fitting procedure the parameters κ, ε, d, and R_m were subject to change, and the region $Q > 0.03$ Å^{-1} was considered where $S(Q) \approx 1$.[7] Other parameters are the same as in Figures 1 and 2 (lower line). The upper line is for the D_{22}-decane-surfactant $(C_{12}E_5)$-D_2O microemulsion system[6] at 10 °C: $\rho_1 = 6.54 \times 10^{10}$, $\rho_2 = 6.36 \times 10^{10}$ cm^{-2}, and $\rho_0 = 2.76 \times 10^{9}$ cm^{-2}. In this case the intensity is divided by the volume fraction $\phi_{hs} = 0.07649$. The results of the fits are described in the text.

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О малоугловом рассеянии нейтронов на каплях микроэмульсии:
роль флуктуаций формы капель

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Рассчитаны формфактор и интенсивность статического рассеяния нейтронов на каплях микроэмульсии. Капли моделируются двухслойными сферами, состоящими из жидкого ядра и тонкого поверхностного слоя сурфактанта и находятся в другой жидкости. Все три компоненты несжимаемы и характеризуются различными плотностями длин рассеяния. В отличие от прежних описаний малоуглового рассеяния нейтронов последовательно учитываются тепловые флуктуации формы капли до второго порядка по флуктуациям радиуса. Свойства поверхностного слоя описываются в рамках модели Хельфриха. Показано, что для интерпретации рассеяния во многих случаях учет флуктуаций является существенным. В условиях сосуществования объемных фаз возможно теперь из эксперимента одновременно получить информацию о двух эластических константах слоя κ и $\bar{\kappa}$, до сих пор извлекаемых из экспериментов в комбинации $2\kappa + \bar{\kappa}$. В качестве иллюстрации теория применена для количественного описания экспериментов по малоугловому рассеянию нейтронов из литературы.

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On Small-Angle Neutron Scattering from Microemulsion Droplets:
the Role of Shape Fluctuations

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The form factor and intensity of static neutron scattering from microemulsion droplets are calculated. The droplet is modeled by a double-layered sphere consisting of a fluid core and a thin surfactant layer, immersed in another fluid. All the three components are incompressible and characterized by different scattering length densities. As distinct from previous descriptions of small-angle neutron scattering (SANS), we consistently take into account thermal fluctuations of the droplet shape, to the second order of the fluctuations of the droplet radius. The properties of the layer are described within Helfrich's concept of the elasticity of curved interfaces. It is shown that in many cases the account for the fluctuations is essential for the interpretation of SANS. Information about two elastic constants κ and $\bar{\kappa}$ (so far extracted from the experiments in the combination $2\kappa + \bar{\kappa}$) can be now simultaneously obtained from SANS for system in conditions of two-phase coexistence. As an illustration, the theory is applied for the quantitative description of SANS experiments from the literature.