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Stability of additive-free water-in-oil emulsions

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Abstract

We calculate ion distributions near a planar oil–water interface within nonlinear Poisson–Boltzmann theory, taking into account the Born self-energy of the ions in the two media. For unequal self-energies of cations and anions a spontaneous charge separation is found, such that the water and oil phases become oppositely charged in slabs with a typical thickness of the Debye screening length in the two media. From the analytical solutions, the corresponding interfacial charge density and the contribution to the interfacial tension is derived, together with an estimate for the Yukawa potential between two spherical water droplets in oil. The parameter regime is explored where the plasma coupling parameter exceeds the crystallization threshold, i.e. where the droplets are expected to form crystalline structures due to a strong Yukawa repulsion, as recently observed experimentally. Extensions of the theory that we discuss briefly, include numerical calculations on spherical water droplets in oil, and analytical calculations of the linear PB-equation for a finite oil–water interfacial width.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The making and breaking of oil–water emulsions is not only a problem of extreme importance in chemical, oil, pharmaceutical, food and cosmetics industries, but is also a scientifically fascinating topic. It is well-known that the intrinsic tendency of oil and water to demix can be slowed-down or delayed by adding surfactants or colloidal particles to the mixture. These additives strongly adsorb to the oil–water interface, which lowers the interfacial tension (the main driving force for demixing) and/or provides a kinetic barrier that prevents droplet coalescence [1, 2]. Recently however, it was observed that emulsions of water droplets dispersed in somewhat polar oils can be stable for a long time (so far, for more than 18 months), *without any additives* [3]. Moreover, the water droplets, which are of micrometer dimensions in these experiments, spontaneously form crystalline structures with lattice spacings of the order of 5–15 μm . These observations suggest long-ranged electrostatic droplet–droplet repulsions due to a net water droplet charge stemming from a preferential uptake of ions from the oil [3–5]. Theoretical calculations, based on Poisson–Boltzmann theory for monovalent ions in the geometry of a planar water–oil interface, showed that the order of magnitude of the charge separation process, caused by the different cationic and anionic Born self-energies in oil

and water, is indeed sufficiently strong to explain the observed stability and crystallization [4, 5], at least qualitatively. These predictions are based on the assumption of a pairwise screened Coulomb potential of the charged water droplets through the oil, and an explicit empirical crystallization condition based on simulations [6, 7].

In this paper we will explore the ionic charge separation at the planar oil–water interface, and the resulting crystallization regime of water droplets dispersed in oil in the high-dimensional parameter space of salt concentration, dielectric constant of the oil, ionic sizes and self-energies, droplet size and droplet concentration. The analytic solution admitted by the nonlinear Poisson–Boltzmann equation in the planar geometry [8, 9] allows for such a detailed exploration efficiently; the effects of droplet curvature were recently studied numerically [10]. We will find that crystallization of water droplets is only possible for sufficiently large droplet radii ($\gtrsim 100$ nm), sufficiently large water content (volume fraction $\gtrsim 10^{-3}$), and sufficiently polar (but not too much) oils with dielectric constants between 4 and 10. In addition we will also give an explicit expression for the change of the interfacial tension between oil and water due to the ionic segregation over the two media. This change is found to be negative, proportional to the square-root of the ionic strength, and small on the scale of the bare oil–water tension, at least

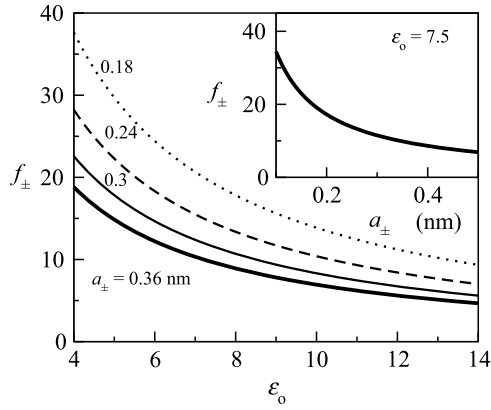


Figure 1. The Born self-energy f_{\pm} in units of $k_B T$ as a function of the dielectric constant ϵ_o , for several ionic radii a_{\pm} , and as a function of the ionic radius at $\epsilon_o = 7.5$ (inset).

within the present model. We will discuss the sensitivity of these findings to details of the interfacial structure as described recently in [11].

2. Poisson–Boltzmann theory for a planar oil–water interface

The liquids are considered as structureless homogeneous linear dielectric media, filling the two half spaces $z < 0$ (water) and $z > 0$ (oil), forming a flat interface at $z = 0$. The relative dielectric constant is a step function, $\epsilon(z) = \epsilon_w$ ($z < 0$) and $\epsilon(z) = \epsilon_o$ ($z > 0$). The grand potential functional per unit area of the variational density profiles $\rho_{\pm}(z)$ of the cations (+) and anions (–) in units of $k_B T \equiv 1/\beta$ is given by [5, 10–12]

$$\beta\Omega[\rho_{\pm}] = \sum_{\alpha=\pm} \int_{-\infty}^{\infty} dz \rho_{\alpha}(z) \times \left(\ln \frac{\rho_{\alpha}(z)}{\rho_w} - 1 + \beta V_{\alpha}(z) + \frac{\alpha}{2} \phi(z, [\rho_{\pm}]) \right), \quad (1)$$

with the self-consistent dimensionless electrostatic potential $\phi(z, [\rho_{\pm}])$, and with the external potential acting on the ions

$$\beta V_{\pm}(z) = \begin{cases} 0, & z < 0; \\ \frac{e^2}{2a_{\pm}k_B T} \left(\frac{1}{\epsilon_o} - \frac{1}{\epsilon_w} \right) + g_{\pm} \equiv f_{\pm}, & z > 0, \end{cases} \quad (2)$$

representing the Born self-energy and an additional specific solvation energy g_{\pm} (e.g. due to hydration, hydrogen bonding, local modification of dielectric constant [13–15]), which is set either to 0 or to 4 here, in order to study specific effects. The salt concentration in bulk water is denoted by ρ_w , e is the elementary charge, and a_{\pm} is the ionic radius. Both $\phi(z)$ and $V_{\pm}(z)$ are gauged to zero in the bulk water phase ($z \rightarrow -\infty$). Figure 1 shows f_{\pm} as a function of the oil dielectric constant ϵ_o , and ionic radius a_{\pm} (inset), for $g_{\pm} = 0$. Typical values for the self-energies are 5–20 $k_B T$, and self-energy differences are of the order of 1–10 $k_B T$ for ionic radii differing by, say, 1 Å.

Minimization of the functional (1) with respect to ρ_{\pm} , together with the Poisson equation, yields

$$\rho_{\pm}(z) = \rho_w \exp(-\beta V_{\pm}(z) \mp \phi(z)), \quad (3)$$

which can be rewritten as the Poisson–Boltzmann equation

$$\phi''(z) = \begin{cases} \kappa_w^2 \sinh(\phi(z)), & z < 0; \\ \kappa_o^2 \sinh(\phi(z) - \phi_D), & z > 0, \end{cases} \quad (4)$$

subject to the Neumann boundary conditions

$$\begin{aligned} \lim_{z \rightarrow -\infty} \phi'(z) &= \lim_{z \rightarrow \infty} \phi'(z) = 0; \\ \lim_{z \uparrow 0} \epsilon_w \phi'(z) &= \lim_{z \downarrow 0} \epsilon_o \phi'(z), \end{aligned} \quad (5)$$

which are dictated by the vanishing of the electric displacement field in the bulk and its continuity at the interface. The Donnan potential of the bulk oil is $\phi(z \rightarrow \infty) \equiv \phi_D = \frac{1}{2}(f_- - f_+)$, the inverse Debye screening lengths are given by $\kappa_i = \sqrt{8\pi e^2 \rho_i / \epsilon_i k_B T}$, $i \in \{o, w\}$, and the bulk salt concentration in oil satisfies $\rho_o = \rho_w \exp(-\frac{1}{2}(f_- + f_+))$. The general solution of (4) is

$$\phi(z) = \begin{cases} 4 \operatorname{arctanh}(C_w e^{\kappa_w z}), & z < 0; \\ 4 \operatorname{arctanh}(C_o e^{-\kappa_o z}) + \phi_D, & z > 0, \end{cases} \quad (6)$$

with integration constants that follow from the boundary conditions (5) as

$$\begin{aligned} C_w &= \frac{n + \cosh \frac{\phi_D}{2} - D}{\sinh(\phi_D/2)}, \\ C_o &= -\frac{1 + n \cosh(\phi_D/2) - D}{n \sinh(\phi_D/2)}, \end{aligned} \quad (7)$$

where $n \equiv \epsilon_w \kappa_w / \epsilon_o \kappa_o$, and $D \equiv \sqrt{n^2 + 2n \cosh \frac{\phi_D}{2} + 1}$. The derivation so far is equivalently presented in [8, 9]. A separation of charge is found near the interface for unequal self-energies, comprising a cloud of net charge in the water phase of typical width κ_w^{-1} and one in the oil phase of typical width κ_o^{-1} , with a charge per area at the water side given in units of e by

$$\sigma_w = \int_{-\infty}^0 dz (\rho_+(z) - \rho_-(z)) = -\frac{8\rho_w}{\kappa_w} \frac{C_w}{1 - C_w^2}; \quad (8)$$

the compensating charge resides at the oil side as the system is globally neutral. In section 3 we will assume that the surface charge density of a water droplet in oil is equal to σ_w in order to calculate the pair potential between the droplets.

3. Screened Coulomb potential between water droplets in oil

We now consider N oil-dispersed water droplets of radius a in a volume V , such that the typical droplet–droplet separation is $R = (V/N)^{\frac{1}{3}}$ and the water volume fraction is $x = \frac{4}{3}\pi a^3 N/V = \frac{4}{3}\pi (a/R)^3$. We assume that each water droplet has a charge $Z = 4\pi a^2 \sigma_w$, where σ_w follows from the nonlinear PB theory (8), and reconsider a screened Coulomb (Yukawa) potential between two droplets

$$V_{\text{Yuk}}(r) = \frac{(Ze)^2}{\epsilon_o} \left(\frac{e^{\kappa_o a}}{1 + \kappa_o a} \right)^2 \frac{e^{-\kappa_o r}}{r}, \quad (9)$$

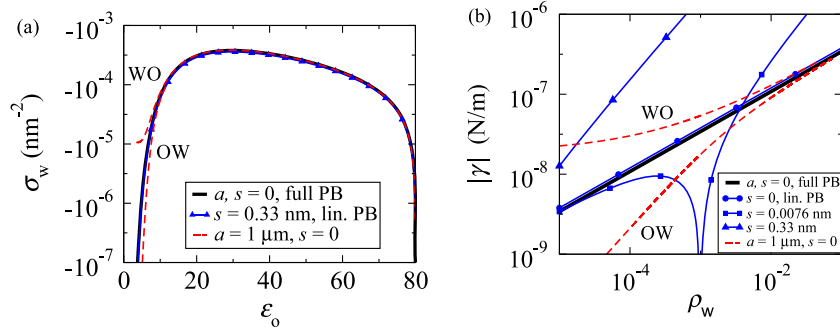


Figure 2. (a) Interfacial charge density as a function of the oil dielectric constant. (b) Excess interfacial tension as a function of ionic strength, at $\epsilon_o = 7.5$. If the interfacial width $s = 0$, the planar calculations clearly show a square-root behavior. The sign of γ is negative. The dashed lines show the numerical results from the PB theory in spherical geometry, for water droplets of radius $a = 1$ μm (WO), and equal sized oil droplets in water (OW) [10]. The thin lines show the result of the planar linearized PB theory with interfacial width s , for which γ has a linear asymptote and positive sign in the high- ρ_w limit [11], if $s \neq 0$.

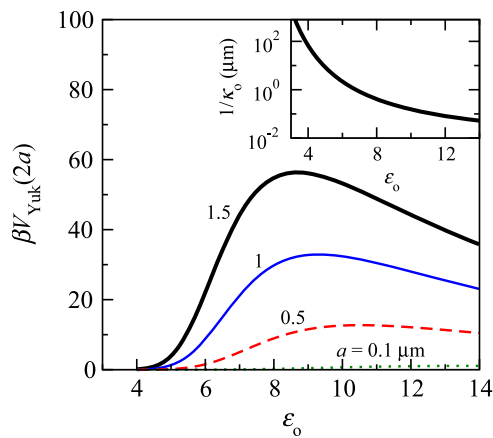


Figure 3. The Yukawa potential at contact and the Debye screening length in oil (inset) as a function of the oil dielectric constant ϵ_o , at $\rho_w = 10^{-3}$ M, $(a_+, a_-) = (0.36, 0.3)$. The contact value $V_{\text{Yuk}}(2a) > 1 k_B T$ only for $\epsilon_o > 4$ and droplet radii $a > 100$ nm. On the other hand, the range of the Yukawa potential decays rapidly for $\epsilon_o > 10$ (inset); for droplets with a radius $a > 100$ nm, the value of $\kappa_o a \gg 1$ above $\epsilon_o \gtrsim 12$. Therefore, significant long range Coulomb interactions are only expected between $4 \lesssim \epsilon_o \lesssim 10$.

with r as the center-to-center separation between the droplets. According to simulation results, crystallization of such a Yukawa system occurs if $\Gamma \gtrsim 106$ [6, 7], with the coupling parameter Γ defined by

$$\Gamma \equiv \beta V_{\text{Yuk}}(R) \left(1 + \kappa_o R + \frac{(\kappa_o R)^2}{2} \right). \quad (10)$$

Although this condition has been confirmed only for point-Yukawa systems, it is expected to hold also for finite droplets as long as $V_{\text{Yuk}}(2a) \gtrsim 10 k_B T$ and $\kappa_o a \lesssim 1$, conditions that are easily met for micron-sized droplets, provided $4 < \epsilon_o < 10$, as can be seen in figure 3.

The electrostatic contribution γ to the interfacial tension can be calculated analytically by evaluating the functional (1) with the equilibrium profiles, minus the functional evaluated with the step profile $\rho_{\pm}(z < 0) = \rho_w$, $\rho_{\pm}(z > 0) = \rho_o$ [10, 11, 15]. After a tedious but straightforward calculation

we find

$$\beta\gamma = -\frac{16\rho_w}{\kappa_w} \frac{C_w}{1 - C_w^2} (C_w - C_o) \propto -\sqrt{\rho_w}, \quad (11)$$

which is symmetric under exchanging $w \leftrightarrow o$ and where the proportionality to $\sqrt{\rho_w}$ follows from $\kappa_w \propto \sqrt{\rho_w}$ and the fact that C_w and C_o are independent of ρ_w . Typical values of the excess interfacial tension are at most $\mathcal{O}(\mu\text{N m}^{-1})$, and are therefore vanishingly small compared to the value of the bare oil–water interfacial tension ($\mathcal{O}(10 \text{ mN m}^{-1})$).

4. Numerical results

As standard parameters we use $\epsilon_o = 7.5$ and $\rho_w = 10^{-3}$ M, which are close to the experimental values of [3, 4], $g_{\pm} = 0$ and $(a_+, a_-) = (0.36, 0.3)$ nm. The surface charge density σ_w of the interface appears to be strongly dependent on the oil dielectric constant, keeping the ionic radii fixed. Typically it is of the order of $\mathcal{O}(10^{-4})$ elementary charges nm^{-2} in the range $10 < \epsilon_o < 70$, and decays rapidly to 10^{-7} nm^{-2} for $\epsilon_o = 4$, see figure 2(a). Numerical calculations in the spherical geometry [10] predict a smaller σ_w for oil-in-water droplets, and a larger one for water-in-oil droplets in the regime $4 < \epsilon_o < 10$, as shown in figure 2(a) for a radius $a = 1$ μm . The excess interfacial tension γ differs correspondingly for finite droplets, figure 2(b). The linearized PB theory that takes into account a finite interfacial width $s \neq 0$ [11] between oil and water agrees quantitatively with the present results for σ_w , indicating that the charge separation is hardly dependent on $s = \mathcal{O}(10^{-1})$ nm, even if the ions are effectively excluded in a band of several tenths of nanometers. On the other hand, above a certain crossover ionic strength, the same theory predicts a qualitatively different asymptotic behavior of the excess interfacial tension, being positive and proportional to the ionic strength ρ_w , figure 2(b). One can understand that as follows: whereas the charge separation is hardly affected by the interfacial width s , the adsorption of particles, and hence the interfacial tension, is sensitive to the effective exclusion in a region of width s . As the absolute value of the excess interfacial tension is vanishingly small compared

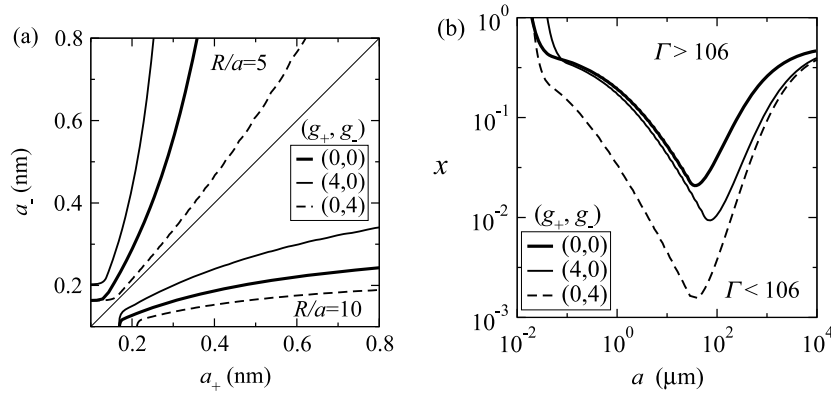


Figure 4. (a) The ionic radii (a_+ , a_-) for which $\Gamma > 106$ for some physically achievable ionic strength ρ_w . The droplets crystallize in the area between the curves and the horizontal axis ($R/a = 10$), and between the curves and the vertical axis ($R/a = 5$), respectively. The lines can be mirrored on the diagonal since there is a symmetry under $a_+ \leftrightarrow a_-$, together with $g_+ \leftrightarrow g_-$. The thin and dashed lines show the results if one of the ionic species has an additional solvation energy (independent of ρ_w and ϵ_o) of $g_{\pm} = 4$. The dielectric constant of the oil is $\epsilon_o = 7.5$ and droplet radius $a = 1.5 \mu\text{m}$. (b) The volume fractions of water x and droplet radii a for which $\Gamma > 106$ for some physically achievable ionic strength ρ_w , for several combinations for g_{\pm} .

to the bare oil–water interface, $\gamma_{ow} = \mathcal{O}(10 \text{ mN m}^{-1})$, γ will be considered not to contribute to the stability of the system of interest here.

We expect that water droplets in oil can only form crystalline structures if long range interactions are present ($\kappa_o a \lesssim 10$), and if the repulsion is sufficiently strong. Figure 3 shows the Yukawa potential (9) at contact, $V_{\text{Yuk}}(2a)$, for several droplet sizes as a function of ϵ_o , revealing that these two conditions already impose strong restrictions on the dielectric constant and the size of the particles. The inset of figure 3 shows for instance that the screening length in oil decays from 10 to 100 μm at $\epsilon_o = 4$ –100 nm at $\epsilon_o = 12$, for $\rho_w = 1 \text{ mM}$, while the main part of figure 3 shows contact potentials that exceed $10 k_B T$ for $\epsilon_o \simeq 6$ –12, provided the droplet size is in the micron regime. Thus one only expects crystallization to be possible for micron-sized water droplets in oils that are sufficiently polar ($\epsilon_o \gtrsim 4$) to have enough charge (see also figure 2(a)), but not too polar ($\epsilon_o \lesssim 12$) to have a long enough range κ_o^{-1} of the repulsions. This regime of ϵ_o is in remarkably good agreement with the experimentally found regime [3, 4].

The actual parameter regime where droplets are expected to form crystalline structures, on the basis of $\Gamma > 106$, is depicted in figure 4, where the varied parameters are the ionic radii a_+ , a_- (figure 4(a)) and the volume fraction and droplet radius x , a (figure 4(b)). The lines show the envelopes of the regimes $\Gamma > 106$ for all physically achievable ionic strengths ρ_w . Variations of the external potential $\beta V_{\pm}(z)$ by taking a non-zero g_{\pm} are seen to result into a significantly modified crystallization regime. Other solvation effects, e.g. hydration, hydrogen bonding, local alignment of dipolar fluid molecules, are therefore expected to be important for a proper quantitative picture. We examined this for $g_{\pm} = 4$ (figure 4), and found it to be considerable compared to $|f_+ - f_-| \simeq 2$ for the present parameters, but small compared to $f_{\pm} \simeq 12$. Figure 4(b) shows that micron-sized droplets, for our standard parameter set, tend to crystallize at $x \simeq 10^{-2}$ – 10^{-1} , which is somewhat higher than the experimentally observed regime $x \simeq 10^{-3}$ – 10^{-2} [3, 4]. A similarly relatively high theoretical value

for the crystallization volume fraction was found in [10], where curvature effects were studied, with $g_{\pm} \equiv 0$. Combining these results with those of figure 4(b) suggests that the experimental results may only be quantitatively explained by taking both curvature and specific solvation effects ($g_{\pm} \neq 0$) into account. This problem is left for future studies.

5. Concluding remarks

By means of a nonlinear Poisson–Boltzmann theory, that takes into account the Born self-energies of the ions [8, 9], and a specific solvation energy [13–15], ionic equilibrium distributions near an oil–water interface were calculated. A difference in self-energy was found to lead to a Donnan potential and charge separation near the interface. The analytical expression for the charge of the medium per area of interface agrees roughly with the numerical results of the Poisson–Boltzmann theory in spherical geometry [10], although the planar charge density is somewhat underestimated compared to the value for micron-sized water droplets in oils with $\epsilon_o < 10$. The charge is in good quantitative agreement with a linearized Poisson–Boltzmann theory that takes into account a finite interfacial width s [11], showing independence of the charge on s . For slightly polar oils, i.e. $4 < \epsilon_o < 10$, the typical charge of micron-sized water droplets ranges between 10 and 1000 elementary charges and the Debye screening lengths range between $0.1 < \kappa_o a < 10$, such that the particles repel each other electrostatically by many $k_B T$, even if their centers are several radii apart. On the basis of an empirical crystallization condition [7] we found a relatively narrow regime in the high-dimensional parameter space, where water droplets in oil are expected to form crystalline structures, namely only when $4 < \epsilon_o < 10$ (in striking agreement with experimental findings [3]), $x \gtrsim 0.001$, $a \gtrsim 100 \text{ nm}$, and a sufficiently large difference exists between the ionic self-energies $|f_+ - f_-| \gtrsim 1 k_B T$. The spontaneous charging of the water droplets might play an important role in the production and stabilization of emulsions with rather polar oils, since we

have seen that by a judicious choice of the type of oil and salt ions, water droplets can be stabilized by these, sometimes surprisingly strong, electrostatic effects alone.

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