

Interpretation of static and dynamic neutron and light scattering from microemulsion droplets: Effects of shape fluctuations

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The theory of static and dynamic scattering of neutrons and light on microemulsion droplets is developed. The droplets are modeled by double-layered fluid spheres immersed in another fluid. The surface layer of arbitrary thickness thermally fluctuates in the shape. The scattering functions are consistently calculated up to the second order of the fluctuations. The bulk fluids and the layer are characterized by different scattering length densities (or dielectric constants). Involving the Helfrich's concept of interfacial elasticity, the theory is applied for the description of small-angle neutron scattering (SANS), neutron spin echo (NSE), and dynamic light scattering (DLS) experiments on dilute microemulsions. From the fits to the experimental data the bending elasticity and the Gaussian modulus are extracted. Due to the corrected account for the fluctuations, their values differ markedly from those obtained in the original works. The theory well describes the SANS experiments. In the case of DLS, we had to assume the shell of the solvent molecules to be built of several layers. Previous theories were in a sharp disagreement with the NSE experiments. A better agreement with these experiments is obtained if the dissipation in the surface layer is included into the consideration. From the experiments, the viscosity of the layer is estimated for a concrete microemulsion system.

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I. INTRODUCTION

Microemulsions, thermodynamically stable dispersions of oil and water, are intensively studied in recent years because of their interesting physical properties and great practical importance [1]. A homogeneous mixture of the two in principle immiscible liquids is achieved by the stabilizing effect of some surfactants or a surfactant and a cosurfactant. In droplet microemulsions, the surface-active molecules are spread at the oil-water interface and form a dense monolayer. The characteristics of the layer determine to a large degree the properties of the microemulsion. Within the widely used Helfrich's model of interfacial elasticity [2], the interface is characterized by a few parameters: the bending and saddle splay moduli κ and $\bar{\kappa}$, the spontaneous curvature C_s , the surface tension coefficient α , and the equilibrium radius of the droplet, R_0 . The determination of these constants has been attempted by several macroscopic and microscopic methods (see, e.g., Refs. [3–6] and citations therein). However, different experimental methods yield very different parameters of the surface film. So, the neutron scattering associated with spin echoes (NSE) [6] gives significantly larger values of κ than indirect macroscopical or optical techniques [7] or a combination of dynamic light scattering (DLS) and NSE [5,8]. The difference between the hydrodynamic radius of the droplets determined from DLS and the mean radius found from NSE and small-angle neutron scattering (SANS) is surprisingly large that can be only attributed to the presence of several hydration layers [5,8]. There are also difficulties with the fit of the intermediate scattering function to the NSE experimental data [6] and the height of the observed peak in the Q (wave-vector transfer) dependence of the effective diffusion coefficient D_{eff} of the microemulsion droplets [5,6,9,10] is in a sharp disagreement [11] with the existing theory [12]. For other problems we refer to our recent studies [13–16].

To our opinion, the above problems are partially due to the fact that the thermal fluctuations of the droplets in microemulsions are not appropriately taken into account in the interpretation of the experiments. It is known that because of the low interfacial tension of the surface film (typically below 10^{-2} mN/m) the droplet shape easily fluctuates at room temperatures. The effect of the fluctuations on the measured scattering functions in the static and dynamic experiments depends mainly on the values of the bending rigidity constants. Often the reported values of κ are of the order of $k_B T$ or even smaller [4] when the effect is essential [11]. However, in the interpretations of the SANS spectra the fluctuations are not taken into account [5,8]. The intermediate scattering function (calculated up to the second order of the small fluctuations [5,6,8,9–12]) used to describe the NSE experiments should be corrected as shown below; in the first place it does not contain all the necessary contributions within the approximation. While the neutron scattering experiments are carried out at conditions of the shell contrast, the light scattering on the same systems should be described taking into account the difference between the dielectric constants of the three microemulsion components, which is not the case [5,8]. Finally, we have already discussed [13,14,16] that the decay rates of the droplet fluctuations used to describe the NSE data (e.g., Refs. [5] and [8]) correspond to the case of highly compressible surface layer while it is generally accepted that the layer is almost incompressible [4,12] (the use of corrected frequencies of the droplet vibrations allowed us recently [14,15] to obtain a very good agreement with the diffusing-wave spectroscopy experiments on emulsions [17]). Owing to the discussed problems, we suggest that the characteristics of the surfactant film of microemulsion droplets have not been reliably extracted from the scattering experiments so far.

In this paper, we calculate the intermediate scattering function $F(Q, t)$ of microemulsion droplets that consistently

takes into account the droplet fluctuations in the shape. This function is appropriate to describe the static and dynamic scattering of neutrons and light from dilute microemulsion and emulsion dispersions. We take into account the difference in the scattering length densities (dielectric constants). The droplet is modeled by a double layered sphere with arbitrary thickness of the layer, d . The layer fluctuates in shape; we account for all the contributions to $F(Q, t)$ up to the second order of the (presumably small) fluctuations of the droplet radius. The theory is applied to the description of SANS, NSE, and DLS experiments on some concrete microemulsions. To do this, we use the Helfrich's theory for fluctuating curved interfaces. From the fits to the experimental data the basic parameters of the systems are extracted: in some cases their values differ markedly from those obtained in the original works. The theory well reproduces the corresponding SANS experiments. To describe the DLS, we had to assume the shell of the solvent molecules to be built of several layers. Previous theories were in a sharp disagreement with the NSE experiments. To obtain an agreement with these experiments, we included into the consideration the viscosity of the surface layer. Its estimation for the octane- $C_{10}E_5$ -water microemulsion system [8] is given. An alternative approach to explain the difference between the radii of the droplets as obtained from the neutron scattering and DLS [5,8] is discussed.

II. SCATTERING FUNCTIONS

For homogeneous systems, in the long-wavelength approximation, the inelastic scattering of neutrons is determined by the temporal evolution of the scattering length density $\rho(\mathbf{r}, t)$ (Ref. [18]) (as far as the scattering of light is considered, $\rho(\mathbf{r}, t)$ has to be simply replaced by $\varepsilon(\mathbf{r}, t)$, ε being the dielectric constant [19,20]). Neglecting multiple effects, the scattering from a single particle is essential. In our case, the particle that models the microemulsion droplet is a double-layered sphere immersed in a fluid. Let the scattering length density is ρ_1 in the droplet interior, ρ_2 in its exterior, and the surface shell is characterized by the constant ρ_0 . The deviation from the mean (R_0) of the inner ($R_1 = R_0 - d/2$) and outer ($R_2 = R_0 + d/2$) radii of the nondeformed shell is described by the quantity $u = R(t) - R_0$. As distinct from the previous theories of the dynamic scattering from fluctuating liquid drops [5,6,10-17,21], the thickness d of the layer is not assumed to be small. The scattering length density of such a system is

$$\rho(\mathbf{r}, t) = \rho_1 \Theta(R_1 + u - r) + \rho_2 \Theta(r - R_2 - u) + \rho_0 \times \{\Theta(r - R_1 - u) + \Theta(R_2 - r + u) - 1\}. \quad (1)$$

Here, Θ is the Heaviside function. To the second order in the small quantity u one has

$$\begin{aligned} \rho(\mathbf{r}, t) \approx & \rho(\mathbf{r}) + u[(\rho_1 - \rho_0) \delta(r - R_1) + (\rho_0 - \rho_2) \delta(r - R_2)] \\ & - (u^2/2)[(\rho_1 - \rho_0) \delta'(r - R_1) + (\rho_0 - \rho_2) \delta'(r \\ & - R_2)], \end{aligned} \quad (2)$$

where δ and δ' are the delta function and its derivative with respect to the argument. The first term in Eq. (2) corresponds to the density in a nonfluctuating system. Its space Fourier transform ($Q \neq 0$)

$$\begin{aligned} \rho(Q) &= \int e^{iQr} \rho(\mathbf{r}) d\mathbf{r} \\ &= 4\pi \left\{ (\rho_1 - \rho_0) R_1^3 \frac{j_1(x_1)}{x_1} + (\rho_0 - \rho_2) R_2^3 \frac{j_1(x_2)}{x_2} \right\}, \end{aligned} \quad (3)$$

[$x_{1,2} = QR_{1,2}$ and $j_1(x)$ is the spherical Bessel function of order 1 (Ref. [22])] determines the well-known form factor of the static scattering, $P(Q) = \rho^2(Q)$ (Ref. [23]) that is used in the conventional description of SANS experiments on microemulsions, e.g., Refs. [5], [8], [21], and [24-27]. The quasielastic scattering of neutrons, in the classical limit when both the energy and momentum transfers are small, in Born approximation, is described by the Van Hove scattering function for coherent scattering (intermediate scattering function) $F(Q, t) = \langle \rho(\mathbf{Q}, t) \rho^*(\mathbf{Q}, 0) \rangle$ (Ref. [18]). To calculate this correlator for our fluctuating droplet, we express the quantity u as an expansion in spherical harmonics $Y_{lm}(\vartheta, \varphi)$ (Refs. [12] and [22]).

$$u(\vartheta, \varphi, t) = R_0 \sum_{l,m} u_{lm}(t) Y_{lm}(\vartheta, \varphi), \quad (4)$$

where $m = -l, -l+1, \dots, l$, and $l = 0, 1, 2, \dots$, 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 [12]. The shape fluctuations with different numbers l and m are uncorrelated, and $\langle u_{lm} \rangle = 0$ for $l > 1$ (Refs. [28] and [29]). With the use of known properties of the spherical harmonics and Bessel functions [22], the intermediate scattering function can be written in the following form (valid to the second order in the fluctuations, when R_0 is the equivalent-volume radius):

$$\begin{aligned} \frac{F(Q, t)}{(4\pi R_0^2 d \Delta)^2} &= \Phi^2 + 2\Phi \Phi_0 \frac{\langle u_{00} \rangle}{\sqrt{4\pi}} + \sum_{l>1} \frac{2l+1}{4\pi} \\ &\times \{ \Phi \Psi \langle u_{l0}^2 \rangle + \Phi_l^2 \langle u_{l0}(0) u_{l0}(t) \rangle \}. \end{aligned} \quad (5)$$

Here, $\Delta = (\rho_1 + \rho_2)/2 - \rho_0$ characterizes the contrast between the scattering length densities of the bulk fluids and the shell, and

$$\Phi(Q) = \frac{\rho(Q)}{4\pi R_0^2 d \Delta},$$

$$\Phi_l(Q) = \frac{1}{R_0 d \Delta} [(\rho_1 - \rho_0) R_1^3 j_l(x_1) + (\rho_0 - \rho_2) R_2^3 j_l(x_2)],$$

$$\Psi(Q) = \frac{1}{d\Delta} [(\rho_1 - \rho_0)R_1\varphi(x_1) + (\rho_0 - \rho_2)R_2\varphi(x_2)],$$

$$\varphi(x) = 2j_0(x) - xj_1(x). \quad (6)$$

The $l=1$ mode was automatically excluded during the calculations that coincides with the fact (known for droplets with thin adsorbed layers) that this mode corresponds to the translational motion of the droplet [12]. For $l=1$ there is no motion in the layer and the droplet moves like a hard sphere [13,30]. The calculations were carried out in the coordinate system connected with the droplet; the effect of translational motion is incorporated into Eq. (5) by assumption that the translational and other degrees of freedom are statistically independent. Then, the right-hand side of Eq. (5) must be multiplied by the factor $\exp(-Q^2Dt)$, where D is the self-diffusion coefficient of the droplet (the same as for a hard sphere with the hydrodynamic radius R_H that is in general larger than the outer radius of the droplet due to the shell of solvent molecules moving together with the droplet).

Equation (5) is the basic result of the paper. Due to the account for all second-order corrections in the fluctuating density expansion (2) it significantly differs from analogous expressions for the function $F(Q,t)$ or the form factor $P(Q) = F(Q,0)$ that can be found in the cited literature so we shall discuss it in more details. The first term in Eq. (5) exactly corresponds to the scattering on the undistorted double-layered sphere [23]. The second term reflects a contribution from the $l=0$ mode. This contribution did not appear in previous works. However, for incompressible bulk fluids, using the constraint on the droplet volume, $\langle u_{00} \rangle \neq 0$, namely [12],

$$\langle u_{00} \rangle = -\frac{1}{\sqrt{4\pi}} \sum_{l>1} (2l+1) \langle u_{l0}^2 \rangle, \quad (7)$$

that should be inserted in Eq. (5). The third (time-independent) term in Eq. (5) does not appear in Ref. [12] where the intermediate scattering function for droplet micro-emulsions was calculated for the first time; it also absents in the interpretation of experimental data [5,8,9]. The expressions for this term that can be found in Refs. [6] and [10] were later corrected [21], however, the $l=0$ contribution is missing in that work. All the above works assume the perfect shell contrast when the scattering length densities of the deuterated bulk fluids $\rho_1 \approx \rho_2$ significantly differ from the density of the hydrogenated layer. The scattering function was obtained for the thickness of the layer, d , negligible in comparison with the droplet radius. In such an approximation $F(Q,t)$ does not contain terms $\sim (\rho_1 - \rho_2)$ and is thus inappropriate for the description of the scattering in conditions far from the shell contrast. In the limit $d \rightarrow 0$, $F(Q,t)$ disappears so it cannot describe the scattering from vesicle or emulsion droplets. As to the last term in Eq. (5), it agrees with the corresponding expressions from the literature for small d/R_0 and $\rho_1 = \rho_2$. Taking into account Eq. (7), the scattering function is

$$F(Q,t) = (4\pi R_0^2 d \Delta)^2 e^{-Q^2Dt} \left\{ \Phi^2 + \sum_{l>1} \frac{2l+1}{4\pi} \right. \\ \left. \times [\Phi(\Psi - 2\Phi_0) \langle u_{l0}^2 \rangle + \Phi_l^2 \langle u_{l0}(0)u_{l0}(t) \rangle] \right\}. \quad (8)$$

When d is small [the density (2) is expanded to the first order in d/R_0], instead of Eq. (6) one has

$$\Phi(Q) = \lambda(R_0) \frac{j_1(x)}{x} - j_0(x),$$

$$\Phi_l(Q) = xj_{l+1}(x) - [l+2 - \lambda(R_0)]j_l(x), \quad (9)$$

$$\Psi(Q) = xj_1(x)[2 - \lambda(R_0)] + j_0(x)[2\lambda(R_0) - 2 + x^2],$$

$$x = QR_0, \quad \lambda(R_0) = \frac{R_0}{d} \frac{\rho_1 - \rho_2}{\Delta}.$$

Contrary to the previous works where $\lambda = 0$, Eqs. (5) and (8) contain the $d \rightarrow 0$ limit,

$$F(Q,t) \approx [4\pi R_0^3 (\rho_1 - \rho_2)]^2 e^{-Q^2Dt} \left\{ \frac{j_1^2(x)}{x^2} + \sum_{l>1} \frac{2l+1}{4\pi} \right. \\ \left. \times [j_l^2(x) \langle u_{l0}(0)u_{l0}(t) \rangle - j_l^2(x) \langle u_{l0}^2 \rangle] \right\}, \quad (10)$$

applicable for (emulsion [17] or vesicle [31] droplets, or cells [32]; in all these systems the thickness of the surface membrane is negligible compared with the radius R_0).

The above equations must be completed by the expressions for the correlators of the fluctuations of the droplet radius. Available equations assume isothermal fluctuations, small thicknesses of the surface layer, and the conservation of the droplet volume as well as the total number of the molecules in the shell. Under these conditions we have [29,33]

$$\langle u_{l0}(t)u_{l0}(0) \rangle \approx \frac{k_B T}{\alpha_l R_0^2 (l+2)(l-1)} \exp(-\omega_l t), \quad (11)$$

$$\alpha_l = \alpha - 2\kappa C_s R_0^{-1} + \kappa l(l+1)R_0^{-1}.$$

Here, $\alpha = \sigma + C_s^2 \kappa / 2$ (σ is the microscopic interfacial tension [34]). The decay rates ω_l for compressible surface layers have been studied in detail in our previous papers [13,16]. The relaxation modes in the limit of incompressible layers were described by the formula (see also Ref. [35])

$$\omega_l \approx \frac{\alpha_1}{R_0} \left[\frac{2l+3}{l(l+2)} \eta_1 + \frac{2l-1}{(l-1)(l+1)} \eta_2 \right]^{-1}, \quad (12)$$

with η_1 and η_2 being the viscosity coefficients of the fluid inside and outside the droplet, respectively.

Finally, the experimental samples always contain droplets with different radii. For the self-consistence of the consideration, instead of the often used Schulz distribution [21] we prefer to employ the distribution $f(R_0)$ of the droplets in radii as it follows from the theory of the droplet formation. Within the phenomenological approach, $f(R_0)$ found through the free energy of a spherical microemulsion droplet [34] is

$$\begin{aligned} f(R_0) &\propto \exp \left[-\frac{1}{2\varepsilon} \left(1 - \frac{R_0}{R_m} \right)^2 \right] \\ &= \exp \left[-\frac{4\pi}{k_B T} (\alpha - R_m \Delta p) (R_0 - R_m)^2 \right], \end{aligned} \quad (13)$$

where R_m is the mean radius of the droplets and Δp is the pressure difference (pressure inside the droplet minus outside). The generalized Laplace condition [34] $R_m \Delta p = 2\alpha - 4\kappa/R_s R_m$ ($R_s = 2/C_s$ is the spontaneous radius of curvature) relates the polydispersity to the characteristics of the layer,

$$\varepsilon = \frac{k_B T}{8\pi R_m^2 (4\kappa/R_s R_m - \alpha)}, \quad \varepsilon_2 \Phi = \frac{k_B T}{8\pi (2\kappa + \bar{\kappa})}, \quad (14)$$

with the second equation written for the case of the so-called two-phase coexistence [4,34] when $\alpha = (2\kappa + \bar{\kappa})/R_m^2 = 2\kappa/R_s R_m$. For small ε the distribution (13) has a sharp maximum 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 $\sim \exp(-1/2\varepsilon)$.

The above formulas can be applied to noninteracting droplets in an infinitely diluted dispersion. For dense microemulsions the scattering function should take into account the interaction between the droplets. Also the expressions for the quantities $\langle u_{l0}^2 \rangle$, the polydispersity and decay rates of the fluctuations should be changed due to the interaction and dispersion of the globules in the continuous phase [4,5,8,21]. This question will be considered below in Sec. III.

The shape fluctuations can have a significant effects on the scattering functions. It can be shown by the following consideration of the form factor $P(Q) = F(Q,0)$ from Eqs. (5)–(9). If the fluctuations were negligible, the minimum of $P(Q)$ would correspond to the first zero of the function $\Phi(x)$, i.e., $x_0 \approx \pi - \lambda/\pi$ in conditions close to the shell contrast. Since the $l=2$ mode of the fluctuations is dominant, $P(Q)$ for a droplet with the mean radius R_m can be approximated by $P(Q) \sim \Phi^2(x) + \chi[\Phi(x)\Psi(x) + \Phi_2^2(x)]$, where $\chi = 5/[96\pi\kappa/k_B T - 2/\varepsilon]$. For very small χ , $P(Q)$ is determined mainly by the function $j_0^2(x)$, its minima are close to $x \approx \pi, 2\pi, \dots$, and a local maximum is at $x \approx 4.5$ [the root of $j_1(x)$]. 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

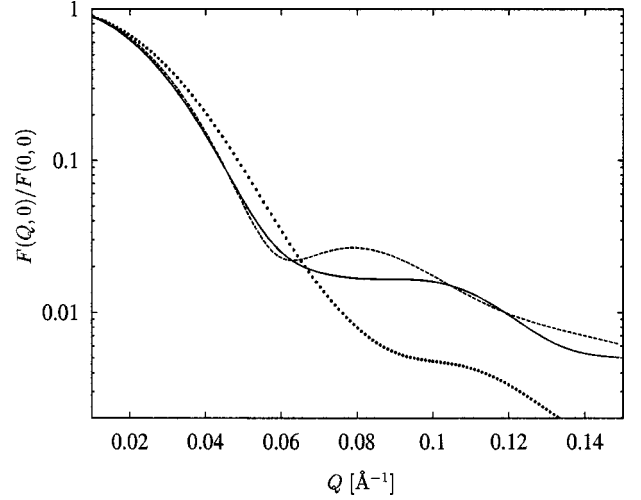


FIG. 1. The normalized formfactor $F(Q,0)$ calculated from Eqs. (8), (13), and (19) for the bending rigidity values $\kappa=0.92$ (full line) and $\kappa=3.0 k_B T$ (dashed line). The octane- d_{18} -surfactant ($C_{10}E_5$)-water microemulsion (Ref. [8]) in conditions of two-phase coexistence at the temperature $T=305.2$ K is characterized by the parameters $\rho_1=6.35 \times 10^{10}$, $\rho_2=6.36 \times 10^{10}$ and $\rho_0=1.65 \times 10^9 \text{ cm}^{-2}$, $\varepsilon=0.04$, $d=10.8 \text{ \AA}$, and $R_m=48 \text{ \AA}$. For illustration (points) the formfactor corresponding to the scattering of light is shown. In this case the dielectric constants are $\varepsilon_1=1.946$, $\varepsilon_2=1.769$, and $\varepsilon_0=2.106$.

maximum and the former maximum at $x \approx 4.5$. This takes place for $\chi \approx 0.025$. With a further growth of χ the location of this new minimum moves towards $x \approx 4.5$, 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 $\chi \approx 0.035$), 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 [they appear because third and higher order terms in u were neglected obtaining Eqs. (5) and (8)]. Unphysical values of the form factor from Eqs. (8) and (9) appear also for large $x \gg 1$ well out of the range of experimental values of Q ; this is a property of the approximation $d/R_0 \ll 1$ [Eqs. (5)–(7) possess the correct limit $P \rightarrow 0$ as $x \rightarrow \infty$].

In Fig. 1, the normalized form factor from Eqs. (5)–(7) is shown for the octane- d_{18} -surfactant ($C_{10}E_5$)-water microemulsion system [8]. The scattering length densities of the deuterated bulk fluids are close [21], $\rho_1=6.35 \times 10^{10}$ and $\rho_2=6.36 \times 10^{10} \text{ cm}^{-2}$, and the surfactant is characterized by the density $\rho_0=1.65 \times 10^9 \text{ cm}^{-2}$ [36]. The system was in conditions of the two-phase coexistence. The thickness of the surface layer is $d=4.3(2\pi)^{1/2} \text{ \AA}$ [8,37], and the mean radius $R_m=48 \text{ \AA}$ and the polydispersity $\varepsilon \approx 0.04$ were determined in the SANS study [8] using the polydisperse shell model without fluctuations. Figure 1 shows the form factor for the bending elasticities $\kappa=3k_B T$ ($\chi \approx 0.006$, small fluctuations) and $\kappa=0.92k_B T$ (when $\chi \approx 0.025$ and the fluctuations are relatively large) found in Ref. [8] by a combination of SANS and NSE. 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 polydis-

perse systems the form factor (5) has to be averaged over the droplet radii. 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 [8] at $Q \approx 0.06 \text{ \AA}^{-1}$) does not satisfy the condition $x \approx \pi$ as assumed in Ref. [8]: if $\kappa = 0.92 k_B T$, the mean radius should be notably larger. For illustration, we show also on Fig. 1 the form factor calculated for the parameters corresponding to the scattering of light. The dielectric constants for the system studied in Ref. [8] are approximately $\varepsilon_1 = 1.946$, $\varepsilon_2 = 1.769$, and $\varepsilon_0 = 2.106$ [38], the rest of the parameters are the same as above. Now the scattering conditions are far from the shell contrast that can be characterized by the parameter λ from Eq. (9): here $\lambda(R_m) \approx -2$ while for the neutron scattering it was approximately -0.015 . It is seen that the changes of the form factor are significant so that a correct analysis of the DLS data cannot be done without the account for the difference in dielectric constants of the three microemulsion components.

III. QUANTITATIVE DESCRIPTION OF THE SCATTERING EXPERIMENTS

In the strict sense the theory developed in the preceding section is restricted to small thicknesses d of the surface layer. This restriction is due to the Helfrich's model of interfacial elasticity that is valid to the second order in d (relative to the principal radii of curvature of the droplet) [2,4], and to the approximations used in obtaining the correlators $\langle uu \rangle$ and decay rates of the shape fluctuations [13,29,35]. However, we shall proceed with Eqs. (5)–(7) obtained with no explicit limitation on d except the natural inequality for a double-layered sphere, $d < 2R_0$. The reason for this is to use the form factor that in the absence of fluctuations exactly corresponds to the form factor [23] used in the analysis of SANS [5,8,24–27]. Comparing our results with the previous analyses we thus have a better possibility to see how the fluctuations influence the values of the microemulsion parameters extracted from the experiments.

A. Small-angle neutron scattering

Using Eq. (5), the SANS intensity is calculated according to the formula [5,8,21,27]

$$I(Q) = N \langle F(Q,0)S(Q) \rangle. \quad (15)$$

Here, the average is over the droplet distribution in radii, N is the number density of the scattering 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 [39] is usually

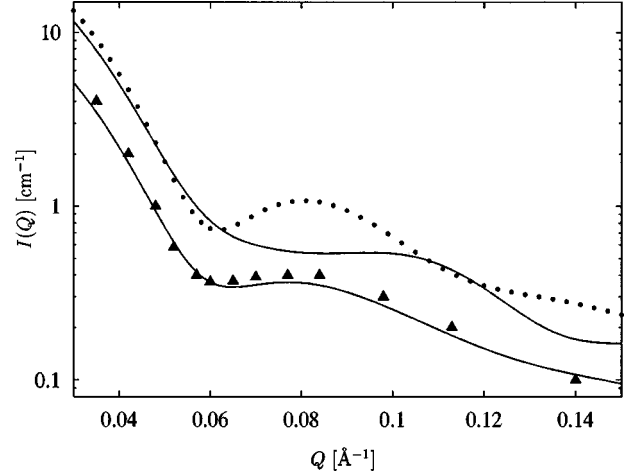


FIG. 2. The SANS intensity calculated from Eqs. (8), (13), and (15), (17)–(19) with (the upper full line) and without (dashed line) the droplet fluctuations in the shape. The experimental points are from the work (Ref. [8]) for the same system and conditions as in Fig. 1. Here, $\kappa = 0.92 k_B T$, $\varepsilon = 0.036$, $d = 10.8 \text{ \AA}$, $R_m = 48 \text{ \AA}$, and the hard-sphere volume fraction of the droplets is 0.049 (Ref. [8]). The lower line is our fit to the experimental data that yielded the values $\kappa = 1.93 k_B T$, $\varepsilon = 0.046$, $R_m = 47.7 \text{ \AA}$ and $d = 6.4 \text{ \AA}$.

employed [21,27]. For larger Q [but smaller than the minimum of $I(Q)$], $S(Q)$ approaches unity [8,40]. Since the value of the droplet radius is fixed by the position of the minimum of $I(Q)$, $S(Q) \approx 1$ is a good approximation in the determination of R_m if the low- Q data are omitted in the fitting procedure [5,8]. The influence of the entropy of dispersion can be taken into account as follows. In conditions of the two-phase equilibrium and within the random mixing approximation [12] the quantity α_i in Eq. (11) becomes

$$R_0^2 \alpha_i = \kappa(l-1)(l+2) - \bar{\kappa} - (k_B T / 4\pi) F(\Phi), \quad (16)$$

and the polydispersity from Eq. (14) is now

$$\varepsilon_{2\Phi} = \frac{k_B T}{8\pi(2\kappa + \bar{\kappa}) + 2k_B T F(\Phi)}, \quad (17)$$

$$F(\Phi) = \ln \Phi + \frac{1-\Phi}{\Phi} \ln(1-\Phi) \approx \ln \Phi - 1, \quad (18)$$

where the approximation is for small volume fractions of the droplets, Φ . The last three equations allow us to rewrite the mean quadrate of the amplitude of fluctuations in the form

$$\langle u_{i0}^2 \rangle = \left\{ (l-1)(l+2) \left[\frac{\kappa}{k_B T} l(l+1) - \frac{1}{8\pi\varepsilon} \right] \right\}^{-1}, \quad (19)$$

that is particularly suitable for the fits to experimental data due to its invariance with respect to the function $F(\Phi)$.

We used Eqs. (5)–(7), (15), (17)–(19) in the case of two-phase coexistence to calculate the SANS intensity as shown on Fig. 2. The microemulsion parameters are taken from the work [8] [$\kappa = 0.92 k_B T$ at $T = 305.2 \text{ K}$, $\varepsilon = 0.0356$, $R_m = 48 \text{ \AA}$, $d = 10.78 \text{ \AA}$ [8,37], $\phi_{hs} = 0.049$ (the hard-sphere

volume fraction), and the scattering length densities are the same as in the calculations to Fig. 1]. The intensity 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 Q s 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. [8], cannot describe the experiment. Figure 2 shows also the result of our own fit of Eq. (15) to the experimental SANS data [8]. The volume fraction of the droplets was the same as in Ref. [8] and following that work the region $Q > 0.03 \text{ \AA}^{-1}$ was considered to have $S(Q) \approx 1$. The best fit to the experiment was achieved for the values $\kappa = 1.93 k_B T$, $\varepsilon = 0.0463$, $R_m = 47.7 \text{ \AA}$, and $d = 6.44 \text{ \AA}$. The difference from the parameters found in Ref. [8] is reflected mainly in the elasticity coefficients: together with a larger κ we have now $\bar{\kappa} \approx -2.68 k_B T$ instead of $\bar{\kappa} \approx -0.38 k_B T$ [8]. If the entropy-of-mixing contributions are not taken into account, the fit yields $|\bar{\kappa}|$ slightly larger ($\approx -3 k_B T$) while κ and ε remain unchanged. One more fit was done for a different D_{22} -decane-surfactant ($C_{12}E_5$)- D_2O microemulsion system at 10°C [21] described by the parameters $\rho_1 = 6.54 \times 10^{10}$, $\rho_2 = 6.36 \times 10^{10}$, and $\rho_0 = 2.76 \times 10^9 \text{ cm}^{-2}$, and the volume fraction $\phi_{hs} = 0.0765$. Instead of the parameters determined in the original work [21], $2\kappa + \bar{\kappa} = 3.42 k_B T$, $\varepsilon = 0.0127$, $R_m = 49.1 \text{ \AA}$, and $d = 15.2 \text{ \AA}$ (the elasticity κ was not found), our fit yielded the values $2\kappa + \bar{\kappa} = 1.97 k_B T$, ($\kappa = 4.05$ and $\bar{\kappa} = -6.13 k_B T$), $\varepsilon = 0.0236$, $R_m = 49.1 \text{ \AA}$, and $d = 14.6 \text{ \AA}$. The presented values should be considered just as estimations of the system parameters within the used approximations. Despite this it allows us to make some conclusions about the studied systems. In both the examples the best fits to the experiments were obtained for such parameters when the fluctuations are relatively small. This is reflected by rather large bending elasticities, especially in the second case. In the first example the bending elasticity is smaller but our calculations suggest that it was underestimated in the original work [8]. The thickness of the layer is relatively large compared with R_m so that a more exact theory, not limited to small values of d , is 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 here (see below).

Despite the approximations used, 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 where it was thought that the SANS results are connected with the fluctuations through the polydispersity formally determined by $\varepsilon = \langle u_{00}^2 \rangle / 4\pi$ [21] with $\langle u_{00}^2 \rangle = k_B T / (-2R_0^2 \alpha_{l=0})$, where α_l is from Eq. (11). However, due to the constraint on 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 [34] is a sum of the terms $k_B T |u_{lm}|^2 / 2 \langle |u_{lm}|^2 \rangle$ that does not contain the $l=0$ mode contribution. With the use of Eq. (7) (before averaging), we thus obtain

$$4\pi \langle u_{00}^2 \rangle = \left(\sum_{l>1} (2l+1) \langle u_{l0}^2 \rangle \right)^2 + 2 \sum_{l>1} (2l+1) \langle u_{l0}^2 \rangle^2. \quad (20)$$

The total polydispersity in a microemulsion sample is not only due to the droplet distribution in radii; it is also affected by the droplet fluctuations in the shape: $\varepsilon_{\text{tot}} = \langle (R - \langle R \rangle)^2 \rangle \langle R \rangle^{-2}$, where $R = R_0 + u$ is the fluctuating radius as given by Eq. (4) and the average is over the fluctuating variables u_{lm} and over the radii R_0 . Since by assumption the volume of the droplets with the equilibrium radius R_0 does not change [Eq. (7)], and the shape fluctuations of different droplets does not influence each other, the average gives in the main approximation [21]

$$\varepsilon_{\text{tot}} \approx \varepsilon + \Sigma, \quad \Sigma = \sum_{l>1}^{l_{\text{max}}} \frac{2l+1}{4\pi} \langle u_{l0}^2 \rangle. \quad (21)$$

This equation again illustrates that the role of the shape fluctuations can be important [for example, for a dilute microemulsion characterized by $\kappa \approx 0.5 k_B T$ [7] and a typical polydispersity $\varepsilon \approx 0.04$ when $2\kappa + \bar{\kappa} \approx k_B T$, Eqs. (18) and (11) give $\varepsilon_{\text{tot}} \approx 2.75\varepsilon$]. Thus, as opposite to the previous studies, the description of the SANS experiments must take into account the fluctuations. 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 through Eq. (14) or (17) connected with $2\kappa + \bar{\kappa}$), both the elasticity coefficients κ and $\bar{\kappa}$ can be found. 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 $R_m, C_s, \kappa, \alpha, d$, and ε is connected with the first three parameters by Eq. (14). Due to a large number of the parameters it is desirable to supply the information from SANS with data obtained from other sources [3–5,8,27]. Below we consider SANS in combination with dynamic scattering experiments. A combined analysis of the static and dynamic data was done in Ref. [8].

B. Dynamic light scattering

In general, the interpretation of dynamic experiments is more model dependent than that of the static ones since it requires additional knowledge of the dynamics of the microemulsion. However, the DLS on microemulsions has an advantage that the knowledge of the decay rates ω_l for individual droplets is of less importance. DLS yields the effective diffusion coefficient D_{eff} of the droplets in the range of the wave-vector transfer Q much smaller than in SANS ($D_{\text{eff}} = \Gamma / Q^2$, where Γ is the first cumulant to the scattering signal, $\Gamma = -\langle dF(Q,t)/dt \rangle / \langle F(Q,0) \rangle$ at $t=0$; the average is over the distribution in radii). In this region D_{eff} is practically constant. It is only weakly influenced by the time-dependent term in Eq. (5) that disappears when $Q \rightarrow 0$ ($x \rightarrow 0$); thus DLS is not so sensitive to a model for ω_l as the dynamic scattering of neutrons. D_{eff} differs from the mutual

diffusion coefficient of the droplets (even in the limit $Q \rightarrow 0$) or, in the case of their small concentration, from the self-diffusion coefficient $D_m = k_B T / 6\pi\eta_2 R_H$, where the hydrodynamic radius $R_H = R_m + d/2 + \delta$ (δ accounts for the shell of solvent molecules). This is because the calculation of D_{eff} must take into account the dielectric constants of the three microemulsion components, as it was done in the calculations of the form factor in Fig. 1. As a result, due to a different functional dependence on R_0 of the numerator and denominator that form D_{eff} , D_{eff} differs after averaging from D_m . Neglecting this, the Stokes' formula for the diffusion coefficient can lead to incorrect values of R_H . In Ref. [8] where the dependence of the autocorrelation function of the scattering amplitude (it corresponds to the intermediate scattering function $F(Q, t)$ when in Eq. (5) the scattering length densities are replaced by dielectric constants) was not considered, a value $D_m = 3.6 \times 10^{-11} \text{ m}^2/\text{s}$ for the translational diffusion coefficient was found. The hydrodynamic radius of 81 Å determined from this value was surprisingly larger than the droplet radius $R_m \approx 48 \text{ Å}$ obtained by SANS. Similar differences were reported for the dodecane- $C_{10}E_5$ -water [5] and decane- $C_{12}E_5$ -water microemulsions [40,41]. To explain such differences between the two radii, in Ref. [8] the presence of four hydration shells was assumed.

Within our theory a smaller hydrodynamic radius follows from the simultaneous description of the SANS and DLS data [8]. The fit to the experimental SANS intensity was carried out as in Sec. III.A, with the additional requirement to satisfy the value of the effective diffusion coefficient measured by DLS, $D_{\text{eff}} = 3.8 \times 10^{-11} \text{ m}^2/\text{s}$ (with the tolerance $\pm 5\%$). The optical characteristics of the microemulsion were the same as in Fig. 1. For the beginning we assumed one monomolecular hydration layer with $\delta = 2 \text{ Å}$ [27]. The fit yielded the following values of the microemulsion parameters: $\kappa = 0.50k_B T$, $\varepsilon = 0.075$, $R_m = 57.4 \text{ Å}$, and $d = 9.6 \text{ Å}$. One thus finds $R_H \approx 64.2 \text{ Å}$ and $D_m = 4.56 \times 10^{-11} \text{ m}^2/\text{s}$. These results essentially differ from the parameters obtained from the fit to SANS data only as well as from the parameters found in Ref. [8]. In agreement with our qualitative consideration of the behavior of the scattering form factor, the bending elasticity is smaller and the radius is larger. This seemingly resolves the discrepancy between the radii found from DLS and SANS in Ref. [8], however, the quantitative agreement with the SANS data is now notably worse than the previous fit to SANS alone, presented in Fig. 2. Since the analysis of the SANS spectra is not influenced by the change of this parameter, we used the droplet parameters as found from the fit to SANS in the previous section and changed δ to obtain the best agreement with the experimental D_{eff} . This was achieved for $\delta = 13 \div 21 \text{ Å}$ (the mean $\delta = 17 \text{ Å}$). In this case the mean $R_H \approx 68 \text{ Å}$ and $D_m = 4.3 \times 10^{-11} \text{ m}^2/\text{s}$. Following Refs. [5] and [8], we thus also have to assume that the hydration shell consists of several layers.

Note that describing the DLS and NSE experiments (see below), in Ref. [8] the scattering function was taken in the form of Eq. (8) but without the first term in the sum and with $\lambda(R_0) = 0$. The used decay rates of the fluctuations corresponded to the expression firstly obtained in our work [33], and only the mode $l=2$ was taken into account. In our calculations we considered the modes up to $l_{\text{max}} = 20$ and use a more adequate, corresponding to incompressible surface lay-

ers, expression for ω_l (12). The employed viscosities at $T = 305.9 \text{ K}$ were $\eta_1 = 0.4675 \text{ cP}$ (*n*-octane) and $\eta_2 = 0.7632 \text{ cP}$ (water) [8].

C. Neutron spin-echo spectroscopy

The microemulsion dynamics is studied by NSE beginning from the works [9,10]. In these experiments the intermediate function $F(Q, t)$ is measured directly. The effective diffusion coefficient D_{eff} determined from this function essentially depends on Q : a pronounced peak is observed in D_{eff} near $QR_m = \pi$ [5,6,8–10]. This peak was attributed to the shape fluctuations of microemulsion droplets and analyzed within the theory by Milner and Safran [12] (the works [8,9]) or alternative theories [5,6,10] that have to be, however, changed as discussed in Sec. II. The values of the bending elasticity of the layer, κ , obtained in such ways are very different from about 1 to $5k_B T$ and differ from the values found in other experiments (see Introduction). The problems with the fit of the theoretical scattering function onto the experimental spin-echo data [6,8] stimulated our detailed analysis of the NSE experiments. We reconsidered the original interpretation of the mentioned experiments. First, we used the theory [12] just generalized for different scattering length densities of the oil, water, and the interfacial surfactant film [11]. As distinct from the previous works, we considered not only the $l=2$ mode of the fluctuations, but took into account the higher l modes and showed that their contribution to the scattering function is essential. The decay rates of the fluctuations were taken in the form of Eq. (12) that reflects the difference between the viscosities of the bulk fluids. As a result, we came to a significant discrepancy with the experiments. The fit to the measured peaks in D_{eff} was not possible for the microemulsion parameters extracted from the NSE studies: the height of the theoretical peak was essentially larger than the experimental one. An agreement with the experiment [8] was not possible for any realistic set of the parameters and to satisfy the experiments [9,10] we had to significantly lower the bending elasticity κ (more than 10 times). We thus conclude that the theory [12], neither its originally proposed form nor its modifications [5,6,10,11], does not adequately describe the NSE experiments.

Here we present the description of the NSE experiments using the intermediate scattering function (5)–(7). Let us return to the experiment [8]. In our calculations of D_{eff} one set of the microemulsion parameters corresponded to those determined in the original work [8] (see Fig. 2), the other two sets were found above from the combined analysis of SANS and DLS. In all the cases there is a disagreement with the experiment: the height of the peak is several times larger compared with the measured one. We propose to solve this problem by taking into account the viscosity of the surface layer. The dissipation in the layer leads to a decrease of the decay rates of the droplet fluctuations. Correspondingly, the contribution in D_{eff} that is mainly responsible for the peak [it comes from the time-dependent term of Eq. (5) and, from the definition of D_{eff} is a sum of terms proportional to ω_l] also decreases. The available decay rates that reflect the internal viscosity η_0 of an incompressible surface layer have been found by Fujitani [42].

$$\alpha_1 = \frac{\alpha_l}{R_0} \frac{l(l+1)(l-1)(l+2)}{4(l-1)(l+2)\eta_0/R_0 + (l-1)(2l^2+5l+5)\eta_1 + (l+2)(2l^2-l+2)\eta_2}. \quad (22)$$

Figure 3 presents the calculation of $D_{\text{eff}}(Q)$ using this equation instead of Eq. (12). The unknown parameter η_0 was found from the correspondence between the calculated and experimental [8] heights of the peak in D_{eff} . As found in the previous section, the best coincidence with the SANS and DLS experiments was achieved for the parameters $\kappa = 1.93 k_B T$, $\varepsilon = 0.046$, $R_m = 47.7 \text{ \AA}$, and $d = 6.4 \text{ \AA}$ determined from the fit to SANS data in Sec. III A, and $\delta \approx 17 \text{ \AA}$ determined from DLS. For these values the estimate of the viscosity of the layer is $\eta_0 = 5.6 \times 10^{-11} \text{ Ns/m}$. Assuming a smaller thickness of the hydration layer, an agreement with the NSE experiment (as well as before for SANS combined with DLS) becomes worse. We thus again come to the conclusion that within the presented model the hydration shell is built of several layers [8].

At this point, we would like to mention a possible alternative approach to the consideration of the scattering by microemulsion droplets. It could come from the assumption that the hydration shell of the water bound to the droplet is characterized by different physical properties (i.e., also the dielectric constant) than the free water [43]. Then, instead of one dielectric constant for the water we have to characterize the hydration layer by one constant and the solvent by another. In such a model there is a possibility to describe the DLS experiments [8] with a smaller δ than it was found in the present work. This can be supported by the following calculations: characterizing the bound and free water by one ‘‘effective’’ dielectric constant ε_{eff} , we calculated D_{eff} mea-

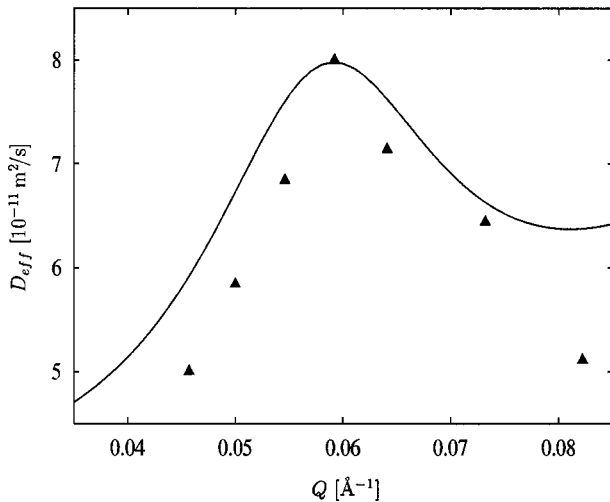


FIG. 3. The effective diffusion coefficient measured by NSE (points) (Ref. [8]) on the same system as in Fig. 1, and calculated as $D_{\text{eff}} = \Gamma/Q^2$, where $\Gamma = \langle dF(Q,t)/dt \rangle / \langle F(Q,0) \rangle$ at $t=0$, from Eqs. (8), (11), (13), (17), (19), and (22) using the parameters found from the fit to SANS (Fig. 2). The height of the peak corresponds to the experimental one if the viscosity of the surface layer $\eta_0 = 5.6 \times 10^{-11} \text{ Ns/m}$ is employed in the calculations. The thickness of the hydration shell $\delta = 17 \text{ \AA}$ was obtained from D_{eff} measured in the DLS experiment (Ref. [8]). The viscosities of the bulk fluids were $\eta_1 = 0.4675$ and $\eta_2 = 0.7632 \text{ cP}$.

sured by DLS as a function of ε_{eff} . This function is practically constant for $\varepsilon_{\text{eff}} < \varepsilon_1 = 1.946$ and $\varepsilon_{\text{eff}} > \varepsilon_0 = 2.106$. When ε_{eff} increases, D_{eff} has near $\varepsilon \approx 2$ a maximum and then a minimum. At the minimum the experimental value for D_{eff} is obtained from our formulas when δ is about 10 \AA .

IV. CONCLUSIONS

We have calculated the intermediate scattering function $F(Q,t)$ that is measured in quasielastic neutron scattering (neutron spin echo) from droplet microemulsions. This function can be also used to describe dynamic light scattering experiments and the form factor and intensity of the static scattering of neutrons. Our aim was to consider the role of the droplet fluctuations in the shape. The droplet was modeled by a double-layered sphere in a fluid. The fluid core, the surfactant layer and the solvent are characterized by different scattering length densities (or dielectric constants in the case of light scattering) and viscosities. We have accounted for all the contributions to the scattering up to the second order of the fluctuations. As a result, the function $F(Q,t)$ differs from the previously known expressions by a time-independent term that is determined by the fluctuations and essentially influences the interpretation of the scattering experiments. The results are applicable for the description of SANS, NSE, and DLS on dilute microemulsions, as well as on emulsion or vesicle systems. From such experiments the crucial parameters determining the properties of the droplets can be extracted, like their mean radius R_m , the polydispersity ε , and the Helfrich’s elasticity coefficients κ and $\bar{\kappa}$. Using SANS, R_m , ε , and, in favorable conditions (two-phase coexistence), the combination $2\kappa + \bar{\kappa}$ have been determined so far fitting the experimental data with the model of nonfluctuating double-layered spheres. In 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 the 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 . Compared with the recent work on octane - $C_{10}E_5$ -water microemulsion [8], a good agreement with the experiment was achieved for a notably larger κ while the radius did not change significantly. The following set of the parameters has been found: $\kappa = 1.93(0.92)k_B T$, $\varepsilon = 0.046(0.036)$, $\bar{\kappa} = -2.68(-0.38)k_B T$, $R_m = 47.7(48) \text{ \AA}$, and $d = 6.4(10.8) \text{ \AA}$ (in parenthesis the values from Ref. [8] are shown). Concerning the dynamic experiments, we have shown that the previous theories do not correctly describe the

DLS and NSE data. These experiments yield an effective diffusion coefficient of the microemulsion droplets, D_{eff} . The peak in $D_{\text{eff}}(Q)$ observed by NSE (connected with the shape fluctuations of the droplets) was significantly smaller than predicted by the existing theories. In our approach, the three experiments can be described more satisfactorily. We have presented two ways of the combined analysis of the SANS, NSF, and DLS data. In the first approach we assumed a small thickness of the hydration shell and fitted the corresponding scattering functions to the experiments. This approach yielded the estimations for the elasticity coefficients that markedly differ from their values found in the work [8] and the obtained hydrodynamic radius was much smaller. However, the agreement with SANS became worse than in the independent description of this experiment alone. Assuming the dissipation in the surfactant layer we found from the NSE experiment a value $\eta_0 = 1.42 \times 10^{-10}$ Ns/m for the viscosity coefficient of the layer. In the second approach, we used the parameters found from the description of SANS. Independent DLS data that are necessary to treat characterizing the microemulsion components by different dielectric

constants allowed us to determine the thickness of the hydration shell, which is now about 17 Å. This assumes the existence of several hydration layers that is a question for future investigations. (We suppose however that first a model should be built that takes into account different physical properties of the bound and free bulk fluids.) Finally, in this case the viscosity coefficient of the layer is $\eta_0 = 5.6 \times 10^{-11}$ Ns/m. This second approach gives the best quantitative description of all the three experiments and on this stage of the theory (when the microemulsion droplets are modeled as double-layered spheres) can be used to estimate the droplet parameters by their extraction from the experiments. We suppose that in further studies the role of the hydration and oil layers bound to the droplets must be considered. Also, more should be known about the interaction between the droplets and the entropy of dispersion [44].

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