February 2014

A Molecular Simulation Study on Micelle Fragmentation and Wetting in Nano-Confined Channels

Mona Habibi
The University of Western Ontario

Supervisor
Dr. Mikko Karttunen
The University of Western Ontario

Graduate Program in Applied Mathematics

A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

© Mona Habibi 2014

Follow this and additional works at: https://ir.lib.uwo.ca/etd

Part of the Biological and Chemical Physics Commons, Condensed Matter Physics Commons, Other Applied Mathematics Commons, and the Physical Chemistry Commons

Recommended Citation

https://ir.lib.uwo.ca/etd/1886

This Dissertation/Thesis is brought to you for free and open access by Scholarship@Western. It has been accepted for inclusion in Electronic Thesis and Dissertation Repository by an authorized administrator of Scholarship@Western. For more information, please contact tadam@uwo.ca, wlswadmin@uwo.ca.
A MOLECULAR SIMULATION STUDY ON MICELLE
FRAGMENTATION AND WETTING IN NANO-CONFINED CHANNELS
(Thesis format: Monograph)

by

Mona Habibi

Graduate Program in Applied Mathematics

A thesis submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

The School of Graduate and Postdoctoral Studies
The University of Western Ontario
London, Ontario, Canada

© Mona Habibi 2014
Abstract

We performed coarse-grained molecular-dynamics (MD) simulations to study the structural and dynamical properties of surfactant micelles in equilibrium and under Poiseuille-like flow in a nano-confined geometry. We used the MARTINI force-field to model the interactions between water molecules, counter-ions, and sodium dodecyl sulfate (SDS) surfactants. SDS surfactant was chosen as the standard model because of its potential application in drug delivery systems.

First, we focused on the self-assembly of SDS in equilibrium. To form stable spherical micelles, we ran simulations in the isothermal-isobaric ensemble (NPT) on a system of free SDS surfactants, counter-ions and water molecules. We studied the aggregation number, shape and radius of the SDS micelles in equilibrium. These results agree well with all-atom simulations of SDS.

Second, we studied the spreading of a spherical micelle on a solid surface over various interaction strengths in a system consisting of a spherical SDS micelle, and counter-ions in the vicinity of a surface and water molecules. The interaction energies between walls and surfactants were parameterized at three distinct levels corresponding to non-, low-, and high-wetting walls surfaces. The wetting properties of the surfaces were determined by calculating the contact angles of the micelle on the surface in equilibrium. We calculated the contact angle from Young’s equation through measuring the surfaces tension of wall-water, wall-SDS, and water-SDS. As the micelle interacts with the surface, it either forms a cap, a bulb-shape structure, or detaches itself and floats away on high-, low-, and non-wetting surfaces respectively.

Third, we explored the effect of flow, confinement, and wetting on SDS micelles when the micelle is forced through a channel slightly smaller than its equilibrium size. We performed simulations on micellar solutions confined in a die geometry in the isothermal ensemble (NVT). We show that the flowing micelle adopts different shapes to pass through the channel. Inside the channel, the micelle may fragment into smaller micelles. We demonstrate that in addition to the flow rate, the wettability of the channel surface dictates whether the micelle fragments and determines the size of daughter micelles.

Keywords: MD simulations, MARTINI model, DPD, SDS, Micelle, Poiseuille flow, Wetting, Fragmentation
Co-Authorship Statement

The work presented in section 6.5 and Chapter 7 in this thesis were co-authored with my supervisors, Dr. Mikko Karttunen and Dr. Colin Denniston.
Acknowledgement

First and foremost, I would like to express my gratitude to my advisors, professor Mikko Karttunen and professor Colin Denniston for their continuous patience, motivation, and thoughtful guidance. Mikko has given me the chance to pursue my research freely. I profoundly thank Colin for always having time for discussions, and for his thoroughness in editing my work. I am also very grateful for their many insightful comments and suggestions on this thesis. Moreover, I would like to express my sincere appreciation to both for their financial support that facilitated the completion of this thesis.

My sincere thanks also goes to my examiners, Dr. Russell Thompson, Dr. Alex Buchel, Dr. David Jeffry, and Dr. Styliani Constas for their invaluable feedbacks, and thoughtful suggestions. It is not an easy task to review a thesis, and I am grateful for their comments.

I would also like to thank Dr. Maria Sammalkorpi with whom I have the chance to work, during early years of my PhD. We exchanged several emails and discussions from which I developed an interest in micelles. I greatly benefited from her scientific insight.

In my years in London, I have been blessed with my friends and group of fellow students. Among many others, I would like to thank Frances, Anna, Susanna, Jirasak, Mohsen, Cristiano, John, and MG for all the emotional support, friendship, entertainment, and caring that they have provided for me throughout these years. I also thank Trang for proof reading a chapter of my thesis.

And at last, I am deeply grateful to my family, my mother and father for their unconditional love and support. I am thankful to my sister and brother who encouraged me to work through some very rough times. At the end, I would like to thank my lovely niece Rasta and my joyful nephew Sadra, who always make me happy and cheerful.
# Contents

Abstract .......................................................... ii

Co-Authorship Statement ........................................ iii

Acknowledgements ................................................ iv

List of Figures .................................................... viii

List of Tables ..................................................... xi

List of Appendices ................................................ xii

1 Introduction ..................................................... 1

2 Essential concepts .............................................. 5

2.1 Surfactants and self-assembly ................................ 5

2.2 Surfactant parameters ...................................... 7

2.3 Micelle size .................................................. 8

2.4 Thermodynamics of self-assembly ......................... 10

Israelachvili approach [1] .................................... 10

Maibaum approach [2][3] ..................................... 12

Nagarjan approach [4][5] ..................................... 13

2.4.1 The critical micelle concentration .................... 16

2.5 Micellar kinetics ............................................. 16

2.6 Sodium dodecyl sulfate .................................... 18

3 Molecular dynamics simulation ............................... 20

3.1 Introduction ................................................ 20

3.2 Coarse-graining methods .................................. 22

3.3 Integration .................................................. 26

3.3.1 Verlet algorithm ....................................... 27
3.3.2 Velocity-Verlet algorithm ........................................... 27
3.3.3 Leapfrog algorithm .................................................. 27
3.4 Force-fields ............................................................... 28
  3.4.1 Van der Waals interactions ........................................ 29
  3.4.2 Electrostatic interactions ......................................... 30
    Ewald sum .................................................................. 30
    Particle-Mesh-Ewald .................................................... 31
  3.4.3 Bonded interactions .................................................. 31
    Bond stretching .......................................................... 32
    Angle bending ........................................................... 32
    Bond rotation (torsion) ................................................ 33
3.5 CG force-fields ............................................................. 33
  3.5.1 MARTINI force-field ................................................ 33
3.6 Thermostats ................................................................. 36
  3.6.1 Langevin thermostat ................................................ 36
  3.6.2 Berendsen weak coupling ......................................... 36
  3.6.3 Andersen ............................................................... 37
  3.6.4 Lowe-Andersen ...................................................... 37
  3.6.5 Dissipative Particle Dynamics .................................... 37
    The DPD formalism ..................................................... 38
3.7 Barostats .................................................................... 39
  3.7.1 Berendsen barostat ................................................ 39
  3.7.2 Parrinello-Rahman barostat ..................................... 40
3.8 Boundary Condition ..................................................... 40
  3.8.1 Periodic boundary condition (PBC) ............................ 40
  3.8.2 Wall .................................................................. 40
3.9 Constraints ................................................................. 41
  3.9.1 SHAKE ............................................................... 41
3.10 Neighbor list .............................................................. 42
  3.10.1 Verlet list ............................................................ 42
  3.10.2 Cell list .............................................................. 42

4 Simulation details .......................................................... 44
  4.1 Simulation set-up for micelle formation .......................... 44
  4.2 Confined micellar solutions ......................................... 45
    4.2.1 Simulation set-up for the slab geometry ..................... 45
List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Representation of free surfactants, micelle, and vesicle.</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>Micelles and vesicles are commonly used in daily life products.</td>
<td>2</td>
</tr>
<tr>
<td>1.3</td>
<td>A schematic representation of a die-extruder.</td>
<td>4</td>
</tr>
<tr>
<td>2.1</td>
<td>Examples of surfactants.</td>
<td>6</td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic representations of different types of structures formed by surfactants in solutions.</td>
<td>7</td>
</tr>
<tr>
<td>2.3</td>
<td>Schematic packing of geometrical shapes of the self-assembled surfactants.</td>
<td>8</td>
</tr>
<tr>
<td>2.4</td>
<td>The size distribution curve of a micellar solution at equilibrium.</td>
<td>9</td>
</tr>
<tr>
<td>2.5</td>
<td>A schematic phase diagram of a surfactant solution at constant pressure.</td>
<td>9</td>
</tr>
<tr>
<td>2.6</td>
<td>A schematic representation of a micellar solution in equilibrium with free surfactants.</td>
<td>10</td>
</tr>
<tr>
<td>2.7</td>
<td>Aggregate concentration as a function of $X_{total}$.</td>
<td>17</td>
</tr>
<tr>
<td>2.8</td>
<td>All atom model and molecular structure of SDS.</td>
<td>18</td>
</tr>
<tr>
<td>3.1</td>
<td>The time and length scales of different molecular dynamics methods.</td>
<td>22</td>
</tr>
<tr>
<td>3.2</td>
<td>Different levels of description of a coarse-grained system.</td>
<td>24</td>
</tr>
<tr>
<td>3.3</td>
<td>The illustration of the leapfrog algorithm.</td>
<td>28</td>
</tr>
<tr>
<td>3.4</td>
<td>A schematic plot of LJ 6-12 potential.</td>
<td>29</td>
</tr>
<tr>
<td>3.5</td>
<td>A point charge distribution is split into a screened point charge distribution and the corresponding screening distribution.</td>
<td>31</td>
</tr>
<tr>
<td>3.6</td>
<td>Illustration of bonded interactions.</td>
<td>32</td>
</tr>
<tr>
<td>3.7</td>
<td>Mapping between the all-atom chemical structure and the coarse-grained model for SDS, water and ion molecule.</td>
<td>35</td>
</tr>
<tr>
<td>3.8</td>
<td>A schematic representation of periodic boundary conditions in two dimensions.</td>
<td>41</td>
</tr>
<tr>
<td>3.9</td>
<td>Verlet neighbor list.</td>
<td>43</td>
</tr>
<tr>
<td>3.10</td>
<td>Cell list.</td>
<td>43</td>
</tr>
<tr>
<td>4.1</td>
<td>A snapshot of the initial configuration of the simulation set-up for formation of micelles, after the energy minimization.</td>
<td>45</td>
</tr>
</tbody>
</table>
4.2 A snapshot of the slab simulation in the $xz$ plane. ........................................... 46
4.3 A cross-section view of the simulation set-up of the die in $xy$ plane in the initial
configuration. ................................................................. 47
5.1 Snapshots of an NPT simulation of 60 SDS at different times (ns). ............... 51
5.2 The radial distribution of counter-ions around head groups. ........................ 52
5.3 A schematic representation of the micelle surface region. ............................... 53
5.4 The radial distribution of water around head groups. Water molecules form
structured shells around the head groups. ................................................... 54
5.5 The radial distribution of water around tail beads. ........................................... 54
6.1 A schematic representation of the planar Poiseuille flow. ............................... 57
6.2 Different degrees of wetting. ........................................................................... 59
6.3 Partial wetting for an ideal solid. ..................................................................... 60
6.4 The slab geometry to calculate $\gamma$ at the interface of SDS/Wall. .............. 62
6.5 A snapshot of frozen water in a die geometry in equilibrium. ....................... 63
6.6 The velocity, temperature and density profile of water molecules. .............. 64
6.7 The configuration of a CG SDS on high-, low-, and non-wetting surfaces. 65
6.8 The pressure profile of water in the slab geometry. ....................................... 67
6.9 The pressure profile of SDS micelle along the radial axis. ............................ 68
6.10 The time evolution of the micelle on the low-wetting surface. .................... 70
6.11 Pressure profile of SDS and wall molecules and density profile of SDS along
the $y$ direction for the low-wetting wall. .................................................... 70
6.12 The time evolution of the micelle on the high-wetting surface. ................... 71
6.13 Pressure profile of SDS and wall molecules and density profile of SDS along
the $y$ direction for the low-wetting wall. .................................................... 71
7.1 Snapshots of the micelle on different surfaces and with different flow rates. ..... 74
7.2 The micelle classification scheme. ................................................................. 76
7.3 Asphericity factor, Eq. 5.2, versus the normalized center of mass position of
the micelle (and micelle fragments) in the die for $F = 0.003$ kcal molÅ. ........... 77
7.4 Gyration radii of the micelle and fragments over time for $F = 0.003$ kcal
molÅ. ............................................................................. 78
7.5 Size distribution of micelles and distribution of the number of micelles inside
the channel for the first passage for non-, low-, and high- wet channel’s surfaces.
79
7.6 Asphericity factor (Eq. 5.2) and gyration radius of the micelle (Eq. 5.3) and its
fragments for $F = 0.0005$ kcal molÅ. ......................................................... 80
7.7 A schematic representation of a bulb micelle on a surface. .......................... 82
7.8 Response of the micelle to an external force on a low-wetting surface. (a) Initial configuration, (b) the micelle spreading on the surface, $t = 1.8$ ns, and (c) fragmentation, $t = 10$ ns.

7.9 (a) Pressure profile of SDS and wall molecules and (b) density profile of SDS along $y$ direction for the non-wetting wall.

7.10 (a) Pressure profile of SDS and wall molecules and (b) density profile of SDS along $y$ direction for the low-wetting wall.

7.11 (a) Pressure profile of SDS and wall molecules and (b) density profile of SDS along $y$ direction for the high-wetting wall.

7.12 $\gamma_{\text{WALL,SDS}}$ for non-, low-, and high-wetting surfaces.
List of Tables

3.1 Energies of interactions ............................................. 35
6.1 LJ energy interactions for wall-water beads. ..................... 65
6.2 LJ energy interactions for wall-surfactant beads. ............... 69
7.1 The optimum number of SDS in micelle caps on the surfaces . 86
List of Appendices

Appendix A ................................................................. 109
Chapter 1

Introduction

If a substance is soluble in water and its molecules form a homogeneous aqueous solution, it is called hydrophilic. On the other hand, molecules that are insoluble in water are referred to as hydrophobic. Surfactants are molecules that contain both hydrophobic (tail) and hydrophilic (head) groups. In aqueous solutions, surfactants re-arrange themselves to minimize unfavorable contacts between water and hydrophilic groups. Depending on the surfactant concentration, chemical properties of the surfactant/solvent, and flow conditions, surfactant can self-assemble into various structures with different shapes and sizes such as micelles and vesicles [1,6]. A micelle is a spherical (or cylindrical) object with hydrophilic groups on the surface of the sphere and hydrophobic groups forming an oily core inside [1,6–8]. A vesicle is a shell; like an inverted micelle inside a larger micelle [1,6–8]. Figure 1.1 shows representations of micelles and vesicles.

![Figure 1.1: A schematic representation of a) free surfactants, b) a micelle, and c) a vesicle.](image)

Surfactants and their self-assembled structures have numerous industrial and biological applications. They are a very common ingredient of many every-day life products such as shampoos, conditioners, toothpastes, and detergents. Surfactants added to water absorb to dirty interfaces, reduce the surface tension of the solution and help to remove and dissolve the dirt. Besides the detergent industry, surfactants are used in oil recovery. In reservoirs, because of the high interfacial tension, oil is trapped between sand, water and natural gas. By injecting surfactants to the reservoir, the surface tension decreases and therefore the oil can flow [11]. Fatty acids and lipids are all examples of surfactant molecules. Cell membranes are made of lipids. Moreover, micelles and vesicles are used successfully in delivery-release of...
various molecules such as drugs and cosmetic substances \cite{12}-\cite{15}. Most drugs are hydrophobic and poorly soluble in aqueous solutions. By setting drug molecules inside a micelle/vesicle, the micelle/vesicle acts as a carrier for the drug. Also, these drug carriers can be useful to target diseased tissues more effectively. For example, the micelles that carry anti-cancer drugs are most likely to be absorbed by cancer tissues because cancer tissues are more permeable than healthy tissues. Over time, the accumulated micelles in the tissue break up and release the drugs \cite{14}-\cite{15}, see Fig. 1.2. Due to the widespread use of micelles in different fields, micelle formation and their morphologies close to equilibrium point have been well-studied \cite{1-5,16-29}. Detailed descriptions of micelle formation, and their shapes and sizes in the bulk are presented in \cite{3,3,5,6,25,28,30}.

![Micelles and vesicles](http://en.wikipedia.org/wiki/File:Afwasmiddel-Una-Aldi.JPG) and ![Micelles and vesicles](http://en.wikipedia.org/wiki/File:Oil_well.jpg)

Figure 1.2: Micelles and vesicles are commonly used in daily life products such as a) dish-washing liquid, and b) oil recovery. Picture (a) is reproduced from http://en.wikipedia.org/wiki/File:Afwasmiddel-Una-Aldi.JPG, licensed under the Creative Commons Attribution-Share Alike 3.0 Unported. Picture (b) is reproduced from http://en.wikipedia.org/wiki/File:Oil_well.jpg under the terms of the GNU Free Documentation License.

In recent years, understanding the rheological properties of micellar solutions in different flow regimes in confined channels has been an active area of research \cite{31}-\cite{33}. In many of the mentioned applications, surfactants and micellar solutions are involved with flow. They are pumped, stirred, mixed, or pressure extruded through micro/nano channels and thin capillaries. For example, to synthesize small vesicles and micelles for pharmacological applications, a solution of vesicles is extruded through an array of nano-channels. With each passage, the vesicle breaks up into smaller sizes, and at the end we have a relatively mono-disperse distribution of vesicles \cite{34,35}. Another example is in material synthesis for encapsulating cells and chemicals where micelles and vesicles are pumped through microfluidic and lab-on-a-chip devices. These systems are used to transport, break, or merge nano-structures. In blood vessels and capillaries, the transport process of the drug-carriers to the diseased tissue is through blood flow. Cell membranes and red blood cells have structures similar to vesicles. These structures are under constant flow in the blood circulatory system. Also, in oil fields, to recover trapped oil in reservoir, the surfactant fluid is injected into the pores of the rock. In all of these examples, a micellar solution (or a solution of vesicles) is pushed through a nano-confined channel. The geometry of the channel can be like a cylindrical pipe, or an expansion-contraction cavity with narrow incoming and outgoing regions.
In response to flow, micelles and vesicles are able to break, recombine or alter their shapes which leads to a variety of interesting phenomena such as transitions and instabilities [36, 37], formation of different structures induced by flow [38–44], shear thinning/thickening [45–47] and shear banding [48, 49]. Because of the promising pharmacological applications [12, 15] as drug-carriers, many studies have been done on the extrusion of vesicles, micelles, and droplets through nano-channels [50–53]. One motivation for these studies is in drug targeting systems where the stability of micelles and vesicles under flow in the bloodstream is a key issue in maintaining the drugs’ targeting potential. Similar problems arise in the deformation of red blood cells in the flow inside vessels and capillaries [41–44]. Although red blood cells are more complex than vesicles, the dynamical behavior of vesicles as a simple mechanical model in flow can give a good understanding of the behavior of red blood cells in blood vessels.

Computer modeling and simulations have been a key component of investigation into micellar solutions [19, 21, 45, 54, 55]. Micelles are dynamic structures and they exchange surfactants between each other. The exchange rate of surfactants is high, therefore experimental studies can not provide much detail of the micellization process at the molecular scale. Furthermore, probing the micellar solution in confined nano-scale geometries by experimental methods can be very difficult. Hence, computer simulations have become a preferred tool in the investigation of micellar solutions in aspects that are harder to study through experimental methods. However, the required time and length scales to study the rheology of complex micellar solutions are beyond atomistic simulations. To overcome these limitations, a coarse-grained approach [56–58] should be used. In coarse-grained modeling, by reducing the degrees of freedom in the system, we can greatly extend the time and length scales, to capture transport properties and shape transitions of micelles. The MARTINI coarse-grained force-field [57, 58] has been successfully used to investigate the self-assembly of a large class of lipids and surfactants into vesicles and micelles [57, 59–64].

In experiments, formation of vesicles is often easier than forming spherical micelles. Vesicles and micelles both exchange surfactants with the surrounding solutions, however, the exchange rate in micellar solutions is typically much faster than the rate in a solution with vesicles. Moreover, there are about 10 times more surfactants involved in vesicle formation than micelle formation [6]. Also, the life time of a vesicle is usually much longer than that for a micelle. Generally, in laboratory experiments, observation of micellization is more difficult than the observation of vesicle formation. On the other hand, in molecular simulation, obtaining the structure of vesicles from aggregation of surfactants can be challenging due to the large size of the vesicle. Studying flowing vesicles with sizes in the range 100 nm to 200 nm with explicit solvents requires very long and multiple massive simulations to verify the accuracy of such systems which is computationally very expensive. In this thesis, we therefore focus on micelles.

In this dissertation, we performed coarse-grained molecular dynamics simulations to investigate the self-assembly of micelles, the effect of Poiseuille-like flows, confinement and wetting on spherical micelles. The sodium dodecyl sulfate (SDS) micelle was chosen as the standard model since SDS is one of the most commonly used surfactants in the detergent industry, and also because of its potential application in drug delivery systems [15] and tissue engineering [65]. The coarse-grained MARTINI parameterization [57, 58] was used to model SDS surfactants, water, and solid surfaces interactions. We are interested in a die-extruder geometry with cross-rectangular profile where a reservoir is linked to a narrow channel. A
schematic representation of a die-channel is shown in Fig. 1.3. This geometry was chosen because of its simplicity and wide applications in industry. Different flow velocities in the range of $1 - 10 \text{ m sec}^{-1}$ under varying degree of wetting (non, low, and high) were studied. We demonstrate that the interplay between flow and the wettability of channel walls determines the micellar solution behavior in the channel. These are the first simulations of flowing spherical micelles with explicit solvent in a nano-confined channel.

![Figure 1.3: A schematic representation of a die-extruder.](image)

The structure of this thesis is as follows:

**Chapter 2** is a review of the chemical background of surfactants, self-assembly, and micelle kinetics;

**Chapter 3** covers the related basic concepts of molecular dynamic simulations, coarse-grained methods such as dissipative particle dynamics, and the MARTINI force-field;

**Chapter 4** is on the simulation details of the systems studied in this thesis. We discuss the system set-up for the micelle formation simulation, the slab system to parameterize the surface interactions, and the flowing micelle in a expansion-contraction channel, the (“die” simulation);

**Chapter 5** presents the formation of SDS micelles by simulations of explicit solvent/surfactant coarse-grained models. The micelles are obtained from the spontaneous aggregation of free MARTINI SDS. We show that properties of the MARTINI SDS micelle agrees well with experiments;

**Chapter 6** starts with a brief review on wall models, Poiseuille flow, surface tension and wetting of surfaces. The remainder of this chapter discusses the wall structure and their parameters in our simulations. This is the original parameterization of the wall atoms to provide no-slip/no-stick boundary conditions while avoiding formation of frozen layers of MARTINI water molecules on the surfaces. In the last section, we study the equilibrium spreading of the coarse-grained micelle droplet on surfaces with different wettability;

**Chapter 7** presents the results of simulations of flowing micelles in a nano-confined channel. This is the first work that investigates the effect of Poiseuille-like flows, confinement and wetting on the flowing micelles. We demonstrate that, in addition to the flow rates, the wettability of the channel surface and the self-assembly forces determine the micelle fragmentation and fragment sizes;

**Chapter 8** summarizes and offers concluding remarks.
Chapter 2

Essential concepts

2.1 Surfactants and self-assembly

Surfactants (or amphiphiles) are a large class of molecules in which both hydrophobic and hydrophilic groups are covalently bonded to each other. The hydrophilic and hydrophobic groups are referred to as head and tail, respectively. Based on the properties of head groups, surfactants are classified as anionic (negatively charged head and positively charged counter-ion), cationic (positively charged head and negatively counter-ion), zwitterionic (both cationic and anionic group) or non-ionic. Examples of anionic ones are surfactants with sulfate, sulfonate or phosphate head groups. Anionic surfactants are commonly used in the detergent industry and oil recovery. Examples of cationic surfactants are benzalkonium chloride and cetrimonium bromide where chloride and bromide carry negative charges. Their applications are in wet wipes, hair conditioners, and also in products for high-level sterilization. The heads in non-ionic surfactants are polar groups e.g. a glucoside group in decyl glucoside surfactant, which is used in products for individuals with sensitive skin like baby shampoos.

The tail group generally consists of one (or two) hydrocarbon chains with straight, branched or ring structure. Lipids in cell membranes are surfactants with two hydrocarbon chains. Another type is gemini (dimeric) surfactants that are made up of two identical head and two tail groups. In a gemini surfactant, the tails (or heads) are linked together by a group of molecules. Some examples of surfactant structure are shown in Fig. 2.1.

In aqueous medium, surfactants re-arrange themselves to reduce the unfavorable contacts between polar water molecules and hydrophobic tails. In systems with a low concentration of surfactants, surfactants tend to locate their hydrophobic tails toward air/water interface while their heads are in the water side of the interface. As a result, an adsorbed layer of surfactants is formed. The additional free energy per unit area to remove molecules from bulk and create interface between two coexisting phases is known as the surface tension. This layer at the air/water interfaces reduces the surface tension of water. As the interfacial area absorbs surfactants, the entropy of the system increases, therefore the free energy and the surface tension decrease. By increasing the concentration of the surfactants, at some point the air/water interface is saturated by absorbed surfactants. From this point, more surfactants may be dissolved in the solution, however the number of unfavorable tail/water contacts and consequently the free energy of the system increase. At a certain concentration, known as critical micelle concentration.
Figure 2.1: Examples of surfactants. (a) Cetrimonium bromide (cationic), (b) sodium dodecyl sulfate (anionic), (c) phosphatidic acid (anionic), (d) pentaerythylene dodecyl ether (non-ionic), and (e) a schematic representation of a conventional surfactant. Head groups are marked with dashed red circles, and tail groups are marked with blue dashed lines.

Concentration (CMC) surfactants spontaneously aggregate into mesoscale structures [1,6,30]. This aggregation occurs to prevent a further increase in the free energy of the system. Self-assembly (spontaneously aggregation) is a hydrophobic effect driven process where surfactants cluster together. Surfactants self-assemble to form a micro-phase where the polar heads orient themselves in such a way as to shield tails from surrounding water molecules. Therefore, the interface between water and the hydrophobic group is minimized and the enthalpy of the system is decreased. At concentrations above the CMC, there is a large cost of entropy for water molecules to cage the hydrophobic tails. The entropic penalty of self-assembling is less than of constraining tails in solution.

Depending on the (i) chemical properties of the solvent/surfactant, (ii) concentration of the surfactants, (iii) temperature and pressure, surfactants aggregate into various shapes and sizes such as micelles, vesicles and lamellar phases [1,6]. Figure 2.2 shows schematic representations of these aggregations. Micelles are the simplest and smallest structures. In a spherical micelle, heads interact with water molecules on the surface of the sphere to coat tails. Tails form an oily core in the center of the sphere, covered by heads. A cylindrical micelle has two ends that are capped with hemispheres covered by the heads. The cylinder micelle can easily take many surfactants into the cylindrical portion of the micelle. Through micelle formation, repulsive interactions, including steric interactions between heads and electrostatic interactions are opposing the hydrophobic forces that drive self-assembly. As a result of balancing between attractive and repulsive forces, the formed micelle has a finite number of surfactants. In section 2.2, we discuss the size and shape of aggregations based on the surfactant parameters [1]. In bilayer structures (see Fig. 2.2), layers of surfactants arrange themselves in such a way that tails of two layers form a flat plane and head groups are exposed to water molecules. When
a bilayer curves back on itself and forms a closed spherical capsule with a hollow spherical structure in the center, a vesicle forms. In the vesicle structures, water (solvent) molecules are trapped in the hollow structures inside the vesicles. Usually surfactants that form vesicles are more hydrophobic; they have double chained tails.

Self-assembly is a physiochemical process and surfactants are not chemically bonded together. Thus, the surfactant aggregations are dynamic micro-structures. They constantly exchange surfactants with the bulk phase and in response to changes in the solution condition; these structures can adopt new shapes or sizes [30].

![Figure 2.2: Schematic representations of different types of structures formed by surfactants in solutions. Depending on the properties of the surfactants/solution, surfactants can self-assemble into spherical micelles, inverted micelles, bilayers or vesicles.](image)

### 2.2 Surfactant parameters

Depending on the surfactant concentrations, micelles may form a sphere, oblate (disc-like) or prolate (elongated, cylindrical, or rod-like). The micelle shape is determined by the value of the surfactant parameter, $\psi [1]$, $\psi = \frac{v}{A\ell_{\text{tail}}}, \quad (2.1)$

where $v$, $\ell_{\text{tail}}$ are the volume and the length of the hydrophobic tail respectively. $A$ is the optimum surface area occupied by one surfactant at the micelle-water interface. The surfactant parameters determine the optimal curvature for a given set of surfactants. $\psi < \frac{1}{3}$ corresponds to spherical micelles, while surfactants with $\frac{1}{3} < \psi < \frac{1}{2}$ form more elongated micelles. For flexible bilayers and vesicles $\psi > \frac{1}{2}$ (see Fig. 2.3).

For alkyl surfactants, the length and volume of a tail having $m$ carbon chains ($C_mH_{2m+1}$) are reasonably approximated by [67],

$$\ell_{\text{tail}} = 0.15 + 0.1265m \quad (\text{nm}), \quad (2.2)$$

$$v = 0.0274 + 0.0269m \quad (\text{nm}^3). \quad (2.3)$$

While $v$ and $\ell$ are molecular properties connected to the geometrical shape and size of the surfactant tail, $A$ is the cross-sectional area of the head group in the aggregation. The value of $A$ is determined by all the interactions involved in micelle formation [1]; in fact, $A$ is a
thermodynamic quantity of the system rather than an individual surfactant property. Thus, any change in thermodynamic variables like temperature, pressure and concentration affects $A$, consequently $\varphi$, and as a result the shape and size of the aggregation vary as well.

### 2.3 Micelle size

Spherical micelles have a preferred aggregation size. The size of a micelle is typically measured by the number of aggregated surfactants ($N$) in the micelle. A spherical micelle typically consists of 20-100 surfactants. Spherical micelles have a size distribution with a standard deviation of $\sigma$ around $N$, see Fig. 2.4. The size distribution in Fig. 2.4 shows that a micellar solution includes monomers (free surfactants that are not aggregated, region I), small size micelles (sub-micellar, region II) and micelles with the “proper” size of $N$ (region III). The size distribution illustrates that by adding more surfactants to a system above the CMC, more micelles with the proper size are formed rather than larger micelles. Although, more ordered phases may form at high enough concentration of surfactant. A phase diagram for a surfactant water-system at constant pressure is shown in Fig. 2.5. At concentrations below the CMC, surfactants are not aggregated. Around the CMC, surfactants form micelles and at higher concentration more ordered structures are formed.
2.3. Micelle size

Figure 2.4: The size distribution curve of a micellar solution at equilibrium with a maximum at \( n = N \) and a minimum at \( n = n_{\text{min}} \). \( n \) is the micelle size and \( N \) is the proper size. \( PDF(n) \) is the probability size distribution of a micelle of size \( n \). Region I corresponds to free surfactants and oligomers (aggregation of a few surfactants), region II (sub micellar region) shows small clusters around the minimum of the curve and region III is where micelles have their proper size. Adapted from Ref. [6].

Figure 2.5: A schematic phase diagram of a surfactant solution at constant pressure. By increasing the surfactant concentration, the system goes from free monomers, spherical micelles (CMC1), rod like micelles (CMC2), hexagonal stacked rocks, cubic structures to bilayer, lamellar crystal structures.
2.4 Thermodynamics of self-assembly

Here, we discuss the thermodynamics of micelle formation. There have been several different theories on molecular-thermodynamics of micelle formation [1–5, 16–18]. In this section, we derive the free energy of micelle formation according to Israelachvili Ref. [1], we briefly review Maibaum approach [2, 3]. At the end, we discuss the method proposed by Nagarajan [4, 5], which is a quantitative formalism based on molecular properties of surfactants and solution.

Israelachvili approach [1]

Consider a micellar solution in equilibrium with a concentration of surfactants above the CMC (see Fig. 2.6). This system includes free surfactants, micelles with different sizes, and water molecules. The chemical potential of an aggregation including \( n \) surfactants, \( \mu \), is

\[
\mu = \frac{1}{n} \mu_n = \frac{1}{n} \mu_n^\circ + \frac{k_B T}{n} \ln (X_n), \quad n = 1, 2, 3, \ldots
\]  

(2.4)

where \( \mu_n^\circ \) is the standard chemical potential and \( X_n \) is the concentration of aggregations with \( n \) surfactants [1]. \( \mu_n \) is the mean chemical potential of an aggregate of size \( n \). In the above equation \( k_B \) is the Boltzmann constant and \( T \) is the temperature. If interactions between aggregations are negligible, e.g. a dilute system, then we can assume that the energy of an aggregation of \( n \) surfactants is \( n \mu_n^\circ \). \( n = 1 \) corresponds to free surfactants. The total concentration of the solute, \( X_{\text{total}} \), is

\[
X_{\text{total}} = \sum_{n=1}^{\infty} n X_n.
\]  

(2.5)

By substituting \( n \mu_1 = \mu_n \) in equation \( 2.4 \), we have

\[
X_n = X_1^n \exp \left[ \frac{n \mu_1^\circ - \mu_n^\circ}{k_B T} \right].
\]  

(2.6)
From equations 2.4 and 2.6, we have a complete definition of the system \([1]\). The free energy difference between a micelle of \(n\) surfactants \((\mu^n)\) and a solution of \(n\) free surfactants \((\mu_1)\) is given by \(\Delta G_n\). Substituting \(\Delta G_n = -(n\mu^n_1 - \mu^n_1)\) in Eq. 2.6, we have

\[
X_n = X^n_1 \exp \left[\frac{-\Delta G_n}{k_B T}\right].
\]

To have stable micelles of size \(n\), there should be some value of \(n > 1\) that satisfies \(G(n) > G_1\). Therefore, \(\frac{G(n)}{n}\) should have a minimum at some value of \(n = N\) which determines the proper size of the micelle, \(N\).

In the micelle formation, the driving force of the self-assembly is the hydrophobic force of transferring tails into the micelle core, \(G_{\text{trans}}\). In addition to this favoring force, there are two opposing forces. The first one is from the entropic penalty of constraining tails in the hydrophobic core of the micelle, \(G_{\text{inter}}\). The second opposing force is due to restricting the surfactant heads to the surface of the micelle, \(G_{\text{head}}\). All three forces contribute to the total free energy of the micellization \([2]\).}

\[
\Delta G_n = G_{\text{trans}} + G_{\text{inter}} + G_{\text{head}}.
\]

The interplay between these forces limits the micellar growth to a finite size. In other word, there is no available configuration that has a dense micelle core while head groups are placed at the micelle surface with proper distances from each other at the same time.

Now, we derive the free energy of a micelle in an aqueous solution. Let’s consider a spherical micelle including \(n\) surfactants with an oily core of radius \(R_{\text{core}}\). If the tail’s length is \(\ell_{\text{tail}}\), the volume \(V_{\text{core}}\) and surface area \(A_{\text{core}}\) of the hydrophobic part are

\[
V_{\text{core}} = \frac{n\ell_{\text{tail}}}{\rho_{\text{core}}} = \frac{4}{3}\pi R_{\text{core}}^3,
\]

\[
A_{\text{core}} = 4\pi R_{\text{core}}^2,
\]

where \(\rho_{\text{core}}\) is the density of the core. From the above equations, we have \(A_{\text{core}} \propto n^{\frac{2}{3}}\). We can then write the free energy of a hydrophobic core of a micelle of \(n\) surfactants as

\[
G_n = G_{\text{trans}} + G_{\text{inter}},
\]

\[
= -n g_{\text{trans}} + A_{\text{core}} \gamma_{\text{core}},
\]

\[
= -n g_{\text{trans}} + 4\pi \gamma_{\text{core}} n^{\frac{2}{3}} \left(\frac{3\ell_{\text{tail}}}{4n\rho_{\text{core}}}\right)^{\frac{2}{3}},
\]

where \(g_{\text{trans}}\) is the free energy of transferring one tail from water into the hydrophobic core and \(\gamma_{\text{core}}\) is the surface tension between the core and water surface. We introduce the effective hydrophobic radius as \(r = \left(\frac{3\ell_{\text{tail}}}{4n\rho_{\text{core}}}\right)^{\frac{1}{2}}\). So far we have calculated the free energy of the oily core of a micelle of size \(n\) without considering the head interactions. Head group interactions include two forces that are opposing each other. The first force is the repulsion force between head groups on the micelle surface that tends to increase the effective area per molecule, \(\bar{a} = \frac{A_{\text{core}}}{n}\).

The second force arises from the surface tension that favors decreasing \(\bar{a}\) and minimizing the
interaction area between the oily core and water molecules. The total interfacial free energy from head groups for \( n \) aggregated surfactants is approximated by

\[
\frac{G_{\text{head}}}{n} = \gamma_{\text{core}} a + \frac{C}{a},
\]

(2.14)

where \( C \) is the constant. By minimizing the free energy with respect to \( a \), the optimal surface area per molecule, \( A \), is obtained as

\[
A = \sqrt{\frac{C}{\gamma_{\text{core}}}}.
\]

(2.15)

Now we can rewrite the interfacial energy per molecule

\[
\frac{G_{\text{head}}}{n} = \gamma_{\text{core}} a + \frac{\gamma_{\text{core}} a^2}{a} = 2\gamma_{\text{core}} a + \frac{\gamma_{\text{core}}}{a} (a - A)^2.
\]

(2.16)

By substituting \( a = 4\pi r^2 n^{-\frac{1}{3}} \), and \( A = 4\pi r^2 N^{-\frac{1}{3}} \) in Eq. 2.17 and combining with Eq. 2.13 we can obtain the free energy \( G(n) \) of a micelle of size \( n \) as follows [2]

\[
G(n) = -n g_{\text{trans}} + 4\pi \gamma_{\text{core}} r^2 n^{\frac{2}{3}} + 4\pi \gamma_{\text{core}} r^2 n^{\frac{4}{3}} N^{-\frac{2}{3}}.
\]

(2.18)

The above equation is an expression for the free energy of a spherical aggregation of \( n \) surfactants. From the free energy profile, Eq. 2.18, the aggregate size distribution can be calculated. And from the size distribution, all other important solution properties such as the CMC and micelle size can be obtained. The functional form of micellar size distribution, \( PDF(n) \), is

\[
PDF(n) = \exp\left[ -\frac{(\Delta G(n))}{k_B T} \right].
\]

(2.19)

By substituting values of \( \gamma_{\text{core}}, \ell_{\text{tail}} \) and \( \rho_{\text{core}} \) in Eq. 2.18, \( G(n) \) and \( PDF(n) \) can be obtained. The value of \( g_{\text{trans}} \) is determined from \( G(1) = G(N) \) [1]. Note that in writing Eq. 2.18 we have a knowledge of the optimal aggregation number, \( N \), which is not always the case.

**Maibaum approach [2,3]**

Maibaum and Chandler [2,3] presented a theory for non-ionic micelle self-assembly based on hydrophobic forces. In their theory micelle formation is seen as creating a cavity in water, filling the cavity with hydrophobic tails, and placing head groups on the micelle surface. The energy to create a cavity in water is \( G_{\text{cav}} = \gamma_{aw} A_{\text{core}} \). \( \gamma_{aw} \) is the air-water surface tension. The free energy of filling the cavity with the \( n \) tail groups includes \( -n g_{\text{trans}} \). Also, because of the interaction between the oily core and water, there is an interfacial contribution that decreases the core-water surface tension. Therefore, the free energy contribution of filling the cavity is \( G_{\text{fill}} = -n g_{\text{trans}} - (\gamma_{aw} - \gamma_{\text{core}}) A_{\text{core}} \). In Israelachvili methods [1], \( G_{\text{head}} \) comes from the interfacial contributions of head groups. While in Maibaum approach [2], the head group contribution is due to the entropy penalty
2.4. THERMODYNAMICS OF SELF-ASSEMBLY

of confining the head groups on the surface of the micelle. The form of this contribution is estimated as $G_{m_{head}} \propto k_B T n^2$. Thus, the free energy of forming a micelle of $n$ surfactants is

$$G(n) = G_{m_{cav}} + G_{m_{fill}} + G_{m_{head}} = -n g_{trans} + h_1 n^{\frac{2}{3}} + h_2 k_B T n^{\frac{5}{3}},$$  \hspace{1cm} (2.20)

where $h_1 \approx 4.8 \times (\frac{a}{\ell})^{\frac{2}{3}}$ and $h_2 \approx 0.75 \times (\frac{a}{\ell})^{\frac{4}{3}}$ \cite{2}. $\ell$ is the mean distance between a head group and an alkyl group within a surfactant molecule.

Nagarjan approach \cite{4, 5}

Nagarajan theory of micelle formation \cite{4, 5} is a quantitative approach to predict micelle properties from surfactant molecular structure and solution condition. In this approach, the physical and chemical factors in self-assembly are identified by the differences in the chemical potential of a single free surfactant in water and a single surfactant when it becomes part of an aggregate. Based on the chemical structure of the surfactant and the solution, the contributions of different factors to free energy of micelle formation are defined via simple analytical equations. The obtained free energy expressions can predict the aggregation properties of surfactants.

Similar to the previous frameworks \cite{1–3}, the total free energy includes contributions from head groups, tail groups interactions, and formation of the core-solvent interface. The Israelachvili approach is limited to spherical micelles, while the Nagarajan theory can predict properties of micelles in any shape. Unlike the previous methods, in the Nagarajan theory counter-ion interactions that play an important role in formation of ionic micelles are considered. Moreover, Nagarajan formalism is expressed in terms of molecular size parameters and does not require prior knowledge of the optimal aggregation number $N$, while the Israelachvili free energy (Eq. 2.18) depends on $N$. Nagarajan theory is based on the chemical potentials between a surfactant molecule present in an aggregate of size $n$ and a singly dispersed surfactant in water. The Israelachvili approach is based on the chemical potential of an aggregate of size $n$.

In the Nagarajan approach \cite{4, 5} micellar solutions are multicomponent systems consisting of $g_w$ water molecules, $g_1$ free surfactants and $g_n$ aggregates of size $n$ where $n = 2 \ldots \infty$. Each micelle with any shape and size is a distinct chemical component with a chemical potential of $\mu_i$, $i \in \{w, 1, n\}$, where $w$ refers to water molecule and $n = 2, 3, \ldots$ represents an aggregation of size $n$. The total Gibbs free energy of the micellar solution is written as

$$G = g_w \mu_w + g_1 \mu_1 + \sum_{n = 2}^{\infty} g_n \mu_n.$$

(2.21)

We have $\mu_n = n \mu_1$ which implies that the chemical potential per surfactant of a micelle with size $n$ equals the chemical potential of a free surfactant. Thus, for a dilute system the chemical potential of a micelle of size n is

$$\mu_n = \mu_n^0 + k_B T \ln \kappa_n,$$

(2.22)

where $\mu_n^0$ is the standard chemical potential of the species $n$ and $\kappa_n$ is the mole fraction. $\Delta \mu_n^0$ is the difference in the chemical potentials between a surfactant molecule present in an aggregate.
of size \( n \) and a singly dispersed surfactant in water \[5\] which is defined as sum of the different free energy contributions as follows

\[
\frac{\Delta \mu_n^o}{k_B T} = \frac{(\Delta \mu_n^o)_{\text{trans}}}{k_B T} \quad \text{transferring of tails} \tag{2.23}
\]
\[
+ \frac{(\Delta \mu_n^o)_{\text{def}}}{k_B T} \quad \text{deformation of tails} \tag{2.24}
\]
\[
+ \frac{(\Delta \mu_n^o)_{\text{int}}}{k_B T} \quad \text{formation of aggregate core-solvent interface} \tag{2.25}
\]
\[
+ \frac{(\Delta \mu_n^o)_{\text{steric}}}{k_B T} \quad \text{steric interactions between heads and absorbed counterions} \tag{2.26}
\]
\[
+ \frac{(\Delta \mu_n^o)_{\text{ionic}}}{k_B T} \quad \text{head group ionic interactions} \tag{2.27}
\]

In the following, each of the contributions for the case of the spherical ionic micelle will be discussed briefly \[4, 5\].

**Transfer of the surfactant tail:** The free energy contribution of transferring a surfactant tail from the solution to the core of the micelle is \( \frac{(\Delta \mu_n^o)_{\text{trans}}}{k_B T} \). It is estimated from solubility of hydrocarbons in water. The expressions for methylene and methyl group free energy contributions from transferring a tail from pure water to the hydrophobic core of the micelle as a function of temperature can be expressed as follows \[4\]:

\[
\left( \frac{(\Delta \mu_n^o)_{\text{trans}}}{k_B T} \right)_{\text{CH}_2} = 5.85 \ln T + \frac{896}{T} - 36.15 - 0.0056T; \tag{2.28}
\]
\[
\left( \frac{(\Delta \mu_n^o)_{\text{trans}}}{k_B T} \right)_{\text{CH}_3} = 3.84 \ln T + \frac{4064}{T} - 44.13 - 0.02595T. \tag{2.29}
\]

In the above two equations, \( T \) is in Kelvin.

**Deformation of the Surfactant tail:** The micelle formation is associated with a positive free energy contribution from the conformational constraints on the surfactant tail. The expression for spherical micelles is \[4\]:

\[
\frac{(\Delta \mu_n^o)_{\text{def}}}{k_B T} = \frac{9\varphi n^2}{80 N_A L^2}; \tag{2.30}
\]

where \( L \) (nm) is the segment length for the tail \[4\] and \( N_A \) is the number of the segments in the tail of the surfactant \( A \). \( \varphi = \frac{1}{3} \) is the packing factor for spherical micelles. For SDS, \( L = 0.46 \) nm and \( N_A = 12 \). \( R_{\text{core}} \) is the radius of the spherical hydrocarbon core which is obtained from geometrical relations for the micelle \[4\]. For a spherical micelle

\[
V_n = n \nu_{\lambda A} = \frac{4\pi R_{\text{core}}^3}{3} \tag{2.31}
\]
\[
\nu_{\lambda A} = \nu_{\text{CH}_3} + (n_c - 1) \nu_{\text{CH}_2} \tag{2.32}
\]
\[
\nu_{\text{CH}_3} = 0.546 + 1.24 \times 10^{-4}(T - 298) \quad \text{nm}^3 \tag{2.33}
\]
\[
\nu_{\text{CH}_2} = 0.0269 + 1.46 \times 10^{-4}(T - 298) \quad \text{nm}^3 \tag{2.34}
\]
where $V_n, \nu_{sA}, \nu_{CH_2}, \nu_{CH_3}$ are the volume occupied by a micelle with size $n$, and one surfactants’
tail with $n_c$ number of carbon, methylene and methyl groups respectively.

**Head-group steric interaction:** The steric interactions between surfactant heads and coun-
terions at the micelle-water interface is [4]

$$\frac{(\Delta \mu_b^c)_{\text{steric}}}{k_B T} = -\ln(1 - (a_p/a))$$

(2.35)

where $a_p$ is the cross-sectional area of the head group near the surface of the micelle and $a$ is
the surface area of the oily core per surfactant.

**Formation of aggregate core-solvent interface:** The contribution of the core-aqueous so-
lution interface to the free energy is calculated by Carale in ref [68] and is given by

$$\frac{(\Delta \mu_b^c)_{\text{int}}}{k_B T} = \frac{\sigma_{agg}}{k_B T}(a - a_0),$$

(2.36)

where $\sigma_{agg}$ represents the macroscopic interfacial tension between bulk hydrocarbon and the
surrounding electrolyte solutions. $a_0$ is the surface area per molecule shielded from contact
with water by head groups [4].

**Head group ionic interactions:** For ionic surfactant self-assembly, electrostatic interactions
between surfactant heads and the solute play an important role. Counter-ions form a charged
spherical shell around an ionic micelle. Electrostatic interactions contribute a large positive
energy to the free energy of micelle formation. This free energy is equal to the work in form-
ing layers around the core by a reversible and isothermal process, which can be estimated by
solving the Poisson-Boltzmann equations. However, the theoretical computation of these in-
teractions is complicated by a number of factors such as the size, shape, and orientation of the
charged groups, the dielectric constant in the region where the head groups are located, the
discrete charge effects, etc.

An approximate analytical solution to the Poisson-Boltzmann equation derived in Ref. [30]
for spherical micelles in $1:1$ electrolyte is used in calculations of ionic free energy [4],

$$\frac{(\Delta \mu_b^c)_{\text{ionic}}}{k_B T} = 2 \ln \left( \frac{s}{2} + \left[1 + \left(\frac{s}{2}\right)^2\right]^{0.5} \right) - \frac{4}{3} \left[1 + \left(\frac{s}{2}\right)^2\right]^{0.5} - 1$$

$$- \frac{4C}{\kappa s} \ln \left( \frac{1}{2} + \frac{1}{2} \left[1 + \left(\frac{s}{2}\right)^2\right]^{0.5} \right),$$

(2.37)

where

$$s = \frac{4\pi e^2}{\epsilon \kappa a_d k_B T},$$

(2.38)

$$C = \frac{2}{R_c + \delta},$$

(2.39)

$$\epsilon = 87.74 \exp[-0.0046(T - 273)],$$

(2.40)

$$\kappa = \sqrt{\frac{8\pi e^2 n_o}{\epsilon k_B T}}, n_o = (C_1 + C_{add}) 10^3 N_{Avo}.$$

(2.41)
$a_\delta$ is the area per surfactant at a distance $\delta$ from the hydrophobic core surface. This distance is estimated as the distance from the hydrophobic core surface to the surface where the center of the counter ion is located. $\epsilon$ is the dielectric constant of the solution (dimensionless), $\kappa$ is the reciprocal Debye length, $n_o$ refers to the number of counterions per $m^3$, $C_1$ is the molar concentration of free surfactants, $C_{add}$ is the concentration of added salt and $N_{Avo}$ is Avogadro’s number. The first term in equation [2.37] is the electrostatic free energy of a planar double layer and the second term is the correction for the curvature of the surface. This solution is valid only for $\kappa R \geq 1$, where $R$ is the radius of the micelle.

### 2.4.1 The critical micelle concentration

So far, we have reviewed the thermodynamics of micelle formation and the free energy of spherical micelles. Here, we discuss that at which concentration micelle formation occurs.

For a low concentration system, most surfactants are free in the solution. Thus, following Eqs. [2.6] one can conclude that for a dilute solution of surfactants, $nG(1) < G(n)$ and $X_{total} \approx X_1$. Based on the Eq. [2.5] $\sum_{n=1}^{\infty} nX_n$ cannot exceed $X_{total}$. Therefore, once $X_1$ approaches $\exp \left[ \frac{\mu}{k_B T} \right]$, it cannot increase anymore. This point is called the critical micelle concentration which is defined by [1]

$$CMC = (X_1)_{critical} = \exp \left[ \frac{\mu}{k_B T} \right]. \quad (2.42)$$

The CMC can be calculated from $nX_n$ against $X_{total}$ plot (see Fig. [2.7]). The CMC is defined as the value of the total surfactant concentration at which a sharp transition in the plotted function occurs. Also, it can be estimated as the value of $X_1$ for which the concentration of the free surfactant is equal to that of the aggregated surfactant $X_1 = \sum nX_n = CMC$.

### 2.5 Micellar kinetics

Although structures, sizes, and the thermodynamics of micelles have been studied extensively through experiments [1, 4, 6, 8, 69] and computer simulations [19, 21, 54], the detailed picture of the micellization kinetics is not fully covered. Many theoretical approaches have been suggested for the micelles formation [22, 70, 81]. One of the most appealing was first introduced by Aniansson and Wall in the 1970s [70–72]. They formalized the aggregation process in terms of chemical kinetic equations in which only one surfactant at a time can associate to/dissociate from micelles. This stepwise process of exchanging one surfactant at a time is expressed as

$$S_1 + S_n \rightleftharpoons K_{n+1,n}^{assoc} S_{n+1} \quad n = 1, 2, ..., \quad (2.43)$$

---

1 The Debye length is the scale over which mobile charges screen out electric fields. Free ions reduce the Coulomb interactions and the electrostatic energy goes to zero beyond the Debye screening length [30].
2.5. Micellar kinetics

Figure 2.7: Aggregate concentration as a function of $X_{total}$. A larger aggregation usually has a sharper transition at the CMC. Adopted from Ref. [1] where $S_n$ refers to micelles that include $n$ surfactants. The association rate of a surfactant joining a micelle with size $n$ is $K^+_{n,n+1}$ and $K^-_{n+1,n}$ is the dissociation rate of a surfactant leaving a micelle of size $n + 1$. The assumption in formulating the stepwise process was that the association and dissociation rates are independent of micelle size ($K^+_{n,n+1} = K^+$, $K^-_{n+1,n} = K^-$). Also, the micellar size distribution is Gaussian with mean $N$ and standard deviation of $\sigma$. The stepwise mechanism with constant association/dissociation rates approach was successfully supported by experiments (Ref. [6] and references therein) and simulation analysis [82,83] for non-ionic surfactant and ionic surfactants with low surfactant concentration. In many studies on micellization theory, the stepwise process is considered to play the most important role in micelle formation [82-86]. However, some simulation studies have shown that constant rates may not be a good assumption [82,83,87,88]. Note that since micellar systems have fast kinetics with a small length scale, it is impossible to obtain size dependent rate constants from laboratory experiments. Burov et al. [82] calculated the rates of an ionic surfactant model from the MD trajectories. The cluster size distribution of their coarse-grained model is in agreement with the estimation of the corresponding kinetic equation of the stepwise mechanism.

The treatment of Aniansson and Wall was refined by Kahlweit in the 1980s [73-75] for higher concentrations of ionic surfactants and stronger ionic strength. In fact, micellar aggregations in high strength ionic solutions happens through both stepwise and sub-micellar aggregations, of which the latter one increases the speed of micellar aggregation. This model includes fusion/fission reactions in which one micelle can split into two daughter micelles or two smaller micelles can join to form a larger micelle. To include the fusion/fission of micelles,
the kinetic equation 2.43 is written as

\[ S_m + S_n \xrightleftharpoons[K_m,n]{K_{m,n}} S_{m+n}. \]  

(2.44)

Pool and Bolhouis [77, 89] have proposed an alternative mechanism for micelle formation. They argued that micelle formation occurs through both nucleation and an auto-catalytic replication process. Through diffusion, surfactants slowly associate to an existing micelle and the micelle grows gradually. When the micelle becomes too large, it becomes unstable because of a shape fluctuation, then instead of surfactants dissociation, micelle breaks up into two micelles with similar size. These daughter micelles subsequently grow. It has been shown in Ref. [77] that around the CMC or for specific non-ionic surfactant topologies this mechanism can contribute significantly to the kinetics of micelle formation.

### 2.6 Sodium dodecyl sulfate

In this thesis, we focus on spherical micelles of [sodium dodecyl sulfate (SDS)] standard model since SDS is one of the most commonly used ionic surfactants in the detergent industry, and also because of its potential application in drug delivery systems [15] and tissue engineering [65].

![SDS Molecular Structure](image)

**Figure 2.8**: Left: SDS molecular structure. Right: All atom model of SDS. Head group molecules are colored by red (O) and yellow (S). Carbon and hydrogen atoms in tail are shown by cyan and white respectively.

Sodium dodecyl sulfate (SDS or NaDS), sodium laurilsulfate or sodium lauryl sulfate (SLS) is an anionic surfactant consisting of 12 carbon groups (11 CH\_2 groups and one CH\_3 group) attached to a sulfate group (NaC\(_{12}\)H\(_{25}\)SO\(_4^-\)). Figure 2.8 shows a representation of a SDS surfactant. The length and volume of the extended SDS tail are 1.67nm and 0.35nm\(^3\) respectively (calculated from equation 2.3). Experimentally, in the absence of the supporting electrolyte the value for the area per head group of SDS, \(A = 0.62\text{nm}^2\) [30] which yields the packing factor \(\varphi < \frac{1}{3}\). Therefore, in the absence of supporting electrolyte, at the CMC, SDS surfactants aggregate to spherical micelles. The mean aggregation number of SDS micelle in water has been reported between 55-77 in experimental [70,90–93] and simulation [94,95] studies. The standard deviation of SDS is reported to be \(\sigma = 13\) [70]. The CMC of SDS in pure water is 8.2 mM [6]. At concentrations above CMC, the association/dissociation rates for SDS are
2.6. SODIUM DODECYL SULFATE

$K^+ = 1.2 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ and $K^- = 1 \times 10^7 \text{s}^{-1}$ [70]. Structural properties of SDS surfactants have been investigated in many all-atom simulations [20,21,54], coarse-grained simulations [23,24] as well as experimental studies [6,30,70].
Chapter 3

Molecular dynamics simulation

3.1 Introduction

Computer simulations are the third paradigm of research, in addition to experiments and theories. Molecular simulations can make predictions about phenomena that are difficult or impossible to achieve in experiments. Micellization is an example of such a process. Micelle formation is a thermodynamically driven process. Due to its fast kinetics, observation of micellization is difficult in laboratory experiments, if not impossible [96]. However, several computational studies on micellization have provided us with a good insight into the solvation of surfactants [19, 21, 54, 77, 83, 89]. Another example is the collective diffusion behavior of lipids in bilayers, which first was predicted by molecular simulations [97] and then later confirmed by experiments [98]. Moreover, molecular simulations can probe controlled systems that are hard, or impossible to set-up in real experiments. For instance, systems under high pressure or temperature are examples. In addition, in any experimental measurement, the systems are always perturbed, and it is not trivial to distinguish the effects caused by these perturbations. For example, to study the properties of lipid bilayers, fluorescent lipid analogues inserted into the lipid bilayer that affect the behavior of the lipids. It is impossible to gain information on these effects in experiments. We can study such effects by simulations [99]. Computer simulations are valuable tools to guide or complement experiments. In treating many-body systems, while theoretical approaches require many approximations, molecular simulations can accurately provide numerical results. However, the accuracy of the molecular simulation results depends on the chosen formulation for molecular models and the interactions of particles with each other.

In principle, the behavior of a real system is described by quantum mechanical rules. All other descriptions of the system are approximations to the quantum level interactions. In quantum level simulations, particles are atomic nuclei, electrons and photons. The methods are based on the Schrödinger equation. In the next level of approximation, by ignoring the electron dynamics, we can model ions and molecules by effective potentials.

In classical molecular dynamics (MD) we treat the motion of atoms classically according to Newton’s laws of motion. The nucleus and the electrons are modeled as a single point-mass particle. Systems that can be studied by MD simulations are limited to those that are consisting of particles with specified mass and charge. These particles interact through averaged effective
potentials in which electronic interactions are not explicitly included but implicitly incorporated into force-fields. The most important part in any MD simulation is the “force-field” that describes the interactions of particles through mathematical functions and a set of parameters. The motion of particles is described by Newton’s equations of motions. In MD, properties of a molecular system are determined by solving the equations of motion numerically over the desired time span. At each time step, the total force on each particle is calculated and from there the position and velocity of the particle at a time step are updated. By repeating this cycle over the desired time span, we can obtain the time development “trajectory” of the molecular system toward equilibrium. In the equilibrium state, the macroscopic quantities of the system, such as temperature, pressure, energy, and radial distribution function do not vary with time; the phase-space averages of all macroscopic thermodynamic variables provide the same information as a long-time-averaged simulation [100].

The direct integration of Newton’s equation of motions in MD simulations leads to reproducing the micro-canonical ensemble, where the energy of the simulated system is constant. However, most experiments are performed at constant temperature and/or pressure. In order to simulate a system at constant temperature/pressure in the canonical ensemble (NVT-ensemble)/the isothermal-isobaric ensemble (NPT-ensemble), the simulated system is coupled to an external thermostat and or barostat by implementation of specified algorithms.

MD simulations have an important role in predicting the average behavior of molecular systems at thermodynamic equilibrium. However, many real systems are not at thermodynamic equilibrium. Phase separation, pattern formation, and flow of fluids are examples of such systems. In this thesis, by “non-equilibrium system” we mean a fluid that is acted upon by an external force. The external force drives the flow. For simulating non-equilibrium systems that are close to equilibrium, linear response theory is a reasonable approach. Thus, we can still use the principles of equilibrium thermodynamics if the spatial non-equilibrium inhomogeneities in the system are larger than intrinsic atomic or molecular distances [101]. Although one should notice that, in order to simulate fluid flow, a thermostat that preserves hydrodynamics (flow) should be used.

In MD simulations, typical systems are (macro)molecules, fluids, solutions, and liquid crystals. The dynamics of the molecular system follows classical mechanics. Although the simulation of a system with all atomic detail gives us a full description at the molecular-level, it is limited to the time scale of nanoseconds and system sizes of 10s nanometer. For instance, a 20 ns all-atom simulation of $10^6$ particles needs 75000 hours of CPU time [102]. In soft matter physics, thermodynamic properties of systems are studied over long time and length scales, that are hard to achieve by all-atom simulations. For example, crystallization, conformational changes of polymers, protein folding, hydrodynamic behavior of complex fluids, self-assembly, and micellization of amphiphilic systems can extend into micro-second range or longer. Therefore, in order to reproduce the long-time behavior of soft matter systems more efficiently, many methods with different approaches have been developed to capture the important atomistic aspects. In coarse-graining methods, the system is simplified in such a way that the “interesting” behavior of the system is well reproduced, but at the expense of uninteresting details. In other words, computation time is being saved by reducing the degree of freedom of the system. The degrees of freedom can be decreased either by simplifying a group of atoms and reducing the number of interaction sites of particles or by replacing particles with a continuum medium. Figure 3.1 shows multiple levels of simulations in different time and length
scales.

<table>
<thead>
<tr>
<th>Length Scale</th>
<th>Å</th>
<th>nm</th>
<th>µm</th>
<th>mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subatomic scale</td>
<td>nuclei/electrons</td>
<td>Atomistic scale</td>
<td>atoms</td>
<td>Mesoscale scale</td>
</tr>
</tbody>
</table>

Figure 3.1: The time and length scales of different molecular dynamics methods. Depending on the length and time scale of the phenomena, the model will include a larger or smaller number of degrees of freedom. Through omission of number of degree of freedom, the model becomes less accurate but the length and time scale increase.

In this chapter, we review the most important aspects of classical MD methods, coarse-graining, and force-fields. We discuss the integration of Newton’s equation in Sec. [3.3]. More details on force-fields is presented in Sec. [3.4]. A brief review of thermostats and barostats is given in Sec. [3.6] and [3.7] and at the end we discuss methods for speeding up simulations.

### 3.2 Coarse-graining methods

Coarse-graining methods are typically divided into two categories, the structure-based, and the effective coarse-grained interactions.

In the structure-based approaches, the structure of atoms are coarse-grained; i.e., not all atomic details are included in the description of systems. A “pseudo-atom” is used to represent a group of atoms and the interactions between them are modeled often through soft potentials (see Fig. 3.1, mesoscale model for the illustration). The parameterization of coarse-grained (CG) force-fields is through matching the behavior of the model to appropriate experimental or all-atom simulations data. Depending on the level of the approximation, additional noise and friction forces may, or may not, be added to the system.

The equation of motion for Langevin dynamics is

\[
\frac{dm_i}{dt} \frac{dv_i}{dt} = -\frac{\partial U}{\partial r_i} - \sum_j \int_0^\tau \zeta_{ij}(\tau)v_j(t-\tau)\,d\tau + \eta_i(t),
\]

(3.1)

where \(m_i\) is the mass of particle \(i\), \(U\) is a potential, and \(v_i(t)\) is the velocity of particle \(i\) at time \(t\). \(\zeta_{ij}(\tau)\) is a frictional kernel for \(\tau > 0\) that decays to zero within a finite time. This friction
term can represent a linear prediction of the velocity derivative based on knowledge of the past trajectory \[101\]. Linearity means that velocity-dependent forces are truncated to first-order terms in the velocities. The last term in the Langevin equation \[3.1\] \(\eta_i(t)\) is a random force with mean zero \[101\]. When systematic forces do not change much on the time scale of the velocity correlation function, we can average the Langevin equation over a time scale \(t > \tau\). The averaged inertial term becomes negligible in Eq. \[3.1\] and yields Brownian dynamics \[101\]. The non-inertial dynamic equation is

\[
0 = -\frac{\partial U}{\partial r_i} - \sum_j v_j(t) \int_0^t \zeta_{ij}(\tau)d\tau + \eta_i(t). \tag{3.2}
\]

Over a long time interval, we can take \(\zeta_{ij}(t)\) approximately constant, i.e. \(\zeta = \int_0^t \zeta_{ij}(\tau)d\tau\). Since the dynamics in Eq. \[3.2\] is non-inertial, it is no longer mass-dependent.

Bead-spring, bead-rod models \[103, 104\], and FENE (finitely extendable nonlinear elastic) \[105–107\] chain models are simplified representation of polymers. From various CG models for alkanes, Nielsen \[108\] introduced a CG model based on Lennard-Jones and harmonic potentials. A successful CG force-field for several surfactants and bimolecular systems is the MARTINI model by Marrink et al. \[57, 58\] that is based on LJ re-parametrization. In this model, every four heavy atoms are mapped to one bead. Details of the MARTINI CG model are discussed in section \[3.5\].

At a different level of coarse-graining, the Dissipative Particle Dynamics (DPD) method \[56, 109–111\] is a popular method for simulations of fluids and complex fluids, in which particles are lump of fluid atoms with noise and friction forces. In DPD, particles are given interactions to represent the correct physical behavior of continuum equations. We discuss this method in more detail in section \[3.6.5\].

In the macroscopic/mesoscopic level of coarse-graining, the systems are not modeled by explicit particles, but by properties of continuum equations. We obtain the equations of fluid dynamics by averaging over space and time. The equations are based on the conservation of mass, momentum and energy, and they do not explicitly give information about the atomistic details of particles. Density as a function of space, pressure, and temperature are obtained from the equation of state. Continuum methods lead to a mesoscopic/macroscopic scale of continuum dynamics. At the first step at the mesoscopic level, only the collective motion of solvent molecules is taken into account. If we look at the solvent from a distance and average over a time longer than that of molecular fluctuations, in a region of space molecules move coherently. The hydrodynamic variables, mass density field \(\rho_r(x)\), the momentum density field \(g_r(x)\), and the energy density field \(e_r(x)\) are variables that capture collective motions of solvent molecules. These variables are defined as

\[
\rho_r(x) = \sum_i m\delta(r - q_i),
\]

\[
g_r(x) = \sum_i p_i\delta(r - q_i),
\]

\[
e_r(x) = \sum_i e_i\delta(r - q_i), \tag{3.3}
\]

where \(q_i\) and \(p_i\) are the position and momentum of the center of mass of particle \(i\) at the microscopic level and \(\delta(r - q_i)\) is a coarse-grained delta function. Equation \[3.3\] gives us information
Figure 3.2: Different levels of description of a coarse-grained system. From left to right: the Classical Mechanics level, Hydrodynamics, Fokker-Planck, and Smoluchowski. The coarse-grained delta function is non zero if $q_i$ is in the cell $r$ which represents a portion of space. Sketched from Ref. [112].

about average velocity and energy in small cells that contain many solvent molecules (see Fig. 3.2).

Solvent molecules enter and leave the cell in which hydrodynamic variables are defined, therefore there are fluctuations in hydrodynamic variables. These fluctuations are described as stochastic terms in the Landau-Lifshitz Navier-Stokes equations [113],

$$\frac{\partial \mathbf{U}}{\partial t} + \nabla \cdot \mathbf{F} = \nabla \cdot \mathbf{D} + \nabla \cdot \mathbf{S}, \quad (3.4)$$

where $\mathbf{U} = \begin{pmatrix} \rho \\ \mathbf{v} \\ e \end{pmatrix}$ is the vector of conserved quantities (mass, momentum, and energy density). $\mathbf{F}$, $\mathbf{D}$ and $\mathbf{S}$ are hyperbolic, dissipative, and stochastic fluxes respectively, given by

$$\mathbf{F} = \begin{pmatrix} \rho v \\ \rho v \mathbf{v} + P \mathbf{I} \\ (e + P) \mathbf{v} \end{pmatrix}, \quad \mathbf{D} = \begin{pmatrix} 0 \\ \tau \\ \kappa \nabla T + \tau \cdot \mathbf{v} \end{pmatrix}, \quad \mathbf{S} = \begin{pmatrix} 0 \\ S \\ Q + \mathbf{v} \cdot S \end{pmatrix}. \quad (3.5)$$

In the above equations, $P$ is the pressure, $T$ the temperature, $\tau$ the stress tensor, and $\kappa$ is the thermal conductivity. The stochastic stress tensor is $S$, and $Q$ represents the heat flux. The lattice-Boltzmann method [114,115] is one of the simulation methods to solve the Navier-Stokes equations at the hydrodynamic level of description. In the case where the hydrodynamic interactions of the solvent are fast compared to the time scale of variation of the solute particles, we can extend the level of coarse-graining to eliminate the hydrodynamics variables. At this level, we use the Fokker-Plank equation (FPE) to describe the time evolution of the probability density function, $\mathcal{P}(x,t)$, at state $x = \{Q_i, P_i\}$ [116],

$$\frac{\partial}{\partial t} \mathcal{P}(x,t) = -\sum_i \left[ U_i \cdot \frac{\partial}{\partial Q_i} + F_{iC}^{cc} \cdot \frac{\partial}{\partial P_i} \right] \mathcal{P}(x,t)$$

$$+ k_B T \sum_{ij} \frac{\partial}{\partial P_i} \cdot \zeta_{ij}(Q) \left[ \frac{\partial}{\partial P_j + \frac{p_j}{m_i k_B T}} \right] \mathcal{P}(x,t). \quad (3.6)$$
3.2. Coarse-graining methods

In equation 3.6, $P_i = m_i U_i$, $F_{i}^{CC}$ is the effective force exerted on solute particle $i$ due to the rest of particles. $\zeta_{ij}(Q)$ is the macroscopic friction tensor in which the hydrodynamic interactions are captured. If the evolution of the positions of the particles occurs on a much longer time than the evolution of the momentum and hydrodynamic modes, $Q_i$ will be enough to describe the system in longer time scales than the FPE equation. For example, in a dilute colloidal system the typical time scale of evolution of the position variables is about $10^3$ s. By using only $Q_i$ we can correctly simulate phenomena that occur above $10^3$ s. By eliminating momenta and mutual interactions between particles, we can rewrite the equation 3.6 as

$$\frac{\partial}{\partial t} P(Q, t) = - \sum_i \frac{\partial}{\partial Q_i} \left[ D_{ij} \cdot \frac{F_{i}^{CC}(Q)}{k_B T} P(Q, t) \right] + \sum_{ij} \frac{\partial}{\partial Q_i} D_{ij} \frac{\partial}{\partial Q_j} P(Q, t), \quad (3.7)$$

where $D_{ij}$ is the diffusion tensor that captures the eliminated interactions between particles. Equation 3.7 is called the Smoluchowski equation. Figure 3.2 shows the different levels of description of a system.

Coarse-graining can be considered a process of renormalization of interactions into a new representation with a lower overall dimensionality. Here we briefly explain the fundamental theoretical concepts of coarse-graining. Consider a system with potential energy $U(r)$ as a function of the atomic coordinates $r$. The free energy of the system in equilibrium, $G$, is

$$\exp (-\beta G) \propto \int \exp \left[ -\beta U(r) \right] \, dr, \quad (3.8)$$

where $\beta = \frac{1}{k_B T}$, with $T$ the thermodynamic temperature and $k_B$ the Boltzmann constant. Equation 3.8 connects the scale of the atoms and molecules to the macroscopic behavior of the system such as temperature, entropy, heat capacity and all free energy derivatives. Since the Eq. 3.8 is rarely solvable directly, coarse-graining eases the complexity of the system by following replacement of variables

$$\int \exp [-\beta U(r)] \, dr = \int \exp [-\beta U_{CG}(R_{CG})] \, dR_{CG}, \quad (3.9)$$

where $R_{CG}$ is the set of coordinates of $N_R$ CG particles. $U_{CG}(R_{CG})$ defines the effective potential for the CG variables which are less than the number of all atom degrees of freedom. However, there are two challenges in CG methods. First, the optimal choice for CG mapping may not be clear in Eq. 3.9, and second, $U_{CG}(R_{CG})$ must be defined and modeled. Therefore, a mapping operator $M_R(r)$ is needed to bridge between real atoms and CG sites, $R_{CG}$. One possibility is the use of the set of integrals over delta functions of all possible CG site positions as follows

$$\int dR_{CG} \delta(M_R(r) - R_{CG}) = 1. \quad (3.10)$$

By inserting Eq. 3.10 in 3.9, we rewrite the left side of Eq. 3.9 as

$$\int \exp [-\beta U(r)] \, dr = \int \, dR_{CG} \delta(M_R(r) - R_{CG}) \exp [-\beta U(r)]. \quad (3.11)$$

Therefore, we define the CG effective potential $U_{CG}(R_{CG})$ as

$$\exp [-\beta U_{CG}(R_{CG})] = \int \, dR \delta(M_R(r) - R_{CG}) \exp [-\beta U(r)] \quad (3.12)$$
Equation 3.12 is a mapping of the atomistic system to CG variables and certain degrees of freedom have been integrated out. As a result, the $U_{CG}(R_{CG})$ must include some entropic effects. Further details on coarse-graining and multiscale methods can be found in [117–120].

### 3.3 Integration

For a system of $N$ interacting particles, Newton’s equation of motion for particle $i$ is written as

$$
\vec{F}_i = m_i \ddot{\vec{r}}_i, \quad i = 1 \ldots N,
$$

(3.13)

where $m_i$ refers to the particle’s mass, $\ddot{\vec{r}}_i$ is the second derivative of the position vector with respect to time, and $\vec{F}_i$ is the force acting on the particle. In MD simulations, we require an “integrator” to solve Newton’s equations of motions numerically subject to a given set of initial velocities and positions. The integrator should satisfy time reversibility since Newton’s equations of motion are time reversible. Also, the integrator should conserve the energy of the system for short and long time scales. This means that, if at some instant all the velocities are reversed, the system can in principle backtrack over its prior trajectory. Most importantly, the integrator should preserve the symplectic property of the Hamiltonian system. A symplectic solver conserves the phase space area of the Hamiltonian. Let us consider a Hamiltonian system with phase space vector $x = q_1, \ldots, q_{3N}, p_1, \ldots, p_{3N}$. The dynamical system is a symplectic structure if the Hamiltonian of the system, $\mathcal{H}$, is expressible in the following form [100]

$$
\dot{x} = M \frac{\partial \mathcal{H}}{\partial x},
$$

(3.14)

where the matrix $M$ is defined as $M = \begin{pmatrix} 0 & I \\ -I & 0 \end{pmatrix}$. $0$ and $I$ are $3N \times 3N$ zero and identity matrices, respectively. Assume that $x_i$ is a solution to eqn. 3.14 from initial condition of $x_0$. Since $x_i$ is the unique solution of $x_0$, $x_i = x_i(x_0)$, there is a Jacobian transformation matrix which maps the initial phase space coordinate $x_0$ to a new set $x_i$ in phase space,

$$
J_{kl} = \frac{\partial x_i^k}{\partial x_0^l}.
$$

(3.15)

Matrix $J$ satisfies the following condition,

$$
M = J^T M J,
$$

(3.16)

where $J^T$ is the transpose of $J$. Equation 3.16 is known as the symplectic property. The integrator algorithm should map the initial phase space point $x_0$ into $x_i$ without violating the symplectic property of classical mechanics. One should notice that numerical solvers do not exactly conserve the Hamiltonian. But the important property of a symplectic solver is that, along the trajectory, there is a conserved “shadow” Hamiltonian, $\tilde{\mathcal{H}}(x, \delta t)$, close to the true Hamiltonian. By close we mean at the limit of $\delta t \to 0$, $\tilde{\mathcal{H}}(x, \delta t)$ approaches the true Hamiltonian. The existence of $\tilde{\mathcal{H}}(x, \delta t)$ ensures that the errors are bounded in a symplectic map [100, 121]. That simply means, at any time step, $x_{\delta t}$ remains on the constant energy surface which is close
to the true constant energy surface and by using a symplectic integrator there is no dramatic drift in the total energy of the system. To develop symplectic algorithms from the equation of motion, a Trotter expansion has been used, details of the Trotter expansion will be discussed in Appendix A.1. Here we briefly review a few integrators.

### 3.3.1 Verlet algorithm

In the Verlet approach [122], the new positions of particles at the time step \( t + \delta t \) are updated as follows

\[
\vec{r}_i(t + \delta t) = 2\vec{r}_i(t) - \vec{r}_i(t - \delta t) + \frac{1}{m_i} \vec{F}_i(t)(\delta t)^2. \tag{3.17}
\]

Equation 3.17 is obtained by adding the Taylor expansions of \( \vec{r}_i(t - \delta t) \) and \( \vec{r}_i(t + \delta t) \) which is known as the Verlet algorithm. This algorithm only generates positions of particles with an error of order \( O(\delta t^4) \). After calculating the position of particle at time \( t + \delta t \), if needed, the velocity of a particle at time step \( t \) can be approximated as

\[
\vec{v}_i(t) = \frac{\vec{r}_i(t + \delta t) - \vec{r}_i(t - \delta t)}{2\delta t} + O(\delta t^2). \tag{3.18}
\]

### 3.3.2 Velocity-Verlet algorithm

The velocity-Verlet algorithm is based on the Verlet algorithm, however it gives both velocities and positions at the same time. First the velocity is computed at half time step and then this is used to update the position. Finally the velocity at next time step is calculated:

\[
\vec{v}_i(t + \frac{\delta t}{2}) = \vec{v}_i(t) + \frac{1}{2m_i} \vec{F}_i(t)(\delta t) \tag{3.19}
\]

\[
\vec{r}_i(t + \delta t) = \vec{r}_i(t) + \vec{v}_i(t + \frac{\delta t}{2})\delta t \tag{3.20}
\]

\[
\vec{v}_i(t + \delta t) = \vec{v}_i(t + \frac{\delta t}{2}) + \frac{1}{2m_i} \vec{F}_i(t + \delta t)(\delta t) \tag{3.21}
\]

Error for both the position and velocity is of the order \( O(\delta t^4) \). This algorithm is stable and time-reversible which makes it a reliable integrator for MD simulations. In our simulations, we use the LAMMPS [123, 124] package, in which the integrator is the velocity-verlet algorithm.

### 3.3.3 Leapfrog algorithm

The leapfrog algorithm is equivalent to the Verlet algorithm algebraically. The only difference is that in the leapfrog algorithm, velocity at half a time step \( \vec{v}(t - \frac{\delta t}{2}) \) is used to update the positions and forces at time \( t \).

\[
\vec{v}_i(t + \frac{\delta t}{2}) = \vec{v}_i(t - \frac{\delta t}{2}) + \frac{1}{m_i} \vec{F}_i(t)(\delta t) \tag{3.22}
\]

\[
\vec{r}_i(t + \delta t) = \vec{r}_i(t) + \vec{v}_i(t + \frac{\delta t}{2})\delta t \tag{3.23}
\]

\[
\vec{v}_i(t + \delta t) = \frac{\vec{v}_i(t + \frac{\delta t}{2}) + \vec{v}_i(t - \frac{\delta t}{2})}{2}. \tag{3.24}
\]
Leap frog is a second order method, with an accuracy of $O(\delta t^2)$. GROMACS \cite{GROMACS} uses the Leapfrog algorithm.

![The illustration of the leapfrog algorithm.](image)

Figure 3.3: The illustration of the leapfrog algorithm. Positions are updated at full time steps while velocities are calculated at half time steps.

## 3.4 Force-fields

To perform molecular simulations of large systems over reasonable time spans, a simple description of the interactions between constitute particles is required. A force-field describes the interactions of particles through mathematical functions and a set of parameters. Thus, for any MD simulations, first we should define an accurate force-field from which forces on particles can be calculated. In the classical regime, we divide force-fields into three main categories: all-atom, united-atom, and coarse-grained. In all-atom force-fields, detailed information about the electronic properties of atoms is not explicitly included, but is considered in interaction potential parameters for every type of atom. All-atom simulations give a good insight into the molecular structure and the important atomistic aspects, in a time span of ns within a reasonable computational time. In the united-atom force-fields, the non-polarized hydrogen atoms of methyl and methylene groups are incorporated in the carbon atom and the parameters involved are adjusted accordingly. Therefore, the united-atom represents a group of atoms, e.g. a carbon group. This approximation can save computational time in simulations. In “coarse-grained” (CG) force-fields, a group of atoms are represented by “pseudo-atoms”. By reducing the degrees of freedom in a system, the behavior of the system can be investigated over experimental time scale. Force-fields are chosen depending on the purpose of the simulations, and time/length scale of the systems. For example, it is impossible to describe hydrodynamic flow by a quantum-mechanical force-field. In conclusion, the chosen force-field should be able to model the real behavior of the system at the desired length/time scales.

Although at the fundamental level molecular interactions have been derived from quantum mechanics, in classical MD, atoms are modeled as spheres that interact through “effective potentials” which are not exactly obtained from quantum mechanical principles. Effective potentials incorporate the average induced dipole moments, as well as average repulsion and dispersion contributions. Interactions are modeled through mathematical functions with the appropriate parameters. In general, interactions are classified into non-bonded interactions, such as van der Waals, and electrostatic interactions, or bonded ones, i.e. bond stretching,
bond rotation, and angle bending. Non-bonded interactions are usually pairwise and additive. Bonded interactions are used to model bonded atoms in a molecule such as hydrogen and oxygen atoms in a water molecule. A two-body potential, such as harmonic or FENE (finitely extendable nonlinear elastic) [126] potential, describes bond stretching between two atoms. Three-body and four-body interactions are mostly used to represent angle bending and bond rotation. We classify non-bonded interactions as short-range or long-range. Short-range interactions are defined as interactions that decrease faster than \( r^{-d} \), \( d \) being the dimension of the system, e.g., van der Waals interactions. Electrostatic interactions are considered long-range interactions. In this section, some commonly used potentials in a CG force-field are discussed.

### 3.4.1 Van der Waals interactions

The Lennard-Jones (LJ) potential is the most used potential to model the van der Waals interactions,

\[
U_{LJ}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right],
\]

where \( \epsilon_{ij} \) represents interaction strength and \( \sigma_{ij} \) sets the length scale of two interactions. \( r_{ij} \) denotes the distance between two particles. These parameters can be fitted to reproduce different levels of interaction between atoms (see Fig. 3.4). The \( -r^{-6} \) term arises from averaging over the random orientations of two permanent dipoles (Keesom interaction), induced dipole-permanent dipole (Debye interaction) and London or dispersion force. The London forces are results of induced dipole-induced dipole interactions. Averaging over Keesom, Debye and the London interactions gives a term \( -r^{-6} \). The repulsive term \( r^{-12} \) is a good approximation for

\[\text{Figure 3.4: A schematic plot of LJ 6-12 potential.}\]
the Pauli repulsion at short ranges. The overlapping electron orbitals cause the Pauli repulsion. The term $r^{-12}$ is computationally efficient to calculate (the square of $r^6$), thus the van der Waals interaction is most commonly modeled by the LJ 12-6 potential. The repulsive term of $r^{-12}$ diverges quickly and prevents the particles from penetrating, so the LJ 12-6 potential is considered to have a “hard core”. The $r^{-12}$ term can be replaced with a softer potential such as any form of $\exp(-\kappa r)$. The combination of the $r^{-6}$ and the $\exp(-\kappa r)$ term is called the Buckingham potential.

LJ 12-6 form has been used extensively in molecular simulations because of its simplicity and short range feature. A cut-off distance $r_{\text{cut}}$ is often introduced. To avoid discontinuity of potentials and forces, the LJ potential is shifted/interpolated to be zero at $r_{\text{cut}}$.

### 3.4.2 Electrostatic interactions

In systems involving electric charges and dipole interactions, the electrostatic interactions between two charged atoms with charges $q_i$ and $q_j$ can be modeled by the Coulomb’s potential,

$$U_{el}(r_{ij}) = \frac{q_i q_j}{4 \pi \epsilon_r \epsilon_0 r_{ij}}, \quad (3.26)$$

where $\epsilon_r$ is the relative permittivity and $\epsilon_0$ is the vacuum permittivity. The potential is truncated at $r_{\text{cut}}$, similar to the short-range interaction. To avoid discontinuity, a smooth function is used to interpolate/shift the forces and potential to zero. The electrostatic interactions are long-range, therefore truncation of potentials may lead to crucial artifacts if the long-range contributions are ignored [127–130].

The electrostatic potential for a system with explicit ions is calculated by adding the individual electrostatic interactions. This Coulomb sum conditionally converges, and the end result depends on the order of doing the sum. Also, in systems with periodic boundary conditions, including all interactions between a charged particle and all its images is not efficient [131]. Therefore, to handle the long-range interactions, the Ewald summation has been developed [132]. In the Ewald’s approach [132] the summation is over periodic images of the system. The particle-particle/particle-Mesh (PPME) method of Eastwood and Hockney [133–136] is basically the Ewald sum but computationally faster.

**Ewald sum**

In the Ewald summation [132], the basic idea comes from the calculation of the total energy of an ionic crystal lattice structure. In a system of $N$ particles, because of the long-range interactions, the total energy of the system includes all contributions of the periodic images of the central cell and is shown in the following sum

$$U_{qq} = \frac{1}{2} \sum_{n} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{q_i q_j}{|r_{ij} + L\vec{n}|}, \quad (3.27)$$

where $q_i$ is the charge of the particle $i$ and $L$ is the box length (cubic box). The sum is over all the integer vectors $\vec{n}$ and the prime sign means that the summation does not include $i = j$ when $|\vec{n}| = 0$. Although self-interaction is avoided, particles interact with their images in
replica cells. In the above equation, we assume that the whole system is neutral. To compute the electrostatic potential from Eq. 3.27, each charged particle is screened by a diffuse charge distribution with the opposite sign. The distribution is chosen to be a Gaussian distribution that rapidly goes to zero at large distances. Then, we add the second distribution with the same charge sign of the particle to cancel out the contribution of the additional charges. In another words, we replace a set of point charges with a set of screened charges minus the smooth screening background [100], see Fig. 3.5 for illustration. We use a Fourier series to represent these rapidly converging functions. At the end, the electrostatic contributions of a set of screened charge can be calculated by the mentioned summation.

![Figure 3.5: A point charge distribution is split into a screened point charge distribution and the corresponding screening distribution. Sketched from Ref. [100]](image)

**Particle-Mesh-Ewald**

In the Ewald sum, the computation time of the Fourier part scales as $N^2$. By using the optimized cut-off, we can improve the scaling to $N^2$ at the best. Particle-Mesh-Ewald [133, 134] and particle-particle-mesh (PPME) [135, 136] are based on Ewald summation; however, since they handle the reciprocal sum by the Fast Fourier transform algorithm, they are more efficient for large scale systems, e.g. biological systems and systems with both long and short range interactions. These two methods both scale with $O(N \log(N))$. In these approaches, charges are distributed on a mesh. The efficiency and accuracy of mesh-particle based models depends on how the charges are mapped onto the discrete mesh points.

### 3.4.3 Bonded interactions

Bonded interactions are between atoms in a molecule. If bonds have high frequency vibrations much larger than $\frac{k_B T}{h}$ then, in a simulation, we should replace them with constraints. Modeling bonds requires much shorter integration time steps; hence the computation time substantially increases. Thus, we replace high frequency vibration bonds with constraints (see section 3.9). In Fig. 3.6 some bonded interactions are depicted.
Figure 3.6: Illustration of bonded interactions: a) bond stretching, 2 body interactions. $r_{ij}$ represents the bond length between particles $i$ and $j$. b) angle bending, 3 body interactions. $\theta$ is the angle formed between three particles. c) torsion, 4 body interactions. $\phi$ is the angle between the normals to the two planes formed by $i, j, k$ and $j, k, l$ particles.

**Bond stretching**

The covalent bond between atoms is usually described by a harmonic potential, obtained by a polynomial expansion around the equilibrium length $r_{bond}$

$$U_{bond}(r_{ij}) = \frac{1}{2} K_{bond} (r_{ij} - r_{bond})^2,$$

(3.28)

where $r_{ij}$ is the bond length, and $K_{bond}$ is the force constant. $K_{bond}$ and $r_{bond}$ are different for each bond type. This potential model is commonly used in both coarse-grained models and all-atom force-fields.

Another widely used model is the FENE potential \[126\] which does not allow stretching beyond a maximum length $R$.

$$U_{FENE}(r_{ij}) = \frac{1}{2} K_{bond} R^2 \ln(1 - \frac{r_{ij}^2}{R^2}),$$

(3.29)

The FENE potential is used in CG modelss of bead-spring polymers.

**Angle bending**

A covalent bond angle formed between three particles $i, j, k$, is typically described by

$$U_{angle}(r_i, r_j, r_k) = \frac{1}{2} K_{angle} (\cos(\theta) - \cos(\theta_0))^2,$$

(3.30)

or by

$$U_{angle}(r_i, r_j, r_k) = \frac{1}{2} K'_{angle} (\theta - \theta_0)^2,$$

(3.31)

where $\theta = \arccos \left( \frac{\vec{r}_{ij} \cdot \vec{r}_{jk}}{r_{ij}r_{jk}} \right)$. 
3.5 CG force-fields

Bond rotation (torsion)

Four sequential particles \(i - j - k - l\) form a dihedral angle \(\phi\) which is defined as the angle between the normals \(n\) and \(m\) to the two planes formed by \(i, j, k\) and \(j, k, l\):

\[
\phi = \arccos \left( \frac{n \cdot m}{nm} \right),
\]

(3.32)

\[
\vec{n} = \vec{r}_{ij} \times \vec{r}_{kj},
\]

\(\vec{m} = \vec{r}_{jk} \times \vec{r}_{lk}.
\)

(3.33)

See Fig. 3.6c for the illustration. The change in energy due to the rotation of the bonds, \(U(\phi_{ijkl})\), is described by the torsion potential. Since the energy barriers for bond rotation are low, compared to the energy barriers of bond stretching or angle bending, large deviations can occur in dihedral angle. Furthermore, the torsional potential is periodic through a 360° rotation of bonds. As a result, the harmonic approximation can not be justified. Therefore, a cosine expansion is chosen which gives a functional form as follows:

\[
U_{\text{torsion}}(\phi) = K_\phi \left( 1 + \cos(n\phi - \phi_0) \right).
\]

(3.34)

3.5 CG force-fields

Mapping a molecular structure to a description with fewer interaction sites reduces the degrees of freedom in the system. In addition, to save computation time, larger time steps are desirable and they are achievable through softer effective potentials. As a result, not all molecular properties are preserved in CG models. The key question in every mapping is: what properties are going to be reproduced by CG models. Thus, there is no unique answer for CG mapping. Several CG models for surfactants [108, 137, 138] have been proposed. In this thesis, we focus on the “MARTINI” model [57] that has been successfully used in several studies including vesicle formation and fusion [57, 59, 61], the structure and dynamics of membrane and lipids [139, 143], and self-assembly [63] and the micellization of different surfactants [62]. The MARTINI approach is based on calibration of the building blocks of the coarse grained force-field against thermodynamic data, and in particular oil/water partitioning coefficients [57]. The CG MARTINI model for sodium dodecyl sulfate (SDS) and water molecules are discussed in more detail in this section.

3.5.1 MARTINI force-field

In the simulations in this thesis, the MARTINI force-field martini-v2.P [57, 58] is used to model the particle interactions. All types of interaction in the MARTINI force field are grouped into four main categories: Polar (P), nonpolar (N), apolar (C), and charged (Q). In order to represent a more realistic description of the chemical properties of a molecular structure, each category is divided into subtypes. Within a main type, subtypes are distinguished based on the hydrogen-bonding capabilities (d = donor, a = acceptor, da = both, 0 = none) and the degree of polarity (from 1, low polarity, to 5, high polarity). In the MARTINI force-field, on average, every 4 heavy atoms are represented by one interaction center.
Non-bonded interactions are described by a LJ 12-6 potential energy function, Eq. (3.25), which is smoothly interpolated to zero at the cut-off distance:

\[ U_{LJ}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + S(r) \]  

(3.35)

\( S(r) \) is a switching function between the \( r_{shift} \) and \( r_{cut} \), discusses in chapter 4.

Electrostatic interactions for charged groups are defined via a Coulombic potential energy function

\[ U_{el}(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 \epsilon r_{ij}} + S(r). \]  

(3.36)

In the above equation, \( S(r) \) is the same as in Eq. (3.35).

In bonded interactions, LJ interactions are excluded between bonded particles. Bond stretches are described by a harmonic potential

\[ U_{bond}(r) = \frac{1}{2} K_{bond} (r_{ij} - r_{bond})^2, \]  

(3.37)

where \( r_{bond} \) is the equilibrium distance between two bonded particles and \( K_{bond} \) is the force constant. Chain stiffness is represented by a weak cosine type harmonic potential \( U_{angle}(\theta) \). The potential \( U_{angle} \) for angles is

\[ U_{angle}(r) = \frac{1}{2} K_{angle} (\cos(\theta) - \cos(\theta_0))^2, \]  

(3.38)

in which \( \theta_0 \) is the equilibrium bond angle, \( K_{angle} \) is the coupling constant and \( \theta \) is the angle formed by triplets of bonded particles.

The atomic structure of SDS is mapped onto four CG beads according to the input files available on [http://md.chem.rug.nl/CGmartini/](http://md.chem.rug.nl/CGmartini/) (MARTINI force-fields for surfactants), see Fig. 3.7. The head group of SDS, \( \text{SO}_4^- \), is modeled by type \( Q_a \), \( \text{Na}^+ \) is a \( Q_d \) particle, and 12 hydrocarbon groups in the tail of the surfactant are reduced to three particles of type \( C_1 \). The mass of the head group is \( m = 96.0576 \text{ g mol}^{-1} \), the first and second tail bead masses are \( m = 56.1088 \text{ g mol}^{-1} \), and the mass of the last bead in the tail is set to \( m = 57.1163 \text{ g mol}^{-1} \). Bond lengths between the head group and the first tail bead is \( l = 4.04 \text{ Å} \) with \( K_{bond} = 23.92 \text{ kcal mol}^{-1} \text{ Å}^{-1} \). Bond lengths and force constants between all tails bead are \( l = 4.7 \text{ Å} \) and \( K_{bond} = 2.99 \text{ kcal mol}^{-1} \text{ Å}^{-1} \) respectively. The equilibrium angle among the head and the first two tail beads is \( \theta_0 = 170^\circ \) with \( K_{angle} = 3.584 \text{ kcal mol}^{-1} \text{ Å}^{-1} \). The angle formed between the three tail beads is set to \( \theta_0 = 180^\circ \) with \( K_{angle} = 5.976 \text{ kcal mol}^{-1} \text{ Å}^{-1} \).

In many CG water models, several water molecules are grouped to a single interaction site. Most models have short-ranged LJ interactions with no electrostatic interactions [57]. Although these models significantly decrease the computation time, there are some known unphysical features of non-electrostatic water. The one bead CG MARTINI water has a tendency to freeze close to interfaces such as membranes and solid surfaces [57]. Furthermore, by neglecting the electrostatic interactions in water models, the water model is blind to explicit polarization effects. It can not probe processes that involve interactions between charged groups and polar groups. Since we have surfaces in our simulations, to avoid known artifacts of MARTINI water, we have chosen the polarizable MARTINI water model [58] as the CG water
3.5. CG force-fields

model in our confined systems. It has been shown that the density-temperature dependency of the polarizable model \[58\] compares well with experiments. Also, the polarizable MARTINI water model has been parameterized to reproduce the orientational polarizability of real water and, consequently, the dielectric constant of bulk water is reproduced \[58\].

The CG model of polarizable MARTINI water \[58\] has three linear beads with equal masses of 24 \(\frac{g}{mol}\) which represents the mass of four water molecules. Side beads \(WP\) and \(WM\) have partial charges of \(q_{\pm} = \pm 0.46e\). The central bead \((W)\) is neutral. Fig 3.7b) shows the water model. The bond length between charged beads and the neutral bead is kept fixed at 1.4 Å. The equilibrium angle is set at \(\theta = 0^\circ\) with \(K_{\text{angle}} = 0.5019 \text{ kcal} / \text{molÅ}\). In the polarizable model, only the central neutral bead has Lennard-Jones interactions with other CG beads. The energy of interaction between the central beads is \(\epsilon_{WW} = 0.956 \text{ kcal} / \text{molÅ}\) with \(\sigma_{WW} = 4.7\) Å. Also, there is no electrostatic and LJ interactions among the beads in the same CG water molecule. A uniform relative dielectric constant helps to implicitly screen electrostatic interactions. In the polarizable water model the relative dielectric constant is \(\epsilon_r = 2.5\) \[58\]. Although the obtained density and diffusion coefficients of this model compare well with the properties of bulk water, the surface tension of the polarizable MARTINI model is 30.5 mN/m \[58\] which is significantly lower than the experimental data, 73 mN/m \[144, 145\]. LJ energies of interactions between water, surfactants and ions are shown in Table 3.1.

![Figure 3.7](image)

Figure 3.7: Mapping between the all-atom chemical structure and the coarse-grained model for SDS, water and ion molecule. a) The sulfate group at the head is modelled as a \(Q_a\) particle (red) and the 12 hydrocarbon groups in the tail of the SDS are mapped to three \(C1\) particles (cyan). b) The polarizable MARTINI model represents the properties of four all-atom water molecules. The central bead is neutral and each charged bead carries \(q = \pm 0.46e\). c) Picture of the MARTINI CG ion which represents the ion and the hydration shell around it.

<table>
<thead>
<tr>
<th>(\epsilon_{LJ} (0.5 \times \frac{\text{kcal}}{\text{mol}}))</th>
<th>Head</th>
<th>Tail</th>
<th>(Na^+)</th>
<th>(W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Head</td>
<td>0.836</td>
<td>0.549</td>
<td>0.956</td>
<td>1.195</td>
</tr>
<tr>
<td>Tail</td>
<td>0.549</td>
<td>0.836</td>
<td>0.549</td>
<td>0.454</td>
</tr>
<tr>
<td>(Na^+)</td>
<td>0.956</td>
<td>0.549</td>
<td>0.836</td>
<td>1.195</td>
</tr>
<tr>
<td>(W)</td>
<td>1.195</td>
<td>0.454</td>
<td>1.195</td>
<td>0.956</td>
</tr>
</tbody>
</table>
3.6 Thermostats

Direct integration of Newton’s equation of motions produces the micro-canonical ensemble, while most experiments are performed at constant temperate and/or pressure. Thus, it is useful to run MD simulations in ensembles such as the canonical ensemble (NVT-ensemble) with constant temperature or the isothermal-isobaric ensemble (NPT-ensemble).

Many algorithms for thermostating have been developed. In general, thermostats act locally or globally. Global thermostats affect all particles, while a local thermostat acts on single/pairwise particles. The Nosé-Hoover thermostat \[146, 147\] and the weak coupling Berendsen thermostat \[148\] are examples of global thermostats. Common local thermostats are Langevin \[149\], Andersen \[150\] and Dissipative Particle Dynamics (DPD) methods \[111\]. In simulations on micelle formation, we used the Berendsen thermostat. We applied the DPD thermostat in the confined systems.

3.6.1 Langevin thermostat

In the Langevin thermostat \[151\], each particle moves as if it is in a viscous fluid. A friction term and a white noise term is added to Newton’s equations of motions (see Eq. 3.1). The noise and friction terms are balanced to keep the solvent molecules at constant temperature \(T\). Langevin dynamics resembles a stochastic heat bath for a system. It reproduces the canonical ensemble if the inverse friction constant is large in comparison to the time steps of the simulated system. Since each particle is coupled to a local heat bath, there is no heat trapped in localized modes. However, momentums transfer is destroyed by the Langevin thermostat. Therefore long-range hydrodynamic interactions can not be described correctly with the Langevin thermostat. Although the Langevin thermostat has been extensively and successfully used in many simulations, particularly in polymer simulations, for systems in which hydrodynamic interactions are important (e.g. diffusion coefficients), the usage of the Langevin thermostat should be avoided.

3.6.2 Berendsen weak coupling

One of the popular velocity rescaling thermostats is the Berendsen thermostat \[148\]. In the Berendsen method, a heat bath with the desired temperature \(T_d\) is weakly coupled to the system. At each time step, the particle velocities are rescaled by the factor

\[ \chi = \frac{1}{2\tau} \left( \frac{T_d}{T(t)} - 1 \right), \]  

(3.39)

where \(T(t)\) is the kinetic temperature of the system at time \(t\) and the time constant \(\tau\) determines the rate of this correction. The produced ensemble depends on the values of \(\tau\). At small \(\tau\), the canonical ensemble is obtained while a large value for \(\tau\) leads to the microcanonical ensemble \[152\]. A weaker coupling means a larger \(\tau\); it takes longer time for the system to reach the desired temperature. Because this algorithm is easy to implement, and it can produce the canonical ensemble by adjusting parameters, this thermostat has been used in many MD simulations, especially in bringing the system close to the equilibrium point. Nevertheless, it has been shown \[153\] that the simulation does not fulfill the equi-partition theorem over time.
There is an increase in transitional and rotational kinetic energy and a gradual loss in vibrational energy. As a result, the “flying ice cube” artifact can occur where the system freezes to a single conformation. To avoid this artifact in simulations, the center of mass of the translational and rotational motion should be removed periodically \[1\]. Apart from the kinetic energy, most properties are sampled correctly in large enough systems.

### 3.6.3 Andersen

In this method \[1\], the system is coupled to an imaginary heat bath with the desired temperature \( T \). To mimic the stochastic collisions between particles and heat bath, the new velocity for randomly selected particles are drawn from the Maxwell-Boltzmann distribution of temperature \( T \) at specified time intervals. The equations of motion for particles are Hamiltonian and the stochastic collision event only affects the momentum of the selected particles. The combination of Newtonian dynamics and the stochastic collisions turns the MD simulation into an irreducible Markov process \[1\]. It has been shown \[1\] that the Andersen thermostat reproduces the correct canonical ensemble in the limit of a long trajectory averaged over heat bath collision. Due to the random velocities there is no continuity of momentum, hence it should not be used to compute dynamical quantities such as diffusion coefficients. Trajectories are not smooth due to random collisions and obviously there is no local momentum conservation in this method and it is not expected to preserve hydrodynamic modes.

### 3.6.4 Lowe-Andersen

The Lowe-Andersen thermostat \[1\], a modification of the Andersen thermostat, conserves the momentum of the system. Also it is Galilean invariant, and local. The thermostat only acts pairwise on particles within the cut-off distance, while the Anderson thermostat rescales the velocity of a single particle. To keep the angular momentum of the system conserved, only components of the relative velocity that are parallel to the line of centers are affected. The new value of the projected relative velocity obtained from the Maxwell distribution is reassigned with probability \( \Gamma dt \). An efficient Lowe-Andersen thermostat requires a high rate of collision, which leads to an increase in the viscosity of the fluid. Although the Lowe-Andersen thermostat preserves the hydrodynamics of the system, having a high viscous fluid with a low diffusion coefficient can be a drawback in some cases.

### 3.6.5 Dissipative Particle Dynamics

Dissipative Particle Dynamics (DPD) is one of the coarsed-grained MD methods which represents the continuum fluid equations by particles. CG particles in the DPD model represent a simplified but realistic molecular structure. DPD particles are basically representing lumps of fluid and their sizes depend on the fluid conditions in the system, varying between atomic size to nanometer for colloidal systems. The DPD particles are more a collections of molecular groups rather than individual atoms.

The DPD method was first introduced by Hoogerbrugge and Koelmann \[1\]. They treated the fluid dynamics problem with particles with short-ranged conservative forces with additional pairwise friction and noise terms that conserve momentum and the average energy. The friction
and noise forces were coupled and acted as thermostats. Español and Warren [109] studied the relation between statistical mechanics and DPD. They showed that in order to recover the proper thermodynamics of systems, the friction and noise terms must be coupled through a fluctuation-dissipation relation. Under this condition, DPD conserves the flow properties of the modeled system and therefore can successfully reproduce the hydrodynamic behavior of the system [109].

In addition to conservation of the total momentum of the system, the DPD method reproduces the proper description of the physical hydrodynamic behavior [56,109]. Due to these advantages with respect to other mesoscale methods, the DPD method has been used in a diverse range of studies in soft matter systems such as self-assembly and micellization [157–159], vesicle formation [160,161] and flow of complex fluids [111,162–166].

The DPD formalism

Assume $N$ particles with mass $m_i$, positions $r_i$ and velocities $\vec{v}_i$. Particles interact through three pairwise forces: a potential-derived conservative force, a dissipative friction force, and a random force. All inter particle forces are pairwise. The sum of all forces is zero and both linear and angular momenta are conserved, even on a local basis. The forces are given by

$$\vec{F}_i = \sum_{i \neq j} \left( F^{C}_{ij} + F^{D}_{ij} + F^{R}_{ij}\right) \hat{r}_{ij}, \quad r < r_{\text{DPD}}$$

$$F^{C}_{ij} = F^{(c)}_{ij}(r)\hat{r}_{ij}$$

$$F^{D}_{ij} = -\gamma_{\text{DPD}} \omega_D(r)(\hat{r}_{ij} \cdot \vec{v}_{ij})$$

$$F^{R}_{ij} = \sigma_{\text{DPD}} \omega_R(r) \alpha \delta t^{-\frac{1}{2}},$$

where $\hat{r}_{ij}$ is the unit vector in the direction of the separation distance between particles $i$ and $j$ and $\vec{v}_{ij}$ stands for the vector difference of velocities between particles. $\alpha$ is a random number generated from a Gaussian distribution with zero mean and unit variance for a pair particles at every time step, $\delta t$ is the time step size, $k_B$ is the Boltzmann constant, $T$ is the temperature, and $\sigma_{\text{DPD}}$ is the amplitude of the noise.

The pairwise conservative force, $F^{(c)}_{ij}$, is completely independent of the random and dissipative forces. The general DPD formalism does not specify the functional form of the conservative force. Hence, $F^{(c)}_{ij}$ can be obtained from any appropriate potential for a given system, such as van der Waals and electrostatic interactions. However, since the DPD method is used to simulate mesoscopic scale simulations, the conservative force is often chosen to be soft, repulsive, and short-scale.

In order to reproduce the canonical distribution in thermodynamic equilibrium in the system, the DPD formalism must satisfy the fluctuation-dissipation theorem which states that perturbations in the system will be dissipated as the system reaches its equilibrium. Therefore, the random and dissipative forces must be coupled together. Español and Warren [109] used a Fokker-Plank equation to derive the conditions that ensure the energy changes from dissipation and random force cancel. They showed that the coupling between the dissipative and random
forces requires that
\[ \omega_D(r) = \omega_R(r)^2, \]  
\[ \sigma_{\text{DPD}} = \sqrt{2K_B T \gamma_{\text{DPD}}}. \] (3.41) (3.42)

The functional form of the weight function is not specified by the fluctuation-dissipation theorem. The functional form of the weight function is arbitrary \( \omega(r) \) however the most common choice is
\[ \omega(r) = \begin{cases} 
1 - \frac{r}{r_{\text{DPD}}} & r < r_{\text{DPD}} \\
0 & r > r_{\text{DPD}} 
\end{cases}, \] (3.43)
where \( r_{\text{DPD}} \) is the cut-off distance of DPD. The above function is simple and fast to compute. Also, it is fairly soft, thus, bigger time steps is stable. Thus, the most common choice in DPD simulations is \( \omega_R(r) = \omega(r) \).

In order to have a canonical distribution in thermodynamic equilibrium, this formalism must be followed [56, 109]. Through this formalism, random and dissipative forces together form a thermostat of temperature \( T \) for particles [56, 110]. In MD simulations, a variety of thermostats (see section 3.6) have been explored, however the DPD-thermostat is the only thermostat that is guaranteed to conserve momenta of the particles, and thus to reproduce the correct hydrodynamic properties of the fluid. Therefore, it is the only thermostat that allows investigating transport processes.

3.7 Barostats

Most experiments are done in the isothermal-isobaric ensemble. In order to simulate such systems, volume must change during simulations. To achieve the desired pressure, several algorithms such as Berendsen and Parrinello-Rahman have been proposed. In this section we briefly review them. In the NPT simulations of micelle formation, we use the Berendsen barostat.

3.7.1 Berendsen barostat

In the Berendsen barostat [148] the system is weakly coupled to an external pressure bath. An extra term is added to the equation of motion
\[ \frac{dP}{dt} = P_d - P \tau_p. \] (3.44)

In above equation, \( P_d \) is the desired pressure, and \( \tau_p \) is a time constant. At each time step, the volume is rescaled by the scale factor \( \chi \) and the coordinates are accordingly adjusted by a factor \( \chi^{1/3} \), where \( \chi \) is defined as
\[ \chi = 1 - \beta_T \frac{\delta t}{\tau_p} (P_d - P). \] (3.45)

In above equation, \( \beta_T \) is the isothermal compressibility. Due to its simplicity, this barostat is often used during the equilibration of the system.
3.7.2 Parrinello-Rahman barostat

The Parrinello-Rahman barostat [167] allows the system to modify its volume anisotropically. The volume of the system is defined by three vectors that can have different lengths and orientations. The box vectors are set to follow an equation of motion; thus the cell shape is also a variable. This barostat is considered reliable for simulation of solids. However, in simulations of liquids, since the box itself is a dynamic and changes its shape, one should use it carefully.

3.8 Boundary Condition

3.8.1 Periodic boundary condition (PBC)

Molecular simulations are aimed at providing information about thermodynamic properties. However, the number of the particles in simulations are up to millions, which is far below the thermodynamic limit of a macroscopic sample ($\approx 10^{23}$). No matter how large the system is, the fraction of surface particles ($\sim N^{1/3}$ in 3 dimensional simulations) is much larger than in realistic samples, therefore the surface effects influence the system’s properties significantly. In order to overcome this problem, and simulate a bulk model system, we use periodic boundary conditions (PBC). In PBC, the main simulation box, called “the central box”, is replicated to form an infinite lattice in all directions. In each cell, particles are moving exactly like the original particles in the central box. When one particle leaves the central box, its image will enter the central box from the opposite side. Each particle in the central box interacts with all other particles in all other cells, including its images. As a result, no surfaces are present and a bulk system is modeled. Figure 3.8 shows the images of the central box in 2D. Despite the effectiveness of the PBC method, it may lead to artificial periodicity in the presence of long-range interactions such as electrostatic interactions [100]. Moreover, macroscopic fluctuations with wavelength longer than the length of the central box are not allowed in the system [100]. Another unphysical problem is that angular momentum is not conserved in systems with PBC. When a particle leaves the box and enters the central box from the opposite side, the traveled distance by the particle from the center of mass of the replica box and the central box are different; the angular momentum of the system will not be conserved. Nevertheless, PBC has no artifacts regarding the equilibrium properties of systems with short-ranged interactions.

3.8.2 Wall

To reproduce bulk properties of fluids at equilibrium, PBC is the best choice in MD simulations. However, in some systems, complicated geometrical boundaries are needed. In non-equilibrium systems, including gradient pressure driven flows and shear flows in channels, the boundary conditions affect the flowing fluid significantly. For studying absorption of molecules on surfaces, and fluid/solid interfaces, other boundary conditions, like walls, must be used. Fixed cell boundaries can be a virtual wall; a simple continuous barrier potential that acts as the repulsive wall or it can be an atomistic rigid/semi-rigid wall with static or dynamic atoms with springs. Atomistic walls can represent various lattice structure with different orientations. In Sec. 6.2 more details on the structure of walls will be discussed.
Figure 3.8: A schematic representation of periodic boundary conditions in two dimensions. The gray particle leaves the central box through top boundary, and consequently re-enters through the bottom boundary.

### 3.9 Constraints

The frequencies associated with bond/angle vibrations within molecules ($\approx 10^{-15}$ s$^{-1}$) are much higher than the translational motion of unbounded atoms. Thus, modeling bonds requires much shorter integration time steps which would lead to substantial increase in computation time. To overcome this problem, bond vibrations can be replaced by frozen bonds in classical MD simulations. In fact we replace high frequency vibration bonds with constraints. The most popular algorithms based on Lagrange multipliers are SHAKE [168], LINCS [169] and SETTLE [170] for smaller molecules. Here we discuss the SHAKE method which is the coordinate resetting method. In our simulations, we use the SHAKE method for water bonds.

#### 3.9.1 SHAKE

The SHAKE algorithm [168], applies an additional force on bonds/angles to reset them to their equilibrium lengths/angles. The equations for the additional force are solved iteratively for each constraint till it converges to an accurate solution or reaches to a specified tolerance. We define each constrain by the following equation

$$\sigma_\alpha(\vec{r}_i, \vec{r}_j) = r_{ij}^2 - d_{ij}^2 = 0,$$

where $\alpha = 1 \ldots K$ is the index for $K$ constrains, $r_{ij}$ is the separation of particle $i$ and $j$, and $d_{ij}$ is the desired separation between particles. The new Lagrangian of the system that includes constraints is

$$L' = L - \sum_\alpha \lambda_\alpha \sigma_\alpha(\vec{r}_i),$$

where $\lambda_\alpha$ are the Lagrange multipliers.
where $\mathcal{L}$ is the Lagrangian of the system without constraints. In the above equation, the Lagrange multipliers, $\lambda_\alpha$, should be defined. By using the Euler-Lagrange equation the new equations of motion can be derived as follows

$$m_i \ddot{\vec{r}}_i = -\frac{\partial U}{\partial \vec{r}_i} - \sum_\alpha \lambda_\alpha \frac{\partial \sigma_\alpha}{\partial \vec{r}_i} \equiv \vec{F}_i + \sum_\alpha \vec{G}_i(\alpha),$$ \hspace{1cm} (3.48)

where $\vec{G}_i$ is the constraint force. To find the positions and momenta of particles in the system, the constraint algorithm determines the values of $\lambda_\alpha$ in a way that all constraints are satisfied simultaneously.

### 3.10 Neighbor list

In this section, we review some time-saving tricks for designing a simulation program. The most time consuming part of the computation is the force calculation. In a MD simulation, for a system with $N$ particles, $N(N-1)/2$ terms of pairwise interactions of particles should be evaluated. We often truncate the interactions within a certain cut-off distance, however even with calculation of forces only withing the cut-off distances $r_{\text{cut}}$, we still have to evaluate $N(N-1)/2$ pair distances, meaning that the time of the computation scales as $N^2$. Here, for short-ranged interactions, we discuss the Verlet list and Cell lists for speeding up simulations.

#### 3.10.1 Verlet list

In the Verlet list [171], a second cut-off distance $r_v$ is introduced that is larger than $r_{\text{cut}}$. Then, for each particle $i$ a list of all particles within the skin radius $r_v$ is built. For the force calculation, only particles in the generated list are considered and the rest of the interactions are excluded. The Verlet list is updated only when the displacement of one of the particles in the list is larger than $r_v - r_{\text{cut}}$. However, updating the list scales as $N^2$, but since we do not update the list every single time step, cpu-time is being saved. The list is usually updated every 10 steps. See Fig. 3.9 for illustration.

#### 3.10.2 Cell list

In the cell list method [100, 172], the simulation is divided into square cells of size $r_{\text{cut}}$ or slightly larger. Each particle only interacts with particles in the same cell or neighbor cells. Fig. 3.10 depicts the cell method. Assigning particles to cells scales as $N$ which is a significant speed-up. Often a combination of the cell-list and verlet-list is used for maximum efficiency.
3.10. Neighbor list

Figure 3.9: Verlet neighbor list: The red particle interacts only with particles within the cut-off distance $r_{\text{cut}}$. The particles interacting with the red one are shown by black circles. Gray particles are on the neighbor list of the red particle, although they do not interact. Particles further than $r_\gamma$, shown by empty circles, are neither interacting nor in the list.

Figure 3.10: Cell list: Particles in the cell within the solid red line only interact with the particles in the neighboring cells (within dashed red lines). $r_{\text{cut}}$ is the cut-off distance.
Chapter 4

Simulation details

We used the molecular dynamic code LAMMPS [123] (Large-scale Atomic/Molecular Massively Parallel Simulator) to perform all simulations except where stated otherwise. Integration of Newton’s equation was done by the velocity-Verlet algorithm. The cut-off radius was $r_{\text{cut}} = 12\,\text{Å}$ for all interactions. Non-bonded interactions were computed with the lj/gromacs/coul/gromacs potential. The energy and forces of the LJ and Coulomb potentials are smoothly interpolated to zero between $r_{\text{shift}}$ and $r_{\text{cut}}$, by adding the switching function $S(r)$,

$$S(r) = \frac{A}{3}(r - r_{\text{shift}})^3 + \frac{B}{4}(r - r_{\text{shift}})^4 + C, \quad r_{\text{shift}} < r < r_{\text{cut}}. \quad (4.1)$$

For LJ and Coulomb potentials $r_{\text{shift}} = 9.0, 0\,\text{Å}$, respectively. Equation (4.1) is a commonly used potential for the MARTINI CG model. The coefficients $A$, $B$, and $C$ are calculated by LAMMPS to ensure smooth interpolation to zero at $r_{\text{cut}}$. Bond lengths between water beads were kept rigid with the SHAKE algorithm [168]. The dielectric constant is $\epsilon = 2.5$.

Data was recorded every 20 ps. All visualization were prepared by using VMD [173].

4.1 Simulation set-up for micelle formation

To obtain the topological configuration of a SDS micelle, we first randomly placed free CG SDS and CG sodium ions in a periodic boundary box with sides of length of $10\,\text{Å}$ consisting of 8960 MARTINI water beads. The concentration of SDS in this system was high enough to ensure the micellization in the system. The initial configurations were minimized by the steepest descent method for 5000 steps. Then, a NPT simulation at $T = 300\,\text{K}$ and $P = 1\,\text{atm}$ with a small time step of $\delta t = 2\,\text{fs}$ for 100 ps was performed to adjust the bonds in the system. Following this, to reach to proper density of CG water, we ran another NPT simulation with a bigger time step $\delta t = 10\,\text{fs}$ for 1 ns. To bring the system close to equilibrium, the surfactants, and the ion-solvent temperature were controlled independently by the weak coupling method described in section 3.6 [148]. The temperature coupling times were set to 1.0 ps. The pressure of the system was kept constant with a Berendsen barostat with coupling times of 10 ps. We used the GROMACS [125] package to minimize the energy of the initial configuration of the system.

After minimizing the initial configuration, to form micelles, the simulation was performed at $T=300\,\text{K}$ and pressure $P = 1\,\text{atm}$. The time step size was $\delta t = 20\,\text{fs}$. The system pressure
was controlled with pressure coupling times of 200 ps. The temperature of the surfactants, and the ion-solvent molecules was kept constant independently with coupling times of 20 ps by the Berendsen thermostat \[148\]. Neighbor lists were updated every 10 steps with a cut-off distance of 15 Å as prescribed by the MARTINI force-field. Data was recorded every 20 ps. Figure 4.1 shows an illustration of the initial configuration of the free surfactants. We studied two systems including 60 and 200 SDS. The structural properties of the micelle were obtained for a micelle of 60 SDS.

Figure 4.1: A snapshot of the initial configuration of the simulation set-up for micelle formation, after the energy minimization. Water and counter-ion molecules are not shown for clarity. The heads and tails are shown in red and cyan, respectively. The system is periodic in all the directions.

### 4.2 Confined micellar solutions

All confined systems were simulated in the NVT ensemble at a temperature of \( T = 300 \, \text{K} \). We used the DPD thermostat with a cut-off distance of 8 Å and friction coefficient 80 kcal fs \(^{-1}\) mol\(^{-2}\). The time step size was 10 fs, and the neighbor list was updated every 2 steps with a cut-off distance of 15 Å. The configuration of a micelle consisting of 60 SDS, obtained from the micellization simulation of free surfactants (see chapter 5) was the micelle model in all confined simulations. All the confined systems consisted of a micelle including 60 SDS, 60 counter-ions and polarizable MARTINI water molecules.

#### 4.2.1 Simulation set-up for the slab geometry

We studied the spreading of the spherical micelle droplet on the CG walls in an open channel geometry (slab). We arranged a slab of polarized water with a spherical micelle on the surface in the \( \chi z \) plane. The distance between the two walls is large enough that the upper wall has little effect on the dynamics of the micelle on the surface. In our simulations, the explicit solvent was present in the system along with the structured walls. The micelle and 60 Na\(^+\) counter-ions were solvated in a box of size 183.8 \( \times \) 88.4 \( \times \) 82 Å\(^3\). The density of water was \( \rho = 1060 \, \text{Kg} \, \text{m}^3 \). The micelle was centered at the top of the surface. We slowly moved the micelle toward the
surface until surfactants’ tails touched the surface in the vicinity of the surface and then we let the system equilibrate. The system was periodic in the $x$ and $z$ directions. All the other simulation parameters were the same as described before, including the DPD thermostat. See Fig. 4.2 for an illustration of the slab simulations.

![Figure 4.2: A snapshot of the slab simulation in the $xz$ plane. Water beads are shown in blue shadow points, and CG counter-ions are yellow spheres. Surfactants’ heads and tails are shown in red and cyan, respectively. The dimension of the box is large enough that the upper surface has a minimal effect and the micelle is not interacting with its images. The system is periodic in $x$ and $z$ directions. The same surface was used as the channel surfaces in the die simulations 4.2.2.](image)

### 4.2.2 Simulation set-up for the die-extruder geometry

To set-up the initial configuration of the micellar solution in the die-extruder geometry, we first ran a simulation of the micelle with 60 surfactants in a box consisting of polarizable water with 60 counter-ions randomly distributed around it. This system was equilibrated for 50 ns and formed the chamber area (larger area) of size $180 \times 199 \times 186 \text{ Å}^3$. We used a similar set-up for temperature and pressure as described in section 4.1 with 3d periodic boundary conditions. Then, an equilibrated slab of water of size $90 \times 50 \times 200 \text{ Å}^3$ was added to the chamber area to form the channel part. In this set-up, the micelle was placed close to the center of the box below the narrow channel. Next, we included fcc static walls with a die-extruder geometry. For the initial configuration, walls were placed within 5 Å from water molecules, then we slowly moved walls toward each other in the $x$ direction to fill the gaps and reach the density of $\rho = 1076 \frac{\text{kg}}{\text{m}^3}$ for water molecules inside the box, about 2% higher than the density of polarized MARTINI water. This system is periodic in the $y$ and $z$ with an overall size of $167 \times 278 \times 185 \text{ Å}^3$. We let the system evolve for 10 ns in the NVT ensemble with the DPD thermostat. The final configuration of the simulation set-up in the $xy$ plane is shown in Fig. 4.3. The inner width of the narrow channel is 34 Å, slightly less than the diameter of the equilibrated micelle. The narrow channel’s length is 86 Å. Walls in the chamber area are set as non-wetting, repulsive to the micelle, but in the narrow channel, walls interactions are set...
for three distinct regimes to be high-wetting, low-wetting or non-wetting toward surfactants as described in chapter 6. The surface of the channel had the same configuration as the surfaces in the slab simulations. After equilibrating the system, each system was subjected to a uniform body-force in the \( y \) direction. For the confined flow, the DPD thermostat was only applied in the direction perpendicular to the direction of flow (\( x \) and \( z \)) and on fluid particles.

Figure 4.3: A cross-section view of the simulation set-up of the die in \( xy \) plane in the initial configuration. Water beads are shown as blue shadow points, and CG counter ions are yellow spheres. Surfactants’ heads and tails are shown in red and cyan, respectively. The outer layer of walls are gray. In the chamber area, white and purple beads of inner layer of walls represent charged beads, with +0.2e and −0.2e charge in order, these beads are repulsive to surfactants molecules. Violet (+0.2e) and blue (−0.2e) beads construct the inner layer of walls in the narrow channel area which are separately parameterized for non, low and high wet surfaces toward micelle. This system is periodic in the \( y \) and \( z \) directions.
Chapter 5

Formation of SDS micelles, MD simulations

5.1 Introduction

In aqueous solution, whenever the concentration of surfactant molecules is higher than the critical mass concentration (CMC), surfactants spontaneously aggregate into micro-structures such as micelles. Micellization plays a major role in nature and in many industrial applications including oil recovery, wetting, lubricants, biomedical products, and delivery-release of various substances, specifically drugs and cosmetic substances [11–15]. Over the past few decades, experimental, computational, and theoretical [19–29, 174] studies have been done on self-assembly of amphiphilic molecules in solution to understand the physical mechanics of micelle formation. In particular, much of the work has focused on prediction of micelle shape, size and shape variations and polydispersity [3, 5, 19, 23, 25, 28, 29, 174].

The general mechanism of self-assembly is well-understood [6, 30]. However, there is an intense effort to investigate the effect of molecular scale interactions on the micelle structures and sizes [3, 25, 28, 29]. In order to find a predictive theoretical framework, since the exchange rate of surfactants in micellar solution is very high, experimental studies can not provide many details of the micellization process at the molecular scale. On the other hand, molecular simulations have become a preferred tool in the investigation of micellization in aspects that are harder to study through experimental methods. The pioneering computational work on micellization was done by Monte Carlo simulations [175] of short hydrocarbon chains in idealized lattice models. Larson [175] used Metropolis Monte Carlo sampling for an amphiphile-oil-water systems to investigate the influence of molecular properties such as the length of the head and tail groups on the self-assembled structure and phase behavior of surfactant systems. They observed lamellar, cylindrical, and spherical microstructures. In recent years, many all-atom MD simulations on SDS and other sodium alkyle sulfates [19, 176] have been performed to predict the aggregation size of micelles [20, 21, 54].

Despite many important predictions made by atomistic simulations, there are still some challenges with fully-atomistic MD simulations on surfactants [177]. The main issue is the inherently long micellization time scale. To reach equilibrium, where micelles have their equilibrium sizes at concentrations close to the CMC, the typical time-scale of the self-assembly
5.1. INTRODUCTION

Processes are often beyond 1 microseconds. This time scale is hard to achieve by atomistic simulations. For instance, the surfactant self-assembly time scale requires $10^9$ time steps of MD simulations on the atomistic level. Moreover, the CMC for most surfactants is less than 200 mM [6] (except for sodium hexyl sulphate that has a CMC of 420 mM [6]); to simulate such conditions the system should be dilute. However, in fully atomistic simulation the size of the system is typically limited to $\sim 10^6$ atoms. Therefore, most extensive atomistic MD simulations are constrained to smaller box sizes and high concentrations around 250-1000 mM [20,21,54] which for most surfactants are about three magnitudes higher than their actual CMC. Due to the computational cost of atomistic simulations, all-atom simulations are limited to nano-second time scales and nanometer length scales. Hence, atomistic simulations are not capable of investigating micellar systems beyond 1 microseconds. To overcome these limitations, various CG methods have been proposed to extend the time and length scales of the simulations. In CG approaches, by replacing several degrees of freedom by one interaction site, the simulation time can surpass microseconds.

To choose a CG model, one should consider its capability to reproduce the key quantities that are relevant for the application. For example, in ionic surfactant micellization the key quantities should be reproducing the hydrophobic/hydrophilic effects realistically, the electrostatic interactions between the counter-ions, head groups and water molecules, and the aggregation size.

The Klein & Shinoda group has proposed multiple CG models to reproduce a variety of thermodynamic properties of non-ionic [178] and ionic surfactants [24]. The updated model for ionic surfactants reproduces the correct interfacial surface tension for water, as well as the free energy of association of a SDS dimer and the micelle aggregation number distribution of SDS as a function of ionic strength [24]. In their model [24,178], a water model maps three actual water molecules into a single CG bead without electrostatic interactions, and the surfactants, lipids, proteins, etc. are coarse-grained in a similar fashion.

The most common and successful model is the so-called MARTINI model [57] in which a CG particle consists of four-five groups of molecules. Simulation time-scales of the MARTINI coarse-grained force field can be up to 6 orders of magnitude longer than the atomistic simulations [179]. Despite the simplicity of the MARTINI model and its computational speed, it has been proven to accurately predict the self-assembly of lipids and surfactants such as DPC and DPPC into micelles [23,62,63] and vesicles [57,59,61]. Since the MARTINI force field allows long simulation times, it is ideal for equilibrating surfactant solutions and studying formation of micelles. Obtaining an equilibrated micellar size distribution depends on the type of the surfactant as well. For example, surfactants with high CMC (ionic surfactants) self-assemble into small micelles pretty fast, but convergence of the size distribution is very slow. Even with coarse-grained methods the time scale for micellization can only be achieved through extensive simulations for more than a microsecond simulation time [138]. The MARTINI force-field has been successfully used to equilibrate systems with less hydrophobic surfactants such as SDS [23].

In order to extend the simulation times, one can coarse-grained the system further by eliminating the explicit solute molecules and replace them with the implicit water [180,181]. For dilute surfactant systems, few models for the interaction between surfactant and implicit solvent have been proposed [180,181]. Nevertheless, there are significant differences between the results of using explicit water and implicit solvent, especially when long-range electrostatics are
involved \([182]\). These differences arise from the fact that head group and counter-ion electrostatic interactions are not captured by the screening potential such as the Yukawa model \([180]\). The electrostatic interactions between counter-ions and head groups play an important role in the self-assembly of ionic surfactants \([20, 54]\).

In the rest of this chapter, we present the results of our simulations of free CG SDS in equilibrium using the MARTINI force-field. We performed MD simulations to obtain the equilibrium size and shape characteristics of CG SDS micelles. In the previous study of MARTINI SDS \([23]\), surfactants were initially formed into a sphere, and then solvated in a water box. While in our system, for the initial configuration, free CG SDS and CG counter-ions were randomly placed in a PBC box. Unlike the previous study \([23]\), we can observe the self-assembly of surfactants into the proper micelle size. The trajectory was long enough to ensure that the micelle is stable. The system included 60 surfactants, 60 counter-ions, and 8960 MARTINI water beads and it was simulated over 850 ns after equilibration. See section \([4.1]\) for details on the simulation set-up.

5.2 Results

5.2.1 CG SDS micelles

Figure \([5.1]\) illustrates the aggregation of free surfactants into a micelle for a system of 60 surfactants. Water molecules are not shown for clarity. After minimizing the energy of randomly placed surfactants, SDS molecules quickly self-assemble into small aggregates in the first few ns of the simulation. Then, the size of the aggregation gradually grows, small micelles associate together and around \(t=20\) ns, a micelle of size 60 forms. The structure of the micelle of 60 SDS is stable for 800 ns after formation of the micelle; no fragmentation occurs during this time. Therefore, the CG SDS micelle consisting of 60 surfactants is chosen as our basis model.

In the system including 200 SDS, at \(T = 300K\), similar behavior of SDS aggregation is observed. After initial minimization, small micelles forms and as the simulation proceeds, the average size of the micelle grows. However, the system did not converge in 800 ns and did not reach an equilibrium state. The micelles were growing and their sizes and structures were still evolving. Since, in the system size of 200 SDS, the observed micelles did not stabilize, the configuration of the micelle of size 60 is taken as our basis model. The same micelle was used for the simulations on the confined systems. The following results are for a micelle of size 60, surrounded by 60 counter-ion in a PBC box of CG water molecules.

5.2.2 Micelle radius and shape

To determine the shape of the aggregates, we calculated the radius of gyration tensor, and the asphericity factor, \(A_d\) every 20 ps. Elements of the radius of gyration tensor are computed as

\[
R_{ij} = \frac{1}{n} \sum_{m=1}^{n} (r_{mi} - R_{cmi}) (r_{mj} - R_{cmj}),
\]

where \(i, j = x, y, z\) are the three directions, \(n\) is the number of surfactants in a micelle, and \(r_m\) is the vector position of the surfactant heads. \(R_{cm}\) is the vector coordinate of the center of
5.2. Results

Figure 5.1: Snapshots of the NPT simulation of 60 SDS at different times (ns). a) Small aggregates of SDS at t=3 ns, b) spontaneous self-assembly of SDS into one micelle, t=800 ns. Head, tail and counter-ion groups are shown in red, cyan, and yellow sphere respectively. For clarity, 8960 water molecules are not shown.

mass of the micelle. The eigenvalues of the gyration tensor, $R_1, R_2, R_3$, are the principal radii of gyration. In the case where all values are approximately equal to each other, the aggregation shape is considered as spherical. If one is larger than the other two ($R_1 > R_2, R_2 = R_3$) this shows that the micelle is elongated in one direction and it has a cigar shaped form. In case of ($R_1 < R_2, R_2 = R_3$) the micelle shape is more like a pancake. We calculated the asphericity factor in order to measure the deviation from the spherical shape:

$$A_d = \frac{\sum_{i<j} \langle (R_i^2 - R_j^2)^2 \rangle}{2 \langle \sum_i R_i^2 \rangle^2}. \quad (5.2)$$

For the perfect spherical micelle $A_d = 0$, and the perfect cylinder has $A_d = 1$.

The mean-square radius of gyration $\langle R_g^2 \rangle$ is the mean of the sum of the squares of the three principal moments of the radius of gyration tensor

$$\langle R_g^2 \rangle = \frac{1}{n} \langle \sum_{m=1}^{n} |r_m - R_{cm}|^2 \rangle \quad (5.3)$$

We define the radius of the micelle as $\sqrt{\langle R_g^2 \rangle}$, which is the root-mean-squared distance of the heads to the center of mass of the micelle. For a micelle of 60 SDS surrounded by polarizable water molecules, $R_g = 20.5 \pm 0.3$ Å which is in good agreement with all-atom simulations and experiments \cite{6}. We obtained $A_d = 0.03 \pm 0.01$; the micelle shape is very close to a perfect sphere.
5.2.3 Micelle structure

To study the structure of the micelle and ions around it, we measured the radial distribution function, \( g(r) \). \( g(r) \) is simply a measure of the probability of finding a particle at a distance \( r \) from a given particle.

The radial distribution function for the ion-head group is depicted in Fig. 5.2. The first peak indicates that the \( \text{Na}^+ \) ions form a shell around head groups at a distance of 5 Å from the head groups. The weak subsequent peaks shows that counter-ions diffuse in the system, forming a charged cloud around the micelle. When ionic surfactants are solvated in water, some counter-ions dissociate from the head groups. The counter-ions either bind onto the micelle surface that is negatively charged or distribute in a layer around the micelle. The scattered counter-ions around the micelle form a charged cloud. The peaks in the radial distribution function correspond to these layers. Figure 5.3 shows a schematic representation of the micelle surface region.

![Figure 5.2](image)

Figure 5.2: The radial distribution of counter-ions around head groups. The peaks in the radial distribution function correspond to the different charged layers around the head groups.

The distribution of water molecules around the head groups is shown in Fig. 5.4. The distinct peaks in the distribution show that water molecules form structured shells around the micelle.

Figure 5.5 shows \( g(r) \) for water molecules around tail beads (C1 (black line), C2 (dashed red line), and C3 (dotted blue line)). C1 is the tail particle that is bounded to the head. C2 is the middle particle in the tail and C3 is the last bead in the tail. The low probability of water particles shows that in the core of the micelle, (hydrophobic region), there is no water molecules inside the SDS micelle. Thus, the structure of the CG SDS micelle agrees well with the previous studies on SDS [6, 20, 23, 54].
5.3 Conclusion

We performed MD simulations of a CG SDS system. The simulation time was long enough to observe the self-assembling of surfactants into small aggregates, and finally larger size micelles. The average number of aggregation for CG SDS micelle is in agreement with all-atom simulations and experimental data \[21, 90\]. The distribution of water molecules shows that in the core of the micelle there are no water molecules. The radial distribution of ions indicates that counter-ions form layers around head groups. The shape of the micelle fluctuates, however the micelle’s shape is close to a sphere. During the simulations of a SDS micelle in a box of polarizable water, the micelle was stable. Thus, we chose the configuration of a micelle of size 60 as our basis model for the simulations on micellar solutions in confined channels.
Figure 5.4: The radial distribution of water around head groups. Water molecules form structured shells around the head groups.

Figure 5.5: The radial distribution of water around tail beads, C1 (black line), C2 (dashed red line), and C3 (blue line). The low probability of the water-tail distribution indicates that there is almost no water molecule in the hydrophobic core of the micelle.
Chapter 6

Walls and the wettability

6.1 Introduction

Recent developments in nano/micro devices, lab-on-chip devices and drug delivery systems have attracted attention to flowing fluid behaviors in nano-channels [36–40, 45–49]. The structure and properties of confined flows are determined by several parameters, such as, the wall roughness, the atomic structure of walls, and the interactions between the fluid and the wall [183–187]. The fluid-surface (wall) interactions can significantly influence the dynamic of confined fluids in narrow pores, channels, and capillaries with dimension on the order of nanometers [188]. The interactions between a solid surface and water can give rise to phenomena distinctly different from those in bulk water [188–190]. For example, in small capillaries, fluid molecules order in distinct layers. The layering leads to an inhomogeneous density profile [188]. The layers close to the wall often absorb high velocity gradients; meaning that there are regions with low viscosity compared to the bulk fluid. In the vicinity of a solid-fluid interface, the density, velocity, stresses and other quantities can vary across the channel as a function of the distance from the wall [1, 190, 191].

To simulate walls and systems of confined flow in nano-channels, several wall models have been proposed over the last decades [184, 186, 187, 192–198]. In this chapter, we briefly discuss some of the wall models in MD simulations in section 6.2. Then we discuss basic concepts of Poiseuille flow (section 6.3). We briefly review wetting and surface tension. In the last section (6.5), we explain the wall structure in our systems. We discuss the parameterization of water/wall interaction and the wetting properties of the SDS micelle and surfaces in equilibrium in our confined systems.

6.2 Wall models

Modeling of walls and surfaces is one of the challenging problems in simulations of confined systems with fixed boundary conditions. In MD simulations, a variety of approaches have been used [184, 186, 187, 192–198]. Realistically, walls should be made up of a large number of particles with realistic bonds to allow heat and momentum transfer. However, this approach is computationally too demanding to be of practical use. Here we briefly mention some models of walls.
The simplest wall model is an implicit smooth surface with an infinite interaction potential that bounds one or more faces of the simulation box \([199,200]\). In stochastic wall models, when a particle collides with the wall, the particle is reflected with a new velocity. If the collision is purely reflective, the particle reflects with the reverted velocity \([192]\). The parallel component of the velocity remains unchanged and the perpendicular component is reversed. In bounce-back \([192]\) reflections, both velocity components are inverted. In a thermal wall, the particles are reflected back into the system with a new velocity from the Maxwellian distribution of the velocity of the wall \([201]\). In all these approaches, the energy of wall-particle interactions are usually described by a LJ potential.

A more realistic approach is an atomistic rough wall. One of the first models was proposed by Koplik \([202]\) in which the solid wall beads were laid on a fcc lattice with heavy masses of \(10^{10}\) times the fluid mass. The large mass preserves the wall from collapsing during simulations, however, there is no heat transfer between the fluid and the wall. In another model, the atomic wall beads vibrate around the fcc lattice sites with harmonic springs and particles interact with each other via a LJ 6-12 potential \([195,203]\). In a similar approach, wall beads are linked together through a harmonic potential with an additional constraint on fixing the center of mass of the wall with a thermostat that is applied to the wall. By using a thermostat, it is ensured that the wall temperature stays constant \([196]\).

A popular model for a wall is using some layers of static frozen beads on a fcc lattice with a LJ interaction potential between the beads and the fluid particles \([184,186,187,197]\). In recent studies of DPD systems, to provide no-slip boundary conditions, a combination of the frozen layers of DPD particles \([198]\) and bounce-back reflections has been used.

In all simulation of this thesis, walls are two layers of frozen beads and are parameterized to provide no-slip no-stick boundary conditions under flow. We discuss details of the structure of walls and the parameters in section 6.5.

### 6.3 Poiseuille Flow

Many industrial and biological applications of micelles, vesicles, droplets, and block-copolymers involve flow through micro/nano-channels and thin capillaries. These deformable objects break, recombine or change their shape to respond to flow \([38–40]\). Hence, the dynamical behavior of flowing micelles and vesicles have been the subjects of many studies \([41–44, 50, 183, 204, 205]\).

A widely studied flow is the confined Poiseuille flow \([41–44, 50, 183, 204, 205]\). In the plane Poiseuille flow, an external force (from a pressure gradient or a uniform body-force) is applied to the fluid particles that are confined between two parallel solid interfaces. Figure 6.1 shows a schematic representation of Poiseuille flow in a confined channel. As the body force pushes the fluid, a steady flow can form with a velocity profile which is typically a quadratic function of the position across the channel. The velocity along the channel, \(u_y\), can be obtained from the Navier-Stokes equation, Eq. 3.4 as \([206]\)

\[
u_y = -\frac{1}{2\eta} \mathcal{F} x(x - h)
\]

where \(\eta\) is the viscosity and \(\mathcal{F}\) is the applied body force. The velocity profile vanishes at the
walls and has its maximum at the center. The assumption in formulations of flow is the “no-slip” boundary condition at the walls \[206\]. If flow confined between parallel walls, the no-slip boundary condition requires that the tangential component of the velocity of the fluid equals the velocity of the wall. Thus, in Poiseuille flow, the velocity profile vanishes at the position of the solid stationary walls \((x = 0, x = h)\); \(u_y(x = 0) = 0, u_y(x = h) = 0\). Since the flow in

![Figure 6.1: A schematic representation of the planar Poiseuille flow. The flow is confined between two parallel walls and a constant force is applied in the y direction. The resulting velocity profile of the fluid is a parabolic. \(F\) is the applying force and \(h\) is the channel width.](image)

the blood circulatory system is pressure-driven channel flow, there have been extensive studies on the behavior of red blood cells (RBC) \[41–44\], vesicles \[42, 43, 50, 204\], micelles \[39, 40\], polymers \[205\] or droplets \[207\] under Poiseuille flow. One of the main motivations has been the possibility to use these objects as drug delivery system \[12\]. Furthermore, it has been shown that understanding the shape transition of RBC under flow can shed some light on the mechanisms involve in arterial diseases and other blood flow-related illnesses \[41\].

To model a Poiseuille flow in MD simulations, an external force acts on individual atoms in the fluid and drives the flow. The equations of motion for fluid atoms are simply Newton’s equations for interacting particles subject to an external force. To solve the equation of motions for the system, we assume that the local thermodynamic equilibrium holds. The challenges of simulating the flowing system are modeling the realistic nearly no-slip boundary conditions and thermostatting the system.

For many types of flow, including plane Poiseuille flow, the ideal boundary condition is the no-slip wall \[206\] in which liquid molecules close to the surface have the same velocity as the surface. Although, there are situations that a non-slip condition may not be true, e.g. in the extrusion of polymer melts from a capillary tube. Polymer melts should slip on a non adsorbing solid surface especially at high shear rate \[208–210\]. Numerous MD studies have been conducted to understand the crucial issue of slip on boundary conditions \[183–187, 193, 194, 199, 200, 211\]. To form a wall with a negligible slip at nano scales,
the effect of various parameters on the behavior of fluid layers close to the walls should be considered. These parameters include the interaction energies between the fluid particles and the wall atoms \cite{186,187,193,194,199,200}, the structure of the wall, the density of the wall, the roughness of the wall \cite{184,185}, and the distances where interacting potentials have their minimum. Furthermore, it has been shown that the same crystal lattice but with different surface orientations \cite{183}, and even the method of heat removal \cite{212} have noticeable effects on the slip length.

Early MD studies on ideal Pouiselle flows showed that using implicit walls (structureless and repulsive) leads to large slip \cite{199,200}. In a more realistic system, where a LJ fluid was confined between atomistic walls, various boundary conditions have been tested \cite{183,186,187}. In a detailed MD study \cite{186,187} using a LJ fluid sheared between two solid walls, flow boundary conditions for different densities of walls and interactions of wall-fluid were studied and a variety of boundary conditions including slip, no-slip, and locking were observed. Thompson \cite{186,187} calculated the slip length for each case. Based on the result \cite{186}, the wall density and the strength of the wall-fluid interaction significantly affects the flow near solid boundaries. If the density of the wall is close to the density of the fluid, the minimum slip for a LJ fluid occurs when the strength of the fluid-wall interaction is about 0.4 of the fluid-fluid interactions. For large interactions between the fluid and wall, the fluid layers lock to the wall. A weak interaction leads to slip \cite{186}. By increasing the density of the walls, the roughness of the walls decreases and this causes more slip \cite{186}. In a more recent study \cite{183}, MD simulations were performed to evaluate the effect of surface orientation of fcc lattice planes (111), (100), and (110) on slip length for both plane Poiseuille and Couette flows of liquid argon. The plane (111), which is the smoothest wall, has the largest slip and the fcc plane (110), the most roughest and the most anisotropic surface, has lower slip length \cite{183}. Generally speaking, in nano-channels, the density of layers, fluid slippage, and the channel flow rate are significantly influenced by the surface orientation, flow orientation \cite{183,185}, wall and fluid densities, and the molecular interaction parameters \cite{183,186}.

Thermostatting an out of equilibrium system may also have significant effects on the dynamics of the flow and layering of the fluid close to the walls \cite{212}. The energy injected to a driven system gradually heats the system. Therefore, to keep the temperature of the system constant, a thermostat must be applied. The thermostat used should be free from undesirable properties such as screening of hydrodynamic interactions and lack of Galilean invariance \cite{111,213} otherwise the dynamical behavior does not represent the actual dynamics of the system. Yong and Zhang \cite{212} compared different combinations of thermostat algorithms for a sheared system (see section 3.6 for details on the thermostats). They showed that in weakly sheared systems, thermostatting only walls, only fluids or both walls and fluid produce similar behaviors. However, in strongly sheared systems only thermostatting the walls resembles experimental conditions. Moreover, the Langevin and DPD methods used in the thermostatting of fluid yield correct dynamics while the Nosé-Hoover thermostat breaks down in strongly sheared systems. For our driven system, we used the DPD thermostat which is a common method for removing heat in MD simulation \cite{56,111,119,213}. The DPD thermostat conserves the momentum of the non-equilibrium systems \cite{56,109,111,119} and reproduces the correct hydrodynamic behavior. Details on the DPD thermostat are explained in section 3.6.5.

In conclusion, one should carefully choose the wall model (and related parameters of interactions between the walls and fluid) and the method of thermostatting the system since they
have significant impact on interfacial characteristics such as density layering, slip length, and consequently on flow rate.

6.4 Wetting

Consider a droplet on a solid surface. Depending on the interactions between the surface molecules and the droplet, the droplet either spreads completely (wets the surface completely) or partially wets the surface. The wettability of the surface, the extent to which a liquid spreads on a given solid, determines the equilibrium shape of the droplet on the surface [1]. The main question is how well the droplet “wets” the surface [214–218]. Wetting phenomena play a fundamental role in technological applications such as coating, emulsions, oil recovery [219] and in the design of nanochannels in microfluidic and nanofluidic applications. In many of these processes, the wettability between the fluid and the micro-channel wall affects the flow behavior [205]. The fluid can be a dye, ink, lubricant or surfactant solution on surfaces, e.g. graphite [220]. Thus, understanding the solid-liquid interactions at a molecular level has been the subject of investigations both from a fundamental point of view and for industrial application. Recent reviews on wetting of surfaces can be found in Ref. [1, 66, 214–217, 221–225].

Consider a droplet on a solid surface that is in equilibrium with its vapor. The droplet shape on the surface is defined from the balance between the surface/droplet interactions and the droplet/vapor interactions. The wettability of the surface is measured by the contact angle. The contact angle, θ, is the angle measured at the interface of the droplet, droplet/vapor and droplet/surface. Figure 6.2 shows different degrees of wetting on a solid surface. When the droplet barely touches the surface the surface has low wettability. In the case where the droplet partially spreads on the surface (90 > θ) the surface is low wetting toward the droplet. In the perfect wetting case, the droplet completely spreads on the surface (θ ≈ 0). It is of obvious interest to determine the wetting properties. The wetting properties are controlled by surface energies. The surface tension (surface energy) is the free energy change per unit area when the surface area of a medium is increased. The surface tension between phases I and J at the interface of two phases is denoted by γ_{IJ} in units of energy per unit area and thus a force

![Figure 6.2: Different degrees of wetting. From left to right: Non-wetting, contact angle θ < 180, low-wetting 90 < θ, and high-wetting with θ < 90.](image-url)
per unit length. This force minimize the corresponding surface energy along the $IJ$ interface. The balance of surface tensions determines the contact angle and the shape of the macroscopic droplets on the surface. In Fig. 6.3 an arbitrary liquid droplet (medium 2) is immersed in medium 3 and settled on a rigid flat surface of medium 1. For an ideal solid substrate (flat and chemically homogeneous) Young \[226\] obtained the macroscopic contact angle from the balancing of surface tensions in equilibrium \[226\]

\[
\cos \theta = \frac{\gamma_{13} - \gamma_{12}}{\gamma_{23}}
\]  

(6.2)

Young originally presented the thermodynamic definition of the contact angle. Laplace provided a mathematical description later \[226\]. Equation 6.2 links the interfacial energies of solid, liquid, and vapor.

One should notice that the contact angle is independent of surface geometry \[227\]; the $\theta$ will be the same on a curved surface like a capillary or any other irregular shaped surface. The contact angle is a macroscopic quantity and is derived from a thermodynamic equation, Eq. 6.2 Therefore, it does not necessarily provide us with information about the microscopic profile of the droplet at the point where it meets the surface \[1,214\]. Since the wetting at the liquid-solid interface takes place at molecular length scales, the actual physics of the wetting dynamics at the interface remains unclear. Also, because of the very rapid time scales, performing experiments are quite difficult.

In the last decade, the estimation of microscopic or nanometre scale contact angle by molecular simulations attracted a lot of attention \[220,228-235,235,236\]. Although, performing MD simulations of a spreading droplet provides details at the molecular level, measuring the contact angle is not without challenges \[237\].

To measure the contact angle of liquid droplets in MD simulations, usually a droplet with the initial shape of a sphere \[220,230,231\] or a cylinder \[230\] is set on a solid surface surrounded by vacuum or solvent. The substrates are usually atoms laid on a lattice structure. The droplet is allowed to spread to reach its equilibrium. Then, the number density \[220,230,231,233\] or atomic density \[232\] profiles with Cartesian or cylindrical grid volumes is calculated \[220,230,231\]. Because of the solid-fluid interactions at the interface of the substrate and the droplet, the density profile fluctuates for several layers close to the
interface. To reduce this fluctuation, points less than a cut-off distance are excluded from the density profile \[233,238\]. And finally, the density profile is fitted with a circular \[233,235,238\], or a polynomial \[236\] function. From the first derivative of the fitted function, the contact angle is calculated. This method is very common for simulation studies of nano-droplet contact angles, although the parameters used for gridding the system and fitting the function vary. The grid size in different studies varies between 0.5-5 Å \[233, 236, 238\]. The cut-off distance to reduce the effect of density fluctuations at the interface has been reported in the range of 0 \[233, 235\]-10 Å \[234\]. The size of the grid size significantly affects the values of the contact angles \[232\]. Furthermore, the arbitrary choice of the cut-off distance and the irregularity of contour lines at the interfaces \[232\] add more ambiguity to the contact angle calculation especially for the small size of the droplets.

Another method for calculating the contact angle is through measuring the surface tensions at the interfaces \[239–241\] and using Young’s equation \[6.2\]. At the molecular scale near the interface, \(\gamma\) is defined as the integrated difference between the normal and tangential pressure through the Kirkwood-Buff formula \[242\]. The formula to calculate the surface tension of an atomic liquid is

\[
\gamma = \int \left[ P_{\perp} - P_\parallel \right] dr_{\perp},
\]

where \(P_{\perp}\) is the perpendicular pressure and \(P_\parallel\) is the lateral pressure components. \(dr_{\perp}\) is the length of the layer normal to the interface. For homogeneous systems, the pressure tensor is defined in terms of the virial terms as

\[
P_{ij} = \frac{1}{V} \left( \sum_k \frac{p_{ki}p_{kj}}{m_i} + \sum_i r_{ki}f_{kj} \right),
\]

where \(i, j = x, y, z\), \(p_{ki}\) is the momentum of particle \(k\) in \(i\) direction, \(r\) is the position, \(f\) is the force, and \(V\) is the volume. The pressure tensor is

\[
P = \begin{pmatrix}
P_{xx} & P_{xy} & P_{xz} \\
P_{yx} & P_{yy} & P_{yz} \\
P_{zx} & P_{zy} & P_{zz}
\end{pmatrix}.
\]

In order to calculate the \(\gamma\) of inhomogeneous interfaces in MD simulations, e.g. micelle/water and water/surface, the local pressure in a small region of the simulation box should be computed. These regions often contain a few particles. Irving and Kirkwood \[243\] first proposed the “planes” method to directly measure the pressure locally, across a region in the simulation box. In calculating the local pressure, only particles inside the region are included. The components of the interaction terms are weighted by the fraction of the line that joins particles \(i\) and \(j\) inside the region.

Figure \[6.4\] shows a snapshot of the slab geometry of our system to calculate the surface tension at the interface of an SDS micelle and wall. We divide the slab geometry system into parallel slabs in Cartesian coordinate \[239–241, 244–246\] (see Fig. \[6.4\]), and then all the relevant quantities are averaged over each slab. In Fig. \[6.4\] the normal pressure is \(P_{\perp} = P_{yy}\) and the lateral pressure is \(P_\parallel = \frac{1}{2} \left( P_{xx} + P_{zz} \right)\). \(P_{\perp}\) and \(P_\parallel\) are different only at the interfaces of different mediums.
Figure 6.4: The slab geometry to calculate \( \gamma \) at the interface of SDS/Wall. The system is divided into thin parallel slabs. The pressure stress components are calculated in every slab and from there the stress profile across the system is obtained. The \( \gamma \) is calculated by integrating the difference of \( P_{\perp}(L_y) \) and \( P_{\parallel}(L_y) \) across the interface. Counter-ions are not shown.

To obtain the pressure profile of a planar system, such as bilayers, the system is divided into slabs perpendicular to the normal of the interface. Then the local pressure tensor in each slab is calculated in terms of the Cartesian coordinates of the planar interface \([239, 241, 244, 246]\). However, in systems with spherical interfaces, for example vesicles and micelles, the pressure profile should be evaluated across the spherical interfaces \([247, 249]\). An expression for using spherical coordinate system for the slice averaged pressure was first proposed in \([247]\). Despite the well-converged pressure tensor for the system, the expression was not invariant against a rotation of the coordinate system. Furthermore, the derived expression was limited only to simple pairwise central force models. In computational study by Ollila \([248]\), the pressure profile along the radial axis of a spherical liposome is obtained as a projection of the three-dimensional pressure field to the radial axis. The computed profile in Ref. \([248]\) had enhanced statistical noises. Nakamura and Shinoda \([249]\) have derived simple expressions for the pressure profile along the radial axis of spherical molecular systems described by conventional molecular force fields. Different expressions for the pressure profile of non-bonded and bonded interactions are proposed. These expressions are advantageous over the previous methods \([247, 248]\) in terms of computational efficiency and convergence.

### 6.5 Parameterization for the wall interaction

In this section, we describe the new parameterization of interactions between polarizable MARTINI water-walls and CG SDS-walls in our systems. Water-wall interactions are parameterized to provide no-slip no-stick boundary conditions. We discuss the tendency of polarizable MARTINI water to form locked layers and even freeze close to solid surfaces. This over structuring is due to artificial organization of water dipoles close to a surface and it can be eliminated by constructing the surfaces with partial charges.

In the current work, we are interested in investigating the effects of Poiseuille-like flows, confinement, and wetting on spherical micelles in the die-extruder geometry. In the die geometry, a reservoir is linked to a channel. This contraction-expansion channel shape is called the “die”. The narrow section is referred to as the channel, and the larger section as the chamber. A snapshot of the simulation set up for a flowing micelle is shown in Fig. 4.5.
6.5. Parameterization for the wall interaction

The configuration of walls are two layers of static beads on the fcc (110) plane with lattice distance of 6.23 Å. The mass of each wall bead is $24\text{ g mol}^{-1}$. The outer layer of walls are neutral, while the inner layers that are in contact with water molecules are randomly charged.

6.5.1 Wall-water interactions

![Figure 6.5: A snapshot of a frozen water in a die geometry in equilibrium. The wall beads are shown in gray. Blue points represent water (W) beads. Water molecules over-structure close to the wall surfaces. Inside the channel, water layers lock to each other leading to frozen regions.](image)

The standard CG MARTINI water [57] has a tendency to freeze and form a hexagonal lattice close to interfaces such as confined membranes, and solid surfaces [57]. Thus, we have chosen the polarizable MARTINI water model [58] as the CG water model in our system. The polarizable MARTINI water corrects many of the artifacts of the standard MARTINI water model. However, even the best available MARTINI water model must be modified to study surface systems. The chosen wall model and the parameters involved with interactions between polarizable MARTINI water model and the surfaces should provide the no-slip no-stick boundary conditions under the flow. We modeled the walls as two layers of static beads on a fcc lattice in a die geometry and we tested the system over various strengths of interactions and lattice distances.

The wall structure was tested over various lattice distances (3.97, 5.65, 6.23, 7.5 Å) and different fcc plane orientations ((111), (100), and (110)). For each, the density profile and the velocity profile was obtained for a range of LJ energy interactions ($\epsilon_{\text{WSURF}} = 0.5, 0.9, 1\epsilon_{\text{WW}}$) and LJ cut-off distances (5.27, 9, 11, 75, 12 Å). Moreover, a thermal wall model was tested in which each wall atom was independently linked to a spring force to tether to its initial position. In all
Figure 6.6: From top to bottom: a) Profile velocity ($\frac{m}{s}$) of water molecules in the $y$-direction of the flow subject to forces $F=0.003$ and $0.0005$ kcal/molÅ. Velocity profile for chamber area is shown in black circle ($F=0.003$) and blue cross ($F=0.0005$). In channel area, red circle and dark blue star shows velocity of high and low forces respectively. Applying a uniform-force on the system yields a Poiseuille-like flow in the system with a negligible slip length at the wall. The velocity smoothly comes to zero at the wall location. b) Temperature profile of the flowing fluid. c) Density profile ($kg/m^3$) of the water molecules at the equilibrium inside the chamber area. The positions of channel walls are marked with vertical gray dashed lines in each plot. The density has peaks near the wall but these are small and typical of liquids near flat surfaces.

In the above simulations, we observed strong layering of polarizable water on the neutral walls. In energy levels close to the water/water interaction ($\epsilon_{WSURF} = 0.5, 0.9, 1\epsilon_{WW}$), water molecules stick to the walls and form a dipolar packing on the surface and eventually the system freezes (see fig. 6.5). For lower energy levels, $\epsilon_{WSURF} = 0.01\epsilon_{WW}$, large slip occurs on the walls and leads to voids in the system. To avoid the strong packing of water molecules on the surfaces, we randomly placed weak charges on the inner layer of wall beads to break the layering. The chosen parameters for the energy and charges on the wall give a strong enough interaction to only break the alignment of the dipoles on the wall without trapping other charged molecules on the wall. The interaction parameters between the polarizable water molecules and the wall beads were chosen to provide a no-slip boundary condition of water molecules under flow.

The beads in the outer layer of walls are neutral, while the beads of the inner layer are randomly charged with $q = \pm 0.2e$. The total charge of the inner surface layer is always zero,
representing a CG mineral surface. The magnitude of $q$ is comparable to the partial charges on atoms in neutral molecules in all-atom force-fields such as OPLS. In Table 6.1, the new wall-water LJ interactions parameters $\epsilon$ are presented. There is no LJ interactions between charged water beads and neutral wall beads, however charged water beads have an LJ interaction with the inner wall beads with $\sigma = 2.35 \text{ Å}$. For neutral water beads and wall beads $\sigma = 4.7 \text{ Å}$. This arrangement of wall beads and interaction energies provides non-stick non-slip surfaces for the polarizable MARTINI water model under flow without strong layering of CG water molecules on the surfaces. The velocity, temperature, and density profiles of water molecules are shown in Fig. 6.6. As is shown in Fig. 6.6, the velocity smoothly comes to zero at the wall location. The density has peaks near the wall but these are small and typical of liquids near flat surfaces.

<table>
<thead>
<tr>
<th>$\epsilon_{\text{LJ}} (0.5 \times \text{kcal mol}^{-1})$</th>
<th>W</th>
<th>WM</th>
<th>WP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wall$_0$</td>
<td>0.04</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Wall$_-$</td>
<td>0.04</td>
<td>0.836</td>
<td>0.956</td>
</tr>
<tr>
<td>Wall$_+$</td>
<td>0.04</td>
<td>0.956</td>
<td>0.836</td>
</tr>
</tbody>
</table>

### 6.5.2 Wetting properties of walls to the micelle

Figure 6.7: From left to right: CG SDS micelle in a) initial configuration, configuration at $t = 1 \text{ ns}$ on b) high-wetting, c) low-wetting and d) non-wetting surfaces. For clarity ions and water molecules are not shown. Walls beads are shown in gray (neutral), violet ($+0.2e$) and blue ($-0.2e$). Depending on the wettability of the wall, the CG micelle forms a cap (a), a bulb shape structure (b) or floats (c).

To characterize the equilibrium wetting properties of walls toward the micelle, we first studied the spreading of a spherical micelle on the walls over various interaction strengths in a system consisting of a spherical SDS micelle in the vicinity of a surface in an open channel of polarizable water (see Section 4.2.1 for simulation details). The LJ interactions between the walls and surfactants were parameterized at three distinct levels corresponding to non-, low-, and high-wetting walls surfaces. The degree of wettability of the surface is determined from
contact angles of the micelle on the surface at equilibrium. The contact angle of a spherical micelle on a solid surface, $\theta$, obeys Young’s equation \[ \cos \theta = \frac{\gamma_{\text{wall},W} - \gamma_{\text{wall},\text{SDS}}}{\gamma_{W,\text{SDS}}}, \tag{6.6} \]

where $\gamma_{\text{wall},W}$, $\gamma_{\text{wall},\text{SDS}}$, $\gamma_{W,\text{SDS}}$ are the surface tensions of wall-water, wall-SDS, and water-SDS surface respectively. The surface tensions were measured using the Kirkwood-Buff formula \[242\]. Following Eq. 6.6, we obtained the contact angle of the micelle for various LJ interaction parameters. As the simulation proceeds, the micelle interacts with the wall and depending on the interactions between the wall and surfactants, it either wets the surface to form a cap, forms a bulb-shape micelle, or totally detaches from the surface. These correspond to high-, low-, and non-wetting surfaces. Figure 6.7 shows snapshots of the micelle on the surface at varying interactions. The degree of the wettability of the surface is determined from calculating the contact angle of the micelle on the surface.

The $\gamma_{\text{wall},W}$, $\gamma_{W,\text{SDS}}$, and $\gamma_{\text{wall},\text{SDS}}$, at equilibrium, are evaluated in separate simulations systems as follows:

**Water/wall surface tension**

A slab geometry (open channel) of walls and polarizable MARTINI model, without SDS and counter-ions, was formed parallel to the $xz$ plane. All other details on simulation parameters of wall/water interactions, the thermostat parameters and the size of the slab are as described in section 4.2.1. The structures of the surfaces are the same as the channel surfaces in the die-simulation. The distance between the two walls is chosen large enough that the upper wall has negligible effect on the lower surface. The system was simulated for 5 ns in the NVT ensemble after equilibrium. The pressure components are measured every 20 ps. Figure 6.8 shows the pressure profile of the system. The bin size is 4.56 Å. The black points represent $P_\perp - P_\parallel$. The $P_\perp$ and $P_\parallel$ are different only at the interfaces of water and walls. In our system, $\gamma_{\text{wall},W} = 47.5 \pm 0.04$ mN/m.

**Water/SDS surface tension**

To measure $\gamma_{W,\text{SDS}}$, a micelle of 60 SDS molecules, 60 counter-ions and 11092 polarizable water molecules were placed in the simulation box with PBC. The size of the box was $110 \times 108 \times 108$ Å$^3$. The center of mass of the micelle was fixed in the center of the box, and counter-ions were randomly placed around it. The simulation was performed in the NVT ensemble at temperature 300 K with DPD thermostat for 5 ns after equilibration. All other parameters were the same as described before.

The pressure profile at the micelle/water interface can not be calculated from the Cartesian coordinates. To measure the surface tension for the micellar system, the pressure profile must be calculated across the spherical interface \[247\]–\[249\]. The pressure field at distance $r$ from the interface is

$$P(r) = (e_\theta e_\theta + e_\phi e_\phi) p_T(r),$$ \tag{6.7} \]

\[1\] All integration is done by trapezoid method.
6.5. PARAMETERIZATION FOR THE WALL INTERACTION

Figure 6.8: The pressure profile of water in the $y$ direction is shown. The black circles show $P_{yy} = \frac{1}{2}(P_{xx} + P_{zz})$. The positions of the walls are marked with dashed gray lines. The error-bars are standard errors. $\gamma_{\text{WALL,W}} = 47.5 \pm 0.04 \text{ mN/m}$.

where $p_{rr}(r)$ and $p_T(r) = 0.5 \times (p_{\theta\theta} + p_{\phi\phi})$ are the radial and the tangential component respectively. $e_r, e_\theta, e_\phi$ are the unit vectors of the spherical coordinate system. Our approach in calculating $p_{rr}(r)$ and $p_T(r)$ is based on the method presented in Ref. [248].

First, we divided the system into cubes with sides of length 4.9 Å. Then, the local pressure tensor, $P(x,y,z)$, in each cube was averaged every 20 ps for the entire system. In each cube, the pressure tensor was transformed to spherical coordinates through

$$P(r, \theta, \phi) = T P(x, y, z) T^T. \quad (6.8)$$

$T$ is the transformation matrix which is defined as

$$T = \begin{pmatrix}
\sin(\theta) \cos(\phi) & \sin(\theta) \sin(\phi) & \cos(\theta) \\
\cos(\theta) \cos(\phi) & \cos(\theta) \sin(\phi) & -\sin(\theta) \\
-\sin(\phi) & \cos(\phi) & 0
\end{pmatrix}. \quad (6.9)$$

Thus, $P(r, \theta, \phi)$ were obtained. $P(r)$ is the average over all cubes at distance $r$;

$$P(r) = \langle P(r, \theta, \phi) \rangle_{\theta,\phi}. \quad (6.10)$$

Note that we have spherical symmetry in the system, $p_{\theta\theta} = p_{\phi\phi}$, therefore instead of using the transformation matrix for all components, we only need to transform the radial component. The tangential component was then calculated as

$$p_{\theta\theta} = p_{\phi\phi} = \frac{1}{2}(Tr[P] - p_{rr}). \quad (6.11)$$

since a coordinate transformation does not change the trace of a tensor ($Tr$). To calculate $\gamma_{\text{W,SDS}}$ as

$$\gamma_{\text{W,SDS}} = \int (p_{rr}(r) - p_T(r)) dr \quad (6.12)$$
we chose $dr = 4.5\ \text{Å}$ using trapezoidal method. Because of the singularity at the core, the summation does not include the pressure difference at the center of the micelle. Although the counter-ions are present in the system, their interactions are not included in the surface tension calculation. When the micelle is on the surface, tails and heads dominate the interaction and the effect of ions is negligible. To be consistent, the pressure tensor was calculated only for heads, tails and water molecules.

Figure 6.9 shows the pressure profile for a SDS micelle (tails and heads only) and polarizable water molecules. The pressure difference inside the micelle and at the interface of heads and water is obvious. In the bulk, the pressure difference is negligible. For a SDS micelle in aqueous solution, we measured $\gamma_{W,SDS} = -9.6 \pm 0.2\ \text{mN/m}$.

\[ \rho \left[ \frac{\text{Å}^3}{\text{Å}} \right] \]

\[ P_{rr} - P_T \ [\text{kbar}] \]

\[ r \ [\text{Å}] \]

\[ \text{Tails} \]

\[ \text{Head} \]

Figure 6.9: Top: The pressure profile of SDS micelle along the radial axis. The circles denote $p_{rr}(r) - p_T(r)$. Bottom: Number density profiles of head (red dashed line) and tail (blue line) molecules. The error-bars are standard errors. $\gamma_{W,SDS} = -9.6 \pm 0.2\ \text{mN/m}$. The bin size is 4.5 \text{Å}.

**SDS/wall surface tension**

To evaluate the surface tensions of surface/SDS, we used the same slab geometry set-up as used for water/wall surface tension measurement. The stress tensor was calculated for groups of tail, head, and wall molecules. Our calculation shows that the interaction of ions has a negligible effect on $\gamma_{WALL,SDS}$. The wetting properties of the wall are mostly determined by the tail and head interactions.

For the non-wetting surface, the LJ energy parameters are scaled accordingly with respect to water(neutral)-wall(neutral) interactions. By tuning the energy parameter of the interaction between heads of the surfactant and the wall beads, and consequently scaling the energy of
tails and ions with walls beads, low and high-wetting surfaces are constructed as well. LJ parameters for varying wetting properties of micelle on the walls’ bead are shown in Table 6.2.

<table>
<thead>
<tr>
<th></th>
<th>ε_{LJ} (0.5 × kcal/mol)</th>
<th>Head</th>
<th>Tails</th>
<th>Na⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>non-wetting</td>
<td>0.05</td>
<td>0.02</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>low-wetting</td>
<td>0.3</td>
<td>0.12</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>high-wetting</td>
<td>0.5</td>
<td>0.2</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>

Each system was simulated for 10 ns in the NVT ensemble. As described before, for systems with planar interfaces, Cartesian coordinates were used to obtain the pressure profiles and consequently $\gamma_{\text{WALL, SDS}}$. In all cases, the bin size is 1.14 Å unless otherwise mentioned. All error estimations are standard errors. Here, we present the details of the measurement of surface tensions for non-, low-, and high-wetting in equilibrium. The contact angles for low- and high-wetting case were calculated by substituting the corresponding surface tensions in Young’s equation, eq. 6.6.

**Non-wetting surface**

For the non-wetting case, the micelle detaches itself from the surface in less than 1 ns and floats away, see Fig 6.7d). For this case, we did not measure the $\gamma_{\text{WALL, SDS}}$. We take the contact angle for non-wetting surface as $180^\circ$.

**Low-wetting surface**

Figure 6.10 shows the time evolution of the micelle on the low-wetting surface. The micelle forms a bulb shape structure on the surface immediately. After about 4.75 ns, some SDS molecules separate themselves from the SDS molecules on the surface. Eventually, the micelle breaks up into two daughter micelles: a cap shape micelle on the surface is formed, and a smaller size of the micelle that floats away. The splitting of the micelle is the result of the balancing between the surface interactions and heads forces. In chapter 7, we discuss this behavior in details.

Pressure components to measure $\gamma_{\text{WALL, SDS}}$ for the low-wetting case were averaged from the formation of the bulb shape until the micelle breaks up. This time frame is about 4.75 ns. The difference between pressure components for the low-wetting case for the SDS and surface molecules are depicted in Fig. 6.11(a). The density of the SDS molecules are shown in Fig. 6.11(b). We measure the surface tension for the low case as $\gamma_{\text{WALL, W}} = 44.9 \pm 4.0 \text{mN/m}$ which corresponds to $\theta = 106 \pm 25$. 
Figure 6.10: The time evolution of the micelle on the low-wetting surface. From left to right: CG SDS micelle in a) initial configuration b) bulb-shape structure at $t = 4.5$ ns, c) after breaking up into a cap and a smaller micelle at $t = 10$ ns.

Figure 6.11: Top: Pressure profile of SDS and wall molecules and (b) density profile of SDS along the $y$ direction for the low-wetting wall. The red circles show $P_{yy} - \frac{1}{2}(P_{xx} + P_{zz})$. The position of the wall is marked with dashed gray lines. Bottom: The black circles denote the SDS density ($\frac{kg}{m^3}$) profile. The error-bars are standard errors. $\gamma_{WALL, SDS} = 44.9 \pm 4.0 \text{ mN/m}$. 
Figure 6.12: The time evolution of the micelle on the high-wetting surface. From left to right: CG SDS micelle in a) initial configuration, b) cap shape structure at $t = 1.5$ ns, c) after breaking up into a cap and a daughter micelle at $t = 10$ ns.

Figure 6.13: Top: Pressure profile of SDS and wall molecules and (b) density profile of SDS along the $y$ direction for the low-wetting wall. The blue circles show $P_{yy} - \frac{1}{2}(P_{xx} + P_{zz})$. The bin size for the last point is 2.3 Å. The position of the wall is marked with dashed gray lines. Bottom: The black circles denote the SDS density ($\text{kg/m}^3$) profile. The error-bars are standard errors. $\gamma_{\text{wall,SDS}} = 51.2 \pm 4.5 \text{ mN/m}$.

**High-wetting surface**

Figure 6.12 shows the time evolution of the micelle on the high-wetting surface. The micelle forms a stretched cap structure on the surface. Similar to the low-wetting case, after about 3 ns, some SDS molecules detach themselves from the ones on the surface. A smaller group of SDS remains on the surface while the rest float away together as one micelle. Figure 6.12 shows the time evolution of the micelle on the high-wetting surface. Local pressure components were averaged over the time that the micelle interacts with surface as one whole structure. This time frame is about 2 ns. The difference between pressure components are depicted in Fig. 6.13(a). The density of the SDS molecules are shown in Fig. 6.13(b). We measure the surface tension
for the high-wetting case as \( \gamma_{\text{WALL,SDS}} = 51.2 \pm 4.5 \text{mN/m} \) which corresponds to \( \theta = 67 \pm 29 \).

### 6.6 Conclusion

In this chapter, we discussed the details of the wall structures. In all our simulations that include walls (slab geometry and die simulation), walls were constructed from two static layers (110 plane) of a fcc lattice with lattice constant 6.23 Å. The beads in the outer layer of walls are neutral, while the beads of the inner layer are randomly charged (±0.2e) and the total charge of the inner surface layer is always zero. Without charges on the walls, there is a strong ordering, and slowing of the dynamics, of water on surfaces due to alignment of dipoles resulting from the MARTINI water properties. This undesirable ordering is eliminated by the random arrangement of weakly charged wall beads which provides a non-stick, non-slip surfaces for the polarizable MARTINI water model under flow. For the first time, we show how to eliminate the strong layering of polarizable MARTINI water molecules close to a surface.

To characterize equilibrium wetting properties of walls toward the micelle, we studied the spreading of a spherical micelle droplet on the walls over various interaction strengths in a slab geometry. The surfaces are classified based on the contact angle of the micelle. To obtain the contact angles, we measured the surface tensions of water/wall, SDS/water and SDS/wall in separate simulations. For the first time, we calculated the surface tension of the SDS micelle and polarizable water model. The radial and tangential pressure components were obtained from an NVT simulation of a SDS micelle in a cubic box of water. \( \gamma_{\text{SDS, Wall}} \) for various sets of parameters were calculated in the slab geometry simulations. We used the same size of the slab of water to measure \( \gamma_{\text{W, Wall}} \). We constructed non-, low-, and high-wetting surfaces toward a SDS micelle.

At equilibrium, the micelle forms a cap shape on the high-wetting surfaces while on the low-wetting surfaces, the micelle shape is bulb like. Although in both cases, the micelle eventually breaks up into two parts. Some SDS molecules dissociate from the micelle. At the end, some SDS molecules equilibrate and form a cap micelle on the surface, while the separated SDS float away as one micelle. The size of the cap (the floated micelle) varies between cases. The size of the cap and the micelle will be discussed in detail in chapter 7.
Chapter 7

Micelle shape and fragmentation in confined flow

7.1 Introduction

In the previous chapters, we discussed the structural properties of CG SDS micelles in bulk solutions and on surfaces in equilibrium. In this chapter, we study the structural and dynamical properties of micelles under Poiseuille-like flow in a nano-confined geometry. We discuss the effect of flow, confinement, and wetting on spherical SDS micelles when the micelle is forced through a channel slightly smaller than the equilibrium size of the micelle.

After equilibrating the micelle and the counter-ions in a box consisting of polarizable water in a die-extruder geometry, a constant force in the \( y \) direction is applied to fluid particles for at least 10 ns. External forces on wall particles were kept at zero. The DPD thermostat was only applied in the direction perpendicular to the direction of flow (\( x \) and \( z \)) and on fluid particles. Each system was subjected to a uniform body-force with varying forces of 0.003 (I), and 0.0005 (II) \( \text{kcal mol}^{-1} \text{Å} \) corresponding to a maximum flow velocity of 27, 4.1 \( \text{m sec}^{-1} \) inside the channel. The behavior of the micelle was studied using various forces and three different wetting properties of the surface. In the following section, we discuss the effects of flow on the shape of the micelle, and the fragmentation and re-assembly of the micelle in the channel with varying wetting properties of the channel’s surfaces.
7.2 Results and Discussion

I. $F = 0.003 \frac{\text{kcal}}{\text{molÅ}}$

(a) Non-wetting wall,
(b) Low-wetting wall,
(c) High-wetting wall,

II. $F = 0.0005 \frac{\text{kcal}}{\text{molÅ}}$

(d) Non-wetting wall,
(e) Low-wetting wall,
(f) High-wetting wall,

Figure 7.1: Snapshots of the flowing micelle on different surfaces and with different flow rates. Non-wetting (7.1a 7.1d), low-wetting (7.1b 7.1c) and high-wetting (7.1e 7.1f) channels. For clarity, water molecules and ions are not shown. Maximum velocities for flow are 27 m/sec (I, top row) and 4.1 m/sec (II, bottom row). As the snapshots show, micelles adopt a cigar shape conformation to pass through the channel. Inside the channel, the SDS molecules reside on the surface. The micelles break up on the non/low-wetting surfaces.

Snapshots for different flow rates and wettability of channel walls are shown in Fig 7.1. In each case, the flowing micelle is shown at multiple times during its first passage through the channel. Figure 7.1 illustrates that the micelle shape and size alters under flow. Depending on the flow rates and the wetting properties of the wall, different behaviors of micelles are observed. Under the high flow velocity (I), the micelle fragments and re-assembles on non/low-wetting surfaces (see Fig. 7.1a,b), while on the high-wetting surface, the micelle passes through the channel as one whole structure. In the case of low flow velocity (II), the micelle spans through the whole channel and wets both sides of the channel, while in high flow velocity, surfactants reside on one side of the channel; the strong lateral force of flow pushes the surfactants to the side. At low flow velocity, the micelle spends more time inside the channel, therefore even in the high-wetting case, the micelle breaks.
7.2.1 Effect of flow in the die simulation

To determine the shape of the micelle under flow, we have calculated the tensor of gyration ($\mathbf{R}$), radius ($R_g$), asphericity parameter ($A_d$) and the number of surfactants in daughter micelles every 20 ps. Elements of the radius of gyration $R_{ij}$ and $A_d$ are computed as described in Eq. 5.1 and Eq. 5.2, respectively. We use the same definition for the micelle radius as in Eq. 5.3. The eigenvalues of the radius of gyration, $R_1, R_2, R_3$, are the principal radii of gyration. In the case where all values are approximately equal to each other, the aggregation shape is considered to be spherical. If one is larger than the other two ($R_1 > R_2, R_2 = R_3$) this shows that the micelle is elongated in one direction and it has a cigar shaped form. In case of ($R_1 < R_2, R_2 = R_3$) the micelle shape is more like a pancake.

Since the flowing micelle can break into multiple micelle fragments with each including different numbers of SDS, we need to identify which SDS belongs to which micelle. Similar to the method presented in Ref. [54], for all pairs of CG SDS molecules, we calculated the distance between the centers of mass, head beads, and the three distances between each bead on the tail with its corresponding bead on the other molecule. Any two SDS molecules are classified to be in one micelle if they meet one of these criteria: (i) one of the calculated distances is less than $R_{cut_1} = 6 \, \text{Å}$, (ii) any of two distances are shorter than $R_{cut_2} = 9 \, \text{Å}$, and (iii) any of three distances are shorter than $R_{cut_3} = 12 \, \text{Å}$. The cut-off distances were chosen after inspecting the configuration of micelles in the snapshots, the results are consistent with the number of micelles that are seen in the visualization. Figure 7.2 illustrates the classification. The tensor of gyration and the eigenvalues of the tensor of gyration are computed only for micelles with more than 5 SDS molecules.

Asphericity factors and radii of micelles for flow with $F = 0.003(I)$ are shown in Fig. 7.3 and Fig. 7.4. Figure 7.3 gives information about where the micelles mostly change shape or fragment in the die. We depict $A_d$ of the micelle and micelle fragments versus the location of their center of mass for different wettability. The center of mass location is normalized to the size of the box in the $y$ direction (flow direction). The $A_d$ of the micelle consisting of 55-60 SDS is shown with red signs in all plots. The micelle fragments with various numbers of surfactants are distinguished with different colors. The position of the beginning of the channel is marked on each plot with gray vertical dashed lines. In equilibrium, the three eigenvalues of the radius of gyration are fairly close to each other, with $A_d = 0.03 \pm 0.01$ which shows that the micelle shape is close to a perfect sphere. After applying a force, the micelle deforms and $A_d$ increases. As is clear in Fig. 7.3 before entering the channel area, the micelle alters its shape and deviates from spherical form. Micelles deform to pass through the channel. The maximum value of $A_d$ is reached inside the channel. The micelle stretches to form a cigar shaped cylinder. Generally speaking, in the cases where micelles break, the first fragmentation occurs inside the channel area, while micelle bulb fission happens before entering the chamber area. After passing the channel for the first time, micelle fragments recombine and form one micelle before entering the chamber area. The (reformed) micelle re-changes its shape to be more spherical in the chamber area where the velocity is less than inside the channel. The micelles pass through the channel 3 times in 10 ns. For the high-wetting surface, the micelle with size 60 flows as one whole structure while in non/low-wetting channels, multiple smaller micelles are formed.
Figure 7.2: The micelle classification scheme. Head ($H$) and tail ($C_1, C_2, C_3$) beads are shown by red and cyan. The CM positions are marked by black crosses. The two SDS molecules belong to the same micelle in a), b), and c). a) The heads distance is less than $R_{\text{cut}_1}$ (blue dashed circle). b) The distances between head beads and $C_3$ beads are less than $R_{\text{cut}_2}$ (purple dashed-dot circle). None of the distances are within $R_{\text{cut}_1}$. c) The distances between the heads, the CM positions, and the $C_3$ beads are within $R_{\text{cut}_3}$ (green dashed-dot-dot circle). None of the distances are within $R_{\text{cut}_1}$ or $R_{\text{cut}_2}$. d) The two micelles do not belong to the same micelle since none of the criteria are met.
Figure 7.3: Asphericity factor, Eq. 5.2, versus the normalized center of mass position of the micelle (and micelle fragments) in the die for $F = 0.003 \text{ kcal mol}^{-1}\text{Å}$. Color scheme for classifying micelles is presented on the right. Each color refers to a micelle including the same number of surfactants in a bin of size 5. Before the micelles enters the channel, $A_d$ increases and reaches maximum while the micelles are inside the channel area. When the micelles enter the chamber area, $A_d$ decrease. When the micelle stretches to a long cigar shape, fragmentation occurs.

Figure 7.4 shows $R_g$ for the micelle and the micelle fragments over simulation time. At equilibrium, the calculated radius of the micelle is $R_g = 20.5 \pm 0.3 \text{ Å}$. Micelles consisting of the same number of SDS are shown with the same color scheme as before. As constant force is applied on the fluid, the micelle stretches in the direction of the flow. The principal radius $R_2$ becomes larger than the other two, whereby the micelle takes a cylindrical cigar shape and passes through the channel. The computed values of radii are consistent with the observation of shape transitions of spherical micelles to cigar shaped micelles (see the snapshots in Fig. 7.1). Inside the channel, the surfactants reside on the surfaces. Inside the non/low-wetting channel, the radii of the micelle increases to more than $30 < R_g < 40$ and the micelle breaks at the first passage.

In the chamber area before the first passage, the flow velocity determines the shape and the radius of the micelle independent of the surface absorption on walls. However, in the narrow channel area, depending on the wetting property of the channel surface, micelles show diverse dynamics. In the perfect wetting case, the micelle totally spreads on the surface of the channel. The surfactant tails wet the the wall, and the micelle crawls through the channel length and then it enters the chamber area as one structure. After entering the chamber area, the micelle alters its shape to regain its spherical shape and $R_g$ decreases. On the other hand, for channels with the low-wetting/non-wetting surfaces, micelle fragmentation is observed. Inside the non-wetting/low-wetting channel, the micelle splits into daughter micelles with varying number of surfactants. Micelle fragments take more bulb-like shapes. Interestingly, as these smaller
micelles fragments are entering the chamber area, some or all associate together and they reassemble into one micelle or more micelles with different sizes. Micelle fragments follow the path through the narrow channel almost with the same pattern, elongating along the direction of the applied force to pass through the channel.

The micelle fragment size distribution in the first passage inside the channel for case I is shown in Fig. 7.5. The distributions was obtained over 10 simulations starting from different initial positions of the micelle, and normalized to give the total cumulative probability distribution. Since the starting size of the micelle is 60 and the micelles spend some time inside the channel before breaking up, the largest peak is 60 for all cases. Figure 7.5 shows that as the wettability of the surface decreases, it is less probable to have micelles of size 60. For the high-wetting surface, the micelle of size 60 passes through the channel without any fragmentation of more than 5 SDS, as the wettability of the surface decreases, the micelle breaks to smaller sizes. The (second) significant peak for the low-wetting case is about 30 while for non-wetting surface, it is about 10. For the low-wetting surface, the micelle splits to 2 daughter micelles inside the channel with average sizes between 25 and 35. While for the non-wetting surface, smaller micelles with average sizes of 10-15 are formed. Therefore, if the micelle repeatedly passes through the non-wetting channel, we can expect to see multiple micelles with average size of 10, on the other hand for the low-wetting surfaces fewer micelles with larger sizes will be formed. Thus, we can conclude if the micelles are pushed through longer channels multiple times, at the end the micellar solution should become relatively mono disperse size.

The asphericity factor and $R_g$ of the micelle subject to the force $F = 0.0005 \text{ kcal mol}^{-1}$ A, II, for 10 ns is shown in Fig. 7.6. During this time micelles only pass through the channel once. Similar
7.2. Results and Discussion

Figure 7.5: Left: Size distribution of micelles inside the channel for the first passage for non-(criss-cross green), low- (solid yellow), and high- (solid blue) wet channel’s surfaces. Right: Distribution of the number of micelles inside the channel for the first time passage. The size distributions are plotted for bin size 5. The second peak for the low-wetting surfaces shows that the size of the micelles has a peak at 30, while for non-wetting surfaces it is more probable to have micelles of size 10. By decreasing the wettability of the surface, more micelles with smaller sizes are formed.

to case II, the micelle elongates in the direction of the flow, adopts a cylindrical shape and enters the channel, although inside the channel the maximum \( R_g \) of the micelle of size 60 is \( R_g < 30 \). For non/low-wetting surfaces, (Fig. 7.1d, 7.1e) at the first time passage, the micelle breaks up into two smaller fragments inside the channel, however no re-assemblies of micelle fragments have been observed for the time of the simulation: two separate micelles are formed. Despite the former simulations (I) showing that the micelle was stable as one whole structure on a high-wetting surface, under the smaller force, even the high-wetting surfaces result in micelle break-ups inside the channel, see Fig. 7.1f. Micelle fragments re-assemble quickly at the beginning of the chamber area.
Figure 7.6: From top to bottom: Asphericity factor (Eq. 5.2) and gyration radius of the micelle (Eq. 5.3) and its fragments for $F = 0.0005 \text{ kcal mol}^{-1}$. Color scheme for classifying micelles is presented on the right. The micelle passes through the channel only once. It elongates before entering the channel and breaks up inside the channel. In non/low-wetting cases two separate daughter micelles form. In the high-wetting case, the micelle fragments quickly recombine before entering the chamber.
7.2.2 Micelle fragmentation

In the last section, we studied the effect of flow on micelles and the ultimate size of the micelles inside the channel of the die. In this section, we construct a model to estimate the number of SDS molecules in the micelle fragments. In the die simulations, the micelle splits up into smaller bulb shaped micelles under flow in the narrow channel. This is an interplay between hydrodynamic forces from water molecules on the micelle, the surface/micelle interactions, and self-assembly. As the micelle enters the channel, it is pushed toward the surface of the channel. The micelle shape is defined by the mechanical equilibrium of the hydrodynamic forces from water molecules, interfacial surface tensions of micelle/solvent and solid surface, and self-assembly forces among SDS molecules. If we measure the macroscopic contact angle of the micelle that is pushed toward the surface, we can estimate the size of the micelle fragments.

In the die simulations, the fragmentation of micelles into smaller bulb shaped micelles under flow in the narrow channel area is an interplay between hydrodynamic forces on the micelle, the wall-micelle interactions, and self-assembly forces. As the micelle enters the channel, it is pushed toward the surface of the channel. If we know the contact angle of a micelle that is pushed toward the surface, we can predict the size of the resulting micelle fragments. To test this assertion, we revisit the slab geometry used to measure the surface tensions. The micelle is pushed toward the surface under an external force similar to the micelle in flow inside the channel. We measure $\gamma_{\text{WALL,W}}$ and $\gamma_{\text{WALL,SDS}}$, and consequently the optimum contact angle of micelle fragments from Young’s Eq. 6.6 \[214, 226\]. One should notice that in equilibrium, when the micelle touches the wall, the interaction is primarily with the head group so these dominate the equilibrium wetting properties. However, when the micelle is forced against the wall, tail groups start to interact with the wall atoms. The wetting properties of the heads and tails are naturally reversed due to the hydrophobic and hydrophilic properties of tails and heads. As a result, the wetting properties of the tails dominate the fragmentation.

For a spherical micelle, the surface area $S = 4\pi R^2 = nA$, where $n$ is the number of surfactants in a micelle, $A = \frac{4\pi R^2}{N_{sd}}$ is the surface area that a surfactant occupies in a spherical micelle consisting of $N_{sd}$ surfactants ($N_{sd} = 60$) and $R = R_g$ is the radius of the micelle in equilibrium. Also, when the micelle is pushed against the surface, its shape is like a spherical cap. We can then approximate the surface area of the micelle as the surface area of the cap, $S = 2\pi Rh$, where $h$ is the height of the cap. By knowing the contact angle $\theta$, $h$ can be defined from $\alpha = \pi/2 - \theta = \arcsin(\frac{R-h}{R}) = \arccos(\frac{a}{R})$ (see Fig. 7.7). Finally, we estimate the number of SDS molecules ($n$) in a micelle fragment from

$$n = \frac{2\pi Rh}{A}. \quad (7.1)$$

In the slab geometry, described in section 4.2.1, we applied a constant force on the SDS molecules to push the surfactants toward the solid surface. The applied force was similar to the average hydrodynamic force exerted on each channel wall molecule in a die simulation. We have calculated the size of the micelle fragments for each case. At the end, following Eq. (6.6), we obtained $\theta$. Figure 7.8 shows the time evolution of the micelle on the low-wetting surface under external force $F = 0.08 \text{ kcal/molÅ}$ for 10 ns.
Figure 7.7: A schematic representation of a bulb micelle on a surface. Each surfactant occupies a cone shape volume with surface area $A$. The surface area of the micelle cap is then approximated by $S = nA$ where $n$ is the number of SDS molecules forming the cap. $R = 20.5 \pm 0.3$ Å is the radius of the micelle in equilibrium.

Figure 7.8: Response of the micelle to an external forces on a low-wetting surface. (a) Initial configuration, (b) the micelle spreading on the surface, $t = 1.8$ ns, and (c) fragmentation, $t = 10$ ns. The micelle breaks up to multiple cap shape aggregations under the external force. After the fragments are formed, they are pushed away from each other. They distort and take a more stretched shape. This fragmentation is similar to the micelles breaking up inside the channel of the die. The sizes of the aggregates can be estimated through measuring the surface tensions. Counter-ions and water molecules are not shown.

Under the external force, we measured $\gamma_{\text{wall,SDS}} = 54.6 \pm 6, 49.2 \pm 6.2, 41.4 \pm 7.4$ mN/m for the non-, low-, and high-wetting cases, respectively. Figures 7.9, 7.10, and 7.11 show the pressure and density profiles of SDS for non-, low-, high-wetting cases, respectively. In all surface tension calculations, the interactions of ions were excluded since tails and heads dominate the surface interactions with walls. The large error-bars at the tip of the micelle is due to the lack of the sampling. There are limited number of SDS particles. In integration, the last 5-6 points are averaged together. Data were averaged, starting from the time that the micelle totally spread over the surface until it split for the first time. For the non-wetting surface, the averaging time is between 0.8-3 ns. In the low-wetting, this time frame is between 0.5-2.5 ns and for the high-wetting case is between 0.3-2 ns.
Our calculation shows that the optimum number of SDS in micelle caps are about \( n_c = 7.8 \pm 18.9, 24.6 \pm 19.3, 49.2 \pm 23.0 \), respectively. These numbers are in good agreement with the size distribution of micelles in the die simulation (see Fig. 7.5). It is clear that under external forces, as the wettability of the surface increases larger micelle fragments are formed. This simple model explains that micelle fragmentation is the result of the hydrodynamic forces and surface tension of the interfaces. Thus, by controlling the wettability of the surface we can control the size distribution of micelles.

Under an external force the wetting properties of the surface toward the micelle are different from the equilibrium cases. For comparison, we show the surface tensions for non-, low-, high-wetting surfaces for equilibrium and under the external force in Fig. 7.12. In equilibrium, the head groups dominate wetting properties. However, when the micelle is forced against the wall, tail groups start to interact with the wall atoms. Due to the hydrophobic and hydrophilic properties of tails and heads, the wetting properties of the heads and tails are naturally reversed. Thus, under the external force, the wetting properties of the tails dominate and consequently the wetting properties are not the same as the equilibrium case. The optimum number of SDS in micelles caps for systems in equilibrium and under external force are shown in Table. 7.1.
Figure 7.10: (a) Pressure profile of SDS and wall molecules and (b) density profile of SDS along $y$ direction for the low-wetting wall. The red circles show $P_n - P_T$. The bin size for the last point is 2.3. The black circles denote the SDS density ($\text{kg m}^{-3}$) profile. The error-bars are standard errors. $\gamma_{\text{wall, SDS}} = 49.2 \pm 6.2 \text{ mN m}$. 
7.2. Results and Discussion

Figure 7.11: (a) Pressure profile of SDS and wall molecules and (b) density profile of SDS along y direction for the high-wetting wall. The blue circles show $P_n - P_T$. The black circles denote the SDS density ($\frac{kg}{m^3}$) profile. The error-bars are standard errors. $\gamma_{WALL, SDS} = 41.4 \pm 7.4 \frac{mN}{m}$. 
CHAPTER 7. MICELLE SHAPE AND FRAGMENTATION IN CONFINED FLOW

Figure 7.12: $\gamma_{\text{wall,SDS}}$ for non-, low-, and high-wetting surfaces. The black circles show the surface tension when the micelle is in equilibrium and resides on the surface. The red stars are the values when the micelle is pushed toward the surface.

Table 7.1: The optimum number of SDS in micelle caps on the surfaces.

<table>
<thead>
<tr>
<th>$n_c$</th>
<th>Non-wetting</th>
<th>Low-wetting</th>
<th>High-wetting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium</td>
<td>38 ± 12.4</td>
<td>18.4 ± 14.0</td>
<td></td>
</tr>
<tr>
<td>Under force</td>
<td>7.8 ± 18.9</td>
<td>24.6 ± 19.3</td>
<td>49.2 ± 23.0</td>
</tr>
</tbody>
</table>

7.3 Conclusion

We performed CG MD simulations of SDS micelles in the die-extruder geometry. We studied the behavior of a micellar solution under Poiseuille-like flow in the presence of different degrees of wetting. Independent of the wetting properties of the channel walls, micelles are always pushed toward the channel walls (at least in the case where the micelle is slightly larger than the channel width). It has been shown that in a confined channel under uniform force-driven flow, the micelle deforms from its spherical shape and adopts a cylindrical conformation to pass through the narrow channel. Generally, the micelle elongates in the direction of the flow before entering the channel. The extent of the micelle stretching depends on the flow rate. As the flow rate increases, the micelle grows into a long cigar-like cylindrical structure. Independent of the wetting properties of the channel walls, the micelles always reside on the wall, although micelle fragmentation inside the channel is controlled by the wall wettability. By decreasing wall wettability inside the channel, micelle fragmentation occurs. On the other hand, for the high-wetting surfaces, with the same flow velocity as before, tails spread on the wall and the micelle crawls along one side of the channel without breaking up. With high-wetting walls, the micelle drags itself as one structure along the channel and it does not split. The micelle fragments may recombine into one whole micelle upon entering the chamber area. We demonstrated the micelle fragmentation occurs due to the balancing of hydrodynamic forces, micelle-wall interactions and self-assembly forces. The number of SDS molecules in the mi-
celle fragments, approximated from the macroscopic contact angle, was in good agreement with the size distribution of micelle fragments of the die simulations. Our analysis and simulations show that micelle fragmentation and the size of the daughter micelles, can be controlled by varying the wetting properties of the surfaces.
Chapter 8

Conclusion

In this dissertation, we performed classical MD simulations to study the structural and dynamical properties of SDS spherical micelles. Since the desired time and length scales required to study the rheology of micellar solutions under flow are beyond atomistic simulations, we applied a coarse-grained approach. We used the MARTINI coarse-grained force-field \cite{57, 58} which has been successfully used to investigate the self-assembly of surfactants into micelles \cite{62-64}.

In chapter 5, the structure of the CG SDS micelle in equilibrium was investigated by performing NPT simulations. The aggregation of CG SDS into small micelles occurs in the first few ns, and then the size of the micelles slowly grow. In equilibrium, we obtained a stable micelle consisting of 60 SDS. This size of the CG SDS micelle agrees well with experimental studies \cite{90} and atomistic simulations \cite{21}. In equilibrium, the radius of the CG micelle of size 60 is \( R_g = 20.5 \pm 0.3 \) Å. Based on the values of the asphericity factor, it is clear that the CG SDS micelle has an almost spherical shape.

In chapter 6, we parameterized the interactions between wall/water molecules and wall/SDS molecules. Due to the properties of the polarizable water molecules, they have a tendency to align their dipoles along the wall atoms. This ordering causes a strong layering of water molecules on the surfaces that slows the dynamics of the system. This undesirable ordering is eliminated by a random arrangement of weakly charged wall beads which provides a non-stick, non-slip surfaces for polarizable MARTINI water model under flow.

We characterized the equilibrium wetting properties of the surfaces toward the micelle. In equilibrium, the contact angle of the micelle corresponds to \( \theta = 67 \pm 29, 106 \pm 25, \) and \( 180 \) for high-, low-, and non-wetting surfaces respectively. Depending on the interactions between the wall and surfactant, the micelle either wets the surface to form a cap, forms a bulb shape micelle, or totally detaches from the surface. These correspond to high-, low-, and non-wetting surfaces. When the micelle touches the wall, the SDS molecules rearrange themselves to balance the surface tension and self-assembly forces. As a result, an optimum number of surfactants can reside on the surface that eventually leads to dissociation of a group of SDS molecules from the micelle. The detached group of SDS floats away from the surface as one daughter micelle. The SDS molecules that remained on the surface form a cap shaped configuration.

In chapter 7, the behavior of the flowing micelle was studied under three different wetting properties of the surface in a die-extruder geometry. In the chamber area, before the first passage, the flow velocity determines the shape and the radius of the micelle. Independent of
the flow rate and wetting properties of the surfaces, the shape of the micelle goes back and forth between a sphere and a cylinder as the micelle passes in and out of the channel. Moreover, the micelle always resides on the channel wall and the tails of the SDS molecules spread on the walls.

Inside the channel, in addition to the flow rate, the wetting properties of the channel surfaces determine the overall behavior of the micelle. Inside the channel, the micelle may fragment into smaller micelles. After leaving the channel, the micelle fragments may or may not recombine into one whole micelle upon entering the chamber area. In fast flow, the micelle crawls along the channel without splitting on the high-wetting surfaces and enters the chamber area as one whole structure. While, on non-, and low-wetting surfaces under the same applied force, the micelle splits into daughter micelles.

We have demonstrated that micelle fragmentation occurs due to a balance between hydrodynamic forces, micelle-wall interactions, and self-assembly forces. The number of SDS molecules in the micelle fragments, approximated from the macroscopic contact angle, was in good agreement with the size distribution of micelle fragments in the die simulations. Our analysis and simulations show that micelle fragmentation and the size of the daughter micelles, can be controlled by varying the wetting properties of the surfaces.

Also, we have shown that the wetting behavior of micelles on the same surface varies in equilibrium and under external force. In equilibrium, when the micelle touches the wall, the interaction is primarily with the head groups, therefore, heads dominate the equilibrium wetting properties. However, when the micelle is pushed against the wall, tail groups start to interact with the wall. The wetting properties of the heads and tails are naturally reversed due to the hydrophobic and hydrophilic properties of tails and heads. As a result, the wetting properties of the tails dominate the fragmentation.
Bibliography


Appendix A

Trotter expansion

In the numerical integration of Hamiltonian systems, the symplectic structure of the equation of motion should be preserved. Hence, to solve the equation of motion numerically, we need to derive a time-reversible and symplectic algorithm. The Trotter expansion \cite{100,121} is a technique to develop such algorithms. Here we use a simplified version of Trotter expansion of time-evolution operator to derive the velocity Verlet algorithm.

If $f(x)$ is any function of the phase space vector, the time evaluation of $f(x)$ along a trajectory $x_t$ is $f(x_t)$. For a Hamiltonian system, the time derivative of $f(x_t)$ in generalized coordinates is defined by

$$\frac{df}{dt} = \sum_{\alpha=1}^{3N} \left( \frac{\partial f}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} + \frac{\partial f}{\partial p_\alpha} \frac{\partial H}{\partial p_\alpha} \right) = \{f,H\}, \quad (A.1)$$

where $\{f,H\}$, the Poisson bracket between $f(x)$ and $H$, is a generator of the time evolution of $f(x_t)$. We introduce the operator, $iL$, on the phase space as

$$iLa = \{f,H\}, \quad (A.2)$$

where $L$ is known as the Liouville operator. By solving Eq.\,[A.1] for $f(x_t)$, we have

$$f(x_t) = e^{iLt}f(x_0). \quad (A.3)$$

$x_0$ is the initial phase space vector elements. The operator $e^{iLt}$ is the classical propagator. By applying Eq.\,[A.3] on the space function $f(x) = x$, we develop approximate solutions to Hamiltonian’s equation.

$$x_t = e^{iLt}x_0. \quad (A.4)$$

We can rewrite the Liouville operator as a sum of two operators $L_1$ and $L_2$, $iL = iL_1 + iL_2$, where

$$iL_1 = \sum_{\alpha=1}^{N} \frac{\partial H}{\partial p_\alpha} \frac{\partial}{\partial q_\alpha}, \quad (A.5)$$

$$iL_2 = -\sum_{\alpha=1}^{N} \frac{\partial H}{\partial q_\alpha} \frac{\partial}{\partial p_\alpha}. $$
The operators $L_1$ and $L_2$ generally do not commute, i.e. $[iL_1, iL_2] \neq 0$; the classical propagator cannot be separated into a simple product of $\exp(iL_1t) \exp(iL_2t)$. However, based on the Trotter theorem, for any two non-commuting operators $A, B$,

$$e^{A+B} = \lim_{P \to \infty} [e^{B/2P} e^{A/2P} e^{B/2P}]^P,$$

(A.6)

where $P$ is an integer. By applying Eq. A.6 to the classical propagator, we obtain

$$e^{(iL_1)} = \lim_{P \to \infty} [e^{iL_2\delta t/2P} e^{iL_1\delta t/P} e^{iL_2\delta t/2P}]^P.$$  

(A.7)

Substituting $\delta t = t/P$ in Eq. A.7 yields

$$e^{(iL_1)} = \lim_{P \to \infty, \delta t \to 0} [e^{iL_2\delta t/2P} e^{iL_1\delta t/P} e^{iL_2\delta t/2P}]^P.$$  

(A.8)

Equation A.8 states that for a finite time $t$ in the limit of the infinite steps, we can exactly propagate a classical system. For a finite $P$, we approximate Eq. A.8 as

$$e^{(iL_1)} \approx [e^{iL_2\delta t/2P} e^{iL_1\delta t/P} e^{iL_2\delta t/2P}]^P + O(P\delta t^3).$$  

(A.9)

Equation [A.9] is a practical equation for $e^{(iL_1)}$ with order error of $P\delta t^3 = \delta t^2$. Note that the error order of $\delta t^2$ is for a full trajectory of $P$ steps. For a single step of $\delta t$

$$e^{(iL_2\delta t)} \approx [e^{iL_2\delta t/2} e^{iL_1\delta t} e^{iL_2\delta t}]^P + O(\delta t^3).$$  

(A.10)

with order of error for a single step is proportional to $\delta t^3$. Equation A.10 can be used to evaluate a numerical propagation scheme for a single time step. Clearly, by choosing small time steps and large $P$, the global errors will be small and the difference between the true Hamiltonian and the Hamiltonian obtained by the integration (“pseudo-Hamiltonian”) becomes small. Since the true Hamiltonian is conserved, there will be no long-term drift in the energy obtained by with algorithms. It has been shown that pseudo-Hamiltonian is very close to a constant of motion for a realistic many-body systems, and for a harmonic system is indeed conserved [121].

Now let us apply the operator $iL = iL_1 + iL_2$ on the coordinate ($q$) and momentum ($p$) of the particles on $f(p^N(0) + q^N(0))$. First, we apply $e^{iL_2\delta t}$ and we obtain

$$e^{iL_2\delta t} f(p^N(0) + q^N(0)) = f\{[p(0) + \frac{\delta t}{2} \dot{p}(0)]^N, q^N(0)\},$$  

(A.11)

then $e^{iL_1\delta t}$ is applied on Eq. A.11 which yields

$$e^{iL_1\delta t} f\{[p(0) + \frac{\delta t}{2} \dot{p}(0)]^N, q^N(0)\} = f\{[p(0) + \frac{\delta t}{2} \dot{p}(0)]^N, [q(0) + \delta t \dot{q}(\frac{\delta t}{2})]^N\}. $$  

(A.12)

At the end, by applying $e^{iL_2\delta t}$ one more time on the right side of the Eq. A.12 we obtain

$$f\{[p(0) + \frac{\delta t}{2} \dot{p}(0) + \frac{\delta t}{2} \dot{p}(\delta t)]^N, [q(0) + \delta t \dot{q}(\frac{\delta t}{2})]^N\}. $$  

(A.13)

From equation A.13 it is obvious that in every step, we have a simple shift in either $q^N$ or $p^N$. The shift in $q$ is a function of $p$ (since $\dot{q} = \frac{p}{m}$) while the shift in $p$ is a function of $q$, $F(q^N)$. 

Chapter A. Trotter expansion
The Jacobian of the transformation from \( \{p^N(0), q^N(0)\} \) to \( \{p^N(\delta t), q^N(\delta t)\} \) is equal to one; the algorithm preserves the area.

By repeating this sequence on the position and momenta, following set of equations is obtained,

\[
\begin{align*}
  p(\delta t) &= p(0) + \frac{\delta t}{2}(F(0) + F(\delta t)), \quad \text{(A.14)} \\
  q(\delta t) &= q(0) + \delta t \dot{q}(0) + \frac{\delta t^2}{2} F(0), \quad \text{(A.15)} \\
  &= q(0) + \delta t \dot{q}(0) + \frac{\delta t^2}{2m} F(0),
\end{align*}
\]

which is in fact the velocity-Verlet algorithm (see chapter 3). Here we demonstrate that the Verlet algorithm conserves the phase-space area, hence symplectic. Also, since the past and future coordinates are symmetrically present in the algorithm, the Verlet algorithm is time-reversible.
Curriculum Vitae

Name: Mona Habibi

Post-Secondary Education and Degrees:
Amirkabir University of Technology
Tehran, Iran
2000 - 2004 B.Sc.

Sharif University of Technology
Tehran, Iran
2005 - 2008 M.Sc.

University of Western Ontario
London, ON
May 2009 - January 2014 Ph.D.

Honors and Awards:
Western Graduate Research Scholarship
2009-2013

Related Work Experience:
Teaching Assistant
The University of Western Ontario
2009 - 2013

Publications: