Chapter 7

Pickering Stabilisation

ABSTRACT

In this chapter we investigate the interfacial properties of Pickering emulsions. Based upon findings that indicate these emulsions to be thermodynamically stable, we devise a thermodynamic theory assuming the droplets to be stable inspired by a theory originally derived for swollen micelles.
7.1 Introduction

It is well known that oil \(^1\) does not mix with water unless when vehemently shaken or when an emulsifying agent is added. The ordinary emulsions then formed, abundant in many food and daily life products, are characterized by big polydisperse oil drops which eventually will demix due to drop coalescence. In order to stabilise these emulsions the oil and water mixtures are usually exposed to prolonged periods of mechanical agitation and emulsifiers are added in the form of surfactants which adsorb to the bare oil-water interface thus preventing drop coalescence.

Another class of emulsions, the microemulsions, are characterized by a small stable droplet size in the order of \(\sim 100 \, \AA\). The small size of the droplets explains the colorless appearance of these emulsions. Unlike ordinary emulsions, microemulsions are usually obtained upon mixing the ingredients\(^2\) without the requirement of the high shear conditions necessary to stabilize ordinary oil-water emulsions yet are considered thermodynamically stable, i.e. microemulsions are a distinct thermodynamic phase. Depending on the type of surfactant and concentration of the components involved several microemulsion phases exist: water-in-oil droplets, oil-in-water droplets and even bicontinuous structures are known to be formed.

In the classical Pickering emulsion [3], the emulsion is stabilised by the adsorption of small colloidal particles at the oil-water interface. Opposed to the case of surfactant stabilised emulsions, where the shape and chemical properties of the surfactant molecules determine the emulsifying behaviour, in Pickering emulsions the oil droplet is stabilised by a reduction of the bare oil-water interface by adsorption of small particles. The parameter of choice here to describe these Pickering emulsions is the contact angle of the adsorbed particles. It has been shown that for contact angles in the range \(30^\circ - 90^\circ\) oil-in-water emulsions are formed, whereas larger values of the contact angle lead to water-in-oil emulsions. Stabilising emulsions using nanoparticles is not limited to the class of Pickering emulsions. In commercial products, particle attachment is controlled by using both surfactants and colloidal particles which lead to a new class of emulsions. Recently, people even succeeded stabilising foams using nanoparticles [167, 168]. Stabilising foams, however, is an active process, i.e. one also has to supply sufficient (mechanical) energy to prepare these particle-stabilised foams.

For a long time, the stabilisation of the Pickering emulsion was attributed to a kinetic barrier resulting from a viscosity increase of the continuous medium between the Pickering droplets, or to the mechanism of particle adsorption itself. Recently, Sacanna et. al. [169] reported on a monodisperse emulsion created from water, oil and nanoparticles. The oil phase was of the methacrylate type and the nanoparticles employed were all charged but varied in nature (silica, iron-oxide and cobalt-ferrite). Under the appropriate conditions these constituents self-assemble into stable, 

\(^1\)“Oil” and “water” are generic terms: one should read oily phase and the water phase which both could contain many components.

\(^2\)In general oil, water, surfactant and co-surfactant.
monodisperse droplets with diameters in the range of $30 - 150$ nm. As in the case of microemulsions, these Pickering emulsions form without the need for any mechanical agitation. This observation in combination with the fact that one observes a spontaneous evolution towards one droplet size after mixing leads to the speculation that the Pickering emulsion is a thermodynamically stable state just like in microemulsions.

From another recent study \cite{170} we can infer that Pickering emulsions are most stable when the Pickering droplets are homogeneously covered by nanoparticles. This implies that the Pickering drops should be large ($> 100$ nm) since small droplets cannot be covered completely. Any “bare” parts of the oil-water interface will lead to drop coalescence/flocculation over time since the system always strives to minimize the total interfacial area of the oil-water interface. This means that Pickering emulsions in which the droplets are small are expected to destabilize (e.g. by creaming) over time.

The goal in this chapter is to analyze the Pickering emulsion using a theory originally derived for microemulsions. By using the Gibbs adsorption equation we derive expressions for the surface tension and compare with the experiments done by Sacanna et al. \cite{169}. We end with some conclusions.

### 7.2 Thermodynamics

In what follows we largely follow the analysis presented by Ruckenstein \cite{171}. We assume water to be the continuous phase and the Pickering droplets to consist of the dispersed oil phase. In order to simplify the analysis it will be assumed that

- the colloidal particles are only soluble in the continuous phase or are adsorbed on the surface of the Pickering droplet.
- the Pickering droplets are spherical with radius $R$ and are uniform in size

In our system we keep the volume $V$, total amount of particles $N_i$ of component $i$ and the temperature $T$ fixed, so that the thermodynamic potential of choice is the Helmholtz free energy. It reads

$$F = \sigma A + \sum_i \mu_i N_i - p_1 V_1 - p_2 V_2 + F_{\text{ent}}, \quad (7.1)$$

where $i$ marks a summation over the components (in this case water, oil and colloid), $V_1, V_2$ are the volumes of the continuous and dispersed phases respectively with pressures $p_1, p_2$ and $F_{\text{ent}}$ is due to the dispersion of the drops in the medium and is entropic in nature. The surface tension $\sigma$ is the surface tension of the oil-water interface coated by the colloidal particles which we will assume to depend on the radius of the Pickering droplet $\sigma = \sigma(R)$. In appendix E we present a detailed analysis of the surface tension in a Pickering droplet.

From the free energy we can construct the phase diagram but here we focus on the equilibrium properties of $N_p$ Pickering droplets.
If \( \phi = \frac{4\pi N_p}{3} R^3 \) denotes the volume fraction of the Pickering droplets, then the interfacial area per unit volume is \( A/V = 3\phi/R \). Using this constraint we then have for the free energy density

\[
f \equiv \frac{F}{V} = \sigma \frac{3\phi}{R} + \sum_i \mu_i \rho_i - p_1 \phi_1 - p_2 \phi_2 + f_{\text{ent}}, \tag{7.2}
\]

where the partial volumes fractions \( \phi_1 \) and \( \phi_2 \) are related to the volume fraction of Pickering droplets by \( \phi_1 = 1 - \phi \) and \( \phi_2 = \phi \). The pressures in the continuous phase and inside the drop are related according to Laplace’s law \( p_2 = p_1 + 2\sigma/R \). The equilibrium drop radius \( R_e \) can be determined by using

\[
\left( \frac{\partial f}{\partial R_{e}} \right)_{N_i, p_1, T} = 0. \tag{7.3}
\]

Performing the differentiation one obtains

\[
-3\phi R_e^2 \sigma(R_e) - p_1 \left( \frac{\partial \phi_1}{\partial R_e} \right) - p_2 \left( \frac{\partial \phi_2}{\partial R_e} \right) + \left( \frac{\partial f_{\text{ent}}}{\partial R_e} \right) = 0. \tag{7.4}
\]

Using Laplace’s law and noting that \( \phi_1 + \phi_2 = 1 \), this can be rewritten as

\[
-\sigma(R_e) \left[ \frac{2}{R_e} \left( \frac{\partial \phi}{\partial R_e} \right) + \frac{3\phi}{R_e^2} \right] + \left( \frac{\partial f_{\text{ent}}}{\partial R_e} \right) = 0. \tag{7.5}
\]

Note that the surface tension now depends on the drop’s radius \( R \). Since in general \( d\phi/dR \ll \phi/R \) we can rewrite Eq.(7.5) to [171]:

\[
-\frac{3\phi}{R_e^2} \sigma(R_e) + \left( \frac{\partial f_{\text{ent}}}{\partial R_e} \right) = 0. \tag{7.6}
\]

This equation determines the equilibrium drop’s radius \( R_e \) to be determined next. The above treatment is valid only if the Pickering drop’s radius \( R_e \) is sufficiently large compared to the interfacial thickness. In order to calculate the equilibrium radius of the Pickering droplets we now turn to the calculation of the interfacial tension.

### 7.2.1 Calculating the Interfacial Tension

We employ an approach which models the interfacial layer as a (curved) surface film. Such a film is characterised by the surface tension \( \sigma_{ow} \) of the water/solvent phase and a surface pressure \( \pi(T, A) \) which in general will depend on the temperature \( T \) and area per adsorbed colloid \( A \). This quantity is experimentally accessible due to the relation \( A = 1/\Gamma \) with \( \Gamma \) the adsorption of colloidal particles. We then have that the surface tension of the film with the adsorbed particles can be calculated from

\[
\sigma = \sigma_{ow} - \pi. \tag{7.7}
\]
The Gibbs adsorption equation reads
\[ d\pi = -d\sigma = \sum \Gamma_i d\mu_i. \] (7.8)

In the following we consider the formation of droplets at constant external pressure and temperature and consider the surface excess of oil and water to be negligible. Double layer effects are also ignored at the moment. The adsorption equation now becomes
\[ d\pi = \Gamma_c d\mu_c. \] (7.9)

Furthermore, when the concentration of colloids \( c \) in the bulk is sufficiently small, its chemical potential can be written as
\[ \mu_c = \mu_c^\ominus + k_B T \ln c/c^\ominus, \] (7.10)

where \( \mu_c^\ominus \) is the standard chemical potential, \( c^\ominus \) a reference bulk concentration, \( k_B \) is Boltzmann’s constant and \( c \) the concentration of colloids in the bulk\(^3\). If we now combine Eq. (7.9) and Eq. (7.10) one obtains
\[ \Gamma_c = \frac{1}{k_B T} \frac{d\pi}{d \ln c}. \] (7.11)

This equation relates the adsorbed amount of colloids to the surface pressure. In order to calculate the surface tension we thus need information regarding the surface pressure \( \pi \). Here we use Szyskowski’s equation given by [172]
\[ \pi = \alpha \ln \left( \frac{c}{\beta c + 1} \right), \] (7.12)

where \( \alpha, \beta \) are constants. Several choices can now be made for the surface excess amount of colloids. Here we take a Langmuir isotherm [173],
\[ \Gamma_c = \Gamma_c^\infty \frac{c}{k + c}, \] (7.13)

where \( \Gamma_c^\infty \) is the adsorption at closest packing and \( k \) is a temperature dependent rate function [174]. It is related to the heat of adsorption via
\[ k = k^\ominus \exp \left( \frac{\Delta \mu_{\text{ads}}}{k_B T} \right), \] (7.14)

where \( k^\ominus \) is the molarity of water (\( k^\ominus = 33.35 \) molecules /\( nm^{-3} \)) and \( \Delta \mu_{\text{ads}} \) is the chemical potential difference for a colloidal particle due to adsorption (a negative quantity in general). Eq. (7.13) is derived by neglecting any interactions between the adsorbed colloidal particles but does describe a monolayer reasonably well [175]. One

\(^3\)Formally the activity \( a \) should replace \( c \). However, here we treat the emulsion as ideal.
of the striking features follows from the fact that the constants $\alpha$ and $\beta$ appearing in Szyskowski’s equation Eq. (7.12) are related to $\Gamma_c$ and $k$:

$$\alpha = k_B T \Gamma_c \infty$$

$$\beta = k. \quad (7.15)$$

With all the model parameters defined, inserting Eq. (7.12) into Eq. (7.7) gives

$$\sigma = \sigma_{ow} - k_B T \Gamma_c \infty \ln\left(\frac{k + c}{k}\right), \quad (7.16)$$

with $k$ defined in Eq. (7.14).

Inserting expression (7.16) for the surface tension into Eq. (7.6) one obtains:

$$\sigma_{ow} - k_B T \Gamma_c \infty \ln\left(\frac{k + c}{k}\right) - \frac{R}{2} \left(\frac{\partial f_{ent}}{\partial R_e}\right) = 0. \quad (7.17)$$

This equation minimizes the free energy in Eq. (7.2). The bulk concentration of colloids $c$ can be determined by considering the condition of mass balance. Denoting by $n_c = N_c/V$ the number of colloids per unit volume in the entire system, one can write

$$\frac{3\phi}{R} \Gamma_c + c(1 - \phi) = n_c. \quad (7.18)$$

Now using this expression in Eq. (7.13) and solving for $c$ one obtains

$$c = \frac{1}{2R(\phi - 1)} \left(-3\phi \Gamma_c \infty + n_c R + R\phi k - Rk \right. + \left. \left(9\phi^2(\Gamma_c \infty)^2 - 6\phi \Gamma_c \infty n_c R - 6\phi^2 \Gamma_c \infty k R + 6\phi \Gamma_c \infty k R \right. \right. 
+ \left. \left. n_c^2 R^2 - 2n_c k R^2 + R^2 \phi^2 k^2 - 2n_c k R^2 - 2R^2 k^2 \phi + R^2 k^2 \right)^{1/2}\right). \quad (7.19)$$

Since the derivative of the dispersion entropy is much smaller than the oil-water surface tension, we can ignore the last term in Eq. (7.17). With this approximation one obtains

$$R_e = \frac{3\phi \Gamma_c \infty \Lambda^{-1}(\Lambda - 1)}{k [(1 - \phi)(1 - \Lambda)] + n_c}, \quad (7.20)$$

where

$$\Lambda \equiv \exp(\sigma_{ow}/\Gamma_c \infty k_B T), \quad (7.21)$$

Note that this result differs slightly from the one obtained in ref. [171] due to a different choice for the mass constraint.

One of the main features of this theory is the fact that the surface pressure $\pi$ is radius dependent. This in turn causes the surface tension to depend on the radius, which is a direct consequence of the fact that the distribution of colloids between the continuous phase and the droplets depends on the surface area of the droplets which itself depends on $R_e$.

In the next section we test this model on the type of emulsions created by Sacanna et al. [169].
7.3 Testing the model on the work of Sacanna et al.

In the work by Sacanna et al. [169] the surface tension of the TPM-water interface was reported as $1.9 \, k_B T/nm^2$ (spinning drop) and the concentration of colloids was $C = 1.2 \cdot 10^{-24} \, g/nm^3$. The magnetite crystal structure is of the inverted spinel type where the unit cell has a dimension of $\sim 15 \, \AA^3$ [176]. The average diameter of the colloids is $11 \, nm$ so each colloid consists of $4.6 \cdot 10^4 \, Fe_3O_4$ molecules. The molecular weight of the colloids is therefore estimated as $M = 1.1 \cdot 10^7 \, g \, mol^{-1}$. The concentration of colloids $n_c$ can now be calculated using

$$n_c \equiv \frac{N_c}{V} = \frac{C}{M} N_A = 6.6 \cdot 10^{-8} \, nm^{-3}, \quad (7.22)$$

where $N_A$ denotes Avogadro’s constant.

Now instead of using a Langmuir isotherm, let us consider the following. Since the amount of free colloidal particles in the bulk is low [169], we may neglect the amount in the bulk as a first order approximation: $\Gamma_c \approx n_c R/3 \phi$, i.e. all the colloids adsorb onto the interface. We then have

$$R \approx \frac{3 \phi \Gamma_c}{n_c}. \quad (7.23)$$

With this additional approximation Eq. (7.6) becomes

$$\sigma_{ow} - k_B T \frac{n_c R_e}{3 \phi} - \frac{R_e^2}{3 \phi} \left( \frac{\partial f_{ent}}{\partial R_e} \right) = 0. \quad (7.24)$$

Again neglecting the entropy term and solving for $R_e$ one finds

$$R_e = \frac{3 \phi \sigma_{ow}}{n_c k_B T}. \quad (7.25)$$

This is the same result as in Ref. [177], where it was derived using an ideal gas approximation for the adsorption isotherm (i.e. Henry’s law). The volume fractions of added oil should be similar to the final volume fraction of Pickering drops. The typical value of the volume fraction of Pickering drops is $\phi \sim 0.002$ [178] so one finds $R_e = 1.7 \cdot 10^5 \, nm$, which overestimates the experimental finding of $R \approx 50 \, nm$ [169] by three orders of magnitude.

From this finding we can infer that in order to reduce the bare oil-water interface by adsorption of colloids, the Pickering drops need to be very large. In the case of microemulsions the adsorption of surfactants (and co-surfactants) can reduce the bare oil-water interface much more efficiently, resulting in an effective surface tension of zero. Here, the oil-water interface is also reduced but apparently not as much as in microemulsions and the oil-water surface tension still dominates the interfacial behavior.

Next, we examine the situation of close-packed layers of colloids.
7.3.1 Close Packing

It is well-known that the droplets in Pickering emulsions are coated with a close-packed layer of colloidal particles. The adsorption at close packing $\Gamma^\infty$ is related to the molecular area at closest packing $A_0$ via $\Gamma^\infty = 1/A_0$. For typical nonionic surfactants $A_0 \approx 50 - 100 \, \text{Å}^2$ [179]. Using this relationship Eq. (7.16) becomes

$$\frac{\sigma}{k_B T} = \frac{\sigma_{ow}}{k_B T} - \frac{1}{A_0} \ln \left( \frac{k + c}{k} \right),$$

(7.26)

with $c$ given in Eq. (7.19). We have plotted the surface tension for several values of $\Gamma_c$ and $\phi$ in Figure 7.1.

The model predicts larger drops for increasing values of the volume fractions of Pickering drops. If the Pickering drops can adsorb more colloidal particles the surface tension drops faster to lower values and on average larger drops will be formed. This confirms the picture that the reduction of the tension in the bare oil-water interface due to adsorption of the colloids is the primary driving force behind the stabilization mechanism. As can be inferred from Figure 7.1 the model is rather insensitive to changes in the volume fraction.

In Figure 7.2 the surface tension is plotted versus the bulk concentration of colloids. It is an empirical rule that in surfactant systems the surface tension scales linearly with $\log c$ for concentrations well below the cmc (i.e. in this regime the surface pressure may be transformed to $\pi \sim \alpha \ln (c/\beta)$). For low concentrations of colloids the surface tension shows linear behavior as can be seen in Figure 7.2. To the author’s knowledge no experimental results for the surface tension as a function of magnetite concentration exists, so whether this surfactant approach is applicable in Pickering emulsions remains an open question.

Better agreement may be obtained if some data becomes available from experiments like better values for the adsorption energy, measurements of the volume fraction of drops and adsorption isotherms for magnetite on water/TPM interfaces. Despite the model’s simplicity it does reproduce the essential features as observed in experiments.

7.4 Discussion

It was shown that if Pickering drops are thermodynamically stable the theory devised for swollen micelles could act as a good starting point for the theoretical description of Pickering emulsions. The key part of the theory is the introduction of a radius dependent surface tension. This has its origin in the fact that the colloids can be distributed between the continuous and dispersed phases and the latter is uniquely defined by the drop’s radius $R$.

When comparing our model to the Pickering emulsions in the work of Sacanna et al. [169], still too many assumptions have to be made in order to make an accurate
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\[
\sigma = \frac{(k_B T)}{1,89995}
\]

\(\phi = 0,01\)

\[
\sigma = \frac{(k_B T)}{1,89995}
\]

\(\phi = 0,001\)
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Figure 7.1 Surface Tension (in units of $k_B T/nm^2$) as function of the droplet radius for different values of $\Gamma_c$ (in units of $nm^{-2}$) for values of $\phi = 0.001$, 0.01 and $\phi = 0.02$. We have taken $k = 33 \exp(-10) nm^{-3}$ and $n_c = 6.6 \cdot 10^{-8} nm^{-3}$.

comparison. Many parameters entering the theory still need to be determined experimentally before we can put them to use. Still, despite the approximations made and using the data available we do find that the model predicted Pickering droplets are of the same order in size. This agreement breaks down however, when we use Henry’s law for the adsorption. It would be of special interest to see what the model predicts when adsorption isotherms become available for these kind of systems.

We have calculated the interfacial tension and found that it decreases with increasing $R$. It should be noted that these radii merely serve to reflect the different stages of the adsorption process and are not to be considered equilibrium radii. To obtain the equilibrium radius the free energy $F_0$ of a reference state needs to be constructed and compared with the free energy presented in this chapter. Only by minimizing the difference between both free energies one obtains the equilibrium droplet shape.

Both in Pickering emulsions and microemulsions (for which the original theory was derived) the reduction of the bare oil-water interface is the driving force towards aggregation. The observation that both the reduction of the surface tension is not that pronounced combined with the fact that Eq. (7.25) overestimates the radius implies that, opposed to the case of microemulsions, the bare oil-water interface still plays a non-negligible role in Pickering emulsions.

This model is far from complete. We have ignored double layer effects which,
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Figure 7.2 Surface Tension (in units of $k_B T/\text{nm}^2$) as function of the bulk concentration colloids $c$ (in units of $\text{nm}^{-3}$) for different values of $\Gamma_c$ (in units of $\text{nm}^{-2}$). Here $k = 33 \exp(-10) \text{nm}^{-3}$, $\phi = 0.001$ and $n_c = 6.6 \cdot 10^{-8} \text{nm}^{-3}$.

especially when constructing the phase diagram, will be important in describing the interactions between drops. Furthermore, the assumption of the nonexistence of interparticle interactions is especially expected to break-down at high surface coverages. Yet, the rationale here is that the colloidal particles adsorb strongly to the interface in a monolayer and we expect the interparticle interactions here to be smaller than in surfactant systems for which the theory was originally derived.