Molecular dynamics simulation of adsorption and lubrication of hydrocarbons and aqueous copolymer lubricants on iron and iron oxide surfaces

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Molecular Dynamics Simulation of Adsorption and Lubrication of Hydrocarbons and Aqueous Copolymer Lubricants on Iron and Iron Oxide Surfaces

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I, Thi Dinh Ta, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Mechanical, Materials and Mechatronics Engineering, Faculty of Engineering and Information Sciences, University of Wollongong, Australia, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other university or academic institution.

Thi Dinh Ta
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Abstract

A classical molecular dynamics (MD) simulation has been used to investigate the adsorption and tribological performance of hydrocarbon lubricant between different iron and iron oxide surfaces. A realistic all-atom model of alkane was employed using the COMPASS force field (FF) while the relaxed surfaces and an effective force field for interactions between surface and lubricant were obtained from ab-initio calculations. A comparative analysis of adsorption of six n-alkanes (C_nH_{2n+2}, n = 4, 6, 8, 10, 12, 16) on Fe(110), FeO(110), and Fe_2O_3(0001) and thin film lubrication of hexadecane between Fe(100), Fe(110), Fe(111), FeO(100), FeO(110), FeO(111), Fe_2O_3(001), and Fe_2O_3(012) surfaces has been carried out. A quantitative surface parameterization was introduced to investigate the influence of surface properties such as crystalline structure, surface corrugation, and crystal plane on the structure, rheological properties, and tribological performance of the n-alkanes. The effects of working conditions such as loading pressure, shear rate, and temperature are also considered.

The results show that alkane molecules orient randomly on Fe(110) and Fe_2O_3(0001) surfaces but they preferentially orient in (010) direction on FeO(110) at low temperature. Additionally, alkanes adsorb physically on iron oxides, in the following decreasing order Fe(110) > FeO(110) > Fe_2O_3(0001). The adsorption energies per saturated carbon site decrease with an increase of molecular chain length and this propensity is similar for different surfaces. In contrast, the saturated carbon density is insensitive to the surface potentials and shows an increasing trend for short alkane chains but it remains steady for longer chains. Although the wall-fluid attraction of hexadecane on pure iron surfaces is significantly stronger than its oxides, there is a considerable reduction of shear stress of confined n-hexadecane film between Fe(100), and Fe(110) surfaces compared with FeO(110), FeO(111), Fe_2O_3(001), and Fe_2O_3(012). It was found that, in thin film lubrication of hexadecane between smooth iron and iron oxide surfaces, the atomic roughness plays a role more important than the wall-fluid adhesion strength.

While the ordering of n-alkane increases slightly with the pressure, it decreases as the shear rate and temperature increase. Slip at the interface between the wall and
the fluid interface increases with the pressure and shear rate but it is insensitive to temperature. The shear stress increases with the pressure whereas the coefficient of friction (CoF) shows a contrasting propensity. Both shear stress and CoF increase with the shear rate and the logarithmic function predicts this correlation properly, whereas they are decrease with an increase in temperature. For different loading pressures, the shear viscosity increases exponentially with the pressure but this rheological component levels off when the pressure exceeds a critical value. For different shear rates, a higher zero-shear-rate viscosity ($\eta_0$) and lower critical shear rate ($\gamma_c$) can be seen at a higher pressure, but an increase in temperature leads to a decrease in $\eta_0$ and an increase in $\gamma_c$. While these tendencies agree with those observed for bulk hexadecane, a higher zero-shear-rate viscosity and lower onset of shear thinning occurred in the confined model, unlike with bulk lubricant.

Although a number of experiments have been carried out to investigate the lubrication of aqueous copolymer lubricant, which is applied widely in metalworking operations, a comprehensive theoretical investigation at atomistic level is still lacking. This study addresses the influence of pressure and copolymer concentration on the structural properties and tribological performance of aqueous copolymer solution of polypropylene oxide – polyethylene oxide – polypropylene oxide (PPO–PEO–PPO) at mixed lubrication using a MD simulation. An effective potential, which has been derived from density functional theory (DFT) calculations, was employed for the interactions between the fluid’s molecules and iron surface.

The simulation results have indicated that physisorption takes place between triblock copolymer and iron surface. Under confinement by iron surfaces, the copolymer molecules form lamellar structure in aqueous solution and behave differently from its bulk state. The lubrication performance of aqueous copolymer lubricant increases with concentration, but the friction reduction is insignificant at high pressure. Additionally, the plastic deformation of asperity is dependent on both copolymer concentration and pressure, and the wear behaviour shows a linear dependence of friction force on the number of transferred atoms between contacting asperities.
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## Abbreviations

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<th>Description</th>
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<tbody>
<tr>
<td>3D</td>
<td>3-Dimensions</td>
</tr>
<tr>
<td>A–B–A</td>
<td>Anchor–Buoy–Anchor</td>
</tr>
<tr>
<td>B–A–B</td>
<td>Buoy–Anchor–Buoy</td>
</tr>
<tr>
<td>CMC</td>
<td>Critical Micelle Concentration</td>
</tr>
<tr>
<td>CMT</td>
<td>Critical Micellization Temperature</td>
</tr>
<tr>
<td>CoF</td>
<td>Coefficient of Friction</td>
</tr>
<tr>
<td>COMPASS</td>
<td>Condensed-phase Optimised Molecular Potentials For Atomistic Simulation Studies</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DFT-D</td>
<td>Density Functional Theory including long-range Dispersion correction</td>
</tr>
<tr>
<td>DME</td>
<td>Dimethoxyethane</td>
</tr>
<tr>
<td>DMP</td>
<td>Dimethoxypropane</td>
</tr>
<tr>
<td>EA</td>
<td>Explicit Atoms</td>
</tr>
<tr>
<td>EAM</td>
<td>Embedded-Atom Method</td>
</tr>
<tr>
<td>EAM/FS</td>
<td>Finnis–Sinclair Embedded-Atom Method</td>
</tr>
<tr>
<td>FF</td>
<td>Force Field</td>
</tr>
<tr>
<td>G06</td>
<td>Grimme 2006</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized Gradient Approximation</td>
</tr>
<tr>
<td>LAMMPS</td>
<td>Large-Scale Atomic/Molecular Massively Parallel Simulator</td>
</tr>
<tr>
<td>L-J</td>
<td>Lenard-Jones</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
</tr>
<tr>
<td>MP2</td>
<td>Møller–Plesset ²nd</td>
</tr>
</tbody>
</table>
Abbreviations

NVE  Number of molecules $N$, Volume $V$, and Energy $E$
NVT  Number of molecules $N$, Volume $V$, and Temperature $T$
OPLS Optimized Potentials for Liquid Simulations
PAW  Projector Augmented-Wave
PBE  Perdew–Burke–Ernzerh
PDMS Poly(dimethylsiloxane)
PE   Polyethylene
PEO  Poly(ethylene oxide)
PP   Polypropylene
PPO  Polypropylene oxide
PPPM Particle–Particle Particle–Mesh
QM   Quantum Mechanics
ReaxFF Reactive Force Field
SDS  Sodium Dodecyl Sulfate
TraPPE-UA Transferable Potentials for Phase Equilibria–United Atom
TS   Tkatchenko–Scheffler
UA   United Atoms
vdW  van der Waals
ZDDP Zinc Dithiophosphate
Symbols

- $a$ - Exponential factor in Carreau equation
- $A_{\text{Buck}}$ (kJ/mol) - Repulsion parameter in Buckingham potential
- $b$ - Bonding distance
- $C_{\text{Buck}}$ (Å$^6$kJ/mol) - Dispersion parameter in Buckingham potential
- $E$ (kJ/mol) - Total energy of a molecular system
- $E_{\text{ad}}$ (kJ/mol) - Total adsorption energy
- $E_{\text{butane}}$ (kJ/mol) - Total energy of butane
- $E_{\text{butane+surface}}$ (kJ/mol) - Total energy of a system including butane and surface
- $E_{\text{surface}}$ (kJ/mol) - Total energy of a surface
- $F(x)$ (kJ/mol/Å) - Resisting force in $X$ direction
- $F_{\text{corr}}$ (kJ/mol/Å) - Corrugation force
- $F_i$ (kJ/mol/Å) - Total atomic force of a molecular system
- $H$ - Hamiltonian operator
- $h_{\text{comm}}$ (Å) - Commensurability height
- $h_{\text{eq}}$ (Å) - Equilibrium distance
- $\bar{h}_{\text{eq}}$ (Å) - Averaged equilibrium distance
- $M$ (g/mol) - Molecular weight
- $m_i$ (g/mol) - Atomic mass of atom $i^{th}$
- $n$ - Exponential factor that controls the slope of the shear thinning region in Carreau equation
- $N$ - Number of atoms
- $P$ (Pa) - Applied pressure
- $q_i$ (e) - Atomic partial charge of atom $i^{th}$
- $R$ (m$^2$kg.s$^{-2}$K$^{-1}$) - Boltzmann constant
- $r_i$ (Å) - Coordinate of atom $i^{th}$
- $s$ - Slip parameter
- $s_{\text{ref}}$ - Reference slip parameter
- $t$ (s) - Time
- $T$ (K) - Temperature
- $V$ (kJ/mol) - Interatomic interaction potential energy
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$V_{corr}$</td>
<td>kJ/mol</td>
<td>Surface energy corrugation</td>
</tr>
<tr>
<td>$V_{scan}$</td>
<td>kJ/mol</td>
<td>Average interaction energies between the scanning atoms and the surface</td>
</tr>
<tr>
<td>$V_{scan}$</td>
<td>kJ/mol</td>
<td>Interaction energies between the scanning atoms and the surface</td>
</tr>
<tr>
<td>$v_x$</td>
<td>m/s</td>
<td>Sliding velocity in X direction</td>
</tr>
<tr>
<td>$x$</td>
<td>Å</td>
<td>Coordinate in X direction</td>
</tr>
<tr>
<td>$y$</td>
<td>Å</td>
<td>Coordinate in Y direction</td>
</tr>
<tr>
<td>$z$</td>
<td>Å</td>
<td>Coordinate in Z direction</td>
</tr>
<tr>
<td>$\beta$</td>
<td>-</td>
<td>Pressure coefficient</td>
</tr>
<tr>
<td>$\dot{\gamma}$</td>
<td>1/s</td>
<td>Shear rate</td>
</tr>
<tr>
<td>$\dot{\gamma}_{app}$</td>
<td>1/s</td>
<td>Apparent shear rate</td>
</tr>
<tr>
<td>$\dot{\gamma}_c$</td>
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<td>$\dot{\gamma}_{eff}$</td>
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<td>Effective shear rate</td>
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<tr>
<td>$\epsilon_{ij}$</td>
<td>kJ/mol</td>
<td>Well-depth energy of a pairwise interaction between atom $i^{th}$ and $j^{th}$</td>
</tr>
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<td>$\zeta_{surf}$</td>
<td>kJ/mol</td>
<td>Surface corrugation parameter</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Pa.s</td>
<td>Viscosity</td>
</tr>
<tr>
<td>$\eta_0$</td>
<td>Pa.s</td>
<td>Zero-shear-rate viscosity</td>
</tr>
<tr>
<td>$\eta_{\infty}$</td>
<td>Pa.s</td>
<td>High-shear-rate viscosity</td>
</tr>
<tr>
<td>$\eta_{eff}$</td>
<td>Pa.s</td>
<td>Effective shear viscosity</td>
</tr>
<tr>
<td>$\theta$</td>
<td>°</td>
<td>Angle</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>s</td>
<td>Coefficient of $\dot{\gamma}$ in Carreau equation</td>
</tr>
<tr>
<td>$\lambda_s$</td>
<td>Å</td>
<td>Interfacial atomic spacing</td>
</tr>
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<td>$\pi$</td>
<td>-</td>
<td>Pi constant = 3.14159</td>
</tr>
<tr>
<td>$\rho_{Buck}$</td>
<td>Å</td>
<td>Parameter $p$ in Buckingham potential</td>
</tr>
<tr>
<td>$\rho_e$</td>
<td>g/cc</td>
<td>Equilibrium density</td>
</tr>
<tr>
<td>$\sigma_{ij}^0$</td>
<td>Å</td>
<td>Equilibrium distance between atom $i^{th}$ and $j^{th}$</td>
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<tr>
<td>$\tau_{ref}$</td>
<td>Pa</td>
<td>Reference shear stress in xz plane</td>
</tr>
<tr>
<td>$\tau_{xz}$</td>
<td>Pa</td>
<td>Shear stress in xz plane</td>
</tr>
<tr>
<td>$\psi$</td>
<td>-</td>
<td>Set of solutions in Schrödinger equation</td>
</tr>
<tr>
<td>$\omega_e$</td>
<td>-</td>
<td>Weighting factor of energy</td>
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### Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$\omega_{ZC}$</td>
<td>Weighting factor of Z coordinate of carbon</td>
</tr>
<tr>
<td>$\omega_{ZH}$</td>
<td>Weighting factor of Z coordinate of hydrogen</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Coefficient of friction</td>
</tr>
<tr>
<td>$\mu_{ref}$</td>
<td>Reference coefficient of friction</td>
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Introduction

Tribology, a study of science and engineering of interacting surfaces in relative motion focuses on three aspects: friction, lubrication and wear. The main aims are to reduce friction and wear through efficient usage of lubricants. Recently it has been prompted by the high demand to save energy. In many manufacturing processes such as rolling, forming, drawing and ironing, machining and others, the friction induced by sliding between mechanical components often causes a short life expectancy of components and an energy loss. Lubricant has been widely used to minimize the friction and consequently reduces the wear. It reduces the friction by separating two sliding surfaces by a thin lubricant film. Additionally, the lubricant also reduces the surface operating temperature, corrosion of metal surfaces, and transports the contaminants out of the system. Nowadays, the development of modern technology demands the lubricant to operate with ultra-thin films of a few molecular layers, which is within the domain of nanotribology. This new area of tribology has attracted many researchers over several decades; however, the fundamentals of molecular structure and rheological property of lubricant, the mechanics of tribological performance have not been well understood. The nanotribology of lubricant confined between sliding surfaces will be the object of this work.

A number of factors affect the friction and lubrication conditions such as surface finish, temperature, operational load, relative speed between the surfaces, and lubricant characteristics. To understand the influence of these factors, researchers have been looking for methods to improve the performance of machine components. Improving the overall lubrication by using an effective lubricant is one approach to reduce the friction. Base oils composed of hydrocarbons have been used widely due to their high-performance in lubrication. However, the environmental impact and economic consideration have prompted researchers to look for an environmentally friendly metal forming lubricants that can mitigate the disposal issues inherent in oil based lubricants. The copolymer-based aqueous lubricant has been applied in cold strip rolling as it satisfies these environmental and economic requirements. Experimental studies of tribological performance of these lubricants have been
carried out; however, it is not possible to observe the behaviour of lubricant at the molecular level.

In metalworking operations, iron oxides are formed on the surface of the tool and product. The changing in oxidation state of iron leads to a formation of several iron oxide compounds. The structural and chemical properties of iron oxides are therefore altered and could result in different adhesive strength and structural behaviour of adsorbed molecules on the surface. Furthermore, these properties can affect the structural and rheological properties of lubricant, as well as tribological performance of a confined system.

The work in this thesis deal with the adsorption and tribological performance of n-alkanes and aqueous copolymer lubricants confined between iron and iron oxide surfaces. A numerical approach using MD simulation has been used to investigate this matter. The roles of adhesive strength, surface corrugation of iron oxide surfaces as well as the influence of working conditions on their lubrication performance have been addressed. Furthermore, the thin film lubrication of aqueous copolymer lubricant in mixed lubrication regime has also been carried to study the effect of copolymer concentration.

This work begins with a literature review (Chapter 1) on adsorption and thin film lubrication from experimental and numerical investigations. The properties of iron oxide surfaces, the adsorption of hydrocarbons on metal and metal oxide surfaces as well as their tribological performance are presented. The theoretical investigations of thin film lubrication of hydrocarbon lubricant using MD simulation are discussed. Additionally, the experimental and numerical studies of structural properties, phase behaviour, adsorption and tribological performance of aqueous triblock copolymer lubricant have also been reviewed.

In Chapter 2, the basic knowledge of DFT and MD methods are introduced. The numerical models of adsorption and thin film lubrication of hydrocarbon and aqueous triblock copolymer lubricants confined between iron and iron oxide surfaces are presented. A force field parameterization has been carried out to derive a new potential for the interactions between iron and iron oxide surfaces and considered lubricants. Moreover, the DFT and MD simulation procedures along with setting parameters are described in details.
Chapter 3 presents the results of DFT calculations of electronic and structural properties for different iron and iron oxide surfaces as well as their adsorption energies with alkane. A new optimized force field has been applied for the interactions between these surfaces and hydrocarbons in MD simulation. The structural behaviour and adsorption energies of linear alkanes on different iron and iron oxide surfaces are investigated.

In Chapter 4, the thin film lubrication performance of hexadecane, a typical hydrocarbon lubricant, confined between different iron and iron oxide surfaces is presented. A surface parameterization has been carried out to characterize the surface properties that influence the structural and rheological properties as well as tribological performance of hexadecane lubricant.

The influences of sliding conditions such as pressure, shear rate, and surface temperature on thin film lubrication of hexadecane are also considered in Chapter 5.

Chapter 6 investigates the influence of copolymer concentration and applied pressure on thin film lubrication of aqueous copolymer lubricant in mixed film lubrication regime. A force field for interactions between triblock copolymers and iron surface has been derived from quantum calculation of adsorption of monomers on iron surface. The behaviour and tribological performance of triblock copolymer from asperity contacts are investigated.

Finally, Chapter 7 presents the major findings of this work and proposes research topics for future work.
Chapter 1 Literature review

Tribology is the science of friction, wear, and lubrication. Although the use of lubrication had been implemented for thousands years ago, but the scientific focus on lubrication technology is relatively new. The term tribology was first introduced in 1966 and has been used globally to describe this far-reaching field of activity since 1985. Even though efforts had been made since the 16th century to describe the whole phenomenon of friction scientifically (Leonardo da Vinci, Amontons, Coulomb), the works always concentrated on single aspects at macroscale and the lubricants were not even considered. Some research work performed up to early nineteen seventies totally ignored the chemical process taking place in lubricated processes.

1.1 Friction in life

There are many disadvantages of friction which is often associated with wear. However, we cannot deny the fact that friction can also be important. Thank to friction, rolling process can be implemented fluently and roller can move product easily, although high friction can result in high rolling force/torque, excessive wear of work roll and poor strip surface quality. There are many researches related to this area in the last few decades from macroscale to nanoscale.

Together with the development of technology, many modern types of equipment have been employed to investigate experimentally the tribology of lubricants on the nanoscale. Besides, thanks to the development of high performance computing, numerical modelling has been used to probe into the molecular behaviour of lubricant in the contacts. The aim of these investigations is to have a better understanding about the tribological behaviours of lubricants under pressure and shear during asperity contacts, in order to reduce the friction losses and wear in the system and improve the working life of mechanical components.

Nowadays, in a wide range of manufacturing applications such as metal forming to automotive industry, more thin film lubricant are subjected to high pressure and shear under confined conditions. In thin film lubrication, three types of contacts should be considered, depending on the film thickness ($h$). The first one is the boundary lubrication regime which contacting surfaces are covered by a molecular
layer of substance. The boundary region depends on the characteristic of interacting surfaces and their roughness. Boundary lubricating films are created from surface-active substances and their chemical reaction products. The second contact type is the mixed film lubrication whose film layer is thicker than boundary lubrication and the interfaces start interacting at asperity level. As a consequence, the load is carried out by lubricant and asperities. The third contact regime is hydrodynamic lubrication mode whose film layer separates the two surfaces. In some situations, elasto-hydrodynamic lubrication regime can involve mixed film and hydrodynamic lubrication. Several factors need to be considered, such as viscous heating, temperature-viscosity, pressure-viscosity and temperature-density relationships, surface roughness, etc …

1.2 Iron oxide surfaces

Iron oxides are basically formed on iron and steel surfaces by electrochemical corrosion or high temperature oxidation in gases. The electrochemical corrosion happens due to electrochemical reaction of iron that acts as an anode, and oxidizing agent such as oxygen when iron/steel surface is partly or completely exposed to water.

When iron/steel is exposure to the air, a surface film of oxide is formed at temperature ranging from below room temperature up to 1200 °C. At room temperature, this film is only a few Å thick; however, a thicker film is produced at higher temperature. The formation of oxide layer depends on temperature, oxygen partial pressure, and crystal plane of iron surface. For instance, at 700 °C and oxygen partial pressure of $10^{-15}$ Pa the FeO oxide is formed on the surface. In practice, this oxide can be found at least in the initial stage of oxidation process on iron/steel surfaces. On a pure iron surface, the oxidation process could be fast initially, but this process will slow down when the oxide layer is formed on the surface.

This oxidation process is further accelerated at higher temperature and results in an increase of the oxide film thickness. At room temperature, the oxide film is a solid solution of $\text{Fe}_3\text{O}_4$ and $\gamma$-$\text{Fe}_2\text{O}_3$ (Cornell & Schwertmann 2004b), whereas a oxide film consisting of $\text{Fe}_3\text{O}_4$ at inner layer and $\alpha$-$\text{Fe}_2\text{O}_3(0001)$ at outer layer has been
observed at 200-300 °C (Seo et al. 1975). This oxide film structure still retains at temperature up to 550 °C even when the oxygen partial pressure is high. At temperature above 600 °C, the oxide film consists of FeO, Fe$_3$O$_4$ and α-Fe$_2$O$_3$, and FeO is formed in the bottom layer (West 1980). Experimental verification has shown that Fe$_3$O$_4$ forms the largest film thickness (2.2 ± 0.8 μm) due to its stability, followed by α-Fe$_2$O$_3$(0001) (1.0 ± 0.6 μm) and FeO at temperature up to 500 °C (Sullivan & Athwal 1983). There are sixteen iron oxides and these compounds could be oxides, hydroxides, or oxide hydroxides (Cornell & Schwertmann 2004b); however, in this study, only two typical iron oxides of Wüstite and Hematite are considered. The general properties of each oxide are described briefly below in Table 1.1.

Table 1.1 General properties of iron oxides (Cornell & Schwertmann 2004b).

<table>
<thead>
<tr>
<th></th>
<th>Wüstite</th>
<th>Hematite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>Fe$_{1-x}$O</td>
<td>α-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Cation</td>
<td>Fe$^{2+}$</td>
<td>Fe$^{3+}$</td>
</tr>
<tr>
<td>Structure type</td>
<td>rock salt</td>
<td>corundum</td>
</tr>
<tr>
<td>Formula units</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>Crystal system</td>
<td>cubic</td>
<td>trigonal</td>
</tr>
<tr>
<td>Anion stacking</td>
<td>fcc (111)</td>
<td>hcp (001)</td>
</tr>
<tr>
<td>Unit cell dimensions (nm)</td>
<td>a = 0.4302-0.4275</td>
<td>a = 0.5034</td>
</tr>
<tr>
<td></td>
<td>c = 1.3752</td>
<td></td>
</tr>
<tr>
<td>Colour</td>
<td>black</td>
<td>red</td>
</tr>
<tr>
<td>Density (g.cm$^{-3}$)</td>
<td>5.9-5.99</td>
<td>5.26</td>
</tr>
<tr>
<td>Mohs scale hardness</td>
<td>-</td>
<td>6.5</td>
</tr>
<tr>
<td>Melting point °C</td>
<td>1377</td>
<td>1350</td>
</tr>
<tr>
<td>Boiling point °C</td>
<td>2512</td>
<td>-</td>
</tr>
<tr>
<td>Type of magnetism</td>
<td>antiferromag.</td>
<td>weak ferromag. or antiferromag.</td>
</tr>
<tr>
<td>Néel (curie) temperature (K)</td>
<td>203-211</td>
<td>956</td>
</tr>
</tbody>
</table>

Hematite (α-Fe$_2$O$_3$(0001)), as shown in Figure 1.1, crystallizes in the corundum structure (Pauling & Hendricks 1925), and similarly with crystalline structure of Al$_2$O$_3$. Wüstite (Fe$_{1-x}$O) takes the cubic rock salt structure (Figure 1.2), where the O$^{2-}$ anions form a close-packed fcc sub lattice with Fe$^{2+}$ cations in octahedral sites. Under thermal equilibrium, this structure is stable only at temperature higher than 567 °C.
but it disproportionates into α-Fe and Fe$_3$O$_4$ if cooled slowly to temperatures below 567 °C (Cornell & Schwertmann 2004a). In practice, this iron oxide is always defective with (1-x) values ranging from 0.83 to 0.95.

![Figure 1.1](image1.png)  
(a) Crystalline structure of Hematite. (a) Side view of the α-Fe$_2$O$_3$ structure that shows hexagonal unit cell contains 6 formula units in which O$^{2-}$ anions are red, Fe$^{3+}$ cations are purple. (b) On top view of the α-Fe$_2$O$_3$ structure that shows Fe$^{3+}$ cations occupy two thirds of the octahedral interstitial sites between hexagonal close packed O$^{2-}$ planes.

![Figure 1.2](image2.png)  
Figure 1.2 Crystalline structure of Wüstite shows cubic unit cell contains 8 formula units in which O$^{2-}$ anions are red, Fe$^{2+}$ cations are purple.

### 1.2.1 Hematite surface

Although α-Fe$_2$O$_3$(0001) is stable at low temperature (below 600 K) and at any oxygen ambient pressure (Weiss & Ranke 2002), the preparation of the Fe$_2$O$_3$
surfaces in experiment is a challenging task as the surfaces differ considerably from the bulk and the resulting surfaces are identical to that observed on Fe$_3$O$_4$(111) or a thin FeO(111) layer on Fe$_2$O$_3$ surface (Kurtz & Henrich 1983; Lad & Henrich 1988). Theoretical calculations using quantum mechanics (QM) has been a useful method to investigate the Fe$_2$O$_3$ surfaces. DFT calculations by Wang et al. revealed that the α-Fe$_2$O$_3$(0001) surface is expected to be terminated by 1/3 monolayer of Fe over the close-packed oxygen layer (Fe-O$_3$-Fe) only at low oxygen pressures, whilst a bulk-derived oxygen-terminated surface (O$_3$-Fe-Fe) becomes lower in energy at high pressures (Wang et al. 1998). However, the stability of termination depends strongly on chosen function in calculation (Adam & Tomasz 2012; Bergermayer et al. 2004; Huang et al. 2016). For example, Adam et al. find that the oxygen and ferryl terminated surfaces (O=Fe-O$_3$-) can be stable at high oxygen pressures using generalized gradient approximation (GGA), but not with GGA+U (Adam & Tomasz 2012). Additionally, the most recent investigation by Huang et al. reveals that the free energy of various terminations depends on DFT methods (Huang et al. 2016).

1.2.2 Wüstite surface

On iron or steel surface, the Wüstite surface is formed prior to the growth of other iron oxides. Recent experimental investigation by Lundgren at al. reported that the grains of Fe$_{1-x}$O(100) were formed via the oxidation of metallic Fe grains on Ag(100) at 623 K and oxygen partial pressure of 2×10$^{-7}$ mbar (Merte et al. 2015). In another experimental work, Abreu et al. showed that the growth of FeO(100) can be achieved at temperature of 773 K and oxygen partial pressure ranging from 5×10$^{-8}$ to 1×10$^{-7}$ mbar (Abreu et al. 2014). However, the FeO(111) surface is generated when Fe is deposited on a single crystal metal surface such as Ag(100) (Merte et al. 2015) or Pt(111) (Lin & Nilius 2008) under a partial pressure of oxygen.

1.3 Adsorption of alkanes on metal and metal oxide surfaces

In lubrication, the adhesive strength between the lubricant’s molecules and the surfaces play a vital role in tribological performance. Several experimental and
theoretical investigations have been carried out to investigate the adsorption behaviour and adhesive strength of alkanes on metal and metal oxide surfaces.

1.3.1 Experimental investigations

Understanding the adsorption of \( n \)-alkanes on the metal and metal oxide surfaces is the topic which has attracted significant attentions from researchers. During the past few decades, experimental investigations using temperature programmed desorption and helium atom reflectivity (Slayton et al. 1995; Tait et al. 2006; Wetterer et al. 1998), along with theoretical studies using molecular dynamic (MD) method (Bolton et al. 1999; de Sainte Claire et al. 1997; Li & Choi 2007; San-miguel & Rodger 2001) have been routinely used to investigate the structural and dynamic properties of alkanes on the solid surfaces.

Experimental measurements reported that at low surface temperature (\( T_s < 200 \) K) \( n \)-alkanes physisorbed molecularly on metal (Cu(111), Pt(111), Au(111)) (Lei et al. 2004; Tait et al. 2006; Wetterer et al. 1998) and metal oxide (MgO(100), Al\(_2\)O\(_3\)) (Slayton et al. 1995; Tait et al. 2005) surfaces with their adsorption energies per additional methylene unit less than 15 kJ/mol. Furthermore, Lei et al. reported the larger desorption energies for linear alkanes compared to those obtained from cyclic alkanes due to the effect of end group CH\(_3\) (Lei et al. 2004). \( n \)-Alkanes bind more weakly on MgO(100) than on graphitic C(0001) and Pt(111), and the desorption energies increase from about 12 to 46 kJ/mol on MgO(100) and from about 15 to 80 kJ/mol on Pt(111) (Tait et al. 2005; Tait et al. 2006). Although many researches have been carried out for metal and metal oxide surfaces, not many experimental investigation of adsorption of alkane on iron and iron oxide have been performed.

For short linear alkanes \( C_nH_{2n+2} \) (\( 1 \leq n \leq 12 \)), the desorption energies can be approximated well by a linear expression with an incremental increase (\( \Delta E \)) of 5–7.5 kJ/mol for Au(111) surface (Wetterer et al. 1998). The source for this linear relationship is the flat- alignment of \( n \)-alkanes on these surfaces and each methyl group contributes a similar additive energy to the total adsorption energy. However, as shown in Figure 1.3, a non-linear dependence on chain length was observed for the entire range of chain lengths (\( 5 \leq n \leq 60 \)) on graphite (Paserba & Gellman 2001).
Experimental studies show that there is an activation of CH bonds of short alkanes such as methane by transition metal catalysts. A theoretical study of the oxidative addition of methane to an iron surface indicated the reaction was exothermic with an activation energy barrier of roughly 88 kJ/mol (Anderson 1977). This activation energy is lower for Ni and Pt, in particular, 51 kJ/mol for Ni(111) (Lee et al. 1986), 27 ± 5 kJ/mol for Ni(100) (Hamza & Madix 1987) and about 46 kJ/mol on Pt(110) (Szuromi et al. 1985).

At molecularly-adsorbed state, alkanes commonly interact weakly with metal oxides; however, an exceptional case has been observed for palladium oxide (PdO). Indeed, Weaver et al. indicated that n-alkanes chemisorbed on a well-defined PdO(101) surface has an activation energy for dissociation of 16 kJ/mol (Antony et al. 2012). The molecularly-adsorbed state in this case serves as the precursor to initial dissociation unlike other metal oxide surfaces where the dissociation is taken place by the collision of molecule with the surface (Weaver et al. 2014).
1.3.2 Theoretical investigations

Although there are many experimental observations of alkane on metal and metal oxide surfaces, the adsorption of this organic molecule on iron and its oxidised surfaces is still poorly understood (Azevedo & Teixeira 2003; Elsharkawy et al. 2000; Montmitonnet et al. 2000). A few attempts had been carried out to investigate the surface chemistry of C\textsubscript{2}H\textsubscript{6} on iron surface (Govender et al. 2013; Shustorovich & Bell 1991). However, these studies were limited to studies of ethane in partial coverage rather than a full coverage with longer alkanes. An MD simulation has been carried out by Li et al. to investigate the adsorption behaviour of normal alkanes on a relaxed α-Al\textsubscript{2}O\textsubscript{3} (0001) surface (Li & Choi 2007). There results agreed with previous experimental investigation that the adsorption energy per methyl group decreased with longer chain length, and the orientation of the adsorbed segments as well as the number of saturated carbons seem to be insensitive to the chain length.

For MD calculation, the force field plays a vital role in describing the structural and dynamic properties of the organic molecules, as well as their adsorption behaviour on the observed surfaces. For instance, by adopting linear alkanes adsorbed on an Al\textsubscript{2}O\textsubscript{3} surface, Bolton et al. found that using simple united-atom (UA) model resulted in a higher adsorption energy relative to explicit-atom (EA) model (Bolton et al. 1999). Moreover, they also disclosed that with the UA model \emph{n}-alkane preferred to slide between two adjacent rows of Al instead of lying directly above the Al rows as in the EA model. The difference in structural behaviour of alkane between UA and EA models could be due to the explicit steric effects of hydrogen atoms in the EA model.

Clearly, a reliable FF for the simulation model is therefore of paramount importance as it governs a proper interfacial behaviour of the organic molecules. Therefore, a realistic force field – condensed phase optimised molecular potentials for atomistic simulation studies COMPASS (Sun 1998) using explicit-atom model is applied for alkanes in this thesis. Additionally, over the last two decades, the FFs for alkanes, iron and iron oxides, such as FeO and Fe\textsubscript{2}O\textsubscript{3}, have been developed (Mendelev et al. 2003; Sun 1998; Zhao, L et al. 2007). Unfortunately, the FF that describes the interactions between alkane and iron as well as its oxide surfaces has not yet been optimized, as this is a particularly challenging task.
DFT could be used to predict precisely the crystal and interfacial properties of iron and its oxide surfaces (Jiang & Carter 2003; Liao & Carter 2010; Trainor et al. 2004), as well as the interactions between short chain alkanes, such as ethane or butane, on the metal surfaces (Govender et al. 2013; Morikawa et al. 2004). Nevertheless, the high computational cost of DFT leads to a simulation model limited to either using shorter chain alkanes or a smaller number of molecules. To overcome this problem attempts have been made using DFT calculation to derive the FF for the interactions between longer chain alkanes and the inorganic surfaces (Bolton et al. 1999; Kong et al. 2009).

In practice alkane based lubricant has played a vital role in metal forming where there is a presence of iron and its oxides. However a thorough understanding of adsorption of alkanes on these surfaces is still lacking. The interest in the tribological performance of alkanes on steel surfaces has motivated us to obtain an insight into its adsorption ability on iron and its oxide surfaces (Askwith et al. 1966; Kajdas et al. 2006; Montmitonnet et al. 2000). Thus, a theoretical study using MD simulation has been employed in the current work to investigate this issue.

1.4 Tribology performance of hydrocarbon lubricant

Alkanes have attracted numerous investigations in thin film lubrication because they possess desirable physical characteristics such as low friction (Jabbarzadeh et al. 2006), and high mechanical and thermal slip at the solid-fluid interfaces (Berro et al. 2011). A wall-induced layering of thin n-hexadecane film has been seen with walls separated by up to ~50 nm (Chan & Horn 1985); this layering structure and almost solid behaviour are beneficial in the most extreme conditions (Jabbarzadeh et al. 2007a).

The slip of shearing fluid in the thin film lubrication of n-alkanes against an adjacent solid wall has attracted the interest of many researchers because this phenomenon results in a remarkable tribological performance (Fillot et al. 2011; Jabbarzadeh et al. 2007b; Savio et al. 2012). Under nano-confinement the shear viscosity of lubricant increases by several orders of magnitude relative to the bulk value (Jabbarzadeh et al. 2006), and when sheared the viscosity also varies as a power function of the
shear rate, but the shear thinning occurs at a high shear rate (Jabbarzadeh et al. 2005).

Indeed, the tribological performance, structural and rheological properties, and transfer of thermal energy and momentum at the interfaces depend almost entirely on the nature of the lubricant, the types of the surface’s crystal plane, the strength of the solid-fluid adhesive, the surface corrugations, the film thickness and the loading pressure, as well as the sliding velocity. Therefore, a comprehensive review on the influences of these factors is necessary to elucidate their roles on thin film lubrication of hydrocarbon lubricant.

1.4.1 Lubricant film thickness

When the thin film was reduced to a thickness approximately the molecular dimension, the structure and rheological property of lubricant differ from its bulk condition. In a study of variation of film thickness and shear stress on the number of cyclohexane molecules, as shown in Figure 1.4, Tamura et al. revealed that there was not only a decrease in film thickness but there was also a decrease in the number of lubricant layers (Tamura et al. 1999). Moreover, their work also disclosed that the obtained shear stress increased for a decrease in the number of lubricant molecules.

![Figure 1.4 Variation of (a) film thicknesses; and (b) average shear stress with the number of cyclohexane molecules between smooth Fe(001) surfaces (Tamura et al. 1999).](image)
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Cui et al. addressed the influence of film thickness on molecular orientation and film density of dodecane between mica surfaces (Cui et al. 2001). Their results indicated that the further reduction in film thickness produced more parallel orientation between alkane chains and shearing direction. Furthermore, the thinner film yields a higher degree of ordering than thicker one. The film thickness affects significantly the rheological property of confined lubricant. In fact, Figure 1.5 demonstrates that a decrease in film thickness from five to three layers results in an increase of almost ten folds in shear viscosity (Jabbarzadeh et al. 2005).

Figure 1.5 Shear viscosities of different dodecane films confined between mica surfaces as a function of shear rate (Jabbarzadeh et al. 2005)

Under confined conditions, the thin alkane film’s behaviour differs from its bulk state due to the solid-like phenomenon (Gao et al. 1997, 2000). A glass transition characterized by an enormous increase in shear viscosity, the epitaxial ordering of surface-adjacent molecules, the density oscillation across the film thickness, and the interfacial velocity slip; all of which have been observed for linear alkanes (Jabbarzadeh et al. 2006). This phenomenon results in low friction, which is necessary for the performance of tribological systems (Jabbarzadeh et al. 2005; Jabbarzadeh et al. 2007b). This solid-like phenomenon becomes more significant when the thin film is subjected to severe conditions, especially when the film thickness goes below a few nanometers (Cui et al. 2001; Tamura et al. 1999). Additionally, interfacial slip decreases linearly as the thickness of the lubricant film increases (Fillot et al. 2011).
1.4.2 Molecular structure

1.4.2.1 Molecular chain length

The nature of lubricant plays a vital role in behaviour, lubrication performance, and rheological property of thin film. Jabbarzadeh et al. addressed the influence of molecular chain length by carried out a MD simulation using different hydrocarbon lubricants (C₄ to C₁₆) between rough sinusoidal walls (Jabbarzadeh et al. 2000). They revealed a substantial influence of molecular chain length on slip phenomenon at solid-fluid interfaces, particularly, when a longer chain length was used a larger slip-length was observed. This phenomenon is confirmed by a similar observation by Jeng et al. (Jeng et al. 2003).

Figure 1.6 Snapshots of n-alkane monolayer confined between counter asperities from (a) top view; and (b) side view (Zheng et al. 2013a).

Additionally, Sivebaek et al. found that the number of atoms contacting with the metal surfaces increased with the chain length. This therefore results in an increase in the wall-lubricant interaction energy as well as the cohesive energy in the lubricant (Sivebaek et al. 2004). However, the cohesive energy in the lubricant increased at a lower rate than at wall-lubricant interfaces. Moreover, the longer chain hydrocarbon tended to have a better boundary condition due to the higher viscosity. This agrees
with the finding from an investigation of the lubrication performance of \( n \)-alkanes in boundary lubrication by Zheng et al. who pointed out that a longer alkane chain length yielded a better anti-wear performance (Zheng et al. 2013a). The explanation for a better tribological performance of long alkane chains is due to the higher atomic mono-layer concentration on the asperity interface and the formation of molecular bridging as seen in Figure 1.6.

For a wider range of molecular lengths (20 to 1400 C atoms), as shown in Figure 1.7, Sivebaek et al. found that the shear stress was independent with molecular length except in case of \( \text{C}_{20} \text{H}_{42} \) which had a distinct lower stress value (Sivebaek et al. 2010). This propensity is consistent with that observed by Savio et al. who reported an increase of shear stress with the chain length up to 20 CH\text{X} groups, then remained roughly constant (Savio et al. 2012).

![Figure 1.7 Variation of shear stress as a function of the sliding velocity for different alkane chain lengths (Sivebaek et al. 2010)](image)

1.4.2.2 Molecular Branching

For molecular structure, besides the influence of chain length, the molecular branching also plays an important role. Experimental observation on the tribological properties of synthetic hydrocarbon oils, Muraki found that the shear stress increases with molecular branches (Muraki 1987). Tamura et al. compared the shear resistance of different types of hexane’s isomer such as cyclohexane, n-hexane, iso-hexane. They found that the branched methyl groups in the iso-hexane molecules resulted in a larger shear stress between the lubricant layers than others. The source
for this observation was the interlocking of branches between molecules (Tamura et al. 1999).

In an alternative approach, Jabbarzadeh et al. investigated the behaviour of thin lubricant films of six different molecules, mainly isomers of C\textsubscript{30} in Couette shear flow (Jabbarzadeh et al. 2002). They found that there was a weaker layering in the case of branched molecules than the linear one. The slip ratio at solid-liquid interfaces increased with the degree of branching. The viscosity of branched molecules was higher than that obtained from linear ones. The density profiles for five isomers of the C\textsubscript{30} molecule, as shown in Figure 1.8a, shows that the strongest layering for linear C\textsubscript{30} molecules occurs at the maxima and minima in the density oscillation near the wall. The oscillation was weakest for C\textsubscript{12}(C\textsubscript{3})\textsubscript{6} which has the largest degree of branching. Additionally, the slip ratio on the wall depends on the molecular degree of branching, and the highest slip is seen for C\textsubscript{12}(C\textsubscript{3})\textsubscript{6} lubricant whereas the lowest slip is found with n-C\textsubscript{30} (Figure 1.8b). Regarding molecular orientation, their results revealed that the branched molecules showed a smaller change in their orientation than linear one. However, a higher parallel alignment tendency was observed for linear alkanes. Furthermore, the branched molecules exhibit a higher shear viscosity but weaker shear thinning effect than the linear one.

![Figure 1.8](image_url)

**Figure 1.8** (a) Density profiles for different isomers of \textsubscript{30}H\textsubscript{62}; and (b) slip against the applied shear rate (Jabbarzadeh et al. 2002).
1.4.3 Surface properties

With regards to the influence of the tribo-pair, the surface structure, the relative orientation and sliding direction, and the wall-fluid adhesion strength have been shown to play vital roles in rheological and tribological properties of confined system. These factors are therefore reviewed in this section.

1.4.3.1 Interfacial adhesion strength

To date, the rapid development of experimental techniques such as the surface forces apparatus, the scanning probe microscopies, or atomic force microscopies has been capable to produce a vast amount of knowledge about interfacial adhesion at the molecular level. However, computer simulations cannot catch up with experimental development due to limitations in modelling. The calculations using QM can predict repulsion and dispersion energies between atoms. However, the expensive computation in QM to predict the dynamic behaviour has been constrained by models containing a few hundreds of atoms. MD simulation can handle a much larger model, but the interaction for each pair of atoms needs to be parameterized properly. In some cases, the force field parameters for lubricant and surface have been well optimized; however, the parameters for interactions between surface and lubricant are still lacking.

To overcome this, a simple assumption has been made by varying the interaction strength between fluid and surface. For example, Manias et al. had adjusted the wall-fluid interaction strength between atomically flat surface and the films of oligomers (Manias et al. 1993). They found that when a more attractive wall was used, a correlation between structural changes caused by shear and the change in flow behaviour of the confined system was observed. The slip at wall-fluid interfaces and between interfacial layers occurred in less attractive wall. When observed the density of complex fluid confined to nanoscale gaps, Cui et al. revealed that the stronger wall-fluid adhesion strength led to an increase in fluid density (Cui et al. 2001).

In an alternative research, Berro et al. addressed the influence of surface-lubricant interaction on the mechanical and thermal interfacial responses (Berro et al. 2010).
Using hexadecane base-oil and 5% zinc dithiophosphate (ZDDP) as an additive, they found that the mechanical slip at surface-lubricant interfaces reduced significantly due to increasing surface energy. The effect of Fe₂O₃ surface used in this model was described by the adhesive strength between this surface and lubricant. Different surface adhesion energies and potential corrugations thus corresponded to the different equivalent wall energies characterized by systematically increasing the strength of the (dispersion) attraction between lubricant and the surface. Their velocity profiles across the hexadecane film revealed that the interfacial slip was observed for low equivalent Lenard-Jones (L-J) wall energies (Figure 1.9a). They explained that the internal lubricant cohesion was stronger than that with the wall, so that the slip took place at the interface rather than inside the lubricant. A similar tendency had also been observed for mixed lubricant of hexadecane and ZDDP additive. Furthermore, the effect of the wall energy on mechanical and thermal slip was also addressed. They found that an increase in the wall energy affected the interfacial thermal resistance which is characterized by the thermal slip length in Figure 1.9b. This resulted in a general decrease in thermal slip and a decrease in the interfacial thermal resistance. In other words, the lubricant was easier to transfer the generated heat to the thermostat in the cases of high wall energies.

![Figure 1.9](image)

Figure 1.9 (a) Mechanical slip length; and (b) thermal slip length as a function of the equivalent wall energy (Berro et al. 2010).

By adjusting the lattice constant of cubic/face-centered-cubic canonical surfaces along with using different metal/metal oxide surfaces, Savio et al. analysed systematically the influence of atomic roughness (corrugation) and surface commensurability that were characterized by a surface interaction parameter ($\zeta_{\text{surf}}$).
They reported an almost linear decrease of interfacial slip with an increase in surface interaction parameter, whereas there was a nonlinear increase in shear stress. The shear stress reached a plateau when the surface interaction parameter increased beyond a critical value (Savio et al. 2012).

1.4.3.2 Surface structure

There are many factors contributing to surface friction such as normal load, shear rate, solid-liquid adhesive strength, but the surfaces roughness is a crucial factor. Kalyanasundaram et al. conducted a simple rough model with only one surface ledge at the bottom gold substrate (Figure 1.10a). Their results revealed that the ledge not only affected the structure organization of molecules immediately close to the solid interface, but it also created asymmetrical density profile of lubricant (Figure 1.10b) (Kalyanasundaram et al. 2009).

Figure 1.10 (a) A ledge (step) on the surface of the substrate with a height equal to one atomic layer was introduced parallel to the (110) direction; and (b) density profile of n-decane within the gap showing the non-uniform distribution of molecular medium due to the presence of the ledge (negative side of Y-position) (Kalyanasundaram et al. 2009).

Regarding the influence of roughness of only fraction of molecular diameter, Jabbarzadeh et al. had investigated the effect of structure, dynamic behaviour, and
rheology of film of dodecane between amorphous surfaces (Figure 1.11) (Jabbarzadeh et al. 2006, 2007b).

Figure 1.11 (a) A crystalline atomically smooth surface with fcc structure; and (b) a wall with amorphous atomic structure (Jabbarzadeh et al. 2006).

When the film thickness was larger than a critical value (2-layers), their results, as shown in Figure 1.12a, revealed that the shear viscosity between amorphous walls was lower than aligned crystalline surfaces (fcc–fcc). However, an interesting phenomenon was that the amorphous surfaces enhanced the fluid viscosity when the film thickness was reduced to this critical value (Figure 1.12b). Additionally, this kind of roughness also influenced the molecular structure of thin film. Particularly, although the roughness was only a fraction of a molecular diameter of the lubricant, it was sufficient to disrupt the formation of the molecular bridging and result in a lower friction.

Figure 1.12 Shear viscosities plotted against the shear rate for: (a) 6 layer film; and (b) 2 layer film (Jabbarzadeh et al. 2007b).
In another investigation, they observed the effect of the wall roughness on slip and rheological property of hexadecane film in Couette shear flow confined between two sinusoidal walls (Jabbarzadeh et al. 2000). They found that slip on the wall increased with an increase in roughness period as well as a decrease of roughness amplitude. Although their rough surface was created by sinusoidal function and did not resemble the practical surface, their findings had been employed for other later studies. As an example shown in Figure 1.13, Savio et al. had developed this model using wettable surfaces of CuO and Fe$_2$O$_3$ with one lower smoothed surface and another upper sinusoidal rough surface (Savio et al. 2013). This model was subjected to a high loading pressure which progressively reduced thin n-alkane film toward solid-body contact. Their results confirmed that the presence of nanometer-scale roughness frustrated the ordering of fluid molecules, but leading to high friction states. Additionally, the local film breakdown was observed when asperities came into contact which produced the higher shear stress.

![Figure 1.13 Typical 2D snap-shot of Savio's model with a lower smoothed surface and an upper sinusoidal rough one (Savio et al. 2013).](image-url)

However, they pointed out that this high shear stress was varied depending on the initial disposition of fluid in the valleys. When the fluid was equally distributed in the pockets (configuration I of Figure 1.14) the maximum friction was obtained since the lubricant pressure was not sufficient to separate the surfaces. In contrast, when it was not equally distributed in the asperities valleys (configuration J of Figure 1.14) the friction was reduced significantly due to the supporting ability of lubricant. Finally, other states featuring an intermediate frictional behaviour could also exist depending on the initial distribution of molecules in the film.
Figure 1.14 Shear stress and surface separation as a function of the quantity of n-hexadecane in the contact, for rough-smooth and smooth – smooth Fe$_2$O$_3$ walls (Savio et al. 2013).

In aforementioned studies, there is an asperity contact between two rough surfaces, but it was not be able to simulate the plastic deformation as well as the wear of the surfaces. The more advanced potentials of embedded-atom method (EAM) and Finnis–Sinclair embedded-atom method (EAM/FS) force field are a good solution of this issue. These force fields are better than L-J and Morse potentials in their ability to depict plastic deformation, atomic dislocation during the asperity contact in the wear of material. For example, Eder et al. employed this potential to perform the solid-solid contact with plastic transformation and material transfer under a range of applied load and different types of asperity such as semi-sphere, truncated cone, slanted pyramid covered with stearic acid lubricant as a monolayer (Eder et al. 2011) (Figure 1.15). When compared the contact area between these asperity types, they found that semi-sphere presented the highest contact area. However, the number of atoms in contact was independent on the asperity shape. Moreover, they also found that the longer two asperities were in contact, the larger the number of deserters was transferred to other asperity during contact.
Figure 1.15 Schematic representation of Eder’s nanotribological system with truncated cone asperity (Eder et al. 2011).

In another attempt, Zheng et al. addressed the effect of n-alkanes (Zheng et al. 2013a) (Figure 1.16). In this work, they concentrated more on behaviour of alkane around the asperity contact and also observed the plastic deformation as well as atomic transferring between two sinusoidal asperities. They pointed out that the alkane film was squeezed out when asperities came into contact and it formed a monolayer on the contacting surfaces to reduce partially direct contact between two asperities. As a consequence, it also reduced the friction during shear process. However, the ability in reducing friction force of different alkane chain lengths varied differently. This difference had already been discussed in section 1.4.2.1 of molecular chain length.

Figure 1.16 A snap shot of thin n-alkanes film confined between sinusoidal rough Fe(100) surfaces (Zheng et al. 2013a).
In the case without lubricant, Spijker et al. conducted wear simulations with a varied range of applied loads, surface roughness, and sliding velocities to observe the plastic deformation of the weak and full-adhesive solid surfaces during wear process (Spijker, P. et al. 2011). Basically, their model was more advanced than other previous works in improving roughness using a real surface using a modified version of the random midpoint displacement algorithm. In this study, they found that the contact area increased linearly with applied load, but this tendency was reversed for an increase in roughness. Furthermore, the contact area for the full adhesive cases was always larger than the cases with weak adhesion. Additionally, in a later work (Spijker, Peter et al. 2011), they revealed that the average CoF in the presence of weak adhesion increased with roughness, and surface topology played a crucial role in the actual amount of friction. Moreover, due to repetitive sliding the rough surfaces rapidly became flat and consequently the friction was reduced significantly (Figure 1.17a). The type of observed surfaces finally resembled a Swiss cheese flat with holes (Figure 1.17b, c).

![Figure 1.17](image_url)

Figure 1.17 (a) Relation between flatness and the CoF; (b) schematic representation of the flattening of a rough surface (depicted in 2D); and (c) flattening of rough surfaces was described as Swiss cheese profiles. The circles represent for holes on the surfaces, and dark and grey colours are upper and lower surfaces, respectively (Spijker, Peter et al. 2011).
Zheng et al. advanced further Spikjer’s model by adding a thin hexadecane film to cover the multi-asperity rough surface model (Zheng et al. 2013b). Their observation agreed with Spijker’s works, nevertheless, the flattening phenomenon and contact area were reduced with the presence of lubricant. They indicated that the lubricant film had a crucial role in reducing surface flattening as it generated more supporting force against the applied load.

1.4.4 Sliding conditions

1.4.4.1 Applied load

Although the applied load is a critical parameter in lubrication, the role of this physical component has not been addressed satisfactorily in the literature. In an effort to investigate the dependence of slip phenomenon on applied pressure of thin n-octane film between CuO surfaces, Fillot et al (Fillot et al. 2011) indicated that the slip increased linearly with applied load. Using Fe(100) surface, Zheng et al. considered the influence of applied load on the surface coverage of n-alkanes (C\textsubscript{8}-C\textsubscript{64}) and found that the surface coverage (number of saturated carbons) increased with applied load (Zheng et al. 2013a). Their work revealed an increase in lubricant density and the degree of ordering with applied load. In addition, when adopted a model of 3D multi-asperities rough surface, they disclosed an increase in friction force with applied load. The increase of asperity contact area with applied load was an explanation for this phenomenon. However, there was a decrease in CoF with an increase in applied load for the cases of lubricated systems (Zheng et al. 2013b).

1.4.4.2 Shear rate

The sliding velocity or shear rate affects significantly the rheological property of lubricant. Under confined and sheared condition, the actual shear rate is commonly lower than that applied on the surface due to the slip phenomenon at solid-fluid interfaces. Fillot et al disclosed that the slip increased nonlinearly with sliding velocity (Fillot et al. 2011). Indeed, this slip rose sharply when the sliding velocity was increased up to 1 m/s; however, a pure slip occurred when the sliding velocity exceeded this critical value.
The slip affects the apparent shear rate of lubricant such that the actual shear is much lower than the apparent one, and as a consequence the shear viscosity of lubricant under confined condition is an order of magnitude higher than that obtained from the bulk state (Jabbarzadeh et al. 2005; Jabbarzadeh et al. 2006, 2007a, 2007b; Jabbarzadeh & Tanner 2011). The exponential function could predict properly the correlation between the shear viscosity and shear rate. Furthermore, the onset of shear thinning regime in confined condition usually begins at a lower shear rate than that observed in bulk condition.

1.5 Experimental and theoretical investigation of aqueous copolymer lubricant

Hydrocarbon based lubricants have demonstrated impressive tribological performance in rolling. However, the surface cleanliness is poor due to lubricant residues remaining on the strip surface after rolling process. The alkane film sticks on the strip surface during annealing and produces the patches of the carbon residue which deteriorates the surface quality and weakens any coating or paint adhesion to the steel. Furthermore, in practice, the rolling fluid usually contains contaminants. Removing them usually leads to the loss of active lubricant so that the volume of active lubricant will be reduced. This issue results in an increase in the cost of rolling process.

Aqueous lubricants have been used widely in metalworking operations such as rolling, cutting, drawing and ironing, machining and others (Holmberg et al. 2003). These lubricants satisfy several product surface quality and cleanliness requirements such as high cooling capacity, high tribological performance, corrosion-inhibiting properties, and stability under operating conditions (Laemmle 1984). The environmental and economic advantages are also important factors that have attracted widespread commercial use of these lubricants. Water is limited as a metal working lubricant due to the low viscosity and high corrosive properties. To date many studies have shown that the lubrication and antiwear properties could be significantly improved by introducing organic surface-acting compositions, polymers, or copolymers to aqueous solution (Kosasih et al. 2014; Laemmle 1984; Lin et al. 2013). The fundamental understanding of aqueous lubricants by the experiment and
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advanced modelling have driven the efforts to improve the tribological performance of this solution.

1.5.1 Triblock copolymer

1.5.1.1 Molecular structure

Pluronic copolymer has been introduced as an aqueous metalworking lubricants (Kosasih et al. 2014; Laemmle 1984). This copolymer is a nonionic macromolecule which is constituted of both poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) blocks with different relative weight fractions. Depending on the molecular structure, this Pluronic copolymer can be classified into two types: the Pluronic L and R series. The normal L copolymer series consist of a central (PPO) block and two outer (PEO) blocks: \((\text{PEO})_n-(\text{PPO})_m-(\text{PEO})_n\) where \(n\) and \(m\) are the number of average degree of polymerization (Almgren et al. 1992). The reverse R series are in a contrasting sequence: \((\text{PPO})_n-(\text{PEO})_m-(\text{PPO})_n\) (Zhou & Chu 1994).

1.5.1.2 Cloud point

The behaviour of polymer containing PEO blocks is quite sensitive with temperature. In aqueous solution, this type of polymer shows a reverse relationship in lubricant solubility with temperature. It was found that the temperature rises up to a certain value, the polymer molecules become cloudy and separate from solution. This point of temperature is therefore defined as cloud point of solution. In practice, the cloud point of aqueous copolymer solution is measured at 1% of surfactant and in the range of temperature between 0°C and 100°C due to the change in phase of water.

In an effort to measure the cloud point for different PEO/PPO block copolymers, Alexandridis revealed that different copolymers had different cloud points, and a cloud point of 35°C has been measured for 17R2 (Alexandridis 1997). His results also showed that the cloud point increased with weight percentage of PEO block in copolymer molecule. For example, the cloud point increased from 24°C for 10% of PEO in L61 to 32°C and 58°C for L62 (20% of PEO) and L64 (40% of PEO), respectively. Additionally, for a same weight percentage of PEO block, the increase in molecular weight or lengths of the polymer blocks also resulted in an increase in cloud point of the solution.
1.5.1.3 Phase behaviour

As indicated above, the molecular structure of triblock copolymer contains two distinct parts: the hydrophilic PEO block and hydrophobic PPO block. The triblock copolymers are soluble in water due to the hydrophilic PEO block which forms the hydrogen bonding with water (Smith et al. 2000). In aqueous copolymer solution, this hydrogen bond is formed by an attractive interaction between a highly electronegative atom of oxygen and a hydrogen atom, which is covalently attached to another oxygen atom. The structure of this hydrogen bond could be expressed as ‘O—H…O’. It has been disclosed that an unimer of PEO polymer could be hydrated into the bulk aqueous phase at the free surface of water (Darvas et al. 2010). In contrast, PPO behaves as a hydrophobic part due to the additional methyl group which makes PPO block less soluble in water than PEO but more soluble in nonpolar solvents such as hydrocarbon solution (Hezaveh et al. 2011, 2012).

However, the phase behaviour of hydrophilic PEO block depends on the temperature and concentration of surfactant (Alexandridis 1997). The temperature dependence of hydrogen bond between oxygen of PEO block and hydrogen of water is the reason for this phenomenon (Yang & Sharma 2001). When the temperature increases above the cloud point, this bonding is broken and the solution forms two separate phases: the bulk aqueous solution and the cloudy phase of triblock copolymers.

For concentration dependence, when the concentration increases up to a certain value, the polymolecular aggregates becomes thermodynamically stable. The micelles are spontaneously formed in the solution. The concentration of copolymer at which this phenomenon happens is defined as critical micelle concentration (CMC). This behaviour was characterized by the aggregation of copolymer in the lubricant to form spherical micelle in which the hydrophobic blocks was within the core whereas the outer hydrophilic blocks exposed to the solvent(Alexandridis & Alan Hatton 1995). The measured temperature at this point is so called critical micellization temperature (CMT). Experimental investigation by Alexandridis and colleague revealed that CMC and CMT decrease with an increase in the copolymer PPO content or molecular weight. Moreover, the micelles had hydrodynamic radii of approximately 10 nm and the aggregation number of the micelles formed at high polymer concentration was determined to be 52 (Alexandridis & Alan Hatton 1995).
They explained that mechanism for this micellization is driven by entropy, and the free energy of micellization is mainly a function of the PPO block (Alexandridis et al. 1994).

In a study of the phase behaviour of Pluronics 25R2 [(PO)$_{22}$–(EO)$_{14}$–(PO)$_{22}$] and 25R4 [(PO)$_{19}$–(EO)$_{33}$–(PO)$_{19}$] in aqueous solution, D’Errico et al. revealed that there were only water-rich and copolymer-rich regimes in equilibrium when the temperature increased (D’Errico et al. 2004). However, as shown in Figure 1.18, there were different phases of 25R4 aqueous solution at different copolymer concentrations and temperatures. In water-rich solutions as denoted as L$_1$, the copolymers were dissolved as unimers at low temperatures and low copolymer concentrations. In the temperature range of 36-52°C and copolymer concentration of 47-52%, a small hexagonal phase (E) formed and was completely encircled as an “island” in the isotropic copolymer solution, L$_1$. The lamellar was formed as the copolymer concentration of 66-78%. An isotropic copolymer-rich liquid phase (L$_2$) formed at copolymer concentration of 82-98%. Finally, an extremely concentrated mixtures (>98%) are a paste.

Figure 1.18 Phase diagram of concentration versus temperature of the 25R4–aqueous solution. L$_1$ = isotropic water-rich solution phase, E = hexagonal LLC phase, W = water and D = lamellar LLC phase, L$_2$ = isotropic polymer-rich solution phase, P = paste-like polymer-rich phase (D’Errico et al. 2004).
1.5.2 Experimental investigations

1.5.2.1 Adsorption of triblock copolymer on the surface

To protect the tribo-surface during lubrication process, the surfactant adsorbs on the surface to form a protective layer. The adsorption behaviour of copolymer has shown many interesting structural behaviours. This attracts the interest of many researchers to carry out different experimental investigations about these behaviours.

An adsorption experimental investigation of Pluronic polyethylene (PE) 6200 and PE 6800 on hydrophobized silica surfaces using ellipsometry, Tiberg and colleagues showed that copolymers adsorbed onto the surface (Tiberg et al. 1991). The driving force for this adsorption seems to be a combined effect of the preferentially anchored PPO segments onto surface and the good solvency of hydrophilic PEO segments which extending away from the surface. For a number of Pluronic copolymers of a total molecular weight of about 15000 adsorbed on hydrophilic silica surface (Malmsten et al. 1992), a thin adsorbed layer with thicknesses of about 2-5 nm was found, and the adsorbed amount remained independent of temperature at temperatures above CMT. Moreover, they also found that the solution micellization affected significantly the adsorption at hydrophilic surfaces, whilst the hydrophobic surfaces were independent with this phenomenon.

Many attempts have been made to observe the adsorption behaviour of Pluronics L on hydrophobized coined surfaces such as gold and silver (Brandani & Stroeve 2003a, 2003b; Green et al. 1997; Liou & Tsay 2011). Brandani et al. revealed that a polymer brush has been observed on these surface with the adsorbed amounts go through a maximum near CMC (Brandani & Stroeve 2003a). Additionally, the micellar aggregated at the surface for a copolymer with a higher relative hydrophobic content whereas a uniform, monolayer-like morphology has been found for copolymers with higher hydrophilic content. Furthermore, when observed the kinetic behaviour of adsorption from solution of these triblock copolymers, they found that the higher hydrophobic content led to enhanced adsorption rates past CMC (Brandani & Stroeve 2003b). Liou and Tsay addressed the effects of molecular mass and PEO/PPO ratio on adsorption of this type of Pluronic (Liou & Tsay 2011). They
confirmed that the adsorbed amount of the copolymer increased with an increase in molar mass as well as with a decrease in the PEO/PPO ratio.

The adsorbed morphology of triblock copolymer is an interesting aspect. In an investigation of morphologies of Pluronic P105 (PEO<sub>37</sub>–PPO<sub>56</sub>–PEO<sub>37</sub>) on surfaces with different hydrophobicity, Liu et al. revealed that a monolayer has been observed on hydrophobic surfaces such as polypropylene (PP), poly(ethylene terephthalate), nylon, and graphite. In contrast, the micellar structures were observed on the hydrophilic silica surfaces of cellulose and silica (Liu et al. 2010). Li and colleges suggest that the micelles formed on the surface of PP and PE were collapsed and transformed into so-called hemi-micelles (Li et al. 2011; Li et al. 2012). Furthermore, they added that the configurations of the triblock copolymer were influenced by the nature of the substrate. A buoy–anchor–buoy (B–A–B) structure, as shown in Figure 1.19, was observed on the hydrophobic PP and PE surfaces, whereas an anchor–buoy–anchor (A–B–A) was proposed on the hydrophilic cellulose.

![Proposed molecular configurations of PEO<sub>19</sub>–PPO<sub>29</sub>–PEO<sub>19</sub> molecules on PP, PE, and cellulose surfaces. Hemimicelles are present on PP and PE surfaces resembling a BAB structure, whilst flat micelles are present on cellulose surface resembling a A–B–A structure (Li et al. 2011).](image)

Although there have been extensive investigations of adsorption of normal Pluronics; however, to the best of our knowledge, very few studies were carried for reverse triblock copolymers. Recently, in an effort to investigate the mechanism of lubrication
performance of reverse Pluronics, Lin et al. used the neutron reflectometry to investigate the adsorbed film structure of 17R2 and 17R4 on Ti coated surface with and without the presence of phosphate ester additive (Lin et al. 2015). They revealed that the Ti coated surface behaved as a hydrophobic surface where the PPO content formed the inner layer and acted as the anchor of the adsorbed film to form an A–B–A structure. This structural behaviour is in contrast with that observed for normal Pluronics on gold (Brandani & Stroeve 2003a, 2003b; Liou & Tsay 2011) and silver (Green et al. 1997) surfaces. Additionally, the measured thickness of this layer was 1.8 nm and 0.5 nm for 17R2 and 17R4, respectively. However, a thicker layer of PEO content of 2.1 nm has been found for 17R4 compared to 1.0 nm for 17R2. Furthermore, they reported that the presence of phosphate ester additive in the solution, as shown in Figure 1.20, affected the adsorbed film structure of copolymer by forming a thicker mixed-layer of PPO and phosphate ester on the Ti surface.

![Figure 1.20 Molecular configurations and adsorbed 17R2 film thickness on Ti coated surface from neutron reflectometry (Lin et al. 2015).](image)

**1.5.2.2 Tribological performance**

As triblock copolymers are developed as a surfactant applied for lubrication, their tribological performance is the object of many researchers. In an effort to improve the strip cleanliness, an easy-cleaning lubricant of aqueous PPO–PEO–PPO triblock copolymer lubricant has been introduced by Laemmle (Laemmle 1984). His experimental work demonstrated that this lubricant was suitable for both hot and cold rolling of aluminium and aluminium alloy material.
Lee et al. investigated the lubrication effect of normal Pluronic copolymers onto poly(dimethylsiloxane) (PDMS) surfaces (Lee et al. 2004). They found that the degree of lubrication was strongly correlated with the structural features of the PEO–PPO–PEO copolymers, and that the higher the PPO molecular weight, the better the lubrication properties. Moreover, the PEO block could also affect the lubrication. It has been reported that a greater amount of adsorbed PEO block also contributes to better lubrication. To explain this observation, they proposed that PEO block facilitated the entrainment of the lubricant into the contact area between PDMS surfaces.

Recently, Kosasih and colleagues (Kosasih et al. 2014; Lin et al. 2015) studied the tribological performance of both normal and reverse Pluronic lubricants on steel surface in cold rolling. They found that the tribological performance of tribo-system was sensitive to temperature. Indeed, it was observed that the friction of tribo-system increased when the temperature exceeded the cloud point of lubricant. The reason for this phenomenon was due to the destruction of adsorbed film when the temperature of aqueous copolymer solutions increased. This resulted in a high friction and a severe wear during the wear test. However, with the presence of phosphate ester additive into the triblock copolymer solution, the tribo-system was improved in the tribological performance (Lin et al. 2015). Additionally, using similar amount of PEO and PPO blocks in molecular structure of triblock copolymers, they compared the tribological performance of between normal (PPO$_{14}$–PEO$_{24}$–PPO$_{14}$) and reverse (PEO$_{13}$–PPO$_{30}$–PEO$_{13}$) Pluronics. The obtained results showed that the dynamics CoF and the amount of volume loss of steel surface were lower for normal Pluronics compared to reverse ones. When considered the influence of PPO/PEO ratio on tribological performance of this tribo-system, they found that an increase in PPO/PEO ratio resulted in a decrease in CoF for reverse Pluronic (PPO$_{21}$–PEO$_{14}$–PPO$_{21}$), whilst it was insensitive to a normal triblock copolymer of PEO$_{6}$–PPO$_{34}$–PEO$_{6}$.

1.5.3 Theoretical investigations

The mesoscale structures of triblock copolymer have a dimension of a few nm and are formed in a few milliseconds (Li et al. 2009), so it is very difficult to determine their growth mechanism experimentally. Hence, the computer simulations have also
been used to investigate the amphiphilic triblock copolymers by both MD and mesoscopic dynamics methods. The brief introduction of methodologies, advantages, limitations, as well as the researching object of each method is discussed in following sections.

1.5.3.1 Mesoscopic dynamics

To the best of our knowledge, the coarse-grained simulation method is commonly used in simulation investigations about Pluronic aqueous solutions. This method is based on the mean-field DFT, and it uses an idealised Gaussian chain that has the same response functions as the “real” molecular chain and specifies the interaction between each species to represent the polymer chains. Each bead is of a certain component type representing covalently bonded groups of atoms, and different beads correspond to different components in the block copolymer (Li et al. 2009).

This method provides a deeper understanding on aggregation formation and the structural behaviour of Pluronic at equilibrium, especially for aggregation formation rate, which is difficult to observe directly by experiment (Li et al. 2009). For example, using mesoscopic dynamics simulation of the binary mixture of triblock copolymer P123 (PEO<sub>20</sub>—PPO<sub>70</sub>—PEO<sub>20</sub>) and water, Zhao et al. discovered the intrinsic feature of various aggregation structure of P123 in water including micelle, hexagonal, and lamellar phases, which could partly reproduce most experimental phase regimes (Zhao, Y et al. 2007). These observations were confirmed by by Li et al. who observed the aggregation behaviour of Pluronic copolymer L64 (PEO<sub>13</sub>—PPO<sub>30</sub>—PEO<sub>13</sub>) and P85 (PEO<sub>26</sub>—PPO<sub>40</sub>—PEO<sub>26</sub>) solutions in the presence of sodium dodecyl sulfate (SDS) (Li et al. 2009). They also showed that the presence of SDS resulted in a micelle formation at a lower concentration compared to the case without this compound. Furthermore, a transition from spherical micelles → rod-like micelles → bicontinuous phases has been found for an increase of copolymer concentration (Figure 1.21). Bedrov et al. conducted a simulations of L64 Pluronic micelles in aqueous solutions and revealed that L64 micelles had a scalene ellipsoidal shape rather than spherical (Bedrov et al. 2007). Moreover, an average aggregation number of approximately 40 chains per micelle had been measured at 298K. This value was within the range between 25 and 70 chains of aggregation.
numbers reported for L64 micelles in water measured by experiment (Almgren et al. 1995).

The temperature, PEO/PPO ratio, and shear play a vital role on phase behaviour of copolymer. Particularly, the formation of aggregates has been found to be more difficult and the formation rate decreased with an increase in temperature. The source for this effects of temperature is that PEO and PPO become more hydrophobic at increasing temperature; hence, their solubilities in aqueous solution decreases (Guo et al. 2002). On the influence of PEO/PPO ratio, Li et al. revealed that a higher PEO/PPO ratio value yielded a larger size of micelle (Li et al. 2009). Their results agree well with a theoretical work by Guo et al. and experimental work of Alexandridis and co-workers (Alexandridis 1997). Yang et al. adopted a solution of Pluronic copolymers with small PEO/PPO ratio such as P103 (PEO₁₇—PPO₆₀—PEO₁₇), P84 (PEO₁₉—PPO₄₃—PEO₁₉), and P65 (PEO₁₉—PPO₂₉—PEO₁₉) to observe the phase separation at low concentration. Their simulated results indicated that, with an increase of the concentration, the micellar phases changed from spherical micelles and micellar clusters to disk-like micelles for the P103 and P84 solutions (Figure 1.22a, d, e and f), and from spherical micelles to worm-like micelles for the P65 solution (Figure 1.22a, b and c) (Yang et al. 2008).

![Figure 1.21 Phase diagram of L64 in aqueous solution with triblock copolymer concentration at 298K (PM, M, RM, B and L denote regions for premicellar, micellar, rod-like micellar, bicontinuous, and lamellar phase, respectively, and green colour denotes PPO isosurface) (Li et al. 2009).]
Zhao et al. addressed the effect of shear on structural properties of micelle and found that different phases could be obtained at various shear rates for the same concentration (Figure 1.23). Additionally, they also reported that the lamellar phases were found for different shear rates and copolymer concentration higher than 30% (Zhao, Y et al. 2007). In an attempt to investigate the effect of adsorbing (hydrophobic) and nonadsorbing (hydrophilic) solid surfaces in contact with aqueous solutions of the polymer, Liu et al. addressed the influence of confined shear on the formation of aggregates of copolymer (Liu, H et al. 2012). They pointed out that the formation of micelles subjected to a confinement between hydrophilic surfaces took place faster than in bulk aqueous solution, whilst a layering structure assemble has been observed for hydrophobic surfaces. Additionally, they presented a new finding that Pluronics acted as a boundary lubricant for hydrophobic surfaces but not for hydrophilic ones.

![Schematic representation of different micelles with increasing concentration](image)

**Figure 1.22** Schematic representation of different micelles with increasing concentration (Yang et al. 2008). (a) Monomers, (b) spherical micelles of P65; (c) worm-like micelles of P65; (d) big-core-size spherical micelles of P103/P84; (e) micellar clusters due to coalescence of spherical micelles; (f) conjugated disk-like micelles.
Although this coarse grained method can be considered as an adjunct to experimentation and can provide mesoscopic information otherwise inaccessible from experimentation, there are still many limitations on investigations using this method. For instance, this method does not consider all the physical details in the polymer/water system such as intra-molecular interactions (bond, angle, dihedral, and improper), intermolecular (van der Waals (vdW), and hydrogen bonding), and electric polarization of polymer and water molecules. Furthermore, the tribological and rheological properties of confined aqueous copolymer lubricant such as friction and viscosity have not been revealed yet.

![Micelle formation](image)

Figure 1.23 Influence of shear rate on morphologies of micelle formation of 45% P123 in water solution at: (a) 0, (b) $10^2$, (c) $10^3$, (d) $10^4$, (e) $10^5$, and (f) $10^6$ (s$^{-1}$) (Zhao et al. 2007).

### 1.5.3.2 Molecular dynamics

The fully atomistic dynamics can calculate the underlying atomic level interactions and hydrogen bonding between copolymers and water molecules. Over the last two decades, the MD simulation of PEO and PPO polymers has been developed progressively. Some initial efforts had been made to develop a force field for these polymers by adopting their monomer chains such as 1,2-dimethoxyethane (1,2—DME) (Smith et al. 1993) and 1,2-dimethoxypropane (1,2—DMP) (Smith et al. 1998) that derived from ab initio electronic structure calculations. Bedrov et al. adopted a model of 1,2—DME in water solution to address the hydrogen bonding between 1,2—DME and water molecules as well as the influence of polarization. However, this quantum chemistry-based force field for PEO and its oligomers in aqueous solution described improperly the hydrophobic binding of water to the ether.
An attempt has been made by Bedrov et al. to revised this force field, and they proved that the updated force field yielded a good agreement with experiment for excess free energy, enthalpy, and volume as well as excess solution viscosity and the self-diffusion of water (Bedrov et al. 1998). Furthermore, in another effort they disclosed that this revised force field can predict the structural and conformational properties of PEO/water, PPO/water, and PPO/PEO/water solutions (Bedrov et al. 2006; Starovoytov et al. 2011).

Although the all-atom model can include all the physical details in the polymer/water system but a higher degrees of freedom is computationally expensive, and it has restricted the use of a large model. An alternative approach using united atoms (UA) model has been widely adopted in MD simulation due to its convenience in reducing the degrees of freedom. The UA force field such as transferable potentials for phase equilibria-united atom (TraPPE-UA) has been developed for this purpose (Fischer et al. 2008; Stubbs et al. 2004). Using this force field, Pal et al. studied the structural properties of a PEO chain in bulk aqueous solution, at the water/vacuum interface and indicated that the PEO chain preferred to penetrate into the aqueous solution from water/vacuum interface due to the amphiphilic nature of PEO (Pal et al. 2006). This observation was confirmed by the work of Darvas et al. who provided details information of penetration structure of PEO polymer. Indeed, as shown in Figure 1.24, they found that the majority (82%) of PEO were immersed into the bulk liquid
phase, 17% of polymer were anchored at the water/vacuum interface, whilst only 1% penetrated into the vacuum space (Darvas et al. 2010).

In an investigation of conformation and dynamics properties of Pluronic P85 at infinite dilution condition in water, methanol, chloroform, carbon tetrachloride, and n-heptane, Hezaveh et al. revealed that in the case of non-polar solvents such as heptane and carbon tetrachloride the polymer chains tend to become more compact than in polar solvents such as chloroform, methanol, and water due to the lower solubility (Hezaveh et al. 2012). The good solvent behaviour of the chloroform is an exception due to the hydrogen bonding between PEO chains and the solvent molecules.

The adsorption behaviour of triblock copolymer on to solid surfaces using MD simulation has also been addressed. Li et al. carried out an investigation of association of a symmetric P65 triblock copolymer adsorbed from aqueous solutions onto PP, PE, and cellulose surfaces using COMPASS force field. They reported a higher affinity of PEO block with the cellulose surfaces compared to the PPO block, whilst the PPO block had a higher affinity with PP and PE. Moreover, the configurations of the triblock copolymer were found to be affected by the nature of the substrate: a B–A–B structure on the hydrophobic PP and PE is expected, while an A–B–A structure was proposed on the hydrophilic cellulose (Li et al. 2012).

Figure 1.25 Schematic illustration of coated like layer of PEO onto 3D rough iron surfaces during the boundary lubrication (Zhu et al. 2015).
Recently, an effort has been made to investigate the lubrication performance of PEO aqueous lubricant in boundary lubrication of 3D rough and charged surfaces (Zhu et al. 2015). It has been found that, as shown in Figure 1.25, the charged tribo-surface attracts the polar PEO molecules to form a coated like layer that separate the positive charged sliding surfaces and reduced the direct asperity contact.

1.6 Gap of current knowledge

1.6.1 Hydrocarbon lubricants

Hydrocarbon based lubricants play an important role in the metal forming of steel materials (Askwith et al. 1966; Kajdas et al. 2006; Montmitonnet et al. 2000), where iron oxides are formed on the surface of the products. Over the last two decades, there have been extensive studies of thin film lubrication of alkane between metal tribo-pairs using MD method (Jabbarzadeh & Tanner 2011; Martini & Vadakkepatt 2010; Tamura et al. 1999). Attempts have been made to assess the role of Fe₂O₃(001) surfaces in thin film lubrication (Berro et al. 2010; Ewen et al. 2016; Savio et al. 2013; Savio et al. 2012); however, a thorough understanding of tribological and structural properties of hexadecane on different iron and iron oxides surfaces as well as their surface orientations is still missing. Additionally, previous investigations employed a simple model in which each methyl or methylene group was described using a UA model and tribo-surfaces was modelled by harmonic spring without a proper consideration of electrostatic contribution. The literature reveals that using a UA model for alkane yields an interfacial molecular structure different from EA models (Bolton et al. 1999). Moreover, a reliable interaction potential between alkanes and the tribo-surface is still lacking due to the limited experimental data and a systematic parameterization. Therefore, a comprehensive study has been carried out in this work using EA model for alkanes with a reliable force field derived from quantum calculations, to investigate the influence of oxidized state of iron surface on adsorption ability of alkanes (Chapter 3) as well as its tribological performance (Chapters 4-5).

Under confinement the actual shear rate of fluid is usually lower than that applied onto the surfaces due to slip at the solid-liquid interfaces (Savio et al. 2012), so the viscosity is normally higher and has a complex propensity. Reviews of the
The UA model is widely used to simulate thin film lubrication for linear alkanes (Berro et al. 2011; Jabbarzadeh et al. 2006; Savio et al. 2012; Tamura et al. 1999), it could yield an improper structural behaviour at the solid surface because it lacks the steric interaction induced by hydrogen (Bolton et al. 1999). The phase behaviour of confined shear liquid has been taken at extreme conditions using MD simulation (Gattinoni et al. 2013; Heyes et al. 2012; Martinie & Vergne 2016); however, the tribological performance nor rheological property of polymeric lubricant is not well understood up to now. The simple L-J liquid was considered in these investigations. It appears that the CoFs increase steadily with sliding velocity in liquid state for monatomic systems (Gattinoni et al. 2013). Additionally, experimental observations in elastohydrodynamic lubrication revealed an increase in viscosity and shear stress of different base oil lubricants with loading pressure (Bair & Winer 1982, 1992). The validity of these propensities for polymeric lubricant can be questioned. Moreover, the key factor which results in a high viscosity lubricant under nano-confinement is a solid-like behaviour characterised by ordering the lubricant molecules adjacent to the solid surfaces. The degree of ordering is defined as the maximum density at the solid-fluid interfaces, it increases with the applied load and decreases as the film thickness and surface corrugations increase (Jabbarzadeh et al. 2006; Zheng et al. 2013a); however, the shear rate-induced ordering of lubricant has yet to be revealed.
Therefore, an advanced conventional force field known as the condensed COMPASS is used to investigate how the sliding conditions affect the behaviour and shear viscosity of lubricant over a wide range of applied pressure, shear rate as well as surface temperature. Although the thin film lubrication of alkanes has been well established at bulk condition in the literature, the dependence of viscosity-shear rate \((\eta - \dot{\gamma})\) curves on the temperature and pressure-invariant under confined condition has yet to be discussed in detail and presented in Chapter 4.

### 1.6.2 Aqueous copolymer lubricant

The lubrication performance of normal and reverse Pluronic copolymers has been experimentally investigated (Kosasih et al. 2014; Lee et al. 2004; Lin et al. 2013; Lin et al. 2015), which reveals a vital role of molecular architecture of the copolymer. In aqueous solution the PPO block is the major constituent that reduces the friction such that a better lubrication performance is achieved with a higher PPO molecular weight (Lee et al. 2004). Moreover, an increase of copolymer concentration also improved remarkably the lubrication performance of the aqueous copolymer lubricant (Lin et al. 2013). Although Pluronic aqueous copolymer solution is a promising lubricant to apply in cold rolling where the mixed lubrication regime is present (Wilson 1997). However, the theoretical investigation of this lubricant at this regime is still limited. Furthermore, the structural properties of reverse Pluronic copolymer under mixed lubrication still have not been investigated.

Due to the slow kinetic of formation and relatively large dimension of the triblock copolymers, the simulation of Pluronic copolymer has been restricted to mean field DFT approach (MesoDyn) (Liu, H et al. 2012; Yang et al. 2008). Therefore, the ability to incorporate important atomistic scale phenomena (i.e., hydrogen bonding, changes in hydration structure, hydrophobic interactions, local conformation, solvent clustering, etc.) in these systems are very limited. Polyethylene oxide polymer was simulated by MD to investigate the tribosurface charge and polar molecules on friction and lubrication during compression and sliding, but it is limited to short chain PEO polymer (Zhu et al. 2015). An attempt has been made by adopting a fully atomistic model in which the water–water and water–copolymer hydrogen bonds were included to investigate the effects of temperature and concentration on the structure of Pluronic P65 in aqueous solution (Dong, S et al. 2011). However, a
theoretical study at atomic scale of tribological performance of reverse Pluronic copolymer in aqueous solution is still missing.

Furthermore, there has not much research on new aqueous PPO-PEO-PPO copolymer-based rolling lubricant. It is necessary to fundamentally understand adsorption behaviour and tribological performance of this lubricant before it is widely applied in industries. Therefore, a systematic investigation of adsorption and tribological performance of reverse triblock copolymer in aqueous solution has been carried out in this thesis. The study will be at atomic scale using MD simulation with a consideration of aforementioned atomistic scale phenomena. The roles of copolymer concentration and applied pressure on adsorbility of copolymer as well as the mechanism of its lubrication performance in boundary regimes will be presented in Chapter 6.
Chapter 2 Numerical model

In this chapter, the basic knowledges about DFT and MD methods are reviewed. The establishment of numerical models and methodology of these methods are described. A force field parameterization to derive a new potential for the interactions between surface and fluid’s has also been introduced. Finally, the simulation procedure along with setting parameters for DFT and MD calculations are provided in details.

2.1 Molecular dynamics algorithm

The classical MD simulation physically captures the motion of each atom in complex geometry like nano-crystalline solid and liquid. The Newton’s equations of motion for all interacting atoms in the molecular system are described by following equations.

\[ m_i \frac{\partial^2 \vec{r}_i}{\partial t^2} = \vec{F}_i \]  

(2.1)

where \( \vec{r}_i \) and \( \vec{F}_i \) are the position of the \( i^{th} \) atom and the force acting on this considered system, respectively. The force acting on each atom is thus determined as the gradient of the interatomic interaction potential energy \( (V) \).

\[ \vec{F}_i = -\frac{\partial V(\vec{r}_i, ..., \vec{r}_N)}{\partial \vec{r}_i} \]  

(2.2)

2.2 Density functional theory

A computational chemistry method using DFT has been used in this thesis to predict the adsorption of butane, oligomers of PEO and PPO polymers, as well as water on iron and iron oxide surface. DFT has been the most popular and versatile approach to finding solutions to the fundamental equation in physics, chemistry and materials science. It facilitates the investigation of the electronic structure of many-body systems, in individual atoms, particular molecules, and the condensed phases. The low computational costs relative to traditional methods, such as Hartree–Fock theory and its descendants based on the complex wave function have prompted the wide application of DFT calculation in theoretical and computational science. In this approach, the properties of a many-electron system can be determined by using
functions of electron density. The basic concept of QM that supports DFT is introduced briefly in Appendix A.

2.3 Establishment of model and methodology

2.3.1 Model for DFT calculation

All DFT calculations were performed by the DMol3 simulation package using the unrestricted Kohn–Sham method (Delley 1990, 2000). For all atoms in the systems, an accurate density functional semi-core pseudopotentials (DSPP)(Delley 2002) was employed for the core treatment in which the local pseudopotential was applied for Fe atoms while a whole electronic basis set was used for C, H, and O. The DFT reference data for validation of the interfacial FF between butane (C₄H₁₀) with iron and iron oxide surfaces were obtained using GGA of Perdew–Burke–Ernzerh(PBE) (Perdew 1996) of functional, while the PBE functional in conjunction with the vdW correction of Tkatchenko–Scheffler (TS) (Tkatchenko & Scheffler 2009) were employed for the surface relaxation. A real understanding of adsorption of butane on a surface can only be obtained from a properly balance of all interactions. Therefore, the DFT calculations including the long-range dispersion correction (DFT-D) using TS and Grimme (G06) (Grimme 2006) schemes were also taken into account to assess the role of long-range vdW interactions. The double numerical plus polarization basis set (DNP) associated with an automatic generation of k-points using a Monkhorst–Pack and dipole corrections along the surface normal direction were applied throughout. A convergence criterion of 10⁻⁵ Ha was applied in all geometry optimizations. Additionally, the model were periodically repeated in the three Cartesian directions to avoid the edge effects leading to a charge localization of the surfaces (Kong et al. 2009).

2.3.1.1 Relaxation of Fe(110), FeO(110), and Fe₂O₃(0001) Surfaces

For the surface, the interfacial structure differs from its bulk due to the propensity of atomic rearrangement in which the interfacial atoms will be allocated at the lowest energy positions. There is not only the changing in structure but also a decrease of atomic charges at interface due to the breaking of bonding. The classical FF for inorganic compounds are often not available or exhibit a large deviation relative to
known surface properties (Heinz et al. 2013). Furthermore, the surface relaxation affected the adsorption of the organic molecules on the solid surfaces (Bolton et al. 1999; Li & Choi 2007). Therefore an appropriate relaxation was carried out to obtain realistic interfacial properties using DFT geometry optimizations. The atomic charges for interfacial atoms were derived from the calculation of electronic population analysis using Mulliken partitioning scheme (Mulliken 1955a, 1955b).

For iron, the (110) surface of body-centered-cubic (bcc) structure is known as the most thermodynamically stable surface (Rufael et al. 1997); hence, this plane is utilized in this study. For iron oxides, there is several iron oxide compounds depend on the oxidation state of iron. In nature, FeO, Fe$_2$O$_3$, and Fe$_3$O$_4$ are three widespread iron oxides. While Fe$_2$O$_3$ and Fe$_3$O$_4$ can be found at low temperature, FeO is only formed at the temperature higher than 570°C. However, a theoretical investigation was carried out in the current work to observe the adsorption of $n$-alkanes on FeO and Fe$_2$O$_3$ surfaces at low temperature. Li et al. indicated that the (110) surface of FeO with a rock-salt structure was the lowest surface energy (Li et al. 2005). Regarding the Fe$_2$O$_3$ surface, from a geochemical point of view, α–Fe$_2$O$_3$ is one of the important oxides. Additionally, the experimental and theoretical works revealed that the single-layer iron-termination of Fe$_2$O$_3$ (0001) was the most stable surface configuration (Chambers & Yi 1999; Trainor et al. 2004; X.-G. Wang 1998). These oxide surfaces were therefore also utilized in the current work.

The surface models were constructed as slabs that were repeated under periodic boundary condition with an added vacuum layer of 20 Å in perpendicular to the surface to prevent any interaction between periodic images in this direction. These surfaces were cleaved from their optimized crystal structures with the atomic layer thicknesses of 6, 5, and 18 layers, which correspond with the number of constituted atoms of 31, 39, and 46 for Fe(110), FeO(110), and Fe$_2$O$_3$(0001), respectively. The first three layers of Fe(110) and FeO(110), and nine layers of Fe$_2$O$_3$(0001) were relaxed while the rest was constrained in their bulk structure as shown in Figure 2.1.
2.3.1.2 Adsorption of $\text{C}_4\text{H}_{10}$ on Fe(110), FeO(110), and Fe$_2$O$_3$(0001)

The substrates were constituted as slabs of two atomic layers for Fe(110) and FeO(110), and two repeat units consisted of six atomic layers for Fe$_2$O$_3$(0001). In addition, a vacuum of 20 Å was also added on these substrates. As seen in Figure 2.2 these slabs were consisted of 2x2 surface unit cell for Fe(110) and FeO(110), and 1x1 for Fe$_2$O$_3$(0001). The first layer of the slabs was relaxed, whereas the rest was constrained to their bulk crystal structure. The total atoms for the model were 39 atoms for Fe(110) and FeO(110), and 41 atoms for $\alpha$–Fe$_2$O$_3$.
For butane, the anticonformer was the most stable conformational geometry (Woller & Garbisch 1972). Experimental and theoretical investigations indicated that \( n \)-alkane was oriented with its molecular planes containing the skeletal carbons aligned parallel to the surfaces (Morikawa et al. 2004; Wetterer et al. 1998). Therefore, a surface-parallel molecular plane \( C-C-C \) configuration along with a symmetry configuration of butane was adopted for training configurations. These configurations were allocated at the interaction sites on the top and between the atomic rows as illustrated in Figure 2.2. For a FF fitting calculation, more than one input structure should be used. Although choosing initial training configurations for interfacial FF parameterization is arbitrary. However, with four chosen training configurations for each surface we expect that the obtained parameters could predict qualitatively the interaction strength between butane and Fe(110), FeO(110), as well as Fe\(_2\)O\(_3\)(0001) surfaces. The structural parameters of butane on these surfaces were optimized with a constraint whereby the molecule only moved along the direction perpendicular to the surface plane. The adsorption energies \( E_{ads} \) were evaluated as the difference
between the sum of total energies for isolated butane \((E_{\text{butane}})\) and bare surfaces \((E_{\text{surface}})\) with those of adsorbed alkane and surface systems \((E_{\text{butane+surface}})\) as given in following equation:

\[
E_{\text{ads}} = E_{\text{butane+surface}} - (E_{\text{surface}} + E_{\text{butane}}) \tag{2.3}
\]

### 2.3.1.3 Adsorption of 1,2–DME, 1,2–DMP, and water on Fe(110)

A frozen periodic iron substrate of \(p(4\times4)\) including 41 atoms was utilized to ensure that the number of atoms in substrate was acceptable to achieve a stable bond energy per atom. A vacuum of 20 Å was added in the direction perpendicular to the surface to neglect the interactions between the original system and its images in this direction. For copolymer, we expected to handle a long molecule; however, owing to the technical reasons that hamper the calculation of adsorption of the whole chain of triblock copolymer, only dimethyl ether (DME) and the smallest oligomers (monomers) of PEO and PPO polymers, i.e. 1,2–DME and 1,2–DMP were used for parameterizing the interactions between the copolymer and iron surface (Hezaveh et al. 2011). The detailed description of DFT calculation had been described in a previous study.

As illustrated in Figure 2.3, two carbon symmetry configurations of DME (Borodin et al. 2003), are utilized to determine the relative interaction strengths of hydrophobic part (CH\(_3\) groups) and hydrophilic part (oxygen) with iron substrate. Additionally, the 1,2–DME and 1,2–DMP molecules with \(ttt\) configuration, which are their most stable configuration, are employed to determine the interaction strength of CH\(_2\) and CH groups in copolymer with iron surface (Smith et al. 1998; Smith et al. 1993).

For water, the experimental study revealed that it could react with iron surface due to the presence of oxygen, the impurity of iron, or temperature to form ferrous hydroxide, or magnetite (Linnenbom 1958). It could be the chemisorption with a dissociative adsorption energy up to 170 kJ.mol\(^{-1}\) at 373 K (Joly et al. 2000). However, the reaction depends on the physical state of the surface, i.e. the smooth surface did not react with water (Thompson 1940). As the classical MD simulation cannot describe the electronic structure and the electron transfer of atoms, the chemical reaction of water with iron surface was neglected in this study and only the
non-bond interactions are utilized to model the interaction between atoms (Kerisit 2011).

![Image of molecular structures](image1)

Figure 2.3 Adsorption of (a) first symmetry configuration and (b) second symmetry configuration of dimethylether; (c) 1,2-DME (ttt configuration) ; and (d) 1,2-DMP (ttt configuration) on a p(4x4x1) Fe(100) substrate.

Studies of the adsorption of water on the metal surfaces indicated that there were three major adsorption sites: on-top, bridge, and hollow. However, the oxygen lone pair (Olp) at the top adsorption was the most stable one (Meng et al. 2004). Additionally, water with an OH bond up (Hup) or down (Hdown) was also a possible adsorption configuration (Schiros et al. 2006). A water molecule with the Olp, Hup, and Hdown configurations at on-top site (Figure 2.4) along with the bridge and hollow sites are therefore considered for its adsorption on Fe(100) surface.

![Image of water molecule configurations](image2)

Figure 2.4 Adsorption configurations of water with (a) oxygen lone pair, (b) hydrogen up, (c) hydrogen down configurations at on-top site of Fe(100) substrate.
2.3.2 Interfacial potential parameterization

In this investigation, a trial-and-error approach was used by adjusting the vdW parameters. The adsorption energy calculations were rerun over chosen configurations until a quantitative agreement with data obtained from ab initio calculation was achieved. The training configurations and adsorption energies obtained from previous ab initio calculations of a lubricant molecules adsorbed on surface were utilized for this process.

2.3.2.1 C₄H₁₀ adsorbed on Fe(110), FeO(110), and Fe₂O₃(0001)

COMPASS FF was applied for butane which was allowed to move along the surface normal direction similar to the constraint applied in ab initio calculation. The interactions between this molecule with the Fe(110), FeO(110), and Fe₂O₃(0001) surfaces including either vdW and Coulombic interactions. For vdW interaction, the L-J 9–6 function was chosen over L-J 12–6 due to the σ–¹² term for the repulsive potential of L-J 12–6 yielded too high repulsive energies (Kramer et al. 2013; Sun 1998). However, a cut-off of 4.8 Å (one-half the box) was applied for electrostatic and vdW interactions due to the small scale of the model (Skelton et al. 2011). The alkane–surface interactions were mapped onto a sum of pairwise Coulomb and L-J 9–6 interactions between each atom pair and with atomic charges qᵢ and qⱼ separated by a distance rᵢⱼ as shown in the following expression:

\[ V = \sum_{ij} \epsilon_{ij} \left[ 2 \left( \sigma_{ij}^0 / r_{ij} \right)^9 - 3 \left( \sigma_{ij}^0 / r_{ij} \right)^6 \right] + \sum_{ij} q_i q_j / r_{ij} \] (2.4)

Here \( \epsilon_{ij} \) and \( \sigma_{ij}^0 \) are respectively the well depth energy and corresponding distance where the L-J term had its minimum between each atom pair i and j. The Mulliken charges obtained from the DFT calculations of crystalline structures of iron and its oxides were employed for the surfaces. For Fe – C₄H₁₀, there were two pairwise interactions FeC and FeH along with four L-J parameters available to fit the training configurations and adsorption energies, i.e., the well depth of each pairwise \( \epsilon_{\text{FeC}} \), \( \epsilon_{\text{FeH}} \) and two minimum distances \( \sigma_{\text{FeC}} \), \( \sigma_{\text{FeH}} \). Besides, there were two additional types of pairwise interactions, OC and OH and four additional L-J parameters \( \epsilon_{\text{OC}} \), \( \epsilon_{\text{OH}} \), \( \sigma_{\text{OC}} \), and \( \sigma_{\text{OH}} \) for the interactions of FeO and Fe₂O₃ with C₄H₁₀. In the COMPASS FF,
the carbons in linear alkanes are classified in generic sp$^3$ hybridization state (Sun 1998). Therefore, the same fitting parameters were subsequently used (Kong et al. 2009).

These L-J parameters were needed to fit to a set of positions $r_i^j = r_1^j, r_2^j, ..., r_n^j$ and adsorption energies $E_j$ with $j$ chosen configurations determined from ab initio calculations. The parameterization algorithm was implemented by finding a set of L-J 9–6 parameters $\epsilon_i = \epsilon_1, \epsilon_2, ..., \epsilon_n$ and $\sigma_i = \sigma_1, \sigma_2, ..., \sigma_n$ satisfying the minimum cost function $f(\epsilon_i, \sigma_i)$, defined as:

$$f(\epsilon_i, \sigma_i) = \omega_e \Delta E + \omega_{zc} \Delta Z_C + \omega_{zh} \Delta Z_H \ (2.5)$$

where the $\omega_x$ were weights and they were set as $\omega_e = \omega_{zc} = \omega_{zh} = 1$ in this study. Here $\Delta E$, $\Delta Z_C$, and $\Delta Z_H$ were measures of the difference between the energies, minimum distances between carbon, hydrogen and the surfaces calculated with DFT and those calculated with our effective interfacial potential. They were defined below:

$$\Delta E = \frac{\sqrt{\sum_j |E(\epsilon_i, \sigma_i, r_i^j) - E_j|^2}}{\sqrt{\sum_j E_j^2}} \ (2.6)$$

$$\Delta Z_C = \frac{\sqrt{\sum_j |Z_C(\epsilon_i, \sigma_i, r_i^j) - Z_{C,j}|^2}}{\sqrt{\sum_j Z_{C,j}^2}} \ (2.7)$$

$$\Delta Z_H = \frac{\sqrt{\sum_j |Z_H(\epsilon_i, \sigma_i, r_i^j) - Z_{H,j}|^2}}{\sqrt{\sum_j Z_{H,j}^2}} \ (2.8)$$

As the $\epsilon$ parameters were positive and their magnitudes lower than the total adsorption energy, they were initially varied in an interval between zero and the highest magnitude of adsorption energy. The $\sigma$ parameters were then adjusted around the respective equilibrium distances between molecular atoms and the surface. These parameters were adjusted simultaneously by ramping them in a loop between the lower to upper bounds with a chosen increment. A disadvantage of this scheme is that the number of iteration, which is a multiple of the numbers of
increment for parameter loops, is quite large. To reduce the iteration, many trials were carried out with the starting point from a crude increment to restrict the interval of parameter space. Then this increment was reduced and previous steps were repeated until a reasonable convergence of \( f(\epsilon_i, \sigma_i) \) was achieved. This process was carried out using LAMMPS code.

2.3.2.2 1,2–DME, 1,2–DMP, and water adsorbed on Fe(110)

The adsorption energies \( (E_{ads}) \) of 1,2–DME, 1,2–DMP, and water on Fe(110) was evaluated as given in Equation 2.3. From these adsorption energies and configurations obtained from the quantum calculations, a force field parameterization similar with aforementioned method was implemented to derive the L-J 12–6 potential parameters for the interaction between fluid and iron surface. The vdw and Coulombic interactions, as given in Equation 2.9, were used to describe the nonbond interactions.

\[
E_{ij} = \sum_{ij} 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}^0}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}^0}{r_{ij}} \right)^{6} \right] + \sum_{ij} q_i q_j / r_{ij} \tag{2.9}
\]

where \( ij = \text{Fe–CH}_3, \text{Fe–CH}_2, \text{Fe–CH}, \text{Fe–O}, \text{Fe–O}_w \). In this parameterization, the optimized potentials for liquid simulations (OPLS)–UA force field and the SPCE–F potential were applied for organic molecules and water, respectively. All fitting variables were varied to fit the adsorption energies and structural configurations obtained from the DFT calculations.

The Fe–DME training configurations were used to fit the pairwise interactions between methyl groups, as well as oxygen with iron. There were four parameters available to fit to the quantum chemistry data \( (\epsilon_{Fe,\text{CH}_3}, \epsilon_{Fe,\text{O}}, r_{Fe,\text{CH}_3}, r_{Fe,\text{O}}) \). Then a Fe–1,2 DME training configuration was used to fit the pairwise interaction between methylene group \( (\text{CH}_2) \) and iron. Consequently, two additional parameters \( (\epsilon_{Fe,\text{CH}_2}, r_{Fe,\text{CH}_2}) \) were needed to fit. The last pairwise was the interaction between CH group and iron with \( \epsilon_{Fe,\text{CH}}, r_{Fe,\text{CH}} \) parameters, which were determined by using a 1,2–DMP molecule. Finally, for water, only its most stable adsorption configuration \( (\text{O}_l) \) was used to fit its pairwise interaction with iron.
2.3.3 Model for MD calculation

A detailed description of MD models is presented in this section. Note that these models were initially identified by means of commercial Material Studio software, and all consequent MD simulations were performed using large-scale atomic/molecular massively parallel simulator (LAMMPS).

2.3.3.1 Adsorption of $n$-alkanes on Fe(110), FeO(110), and Fe$_2$O$_3$(0001) surfaces

To observe the adsorption behaviour of $n$-alkanes on Fe(110), FeO(110), and Fe$_2$O$_3$(0001), a series of $n$-alkanes ($C_nH_{2n+2}$, $n = 4, 6, 8, 10, 12, 16$) have been employed. Before carrying out a measurement of adsorption energy of alkanes on these surfaces we considered the effect of surface coverage to the adsorption capability of alkanes. A generic observation was carried out with butane molecules in the range from 4 to 160 molecules which correspond to the film thickness from one to four atomic layers on Fe(110). Then the dependence of adsorption of alkanes on surface relaxation was also taken into account. A comparison of adsorption of alkane on unrelaxed, relaxed, and relaxed without charge surfaces of Fe(110), FeO(110), and Fe$_2$O$_3$(0001) were analysed. Finally, a full coverage of thin alkane film including 640 carbon atoms on the highly relaxed Fe(110), FeO(110), and Fe$_2$O$_3$(0001) surfaces was carried out to observe the structural behaviour of alkanes, adsorption energies, and the number of saturated carbon sites. For these MD calculations, the slab models were employed with the surfaces lying in the $xy$ plane and having $\sim 35 \times 35$ Å$^2$ dimensions, and a vacuum of 100 Å was added in the $z$ direction. These slab models contained 6, 5, and 12 atomic layers for Fe(110), FeO(110), and Fe$_2$O$_3$(0001), respectively. The thin film was prepared by building a cell of $\sim 35 \times 35 \times 20$ Å$^3$ containing random alkane molecules.

2.3.3.2 Thin film lubrication of hexadecane confined by iron and iron oxide surfaces

Behaviour of non-equilibrium MD model of confined pressurised and sheared liquid depends on a set of parameters such as film thickness, applied normal load, shear rate, and solid-liquid atom interaction parameters (Gattinoni et al. 2013; Heyes et al.
2012). As this section aimed to study structural alteration and tribological performance of lubricant confined between different surfaces, only case of similar external load and film thickness was considered. A MD simulation was performed to compare the tribological performance of hydrocarbon lubricant between iron and iron oxide surfaces when the film thickness was confined to an order of magnitude of a few nanometers. A snapshot of a representative model is shown schematically in Figure 2.5. It was constructed by a ~2.4 nm-thick alkane lubricant sandwiched between geometrically smooth iron and iron oxide surfaces. As shown in Table 2.1, different surface structures as well as surface orientations were utilized in this study. The initial domain sizes for these surfaces were chosen in such a way that a surface area of \( \sim 35 \times 35 \, \text{Å}^2 \) was kept for all surface models and the periodic boundary condition was applied in shear and transversal directions. This size domain is optimised when the effects of itself and the simulation time are considered. A larger domain size could yield a more stable result, but limits the simulation time when a low shear rate and an advanced conventional force field are considered. The lateral dimensions are almost twice as long as the molecular chain length of \( n \)-hexadecane to ensure that the lubricant molecule did not interact with itself across the periodic boundaries. Each surface was 10 Å thick and was created by cleaving from its regular crystalline structure through Miller indexing. As the domain size was a little different for each type of surface model, the number of lubricant molecules was therefore chosen such that the film thickness and an initial lubricant density (0.7 gram/mol) were almost identical for all types of surface models.
Figure 2.5 Snapshot of molecular model of hexadecane lubricant confined between Fe$_2$O$_3$(001) surfaces under different applied pressures, sliding velocities, and surface’s temperatures. Fe, O, C, and H atoms are presented as purple, red, grey, and white colours, respectively.

In practical industrial processes such as metal forming, ball-bearing, and others (Askwith et al. 1966; Kajdas et al. 2006; Montmitonnet et al. 2000), the hydrocarbon based lubricant is subjected to high applied pressures and shear load by metal surfaces. A uniform normal load, as given in Table 2.1, was therefore applied on atoms of the top layer during compression and shearing states. Because the interaction between iron atoms of iron oxide surfaces described by Columbic repulsive force was weak the uniform load was applied only on the top oxygen layer. This uniform load corresponded to an applied pressure of 500 MPa.

The tribosurfaces of Fe(100), Fe(110), FeO(100), FeO(110), and Fe$_2$O$_3$(001) were used to investigate the influence of loading pressure; these realistic surfaces are introduced because they are commonly found on iron and iron oxide surfaces due to their stability (Chambers & Yi 1999; Li et al. 2005; Rufael et al. 1997). A thin film of
hexadecane lubricant is confined between these tribosurfaces to an order of magnitude of a few nanometers (6-7 layers). In practical applications such as rolling, metal forming, ball bearings, and others, the tribosurfaces usually experience a high pressure, shearing load, and different surface temperature so pressures of 50-2000 MPa, surface temperatures of 300-500K, and shear rates of $10^8$-$10^{11}$ s$^{-1}$ are considered to investigate the influence of sliding conditions.

Table 2.1 Surface structures, lattice constants, Miller indices, domain sizes, number of hexadecane molecules, scanning distances, and applied load for different employed iron and iron oxide surfaces.

<table>
<thead>
<tr>
<th>Surfaces</th>
<th>Structures</th>
<th>Miller indices</th>
<th>Lateral lattice constants</th>
<th>Domain sizes</th>
<th>No. C$<em>{16}$H$</em>{34}$</th>
<th>Sampling steps</th>
<th>Applied load $10^3$ nN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>BCC</td>
<td>(100)</td>
<td>2.867 2.867 34.40 34.40</td>
<td>82</td>
<td>0.205 0.205</td>
<td>41.081</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(110)</td>
<td>4.054 2.867 36.48 34.4</td>
<td>87</td>
<td>0.217 0.205</td>
<td>29.049</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(111)</td>
<td>4.965 4.054 34.75 36.48</td>
<td>88</td>
<td>0.207 0.217</td>
<td>50.315</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(111)(010)</td>
<td>4.054 4.965 36.48 34.75</td>
<td>88</td>
<td>0.217 0.207</td>
<td>50.315</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>Cubic</td>
<td>(100)</td>
<td>4.332 4.332 34.66 34.66</td>
<td>83</td>
<td>0.206 0.206</td>
<td>23.457</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(110)</td>
<td>3.063 4.332 36.76 34.66</td>
<td>87</td>
<td>0.219 0.206</td>
<td>66.349</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(111)</td>
<td>7.503 3.063 37.52 36.76</td>
<td>96</td>
<td>0.223 0.219</td>
<td>114.919</td>
<td></td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>Rhombohedral</td>
<td>(001)</td>
<td>8.721 5.035 34.88 35.25</td>
<td>85</td>
<td>0.208 0.210</td>
<td>36.592</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(012)</td>
<td>5.035 5.419 32.51 40.28</td>
<td>91</td>
<td>0.194 0.240</td>
<td>68.213</td>
<td></td>
</tr>
</tbody>
</table>

2.3.3.3 Aqueous copolymer lubricant in mixed lubrication regime

As illustrated in Figure 2.6, the model of aqueous copolymer lubricant is confined between iron surfaces, and periodic in X and Y directions. Each surface is comprised of 24180 iron atoms, and has a sinusoidal asperity assembled on a 10 Å thick surface. The sinusoidal asperity was set up with amplitude of 25 Å and a period of 145 Å. The chosen asperities are consistent with the experimentally measured roughness of ~2 nm of high Cr–steel balls (Lin et al. 2015). The surfaces were then divided into three sublayers: rigid layers (1, 4), thermostat layers (2, 5), and deformable layers (3, 6) (Zheng et al. 2013a).
Figure 2.6 Representative model of 17R2 aqueous copolymer lubricant confined between sinusoidal rough iron surfaces, the model is subject to an applied pressure varying from 0.25 to 1.0 GPa on the top rigid layer (layer 4), and shear at sliding velocity of 10 m/s for layers 1 and 4. For clarity, water is excluded in this figure.

Figure 2.7 Molecular structure of 17R2 triblock copolymer: (a) EA model; and (b) UA model.

The lubricant was prepared by packing randomly the copolymer and water molecules in a rectangular box with initial dimensions of 215 Å, 86 Å, and 60 Å for \(X\), \(Y\), and \(Z\) directions, respectively. The copolymer 17R2, as illustrated in Figure 2.7, is employed in this study. This copolymer has a chemical formula of \(H–[C^*H–CH_2–O]_{15}–[CH_2–CH_2–O]_{10}–[C^*H–CH_2–O]_{15}–CH_3\), where \(C^*\) is chiral carbon with an attached methyl group.

To consider the influence of copolymer concentration, the lubricant with different concentrations between 1.0-20 Wt% of the composition was used (Laemmle 1984).
To keep the same lubricant volume for different concentrations of copolymer, the number of water molecule was adjusted according to an increase of copolymer concentration (Table 2.2).

Table 2.2 Number of 17R2 and water molecules with different copolymer concentrations in the solution.

<table>
<thead>
<tr>
<th>17R2 Wt%</th>
<th>no. 17R2</th>
<th>no. water</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4</td>
<td>23144</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>22690</td>
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<td>6</td>
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<td>8</td>
<td>16</td>
<td>21696</td>
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<tr>
<td>12</td>
<td>24</td>
<td>20880</td>
</tr>
<tr>
<td>16</td>
<td>32</td>
<td>19984</td>
</tr>
</tbody>
</table>

2.3.4 Force field

2.3.4.1 Adsorption of n-alkanes on Fe(110), FeO(110), and Fe₂O₃(0001) surfaces

All-atoms model in which each CH₂ or CH₃ group of linear alkane molecules represented as explicit atoms (EA) was used. COMPASS FF combined with the sixth order combination law was employed to model the intra- and intermolecular interactions for alkane (Sun 1998). Detail information about the expressions and parameters of this FF can be found from Appendix B. For simplification, the surfaces were constrained into the optimized configurations and the interactions between their atoms were ignored. The nonbond interactions between atoms of lubricant as well as between these atoms and the solid surfaces were represented by the vdw interactions using the L-J 9–6 potential along with the long-range Columbic interactions with a cut-off distance of 9.5 Å.

The Coulomb interactions considering as atomic charges was used to treat the electrostatic potential and the long range correction was implemented by a particle–particle particle–mesh (PPPM) (Hockney & Eastwood 1988). The atomic charges for iron oxides were obtained from DFT calculations using aforementioned Mulliken partitioning method, whereas the charges on alkane molecules were set equal to those of COMPASS FF (Sun 1998).
2.3.4.2 Thin film lubrication of hexadecane confined by iron and iron oxide surfaces

The employed potential for hexadecane and its interactions with iron and iron oxide surfaces are similar to those used in aforementioned adsorption simulation. However, the Buckingham potential, as presented in Table 2.3, was applied for the oxide surfaces (Guillot & Sator 2007a, 2007b). This potential had reproduced thermodynamic and structural properties of FeO and Fe₂O₃ in natural silicate melt at both low and high pressure (Guillot & Sator 2007a, 2007b). A EAM/FS potential (Mendelev et al. 2003) was applied for pure iron. The atomic charges of surface’s atoms obtained from the work by Guillot and Sator (Guillot & Sator 2007a, 2007b) were used in this simulation. These atomic charges, as presented in Table 2.3, are a little higher than those obtained from our DFT calculation. However, this charge discrepancy does not affect significantly the current models due to the minor contribution of electrostatic energy in the interaction between hexadecane film and iron oxide surfaces. A cut-off distance of 12.5 Å was applied for both vdW and long-range Columbic interactions.

The effectiveness of using the Columbic charges in the calculations for “pure” alkanes, as Sun (Sun 1998) also concluded that inclusion of expensive long range electrostatic calculation using Ewald sum is not needed and these columbic interaction can be cut off at 0.85-1.25 nm. However, in a complex surface model of iron oxides, where the columbic interactions contribute a significant amount of electrostatic energy, using Ewald sum is necessary to guarantee an accurate obtained result.

Table 2.3 Potential parameters of Buckingham potential for FeO and Fe₂O₃.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Partial charge</th>
<th>Aₑ</th>
<th>Pₑ</th>
<th>Cₑ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Aₑ</td>
<td>Pₑ</td>
<td>Cₑ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>kJ/mol</td>
<td>Å</td>
<td>Å⁹.kJ/mol</td>
</tr>
<tr>
<td>O</td>
<td>-0.945</td>
<td>870569.659</td>
<td>0.265</td>
<td>8210.128</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.945</td>
<td>1257488.092</td>
<td>0.190</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>1.4175</td>
<td>773839.664</td>
<td>0.190</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Aₑ, Pₑ, and Cₑ, which obtained from the works of Guillot and Sator (Guillot & Sator 2007a, 2007b), correspond to iron cation-oxygen and oxygen-oxygen interaction, the cation-cation interaction is described only by Columbic repulsive force.
2.3.4.3 Aqueous copolymer lubricant in mixed lubrication regime

The OPLS UA potential was applied for triblock copolymer (Hezaveh et al. 2011, 2012). The detailed information and parameters of this potential are presented in Appendix C. In aqueous solution, the density, diffusion coefficients, and concentration dependent conformers of 1,2–DME and 1,2–DMP obtained from this potential resulted in a good agreement with experiment (Hezaveh et al. 2011). Moreover, this potential also described properly the conformation and radii of gyration of PEO and PPO polymer chains, as well as triblock copolymer at 298 K (Hezaveh et al. 2012). A simple point charge (SPCE–F) water model was applied for water (López-Lemus et al. 2008). Although the L-J potential is applicable to metallic surfaces, it is not accurate at reproducing the surface properties (ductility, plastic deformation, and material transfer) compared to the EAM potential (Abraham et al. 1994; Eder et al. 2011). Therefore, the EAM/FS potential was applied for rough iron surfaces (Mendelev et al. 2003).

The inter- and intra-molecular interactions of copolymers such as bond stretching, angle bending, and dihedral were included in this model. Details about the expressions and parameters of this force field can be found in a series of works by Hezaveh and colleagues (Hezaveh et al. 2011, 2012). Due to the complex expressions along with a large number of parameters, for clarity only parameters from the force field parameterization for the interaction between polymer/water and iron surfaces are presented. The nonbond interactions between iron and polymer/water were modelled by L-J 12–6 potential. A cut-off distance of 12.5 Å was applied for both L-J 12–6 potential and the Coulombic interaction. The PPPM solver technique was utilized to treat the Coulombic interactions (Hockney & Eastwood 1988).

2.3.5 Simulation procedure

2.3.5.1 Adsorption of n-alkanes on Fe(110), FeO(110), and Fe$_2$O$_3$(0001) surfaces

In simulation of adsorption of n-alkanes, the thin alkane film was relaxed during 1 ns at low temperature (150 K) to generate a stable coverage of adsorbed molecules.
Then, the obtained results were averaged during the last 500 ps of the dynamic simulation. The time step was set to 1 fs using velocity Verlet integration under Nose–Hoover thermostat condition in canonical ensemble (NVT—constant number of molecules N, constant volume V, and constant temperature T).

2.3.5.2 Thin film lubrication of hexadecane confined by iron and iron oxide surfaces

The simulation procedure was divided into three simulation stages: In the first stage the model was relaxed for 0.5 ns to neglect unrealistic atomic contacts, followed by a dynamic stage for the next 0.5 ns with applied load on the top region while the bottom region was fixed. The temperature of the system was controlled at 300 K by applying Nose-Hoover thermostat during with a damping parameter of 100 fs on thermostated layer of surfaces (Figure 2.5). After that the surface was moved in x direction (it is a default for all cases except for Fe(111) surface model which moved in both x and y (denoted as (010) direction)) with a constant sliding velocity of 10 m/s for 20 ns, while the applied load and thermostat were kept constant. The rheological and tribological properties of lubricant and lubricated systems were averaged during the last 10 ns of shearing state. The simulation timestep of 1 fs was chosen as with the total simulation time of 40 ns (40,000,000 timesteps).

During the confined shear simulation, the NVT ensemble was applied to the layers 2 and 5, thus allowing a dissipation of local heating of the lubricant film and asperities through these layers (Eder et al. 2011; Zheng et al. 2013a). Therefore, the NVE ensemble should be utilized for the fluid and asperities (layers 3 and 6) which were specified as free deformable bodies (Spijker, P. et al. 2011; Zhu et al. 2015).

To investigate the shear rate, different sliding velocities of 0.002-1 Å.ps⁻¹ were imposed onto the surfaces to induce apparent shear rates of 10⁸-10¹¹ s⁻¹. Note that when the velocity decreases below this range the hydrodynamic velocity of the lubricant atoms are then too low to be properly detected due to thermal noise. The shear rate cannot be lower than this lower bound due to the high sensibility of velocity profile and the need for a long calculation time. A sliding velocity of 1 Å.ps⁻¹ becomes the speed limit because viscous heat induces an increase in the temperature, and this could lead to a transition in the liquid stage of hexadecane.
The simulation time varied from 30-80 ns to achieve stable results for different shear rates. The applied shear rates are several orders of magnitude higher than the experimental values, but they are commonly used in MD simulation (Jabbarzadeh et al. 2005; Tseng et al. 2008). Because of such small values of dimension, time scale, and the number of molecular layers, so the very high shear rates are used to obtain reasonable statistics (Martinie & Vergne 2016). The Fe$_2$O$_3$(001) tribo-surface with 100, 250, 500, and 1000 MPa loading pressures as well as surface temperature of 300K, 400K, and 500K are used to study the effect of shear rate.

2.3.5.3 Aqueous copolymer lubricant in mixed lubrication regime

The simulation of aqueous copolymer lubricant in mixed lubrication regime involved three stages: The model was relaxed for 0.1 ns (100,000 timesteps) with the fixed constraint for rigid layers while other layers were set free in the first stage. The rest was thermostated at a temperature of 300 K using the Nose–Hoover NVT ensemble with a damping parameter of 100 fs. The thermostat was applied throughout the simulation to control the system’s temperature. Since 17R2 is a long chain molecule that has many local minima in the energy, a temperature annealing, i.e. thermostating the fluid at 500 K for 0.3 ns (300,000 timesteps), was therefore applied for confined lubricant to overcome energy barriers and move into the optimal equilibrium configuration (Harris et al. 2013). In the second stage, the temperature was reduced to 300 K to obtain stable solution at room temperature, while the system was slowly compressed for 2.6 ns (2,600,000 timesteps) by applying a constant load. This applied load corresponds to pressures between 0.25-1.0 GPa acting on the top rigid layer. The range of applied pressure is consistent with that used in pin-on-disk tests by Lin et al. (Lin et al. 2013; Lin et al. 2015). During the compression, the atoms in the top rigid layer were constrained in the direction perpendicular to the surface, whereas the bottom rigid layer was fixed. In the last stage, the rigid layers 1 and 4 moved at a constant sliding velocity of 10 m/s in the opposite direction to create the shear effect. This velocity is significantly larger than that applied in experiments (0.01-0.1 m.s$^{-1}$) due to the expensive computation of MD (Lin et al. 2015). The lowest shear rate that could be used in MD simulation is $10^7$ s$^{-1}$; however, the simulations should be carried out for up to 94 ns (Jabbarzadeh & Tanner 2011). It is not easy to handle such a long calculation time for a huge model.
in MD simulation. A sliding speed of 10 m/s (corresponding to the shear rate of \( \sim 5 \times 10^9 \) s\(^{-1} \)), which is commonly used in MD simulation, is therefore applied for the current model (Berro et al. 2010; Savio et al. 2012). The applied load was still retained during confined shear process. The rough substrates were sheared for 7.0 ns (7,000,000 timesteps), which correspond to six asperity contacts, to obtain quantitatively the tribological results. The Verlet algorithm was used for the numerical integration of atomic classical equations of motion with an incremental time step of 1 fs.

### 2.4 Confined shear viscosity

In this work, the shear viscosity have been evaluated to investigate the rheological property of hexadecane confined between different iron oxide surfaces and subjected to variety of loading pressures and surface temperatures. The viscosity in the shear flow field is defined by

\[
\eta(\dot{\gamma}) = \frac{\tau_{xz}}{\dot{\gamma}} \quad (2.10)
\]

where \( \tau_{xz} \) is the shear stress measured by the fraction of the force exerted by an atomic interaction of lubricant molecules to surface atoms in a shearing direction and on the surface area, and where \( \eta(\dot{\gamma}) \) denotes the shear rate dependence of shear viscosity. As the shear rate approaches zero, the fluid exhibits Newtonian behaviour so that a zero shear rate can be determined by

\[
\eta_0 = \lim_{\dot{\gamma} \to 0} \eta(\dot{\gamma}).
\]

The Carreau equation is used to extrapolate the zero shear rate viscosity; this equation is described by following formula:

\[
\eta(\dot{\gamma}) = \eta_\infty + \frac{\eta_0 - \eta_\infty}{[1 + (\lambda \dot{\gamma})^a]^{n-1}} \quad (2.11)
\]

where \( \eta_\infty \) is the very high shear rate viscosity, \( \lambda \) is the dimension of time, \( a \) is the exponent which describes the curvature of the transition region between the first Newtonian plateau and the shear thinning slope, and \( n \) is the exponent which controls the slope of the shear thinning region. For liquid polymeric, \( \eta_\infty = 0 \) and \( a = 2 \) are set for the Carreau model.
Chapter 2 Numerical model

The critical shear rate ($\gamma_c$) indicates the onset point of shear thinning, and $\gamma_c \approx \tau_R^{-1}$ (Berker et al. 1992). Here, $\tau_R^{-1}$ is the rotational relaxation time calculated by the modified Rouse model with the following equation:

$$\tau_R = \frac{6\eta_0 M}{\pi^2 \rho_e R T} \quad (2.12)$$

where $M$ and $\rho_e$ are the molecular weight and equilibrium density, respectively (Berker et al. 1992).

2.5 Non-equilibrium shear viscosity

A non-equilibrium MD simulation has been conducted to evaluate the zero-shear viscosity of hexadecane at ambient condition. The shear of the fluid was performed using Forcite package in Material Studio 7.0.

A triple periodic box shaped domain of $45 \times 45 \times 45 \, \text{Å}^3$ (Figure 2.8) containing 182 randomly distributed hexadecane molecules, was used for this calculation. Initially, the geometry was optimized followed by a dynamic calculation for 1.0 ns using NPT ensemble at 298 K and $10^5 \, \text{Pa}$ (1 bar) to obtain the bulk properties of hexadecane at ambient condition. The Berendsen barostat ensemble was utilized with decay constant of 0.1 ps, and the COMPASS force-field was applied for hexadecane. Ewald and atom-based summation method were applied respectively for the electrostatic and Van der wall interactions with cut-off distance of 12.5 Å.

A boundary driven condition so-called Lee and Edwards boundary conditions (Lees & Edwards 1972) was applied to the model in which the image cells moved continuously over the central one at a defined strain rate $\gamma \equiv \partial u_x / \partial y$ of the flow. The periodic boundary condition ensured that the particles leaving the central cell were replaced by their periodic image. The shear of the fluid took place by deforming the boundary in such a way using the sliding-brick or deforming cube presentation. The cells were distorted with the flow, and particles also deformed with the cell. This simulation was carried out under constant pressure, and the thermostat was applied to remove sheared induced heat. The simulation time for this shear calculation was varied from 5.0 to 10 ns for different shear rate. A steady shear rate ($\dot{\gamma}$) from $10^9$ to $10^{12} \, \text{s}^{-1}$, which correspond to the upper and lower shear rate bounds in MD
simulation (Berro et al. 2009; Jabbarzadeh et al. 2005), is applied in this calculation. The shear viscosity was defined as the ratio of the shear stress to the applied shear rate and given in Equation 2.10.

\[ \text{Shear viscosity} = \frac{\text{shear stress}}{\text{applied shear rate}} \]

Figure 2.8 Simulation domain size ($45 \times 45 \times 45 \text{Å}^3$) of hexadecane with a central cell and their image cells for: (a) initial stage; and (b) sheared stage.

### 2.6 Surface characterization

It was revealed in the literature that the tribo-surface properties have a substantial influence on the lubricity of fluid in nanotribology (Gao et al. 2000; Jabbarzadeh et al. 2006). Many simple surface characterization approaches had been employed such as surface energy (Berro et al. 2010; Cui et al. 1999) or surface commensurability (Thompson & Robbins 1990).

The oxidation of iron not only yields the difference in surface properties, including crystalline structure, of tribo-surface; but also results in different molecular behaviour and adhesion strength of the thin alkane film. To analyse the role of these influences in thin film lubrication of alkane between iron and its oxides surfaces, a comprehensive surface parameterization proposed by Savio et al. (Savio et al. 2012) was employed to consider the interaction energy and commensurability between surface and lubricant molecules by the concept of surface corrugation. Although this
method was implemented at zero temperature, it could quantitatively predict the surface properties under standard conditions (Savio et al. 2012).

As shown in Figure 2.9, a representative scanning technique on Fe$_2$O$_3$(012) surface using a uniform layer of scanning atoms with the sampling steps of $\sim 0.2$ Å was used. The scanning distances ($\Delta x, \Delta y$) in lateral directions for each surface are shown in detail in Table 2.1. To simplify the scanning model, only the carbon site of the alkane, without explicit hydrogen atoms was used. A new interfacial potential obtained from a parameterization of interfacial interaction between butane using UA model and iron as well as iron oxides surfaces, was applied for scanning atoms. The adsorption energies and configurations obtained from previous DFT calculation were utilized as the training set for this parameterization. As the contribution of electrostatic component in the interaction between alkane and the surfaces was insignificant (Li & Choi 2007), it was not taken into current surface parameterization. The fitting procedure was similar to that described in previous interfacial potential parameterization.

The coordinates of scanning atoms were fixed in lateral directions, whilst they were set free in a direction normal to the surface during the optimization process. This is to allow the scanning atoms to stay at equilibrium distances that corresponded to the lowest surface potential. The surface potential energy landscape, surface commensurability, and resisting force were investigated to determine these influences on the structural and tribological properties of confined lubricant. The surface commensurability was determined based on the commensurability height expressed in following equation (Savio et al. 2012):

$$h_{comm} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (h_{eq}(x,y) - \bar{h}_{ep})^2} \quad (2.13)$$

where $h_{eq}(x,y)$ presents equilibrium distance at atom $i^{th}$ and $\bar{h}_{ep}$ is the averaged equilibrium distance over N atoms of scanning layer.

It has been shown from the literature that the surface potential energy plays a vital role in thin film lubrication (Berro et al. 2010). To quantify the potential energy of a surface, a physical component ($\bar{V}_{scan}$) was evaluated by averaging the interaction
energies between the scanning atoms and the surface over all scanning atoms. The surface energy corrugation was then determined by the root-mean-square of the sum of deviations between local interaction energy $V_{\text{scan}}(x, y)$ at atom $i^{th}$ and the mean value $\bar{V}_{\text{scan}}$ in the following expression (Savio et al. 2012):

$$V_{\text{corr}} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (V_{\text{scan}}(x, y) - \bar{V}_{\text{scan}})^2} \quad (2.14)$$

For different scan lines on a surface, the distinct force traces are obtained in spite of having the same potential energy landscape (Dong, Y et al. 2011). However, the sliding atom favours to stay at the minimum energy level, and as a result, the minimum force path deviates from a straight scanning direction to form a zigzag pattern (Dong, Y et al. 2011; Savio et al. 2012). The resisting force was therefore defined as the minimum gradient of corrugation potential in the sliding direction.

$$F(x) = \min_{\Delta y} \left( \frac{(V_{\text{scan}}(x, y) - V_{\text{scan}}(x + \Delta x, y + \Delta y))/\sqrt{\Delta x^2 + \Delta y^2}}{\sqrt{\Delta x^2 + \Delta y^2}} \right) \quad (2.15)$$

To quantify the maximum resistance of atom movement, Savio et al. assumed that the corrugation force ($F_{\text{corr}}$) was the maximum value of resisting force ($F(x)$) (Savio et al. 2012). However, in some circumstances discussed in section 4.3, this value could be negative or zero. In this work, the corrugation force was defined as the amplitude of resisting force and given in following expression:

$$F_{\text{corr}} = |F(x)_{\text{max}} - F(x)_{\text{min}}| \quad (2.16)$$

The surface parameter was then determined as a function of surface commensurability and corrugation force by the following equation (Savio et al. 2012):

$$\xi_{\text{surf}} = F_{\text{corr}} \cdot h_{\text{comm}} \quad (2.17)$$
Figure 2.9 A representative scanning technique is presented on Fe$_2$O$_3$(012) surface. For clarity the atoms on the top layer of the surface are highlighted with the darker colours than those underneath.
Chapter 3 Adsorption of normal-alkanes on Fe(110), FeO(110), and Fe₂O₃(0001) surfaces

This chapter presents the results of DFT calculation of electronic and structural properties for different iron and iron oxide surfaces, and the adsorption energies of butane onto these surfaces. A new force field for the interactions between these surfaces and hydrocarbon, which was parameterized from DFT calculation, has been applied for MD simulation. In addition, the structural properties and adsorption energies of linear alkanes on different iron and iron oxide surfaces are investigated.

3.1 Relaxation of surfaces

The resulting bulk lattice parameters for iron and its oxides obtained from the DFT calculation are presented in Table 3.1. The difference between the current results and the obtained experiments are 3.5% and 0.4% for Fe and FeO, respectively. For Fe₂O₃, this difference is 0.6% for lateral parameters and 0.4% for vertical one. These structural properties agree well with experimental measurements. The atomic charges derived from Mulliken partitioning of charge density are also shown in Table 3.1. There is zero charge for pure iron while the respective charges for six-coordinate iron in FeO and seven-coordinate iron in Fe₂O₃ are +0.717e and +0.887 e, respectively. Likewise, the six-coordinate oxygens in FeO have a smaller negative charge (-0.707 e), while the four-coordinate oxygens in Fe₂O₃ have a partial charge of -0.559 e. It is noted that charge magnitude of ions increases with their coordinate number.

The results for the surface relaxation of Fe(110) in Table 3.2 indicate that the topmost atoms of the surface extended 3.02% of the associated bulk spacing, which agrees with the experimental measurement by Shih et al. (Shih et al. 1980). However, this observation is contrasting with the DFT calculation by Jiang and Carter (Jiang & Carter 2003) using GGA exchange–correlation functional of Perdew et al. (PW91) (Perdew 1992). Their results reported an inward relaxation of 0.36% of the interfacial atoms. Although there is a discrepancy between the current results and those obtained from their study; however, the difference in magnitudes of relaxation is quite small.
Chapter 3 Adsorption of normal-alkanes on Fe(110), FeO(110), and Fe2O3(0001) surfaces

Table 3.1 Lattice parameters for iron and its binary oxides obtained from current DFT results and experiments.

<table>
<thead>
<tr>
<th>compound</th>
<th>current DFT</th>
<th>expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>a = b = c = 2.966 Å</td>
<td>a = b = c = 2.867 Å&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>α = β = γ = 90°</td>
<td>α = β = γ = 90°&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>q&lt;sub&gt;Fe&lt;/sub&gt; = 0.0 e</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>a = b = c = 4.347 Å</td>
<td>a = b = c = 4.33 Å&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>α = β = γ = 90°</td>
<td>α = β = γ = 90°&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>q&lt;sub&gt;Fe&lt;/sub&gt; = +0.717 e, q&lt;sub&gt;O&lt;/sub&gt; = −0.707 e</td>
<td></td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>a = b = 5.064 Å</td>
<td>a = b = 5.035 Å&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>c = 13.693 Å</td>
<td>c = 13.747 Å&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>α = β = γ = 90°</td>
<td>α = β = γ = 90°&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>γ = 120°</td>
<td>γ = 120°&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>q&lt;sub&gt;Fe&lt;/sub&gt; = +0.887 e, q&lt;sub&gt;O&lt;/sub&gt; = −0.559 e</td>
<td></td>
</tr>
</tbody>
</table>

experimental lattice parameters for:

<sup>a</sup> Iron obtained from the work of Ackland et al. (Ackland et al. 1997)

<sup>b</sup>FeO obtained from the work of Fjellvåg et al. (Fjellvåg et al. 1996)

<sup>c</sup> Fe<sub>2</sub>O<sub>3</sub> obtained from the work of Finger et al. (Finger & Hazen 1980)

For FeO(110), the results show an averaged inward relaxation of −1.9% of all interfacial atoms as shown in Table 3.3. Alternatively, the Fe and O ions of the relaxed layers deviate from linear to form a wave-like pattern. This finding is consistent with that reported by Liao and Carter by using the projector augmented-wave (PAW) method (Liao & Carter 2010). However, the current results show a larger relaxation of −3.2% for oxygen greater than −0.6% for iron, which are different from their work that reported a preferred inward movement for iron rather than oxygen.

Table 3.2 Structure of Fe(110) surface containing the top three layers after relaxation

<table>
<thead>
<tr>
<th>layer</th>
<th>current DFT</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d&lt;sub&gt;y&lt;/sub&gt; (Å)</td>
<td>d (Å)</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;1&lt;/sub&gt;</td>
<td>2.097</td>
<td>2.161</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.097</td>
<td>2.134</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.097</td>
<td>2.128</td>
</tr>
</tbody>
</table>

For α–Fe<sub>2</sub>O<sub>3</sub>(0001), the first eight layer spacings are −42.2, +13.1, −53.6, +22.9, +6.9, −6.6, +6.4, and 0% of the associated bulk values, respectively. These results indicate
Chapter 3 Adsorption of normal-alkanes on Fe(110), FeO(110), and Fe2O3(0001) surfaces

that the relaxation from our calculation confirms those obtained from the literature, in particular, there is an inward relaxation of the first, third, sixth layers while an extension is found for the second, fourth, fifth, and seventh layers (Chambers & Yi 1999; Trainor et al. 2004; Wasserman et al. 1997). Alternatively, the obtained relaxation magnitudes are in the range of that predicted from the DFT calculations and experiment, previously reported in the literature for Fe-terminated surface except the third layer as presented in Table 3.4. There is a higher inward relaxation of the third layer in the current results than that gained from literature. This relaxation magnitude is -53.6% compared to -26, -41, and -8% from the results of Trainor et al. (Trainor et al. 2004), Wasserman et al. (Wasserman et al. 1997), and Chambers and Yi (Chambers & Yi 1999), respectively.

Table 3.3 Structure and atomic charges of FeO(110) surface containing the top three layers after relaxation.

<table>
<thead>
<tr>
<th>Current DFT</th>
<th>Liao</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔZ_Fe/ %</td>
<td>layer1</td>
</tr>
<tr>
<td>ΔZ_O/ %</td>
<td>-0.6</td>
</tr>
<tr>
<td>ΔZ/ %</td>
<td>-3.2</td>
</tr>
<tr>
<td>q_Fe(e)</td>
<td>+0.55</td>
</tr>
<tr>
<td>q_O(e)</td>
<td>-0.63</td>
</tr>
<tr>
<td>Δd_Fe-O/ %</td>
<td>+10.6</td>
</tr>
<tr>
<td>Δd_O-Fe/ %</td>
<td>-14.4</td>
</tr>
</tbody>
</table>

The relaxation does not only yield to the changing in structural properties of interfacial atoms but also leads to the changing in the charges of iron oxides as shown in Figure 2.1. The charge’s magnitude for the interfacial atoms is lower than that in the inner layers. In particular, the respective charges for iron and oxygen are +0.55e and -0.63 e in the first layer of FeO(110) surface. The magnitudes of these charges are lower than the bulk values obtained in the previous section and it increases with layers closer to the bulk structure. However, a contrasting tendency is found for iron in the third layer. The charge of +0.73 e for iron in the third layer is lower than+0.76 e in the second one (Table 3.3). For α–Fe2O3(0001) there is also a decrease in magnitude of atomic charges for atoms at the outermost layers relative
Chapter 3 Adsorption of normal-alkanes on Fe(110), FeO(110), and Fe2O3(0001) surfaces
to those in the inner layers. The charges of +0.77 e for outermost iron and -0.53 e for outermost oxygen are found for this surface (Table 3.4).

Table 3.4 Structure and atomic charges of Fe2O3(0001) surface containing the top eight layers after relaxation.

<table>
<thead>
<tr>
<th>layer</th>
<th>initial</th>
<th>current DFT</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d0(Å)</td>
<td>d(Å)</td>
<td>Δd/%</td>
</tr>
<tr>
<td>Fe[1]</td>
<td>0.904</td>
<td>0.522</td>
<td>-42.2</td>
</tr>
<tr>
<td>O[2]</td>
<td>0.904</td>
<td>1.023</td>
<td>+13.1</td>
</tr>
<tr>
<td>Fe[3]</td>
<td>0.474</td>
<td>0.220</td>
<td>-53.6</td>
</tr>
<tr>
<td>Fe[4]</td>
<td>0.904</td>
<td>1.111</td>
<td>+22.9</td>
</tr>
<tr>
<td>O[5]</td>
<td>0.904</td>
<td>0.967</td>
<td>+6.9</td>
</tr>
<tr>
<td>Fe[6]</td>
<td>0.474</td>
<td>0.443</td>
<td>-6.6</td>
</tr>
<tr>
<td>Fe[7]</td>
<td>0.904</td>
<td>0.962</td>
<td>+6.4</td>
</tr>
<tr>
<td>O[8]</td>
<td>0.904</td>
<td>0.904</td>
<td>0</td>
</tr>
</tbody>
</table>

For iron oxides, the ionic interaction between iron and oxygen is the crucial potential, and the charge of a type of atom depends on its coordinate number (Batra et al. 2013). In bulk material, this coordinate number is the same so that the charge of a type of atom is consequently similar. However, when these oxide crystals are cleaved to generate the surfaces, the ionic bonds between ions in the cleavage plane are broken and the coordinate numbers of these ions decrease. The surfaces are then relaxed to lower the surface Gibbs energies to attain the thermodynamically more stable systems. This surface relaxation is determined by the change in the ionic size due to the reduction surface charge transfer resulting from Madelung potential at the surface, the imbalance of the ionic forces due to the termination of the lattice (Kung April 1989). The charges on surface’s atoms are therefore dynamically varied and differ from their bulk.

Overall, the geometry optimization of the Fe(110) and FeO(110) surfaces induce quite small relaxations with small errors in the range of the experiment and DFT predictions. This indicate that the surfaces of Fe(110) and FeO(110) are basically bulk terminated. In contrast, there is a significant relaxation of interfacial atoms of the Fe2O3(0001) surface. Additionally, the changing of interfacial atomic charges relative
to its bulk values is not significant for iron oxide surfaces, in particular, the difference is less than 0.2 e.

3.2 Adsorption energies and interfacial potential between butane and surfaces

The results summarized in Table 3.5 show a significant reduction of $\Delta z$ for both carbon and hydrogen of butane molecule for DFT-D calculations. Additionally, the adsorption energies obtained from DFT-D calculations are nearly twice larger than those obtained from ordinary DFT. In fact, the largest adsorption energies obtained from TS scheme are 125.4, 96.0, and 85.9 kJ/mol for Fe(110), FeO(110), and Fe$_2$O$_3$(0001), respectively, while the relevant values for G06 scheme are 102.1, 81.7, and 80.2 kJ/mol. For DFT calculations, these values are only 48.15, 40.04, and 35.89 kJ/mol, respectively. There is a small difference between the adsorption energies of butane on iron oxide surfaces obtained from the current DFT calculations with those from experimental measurements for $\alpha$–Al$_2$O$_3$ (35.12 ± 5.02 kJ/mol) (Slayton et al. 1995) and MgO(100) (34.93 kJ/mol) (Tait et al. 2006). Furthermore, the corresponding adsorption energies per saturated carbon site for Fe(110), FeO(110), and Fe$_2$O$_3$(0001) surfaces are 12.04, 10.01, and 8.97 kJ/mol, respectively. It is a reasonably good agreement between the results obtained from DFT calculations and those obtained from experimental and theoretical measurements for iron surface. For instance, Shustorovich and Bell experimentally reported an adsorption energy per methyl group of 12.55 kJ/mol for C$_2$H$_6$ on Fe(110) surface (Shustorovich & Bell 1991). Alternatively, Govender et al. reported an adsorption energy per methyl group of 11.10 kJ/mol for a molecule of ethane adsorbed on the Fe(100) surface using \textit{ab initio} calculation (Govender et al. 2013). Clearly, DFT calculations show a good prediction of adsorption of butane on iron and its oxide surfaces, and this is a physisorption with the adsorption energies per saturated carbon site lower than 15 kJ/mol. Moreover, butane prefers to adsorb on Fe(110) surface rather than FeO(110) and $\alpha$–Fe$_2$O$_3$, and the adsorption energy decreases in the order Fe(110) > FeO(110) > Fe$_2$O$_3$(0001). This observation indicates that higher oxidation state of iron surface results in lower adsorption energy with butane.
Chapter 3 Adsorption of normal-alkanes on Fe(110), FeO(110), and Fe2O3(0001) surfaces

The account of dispersive interactions at the surfaces by aforementioned schemes likely overestimates the adsorption energy. This observation is similar to the work by McNellis et al. who carried out the investigation of adsorption of an azobenzene at coinage metal surfaces to assess the role of vdw interactions (McNellis et al. 2009). A possible reason is that the introduction of simple correction potential to the ordinary DFT xc-functional, which approximates the contribution of missing dispersion, is uncertain and can result in large errors (Thonhauser et al. 2007). Besides, the semi-empirical dispersion corrections still have some weaknesses, especially for transition metal surfaces. For instance, the effect of hybridization states on effective polarization for effective ‘atoms’ of the same species in the molecules is ignored and the lowering of the effective electric constant due to screening (Rehr et al. 1975) is not reflected by reduced dispersion coefficients of atoms in deeper layers (McNellis et al. 2009).

Table 3.5 Geometry parameters and adsorption energies of C₄H₁₀ on Fe(110), FeO(110), and Fe₂O₃(0001) surfaces as defined in Figure 2.2 and obtained from DFT, DFT-D using Grimme (G06) and TS schemes, as well as MD calculations

<table>
<thead>
<tr>
<th>surface</th>
<th>Δzc (Å)</th>
<th>error (%)</th>
<th>Δzh (Å)</th>
<th>error (%)</th>
<th>−E_ads (kJ/mol)</th>
<th>error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DFT</td>
<td>DFT MD</td>
<td>DFT</td>
<td>DFT MD</td>
<td>DFT MD</td>
<td>DFT MD</td>
</tr>
<tr>
<td></td>
<td>TS G06</td>
<td>TS G06</td>
<td>TS G06</td>
<td>TS G06</td>
<td>TS G06</td>
<td>TS G06</td>
</tr>
<tr>
<td>Fe(110)</td>
<td>a</td>
<td>3.523.24</td>
<td>3.923.85</td>
<td>-1.8</td>
<td>2.60 2.982.94</td>
<td>-1.3</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>3.463.31</td>
<td>3.853.83</td>
<td>-0.5</td>
<td>2.53 2.962.93</td>
<td>-1.0</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>3.303.13</td>
<td>3.773.71</td>
<td>-1.6</td>
<td>2.65 2.433.083.04</td>
<td>-1.3</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>3.303.16</td>
<td>3.753.7</td>
<td>-1.3</td>
<td>2.58 2.473.043.02</td>
<td>-0.7</td>
</tr>
<tr>
<td></td>
<td>e</td>
<td>3.333.14</td>
<td>3.333.34</td>
<td>0.3</td>
<td>2.432.2342.432.49</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>f</td>
<td>3.293.25</td>
<td>3.793.54</td>
<td>-6.6</td>
<td>2.382.3292.872.64</td>
<td>-8.0</td>
</tr>
<tr>
<td></td>
<td>g</td>
<td>3.742.98</td>
<td>3.213.28</td>
<td>2.2</td>
<td>3.072.3102.532.64</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>h</td>
<td>3.692.98</td>
<td>3.553.21</td>
<td>-9.6</td>
<td>2.992.2832.882.54</td>
<td>-11.8</td>
</tr>
<tr>
<td></td>
<td>i</td>
<td>2.842.85</td>
<td>3.463.29</td>
<td>-4.9</td>
<td>1.92 1.90 2.532.36</td>
<td>-6.7</td>
</tr>
<tr>
<td></td>
<td>j</td>
<td>3.072.86</td>
<td>3.543.5</td>
<td>-1.1</td>
<td>2.17 1.90 2.622.62</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>k</td>
<td>2.692.64</td>
<td>3.213.15</td>
<td>-1.9</td>
<td>1.97 1.92 2.492.47</td>
<td>-0.8</td>
</tr>
<tr>
<td></td>
<td>l</td>
<td>2.832.80</td>
<td>3.263.25</td>
<td>-0.3</td>
<td>2.16 2.04 2.582.57</td>
<td>-0.4</td>
</tr>
</tbody>
</table>

As a result, the reference data obtained from DFT calculations was used to parameterize the FF for the interaction between alkanes and iron, as well as its oxide
surfaces. A comparison of obtained geometrical properties and adsorption energies between DFT and MD calculations of an adsorbed butane on Fe(110), FeO(110), and Fe$_2$O$_3$(0001) over all chosen configurations shown in Figure 2.2 are presented in Table 3.5. The distance of carbon or hydrogen from the surface is determined by the smallest difference in z coordinate between that atom and the outermost atom of the surface ($ΔZ_C, ΔZ_H$). This separation is the largest for pure iron and the lowest for α-hematite. The largest $ΔZ_C$ and $ΔZ_H$ obtained from DFT calculation for Fe(110) surface are 3.92 Å and 3.04 Å, respectively. Similar, the respective largest $ΔZ_C$ and $ΔZ_H$ for FeO(110) are 3.79 Å and 2.88 Å. For Fe$_2$O$_3$(0001), these values are 3.54 Å and 2.62 Å, respectively. It is noted that in the case of FeO(110), the derived interfacial potential for MD calculations results in larger errors compared to other cases. Particularly, the root-means-square errors of $ΔZ_C$ and $ΔZ_H$ between DFT and MD calculation over four chosen configurations of butane adsorbed on Fe(110) are 1.4% and 1.1% respectively. Similar, for FeO(110), the errors are 6.2% and 8.0% for $ΔZ_C$ and $ΔZ_H$, respectively. For Fe$_2$O$_3$(0001), the respective calculated errors for $ΔZ_C$ and $ΔZ_H$ are 2.7% and 3.4%.

Comparing with MD calculation, the root-mean-square errors of adsorption energies from derived interfacial potential over four chosen configurations of butane adsorbed on Fe(110), FeO(110), and Fe$_2$O$_3$(0001) are respectively 1.3, 4.5, and 4.7%. Notice that these errors are small, which indicates that the prediction of adsorption energies between alkane and Fe(110), FeO(110), and Fe$_2$O$_3$(0001) surfaces is reasonable. Additionally, the results also show similar preferred adsorption sites between current MD and DFT calculations. Particularly, both observations clearly suggests a preferred alignment of butane with its backbone plane parallel to the Fe(110) and FeO(110) surfaces, and aligns between two atomic rows. Similar, for α–Fe$_2$O$_3$, the molecular plane C–C–C of butane is also parallel to the surface. However, it preferentially aligns on the row of iron ions rather than other cases. This propensity is consistent with that observed by Bolton et al who also reported a preferred alignment of octane on the atomic cation row of α–Al$_2$O$_3$ (Bolton et al. 1999).

The results for parameterization of interfacial potential between alkane and Fe(110), FeO(110), and Fe$_2$O$_3$(0001) are shown in Table 3.6. The fitting results show that there are the higher well depth energies and minimum distances between carbon
and surface atoms compared with hydrogen. Moreover, both carbon and hydrogen interact much more strongly with the small iron cation than the much larger oxygen anion. This trend is consistent with the observations of alkanes on α-Al₂O₃ (Bolton et al. 1999; Li & Choi 2007).

Table 3.6 L-J 9-6 Potential parameters for the interactions between C₄H₁₀ and Fe(110), FeO(110), and Fe₂O₃(0001).

<table>
<thead>
<tr>
<th>surface</th>
<th>Pairwise</th>
<th>$\epsilon_i$</th>
<th>$\sigma_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fe–C</td>
<td>0.820</td>
<td>4.22</td>
</tr>
<tr>
<td></td>
<td>Fe–H</td>
<td>0.193</td>
<td>3.02</td>
</tr>
<tr>
<td>Fe–C</td>
<td>0.675</td>
<td>3.35</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>Fe–H</td>
<td>0.241</td>
<td>3.40</td>
</tr>
<tr>
<td>O–C</td>
<td>0.482</td>
<td>4.45</td>
<td></td>
</tr>
<tr>
<td>O–H</td>
<td>0.096</td>
<td>3.50</td>
<td></td>
</tr>
<tr>
<td>Fe–C</td>
<td>0.772</td>
<td>4.02</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Fe–H</td>
<td>0.434</td>
<td>3.20</td>
</tr>
<tr>
<td>O–C</td>
<td>0.145</td>
<td>4.21</td>
<td></td>
</tr>
<tr>
<td>O–H</td>
<td>0.096</td>
<td>3.40</td>
<td></td>
</tr>
</tbody>
</table>

3.3 Adsorption behaviour of n-alkanes

For adsorption of the organic molecules on a surface, the adsorption energy and the surface coverage are crucial components which reflect the adhesive capability of these molecules. In the current MD simulation, the adsorption energy is evaluated as the sum of interaction energies between the molecules and the substrate. The surface coverage is defined as the density of saturated carbon sites per 100 Å². These carbon sites are accounted for the first adsorbed layer only.

The influence of the film thickness on adsorption of butane on Fe(110) shown in Table 3.7 demonstrates that the total adsorption energy and the number of saturated carbon sites increase linearly with the number of molecules within a monolayer. When this layer is nearly filled up with 155.3 saturated carbon sites, corresponding to the surface coverage of 12.6 C atoms/100 Å², the adsorption energy as well as the surface coverage increase slightly with the number of molecules. In fact, although the film thickness increases to four layers but only 163.4 saturated carbon atoms of surface coverage and 1878.9 ± 12.6 kJ/mol of adsorption energy were obtained.
These results are compatible with the case of three atomic layers, where the adsorption energy and the number of saturated carbon atoms are respectively 4.1% and 2.6% higher than that obtained for the case of two atomic layers with 60 butane molecules. In contrast, the calculated adsorption energy per saturated carbons site decreases slightly with an increase of butane molecules within a monolayer. Particularly, this energy component decreases from $10.88 \pm 0.20 \text{ kJ/mol}/\text{CH}_2$ to $10.10 \pm 0.09 \text{ kJ/mol}/\text{CH}_2$ with an increase of the film thickness from 4 to 50 butane molecules. However, there is a light increases of adsorption energy per saturated carbons site with the film thickness, in particular, this energy component increase from $10.10 \pm 0.09 \text{ kJ/mol}/\text{CH}_2$ to $11.50 \pm 0.08 \text{ kJ/mol}/\text{CH}_2$ with an increase of molecular layers from partly formed two layers (50 molecules) to four layers (160 molecules). This energy increment is not significant and just within 11.1%. This finding attributes to the fact that the adsorption of thin alkane film on a surface is mainly contributed by the first adsorbed layer.

Table 3.7 Dependence of adsorption energy on the number of C$_4$H$_{10}$ molecules on Fe(110) surface at 150K.

<table>
<thead>
<tr>
<th>No. layers</th>
<th>No. C$<em>4$H$</em>{10}$ (molecules)</th>
<th>No. adsorbed C (atoms)</th>
<th>No. adsorbed carbon/100Å$^2$ (atoms)</th>
<th>$-E_{ads}$ (kJ/mol)</th>
<th>$-E_{ads}/\text{CH}_2$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>one</td>
<td>4</td>
<td>16.0</td>
<td>1.3</td>
<td>174.1 ± 3.2</td>
<td>10.88 ± 0.20</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>108.0</td>
<td>8.7</td>
<td>1152.7 ± 11.8</td>
<td>10.67 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>155.3</td>
<td>12.6</td>
<td>1584.6 ± 22.1</td>
<td>10.20 ± 0.14</td>
</tr>
<tr>
<td>two</td>
<td>50</td>
<td>165.2</td>
<td>13.4</td>
<td>1669.8 ± 15.2</td>
<td>10.10 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>162.0</td>
<td>13.1</td>
<td>1709.6 ± 15.0</td>
<td>10.55 ± 0.09</td>
</tr>
<tr>
<td>three</td>
<td>80</td>
<td>166.3</td>
<td>13.5</td>
<td>1782.9 ± 14.3</td>
<td>10.72 ± 0.09</td>
</tr>
<tr>
<td>four</td>
<td>160</td>
<td>163.4</td>
<td>13.2</td>
<td>1878.9 ± 12.6</td>
<td>11.50 ± 0.08</td>
</tr>
</tbody>
</table>

The adsorption energy between the film and the substrate can increase after one monolayer is due to the dispersive interactions of outer layers inducing on inner ones and the surface. Particularly, the second layer is roughly 6 Å away from the surface and still lower than the cut-off distances of pairwise interactions between the surfaces and the second layer. Additionally, as shown in Figure 3.2, the dispersive interactions between the outer layers with inner ones and the surfaces condense the thin film further. This factor causes as light increase of both adsorption energy and the number of saturated carbon sites on the surface.
Regarding the influence of surface relaxation, the results indicate that the effect of the relaxation of the surfaces on the adsorption of butane is not significant. As shown in Table 3.8, the adsorption energy per carbon site on relaxed Fe(110) is $11.48 \pm 0.08$ kJ/mol, which is within 0.01 kJ/mol less than that obtained from the unrelaxed surface. Similarly, the differences between the cases of relaxed with the optimized charge and unrelaxed with the bulk charge are also only 0.02 and 0.88 kJ/mol for the case of FeO(110) and Fe$_2$O$_3$(0001) surfaces, respectively. These values correspond to the energy differences of 0.1, 0.2, and 9.1% for Fe(110), FeO(110) and Fe$_2$O$_3$(0001), respectively. Additionally, it is noted that the contribution of electrostatic interaction between butane and the surfaces was also quite small. The adsorption energy of C$_4$H$_{10}$ on FeO(110) for the case without atomic charge was 7.3% lower than that including the optimized charge, and only 0.6% for Fe$_2$O$_3$(0001). This can be attributed to the insignificant electrostatic interaction between alkane and the iron oxide surfaces, and the major contribution is the vdW interactions. This finding is consistent with the statement by Li and Choi who explained that alkane-inorganic interface carried relatively small partial atomic charges as this organic molecule was nonpolar in its bulk state (Li & Choi 2007).

The adsorption behaviour of $n$-alkanes on the considered surfaces can be considered in Figure 3.1 where a representative $n$-alkane molecule - C$_4$H$_{10}$ is shown. It should be pointed out that the alkane molecules in the thin film are pulled toward the surfaces during the dynamic relaxation and the layer forming was found on the surfaces. Figure 3.2 shows the atomic density profile of C$_4$H$_{10}$ across the thin film thickness for Fe(110), FeO(110), and Fe$_2$O$_3$(0001). The averaged separations between the first nearest layer of butane and the outermost surface’s atom are respectively 3.61, 3.52, and 3.26 Å for Fe(110), FeO(110), and Fe$_2$O$_3$(0001). There is a decrease of distance between the first alkane layer and the surface with an increase of oxidized state of iron surface. This decreasing trend at 150 K using MD calculation is consistent with that observed from DFT calculation at 0 K.

Although the interaction strength ($\varepsilon$) between carbon and iron is strongest for Fe(110) surface, as shown in Table 3.8, the butane film is furthest away for this case (Figure 3.1). Iron is the outermost atom of both all relaxed surfaces (Figure 2.1), and its contribution to the interaction between the surface and alkane is significant in
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comparison with hydrogen (Table 3.8). The largest equilibrium distance ($\sigma$) between carbon and iron on Fe(110) surface could be the source of this observation. The surface corrugation, i.e., the wall-fluid commensurability also plays a vital role on the behaviour of fluid at the surface (Savio et al. 2012; Thompson & Robbins 1990). In fact, it is found that Fe2O3(0001) surface is more corrugated than pure iron (Savio et al. 2012), and the size of lattice constant of Fe(110) is smaller than FeO(110) and Fe2O3(0001) (Table 3.1). The butane molecules are therefore easier to fit between atoms on the oxide surfaces than pure iron. It is due to the commensurability of CHx groups and the lattice constants of the surfaces (Savio et al. 2012). These factors affect the distance between the butane film and surfaces.

Table 3.8 Comparison of adsorption of thin C4H10 film on relaxed and unrelaxed FeO(110), FeO(110), and Fe2O3(0001) surfaces at 150K.

<table>
<thead>
<tr>
<th>surface</th>
<th>-E_ads  (kJ/mol)</th>
<th>No. adsorbed carbon (atoms)</th>
<th>-E_ads/CH2 (kJ/mol)</th>
<th>No. adsorbed carbon/100Å² (atoms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(110)</td>
<td>1876.5 ± 9.6</td>
<td>163.6</td>
<td>11.47 ± 0.06</td>
<td>13.2</td>
</tr>
<tr>
<td>unrelaxed</td>
<td>1876.1 ± 13.2</td>
<td>163.4</td>
<td>11.48 ± 0.08</td>
<td>13.2</td>
</tr>
<tr>
<td>relaxed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeO(110)</td>
<td>1532.0 ± 16.7</td>
<td>163.2</td>
<td>9.40 ± 0.10</td>
<td>12.7</td>
</tr>
<tr>
<td>unrelaxed with bulk charge</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>relaxed with optimized charge</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe2O3(0001)</td>
<td>1606.2 ± 23.5</td>
<td>166.8</td>
<td>9.63 ± 0.14</td>
<td>13.6</td>
</tr>
<tr>
<td>unrelaxed with bulk charge</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>relaxed with optimized charge</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>relaxed without charge</td>
<td>1434.7 ± 15.2</td>
<td>164.9</td>
<td>8.75 ± 0.09</td>
<td>13.4</td>
</tr>
<tr>
<td>relaxed without charge</td>
<td>1434.8 ± 13.8</td>
<td>164.1</td>
<td>8.74 ± 0.08</td>
<td>13.3</td>
</tr>
</tbody>
</table>

In addition, there is a decrease of the peak atomic density of molecular backbone carbon with adsorption strength. In particular, Figure 3.2 shows the peak atomic density for Fe(110) surface is 31.4 carbon atoms, compared with 30.2 and 27.6 carbon atoms for FeO(110) and Fe2O3(0001), respectively. The peak atomic density decreases in the order Fe(110) > FeO(110) > Fe2O3(0001) followed the same trend with adsorption energy as previously stated. However, the surface coverage of butane on these surfaces is quite insensitive to the surface potential. In particular, the total numbers of 163.4, 167.5, and 164.9 saturated carbon atoms are respectively for Fe(110), FeO(110), and Fe2O3(0001) surfaces. These values correspond to the saturated carbon atom per 100 Å² of 13.2, 13.1, and 13.4 (Table
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3.8) which is consistent with that observed by Li and Choi (Li & Choi 2007). Our findings attributed to the interfacial potential effects on the in-plane order structure of alkane but not to surface coverage.

![Figure 3.1 Snapshot of thin C₄H₁₀ film adsorbed on the surfaces at 150K: (a) Fe(110); (b) FeO(110); and (c) Fe₂O₃(0001).](image)

The interlayer distance between the first two consecutive layers of butane can be estimated from the separation between the peaks of the first and second layers. The estimated interlayer distance for Fe(110) is 3.93 Å, compared with 3.98 Å for FeO(110) and 3.95 Å for Fe₂O₃(0001). However, for the rest of the thin alkane film, the same interlayer distance of 4.32 Å is found for all cases. In fact, the influence of attractive force from the surfaces on the outer layers is quite weak so there is no such difference for the interlayer distance between these layers, and their interlayer distances are consequently larger than the inner ones.

![Figure 3.2 Atomic density profiles across the film thickness of butane along the surface normal direction of Fe(110), FeO(110), and Fe₂O₃(0001) surfaces at 150K.](image)
Chapter 3 Adsorption of normal-alkanes on Fe(110), FeO(110), and Fe$_2$O$_3$(0001) surfaces

The snap-shots of the first layers of adsorbed butane molecules on iron and its oxide surfaces are presented in Figure 3.3, which shows an interesting observation: the skeletal backbone chains of alkane molecules almost align parallel to the surfaces. However, for Fe$_2$O$_3$(0001), there is small fraction of butane molecules perpendicular to this surface. Additionally, the in-plane alignment is not in any preferred direction for Fe(110) and Fe$_2$O$_3$(0001) surfaces. However there is a preferred alignment of alkane in (010) direction on the FeO(110) surface.

Figure 3.3 Snap-shots of the first adsorbed C$_4$H$_{10}$ layer on the surfaces at 150K: (a) Fe(110); (b) FeO(110); and (c) Fe$_2$O$_3$(0001).

The adsorption energy of thin alkane film on Fe(110), FeO(110) and Fe$_2$O$_3$(0001) is shown in Figure 3.4. The results reveal that there is a nonlinear dependence of the adsorption energy of the thin alkane film on the molecular chain length. When the molecular backbone increases from C$_4$ to C$_6$ the adsorption energy increases. For Fe(110), it still keeps increasing but very slightly with the molecular chain length until a peak is reached at C$_{10}$, followed by a gradual decrease then on to C$_{16}$. This decreasing trend of adsorption energy for the case of oxide surfaces is earlier and clearer at C$_6$. Furthermore, the adsorption energies are also different for the respective surfaces. The results show that the maximum adsorption energy for the case of Fe(110) is 2200.8 ± 19.4 kJ/mol, following by 1629.1 ± 12.6 and 1596.2 ± 18.1 kJ/mol respectively for FeO(110) and Fe$_2$O$_3$(0001), in a decreasing order Fe(110) > FeO(110) > Fe$_2$O$_3$(0001).
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Figure 3.4 Dependence of adsorption energy on molecular chain length of $n$–alkane on Fe(110), FeO(110), and Fe2O3(0001) at 150K.

The relationship between surface coverage and molecular chain length presented in Figure 3.5 shows a nonlinearly increase of number of saturated carbon site per 100 Å² with an increase of molecular chain length. At the molecular chain length of C₄ there are only 13.22, 13.06, and 13.41 carbon atoms per 100 Å² on Fe(110), FeO(110), and Fe2O3(0001), respectively. However these values increase dramatically with a further increase of the chain length and they become steady at ~16C atoms/100 Å² when the chain length is C₁₀. This propensity is similar for all surfaces and there is no significant difference in the number of saturated carbon site per 100 Å² between these surfaces. This observation shows that the coverage of alkane on the surface was insensitive to the interfacial potential.

Remarkably, the long-chain alkanes have larger adsorbed carbon density than shorter alkanes in spite of the fact that the short alkanes have more flexibility to get closer to the surface. It is due to the end carbon effect. Particularly, for the same surface area, the number of short-chain molecules adsorbed on surface is larger than longer ones. The number of end carbon sites therefore increases with number of molecules while the sites occupied by the middle carbons decreases. As the space occupied by the end carbon sites is larger than the middle carbons, the saturated carbon density for short alkanes is consequently lower than longer alkanes.
Figure 3.5 Dependence of surface coverage on molecular chain length of $n$-alkane on Fe(110), FeO(110), and Fe$_2$O$_3$(0001) at 150K.

An important physical component to examine the adsorption capability of alkane on a surface is the adsorption energy per saturated carbon site. The results for Fe(110), FeO(110), and Fe$_2$O$_3$(0001) surfaces in Figure 3.6, show that there is a linear decrease of adsorption energy per saturated carbon atom with an increase of molecular chain length. This observation demonstrates that smaller alkanes bind strongly to the surface than their longer chain counter parts. This propensity is consistent with an experimental observation of adsorption of $n$-alkanes on Au(111) (Wetterer et al. 1998). For Fe(110) surface, the adsorption energy per saturated methylene group decreases linearly from 12.25 to 10.74 kJ/mol for an increase of alkane’s chain length from C$_4$ to C$_{16}$. A similar trend holds for FeO(110) as well as Fe$_2$O$_3$(0001) surface. Particularly, the adsorption energy per methylene group also decreases from 9.64 to 7.84 kJ/mol, and 8.59 to 7.03 kJ/mol with an increase of molecular chain length for FeO(110) and Fe$_2$O$_3$(0001), respectively. Thus, these results indicate that $n$-alkanes physisorb on iron and its oxide surfaces and the evaluated adsorption energy per saturated carbon site in a decreasing order Fe(110) $>$FeO(110) $>$Fe$_2$O$_3$(0001). This observation is in the same trend with that reported by Tait et al. who found that $n$-alkane bound more weakly on metal oxide than metal at different $n$-alkane chain lengths and observed temperatures (Tait et al. 2006). An explanation could be due to the higher electric polarizability of the metal which strengthens the molecule-surface dispersion interactions (Weaver et al. 2014).
Figure 3.6 Dependence of adsorption energy per saturated carbon site on molecular chain length of \( n \)-alkane on Fe(110), FeO(110), and Fe\(_2\)O\(_3\)(0001) at 150K.

Figure 3.6 shows the variation of the adsorption energy per saturated carbon with the chain length for different surfaces. The adsorption energy per saturated carbon is defined as ratio of total adsorption energy to the surface coverage (adsorption density). As the total adsorption energy depends on the type of surface (Figure 3.4), although the surface coverage density does not (Figure 3.5), the ratio of the two (Figure 3.6) would still be dependent on the surface types.

3.4 Conclusion

MD simulation has been carried out to provide an understanding of fundamental adsorption of normal-alkanes on Fe(110), FeO(110), and Fe\(_2\)O\(_3\)(0001) surfaces. DFT geometry optimization has been also carried out to fully relax the surfaces and derive an effective interfacial force field for the interaction between alkane and these surfaces. The findings can be summarized as follows:

(i) The Fe(110) and FeO(110) surfaces are basically bulk terminated while a significant relaxation is observed for Fe\(_2\)O\(_3\)(0001). However, the surface relaxation does not play a vital role in adsorption capability of alkanes on these surfaces.

(ii) The adsorption energies per saturated methylene group decrease with an increase of molecular chain length on both iron and its oxide surfaces. For short alkane molecules, the saturated carbon density increases with the
(iii) Alkanes physisorb more strongly on Fe(110) surface than FeO(110) and Fe$_2$O$_3$(0001). Additionally, they form layers with their molecular plane parallel to the surfaces and there is a preferred orientation of alkane chain in (010) direction on FeO(110) at low temperature.
Chapter 4 Thin film lubrication of hexadecane: A crucial role of surface structure

In this chapter, the shear viscosity of hexadecane lubricant at ambient condition as well as its lubrication performance between iron and iron oxide surfaces is presented. The influences of iron oxide surfaces and relative sliding direction on tribological and rheological properties of hexadecane have been analyzed using a surface parameterization that includes the influence of surface corrugation and commensurability.

4.1 Lubrication of hexadecane between iron and iron oxide surfaces

Under confinement and sliding motion of the surfaces, the momentum was transferred into the fluid resulting in layering structure and solid-like behaviour of molecules adjacent to the surfaces (Ohara & Torii 2005; Suzuki 2001). This layering density profile oscillated with the highest degree of layering at the wall-fluid interface, then gradually reduced toward the bulk material in the middle of the film gap. There are seven distinct layers across the film thickness for all surface models due to the similar initial film thickness (Figure 4.1). However, there is a difference in in-plane ordering of each surface which is characterized by the degree of layering at the interface. In fact, as reported in Table 4.1, the largest peak of 3.33 g/cc in the density profile is found on the Fe(110) surface; whilst it is only 0.93 g/cc for FeO(111). This statistical component decreases in the following order Fe(110) > FeO(100), Fe(100) > FeO(110) > Fe₂O₃(012) > Fe(111) > Fe(111)(010) > Fe₂O₃(001) > FeO(111). This order is consistent with our previous finding for the adsorption of butane on Fe(110), FeO(110), and Fe₂O₃(001). Generally, there is a less ordering of hexadecane between Fe₂O₃ surfaces when compared with pure iron and FeO; except FeO(111).

It is noted that although there is a remarkable difference in the degree of layering, the summation of density in this layer differs insignificantly. Particularly, as presented in Table 4.1, this component varies in a range from 11.23 g/cc to 13.76 g/cc. It is due to the insensitivity of surface coverage of hexadecane with surface potential. The
results also show that the obtained film thickness is dependent on surface model, although it was initially similar. As a result, the average lubricant density is also different, but this difference is quite small and within 0.1 g/cc.

Figure 4.1 Density profile of hexadecane film across film thickness for: (a) Fe; (b) FeO; and (c) Fe₂O₃ surfaces at applied pressure of 500 MPa, sliding velocity of 10 m/s, and temperature of 300 K.

The high in-plane ordering of hexadecane on Fe(110), FeO(100), Fe(100), FeO(110), Fe₂O₃(012), and Fe(111) surfaces yields a solid-like behaviour in the thin film lubricant. As shown in Figure 4.2, this solid-like phenomenon is characterized by a substantial slip of lubricant at both walls. An interesting observation is that there appears to be a plug-slip phase, whereby the whole film acts as a rigid solid-like
block for Fe(110), FeO(100), Fe(100), FeO(110), Fe(111), and Fe$_2$O$_3$(012) surfaces. For the films at the same thickness confined by FeO(111), Fe$_2$O$_3$(001), and Fe(111) surfaces, an inhomogeneous velocity profile shows almost stick boundaries as well as linear internal deformation. Remarkably, for the same system model of Fe(111), the velocity profiles are different for different sliding directions, in particular, an inhomogeneous velocity profile, with internal deformation, is seen for the case of sliding in the (010) direction, whereas full slip is observed at the interface for the (100) direction. This effect could stem from a number of sources; however, in this work, we only focus on the influence of surface corrugation and interaction strength of the studied surfaces.

A linear function was used to fit the velocity profile of these surface models based on obtained statistical data of lubricant velocity. Then the effective shear rate $\partial u/\partial z$, which was the slope of the linear function, was determined for each surface model. The obtained results, as presented in Table 4.1, show that the shear rate for Fe(110) surface is nearly zero, whilst it is significant for Fe$_2$O$_3$(001) (5.95 ns$^{-1}$), Fe(111)(010) (6.14 ns$^{-1}$), and FeO(111) (7.62 ns$^{-1}$).

![Figure 4.2 Velocity profiles of hexadecane film across film thickness and their appropriate fitting lines for different iron and iron oxide surfaces sliding in (100) direction (except Fe(111)(010) surface model) at applied pressure of 500 MPa, sliding velocity of 10 m/s, and temperature of 300 K.](image)

In tribology, the shear stress and coefficient of friction are crucial physical components to assess the tribological performance a tribosystem. The coefficient of friction is evaluated as the ratio of the shear stress and loading pressure. It is noted
that the shear stresses increase in an order contrasting with that observed for degree of layering. Particularly, the highest shear stress of 65.81 MPa is found for FeO(111) and the lowest value of 2.56 MPa for Fe(110). Notably, the shear stress of 56.44 MPa for Fe$_2$O$_3$(001) is higher than the value of 45.5 MPa obtained from the work by Savio et al. using a UA model (Savio et al. 2012). Furthermore, by varying the Lennard-Jones energy parameter (0.5-15 times) of the iron atoms of Fe$_2$O$_3$(001) surface, Berro et al. reported a CoF of 0.073-0.09 (Berro et al. 2010); lower than that obtained from this work (Table 4.1). This discrepancy could be due to the employed model for alkane, in which the explicit steric effects of hydrogen atoms are taken into account in the current EA model, and to the difference in the interfacial interaction parameters (Bolton et al. 1999).

To assess the solid-like behaviour of hexadecane on the considered surfaces, the shear viscosity, which is defined as the ratio of shear stress and effective shear rate, is shown in Table 4.1. It is noted that the viscosity of lubricant confined between Fe(110), FeO(100), FeO(110), Fe(111), Fe(100) surfaces – in a decreasing order, is higher than Fe$_2$O$_3$(001), FeO(111), and Fe(111)(010).

Table 4.1 Rheological and tribological properties of hexadecane confined between different iron and iron oxide surface models at 500 MPa, 10 m/s, and 300K.

<table>
<thead>
<tr>
<th>Surfaces</th>
<th>$\rho_{\text{max}}$</th>
<th>$\sum_{n\text{bins in }1^{\text{st}}\text{layer}}\rho_{i}$</th>
<th>$\rho_{\text{ave}}$</th>
<th>$\tau_{xx}$</th>
<th>$\Delta\tau_{xx}$</th>
<th>$\mu$</th>
<th>$h$</th>
<th>$\Delta v_x/\Delta z$</th>
<th>$\eta_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(100)</td>
<td>2.59</td>
<td>11.65</td>
<td>0.937</td>
<td>6.18</td>
<td>± 4.88</td>
<td>0.012</td>
<td>27.35</td>
<td>0.06</td>
<td>108.04</td>
</tr>
<tr>
<td>Fe(110)</td>
<td>3.33</td>
<td>11.51</td>
<td>0.948</td>
<td>2.56</td>
<td>± 3.06</td>
<td>0.005</td>
<td>27.06</td>
<td>0.02</td>
<td>129.29</td>
</tr>
<tr>
<td>Fe(111)</td>
<td>1.73</td>
<td>11.69</td>
<td>0.939</td>
<td>15.36</td>
<td>± 7.03</td>
<td>0.031</td>
<td>27.36</td>
<td>0.22</td>
<td>68.97</td>
</tr>
<tr>
<td>Fe(111)(010)</td>
<td>1.62</td>
<td>13.76</td>
<td>0.918</td>
<td>35.95</td>
<td>± 9.39</td>
<td>0.062</td>
<td>27.98</td>
<td>6.14</td>
<td>5.04</td>
</tr>
<tr>
<td>FeO(100)</td>
<td>2.59</td>
<td>11.33</td>
<td>0.940</td>
<td>8.44</td>
<td>± 6.35</td>
<td>0.017</td>
<td>27.20</td>
<td>0.43</td>
<td>19.82</td>
</tr>
<tr>
<td>FeO(110)</td>
<td>2.54</td>
<td>11.35</td>
<td>0.940</td>
<td>8.19</td>
<td>± 6.17</td>
<td>0.016</td>
<td>26.89</td>
<td>0.12</td>
<td>70.60</td>
</tr>
<tr>
<td>FeO(111)</td>
<td>0.93</td>
<td>11.60</td>
<td>0.841</td>
<td>65.81</td>
<td>± 9.75</td>
<td>0.144</td>
<td>30.63</td>
<td>7.62</td>
<td>9.42</td>
</tr>
<tr>
<td>Fe$_2$O$_3$(001)</td>
<td>1.55</td>
<td>11.23</td>
<td>0.909</td>
<td>56.44</td>
<td>± 9.70</td>
<td>0.114</td>
<td>28.12</td>
<td>5.95</td>
<td>9.48</td>
</tr>
<tr>
<td>Fe$_2$O$_3$(012)</td>
<td>1.85</td>
<td>12.73</td>
<td>0.903</td>
<td>19.00</td>
<td>± 6.53</td>
<td>0.040</td>
<td>28.46</td>
<td>0.99</td>
<td>19.24</td>
</tr>
</tbody>
</table>

The molecular alignment of hexadecane molecules of aforementioned surface models was also considered. The snapshots of molecular configuration of the first layer of thin hexadecane film confined between different iron and its oxide surface are shown in Table 4.3. It is noted that there is a parallel alignment of hexadecane
molecules on the surfaces. This observation is consistent with the experimental observation of adsorption of alkanes on Au(111) surfaces (Wetterer et al. 1998), and other theoretical investigations (Li & Choi 2007; Morikawa et al. 2004). However, there is a random alignment of hexadecane molecules with Fe(100), Fe(110), Fe₂O₃(001), and FeO(111) surfaces whilst the preferred aligning directions are seen with Fe(111), Fe(111)(010), FeO(100), FeO(110), and Fe₂O₃(012). Remarkably, a favoured molecular alignment in the (100) direction of Fe(111) surface is found for the case of sliding in this direction (Table 4.3c) and (010) (Table 4.3d). Thus it can be concluded that the local alignment of molecules at the Fe(111) surface is insensitive with the sliding direction.

![Figure 4.3 Snapshots of molecular configuration of hexadecane at the first layer of thin film confined between different iron and iron oxide surfaces sliding in (100) direction (except Fe(111)(010) surface model) at applied pressure of 500 MPa, and temperature of 300 K.](image-url)
4.2 Shear viscosity

The calculated density of hexadecane using COMPASS force-field at ambient condition is 0.77 g/cc, which is consistent with experimental measurement (Tanaka et al. 1993). The obtained results, as presented in Table 4.4, show that the viscosity decreases with the increase of shear rate. However, the predicted zero-viscosity and the thinning regime from the current work are different from those obtained by Berro et al. who employed the AMBER96 force-field for hexadecane (Berro et al. 2009). Particularly, the zero-viscosity in this work is 3.082 mPa.s, which is close to the experimental measurement of 3.0248 mPa.s (Lorenzo De Lorenzi 1995; Stevens et al. 1996), but it is higher than 2.43 mPa.s and 2.08 mPa.s that obtained from their work using the hybrid diffusion method and 2D thermostat method, respectively. Thus it can be noted that the COMPASS force-field can describe properly the density and viscosity of hexadecane. The onset of thinning regime for COMPASS force-field is $2 \times 10^9 \text{s}^{-1}$, whilst it is $4 \times 10^9 \text{s}^{-1}$ for AMBER96.

Figure 4.4. Variation of viscosity of hexadecane determined from MD simulation at ambient condition. The dash line, dot line, and dash-dot lines are respectively correspond to Carreau fits of COMPASS-NEMD, AMBER-2D thermostat, and AMBER-hybrid diffusion methods. The asterisks indicate the results obtained by Berro et al. (Berro et al. 2009), and the arrow presents the experimental Newtonian viscosity.
Table 4.2 Comparison of Newtonian viscosities for different employed potentials of hexadecane.

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Model</th>
<th>$\eta_0$ (mPa.s)</th>
<th>$\eta_0$ (exptl) (mPa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexadecane</td>
<td>COMPASS-NEMD</td>
<td>3.082</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AMBER-2D thermostat</td>
<td>2.08$^a$</td>
<td>3.0248$^b$</td>
</tr>
<tr>
<td></td>
<td>AMBER-hybrid diffusion method</td>
<td>2.43$^a$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Results obtained by Berro et al. (Berro et al. 2009)

$^b$ Result obtained from experiment (Lorenzo De Lorenzi 1995; Stevens et al. 1996)

4.3 Surface characterization

Table 4.3 shows a comparison of the adsorption energies and the carbon site’s minimum equilibrium distances from the surfaces between the current MD calculation using UA model and the reference data obtained from previous DFT calculation. The errors within 5% are found for Fe(110) and F$_2$O$_3$(001) surfaces, whilst some higher deviations are reported for FeO(110). The minimum cost ($f(\epsilon_i, \sigma_i)$) of the potential parameterization over chosen molecular configurations of butane adsorbed on Fe(110), FeO(110), and F$_2$O$_3$(001) surfaces are 1.2%, 8.6%, and 2.7%, respectively.

The fitting results are shown in Table 4.4. The adhesive strengths ($\epsilon_{ij}$) of atomic interactions between the surface’s atoms with the carbon site (CH$_x$) are higher than those obtained from previous interfacial potential parameterization for carbon. This new interfacial potential was then utilized for the surface parameterization.

Table 4.5 shows that there is a correlation between the atomic structure and the scanned potential energy landscape of the surface. In this study, the surface potential energy is defined as the interaction energy between the scanning atom and surface. For pure iron, the lowest surface energy is found on the top of interfacial iron atoms (on-top sites) while the highest surface energies are found on hollow sites (Table 4.5a-c). This observation is consistent with our previous DFT calculation which shows that n-butane molecule is more stable at location between iron rows of Fe(110) surface rather than at on-top sites. Furthermore, from *ab initio* calculations, Lo and Ziegler found that most two-carbon species preferred to adsorb at the hollow site on Fe(100) (Lo & Ziegler 2007). A similar propensity is found for iron oxides;
however, the higher surface energy is observed at iron atom rather than oxygen. It could be due to the stronger interaction strength between scanning atom (characterized by a carbon site) and iron.

Table 4.3 Adsorption energies (-$E_{ad}$) and structural parameters ($\Delta Z_{CHx}$) of C$_4$H$_{10}$ on Fe(110), FeO(110), and Fe$_2$O$_3$(0001) surfaces obtained from previous DFT calculation and the current MD calculation.

<table>
<thead>
<tr>
<th>Surfaces</th>
<th>Figure 2.2</th>
<th>$E_{ad}$</th>
<th>Error</th>
<th>$\Delta Z_{CHx}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(110)</td>
<td>a</td>
<td>48.050</td>
<td>1.24</td>
<td>3.92</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>48.146</td>
<td>1.06</td>
<td>3.85</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>42.550</td>
<td>-0.34</td>
<td>3.77</td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>42.647</td>
<td>-0.46</td>
<td>3.75</td>
</tr>
<tr>
<td></td>
<td>e</td>
<td>36.182</td>
<td>9.37</td>
<td>3.33</td>
</tr>
<tr>
<td></td>
<td>f</td>
<td>40.041</td>
<td>3.13</td>
<td>3.79</td>
</tr>
<tr>
<td>FeO(110)</td>
<td>g</td>
<td>33.673</td>
<td>1.32</td>
<td>3.21</td>
</tr>
<tr>
<td></td>
<td>h</td>
<td>36.857</td>
<td>3.37</td>
<td>3.55</td>
</tr>
<tr>
<td></td>
<td>i</td>
<td>35.893</td>
<td>4.72</td>
<td>3.46</td>
</tr>
<tr>
<td></td>
<td>j</td>
<td>35.893</td>
<td>-1.64</td>
<td>3.54</td>
</tr>
<tr>
<td></td>
<td>k</td>
<td>33.866</td>
<td>2.25</td>
<td>3.21</td>
</tr>
<tr>
<td>Fe$_2$O$_3$(0001)</td>
<td>l</td>
<td>32.612</td>
<td>-3.75</td>
<td>3.26</td>
</tr>
</tbody>
</table>

* Data obtained from previous DFT calculation

Table 4.4 L-J 9-6 interfacial potential parameters for the interactions between C$_4$H$_{10}$ and Fe(110), FeO(110), and Fe$_2$O$_3$(0001).

<table>
<thead>
<tr>
<th>Surface</th>
<th>Pairwise</th>
<th>$\varepsilon_{ij}$</th>
<th>$\sigma_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fe–C(H$_x$)</td>
<td>0.868</td>
<td>4.35</td>
</tr>
<tr>
<td>FeO</td>
<td>Fe–C(H$_x$)</td>
<td>0.965</td>
<td>3.78</td>
</tr>
<tr>
<td></td>
<td>O–C(H$_x$)</td>
<td>0.386</td>
<td>4.53</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>Fe–C(H$_x$)</td>
<td>1.544</td>
<td>3.75</td>
</tr>
<tr>
<td></td>
<td>O–C(H$_x$)</td>
<td>0.289</td>
<td>4.43</td>
</tr>
</tbody>
</table>
Chapter 4 Thin film lubrication of hexadecane: A crucial role of surface structure

Figure 4.5 Atomic surface structures and their relevant scanned potential energy landscapes for different iron and iron oxide surfaces. The contour level of potential energy for each surface can be referred to Figure 4.6-4.8.

As reported in Table 4.5, pure iron surfaces have larger surface energies ($-\bar{V}_{\text{scan}}$) than iron oxides. This tendency is consistent with our previous observation in which the largest interaction energy between alkane and surface is found on Fe(110). The Fe$_2$O$_3$(001) surface shows the highest energy corrugation of 0.707 kJ/mol while it is only 0.071 kJ/mol for Fe(110). This energy corrugation strongly depends on the surface structure. For instance, for nearly the same surface energies such as Fe(111) ($-\bar{V}_{\text{scan}}$ = 5.628 kJ/mol) and Fe(100) ($-\bar{V}_{\text{scan}}$ = 5.770 kJ/mol), the Fe(111) surface ($V_{\text{corr}}$ = 0.561 kJ/mol) is more corrugated than Fe(100) ($V_{\text{corr}}$ = 0.184 kJ/mol). A similar observation was found with FeO, where in which the (111) surface is significantly more corrugated than (100) and (110). The surface corrugation increases in the following order Fe(110) < FeO(100) < Fe(100) < FeO(110) < Fe(111) < Fe(111)(010) < FeO(111) < Fe$_2$O$_3$(012) < Fe$_2$O$_3$(001).

The surface energy affects the lubricant’s properties, i.e. the in-plane ordering, density profile, and the shear stress of confined shear model (Berro et al. 2010). However, even surfaces with the same interaction strength and energy corrugation of Fe(111), the shear stresses can be different, for the case of sliding in different directions (Table 4.1). The role of resisting force can be used to explain this issue.
As shown in Figures 4.6-4.8, there is a correlation between the resisting force and surface potential energy landscape. In fact, the periodicity of resisting forces is consistent with potential energy landscape and atomic structure of the surfaces in sliding direction. For Fe(111) surface, for example, the resisting force differs in different sliding directions although it has the same potential energy landscape, in particular, a corrugation force of 0.469 kJ/mol/Å is found for the case of sliding in (100) direction while there is 1.950 kJ/mol/Å for (010) direction. This corrugation force discrepancy could be explained by the difference of atomic spacing in these directions. Particularly, for an approximate sliding distance, there are 14 periodicities of resisting force, which is also appropriate with 14 atomics spaces, in (100) direction (Figure 4.6c) while this is only nine periodicities in (010) (Figure 4.6d).

Figure 4.6 Resisting forces and surface energy landscapes for different iron surfaces: (a) Fe(100); (b) Fe(110); (c) Fe(111); (d) Fe(111)(010).
Chapter 4 Thin film lubrication of hexadecane: A crucial role of surface structure

Figure 4.7 Resisting forces and surface energy landscapes for different FeO surfaces: (a) FeO(100); (b) FeO(110); (c) FeO(111).

For iron oxides, the correlation between resisting force and surface energy is shown in Figures 4.7-4.8. The corrugation force obtained on Fe$_2$O$_3$(012), FeO(100), and FeO(110) surfaces is small (<0.8 kJ/mol/Å) but it is remarkably larger for Fe$_2$O$_3$(001) (1.749 kJ/mol/Å) and FeO(111) (2.749 kJ/mol/Å). It is noted that there are two frequencies of resisting force for FeO(111) surface (Figure 4.7c). This could be due to the influence of the surface potential; in particular, both iron and oxygen are presented on the top atomic layer of FeO(111) surface; however, the minimum surface energy is seen at the iron’s row (Table 4.5f), which correspond to the largest resisting force (Figure 4.7c). The second peak of resisting force occurs at the position of the second iron layer, underneath and between the iron and oxygen of the first atomic layer. Clearly, the difference in interaction strength and equilibrium distance between the scanning atom and the iron oxide surface’s atoms has resulted
in a complex potential energy landscape and resisting force. As presented in Table 4.5, the corrugation force increases in following order Fe$_2$O$_3$(012) < Fe(110) < FeO(100) < Fe(111) < Fe(100) < FeO(110) < Fe$_2$O$_3$(001) < Fe(111)(010) < FeO(111).

Figure 4.8 Resisting forces and surface energy landscapes for different Fe$_2$O$_3$ surfaces: (a) Fe$_2$O$_3$(001); (b) Fe$_2$O$_3$(012).

It is also noted that there is a correlation between the surface commensurability ($h_{comm}$) and the interfacial atomic spacing ($\lambda$) (Table 4.5). This correlation is confirmed through the fact that when the denser packed crystal surface, which corresponding to lower atomic spacing, is observed the smoother surface is obtained. This observation is consistent with the work by Savio et al. (Savio et al. 2012) and Cui et al. (Cui et al. 1999).

The corrugation force, which was defined as the maximum resisting force by Savio et al., and its relevant surface parameter are also taken into account in this study (Savio et al. 2012). However, it should be noted that there are either negative corrugation force for the cases of Fe(110) and Fe$_2$O$_3$(012) surfaces or zero for FeO(100). These values consequently result in unphysical meaning of surface energy parameter. A modified corrugation force, as expressed in Equation 2.16, was used in this study and the obtained results for this component as well as the surface energy parameter are shown in Table 4.5.
Table 4.5 Average scanned surface energies ($\overline{V}_{\text{scan}}$), surface corrugation energies ($V_{\text{corr}}$), corrugation forces ($F_{\text{corr}}$), commensurability heights ($h_{\text{comm}}$), and surface parameters ($\zeta$) for different iron and iron oxide surfaces.

<table>
<thead>
<tr>
<th>Surfaces</th>
<th>$\overline{V}_{\text{scan}}$</th>
<th>$V_{\text{corr}}$</th>
<th>$F_{\text{corr}}$</th>
<th>$F_{\text{corr}}$</th>
<th>$h_{\text{comm}}$</th>
<th>$\zeta$</th>
<th>$\zeta$</th>
<th>$\lambda_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ/mol</td>
<td>kJ/mol</td>
<td>kJ/mol/Å</td>
<td>kJ/mol/Å</td>
<td>Å</td>
<td>10^{-3} kJ/mol</td>
<td>10^{-3} kJ/mol</td>
<td>Å</td>
</tr>
<tr>
<td>Fe(100)</td>
<td>5.770</td>
<td>0.184</td>
<td>0.180</td>
<td>0.552</td>
<td>0.063</td>
<td>11.339</td>
<td>34.811</td>
<td>2.87</td>
</tr>
<tr>
<td>Fe(110)</td>
<td>6.473</td>
<td>0.071</td>
<td>-0.025</td>
<td>0.268</td>
<td>0.020</td>
<td>-0.502</td>
<td>5.356</td>
<td>2.03</td>
</tr>
<tr>
<td>Fe(111)</td>
<td>5.627</td>
<td>0.561</td>
<td>0.138</td>
<td>0.469</td>
<td>0.166</td>
<td>22.928</td>
<td>77.781</td>
<td>2.48</td>
</tr>
<tr>
<td>Fe(111)(010)</td>
<td>5.627</td>
<td>0.561</td>
<td>0.866</td>
<td>1.950</td>
<td>0.166</td>
<td>143.762</td>
<td>323.674</td>
<td>4.05</td>
</tr>
<tr>
<td>FeO(100)</td>
<td>4.619</td>
<td>0.126</td>
<td>0.000</td>
<td>0.289</td>
<td>0.042</td>
<td>0.000</td>
<td>12.134</td>
<td>2.17</td>
</tr>
<tr>
<td>FeO(110)</td>
<td>4.100</td>
<td>0.343</td>
<td>0.289</td>
<td>0.720</td>
<td>0.118</td>
<td>34.058</td>
<td>84.935</td>
<td>3.06</td>
</tr>
<tr>
<td>FeO(111)</td>
<td>3.837</td>
<td>0.669</td>
<td>0.791</td>
<td>2.749</td>
<td>0.235</td>
<td>185.853</td>
<td>646.010</td>
<td>7.50</td>
</tr>
<tr>
<td>Fe_{2}O_{3}(001)</td>
<td>5.117</td>
<td>0.707</td>
<td>0.448</td>
<td>1.749</td>
<td>0.251</td>
<td>112.382</td>
<td>438.985</td>
<td>4.36</td>
</tr>
<tr>
<td>Fe_{2}O_{3}(012)</td>
<td>4.983</td>
<td>0.669</td>
<td>-0.163</td>
<td>0.218</td>
<td>0.201</td>
<td>-32.803</td>
<td>43.723</td>
<td>2.71</td>
</tr>
</tbody>
</table>

*a* Parameters evaluated based on expressions proposed by Savio et al. (Savio et al. 2012)

Notably, for Fe(100) and Fe_{2}O_{3}(001) surfaces, the surface energy parameters are an order of magnitude lower than those obtained from the work of Savio et al. (Savio et al. 2012). They reported the values of 1.084 and 0.027 kJ/mol for Fe(100) and Fe_{2}O_{3}(001), respectively. This discrepancy is due to the chosen scanning potential in which, shown in Table 4.4, the energy interaction parameter $\varepsilon_{ij}$ of wall atoms in contact with the fluids are significantly smaller than those used by them (Savio et al. 2012). Among considered iron and iron oxide surfaces, the FeO(111) surface shows the highest surface energy parameter, due to its largest corrugation force and surface commensurability. For Fe(111) surface, despite the same surface commensurability of 0.166 Å, the surface parameter for the case of sliding in (010) direction is higher than that in (100) direction due to its significant larger corrugation force.

### 4.4 Discussion

The adhesion strength between hexadecane and iron surfaces, as reported in Chapter 3, is stronger than its oxides in an decreasing order of Fe > FeO > Fe_{2}O_{3} which is consistent with that observed in adsorption investigations of this molecule. However, the obtained results show a more solid-like behaviour and considerably lower shear stresses for Fe(100), Fe(110), and Fe(111) surfaces than FeO(111) and
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Fe$_2$O$_3$(001). The reason for this observation could be due to the weak interaction strength between alkane and iron, which is reported as a physisorption (Govender et al. 2013; Lo & Ziegler 2007), is not large enough to have a crucial influence on the tribological performance of hexadecane film in iron oxides.

![Figure 4.9](image.png)

Figure 4.9. Correlation of degree of layering characterized by the peak of density profile of the first lubricant layer adjacent to the surface with: (a) corrugation potential; (b) corrugation force; (c) surface commensurability; and (d) surface parameter. Data points are results obtained from MD simulation, the dash-dotted lines are fitted curves.

For the same number of seven layers, the degree of ordering, as shown in Figure 4.1, are lower than that obtained by Cui et al. (Cui et al. 2001). There are many reasons for this discrepancy: The weak interaction strength could be a possible reason. In fact, the wall–fluid interaction strength, as given in Table 4.4, is smaller than that used in their work ($\varepsilon_{wf} = 1.747$ kJ/mol). Moreover, the thickness of the simulated film of 2.4 nm is thicker than ~2 nm used in their work. The increase of the film thickness leads to a decrease of order. Importantly, the employed EA model for
lubricant could result in less order than UA model because a weaker layering and larger slip near the wall is observed for branched molecules (Jabbarzadeh et al. 2002).

Figure 4.10. Dependence of shear stress of molecular system on: (a) corrugation potential; (b) corrugation force; (c) surface commensurability; and (d) surface parameter. Data points are results obtained from MD simulation, the dash-dotted line is fitted curve.

An interesting observation is that the in-plane ordering of lubricant depends on the crystal orientation of the surfaces but it is insensitive with the sliding orientation. In fact, Table 4.1 shows that the peak of the density profile for the first lubricant layer is different for distinct surface orientations, but it is similar for Fe(111) and Fe(111)(010). This observation shows a good agreement with the work by Soong et al. who investigated a Couette flow in a nanochannel of different face-centered cubic crystal lattices (Soong et al. 2007). However, the results also reveal that there is a dependence of effective shear rate and shear viscosity on both surface orientation and sliding direction. These observations point out that the surface structure has a
significant influence on structural and rheological properties of lubricant. A quantitative correlation between the surface properties and the degree of layering is illustrated in Figure 4.9; this shows a decrease of the peak of density profile with an increase of surface corrugation energy, corrugation force, and surface commensurability. This finding is consistent with the work by Jabbarzadeh et al. who found that the in-plane order of dodecane confined between amorphous surfaces was reduced significantly compared to crystalline surfaces (Jabbarzadeh et al. 2006).

There is an inverse relationship between the surface corrugation parameter, which are described as a function of corrugation force and surface commensurability, and the degree of layering of confined lubricant (Figure 4.9d). In fact, as shown in Table 4.1 and Table 4.5, the highest degree of layering and lowest shear stress are found for Fe(110) surface which possesses the lowest surface corrugation parameter. In contrast, the FeO(111) surface with highest surface corrugation parameter shows the lowest in-plane ordering and a remarkably high shear stress. One can notice that there are two main trends: the density peak increases significantly when the surface interaction parameter tends to zero; however, the density peak becomes plateau at bulk lubricant density when $\zeta_{surf}$ approaches an infinite value.

The statistical correlation between the surface properties and tribological performance is presented in Figure 4.10. The shear stress, as well as CoF (for a similar applied pressure), increases nonlinearly with the corrugation energy. However, there is a difference in shear stress for some surfaces having the similar corrugation energy. For instance, the FeO(111) and Fe$_2$O$_3$(012) surfaces have same corrugation energy of 0.669 kJ/mol, but shear stress is higher for FeO(111) surface than Fe$_2$O$_3$(012). Similarly, for the same corrugation energy of 0.561 kJ/mol, higher shear stress is found in (010) direction of Fe(111) surface than (100). The role of sliding direction, which was characterized by corrugation force, and surface commensurability were taken into account to explain the relationship between surface’s properties and shear stress of molecular system. Figure 4.10b-c shows an increase of shear stress with corrugation force and surface commensurability; however, this increasing tendency is still uncertain. A comprehensive surface energy
parameter $\zeta_{surf}$, as a function of corrugation force and surface commensurability, predicts the tendency of increasing shear stress (Figure 4.10d).

By varying the crystalline lattice spacing, Savio et al. reported two major regions for shear stress, the linear and plateau regions, and the onset of plateau region for hexadecane was at a surface corrugation parameter of 2.761kJ/mol (Savio et al. 2012) which correspond to a maximum shear stress of ~ 44 MPa. Our results reveal that when the shear stress increases up to 65.81 MPa, this plateau region still does not occur. This discrepancy could be due to the difference in lubricant model and the interfacial interaction potential, in particular, an EM model of lubricant with a QM/MM potential was employed in our work while a UA model was applied in their model. However, there is an agreement between their work and the current result is that the shear stress increases with the surface corrugation parameter. The hyperbolic tangent function was adequately employed to present the correlation between shear stress and the surface interaction parameter (Figure 4.10d).

The mechanism of high shear stress on molecular-scale rough surfaces such as Fe$_2$O$_3$(001), Fe(111)(010), and FeO(111) could be in the behaviour of the liquid layer adjacent to the wall. This first layer is completely fixed into the surfaces. As a result, the stick boundary is moved into the thin film and lies between the first and second layers (Jabbarzadeh et al. 2006). A relatively stronger momentum and energy exchange between the wall and fluid via this boundary, and consequently it yields an internal deformation of lubricant (Ohara & Torii 2005). The shear stress as well as the momentum resistance of the lubricant therefore increases for these surface models.

Another influence of surface on structural properties of lubricant is the local orientation of molecules. The snapshots of molecular configuration of the first layer of thin hexadecane film confined between different surfaces, as illustrated in Table 4.3, reveal that the lubricant molecules do not align in a preferred direction for isotropic surfaces such as Fe(100) and Fe$_2$O$_3$(001). It could be due to the potential of the isotropic surfaces that create the similar energy potential landscape in both lateral directions. In contrast, the favoured molecular alignments are seen on anisotropic surfaces such as Fe(111), Fe(111)(010), FeO(100), FeO(110), and Fe$_2$O$_3$(012). The relative wall-fluid incommensurability is a possible explanation for
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the distinct molecular orientation on these surfaces (Savio et al. 2012). The atomic spacing on the top layer of Fe(110) surface in sliding direction, as reported in Table 4.2, is comparable with the size of CH₆ groups of hexadecane molecule (~2 Å) (Sun 1998); hence, it is not be able to fit between interfacial atomic rows. However, for Fe(111), Fe(111)(010), FeO(100), FeO(110), and Fe₂O₃(012) surfaces, this atomic spacing is larger allowing the hexadecane molecules to align between atomic rows, where the energy is minimal (Table 4.5). However, this explanation is not reasonable for Fe(100), Fe₂O₃(001) and FeO(111) surfaces, where their respective relevant atomic spacings are 2.87 Å, 4.36 Å and 7.50 Å; larger than the size of CH₆ groups. The isotropy of surface (Soong et al. 2007) can be considered as an explanation for the uncertainty in local molecular alignments at Fe(100) and Fe₂O₃(001) surfaces. For FeO(111), this scenario is may be more complicated. The atomic space of 7.50 Å for this surface is much larger than the size of CH₆ groups, and so the hexadecane molecules therefore could be able to adopt a non-linear conformation in order to fill up the large available space between atomic rows.

Table 4.1 reveals that the shear rate of Fe₂O₃(001), Fe(111)(010), and FeO(111) surfaces is beyond the shear thinning of bulk hexadecane, while it is lower for other surfaces. The onset of shear thinning under confined condition depends on the structural properties of surface and thin film thickness (Jabbarzadeh et al. 2006). For rough surfaces, e.g. Fe₂O₃(001), Fe(111)(010), and FeO(111), the onset of shear thinning could be much higher than smooth crystalline surfaces, e.g. Fe(100), Fe(110), Fe(111), FeO(100), FeO(110), Fe₂O₃(012). Additionally, the obtained effective viscosity for Fe(111)(010) (5.04 mPa.s) is close to the bulk viscosity of hexadecane (~3 mPa.s). This effective viscosity is enhanced by two orders of magnitude for other cases in which the surfaces are smoother. A similar observation had been found by Jabbarzadeh et al. who reported a viscosity of dodecane film (6 layers) confined between crystalline walls was enhanced 20 times compared to the amorphous walls (Jabbarzadeh et al. 2006). The lower shear viscosity of hexadecane confined by Fe(111)(010) can be explained that the effective shear rate for hexadecane confined by this surface is larger and this results in shifting to shear thinning regime, hence a lower viscosity.
4.5 Conclusion

The current study has carried out an MD simulation to investigate the thin film lubrication of hexadecane, which is widely used as a model lubricant in simulation and experimental studies, between different iron and its binary oxide surfaces. The realistic tribosystems have been constructed using EA model for lubricant with a reliable force-field – COMPASS, and a QM/MM potential obtained from our previous study to describe the wall-fluid interaction. Different surface structures as well as their crystal orientations were utilized to analyse the influences of iron oxides on rheological and tribological properties of the confined lubricant. A comprehensive surface parameterization method suggested by Savio et al. has been implemented to address the role of surface corrugation (Savio et al. 2012). The findings can be summarized as follows:

(i) Despite a stronger adhesion strength of hexadecane on metal iron surfaces than its oxides, there is a higher degree of layering and lower shear stress of FeO(100), FeO(110), and Fe$_2$O$_3$(001) surfaces compared to Fe(111). The role of wall-fluid interaction strength in tribological performance of hexadecane between smooth iron and its oxide surfaces found to be less significant than the surface corrugation. The highest shear stress has been found for FeO(111) surface while the lowest one is for Fe(110). A plug-slip phase of lubricant has been found for all but Fe$_2$O$_3$(001) and FeO(111) surfaces which have highest shear stress.

(ii) The in-plane ordering of lubricant depends on the crystal orientation of the surfaces, but it is insensitive to the sliding orientation. In contrast, there is a dependence of effective shear rate and shear viscosity on both surface orientation and sliding direction.

(iii) The surface properties have a significant influence on structural, rheological, and tribological of lubricant. The molecular in-plane ordering and the density of lubricant decreases with an increase of surface commensurability and the shear stress increases with surface corrugation parameter whilst there is an inverse decrease of molecular in-plane ordering with this parameter.
The commensurability and isotropy of the surface affect the local orientation of lubricant molecules. There is a favoured molecular alignment of hexadecane molecules on Fe(111), FeO(110), and Fe₂O₃(012)surfaces while there is an uncertainty in local alignments at other surfaces.
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A comprehensive investigation of influence of working conditions such as loading pressure, sliding velocity or shear rate, and surface temperature on tribological performance and rheological properties of hexadecane film confined between different iron and iron oxide surfaces has carried out in this chapter. To the best of our knowledge, this comprehensive study has not been done previously.

5.1 Effect of loading pressure

![Image of graph showing variation of film thickness and average density with loading pressure]

Figure 5.1 Variation of: (a) film thickness; and (b) average density of hexadecane on loading pressure for different iron and iron oxides surfaces at 300K and sliding velocity of 0.1 Å·ps⁻¹.

After equilibration, a load is applied onto the top surfaces during the compressive stage; this load causes the lubrication density to increase and oscillate until it reaches a state of equilibrium where its film thickness and mass density correlate with the loading pressure for different iron and iron oxide tribosurfaces, as shown in Figure 5.1; this is a nonlinear relationship with a propensity that is consistent with other studies (Martini & Vadakkepatt 2010; Zheng et al. 2013a). However, there is a slightly difference in the averaged lubricant density and film thickness for different tribo-surfaces, possibly due to differences between the chosen number of molecules and surface corrugation. Note that the temperature rise (ΔT) shown in the Figure 5.2,
which is defined as the temperature difference between the lubricant molecules and sliding surfaces, is insensitive with loading pressure.

![Graph showing temperature rise of thin hexadecane film on loading pressure for different iron and iron oxides surfaces at 300K and sliding velocity of 0.1 Å.ps⁻¹.]

Figure 5.2 Dependence of temperature rise of thin hexadecane film on loading pressure for different iron and iron oxides surfaces at 300K and sliding velocity of 0.1 Å.ps⁻¹.

As the surfaces slide, momentum is transferred into the fluid, which causes the molecules adjacent to the surfaces to form layers (Berro et al. 2011; Ohara & Torii 2005). As Figure 5.3 shows, the density profile oscillates with the highest peak at the interfacial layers then gradually decreases towards the bulk material in the middle of the fluid. The degree of ordering is determined by averaging the peaks of the density profile at positions close to the surfaces to evaluate the dependence of layering on the loading pressure; as Figure 5.4 shows, the degree of ordering increases with the applied load. This agrees with findings from Zheng et al. (Zheng et al. 2013a), but this is not a linear relationship and the degree of orderings are different for distinct surfaces. A local lubricant density one and a half times larger than the bulk film occurs at the Fe₂O₃(001) surface, but it is two to three times larger for other surfaces. The degree of ordering for different loading pressure decreases in the following order: Fe(110) > Fe(100) > FeO(100) > FeO(110) > Fe₂O₃(001). Surface corrugation is the major factor affecting the ordering of lubricant, an observation that has been investigated comprehensively in previous studies (Jabbarzadeh et al. 2006). Note that the degree of ordering increases at low loading pressures of 50-500 MPa, becomes steady at the Fe₂O₃(001) and Fe(110) surfaces, and then increases again for other surfaces.
Figure 5.3 Density profiles across hexadecane film thickness for: (a) Fe(100); (b) Fe(110); (c) FeO(100); (d) FeO(110); and (e) Fe$_2$O$_3$(001) surfaces for different loading pressures at surface temperature of 300K and sliding velocity of 0.1 Å.ps$^{-1}$.

Furthermore, the increasing loading pressure yields to a transition of the number of layers; for instance, Figure 5.3 shows that as the load increases to 2000 MPa, the number of ordering layers for all the tribo-surfaces drops to six.
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Figure 5.4 Evolution of degree of ordering as a function of loading pressure for thin $n$-hexadecane film confined between iron and iron oxide surfaces.

The velocity profiles for iron and iron oxides surfaces are presented in Figure 5.5 where the velocity across the film thickness varies for the Fe$_2$O$_3$(001) surface, and is almost constant for the other surfaces. In fact at the Fe$_2$O$_3$(001) surface there is some slip at the solid-liquid interface and inside the thin film, but only interfacial slip on the other ones. The lubricant is expected to shear with an apparent shear rate defined as a ratio of the surface velocity ($v_x$) to the lubricant film thickness ($\dot{\gamma}_{app} = 2v_x/h$). However, when confirmed molecularly the lubricant actually sheared with a different shear rate to that imposed onto the surfaces where an effective shear rate ($\dot{\gamma}_{eff}$) is determined from the gradient of the velocity profile across the film thickness. To quantify the slip at the solid-fluid interface, a dimensionless parameter $s$ is defined as (Fillot et al. 2011):

$$s = 1 - \frac{\dot{\gamma}_{eff}}{\dot{\gamma}_{app}} \quad (5.1)$$

Figure 5.6 shows that the momentum slip increases with the loading pressure. The slip parameter seen on the Fe$_2$O$_3$(001) surface agrees with the study by Fillot et al. , who reported a linear dependence of slip parameter on loading pressure (Fillot et al. 2011). However, the slip parameter increases with the loading pressure from 50 to 250 MPa, and a “pure” slip where the slip parameter is close to one, occurs at a higher loading pressure for others surfaces. Moreover, linear dependence is no
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longer enough for a loading pressure higher than a critical value of 250 MPa for Fe(100), Fe(110), FeO(100), and FeO(110) surfaces.

Figure 5.5 Velocity profiles across hexadecane film thickness for: (a) Fe(100); (b) Fe(110); (c) FeO(100); (d) FeO(110); and (e) Fe$_2$O$_3$(001) surfaces for different loading pressures at surface temperature of 300K and sliding velocity of 0.1 Å.ps$^{-1}$. 
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Figure 5.6 Variation of slip parameter in respect with loading pressure for confined system of thin \( n \)-hexadecane film between iron and iron oxides tribosurfaces.

The shear stress is defined as a ratio of the friction force divided by the interfacial area, where the friction force is averaged during the shearing process. Figure 5.7 shows the correlation between the shear stress and the applied load. The shear stress increases with loading pressure, and it is more significant for Fe\(_2\)O\(_3\)(001) surface than the others. Given that the solid-fluid interfacial area is constant, the friction force is almost linearly proportional to the applied load, an observation that agrees with Amonton’s law in a macroscopic scale.

The CoF evaluated as the ratio of the shear stress and loading pressure is a critical component used to assess the performance of a tribo-system. As Figure 5.8 shows, there is a decreasing relationship between the calculated CoF and the loading pressure. However, the CoF plunges when the loading pressure increases from 50 to 500 MPa, but it remains steady when the load is more than 500 MPa. These figures indicate there is a very high CoF of thin hexadecane film between Fe\(_2\)O\(_3\)(001) surfaces compared to other considered tribosurfaces.
Figure 5.7 Evolution of shear stress as a function of loading pressure for confined system of thin $n$-hexadecane film between iron and iron oxides tribosurfaces.

Figure 5.8 Evolution of CoF as a function of loading pressure for confined system of thin $n$-hexadecane film between iron and iron oxides tribosurfaces.
The viscosity of a lubricant is an important rheological property in thin film lubrication because in such a confined regime this physical component is quite different with the bulk value due to the ordering arrangement of lubricant molecules and the effect of confined surfaces. Therefore, the shear viscosity of hexadecane with respect to each type of surface and applied load is calculated to observe the effect that iron oxide surfaces have on this rheological property. As Figure 5.9 shows, hexadecane increases in viscosity with respect to the applied load and viscosity depends on the loading pressure which follows an exponential function at loading pressure lower than a critical value; this can be expressed by Barus’ equation (Li et al. 2015):

\[ \eta_{eff}(P) = \eta_0 \cdot e^{\beta P} \quad (5.2) \]

where \( \eta_{eff}(P) \) is the effective viscosity of hexadecane at pressure \( P \), \( \eta_0 = 3.03 \) is the viscosity of hexadecane under atmospheric conditions (Stevens et al. 1996), \( \beta \) is the pressure coefficient, and \( P \) is the loading pressure. The fitted pressure coefficient of \( \beta = 1.011, 1.009, 1.008, 1.006, \) and 1.002 are for Fe(110), Fe(100), FeO(110), FeO(100), and Fe\(_2\)O\(_3\)(001), respectively.

Figure 5.9 Variation of shear viscosity of thin \( n \)-hexadecane film in respect to the loading pressure for different iron and iron oxides tribosurfaces under sliding velocity of 10 m/s at 300K. The dash lines present fitted results of Barus equation.

However, this exponential relationship is only applicable for a loading pressure less than 400 MPa for Fe(110) as well as FeO(100), 450 MPa for Fe(100), 750 MPa for FeO(110), and 1000 MPa for Fe\(_2\)O\(_3\)(001), so when the loading pressure increases
beyond these critical values, the viscosities are below the fitted curves of Barus’ equation.

5.2 Effect of shear rate

Using a highly corrugated surface of Fe$_2$O$_3$(001), a wide range of shear rates are considered. As shown in Figure 5.10, the film thickness of the lubricant increases slightly with the apparent shear rate. This enhancement in the shear rate increases the work applied to the system, and since this work is a function of the volume and pressure of the lubricant, its volume or film thickness will increase under a constant loading pressure, which is why there is a decrease in the average density as the shear rate increases. This tendency is similar to that gained for bulk hexadecane where there is a decrease in the average density with an increase in the apparent shear rate (Tseng et al. 2008). There is a significant difference (~75 kg/m$^3$) in the average density of the bulk system compared with confined shear model at 250 MPa. This is because the solid-like behaviour of lubricant that characterized by a crystalline structure and layering structure due to applied load and sliding condition.

Figure 5.10 Variation of: (a) film thickness; and (b) average density on apparent shear rate for thin hexadecane film confined between Fe$_2$O$_3$(001) surfaces subjected to different loading pressures at surface temperature of 300K. The bulk density of hexadecane at 250 MPa is obtained by Tseng et al. (Tseng et al. 2009).
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Figure 5.11 Variation of temperature rise as a function of the apparent shear rate of thin hexadecane film confined between Fe$_2$O$_3$(001) surfaces for different loading pressures at surface temperature of 300K.

Figure 5.12 Density profiles across film thickness of hexadecane confined between Fe$_2$O$_3$(001) surfaces at different shear rates and subjected to loading pressure of: (a) 100 MPa; (b) 250 MPa; (c) 500 MPa; and (d) 1000 MPa at surface temperature of 300K.
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Figure 5.11 shows an increase in temperature with the apparent shear rate, which is consistent with Berro et al.’s observations, however this rise in temperature is not sensitive to the loading pressure within the range of shear rates considered (Berro et al. 2011).

The density profiles of lubricant at different sliding velocities and subjected to different loading pressures are shown in Figure 5.12. At a loading pressure lower than 1000 MPa, six layers of hexadecane across the film thickness are found for all the sliding velocities, but there is a transition in the number of layers for a sliding velocity higher than 0.01 Å·ps\(^{-1}\) under a loading pressure of 1000 MPa. This degree of ordering, as shown in Figure 5.13, decreases with an increase in the apparent shear rate and it is similar to the average lubricant density (Figure 5.10b). The figure also shows that the local density profiles at solid-fluid interfaces are more than one and a half times larger than the bulk density at 250 MPa.

![Figure 5.13](image.png)

Figure 5.13 Variation of degree of ordering on apparent shear rate for thin n-hexadecane film confined between Fe\(_2\)O\(_3\)\((001)\) surfaces under different loading pressures at 300K. The reference data of bulk hexadecane is obtained by Tseng et al. (Tseng et al. 2009).

At different sliding velocities, the Fe\(_2\)O\(_3\)\((001)\) surface in Figure 5.14 shows that slip occurs at solid-fluid interfaces, which is defined as an exponential function of the apparent shear rate (Fillot et al. 2011). This correlation can be described as the following function:

\[
s = s_{ref}(1 - e^{-\alpha \dot{\gamma}_{app}}) \quad (6)
\]
where $s_{\text{ref}}$ is the reference data of slip parameter, $\alpha$ is the slip coefficient at loading pressure $P$, and $\dot{\gamma}_{\text{app}}$ is the apparent shear rate; slip at different loading pressures is shown in Figure 5.15. The fitted curves indicate that $s_{\text{ref}}$ of 0.157, 0.205, 0.362, and 0.739 are for loading pressures of 100, 250, 500, and 1000 MPa, respectively, and the corresponding respective slip coefficients are $2.99 \times 10^{-11}$, $7.41 \times 10^{-11}$, $1.40 \times 10^{-10}$, and $1.48 \times 10^{-10}$, respectively. Note that these parameters increase with the loading pressure.

Figure 5.14 Velocities profiles across film thickness of hexadecane confined between Fe$_2$O$_3$(001) surfaces at different shear rates and subjected to loading pressure of: (a) 100 MPa; (b) 250 MPa; (c) 500 MPa; and (d) 1000 MPa at surface temperature of 300K.
Figure 5.15 Correlation between slip parameter and apparent shear rate for confined system of thin \( n \)-hexadecane film between \( \text{Fe}_2\text{O}_3(001) \) surfaces under different loading pressures at 300K.

The dependence of shear stress and the CoF on the apparent shear rate is shown in Figure 5.16, and these tribological components increase with the apparent shear stress. The correlation between shear stress and apparent shear rate can be depicted by an exponential function given as follows:

\[
\tau_{xz} = \tau_{ref}(a \ln \dot{\gamma}_{app} - 1) \quad (5.3)
\]

where \( \tau_{ref} \) is the reference data, and \( a \) is the shear stress coefficient at loading pressure \( P \). The fitted results indicate that \( \tau_{ref} \) of 144.06, 171.4, 180.5, and 102.5 MPa for loading pressure of 100, 250, 500, and 1000 MPa, respectively, and the corresponding \( a \) parameters for these loading pressures are 0.052, 0.053, 0.057, and 0.079, respectively; in fact the shear stress coefficient increases with the loading pressure. By dividing the shear stress \( \tau_{xz} \) by its corresponding loading pressure \( P \), the CoF is shown in Figure 5.16b. For a similar loading pressure \( P \), the relationship between the CoF and the apparent shear rate could also be described by Equation 5.3, but the stress components will be replaced by relevant CoFs, so this relationship is given as the following equation:

\[
\mu = \mu_{ref}(a \ln \dot{\gamma}_{app} - 1) \quad (5.4)
\]

The calculated reference data of the CoF (\( \mu_{ref} \)) of 1.44, 0.69, 0.36, and 0.10 are for loading pressures of 100, 250, 500, and 1000 MPa, respectively. The relevant
parameters $a$ are consistent with those measured for shear stress, so the CoF increases at a lower loading pressure. Moreover, the order of the CoF is consistent with that for shear stress when the apparent shear rate is lower than $10^9 \text{ s}^{-1}$, whilst there is an inverse order when the shear rate is higher than this value.

Figure 5.16 Variation of: (a) shear stress; and (b) CoF on apparent shear rate for thin $n$-hexadecane film confined between Fe$_2$O$_3$(001) surfaces under different loading pressures at 300K.

The viscous response for films in Figure 5.17 typifies the behaviour of melted $n$-hexadecane at different loading pressures. At a shear rate that is less than the critical value of $10^9 \text{ s}^{-1}$ the film acts like an ideal Newtonian fluid, although the shear viscosities are greater than the bulk viscosity for all loading pressures, where viscosity increases with the loading pressure. At a higher shear rate the viscosity falls to a Newtonian bulk value and shows substantial shear thinning, where the viscosity obeys the power law. In a shear thinning regime, a higher loading pressure still results in a higher viscosity.

The Carreau equation is used to fit the $\eta-\dot{\gamma}$ data, with the results shown in Figure 5.17. The zero-shear viscosities obtained from the fitted results are $6.86 \pm 0.53$, $28.37 \pm 1.15$, $78.96 \pm 12.04$, and $460.72 \pm 87.73 \text{ mPa.s}$ for loading pressures of 100, 250, 500 and 1000 MPa, respectively. Note that a remarkable $\sim 10^2$ folds larger of zero-shear viscosity has been measured for a 10 folds increase in the loading pressure. Furthermore, confinement resulted in a higher zero-shear viscosity of
lubricant compared to its bulk state; in fact the zero-shear viscosity calculated for bulk hexadecane is only 8.253 mPa.s at 250 MPa (Tseng et al. 2009).

![Graph showing variation of shear viscosity as a function of shear rate for confined system of thin n-hexadecane film between Fe₂O₃(001) surfaces under different loading pressures.](image)

Figure 5.17 Variation of shear viscosity as a function of shear rate for confined system of thin n-hexadecane film between Fe₂O₃(001) surfaces under different loading pressures. The reference data of bulk viscosity at 250 MPa and 300 K is obtained by Tseng et al. (Tseng et al. 2009).

The fitted results also reveal that the critical shear rate $\dot{\gamma}_c$ increases with the loading pressure, with critical shear rates of $1.6 \times 10^9$, $5.5 \times 10^8$, $1.9 \times 10^8$, and $2.3 \times 10^7$ s⁻¹ having been measured for loading pressures of 100, 250, 500, and 1000 MPa, respectively. For the same pressure of 250 MPa, the calculated critical shear rate for confined lubricant is significantly higher than $1.8 \times 10^9$ s⁻¹ for bulk hexadecane (Tseng et al. 2009).

### 5.3 Effect of surface temperature

The film thickness and average density of lubricant depends on the shear rate, as shown in Figure 5.18; this trend is similar for different surface temperatures, although a higher surface temperature results in a higher film thickness and a lower density. This decreasing density of lubricant confined between surfaces is consistent with those observed for bulk hexadecane solution (Tseng et al. 2008), and while the increment of film thickness and reduction in lubricant density are higher at a lower temperature. In fact, an increase of 1.62 Å of film thickness and a reduction of 0.047
g/cc of density occurs at 300K, but they are only 0.83 Å and 0.02 g/cc for 500K, respectively.

Figure 5.18 Variation of: (a) film thickness; and (b) average density of hexadecane between Fe₂O₃(001) surfaces on apparent shear rate for different surface temperatures under loading pressure of 250 MPa.

Figure 5.19 shows the linear dependence of the rise in temperature (ΔT) as a function of the apparent shear rate. Here, the rise in temperature increases with the shear rate; however, more significant differences in temperature between the surface and fluid at high shear rates also occur with a lower surface temperature.

Figure 5.19 Variation of temperature rise of thin hexadecane film confined between Fe₂O₃(001) surfaces as a function of the apparent shear rate for different wall surface temperatures under loading pressure of 250 MPa.
Chapter 5 Thin film lubrication of hexadecane: Influences of sliding conditions

The profile of lubricant density across the film thickness, as shown in Figure 5.20, indicates that although the number of layers remains at 6, the degree of ordering decreases for layers at the solid-fluid interfaces and inside the lubricant, so to quantify the effect that temperature has on this layering structure, the degree of ordering at the solid-fluid interfaces is shown in Figure 5.21. Note that the degree of ordering is not sensitive to the apparent shear rate at surface temperature of 500K, but it decreases as the shear rate increases at lower temperatures.

Figure 5.20 Density profiles across film thickness of hexadecane confined between Fe$_2$O$_3$(001) surfaces for different shear rates at different surface temperatures of: (a) 300K; (b) 400K; and (c) 500K under loading pressure of 250 MPa.

Figure 5.22 shows the velocity profiles of lubricant across the film thickness for different sliding velocities and surface temperatures. The influence that surface temperature has on velocity slip at solid-fluid interface is shown in Figure 5.23 where a higher surface temperature results in a higher velocity slip. However, the difference
is insignificant because the fitting curve of slip for a surface temperature of 400K is almost with the same as that obtained at 300K.

Figure 5.21 Dependence of degree of ordering on effective shear rate for thin n-hexadecane film confined between Fe$_2$O$_3$(001) tribosurfaces at different surface temperatures under an applied pressure of 250 MPa.

The effect that temperature has on the tribological properties is shown in Figure 5.24, where, at different shear rates a higher surface temperature results in a lower shear stress and CoF. The friction detected for temperatures of 400K and 500K and at an apparent shear rate less than $10^9$ s$^{-1}$ is very low; in fact there is almost no friction at a shear rate less than this critical value, although it is significant for a surface temperature of 300K.

The influence that the surface temperature has on the rheological property of lubricant is shown in Figure 5.25. The shear viscosity measured at different surface temperatures has been compared with those obtained for bulk hexadecane lubricant from work by Tseng et al. (Tseng et al. 2009). Figure 5.25 shows that a lower surface temperature yields a higher shear viscosity, which is consistent with their work, but the shear viscosity of the confined model is higher than the bulk value, and this difference is greater for lower surface temperatures. Zero shear viscosities of $28.37 \pm 1.15$, $4.08 \pm 0.35$, and $1.86 \pm 0.03$ mPa.s are found for the confined shear model at surface temperatures of 300, 400, and 500K, respectively, whereas the corresponding viscosities at a bulk state are only 8.253, 2.637, and 1.363 mPa.s, respectively (Tseng et al. 2009). These results show there is a distinct difference in
fluid viscosity under confinement, unlike that in a bulk condition at low temperatures. Moreover, the fitted results also show that the slope of Carreau curve decreases with an increase of surface temperature.

Figure 5.22 Velocity profiles across film thickness of hexadecane confined between Fe₂O₃(001) surfaces for different shear rates at different surface temperatures of: (a) 300K; (b) 400K; and (c) 500K under loading pressure of 250 MPa.
Chapter 5 Thin film lubrication of hexadecane: Influences of sliding conditions

Figure 5.23 Variation of slip parameter as a function of apparent shear rate for thin \(n\)-hexadecane film confined between \(\text{Fe}_2\text{O}_3(001)\) tribosurfaces at different surface temperatures under a loading pressure of 250 MPa.

Figure 5.24 Effective shear rate dependence of: (a) shear stress; (b) coefficient of viscosity of thin \(n\)-hexadecane film confined between \(\text{Fe}_2\text{O}_3(001)\) tribosurfaces at different surface temperatures under loading pressure of 250 MPa.

Figure 5.25 Variation of shear viscosity as a function of shear rate for thin \(n\)-hexadecane film confined between \(\text{Fe}_2\text{O}_3(001)\) tribosurfaces at different temperatures under loading pressure of 250 MPa. The reference data of bulk viscosities of hexadecane is obtained from the work of Tseng et al. (Tseng et al. 2008).
Moreover, the critical shear rate where the shear thinning regime of confined lubricant occur increases with the surface temperature, this trend agrees with that observed for bulk hexadecane solution (Tseng et al. 2009). However, the critical shear rate between two models is completely different; Figure 5.25 and the calculated results show that the shear thinning regime starts at $5.49 \times 10^8$, $3.56 \times 10^9$, and $7.52 \times 10^9$ s$^{-1}$ for the confined shear model at surface temperatures of 300, 400, and 500K, respectively, whilst the corresponding critical shear rates of $1.8 \times 10^9$, $7.4 \times 10^9$, and $1.7 \times 10^{10}$ s$^{-1}$ are for bulk values of the lubricant (Tseng et al. 2009).

5.4 Discussion

The dependence of confined lubricant’s density on the pressure, shear rate, and temperature is similar to that observed for bulk lubricant, where the density increases with pressure and decreases with an increase in the shear rate as well as temperature (Tseng et al. 2008); however, the densities of confined lubricant are higher than the bulk values (Figure 5.10). Under confinement between surfaces the lubricant molecules align at the solid-fluid interfaces better, which results in a higher local density than in the middle regime and reduces the volume the lubricant atoms occupy; as a consequence, the lubricant is lower in density than its bulk value. At a shear rate higher than $10^{10}$ s$^{-1}$, the density of the lubricant decreases rapidly as the shear rate increases, and this decreasing rate is higher than the bulk value due to the viscous heat induced by shearing. In a dynamic simulation at a bulk state, the temperature of hexadecane is retained (Tseng et al. 2009), whereas it increases significantly with the shear rate in the current non-isothermal MD simulation; this increase in temperature is the source of a rapid decrease in the density of lubricant (Tseng et al. 2008).

A previous study reported very low shear rates of Fe(100), Fe(110), FeO(100), FeO(110) at 500 MPa where the surface corrugation, as reflected by a comprehensive surface energy parameter, plays a vital role in this phenomenon. At a wider range of loading pressure, a complete slip begins at a lower pressure, but this slip depends on the surface properties. For example, although the loading pressure has increased to 2000 MPa, the velocity slip for the Fe$_2$O$_3$(001) tribosurface is not complete. That slip depends on the pressure and shear rate is consistent with Fillot et al.’s report (Fillot et al. 2011), whereas the current study reveals that the slip also
depends significantly on the surface properties. This observation agrees with recent experimental work by Ponijavic et al. who reported a decrease of shear rate ratio with an increase in applied pressure, and the plug flow of poly-butene confined between sapphire surfaces was seen when the applied pressure was higher than a critical value of 463 MPa (Ponjavic et al. 2014).

A similar degree of ordering at the solid-fluid interface occurs for adsorbed hexadecane on iron and iron oxide surfaces under vacuum conditions, but as Figure 5.4 shows, there is a distinct difference in the degree to which these surfaces are ordered. Indeed, the surface corrugation plays an important role under confined condition. Additionally, there is an increase in ordering with the loading pressure, but this increase is not substantial when the loading pressure exceeds the critical value. However, Figure 5.21 shows a decrease in degree of ordering with an increase in surface temperature. The decrease of lubricant density is the source for this observation.

There is a correlation between the degree of ordering and velocity slip; Figure 5.4 and Figure 5.6 shows that the degree of ordering and slip increase with the loading pressure at a constant shear rate and pure slip occurs on Fe(100), Fe(110), FeO(100), FeO(110) surfaces, which have a higher degree of ordering than the bulk and Fe$_2$O$_3$(001) surface. However, varying the sliding velocity can reduce the degree of ordering with the shear rate, whereas velocity slip shows a contrasting tendency. This decrease of ordering with an increase in the shear rate could be due to a decreasing lubricant density (Figure 5.10), whereas the increase of slip is due to the momentum imposed on the surfaces being higher than the momentum transferred at the solid-fluid interfaces.

A previous study reveals that the Fe$_2$O$_3$(001) surface has a higher shear stress than the iron and iron oxide surfaces because its corrugation parameter is larger. Figure 5.7 shows that this propensity is retained for a wide range of loading pressures. There is almost a linear dependence of shear stress with loading pressure, although Figure 5.8 shows a constant CoF only at pressures higher than 500 MPa. It is observed that the CoF decreases with an increase in loading pressure. The Fe$_2$O$_3$(001) surface shows a significant reduction, but it is not substantial for other surfaces.
Under nano-confinement, Figure 5.17 and Figure 5.25 show that the effective shear viscosity is higher than the viscosity of bulk $n$-hexadecane. At different loading pressures Figure 5.9 shows the shear viscosities on Fe(100), Fe(110), FeO(100), and FeO(110) surfaces are an order of magnitude higher than Fe$_2$O$_3$(001). As a previous study indicates, the Fe(100), Fe(110), FeO(100), and FeO(110) surfaces are less corrugated than the Fe$_2$O$_3$(001) surface. This fact results in a reduction in the effective shear rate (Figure 5.6) and shear stress (Figure 5.7), but much lower shear rates on Fe(100), Fe(110), FeO(100), and FeO(110) surfaces yielded higher shear viscosities than the Fe$_2$O$_3$(001) surface. An interesting observation is that although the slip increases with temperature (Figure 5.23), but a lower viscosity has been observed for a higher surface temperature. It could be due to the substantial decrease in shear stress with an increase in temperature (Figure 5.24), while there is a slight increase in slip.

Additionally, Figure 5.9 shows the Barus equation describes properly the relationship between the viscosity and loading pressure when the loading pressure is less than a critical value. However, when the applied pressure is higher than this critical pressure, the lubricant solidifies such that it results in a steady, almost zero shear rate (Figure 5.6) and a steady shear stress (Figure 5.7). These factors reduce the increasing rate of viscosity at higher loading pressures; unlike the linear decrease in the shear rate and increasing shear stress when the applied pressure is below the critical value. Experimental investigation commonly uses Barus equation to estimate the viscosity of confined fluid (Ponjavic et al. 2014); however, this study reveals that the actual viscosity could be lower than the estimated one due to the glassy transition of polymeric lubricant.

The rise of lubricant’s temperature depends to a degree on the viscous heat induced by the internal friction between the layers of lubricant which increases with the sliding velocity of the surfaces. This is why a linear increase in the temperature of lubricant with the shear rate can be seen in Figure 5.11 and Figure 5.19. Moreover, more pressure is applied onto the surfaces, more work is imposed into the tribo-system, and therefore more viscous heat is induced into lubricant and its temperature will be higher (Figure 5.2 and Figure 5.11). Note that a lower rise of lubricant’s temperature is found for a higher surface temperature (Figure 5.11). It could be due to the
increase of slip with temperature (Figure 5.23), which consequently results in the lower effective shear rate and viscous heat induced in lubricant.

5.5 Conclusion

An MD simulation was carried out to determine how the loading pressure, shear rate, and surface temperature affected the thin film lubrication of hexadecane confined between iron and iron oxides surfaces. The effect that these working conditions has on the structural, tribological, and rheological properties were analysed systematically, and the following major findings were discovered:

i) The ordering and slip of lubricant at the solid-fluid interface increases with loading pressure, but this ordering increase is insignificant and pure slip occurs when the loading pressure exceeds a critical value. The wall surface structure has a substantial effect on these phenomena. A low degree of ordering and slip occurred on an Fe$_2$O$_3$(001) surface under a wide range of loading pressures, they were significant on Fe(100), Fe(110), FeO(100), and FeO(110) surfaces. Friction on the Fe$_2$O$_3$(001) surface was much higher, while the lubrication was ideal on the other surfaces. The CoF decreases as the loading pressure increases, but it remains steady at high loading pressures. The shear viscosity of lubricant increases as an exponential function, but this rheological component levels off when the loading pressure exceeds a critical value.

ii) An increase in the shear rate leads to a decrease in the ordering structure and an increasing velocity slip. There is an exponential relationship between the slip and shear rate, and a higher loading pressure increases the slip. Moreover, the shear stress and coefficient of friction increase with shear rate. Logarithmic functions have been proposed to correlate the variation of shear stress and coefficient of friction with shear rate. The shear viscosity increases with the loading pressure, and the shear thinning regime begins at a lower shear rate for a higher loading pressure.

iii) The layering structure decreases considerably as the surface temperature increases, whereas the velocity slip is not sensitive to surface temperature. An increase in surface temperature causes a decrease in the
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shear stress, coefficient of friction, and the zero-shear-rate viscosity, whereas the onset of shear thinning increases with surface temperature. These tendencies agreed with those observed for bulk hexadecane; however a higher shear viscosity and lower onset of shear thinning occurred in the confined model, unlike the bulk lubricant.
Chapter 6 Tribological performance of aqueous copolymer lubricant

This chapter studies the influence of copolymer concentration and loading pressure on thin film lubrication of aqueous copolymer lubricant in boundary regime. The structural behaviour of 17R2 triblock copolymer and tribological performance of this tribo-system are presented. Moreover, the wear of materials during asperities contact with a presence of covered copolymer layer is analyzed.

6.1 Interfacial force field

The obtained adsorption energies \( E_{\text{ads}} \) of water on iron surface were 0.505, 0.349, and 30.586 kJ/mol, and the corresponding equilibrium distances between Fe and O \( d_{\text{Fe-O}} \) are 2.23, 3.67, and 2.48 Å for \( \text{O}_{\text{lp}} \), \( \text{H}_{\text{down}} \), and \( \text{H}_{\text{up}} \) configurations at on-top site, respectively. These calculated results are consistent with the theoretical study by Bedolla et al. who adopted a DFT calculation using the plane–wave basis including the vdW interactions (Bedolla et al. 2014). They reported an average adsorption energy of 49.208 kJ/mol of a water molecule on bare Fe(100) surface with the equilibrium distances between oxygen and the closest iron atom of 2.28 Å and 3.35 Å for \( \text{O}_{\text{lp}} \) and \( \text{H}_{\text{down}} \) configurations, respectively. Regarding the hollow and bridge sites, the corresponding adsorption energies are 38.401kJ/mol and 33.963 kJ/mol, and the respective equilibrium distances are 3.90 Å and 3.03 Å. It is noted that water with \( \text{O}_{\text{lp}} \) configuration at on-top site of Fe(100) surface is the most stable adsorption site. The adsorption energy of water on this substrate is higher than those of 39.463, 39.366, 29.332, 28.077, and 10.131 kJ/mol for top site on Ru(0001), Rh(111), Pd(111), Pt(111), and Au(111) surfaces, respectively (Meng et al. 2004). An interesting observation is that water adsorbs nearly twice stronger on the iron surface than Pt. This observation is consistent with the investigation by Anderson et al. (Anderson 1981). It is due to iron atom orbitals are more diffuse and overlap more strongly with oxygen orbitals.

The adsorption energy in Table 6.1 for the second symmetry path of DME on Fe(100) obtained from the current DFT calculation, is lower than the binding energies 45.155 kJ/mol, and 46.217 kJ/mol of the DME/TiO\(_5\)H\(_9\) complex reported by
Chapter 6 Tribological performance of aqueous copolymer lubricant

Borodin et al. (Borodin et al. 2003). These binding energies were calculated at Hartree–Fock (HF) level using Møller–Plesset second order perturbation theory (MP2) with the basis set of 6-311+G(3f2g) for Ti; whilst the basis set of augcc–pvDz or aug–cc–pvTz was applied for O, C, and H.

Table 6.1 Adsorption energies and equilibrium distances from the iron surface of constituent groups of water, DME, 1,2–DME, and 1,2–DMP molecules obtained from DFT and MD calculations.

<table>
<thead>
<tr>
<th>models</th>
<th>-E_{ads} DFT</th>
<th>MD</th>
<th>error</th>
<th>distances CH_{3} DFT</th>
<th>MD</th>
<th>error</th>
<th>CH_{2} DFT</th>
<th>MD</th>
<th>error</th>
<th>CH DFT</th>
<th>MD</th>
<th>error</th>
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<tbody>
<tr>
<td></td>
<td>kJ/mol</td>
<td>kJ/mol</td>
<td>%</td>
<td>Å</td>
<td>Å</td>
<td>%</td>
<td>Å</td>
<td>Å</td>
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<td>Å</td>
<td>%</td>
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<tr>
<td>DME 1st path</td>
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<td>3.82</td>
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<td>7.24</td>
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<td>2.54 2.81 10.52</td>
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<tr>
<td>DME 2nd path</td>
<td>47.567</td>
<td>43.322</td>
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<td>3.88</td>
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<td>4.66 4.36 -6.38</td>
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<tr>
<td>1,2–DME</td>
<td>71.592</td>
<td>77.960</td>
<td>8.89</td>
<td>3.77</td>
<td>3.49</td>
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<td>3.80</td>
<td>3.31</td>
<td>-12.90</td>
<td>-</td>
<td>-</td>
<td>3.77 4.03 6.84</td>
<td></td>
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</tr>
<tr>
<td>1,2–DMP</td>
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<td>82.013</td>
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<td>2.23 2.22 -0.5</td>
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</tbody>
</table>

Table 6.1 shows the results of DFT and MD calculations of adsorption energies and equilibrium distances from the surface of constituent groups of DME, 1,2–DME, and 1,2–DMP molecules from the iron surface. Additionally, the deviations of adsorption energy and equilibrium distance between MD and DFT calculations are also presented. A consistent result of adsorption energy between MD and DFT calculations for DME with the first symmetry configuration, 1,2–DMP, and water is seen. However, larger deviations of -8.92% and 8.89% are observed for DME with the second symmetry configuration and 1,2–DME. It could be due to the UA model using nonbond interactions without taking into account the steric effect and polarization cannot describe the electronic and structural properties of an organic molecule on a surface as properly as quantum calculation (Bolton et al. 1999; Borodin & Smith 2003; Starovoytov et al. 2011). Furthermore, it is not easy to obtain a unique solution for a large number of force field parameters. With regard to the equilibrium distances between constituent parts of organic molecules and the surface, the deviations are within 10%.

The fitted results in Table 6.2 show that the adhesive strength (\(\epsilon_{ij}\)) of methyl group of triblock copolymer is larger than other constituent groups and this adhesive strength
increases with the number of attached hydrogens in carbon sites. Additionally, the adhesive strength of carbon sites is significantly larger than the value 0.868 kJ/mol for the interaction between carbon sites of hydrocarbon and iron, while the equilibrium distances are shorter than that between hydrocarbon and iron (4.35 Å). It is further noted that the adhesive strength between iron and oxygen of water is an order of magnitude higher than that between iron and oxygen of copolymer.

Table 6.2 Nonbond interaction parameters between lubricant and iron surface obtained from DFT.

<table>
<thead>
<tr>
<th>Pairwise</th>
<th>$\varepsilon_{ij}$ (kJ/mol)</th>
<th>$r_{ij}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-CH₃</td>
<td>2.798</td>
<td>3.68</td>
</tr>
<tr>
<td>Fe-CH₂</td>
<td>2.026</td>
<td>3.50</td>
</tr>
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<td>Fe-CH</td>
<td>1.930</td>
<td>3.70</td>
</tr>
<tr>
<td>Fe-O</td>
<td>1.351</td>
<td>2.10</td>
</tr>
<tr>
<td>Fe-O₆w</td>
<td>26.051</td>
<td>2.02</td>
</tr>
</tbody>
</table>

6.2 Compression stage of simulation

Figure 6.1 shows that the film thickness decreases with an increase of the applied pressure. This tendency is similar for different copolymer concentrations. This figure indicates that the number of selected copolymer and water molecules, as described in Table 2.2, is reasonable to obtain similar film thicknesses for different solutions.

Figure 6.1 Dependence of lubricant film thickness on applied pressure for different copolymer concentrations of 17R2 in aqueous solution.
The molecular structure of copolymer in thin aqueous film is an important feature that needs to be analysed to understand its lubrication mechanism. Figure 6.2 exhibits the structural behaviour of 17R2 molecules in thin aqueous film confined by flat iron surfaces. The copolymer molecules are favoured to adsorb to iron surfaces. This could be a complete adsorption at a surface or in a manner that an end group adsorbs to a surface while another end group adsorbs to the counter one.

Figure 6.2 Snapshots of 17R2 molecules in thin aqueous film with different copolymer concentrations confined by iron surfaces at flat section.

The density profiles of copolymer, as shown in Figure 6.3, are asymmetric, and the layering is found at solid–fluid interfaces. These density profiles were evaluated by determining the atomic mass density in each divided slab along the lubricant film thickness. The domain where there is no presence of asperities (Figure 2.6) is chosen for density profile calculation.
Figure 6.3 Density profile of 17R2 triblock copolymer across the thin aqueous film thickness for different copolymer concentrations at 0.25 GPa.

To quantify the influence of copolymer concentration and applied pressure on the layering of copolymer, the correlation between the degree of layering and these components is presented in Figure 6.4. This degree of layering was evaluated by averaging the peaks of density profile at both upper and lower solid-liquid interfaces to remove the random adsorption of copolymer to the surface. This figure indicates that there is an increase in degree of in-plane ordering of copolymer with its concentration, whilst it is insensitive with applied pressure at low concentration and increases a little at concentration higher than 8%.

Figure 6.4 Correlation between the degree of layering of 17R2 triblock copolymer with concentration and applied pressures.
As presented in Figure 6.5, a large degree of ordering of water has been observed at solid–fluid interfaces. Moreover, this layer is larger and closer to the surface than copolymer. For triblock copolymer, the PPO block tends to stick better on the substrate than the PEO block. The peaks of density profile of 0.51 g/cc and 0.82 g/cc are respectively for PPO block at the lower and upper solid-fluid interfaces. By contrast, there is only 0.20 g/cc and 0.16 g/cc for PEO block.

![Figure 6.5 Density profiles of water, triblock copolymer, and constituent blocks of PPO and PEO across the thin aqueous film thickness for 16% 17R2 aqueous solution under applied pressure of 0.25 GPa.](image)

### 6.3 Confined shear stage of simulation

For mixed lubrication simulation, the motion of upper surface in the direction perpendicular to the surface, as well as the lubricant film thickness are varied with sliding time (Zheng et al. 2013a). The system height, which was determined as the distance between the bottom and top rigid layers, was evaluated to observe this motion. It can be found from Figure 6.6 on the time evolution of system height for different concentration models and loading pressures, all curves exhibit the same general shape. One feature common to all concentration models is a moderate slope of the curve up to the peak, with a steeper decline after the maximum. Compared to the first contact, a slight reduction of the peak of system height at later asperity contacts has been observed for loading pressure of 0.25 GPa while a significant reduction is found for higher pressures due to the wear of asperity which causes the flattening and plastic deformation of the asperity.
Figure 6.6 Time evolution of system height for different 17R2 concentrations (2-16%) and loading pressures of: (a) 0.25 GPa; (b) 0.5 GPa; (c) 0.75 GPa; and (d) 1.0 GPa.

The time evolution of friction force, which was measured by the sum of lateral forces ($F_x$) exerted by the mobile layer’s atoms (layer 5) on the top rigid layer (layer 4), is presented in Figure 6.7 (Zheng et al. 2013a). The peak of friction force increases during the first three sliding cycles; however, it becomes stable for subsequent contacts. A common feature shown in this figure is the variation of friction force with asperity contact cycle. To quantify this relationship, the average friction force for each sliding cycle were evaluated and presented in Figure 6.8. This statistical component increases with the number of sliding cycles (asperity contacts) for the first three sliding cycles. By contrast, the friction almost starts to level off after the third contact. Furthermore, one observes that there is a dependence of friction force on copolymer concentration. In particular, the curves of friction force obtained for low copolymer concentrations are higher than higher concentrations, and this
discrepancy is quite clear for low loading pressure of 0.25 GPa whilst it is insignificant at higher pressure of 1.0 GPa due to the severe wear of asperities.

![Graphs showing friction force evolution for different copolymer concentrations and pressures.](image)

Figure 6.7 Time evolution of friction force of tribosystem for different 17R2 copolymer concentrations under applied pressure of: (a) 0.25 GPa; (b) 0.5 GPa; (c) 0.75 GPa; and (d) 1.0 GPa.

The effects of copolymer concentration and loading pressure on tribological performance of molecular system have been shown in Figure 6.9. The time average friction force $F_x$ and its deviation $\Delta F_x$ during the last three asperity contacts are plotted over the copolymer concentration. The force deviation was defined as the root mean square error between the friction forces and their average value. The obtained statistical results show that these components increase with applied pressure. In contrast, as expected, they decrease for an increase of copolymer concentration. For instance, for a loading pressure of 0.25 GPa, the friction force for a concentration of 16% has been reduced by a half compared to the case of 2% concentration; however, the reduction in friction is insignificant for a higher applied pressure.
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Figure 6.8 Dependence of friction on the number of asperity contacts for different copolymer concentrations under loading pressure of: (a) 0.25 GPa; (b) 0.5 GPa; (c) 0.75 GPa; and (d) 1.0 GPa.

Figure 6.9 Correlation between the average friction force (a) and its deviation (b) with copolymer concentration for different applied pressures.

It is noted that there is a discrepancy between the simulated results and experimental measurements. Kosasih et al. revealed the CoFs of 0.39 for 17R4
(PPO_{14}\text{-PEO}_{24}\text{-PPO}_{14}) and 0.29 for 25R2 (PPO_{21}\text{-PEO}_{14}\text{-PPO}_{21}) between mild steel surfaces at 1.5GPa (Kosasih et al. 2014). Additionally, Lin et al. reported a CoF of 0.217 for 17R2 between Ti coated surfaces at 0.9 GPa (Lin et al. 2015). These coefficients of friction are lower than the value of 0.675 at 1GPa for 16% 17R2 in the current model. This discrepancy could be due to the difference in scale of the investigated models and the operating conditions. The experimental results were carried out on the macroscale with the surface fully covered with a copolymer layer of ~28 Å of 17R2 at a slow sliding velocity of 0.01 m.s\textsuperscript{-1} (Lin et al. 2015). In the current atomic model, the parameters of the maximum 32 polymer molecules corresponding to 16% concentration at the contact region and very high relative sliding velocity 20m/s contribute to the higher CoF. Furthermore, there is a direct contact of two sinusoidal metal asperities at applied pressure in the simulation, which can significantly incurs the high friction force, whereas the roughness of 20 Å in the experiment is considered very smooth.

It is necessary to understand the correlation of time evolution of both system height and friction force with the normal force. The 16% 17R2 copolymer concentration under loading pressure of 0.5 GPa, as shown in Figure 6.10, was used as an representative model to analyse this relationship. It is noted that there is a contrasting relationship between the system height and friction force. The fluid was compressed under the applied pressure and counter sliding of surfaces. The confined fluid gradually pushes the upper surface up during the shear process. When the top asperity slides over the surface of the bottom asperity the friction forces deviate significantly as the upper surface moves in an up and down hill motion. The system height increases when the upper asperity slides up the lower asperity surface (uphill motion), at the same time, the value of friction force increases. In contrast, for downhill motion, the system height and friction force decrease. For the first two repeated asperity contacts, there is not much change of friction force and system height between these sliding cycles. However, the friction force increases slightly for later cycles while the system height is reduced.

The normal force, which was measured as the sum of normal forces exerted by the mobile layer’s atoms on the top rigid layer of the upper surface, remains constant during the sliding stage. It is due to the constant load applied on the upper rigid layer
(Layer 4). The deviation for this force is quite small (Figure 6.10). This reflects that the normal pressure of the tribosystem has been well controlled during shear.

![Figure 6.10](image)

Figure 6.10 Relationship between the normal force, friction force, and system height during sliding time for the tribosystem of 16% 17R2 aqueous copolymer lubricant under loading pressure of 0.5 GPa.

The snap-shots of copolymer molecules at the first asperity contact, as exhibited explicitly in Figure 6.11, show that there is a presence of stretched copolymer molecules across the asperity’s surface in the sliding direction. These molecules were stretched due to the adsorption of different end blocks onto counter sliding surfaces (Figure 6.2), and the contact of counter asperity. The number of copolymer molecules that covers the asperity surface increases with the copolymer concentration. In fact, there is only one molecule of triblock copolymer across the asperity’s surface for the cases of 2% and 4% concentrations but there are three molecules for 6% and four molecules for 8-16% respectively.
Figure 6.11 Perspective snap-shots of 17R2 triblock copolymer and the lower surface during the first asperity contact cycle for different concentrations of 17R2 under loading pressure of 0.5 GPa. The dependence of covered molecules on the asperity surface with different copolymer concentrations is shown. For clarity the water molecules and the upper surface are excluded.

The friction of the model originates from the adsorbed lubricant molecules on the solid surfaces and atomic attractive force between the two asperities. Figure 6.12 shows that the sinusoidal asperities have been deformed during the contact, and this profile is more severe for later asperity contacts. It can be found a transfer of atoms between asperities and the sinusoidal surface has been modified to a complex shape with a larger contact area. To investigate this phenomenon, the number of
transferred atoms between two asperities is considered. This number was determined by counting the number of atoms on an asperity transferred to the counter asperity after the asperity contact.

Figure 6.12 Snapshots of confined model during the asperity contact for different sliding time under applied pressure of 0.5 GPa.

The number of transferred atoms (deserters), which reflect the wear of material, is shown in Figure 6.13. The figure reveals an increase of transferred atoms with the number of contact cycles. However, the number of transferred atoms during the simulation is not quite similar for both contacting asperities. Figure 6.14 shows that the applied pressure affects significantly the wear of asperities, in particular, there is no transferred atom between asperities for the loading pressure of 0.25 GPa;
however, the number of transferred atoms increases remarkably for higher pressure. The number of transferred atoms increases dramatically during the first four asperity contacts, but it levels off for later contacts.

Figure 6.13 Dependence of total transferred atoms and from each asperity on the number of asperity contacts for 16% 17R2 under the applied pressure of 0.5 GPa.

Figure 6.14 Dependence of total transferred atoms on the number of asperity contacts for different applied pressures.

The concentration of copolymer plays a vital role on the wear of asperity. As shown in Figure 6.15, a decrease of number of transferred atom with an increase of copolymer concentration has been found. This tendency is similar for all cases of loading pressure.
Figure 6.15 Dependence of average transferred atoms on the copolymer concentration for different applied pressures.

Figure 6.16 Friction force as a function of the number of transferred atoms between asperities.

Previous study reported a linear dependence of contact area on the number of transferred atoms; however, the relationship between the transferred atoms and friction force of system was not disclosed (Eder et al. 2011). The correlation between the number of transferred atoms and friction force for all sliding cycles of different concentration models and applied pressures are presented in Figure 6.16. The statistical data reveals that this is almost a linear relationship, and the friction force increases with the number of transferred atoms.
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Figure 6.17 Snapshots taken for von Mises stress contour of (a) confined system without the presence of water; and (b) 17R2 in contact region under applied pressure of 1.0 GPa for 16% of 17R2.

6.4 Discussion

The adsorption energy per constituent group is commonly utilized to determine the adsorption of a linear molecule on a surface (Li & Choi 2007). A linear hydrocarbon is considered as physisorption on a surface if the adsorption energy per carbon site is within 15 kJ.mol\(^{-1}\) (Weaver et al. 2014). Although a copolymer includes different constituent groups, this definition is also used in this work to assess the adsorption ability of the organic molecules. The adsorption energy per constituent group obtained from DFT calculation are 15.824, 11.868, and 11.771 kJ.mol\(^{-1}\) respectively for DME, 1,2–DME, DMP. These values reveal that there is a physisorption of DME, 1,2–DME, DMP on iron surface. The adsorption energy attained by interfacial potential, which is derived from short chain molecules, normally results in a higher value than experiment (Bolton et al. 1999). This is due to the fact that the adsorption energy per constituent group of triblock copolymer could be lower than those obtained from oligomers. Therefore, it is considered that the adsorption of triblock copolymer on iron surface is a physisorption. Moreover, it is noted that the adsorption energy per constituent group for oligomers decreases with an increase of molecular chain length. This observation is consistent with that observed by
experimental investigation and theoretical calculation for linear hydrocarbons (Tait et al. 2006). It is due to the steric effect of attached hydrogen atoms in the molecule (Bolton et al. 1999).

The atomic density profile of water, as presented in Figure 6.5, shows a strong layer with a separate distance of 1.68 Å from the Fe(100) surface. The strong adhesive strength and the ordered hydrogen-bonding network, which results in an ice-like structure of water at crystalline surface, could be the explanation for the layering of water on iron surface (Du et al. 1994). This observation is consistent with the theoretical investigations of thin water film confined by MgO(100) using MD calculation and kaolinite(001) using ab initio MD simulation (Deshmukh & Sankaranarayanan 2012; Feibelman 2013). Additionally, the copolymer also forms layering structure at a distance of 4.27 Å from the Fe(100) surfaces. This distance is larger than that evaluated for water. It could be due to the consequence of the considerably stronger adhesive strength and shorter equilibrium distance between water and iron compared to the constituent groups of copolymer as shown in Table 6.2. For copolymer, the PPO blocks form a stronger layer at solid-fluid interface than PEO due to the larger weight ratio (80 Wt%) (Lin et al. 2015) in molecular structure and stronger adhesive strength of PPO block compared to PEO. This observation is consistent with the experimental investigation by Lin. et al who found that the adsorption of 17R2 molecules yields distinct layers in which a thicker layer of PPO block has been found on the titanium oxide surface compared to PEO (Lin et al. 2015). However, the obtained layer of PPO in the current study is quite thin and the PEO blocks adsorb flatly at solid-fluid interfaces. The discrepancy could be due to a number of sources including the roughness of the observed surface (Li et al. 2011), the chosen number of simulation molecules, and the adhesive strength between the copolymer and surface. Particularly, the thin aqueous copolymer film confined between the pure iron surfaces was used in this theoretical study, whilst a full coverage of 17R2 on a rough titanium oxide surface has been observed by experiment. Importantly, in order for PEO blocks to be fully extended into aqueous solution, the adsorbed layer of Pluronic has to pass a transition zone of the flatly adsorbed PEO segments (Liou & Tsay 2011). The film thickness for this transition zone could be up to a few nanometers (Liou & Tsay 2011), while the adsorbed layer of copolymer in this model is only a few Angstroms due to the chosen limited number.
of copolymer molecules. The flat adsorption of triblock copolymer observed in current work can yield to an assumption that the adsorbed film on each iron surface still stay in the transition zone. Furthermore, the adhesive strength between copolymer with iron surface could be higher than titanium oxide. In fact, it is noted that the DFT calculation for adsorption of a monomer of PEO, as presented in Table 6.1, show that the Fe(100) surface possesses stronger adhesive strength than titanium oxide (Borodin et al. 2003).

As shown in Figure 6.6, the system height varied at the crash points, so the density of fluid could be changed a fair bit. For the NVE employed, it is expected that there was a presence of vacuumed space (cavity) in fluid when two asperities were crashed. The impact of vacuumed space on nanotribological system is a topic beyond the scope of this manuscript. From the literature it was revealed that the cavity decreased with an increase of applied load, and it is different for distinct asperity shapes (Eder et al. 2011). Furthermore, in regions with high cavity volumes, asperity contact plays little or no role, and vice versa (Eder et al. 2011).

Although a few PEO blocks, as shown in Figure 6.2, remain in the inner part of the thin film, a majority of them adsorbs on the surface. Experimental and theoretical observations of normal Pluronic triblock copolymer onto polymer surfaces reported a phenomenon in which the PPO blocks are expected to strongly bind to the substrate, whereas the hydrophilic PEO blocks dangle in the aqueous solution from the surface (Green et al. 1997; Li et al. 2011). This behaviour is in contrast with the current observation for metal surface like iron. Again the adhesive strength of copolymer is the main reason for this difference. The polymer surfaces, such as PP and PE, as well as polystyrene, are mainly constituted by carbon and hydrogen which possess a stronger dispersion interaction strength with CH$_3$ group of PPO block compared to water (Green et al. 1997; Hezaveh et al. 2011; Li et al. 2011). In contrast, the dispersion interaction between oxygen in PEO unit with water is higher than those with carbon and hydrogen of polymer (Smith et al. 2002). Therefore, the PPO block is favoured to adsorb on the polymer surface compared to PEO. This scenario is different for iron surface where the interaction strength of both oxygen and carbon sites in PPO and PEO block with iron, as shown in Table 6.2, are significantly stronger than with water (Hezaveh et al. 2011). A similar observation has been found by Bedrov et al. who reported a stronger adhesive strength of PEO on graphite
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surface than oily surface due primarily to the relative strength of dispersion interactions between PEO and the atomically dense graphite compared to oily surface (Bedrov & Smith 2006).

It is noted that the triblock copolymer confined between surfaces at mixed regime behaves differently from its bulk state. In bulk state, the copolymer behaves like single unimer at low concentration and micelle at high concentration (D’Errico et al. 2004). However, under confinement by surfaces, copolymer molecules adsorb on the surface and form a layering at the solid–fluid interface (Figure 6.3). The PPO block plays a vital role in this behaviour (Figure 6.5) due to its stronger adhesive strength of CH$_3$ compared to other constituent groups (Table 6.2). This observation is consistent with that observed by Liu et al. for normal Pluronic on hydrophobic surface (Liu, H et al. 2012). For homogeneous fluid such as hydrocarbons, it has been widely acknowledged that the density profile across the film thickness under compression is symmetrical for symmetry system (Martini & Vadakkepatt 2010; Vadakkepatt & Martini 2011). However, an interesting phenomenon in this study is that the density profile of copolymer across the film thickness is asymmetric. It is due to the effect of inhomogeneous distribution of mixed lubricant in which the copolymers are distributed randomly, and the limited number of copolymer molecules. This observation is in contrast with that observed for homogeneous lubricant such as hydrocarbon (Zheng et al. 2013a). The increase of degree of ordering with copolymer concentration is due to the increase of copolymer molecules adsorbed on the surfaces. For the same lubricant and surface model, the independence of degree of ordering from the applied pressure could be explained by the significant dependence of ordering on the adhesive strength of lubricant’s molecule and the feature of surfaces rather than loading pressure (Thompson & Robbins 1990).

It can be seen from Figure 6.9 that, for different applied pressure, a better lubrication performance is observed for higher copolymer concentration. This observation shows a good agreement with previous experimental study (Lin et al. 2013). The better antiwear performance of high copolymer concentration is due to the higher coverage of copolymer on the asperity surface (Figure 6.11). However, for a strong confinement with applied pressure up to 1.0 GPa, the high concentration of copolymer (16%) has little influence on the friction performance of this solution. It
could be due to the major contribution to the friction force is that produced by direct asperity interaction. Figure 6.17 shows that the copolymer undergoes a high stress during asperity contact, and it could be broken. Moreover, in practice, PPO and PEO are soft organic chains and they hardly survive under severe crash and high temperature. So this finding is limited by the assumption that the bonds in copolymer molecules are unbreakable.

For the case of high copolymer concentration (8-16%), the adsorbed copolymers on the asperity surface, as shown in Figure 6.11, prevent the adhesion of two asperities and the friction between the tribosurfaces. A low friction (Figure 6.9a) and small number of transferred atoms between asperities (Figure 6.15) have been found. However, these components then increase with the number of sliding cycle (Figure 6.8 and Figure 6.14). The increase of contact area could be the reasons for this phenomenon. In fact, during the asperity contact, the film thickness between asperities is reduced to quite a small gap compared to the size of copolymer molecules. This confinement reduces the number of copolymer adsorbed on the asperity surfaces (Liu, S et al. 2012). Moreover, the smooth surface of sinusoidal asperities, as shown in Figure 6.11, has been deformed and results in a rougher surface with a higher contact area which induces a strong adhesive force between asperities (Eder et al. 2011). The wear of asperity becomes more severe for higher loading pressure (Figure 6.15). As shown in Figure 6.11, the clusters of copolymer are found at high concentration (8-16%) rather than the single unimer at low concentration (2-6%). It is due to the aggregation of PPO block at a high concentration (Alexandridis & Alan Hatton 1995). Further, as a consequence of momentum transferring from sliding surface into fluid, the lubricant is sheared and the copolymer is stretched out in sliding direction (Figure 6.12) (Ohara & Torii 2005).

It can be seen that the spherical micelle, where the PPO blocks aggregated in the core of the micelles, is not found at mixed regime although the copolymer concentration increases up to 16%. It could be due to many reasons (Liu, H et al. 2012): The lubricant film thickness is quite thin (4 nm) and not enough space to form the micelle structure between surfaces. Moreover, the strong interaction strength between PPO block and iron surface causes the copolymer molecules to adsorb preferentially on the surface and form lamellar phase rather than stay in bulk aqueous solution. Further, the high shear rate (5x10^9 s^{-1}) applied on this model
causes this lamellar phase to occur faster than at static confined condition (Liu, H et al. 2012).

6.5 Conclusion

A theoretical MD study has been carried out to investigate the lubrication performance and structural properties of aqueous triblock copolymer lubricant confined between rough iron surfaces. The influence of copolymer concentration and loading pressure has been discussed in detail, and the following summaries can be made:

i) Under confinement, the copolymer forms lamellar structure at the solid-fluid interfaces with an asymmetric density profile across the film thickness. The triblock copolymer physisorbs on the iron surface and the PPO block adsorbs stronger compared to PEO.

ii) The obtained statistical results on the tribological performance of aqueous copolymer lubricant show a good agreement with the previous experimental investigation. The friction of tribosurface model decreases with an increase of copolymer concentration, but the friction force changes little at a high applied pressure.

iii) The friction of tribosurface model increases linearly with the number of transferred atoms between contacting asperities. Based on the classical MD model, the lubricant with a higher copolymer concentration shows a better antiwear performance than that with a lower concentration.

The applied pressure significantly affects the wear of asperity and friction of confined system. However, the density profile of copolymer across the film thickness is insensitive with applied pressure.
Chapter 7 Conclusion and future work

MD simulations have been carried out to provide an understanding of fundamental adsorption of normal-alkanes on iron and iron oxide surfaces which have been fully relaxed using DFT geometry optimization. The reliable interfacial force fields derived from quantum calculations have been applied for the interaction between alkane and these surfaces as well as between aqueous copolymer lubricant and iron. The realistic model using EAM model along with COMPASS force field has been used for hydrocarbon, while a UA model using OPLS potential was applied for triblock-copolymer. Using numerical method, the adsorption properties of a wide range of linear alkanes have been observed. The role of surface corrugation in thin film lubrication of hexadecane between different iron and iron oxide surfaces has been analysed systematically using a comprehensive surface parameterization method. Furthermore, the role of working conditions such as loading pressure, shear rate, and surface temperature on the structural, tribological, and rheological properties of hexadecane have been addressed in this work. Additionally, the lubrication performance and structural properties of aqueous triblock copolymer lubricant in mixed lubrication was also investigated to consider the influence of copolymer concentration and loading pressure. The major findings are summarized as following:

The Fe(110) and FeO(110) surfaces are basically bulk terminated while a significant relaxation is observed for Fe$_2$O$_3$(0001). However, the surface relaxation does not play a vital role in adsorption capability of alkanes on these surfaces. The adsorption energies per saturated methylene group decrease with an increase of molecular chain length on both iron and its oxide surfaces. For short alkane molecules, the saturated carbon density increases with the chain length but it remains steady and seems to be insensitive to the interfacial potential for longer molecules. Alkanes physisorb more strongly on Fe(110) surface than FeO(110) and Fe$_2$O$_3$(0001). Additionally, they form layers with their molecular plane parallel to the surfaces and there is a preferred orientation of alkane chain in (010) direction on FeO(110) at low temperature.
For thin film lubrication of hexadecane lubricant, despite a stronger adhesion strength of hexadecane on metal iron surfaces than its oxides, there is a higher degree of layering and lower shear stress of FeO(100), FeO(110), and Fe$_2$O$_3$(001) surfaces compared to Fe(111). The role of wall-fluid interaction strength on the tribological performance of hexadecane between smooth iron and its oxide surfaces is found to be less significant than the surface corrugation. The highest shear stress has been found for FeO(111) surface while the lowest one is for Fe(110). A plug-slip phase of lubricant has been found for all but Fe$_2$O$_3$(001) and FeO(111) surfaces which are subjected to the highest shear stress. The in-plane ordering of lubricant depends on the crystal orientation of the surfaces, but it is insensitive to the sliding orientation. In contrast, there is a dependence of the effective shear rate and shear viscosity on both surface orientation and sliding direction.

The surface properties have a significant influence on structural, rheological, and tribological of lubricant. The molecular in-plane ordering and the density of lubricant decreases with an increase of surface commensurability, and the shear stress increases with surface corrugation parameter whilst there is an inverse decrease of molecular in-plane ordering with this parameter. The commensurability and isotropy of the surface affect the local orientation of lubricant molecules. There is a favoured molecular alignment of hexadecane molecules on Fe(111), FeO(110), and Fe$_2$O$_3$(012) surfaces while there is an uncertainty in local alignments on other surfaces.

The ordering and slip of hexadecane at the solid-fluid interface increases with loading pressure, but this ordering increase is insignificant and pure slip occurs when the loading pressure exceeds a critical value. The surface structure has a substantial effect on these phenomena. A low degree of ordering and slip occurred on an Fe$_2$O$_3$(001) surface under a wide range of loading pressures, they were significant on Fe(100), Fe(110), FeO(100), and FeO(110) surfaces. Friction on the Fe$_2$O$_3$(001) surface was much higher, while the lubrication was ideal on the other surfaces. The coefficient of friction decreases as the loading pressure increases, but it remains steady at high loading pressures. The shear viscosity of lubricant increases as an exponential function, but this rheological component levels off when the loading pressure exceeds a critical value.
An increase in the shear rate leads to a decrease in the ordering structure and an increasing velocity slip. There is an exponential relationship between the slip and shear rate, and a higher loading pressure increases the slip. Moreover, the shear stress and coefficient of friction increase with shear rate, and the logarithmic function predicts this correlation properly. The shear viscosity increases with the loading pressure, and the shear thinning regime begins at a lower shear rate for a higher loading pressure.

The layering structure decreases considerably as the temperature increases, whereas the velocity slip is not sensitive to temperature. An increase in temperature causes a decrease in the shear stress, coefficient of friction, and the zero-shear-rate viscosity, whereas the onset of shear thinning increases with temperature. These tendencies agreed with those observed for bulk hexadecane; however a higher shear viscosity and lower onset of shear thinning occurred in the confined model, unlike the bulk lubricant.

For aqueous triblock copolymer lubricant, the copolymer forms lamellar structure at the solid-fluid interfaces with an asymmetric density profile across the film thickness under confinement. The triblock copolymer physisorsbs on the iron surface and the PPO block adsorbs stronger compared to PEO. The obtained statistical results on the tribological performance of aqueous copolymer lubricant show a good agreement with the previous experimental investigation. The friction of tribosurface model decreases with an increase of copolymer concentration, but the friction force changes little at a high applied pressure. The friction of tribosurface model increases linearly with the number of transferred atoms between contacting asperities. Based on the classical MD model, the lubricant with a higher copolymer concentration shows a better antiwear performance than that with a lower concentration. The applied pressure affects significantly the wear of asperity and friction of confined system. However, the density profile of copolymer across the film thickness is insensitive with applied pressure.

Although the UA model and OPLS potential have been employed for triblock copolymer, this conventional force field cannot describe the bond breaking of copolymer chains when these molecules are subject to a high shear stress during asperity contact. In practice, PPO and PEO are soft organic chains and they hardly survive under severe shear/contact and high temperature. An advance reactive force
field (ReaxFF) could be used to investigate this phenomenon in boundary lubrication. As the iron surface is usually oxidized to form different iron oxides, a force field parameterization will be carried out to develop a model of aqueous copolymer lubricant in boundary lubrication between iron oxide surfaces. For future works, a 3D model of multi-asperities surface roughness will be adopted to test different normal and reverse Pluronic triblock copolymers and phosphate ester additive compounds. The aims of this model are to investigate the tribological performance of tribo-system and the influence of surface structure, molecular structure, and PEO/PPO ratio on adsorption behaviour with and without phosphate ester.
Appendix

Appendix A: Basic knowledges about DFT

The basic concept of QM that supports DFT is introduced briefly in this appendix.

The electron responds more rapidly to changes in its surroundings than nucleus due to the light mass of electron. The equation that describes the electron motion is therefore firstly solved for fixed position of the nuclei. The separation of the nuclei and electrons into separation mathematical problems is known as Born-Oppenheimer approximation. For $M$ nuclei at positions $R_1, ..., R_M$, the lowest energy configuration of the electron is the ground state energy $E(R_1, ..., R_M)$. The simple form of Schrödinger equation is $H \Psi = E \Psi$ where, $H$ is Hamiltonian operator, $E$ is the ground state energy, and $\Psi$ is a set of solutions. Each of these solutions, $\Psi_n$, has an association eigenvalue, $E_n$.

For model where multiple electrons interact with multiple nuclei, the complete expression of Schrödinger equation is expressed as following:

$$H \Psi = \left[ \hat{T} + \hat{V} + \hat{U} \right] \Psi = \left[ -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V(r_i) + \sum_{i=1}^{N} \sum_{j<i}^{N} U(r_i, r_j) \right] \Psi = E \Psi$$

Here, $m$ is electron mass, $N$ is the number of electrons, $\hat{T}$ is kinetic energy, $\hat{V}$ is the energy from external field due to positively charged nuclei, and $\hat{U}$ is the electron-electron interaction energy.

For the chosen Hamiltonian, $\Psi$ is the electronic wave function of each of spatial coordinates of each of electron, so $\Psi = \psi(r_i, ..., r_n)$. This is a time-independent Schrödinger equation because the ground state energy is independent of time.

Here DFT provides an appealing alternative, being much more versatile as a way to systematically map the many-body problem, with $\hat{U}$, on to a single-body problem without $\hat{U}$. The quantity that can be measured is the probability that $N$ electrons are at a particular set of coordinate, $r_i, ..., r_n$. This probability is equal to
\[ \Psi^* (r_i, ..., r_n) \Psi (r_i, ..., r_n), \] where the asterisk indicates a complex conjugate. In DFT the key variable is the particle density \( n(\vec{r}) \) which is for a normalized \( \Psi \) is given by:

\[
n(\vec{r}) = 2 \sum_i \Psi^* (r_i, ..., r_n) \Psi (r_i, ..., r_n)
\]

Here, the summation goes over all the individual wave functions that occupied by electrons.
Appendix B: COMPASS force field

The functional forms of COMPASS force field is the same as those used in CFF force field

\[
E_{\text{total}} = \sum_b [k_2(b - b_0)^2 + k_3(b - b_0)^3 + k_4(b - b_0)^4] \\
+ \sum_\theta [k_2(\theta - \theta_0)^2 + k_3(\theta - \theta_0)^3 + k_4(\theta - \theta_0)^4] \\
+ \sum_\varphi [k_1(1 - \cos \varphi) + k_2(1 - \cos 2\varphi) + k_3(1 - \cos 3\varphi)] + \sum_\chi k_2\chi^2 \\
+ \sum_{b, b'} k(b - b_0)(b' - b'_0) + \sum_{b, \theta} k(b - b_0)(\theta - \theta_0) \\
+ \sum_{b, \psi} (b - b_0)[k_1 \cos \psi + k_2 \cos 2\psi + k_3 \cos 3\psi] \\
+ \sum_{\theta, \phi} (\theta - \theta_0)[k_1 \cos \phi + k_2 \cos 2\phi + k_3 \cos 3\phi] + \sum_{\theta, \theta'} k(\theta' - \theta_0')(\theta - \theta_0) \\
+ \sum_{\theta, \varphi, \chi} k(\theta - \theta_0)(\theta' - \theta'_0)\cos \phi + \sum_{i,j} \frac{q_i q_j}{r_{ij}} + \sum_{i,j} \epsilon_{ij} \left[ 2 \left( \frac{r_{ij}^\phi}{r_{ij}} \right)^9 - 3 \left( \frac{r_{ij}^\phi}{r_{ij}} \right)^6 \right]
\]

The functions are divided into two terms:

\[
\begin{align*}
\text{valence terms} & \quad \begin{cases} \text{diagonal terms} \\
\text{off-diagonal cross-coupling terms} \\
\text{nonbond interaction terms} \end{cases} \\
\end{align*}
\]

The valence terms include internal coordinates of bond (b), angle (\theta), torsion angle (\varphi), and out-of-plane angle (\chi), and cross-coupling terms involve the combinations of two or three internal coordinates.

The parameters of COMPASS force field for hexadecane were obtained from (Sun 1998). The partial charges for atoms in hexadecane molecule are the sum of all charge bond increments. The CH\textsubscript{3} group has three H atoms that have a partial charge of 0.053e for each H atom. Therefore, the C atom in this group should have a partial charge of \(-0.053\times3 = -0.159\) e to maintain a neutral charge group. Similarly, the C atom in CH\textsubscript{2} group have a charge of \(-0.053\times2 = -0.106\) e.
### Atomic Charge (e)

<table>
<thead>
<tr>
<th>elements</th>
<th>$C(H_3)$</th>
<th>$C(H_2)$</th>
<th>$H$</th>
<th>$Fe$</th>
<th>$Fe^{2+}$</th>
<th>$Fe^{3+}$</th>
<th>$O$</th>
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</thead>
<tbody>
<tr>
<td>charge</td>
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<td>-0.106</td>
<td>0.053</td>
<td>0</td>
<td>+0.945</td>
<td>+1.4175</td>
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</table>

### Quartic Bond

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<tr>
<th>$I - J$</th>
<th>$b_0$ (Å)</th>
<th>$k_2$ (kJ/mol/Å²)</th>
<th>$k_3$ (kJ/mol/Å³)</th>
<th>$k_4$ (kJ/mol/Å⁴)</th>
</tr>
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<tbody>
<tr>
<td>$C - C$</td>
<td>1.5300</td>
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### Quartic Angle

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<th>$\theta_0$</th>
<th>$k_2$ (kJ/mol/Å²)</th>
<th>$k_3$ (kJ/mol/Å³)</th>
<th>$k_4$ (kJ/mol/Å⁴)</th>
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</thead>
<tbody>
<tr>
<td>$C - C - C$</td>
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### Torsion

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<th>$k_2$ (kJ/mol)</th>
<th>$k_3$ (kJ/mol)</th>
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<tr>
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<td>$H - C - C - C$</td>
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### Bond-Bond

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<th>$k$ (kJ/mol/Å²)</th>
<th>$b_0$ (Å)</th>
<th>$b_0'$ (Å)</th>
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<tr>
<td>$H - C/C - C$</td>
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<td>1.5300</td>
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<td>$H - C/C - H$</td>
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### Bond-Angle

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<th>$k$ (kJ/mol/Å²)</th>
<th>$b_0$ (Å)</th>
<th>$k'$ (kJ/mol/Å²)</th>
<th>$b_0'$ (Å)</th>
<th>$\theta_0$</th>
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<tbody>
<tr>
<td>$C - C - C$</td>
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<tr>
<td></td>
<td>$b_0$</td>
<td>$k_1$</td>
<td>$k_2$</td>
<td>$k_3$</td>
<td>$b'_0$</td>
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<td></td>
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<td>kJ/mol</td>
<td>kJ/mol</td>
<td>kJ/mol</td>
<td>Å</td>
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<td>$H - C - C - C$</td>
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<td>$H - C - C - H$</td>
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<td>0.328</td>
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**Middle Bond-Torsion**

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<tbody>
<tr>
<td></td>
<td>$b_0$</td>
<td>$k_1$</td>
<td>$k_2$</td>
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<tr>
<td></td>
<td>Å</td>
<td>kJ/mol</td>
<td>kJ/mol</td>
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<td>$C - C - C - C$</td>
<td>1.5300</td>
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**Angle-Torsion**

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</thead>
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<td></td>
<td>$\theta_0$</td>
<td>$k_1(kJ/\text{mol})$</td>
<td>$k_2(kJ/\text{mol})$</td>
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<td>112.67</td>
<td>1.631</td>
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<tr>
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<td>1.891</td>
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<tr>
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**Angle - Angle Torsion**

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<thead>
<tr>
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<th>$I - J/K - L$</th>
<th>$I - J/K - L$</th>
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</thead>
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<tr>
<td></td>
<td>$k(kJ/\text{mol})$</td>
<td>$\theta_0$</td>
</tr>
<tr>
<td>$C - C - C - C$</td>
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</tr>
<tr>
<td>$H - C - C - C$</td>
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<td>$H - C - C - H$</td>
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**Nonbond (L-J-9-6)**

<table>
<thead>
<tr>
<th>Atoms</th>
<th>$\epsilon_0(kJ/\text{mol})$</th>
<th>$r_0(\text{Å})$</th>
<th>Mass(amu)</th>
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</thead>
<tbody>
<tr>
<td>$C$</td>
<td>0.261</td>
<td>3.854</td>
<td>12</td>
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<tr>
<td>$H$</td>
<td>0.096</td>
<td>2.878</td>
<td>1</td>
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</table>
Appendix C: OPLS UA potential for triblock-copolymer

The OPLS UA potential parameters for intra- and interaction of different constituent groups in PEO and PPO blocks of triblock-copolymer as well as their interactions with water are shown in this appendix. These parameters were obtained from the work of Hezaveh et al. (Hezaveh et al. 2011).

Force-field parameters for PEO block

<table>
<thead>
<tr>
<th>Atom types</th>
<th>$C_6$</th>
<th>$C_{12}$</th>
<th>q(e)</th>
<th>Mass (uma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(H$_3$)</td>
<td>$9.3547 \times 10^{-3}$</td>
<td>$3.6075 \times 10^{-5}$</td>
<td>0.225</td>
<td>15.035</td>
</tr>
<tr>
<td>C(H$_2$)</td>
<td>$5.9491 \times 10^{-3}$</td>
<td>$1.7912 \times 10^{-5}$</td>
<td>0.225</td>
<td>14.027</td>
</tr>
<tr>
<td>O</td>
<td>$2.0751 \times 10^{-3}$</td>
<td>$1.5127 \times 10^{-6}$</td>
<td>-0.450</td>
<td>15.999</td>
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</tbody>
</table>

Modified atom pairs

<table>
<thead>
<tr>
<th>Atom pair type</th>
<th>$C_6$</th>
<th>$C_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O–O$_W$</td>
<td>$0.6082 \times 10^{-2}$</td>
<td>$0.5475 \times 10^{-5}$</td>
</tr>
<tr>
<td>O–O$_{Meth}$</td>
<td>$0.2401 \times 10^{-2}$</td>
<td>$0.5970 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Bond constraints

<table>
<thead>
<tr>
<th>Bonds</th>
<th>Distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C</td>
<td>0.153</td>
</tr>
<tr>
<td>C–O</td>
<td>0.141</td>
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</table>

Bond angles

<table>
<thead>
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<th>Angles</th>
<th>$\phi_0$ (deg)</th>
<th>$K\phi$ (kJmol$^{-1}$rad$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C–O</td>
<td>109.5</td>
<td>418.68</td>
</tr>
<tr>
<td>C–O–C</td>
<td>109.5</td>
<td>501.22</td>
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Proper dihedrals

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<th>$C_0$</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
<th>$C_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O–C–C–O</td>
<td>-3.1</td>
<td>-0.74</td>
<td>-4.69</td>
<td>-6.87</td>
<td>15.4</td>
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<tr>
<td>C–O–C–C</td>
<td>1.12</td>
<td>-3.51</td>
<td>-2.54</td>
<td>0.03</td>
<td>4.9</td>
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</table>

Force-field parameters for PPO block

| Atom types, Lennard-Jones parameters, partial charges, masses |
## Appendix

### Atom types

<table>
<thead>
<tr>
<th>Atom types</th>
<th>$C_6$</th>
<th>$C_{12}$</th>
<th>$q(e)$</th>
<th>Mass (u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(H₃)</td>
<td>$9.3547 \times 10^{-3}$</td>
<td>$3.6075 \times 10^{-5}$</td>
<td>0.15</td>
<td>15.035</td>
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<tr>
<td>C(H₃)–[C*]</td>
<td>$9.3547 \times 10^{-3}$</td>
<td>$3.6075 \times 10^{-5}$</td>
<td>−0.15</td>
<td>15.035</td>
</tr>
<tr>
<td>C*(H)</td>
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<tr>
<td>O</td>
<td>$2.0751 \times 10^{-3}$</td>
<td>$1.5127 \times 10^{-6}$</td>
<td>−0.30</td>
<td>15.999</td>
</tr>
<tr>
<td>O–[C*]</td>
<td>$2.0751 \times 10^{-3}$</td>
<td>$1.5127 \times 10^{-6}$</td>
<td>−0.40</td>
<td>15.999</td>
</tr>
<tr>
<td>C(H₂)</td>
<td>$5.9491 \times 10^{-3}$</td>
<td>$1.7912 \times 10^{-5}$</td>
<td>0.05</td>
<td>14.027</td>
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### Modified atom pairs

<table>
<thead>
<tr>
<th>Atom pair type</th>
<th>$C_6$</th>
<th>$C_{12}$</th>
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</thead>
<tbody>
<tr>
<td>O–O₇W</td>
<td>$0.6082 \times 10^{-2}$</td>
<td>$0.5475 \times 10^{-5}$</td>
</tr>
<tr>
<td>O–O₇Meth</td>
<td>$0.2401 \times 10^{-2}$</td>
<td>$0.5970 \times 10^{-6}$</td>
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<tr>
<td>C(H₃)–[C*]–O₇W</td>
<td>$0.8960 \times 10^{-2}$</td>
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### Bond constraints

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<tr>
<td>C–O</td>
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### Bond angles

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<th>Angles</th>
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<th>$K_{ijk}$ (kJ mol⁻¹ rad⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>623.416</td>
</tr>
<tr>
<td>C–O–C</td>
<td>108.33</td>
<td>623.416</td>
</tr>
<tr>
<td>O–C*–C(H₂)</td>
<td>107.66</td>
<td>497.896</td>
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<tr>
<td>O–C*–C(H₃)</td>
<td>111.17</td>
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<td>O–C–C*</td>
<td>105.95</td>
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### Proper dihedrals

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<th>$C_3$</th>
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<td>C–O–C*–C(H₃)</td>
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<td>−0.30</td>
<td>−0.50</td>
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<td>O–C*–C(H₂)–O</td>
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<td>0.45</td>
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<tr>
<td>C(H₃)–C*–C(H₂)–O</td>
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<td>4.10</td>
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<td>C*–C(H₂)–O–C</td>
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<td>aC*–C(H₂)–O–C</td>
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### Improper dihedrals

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<th>$K_\zeta$ (kJ mol⁻¹ rad⁻²)</th>
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</table>


The proper dihedrals parameters for connection between PEO and PPO blocks obtained from (Hezaveh et al. 2012)

| C(H₃)–C(H₂)–O–C* | 35.264 | 334.8 |

*The proper dihedrals parameters for connection between PEO and PPO blocks obtained from (Hezaveh et al. 2012)*
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Anderson, AB 1981, ‘Reactions and structures of water on clean and oxygen covered Pt(111) and Fe(100)’, *Surface Science*, vol. 105, no. 1, pp. 159-76.


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Govender, A, Curulla-Ferré, D, Pérez-Jigato, M & Niemantsverdriet, H 2013, ‘First-Principles Elucidation of the Surface Chemistry of the C2Hx (x = 0–6) Adsorbate Series on Fe(100)’, *Molecules*, vol. 18, no. 4, pp. 3806-24.


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