



Historical perspective

Structure, interfacial film properties, and thermal fluctuations of microemulsions as seen by scattering experiments

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ABSTRACT

The physics of microemulsions and in particular Dominique Langevin's contributions to the understanding of microemulsion structure and bending properties using scattering techniques are reviewed. Among the many methods used by her and her co-workers, we particularly emphasize optical techniques and small angle neutron scattering (SANS), but also neutron spin echo spectroscopy (NSE). The review is then extended to more recent studies of properties of microemulsions close to surfaces, using reflectometry and grazing-incidence small angle neutron scattering (GISANS).

1. Introduction

Microemulsions are thermodynamically stable, isotropic, liquid mixtures of two immiscible fluids, typically oil and water, stabilized by surfactant and in some cases by an additional co-surfactant [1]. Such systems exhibit a low interfacial tension, combined with a high interfacial area between the immiscible fluids. Their phase diagrams and mesoscale structures have been intensely studied over the past seventy years, both for fundamental reasons – understanding the structure and dynamics of a large variety of tunable, complex morphologies from a few simple principles – and industrial applications, namely enhanced oil recovery, further motivated by successive oil crises, extraction, decontamination, new fuels, and drug or cosmetic formulation. The founding fathers of the discipline have proposed the name of ‘microemulsion’ when they realized the internal structure of these solutions which were thought to be micron size, namely emulsified oil or water droplets in the appropriate continuous phase [2–4]. The adjective “isotropic” may be surprising, as some might still consider, e.g., a swollen lamellar phase a microemulsion [6,7], which however may also be counted to the separate class of liquid crystals, depending on if you consider structure or oil solubilization the most remarkable property. Meanwhile microemulsion research is a mature field. This manifests in about 6000 publications since 2010 which are related to microemulsions. Most of these articles are dealing with applications of microemulsions in the mentioned areas.

This review aims at highlighting progress in fundamental understanding of microemulsion structure and properties since the 1980s, in

particular using scattering techniques, as pioneered by the group of Dominique Langevin. After a brief introduction to microemulsions in general, where we summarize our understanding of the bending properties of surfactant layers, early and dominantly optical bulk studies are discussed. In the following years, the experimental approach was considerably deepened: thanks to small-angle scattering and quasi-elastic neutron scattering (QENS, in particular neutron spin-echo spectroscopy (NSE)) combined with contrast variation, access to static and dynamic microemulsion properties on the molecular scale became available. The review is then extended to more recent results on microemulsions close to interfaces (see Section 4). Finally, dynamics as seen by NSE are discussed in a separate section (see Section 5).

2. The physics of microemulsions

Due to the strong molecular immiscibility of oil and water, domains of both solvents are usually formed, separated by a surfactant (mono-) layer. The size and shape of these domains depend on the relative amount of oil and water, and surfactant. The usually encountered morphology for minority compounds, like a little oil with much water, are (discontinuous) oil droplets suspended in a continuous water phase, or vice versa. In mixtures with approximately equal volumes, both phases may become continuous, and bicontinuity will be discussed below. For more detailed information, we refer the reader to a general introduction to both physics and characterization of microemulsions published by Chevalier and Zemb [5].

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2.1. Bending properties

Besides the volumes of the phases, microemulsion structure depends crucially on the quantity and properties of the surfactant. Indeed, the amount of the latter defines the available specific surface S/V , as all oil-water interfaces need to be covered for energetical reasons: S/V is given by the product of surfactant concentration and head group area σ (σ contains not only steric interaction and might vary a bit with experimental conditions). Moreover, if we ignore solubility issues, the bending properties of the surfactant layer determine which type of morphology is accessible, and the strength of thermal fluctuation around these morphologies. The bending properties of surfactant monolayers depend on the molecular architecture and interactions, and may be tuned chemically [8]: e.g., by modifying the surfactant, or adding a co-surfactant [9], changing the temperature [10], adding salt [11], or more complex molecules like copolymers which can induce changes in the phase diagram, or contribute to changes in viscosity of the different phases [12–15]; similar effects have already been reviewed by Sottmann and co-workers [16].

The bending properties of surfactant layers were described in the 70s by Helfrich [17]. The Helfrich approach was originally developed for the description of lipid vesicles. However, it perfectly treats the bending properties of microemulsions of arbitrary morphology, including bicontinuous and in particular spherical microemulsion droplets [18,19]. This is due to the fact that microemulsion droplets only comprise a surfactant monolayer which much better corresponds to the Helfrich bending free energy as compared to vesicles. It is commonly expressed as a series expansion of the bending energy for the lowest curvatures. The free energy dF needed to bend a piece of monolayer of surface dA can then be expressed in terms of the two principal curvatures c_1 and c_2 , which are related to the principal radii of curvature by $c_i = 1/R_i$. The so-called Helfrich Hamiltonian [17] of the bending free energy reads:

$$F = \int_A \left[\frac{1}{2} \kappa (c_1 + c_2 - 2c_0)^2 + \bar{\kappa} c_1 c_2 \right] dA \quad (1)$$

The spontaneous curvature, c_0 , describes the state of lowest bending energy of the monolayer. Due to symmetry reasons, this term is zero for bilayers or balanced monolayers. Alternatively, the free energy can be formulated based on the total curvature $H = c_1 + c_2$, and the Gaussian curvature given by the product $K = c_1 c_2$. Note that different notations exist in the literature, sometimes preferring the average curvature ($H/2$), or the total spontaneous curvature $H_0 = 2c_0$, and similar variants. The above expression for the bending energy serves as definition of two material constants of the monolayer, the bending moduli, κ and $\bar{\kappa}$, which are sometimes called bending rigidity and saddle-splay modulus, respectively. Following Helfrich's approach, they have been related by Safran and coworkers to the molecular conformation of the surfactant chains [20], and by Kabalnov et al. to ion concentrations [11]. Their magnitude may further depend on additional interactions, like added electrostatic terms [21–23] and studies of electrostatic effects in both microemulsion systems [24] and pure surfactant systems [9,25,26] exist. Both moduli are in units of energy, i.e. do not refer to any length scale, which has the surprising consequence that the bending energy of a spherical shell (with $c_0 = 0$) is independent of its radius: $8\pi(\kappa + \bar{\kappa}/2)$. A non-zero spontaneous bending, however, introduces a length-scale, and a preferred radius is selected. In a droplet microemulsion, e.g., the maximum droplet radius obtained at emulsification failure leading to an excess phase is given by the inverse of c_0 , with corrections due to translational entropy and the bending moduli, see the discussion and references reported in Section 3.

The roles of κ and $\bar{\kappa}$ are quite different. It can be shown with the Gauss-Bonnet theorem, that the second term in Eq. (1), which is related to the Gaussian curvature, depends only on the topology of the surface, and in particular on the number of handles and independent pieces of membrane or monolayer [27]. This is particularly obvious in the phase

sequence of non-ionic bilayer phases governed by the surfactant-co-surfactant ratio, where $\bar{\kappa}$ can be shown to trigger morphology changes from vesicular [28], to lamellar, and finally to sponge phases [29,30]. Concerning this last and most intriguing phase, it should be noted that there is a close relationship between the sponge phase and bicontinuous microemulsions to be discussed below [31]. Having understood the influence of $\bar{\kappa}$, it follows that for a fixed topology of any given structure, local topology-preserving bending fluctuations are entirely determined by κ . Alternatively to Eq. (1), the bending energy can also be expressed in terms of the deviation of the packing parameter $p = \frac{V}{l\sigma}$ [32,33] of the molecules from their spontaneous value p_0 . Here, V is the molecular volume, and l the extended chain length. σ indicates the area per headgroup of the surfactant. Indeed, if one integrates over the monolayer thickness δ , the packing parameter is found to be linked to the curvature in order to comply to complete surface coverage:

$$p = 1 + H\delta + \frac{1}{3}K\delta^2 \quad (2)$$

as long as the topology remains unchanged [34]. This covering relationship allows rewriting the Helfrich Hamiltonian as $\kappa \cdot (p - p_0)^2$, with $\kappa^* = 2\kappa + \bar{\kappa}$ [35]. One sees that monolayers adopting configurations close to spontaneous packing can only be stable with respect to bending if κ^* is positive. Finally, the modulus κ can also be used to define a persistence length, exponentially increasing with κ , as the characteristic length above which fluctuations are large enough to decorrelate the orientation of the layer [36]:

$$\xi_k = \xi_0 \exp \frac{4\pi\kappa}{3kT} \quad (3)$$

where ξ_0 is a molecular length. Choice of pre-factors and renormalization of the bending constant by fluctuations are discussed by Binks et al. [37]. The concept of persistence allows understanding the formation of the sponge phase as a lamellar phase which loses its orientational order on scales of the persistence length and thus approaches a random surface. One may note that an alternative view of the sponge phase as a 'molten' periodic minimal surface favored by positive values of $\bar{\kappa}$ has been proposed [30]. Moreover, the bicontinuous microemulsion can be seen as an oil-swollen lamellar phase, and such pathways have been described in the literature [10].

As indicated above, the relative amount of oil and water, and the amount and the bending properties of the surfactant determine the microstructure. Using our knowledge of the evolution of the spontaneous curvature of the monolayer, the complex phase diagrams of microemulsions, like e.g. the different Winsor-phases, can be understood [38–40]. A high curvature towards oil may set a typical droplet size, and the surfactant concentration the number of droplets. This defines how much oil can be solubilized, and emulsification failure with supernatant oil will in general be found for higher oil concentrations – forming what is called a Winsor I domain in the phase diagram. If the spontaneous curvature is of opposite sign, inverse systems with solubilized water in a continuous oil phase will be found – in case of emulsification failure an excess water phase appears, forming a Winsor II domain. Close to zero curvature, bicontinuous structures have been conjectured [41] and been proven to exist by NMR self-diffusion and conductivity experiments [42–45]. In these Winsor III domains, both excess oil and water exist. If one now increases the amount of surfactant, more and more oil and water can be solubilized, up to a point where the excess phases disappear forming a single bicontinuous microemulsion phase. The phase behavior described here in the curvature-surfactant phase plane for equal quantities of oil and water has the shape of a fish and is called the Kahlweit-Strey fish diagram [39,46]. It gives a direct illustration of the fact that the topology of the phases can be tuned and even inverted [47,48], opening the road to chemical reactions either in droplets of either type used as micro-reactors, or at the (giant) interface of bicontinuous microemulsions, making use of both available solubility channels in the samples. The last point is e.g. of

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