Predicting the Stability of Emulsions in the Presence of Surfactants and Nanoparticles Using Coarse-Grained Simulations

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Declaration of Originality

I, Abeer Mohamed Safwat Salah Khedr confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that they have been properly indicated in the thesis.

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Signature

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Date
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Abstract

Understanding the molecular mechanisms and processes that control the stability of emulsions is of great interest for many practical applications. Both surfactants and particles have been developed and optimised to control the emulsions stability. Due to the complexity of the emulsion system, it is challenging to understand the effect of these emulsifiers on the various demulsification processes, which can occur simultaneously or consecutively during phase separation. Molecular dynamics simulations are useful to identify some of the molecular mechanisms responsible for emulsions stability by providing algorithms designed to study the phenomena of interest.

This work presents advances obtained via the implementation of the coarse-grained Dissipative Particle Dynamic simulation framework, DPD. First, a systematic approach was conducted to estimate the parameters to describe immiscible liquids containing surfactants. Starting from the Hansen theory of solutions, the model proved its ability to reproduce experimental water/oil interfacial tension as well as the micellar properties of aqueous non-ionic surfactants representative of the octyl polyethylene oxide family. Using this model, an algorithm was designed to study the Ostwald ripening phenomenon in an oil-in-water emulsion. The DPD simulation results are consistent with theoretical expectations, as well as with experimental observations. When surfactants were introduced to the system, the results show an enhancement in the emulsion stability due to the reduction in the interfacial tension, with a possible effect of the surfactant film properties on the Ostwald ripening rate. Finally, the effect of particle size on the arrangement of nanoparticles (NPs) on a curved oil/water interface was investigated. The arrangement of NPs showed a dependency on the particle size when the emulsion was subjected to a change in the NP-NP interaction, with a prompt self-organization of the smaller NPs. When a mixture of NPs of different sizes were introduced to the system, the NPs self-assembly on the droplet surface showed a dependency on the initial configuration. These findings could prove useful to understand the morphological changes occurring in Pickering emulsions affecting their stability, when subjected to a change in the interaction between its constituents.
The main impact of this work is to provide insights into the effect of emulsifiers, e.g. surfactants and particles, on the stability of emulsions. In view of the experimental and theoretical contribution attempts to understand the different processes affecting the stability of emulsions, molecular simulations can provide a descriptive and visual explanations of certain demulsification processes. To simulate such complex systems, coarse-grained simulations are necessary.

Among other coarse-grained approaches, the Dissipative Particle Dynamics (DPD) formalism is attracting significant attention due to its capability to simulate large systems over relatively long time scale. The outcome of the simulations strongly depend on the choice of the parameters between different species. This thesis provides a systematic approach, based on solubility parameter theories, to derive the proper force field of a water/oil interface in presence of surfactants. The parameters driven from this approach was found to be suitable for reproducing both thermodynamic and structural properties of interest.

Using the validated parameters, a new algorithm was introduced, which takes advantage of the coarse-grained DPD formalism, to study Ostwald ripening. Several experimental investigations focused on the problem, but so far, directly investigating this phenomenon using simulations was prohibitive due to the complexity of the system. The new algorithm is specifically designed to prevent creaming, flocculation and coalescence, so that Ostwald ripening is the only mechanism allowed for breaking the emulsion. The results show quantitative agreement with experimental and theoretical expectations for emulsions in absence and presence of surfactants. The algorithm proposed in this thesis could become a tool for predicting the long-term stability of various emulsions.

On the other hand, several investigations proved the superiority of particles over surfactants to promote emulsion stability by referring to the high interfacial adsorption energy, which makes the particle irreversibly attached to the interface. Although many researches were conducted to understand the effect of the particles physical/chemical properties on the particle adsorption and distribution, yet, several open fundamental questions remain. This work provides insights on the possible synergistic and antagonistic effects between spherical particles of two different sizes on an oil droplet immersed in water. These findings could prove useful to understand the mechanism by which particles of different sizes could stabilise a
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<th>Density</th>
<th>Interfacial Tension</th>
<th>Ostwald Ripening Rate</th>
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</tr>
<tr>
<td>2.0</td>
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<td>4.0</td>
<td>0.02</td>
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</table>
Chapter 1  Introduction

1.1.  Emulsions

Emulsions are mixtures of immiscible liquids, consisting of a liquid dispersed as droplets into a continuous phase. A wide variety of commercial important materials exists in an emulsion state, including agrochemicals, cosmetics, petrochemicals, pharmaceuticals and foods [1-4]. In some applications the stability of emulsions is crucial while in others phase separation is desirable.

Depending on the droplet size, emulsions are categorized into macro- or micro-emulsions. Emulsions are kinetically stable, but thermodynamically unstable [5]. The free energy of the emulsion system is minimized with time by reducing the interfacial area until the system reaches a phase separation. However, the stability of emulsions could be controlled by the addition of emulsifiers, e.g. surfactants or particles, which will create a kinetically stable emulsion, by imposing energy barriers or by reducing interfacial tension in the system, important in applications where the stability of emulsion is crucial. A kinetically stable emulsion is an emulsion where the number, the distribution and the arrangement of droplets are relatively constant within a certain timescale. Emulsion breakdown involves four main processes that can happen simultaneously or consecutively. The instability processes are; creaming (sedimentation), flocculation, coalescence and Ostwald ripening as shown in Figure 1-1 [5, 6].

![Emulsion Breakdown]

Figure 1-1. Emulsion breakdown mechanisms
**Creaming** in oil-in-water emulsion is the movement of oil droplets, due to the difference in densities between the dispersed and the continuous phases, to form concentrated layers at the top of the emulsion. **Flocculation** is the process appearing due to the aggregation of droplets without interfacial films rupture. Flocculation may be reversible or irreversible, depending on the strength of the forces between droplets. In an emulsion, flocculation appears more significantly in case of polydispersity, due to the diversity in the creaming speed depending on the droplet size; consequently, they come into close proximity more often compared to a monodisperse system. **Coalescence** is the fusion of two or more drops together forming one emulsion drop. Coalescence happens due to thinning of the film separating the droplets. Film thinning occurs due to flow of the bulk phase out of the film when the droplets come into proximity from each other. The thickness of the film and its mechanical properties affect the rate of the film rupture. The mechanical properties of the film could be enhanced by the addition of surfactant or nanoparticles. Finally, **Ostwald ripening** is a diffusional mass transfer process. This mass transport occurs due to the solubility difference of dispersed material in an emulsion in case of polydispersity. As a consequence of the solubility increase in relatively small droplets, the material contained in the droplets tends to dissolve and diffuse into the continuous phase. When the continuous phase is saturated with these excess molecules, the later will re-condense on the surface of the larger droplets, creating an increase in the emulsion droplet size, and subsequently a decrease in the interfacial area. In experiments, they observe a reduction in the average droplet size of the dispersed phase and the disappearance of small droplets with time [7].

It is of great interest to understand each process involved in the separation of the emulsion in order to control its stability. Many investigations were conducted to quantify the rate of each mechanism and identify which mechanism is the controlling step in the destabilization process. For example, coalescence and flocculation are two processes that are strongly related to one another. In fact, sometimes it is difficult to identify which process is the rate limiting step in the separation of emulsion. In order to quantify the coalescence and flocculation rates, there is a proposed methodology introduced by Borwanker et al. [8]. In this approach, they derived a mathematical model representing the variation in the number of droplets with time in an agitated emulsion due to coalescence and flocculation processes. They found that the curve of the normalized number of droplets changes from linearity to a non-linear curve with time. From this change, they deduced a shift in the process-controlling step from coalescence to flocculation. They showed that the model provides a good fit with the experimental data.
Many other investigations and theories were conducted to understand the film rupture mechanism in the coalescence process [9, 10], while others focused on the Ostwald ripening phenomena. A detailed study is conducted in Chapter 4 to understand the Ostwald ripening phenomena, including a comparison between experiments, theory and computational simulations.

1.2. Surfactants as emulsifiers

In order to control the rate of the aforementioned processes, particles with various chemical/physical properties are introduced in the emulsion system. In this work, I focus on the effect of non-ionic surfactants on the stability of emulsions, and specifically the polyethylene oxide surfactants. In general, surfactants are amphiphilic molecules, constituted of hydrophilic head and hydrophobic tail. When surfactants are added to water, they tend to disperse at the water/air interface, and with increasing the surfactant concentration the interface becomes saturated and the surfactant molecules start to aggregate in the bulk forming micelles. The concentration of surfactant molecules in aqueous solution at the formation of the first micelle is defined as the critical micelle concentration (CMC). Self-assembly of surfactant aggregations creates generally spherical micelles, and with a further increase in the surfactant concentration, these spherical shapes tend to transform into ellipsoidal, hexagonal or lamellar shapes.

Furthermore, the amphiphilic characteristic nature of the surfactant molecules provides them the ability to adsorb at the interface. While adsorbed at the interface, surfactants tend to reduce the interfacial energy. With the increase of the surfactant concentration, the surface will be filled with surfactants reducing its interfacial tension until it becomes saturated. When the surface is saturated with surfactants, the interfacial tension reaches a plateau, which is an indication of the formation of micelles in the bulk. This criterion is useful for the determination of the CMC in experiments [11, 12]. All these properties will be discussed in Chapter 3, providing a comparison between experimental observations and simulation results.

Many experimental investigations and theoretical studies were conducted to understand the effect of surfactant on the type of the emulsion formed and its stability [13-17]. For example, surfactants could affect the rate of film thinning in the coalescence mechanism. When two droplets come in proximity, liquid flows out of the film between droplet surfaces and film thinning occurs. A convective flux, created by the flow of the liquid flowing out, drives the
surfactant out from the interior of the film, which creates a concentration gradient at the interface. Thus, an opposite flow occurs due to the variation in the local value of the interfacial tension, which is known as the Marangoni effect. This results in a reduction in the mobility of the film surface and a decrease in the rate of film thinning [5, 18]. Furthermore, in case of ionic-surfactants, the electrostatic repulsion between the surfactants head adsorbed on the droplet surface provide an energetic barrier against coalescence or flocculation [19].

On the other hand, the surfactant concentration is an important factor affecting the stability of emulsions. For example, increasing the surfactant concentration above the CMC may lead to the increase of flocculation and coalescence due the depletion forces created by micelles in the bulk [20]. Depletion is an attraction force occurring between droplets created by the presence of depletants in the continuous phase, such as micelles. Moreover, the surfactant’s ability to reduce the interfacial tension has an effect on the Ostwald ripening rate. However, with the increase of surfactant concentration, micelles could act as carriers between droplets in the emulsions, leading to an increase in the Ostwald ripening rate. In our simulations, micelles are clusters of surfactant molecules, which tend to trap oil inside their cores during the simulation time, while a droplet is a cluster of, for example oil beads, at the surface of which surfactants are adsorbed and increases in surface density with time. The Ostwald ripening phenomena is discussed in details in Chapter 4 with a comparison between experimental observations, theoretical models and simulation results.

1.3. Particles as emulsifiers (Pickering Emulsions)

The stability of emulsions shows enhancement through the self-assembly of particles on droplet surfaces. These particle-stabilized emulsions are known as Pickering emulsions. Binks provided a comparison between the abilities of surfactants and particles to stabilize emulsions [21]. Among different reasons, he reported the superiority of particles over surfactants to promote emulsion stability by referring to the high interfacial adsorption energy, which makes the particle irreversibly attached to the interface, once adsorbed. While adsorbed at the interface, the particles could provide energy barrier against emulsion breakdown. When two droplets come in proximity, the particle layers adsorbed on each droplet prevent their coalescence by steric hindrance effect [6].

The particle wettability, defined by its contact angle, affects the amount of energy required to remove a particle from the interface as discussed in detail in Chapter 5. The particle
wettability depends on many aspects including the particle chemical/physical nature. Many studies were carried out to control the interfacial particle self-assembly, e.g., by changing the degree of wettability of particles. For example, Maestro et.al. [22] were able to control the adsorption of silica nanoparticles at the interface by modifying the particles surface with hexadecyl-trimethylammonium bromide (CTAB) and dodecyl-trimethylammonium bromide (DTAB). Another route typically used in the literature to enhance the particle adsorption capability is by changing the chemical nature of the particle surface creating Janus particles [23]. Janus particles are colloidal particles with amphiphilic properties, having both hydrophilic and hydrophobic surfaces, showing a higher surface activity compared to particles with homogenous surfaces.

Furthermore, the surface coverage and the arrangement of particles at the interface could affect the stability of emulsions. Depending on fluids type and nanoparticles (NPs) properties, different structures are observed [24-26]. Particles can assemble on droplet surfaces forming monolayers or multilayers, yielding complete surface coverage, and could cluster into continuous 2D structures that cover the entire interface, or into closely-packed single-layer domains that leave large interfacial areas uncovered. These structures depend on both the particle/interface interactions and particle-particle interaction. A control over these structures could help modulating the interfacial properties. In particle-stabilized emulsions, for instance, the stability mechanisms could be affected by such arrangements [6]. For example, some investigations pointed out the importance of the presence of high surface coverage and a sufficiently dense layer of particles at the interface to achieve stability [27], while others showed that it is not essential to completely cover the droplet surfaces [26]. These different phenomena can occur in different systems due to the change in the interactions occurring at the interfaces. Vignati et al. [28] for example, found that particles could diffuse and relocate on droplet surfaces in order to stabilise emulsions at very low surface coverage. In his investigation, Vignati et al. compared the stability, surface coverage and layer morphology of monodisperse fluorescent silica colloids with smooth surface of diameter 0.51 ± 0.04 μm and 1 μm and rough surface with diameter 0.77 ± 0.05 μm in isooctane-in water emulsion. In their study, they reported the absence of a straightforward relation between the extent of particle interfacial adsorption and emulsion macroscopic stability; stable emulsions are obtained even at very low surface coverage. They found that the particle diffusion coefficient, on poorly covered droplets, is very close to the bulk value concluding that the surface diffusion and
particle relocation on the surface of droplets with low or inhomogeneous particle coverage has an effect on the stability of the emulsion.

In other cases, particles have been shown to yield multilayer domains extended into the continuous phase between emulsion droplets [6]. These particle 3D structures can create particle/droplet networks due to particle flocculation and clustering and can highly affect the emulsion stability [25, 29]. For example, Thieme et al. [24] showed the formation of a 3-D network of lamellae of sodium montmorillonite with spherical particles of layered double hydroxide (LDH). They reported that this network cannot stabilize the emulsion alone, and that an optimal stability is attained when particles are adsorbed at the surface and trapped in a network of additional particles.

The structure and arrangement of particles on droplet surfaces can be manipulated by applying external forces and/or controlling the interparticle interaction, hence affect the emulsion stability. For example, a change in the pH or the ionic strength of the system can alter the interparticle interaction rendering the particle more repulsive/attractive to each other. This change in the interparticle interaction has an effect on the morphological and rheological properties of emulsions [30-33]. For example, as an attempt to understand the effect of changing the pH and the ionic strength on the stability of emulsions, Gautier et al. [30] proved the ability to control the average droplet size, particles arrangement on droplet surfaces and the stability of a hexadecane-in-water emulsion in presence of pH-sensitive particles. Furthermore, Binks and co-workers [29] studied the effect of adding NaCl as electrolyte with different concentrations to a silicone oil-in-water emulsion. In general, the emulsion was stable against coalescence over the whole electrolyte concentration range, while above a certain electrolyte concentration (critical flocculation concentration c.f.c) the creaming rate and extent decreased drastically due to the formation of a 3D network of interconnected particles and emulsion droplets.

Controlling the forces acting on particles at the interfaces can lead to a switch from stable to unstable emulsions, useful in applications such as drug delivery where, for example, pH changes is useful to trigger therapeutic release directly at a site of disease [4]. However, it is difficult to investigate the effect of the change in the interparticle interaction on the arrangement of particles at the droplet surface in experiments. This is due to the complexity of emulsion of interactions occurring between its different constituents. That is why, in Chapter 5, using coarse-grained simulations, a detailed study was conducted to understand the change
in the arrangement of nanoparticles adsorbed on droplet surface when subjected to a change in interparticle interactions.

1.4. Emulsions in Simulations

In view of the experimental and theoretical contributions aiming to understand the different processes affecting the stability of emulsions, molecular simulations can provide descriptive and visual explanations of the interaction between droplets inside emulsions. For example, Rekvig et al. [34] studied the coalescence mechanism of droplets covered with surfactant molecules with the aid of Dissipative Particle Dynamics (DPD) simulations. They were able to observe a difference in the rate of coalescence in presence and absence of surfactant, and they were able to relate the film thickness to this rate. They categorized the film between two droplets into two categories; thin and thick (in nm scale), where each category shows a different rate dependency. The rate of thin film rupture shows an exponential decrease with its thickness, while in case of thick films, a critical channel radius defines the rupture. They were also able to relate the surfactant natural curvature to the rate of the film rupture.

Furthermore, Alvarez et al. [35] investigated the effect of different molecular weights of a triblock co-polymer ethylene oxide/propylene oxide, bi-functionalized with ethylamine, on the coalescence of water drops in a crude oil environment. They started their simulation with two water drops inside the bulk oil, and they monitored the time evolution of the emulsion. They observed a drastic change of the coalescence rate of the two water droplets for a short co-polymer length compared to long co-polymer lengths. For short length, the coalescence is completely stopped by the presence of the polymer forming a film around the water droplets over their simulation time. With increasing the length, the polymeric chain becomes large enough to interconnect the water drops, and then the polymer works as a route for the water bead exchange between droplets.

Kurokawa et al. [36] investigated the change of the shape of water-in-oil droplet with the variation of number of polymer chain and the type of the surfactant hydrophilic group using molecular dynamic simulation. Lin et al. [37] also studied the morphological change of n-octadecane droplets in water in presence of styrene-maleic acid co-polymers using DPD simulations. They studied the kinetics of emulsion formation by analysing the time evolution of droplet numbers, the end-to-end distance and the morphologies of the emulsified oil droplets.
They found that increasing the styrene maleic acid concentration transform the shape of the droplets from a nearly spherical droplet to an ellipsoidal droplet.

Using DPD technique, an investigation of demulsification efficiency caused by coalescence and flocculation of water-in-crude oil emulsions was conducted by Song et al. [38] using the approach proposed by Borwankar et al. [8]. In the DPD model, they studied the change in the coalescence and flocculation rate constants using the slopes of the curves defining the two processes. In their work, they investigated the effect of changing the hydrophobic group of a demulsifier initiator of dimethyl ethanolamine from propylene oxide (DPO) to butylene oxide (DBO) and tetrahydrofuran (DTE) by plotting the former graph to show the decrease of the normalized number of droplets \( \frac{N}{N_0} \) with time in DPD unit \( \tau \). Their results show that the demulsifiers have almost the same rates of coalescence and flocculation with relatively higher rates in case of DBO.

Pickering emulsions were also studied using DPD. For example, Fan et al. [39] studied the influence of nanoparticles (NPs) on the water-oil interfacial tension using the Wilhelmy plate method. They used both homogenous and Janus particles. They found that the reduction in interfacial tension depends on the particle-particle interaction especially when high loadings of NPs are considered.

The structure of the monolayer created at the planar water-oil interface by homogenous and Janus NPs was studied by Luu et al. [40]. They observed a transition from a liquid-like to a solid-like state of uniformly distributed NPs when the surface coverage increases regardless of the nature of NPs. A reduction in the self-diffusion coefficient of NPs at the interface was reported when the surface coverage increases with the formation of hexagonal structures resulting in a reduction in interfacial tension. Furthermore, they studied the orientation of ellipsoidal Janus NPs adsorbed at spherical oil/water interfaces and their equilibrium behaviour [41]. This orientation was found to depend on the characteristic of the NP considering the surface chemistry and the NP surface coverage.

Other studies focused on the effect of the NPs on the stability of emulsion droplets against coalescence. For example, Fan and Striolo [39, 42] studied the stability of droplets surrounded by NPs against coalescence by investigating the effect of both the surface coverage and the contact angle of NPs. In their study they used different types of homogenous and Janus NPs. They found that the surface coverage is an important parameter regarding the force experienced by the droplet during collision, with Janus NPs being more effective imposing a higher energy
barrier against coalescence. Sicard et al. [43] implemented a numerical analysis on the stability of Pickering emulsions using dissipative particle dynamics simulations within the Adiabatic Biased Molecular Dynamics framework. They studied the early stage of the coalescence process between two water droplets stabilized with homogenous and Janus NPs in a decane solvent. They showed that the coalescence mechanism is sensitive to the NP type and shape. They also observed that the formation of the water bridge during the coalescence depends on the shape of the NPs used to stabilize the emulsion droplets whether the NPs are spherical or ellipsoidal. In case of spherical NPs, two NPs each belonging to different droplet create the water bridge is due to their interaction with water molecules from the other droplet. However, in case of ellipsoidal NPs, only one NP is able to create the molecular bridge between the two droplets. This is due to the longitudinal orientation of the ellipsoidal NPs at the interface, which facilitate the interaction of water from the second droplet with the polar NP beads on the approaching droplet.

Qin and Yong [44] also investigated the stability of Pickering emulsion stabilized with pH-responsive NPs (polyelectrolyte-grafted NPs) showing the different mechanism of preventing the coalescence at different degree of ionization. At low surface coverage and relatively high degree of ionization, the polyelectrolyte swells under stronger intramolecular electrostatic repulsions. The extended polymer chains form a shell that can generate stronger steric repulsions during impact, which effectively hinder the collision process. Hence, when the degree of ionization is relatively high, both steric and electrostatic repulsions impede coalescence and enhance emulsion stability. However, they found that rising the degree of ionization reduces emulsion stability when the surface coverage is high. As with increasing the degree of ionization at high surface coverage, a large number of NPs desorbed from the droplet surface and the residual NPs at the interface are insufficient to cover the droplet surface well.

The aforementioned investigations could provide insights into the importance on the coalescence mechanism between droplets in Pickering emulsions where the NPs are homogenously distributed on the droplet surface. More studies are need to understand the effect of the different structures formed by the NPs on the droplet surface, on the stability of Pickering emulsions, and how the size of NPs might affect this stability.

To complement the previous experimental and simulations studies, in Chapter 3, a systematic approach is implemented to describe the interface between immiscible liquids containing surfactants. This study includes a comparison between the different solubility parameter theories to estimate the simulation parameters. Starting from the Hansen theory of
solutions, a validated model is obtained. This model is able to reproduce experimental water/oil interfacial tension as well as the micellar properties of aqueous non-ionic surfactants representative of the octyl polyethylene oxide family. Using this validated model, in Chapter 4, the Ostwald ripening phenomenon in an oil-in-water emulsion was investigated. The results are compared to experimental observations and theoretical models showing good agreement. This investigation also emphasizes the effect of surfactants on the Ostwald ripening rate reporting a possible effect of the surfactant interfacial film. In Chapter 5, the effect of particle size on the arrangement of NPs at the droplet surfaces of an oil-in-water emulsion. The different response of particles with different sizes was also studied when changing the interparticle interaction. The results agree with recent experimental and simulations results and are used to provide phenomenological suggestions on approaches to both control emulsion stability and the self-assembly of particles at liquid-liquid interfaces.
Chapter 2  Modelling and Methodology

2.1. Dissipative particle dynamic simulation

One of the most widely used coarse-grained techniques, for studying colloidal systems, is the Dissipative Particle Dynamics formalism. This technique was introduced by Hoogerbrugge and Koelman [45, 46] in 1992 and modified subsequently by Groot and Warren and others [47, 48]. DPD formalism has been used in many applications, in order to investigate large systems over long time scales [39, 42, 49-51]. In this coarse-grained methodology, a group of molecules is represented by the so called ‘‘beads’’ as shown in Figure 2-1.

Figure 2-1. A schematic representation of the coarse-grained model in DPD. A water bead (blue sphere) represents 5 water molecules, while an oil bead (brown sphere) represents one benzene molecule. The interaction between similar beads is $a_{ii}$, and the interaction between different beads is $a_{ij}$.

The interaction between beads is defined by a pairwise additive forces in which the momentum is conserved, and the hydrodynamic behaviour is reproduced correctly. The total force acting on particle $i$ ($F_i$) is a summation of three types pair interactions: conservative $f^C(r_{ij})$, dissipative $f^D(r_{ij}, v_{ij})$, and random $f^R(r_{ij})$, as shown in the following Equation (2.1):
\[ \mathbf{F}_i = \sum_{j \neq i} [\mathbf{f}^C(\mathbf{r}_{ij}) + \mathbf{f}^D(\mathbf{r}_{ij}, \mathbf{v}_{ij}) + \mathbf{f}^R(\mathbf{r}_{ij})] \]  

(2.1)

### 2.1.1. Conservative force

The conservative force \( \mathbf{f}^C(\mathbf{r}_{ij}) \) is a soft repulsive force given by:

\[ \mathbf{f}^C(\mathbf{r}_{ij}) = \begin{cases} \alpha_{ij} \left(1 - \frac{\mathbf{r}_{ij}}{\mathbf{r}_c}\right) \mathbf{\hat{r}}_{ij} & \mathbf{r}_{ij} < \mathbf{r}_c \\ 0 & \mathbf{r}_{ij} \geq \mathbf{r}_c \end{cases} \]  

(2.2)

The pair DPD interaction parameter \( \alpha_{ij} \) determines the strength of the conservative forces, and describes the interaction between particles. A systematic approach was conducted in Chapter 3 to estimate both the self-interaction parameter \( \alpha_{ii} \) and the repulsion parameter between different beads \( \alpha_{ij} \), based on the DPD equation of state and on different solubility parameter theories. \( \mathbf{\hat{r}}_{ij} \) is the unit vector in the direction of \( \mathbf{r}_{ij} \). The vectors \( \mathbf{r}_{ij} \) is the distance \( (\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j) \) and \( \mathbf{r}_{ij} = |\mathbf{r}_{ij}| \). \( \mathbf{r}_c \) is the cut-off distance, which defines the effective interaction range, and represents the length scale in the DPD simulation. As shown in Equation (2.2), the conservative force is modelled as a linear function of the distance between two beads and drops to zero at the cut-off length \( r_c \).

### 2.1.2. Dissipative and Random forces

In colloidal systems, the particles exert collisions with solvent molecules, creating the so called ‘‘Brownian motion’’ of the colloid. This generated Brownian motion depends on the temperature, density and viscosity of the system, and does not depend on the detailed description of the molecules. This means that to simulate these systems, there is no need for a detailed atomic model description. However, the model should represent the hydrodynamic behaviour, and thermal fluctuations that can derive Brownian motion due to the collision between suspensions and solvent molecules. In the DPD approach, the Brownian motion is mimicked by the combination of an effective friction and a fluctuation force between moving fluid elements.

The dissipative force \( \mathbf{f}^D(\mathbf{r}_{ij}, \mathbf{v}_{ij}) \) corresponds to a frictional force that depends on both the positions and the relative velocities of the particles according to Equation (2.3)
\[ f^D(n_{ij}, v_{ij}) = -\gamma \omega^D(n_{ij})(v_{ij}, \hat{r}_{ij}) \hat{r}_{ij} \]  

(2.3)

Where \( \gamma \) is a coefficient controlling the strength of the frictional force between the DPD particles. The vector \( v_{ij} \) is the relative velocity \( (v_{ij} = v_i - v_j) \) between particle \( i \) and \( j \). \( \omega^D \) describes the variation of the frictional force with distance according to Equation (2.4)

\[
\omega^D(r_{ij}) = \begin{cases} 
(1 - r_{ij}/r_c)^2 & r_{ij} < r_c \\
0 & r_{ij} \geq r_c 
\end{cases}
\]  

(2.4)

On the other hand, the random force is given by:

\[ f^R(n_{ij}) = \sigma \omega^R(n_{ij}) \xi_{ij} \Delta t^{-1/2} n_{ij} \]  

(2.5)

In Equation (2.5), \( \sigma \) determines the magnitude of the random pair force between the DPD particles. \( \xi_{ij} \) is a randomly fluctuating variable with Gaussian statistics, and \( \omega^R(n_{ij}) \) describes the variation of the random force with distance. \( \Delta t \) is the time step used to integrate the equations of motion as will be discussed later in Section 2.2. The functions \( \omega^D(n_{ij}) \) and \( \omega^R(n_{ij}) \) are related according to Equation (2.6)

\[
\omega^D(n_{ij}) = \left[ \omega^R(n_{ij}) \right]^2
\]  

(2.6)

This relation ensures the configurations of the systems to occur with the proper Boltzmann weight for the system to be defined as a canonical ensemble [47, 48]. Finally, \( \sigma \) and \( \gamma \) are related to the temperature according to:

\[
\sigma^2 = 2 \gamma K_B T
\]  

(2.7)

2.1.3. Bonding forces

In the model presented here, the surfactant molecules are simulated as a chain of bonded beads representing the hydrophilic head and hydrophobic tail of two surfactants in the octyl polyethylene oxide \( \text{C}_8\text{H}_{17}\text{O}(\text{C}_2\text{H}_4\text{O})_m\text{H} \) aqueous non-ionic surfactants family. To describe
chemical bonds within a molecule, spring forces are introduced, which are described by $k_s$, the spring constant, and $r_0$, the equilibrium bond length according to:

$$f^S(r_{ij}) = -k_s(r_{ij} - r_0)\hat{r}_{ij} \tag{2.8}$$

### 2.2. Parameters in simulations

In this coarse-grained technique, all the units are in reduced units. The degree of coarse graining of the water beads is chosen to be 5, which means that each DPD water bead represents 5 water molecules. Thus, the volume of one DPD bead ($V_{\text{bead}}$) equals ~150 Å$^3$. The density ($\rho_{\text{DPD}}$) in the simulation box is taken as 3 beads/r$_c^3$. The cut-off distance ($r_c$) is taken as 1 reduced to unit lengths, and according to the relation $r_c = \sqrt[3]{\rho_{\text{DPD}}V_{\text{bead}}}$, $r_c$ is equal to 7.66 Å and the diameter of one bead equals 0.86 $r_c$. All the parameters used in our work are summarised below in Table 2-1.

**Table 2-1.** Parameters used in the DPD simulations presented in this work

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length, $r_c$</td>
<td>7.66 Å</td>
</tr>
<tr>
<td>Time, $\tau$</td>
<td>136.26 µs (when $a_{ii} = 131.5$ $K_B T/r_c$)</td>
</tr>
<tr>
<td>Volume of one bead</td>
<td>150 Å$^3$</td>
</tr>
<tr>
<td>Temperature</td>
<td>Equivalent to 25°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>Equivalent to 1 bar</td>
</tr>
</tbody>
</table>

### 2.3. Solving the equation of motion

DPD is a coarse-grained methodology emerging from the classical Molecular dynamics (MD) technique. In MD simulations it is assumed that the atoms in a system are in continuous motion that can be defined according to the classical mechanics [52]. The basic idea behind MD method is to solve the equations of motion of a set of interacting atoms and use the resulting trajectories to calculate the microscopic and macroscopic properties. In MD simulations, the time evolution of a set of interacting atoms is followed by integrating Newton’s equations of motion:
\[
\frac{dr_i}{dt} = v_i, \quad \frac{dv_i}{dt} = F_i
\]  

(2.9)

Where \(r_i, v_i\) are the position and the velocity of bead \(i\), respectively. \(F_i\) is the sum of the forces acting on bead \(i\). For simplicity, the masses of the particles are put at 1, so that the force acting on a particle equals its acceleration. To start the simulation, it is necessary to specify initial positions and velocities to the atoms. The initial positions may be assigned randomly, with the beads placed on a simple cubic lattice, obtained from an experimental data, or taken from a theoretical model. In DPD, the force acting on each bead in the system is obtained from the sum of forces exerted by the neighbour beads described in Section 2.1, and the position and velocities of each bead are updated with time. Many algorithms are used to integrate the equation of motions. In this work, the velocity-Verlet algorithm is implemented.

We start first by defining the initial configuration of each bead in the system \(r(t)\), then initial velocity is assigned to each bead in the simulation box \(v(t)\) based on a Gaussian distribution at the desired temperature [53]. The forces acting on each bead is then calculated as described previously using the neighbour beads within a cut-off distance equal \(r_c\).

First, the velocity is calculated after half time step according to:

\[
v_i \left( t + \frac{1}{2} \Delta t \right) = v_i(t) + \frac{F_i(t)}{2m} \Delta t
\]

(2.10)

Then, the coordinates are determined after a full-time step according to:

\[
r_i(t + \Delta t) = r_i(t) + v_i(t)\Delta t + \frac{F_i(t)}{2m} \Delta t^2
\]

(2.11)

The forces are then calculated as a function of \(r_i(t + \Delta t)\) and \(v_i \left( t + \frac{1}{2} \Delta t \right)\). Finally, the velocity is updated by half time step according to:

\[
v_i(t + \Delta t) = v_i \left( t + \frac{1}{2} \Delta t \right) + \frac{F_i(t + \Delta t)}{2m} \Delta t
\]

(2.12)
The integration time step (Δt) should be chosen carefully, as using too large time step can cause the simulation to become unstable as the energy increases rapidly with time, while using too small time step requires a large amount of computational time.

2.4. **Periodic Boundary Condition**

To remove boundary effects caused by the finite size of the simulation box, periodic boundary conditions are commonly used in MD simulations. In Figure 2-2, an illustration of the periodic boundary conditions is shown. When using periodic boundary conditions, a computational box is surrounded by periodic images of itself, and its atoms move in a way similar to their images. The atoms near the boundary of the simulation box interact with other atoms in their own box as well as in their periodic images. For each atom leaving the box, at the same time, one of its images enters through the opposite side. As a result, there are no physical boundaries. For all simulations presented in this thesis, periodic boundary conditions were applied in all the directions.

![Figure 2-2](image.png)

**Figure 2-2.** Three-dimensional example of periodic boundary conditions. The simulation box is highlighted at the centre and is surrounded by periodic images of itself.
Chapter 3 DPD Parameters Estimation for Simultaneously Simulating Water-Oil Interfaces and Aqueous Non-Ionic Surfactants

The material presented in this chapter was published in 2018 in volume 14, pages 6460-6471 of the Journal of Chemical Theory and Computation.

3.1. Chapter overview

The outcome of a coarse-grained simulation within the Dissipative Particle Dynamics framework strongly depends on the choice of the repulsive parameter between different species. Different methodologies have been used in the literature to determine these parameters towards reproducing selected experimental system properties. In this chapter, a systematic investigation on possible procedures for estimating the simulation parameters is conducted. A comparison is conducted between methods based on the Hildebrand and the Hansen solubility parameter theories, mapped into the Flory-Huggins model. By using the Hansen solubility parameters, a high degree of coarse graining is achieved, with parameters that yield realistic values for the interfacial tension. The procedure was first applied to the water/benzene system, and then validated for water/n-octane, water/1,1-dichloroethane, water/methyl cyclohexane, and water/isobutyl acetate. In all these cases, the experimental interfacial tension could be reproduced by adjusting a single correction factor. In the case of the water-benzene system, the Dissipative Particle Dynamics parameters derived using this approach were able to simultaneously describe both the interfacial tension and micellar properties of aqueous non-ionic surfactants representative of the octyl polyethylene oxide $C_8H_{17}O(C_2H_4O)_mH$ family. The estimated parameters can be used, within the Dissipative Particle Dynamics framework, to simulate the water/oil interface in presence of surfactants at varying concentrations. The results show, as expected, that as the surfactant concentration increases, the interfacial tension decreases and micelles form in bulk water.
3.2. Introduction

Molecular simulations are widely used to provide molecular-level information to complement experimental data. Striolo and Grady [54] recently reviewed, for example, how experiments and simulations have been synergistically combined to investigate the adsorption of surfactants on a variety of substrates. While electronic-structure calculations are useful, e.g., in catalysis, and atomistic simulations reveal details such as the orientation of solvent molecules near surfaces, coarse-grained simulations can be implemented to investigate the emergent properties of complex fluids, e.g., surfactants [49-51] and emulsions [35, 37, 38]. Coarse-grained simulations allow us to sample length and time scales that approach experimental values, but at the expense of atomic-level descriptions of the phenomena. Among other coarse-grained approaches, the Dissipative Particle Dynamics (DPD) formalism is attracting significant attention [45, 47]. In such technique the particles (beads) represent groups of molecules rather than atoms, and they interact with each other via soft potentials as discussed in Chapter 2. DPD was introduced by Hoogerbrugge and Koelman [45], and modified later on [47, 48, 55]. Compared to other coarse-graining techniques based on ‘soft’ effective interaction potentials [56], the simple soft DPD potential allows practitioners to use relatively long time steps, while providing a correspondence between DPD interaction parameters and thermodynamic properties (e.g., solubility parameters, as discussed below) without invoking complicated calculations [47].

One of the most important parameters that can be tuned within a DPD simulation is the one describing repulsions between DPD beads. For pure fluids, this parameter is referred to as the ‘self-repulsion parameter’. Building on results for the compressibility of water, Groot and Warren [47] related the self-repulsion parameter to the density within the simulation box and to the degree of coarse graining, as shown in Equation (3.1) [47, 57, 58]:

$$a_{ii} = k_B T \frac{\kappa^{-1} N_m - 1}{2\dot{\alpha} \rho_{DPD}} \quad (3.1)$$

In this equation $a_{ii}$ is the repulsion parameter between same beads, $k_B$ is the Boltzmann constant, $T$ is the temperature of the system, $\kappa^{-1}$ is the compressibility of water (equals to 15.9835 at 300 K), $N_m$ is the degree of coarse-graining, $\rho_{DPD}$ (beads/ $r_c^3$) is the density inside the simulation box, and the coefficient $\dot{\alpha}$ is estimated empirically to be equal to 0.101 ± 0.001.
When different fluids are simulated, one could tune the repulsive parameter between different beads to reproduce selected experimental properties or to match results obtained from atomistic simulations [39, 40, 42]. Alternatively, one could define the repulsive DPD parameter ‘a priori’, starting from the thermodynamic properties of the pure components, e.g. solubility parameters. For example, Groot and Warren [47] showed how to extract the DPD repulsive parameter from the $\chi_{ij}$ parameter of the Flory-Huggins model via the Equation (3.2):

$$a_{ij} = (a_{ii} + 3.27 \chi_{ij}) \quad \text{at} \quad \rho_{\text{DPD}} = 3 \text{ beads}/r_c^3$$  \hspace{1cm} (3.2)

In Equation (3.2), $a_{ii}$ is the self-repulsion parameter calculated from Equation (3.1), $a_{ij}$ is the repulsion parameter between different beads, $\chi_{ij}$ is the Flory-Huggins parameter between component i and j. The parameter $a_{ij}$ is expressed in units of $k_B T/r_c$, where $r_c$ is the cut-off distance, which defines the range of interaction between two beads. Maiti et al. [58] showed that increasing the repulsion parameter to match relatively high degree of coarse-graining could yield a deviation from the experimental values of the interfacial tension. Instead of using parameters as calculated from Equation (3.1), a reduced value of $a_{ii}$ is often used in Equation (3.2) to reproduce experimental interfacial tension data [59].

The $\chi_{ij}$ parameter can be estimated experimentally, as well as via other approaches. Oviedo-Roa et al. [60], for example, reproduced the critical micelle concentration of dodecyltrimethyl ammonium chloride when the Flory-Huggins $\chi_{ij}$ parameter between different entities was estimated using the infinite dilution activity coefficients as produced from quantum-atomistic simulations. On the other hand, according to the regular solution theory, the $\chi_{ij}$ parameter could be related to the solubility parameters of different species [61, 62]:

$$\chi_{ij}(T) = \frac{V_i}{RT} \left( \delta_i(T) - \delta_j(T) \right)^2$$  \hspace{1cm} (3.3)

In Equation (3.3), $\delta_i(T)$ and $\delta_j(T)$ are the solubility parameters of component i and j, $V_i$ is the molar volume of component i (in this notation, coefficient i represents the solvent, and j the solute), and R is the gas constant. It is worth noting that when DPD simulations are employed, it is common practice to use the volume of one bead as partial molar volume in Equation (3.3) [37, 58, 59].
Lindvig et al. [63] discussed how the $\chi_{ij}$ parameter can be obtained from Hansen solubility parameters. The model proposed yielded a good prediction of the solubility of different polymers in a large group of solvents. The Hansen solubility parameters for component $i$ results from contributions due to dispersion interactions ($\delta_{i,d}$), dipolar interactions ($\delta_{i,p}$), as well as hydrogen bond effects ($\delta_{i,hb}$), all related to the Hildebrand solubility parameter $\delta_{i}$ according to:

$$\delta_{i}^2 = \delta_{i,d}^2 + \delta_{i,p}^2 + \delta_{i,hb}^2$$ \hspace{1cm} (3.4)

In the Hansen theory, the solubility parameters provide an accurate description of polar systems [61]. Lindvig and co-workers proposed to extract $\chi_{ij}$ from Hansen solubility parameters, using Equation (3.5):

$$\chi_{ij} = \alpha \frac{V_i}{RT} \left( (\delta_{i,d} - \delta_{j,d})^2 + 0.25(\delta_{i,p} - \delta_{j,p})^2 + 0.25(\delta_{i,hb} - \delta_{j,hb})^2 \right)$$ \hspace{1cm} (3.5)

In Equation (3.5) $\alpha$ is a correction factor. These authors showed that changing this correction factor allows them to provide a good prediction of the thermodynamic property and solubility of four polymers [poly (butyl methacrylate), poly (methyl methacrylate), poly (ethyl methacrylate), and poly (vinyl acetate)] in various solvents (polar, non-polar, and hydrogen-bonding ones), and suggested a value of 0.6 as optimum for their systems.

In this chapter, a procedure is introduced to determine the DPD repulsive parameters for a water/oil system in the presence of surfactants. The model parameters are validated by simultaneously representing the water/oil interfacial tension and the properties of the aqueous surfactant system. The estimated parameters are screened using different solubility theories first, and then simulations are conducted to identify the micellar properties in water. Finally, a water/oil system is simulated in presence of surfactants, proving that the simulations show a good representation of such a system. This study is conducted for a system composed of water/benzene containing a family of non-ionic polyethylene oxide surfactants. The reliability of the approach is then extended to a few water/organic liquid binary systems.

The remainder of this chapter is organised as follows: In Section 3.3, the computational details are presented. In Section 3.4, the force fields are validated by comparing the simulations results obtained when the DPD parameters derived from different methodologies are implemented. In this section, the water/benzene system is considered as a test case, and then
the procedure is applied to a few other binary fluid systems. In Section 3.5, a detailed characterization of non-ionic surfactant aggregates in aqueous systems is provided. Finally, in Section 3.6, the results of the simulations for the water/benzene system are discussed in the presence of surfactants. Finally, a brief conclusion is presented to provide a summary of the main findings.

### 3.3. Simulation Models and Algorithms

#### 3.3.1. Coarse-Grained Models and Algorithms

All simulations presented here are conducted using the simulation package LAMMPS [53], with the isothermal pair style DPD force fields. The random and dissipative parameters are set to $\sigma = 3$ and $\gamma = 4.5$ [47]. The time step $\Delta t = 0.04 \tau$ is used to integrate the equations of motion. Simulations are performed in a rectangular box of dimensions $30 \times 30 \times 40 \, r_c^3 \, (L_x \times L_y \times L_z)$. The simulations are intended to reproduce ambient conditions.

In the first instance, water, benzene, and surfactants are simulated. The degree of coarse graining of the water beads is chosen to be 5, which means that each DPD water bead represents 5 water molecules. Thus, the volume of one DPD bead ($V_{\text{bead}}$) equals $\sim 150 \, \text{Å}^3$. The density ($\rho_{\text{DPD}}$) in the simulation box is taken as 3 beads$/r_c^3$, which means that the total number of beads is 108000 in all simulations. The cut-off distance ($r_c$) is taken as 1 reduced to unit lengths, and according to the relation $r_c = \sqrt[3]{\rho_{\text{DPD}} V_{\text{bead}}}$, $r_c$ is equal to 7.66 Å and the diameter of one bead equals 0.86 $r_c$. Because this volume approximates that of one benzene molecule, in this work, one benzene molecule is represented by one DPD bead.

To validate the approach optimised for the water/benzene system, other interfaces are considered, such as; water/n-octane, water/1,1-dichloroethane, water/methyl cyclohexane, water/isobutyl acetate. For consistency, the degree of coarse graining was not changed compared to the water/benzene system.

Two non-ionic surfactants of the $C_8H_{17}O(C_2H_4O)_mH$ family are considered. In the first one, the surfactant molecule is represented by three connected beads: one head represents one diethylene glycol group, and two tail beads represent three ethylene molecules, as shown in Figure 3-1. This surfactant is denoted as $H1T2$ in what follows. In the second surfactant, there are 3 head beads and 2 tail beads. This surfactant is denoted as $H3T2$. Consecutive beads in the surfactant molecule are connected with harmonic springs (see Equation (2.8) in Chapter 2)
having an equilibrium bond length approximately equal to the bead diameter \( r_0 = 0.9 \, r_c \), and spring constant \( k_s = 100 \, k_B T/r_c^2 \) [64].

**Figure 3-1.** Schematic representation of the coarse-grained DPD beads representing the different components simulated in the systems considered in this chapter.

### 3.3.2. DPD Interaction Parameters

As briefly discussed above, in a DPD simulation box with density 3 beads/\( r_c^3 \) and degree of coarse graining 5 water molecules/bead, the self-repulsion parameter \((a_{ii})\) should be 131.5 [see Equation (3.1)]. However, the value 25 has often been used in the literature [58, 59], in an effort to reproduce experimental properties, as the estimation of \( a_{ij} \) depends on \( a_{ii} \) as discussed above [Equation (3.2)]. It is worth noting that, in this study, all systems are simulated to mimic real systems at conditions equivalent to 25°C and 1 bar.
Figure 3-2. Different combination of parameters estimated using two different values of self-repulsion parameters $a_{ii}$ (25 and 131.5). Equation (3.2) is applied along with Equations (3.3) and (3.5) to estimate the repulsion between different beads ($a_{ij}$) starting from both values $a_{ii}$, to provide a comparison between models based on DPD parameters estimated from both Hildebrand and Hansen solubility parameter theories.

Using either $a_{ii} = 25$ or $a_{ii} = 131.5$, different combinations of $a_{ij}$ DPD parameters were considered, as shown schematically in Figure 3-2. A systematic comparison is conducted to derive parameters from different solubility parameter theories, as well as to understand the effect of the correction factor ($\alpha$) in Equation (3.5) [63]. Ultimately, the ability of coarse-grained simulations to reproduce the water-benzene interfacial tension is tested for each of the 10 combinations of parameters shown in Figure 3-2. To obtain the DPD parameters using different solution theories, the Hansen and the Hildebrand solubility parameters are required, which are listed in Table 3-1 [61]. The values for $\delta_{\text{Hildebrand}}$ as listed in Table 3-1 are calculated from Equation (3.4). All the parameters used for the 10 combinations of Figure 3-2 are listed in Appendix A (Table A-1).
Table 3-1. Hansen and Hildebrand solubility parameters estimated at 25°C, in (MPa$^{1/2}$), and molar volume in cc/mol for some of the compounds used in this study [61].

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta_D$</th>
<th>$\delta_P$</th>
<th>$\delta_H$</th>
<th>$\delta_{\text{Hildebrand}}$</th>
<th>$V_{\text{molar}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>15.5</td>
<td>16</td>
<td>42.3</td>
<td>47.81</td>
<td>18</td>
</tr>
<tr>
<td>Benzene</td>
<td>18.4</td>
<td>0</td>
<td>2</td>
<td>18.51</td>
<td>89.4</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>16.6</td>
<td>12</td>
<td>20.7</td>
<td>29.12</td>
<td>94.9</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>16</td>
<td>0.8</td>
<td>2.8</td>
<td>16.26</td>
<td>63</td>
</tr>
</tbody>
</table>

3.3.3. Computational details

The procedure is optimized for the water/benzene system. The interfacial tension is calculated by performing simulations for systems with equal number of beads of water and benzene (54000 beads each). Water and benzene phase separate. Water is at the bottom of the simulation box, benzene at the top, as shown in Figure 3-3. Note that the Z direction of the simulation box is perpendicular to the liquid-liquid interface. The interfacial tension between the two liquids is determined using the pressure tensors as shown in Equation (3.6) [58]. The interfacial tension, $\gamma_{\text{DPD}}$, is averaged over the last $10^5$ steps of a total $10^6$ steps, after equilibrium has been reached.

$$\gamma_{\text{DPD}} = \frac{1}{2} \left( P_{zz} - \frac{P_{xx} + P_{yy}}{2} \right) L_z$$  \hspace{1cm} (3.6)

To convert the calculated interfacial tension from the DPD units to mN/m, the simulated value is multiplied by $k_B T/r_c^2$ [58]. It is worth noting that the factor $\left(\frac{1}{2}\right)$ in Equation (3.6) is due to the presence of two interfaces in the simulations, as shown in Figure 3-3.
Figure 3-3. The water (transparent blue beads) - benzene (grey beads) system simulated in Chapter 3.

To quantify the properties of aqueous surfactants, simulations were conducted in bulk water at increasing surfactant volume fraction $\phi$. As $\phi$ increases, surfactants might aggregate. To identify a cluster of surfactant molecules, the approach proposed by Johnston et al. was followed [65]. In this approach it is estimated that two surfactants belong to the same cluster when the distance between any of their hydrophobic tail beads is lower than $1 \, r_c$; note that this is the cut-off distance for the conservative interactions between DPD beads in simulations presented here. Once a micelle is identified, its properties are quantified as ensemble averages. Properties of interest include aggregation number, number of micelles in the simulation box, and the free surfactant volume fraction in the presence of micelles, which is used to estimate the critical micelle concentration (CMC). These properties are estimated after a total $2 \times 10^6$ simulation steps and averaged over $1.9 \times 10^6$ steps. The first $0.1 \times 10^6$ steps are considered as the equilibrium time. Regarding the micellar shape, qualitative information is obtained by analysing snapshots taken at the end of $10^6$ simulations steps.

The micellar properties depend on the cluster size cut-off, which means the aggregation number at which a cluster is considered as a micelle or as a surfactant aggregate (submicelles). Johnston et al. reported the cluster size distribution for different surfactants [65]. They used a minimum, or a gap in the cluster size distribution as the cluster size cut-off: clusters smaller than such cut-off were not considered micelles, clusters larger than such cut-off were considered as micelles. They found that this cut-off number could depend on the concentration of surfactant and the surfactant type. Building on this analysis, the cluster size distribution (based on aggregation number) of the simulated surfactants was calculated at different surfactant volume fractions with respect to the water beads ($\phi$) as shown in Appendix A (Figure
A- 1 and Figure A- 2). In agreement with the previous studies, the cut-off number was found to be dependent on the surfactant type and its volume fraction $\varphi$.

To calculate the critical micelle concentration (CMC) the approach proposed by Santos et al. was implemented [66]. They demonstrated that the CMC can be estimated by the constant value of the volume fraction free surfactant ($\varphi_{\text{oligomer}}$) in the accessible volume of aqueous phase (water beads in this case) when the total surfactant volume fraction in water ($\varphi$) increases.

In Figure A- 3 and Figure A- 4 in Appendix A, the number of micelles and $\varphi_{\text{oligomer}}$ found in the simulation box as a function of simulation time is reported for both surfactant molecules considered in this study. The results proved that $0.1 \times 10^6$ steps are enough to reach a dynamic equilibrium for systems presented here.

The correspondence between simulation time $\tau$ and real time can be estimated by comparing the experimental diffusion constant of water $D_{\text{water}}$ ($2.43 \times 10^{-5}$ cm$^2$/s), at 25°C and 1 bar, to the diffusion constant of the water beads in the DPD simulation, $D_{\text{sim}}$, as shown in Equation (3.7) [55]. Following standard protocols, the simulated diffusion constant is calculated by the slope of the mean square displacement (MSD) of the water beads against time (in $r_c^2/\tau$), as described by Equation (3.8).

$$\tau = \frac{N_m D_{\text{sim}} r_c^2}{D_{\text{water}}}$$  \hspace{1cm} (3.7)

$$D_{\text{sim}} = \frac{\text{MSD}}{6t}$$  \hspace{1cm} (3.8)

Based on the procedure just summarized, it is concluded that the time step in the simulations presented here is equal to 15.2 ps and 5.45 ps in case of self-repulsion parameter equals 25 and 131.5 respectively. This decrease in the diffusion coefficient of the beads might be due to the fact that, as proved previously by Goicochea at al.[64], increasing the self-repulsion parameter to match a high degree of coarse graining increases the excess pressure inside the simulation box according to:

$$P = \rho k_B T + \dot{\alpha} \rho^2$$ \hspace{1cm} (3.9)

This increase in the excess pressure hinders the movement of the beads inside the simulation box, and by consequence, decreases the diffusion coefficient in DPD unit even if the density is
constant. The dependency of the diffusion coefficient on the degree of coarse graining and the self-repulsion parameter were also studied by Pivkin et al. [57] and they also found that increasing $a_{ii}$ to match a high degree of coarse graining leads to a decrease in the diffusion coefficient.

3.4. Simulation Results – Model Validation

3.4.1. Interfacial tension

The experimental interfacial tension between water and benzene is 32.5 mN/m at 25°C [67]. The water-benzene interfacial results as obtained from the simulations are summarized in Table 3-2. As expected based on literature observations [58, 59], in case of deriving the DPD parameters using the Hildebrand theory, realistic value for the interfacial tension is only produced at a self-repulsion parameter equals to 25. On the other hand, deriving the DPD parameters using the Hansen solubility theory yields interfacial tension values in reasonable agreement with experiments when the self-repulsion parameter equals either 25 or 131.5, although for different values of the correction parameter $\alpha$.

When the self-repulsive parameter is 25, the correction parameter $\alpha$ needs to be exceedingly high (2), while when the self-repulsive parameter is 131.5 (representing accurately the degree of coarse graining of 5 water molecules/bead), a reasonable value for $\alpha$ (0.7), yields a value for the simulated interfacial tension that is in good agreement with the experimental value. Presumably, adjusting $\alpha$ slightly above 0.7 could optimize the match between simulated and experimental interfacial tension when $a_{ii}$ is 131.5. These results suggest that maintaining the original formalism and its relation to experimental observables (i.e., see Section 3.3.2) is critical for deriving sensible coarse-grained parameters.

The three sets of parameters that yield water/benzene interfacial tensions that are in reasonable agreement with experiments are identified as Model 1, Model 5 and Model 8 in Table 3-2. These are the sets of parameters that are used below to determine which one is also able to predict a realistic behaviour of surfactants in water.
Table 3-2. The simulated water/benzene interfacial tension using ten models presented in Figure 3-2. All values are estimated in condition equivalent to 25°C and 1 bar. The underlined values are in reasonable agreement with experimental data.

<table>
<thead>
<tr>
<th>Model</th>
<th>IFT (mN/m)</th>
<th>( a_{ii} )</th>
<th>Solubility parameter theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model 1</td>
<td>32 ± 5</td>
<td>25</td>
<td>Hildebrand</td>
</tr>
<tr>
<td>Model 2</td>
<td>17.5 ± 5</td>
<td>25</td>
<td>Hansen (( \alpha = 0.6 ))</td>
</tr>
<tr>
<td>Model 3</td>
<td>20 ± 5</td>
<td>25</td>
<td>Hansen (( \alpha = 0.7 ))</td>
</tr>
<tr>
<td>Model 4</td>
<td>25.5 ± 5</td>
<td>25</td>
<td>Hansen (( \alpha = 1 ))</td>
</tr>
<tr>
<td>Model 5</td>
<td>33 ± 5</td>
<td>25</td>
<td>Hansen (( \alpha = 2 ))</td>
</tr>
<tr>
<td>Model 6</td>
<td>61 ± 9</td>
<td>131.5</td>
<td>Hildebrand</td>
</tr>
<tr>
<td>Model 7</td>
<td>26 ± 8.5</td>
<td>131.5</td>
<td>Hansen (( \alpha = 0.6 ))</td>
</tr>
<tr>
<td>Model 8</td>
<td>30 ± 8</td>
<td>131.5</td>
<td>Hansen (( \alpha = 0.7 ))</td>
</tr>
<tr>
<td>Model 9</td>
<td>41.5 ± 8.5</td>
<td>131.5</td>
<td>Hansen (( \alpha = 1 ))</td>
</tr>
<tr>
<td>Model 10</td>
<td>65 ± 8</td>
<td>131.5</td>
<td>Hansen (( \alpha = 2 ))</td>
</tr>
</tbody>
</table>

3.4.2. Micelle formation

To identify the formation of micelles in aqueous systems Model 1, Model 5 and Model 8 are used, as identified in Table 3-2. The simulations are conducted in bulk water at increasing surfactant volume fraction \( \phi \). The results obtained for \( \phi \) equal to 0.001, 0.003 and 0.05, in the form of simulation snapshots, are shown for the H1T2 surfactant in Figure 3-4. The results show that force fields Model 1 and Model 5 yield surfactant aggregates already for surfactant volume fraction 0.001. Note that no free surfactants are observed for these parameterizations until \( \phi \) equals 0.05. For the Model 8 parameterization, the results show that at low \( \phi \) the surfactants are well dispersed in water. As the surfactant volume fraction increases, a micelle appears surrounded by free surfactant. This representation seems realistic, as it allows for the surfactants to exchange between the micelle and the free surfactants.
Figure 3-4. Aqueous surfactant H1T2 simulated at increasing volume fraction $\phi$ (top: 0.001; middle: 0.003; bottom: 0.05). From left to right, the snapshots represent results obtained for different force fields: Model 1 (left); Model 5 (middle); Model 8 (right). The snapshots are obtained after $10^6$ simulation steps (5.45 $\mu$s).

Although the simulation results presented in Figure 3-4 suggest that Model 8 yields parameter that reproduce the properties of H1T2 surfactants in water, when the surfactant volume fraction is increased further, the single micelle grew, rather than multiple micelles appearing in equilibrium with free surfactant. The expected behaviour for surfactants instead is that as the surfactant volume fraction $\phi$ increases above the critical micelle concentrations, multiple micelles form [65]. The simulations showed therefore evidence of phase separation between surfactant and water, rather than surfactant micelles formation in water.
To prevent phase separation, the repulsion parameter between water and the surfactant hydrophilic groups (head) was set to zero, following literature simulations for the STS [68], as well as for the SDS surfactant in water [49, 51]. The simulations discussed in Figure 3-4 are repeated for the three force fields (Model 1, Model 5 and Model 8) but with the reduced repulsion between water and surfactant head-groups. The results are shown in Figure 3-5 for surfactant volume fraction $\phi$ equal to 0.001 and 0.003.

**Figure 3-5.** Aqueous surfactant H1T2 simulated at increasing volume fraction $\phi$ (top: 0.001; bottom: 0.003). From left to right, the snapshots represent results obtained for different force fields: Model 1 (left); Model 5 (middle); Model 8 (right). As opposed to the results shown in Figure 3-4, the water-surfactant head-group repulsion parameter has been set to zero in these simulations. The snapshots are obtained after $10^6$ simulation steps (5.45 µs).

The results show that the surfactants yield multiple micelles for each of the force fields considered. However, the parameterization based on Model 1 and Model 5 does not allow for free surfactants in coexistence with the micelles. The Model force field instead allows the description of multiple micelles in equilibrium with free surfactant. This force field is summarized in Table 3-3. Based on my results, DPD simulations based on such parameters
predict realistic values for the water-benzene interfacial tension and describe realistic behaviour of aqueous H1T2 surfactants.

It is possible that Model 8 yields a realistic representation of the simulated system because the parameters are mapped from the proper coarse-graining degree and derived from the solubility parameters of the Hansen theory, which accounts for the contribution of dispersion, polar and hydrogen-bond effects [61]. Model 1 and Model 5 were derived from Hildebrand solubility parameters, based on the regular solution theory, which works best for nonpolar compounds where solvation and association effects are negligible [69].

**Table 3-3.** DPD parameters, derived from Model 8 (see Table 3-2) that are able to both predict realistic water/benzene interfacial tension and realistic behaviour of aqueous H1T2 surfactants.

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Benzene</th>
<th>Head</th>
<th>Tail</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>131.5</td>
<td>171.43</td>
<td>0</td>
<td>168.9</td>
</tr>
<tr>
<td>Benzene</td>
<td>131.5</td>
<td>142.07</td>
<td>132.01</td>
<td></td>
</tr>
<tr>
<td>Head</td>
<td>131.5</td>
<td>131.5</td>
<td>140.83</td>
<td></td>
</tr>
<tr>
<td>Tail</td>
<td>131.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**3.4.3. Other binary fluid systems**

To assess the reliability of the approach described above to study the water/aromatic hydrocarbon interface, in this section, other interfaces are considered, e.g. between water and (a) one aliphatic hydrocarbon (n-octane), (b) one aliphatic halocarbon (1,1-dichloroethane), (c) one saturated cyclic compound (water/methyl cyclohexane), and (d) one ester (water/isobutyl acetate). These systems represent a variety of structural characteristics. For each binary system, the simulated interfacial tension is compared against experimental data. As discussed above for Model 8, \( \alpha_{ii} = 131.5 \) is employed, and \( \alpha_{ij} \) is calculated via Equation (3.2) once \( \chi_{ij} \) is estimated from Equation (3.5) and the Hansen solubility parameter for the chosen compounds. In Table 3-4, the number of beads that represents the different fluids are listed according to their molar volume and the chosen degree of coarse-graining. It is found that the correction factor varied from 0.4 to 1.4. This large variation reflects the fact that some interfaces require strong repulsion between different beads to yield high interfacial tension. In fact, the results
show that the correction factor increases as the interfacial tension increases. A final note, for the 1,1-dichloroethane IFT with water, it is compared to the available experimental values of 1,2-dichloroethane at 25°C.

**Table 3-4.** Calculated IFT (mN/m) (at conditions equivalent to 1 bar) of water/liquid systems from DPD simulations using Hansen solubility parameters and tuning the correction factor \( \alpha \) in Equation (3.5) to match the experimental data [67, 70, 71].

<table>
<thead>
<tr>
<th>Model</th>
<th>Model</th>
<th>Correction factor ( \alpha )</th>
<th>Water/liquid repulsion parameter</th>
<th>Experimental IFT at 25°C</th>
<th>Simulated IFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>1 bead represents 1 molecule</td>
<td>0.7</td>
<td>171.43</td>
<td>32.5</td>
<td>30 ± 8</td>
</tr>
<tr>
<td>n-octane</td>
<td>2 beads represent 1 molecule</td>
<td>1.4</td>
<td>216.86</td>
<td>51.22</td>
<td>48 ± 11.5</td>
</tr>
<tr>
<td>1,1-dichloroethane</td>
<td>1 bead represents 1 molecule</td>
<td>0.8</td>
<td>170.03</td>
<td>28.4</td>
<td>29 ± 9</td>
</tr>
<tr>
<td>Methyl cyclohexane</td>
<td>3 beads represent 2 molecules</td>
<td>1</td>
<td>190.01</td>
<td>41.9</td>
<td>41.5 ± 13</td>
</tr>
<tr>
<td>Isobutyl acetate</td>
<td>3 beads represent 2 molecules</td>
<td>0.4</td>
<td>148.77</td>
<td>13.2</td>
<td>13.5 ± 12</td>
</tr>
</tbody>
</table>

### 3.5. Simulation Results – Aqueous Micellar Properties

#### 3.5.1. Size distribution

Using the parameterisation discussed in Table 3-3, the surfactants H1T2 and H3T2 were simulated in water at different \( \phi \). The snapshots are reported after \( 2 \times 10^6 \) simulation steps in Figure 3-6 and Figure 3-7, together with the enlargement of a representative micelle, respectively.

The aggregation number distribution (cluster size distribution) is reported at \( \phi = 0.18 \) in Figure 3-8 (a) and (b) for H1T2 and H3T2 surfactants, respectively. Based on the cluster size distributions, the cluster cut-off is chosen as 10 for both surfactant types at this \( \phi \). This aggregation number shows a gap (Figure 3-8 (a)) and a minimum (Figure 3-8 (b)) in the cluster size distribution. All cluster size distributions as obtained for different volume fractions \( \phi \) of both surfactant molecules are shown in Appendix A.

Once the cluster cut-off is identified, it is possible to classify clusters as micelles (their size is larger than the cut-off) or submicelles. The average number of micelles obtained at increasing
surfactant volume fraction is shown in Figure 3-9 for both H1T2 and H3T2 surfactants. It is expected that the number of micelles in the systems increases linearly with \( \varphi \). Instead, the results show a curvature, especially for the H3T2 surfactant. These results show that, as \( \varphi \) increases, the micelles increase in size. This behaviour is reported experimentally and, in some cases, leads to a micellar shape transformation (see the micellar shape section below).

In Figure 3-10, the mean aggregation number is calculated for the systems considered in Figure 3-9. Note that the submicelles are excluded from this analysis. At low surfactant volume fraction \( \varphi \), a sudden increase in the aggregation number is observed due to the formation of the first micelles in the system. Instead of a constant aggregation number at high surfactant volume fraction, the results show a slow increase in the aggregation number. The results just discussed are consistent with the results shown in Figure 3-9. It should be noted that previous DPD simulations also reported that the aggregation number is not constant after the formation of micelles [65]. Instead, it depends on the surfactant volume fraction \( \varphi \), and in general increases with \( \varphi \) following the law of mass action.
Figure 3-6. The aqueous H1T2 surfactant simulated at increasing volume fraction $\varphi$ (left to right, top to bottom: 0.001, 0.002, 0.003, 0.005, 0.05, 0.11, 0.14, and 0.18). The snapshot at the bottom is an enlargement of a representative spherical micelle at conditions equivalent to 25°C and 1 bar.
Figure 3-7. The aqueous H3T2 surfactant simulated at increasing volume fraction $\phi$ (left to right, top to bottom: 0.002, 0.003, 0.0042, 0.01, 0.02, 0.053, 0.087, 0.11, 0.176 and 0.2). The snapshot at the bottom is an enlargement of a representative spherical micelle at conditions equivalent to 25°C and 1 bar.
Figure 3-8. Cluster size distribution for aqueous (a) H1T2 and (b) H3T2 surfactants when $\phi$ equals 0.18. The red circle in the X-axis identifies the cluster cut-off.
Figure 3-9. The increase in the number of micelles with increasing the surfactant volume fraction for both H1T2 and H3T2 surfactant molecules at conditions equivalent to 25°C and 1 bar.

Figure 3-10. Mean aggregation number as a function of surfactant volume fraction for H1T2 and H3T2 surfactants (volume of surfactant beads/volume of water beads).

3.5.2. Critical Micelle Concentration (CMC)

To estimate the critical micelle concentration (CMC) for H1T2 and H3T2 surfactants, the volume fraction of the surfactant oligomers ($\phi_{\text{oligomer}}$) is calculated as the surfactant volume fraction increases in the simulations. In Figure 3-11, the results are reported: $\phi_{\text{oligomer}}$ increases as $\phi$ increases until the CMC is reached, after which $\phi_{\text{oligomer}}$ remains constant. This plateau is reached at $\phi_{\text{oligomer}} = 0.00125$, equivalent to 0.004624 ± 0.0004 mole/litre for H1T2, and at $\phi_{\text{oligomer}} = 0.006$, equivalent to 0.01402 ± 0.0017 mole/litre for H3T2. In the case of H3T2, it was found that at surfactant volume fraction 0.0042, just below the CMC, unstable micelle was found then it dissolved in the bulk water again. This
concentration is not included in the calculations of the CMC or in the properties mentioned above.

Figure 3-11. Volume fraction of the free surfactant ($\phi_{\text{oligomer}}$) as a function of $\phi$ for aqueous H1T2 and H3T2 surfactants (volume of surfactant beads/volume of water beads). The results are averaged over the last $1.9 \times 10^6$ steps of the total $2 \times 10^6$ steps for each simulation.

The CMC results are compared in Table 3-5 to experimental values reported for polyethylene oxide non-ionic surfactants [11, 12, 72]. The simulated CMC for H1T2 is similar to the experimental one for octyl polyethylene oxide $C_8E_1$ (0.0049 mole/litre) [12, 72]. The simulated CMC increases as the length of the hydrophilic group increases (i.e., compare results for H1T2 to H3T2 surfactants). This is consistent with experiments, as the simulated CMC for H3T2 is similar to the experimental one for $C_8E_9$ (0.013 mole/litre) [11, 72].

Table 3-5. CMC in mole/litre determined from simulations and reported from experiments at conditions equivalent to 25°C and 1 bar.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0046 ± 0.0004</td>
<td>0.0049</td>
</tr>
<tr>
<td>H1T2</td>
<td>$C_8E_1$ (octyl glycol ether)</td>
</tr>
<tr>
<td>0.014 ± 0.0017</td>
<td>0.013</td>
</tr>
<tr>
<td>H3T2</td>
<td>$C_8E_9$ (nonaoxyethylene glycol monoether)</td>
</tr>
</tbody>
</table>
3.5.3. Micellar shape

It has been reported that micelles for some non-ionic polyethylene oxide surfactants transform from spherical to rod-like as the surfactant concentration increases [73, 74]. For example, Nilsson et al. [75] reported that the size of \( \text{C}_{12}\text{E}_5 \) micelles increases and exhibit a shape transition from spherical to rod-like micelles with increasing surfactant concentration. Consistently with these experimental observations, at low surfactant volume fractions, spherical micelles with different aggregation numbers are observed for both H1T2 and H3T2 simulated surfactants (Figure 3-6 and Figure 3-7). When the volume fraction of aqueous H1T2 is increased to \( \varphi = 0.43 \) (volume of surfactant beads/volume of water beads), micelles with ellipsoidal shape are observed, as well as rod-like micelles. A similar shape transformation is observed for H3T2 in water when the volume fraction is increased to \( \varphi = 1 \) (volume of surfactant beads/volume of water beads). Snapshots of these two simulations are shown in Figure 3-12 along with examples of micelles observed in both systems.

![Figure 3-12](image)

Figure 3-12. The ellipsoidal and rod-like micelles observed for H1T2 (left) and H3T2 (right) at \( \varphi = 0.43 \) and 1 (volume of surfactant beads/volume of water beads), respectively, after \( 10^6 \) simulations steps at conditions equivalent to 25°C and 1 bar.
3.6. Water/Benzene/Surfactant Systems

The parameterization of Table 3-3 is able to reproduce the water/benzene interfacial tension as well as several properties of aqueous micelles for both H1T2 and H3T2 surfactants. This parameterization is implemented here to simulate water/benzene interfaces in the presence of surfactants. A simulation box with an equal amount of beads representing water and benzene is prepared (number of beads of each constituent are listed in Table 3-6 for different simulations). As the simulation progresses, water and benzene phase separate. The Z direction of the simulation box is perpendicular to the water-benzene interface. When surfactants are present in the system, they are expected to accumulate at the water/benzene interfaces. Figure 3-13 (a) and (b) show representative simulation snapshots obtained when 300 surfactants (either H1T2 or H3T2) are introduced to water/benzene system.

<table>
<thead>
<tr>
<th>Molecules</th>
<th>H1T2</th>
<th>H3T2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>53550</td>
<td>52500</td>
</tr>
<tr>
<td>Benzene</td>
<td>53550</td>
<td>52500</td>
</tr>
<tr>
<td>Surfactants (Head/Tail)</td>
<td>300/600</td>
<td>1000/2000</td>
</tr>
</tbody>
</table>

At these conditions, little, if any surfactant exists in the bulk phases. As mentioned before, these simulations are conducted at temperature equivalent to 25°C and pressure 1 bar. The water/benzene interfacial tension (30 mN/m) is reduced to 26.3 ± 9.6 and 26.6 ± 9.2 mN/m by 300 H1T2 and H3T2 surfactants, respectively. When the number of H1T2 and H3T2 surfactant molecules is increased to 1000 and 700, respectively, the interfacial tension is reduced to 17.4 ± 8.5 and 16.3 ± 10 mN/m, respectively. The correspondent snapshots are shown in Figure 3-13 (c) and (d). The surfactant concentrations were chosen, via trial and error, to achieve maximum interfacial saturation before surface deformation.

Increasing the surfactant concentration further to 1200 molecules, the water/benzene interfaces saturate, and micelles appeared in bulk water. At these conditions, oil beads were found inside the micelles, suggesting that the simulations are consistent with the formation of
micro-emulsions. A schematic representation of these later simulations is shown in Figure 3-14 with snapshots of the micelles contain benzene beads in both surfactant molecules.

It is concluded that the DPD parameterization of Table 3-3 yields properties of the water/benzene/H1T2 and water/benzene/H3T2 systems that are qualitatively consistent with experimental expectations, where surfactant molecules diffuses to the interface resulting in the reduction of interfacial tension. With the increase of surfactants concentration, micelles start to from trapping oil inside mimicking a micro-emulsion systems.

Figure 3-13. Representative snapshots for water/benzene/H1T2 (left) and water/benzene/H3T2 (right) systems containing 300 (a and b), 1000 H1T2 (c) and 700 H3T2 (d) surfactants.
Figure 3-14. Snapshots of water/benzene system in presence of 1200 molecules of H1T2 (left) and H3T2 (right), with oil beads entrapped inside micelles found in each simulation (bottom), at conditions equivalent to 25°C and 1 bar. Oil beads are shown in grey.

3.7. Conclusions

In this chapter, a systematic process for determining DPD parameters is implemented for simulating water/oil interfaces in the presence of non-ionic surfactants. The Hansen/Flory-Huggins theory proved its ability to provide parameters that reproduce experimental interfacial tension consistent with the degree of coarse graining selected for the simulations. The approach was optimised for the water/benzene system and validated for other binary liquid systems. The results show that to reproduce the properties of aqueous micelles formed by non-ionic surfactants of the $C_8H_{17}O(C_2H_4O)_mH$ family, it is necessary to strongly reduce the repulsive parameters between water and surfactant head groups.

The resultant parameterization is able to simulate the expected behaviour of non-ionic surfactants in water and to predict their critical micelle concentration in good agreement with experiments, including the dependency of the CMC on the length of the surfactant head group and the shape transformation of micelles as the surfactant volume fraction increases. When the parameterization is implemented to simulate water/benzene/surfactant systems the results are in qualitative agreement with experiments. They show that the surfactants accumulate at the liquid/liquid interface reducing the interfacial tension; that the surfactants do not distribute significantly on either pure bulk phase until the interfaces are saturated by surfactants; and that
when the surfactant amount increases further, the surfactants deform the interface and distribute preferentially in the aqueous phase where they form micelles containing oil beads.
Chapter 4  Quantification of Ostwald Ripening in Emulsions via Coarse-Grained Simulations

The material presented in this chapter was published in 2019 in volume 15, pages 5058-5068 of the Journal of Chemical Theory and Computation.

4.1. Chapter overview

Ostwald ripening is a diffusional mass transfer process that occurs in polydisperse emulsions, often with the result of threatening the emulsion stability. In this chapter, a simulation protocol is designed to quantify the process of Ostwald ripening at the molecular level. To achieve experimentally relevant time scales, the Dissipative Particle Dynamics (DPD) simulation protocol is implemented. The simulation parameters are tuned to represent two benzene droplets dispersed in water. The coalescence between the two droplets is prevented via the introduction of membranes, which allow diffusion of benzene from one droplet to the other. The simulation results are quantified in terms of the changes of the droplets volume as a function of time. The results are in qualitative agreement with experiments. The effect of two different surfactants was also investigated. In agreement with both experimental observations and theory, the addition of surfactants at moderate concentrations decreased the Ostwald ripening rate because of the reduction in the interfacial tension between benzene and water; as the surfactant film becomes dense, other phenomena are likely to further delay Ostwald ripening. In fact, the results suggest that the surfactant that yields higher density at the benzene-water interface delayed more effectively Ostwald ripening. The formation of micelles can also affect the ripening rate, in qualitative agreement with experiments, although the simulations presented in this chapter are not conclusive on such effects. The simulations show that the coarse-grained DPD formalism is able to capture the molecular phenomena related to Ostwald ripening, and reveal molecular-level features that could help to understand experimental observations. The results could be useful for predicting, and eventually controlling the long-term stability of emulsions.
4.2. Introduction

An emulsion is a system of at least 2 immiscible fluids, yielding one phase in the form of droplets dispersed in a continuous phase. Depending on the droplet size, emulsions are categorized into macro- or micro-emulsions [5]. In general, emulsions are kinetically stable, but thermodynamically unstable, as the system free energy is minimised when the two fluids separate and yield two continuous phases. The phase-separation process can be slow, for example because of the presence of surfactants known as emulsifiers. Various surface-active compounds are used for such applications, including solid particles [5, 6, 17, 21, 33, 35, 37]. A kinetically stable emulsion is obtained when the number of droplets, the distribution of their sizes and their arrangement within the continuous phase remain relatively constant within a certain timescale [5]. Over time, an emulsion is expected to become unstable, and the liquids to phase separate. This can occur by four processes: creaming, flocculation, coalescence and Ostwald ripening [5, 6]. Previous computational studies focused on the effect of surfactants and co-polymers on flocculation and coalescence of emulsion droplets [34, 35, 37, 38]. Only few molecular dynamics simulations explicitly considered Ostwald ripening or oil solubilisation into micelles [76-80], despite the fact that ripening could be the principal cause for emulsion destabilization in applications such as amorphous drug nanosuspensions and foodstuff [1-3, 81-83]. Molecular level observations are required to better understand Ostwald ripening as it occurs in oil-in-water emulsions.

Ostwald ripening occurs due to the solubility difference of dispersed fluids due to different droplet sizes. The Kelvin equation describes how solubility depends on droplet size [84]:

\[
c(r) = c(\infty) \exp\left(\frac{2 \gamma V_m}{r_{\text{droplet}} RT}\right)
\]  

(4.1)

Assuming an oil-in-water emulsion, in Equation (4.1), c(r) is the aqueous solubility of the oil (dispersed phase) contained in a droplet of radius \( r_{\text{droplet}} \), while \( c(\infty) \) is the correspondent solubility at a planar interface. \( \gamma \) is the interfacial tension between the two liquids, \( V_m \) is the molar volume of the dispersed phase, \( R \) is the gas constant and \( T \) the absolute temperature. Because, based on Equation (4.1), solubility increases as the droplet radius decreases, the fluid contained in the smaller droplets dissolves preferentially into the continuous phase, where it diffuses to the larger droplets. When the fluid condenses on the surface of the larger droplets,
the overall emulsion droplet size increases, eventually yielding a decrease in the total interfacial area.

Among theories developed to describe Ostwald ripening, the Lifshitz-Slyozov-Wagner (LSW) theory [85, 86] reproduces experimental Ostwald ripening rate data ($\omega_T$) for many emulsions, including benzene-in-water ones [7]. The LSW theory is expressed as:

$$\omega_T = \frac{dr_{\text{critical}}^3}{dt} = \frac{8 \gamma C_w^{\text{eq}} D_w V_m}{9 RT} \quad (4.2)$$

In Equation (4.2), $\omega_T$ is estimated by the linear increase of the cube of the ‘critical radius’ ($r_{\text{critical}}^3$) over time. The critical radius ($r_{\text{critical}}$) is defined as the radius of a droplet whose size does not change, while the droplets of radius ($r_{\text{droplet}} < r_{\text{critical}}$) decrease in size, and droplets of radius ($r_{\text{droplet}} > r_{\text{critical}}$) increase in size. In Equation (4.2), $C_w^{\text{eq}}$ and $D_w$ are the solubility (volume fraction) and the diffusivity of the dispersed phase in the continuous one, expressed in m$^3$/m$^3$ and cm$^2$/s, respectively. Equation (4.2) provides an expression of the Ostwald ripening rate for dilute emulsions, where the effect of the dispersed phase concentration is not considered. In fact, the Ostwald ripening rate can increase when the dispersed phase volume fraction increased from 0 to 0.3 [87]. Kabalnov et al. [88], e.g., included a correction factor of 1.75 when the oil volume fraction increased to 0.1.

Kabalnov et al. [7] showed that the LSW theory satisfactorily reproduces experimental Ostwald ripening rates for several oil-in-water emulsions, including as oil 1,2-dichloeroethane, benzene, nitrobenzene, toluene, and p-xylene. They found that the critical radius coincides with the mean droplet radius ($\bar{r}_{\text{droplet}}$), and that this value changes over time. They showed that increasing the concentration of the surfactant sodium dodecyl sulfate (SDS) within 1,2-dichloeroethane-in-water emulsions reduces the interfacial tension from 31 mN/m (when no surfactant is present) to 3.8 mN/m at 0.1 M surfactant concentration, which would decrease the Ostwald ripening rate by ~ one order of magnitude. In a further study, Kabalnov et al. [88] studied the dependency of the Ostwald ripening rate on the aqueous solubility in water of a series of C$_9$-C$_{16}$ aliphatic hydrocarbons stabilized by SDS. The Ostwald ripening rate decreases by ~ one order of magnitude when the oil chain length increased by two CH$_2$ groups, because of the reduced solubility in water. Although they also observed oil solubilisation into the core of surfactant micelles, they concluded that such phenomenon has negligible effect on Ostwald ripening rate. In a further investigation [89], no changes in Ostwald ripening rate were reported.
as SDS concentration was increased from 0.03 to 1 M (the SDS CMC is ~ 0.0082 M). Taylor et al. [90] reported that the Ostwald ripening rate falls linearly as the SDS concentration increases to the CMC, due to the decrease in the interfacial tension, and then it increases very slightly above it. It was suggested that the micelles have a negligible effect on the ripening rate because of their short lifetime: when the micelles break, they release the oil in the aqueous phase.

In a series of reports, McClements and his group [1, 3, 91-95] described the dependency of the Ostwald ripening rate on surfactant concentration. With the aid of static light scattering [91], they reported that micelles of the non-ionic surfactant Tween 20 formed micelles with oil in their core. The results showed an increase in the droplet size, contrary to expectations. The results were explained as follows: oil solubilisation in micelles caused some droplets to become smaller; these smaller droplets favoured Ostwald ripening, leading to the formation of the larger droplets observed. These authors reported that short unsaturated hydrocarbons have higher solubilisation rate and maximum solubility capacity in the micelles compared to long saturated ones. McClements and co-workers [95] investigated the Oswald ripening rate as a function of surfactant concentration for SDS (ionic) and Tween 20, Brij 35 and Triton X-100 (non-ionic) above their CMC. In these experiments the oil was n-tetradecane, at 5 wt. %. They found a clear dependency of the Ostwald ripening rate on the interfacial tension for non-ionic surfactants. However, the Ostwald ripening rate was the slowest in the presence of SDS, although this surfactant did not yield the lowest interfacial tension. They suggested that surfactants affect the Ostwald ripening rate via their effect on the interfacial tension, and also via the effective interactions between micelles and the droplet surface. For example, in the case of ionic surfactants, the electrostatic repulsion between micelles and droplets surface could prevent oil exchange between the two. Finally, they suggested that the maximum solubilizing capacity of micelles could affect Ostwald ripening, although the results were not conclusive. They found no clear dependency of the Ostwald ripening rate on the solubilisation kinetics or on the solubilisation capacity of micelles of non-ionic surfactants for emulsions containing n-tetradecane [92, 93].

Ariyaprakai et al. [96] reported that the presence of micelles enhanced the rate of Ostwald ripening for different surfactants by factors of up to 50, depending on the surfactant type and concentration. They studied Ostwald ripening of decane-in-water emulsions stabilized by dodecyl ether surfactants with different ethylene oxide (EO) chain lengths: \( \text{C}_{12}\text{E}_7, \text{C}_{12}\text{E}_8, \text{C}_{12}\text{E}_{10} \) and Brij 35 (with ~ 23 EO groups). The results showed that the repulsion between micelles and
droplet surfaces, due to different hydrophilic groups, has no systematic effect on the Ostwald ripening rate. In fact, Ariyaprakai et al. suggested that micelle collision and coalescence with the droplets does not contribute significantly to Ostwald ripening, while the observed increase in Ostwald ripening rate is due to the enhanced oil transport across the aqueous phase facilitated by the ability of micelles to become supersaturated with oil.

Han et al. [82] quantified how Ostwald ripening depends on the characteristic of the interfacial membrane formed by surfactants adsorbed on the droplet surfaces. They quantified the performance of non-ionic polyethylene alkyl ether surfactants as stabilizers for flavour oil emulsions. The surfactants considered were S10 (polyoxyethylene 10 stearyl ether), S20 (polyoxyethylene 20 stearyl ether), L23 (polyoxyethylene 23 lauryl ether) and S100 (polyoxyethylene 100 stearyl ether). Out of these surfactants, S10 was effective at preventing Ostwald ripening, while others, including S100, were not. While no systematic trend was observed, the results were explained by the ability of S10 to yield a dense interfacial membrane, which could delay oil transport. McClements and co-workers [97] reported that SDS-chitosan films could delay ripening of n-tetradecane droplets in water, because the thickness of the interfacial film can provide mechanical resistance to droplets shrinkage and growth. These findings show that the density and the thickness of the interfacial membrane could play a major role on Ostwald ripening and on the stability of emulsions, although systematic trends as a function of surfactants molecular architecture might not be evident because different phenomena take place simultaneously.

Several computational studies related to this topic have also been reported. Karaborni and co-workers [76, 77], for example, studied the solubilisation of oil in aqueous micelles using molecular dynamics (MD) simulations. The oil was an equimolar mixture of two components with different chain lengths [77]. Increasing the chain length was found to decrease the molecular exchange between droplets and aqueous surfactant phase, due to the decrease of oil solubility in water, which agrees with previous experimental observations [91, 96]. In fact, oil molecules were found to diffuse from the droplet to the aqueous phase, and then to the micelle core. Transport of oil molecules from the droplet to the micelles was also detected upon collision between micelles and the droplet. Karaborni and co-workers described the ‘budding-off’ mechanism, according to which adsorbed surfactants depart the droplet surface with some oil molecules, yielding a micelle [76]. The three mechanisms observed during the simulations correspond to those generally considered to interpret experimental data [91, 92, 96]. Mondal et al. [78] carried out MD simulations to study the solubilisation of aromatic compounds such as
benzene, toluene, pyridine and phenol in SDS micelles. They found that pyridine and phenol are solubilized in the Stern layer and the micelle-water interface while non-polar aromatics (benzene and toluene) tend to accumulate in the palisade and inner core of the micelles. The type of the aromatics also affected the shape of the micelles, with polar aromatics deforming the SDS micelles.

Directly simulating Ostwald ripening has been attempted only in idealised systems, presumably because of the high computational requirements. For example, Jung et al. [98], while studying droplet formation and growth in dilute Lennard-Jones (LJ) fluids using Brownian dynamics (BD) simulations, reported evidence of Ostwald ripening. The cluster size was estimated by the number of particles existing in the cluster, which was increasing with time for the large clusters in expense of the size of smaller clusters. Jung et al. [99] also studied the growth of LJ fluid droplets dispersed in a polymer network using MD. Ostwald ripening was observed when the polymer network had an intermediate mesh size, because when the mesh size was too small, the droplets could not form, while when the mesh size was large, droplets coalescence occurred. Kraska [80] explicitly simulated Ostwald ripening using MD, but for two argon clusters dispersed in vapour. To retard coalescence between the clusters, Ostwald ripening was accelerated via adding biases to the system. Zhang et al. [100] simulated coarsening and crystallization of solid particles, and reported that after aggregation, nanoparticles started to coarsen due to atomic diffusion. The two nanoparticles were however at contact. Other computational attempts to understand Ostwald ripening were conducted using phase-field simulations [101, 102].

To complement the experimental observations in the literature, and to provide synergistic molecular-level insights, a simulation set up is introduced here to directly simulate Ostwald ripening for an oil-in-water emulsion. An algorithm specifically designed to prevent creaming, flocculation and coalescence is employed, so that Ostwald ripening is the only mechanism allowed for breaking the emulsion. Benzene-in-water emulsions are selected because Kabalnov et al. [7] reported both experimental and theoretical results for a similar system. Once the capability of the proposed algorithm to replicate Ostwald ripening is demonstrated, the effect of surfactants on the Ostwald ripening rate is quantified. Surfactants concentrations are selected just before the formation of micelles. Focus is on the effect of the hydrophilic group length, and on the effect that could be due to the density and the thickness of the interfacial surfactant film. Two surfactants with different hydrophilic groups are considered, and the results are
compared to experimental data reported by Ariyaprakai et al. [96], Han et al. [82], and McClements and co-workers [97].

The Dissipative Particle Dynamics methodology (DPD) is selected because it is suitable for the investigation of relatively large systems over time scales that are experimentally relevant. The parameters used in this chapter were taken from parameters estimated in Chapter 3.

The remainder of this chapter is organized as follows: in Section 4.3, the simulation methodology, algorithms and parameters are briefly summarised. In Section 4.4, the main simulation results are summarised with a discussion on how they favourably compare to experimental and theoretical observations from literature. Finally, the main outcomes of this chapter are concluded in a brief summary, including some limitations of the method proposed.

4.3. Simulation Models and Algorithms

The Dissipative Particle dynamics (DPD) coarse-grained methodology is implemented. The DPD parameters estimated in Chapter 3 are used in this investigation. These parameters are able to reproduce water-benzene interfacial tension, as well as some of the properties of the octyl polyethylene oxide \(\text{C}_8\text{H}_{17}\text{O(C}_2\text{H}_4\text{O)}_m\text{H} \) aqueous non-ionic surfactants. All the repulsion parameters used are listed in Table 4-1. The other parameters are discussed later in this section. All simulations presented in this chapter are conducted using the simulation package LAMMPS [53], with the isothermal pair style DPD force fields.

Simulations were performed in a rectangular box of dimensions \(74 \times 36 \times 36 \, \text{r}_c^3 \, (L_x \times L_y \times L_z)\), which is shown in Figure 4-1. The simulation methodology is discussed previously in Chapter 3. To study Ostwald ripening, it is necessary to prevent flocculation or coalescence between the droplets. Thus, membranes were inserted between two droplets. Note that two membranes are required because of periodic boundary conditions. Each membrane has channels large enough to allow molecular exchange between the droplets, yet small enough to prevent the droplets from diffusing across the membrane. The height of each channel is equal to \(5 \, \text{r}_c\). The interaction between the membrane and water beads is equal to the self repulsion parameter \((a_{\text{membrane-water}} = 131.5)\) to facilitate the passage of water through the channels, while the repulsion parameter between the membrane and the other constituent is set to a much
higher value \( a_{\text{membrane-oil}} = 200 \) and \( a_{\text{membrane-surfactant}} = 400 \) to prevent any interaction with the membrane. The parameters are reported in Table 4-1.

Two benzene droplets are inserted in water. To observe ripening, it is necessary that the droplets have different sizes. The droplets are of diameter 9.7 (droplet 1) and 26.15 \( r_c \) (droplet 2), equivalent to 7.4 and 20.04 nm, respectively. The number of benzene beads in the two droplets at the beginning of the simulations are 1385 and 27984, respectively.

![Figure 4-1](image)

**Figure 4-1.** Two oil droplets (grey beads) in water (transparent), separated by membranes (yellow beads) located in the middle and at the edges, at conditions equivalent to 25°C and 1 bar.

**Table 4-1.** DPD repulsion parameters in \( k_B T/r_c \).

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Benzene</th>
<th>Head</th>
<th>Tail</th>
<th>Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>131.5</td>
<td>171.43</td>
<td>0</td>
<td>168.9</td>
<td>131.5</td>
</tr>
<tr>
<td>Benzene</td>
<td>131.5</td>
<td>142.07</td>
<td>132.01</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Head</td>
<td>131.5</td>
<td>140.83</td>
<td>400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tail</td>
<td>131.5</td>
<td>400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane</td>
<td>131.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To quantify Ostwald ripening, it is required to identify and count the oil beads that belong to a certain droplet / cluster. The approach proposed by Johnston et al. is followed [65], as
implemented in Chapter 3. In this approach, two surfactants belong to the same droplet / micelle when the distance between any of their hydrophobic tail beads is lower than $1 \, r_c$. If an oil or tail bead is separated by a distance shorter than $1 \, r_c$ from any of the oil beads in a droplet, they are considered as part of that droplet.

The radius of the droplet was estimated from the radius of gyration according to:

$$r_{GYR}^2 = \frac{3}{5} \, r_{droplet}^2$$  \hfill (4.3)

To estimate the radius of gyration, the gyration tensor is required, which is defined as [103, 104]:

$$\mathcal{T}_{GYR} = \frac{1}{N} \begin{bmatrix}
\sum x_i^2 & \sum x_i y_i & \sum x_i z_i \\
\sum x_i y_i & \sum y_i^2 & \sum y_i z_i \\
\sum x_i z_i & \sum y_i z_i & \sum z_i^2
\end{bmatrix}$$  \hfill (4.4)

The summations in Equation (4.4) are performed over N droplet beads, whose x, y and z coordinates are related to the droplet centre. By the diagonalization of the gyration tensor:

$$\mathcal{T}_{GYR}^{diag} = \begin{bmatrix}
S_1^2 & 0 & 0 \\
0 & S_2^2 & 0 \\
0 & 0 & S_3^2
\end{bmatrix}$$  \hfill (4.5)

The radius of gyration is related to the Eigen values, according to:

$$r_{GYR}^2 = S_1^2 + S_2^2 + S_3^2$$  \hfill (4.6)

To calculate the radius of gyration, each droplet was simulated in isolation, surrounded by solvent, within separate simulations. Each of these droplets were simulated for $10^5$ steps; during these simulations, one frame was extracted every 1000 step, yielding 100 frames. The radius of gyration reported below was the average over these 100 frames.

Two different surfactants were used, with short and long hydrophilic head-groups, respectively. The surfactants are shown schematically in the previous chapter in Figure 3-1.
Consecutive beads in the surfactant molecule are connected with harmonic springs (see Equation (2.8) in Chapter 2) having an equilibrium bond length $r_0 = 0.9 \, r_c$ and spring constant $k_s = 100 \, k_B T/r_c^2$ [64]. The force field parameters used to describe the beads in the surfactant molecules are represented in Table 4-1. To mimic the experimental procedure of introducing surfactants to emulsions, surfactants were added to water (solvent) at different positions within the simulation box. The initial configurations are shown in Figure 4-2. Starting the simulations from different initial configurations yielded consistent results. The results obtained from initial configurations shown in panels (b) and (e) are shown in this chapter, while a comparison between all results is included in Appendix B.

To quantify the number of surfactant molecules needed to saturate both droplet surfaces, a large number of surfactants is introduced in the system, and the amounts of surfactants adsorbed on each droplet were monitored, as a function of time. Once a plateau was reached, the correspondent amount was considered to be the surface coverage at saturation. Results are discussed in Section 4.4, with additional details provided in Figure B- 4 to Figure B- 6 in Appendix B.

Figure 4-2. Three initial configurations for the benzene-in-water droplets simulated in the presence of H1T2 (panels a, b and c) and H3T2 (panels d, e and f), at conditions equivalent to 25°C and 1 bar.
Additional simulations were conducted to extract the parameters used in Equation (4.2). Explicitly, the solubility of simulated benzene in water was calculated by estimating the ratio of the benzene beads dissolved in bulk water to the number of bulk water beads. The results were averaged over $10^6$ simulation steps, which is equivalent to 5.45 µs.

To estimate the simulated oil beads diffusivity in water ($D_{\text{oil in water}}$), the diffusion coefficient ($D_{\text{sim}}$) is calculated from the mean square displacement (MSD) of oil beads in water (see Equation (3.8)). The reported value of $D_{\text{sim}}$ is the average over three simulations, each running for $10^6$ steps. Then, knowing that in the simulated system $\tau = 136.3$ ps [105], the diffusion coefficient $D_{\text{oil in water}}$ was calculated as:

$$\tau = \frac{N_m D_{\text{sim}} r_c^2}{D_{\text{oil in water}}} \quad (4.7)$$

To apply the LSW theory to the simulation results, it is important to describe how the interfacial tension depends on droplet curvature [106]:

$$\frac{\gamma(t)}{\gamma_{\text{curved}}(t)} = 1 + 2\delta/r_{\text{droplet}}(t) \quad (4.8)$$

In Equation (4.8), $\gamma_{\text{curved}}(t)$ and $\gamma(t)$ are the interfacial tensions at curved and planar interface, respectively; $\delta$ is the Tolman length, $\sim 10^{-8}$ cm [106, 107]. Based on DPD parameters estimated in Chapter 3, $\gamma = 30 \pm 8$ mN/m for a water-benzene planar interface. Using Equation (4.8), $\gamma_{\text{curved}}(t)$ is equal to $28.5 \pm 8$ and $29.4 \pm 8$ mN/m for droplets 1 and 2, respectively. Due to the small differences between $\gamma_{\text{curved}}(t)$ and $\gamma(t)$, $\gamma(t)$ were used for the calculations below.

### 4.4. Simulation Results

#### 4.4.1. Ostwald Ripening for Benzene Droplets Dispersed in Water

The size of the two simulated benzene droplets, expressed as number of beads per droplet, was monitored during simulations that lasted up to $48 \times 10^6$ steps, equivalent to 262 µs. The results are shown in Figure 4-3, in which the two horizontal dashed lines indicate the sizes of
the two droplets at the beginning of the simulation, provided for reference. It can be seen that the simulations were long enough for the smaller droplet, droplet 1, to completely disappear, when all its beads diffused to the larger droplet 2. Qualitatively, these results demonstrate that the DPD formalism is able to capture the fundamental phenomena responsible for Ostwald ripening. To ensure the reliability of the results, additional simulations were carried out for the same system, but starting from the two benzene droplets with sizes similar to the ones obtain after 94.7 µs of the simulation just discussed. The results, shown in Figure B-1 in Appendix B, are consistent with those presented in Figure 4-3.

Because of experimental limitations faced when attempting to track the molecular exchange between droplets in an emulsion, evidence of Ostwald ripening is obtained experimentally by collecting size distributions of emulsion droplets, and by studying changes in the mean droplet size over time. To compare the simulation results with experiments and theory, in Figure 4-4, the cube of the mean radius of droplet 2 is plotted as a function of time. The droplet radius is estimated following the procedure discussed in Section 4.3. The results (Figure 4-4) show a linear relation with slope $0.17 \pm 0.01 \text{ nm}^3/\mu\text{s}$, in agreement with Equation (4.2).

A comparison of the simulated Ostwald ripening rate vs. experimental data and theoretical predictions is presented in Table 4-2. The predictions are those by Kabalnov et al. [7], who employed the LSW theory at 20°C. To predict the Ostwald ripening rate at conditions equivalent to 25°C and 1 bar, the LSW theory (Equation (4.2)) is applied using the experimental values listed in Table 4-3. The comparison provided by Table 4-2 shows that the simulations underestimate the Ostwald ripening rate by one order of magnitude compared to experimental data and theoretical estimations. To reconcile the difference, the LSW theory (Equation (4.2)) is applied using solubility and diffusivity of benzene beads in water as estimated from simulations (see Section 4.4 for a discussion on methods). Note that the simulations underestimate the solubility of benzene in water by two orders of magnitude compared to experiments; while they overestimate benzene diffusivity in water by a factor of 2 (see Table 4-3). These differences are in part due to the soft potentials implemented in the DPD framework. While such potentials are suitable to achieve relatively long simulation times, they yield un-naturally high transport properties. Perhaps other coarse-grained simulation approaches could mitigate such limitations. However, it should be noted that, when this simulation data is used in the LSW theory (Equation (4.2)), along with the simulated benzene-water interfacial tension estimated in Chapter 3 (~30 mN/m), an Ostwald ripening rate
of $0.12 \pm 0.06$ nm$^3$/μs is predicted, which favourably compares to the $0.17 \pm 0.01$ nm$^3$/μs value obtained from the simulations of Figure 4-4. Thus, it is concluded that this simulation approach and set up is suitable for reproducing Ostwald ripening for the benzene-water system, yielding results that are in satisfactory agreement with the LSW theoretical predictions.

**Figure 4-3.** Number of beads belonging to the two droplets during Ostwald ripening simulations. The left and right axis show the number of beads in droplet 1 (small) and droplet 2 (large), respectively, at conditions equivalent to 25°C and 1 bar. The horizontal dashed lines indicate the droplets size at the beginning of the simulations.

**Figure 4-4.** Cube of the mean radius of droplet 2 as a function of time. The horizontal dashed line indicates the final radius of the droplet, when the first droplet has disappeared.
Table 4-2. Ostwald ripening rate in nm$^3$/µs of benzene-in-water emulsion estimated from simulation (in Chapter 4), experiment and theory [7].

<table>
<thead>
<tr>
<th>Results from</th>
<th>Ostwald ripening rate ($\omega$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulations (Figure 4-4)</td>
<td>$0.17 \pm 0.01$</td>
</tr>
<tr>
<td>Experiment (Literature)</td>
<td>$3.1$</td>
</tr>
<tr>
<td>LSW theory at 20°C (Literature)</td>
<td>$2.2$</td>
</tr>
<tr>
<td>LSW theory at 25°C (Estimated here)</td>
<td>$1.72$</td>
</tr>
<tr>
<td>LSW theory using data estimated from</td>
<td></td>
</tr>
<tr>
<td>simulations and reported in Table 4-3</td>
<td>$0.12 \pm 0.06$</td>
</tr>
</tbody>
</table>

Table 4-3. Benzene solubility and diffusivity in water at 25°C (experiments [108] and simulations) and 1 bar.

<table>
<thead>
<tr>
<th>Experimental at 25°C.</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility</td>
<td>$2.28 \times 10^{-2}$M</td>
</tr>
<tr>
<td>$\equiv 2 \times 10^{-3}$ m$^3$/m$^3$</td>
<td>$7.4 \pm 4 \times 10^{-5}$ m$^3$/m$^3$</td>
</tr>
<tr>
<td>Diffusivity</td>
<td>$8.1 \times 10^{-6}$ cm$^2$/s</td>
</tr>
<tr>
<td></td>
<td>$(average$ of 4 benzene beads dissolved in 54000</td>
</tr>
<tr>
<td></td>
<td>$water$ beads$)$</td>
</tr>
<tr>
<td></td>
<td>$1.7 \pm 0.02 \times 10^{-5}$ cm$^2$/s</td>
</tr>
</tbody>
</table>

4.4.2. Characteristics of the surfactants’ interfacial films

The rest of this study will focus on the effect of two surfactants on Ostwald ripening. First, the number of surfactant molecules needed to fully cover each of the two droplets is estimated. A large number of surfactants (2500 H1T2 and 1600 H1T2) were added to bulk water. Starting with the initial configurations showed in Figure 4-2, the surfactants first form micelles. These micelles tend to gather oil beads from both oil droplets. This is evident for H1T2 surfactants in the results discussed later (Section 4.4.4). The micelles are then driven to the oil droplet/water interface. These observations appear consistent with results from Karaborni and co-workers.
[76, 77], who observed three mechanisms of surfactant adsorption on droplets. The first mechanism involves the adsorption of monomeric surfactant molecules, the second is the coalescence between the micelle and oil droplets, and the third is the exchange of surfactant molecules through micelle/oil collisions.

As the simulations progressed, the amounts of surfactants adsorbed on the two droplets are monitored. Representative results are shown in Figure 4-5. From the plateaus, it is estimated that ~313 H1T2 surfactants are needed to saturate droplet 1 and ~1993 to saturate droplet 2. The correspondent values for H3T2 surfactants are ~194 and ~1114. These differences are probably related to the size and interaction differences between the two surfactant molecules.

![Figure 4-5. Number of surfactants molecules adsorbed to each droplet when 2500 and 1600 molecules of H1T2 and H3T2 surfactants are added, respectively.](image)

From the results shown in Figure 4-5, it was determined that, in total, ~2300 H1T2 and ~1310 H3T2 surfactants saturate both droplet surfaces. In agreement with experimental observations [82], the surfactants with shorter hydrophilic groups can more densely pack at the droplet surfaces compared to the surfactant with longer head-groups. A slight deformation in the droplet is observed in the presence of H1T2 surfactants (see Figure 4-6, where the cross-sectional views are shown together with the covered droplets).
Figure 4-6. Droplet 2 saturated with ~1993 H1T2 (top) and ~1114 H3T2 surfactants (bottom). Panels (b) and (d) provide cross-sectional views of the droplets.

4.4.3. Surfactants Effects on Ostwald Ripening

Ostwald ripening is simulated in the presence of 2000 and 1300 molecules of H1T2 and H3T2 surfactants, respectively. These concentrations yield interfacial films just below saturation. These conditions were chosen to limit the likelihood of micelles formation, once the surfactants are adsorbed on the droplets. In Figure 4-7, snapshots of the two systems in the presence of H1T2 and H3T2 surfactants are shown, once the surfactants have been adsorbed on both droplets. Visual inspection confirms that micelles are not present.

Figure 4-7. Simulated systems with a) 2000 H1T2 and b) 1300 H3T2 surfactants adsorbed on the benzene droplets.
In Figure 4-8, the number of oil beads in the two droplets is reported as a function of simulation time. It should be noted that, because the surfactants delayed Ostwald ripening, it was not possible to continue the simulations until droplet 1 completely vanished. To be consistent with the results presented in Section 4.4.1, the simulations were conducted in presence of surfactants for up to 262 µs. The results are compared to those with no surfactants (Figure 4-3). Visual observation confirms that both surfactants slow down Ostwald ripening, as evidenced by the fact that the curves change slope after the complete adsorption of surfactants on the droplets. It is worth noting that, at the beginning of the simulation, micelles were formed and during their diffusion to the droplet surfaces, they tend to solubilize oil inside their core. This phenomena lead to the observation of a different regime at the beginning of simulation as shown in Figure 4-8, where both the oil droplets lost molecules which were trapped inside the micelles cores.

To quantify the change in Ostwald ripening rate, the increase in the cube of the mean radius of droplet 2 is plotted as a function of time (Figure 4-9), and the ripening rate is extracted from fitting the data after complete adsorption of surfactants on the droplet surfaces. Table 4-4 presents the average Ostwald ripening rate as obtained from the different simulations.

The simulation results show that the surfactants reduce the Ostwald ripening rate from $0.17 \pm 0.01 \text{ nm}^3 / \mu\text{s}$ to $0.02 \pm 0.01$ (H1T2) and $0.03 \pm 0.01 \text{ nm}^3 / \mu\text{s}$ (H3T2). These results yield a decrease in Ostwald ripening rate by a factor of $\sim 8$ and $\sim 5$ in presence of H1T2 and H3T2 surfactants, respectively. These results qualitatively agree with Kabalnov et al. [7], whose experiments showed a decrease by a factor of 8 in Ostwald ripening rate when surfactants were added to their emulsions. This group reported that the dominant effect in reducing Ostwald ripening rate was due to the reduction in interfacial tension. Although the results generally agree with this conclusion, within the accuracy of my simulations, other effects might arise in the systems simulated.
Specifically, the results in Chapter 3 showed that the water-benzene interfacial tension at a planar interface is reduced from $30 \pm 8$ mN/m to $17.4 \pm 8.5$ and $16.3 \pm 10$ mN/m by H1T2 and H3T2 surfactants at high surface density, respectively. Using these interfacial tensions in Equation (4.2) yields predicted Ostwald ripening rates of $0.07 \pm 0.04$ nm$^3$/μs and $0.06 \pm$
0.04 nm$^3$/μs for H1T2 and H3T2 surfactants, respectively, which are faster by a factor of ~3 and ~2, respectively, compared to my direct simulation results. Thus, in addition to reducing the interfacial tension, the surfactants must reduce Ostwald ripening rate via additional mechanisms. To further probe these systems, additional simulations were conducted in which the droplets were covered by fewer surfactants. The obtained Ostwald ripening rates, presented in Appendix B (Table B-1 and Figure B-10), are in excellent agreement with the LSW predictions when the interfacial tension values at the correspondent surface coverage are used. It is concluded that the reduction in interfacial tension is the primary mechanism by which surfactants reduce the Ostwald ripening rate, but only until a dense interfacial layer is obtained.

Experimental observations, summarized in the introduction, suggest that various mechanisms could determine how surfactants affect Ostwald ripening. For example, Han et al. [82] and McClements and co-workers [97] suggested that density and thickness of the surfactants film on the droplets surface might affect Ostwald ripening. These groups attempted to quantify the effect of the interfacial films formed by surfactants with different head-group length on Ostwald ripening. It is possible that once the surfactants simulated in my systems yield a dense surface film, barriers to Ostwald ripening in addition to interfacial tension reduction arise. For example, because my simulations show a slower Ostwald ripening rate in the presence of H1T2 surfactants, which yield higher surface density on the two droplets compared to H3T2, it is possible that my results reflect the possibility that H1T2 surfactants introduce a stronger resistance to benzene beads from diffusing across the interfacial film at the droplet-water interface, which seems to be consistent with the experiments just summarised. To provide a quantitative comparison against the results reported by Han et al. [82], models are needed to replicate the molecular-level features of the surfactant-laden interfaces, especially when surfactants with different head-groups are considered.

For completeness, it should be pointed out that, as the simulations progress, the surfactant films on the droplets change because the surface density increases as a droplet shrinks and decreases as a droplet grows. Figure B-9 in Appendix B shows how the number of surfactants adsorbed on the two droplets change as a function of simulation time. This affects surface packing, which directly affects the ability of oil beads to transfer to the continuous aqueous phase, as just discussed. However, within the conditions considered here, these changes do not affect significantly the results presented.
Figure 4-9. Cube of the mean radius of droplet 2 as a function of time in the presence of 2000 H1T2 and 1300 H3T2 surfactants, starting from the three initial configurations (IC) shown in Figure 4-2.

Table 4-4. Ostwald ripening rate in nm$^3$/µs estimated from simulations and theory in the presence of H1T2 and H3T2 surfactants.

<table>
<thead>
<tr>
<th>Results from</th>
<th>Ostwald ripening rate ($\omega$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulations (Figure 4-9)</td>
<td>H1T2: 0.02 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>H3T2: 0.03 ± 0.01</td>
</tr>
<tr>
<td>LSW using the reduced interfacial tension</td>
<td>H1T2: 0.07 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>H3T2: 0.06 ± 0.04</td>
</tr>
</tbody>
</table>

4.4.4. Ostwald ripening in the presence of micelles

It has been suggested that the presence of micelles could affect Ostwald ripening [91, 96]. In one of the simulations, conducted in the presence of H1T2 surfactants, one swollen micelle formed because of the coalescence between small micelles and the accumulation of oil beads (see Figure 4-10). The swollen micelle was not able to traverse the membrane and coalesce with droplet 2. While the micelle was present, the sum of the number of benzene beads plus surfactants on droplet 1 is constant (Figure 4-11), while droplet 2 seems to grow at the expense of the micelle. In fact, detailed analysis (see Figure B-11 in Appendix B) shows a more complex molecular exchange; the benzene beads transferred because of Ostwald ripening between the micelle and droplet 1, while some surfactant molecules diffused from droplet 1 to droplet 2. Some benzene beads also diffused from the micelle to droplet 2. Once the micelle
disappeared (vertical line in Figure 4-11), Ostwald ripening started between droplets 1 and 2, as discussed in Section 3.3. Although this detailed molecular exchange occurring in presence of a micelle is difficult to observe experimentally, the overall change in the size of droplet 2 in the presence of the micelle seems to be in qualitative agreement with the experimental observations by Ariyaprakai and Dungan [96], who however reported a much more pronounced effect due to micelles. Depending on surfactant type and concentration, the Ostwald ripening rate increased by a factor up to 50. The difference between simulated and experimental results is probably due to the high surfactant concentration used in the experiments. In fact, as the surfactant concentration increases, the experimental Ostwald ripening rate increases as well. It is possible that when many micelles are present, they enhance Ostwald ripening rate by increasing the oil solubility in water (due to the small micellar size). It is also possible that micelles contribute to enhance the transport of oil from small to large droplets, via their diffusion. This was not observed in my simulations, by design, mostly because of the low surfactant concentration used.

**Figure 4-10.** Simulation snapshots showing droplets 1 and 2, both covered by the H1T2 surfactant, as well as a swollen micelle, highlighted by an arrow.
Figure 4-11. Number of oil + number of tail beads in droplet 1 (red), droplet 2 (black) and in the swollen micelle (blue) as a function of simulation time. Note that, while the number of beads in droplet 2 increase, those in droplet 1 remain approximately constant until the micelle completely disappear. This condition is highlighted by the dashed vertical black line.

4.5. Conclusions

Ostwald ripening is a natural mechanism responsible for the destabilisation of emulsions. Its effects are important, sometimes deleterious, for a variety of industrial applications, ranging from the formulation of specialty chemicals to foodstuff, as well as pharmaceuticals. Molecular models able to quantitatively relate the molecular features of surfactants and other chemical compounds used in a formulation to the Ostwald ripening rate could facilitate the prediction of the long-term stability of industrial formulations. Because many mechanisms contribute to Ostwald ripening, as a first step towards a general approach to quantify Ostwald ripening rates in surfactants-stabilised emulsions, a simulation approach is described in this chapter, based on the coarse-grained Dissipative Particle Dynamics formalism, which is able to qualitatively replicate Ostwald ripening rates for benzene droplets dispersed in water. Nearly quantitative reproduction of experimental observations is achieved when simulation results for solubility and diffusivity of benzene in water are used.
When applied to systems containing surfactants, the approach shows that the Ostwald ripening rate is reduced in large part because the surfactants reduce the benzene-water interfacial tension. However, other phenomena might also be important, especially when the surfactants yield a compact interfacial layer on the droplets. These additional phenomena include the resistance to transfer of benzene from the oil droplet to the continuous aqueous phase, due to the surfactant film at the benzene-water interface, as well as the possible formation of micelles. The former mechanism delays Ostwald ripening rate, while the latter seems to speed it up.

The results presented prove that coarse-grained simulations are able to capture the essential phenomena leading to Ostwald ripening, where molecular transfer occurs between two droplet with different sizes. For future practical applications of the methods described in this chapter, it should be emphasized that the simulations allow us to identify the molecular mechanisms responsible for either speeding up or delaying Ostwald ripening. A detailed analysis of the effect of micelles on Ostwald ripening is feasible using the set up presented in this chapter, but it requires simulating systems at high surfactant concentration. When implementing coarse-grained simulations to study kinetic phenomena, one should remember that soft potentials, such as those employed in dissipative particle dynamics, tend to over-estimate diffusion coefficients, which needs to be accounted for when interpreting the simulation results to match experimental observations.
Chapter 5 Self-Assembly of Mono- and Poly- Dispersed Nanoparticles on Emulsion Droplets: Antagonistic vs. synergistic Effects as a Function of Particle Size

The material presented in this chapter is submitted to the Journal of Physical Chemistry Chemical Physics.

5.1. Chapter overview

In this chapter, using Dissipative Particle Dynamics simulations, fundamental insights are provided into the self-assembly of nanoparticles (NPs) on droplet surfaces in an oil-in-water emulsion. The effect of particle size on the arrangement of NPs at different interparticle interactions is highlighted. NPs of two different sizes were considered. In general, when the NP-NP interaction is changed from repulsive to attractive, a transition in the NPs arrangement occurs from weekly-connected networks to clusters of NPs separated by particle-free domains. When NP-NP interactions are strongly attractive, NPs yield small 3D aggregates on the droplet surface. These arrangements seem to be in agreement with experimental observations reported in the literature. In addition, simulations conducted in this chapter suggest that small NPs are able to diffuse more easily on the droplet surface, which leads to prompt self-organisation, while large NPs are more likely to form metastable structures, perhaps because of slow mobility and strong adsorption to the interface. The analysis suggests that thermal fluctuations could provide the activation energy for the small NPs to escape local minima in the free energy landscape.

The results obtained for systems containing NPs of two sizes provide evidence of size segregation on the droplet surface, which could be useful when NPs self-assemblies are used, for example, to template supra-molecular materials. However, analysis of the simulated trajectories suggests that the results depend strongly on the initial configuration, as larger NPs impose barriers for the small NPs to adsorb and diffuse on the droplet surface.
5.2. Introduction

The self-assembly of particles at interfaces is a key step in many applications, from materials design to emulsions stabilisation. While adsorbed at fluid-fluid interfaces, the particles can arrange yielding structures useful to produce, for example, NP films with unique properties, including reflecting ones [109]. On the other hand, assembled particles on droplet surfaces can provide an energetic barrier useful to stabilise dispersed systems in the so-called Pickering emulsions [6, 21].

The adsorption and distribution of particles and nanoparticles (NPs) at interfaces is controlled by particles physical/chemical properties such as wettability, size, shape, surface charge, and chemical nature [41, 110-113]. A macroscopic quantity often used to quantify the affinity between particles and the two liquids at the interface is the three-phase contact angle, $\theta_C$. The desorption energy, e.g., depends on particle size and contact angle, as described by [21]:

$$\Delta E_p = \pi R_p^2 \gamma (1 \pm \cos \theta_C)^2$$  \hspace{1cm} (5.1)

In Equation (5.1), $R_p$ is the particle radius, $\gamma$ is the fluid-fluid interfacial tension, negative and positive signs represent the detachment to one of the two liquids at contact, e.g., water and oil. Because, as shown in Equation (5.1), the desorption energy depends on $\theta_C$, particles adsorption can be manipulated by changing the particles wettability, using, e.g., polymers or surfactants [22, 114, 115], or by manufacturing amphiphilic particles [23, 116, 117]. The importance of particle size should be emphasized as, for example, when adsorbed at fluid-fluid interfaces, NPs are subjected to thermal fluctuations and Brownian motion, which might affect contact angle measurements [110]. For example, Isa et al. [118] reported a broad distribution of three-phase contact angles for NPs of size from 20 to 500 nm prepared from different materials. The broad distribution of contact angles could be due to NPs heterogeneous surface properties, fluctuations in the direction perpendicular to the interface due to Brownian motion coupled with weak adsorption energy, and because the line tension becomes more and more important as the NP size decreases.

The dependency of the adsorption energy on the particle size could yield a competition between particles of different size to self-assemble at the interface. Lin et al. [119, 120], e.g., studied the self-assembly of cadmium selenide NPs of two sizes on water-in-toluene emulsion...
droplets. The NPs were covered with tri-n-octylphosphine-oxide. The small NPs (2.8 nm) were able to stabilise the emulsion for days [119]. These NPs yield monolayers on the droplets in which NPs arranged in liquid-like structures. These NPs were mobile and diffused laterally over the droplet surface. Upon the addition of large NPs (4.6 nm), some small NPs were displaced from the droplet surface. This observation was ascribed to the dependency of the adsorption/desorption energy on particle size [i.e., see Equation (5.1)]. Lin et al. reported that, over time, the NPs underwent a phase separation on the droplet surface, and an assembly of large NPs surrounded by small ones was observed after 48 hours [120]. They concluded that adsorbed NPs of different sizes tend to phase separate, but that for the phase separation to be complete, the NPs need to diffuse, a process which can be slow [40].

The in-plane diffusion of NPs at an interface depends on particle size and fluid viscosity. Wang et al. [121], e.g., showed that the diffusion coefficient of quantum dots (QDs) of radius 5, 8, and 11 nm at the water/oil interface increases as the particle size decreases. Tarimala and Dai investigated the arrangement of polystyrene particles with diameters 1 and 4 µm on a poly(dimethyl siloxane) droplet dispersed in water [122]. The small NPs formed patches of hexagonally ordered monolayers separated by particle-free domains. When both particles coexisted on the droplet surface, the large NPs compromised the ordered assembly among small NPs. As opposed to Lin et al. [119, 120], Tarimala and Dai did not report size-dependent phase separation on the droplet surface, which could be due to slow diffusion.

Reincke et al. [123], among others, demonstrated that the adsorption of NPs at the water/oil interface is a balance between the NPs chemical potential in the bulk aqueous phase and that at the interface. Both van der Waals and electrostatic interactions contribute to these effects. When Reincke et al. compared their theoretical predictions to experiments, they observed that the results were dependent on particle size. They reported a switchable interfacial self-assembly of small carboxylic acid – functionalized gold NPs of size < 10 nm when increasing the aqueous solution pH from 2 to 9. They also reported evidence of hysteresis effects, as once the large NPs adsorbed at the interface, changing the solution pH was not sufficient to desorb them.

Others used external stimuli to control NP-NP interactions. Luo et al. [109], e.g., considered gold NPs of size 5 and 10 nm at the planar toluene-water interface. The NPs surface was modified using ion-pair complexes, so that changing the aqueous solution pH could affect the NPs interactions. For both NPs sizes, they found that at pH >10, the NP-NP interactions become so repulsive that the NPs desorbed from the interface. At pH ≤10, the NPs assembled at the interface yielding films, probably monolayers, with a mirror-like reflectance. The reflective
properties of the film could be manipulated by controlling the interparticle distances, which decrease when the ionic strength increases from 0.1 to 5 mM.

Controlling NP-NP interactions at interfaces could affect the stability of Pickering emulsions as well. For example, in drug delivery applications, pH changes could trigger the release of therapeutics [4]. However, effective NP-NP interactions are the result of multiple phenomena, which might occur simultaneously. For example, McClements and co-workers [124, 125] reported extensive droplet flocculation and aggregation near the isoelectric point of particles adsorbed on droplets surfaces, leading to creaming instability. Other experiments showed an enhancement in the emulsion stability against creaming due to the formation of a 3D network of interconnected particles and emulsion droplets above a certain electrolyte concentration [29].

To quantify how NPs adsorbed at interfaces respond to changes in the effective NP-NP interactions, computational studies could be useful, as they allow practitioners to modify systematically individual parameters and test the effect of such changes. While atomistic molecular simulations provide useful information on the properties of individual particles at fluid-fluid interfaces [126], to investigate emergent effects, one needs to implement coarse-grained simulations or other approaches [127]. For example, Qin and Yong [128, 129], using a bespoke coarse-grained simulation approach that accounts for electrostatic interactions, were able to describe a disorder-to-order phase transition in the arrangement of functionalized NPs on a planar fluid interface upon increasing the particles’ degree of ionization. In a further study [44], the same group found that it is possible to induce the desorption of NPs from the droplets surface when a high degree of ionisation is combined with high surface coverage. These findings were found in agreement with experimental observations. As another example, Cerbelaud et al. [130], using Brownian dynamics, investigated the self-assembly of NPs on octane droplets dispersed in water upon changing the density of carboxylic acid fragments adsorbed on the NPs’ surface. At low carboxylic acid densities, the particles yield a homogeneous layer and remain well dispersed due to repulsive interactions. Higher carboxylic acid densities reduce the repulsive forces between NPs, leading to the formation of closely packed arrays on the surface of the droplets. A further increase in carboxylic acid density results in extensive agglomeration among NPs, both on the droplet surface and in the continuous aqueous phase.

Schwenke et al. [131] combined Monte Carlo and molecular dynamics simulations with experiments to investigate the self-assembly of NPs at planar water/oil interfaces. They
considered both mono- and poly-dispersed NPs. They studied the kinetics of NPs adsorption at the interface by measuring the surface coverage as a function of time. When starting with a high concentration of NPs in the bulk, the rate of adsorption was initially fast, but then it slowed down once a plateau in the estimated surface coverage was seemingly approached. However, once the adsorbed NPs organised, more NPs adsorbed from the bulk, filling in available defects on the interfacial NP film.

To complement the previous investigations, in this chapter Dissipative Particle Dynamics (DPD) simulations is implemented to (1) quantify the effect of particle size on the NP contact angle and in-plane diffusion at planar interfaces and compare my results to available experimental data [118, 121]; (2) describe the effect of NP size on the arrangement of mono-dispersed NPs on a curved oil/water interface as a function of the effective NP-NP interactions, with emphasis on the transition of NP-NP interactions from repulsive to attractive and on available experimental observations [29, 122, 124, 125]; and (3) investigate the adsorption and the arrangement of poly-dispersed NPs on droplet surfaces, with emphasis on possible competing effects and on the comparison against available experimental observations [119, 120, 122].

The remainder of this chapter is organized as follows: in Section 5.3, the parameters and computational details are briefly summarised. In Section 5.4, the main simulation results are presented with a discussion on how they favourably compare to experimental and theoretical observations from literature. Finally, the main outcomes of this chapter are concluded in Section 5.5.

5.3. Methods and Algorithms

The in this chapter, the Dissipative Particle Dynamics (DPD technique was employed) [45, 47, 52, 55]. The methodology and the parameterization details are fully described in the previous chapters [105, 132]. All simulations presented here were conducted using the simulation package LAMMPS [53], with the isothermal pair style DPD force fields set at a scaled temperature of $K_B T = 1$. All simulations were conducted in the NPH ensemble, with constant number of particles, N, constant pressure, P, and constant enthalpy, H. The temperature is maintained constant because of the use of the DPD pair-style. The volume of the box was adjusted to maintain a pressure similar to the one obtained when only water beads are present in a simulation box with a density of 3 beads/$r_c^3$. 

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The degree of coarse graining ($N_m$) was chosen to be 5, which means that each DPD water bead represents 5 water molecules. Distances are measured in terms of the cut-off distance ($r_c$), which in reduced units is 1. According to the relation $r_c = \sqrt[3]{\frac{\rho_{DPD}V_{bead}}{N}}$, $r_c \approx 7.66 \text{ Å}$. The radius of one DPD bead is equal to 0.43 $r_c$, which is equivalent to 3.3 Å. As explained elsewhere [105, 132], in my model the simulation time scale $\tau = 136.3 \text{ ps}$ obtained by fitting the self-diffusion coefficient of water in DPD simulations to the experimental one. All the DPD interaction parameters implemented here are listed in Table 5-1. The interaction potential between water and oil beads is taken from Chapter 3, where it is shown that these parameters are able to reproduce the water-benzene interfacial tension. As it is intended to model hydrophilic NPs, the repulsion parameter between water and NP beads ($a_{\text{NP-Water}}$) is chosen to be equal to the self-repulsion parameter ($131.5 \text{ K}_B T/r_c$), whereas the interaction between the NP and oil beads is relatively more repulsive, with $a_{\text{NP-Oil}} = 150 \text{ K}_B T/r_c$, as shown in Table 5-1. The $a_{\text{NP-NP}}$ was set equal to 1, 50, 131.5 and 200 $\text{ K}_B T/r_c$. These values were chosen to mimic the changes in the NP-NP interactions observed in experiments.

**Table 5-1. DPD repulsion parameters in $\text{ k}_B T/r_c$.**

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Oil</th>
<th>Nanoparticle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>131.5</td>
<td>171.43</td>
<td>131.5</td>
</tr>
<tr>
<td>Oil</td>
<td>131.5</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>Nanoparticle</td>
<td>1/50/131.5/200</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For the simulations conducted in this chapter, hollow spherical NPs of two diameters are considered. The DPD beads are distributed over surfaces with diameter $1r_c$ and $2r_c$ for small and large NPs, respectively. As shown in Figure 5-1, the resultant diameter of the NPs is 1.86 and 2.86 $r_c$, respectively, which correspond to ~1.4 nm (small NP) and ~2.2 nm (large NP). To cover small and large NPs, 50 and 200 beads are required, respectively, yielding a surface density of ~16 beads/$r_c^2$ on the NPs surface. This is sufficient to prevent other beads (e.g., solvent beads) from entering the hollow NPs, which would be unphysical. One bead is located...
at the centre of each NP; its position is used for estimating, for example, the NPs diffusion coefficients.

\[ D_{\text{nanoparticle}} = 2.2 \text{ nm} \]

\[ D_{\text{nanoparticle}} = 1.4 \text{ nm} \]

\[ 0.43 r_c, 0.43 r_c \]

\[ 2 r_c \]

\[ 1 r_c \]

\[ 43 r_c \]

\[ 43 r_c \]

\[ 1 r_c \]

\[ 2 r_c \]

\[ 20 \times 20 \times 40 \] (\( L_x \times L_y \times L_z \)) with the NP placed at the interface between water and oil as shown in Figure 5-2. To estimate the three-phase contact angle (\( \theta_C \)), the fraction of the spherical NP surface area that is wetted by water is calculated according to [42, 43]:

\[
\theta_C = 180 - \arccos \left( 1 - \frac{2A_w}{4\pi R_p^2} \right)
\]  

(5.2)

In Equation (5.2), \( A_w \) is the area of the NP surface that is immersed in water phase. The ratio \( A_w/4\pi R_p^2 \) is obtained by dividing the number of NP surface beads immersed in the water phase, by the total number of beads on the NP surface. One surface bead is immersed in water if a water bead is the solvent bead nearest to it. The contact angle was estimated over \( 1 \times 10^6 \) simulation steps (equivalent to 5.45 \( \mu s \)), during which one frame was collected every 1000 steps, yielding 1000 frames for my analysis. The contact angle was averaged over these 1000 frames.
The diffusion of NPs at the water/oil interface was also studied. For these calculations, the mean squared displacement (MSD) was estimated for a single NP adsorbed at a planar water/oil interface parallel to the x - y plane. The simulation box dimensions are $20 \times 20 \times 40$ ($L_x \times L_y \times L_z$). For each particle size, the MSD is an average over 30 simulations conducted for 5.45 µs. The simulated diffusion coefficient is estimated according to:

$$D_{x-y} = \frac{1}{4} \lim_{t \to \infty} \frac{\langle |r_i(t) - r_i(0)|^2 \rangle}{t} \quad (5.3)$$

In Equation (5.3), $r_i(t)$ is the position of the particle i at time t on the plane of the interface.

To study the arrangement of monodispersed NPs on a curved surface, an oil droplet with diameter 26.15 $r_c$ was considered, which corresponds to ~20 nm. At the beginning of each simulation, the NPs are randomly placed at the droplet surface. For the small NPs, systems were simulated with either 200 or 430 NPs on the droplet. For the large NPs, three systems simulated were simulated with 128, 200, and 250 NPs on the droplet surface, respectively, as shown in Figure 5-3. The dimensions of the simulation boxes used for each system are listed in Table 5-2. The simulation box size is adjusted to prevent unphysical interactions between NPs adsorbed on the same droplet across the periodic boundary conditions. These simulations were conducted for up to 65 µs with no obvious change in the NPs arrangement over the last 44 µs.
Table 5-2. Composition and simulation box dimensions of systems for NPs adsorbed on an oil droplet dispersed in water.

<table>
<thead>
<tr>
<th>Number of small NP</th>
<th>Number of large NP</th>
<th>Number of oil beads</th>
<th>Number of water beads</th>
<th>Dimensions of simulation box $(L_x \times L_y \times L_z)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>----</td>
<td>27988</td>
<td>111980</td>
<td>$39 \times 36 \times 39$</td>
</tr>
<tr>
<td>430</td>
<td>----</td>
<td>27988</td>
<td>111980</td>
<td>$38 \times 36 \times 40$</td>
</tr>
<tr>
<td>----</td>
<td>128</td>
<td>27988</td>
<td>111980</td>
<td>$36 \times 36 \times 40$</td>
</tr>
<tr>
<td>----</td>
<td>200</td>
<td>27988</td>
<td>111980</td>
<td>$39 \times 36 \times 39$</td>
</tr>
<tr>
<td>----</td>
<td>250</td>
<td>27988</td>
<td>245387</td>
<td>$45 \times 45 \times 45$</td>
</tr>
<tr>
<td>200</td>
<td>200</td>
<td>27988</td>
<td>111980</td>
<td>$39 \times 37 \times 39$</td>
</tr>
</tbody>
</table>

Finally, the adsorption and structure of polydisperse NPs on the droplet surface were studied. For this study, $a_{\text{NP-NP}}$ was set to $131.5 \text{ K}_B T / r_c$, because larger values lead to strong repulsion between NPs, while smaller values lead to strong attractions between NPs, as discussed in the results section. Systems of 200 small NPs and 200 large NPs were considered. The simulation box dimensions are listed in Table 5-2. Three different initial configurations were considered, in all of which one oil droplet was immersed in water as shown in Figure 5-4. In the first initial configuration, all the NPs were dispersed in the bulk water. In the second initial configuration, the small NPs were adsorbed on the droplet while the large NPs were dispersed in bulk water. In the third initial configuration, the large NPs were adsorbed on the droplet while the small NPs were dispersed in bulk water. Each of these systems was simulated for 403 $\mu$s.
Figure 5-3. Initial configurations of 200 (a) and 430 (b) small NPs and 128 (c), 200 (d) and 250 large NPs arranged on an oil droplet (grey) immersed in water. Water beads are not shown for clarity.

Figure 5-4. The three initial configurations for systems with poly-dispersed NPs adsorbing on an oil droplet dispersed in water: (a) all the NPs were dispersed in bulk water; (b) small NPs were on the droplet, while the large NPs were in bulk water; and (c) large NPs were on the droplet, and the small ones were in bulk water.
5.4. Simulation Results

5.4.1. Effect of NP Size on Structure and Dynamics at Water-Oil Interfaces

The three-phase contact angles ($\theta_c$) of NPs are calculated at the planar oil/water interface, starting from configurations shown in Figure 5-2. In Figure 5-5, the estimated contact angle for both NPs over 5.45 µs are reported. A fluctuation in the estimated contact angles was observed over the simulation time. These fluctuations reflect the perpendicular movement of NPs at the interface, due to the thermal fluctuations, in agreement with experimental observations [118]. The resultant contact angles are $\sim 80^\circ \pm 11^\circ$ and $81^\circ \pm 8^\circ$ for small and large NPs, respectively. From the error bars observed, it is clear that the small NPs are more sensitive to thermal fluctuations at the interface compared to the large ones. This is in agreement with Equation (5.1), which shows that the adsorption energy increases with the particle radius.

![Figure 5-5](image_url). Contact angle estimated over 1000 frames (equivalent to 5.45 µs) for small and large NPs (green and blue, respectively) adsorbed at planar water/oil interfaces.

In Figure 5-6, the calculated mean squared displacement (MSD) is presented as a function of time for small and large NPs at planar interfaces, averaged over 30 simulations. From these results, the diffusion coefficient of small and large NPs equals $9 \pm 6 \times 10^{-7}$ cm$^2$/s and $5.5 \pm 3.75 \times 10^{-7}$ cm$^2$/s, respectively. As expected, large NPs are less diffusive than smaller ones, in agreement with experimental observations [121]. It should be noted that the change in
diffusion coefficient with the NP radius as predicted by my simulations is consistent with the Stokes-Einstein relation for the diffusion of spherical particles in uniform mediums.

Figure 5-6. MSD as a function of simulation time for small and large NPs at water/oil planar interfaces. For these simulations single NPs were considered (see Figure 5-2), at conditions equivalent to 25°C and 1 bar.

5.4.2. NPs Aggregates on Oil Droplets: Effects of NP Size and NP-NP Interactions

To quantify the structure of NPs aggregates on oil droplets, several initial configurations were prepared, as well as several NP densities on the droplet surfaces. Starting from the initial configurations shown in Figure 5-3, equilibrium simulations were conducted. In addition to varying the surface density, the effective NP-NP interactions were also changed. The $\alpha_{\text{NP-NP}}$ values reported in Table 5-1 (i.e., from 1 to 200 $k_B T/r_c$) are considered. These values reflect conditions at which the effective NP-NP interactions are strongly attractive, to strongly repulsive. First, the results of the small NPs are discussed, followed by those of the large ones.

5.4.2.1. Small NPs

In Figure 5-7, I report the final simulation snapshots obtained when 430 small NPs are simulated on the oil droplet, as a function of the $\alpha_{\text{NP-NP}}$ parameter. When this parameter is large, the NPs are effectively repulsive to each other. The results show that, when the $\alpha_{\text{NP-NP}}$ is
set to 200 (i.e., very repulsive), the NPs yield a homogeneous distribution over the droplet surface with no cluster formation. It might be possible to observe weakly interconnected NP networks. At these conditions, some NPs desorb from the droplet surface, as can be seen in the snapshot of Figure 5-7 and as also shown in Figure C-1 in Appendix C. Desorption of NPs from the droplet surface is attributed to the repulsive interaction between the NPs, coupled with the large surface density of the NPs on the droplet for the system considered here, in qualitative agreement with literature observations [44, 109, 123].

When the $a_{\text{NP-NP}}$ interaction is reduced to 131.5 $K_B T/r_c$, the small NPs form patches on the droplet surface separated by particle-free domains, as shown in Figure 5-7. Hexagonal order is observed in some of the patches, although such order is not pervasive. The structure just described becomes less evident when the NP surface coverage decreases to 200 NPs, as shown in Figure C-1 in Appendix C. Similar monolayers were reported in several experiments [30, 33, 122].

When $a_{\text{NP-NP}}$ is reduced to 50 $K_B T/r_c$, the small NPs yield very dense clusters. In some of these clusters, a bilayer is formed by the NPs, while in others, hexagonally ordered structures are observed. A representative snapshot is provided in Figure 5-8.

When $a_{\text{NP-NP}}$ is further reduced to 1 $K_B T/r_c$, the very attractive NPs yield 3D clusters (flocs) on the droplet surface. Snapshots of a few such flocs are provided in Figure 5-9 and in Figure C-2 in Appendix C. Each floc is formed by a different number of NPs. In Figure 5-10, the number distribution of NPs in the flocs are presented when 200 or 430 NPs are adsorbed on the droplet.

From the findings just summarised, it is concluded that when $a_{\text{NP-NP}}$ is high, the NPs repel each other and uniformly cover the droplet, while when $a_{\text{NP-NP}}$ is low, the NPs attract each other and form 3D flocs. When $a_{\text{NP-NP}}=131.5$ $K_B T/r_c$, an intermediate behaviour is observed, at which the NPs begin to assemble. The transition in the NPs arrangement from a dispersed structure, to patches, and then to 3D agglomerates resembles the simulation results reported by Cerbelaud et al. [130], when the NPs interaction changed from repulsive to attractive with the increase in the carboxylic acid density on NPs surfaces.
Figure 5-7. Simulation snapshots of the arrangement of 430 small NPs on the surface of the oil droplet, when changing $a_{NP-NP}$ to 200, 131.5, 50 and 1 $k_B T/r_c$ from left to right, respectively. Snapshots are taken after 65 µs.

Figure 5-8. The formation of a second NPs layer on the oil droplet surface when $a_{NP-NP}$ is equal to 50 $k_B T/r_c$. Snapshot was taken after 65 µs.
Figure 5-9. 3D flocs created by small NPs at the droplet surface when $\alpha_{NP-NP} = 1 \text{ kBT} / r_c$. Snapshots were taken after 65 $\mu$s. The insets show top views of each floc.

Figure 5-10. The number distribution of small NPs in flocs in presence of 200 (left) and 430 (right) NPs on the droplet surface when $\alpha_{NP-NP}$ is equal to $1 \text{ kBT} / r_c$. The flocs obtained during the last 20 $\mu$s of the simulations were used for analysis.
5.4.2.2. Large NPs

Figure 5-11 reports the final simulation snapshots obtained when 250 large NPs are simulated on the oil droplet, as a function of the $a_{NP-NP}$ parameter. From left to right, the results are shown for $a_{NP-NP}$ equal to 200, 131.5, 50, and $1 \, k_B T / r_c$, respectively. Top and bottom panels in this figure are obtained following two different procedures. In the top one, the entire simulations are conducted at the reduced temperature of $k_B T = 1$. The results shown in the bottom panels are obtained from simulations conducted as follows: starting from the initial configurations shown in Figure 5-3, first, equilibrium simulations are conducted at the temperature $k_B T = 2$ for 11 µs, and then the temperature was reduced to $1 \, k_B T / r_c$ and the simulations were continued for 20 additional µs. The results show that the structures obtained can differ depending on the simulation protocol. This suggests that in some cases the NPs aggregates are trapped in local minima of the free energy landscape.

In details, when $a_{NP-NP}$ equals $200 \, K_B T / r_c$, the large NPs distribute rather uniformly on the droplet (see also results in Figure C- 3 in Appendix C). This result does not seem to depend on the simulation procedure nor on the initial configuration. At the other extreme, when $a_{NP-NP}$ equals $1 \, k_B T / r_c$, the NP-NP interactions are very attractive, and the NPs yield 3D flocs on the droplet surface. This result does not depend on initial configuration nor simulation protocol either. Snapshots of a few 3D flocs are provided in Figure 5-12 and in Figure C- 4 in Appendix C. Each floc can contain up to 14 NPs when there are 250 NPs on the droplet surface. At lower surface density, the flocs are still present, but they contain, for the most part, 4 NPs. In some cases, they contain 7 large NPs. The number distribution of NPs in the flocs is shown in Figure 5-13.
Figure 5-11. Simulation snapshots of the arrangement of 250 large NPs on the surface of the oil droplet, when changing $\alpha_{\text{NP-NP}}$ to 200, 131.5, 50 and 1 $k_B T/r_c$ from left to right, respectively. All results are obtained at the same temperature but following two simulation protocols for snapshots in panels (a) and (b), respectively. See narrative for details.

For the simulations conducted at intermediate values for the $\alpha_{\text{NP-NP}}$ parameter (131.5 and 50 $k_B T/r_c$), the structures formed by the large NPs depend on the simulation algorithm. Some small patches or networks are visible, especially at $\alpha_{\text{NP-NP}} = 50 \frac{k_B T}{r_c}$, and some NPs desorb from the interface, with the effect being more pronounced as both the surface density and the repulsive parameter increase (more details in Figure C-3 in Appendix C). In some cases, specifically when the NPs are provided increased thermal energy for a short period of time at the beginning of the simulations (bottom panels in Figure 5-11), patches of NPs are obtained, which are similar to those observed for the small NPs. Analysis of the simulation trajectories suggest that once NP aggregates are formed, they are persistent in the simulations.

Comparing the results obtained for small and large NPs, it is concluded that large NPs are more likely to form metastable structures on a droplet surface. This could be due to lower mobility of the large NPs (e.g., see Figure 5-6), to stronger adsorption to the interface (e.g., see Equation (5.1) and Figure 5-5), as well as to stronger NP-NP adhesion forces.
Figure 5-12. 3D flocs formed by large NPs at the droplet surface when $a_{\text{NP-NP}} = 1 \, k_B T / r_c$. Snapshots were taken after 65 $\mu$s. The insets show top views of each floc.

Figure 5-13. The number distribution of 200 (left) and 250 (right) large NPs in flocs on the droplet surface when $a_{\text{NP-NP}}$ is equal to $1 \, k_B T / r_c$, at a scaled temperature $k_B T = 1$. The analyses were performed on the flocs obtained during the last 20 $\mu$s of the simulations.

5.4.3. Poly-dispersed NPs

In this section, poly-dispersed NPs systems are investigated, in which 200 ‘small’ and 200 ‘large’ NPs are introduced near the surface of the oil droplet in water. The initial configurations
shown in Figure 5-4 are used for comparison. These simulations were conducted using $a_{\text{NP-NP}} = 131.5 \, k_B T / r_c$. As shown previously, for small NPs, this value of the interaction parameter is intermediate between effectively repulsive and attractive interactions between the NPs. Several NPs aggregates, as obtained from different initial configurations, are shown in Figure C-5 to Figure C-7 in Appendix C. Those snapshots suggest that the results depend on the initial configurations.

When all NPs are initially in the bulk, or when the small NPs are initially on the droplet surface, the small NPs yield aggregates reminiscent of those observed where only small NPs are present on the droplet (see Figure 5-7), while the large NPs occupy the empty spaces separating the clusters of small NPs. In Figure 5-14 (bottom left panel), the final structure is shown, after 403 µs of simulations, which suggests some sort of size segregation between the NPs on the droplet surface. At the end of the simulations, some NPs of both sizes are found in the bulk water. Assuming that the contact angle in Figure 5-5 does not depend on the curvature of the interface, nor on NP-NP interactions, it is estimated that the final surface coverage obtained from these initial configurations (left and middle in Figure 5-4) is ~ 74%.

Experimental results reported by Lin et al. [119, 120] are consistent with the possibility that NPs of different sizes segregate on a droplet interface. In my simulations, a complete phase separation is not observed, which might be due to the relatively short simulation times compared to experiments, to the small size of the droplets simulated as well as that of the simulated system, to the possibility that the system is trapped in local minima in the free energy landscape, as well as to the possibility that the interaction parameters implemented in my models do not precisely match the experimental conditions.
It should be however noted that when the simulations are started from a different initial configuration, i.e., with the large NPs adsorbed on the oil droplet surface (panel (c) in Figure 5-4), the final configuration observed differs somewhat from the one just described. The small NPs reach the droplet surface either particle-by-particle or as clusters. Single particles tend to occupy the interparticle spaces between large NPs on the droplet surface. While a small NP cluster adsorbing on the droplet can gradually push the large NPs until all the small NPs in the cluster adsorb, as shown in Figure C-8 of in Appendix C. When clusters of small NPs adsorb on the droplet, it is possible that they remain ‘dangling’ towards the bulk, as shown in Figure 5-14 (right), as well as in Figure C-7 in Appendix C. As observed for the other two initial
configurations, even in this case some NPs remain in the bulk, and the estimate surface coverage is \( \sim 77.8\% \) at the end of the simulations, which is somewhat larger than what was mentioned above. In some regions, high NPs packing on the droplet surface leads to changes in contact angle, which is probably due to crowding effects \([104]\). It is possible that the right panel in Figure 5-15 differs from the left one because the large NPs distributed over the droplet surface delay the mobility of the small NPs on the droplet surface via, e.g., caging, which would prevent size segregation within the length of my simulations. Dai et al. \([122]\) also reported that large NPs could prevent the formation of ordered structures of small NPs. Such effects could become more pronounced as the surface coverage increases as suggested by prior simulation results \([40]\).

Noting that the final surface coverages for the structures observed in Figure 5-15 are similar, the adsorption kinetics of small and large NPs on the droplet surface are monitored, starting from the initial configurations shown in Figure 5-4. As shown in Figure 5-15 (a), when both NPs are initially in the bulk, the small NPs reach the droplet surface first. When the small NPs are initially on the droplet surface, the results in Figure 5-15 (b) suggest that the fast initial adsorption of the large NPs causes the displacement of some small NPs during the first few \( \mu s \) of simulations. After that, the large NPs continue to adsorb, slowly (see, e.g., plateaus such as the one from 207 to 240 \( \mu s \) of simulations), showing evidence of bursts of additional adsorption. During the latter events, a few small NPs desorbed, suggesting that large NPs are preferentially adsorbed at those conditions. However, when the large NPs are initially on the droplet, and the small ones in the bulk, the results in Figure 5-15 (c) show that as the small NPs adsorb, some of the large ones desorb, suggesting that a competition between the two NPs for adsorption is indeed taking place in the investigated system. This competition, combined with the slow mobility of NPs within a crowded interface, is probably the reason why the systems considered here seem to sample a free energy landscape characterised by deep local minima, from which the system is not always able to escape. It is however interesting to observe that the rate of adsorption of the small NPs on the droplet covered by large NPs is much slower than that observed for all the other systems (compare Figure 5-15 (c) to Figure 5-15 (a) and Figure 5-15 (b)), especially at the beginning of the simulations, suggesting that the large NPs are more strongly adsorbed at the interface, as expected based on Equation (5.1), and that perhaps they also prevent the mobility of both small and large NPs on the droplet interface. The general trend of the results shown in Figure 5-15, namely a fast initial adsorption rate followed by a much slower adsorption rate, is consistent with the simulation results reported
by Schwenke et al.[131]. In particular, this group showed that when the adsorption rate is fast (i.e., when the NP concentration in the bulk is high), a pseudo plateau is observed in the amount of NPs adsorbed, which is followed by additional adsorption after some time, presumably because the adsorbed NPs require some time to rearrange on the surface. These results suggest that a few such events can occur during a long simulation, because successive relaxations of the adsorbed NPs (see, e.g., Figure C-8 in Appendix C).

**Figure 5-15.** The number of small and large NPs adsorbed on the droplet surface as a function of simulation time, when starting from the three initial configurations shown in Figure 5-4.

### 5.5. Conclusions

Nanoparticles (NPs) of two sizes were simulated on oil droplets dispersed in water. The coarse-grained Dissipative Particle Dynamics formalism was implemented, which allows me to simulate the systems considered for up to several hundreds of micro-seconds. This allows for semi-quantitative comparison to experimental observations available in the literature, although the simulated systems are smaller than experimental ones, and the force fields represent significant simplifications of the reality.

When mono-dispersed NPs were considered, the simulations showed larger fluctuations in the contact angle for small than for large NPs, which is consistent with the adsorption energy increasing with the square of the particle radius. The simulations also showed that small NPs diffuse faster at the oil-water interface than the large NPs, consistently with expectations based on the Stokes-Einstein relation for particles diffusing in homogeneous fluids. When the NPs
are adsorbed on curved interfaces, the NP-NP interactions determine the structure of the resultant aggregates. Small NPs yield uniform distributions on the droplet surface, interconnected patches of NPs with some evidence of order, incipient multi-layered aggregates, and eventually small 3-dimensional clusters of NPs as the effective NP-NP interactions transition from strongly repulsive to strongly attractive. The aggregates formed by large NPs seem to follow the same trend, although evidence of multi-layered structures was not observed, and analysis of the simulation results suggests that large NPs could in some cases be trapped in local minima of the free-energy landscape.

When equimolar mixtures of NPs with different sizes were simulated, the simulation results suggest that size segregation is likely to occur. The simulation results are dependent on the initial configurations, possibly because of the strong adsorption energy of large vs. small NPs at the oil-water interface. Differences in diffusion coefficients both in the bulk and at the interface yield differences in the kinetic of adsorption of the two NPs, which can be linked with the structure of the final NP aggregates obtained on the droplet surface.

The results present are in general agreement with experimental observations related to the structural changes observed when changing the NP-NP interaction reported in the literature, which suggests coarse-grained simulations within the formalism implemented here could be useful for interpreting experiments as well as for designing practical approaches to advance applications in materials sciences.
Chapter 6  Summary and Outlook

This work aims to provide insights on the effect of surfactants and nanoparticles on the stability of emulsions using Dissipative Particle Dynamics (DPD) coarse-grained technique. First, in Chapter 3, a systematic approach was conducted to derive the DPD force field using different solubility parameter theories. The parameters derived from the Hansen solubility parameter theory proved their ability to reproduce the experimental water/benzene interfacial tension and the aqueous micellar property of two surfactants in the $\text{C}_8\text{H}_{17}\text{O}(\text{C}_2\text{H}_4\text{O})_m\text{H}$ family. When surfactants were added to the water/oil system, they diffuse in the bulk until they reach the interface, reducing the interfacial tensions. With the increase of surfactant concentration, the interface was saturated and micelles start to form in bulk water.

The resultant parameterization was then used to investigate the Ostwald ripening phenomena in an oil-in-water emulsion. In Chapter 4, two oil droplets having different sizes were immersed in water, separated by membranes to prevent coalescence and flocculation. Ostwald ripening occurred between the two droplets and the rate was estimated. When compared to experimental results and theoretical model, Ostwald ripening rate showed an agreement with the LSW theory when the solubility and the diffusion coefficient of oil in water was used as estimated from simulations. When surfactants are introduced to the emulsion system, a reduction in the Ostwald ripening rate was observed. At low surface coverage, the Ostwald ripening rate was reduced corresponding to a reduction in the interfacial tension. While at high surface coverage, the surfactant interfacial film showed a possible effect on the Ostwald ripening rate.

In Chapter 5, Pickering emulsions were investigated. While in the literature many researchers studied the coalescence mechanism between droplets stabilized with particles, in this work, the different structures and arrangement of NPs adsorbed on droplet surface are considered. This study aims to provide insights to the changes occurring in emulsions subjected to a change in the interparticle interaction. In general, the arrangement of NPs changes from randomly distribution over the droplet surface to patches separated by particle free domains and finally to 3D flocs, when the NP-NP interaction changes from repulsive to attractive.

However, the response of NPs to the change in their interaction showed a dependency on the particle size, with a prompt response reported in case of small NPs. Furthermore, when a
mixture of NPs of different particle sizes was introduced to the emulsion system, the results showed a dependency on the initial configuration.

In summary, this work (1) provides a new methodology for identifying suitable parameters for coarse-grained simulations of soft matter, (2) provides a new computational approach that could be used in the future to either predict or interpret stability results for systems with large interfaces to investigate phenomena such as Ostwald ripening, and (3) provides new insights into the possible antagonistic/synergistic effects of the nanoparticle on droplet surface as a function of particle size.

**Future Work**

According to the literature review presented in Chapter 4, the concentration of surfactants in the system affects the Ostwald ripening rate. Above the critical micelle concentration, experiments showed that the micelles act as carriers, which facilitate the molecular transport between oil droplets, and affect the Ostwald ripening rate. However, it is challenging to quantify such an effect from experiments, and usually it is a matter of a trial and error process. With the algorithm presented here, the effect of micelles could be investigated providing a possible empirical relation between the number of micelles in the system and the Ostwald ripening rate. First, the investigation could provide information on the aggregation number of specific surfactant molecules, the maximum oil solubilisation capacity of its micelles and the diffusion of these micelles in the continuous phase. Then, the Ostwald ripening rate could be quantified through the molecular transport between droplets. Furthermore, a systematic study could be conducted to investigate the effect of surfactant film thickness and density on the Ostwald ripening rate. The results presented in Chapter 4 showed the dependency of Ostwald ripening on the characteristic of the surfactant film surrounding the oil droplet. However, DPD formalism could not provide detailed molecular information on such effect. Hence, results obtained from Chapter 4 could be integrated with MD simulations to understand first the diffusion of oil molecules through different surfactant films surrounding the droplet. This molecular diffusion would be related to the Ostwald ripening rate reported from DPD simulations. These proposed studies could provide predictions of the emulsion stability against Ostwald ripening mechanism.

On the other hand, the self-assembly of NPs on droplet surfaces provides an energy barrier against droplets coalescence. Many experimental and theoretical attempts were conducted to
understand the effect of the particles arrangement on the mechanism of coalescence. Some investigations pointed out the importance of the complete surface coverage, while others reported emulsion stability in case of incomplete surface coverage. For example, at low droplet surface coverage, Vignati et al. [28] reported the stability of emulsions with a possibility of particle relocation on droplet surface. The particle relocation requires an appreciable rate of diffusion on the droplet surface, which would depend on the particle size, as proved in Chapter 5. Hence, the mechanism by which NPs could stabilise emulsion droplets could also depend on the particle size. Therefore, the work presented in Chapter 5 could be extended by investigating the coalescence mechanism of two emulsion droplets surrounded by NPs in cases of different particle sizes. Furthermore, the 3D structures reported in Chapter 5 could possibly be the building block of the particle/droplet networks observed in the literature [25, 29], which can highly affect the emulsion stability. This could be investigated using energy calculation to study the coalescence of two droplets in presence of a network of NPs extended in the continuous phase.

The work presented in Chapter 4 and Chapter 5 could be extended by investigating the possible synergistic effect emerging from the introduction of both surfactants and nanoparticle to the emulsion systems. Many previous investigations were conducted to understand the effect of increasing the surfactant concentration on the stability of Pickering emulsions [133, 134]. Other studies pointed out the importance of the preparation protocol on the stability of oil-in-water emulsion in presence of a mixture of non-ionic surfactant and surface-active silica nanoparticles [135]. These investigations focused on the synergistic effect of NPs and surfactants on the droplet surface; however, other effects could also occur in the continuous phase affecting the emulsion stability. Previous experimental observations reported the formation of small droplets in presence of surfactants creating particle/droplet networks enhancing the emulsion stability [136]. To complement these experimental investigations, DPD could be implemented to understand the synergistic effect emerging from the interaction between NPs and surfactant on the droplet surface as well as in the continuous phase. For example, in Figure 6-1, preliminary simulations were conducted as an attempt to understand first the interaction of NPs and surfactant on droplet surface. The systems consist of oil droplets immersed in water with NPs adsorbed on the surface. The surface coverage was changed. When surfactants are introduced to the systems, a competition between NPs and surfactants is observed depending on the surfactant concentration as shown in Figure 6-1.
Other interactions between NPs and surfactants emerge in the bulk water. For example, in Figure 6-1, at high NP surface coverage (highlighted in red boxes) and low and intermediate surfactant concentrations, micelles were formed in the bulk phase. These micelles start to solubilize oil inside its core, creating very small oil droplets on the surface of which NPs start to adsorb. These small droplets are shown in Figure 6-2. With these preliminary results, it is possible that the small droplets observed in previous experiments are formed due to the presence of micelles solubilizing oil inside its core. The networks of NPs and small droplets could depend on the NPs and surfactants concentrations as well as the interaction between their molecules. Therefore, a systematic study could be conducted to investigate the effect of surfactants on the stability of Pickering emulsions, including a change in the concentration of the system constituents as well as the interaction between the different molecules.

**Figure 6-1.** The effect of increasing surfactant concentration on the number of NPs adsorbed on the droplet surface.
Figure 6-2. Effect of surfactant at low concentrations on droplet with high NPs surface coverage.
Appendix A. Supporting Information for Chapter 3

In Table A-1, DPD parameters for the simulations discussed in Chapter 3 are reported. In Figure A-1 and Figure A-2, the size distributions of the surfactant aggregates is shown as observed in the simulations. These results are used to determine the cut-off value for the micelle size. Note that at low surfactant volume fraction \( \varphi \), there was no gap, nor minimum value in the distributions shown in Figure A-1 and Figure A-2. At these conditions, the cut-off is considered to be equal to the sub-micelle peak just before the micelle size distribution.

Figure A-3 reports the number of micelles monitored during the course of my simulations for different concentration of both surfactant molecules (H1T2 and H3T2). The volume fraction of free surfactants, \( \varphi_{\text{oligomer}} \), as a function of the simulation time as observed during the simulations is shown in Figure A-4. The results shown in Figure A-3 and Figure A-4 are used to determine the length of the simulations required to achieve reliable statistics. It was found that \( 0.1 \times 10^6 \) steps are sufficient to reach the equilibrium. After these equilibration stages, the average number of micelles found in the system and \( \varphi_{\text{oligomer}} \) at different \( \varphi \) are fluctuating around constant values for both surfactant types, as shown in Figure A-3 and Figure A-4. All results presented in Chapter 3 are ensemble averages collected over the last \( 1.9 \times 10^6 \) steps of simulations that lasted in total \( 2 \times 10^6 \) steps.
### Table A-1. The repulsion parameters of the 10 models shown in Figure 3-2 in Chapter 3.

<table>
<thead>
<tr>
<th>Model</th>
<th>Water</th>
<th>Benzene</th>
<th>Diethylene glycol</th>
<th>Polyethylene</th>
</tr>
</thead>
<tbody>
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<td>Water</td>
<td>25</td>
<td>127.36</td>
<td>66.64</td>
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<td></td>
<td>Benzene</td>
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<td>38.43</td>
<td>25.6</td>
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<tr>
<td></td>
<td>Diethylene glycol</td>
<td>25</td>
<td>44.72</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polyethylene</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Water</td>
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<td>59.23</td>
<td>33.72</td>
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<tr>
<td></td>
<td>Diethylene glycol</td>
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<td>Water</td>
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<td>64.93</td>
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<td>25.51</td>
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<td>Diethylene glycol</td>
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<td>34.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polyethylene</td>
<td>25</td>
<td></td>
<td></td>
</tr>
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<td>25.72</td>
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<td>Water</td>
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<td>51.67</td>
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<tr>
<td></td>
<td>Polyethylene</td>
<td>25</td>
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<td></td>
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<tr>
<td>6</td>
<td>Water</td>
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</tr>
<tr>
<td></td>
<td>Polyethylene</td>
<td>131.5</td>
<td></td>
<td></td>
</tr>
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<td></td>
<td>Diethylene glycol</td>
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<td>139.5</td>
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</tr>
<tr>
<td></td>
<td>Polyethylene</td>
<td>131.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Water</td>
<td>131.5</td>
<td>171.43</td>
<td>141.67</td>
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<td>Diethylene glycol</td>
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</tr>
<tr>
<td></td>
<td>Polyethylene</td>
<td>131.5</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>Water</td>
<td>131.5</td>
<td>188.55</td>
<td>146.03</td>
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<td>131.5</td>
<td>146.6</td>
<td>132.22</td>
</tr>
<tr>
<td></td>
<td>Diethylene glycol</td>
<td>131.5</td>
<td>144.83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polyethylene</td>
<td>131.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Water</td>
<td>131.5</td>
<td>245.6</td>
<td>160.56</td>
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<td>161.71</td>
<td>132.95</td>
</tr>
<tr>
<td></td>
<td>Diethylene glycol</td>
<td>131.5</td>
<td>158.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polyethylene</td>
<td>131.5</td>
<td></td>
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</tr>
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</table>
Figure A-1. The cluster size distribution of H1T2 micelles at different surfactant volume fraction $\phi$. Cut-off numbers for each $\phi$ are highlighted with red circles.
Figure A-2. The cluster size distribution of H3T2 micelles at different surfactant volume fraction $\phi$. Cut-off numbers for each $\phi$ are highlighted with red circles.
Figure A-3. Number of a) H1T2 and b) H3T2 micelles in water at different φ.
Figure A-4. \( \phi_{\text{oligomer}} \) change with time for a) H1T2 and b) H3T2 in water at different \( \phi \).
Appendix B. Supporting Information for Chapter 4

Figure B-1 shows that the Ostwald ripening rate does not change when I start from different initial configurations, as well as when different oil droplets sizes were simulated in water. In these simulations, no surfactants are present.

Figure B-2 shows that the rate by which oil beads leave droplet 1 does not change when droplet 2 has either finite or infinite curvature. The infinite curvature droplet was simulated as a flat interface, as shown in the snapshot of Figure B-3.

In Figure B-4, the number of surfactant molecules attached to the surfaces of the droplets are shown as a function of time, when 2000 H1T2 molecules and 1300 H3T2 molecules are added to the emulsions. For these simulations, the initial configuration is the second of those shown in Figure 4-2 in Chapter 4. From the plateaus in Figure B-4, it is estimated that ~252 H1T2 surfactants are needed to cover droplet 1 and ~1728 to cover droplet 2. The correspondent values for H3T2 surfactants are ~168 and ~1026, respectively. Figure B-5 and Figure B-6 report similar results for H1T2 and H3T2 surfactants, respectively, starting from 3 different initial configurations. The plateaus are independent of the initial configuration.

In Figure B-7 and Figure B-8, the number of oil beads in the two droplets is reported as a function of simulation time, starting from different initial configurations, when 2000 H1T2 and 1300 H3T2 surfactants are present, respectively. The horizontal dashed lines indicate the sizes of the two droplets at the beginning of the simulations, provided for reference.

Figure B-9 shows the number of both oil beads within, and surfactant molecules on the surface of droplet 1 as a function of simulation time. The results are shown in the presence of H1T2 (top) and H3T2 (bottom) surfactants.

In Figure B-10, the cube of the mean radius of droplet 2 is compared as a function of simulation time when H1T2 (top) or H3T2 (bottom) surfactants are present. In both cases, the results are shown for different amounts of surfactants adsorbed in droplet 1 (~252, ~125, and zero for H1T2 surfactants; ~168, ~88, and zero for H3T2 surfactants).

In Table B-1, results for surface density, interfacial tension, Ostwald ripening rate are reported from simulation results such as those of Figure B-10, and Ostwald ripening rate from the LSW theory when simulation data are used as input. Direct simulations agree well with LSW predictions for both H1T2 and H3T2 surfactants at low surface coverage.
Figure B-11 shows a detailed analysis of the molecular exchange between the two droplets and the micelle in the presence of the micelle. Figure B-11(a) shows the transfer of oil beads from the micelle to droplet 1 and droplet 2, and in Figure B-11(b) the transfer of H1T2 surfactant molecules from the micelle and droplet 1 to droplet 2.

**Figure B-1.** The molecular exchange between two droplets of different sizes in two simulations starting from different starting points.

Figure B-2. The molecular exchange between small and big droplets, varying the curvature of droplet 2 (see Figure B-3 for a snapshot representing the system with a flat interface).
**Figure B-3.** A snapshot of the oil-in-water emulsion when droplet 2 has infinite curvature.

**Figure B-4.** The number of surfactants molecules attached to each droplet when 2000 and 1300 molecules of H1T2 and H3T2 surfactants are added to the system, respectively, starting from the second of the initial configurations shown in Figure 4-2 in Chapter 4.
Figure B-5. H1T2 surfactant molecules attached to the droplet surfaces as a function of simulation time, starting from three different initial configurations.

Figure B-6. H3T2 surfactant molecules attached to the droplet surfaces as a function of simulation time, starting from three different initial configurations.
Figure B-7. Number of oil beads in the two droplets, as a function of simulation time, in the presence of 2000 H1T2 molecules. The results obtained for three different initial configurations are shown in different colors.

Figure B-8. Number of oil beads in the two droplets, as a function of simulation time, in the presence of 1300 H3T2 molecules. The results obtained for three different initial configurations are shown in different colors.
Figure B-9. Number of surfactant molecules adsorbed on, and of oil beads within droplet 1 as a function of simulation time (starting from the second initial configuration in Figure 4-2, in Chapter 4). Top and bottom plots are for simulations conducted in the presence of 2000 H1T2 or 1300 H3T2 surfactants, respectively.
Figure B-10. The cube of the mean radius of droplet 2 as a function of simulation time when droplet 1 is covered with ~252, ~125, and zero H1T2 surfactants (top), and ~168, ~88, and zero H3T2 surfactants (bottom).
**Table B-1.** The interfacial tension at different surface densities of H1T2 and H3T2 surfactants; Ostwald ripening rate from simulation (Figure B-10); Ostwald ripening rate estimated from the LSW theory when simulation data are used as input.

<table>
<thead>
<tr>
<th>Surfactant Type</th>
<th>Surface Density moleculenm²</th>
<th>Interfacial Tension mN/m</th>
<th>Ostwald ripening rate Simulated nm³/μs</th>
<th>Ostwald ripening rate LSW prediction nm³/μs</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>NA</td>
<td>30 ± 8</td>
<td>0.17 ± 0.01</td>
<td>0.12 ± 0.06</td>
</tr>
<tr>
<td>H1T2</td>
<td>1.5</td>
<td>17.4 ± 8.5</td>
<td>0.02 ± 0.01</td>
<td>0.07 ± 0.04</td>
</tr>
<tr>
<td>H1T2</td>
<td>0.7</td>
<td>19.7 ± 8</td>
<td>0.074 ± 0.01</td>
<td>0.077 ± 0.04</td>
</tr>
<tr>
<td>H3T2</td>
<td>1</td>
<td>16.3 ± 10</td>
<td>0.03 ± 0.01</td>
<td>0.06 ± 0.04</td>
</tr>
<tr>
<td>H3T2</td>
<td>0.5</td>
<td>20.98 ± 9</td>
<td>0.081 ± 0.01</td>
<td>0.082 ± 0.05</td>
</tr>
</tbody>
</table>
Figure B-11. Molecular exchange occurring in presence of a micelle and two droplets. Panel (a) illustrates the transfer of oil molecules from the micelle (top) to droplet 1 and droplet 2. Panel (b) shows the transfer of H1T2 molecules from droplet 1 and the micelle (bottom) to droplet 2.
Appendix C. Supporting Information for Chapter 5

In Figure C-1, simulation snapshots are reported to represent the arrangement of small NPs on the droplet surface after 65 μs of simulations. The results are for low and high surface coverage in left and right panels, respectively.

In Figure C-2, simulation snapshots are reproduced for three-dimensional flocs of small NPs formed on the droplet surface. Flocs composed by increasing number of NPs are shown from top to bottom as obtained when \( a_{\text{NP-NP}} = 1 \) \( K_B T/r_c \).

In Figure C-3, simulation snapshots are reported to represent the arrangement of large NPs on the droplet surface after 65 μs of simulations. The results are for three increasing surface coverages from left to right panels, respectively.

In Figure C-4, simulation snapshots for 3D flocs of large NPs are provided when \( a_{\text{NP-NP}} = 1 \) \( K_B T/r_c \).

Figure C-5, C-6 and C-7 provide details regarding the arrangement of small and large NPs on the oil droplet as obtained after 403 μs of simulations starting the simulations from the three different initial configurations shown in Figure 5-4 in Chapter 5.

In Figure C-8, two simulation snapshots are provided to highlight the mechanism by which a small cluster of small NPs adsorbs from the bulk water to the oil droplet surface. This simulation was started from initial configuration (c) shown in Figure 5-4 in Chapter 5.
Figure C-1. Representative simulation snapshots illustrating the arrangement of 200 (left) and 430 (right) small NPs on the oil droplet when $a_{NP-NP}$ is equal to 200, 131.5, 50 and 1 $k_B T/r_c$ from top to bottom, respectively. Snapshots were taken after 65 µs of simulations.
Figure C- 2. Representative snapshots illustrating the structure of 3D flocs formed by small NPs on the droplet surface when $a_{\text{NP-NP}} = 1 \text{k}_{\text{B}} T/\kappa_c$. Snapshots were taken after 65 $\mu$s for flocs with different NPs densities. Top (left) and side (right) views are provided. From top to bottom, the results are for flocs composed of the number of NPs indicated in the left.
Figure C-3. Representative simulation snapshots illustrating the arrangement of 128 (left), 200 (middle) and 250 (right) large NPs on the oil droplet when $a_{\text{NP-NP}}$ is equal to 200, 131.5, 50 and 1 $\text{k_B} T/r_c$ from top to bottom, respectively. Snapshots were taken after 65 $\mu$s of simulations.
Figure C-4. Representative snapshots illustrating the structure of 3D flocs formed by large NPs on the droplet surface when $a_{\text{NP-NP}} = 1 \text{ k_BT}/r_c$. Snapshots were taken after 65 $\mu$s for flocs with different NPs densities. Top (left) and side (right) views are provided. The floc in the top panels is formed by 4 NPs, that in the bottom panels are formed by 14 NPs.
Figure C-5. Arrangement of a mixture of small and large NPs, 200 NPs each, after 403 µs (bottom) when starting with an initial configuration where both NPs were dispersed in bulk water (top). Arrangement of only small NPs on the droplet is shown in the middle panels. Snapshots from three different angles are provided.
Figure C-6. Arrangement of a mixture of small and large NPs, 200 NPs each, after 403 µs (bottom) when starting with an initial configuration (top) of the small NPs adsorbed on the droplet surface while the large NPs were in the bulk. Arrangement of only small NPs on the droplet is shown in the middle panels. Snapshots from three different angles are provided.
Figure C- 7. Arrangement of a mixture of small and large NPs, 200 NPs each, after 403 µs (bottom), when starting with an initial configuration (top) with the large NPs adsorbed on the droplet surface while the small NPs were in the bulk fluid. Arrangement of only small NPs on the droplet is shown in the middle panels. Snapshots from three different angles are provided. The circle highlights a cluster of small NPs adsorbed on the droplet.
Figure C-8. A cluster of small NPs diffuses to the droplet surface by pushing the large NPs. Snapshots are taken from the simulations after 8.2 (left) and 8.7 µs (right), illustrating how the cluster of small NPs makes room among the large NPs on the droplet surface.
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