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Perturbations of microemulsion droplets by confinement and adsorption of polymer

Jyotsana Lal and Loïc Auvray

Laboratoire Léon Brillouin (CEA-CNRS), CEN Saclay, 91191 Gif sur Yvette Cedex, France

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Abstract. — We perturb the structure of dilute microemulsion droplets by confining polymer chains inside the droplets and by adsorbing polymer on the surfactant shells from the outer phase. We observe the local structure changes by small-angle neutron scattering. The curvature fluctuations and the size distribution of the droplets increase by different possible mechanisms, an induced size polydispersity minimizing osmotic stresses in the first case, a lowering of the film rigidity in the second one. The polymer adsorption is observed by measuring the polymer-droplet cross-structure factor.

Polymers interacting [1a] with flexible surfactant layers [1b] may change their elasticity parameters, their shape, fluctuations, mutual interactions and affect deeply the system phase behaviour and rheological properties. These effects have important applications in food industry, cosmetics, oil recovery, but are still poorly understood. They begin to be investigated theoretically [2-5] and also experimentally in vesicles [6], lamellar phases [7] and microemulsions [8-11].

Microemulsions in particular allow the polymer chains to be localized in different geometries and in different solvents, polar or non-polar, and different types of polymer-surfactant interactions to be probed: hydrophobic, hydrophilic, attractive or repulsive.

We raise here two sets of questions: 1) to what extent can we confine non-adsorbing polymer chains inside microemulsion droplets, how do they probe the elastic properties of the layers, what are the induced structure changes? 2) what are the effects of polymer on the droplet structure and interactions when the chains are adsorbed from the outer phase?

The first question has already been investigated in references [9-11] by conductivity measurements, light scattering, fluorescence techniques [9, 10] and small-angle neutron scattering [11], at a rather macroscopic level. Here we focus our study on the local deformations of the droplets. The second question is still open to our knowledge. In both situations of polymer confinement and polymer adsorption, we characterize the local deformations of the droplets by small-angle neutron scattering and contrast matching methods. In most cases we adjust the neutronic indices of refractions of the constituents by mixing hydrogenated and deuterated compounds so that the polymer is invisible and the scattering signal arises either from the core
of the droplets or just from the surfactant layer.

The polymer confinement studies were performed mainly with poly(ethyleneglycol) (PEG) in water-in-oil microemulsions made of cyclohexane (a non-solvent of PEG), SDS (sodium dodecylsulfate), butanol as cosurfactant and brine at two salinities $I = 5.8\%$ (1 M) and 9% (in g/cm$^3$). These two values of the ionic strength yield a different spontaneous curvature of the surfactant layer $C_\theta$. $I = 1$ M is the optimal salinity of the Winsor system associated with the constituents and should correspond to a very small or vanishing spontaneous curvature [12]. $I = 9\%$ provides on the other hand a large spontaneous curvature stabilizing water in oil phases. We vary the droplet radius $R$ (determined by the water to surfactant ratio W/S in ml/g), the polymer concentration in water expressed here by the average number of chains per droplet, n and the polymer molecular weight ($M_w = 10000$ (Aldrich, polydispersity 1.08) and 36000 (Polymer Laboratory, polydispersity 1.04). Attempts of getting stable microemulsions with higher molecular weight $M_w = 50000$ were unsuccessful.

The maximum number of chains per droplet depends on the droplet radius and polymer molecular weight. For $M = 10000$, $n_{\text{max}} = 1.5$ at $R = 50$ Å ($W/S = 2$, $I = 5.8$ and 9%), it increases to $n_{\text{max}} = 2$ at $R = 75$ Å ($W/S = 3$, $I = 5.8$%) and $R = 100$ Å ($W/S = 4$, $I = 5.8$%). For $M = 36000$ $n_{\text{max}} = 1$ for $R = 75$ Å ($W/S = 3$, $I = 5.8$%). Let us investigate in detail the case $n = 1$ with 10000PEG. One chain in a 50 Å droplet represents an average polymer concentration in water $c_p = 3.17 \times 10^{-2} g/cm^3$, this is about 1/4 of the overlap concentration $c_p^*$ estimated from the value of the chain radius of gyration $R_g = 30$ Å with $c_p^*$ defined as $3N/4\pi R_g^3$ ($N$ polymerization index). However the chain end-to-end distance $R_t \approx 2.4R_g = 73$ Å is larger than the droplet radius, we thus approach a regime of strong confinement. In figure 1 we present a few scattering spectra of the microemulsions with and without polymer. In each case the spectra are observed in core contrast (hydrogenated polymer, H$_2$O, hydrogenated SDS and butanol, deuterated cyclohexane) and the water-to-oil volume ratio is 4%. The scattering intensity $S(q)$ from dilute, monodisperse bulk spheres of radius $R$ at concentration $c$ is given by $cV_c^2(\Delta n)^2[3(\sin qR - qR\cos qR)/(qR)^3]^2$ oscillating around a $q^{-4}$ decay at large scattering vector $q$, $V_c$ is the volume of the sphere, $\Delta n$ a contrast factor. Therefore the eventual deviations from the perfect spherical shape are observed in the most sensitive way by plotting the data as $q^4S(q)$ versus $q$. The curves exhibit classical features: i) an asymptotic Porod’s plateau proportional to the specific area $c_s \Sigma (c_s$ surfactant concentration, $\Sigma$ area per polar head), ii) a bump related to the droplet radius or, more precisely, to a quadratic average of the curvature [12] which depends on the size and shape polydispersity of the droplets [13]. There is no observable oscillation in the droplet form factor. This implies that the water droplets are very polydisperse and fluctuating, even without polymers [13]. The confinement of polymer does not change the asymptotic limit of the intensity, i.e. the area per polar head but enlarges the width of the bump and slows down the decays towards the Porod limit. This immediately implies that the size or shape polydispersity of the droplets is increased by the polymer. This effect decreases as the size of the droplets increases at constant $n$ and $M$ but increases as $M$ increases. We have also noticed that the effect of the polymer is much smaller on the microemulsions with the largest spontaneous curvature, the spectra (not displayed in Fig. 1) exhibit only very small changes.

This analysis can be made more quantitative by comparing the data with a particular model of polydisperse spheres (Fig. 1) [14-16], this will be reported in a forthcoming publication [17]. One might however argue that it is not fully satisfying to analyse the data only in terms of size polydispersity because the droplets exhibit both size and shape fluctuations [13, 15]. We take up this discussion at the end of this article. Clearly here the distribution of the droplet volumes is the important parameter which controls in first approximation the balance
between the confinement free energy of the chains \([17]\) and the droplet elastic energy. One may estimate, in agreement with our observations, that one or several chains imposing a local monomer concentration \(c_p\) cannot enter in a single droplet if \(c_p\) is larger than \(c_{p}^{*}\) and the film rigidity is of order \(k_B T\). Of course, it might be more favourable for the system to form larger droplets containing two or more chains while some smaller droplets would be empty. This induced polydispersity then depends on the spontaneous curvature of the surfactant layer, and should decrease if \(C_0\) is larger. This conclusion is also in agreement with our observations. Confining polymer is thus a sensitive way to probe the elasticity of surfactant film. By adjusting the elasticity parameters, one should be able to separate or sieve different molecular weight polymer chains (including proteins) by microemulsion droplets.

Our second way of perturbing the surfactant layers was to dissolve the polymer in the continuous phase outside the droplets. We used water-in-oil microemulsions (cyclohexane/brine \((I = 5.8\) or \(1\%) /\text{SDS}/\text{butanol or pentanol}\) where we dissolved several different hydrophilic polymers: POE (polyethyleneoxide, \(M_w = 105\), PVP (polyvinylpyrrolidone, \(M_w = 3 \times 10^5\), PNIPAM (poly-N-isopropylacrylamide, \(M_w = 2.2 \times 10^5, 10^6\)) known for interacting strongly with pure SDS \([1a]\).

Figure 2 shows one series of microemulsion spectra with and without polymers observed in core contrast (normal water, deuterated cyclohexane in volume fraction \(\Phi = 4\%\)). The scattering intensity decreases with POE and PVP and increases with PNIPAM. Thus POE and PVP increase the repulsive interactions between the droplets while PNIPAM seems to induce attractive interactions between the droplets. These attractive interactions may have different origins: i) repulsive polymer-surfactant interactions lead to depletion forces between the droplets \([19]\), ii) attractive polymer-surfactant interactions may lead to bridging the droplets by the chains \([20]\). The most sensitive way of characterizing these interactions is therefore to study the polymer-surfactant correlations. This is possible by measuring the polymer-droplet cross-structure factor with the contrast variation technique. This cross structure factor has to
be positive (at angle tending to zero) if the polymer-droplet interactions are attractive, it is negative or vanishing in the opposite case. For dilute droplets of volume \( V \) in concentration \( c \), the value at the angle tending to zero, \( S_{\text{mp}}(0) \), can be explicitly calculated, one gets:

\[
S_{\text{mp}}(0) = cV \int_{R}^{\infty} d^3r \delta \phi_p(r)
\]

where \( \delta \phi_p(r) \) is the integral of the profile of excess polymer volume fraction around one droplet. In our case, the contrast variation experiments are not easy. We have to match the core of the droplets with the film using deuterated surfactant and to take into account the cosurfactant (knowing the composition of the phases from dilution experiments). We have also to deal with a weak signal due to low concentrations of polymer. We did several series of experiments, one with POE (butanol as cosurfactant, water 1 M) and five with PNIPAM at different molecular weights, concentrations and droplet radii (pentanol as cosurfactant, water 1% salinity). This change was imposed because PNIPAM precipitates in the presence of butanol and also at high salinity. In order to minimize systematic errors and to obtain reproducible results, we observed that the signal of the droplets had to be weak and that the microemulsion contrast had to be chosen close to the droplet-water matching point. For POE, we could not detect any significant correlation between the polymer and the microemulsion structure, \( S_{\text{mp}}(q) = 0 \pm 0.1 \times 10^{-20} \text{ cm}^3 \) (Fig. 3). On the contrary, the PNIPAM cross structure factors are always positive at small angle. This shows clearly that PNIPAM does adsorb on the droplets, while POE does not, at least in a measurable amount. If we come back shortly to the experiments discussed in the first part, this implies that the effects observed with PEG chains (chemically identical to PEO) inside droplets are primarily sterical and not due to polymer adsorption. This PEO behaviour is at variance with the phenomena observed in SDS-PEO water systems [1a]. It could be an effect of the cosurfactant, but this has to be checked. As regards PNIPAM, we can now conclude that the rise in the intensity scattered at low \( q \) by the microemulsion is probably due to the adsorption of the chains and to a reversible bridging of

Fig. 2. — Intensity scattered by cyclohexane in water microemulsions in core contrast (pentanol, \( \text{H}_2\text{O} \) salinity 1%, \( \text{O}/\text{S} = 2 \), water to oil volume ratio 4%) with different hydrosoluble polymers (PVP, PEO, PNIPAM) in solution (\( c_p = 5 \times 10^{-3} \text{ g/cm}^3 \)).
Fig. 3. — Polymer droplet cross-structure factors (in $10^{20}$ cm$^{-3}$) for different polymers, different droplet sizes and different polymer concentrations. 

**PEO series:** ($\bigcirc$) $O/S = 2$, $M_w = 10^5$, $c_p = 5 \times 10^{-3}$; 
**PNIPAM series** $M_w = 10^6$: ($\times$) $O/S = 2$, $c_p = 5 \times 10^{-3}$, ($\bullet$) $c_p = 10^{-2}$; $O/S = 3$, ($\ominus$) $c_p = 3.3 \times 10^{-3}$, ($+$) $c_p = 6.6 \times 10^{-3}$; 
**PNIPAM series** $M_w = 2.2 \times 10^5$: ($\triangle$), $O/S = 2$, ($-$) $c_p = 5 \times 10^{-3}$

the droplets by the polymer, which remains to be studied more deeply.

To discuss the PNIPAM data more quantitatively, we use equation (1). Up to the (large) experimental uncertainties the values of $S_{mp}(q)$ at the lowest measured angle ($q = 10^{-2}$ Å$^{-1}$) only depend on the droplet radius but not on polymer concentration, nor on molecular weight, $S_{mp}(0) = (0.3 \pm 0.1) \times 10^{-20}$ cm$^3$ for the oil to surfactant ratio $O/S = 2$ ($R = 50$ Å) and $(0.8 \pm 0.3) \times 10^{-20}$ cm$^3$ for $O/S = 3$ ($R = 75$ Å). If all the polymer were adsorbed, the product $c \int_R^{\infty} d^3r \delta \phi_p(r)$ should be equal to the total polymer volume fraction in the sample $\phi_p$ and $S_{mp}(0)$ should be equal simply to the product $V \phi_p$. By comparing the experimental and calculated values of $S_{mp}(0)$, e.g. $S_{mp}(0) = 0.26 \times 10^{-20}$ cm$^3$ for $O/S = 2$, $\phi_p = 5 \times 10^{-3}$ and $S_{mp}(0) = 0.58 \times 10^{-20}$ cm$^3$ for $O/S = 3$, $\phi_p = 3.3 \times 10^{-3}$ (corresponding to the same polymer-to-surfactant ratio as for $O/S = 2$, $\phi_p = 5 \times 10^{-3}$), we observe that they are equal within the uncertainties for the given values of $\phi_p$ and deduce that the polymer adsorption saturates at these values. Assuming an area per polar head of 60 Å$^2$, we calculate then an adsorbed amount equal to 0.2 mg/m$^2$.

Finally, we return to the observation of the local microemulsion structure. To eliminate possible contamination by the polymer signal, we have made samples by matching exactly the PNIPAM and the water phase (with a 21% D$_2$O/H$_2$O mixture). In figure 4 we present the spectra obtained in film contrast, plotted as $q^2 S(q)$ because of the classical $q^2$ asymptotic behaviour of $S(q)$. We notice first that the oscillations in the spectrum of the microemulsion without polymer are very pronounced. The bare-oil-in water droplets are thus less fluctuating and more monodisperse than the equivalent inverse droplets. On the contrary the oscillations are smeared when polymer is added. This directly implies that polymer adsorption increases the fluctuations of the surfactant layer. Such an effect has been predicted theoretically but is still a subject of controversy [2, 3]: reversible polymer adsorption could decrease the surfactant film rigidity $K$ [3]. We can analyse the spectra in terms of sphere polydispersity (Fig. 4) and relate the polydispersity parameters to the elastic constants of the surfactant interfacial film [13, 16].
Fig. 4. — Intensity $S(q)$ of oil-in-water microemulsion without polymer (above) and with adsorbed invisible PNIPAM (below) observed in film contrast, plotted as $q^2 S(q)$ (in $\text{Å}^{-2} \text{cm}^{-1}$) versus $q$. The spectrum with polymer has been shifted downwards for clarity, the heights of the asymptotic plateaux of the two samples are otherwise identical. The continuous lines are best fits to the scattering by polydisperse spherical shells distributed according to the Schultz-Flory law.

Assuming that the mean square amplitude of the droplet fluctuations scales as $k_B T / K$ [13], we can estimate the ratio of the two values of $K$ before and after adsorption if one neglects the variations of the other elastic parameters, the spontaneous curvature and the Gaussian rigidity. We find $K_{\text{ads}} / K_0 \approx 0.6$. The increase of flexibility is, as predicted, rather large. To justify our assumptions and measure the different elastic constants, independently, one should distinguish the fluctuations of size (fluctuations of the droplet radii) from the fluctuations of shape (fluctuations of the local curvature). This is a difficult problem which will be solved hopefully by future neutron spin echo experiments [15]. There is however another way (in principle) to solve this problem that we briefly mention here. The asymptotic behaviour of the intensity scattered by the surfactant layer (of thickness $d$) is given by the following expression [21], valid in the range $qR \gg 1$, $qd \ll 1$:

$$q^2 i_r(q) = 2\pi c_0 \Sigma d^2 (\Delta n)^2 \left\{1 - \langle (C_1 - C_2)^2 \rangle / 8q^2 \right\}$$

(2)

$\Delta C^2 = \langle (C_1 - C_2)^2 \rangle$ is the quadratic average of the difference between the principal curvatures of the surfactant layer, it shows the droplet asphericity and shape fluctuations independently of the size polydispersity. This expression predicts that the $q^2 i_r(q)$ plateau is reached from below if the oscillations of the droplet form factor are averaged (see Fig. 4). It also predicts a straight line and a negative intercept proportional to $\Delta C^2$ if one plots $q^4 i_r(q)$ vs. $q^2$. In our experiment $\Delta C^2$ (the intercept) is very small and not measurable in the absence of polymer, whereas we measure a non-vanishing $\Delta C^2 = 1.4 \times 10^{-2} \pm 10^{-2} \text{Å}^{-2}$, when the polymer is adsorbed. This value is surprisingly large since $\Delta C^{-1}$ is of order of the layer thickness. Its possible physical origin and the technical problems associated with the use of expression (2) will be discussed in a more detailed publication [17].

In conclusion we have shown that polymer may strongly perturb surfactant layers and that the induced deformations are directly observable. Both confinement and adsorption of polymers may increase the fluctuations of the surfactant layers of microemulsion droplets by different
mechanisms: induced size polydispersity minimizing osmotic stresses in the first case, possible lowering of the film rigidity in the second one.

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References

[21] This expression has been discovered independently by many people (including us):
   but it has to be credited to Crowley T., Ph. D. Thesis Oxford (1984).