Computer Simulations of Alkali Phosphate/Borate Lubricant at Sliding Interface in Metal Forming

Thi Thuy Huong Ta

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Computer Simulations of Alkali Phosphate/Borate Lubricant at Sliding Interface in Metal Forming

THI THUY HUONG TA

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This thesis is presented as part of the requirement for the conferral of the degree:
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School of Mechanical, Materials, Mechatronics and Biomedical Engineering
Faculty of Engineering and Information Sciences
University of Wollongong

March 2020
Abstract

Inorganic glasses such as alkali metal phosphate or borate have been proven to be the most effective lubricants for high temperature lubrication in hot metal forming. When the lubricants are introduced into a metal-metal contact, multiple physical/chemical phenomena such as adsorption, tribochemical reactions and tribofilm formation occur under the effects of heavy loads, sliding motion, and high temperature. These processes not only transform lubricant structures but also modify profoundly the contacting interface and induce surface complexity, which eventually affect the overall lubricant effectiveness. In recent years, experimental measurements on friction, wear, and tribofilms obtained from alkali phosphate/borate lubricated systems have been reported, however little research has been done to understand the functioning mechanisms of alkali phosphate/borate and steel surface interactions and chemical reactions, and the structural transformation inside the systems under harsh operating conditions.

In this work, density functional theory (DFT) and ab initio molecular dynamics (AIMD) simulations were used to investigate the physical/chemical interactions and tribochemical reactions between alkali phosphate/borate and iron oxide (Fe$_2$O$_3$) surface. First, the adsorption of sodium sodium pyrophosphate (Na$_4$P$_2$O$_7$) and orthophosphate (Na$_3$PO$_4$) on Fe(110) and Fe$_2$O$_3$(0001) surfaces was carried out to study the correlation between the adsorption behaviors and frictional performance of sodium phosphate lubricants. This was accompanied by electronic structure analyses to unveil atomic mechanisms and chemical insights into the phosphate-ion/iron oxide interactions. The results indicate that sodium phosphates chemically adsorbed on the iron and iron oxide surfaces by forming Fe–O bonds and stabilize on the surfaces through Fe–O–P linkages. The stronger binding of Na$_3$PO$_4$ than that of Na$_4$P$_2$O$_7$ on Fe$_2$O$_3$(0001) surfaces is consistent with its better antiwear performance observed by the experiments. It was found that Fe–O bonds formed during the phosphate adsorption are stable covalent bonds that are as strong as P–O bonds of the Fe–O–P linkages. However, the binding of Fe–O–P on Fe is caused by a donor-acceptor mechanism; which is in contrast to the donation/back-donation interaction mechanism between the Fe–O–P and the Fe$_2$O$_3$ surface. The results suggested a strong adhesion of sodium phosphate lubricant on the oxidized surface which is essential to maintain a protective layer on steel surfaces.
In order to unveil the effects of elevated temperature on the glass lubricant behaviors, AIMD simulations were carried out to study the interactions of sodium tetraborate (Na$_2$B$_4$O$_7$) and boron oxide (B$_2$O$_3$) on an iron oxide surface Fe$_2$O$_3$(0001) at 1073 K. It was found that high temperature transformed Na$_2$B$_4$O$_7$ structure by activating sodium mobility and decomposing BO$_4$ complexes into BO$_3$ and non-bridging oxygen. These products engage in chemical reactions with the Fe$_2$O$_3$ surface by forming O–Na ionic and Fe–O–B covalent bonds, which make Na$_2$B$_4$O$_7$ adhere strongly on the surface. Density profile and charge analysis showed that sodium cations play a critical role at the interface by forming O–Na–O stacking and acting as a bridge to connect the surface with the lubricant. On the contrary, the molten B$_2$O$_3$ remained intact with no chemical reactions which accounts for its poor adhesion on the Fe$_2$O$_3$ surface.

To further investigate the effects of pressure on Fe$_2$O$_3$-sodium borate systems with different concentrations, the compression and decompression processes were conducted on sodium borates xNa$_2$O·(100-x)B$_2$O$_3$ (x = 25, 33, 50, and 60 mol %) confined between two Fe$_2$O$_3$ surfaces from 0 and 10 GPa. The compressed structures revealed that the borates responded to the applied load through a two-stage transformation: rearrangement at low pressure and polymerization at high pressure. The polymerization occurred through three different mechanisms to form BO$_4$ tetrahedra with the surface’s oxygen, non-bonding, and bonding oxygen. The conversions from BO$_3$ to BO$_4$ were mostly irreversible as a large number of newly formed BO$_4$ remained unchanged under the decompression. In addition, the formation of a sodium-rich layer can be observed when the systems were compressed to high pressure.

When the compression is completed, the sliding was applied at 1 and 3 GPa. In order to account for the effects of alkali elements, apart from xNa$_2$O·(100-x)B$_2$O$_3$ (x = 25, 33, and 50 mol %), lithium borate (Li$_2$O·B$_2$O$_3$), and potassium borate (K$_2$O·B$_2$O$_3$) have been confined between two Fe$_2$O$_3$ surfaces and subjected to the sliding motion. A significant impact of alkali elements on the energy shape and bonding behavior in the systems has been identified. In fact, the lower energy variation, which is associated with the formation of an easy-shear layer was obtained in systems with the highest content of Na$_2$O (50%). Meanwhile, high energy variation was encountered with low Na$_2$O concentration systems, lithium borate and potassium borate at 3 GPa. The high shearing energy variation was closely associated with the dissociation of the interfacial bonds and the subsequent rupture of the bonds inside the surface. Based on the current
simulations, the possible interfacial layering has been proposed to correlate with experimental findings on friction and wear of borate lubricated oxide surfaces.

By adding graphene to sodium borate-Fe$_2$O$_3$ systems, the graphene-borate and Fe$_2$O$_3$ graphene interactions have shown that graphene weakly interacts with both the surface and the sodium borate. A doping of highly adhesive atoms such as boron (B), sulfur (S), phosphorus (P), and silicon (Si) in graphene lattice suggested that doped-graphene adsorbed well on the Fe$_2$O$_3$ surface by chemical bonds between Fe and dopant atoms. In addition, these doped-graphene structures showed a comparable thermal stability with the pure graphene when interacted on the Fe$_2$O$_3$ surface at high temperature.
Acknowledgments

First, my deep gratitude goes to my supervisor Prof. Kiet Tieu for his intellectual guidance and enthusiastic support during my study at the University of Wollongong. From the first day I arrived in Australia, he has always been patient and given me opportunities to broaden my horizons. I also wish to thank my co-supervisors Dr. Hongtao Zhu and A/Prof. Haibo Yu who always shared with me their brilliant advice and knowledge. Without my supervisors, I would never have been able to complete this work and reach this point. I am so grateful to have them as my supervisors.

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I’d like to thank the University of Wollongong for providing the HDR scholarships and financial support for the duration of my studies. I would like to thank the staff and students within the School of Materials, Mechanical, and Mechatronics and Biomedical Engineering for all the help and assistance given. I’d like to thank Dr. Guillaume Michal for his support of Eukles's supercomputer, and Australian National Computational Infrastructure (NCI) for high performance computing.

Finally, I’d like to acknowledge my fiancé Thanh Nhan Nguyen, my family, and his family, who are the most important people in my life. Thank you for always standing beside and supporting me unconditionally through the years. Thank you for letting me pursue my dreams even when I was thousands of miles away for years, and most of all you are the greatest inspirations to help me overcome many difficulties during the time in a faraway land.
Declaration of authorship

I, Thi Thuy Huong Ta, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Mechanical, Materials, Mechatronics, and Biomedical 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 Thuy Huong Ta

March 2020
List of publications


# List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>[2]O</td>
<td>Bridging oxygen</td>
</tr>
<tr>
<td>(NaPO₃)₆</td>
<td>Sodium Metaphosphate</td>
</tr>
<tr>
<td>[3]O</td>
<td>Three coordinated oxygen</td>
</tr>
<tr>
<td>AIMD</td>
<td>Ab initio Molecular Dynamics</td>
</tr>
<tr>
<td>B</td>
<td>Boron</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>Boron oxide</td>
</tr>
<tr>
<td>B³</td>
<td>Three coordinated boron</td>
</tr>
<tr>
<td>B⁴</td>
<td>Four coordinated boron</td>
</tr>
<tr>
<td>BB</td>
<td>Bidentate-binuclear</td>
</tr>
<tr>
<td>B-G</td>
<td>Boron-doped graphene</td>
</tr>
<tr>
<td>BN</td>
<td>Boron Nitride</td>
</tr>
<tr>
<td>BOMD</td>
<td>Born-Oppenheimer Molecular Dynamics</td>
</tr>
<tr>
<td>BOP</td>
<td>Bond Overlap Population</td>
</tr>
<tr>
<td>BT</td>
<td>Bidentate-Trinuclear</td>
</tr>
<tr>
<td>BTetra</td>
<td>Bidentate-Tetranuclear</td>
</tr>
<tr>
<td>CDD</td>
<td>Charge Density Difference</td>
</tr>
<tr>
<td>COF</td>
<td>Coefficient of Friction</td>
</tr>
<tr>
<td>CP</td>
<td>Compression</td>
</tr>
<tr>
<td>CPMD</td>
<td>Car-Parrinello Molecular Dynamics</td>
</tr>
<tr>
<td>D</td>
<td>Dopant</td>
</tr>
<tr>
<td>DC</td>
<td>Decompression</td>
</tr>
<tr>
<td>DDEC6</td>
<td>Density derived electrostatic and chemical</td>
</tr>
<tr>
<td>DDP</td>
<td>Dialkyldithiophosphate</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DG</td>
<td>Doped-graphene</td>
</tr>
<tr>
<td>DLC</td>
<td>Diamond-like carbon</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of State</td>
</tr>
<tr>
<td>EP</td>
<td>Extreme Pressure</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Iron (III) Oxide</td>
</tr>
<tr>
<td>FeKB</td>
<td>Fe₂O₃-Potassium Tetraborate</td>
</tr>
<tr>
<td>FeLiB</td>
<td>Fe₂O₃-Lithium Tetraborate</td>
</tr>
</tbody>
</table>
FeNaB  Fe$_2$O$_3$-Sodium Tetraborate
FeNaB25%  Fe$_2$O$_3$-Na$_2$O.3B$_2$O$_3$
FeNaB33%  Fe$_2$O$_3$-Na$_2$O.2B$_2$O$_3$
FeNaB50%  Fe$_2$O$_3$-Na$_2$O.B$_2$O$_3$
FeNaB60%  Fe$_2$O$_3$-3Na$_2$O.2B$_2$O$_3$
G  Graphene
G-F  Graphene Flake
GGA  Generalized Gradient Approximation
G-S  Graphene Sheet
h-BN  Hexagonal Boron Nitride
H$_3$BO$_3$  Boric acid
HOMO  Highest Occupied Molecular Obital
HSAB  Hard and soft acids and bases
K  Potassium
LA  Local density approximation
Li  Lithium
LUMO  Lowest unoccupied molecular orbitals
MB  Monodentate-Binuclear
MD  Molecular Dynamics
MeCHO  Aldehydes
MM  Monodentate-Mononuclear
MoS$_2$  Molybdenum disulfide
MSD  Mean Squared Displacement
MT  Monodentate-Trinuclear
MTPs  Meta-thiophosphates
Na  Sodium
Na$_2$B$_4$O$_7$  Sodium Tetraborate
Na$_3$PO$_4$  Sodium Orthophosphate
Na$_4$P$_2$O$_7$  Sodium Pyrophosphate
NVT  NVT ensemble
O  Oxygen
O$^b$  Bridging oxygen
O$_B$  Oxygen of Sodium/Lithium/Potassium Borate
O$^{nb}$  Non-bridging oxygen
Os  Oxygen of the Fe$_2$O$_3$ surface
P   Phosphorus
PAO Polyalphaolefine
PAW Projector augmented-wave
PBE Perdew–Burke–Ernzerhof
PDOS Partial Density of State
P-G Phosphorus-doped graphene
PTFE Polytetrafluoroethylene
QM/MM Quantum Mechanics/Molecular Dynamics
RDF/g(r) Radial Distribution Function
S   Sulfur
SAM Self-assembled monolayers
S-G Sulfur-doped Graphene
Si  Silicon
Si-G Silicon-doped Graphene
T   Temperature
TBQC Tight-Binding quantum chemical
TDOS Total Density of State
Tetra-Tetra Tetrادentate-Tetranuclear
TH  Tridentate-hexanuclear
TP  Tridentate-pentanuclear
TPs Triphosphates
TS  Transition State
TT  Tridentate-trinuclear
TTetra Tridentate-tetranuclear
VASP Vienna Ab Initio Simulation Package
ZDDP Zin dialkyl dithiophosphate
ZP  Zinc phosphate
# Table of Contents

ABSTRACT .......................................................................................................................... 1

ACKNOWLEDGMENTS ......................................................................................................... 4

DECLARATION OF AUTHORSHIP ...................................................................................... 5

LIST OF PUBLICATIONS ...................................................................................................... 6

LIST OF ABBREVIATIONS .................................................................................................... 8

TABLE OF CONTENTS .......................................................................................................... 11

LIST OF FIGURES ................................................................................................................ 14

LIST OF TABLES .................................................................................................................. 22

CHAPTER 1. INTRODUCTION ............................................................................................... 24

CHAPTER 2. LITERATURE REVIEW ....................................................................................... 27

2.1. HOT METAL FORMING AND HIGH TEMPERATURE LUBRICATION ......................... 27

2.2. LUBRICANTS FOR HIGH TEMPERATURE LUBRICATION ........................................ 30

2.2.1. Phosphate based lubricants .................................................................................. 30

2.2.2. Alkali Borate lubricants ...................................................................................... 33

2.2.3. Silicate lubricants ............................................................................................... 40

2.2.4. Solid lubricants ................................................................................................... 42

2.3. LUBRICANT-SURFACE INTERACTIONS: PHYSICAL/CHEMICAL ADSORPTION,

TRIBOCHEMICAL REACTIONS AND TRIBOFILM FORMATION ........................................ 43

2.3.1 Physical and chemical adsorption .......................................................................... 43

2.3.2 Tribochemical reactions ....................................................................................... 45

2.3.3 Mechanisms of tribofilm formation ...................................................................... 46

2.4. COMPUTER SIMULATIONS OF TRIBOCHEMICAL REACTIONS ................................ 49

2.4.1. Studies by Molecular Dynamics simulations ....................................................... 49

2.4.2. Tribochemical reactions by Density Functional Theory ..................................... 52

2.4.3. Studies by Ab initio Molecular Dynamics ............................................................. 55

2.4.4. Studies by Coupling Methods (QM/MM) ............................................................. 57

2.5. SUMMARY, KNOWLEDGE GAPS, AND OBJECTIVE ................................................. 59

2.5.1 Summary and knowledge gaps .............................................................................. 59
6.2 SIMULATION MODEL ........................................................................................................ 133
6.3 STRUCTURES OF SODIUM BORATE GLASSES AT 300 K AFTER COOLING .......... 135
6.4 ENERGETIC PROPERTIES UNDER COMPRESSION AND DECOMPRESSION .......... 137
6.5 STRUCTURAL TRANSFORMATION UNDER COMPRESSION AND DECOMPRESSION .......................................................... 140
6.5.1. Low pressure region: Structural reorientation ............................................ 142
6.5.2. High pressure region: Three Mechanism Polymerization .................................... 143
6.6 SODIUM DISTRIBUTION IN THE COMPRESSION AND DECOMPRESSION .......... 149
6.7 CONCLUSIONS ........................................................................................................ 153

CHAPTER 7. ALKALI BORATE GLASSES UNDER SLIDING CONDITIONS ............................................................... 154
7.1 INTRODUCTION ........................................................................................................ 154
7.2 SIMULATION DETAILS ............................................................................................... 155
7.3 ENERGIES AND BONDING BEHAVIORS DURING THE SHEAR ...................................... 157
7.4 FORMATION OF “EASY-SHEAR” LAYERS ................................................................ 162
7.5 FE REMOVAL FROM THE SUBSTRATES .................................................................. 164
7.6 EFFECTS OF HIGH TEMPERATURE .......................................................................... 170
7.7 PROPOSED INTERFACIAL LAYERING ................................................................... 173
7.8 CONCLUSIONS ........................................................................................................ 175

CHAPTER 8. GRAPHENE AND ITS MODIFICATIONS FOR HIGH TEMPERATURE LUBRICATION ......................................................... 177
8.1 INTRODUCTION ........................................................................................................ 177
8.2 SIMULATION DETAILS ............................................................................................... 178
8.3 INTERACTIONS OF GRAPHENE WITH SODIUM BORATE AT HIGH TEMPERATURE … 180
8.4 GRAPHENE DOPING .................................................................................................. 184
8.5 INTERACTIONS OF GRAPHENE AND DOPED-G ON Fe2O3 SURFACE ..................... 187
8.6 STABILITY OF GRAPHENE AND DOPED-G AT HIGH TEMPERATURE ..................... 190
8.7 CONCLUSIONS ........................................................................................................ 197

CHAPTER 9. CONCLUSIONS AND FUTURE WORK .............................................................. 198
9.1 CONCLUSIONS ........................................................................................................ 198
9.2 FUTURE WORK ......................................................................................................... 201

REFERENCES .................................................................................................................... 203
List of Figures

Figure 2.1 Schematic description of the interface in the hot metal forming processes.\textsuperscript{9} ............27

Figure 2.2 Structure of a phosphate ester, a thiophosphate ester and a dialkyldithio phosphoric acid.\textsuperscript{40} ..................................................................................................................31

Figure 2.3 Coefficient of friction as a function of time and (b) average coefficient of friction in steady-state lubrication for the steel/steel pairs at 800°C.\textsuperscript{47} ...........................................................................32

Figure 2.4 Friction coefficients and wear loss volumes of dry and sodium borate-lubricated steel tribo-pair (at 800°C, nominal load of 10 N, and sliding speed of 0.1 m/s)\textsuperscript{15} .........................37

Figure 2.5 Layered structure of boric acid.\textsuperscript{26} ..................................................................................39

Figure 2.6 Friction coefficients (u) measured in unlubricated (dry) and sodium metasilicate (NSO) lubricated condition at various temperatures of 530, 645, 730, 825, 920 and 960°C.\textsuperscript{111} 42

Figure 2.7 Schematic description of the hierarchical structure at steel tribo-interfaces lubricated by sodium/potassium polyphosphate at elevated temperatures \textsuperscript{142} ...............................................................................48

Figure 2.8 Bi-layered tribofilm obtained from sodium tetraborate lubricant at 800°C.\textsuperscript{15} .............49

Figure 2.9 MD simulation model of ZP or ZDDP confined between iron substrates, Fe\textsubscript{2}O\textsubscript{3} in the center of the lubricant layer and plays as a wear particle.\textsuperscript{31} ........................................51

Figure 2.10 Dissociation path of trimethyl phosphite on Fe(110) surface obtained from DFT calculation.\textsuperscript{154} ........................................................................................................53

Figure 2.11 Visualization of the structures of zinc phosphate during the AIMD simulation: (a) initial structure, (b) the final structure of the compression – decompression cycle, and (c) structure of zinc phosphate at 17 GPa.\textsuperscript{136} ..........................................................56

Figure 2.12 Simulation models of aldehydes (MeCHO) positioned between α-Al\textsubscript{2}O\textsubscript{3} surfaces using the modified Quantum Espresso code.\textsuperscript{179} .................................................................57

Figure 2.13 QM/MM simulation model of trimethyl phosphate between iron substrates.\textsuperscript{137} ......59

Figure 3.1 Schematic diagram of BOMD simulation ....................................................................................68

Figure 3.2 Schematic diagram of CPMD simulation......................................................................................69

Figure 3.3 Crystalline lattices of Fe (bcc), FeO (cubic) and Fe\textsubscript{2}O\textsubscript{3} (rhombohedral): Fe (blue), O red). ..................................................................................................................................................70

Figure 3.4 Molecular structures of (a) Na\textsubscript{4}P\textsubscript{2}O\textsubscript{7} and (b) Na\textsubscript{3}PO\textsubscript{4}: Sodium (purple), Phosphorus (magenta), Oxygen (red). The non-bridging oxygen is P–O, and the bridging oxygen is P–O–P (O\textsuperscript{b}). .........................................................................................................................71

Figure 3.5 Models for the construction alkali borate glasses (a) the Fe\textsubscript{2}O\textsubscript{3} slab and (b) an
orthorhombic box of alkali borate glasses. $a = 8.72 \, \text{Å}$, $b = 10.07 \, \text{Å}$, and $c$ is adjusted based on the density of alkali borate. $Z_{\text{surf}}$ includes the surface thickness and 15 Å of the vacuum layer. Iron (blue), oxygen (red), boron (green), and sodium (yellow). The color assignment is applied for all Fe$_2$O$_3$ and sodium borate systems. 

Figure 3.6 Confined model of alkali borate glasses between two Fe$_2$O$_3$ substrates.

Figure 4.1 Top view of the possible adsorption sites on Fe(110) and Fe$_2$O$_3$(0001) surfaces: (a) on-top of Fe atom (T), long bridge (LB), short bridge (SB), pseudo-threefold coordinated hollow (3F); (b) on-top of Fe atom (Fe T), on hollow of Fe atom (Fe H1 and Fe H2), on top of oxygen atom (O T) and bridge (B). Fe (blue), O (red).

Figure 4.2 Side view (a), (b), and (c), and top view (d), (e) and (f) of three molecular orientations of Na$_4$P$_2$O$_7$ on Fe(110)/Fe$_2$O$_3$(0001) surface. Sodium is presented in purple.

Figure 4.3 Side view (a), (b), and (c), and top view (d), (e) and (f) of three molecular orientations of Na$_3$PO$_4$ on Fe(110)/Fe$_2$O$_3$(0001) surface.

Figure 4.4 Different adsorption configurations of Na$_4$P$_2$O$_7$ and Na$_3$PO$_4$ on Fe surface. Each interaction mode is represented by two letters; the first one is related to the oxygen atoms in phosphate molecules involving Fe-O bonds, and the second one is the number of Fe atoms of the surfaces that bonded to oxygen atoms of the phosphates. M (mono-), B (bi-), T (tri-), Tetra (tetra-), P (pen-), and H (hexa-). Blue (Fe), Red (O), Purple (Na), Magenta (P). The name of the adsorption modes and color assignment are applied through this chapter.

Figure 4.5 CDD for the most favorable configuration in each system: Fe- Na$_4$P$_2$O$_7$ TP mode (a) side view, (b) top view, and Fe$_2$O$_3$- Na$_3$PO$_4$ system BB mode (c) side view and (d) top view. The yellow and cyan represent the positive (electron accumulation) and negative (electron depletion) regions, respectively. Isosurfaces are 0.007 e/Å$^3$ for (a) and (c) and 0.004 e/Å$^3$ for (b) and (d). For clarity, sodium ions in (a) and (c) have been removed, and only the topmost layer of the surface is shown.

Figure 4.6 PDOS of Fe and O atoms in isolated phosphates and adsorbed on Fe surfaces: (a) isolated Na$_4$P$_2$O$_7$, and (b) adsorbed Na$_4$P$_2$O$_7$ on Fe surface, (c) isolated Na$_3$PO$_4$, (d) adsorbed Na$_3$PO$_4$ on Fe surface. The horizontal scales are set differently for the (a), (c) and (b), (d).

Figure 4.7 Total density of state (TDOS) and corresponding electronic band decomposition of Na$_4$P$_2$O$_7$ and Na$_3$PO$_4$.

Figure 4.8 Different adsorption configurations of Na$_4$P$_2$O$_7$ and Na$_3$PO$_4$ on Fe$_2$O$_3$ surface.

Figure 4.9 CDD for the most favorable configuration in each system: Fe$_2$O$_3$- Na$_4$P$_2$O$_7$ BB mode (a) side view, (b) top view, and Fe$_2$O$_3$- Na$_3$PO$_4$ system MM mode (c) side view and (d) top view. The yellow and cyan represent the positive (electron accumulation) and negative (electron depletion) regions, respectively. Isosurfaces are 0.005 e/Å$^3$ for (a) and (c) and 0.004 e/Å$^3$ for (b).
and (d). $O_3$ is oxygen of the surface. For clarity, only the topmost layers of the surface are shown.

Figure 4.10 PDOS of Na$_3$PO$_4$ and iron atoms of Fe$_2$O$_3$(0001) surface in the isolated and adsorbed systems: (a) isolated Fe$_2$O$_3$ surface, (b) isolated Na$_3$PO$_4$, and (c) Fe$_2$O$_3$-Na$_3$PO$_4$. For iron, only the atoms at the first layer are used. mol.s and mol.p are the s and p states of the total DOS of Na$_3$PO$_4$, respectively.

Figure 4.11 BOP (e) of P–O bonds in Na$_3$PO$_4$ in the isolated and adsorbed states. The BOP values after adsorption are independent in each configuration. The colors and symbols are only for the identification of different bonds. ads. P–O–Fe means the P–O bonds in Fe–O–P linkages, and ads. P–O means the remaining P–O bonds of Na$_3$PO$_4$.

Figure 4.12 BOP of P–O, P–O$_b$, and Fe–O bonds in the isolated and the adsorbed Na$_3$P$_2$O$_7$ on Fe and Fe$_2$O$_3$ surfaces. Sodium has been removed for clarity.

Figure 4.13 PDOS of $d$ orbitals of Fe in (a) free Fe surface, (b) Fe-Na$_3$PO$_4$, (c) free Fe$_2$O$_3$ surface and (d) Fe$_2$O$_3$-Na$_3$PO$_4$ system. The scales are set differently for (a), (b) and (c), (d). For clarity, only energy range around Femi level is displayed.

Figure 4.14 PDOS of non-bridging oxygen (O) and bridging oxygen (P-O-P/O$_b$) in isolated Na$_3$P$_2$O$_7$. DOS of oxygen is averaged for six non-bridging oxygen atoms.

Figure 5.1 Structures of Na$_2$B$_4$O$_7$ (a) at 300 K and (d) at 1073 K; polyhedral presentation (b) at 300 K and (e) at 1073 K; and RDFs of Na–O, B–O, and O–O (c) at 300 K and (f) at 1073 K. O$^{nb}$ atoms are colored Blue in (a) and (d), sodium in (b) and (e) has been remove for clear visualization.

Figure 5.2 Structures of B$_2$O$_3$ (a) at 300 K, (b) at 1073 K, and (c) B–O and O–O RDFs at 300 and 1073 K.

Figure 5.3 Building units and the corresponding BOP values of BO bonds in (a) Na$_2$B$_4$O$_7$ and (b) B$_2$O$_3$.

Figure 5.4 MSD of Na, B, and O at 300 K and 1073 K. The MSD values were averaged over all atoms of the same type in the system.

Figure 5.5 Potential energy and temperature of Fe$_2$O$_3$-Na$_2$B$_4$O$_7$ during the simulation at 1073 K.

Figure 5.6 Snapshots of Fe$_2$O$_3$-Na$_2$B$_4$O$_7$ configurations during the simulation at 1073 K: (a) 0 ps, (b) 2 ps, (c) 5 ps, and (d) 10 ps, (e) MSD of Na$_2$B$_4$O$_7$’s atoms and (f) average distance from Na ions to the Fe$_2$O$_3$ surface during the interaction of sodium borate on the surface.

Figure 5.7 Atomic density profile of atoms across the z direction of all elements in the system. The vertical dotted line separates the surface and the lubricant areas. O is the oxygen of
Na$_2$B$_2$O$_7$ and O$_3$ is the oxygen of the Fe$_2$O$_3$ surface…………………………………………………………….117

Figure 5.8 Potential energy and temperature of the Fe$_2$O$_3$-B$_2$O$_3$ system during the simulation at 1073 K…………………………………………………………………………………………………………..119

Figure 5.9 Snapshots of Fe$_2$O$_3$-B$_2$O$_3$ configurations at (a) 0 ps, (b) 10 ps, and (c) the corresponding closest distance from the B$_2$O$_3$ block to the Fe$_2$O$_3$ surface during the simulation at 1073 K…………………………………………………………………………………………………………..119

Figure 5.10 Binding energies of Fe$_2$O$_3$-Na$_2$B$_2$O$_7$ and Fe$_2$O$_3$-B$_2$O$_3$ as a function of separate distance d. The scales are different in (a) and (b). ………………………………………………………………………………………………………..121

Figure 5.11 Partial charge distribution of Fe$_2$O$_3$-borate systems: (a) initial Fe$_2$O$_3$ surface at 0 ps, (b) Fe$_2$O$_3$-Na$_2$B$_2$O$_7$ at 10 ps, and (c) Fe$_2$O$_3$-B$_2$O$_3$ at 10 ps. (+) means a positive charge and (−) means a negative charge. The partial charges are the averaged values over atoms of the same type in the system…………………………………………………………………………………………………………..122

Figure 5.12 Constraint forces at some reaction coordinates ("ξ") for the Fe-O bond dissociation at 300 K: (a) Fe−O$^b$ bond, (b) Fe−O(B$^3$) bond, and (c) evolution of mean constraint forces of the Fe−O$^b$ and Fe−O(B$^3$) bonds along the reaction coordinates ("ξ")……………………………………………………………..126

Figure 5.13 Dissociative configurations and the corresponding activation energies of Fe−O bonds in the system. (a) and (d) are the initial configurations; (b) and (e) are the transition states; (c) and (f) are the corresponding free energy profiles. Sodium has been removed for clear visualization. ………………………………………………………………………………………………………127

Figure 5.14 Constraint forces at some reaction coordinates ("ξ") for the B−O bond dissociation at 300 K: (a) B$_4$−O bond, (b) B$_3$−O bond, (c) B$_3$−O(−Fe) bond, and (d) evolution of mean constraint forces of the B$_4$−O, B$_3$−O, and B$_3$−O(−Fe) bonds along the reaction coordinate ξ…128

Figure 5.15 Bond dissociation and the corresponding activation energies of B−O bonds in the systems. (a), (d), and (g) are the initial configurations; (b), (e), and (h) are the transition states; (c), (f), and (i) are the corresponding energy profiles. Sodium has been removed for better visualization. ………………………………………………………………………………………………………129

Figure 6.1 Model of sodium borates confined between two Fe$_2$O$_3$ substrates for compression. In the compression, the upper surface was shifted along the z direction with a distance Δz = 0.05 Å………………………………………………………………………………………………………………..134

Figure 6.2 Visualization structures of sodium borate glasses at 300 K obtained from the cooling process by AIMD simulation. ………………………………………………………………………………………………..135

Figure 6.3 Radial distribution function g(r) of B−O, Na−O, and O−O pairs in xNa$_2$O-(100-x)B$_2$O$_3$ systems at 300K. The first peaks of g(r) correspond to the bond length of each pair presented in Table 5.1……………………………………………………………………………………………………..136
Figure 6.4 Optimization of the simulation cells of FeNaB systems. The green dot is the equilibrium distance of each system. The red line is the fitted curve. The lowest energy at the distance $d_0$ in each system was shifted to zero.

Figure 6.5 Relative energy versus the gap distance during the compression (CP) and decompression (DC) processes. The zero energy is the energy of the system at the equilibrium distance obtained from cell optimization. Each red circle represents one $[3]B \rightarrow [4]B$ conversion while each green circle corresponds to one $[4]B \rightarrow [3]B$ conversion.

Figure 6.6 Correlation between the percentage of $[4]B$ (open symbols) and starting pressure of the polymerization (filled symbols, right axis) with different Na$_2$O concentration in FeNaB systems. DFT bulk is the results of xNa$_2$O·(100-x)B$_2$O$_3$ by AIMD for 10 ps at 300 K.

Figure 6.7 Evolution of four-coordinated boron as a function of pressure during the compression (a) and decompression processes (b). The boron coordination number was identified with a cutoff distance of 1.6 Å.

Figure 6.8 Reorientation of borate structure in FeNaB60%: (a) initial system at 0 GPa, (b) at 1.8 GPa. Sodium has been removed for clear visualization.

Figure 6.9 Ball and stick model of the selective configurations before (the left) and after (the right) the polymerization in the system following three mechanisms M1 (a) and (b), M2 (c) and (d), and M3 (e) and (f). These configurations before and after the chemical reactions were captured from two consecutive steps with $\Delta z = 0.05$ Å. Sodium has been removed for better visualization.

Figure 6.10 Polymerization mechanisms of sodium borates under compression as a function of pressure. M1 (black circles), M2 (red stars), and M3 (green diamonds) refer to three polymerization pathways. The dotted lines connect the first points when each mechanism was observed in each system.

Figure 6.11 Total density of state of boron and oxygen in the polymerization: (a) M2 and (b) M3. The arrows show how DOS of oxygen changes before (dash line) and after (solid line) the reaction.

Figure 6.12 Total DOS of sodium borate Na$_2$O·2B$_2$O$_3$ at 0, 4 and 8 GPa.

Figure 6.13 Number of Na$^+$ ions adsorbed on Fe$_2$O$_3$ substrates during the compression (solid lines) and decompression (dotted lines). Only Na$^+$ within a distance of 2.3 Å from the surface is counted.

Figure 6.14 Density profile of sodium ions (the yellow in the lower row) along the z direction (upper row) and ball-and-stick models at 6 GPa of FeNaB33% (a, d), FeNaB50% (b, e) and FeNaB60% (c, f) borates systems. The center of the simulation cells has been shifted to zero.
Figure 6.15 Evolution of RDFs g(r) of Na–O pair (a) and number of O\textsuperscript{nb} (solid lines) and [\textsuperscript{3}]O (dotted lines, including [\textsuperscript{3}]O in B–O–Fe cluster, (b)) in sodium borates versus pressure during the compression. The dotted lines in (a) connect the peaks of RDF at different pressures. In (b), black (FeNaB25\%, blue (FeNaB33\%, green (FeNaB50\%, and red (FeNaB60\%).

Figure 7.1 Model of alkali borate glasses confined between two Fe\textsubscript{2}O\textsubscript{3} surfaces for the shearing process. Iron (blue), oxygen (red), boron (green), and sodium (yellow); the colors assignment is applied throughout this work. At each step, two surfaces are manually shifted relatively to each other along the x-direction with a distance of $\Delta x = 0.025$ Å. Therefore, the relative displacement between the two surfaces is 0.05 Å per step. At least 400 sliding steps are applied, which introduces a total relative displacement of 20 Å. The dimensions of the Fe\textsubscript{2}O\textsubscript{3} surface are $8.72 \times 10.07$ Å\textsuperscript{2}.

Figure 7.2 Variation of the total energy in the systems during the shear at 1 GPa and 3 GPa.
The minimum energy in the whole shearing process was shifted to 0.

Figure 7.3 Energy variation and Fe–O bond length of FeNaB50\% during the shearing at 1 and 3 GPa: (a) and (c) energy variation at 1 and 3 GPa, respectively; (b) and (d) bond distance of all Fe–O\textsubscript{B} formed between Fe and oxygen of the borate during the shearing process at 1 and 3 GPa. Different colors represent different Fe–O\textsubscript{B} bonds. There are totally 5 and 7 Fe–O\textsubscript{B} interfacial bonds in the system including the initial and the newly formed bonds at 1 and 3 GPa, respectively.

Figure 7.4 Number of bonds between the Fe\textsubscript{2}O\textsubscript{3} surface and the borates including Fe–O\textsubscript{B} and B–O\textsubscript{S} during the shearing. The legends are the same in (a) and (b).

Figure 7.5 Rearrangement of the lubricant under the shearing of FeNaB50\% at 1 GPa: (a) initial shearing at 0 Å; (b) shearing at a distance of 12 Å; (c) The bonding network within one layer marked by the blue dotted lines in (b).

Figure 7.6 Formation of wear particles when Fe moves up from the surface when shearing at 3 GPa (a) FeNaB25\%, (b) FeLiB, and (c) FeKB: lithium (green) and potassium (purple). The circled areas show the Fe atom moving out from the surface and forming clusters with atoms in the lubricant.

Figure 7.7 Fe-surface distance of the Fe atoms that breaks from the surface at 1 GPa (a) and 3 GPa (b). FeNaB25\% (black), FeLiB (red), and FeKB (green). Only the Fe atom that has the highest z coordinate in each system is reported. The dotted line marks the distance of 0 Å corresponding to the height of the initial surface. There is no Fe removal for FeKB at 1 GPa.

Figure 7.8 Snapshots of the Fe removal from the surface when shearing at 1 and 3 GPa. The snapshots were taken at the largest Fe-surface distance from Figure 7.7. Result for FeKB at 1 GPa was not shown as there is no Fe atom moving out from the surface. O\textsubscript{S} is the oxygen atom.
of the surface that completely dissociates and has no direct bonds with surface’s atoms. Fe_{L1} is the Fe atoms in the top layer, and Fe_{L2} is the Fe atom in the second Fe layer from the top surface. Alkali ions were removed for clear visualization.

Figure 7.9 Comparison of Fe$_2$O$_3$-alkali borate structure at 0 K and 1073 K at the shearing distance of 20 Å, pressure of 1 GPa. The results at 0 K are obtained from the shear by DFT.

Figure 7.10 Z-coordinate of all Li, Na, and K ions in the systems FeLiB, FeNaB, and FeKB during the shear at 1 GPa and 1073 K. There are 12 alkali ions in each system. Different colors represent different Li/Na/K cations.

Figure 7.11 Schematic description of the possible tribofilm composition and its lubricating mechanism of alkali borate.

Figure 8.1 G 4×4 supercell (a), the doping sites on the G lattice (b), and 2×2 Fe$_2$O$_3$ surface. Carbon (brown), doped atom (blue), oxygen (red), iron (navy). The blue cell in (a) shows the 1x1 G unit cell. The numbers in (b) indicate the doping positions corresponding to the number of dopants in the supercell. Green atoms in (c) represent the Fe topmost atoms.

Figure 8.2 Interactions of G-F and G-S in Fe$_2$O$_3$-sodium borate system at 1000 and 1000 K for 20 ps.

Figure 8.3 Top view of G-F and G-S layers in FeBG-F and FeBG-S at initial structure (a) and (c) and after relaxed in Fe$_2$O$_3$-sodium borate systems at 1100 K for 20 ps (c) and (d).

Figure 8.4 Optimization of the lattice constants for doped-G structures with the number of doping atoms: (a) B-G, (b) P-G, (c) S-G, and (d) Si-G.

Figure 8.5 Top view and side view of the optimized structures of 4×4 G and doped-G supercells. Only the doping with 4 dopant atoms is shown. C (brown), B (green), P (pink), S (yellow), and Si (orange).

Figure 8.6 Binding energy per atom of graphene and doped-G adsorbed on Fe$_2$O$_3$ surface. The red dot shows the binding energy of the pure graphene on Fe$_2$O$_3$ surface.

Figure 8.7 Adsorption configurations (top row in each sub-figure) and CDD (bottom row in each sub-figure) of graphene and doped-G on the Fe$_2$O$_3$ surface. Only doped-G configurations with 4 dopant atoms are shown in the figure. The red and blue regions in CDD signify the electron gain and loss areas, respectively.

Figure 8.8 Top view and side view of graphene structures after relaxed at (a) 1000 K and (b) 1200 K for 10 ps. The number in (b) shows the defect site in the graphene lattice. The cutoff distance for C–C bonds is 1.6 Å.

Figure 8.9 Top view and side view of doped-G geometries from AIMD simulations at 1000 K and 10 ps. The name of the systems and number of dopant atoms remains as the 4×4 supercell.
for DFT optimization. \( n \) is the number of defects in the systems. The cutoff radii for C–C, C–B, C–P, C–S, and C–Si are respectively 1.60, 1.64, 1.80, 1.82, and 1.86, which are 10% larger than the equilibrium bond lengths obtained from DFT optimization.

Figure 8.10 Top view and side view of doped-G geometries from AIMD simulations at 1200 K and 10 ps.

Figure 8.11 Top view and side view of doped-G relaxed on Fe\(_2\)O\(_3\) surface by AIMD simulation at 1200 K and 10 ps.
List of Tables

Table 3.1 Details of the sodium, lithium, and potassium borate glasses ........................................ 72

Table 4.1 Simulation models of Na₄P₂O₇ and Na₃PO₄ on Fe(110) and Fe₂O₃(0001) surfaces ........................................ 81
Table 4.2 Bond lengths (Å) and angles of optimized Na₄P₂O₇ and Na₃PO₄ by current DFT calculations and relevant experiments and theoretical calculations ............................................................................. 82
Table 4.3 Interaction energy (E_{ads}) and interaction energy per phosphate group [-PO_3] (ΔE_1) of Na₄P₂O₇ and Na₃PO₄ adsorbed on Fe surface. Energies are in eV .......................................................... 85
Table 4.4 Charge transfer by the Bader charge analysis method for alkali phosphates adsorbed on Fe surface (unit e). Δq₁, Δq₂, and Δq₃ are the absolute values of average charge transfer per atom in the 1ˢᵗ, 2ⁿᵈ, and the 3ʳᵈ layer, respectively. q_{Fe} and q_{mol} are the total charge transfer of the iron surface, and alkali phosphate molecules, respectively. (−) and (+) mean charge loss and charge gain, respectively ........................................................................................................... 89
Table 4.5 Bond Overlap Population (BOP) of ionic and covalent bonds in adsorbed Fe-Na₄P₂O₇ and Fe-Na₃PO₄ systems. Atomic orders follow the orders in the CDD in Figure 4.5 ................................................................. 92
Table 4.6 Interaction energy (E_{ads}) and interaction energy per phosphate group [-PO_3] (ΔE_1) of Na₄P₂O₇ and Na₃PO₄ adsorbed on Fe₂O₃ surface. Energies are in eV .......................................................... 94
Table 4.7 Charge transfer by the Bader charge analysis method and Bond Overlap Population (BOP) for alkali phosphates adsorbed on Fe₂O₃ surfaces. Δqᵢ is the absolute average charge transfer per atom in the ith layer. Δq_{4,5,6} is the absolute average charge transfer per atom in the 4ᵗʰ, 5ᵗʰ and 6ᵗʰ layers. q_{s} and q_{mol} are the total charge transfer of the surface and alkali phosphate molecules, respectively. (−) means charge gain, and (+) means charge loss ........................................................................................................... 96
Table 4.8 Bader charges (e) and charge transfer (e) of some atoms in adsorbed phosphates on the Fe₂O₃ surface. qᵢ and q_{a} are the charges of atoms in the isolated and adsorbed systems, respectively. For Bader charges (qᵢ/q_{a}), (−) means negative charge, (+) for positive charge is not shown here. For charge transfer (Δq), (−) means charge gain and (+) means charge loss. Only atoms that have significant charge differences in the CDD are presented. The order of atoms follows the order in the CDD in Figure 4.2 ........................................................................................................... 98

Table 5.1 Densities, structural parameters, and diffusion coefficients of Na₂B₄O₇ and B₂O₃ at 300 K and 1073 K .................................................................................................................. 112
Table 5.2 Diffusion coefficients of Na, O, and B in Na₂B₄O₇ at 300 K and 1073 K .................. 114
Table 5.3 Changing of four-fold coordinated boron (B\textsuperscript{4}) and O\textsuperscript{nb} in Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} interacting on the iron oxide surface at 1073 K with the simulation time\textsuperscript{*}, B\textsuperscript{3} is the three-fold coordinated boron. ................................................................................................................. 118

Table 5.4 Charge transfer (\Delta q)\textsuperscript{*} between Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7}/B\textsubscript{2}O\textsubscript{3} and the Fe\textsubscript{2}O\textsubscript{3} surface of the selected configurations at 0, 5, 10, 15, and 20 ps, and friction and wear data of Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} and B\textsubscript{2}O\textsubscript{5} lubricated systems collected from experiments. ................................................................................................................. 124

Table 6.1 Structural parameters of xNa\textsubscript{2}O·(100-x)B\textsubscript{2}O\textsubscript{3} at 300 K compared with experimental data (where available). ................................................................................................................. 136

Table 7.1 Maximum energy variation in the systems induced by the shearing motion at 1 and 3 GPa. The maximum energy variation was calculated by the difference between the lowest and the highest peaks of the energy curve. ................................................................................................................. 158

Table 7.2 Variation of BOP (e) during the shearing motion. For FeNaB25\% and FeLiB, only results at 1 GPa are shown as a representative for each system. For FeKB, BOP was calculated at 3 GPa as there is no Fe removal at 1 GPa. ................................................................................................................. 168

Table 8.1 Optimized lattice constants for 4×4 supercell of G and doped-G ........................................ 184

Table 8.2 Formation energies (eV) of doped graphene and the bond length between carbon and the dopant atoms. ................................................................................................................. 186

Table 8.3 Interacting distances from graphene and doped-G on Fe\textsubscript{2}O\textsubscript{3} surface ........................ 188
Chapter 1. INTRODUCTION

The majority of mechanical systems are built from individual components that are fabricated from metals. They are assembled together to create a moving mechanical system. During the operation of those machines, the interaction between two sliding contact surfaces produces heat, oxidation, high friction and wear that result in undesirable effects such as a shorter service life of machines, higher fuel and energy consumption, reduced efficiency of mechanical processes, and eventually high operating costs.1

In hot forming operations, the sliding contact between two metal surfaces operates in the boundary lubrication regime, i.e., mostly solid metal to metal contact, subjected to harsh working conditions of high pressure and shear at temperatures up to 1000°C (usually above the recrystallization temperature of the material). Those severe working conditions can produce serious friction, severe tool wear and oxidation at the interface. A certain amount of friction is necessary for some metal forming process, but excessive friction always leads to undesirable consequences of wasted energy and unreliability of machine elements. In the manufacturing process, energy is needed to overcome friction, which also causes wear and produces surface defects on the products. Thus the control of friction in metal forming processes, thermal engines and general moving mechanical systems can reduce energy consumption and bring economic benefits. To this point, the introduction of lubricant in those areas is an effective solution to reduce friction forces and tool wear, thus improving the reliability of equipment and the quality of the products.

Lubricants used in industry are varied depending upon the type of metal forming process, the temperature at which the operation occurs, and the types of materials formed. There are various types of lubricants, which can be sorted into base oil group, aqueous and solid lubricants. Water-based and oil-based lubricants have been widely used in many industrial applications, but most of them suffer from thermal decomposition and burn at high temperature. To sustain the elevated temperature and extreme pressure, the lubricants are not only required to provide friction reduction, wear mitigation and anti-oxidizing function, but also possess excellent thermal stability. Therefore, an effective lubricant needs to cover evenly the contacting interface, and maintain the separation between two surfaces to prevent a direct metal-to-metal contact
in the boundary lubrication regime. Moreover the lubricant should adhere well onto the metal surfaces to protect the underlying material and facilitate the sliding between two mating contacts.

Phosphate based lubricants have been found to be an effective solution that is responsible for friction reduction, anti-wear and anti-oxidation function. One of the most common types of phosphate lubricant species is zinc dialkyl dithiophosphate (ZDDP) that has been widely used in industry, aerospace, automotive engines and metal forming fabrications for a century.\textsuperscript{2-4} However, the extensive use of ZDDP in industries particularly in automotive engines, poses major concerns of environmental issues from the release of zinc- and sulfur-containing wastes. On the other hand, since the 1960s, US patents no. 313727 (1967), no. 3997454 (1975), and no. 4400284 (1983),\textsuperscript{5-7} have shown potential applications of alkali metal borates in extreme conditions, by providing good lubrication between two moving surfaces and maintaining the lubricating film during the relative sliding. The boron-containing lubricants exhibit a high load-bearing capacity under extreme pressure and at high sliding speed.\textsuperscript{8} They are also non-volatile, relatively non-toxic, and have a pleasant odor.

Recently, scientists have found that alkali inorganic compounds such as alkali metal phosphates/silicates/borates can potentially be used to replace oil-based or water-based lubricant in high temperature metal forming due to the following advantages: good adhesion to the surface, high viscosity at high working temperature from 500 to 1200°C, excellent thermal stability, and environmental friendliness.\textsuperscript{9} There are a number of research papers published, which are related to the lubricant’s performance as well as investigating their friction and wear reduction mechanism and oxidation inhibition.\textsuperscript{10-16} These alkali metal glass compounds usually consist of two principal components: network builders (such as phosphorus/boron/silicate combined with oxygen) that bind onto the surface, and free cations usually of alkali metals (K\textsuperscript{+}, Na\textsuperscript{+}, Ca\textsuperscript{2+}) that act as network compensator. Their molecular assembly creates a hierarchical structure of nanoscale tribofilm in hot rolling. The superior hardness of borate tribofilms provides an excellent load carrying capacity in extreme pressure conditions. However, exact mechanisms and chemical behaviors leading to a good and effective lubrication performance, especially at high temperature are unclear and cannot be explained satisfactorily by advanced microscopy techniques.
Non-experimental methods such as computer simulations are powerful tools to support the experimental findings and can describe the working mechanics of the lubricating tribofilm at an atomic or molecular level. Computer simulations and modelling have provided multiscale pictures of tribological systems from nano- to macro-scale.\textsuperscript{17} When a tribochemical reaction in tribo-systems is initiated, multiple physical/chemical phenomena occur among participating substances. A detailed understanding of the tribochemical reactions between the lubricant and the metal surface is important to rationalize the friction and wear reduction mechanisms and to improve lubricant performances. In the current project, we used computer simulations by DFT and AIMD to investigate the tribo-chemical interactions between phosphate/borate lubricants with steel surface, the structural transformations of lubricant subjected to high temperature, compression and shear. The simulation methods which consider the tribofilm at the atomic and electronic levels will allow us to study mechanisms and nature of tribochemical reactions occurring in the systems and rationalize experimental findings that could not explain chemical reactions and working mechanisms at the interface.
Chapter 2. LITERATURE REVIEW

2.1. Hot Metal Forming and High Temperature Lubrication

Hot rolling processes are processes that work at temperatures higher than 0.5 melting temperature of the material.\textsuperscript{18} Generally, in hot rolling processes, the working temperature of strips can reach 600 – 1200°C, while the temperature of the roll surface varies between 100 and 550°C in one revolution (Figure 2.1). In addition, when two surfaces are brought into contact, a high pressure up to 1 GPa is applied with the strip speed up to 10 m/s. The direct contact of two sliding surfaces and their asperities can induce a flash temperature which is few times higher than that of the bulk fluid.\textsuperscript{19} The control of tribology in hot rolling is related to a number of variables such as materials, surface properties, applied loads, temperature, shearing rate, and lubricants.

![Figure 2.1 Schematic description of the interface in the hot metal forming processes.\textsuperscript{9}](image)

The most challenging problems from hot forming processes that affect the efficiency of the whole process and the quality of the final products are high friction, abrasive wear, and oxidation.\textsuperscript{20} Several experiments have been carried out to study the lubricant behaviors, friction and wear in tribo-systems during hot metal forming processes. First, the high temperature combined with environmental factors such as moisture, contaminations, and the availability of oxygen can initiate oxidation and create oxide layers on the surfaces of the roll and strips. Below 570°C, the scale mostly comprises magnetite (Fe\textsubscript{3}O\textsubscript{4}) and hematite (Fe\textsubscript{2}O\textsubscript{3}) layers. Above 570°C wüstite (FeO)
starts to form at the innermost layers from the metal surface together with the other two oxides, (Fe$_2$O$_3$ and Fe$_3$O$_4$) while Fe$_2$O$_3$ covers the outermost layer, forming a compositionally complex surface. At temperatures above 400°C, Fe$_2$O$_3$ particles are hard, thus are responsible for increasing abrasive wear. Secondly, wear can be caused by physical or chemical interactions between two contacting surfaces. Batchelor and Stachowiak (1995) have discussed several mechanisms of wear which include abrasive, fatigue, erosive, cavitation, and adhesive wear. Among them, abrasive wear is considered the most serious type under heavy loads. The abrasive wear is caused by the ploughing action between the hard oxide asperities when two surfaces are in a relative motion, or by three-body wear involving loose oxide/wear particles between two sliding surfaces. Thirdly, sliding friction is generated when two surfaces rub against each other. At elevated temperature, friction in hot rolling is usually higher than that in cold and warm rolling processes. Particularly, high friction in hot metal forming comes from several sources such as surface roughness, adhesive/abrasive wear, deformation of the asperities peaks and plastic deformation. This type of friction occurs when the lubricated film is very thin and unable to separate asperities. Another factor that influences friction is the adhesion, which is initiated by chemical interactions between the metal surfaces and the lubricant. A high friction will cause surface seizure, and thus should be reduced as much as possible.

There are two common ways to control friction, wear, and reduce oxidation at the interacting surfaces in hot metal forming, namely tribo-coatings and lubrication. Tribo-coatings are the technique that is used to cover the metal surfaces with different materials to reduce friction, wear, corrosion and oxidation. The main purpose of tribo-coatings with different materials such as high strength alloys or wear resistant materials is to lower the adhesive forces and hence sliding friction between the metal and the tool, thus improve surface quality and prevent oxidation. The tribo-coatings are quite effective in a wide range of temperature from 500 to 950 °C. Nevertheless, one of the biggest problems with tribo-coatings is that the technique is inapplicable for small scale tool surfaces that require a relatively high level of precision in fabrication and processing. Another significant aspect of tribo-coatings is the requirement of a strong adhesion between the coating material and the metal surface. However, it is technically challenging to maintain the adhered coating layer on the material surface especially when the systems undergo severe pressure/shearing at elevated temperature.
Lubrication is the introduction of a gas, liquid, or solid layer to the interface between two contacting objects in order to separate or create a protective film between the two surfaces. The ultimate purpose of lubrication in metal forming is to control friction and wear and reduce oxidation at the contacting interfaces. When lubricants are introduced between two sliding surfaces, it can operate under one of the three main lubrication regimes: boundary lubrication, mixed film lubrication, and hydrodynamic (full film) lubrication. Boundary lubrication takes place when two metal surfaces are in a completely direct contact, mixed film lubrication occurs when two surfaces partially contact which is the mixed regime of boundary and hydrodynamic lubrication, and hydrodynamic lubrication occurs when there is a complete separation between the two surfaces. In hot metal forming, a number of lubrication regimes are initiated as a result of sliding speed, applied load, lubricant viscosity and surface roughness. Generally, several regimes can dominate at different positions on the working surface, or can alter at any one position during the operation. Under the combination of heavy loads, elevated temperature and sliding motion, boundary lubrication regime usually dominates when asperities of two metal surfaces come into a physical contact, leading to undesirable effects such as high friction and wear and poor surface finishing of the end-products.

The introduction of lubricants into the contacting area between two sliding objects is intended to minimize the effects of the boundary lubrication and direct metal-to-metal contact. Lubricants with sufficient viscosity are required to provide a high load carrying capability yet to ensure easy-shearing and low friction. Another effective way to avoid boundary regimes is to use lubricants and/or additives to form a protective layer on the surface. When two surfaces are in contact, these lubricants/additives react with the metal surface, and instantly form a so-called “tribofilm” on the metal surface. This tribofilm plays as a padding layer that can prevent a direct metal-to-metal contact and protect the surface underneath from wear and oxidation.

The temperature can affect the lubricated contact through viscosity, thermal degradation, and surface oxidation. Therefore, the selection of lubricants suitable for those harsh working environments must be considered carefully. Such lubricants are required to reduce friction and wear to a minimum and offer high load carrying capability. They also need to maintain a good performance at elevated temperatures and the high pressure and shear rate in hot metal forming. In terms of high temperature
aspect, those lubricants must be able to withstand thermal degradation and structural collapse in extreme heat. The ability of transferring heat between metal parts is also important. Conventional lubricants are, therefore, not suitable for such working environments. Instead, solid lubricants such as graphite-containing compounds, hexagonal boron nitride, molybdenum disulfide, metal alloys or composites and glass lubricants have shown effectiveness at high temperature.

2.2. Lubricants for high temperature lubrication

As discussed in the previous section, the lubricants used in hot metal forming must be stable and perform well at high load and temperature conditions. Two common groups of lubricants have been reported for high temperature applications: alkali glass lubricants such as alkali borates, alkali silicates, alkali phosphates, and solid lubricants such as graphite-based lubricants and 2D materials.

2.2.1. Phosphate based lubricants

Phosphate-based lubricants are one of the most common lubricants/additives in automobiles, rolling processes, engines and manufacturing industries. Phosphate lubricants are famous for their excellent corrosion resistance, wear inhibition, adhesion and lubricating properties. Many phosphate lubricants have been introduced and commercialized in recent decades. Among them, zinc dialkyl dithiophosphates (ZDDP) have been widely used as antioxidants, corrosion inhibitors, and anti-wear agents since the late 1930s (Figure 2.2). Ito et al. found that only 1% of ZDDP added into polyalphaolefine (PAO) could reduce the friction coefficient to 0.06 – 0.08, which is 20% lower than using PAO alone and approximately 50% lower than that of the dry sliding conditions. The tribofilm analysis indicated that the friction reduction of ZDDP is provided by a multi-layer film with a thickness of 30-130 nm including Zn, Fe, S, P, and O in composition. The mechanisms of the ZDDP tribofilm that accounts for low friction, anti-wear and anti-oxidation behaviors were proposed later Martin et al., and it will be discussed in detail in Section 2.3.3. Generally, the strong adhesion of sulfur and phosphorus is critical to the function of ZDDP tribofilm under extreme conditions. Many researches have been carried out to confirm the effectiveness of wear and oxidation resistance of ZDDPs as well as explain the mechanisms of tribofilm formation and its function. For example, in automotive engines, when ZDDP additives are
burnt, their decomposed derivatives (mostly P- and S-containing species) can drastically diminish the efficiency of a catalytic converter, which is a device to convert engine toxic exhaust gas to more environmentally friendly emission, and significant amount of toxic components released during service. As a result, scientists have tried to lower the amount of hazardous release by mixing ZDDP with other potential additives, or looked for alternatively comparable phosphate-containing compounds. For example, Martin and Miyamoto groups introduced zinc dialkyl phosphate (ZP) additive which provides better anti-wear function than ZDDP at room temperature and slow sliding speed (25 mm/s), yet appears to be more friendly to the environment due to the removal of sulfur from its composition. By molecular dynamics (MD) simulations, they found that the large radius of sulfur atom can restrict the diffusion of iron into the ZDDP film, thus the migration of Fe in Zn(PO₃)₂ is greater than in Zn(S₀.₅O₂.₅)₂ and the wear prevention of Zn(PO₃)₂ can be potentially better than that of Zn(S₀.₅O₂.₅)₂. In contrast, at 100°C and a higher sliding speed of 100 mm/s, ZP is easily dissolved in oil due to the presence of alkyl groups in its molecules. Nevertheless, the combination of ZP and ZDDP could be considered a compromising solution, which could balance the efficiency of an additive and the environmental concern. Spencer et al. observed that a transfer film formed as a result of the shortening of zinc metaphosphate chains during the sliding of steel ball against a steel disc plays a role to reduce friction and wear. Some researchers proposed the addition or replacement of zinc in ZDDPs or ZP with different metals such as molybdenum.

![Structure of a phosphate ester, a thiophosphate ester and a dialkylidithio phosphoric acid.](image)

Figure 2.2 Structure of a phosphate ester, a thiophosphate ester and a dialkylidithio phosphoric acid.

Apart from ZDDP and ZP, anti-wear and anti-oxidation properties of a number of phosphate esters (Figure 2.2) have been considered by Yamamoto et al., and Johnson et al. Yamamoto and Hirano have found that using tricresyl phosphate as a lubricant
can prevent scuffing more effectively than using base oils, while the addition of trioctyl phosphate improves the lubricating performance by thickening the oil films due to its high reactivity to the surface.\textsuperscript{41} The reactions between the steel surface and phosphate esters in oil create beneficial lubricating films that support frictional processes, especially the anti-wear function at extreme pressure.\textsuperscript{42}\textsuperscript{43} These tribofilms are durable and act as a lubricant when the liquid lubricant flow is absent. Aswath \textit{et al.} studied the wear mechanism of six phosphate additives in a base oil under the harsh boundary lubrication.\textsuperscript{44} Najman \textit{et al.} studied the chemistry of anti-wear films generated from phosphate ester additives on steel surface.\textsuperscript{43} Saba \textit{et al.}\textsuperscript{45} and Tysoe \textit{et al.}\textsuperscript{46} investigated reactions of phosphate esters with iron and its oxide surfaces. Their results showed that phosphate esters react to iron and its oxides to form a stable protective tribofilm, but the films were largely decomposed on the surface by either P–O bond breaking or carbon desorbing when the temperature reaches 300 °C or higher.

Figure 2.3 Coefficient of friction as a function of time and (b) average coefficient of friction in steady-state lubrication for the steel/steel pairs at 800°C.\textsuperscript{47}

Polyphosphate and soluble metal phosphate glasses have shown superior performances in corrosion inhibition and oxidation resistance at high temperatures and severe conditions thanks to their high thermal stability. Recently, Tieu \textit{et al.}\textsuperscript{10}\textsuperscript{13} have unveiled excellent lubrication properties of alkali metal phosphate glasses. In particular, experiments on alkali metal polyphosphate glasses at elevated temperature indicated that alkali metal phosphate glasses possess high thermal stability, high viscosity when melted without decomposition, and good adhesion to the metal surface. The experiments have found that under phosphate-lubricated condition, friction coefficient was reduced up to 60% (from 0.42 in unlubricated condition to 0.19 in the lubricated one) and the wear in rubbing steel/steel contact was reduced more than 50% compared
to the unlubricated one. In addition, the melting of phosphate species covers evenly the steel surface, reacts with metal surface to form a phosphate compound film, and creates a protective barrier against oxidation. The polyphosphate lubricant was fully melted at 800 °C when the viscosity was lower than that in the dry condition. It has been found that alkali polyphosphate lubricant performs well in the temperature range from 650-850°C. The contribution of alkali ions in the polyphosphate lubricants has been proposed. Accordingly, the cation exchange between Fe³⁺ and Na⁺ promoted the shortening of the phosphate chain length, and the tribochemical reactions between phosphate species and iron oxide surface occurred. As a result, a mixed layer of short chain Fe/Na polyphosphates settles in the bulk of the tribofilm. Additionally, melting of sodium or potassium compounds create high mobility Na⁺ and K⁺ cations which lower the viscosity of the lubricants. It is unclear if the resultant low friction of the hot rolling processes was due to the melt viscosity, the cation effects, or the composite tribofilm. Similarly, tribological testing on sodium poly-phosphates with different chain lengths, i.e., sodium ortho- (Na₃PO₄), pyro- (Na₄P₂O₇), and metaphosphate ((NaPO₃)₆), reported that long chain sodium metaphosphate has a tendency to be depolymerized into shorter chains under harsh tribological conditions, while the short chain Na₃PO₄ provides a better antiwear performance than the longer counterparts (Figure 2.3). The superior performance of the shorter chain phosphate could be due either to the chain length effects or the ratio of sodium cations in the lubricant. Neither of the proposed factors has been confirmed to provide an in-depth understanding of the underlying lubricating mechanisms. Nevertheless, these findings indicated that this kind of alkali phosphate lubricant performs effectively for wear inhibition, oxidation resistance and friction reduction at elevated temperature, and can be considered as a promising class of environmentally friendly lubricants.

2.2.2. Alkali Borate lubricants

Boron-containing compounds, such as boric acid, boric oxide, and other organic and inorganic borates have been employed for lubrication purposes, particularly in extreme environments. Boron is an electron-deficient element and has a great affinity toward oxygen. In nature, boron always occurs as borates. Boron compounds have some important features such as: capacity to absorb thermal neutrons, antioxidant characteristics, relatively low toxicity, good fire resistance, pleasant odor, non-volatility, and ready availability. Frictional behaviors of boron compounds come from their
layered structures and load-bearing capacity.

**Alkali borate glasses: Structural, physical and mechanical properties**

Fundamentally, an alkali borate glass is composed of two intrinsic components including network formers and network modifiers. The former component is represented by boron connecting with oxygen to create a three-dimensional network, and the latter operates as charge compensators for [BO$_4$]$^-$ anions or as network modifiers for non-bridging oxygen (O$_{nb}$). The boron oxide complexes can exist in the basic structural units of BO$_4$ tetrahedra, planar triangular BO$_3$ with/without non-bridging oxygen, or in superstructural units of B$_3$O$_3$ boroxol rings, di-/tri-/penta-/di-penta- borate groups. A small amount of alkali content can lead to an increase in the network connectivity by increasing boron coordination number, while an excessive amount of alkali cations leads to the appearance of non-bridging oxygen and the loss of network connectivity. The fraction of BO$_4$ tetrahedra as well as non-bridging oxygen in an alkali borate glass depends directly on the concentration of alkali cations in the system. Accordingly, alkali borates reach the highest connectivity when the system contains an amount of 33% X$_2$O (where X is the alkali metals), corresponding to X$_2$O.2B$_2$O$_3$ or alkali tetraborate glasses (Figure 2.4). The ability of borate glasses to change from triangular to tetrahedral coordination makes them flexibly adaptable to severe working conditions without structural cracking or collapse. This characteristic exists in borate thanks to the abnormal property of boron which can be hybridized into either sp$^2$ or sp$^3$ configuration.

![Figure 2.4 Ratio of 4-fold coordinated boron atoms (X$_4$) in alkali borate systems: Li$_2$O–](image)
B$_2$O$_3$ (blue filled circles), Na$_2$O–B$_2$O$_3$ (red filled squares), K$_2$O–B$_2$O$_3$ (green filled triangles), Rb$_2$O–B$_2$O$_3$ (magenta inverted filled triangles), and Cs$_2$O–B$_2$O$_3$ (cyan asterisks). $^{49}$ $X_M$ is the ratio of alkali metal oxide in the systems.

Shaw and Uhlmann investigated the phase transition in alkali borate glasses and indicated the glass-liquid transition region from 500 to 900°C depending on the alkali metals and their concentrations. $^{52}$ The melting temperature of alkali borate glasses is compositional dependent, i.e., it increases with the percentage of alkali content. At high temperature, there is a remarkable change in boron coordination number and short-range order structures. $^{53}$-$^{57}$ Yano et al. reported that the main conversion occurs by $\text{BO}_4 \leftrightarrow \text{BO}_3 + \text{O}^{\text{nb}}$, where one $\text{O}^{\text{nb}}$ is created from the tetrahedral group. $^{53}$, $^{56}$ This reaction is more preferable in the system containing more than 25% Na$_2$O than those with lower Na$_2$O concentrations. In addition to the decomposition of $\text{BO}_4$ groups, $\text{O}^{\text{nb}}$ can also be created by breaking $\text{BO}_3$ in boroxol rings by transforming $\text{BO}_3$ triangle unit into $\text{BO}_2\text{O}^-$ triangle unit. $^{54}$ These modifications of borate structure can result in the changes in cation environment. Cormier et al. indicated that Li cations act as a charge-compensation role in borate glass and network modifying role in the liquid phase. $^{55}$ The network modifying cations can restructure their local environment in order to minimize the volume of the cavities caused by the network breaking from the boron oxide groups and optimize their first coordination shell with the surrounded non-bridging oxygen. Jaccani and Huang indicated that the elastic properties of sodium borate glasses are sensitive to temperature, especially those with lower Na$_2$O concentrations. $^{58}$ This attribute is associated with the change in the intermediate range order structure under the temperature onset. $^{58}$ Viscosity is another property of alkali borates that depends closely on temperature. Due to the breaking of borate networks and the loss of connectivity, viscosity decreases continuously with increasing temperature. $^{59}$-$^{60}$ Nevertheless, Maje´rus et al. suggested that the viscosity of the borate glasses is determined by both alkali migration activities and oxygen exchange between structural units. $^{56}$

Many researches have investigated the adaptation of structural, physical and mechanical properties of alkali borate glasses at high pressure. When compressed, the coordination flexibility of network forming agents is the origin of structural transformation and compressibility of inorganic glasses. $^{61}$-$^{64}$ Taking lithium borate glass as an example, Vegiri and Kamitsos indicated that four-fold boron is stabilized in the
pressure range of 15 to 80 GPa, while five- and six-fold boron start forming from 80 to 300 GPa.\textsuperscript{65} When boron coordination number rises, it creates a highly compact glass, increases the degree of network connectivity,\textsuperscript{61, 63} as well as glass hardness.\textsuperscript{66} On the other hand, Svenson et al. revealed that molecular stacking instead of structural conversion is the major contribution to the borate densification.\textsuperscript{67} By using X-ray scattering, the nature of structural transformation of pure boron oxide at high pressure has been experimentally unveiled.\textsuperscript{64} Meanwhile, their response to pressure in the presence of network-modifying cations has not been discussed. A small amount of added alkali metal oxides in the boron oxide can enhance the network connectivity, while a higher concentration conversely induces the breaking of the polymerized network.\textsuperscript{68-70} As a result, their responses to external stimuli differ from mechanical-physical behaviors to chemical nature and electronic/atomic mechanism. In fact, the compressibility is composition-dependent and appears to be reversed with high and low alkali contents.\textsuperscript{71}

**Alkali borate glasses as lubricants**

In the case of alkali metal borates such as sodium borates and potassium borates, a number of publications have reported the wear resistance and load carrying capacity of borate-containing oils for extreme pressure (EP) lubrication in the US patent no. 3,313,727, no. 3,227,739, no. 3997454 etc.\textsuperscript{5-6, 72-73} The initial models that include alkali borates in oils were to improve load bearing capacity in EP conditions. In particular, the US patent no. 3,313,727 proposed a range of alkali borate-containing oils including sodium/potassium meta-/tetra-borate or the mixtures thereof dispersed in a nonpolar lubricating oil which can provide excellent EP properties a long periods of time in metal forming.\textsuperscript{5} The US patent no. 3,997,454 introduced the lubricant containing potassium borate with a boron-to-potassium ratio from 2.5 to 3.5. The lubricant not only can provide excellent EP properties but also improve anti-wear function by adding the agent zinc dihydrocarbyl dithiophosphate.\textsuperscript{6} The US patent no. 4,400,284 reported the synthesis of boron derivatives as reaction products of boramids and metal salts in an lubricating oil to reduce friction.\textsuperscript{7} In order to achieve a high friction reduction, the modification of borate lubricants with N-containing compounds was carried out.\textsuperscript{74-76} The reactions resulted in some major boron compounds such as FeB, O–Fe–B, BN, and Na$_3$B$_3$O$_6$ which created a separating film in the boundary lubrication regime.\textsuperscript{74} Hu et al. investigated friction and wear performance of n-Na$_2$B$_4$O$_7$/ion nitrocarburized duplex
layer and found that Na$_2$B$_4$O$_7$ particles play the “micron nano bearing” role while BN layers act as an effective solid lubricant that can reduce friction remarkably even at the temperature higher than 100°C.\textsuperscript{75} Moreover, Chen et al. reported the anti-wear and friction reduction of water containing sodium/potassium borates at extreme pressure, and their frictional function can be further enhanced by a combination of borates with lanthanum chloride.\textsuperscript{77} Their XPS analysis suggested that mechanism of anti-wear and friction reduction abilities are attributed to the tribochemical reactions in which a tribofilm composed of La$_2$O$_3$, B$_2$O$_3$, Fe$_2$O$_3$ and Fe$_3$O$_4$ was formed.\textsuperscript{77} Apart from that, other metal borates such as calcium borate and the mixtures of them with other lubricant additives such as ZDDP and MoS$_2$ have also been reported to provide good friction and anti-wear properties.\textsuperscript{78-80} At 60°C and the contact pressure of 0.26 GPa, the addition of borates in these cases can improve friction behavior, wear reduction properties and prevent metal-to-metal contact as compared to ZDDP or MoS$_2$ alone.\textsuperscript{78} Recently, Cui et al. tested borates as a slow-release inhibitor to eliminate long-term pipeline corrosion in simulated recirculating water. The testing results show a passivated film consisting of Fe–O–B structure on the mild steel surface which was responsible for the corrosion reduction.\textsuperscript{81}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{friction coeffs and wear loss.png}
\caption{Friction coefficients and wear loss volumes of dry and sodium borate-lubricated steel tribo-pair (at 800°C, nominal load of 10 N, and sliding speed of 0.1 m/s).\textsuperscript{15}}
\end{figure}

The above lubricants/additives were designated to deal with the environment where temperature is under 300°C. One critical requirement of hot rolling lubrication is the thermal stability of lubricants at elevated temperatures. Most recently, a novel lubricating mechanism has been proposed in sodium tetraborate, where the tribofilm is developed from an ionic sodium-rich layer at 800°C.\textsuperscript{15} On the contrary, pure boron
oxide fails to serve as a proper lubricant in terms of friction, wear, and oxidation reduction (Figure 2.4).\textsuperscript{16} The incorporation of sodium in the tetraborate was acknowledged as the main factor that was responsible for its outstanding performance over the pure boron oxide. The critical finding with Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} lubrication is the formation of a bi-layered tribofilm, which composes of an underlying Na-rich layer covered by the upper polymerized borate.\textsuperscript{15-16} It is worth noting that without tribological operations of pressure/shearing, the melting of Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} also induced a significant amount of Na on the steel-borate interface.\textsuperscript{14} Furthermore, there is no indication whether oxygen or boron contributes to the Na-rich tribofilm, thus the layering of sodium on the top of the iron oxide surface requires a detailed interpretation from atomic and electronic points of view.

\textit{Boric acids and borate esters}

Boric acid is one of the most important boron compounds because it is the essential material to produce borates and other boron-containing materials. Boric acid and boric acid-forming surfaces are of importance in new lubrication concepts for tribological performance. The acid has a lamellar structure that plays a crucial role for friction reduction (Figure 2.5). The frictional behavior of a boric acid-containing tribosystem is a function of temperature; a sharp increase in temperature increases the decomposition of boric acid into boric oxide and water. The US patent no. 2,987,476 presented a method to solubilize boric acid and metal borates in fuels and lubricating oils.\textsuperscript{82} Bindal \textit{et al.} carried out the experiment on borided steel surface at high temperature around 600 – 800\textdegree C and concluded that the formation of boric acid (H\textsubscript{3}BO\textsubscript{3}) film was the main reason for the stably low friction coefficient.\textsuperscript{83} Boric acid film formed when boron oxide (B\textsubscript{2}O\textsubscript{3}) was exposed to humid air was also found in the work of Ma \textit{et al.}\textsuperscript{84} At high temperature, boron oxide could react spontaneously with water vapor to form boric acid; however, the author suggested that surface structures in boron – water system were complex and the mechanism of lubricity in the boron-oxide system was not clearly evaluated. On the other hand, Philippon and co-author reported that the friction reduction by trimethylborate-lubricated system was due to the formation of tribofilm and the digestion of iron oxide particles by borate glass rather than from the boric acid. In contrast, the presence of boric acid could be detrimental to the surface because of its abrasive property and they also ruled out the possibility of friction reduction by boric acid.\textsuperscript{85}
Boron nitride

Apart from boric acid, boron nitride (BN) is one of the promising solid lubricants, especially for high temperature bearings. BN is usually used in the conditions with the working temperatures above 850°C, and this boron nitride based material can sustain a temperature as high as 1500°C. Kimura et al. reported the wear reduction of BN when the material was used as an additive added into lubricating oil. Celik showed that the addition of nano hexagonal boron nitride (h-BN) in engine oil could result in an improvement of 14.4% in friction and 65% reduction in wear. It has been shown that boron nitride was well-dispersed and stable in oils and played an important role in the wear protective tribofilm. Under extreme condition such as high temperature, Eichler et al. found that the structure of boron nitride was very versatile thanks to its unique combination of properties. Lavrenko and Alexeev indicated that BN structures can transform from wurtzite-like into thermodynamically more stable hexagonal lattice of boron nitride (h-BN) as a result of high-temperature oxidation reaction at temperatures above 1300°C. Another superior property of BN compounds is the effective oxidation resistance at elevated temperatures. Thanks to the thermal stability, BN can be used as a coating material for oxidation resistance. A monolayer h-BN nanosheet can be stable up to 850°C while a slightly higher oxidation temperature was registered for bi-/tri-layer h-BN nanosheets. On the other hand, Liu and his coauthors indicated that the diamond-like structure of bilayer h-BN can be stable at 1500°C in air without any chemical reactions when coated on nickel metal. Such inert property can create a barrier to prevent the oxidation and protect the
underlying surfaces.

A variety of boron compounds used as lubricant or lubricant additives have been investigated and shown their effectiveness in friction reduction, wear inhibition, load bearing capacity in extreme condition, and high temperature oxidation resistance. In terms of biocompatibility and environmental safety, borates are promising candidates as an alternative solution for the traditional ZDDPs and other conventional lubricant additives. However, there are some shortcomings about alkali borate lubrication such as the dispersion in base oils and poor adhesion to the working surfaces, and its inability to form strong and stable tribofilms to prevent direct metal-to-metal contact.\(^{26}\) These drawbacks should be overcome to enable widespread applications of borate compounds in lubrication technology.

### 2.2.3. **Silicate lubricants**

Inorganic silicate compounds have been used for the lubrication of bearings or gear boxes in which steel surface and steel/bronze surface are in contact. The compounds are well-known not only for the thermal and mechanical stability under heavy loads and elevated temperature but also for the low costs. In addition, the high specific heat and high latent heat of alkali silicates can protect the systems from local overheating. The US patent 3,350,307 and 3,375,729 have reported the use of an aqueous solution of sodium/potassium silicate and their mixtures, and a thickening agent as lubricating grease.\(^{97-98}\) They have found that the sodium silicate provides the best performance with the \(\text{SiO}_2/\text{Na}_2\text{O}\) weight ratio between 1.0 – 2.5, and those of potassium silicate 1.0 – 2.2.\(^{97}\) The reaction between the lubricant and the metal or with the oxide layer present on the surface produces a strong metal silicate film which remains stable under high pressure and temperature.\(^{98}\) Layered sodium silicate with different modifications including \(\alpha-\text{Na}_2\text{SiO}_3\), \(\delta-\text{Na}_2\text{SiO}_3\), \(\beta-\text{Na}_2\text{SiO}_3\), and kanemite (\(\text{NaHSi}_2\text{O}_5\cdot3\text{H}_2\text{O}\)) have been reported as excellent lubricant additives which showed good load carrying capacity and anti-wear property because of the pillared layers similar to typical solid lubricants such as MoS\(_2\) and graphite.\(^{99-101}\) Chen et al. have reported that with only 1% of Ca- and Mg- kanemite added to the oil, the maximum seizure loads increased by over 27% and the wear scar diameter decreased by over 50%.\(^{99}\) However, the layered structure of kanemite collapsed after a long wear test, while \(\alpha-\text{Na}_2\text{SiO}_3\) and \(\beta-\text{Na}_2\text{SiO}_3\) remained in layered structures and provides better tribological properties.\(^{100}\)
On the other hand, lower friction coefficient and wear protection were obtained for a wide range of temperatures from 100 to 1200°C with a mixture of sodium silicate and graphite powder called “water glass”. It was found that the liquid glass provides the best performance at the liquid state, i.e., 900, 1000, and 1200°C for SiO₂/Na₂O ratios of 2.0, 3.0, and 4.0, respectively. Meanwhile, the addition of graphite provides better adhesiveness of the lubricant onto the hot surface.

The combinations of silicate with other chemical substances to create silicate compounds also serve as effective lubricants or additives under extreme conditions. Yu et al. found that the doping of silicate or Si-O to diamond-like carbon (DLC) additive can improve the adhesion of the DLC film, which can restore the rough surface and provide excellent steel-steel friction pairs. On the other hand, Zhang et al. found that silicate additive itself can resemble DLC films and reduce the friction coefficient from a pin-on-disk test by ~40%. The author recorded “negative wear”, which was explained by a series of tribological events including the adsorbed broken carbon chains from the lubricant oil, embedded partial iron debris, and a self-repairing DLC layer on the worn surface. The self-repairing function has also found in some silicate mineral acting as lubricating additives such as Al₄[Si₄O₁₀](OH)₄. Yue et al. studied the mechanism of the self-repairing function of Al₄[Si₄O₁₀](OH)₄ additive and revealed that the silicate particles in the additive act as a catalyst to activate a series of tribochemical reactions to form a carbon-rich film which can reduce the roughness of the worn surface. Nan et al. found that the tribofilm formed from ultrafine magnesium aluminum silicate lubricant additive contains mainly iron oxides and SiO which were responsible for the friction reduction and anti-wear properties. Apart from that, silicon nitride is also a potential high temperature lubricant with an operating range up to 1500°C.
Figure 2.6 Friction coefficients ($u$) measured in unlubricated (dry) and sodium metasilicate (NSO) lubricated condition at various temperatures of 530, 645, 730, 825, 920 and 960°C.$^{111}$

Recently, a series of environmentally friendly sodium silicate lubricants and their mixtures with borate and expanded graphite has been reported.$^{111-114}$ The tribotests indicated that the sodium silicate compounds provide excellent lubricating functions such as the reduction of friction, wear and oxidation. One of the important properties of the silicate lubricants is the high working temperature, i.e., 920 to 960°C (Figure 2.6).$^{111,113-114}$ Similar to the achievement with alkali borates or alkali phosphate/borate, the findings with these sodium silicates have opened a promising potential of using alkali silicate with a variety of chemical compounds to create new lubricants/additives that could sustain extreme conditions of high temperature, heavy loads, and frictional shearing.

2.2.4. **Solid lubricants**

Solid lubricants can also be applied to reduce friction and wear and protect the surface finish in metal forming processes. The lubricants can be used in the form of powders, films, or composite materials, which can be applied with mixed fatty acids or fatty oils or applied directly onto the sliding surfaces. The most common examples of solid lubricants are graphite, molybdenum disulfide ($\text{MoS}_2$), hexagonal boron nitride ($h$-
BN), and polytetrafluoroethylene (PTFE). Among them, graphite and MoS$_2$ lubricants have a long history and have been widely applied in the metal forming processes. These types of lubricants have been used at a temperature range from 100°C to 1200°C, offering low friction and anti-oxidation properties. The low-friction characteristics of those lubricants are attributed to their layered structure on the molecular level with weak interlayer bonds. Therefore, such layers are able to slide relatively to each other under applied loads.

However, graphite lubricant suffers from the bond weakening of hexagonal planes that leads to the loss of planar form and easy-shear function in extreme pressure. The weak adhesion between the substrate and the graphite could result in the easy removal of the material from the wear track. In addition, galvanic corrosion can also occur as a result of the heightened electrical conductivity. Meanwhile, MoS$_2$ contains a significant amount of sulfur that suffers from the harmful release to the environment.

**2.3. Lubricant-Surface interactions: physical/chemical adsorption, tribochemical reactions and tribofilm formation**

Surface-lubricant interactions play a crucial role in determining the wear and friction reduction capability of a tribosystem where most chemical reactions and frictional behaviors are initiated at the interfaces. Therefore, the performance of a lubricating system is dictated by the surface-lubricant interactions and the resulting tribofilm formation, which include physical/chemical adsorption; tribochemical reactions: bond formation and dissociation, cation exchange, polymerization and depolymerization of lubricant molecules. In some tribosystems, the bearing layer is bonded to the surface through a molecular adsorption, while in extreme conditions, tribochemical reactions and tribofilm formation all interact.

**2.3.1 Physical and chemical adsorption**

In less extreme tribosystems, the physical adsorption of lubricant or additive molecules on metal surfaces often occurs with organic and fluid lubricants. In this case, lubricant molecules only adsorb physically or chemically on a metal surface via weak van der Waals or electrostatic interactions without any chemical reactions and the formation of resultant products. The adsorption of lubricant molecules on the surface creates an adsorbed layer to support load-bearing function. The adsorbed layers can be
formed by stacking lubricant/additive molecules in a certain direction, i.e. vertically or horizontally. In this case, surface texture, molecular arrangement, and binding strength are critical factors to determine the stability and the performance of a lubricant, and therefore its lubricating effectiveness. Jabbarzadeh et al. indicated that the adsorbed dodecane produces a lower friction at even thinner film thickness on amorphous walls than crystalline walls due to the absence of “solid-like” behavior from high viscosity. The high density and solid-like behavior becomes more severe when the thin film undergoes extreme conditions, for example the film thickness is reduced to a few atomic layers at the asperity contact due to high applied loads in the boundary lubrication regime. Ta et al. have shown that hexadecane molecules adsorbs stronger on iron metal than on its oxide surface, but the reduced shear stress of the iron surface stems from the surface corrugation rather than the metal-fluid adsorption strength. As in a liquid phase, the lubricant molecules are able to fill the surface cavities at atomic scales and thus support the load. Within a thickness of a monolayer, longer chain lubricants are able to cover the valleys between two asperities and keep these asperities separated from a direct contact.

In order to best cover and protect the underlying material, a strong adsorption or chemical binding is needed to avoid being removed by shear under the relative motion of tribopairs. In some ionic liquid lubricants, the alkali cations stabilize and thicken the lubricant layer by ionic interactions. These alkali cations with positive charges can act as a bridge to connect between the surface and the lubricant molecules, thus enhance lubricant adhesion and stability. It has been found that when the lubricant adsorbs chemically on the surface, the binding strength relates to the effective friction and wear performance. Previous research has revealed that a better surface-lubricant binding provides a better wear resistance and surface protection than a poorer mating system. The reason is that the better adhered lubricant requires stronger effort to be dislodged by horizontal forces or shear, therefore it remains covered on the surface under harsh conditions. On the other hand, those with the lower adsorption strength fail to protect the surface and maintain the gap between two contacting surfaces. Under extreme conditions of high temperature and heavy loads, such physical and chemical adsorption only appears at the initial phase of lubricant–surface interactions. As the frictional process proceeds, tribochemical reactions occur, which transform lubricant chemical properties and composition at the interface. Therefore, the adsorption plays a major role
in providing precursors for further tribochemical reactions with the metal surface.

### 2.3.2 Tribochemical reactions

Many researches have been carried out in order to find out the mechanism of friction reduction and anti-wear property of phosphate lubricants. In general, during hot rolling processes, high temperature and extreme pressure, iron oxides such as hematite (Fe₂O₃) and magnetite (Fe₃O₄) can readily be formed through the chemical reaction with oxygen dissolved in the lubricants. These iron oxides are hard particles with a relatively high melting point (usually > 1200°C) and they can cause severe damage to the surface by abrasive wear. In addition, further third body wear debris is also produced from the original oxide particles and the nascent surface itself under high pressure/shear treatment that could eventually result in accelerated wear. Those abrasive iron oxide particles at the contacting interface can be digested by the tribofim that is produced by the tribochemical reactions between the iron oxide and the lubricant or additive molecules.

The mechanism of the tribochemical reactions between phosphate lubricants/additives has been intensively investigated. Martin proposed the mechanism of the tribochemical reaction between ZDDP and iron oxide surface on the basis of the hard and soft acids and bases (HSAB) theory. Accordingly, Fe³⁺ in Fe₂O₃ is a harder Lewis acid than Zn²⁺ while PO₄³⁻ is a hard base, and that makes the cation exchange of Zn²⁺ and Fe³⁺ more energetically favorable. The cation exchange process of Fe³⁺ and Zn²⁺ causes the de-polymerization of the polyphosphate chains and creates the mixed Fe/Zn short-chain phosphate in the bulk of the tribofilm. Therefore, a layered structure with a short chain Zn/Fe phosphate covered by zinc-polymer phosphate is created through the tribochemical process. HSAB theory has been a useful tool to predict the tribochemical reactions. Subsequently, Minfray et al. indicated that during the friction test, two kinds of chemical reactions were identified. The first one was the reaction of zinc phosphate and the native iron oxide to form a tribofilm containing mixed Zn and Fe phosphate glasses that adhere well to the surface. The second reaction was between the nascent iron surface and sulfur atoms in the ZDDP tribofilm. Therefore, the antiwear protection of the phosphate layer on the friction surface is mainly supported by the strong adhesion through the chemical bonding. The iron
oxide particles are decomposed to take part in the chemical reaction and thus those abrasive wear particles are eliminated. Through computer simulations, Onodera et al. 31 found that the digestion of wear particles was caused by both pressure and shear conditions. Muser group reported an alternative cross-linking mechanism through theoretical models to explain the tribochemical reactions.134-136 The authors proposed that pressure can induce the polymerization in phosphate chains by linking short chain phosphates into a highly connected network. This pressure-induced cross-linking plays an important role in the formation and functionality of the tribofilm and improves mechanical properties of the materials. Miyamoto group developed a simulation package that combine Molecular Dynamics and Tight Binding Quantum mechanics to investigate the atomistic behaviors of the tribochemical reactions.136-140 When phosphoric ester additive is used, a chemical reaction occurs due to the bond formation between O of phosphate ester and Fe of the iron surface. Stable Fe–O bonds were obtained and accompanied by bond breaking of these oxygen atoms and phosphorus atom during the friction process.137 This method has been applied successfully for other tribological systems such as zinc phosphate confined between iron substrates, MoS2 on iron surfaces.139-141

2.3.3 Mechanisms of tribofilm formation

The formation of tribofilms as a result of tribochemical reactions is responsible for the anti-wear and anti-oxidation characters of phosphate lubricants/additives. Physical/chemical mechanisms of the tribofilm formation have been experimentally investigated.3, 34, 36 In particular, Bancroft et al. 34 proposed that the mechanism of ZDDP tribofilm formation follows three steps. Step 1 is the physical/chemical adsorption of ZDDP on the steel surface. Step 2 is the formation of long chain polyphosphate, and step 3 is the formation of short chain polyphosphate. Subsequently Zhang et al. 36 investigated ZDDP and dialkyldithiophosphate (DDP) and suggested a general mechanism of the tribofilm formation which is slightly different to that proposed by Bancroft. In Zhang work, the mechanism follows four stages. Stage 1 is physical/chemical adsorption of ZDDP and DDP on the steel surface. The adsorption layer plays a role as a precursor for the tribofilm in the subsequent steps;3 Stage 2 is the initial film formation with the thickness of around 10 nm. In this step, the decomposition of ZDDP and DDP occurs when the rubbing begins. Sulfur and phosphorus of ZDDP/DDP react with the steel surface while some decomposed
products adsorb on the rubbing surface. Therefore, the surface is initially covered by a thin composite layer of short-chain Zn/Fe phosphates and Zn/Fe sulfide; In Stage 3, the reactions continue to occur following stage 2, and Fe diffuses into the lubricant to engage in the reaction with long chain Zn phosphate to shorten the phosphate chains; Stage 4 is the polymerization of short chain zinc phosphates to form a long chain zinc polyphosphate. This chain length will increase as the rubbing process continues. On the other hand, short chain phosphates produced from stage 2 and stage 3 dominate the rubbing surface. Further sliding may lead to an increase of the tribofilm thickness. As a result, a multi-layer film is formed which consists of long chain polyphosphates on the top and mixed short-chain phosphates and inorganic Zn/Fe sulfide in the bottom layer. In this proposed mechanism, the decomposition of phosphate chains into short chains occurs first and follows by the formation of long chain phosphate as rubbing continues. In an approach using an adsorption model similar to Bancroft et al.,26 Zhang et al.,28 and Ito et al. 3 explained the tribofilm formation by the mechanical mixing process which occurs during sliding, leading to the rupture of chemical bonds and the promotion of the cation exchange reactions between Zn$^{2+}$ and Fe$^{3+}$. This mixing process makes the tribofilm thicker and can be considered to play a significant role in the tribofilm formation.

With alkali metal polyphosphate as a lubricant, Tieu et al. carried out the characterization of the tribofilm from tribological tests at 800°C.11 The tribofilm analysis indicated that at high temperature, the mechanism of friction reduction, anti-wear and anti-oxidation is mainly due to the pressure/shearing of the melted alkali metal phosphate that creates a hierarchical tribo-interface consisting of 4 regions at the interface above the iron oxide layer (Figure 2.7). Region (I) contains alkali metal phosphate which acts as lubricant and anti-wear film, region (II) includes Fe, Na, K, P which act as network modifiers, region (III) is phosphate subscale (Na, K, P) acting as a barrier to oxygen penetration into region (IV). Region (IV) is the iron oxide layer.
Figure 2.7 Schematic description of the hierarchical structure at steel tribo-interfaces lubricated by sodium/potassium polyphosphate at elevated temperatures.

Similar to the phosphate based lubricant, boron-containing tribofilms are responsible for the friction reduction and anti-wear property of borate lubricants which include boric acids, sodium borate, and boron esters. The tribofilm formed by the chemical interaction between borate additives and the steel surface reduces metal-to-metal contact, especially at high contact loads and thus prevents excessive wear. In addition, vacant $p$-orbital of boron, which acts as an electron carrier make borates a catalyst in the tribochemical reactions. The borate film has a heterogeneous non-destructive structure which contains both inorganic and organic components. Furthermore, it was suggested that the borate film was hard and contained a mixture of iron oxide and boric oxide. At a high temperature of 800°C, a novel lubricating mechanism of sodium tetraborate has been proposed. The critical finding with Na$_2$B$_4$O$_7$ lubrication is the formation of a bi-layered tribofilm which composes of an underlying Na-rich layer and an upper polymerized borate film (Figure 2.8). The tribofilm was believed to serve multiple functions including friction and wear reduction, antioxidation, and load supporting function.
2.4. Computer simulations of tribochemical reactions

Many experiments have been carried out to characterize the tribochemical reactions as well as the tribofilm formations. However, due to the complexity of the reaction processes in the contact regions, it is challenging to unveil the precise mechanism of the reactions in the dynamic systems. To this point, theoretical methods such as molecular dynamics simulation, first-principle calculations have been proven to be powerful techniques that can capture the details of chemical processes at the molecular or atomic level. There are four common methods that have been currently utilized to study tribochemical reactions between lubricants/additives and surfaces including molecular dynamics (MD), density functional theory (DFT), first-principle molecular dynamics or \textit{ab initio} molecular dynamics (AIMD), and coupling methods such as the combination of quantum mechanics and molecular dynamics (QM/MM). This session reviews the work that has been carried out by those simulation methods.

2.4.1. Studies by Molecular Dynamics simulations

MD simulations with bond order potential such as REBO/AIREBO, COMB or ReaxFF force fields can be used to study tribochemical reactions as they are able to account for bond formation and bond breaking. These force fields are usually empirical force fields that use a bond order/bond distance relationship to describe the chemical interactions. One of the earliest MD simulations of tribochemical reaction was carried

Figure 2.8 Bi-layered tribofilm obtained from sodium tetraborate lubricant at $800^\circ$C.\textsuperscript{15}
out by Harrison et al.\textsuperscript{143} using empirical hydrocarbon potential to study the chemistry of wear occurred when ethyl (\(-\text{CH2CH3 or -R}\)) groups chemisorbed between two diamond surfaces. Sliding was achieved by moving the rigid upper surface at constant velocity of 1 Å/ps in the sliding direction. The study observed the hydrogen detachment/recombination, carbon-carbon bond formation, and the creation of molecular wear debris. This group later used AIREBO force field to investigate the chemical reaction in alkyne chains containing diacetylene on diamond surface during shear and compression.\textsuperscript{144} The simulation showed that both compression and sliding process caused the cross-linking or the polymerization of carbon chains. Martin and Miyamoto groups modeled the digestion of Fe\textsubscript{2}O\textsubscript{3} wear particles in ZDDP and ZP,\textsuperscript{31} zinc metaphosphate (Zn(PO\textsubscript{3})\textsubscript{2}),\textsuperscript{32} \textsuperscript{,145} calcium borate (Ca\textsubscript{3}(BO\textsubscript{3})\textsubscript{2})\textsuperscript{79} under the effects of pressure and shear. In the simulation model, Fe\textsubscript{2}O\textsubscript{3} particles were embedded in the center of lubricant/additive and the whole lubricant layer confined between two Fe substrates as shown in Figure 2.9. The two-body Buckingham potential was applied for zinc metaphosphate/calcium borate while Lennard-Jones potential was applied for interfacial interactions between metaphosphate/calcium borate and Fe surfaces. It was indicated that under the combination of compression and shear, the digestion of Fe\textsubscript{2}O\textsubscript{3} particles by a complete diffusion of iron and oxygen atoms into the lubricant and thus eliminated the abrasive particles in the contact area. In spite of the modeling simplicity, the simulations provided a general picture of interfacial interactions and explained the wear protection of the lubricant additives. However, the diffusion has already been predetermined by embedding Fe\textsubscript{2}O\textsubscript{3} particles at the center of lubricant/additive and the surfaces. In addition, the use of pure iron surface rather than the oxidized surface such as Fe\textsubscript{2}O\textsubscript{3} or Fe\textsubscript{3}O\textsubscript{4} made the simulation unrealistic.
Figure 2.9 MD simulation model of ZP or ZDDP confined between iron substrates, Fe$_2$O$_3$ in the center of the lubricant layer and plays as a wear particle.\textsuperscript{31}

The ReaxFF force field has been an advanced solution that can overcome the shortage of bond order in traditional force fields to study the tribochemical reactions by MD simulations. The force field is able to describe the chemical reactions in terms of bond order and it is parameterized and trained from quantum mechanics and/or experimental data. However, due to the complexity of the training process, the application of ReaxFF in tribochemical reaction has been limited to a number of systems such as phosphoric acid and silicate systems.\textsuperscript{146-148} The models included two quartz surfaces or amorphous silica asperities pressing against flat $\alpha$-SiO$_2$ substrate and were separated by phosphoric acid or water.\textsuperscript{147-148} Pressure, sliding and high temperature up to 1400 K were applied in these simulations. The studies observed bond formation and bond dissociation in Si–O, P–O, and H–O bonds. In addition, the polymerization of phosphoric acid by condensing phosphoric acid molecules was also obtained. The authors also investigated the temperature dependence of reaction behaviors and the information on the optimum lubricating properties.

The advantages of MD simulations in tribology and tribochemical is that it can model huge and complex systems up to millions of atoms, and it can describe the effects of pressure, shear and temperature with suitable thermodynamic ensembles that make the simulation models more realistic and practical. However, MD simulations with conventional simple force fields are incapable of embracing complex and reactive systems due to the shortage of electron transfer information. On the other hand, reactive
force fields need to be trained properly as it requires reliable quantum mechanics or empirical data. ReaxFF force field for more practical tribo-systems such as iron/iron oxides – phosphates, iron/iron oxides – alkali metal borates is not currently available and it has been preliminarily developed in our research group.\textsuperscript{149}

\subsection{2.4.2. Tribochemical reactions by Density Functional Theory}

DFT is a powerful method to study chemical reactions because of its high accuracy, parameter-free characteristics, and atomic and electronic level of description. However, the application of DFT method in tribochemical reactions is scarce due to the complexity and the huge size of the ensemble of tribological models and lubricant molecules. Details of structures of reactants, products, intermediates as well as possible mechanisms of the tribochemical reactions can be considered properly with the DFT method. For example, Jiang \textit{et al.}\textsuperscript{150} used \textit{ab initio} quantum mechanics methods to examine structures, vibrations, and energy of zinc dithiophosphates. Armstrong \textit{et al.}\textsuperscript{151} used a semi-empirical quantum chemistry method to predict the structures of complexes formed during the reactions between ZDDP with an oxygen rich steel surface. Mosey group reported some reaction pathways leading to the formation of ZDDP anti-wear film precursors, the isomerization and decomposition of ZDDP molecules by alkyl group transfer and olefin elimination. The decomposition pathways of ZDDP with different constituents series comprising of hydrogen, ethyl, isopropyl, and isobutyl groups were also found to contribute to the reaction mechanism and origin of products during the tribofilm formation.\textsuperscript{152} Kolesnikov \textit{et al.}\textsuperscript{153} reported the adsorption of alkali metal phosphate on iron surface and the possible transformation of phosphate structure during the interaction with iron surface. Considering (PO$_4$)$_3^-$ fragment, the author found that the most favorable configuration of phosphate group adsorption on iron surface is through two oxygen atoms. However, an iron cluster was used in this research, which is insufficient to embody the property of the surface.
Onodera group has applied the transition state search to find reactants, products and transition states of the tribochemical reaction between polytetrafluoroethylene (PTFE, C₅F₁₂ was chosen) and aluminum/aluminum oxide/copper oxide surfaces. Reactions occurred by breaking C-F bonds accompanied by the formation of two chemical bonds between aluminum and fluorine on the aluminum surface. Therefore, after the reaction, the aluminum surface was terminated by fluorine atoms. It was experimentally proven that aluminum fluoride formation decreases the tribological performance of PTFE as it restricted the transfer film formation. Apart from that, the effects of environmental factors such as humid air on the performance of PTFE was also considered. DFT-optimized structures and transition state search technique indicated that depolymerized chain (C₅F₁₀) of PTFE preferentially reacted with water vapor than with oxygen or nitrogen. On the basis of DFT results, subsequent MD simulations were carried out to survey the frictional behavior of PTFE-aluminum with various surface terminations. Therefore, the MD simulation model contained properties of the tribological system as a result of the tribochemical reactions predetermined from the DFT calculations. This combination can solve the chemical reaction problem in MD simulations. Recently, decomposition mechanism of trimethyl phosphite on iron surface Fe(110) was reported by the Martin group. Reaction path of trimethyl phosphite dissociation was proposed in terms of energy barrier calculations and
depicted in Figure 2.10. In particular, trimethyl phosphite dissociated on iron surface through the detachment of each –CH₃ group leaving P-Fe bond on the surface as the most stable one. In order to account for pressure application, Yubo et al. built the model of benzene placed between Pt/Au substrates, and the applied load was controlled by decreasing the distance between each pair of the metal surface by Δa ranging from 0.2 to 0.02 Å. This process corresponds to the compression of the system with a certain pressure depending on the value of Δa. During the compression, C–H bond breaking and the linking of broken C–C bonds were observed on the Pt surface as a result of mechanical load rather than catalytic effect. Although those DFT results provided insights of the reaction mechanism, it is not able to account for the effects of tribological conditions (loads, shear, and temperature).

It has been found that the interaction strength of lubricant – surface reflects the antiwear capability of the lubricant, i.e. a better surface-lubricant binding provides a superior wear resistance and surface protection than a weaker mating system. A tribofilm made up from stable bonds requires a higher barrier to be dislodged from the metallic surface. An alternative way to assess metal-lubricant reaction and wear inhibition of a lubricant is by estimating the energy gap of valence electrons in lubricant and metal surface, as it represents the chemical reactivity of substances. For example, Jaiswal et al. proposed that the tendency of antiwear effectiveness of lubricant additives with respect to the metal surface is correlated with their band gaps, and it has been proven to be consistent with antiwear inhibition evaluated from experiments. Accordingly, the capability of an additive molecule and metal surface system to undergo a chemical reaction depends upon their band gap which is defined by the energy difference between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO). Furthermore, reaction pathways and possible intermediates/products of lubricant additives on steel surface provide a better understanding of the tribochemical reaction processes. More importantly, the effectiveness of new antiwear additive lubricants can be predicted by theoretical calculations without costly experimental testing.

DFT calculation is also an effective method to determine nanoscale friction by mapping the potential energy landscape of two flat shearing surfaces. This method was first applied for metal-metal contact of two flat surfaces, then for 2D materials such as graphene, h-BN, or MoS₂ as lubricants. Friction estimated from the
method is based on the variation of the total energy of the system against the relative motion of two bodies across the surface under a certain load. Therefore, it provides a quantitative assessment of friction and electronic analyses of charges and chemical bonding behaviors that accounts for the frictional properties. However, apart from flat surfaces and 2D materials, it is unadaptable for 3D tribosystems with disordered or anisotropic lubricant molecules such as polymers or glasses.

2.4.3. Studies by Ab initio Molecular Dynamics

Mosey and his group were one of the pioneers who used AIMD in the study of tribochemical reactions and prediction of anti-wear precursors. In particular, the combination of static DFT and AIMD was carried out in order to investigate the thermal decomposition of ZDDP monomers, dimers and isomers. Some proposed thermal decomposition pathways involving the loss of radicals, olefins, and sulfides led to the components of anti-wear film precursors. On the other hand, reaction of meta-thiophosphates (MTPs), ZDDPs and the formation of phosphate chain under a high pressure condition were performed. Pressure-induced changes in bonding and coordination number of triphosphates (TPs) and zinc phosphate (ZPs) was reported in (Figure 2.11). Accordingly, separated phosphate molecules (P$_3$H$_{10}$O$_5$) were heated up to 1000 K and quenched down to around 300 K while the pressure changed from 0 to 20 GPa. Under compression polymerization occurred via bridging oxygen atoms and involved in the modification of bonding at phosphorus sites. In contrast, ZPs underwent a cross-linking process, which was dominated by the change in the coordination number from tetra-coordinate into penta-coordinate at zinc sites rather than phosphorus sites. The cross-linking network of phosphates explained the existence of long-chain phosphates on the top of the tribofilms. Zn can act as cross-linking agents because of its flexible coordination numbers and can also be called ‘smart material behaviors.' Zinc atom was able to fluctuate between di-, tri-, and tetra-coordination during the initial compression and penta-coordinate one at high pressure. This characteristic is important for the elasticity of the material in response to pressure fluctuation.
To account for friction and pressure in tribological systems, AIMD packages such as Quantum Espresso were modified to deal with these simulation conditions.\textsuperscript{177-181} The general idea of this method is to build a model of two substrates terminated by a hydroxyl group at the interface or separated by molecules. The upper surface can be sheared with a certain rate while the pressure is applied as shown in Figure 2.12. In hydroxylated $\alpha$-$\text{Al}_2\text{O}_3$ (0001/0001) interfaces, the sliding and frictional behaviors of the system depends on the Al–O bond formation across the interfaces.\textsuperscript{178, 181} The tribochemical reaction and slip mechanism of $\alpha$-$\text{Al}_2\text{O}_3$ surfaces separated by aldehydes (MeCHO) molecules were reported. The authors concluded that high pressure led to the formation of MeCHO dimers, trimers and even higher order oligomers. Furthermore, the slip mechanism at high pressure was associated with the bond rupture of the dimers/oligomers or of the dimers and surfaces.\textsuperscript{179} By using large scale AIMD simulation, Righi et al., the passivation of diamond surfaces under the loading effect can reduce the energy of the contacting surfaces, thus decrease friction.\textsuperscript{182} The advantage of this method is the observation of tribochemical reaction under the consideration of temperature, loads and sliding. However, the computational expense is a big issue since it limits the size of the systems (usually less than 200 atoms), which is far from large realistic systems and suffers from time-consuming problems. On the other hand, the modification of DFT codes is a tricky task that requires experiences on coding as well as an in-depth knowledge of DFT.
2.4.4. **Studies by Coupling Methods (QM/MM)**

The Miyamoto group from Tohoku university developed a new code called TB-QCMD to simulate tribochemical reactions by combining Tight-Binding quantum chemical (TBQC) and Molecular Dynamics methods. This combined code performs both MD and TBQC at the same time by partitioning the system in quantum part and MM part. The quantum part is the central and most reactive part that is chosen to be treated self-consistently by quantum tight-binding level while the rest of the system is described by the classical MD. Figure 2.13 describes the model for the QM/MM simulations which consists of a confined system for MD simulations and a small QM system to account for chemical reactions. This method can deal with large complex systems including dynamics properties and chemical reactions and has been widely applied for various tribological systems.

For example, iron substrates lubricated by 45 phosphoric ester molecules, one phosphoric ester molecule and some adjacent iron atoms were selected for the quantum system and the remainder of the system treated by a classical force field. The temperature of 80°C (423 K), pressure of 1 GPa, and sliding velocity 100 m/s were selected for the calculations. Electronic structures such as bond overlap population and density of state (DOS) were considered to determine the chemical interactions occurring inside the QM system. The simulation results indicated that the bond formation between the nascent iron surface and oxygen atoms of phosphoric ester was stable only under both pressure and sliding applications. Otherwise, the Fe surface and phosphoric ester
interacted through a long-range electrostatic interaction and not through stable covalent bonds. In addition, the P–O bond dissociation occurred as the initial step of tribofilm formation. Similar method was applied to study the formation of MoS₂ tribofilms. In those systems, the mechanism of low friction of MoS₂ lubricant can be explained satisfactorily via TB-QCMD combined with static DFT calculations. In particular, the covalent bond formation between Fe and S at the interface was the main reaction. The charge transfer from Fe surface to S atoms made MoS₂ chains more negative and increased the repulsive Coulombic interaction between MoS₂ layers that eventually reduced friction in the whole system. The effect of friction on the bond dissociation of Molybdenum Dithiocarbamate molecules on Fe(001) surface was reported by Onodera et al. In this system, Mo–O was completely dissociated under the combination friction condition and catalysis of nascent Fe surface. Only bond elongation was found in the non-friction model. Bond dissociation in this situation could be the initial stage for the tribofilm formation. Hayashi et al. used TB-QCMD to explain the mechanism of low friction obtained from hydrogen terminated Diamond-like carbon (DLC) sliding surfaces compared to non-terminated DLC ones at 1 GPa. Accordingly, the C–C bond formation in the model was the factor that increased friction in the system. By contrast, hydrogen termination prevented the formation of C–C bonds in the contacting surfaces. Also, hydrogen molecules generated at the friction surfaces separated the direct carbon-carbon contact and reduced friction. Onodera et al. reported the transfer film formation from polytetrafluoroethylene (PTFE) on aluminum oxide surface in both OH-terminated and non-terminated conditions. During the friction condition, TB-QCMD simulation, bond dissociations between carbon and fluorine atoms were observed together with the bond formation of the dissociated fluorine atoms and aluminum atoms of the surface. The charge transfer from PTFE polymer to aluminum indicated that aluminum atoms on the α-Al₂O₃ surface acted as a catalytic Lewis acid, and removed fluorine atoms from its PTFE backbone. Two main reactions were observed: the formation of aluminum fluorine and the double bond between carbon atoms inside PTFE backbone. The aluminum fluorine formation was the main reason that reduces the tribological performance due to the high electrostatic repulsive interactions with fluorine atoms in PTFE. Recently, Righi et al. developed a QM/MM platform by coupling Lammps and Quantum Espresso for graphene and water reactions, and for MoDTC lubricant additive and iron reaction. The research has provided a real-time observation of the effects of moisture on graphene/graphite lubricity and
highlighted a great potential of using hybrid methods in describing tribochemical systems.

Figure 2.13 QM/MM simulation model of trimethyl phosphate between iron substrates.\textsuperscript{137}

As reported in the above references, QM/MM method is able to capture the tribochemical reaction dynamics which includes the effects from loads, shear and temperature during the simulations. In addition, this method is less computationally expensive than AIMD since only the most reactive part of the system is treated at quantum chemical level. The MM part can be large enough to model more practical models.

2.5. Summary, knowledge gaps, and objective

2.5.1 Summary and knowledge gaps

Through the literature review, many types of lubricants have been carried out from graphene, silicates, borate glasses as lubricants to phosphate lubricants. Among them ZDDPs have been one of the most common anti-wear and anti-oxidation agents and played a crucial role in tribology. Those ZDDP compounds have been studied extensively by experiments and computer simulations for over 80 years. However, environmental safety is the biggest concern about ZDDP’s widespread applications.

Four simulation methods including MD with reactive force fields, DFT, AIMD,
and QM/MM have been used to uncover the dynamics and tribochemical reactions of lubricants with surfaces for a variety of conditions from low to high temperature, under compression and sliding effects. MD simulations with reactive force fields take advantage of large-scale modeling and computation time, but the lack of force field parameters and the complexity of force field training make it challenging to deal with multi-element systems. QM/MM can describe both chemical reactions and dynamic behaviors (temperature, pressure, and shear) but the scale of the QM model is still small. In addition, in order to describe the tribological properly, there still requires reliable force fields for the surface, the lubricant, and the surface-lubricant interface. DFT and AIMD simulations are reliable for studying chemical reactions and structural transformation at an atomic level. Furthermore, the external variables such as temperature, pressure and sliding effects can be taken into account in AIMD simulations. However, the biggest issues from DFT and AIMD are small system sizes and computational expenses.

In the case of high temperature lubricants, test results have indicated that alkali phosphate/silicate/borate are excellent candidates for hot metal forming processes. Experimental testing based on these lubricants has shown good performances in terms of friction reduction, antiwear function and antioxidation, especially at elevated temperature and under severe loads. However, detailed questions behind the good performance of these lubricants have not fully explained by current experiments:

i) The mechanisms and tribochemical reactions of the alkali metal phosphate/borate/silicate with the steel surface at high temperature, under pressure and shearing conditions have not been fully understood.

ii) The chemical reactions between the lubricant and the surface and the applications of pressure and sliding motion at high temperature result in a variety of structural responses from the lubricants. The insights into the structural transformation have not been reported from experiments.

iii) Experimental results have shown that alkali cations play an important role in friction reduction and defining layering structures at the contacting interface. However, the role of alkali metals in cooperation with other lubricant’s components has not been quantified and clarified.
iv) The effectiveness of the alkali glass lubricants is based on the formation of multifunctional layered tribofilms in which each layer plays a certain role in reducing friction, mitigating wear, or preventing oxidation. However, the formation of a hierarchical structure and the distribution of layers and their contribution to the overall performance of the lubricants remain unclear.

2.5.2 Objective

DFT and AIMD have been used to study the interactions and chemical reactions of alkali metal phosphate/borate lubricant on an oxidized (Fe2O3) surface as these methods are reliable to describe chemical reactions and time-dependent chemical events in a dynamic system. To provide a complete picture of the tribochemical reactions and frictional and the effects of pressure, temperature, and sliding, the following tasks will be carried out in this thesis:

i) The adsorption of sodium phosphate on the iron oxide surfaces will be investigated by DFT calculations. The electronic structure of the adsorbed configurations will be analyzed to rationalize the chemical nature of the interactions. The comparison between two phosphates with different chain length is made to clarify the relationship between the adsorption behaviors and the frictional performance.

ii) In order to investigate the effects of high temperature on surface-lubricant interactions, AIMD simulations will be performed for sodium borate and boron oxide at 1073 K. The melting behaviors and interactions of Na2B4O7 and B2O3 on the Fe2O3 surface will be compared and correlated with their friction and wear results.

iii) The effects of pressure on structural transformation in sodium borate lubricants with different sodium concentrations will be investigated by the compression of sodium borate confined between two Fe2O3 surfaces.

iv) Chemical reactions between alkali borate lubricants and the Fe2O3 surface under shearing condition will be studied by applying the sliding motion on two Fe2O3 substrates. The effects of alkali metals will be qualified by the
comparison between sodium borate with different Na$_2$O concentrations, lithium borate, and potassium borate.

v) The effects of graphene on the Fe$_2$O$_3$-sodium borate systems will be investigated. In addition, the stability of graphene and its doped structures on Fe$_2$O$_3$ surface will be studied at high temperature by AIMD simulations.
3.1 Simulation Methods

3.1.1 Density Functional Theory

Kohn-Sham equation

All the information of a system can be obtained by solving the Schrödinger equation. Formally, the Hamiltonian of such a many-body system can be written in the following form (1).192 For a limited simple case such as a hydrogen atom or simple 2-D square potential, we can solve the equation and find the wave function for the system as well as determine the allowed energy states of the system.

\[
\hat{H} = -\sum_{l=1}^{P} \frac{\hbar^2}{2M_l} \nabla_l^2 - \sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \nabla_i^2 + \frac{e^2}{4\pi\varepsilon_0} \left[ \frac{1}{2} \sum_{l=1}^{P} \sum_{j \neq l}^{P} \frac{Z_l Z_j}{|R_l - R_j|} + \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \frac{1}{|r_i - r_j|} \right]
\]

(1)

Where \( R = \{R_l, l = 1, \ldots, P\} \) and \( r = \{r_i, i = 1, \ldots, N\} \) is a set of \( P \) nuclear and \( N \) electronic coordinates, respectively. \( M_l \) and \( Z_l \) are the nuclear masses and charges, \( m_i \) is the electronic masses. The time-independent Schrödinger equation which describes all the properties of a system is then written as:

\[
\hat{H} \psi_n(R, r) = \varepsilon_n \psi_n(R, r)
\]

(2)

Where \( \psi_n(R, r) \) and \( \varepsilon_n \) are eigenstates (wavefunction) and their corresponding energy eigenvalues.

In practice, only a limited number of cases such as hydrogen atoms or \( H^2^+ \) molecule, and very small molecules can be treated as a full quantum mechanical framework. In most problems, it is almost impossible to solve the full Schrödinger equation for all electron systems due to the complexity of the multi-component equation. In order to fix the idea, approximation methods have been introduced to simplify the problem. Born-Oppenheimer approximation is the first method used to approximate the motion of nuclei. The idea of the Born-Oppenheimer method is based on the fact that nuclear masses are much heavier than electronic masses, and the movement of electrons is much higher than that of the nuclei. Therefore, under a certain condition, the movement of nuclei can be ignored and the nuclei can be considered as stationary states. The Hamiltonian is then can be decomposed as below:
\[ \hat{H} = \hat{T} + \hat{V} + \hat{W} \quad (3) \]

In which \( \hat{T} \) is the kinetic energy of electrons, \( \hat{V} \) and \( \hat{W} \) are the interaction of electrons with external fields and the electron-electron interaction, respectively. Although we can eliminate the kinetic energy of stationary nuclei and consider the potential energy of the nuclei a constant potential, solving Schrodinger equation for a many-body system remains too complicated as the equation is inseparable. Therefore, DFT has been invented to tackle the issue.

The idea of solving Schrodinger equation through electronic density was originally proposed by Thomas and Fermi, and then developed by Hohenberg, Kohn and Sham through Hohenberg – Kohn – Sham theorem.\(^{192} \) The basic concept of this method is that instead of dealing with original Schrodinger equation of a many-body, which involves in the many-body wave function \( \psi_n(r_i) \), we only have to solve an Schrodinger-like equation that involves in the total density of electrons \( \rho(r) \).

The external potential is a unique functional of electronic density, and thus the total energy depending on electronic density becomes:

\[ H[\rho] = T[\rho] + V[\rho] + W[\rho] \quad (4) \]

With \( \rho(\vec{r}) = N \int ... |\psi|^2 \, d\vec{r}_1 \, d\vec{r}_2 ... d\vec{r}_N \), and \( \int \rho(\vec{r}) \, d\vec{r} = N \).

The electron-electron interaction term \( W[\rho] \) includes two parts: the classical Coulombic interaction of electrons \( W_{CL}[\rho] \) and the non-classical interaction \( W_{NCL}[\rho] \), while the electronic kinetic energy is separated into kinetic energy of non-interacting single electron \( T_s[\rho] \) and the unknown term \( T_c[\rho] \). Finally, total energy of the system can be rewritten as:

\[ H[\rho] = T_s[\rho] + T_c[\rho] + V[\rho] + W_{CL}[\rho] + W_{NCL}[\rho] \quad (5) \]

\[ H[\rho] = T_s[\rho] + V[\rho] + W_{CL}[\rho] + E_{XC}[\rho] \quad (6) \]

Where, \( E_{XC}[\rho] \) in equation (6) is the exchange – correlation term that contains all the unknown terms in the equation (5).

**Exchange and correlation function in DFT**

The total energy of a many-body system discussed in the previous section has been summarized in equation (6). In (6), the first three terms are well-defined in terms of the electronic density, while the last term which describes the exchange and correlation energy does not have a specific form. The idea is now to look for an appropriate approximation for the exchange-correlation functional. The first and also
the most simple method for approximating the $E_{XC}$ energy is the homogeneous electron
called local density approximation (LDA).\textsuperscript{192-193} The central idea of this method is to
consider the general inhomogeneous electron density of a system is homogeneous at a
local region. By using the approximation, we can use the exchange-correlation hole
corresponding to the homogeneous electron gas. Then, the $E_{XC}$ energy is calculated by
integrating over the volume corresponding with the exchange correlation energy density
at every point in the volume of the system as shown in equation (7).

$$E_{XC}^{LDA}(\rho) = \int \rho(r) \varepsilon_{XC}^{LDA}[\rho(r)]dr$$ (7)

Where, $\varepsilon_{XC}[\rho(r)]$ is the average of an exchange correlation energy density of a
local uniform electron gas. Since LDA method considers the electron density locally
homogeneous where $\rho(r)$ is the same. This approximation method is suitable for
systems whose electronic density is relatively uniform such as bulk metals. However, in
less uniform systems such as molecules, ionic crystals, and semiconductors, the LDA
approximation fails to reproduce correct properties.

The LDA method can be improved by including the dependent term of the
gradient of the density. The procedure leads to “gradient corrected” functionals or
“generalized gradient approximation” (GGA) functionals.\textsuperscript{193-195}

$$E_{XC}^{GGA}(\rho) = \int A_{XC}[\rho] \rho$$ (8)

There are several versions of GGA such as BLYP, PBE, and the revised versions
of PBE or RPBE. The BLYP exchange functional was proposed with the parameters
fitted to experimental molecular data. GGA-PBE is very good functional from the
theoretical point of view, since it confirms many exact conditions of the XC hole, and
does not include any fitting parameters. Furthermore, the accuracy of this functional is
equivalent or sometimes better than that of BLYP. The RPBE appears to provide an
improved description of adsorption and hydrogen-bonded systems.

**Pseudopotential**

Since the electrons near to the nuclei do not participate actively in chemical bonding,
we can replace the complicated effects of the motion of those core electrons of an atom
and its nucleus with an effective potential. This effective ionic core represents the
nucleus together with its core electrons. In this way, the number of electrons treated
explicitly is much smaller, thus reducing significantly the number of required electronic
states and the size of the basis set. However, the interaction of the valence electrons
with the nuclei is not the bare Coulomb interaction anymore; it now includes that part of the electron-electron interaction related to the screening of the nuclear charge by the core electrons. The Coulomb potential must be replaced by a softer pseudopotential that takes into account the orthogonalization of the valence orbitals with respect to core orbitals of the same angular momentum, thus producing valence wave function. The important aspect of the pseudopotential is that the pseudo-wave function outside the core region must be the same as the full-electron wave function.

### 3.1.2 Ab initio Molecular Dynamics

In any molecular-dynamics (MD) simulation including Ab initio Molecular Dynamics (AIMD), the microscopic trajectory of each individual atom in the system can be determined by integrating Newton’s equations of motion. In order to accomplish the task, several algorithms have been implemented to integrate the equation such as Verlet and Leapfrog, etc.\(^{196-197}\) The main difference between classical and first principle MD is in the way the potential energy is evaluated. While classical MD calculates the potential energy through the classical force field\(^ {198}\) or Buckingham, AIMD includes the interaction between electrons into the many-body system. In AIMD, the potential energy can be obtained by solving the Schrodinger equation (9).

\[
M_I \ddot{R}_I = F_I ; F_I = - \frac{\partial U(R)}{\partial R_I} ; \quad U = \langle \Psi | \hat{H} | \Psi \rangle
\]

Where \( R_I \) and \( F_I \) are the position and force of the nuclei I, \( \Psi \) is electronic wavefunction of the many-body system at ground state and \( \hat{H} \) is the Hamiltonian of the system. Once the electronic wavefunction at the ground state is defined, the potential energy can be calculated easily. However, solving the exact electronic wavefunction for a complex many-body system is impossible in practice. Therefore, there are several approximation methods that have been used to find the wavefunction i.e. Tight Binding, Hartree-Force or DFT. In fact, DFT has become the method of choice for most applications because of its combination of good scaling with system size and high accuracy in reproducing most ground state properties.

The calculated potential energy based on \textit{ab initio} techniques provides AIMD
both advantages and disadvantages over classical MD. Since the electronic interactions are included, the method is able to describe chemical reactions that are impossible with classical MD such as bond formation/dissociation, charge transfer and more. Another crucial advantage of using AIMD is that it does not rely on empirical parameters regarding the reactivity of the system, which is based on the fact that *ab initio* methods only use the fundamental quantum mechanical laws of nature and nothing else. Meanwhile, classical MD requires to retrain its force field if the system of interest is changed. The main drawback of AIMD is the computational expense. Although approximation techniques have been used, the computational cost of AIMD is far more expensive compared to that of classical MD. The disadvantage of AIMD simulations is that its system size is limited up to thousands of atoms while the system size of classical MD calculations can reach millions of atoms.

There are two most popular classes of AIMD which are Born-Oppenheimer MD (BOMD) and Car-Parrinello MD (CPMD).

**Born-Oppenheimer Molecular Dynamics**

The concept of Born-Oppenheimer Molecular Dynamics is very straightforward. In this method, the electronic wave function at the ground state is optimized at each step of the simulation. The wave function is then used to evaluate the potential energy as described in the previous section. The procedure can be illustrated in Figure 3.1. For an initial system in which the specific positions of each atom are defined, the electronic wave function can be optimized using *ab initio* methods. The obtained wave function is then substituted in equation (9) and (10) to calculate the force on each atom. Later, the force is used to update the atomic position using the Verlet or Leapfrog algorithm. After the coordinates of the atoms are updated to the new position, we repeat the whole procedure again by optimizing the electronic wave function regarding the new atom coordinates.
The BOMD method allows us to use a large timestep. In practice, a timestep of ~1.0 fs can be used in BOMD simulations. However, the computational cost of the method is relatively expensive due to the optimizing process of the electronic wavefunction at each ionic step.

**Car-Parrinello Molecular Dynamics**

As discussed in the previous section, the main drawback of BOMD is due to the optimization of the electronic wave function at every time step. The CPMD method overcomes this disadvantage by considering both atomic positions and the electronic wavefunction as dynamic variables. We then are able to propagate these variables using Newton’s equations of motion. This can be done by using an extended Lagrangian.\(^{199}\)

\[
L = \frac{1}{2} \sum_{i=1}^{N_{\text{atoms}}} M_i \dot{R}_i^2 + \frac{1}{2} \sum_{i=1}^{N_{\text{orbitals}}} \mu_i \langle \psi_i \mid \psi_i \rangle - \langle \Psi \mid \hat{H} \Psi \rangle + \sum_{i,j} \Lambda_{ij} \left( \langle \psi_i \mid \psi_j \rangle - \delta_{ij} \right) \tag{11}
\]

In which, the electronic wavefunction of the many-body system \(\Psi\) is constructed from a set of molecular orbitals \(\Psi_i\) with a fictional mass of \(\mu_i\). \(\hat{H}\) is the Hamiltonian of the system. \(\Lambda_{ij}\) is Lagrange multipliers and \(\delta_{ij}\) is Kronecker delta function. By using the extended Lagrangian we can obtain the equations of motion of both electron and nuclear.

\[
M_i \ddot{R}_i = -\frac{\partial \langle \Psi \mid \hat{H} \Psi \rangle}{\partial R_i} \tag{12}
\]

\[
\mu_i \ddot{\psi}_i = -\frac{\delta \langle \Psi \mid \hat{H} \Psi \rangle}{\delta \psi_i} + \sum_{i,j} \Lambda_{ij} \psi_j \tag{13}
\]
Equation (12) is similar to that of BOMD which allows us to update the nuclear positions. However, instead of optimizing electronic wavefunction at each ionic step, CPMD uses equation (13) to propagate the wavefunction. The process of CPMD can be illustrated in Figure 3.2. At first, the wavefunction is optimized using ab-initio methods, it is then used to evaluate the force and update the position of each individual atom. After that, the wave function is propagated using equation (13). In the following step, the new wavefunction is used to calculate the force and the process is repeated over again. Since the CPMD scheme allows us to avoid optimizing electronic wavefunction at each timestep which is costly, the computational expense is lower than that of BOMD.

Figure 3.2 Schematic diagram of CPMD simulation.

3.2 Simulation models

3.2.1 Iron and iron oxide substrate

Iron oxide (Fe₂O₃) is usually formed as a result of oxidation of iron when it is exposed to the environment, particularly at high temperature. Therefore, it is the most suitable material to be used as a substrate in metal forming. Iron oxide (Fe₂O₃) surface was built up from the crystalline structure of the Fe₂O₃ bulk systems. The geometry of Fe₂O₃ is a rhombohedral crystal which is presented in Figure 3.3a. Fe₂O₃(0001) slab was created from six stoichiometric layers of Fe₂O₃ bulk with a size of 1×2 orthorhombic unit cell. It has been reported by Ta et al.²⁰⁰ that those selected layers and
Fe₂O₃ are sufficient to describe properly the structural properties and electronic structures of their bulk systems after surface relaxation. In this work, Fe₂O₃(0001) surface with Fe–O₃–Fe termination was chosen for modeling as it has been proven to be the most thermodynamically stable surface morphology of Fe₂O₃. The surface was geometrically optimized to obtain the equilibrium positions for atoms at the surfaces before loading lubricant molecules for subsequent simulations. An additional vacuum of 15 Å was added on the top of the surface to avoid the interactions of the periodic images along the z direction. The bulk crystal structure consisting of three bottom layers of the Fe₂O₃(0001) slab was fixed during the geometrical optimization and the AIMD simulations.

![Crystalline lattices of Fe (bcc), FeO (cubic) and Fe₂O₃ (rhombohedral): Fe (blue), O red).](image)

Figure 3.3 Crystalline lattices of Fe (bcc), FeO (cubic) and Fe₂O₃ (rhombohedral): Fe (blue), O red).

Nascent iron surface contacts directly with lubricant right after the detachment of the upper Fe₂O₃ layer. Therefore, the iron surface was also selected to study the adsorption of sodium borate lubricants. A Fe (110) slab containing three stoichiometric Fe layers was built from the Fe bcc crystal presented in Figure 3.3b. The surface was fully optimized before adding sodium phosphate for further geometrical adsorption of the adsorption. During the simulation, a vacuum layer of 15 Å was added on the top of the surface to reduce the effect of the periodic boundary condition. One bottom layer of the Fe surface was fixed to represent the bulk crystal structure.
3.2.2 Sodium phosphate lubricants

Sodium pyro- \((\text{Na}_4\text{P}_2\text{O}_7)\) and ortho-phosphate \((\text{Na}_3\text{PO}_4)\) were chosen to investigate the adsorption behaviors on the iron oxide surface. The ball-and-stick models of \(\text{Na}_2\text{B}_4\text{O}_7\) and \(\text{Na}_3\text{PO}_4\) are shown in Figure 3.4. These molecules were optimized in the simulation boxes that have the same size with the \(\text{Fe}_2\text{O}_3\) slab model created from the previous step. After fully optimized, the structural parameters such as bond length and bond angles were compared with the corresponding experimental values to validate the results. It is noted that there are available experimental data on tribochemical behaviors of sodium ortho-\((\text{Na}_3\text{PO}_4)\), pyro-\((\text{Na}_4\text{P}_2\text{O}_7)\) and metaphosphates \((\text{NaPO}_3)_6\).\(^{47}\) The meta-phosphate was not included in this work because it would require a large simulation model with a huge computational expense.

![Figure 3.4 Molecular structures of (a) \(\text{Na}_4\text{P}_2\text{O}_7\) and (b) \(\text{Na}_3\text{PO}_4\): Sodium (purple), Phosphorus (magenta), Oxygen (red). The non-bridging oxygen is P–O, and the bridging oxygen is P–O–P (O\(^b\)).](image-url)

3.2.3 Alkali borate glasses

Sodium borate glasses \(x\text{Na}_2\text{O}·(100-x)\text{B}_2\text{O}_3\) \((x = 0, 25, 33, 50, \text{and} 60 \text{ mol} \%)\), lithium \((\text{Li}_2\text{B}_4\text{O}_7)\) and potassium tetraborate \((\text{K}_2\text{B}_4\text{O}_7)\) glasses were prepared by the melt-and-quench technique in orthorhombic boxes. In order to eliminate the mismatch when transferring the \(\text{Na}_2\text{B}_4\text{O}_7\) and \(\text{B}_2\text{O}_3\) boxes onto the \(\text{Fe}_2\text{O}_3\) substrates, the \(a\) and \(b\) dimensions of the boxes were set identical to those of the \(\text{Fe}_2\text{O}_3\) substrate (Figure 3.5), while the \(c\) direction was calculated based on the experimental densities of the materials as presented in Table 3.1. The purpose of this setting was to maintain the periodicity along the \(x\) and \(y\) directions of \(\text{Fe}_2\text{O}_3\)-borate systems when the alkali glasses were
transferred on the Fe₂O₃ slab or confined between two Fe₂O₃ substrate.

Table 3.1 Details of the sodium, lithium, and potassium borate glasses

<table>
<thead>
<tr>
<th>Sodium borate glass</th>
<th>Na₂O (mol %)</th>
<th>Density (g/cm³)</th>
<th>No. atoms</th>
<th>No. alkali ion</th>
<th>No. boron</th>
<th>No. oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₂O₃</td>
<td>0%</td>
<td>2.25ᵃ</td>
<td>60</td>
<td>0</td>
<td>24</td>
<td>36</td>
</tr>
<tr>
<td>Na₂O·3B₂O₃</td>
<td>25%</td>
<td>2.25ᵇ</td>
<td>72</td>
<td>8</td>
<td>24</td>
<td>40</td>
</tr>
<tr>
<td>Na₂O·2B₂O₃</td>
<td>33%</td>
<td>2.36ᵇ</td>
<td>78</td>
<td>12</td>
<td>24</td>
<td>42</td>
</tr>
<tr>
<td>Na₂O·B₂O₃</td>
<td>50%</td>
<td>2.76ᵇ</td>
<td>72</td>
<td>18</td>
<td>18</td>
<td>36</td>
</tr>
<tr>
<td>3Na₂O·2B₂O₃</td>
<td>60%</td>
<td>2.56ᵇ</td>
<td>76</td>
<td>24</td>
<td>16</td>
<td>36</td>
</tr>
<tr>
<td>Li₂O·B₂O₃</td>
<td>33%</td>
<td>2.23ᵇ</td>
<td>78</td>
<td>12</td>
<td>24</td>
<td>42</td>
</tr>
<tr>
<td>K₂O·B₂O₃</td>
<td>33%</td>
<td>2.31ᵇ</td>
<td>78</td>
<td>12</td>
<td>24</td>
<td>42</td>
</tr>
</tbody>
</table>

ᵃ experimental data from Spinner et al. ᵇ experimental data from Riebling

Figure 3.5 Models for the construction alkali borate glasses (a) the Fe₂O₃ slab and (b) an orthorhombic box of alkali borate glasses. a =8.72 Å, b=10.07 Å, and c is adjusted based on the density of alkali borate. Zₙₐᵥₙ includes the surface thickness and 15 Å of the vacuum layer. Iron (blue), oxygen (red), boron (green), and sodium (yellow). The color assignment is applied for all Fe₂O₃ and sodium borate systems.

For the melt-and-quench technique, first the alkali borates were melted at 4000 K for 20000 steps corresponding to 20 ps (using the time step of 1.0 fs). This process is to ensure that all atoms in the systems are adequately randomized before quenching to obtain glassy states. Then in the quenching process, the temperature was rapidly reduced from 4000 K to 300 K with a certain cooling rate to obtain glassy states. The effect of cooling rate on the obtained glass structures was also tested with three cooling rates: 5.0 × 10¹³ K·s⁻¹, 1.0 × 10¹³ K·s⁻¹, 5.0 × 10¹² K·s⁻¹. The cooling rate of 1.0 × 10¹³
K·s\(^{-1}\) was used based on the reasonable cooling rate used in AIMD simulations. The radial distribution function of the melting and quenching processes was calculated to confirm the fully liquid state of the systems at 4000 K and the glassy state at 300 K. The obtained alkali borate glasses were used for subsequent AIMD simulations.

### 3.2.4 Confined models

The alkali borate glasses obtained from the melt-and-quench technique were sandwiched between two Fe\(_2\)O\(_3\). A minimum gap of 2.3 Å was set between the surface and the lubricant, which corresponds to the ionic Na–O distance (Figure 3.6). The systems were subjected to AIMD simulations, compression, and shear. The corresponding procedures of such simulations will be presented in the appropriate chapters.

![Figure 3.6 Confined model of alkali borate glasses between two Fe\(_2\)O\(_3\) substrates.](image)

### 3.3 Simulation details

DFT and AIMD simulations were performed by the Vienna Ab Initio Simulation Package (VASP). A plane wave basis set and the projector augmented-wave (PAW) method (PAW potentials) were used to model core potentials. The electron exchange and correlation was estimated by using the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) exchange and correlation functional.\(^{194-195}\)
Geometrical optimization and electronic structure calculations were performed by DFT calculations. A cutoff energy of 450 eV was used for the plane wave basis set, and the optimization with the convergence criteria of $10^{-4}$ eV and $10^{-3}$ eV were applied for the electronic wave function and ionic relaxation, respectively. The Monkhorst – Pack scheme was used to sample the Brillouin zone. A k-points set of 3x3x1 was used for the geometrical optimization, while the higher accuracy with k-points set of 5x5x1 was used for energy calculations and electronic structure calculations. The parameters used in the thesis are standard parameters recommended in the document of the VASP simulation package. These parameters have been tested with each system, compared with the available experimental data, and presented in an appropriate section in each chapter. In general, the testing results using the parameters in this work showed good agreements with the corresponding experimental results such as geometrical parameters of bond length, bond angles; structure parameters of $\text{B}_4/\text{B}_3$ and $\text{O}_{1b}/\text{O}_{2b}$ ratios.

For AIMD simulations, the Nose-Hoover thermostat with the algorithm of Nosé was used to maintain the temperature in the system. In the Nosé algorithm, the Nosé mass controls the frequency of the temperature oscillations every a period of 40 time steps. Due to the large size of the supercells, Brillouin zone integrations were sampled over the $\Gamma$ point, and the plane-wave expansion of the electronic wave function was truncated by setting the energy cutoff to 350 eV. The time step of 1 fs was used in the AIMD simulations.

Electronic structure was analyzed by density of state (DOS), partial charges, charge density difference (CDD), and bond overlap population (BOP) calculations. The partial charges were estimated by Bader, or density derived electrostatic and chemical (DDEC6) method. CDD ($\Delta \rho$) was estimated by the subtraction of the electron density of the total systems ($\rho_{\text{total}}$) to the corresponding isolated ones ($\rho_{\text{surface}}$ and $\rho_{\text{mol}}$) by Equation 14.

$$\Delta \rho = \rho_{\text{total}} - \rho_{\text{surface}} - \rho_{\text{mol}}$$  \hspace{1cm} (14)

Bond overlap population was estimated by the Lobster code to analyze the bonding behaviors in the systems. The BOP was calculated by estimating the shared electron density between two atoms. Therefore, the change in BOP values of a bond
reflects the variation in its bonding behaviors such as new bond formation, bond strengthening, weakening, or dissociation.
Chapter 4. ADSORPTION OF SODIUM PHOSPHATE LUBRICANTS ON IRON AND IRON OXIDE SURFACE

4.1 Introduction

Phosphate additives are well-known for their excellent friction reduction and antiwear functions and have been extensively used in engines and industrial lubricants for a long time. Apart from ZDDP, alkali metal polyphosphates have been recently proved to form an effective tribofilm that can reduce friction, and protect workpieces from wear and oxidation at high temperature. \(^{10-13}\) Remarkably, this kind of lubricant is environmentally friendly and works well at elevated temperatures due to its exceptionally thermal stability that can withstand structural corruption during its melting. \(^{6-7, 41-42}\) Although experimental observations about frictional behaviors and tribofilm characterizations obtained from these alkali metal phosphates at the macroscopic scale have been reported, an in-depth understanding of the chemical nature of the iron – phosphate tribofilm formation remains unclear due to the complexity of tribological systems, such as high pressure, elevated temperature and large sliding velocity.

It has been found experimentally that during the tribological processes, rubbing surfaces are covered by a well-adhered layer which consists of mixed short-chain and long-chain iron phosphate glasses. \(^{47}\) This protective layer also called tribofilm, is formed as a result of a series of chemical reactions between phosphate glasses and the metal surface in response to the extreme pressure and temperature under sliding contacts. Zhang \textit{et al.} \(^{36}\) proposed four steps of ZDDP tribofilm formation including the adsorption, the reactions between the lubricants and rubbing surface, the diffusion of Fe atoms and shortening the phosphate chains, and the polymerization of the short chain zinc phosphate. In general, lubricant molecules are initially adsorbed chemically or physically on the metal surface creating an adsorbed layer. It has been indicated that this step plays a crucial role as it provides the precursors for the tribofilm in the following steps. \(^{3}\) If the interaction of lubricant additives and the surface is strong enough, the chemisorbed layer will be formed and prevent the direct surface – surface contact as well as the further penetration of other species to the underlying layers. The strength of this adsorbed layer is dependent upon the bonds formed between the phosphates and

\(^{1}\) The content of this chapter was published on J. Phys. Chem. C 2018, \textbf{122}, 1, 635-4447.
iron surface which are inherently governed by their own electronic structure. Thus, understanding the adsorption in the first step is essential for the optimization of the tribofilm formation process.

In recent decades, computer simulations have been proven as effective methods to study surface – lubricant interactions and tribochemical reactions between them. It has been found that the interaction strength of lubricant – surface reflects the antiwear capability of the lubricant. In particular, the correlation between adsorption strength and the antiwear property of lubricants has been revealed by molecular dynamics (MD) simulation. The result confirmed that the increase of cohesive energy in the self-assembled monolayers (SAM) is correlated with an improvement of wear performance observed by experiments. These studies have provided fundamental understanding and strategies to evaluate the effectiveness of lubricants despite the limitations of classical force fields in describing chemical surface-lubricant relationship. Complementarily, first principle calculations have become useful tools when it comes to chemical reactions as they provide more accurate information at the electronic level and additional insights into the lubricant structures as well as the nature of lubricant – surface interactions. For example, Righi et al. reported the dissociation pathway of trimethyl phosphite on nascent iron surface by DFT calculation in which Fe surface acts as a catalyst. The decomposed products leading to the generation of P-passivated interface to help reduce friction and interfacial adhesion has been confirmed by experiments. Jaiswal et al. proposed that the tendency of antiwear effectiveness of lubricant additives with respect to the metal surface is correlated with their band gaps, and it has been proven to be consistent with antiwear inhibition evaluated from experiments. Accordingly, the capability of an additive molecule and metal surface system to undergo a chemical reaction depends upon their band gap which is defined by the energy difference between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO). Furthermore, reaction pathways and possible intermediates/products of lubricant additives on steel surface provide a better understanding of the tribochemical reaction processes. More importantly, the effectiveness of new antiwear additive lubricants can be predicted by theoretical calculations without costly experimental testing.

In ZDDPs, long - chain polyphosphates are usually decomposed into shorter chains. Interactions between metal surface and additives are in fact based on the short-
chain precursors. Similarly, tribological testing on sodium polyphosphates with different chain lengths, i.e., sodium ortho- (Na$_3$PO$_4$), pyro- (Na$_4$P$_2$O$_7$) and metaphosphate (Na$_4$P$_2$O$_7$) reported that long chain sodium polyphosphate has a tendency to be depolymerized into Na$_4$P$_2$O$_7$ under harsh tribological conditions, while shorter chain Na$_3$PO$_4$ provides better antiwear performance than the two other longer chain ones. These findings raise a question regarding how their interactions with the surfaces lead to the differences in their antiwear behaviors. Meanwhile, previous DFT calculations for phosphates have focused on PO$_4$ group on hydroxyl or goethite surfaces or iron-phosphate clusters, but neither the surfaces nor the phosphate molecules can be applied to sodium phosphates – steel system due to the presence of sodium and complicated tribo-stressed conditions including high temperature, pressure and shearing. Furthermore, the study of longer chains such as P$_2$O$_7$ on metal surfaces so far is rare because it needs a huge computational cost.

Therefore, the aim of this chapter is to investigate the behaviors of the adsorption of sodium ortho- (Na$_3$PO$_4$) and pyro- (Na$_4$P$_2$O$_7$) phosphates on nascent iron and iron oxide (Fe$_2$O$_3$) surfaces. The comparison between the adsorption on Fe and Fe$_2$O$_3$ surfaces was implemented to determine the electronic mechanism of phosphate – iron/iron oxide interactions. Furthermore, a detailed electronic structure analysis of alkali phosphates and their adsorption on metal surfaces is also discussed to investigate the influence of their chemical nature on the antiwear performance as additives in tribology.

### 4.2 Simulation model

The phosphate molecules are put on Fe(110) and Fe$_2$O$_3$(0001) surfaces at different interaction sites with three orientations of the molecules. The possible adsorption sites on Fe(110) and Fe$_2$O$_3$(0001) surfaces are depicted in Figure 4.1. Due to the symmetry in Na$_4$P$_2$O$_7$ configuration, we choose bridging oxygen for setting on the initial adsorption sites on Fe surface. For Na$_3$PO$_4$, P atom located in the center of Na$_3$PO$_4$ unit is chosen to set up the adsorption sites in the initial configurations. The orientations of Na$_4$P$_2$O$_7$ and Na$_3$PO$_4$ on the surface are presented in Figure 4.2 and Figure 4.3, respectively.
Figure 4.1 Top view of the possible adsorption sites on Fe(110) and Fe$_2$O$_3$(0001) surfaces: (a) on-top of Fe atom (T), long bridge (LB), short bridge (SB), pseudo-threefold coordinated hollow (3F); (b) on-top of Fe atom (Fe T), on hollow of Fe atom (Fe H1 and Fe H2), on top of oxygen atom (O T) and bridge (B). Fe (blue), O (red).

Figure 4.2 Side view (a), (b), and (c), and top view (d), (e) and (f) of three molecular orientations of Na$_4$P$_2$O$_7$ on Fe(110)/Fe$_2$O$_3$(0001) surface. Sodium is presented in purple.
Figure 4.3 Side view (a), (b), and (c), and top view (d), (e) and (f) of three molecular orientations of Na$_3$PO$_4$ on Fe(110)/Fe$_2$O$_3$(0001) surface.

The geometrical optimization of the sodium phosphate on the Fe$_2$O$_3$ surface was carried out by DFT using GGA-PBE exchange-correlation functional. A plane wave basis set and the projector augmented-wave (PAW) method (PAW potentials) were used to model core potentials. The details about the dimension and number of atoms in these systems are listed in Table 4.1. Brillouin zone is sampled using Monkhorst – Pack scheme. For Fe and Fe$_2$O$_3$ systems, $4 \times 4 \times 1$ and $2 \times 4 \times 1$ k-points grids are used for the geometry optimization while the sets of $8 \times 8 \times 1$ and $4 \times 8 \times 1$ are used for high accurate electronic structure calculations. A cutoff energy of 450 eV was used for the plane wave basis set, and the convergence criteria of $10^{-4}$ and $10^{-3}$ were applied for the electronic wave function and the ionic relaxation during the optimization. Multiple interacting configurations of Na$_4$P$_2$O$_7$ and Na$_3$PO$_4$ on Fe(110) and Fe$_2$O$_3$(0001) surfaces are considered systematically with various adsorption sites and molecular orientations on the surfaces.
Table 4.1 Simulation models of Na₄P₂O₇ and Na₃PO₄ on Fe(110) and Fe₂O₃(0001) surfaces.

<table>
<thead>
<tr>
<th>System</th>
<th>Dimension (Å³)</th>
<th>No. layer</th>
<th>No. of atoms</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Na₄P₂O₇</td>
<td>11.46 × 12.16 × 19.15</td>
<td>3</td>
<td>85</td>
<td>72</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Fe-Na₃PO₄</td>
<td>11.46 × 7.10 × 19.15</td>
<td>3</td>
<td>56</td>
<td>48</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃-Na₄P₂O₇</td>
<td>17.44 × 10.07 × 19.97</td>
<td>6</td>
<td>93</td>
<td>80</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃-Na₃PO₄</td>
<td>8.72 × 10.07 × 19.97</td>
<td>6</td>
<td>48</td>
<td>40</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>

The interaction energies of sodium phosphate with Fe/Fe₂O₃ surfaces are calculated following equation 15. It is worth noting that the equation yields negative adsorption energies when the adsorbed system is more stable than the reactants, and the more negative energies indicate the more stable adsorbed systems.

\[
E_{\text{ads}} = E_{\text{total}} - (E_{\text{surface}} + E_{\text{mol}}) \tag{15}
\]

where, \( E_{\text{ads}} \) is the interaction energy between the Fe₂O₃ surface and Na₄P₂O₇/Na₃PO₄; \( E_{\text{total}} \), \( E_{\text{surface}} \), and \( E_{\text{mol}} \) are the total energy of Na₄P₂O₇/Na₃PO₄ adsorbed on the Fe₂O₃ surface, the energy of isolated Fe₂O₃, and the energy of isolated Na₄P₂O₇/Na₃PO₄ molecules, respectively.

The electronic structure of the systems was analyzed by calculating Bader charges, CDD, DOS, and BOP upon the adsorption. In this case, the antiferromagnetic Fe₂O₃ was used. In addition, GGA calculations usually underestimate the band gap for transition metals like iron.\(^\text{220}\) Meanwhile, Hubbard U correction\(^\text{221}\) usually provides more accurate electronic descriptions of frontier orbitals, which are the key to understand chemical reactions.\(^\text{222}\) An GGA + U with \( U_{\text{eff}} = 4 \text{eV} \) (\( U = 5 \text{ eV} \) and \( J = 1 \text{ eV} \)) was used in electronic structure calculations (DOS, charges) since those values have been indicated to provide comparable bulk lattice parameters and band gap to experimental measurements.\(^\text{201}\)
4.3 Sodium phosphate molecules

Sodium pyro- (Na₄P₂O₇) and ortho-phosphate (Na₃PO₄) are optimized by DFT calculations and the obtained structural parameters are presented in Table 4.2. The structures of Na₄P₂O₇ and Na₃PO₄ show a good agreement with the experimental data and other DFT calculations in terms of bond length and bond angle.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Current DFT *</th>
<th>Other DFT</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Na₄P₂O₇</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P – Oₖ</td>
<td>1.658</td>
<td>1.595a</td>
<td>1.631 – 1.642b</td>
</tr>
<tr>
<td>P – O</td>
<td>1.527 – 1.573</td>
<td>1.541</td>
<td>1.512 – 1.514b</td>
</tr>
<tr>
<td>P – P</td>
<td>3.06</td>
<td></td>
<td>2.936</td>
</tr>
<tr>
<td>O – Na</td>
<td>2.211 – 2.217</td>
<td></td>
<td>2.313 – 2.517b</td>
</tr>
<tr>
<td>Oₖ – P – O</td>
<td>105.3 – 108.9</td>
<td>99.7 – 112.3a</td>
<td>102.5 – 108.8b</td>
</tr>
<tr>
<td>O – P – O</td>
<td>108.8 – 116.6</td>
<td>111.6 – 112.3a</td>
<td>111.6 – 113.9b</td>
</tr>
<tr>
<td>P – Oₖ – P</td>
<td>134.9</td>
<td>134.6a</td>
<td>127.5b</td>
</tr>
<tr>
<td><strong>Na₃PO₄</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P – O</td>
<td>1.54 – 1.58</td>
<td>1.513 – 1.544c</td>
<td></td>
</tr>
<tr>
<td>Na – O</td>
<td>2.21 – 2.34</td>
<td>2.269 – 2.714c</td>
<td></td>
</tr>
<tr>
<td>O – P – O</td>
<td>107.9 – 108.9</td>
<td>108.23 – 110.24c</td>
<td></td>
</tr>
</tbody>
</table>

* The current DFT results are for the gas phase molecules.

a DFT calculation for H₂P₂O₅Na₂ cluster by Uchino and Ogata.223

b Experimentally determined structure of Na₄P₂O₇ at 22°C by Leung and Calvo.224

c Average values, experimentally determined crystal structure of Na₃PO₄·1/2H₂O by Averbuch-Pouchot and Dufif.225

4.4 Interaction on Fe(110) surface

4.4.1 Interaction modes and interaction energies

Na₃PO₄ and Na₄P₂O₇ structures were optimized on Fe surface at multiple adsorption sites and molecular orientations. Geometry optimization of those initial structures reveals that oxygen atoms of phosphates tend to interact with their nearest Fe atoms to establish Fe–O–P linkages, leading to a variety of phosphate-surface binding modes, such as, monodenate, bidentate, tridentate and tetradentate. Different binding modes obtained from the adsorption configurations of Na₃PO₄ and Na₄P₂O₇ on the Fe surface are presented in Figure 4.4. The binding modes are classified in terms of the
differences in the number of iron and oxygen atoms in Fe–O–P linkages. In particular, the geometry optimization of Na₄P₂O₇ on Fe surface yields three different interaction modes represented by eight stable configurations including bidentate- (binuclear (BB), trinuclear (BT) and tetranuclear (BTetra)); tridentate- (trinuclear (TT), tetranuclear (TTetra), pentanuclear (TP) and hexanuclear (TH)); and tetradaentate tetrnucler (Tetra-Tetra). For Na₃PO₄, there are also three different binding modes with seven representatives including monodentate- (mononuclear (MM), binuclear (MB), and trinuclear (MT)); bidentate (binuclear (BB), trinuclear (BT), and tetranuclear (BTetra)); and tridentate trinuclear (TT). There is no mono-dentate in the Na₄P₂O₇ system and tetra-dentate in the Na₃PO₄ system.

In general, the interaction energies range from −4.16 to −2.93 eV for Na₄P₂O₇ and from −4.17 to −2.45 eV for Na₃PO₄ adsorbed on Fe surface, respectively. The low adsorption energies of the two phosphates demonstrate a strong phosphate – iron interaction. There is a tendency of forming multi-bridge interaction and the interaction energy depends on the number of Fe–O–P bridges formed.¹⁵⁴,²²⁶ Systems with a large number of Fe-O bonds formed are more stable with lower adsorption energies than those with less Fe-O bonds. In particular, mono-dentate (MM) in Fe-Na₃PO₄ system is the least favorable binding mode with an adsorption energy of −2.45 eV (Figure 4.4i), followed by either bidentate (BB) or binuclear (MB) with Eₐds from −2.93 to −2.84 eV. From tridentate or trinuclear mode, there is no clear correlation between binding modes and interaction energies, but lower binding energies than mono- and bi- modes are obtained, i.e., from −4.17 to −3.21 eV. Tri-dentate mode with five Fe atoms bonded to oxygen atoms of the phosphate (TP) is the most stable configuration in Fe-Na₄P₂O₇ (Figure 4.4f) and bidentate mode with four Fe atoms bonded to two O (BTetra) is the most favorable one in Fe-Na₃PO₄ system (Figure 4.4n). This result is consistent with that observed by Zhong and Adams who reported the favorable tri-bridged over bi- and unidentate coordinations of vinyl phosphonic acids on the Al(111) surface.²²⁷
Figure 4.4 Different adsorption configurations of Na$_4$P$_2$O$_7$ and Na$_3$PO$_4$ on Fe surface. Each interaction mode is represented by two letters; the first one is related to the oxygen atoms in phosphate molecules involving Fe-O bonds, and the second one is the number of Fe atoms of the surfaces that bonded to oxygen atoms of the phosphates. M (mono-), B (bi-), T (tri-), Tetra (tetra-), P (pen-), and H (hexa-). Blue (Fe), Red (O), Purple (Na), Magenta (P). The name of the adsorption modes and color assignment are applied through this chapter.

In order to compare adsorption strength of Na$_4$P$_2$O$_7$ and Na$_3$PO$_4$ on Fe surface, we estimate the interaction energy per [−PO$_3$] group by dividing the interaction energy by number of phosphorus atoms in the phosphate, $\Delta E_1 = E_{ads}/n$; where, $n$ is the number of
\([-\text{PO}_3]\) groups and the results are shown in Table 4.3. Noticeably, \(\Delta E_i\) values for Fe-Na\(_3\)PO\(_4\) are much lower than those for Fe-Na\(_4\)P\(_2\)O\(_7\). In fact, \(\Delta E_i\) values of Na\(_3\)PO\(_4\) are nearly twice as large as those of Na\(_4\)P\(_2\)O\(_7\) for binding modes BB, BT, BTetra and TT, and substantially higher in other binding modes. It is noted that the interaction energy reflecting the binding strength of lubricant-surface systems has been proven to be correlated with its antiwear and adhesion capability.\(^{130-131}\) The lower interaction energies of Na\(_3\)PO\(_4\) indicate a stronger Fe-Na\(_3\)PO\(_4\) interaction and a better adhesion than Fe-Na\(_4\)P\(_2\)O\(_7\), which is consistent with the experimental finding of their antiwear performance,\(^47\) i.e. Na\(_3\)PO\(_4\) can reduce 90\% wear while it is only 82\% for Na\(_4\)P\(_2\)O\(_7\).

Table 4.3 Interaction energy (E\(_{\text{ads}}\)) and interaction energy per phosphate group \([-\text{PO}_3]\) (\(\Delta E_i\)) of Na\(_4\)P\(_2\)O\(_7\) and Na\(_3\)PO\(_4\) adsorbed on Fe surface. Energies are in eV.

<table>
<thead>
<tr>
<th>Interaction mode</th>
<th>Fe-Na(_4)P(_2)O(_7)</th>
<th>Fe-Na(_3)PO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BB</td>
<td>-2.93 (-1.47)</td>
<td>BB -2.85 (-2.85)</td>
</tr>
<tr>
<td>BT</td>
<td>-3.10 (-1.55)</td>
<td>BT -3.99 (-3.99)</td>
</tr>
<tr>
<td>BTetra</td>
<td>-3.76 (-1.88)</td>
<td>BTetra -4.17 (-4.17)</td>
</tr>
<tr>
<td>TT</td>
<td>-3.50 (-1.75)</td>
<td>TT -3.21 (-3.21)</td>
</tr>
<tr>
<td>TTetra</td>
<td>-3.86 (-1.93)</td>
<td>MM -2.45 (-2.45)</td>
</tr>
<tr>
<td>TP</td>
<td>-4.16 (-2.08)</td>
<td>MB -2.84 (-2.84)</td>
</tr>
<tr>
<td>TH</td>
<td>-3.94 (-1.97)</td>
<td>MT -3.55 (-3.55)</td>
</tr>
<tr>
<td>Tetra-Tetra</td>
<td>-3.66 (-1.83)</td>
<td>- - -</td>
</tr>
</tbody>
</table>

In the adsorbed stage, phosphate molecules anchor to the surface with Fe-O distances ranging from 1.82 to 2.20 Å, depending on the binding mode. The shortest Fe-O distance of 1.82 Å is achieved in MM, where O directly anchors on the top of Fe surface (Figure 4.4i). For other configurations, the average distance is around 2.0 Å, which is typical for Fe-O chemical bonds in other Fe-phosphate complexes;\(^{217, 228}\) for instance, Fe-O distance in iron phosphate clusters 1.92 to 2.14 Å,\(^{216-218}\) and 1.98 to 2.0 Å which is defined for Fe–O distances in Fe\(_2\)O\(_3\) bulk system.\(^{229}\) Additionally, the obtained Fe-O distance in this work is close to the covalent bond length between O and Fe (1.98 Å), which is defined by the summation of O and Fe covalent radii (0.66 Å for O and 1.32 Å for Fe).\(^{230}\) These results suggest that Fe–O chemical bonds are formed as a result of the interactions between alkali phosphates and Fe surface, indicating a
chemical adsorption process.

Furthermore, alkali phosphates undergo a significant molecular distortion in phosphate groups especially the elongation of P–O bonds in P–O–Fe linkages. The greater bond lengthening was found for mono-dentate and bidentate modes, and the P-O bond lengthening in Na₃PO₄ is larger than that in Na₄P₂O₇. In fact, P–O bonds are elongated from the initial 1.53 Å of the isolated Na₄P₂O₇ (Table 4.2) to 1.56 Å (in BB) and 1.62 Å (in TP) of the adsorbed Na₄P₂O₇. Moreover, the longest P–O bond obtained in Na₄P₂O₇ is 1.62 Å, which belongs to the lowest adsorption energy configuration (TP). Meanwhile, P-O bond is 1.57 Å in isolated Na₃PO₄, in mono-dentate of adsorbed Fe-Na₃PO₄, this bond is elongated up to 1.66 Å (in MB) and 1.71 Å (in MT), and the average P–O distance in other structures is around 1.62 Å. This can be explained by the stronger Fe-Na₃PO₄ interaction than that of Fe- Na₄P₂O₇, leading to a greater P–O bond lengthening with Na₃PO₄ than that found with Na₄P₂O₇. In addition, bond lengthening can also result in the weakening of P-O bonds and this will be discussed in the next section.

Phosphate molecules also undergo the structural bending to adapt for the bond formation with the surface in the adsorbed states. The bending occurs mainly at the P–O–P bridges where bridging oxygen connects two PO₃ groups. More severe changes are witnessed in low-energy configurations. As can be seen in Figure 4.4, there is almost no change at P–O–P angles in bidentate modes (Figure 4.4a, b, and c), whilst the shape of P–O–P angles are broadened in TTetra (Figure 4.4e) and narrowed in TP (Figure 4.4f) and Tetra-Tetra (Figure 4.4h), respectively. Those changes are attributed to the formation of Fe–O–P bonds in each PO₃ group of the Na₄P₂O₇ unit. Therefore, more Fe–O–P bonds formed in tridentate (Figure 4.4e) and tetradentate (Figure 4.4f) lead to more significant P₂O₇ structural bending. In Fe-Na₃PO₄, due to the absence of P–O–P bridges, modest geometrical modification occurs as the adsorption only affects the local PO₄ unit (Figure 4.4i-o).

Overall, the optimized structures of Na₃PO₄ and Na₄P₂O₇ on Fe surface suggest a strong chemical adsorption with a variety of interaction modes through Fe–O–P linkages. In comparison, interaction strength of Na₃PO₄ on Fe surface is stronger than that of Na₄P₂O₇, which is consistent with their antiwear performance measured by the experiment.⁴⁷
4.4.2 Electronic structure

The strength of the interaction of the sodium phosphates on the Fe surface depends on the type of the interaction, which in turn, is originated from the electronic structure transformation inside the system. As presented in the previous section, despite multiple interaction modes observed, the attachment of phosphate on the surface is consistently through P–O–Fe bridges. For this reason, only the most favorable configuration of each system is selected for further electronic structure analyses, i.e., TP for Na$_4$P$_2$O$_4$ and BTetra for Na$_3$PO$_4$ on Fe(110) surface, respectively.

CDD which visualizes the redistribution of the electron density in the system during the adsorption is presented in Figure 4.5. The result reveals that Fe-phosphate interactions perturb the electronic distribution of the system, particularly at the Fe–O–P linkages in the first layer. This is confirmed by the Bader charge analysis in Table 4.4 as the major charge modification occurs at the first layer of the surface i.e., 0.125e, 0.115e for Fe-Na$_4$P$_2$O$_7$ and Fe-Na$_3$PO$_4$, respectively. This magnitude of Δ$q_i$ is reduced when moving inward lower layers and minor change is observed for the third layer; in particular, the charge difference is negligible around 0.006e. In addition, there are massive electron depletion regions around P and Fe (Fe1-Fe5 in Fe-Na$_4$P$_2$O$_7$ and Fe1-Fe3 in Fe-Na$_3$PO$_4$) of the Fe–O–P, while O (O1-O3) and Fe atoms near Na (Fe5-Fe9) accumulate electron (Figure 4.5b, 3d and Table 4.4). The charge loss on phosphate molecules is due to the electron withdrawal from P–O to share with Fe, resulting in P–O bond elongation observed in the previous section. However, the total charge transfer of the surface and molecules suggests that during the interaction phosphate molecules lose charge while iron surface gains charge. Most of the charge loss from the molecule is donated to the surface as the surfaces gain total 0.261e and 0.258e while Na$_4$P$_2$O$_7$ and Na$_3$PO$_4$ donate 0.182e and 0.201e, respectively (Table 4.4). The back-donation electron from the surface to phosphate is also found by charge accumulation around O$_p$, but the donation from phosphate to surface is stronger and dominates the interaction. This suggests a donor–acceptor interaction mechanism through Fe–O–P bonds by charge transfer, where phosphates act as donors and the Fe surface acts as an acceptor. This result is similar to what proposed by Kalyani et al. and Jaiswal et al.,$^{132, 213}$ who reported the possibility of lubricant additives to donate their electrons to the iron surface. The underlying bonding mechanism holds true for both Fe-Na$_4$P$_2$O$_7$ and Fe-Na$_3$PO$_4$ systems indicating that the strength of the iron–phosphate interaction is apparently dependent on
the number of atoms in the surfaces and the molecules involved in Fe–O–P bonds.

![Figure 4.5 CDD for the most favorable configuration in each system: Fe-Na₄P₂O₇ TP mode (a) side view, (b) top view, and Fe₂O₃-Na₃PO₄ system BB mode (c) side view and (d) top view. The yellow and cyan represent the positive (electron accumulation) and negative (electron depletion) regions, respectively. Isosurfaces are 0.007 e/Å³ for (a) and (c) and 0.004 e/Å³ for (b) and (d). For clarity, sodium ions in (a) and (c) have been removed, and only the topmost layer of the surface is shown.](image)

There is no significant difference in the total charge transfer of Fe-Na₄P₂O₇ and Fe-Na₃PO₄ systems as their adsorption energies and interaction strength are similar. Additionally, no significant density difference is observed around sodium ions, as sodium is a hard metal which usually interact through weakly polarization contribution. Consequently, Na only forms weak ionic bonds with its adjacent atoms such as oxygen or iron and result in the electron accumulation around Fe atoms (Fe5-Fe9) nearby due to the polarization effect from positive charged Na (Figure 4.5b, d). This ionic bond can make sodium more mobile during the shearing process, generating mixed sodium–iron–phosphate surface complexes.
Table 4.4 Charge transfer by the Bader charge analysis method for alkali phosphates adsorbed on Fe surface (unit e). $\Delta q_1$, $\Delta q_2$, and $\Delta q_3$ are the absolute values of average charge transfer per atom in the 1st, 2nd, and the 3rd layer, respectively. $q_{Fe}$ and $q_{mol}$ are the total charge transfer of the iron surface, and alkali phosphate molecules, respectively. (–) and (+) mean charge loss and charge gain, respectively.

<table>
<thead>
<tr>
<th>System</th>
<th>Surface</th>
<th>Mol.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta q_1$</td>
<td>$\Delta q_2$</td>
</tr>
<tr>
<td>Fe-Na$_4$P$_2$O$_7$</td>
<td>0.125</td>
<td>0.018</td>
</tr>
<tr>
<td>TP mode</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-Na$_3$PO$_4$</td>
<td>0.115</td>
<td>0.022</td>
</tr>
<tr>
<td>BTetra mode</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Additional insights into the electronic structure of iron – alkali phosphates interactions can be seen from partial electronic density of state (PDOS) in Figure 4.6. At the isolated state, PDOS of oxygen atoms in both Na$_3$PO$_4$ and Na$_4$P$_2$O$_7$ shows sharp peaks implying the localized molecular orbitals. Partial charge decomposition corresponding to their energy levels of these phosphate molecules is presented in Figure 4.7. It can be clearly seen that those peaks that are closest to the Fermi level belong to the lone pair orbitals of oxygen as they do not share electrons with either phosphorus or sodium. Those frontier orbitals play a crucial role in HOMO – LUMO interaction of lubricant additive and metal surface because of their capability in donating electron to the vacancies of iron atoms.$^{132, 213}$
Figure 4.6 PDOS of Fe and O atoms in isolated phosphates and adsorbed on Fe surfaces: (a) isolated Na$_4$P$_2$O$_7$, and (b) adsorbed Na$_4$P$_2$O$_7$ on Fe surface, (c) isolated Na$_3$PO$_4$, (d) adsorbed Na$_3$PO$_4$ on Fe surface. The horizontal scales are set differently for the (a), (c) and (b), (d).

When adsorbed on Fe surface, all states of oxygen atoms are homogeneously downshifted far away from the Femi level, meaning that bonding interaction occurs and the systems get more favorable than the isolated ones. The chemical reaction mainly takes place at the high energy levels, where witness profound overlaps in a wide range from -9 to -3 eV between valence orbitals, i.e., lone pairs (2p) of oxygen and 3d/4s orbitals of iron, but the greater contribution is from Fe 3d. As a result, oxygen’s lone pairs with initially sharp peaks are hybridized with Fe 3d and become smeared and broadened band from -7 eV to -3 eV because of the electron delocalization to transfer between oxygen and iron, especially electron shared between oxygen’s lone pairs and partially unfilled d band of iron, establishing the donor – acceptor mechanism$^{232}$ as discussed previously. The peaks located in the low energy levels between -12 and -7 eV are also smeared by the profound effects from the surface. The whole hybridization region is distributed in a wide energy range below the Femi level, which again confirms the bonding interaction and Fe–O covalent bond formed.
Figure 4.7 Total density of state (TDOS) and corresponding electronic band decomposition of Na$_4$P$_2$O$_7$ and Na$_3$PO$_4$.

The strength of Fe–O bonds was evaluated by bond overlap population (BOP) which quantitatively measures the magnitudes of shared electrons between two atoms. Accordingly, BOP value close to zero means there is no significant interaction between the electronic populations of the two atoms, i.e., ionic bond, while value greater than zero indicates increasing levels of covalence. In our calculation, BOP values of Fe–O bonds range from 0.160 $e$ to 0.230 $e$ in Fe-Na$_3$PO$_4$ and from 0.090$e$ to 0.232$e$ in Fe-Na$_4$P$_2$O$_7$, while BOP of Na-O ionic bonds are of small values 0.074$e$ and 0.078$e$, and negative values of $-0.026e$ and $-0.052e$ are attributed to anti-bonding Fe-Fe and Fe-Na, respectively (Table 4.5). This demonstrates that Fe–O bonds are covalent bonds and their strength is quantitatively comparable with P-O bonds in Fe–P–O linkages, which also confirms the adhesion capability of the alkali phosphate to metal surface. Therefore, iron – phosphate reaction provides a predominant well-adhered layer stuck on the surface that can withstand the detachment under tribo-stressed conditions. In addition, Na atoms do not form any stable bond with phosphates or iron surface as neither Na-Fe nor Na–O ionic bonds are strong interactions. Their interaction is mainly
based on electrostatics that can be flowed from the surface if the surface is predominantly covered by chemi-adsorbed Fe–O–P precursors. During the shearing process, there could be a mixed layer of Na, Fe, and those phosphates that are not bonded to Fe supported by the underlying Fe–O–P film.

Table 4.5 Bond Overlap Population (BOP) of ionic and covalent bonds in adsorbed Fe–Na$_4$P$_2$O$_7$ and Fe–Na$_3$PO$_4$ systems. Atomic orders follow the orders in the CDD in Figure 4.5.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>BOP (e)</th>
<th>Bond</th>
<th>Distance (Å)</th>
<th>BOP (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1-O1</td>
<td>2.03</td>
<td>0.175</td>
<td>Fe1-O1</td>
<td>2.08</td>
<td>0.174</td>
</tr>
<tr>
<td>Fe2-O1</td>
<td>2.27</td>
<td>0.090</td>
<td>Fe2-O1</td>
<td>2.07</td>
<td>0.168</td>
</tr>
<tr>
<td>Fe3-O2</td>
<td>2.02</td>
<td>0.232</td>
<td>Fe3-O2</td>
<td>2.06</td>
<td>0.178</td>
</tr>
<tr>
<td>Fe4-O3</td>
<td>2.13</td>
<td>0.142</td>
<td>Fe4-O2</td>
<td>2.07</td>
<td>0.160</td>
</tr>
<tr>
<td>Fe5-O3</td>
<td>2.03</td>
<td>0.176</td>
<td>P-O1</td>
<td>1.62</td>
<td>0.230</td>
</tr>
<tr>
<td>O1-P1</td>
<td>1.62</td>
<td>0.221</td>
<td>P-O2</td>
<td>1.63</td>
<td>0.228</td>
</tr>
<tr>
<td>O3-P2</td>
<td>1.59</td>
<td>0.255</td>
<td>O - Na$^a$</td>
<td>2.35</td>
<td>0.077</td>
</tr>
<tr>
<td>O - Na$^a$</td>
<td>2.36</td>
<td>0.074</td>
<td>Fe - Fe$^b$</td>
<td>2.57</td>
<td>-0.026</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe - Na$^b$</td>
<td>3.12</td>
<td>-0.052</td>
</tr>
</tbody>
</table>

$^a$ averaged values of four Na–O bonds in Na$_4$P$_2$O$_7$ and three Na–O bonds in Na$_3$PO$_4$.
$^b$ averaged values for the closest Fe-Fe in Fe–Fe–O–P and the closest Fe–Na distances.

4.5 Interaction on Fe$_2$O$_3$(0001) surface

4.5.1 Adsorption modes and adsorption energies

Geometry optimization of those initial structures reveals that oxygen atoms of phosphates tend to interact with their nearest Fe atoms to establish Fe–O–P linkages, leading to a variety of phosphate – surface binding modes, such as, monodenate, bidentate, trideterminate and tetradeinate. Different binding modes obtained from the adsorption configurations of Na$_3$PO$_4$ and Na$_4$P$_2$O$_7$ on the Fe$_2$O$_3$ surface are presented in Figure 4.8. The binding modes are classified in terms of the differences in the number of iron and oxygen atoms in Fe–O–P linkages. In particular, the geometry optimization of Na$_4$P$_2$O$_7$ on the Fe$_2$O$_3$ surface yields three different interaction modes represented by 4 stable configurations including monodenate-monomonuclear (MM), bidentate-monomonuclear (BM), bidentate-binuclear (BB) and trideterminate-trinuclear (TT). For Na$_3$PO$_4$, there are also three different binding modes with 3 representatives including
monodentate-mononuclear (MM), bidentate-binuclear (BB), and tridentate trinuclear (TT).

Figure 4.8 Different adsorption configurations of Na₄P₂O₇ and Na₃PO₄ on Fe₂O₃ surface.

For the adsorption on Fe₂O₃ surface, three interaction modes of mono-dentate, bidentate and tri-dentate are observed for both Fe₂O₃-Na₄P₂O₇ and Fe₂O₃-Na₃PO₄ systems. There is one O_p anchoring on the top of one Fe atom except for configuration BM (Figure 4.8b) where one Fe atom bonds to two oxygen atoms of the phosphate (O_p). This can be explained by the sparse iron terminated atom distribution on the Fe₂O₃ surface, while the bond is expected to occur between Fe and O_p. In Fe₂O₃-Na₄P₂O₇, bidentate as shown in Figure 4.8c is the most energetically favorable structure (E_ads = −3.93 eV) while it is mono-dentate in Figure 4.8(e) for Fe₂O₃-Na₃PO₄ system (E_ads = −3.65 eV). Both of them have oxygen (O_p) located on the top of Fe atoms, which means end-on mode is preferable than multi-point binding interaction like that found on the pure iron surface. Bidentate binuclear has been found to be predominant adsorption mechanism at lower coverage on goethite surface, while monodentate complexes are more likely to be formed on gibbsite. In our calculation, tri-dentate mode has been found although it is less energetically favorable than the other two modes. However, under severe loads and shearing rate, it is possible to generate the mixed adsorbed
Table 4.6 Interaction energy (E_{ads}) and interaction energy per phosphate group [-PO3] (ΔE1) of Na4P2O7 and Na3PO4 adsorbed on Fe2O3 surface. Energies are in eV.

<table>
<thead>
<tr>
<th>Interaction mode</th>
<th>Fe2O3-Na4P2O7</th>
<th>Fe2O3-Na3PO4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E_{ads}</td>
<td>ΔE1</td>
</tr>
<tr>
<td>MM</td>
<td>-2.47</td>
<td>-1.24</td>
</tr>
<tr>
<td>BM</td>
<td>-2.32</td>
<td>-1.16</td>
</tr>
<tr>
<td>BB</td>
<td>-3.93</td>
<td>-1.97</td>
</tr>
<tr>
<td>TT</td>
<td>-3.50</td>
<td>-1.75</td>
</tr>
</tbody>
</table>

P–O bond elongation has been found in Fe2O3-phosphates analogous to what has been obtained on the Fe surface. Briefly, we only focus on the different behaviors of phosphates adsorbed on these two different surfaces. One thing worth emphasizing is that Fe–O_p bonds in end-on binding mode, i.e., MM and BB, are shorter than those in side-on mode, which is attributed to their lower interaction energies trend. Remarkably, there is no bond formation between Fe of Fe2O3 surface and bridging oxygen (P–O–P/O_b) of Na4P2O7. This could be due to the fact that bridging oxygen is less chemically active than non-bridging oxygen and Fe2O3(0001) surface has fewer Fe-terminated points than Fe(110) surface. Furthermore, comparison of interaction energy per phosphate group of Na3PO4 and Na4P2O7 on Fe2O3 surface (Table 4.6) yields the same conclusion to that has been drawn for phosphates on Fe surface; in particular, the binding strength of Na3PO4 on both Fe and Fe2O3 surfaces is always greater than that of Na4P2O7. This agrees well with the experiment as the trend holds true for both iron and its oxide surfaces.

4.5.2 Electronic structure

Both CDD in Figure 4.9 and the Bader charge calculation in Table 4.7 reveal that electron redistribution mainly occurs on the 1st layer of the surface where Fe bonds to O_p of the phosphates. The Bader analysis indicates that an average of 0.087e for Na4P2O4 and 0.103e for Na3PO4 is lost or gained at the 1st layer of Fe2O3 surface. While that value drops dramatically to 0.027e, 0.008e, and 0.005e for the 2nd, 3rd and 4th, 5th and 6th layer for Fe2O3–Na4P2O7 system, respectively. Similar trend is found in Fe2O3–Na3PO4 as the charge transfer per atom is 0.27e for the 2nd layer, 0.005e for the 3rd and
0.006\(e\) for the 4\textsuperscript{th}, 5\textsuperscript{th} and 6\textsuperscript{th} layer. Besides, CDD shows massive electron accumulation and depletion areas around Fe–O–P linkages, indicating profound interaction through Fe–O chemical bond formation.

Figure 4.9 CDD for the most favorable configuration in each system: \(\text{Fe}_2\text{O}_3\)-Na\textsubscript{4}P\textsubscript{2}O\textsubscript{7} BB mode (a) side view, (b) top view, and \(\text{Fe}_2\text{O}_3\)-Na\textsubscript{3}PO\textsubscript{4} system MM mode (c) side view and (d) top view. The yellow and cyan represent the positive (electron accumulation) and negative (electron depletion) regions, respectively. Isosurfaces are 0.005 \(e/\text{Å}^3\) for (a) and (c) and 0.004 \(e/\text{Å}^3\) for (b) and (d). \(\text{O}_8\) is oxygen of the surface. For clarity, only the topmost layers of the surface are shown.

Unlike interaction on Fe surface, charge transfer in \(\text{Fe}_2\text{O}_3\) – alkali phosphate systems is through mutual electron transfer between the surface and the molecules. In fact, CDD presented in Figure 4.2 shows alternative distribution of accumulation and depletion regions around Fe and O\textsubscript{p} atoms, meaning that O\textsubscript{p} and Fe can simultaneously gain and lose charge when Fe–O\textsubscript{p} bonds are formed. This suggests a donation/back-donation mechanism that happens in transition metal-ligand systems when they have similar HOMO and LUMO.\textsuperscript{236-237} Density of state showing the comparability of the gaps in the Fe of \(\text{Fe}_2\text{O}_3\) surface and the isolated Na\textsubscript{3}PO\textsubscript{4} is presented in Figure 4.10. In this case, the highest occupied non-bonding \(p\) orbitals of alkali phosphate share their
electrons with the partially unfilled $d$ orbitals of iron (donation), and alternatively a part of electrons in Fe transfers back to the anti-bonding states of the lubricant creating back-donation interaction. Partial band decomposition reveals that the HOMO of lubricant molecules is located at the lone-pairs of oxygen atoms (Figure 4.7). In Na$_4$P$_2$O$_7$, the peaks 1 to 4 are the states of non-bonding orbitals of oxygen atoms. From peak 5, there are hybridizations of orbitals in Na$_4$P$_2$O$_7$. A vast majority of electrons are from non-bridging oxygen while only a small contribution is from bridging oxygen (peak 2). For Na$_3$PO$_4$, non-bonding states are distributed in energy range between $-1$ and 0 eV.

Table 4.7 Charge transfer by the Bader charge analysis method and Bond Overlap Population (BOP) for alkali phosphates adsorbed on Fe$_2$O$_3$ surfaces. $\Delta q_i$ is the absolute average charge transfer per atom in the $i$th layer. $\Delta q_{4,5,6}$ is the absolute average charge transfer per atom in the 4$^\text{th}$, 5$^\text{th}$ and 6$^\text{th}$ layers. $q_s$ and $q_{mol.}$ are the total charge transfer of the surface and alkali phosphate molecules, respectively. (–) means charge gain, and (+) means charge loss.

<table>
<thead>
<tr>
<th>System</th>
<th>Charge transfer (e)</th>
<th>BOP (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta q_1$</td>
<td>$\Delta q_2$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-Na$_4$P$_2$O$_7$, BB mode</td>
<td>0.087</td>
<td>0.027</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-Na$_3$PO$_4$, MM mode</td>
<td>0.103</td>
<td>0.027</td>
</tr>
</tbody>
</table>
Figure 4.10 PDOS of Na$_3$PO$_4$ and iron atoms of Fe$_2$O$_3$(0001) surface in the isolated and adsorbed systems: (a) isolated Fe$_2$O$_3$ surface, (b) isolated Na$_3$PO$_4$, and (c) Fe$_2$O$_3$-Na$_3$PO$_4$. For iron, only the atoms at the first layer are used. mol.s and mol.p are the s and p states of the total DOS of Na$_3$PO$_4$, respectively.

The donation/back-donation interaction regime strengthens Fe−O$_p$ bond, yet weakens the remaining part O$_p$−P bond in the Fe−O−P linkage because the electron withdrawal from P−O$_p$ bonds. In comparison, the donation interaction is stronger than the back-donation one as the Bader charge analysis result shows charge loss on phosphate and charge gain on the surface. In fact, the total charge gain of the surface is 0.557$e$ and 0.552$e$, and the charge loss of the phosphates is 0.463$e$ and 0.491$e$ for Fe$_2$O$_3$-Na$_4$P$_2$O$_7$ and Fe$_2$O$_3$-Na$_3$PO$_4$, respectively. However, the donation and back-donation strength cannot be used as the evidence for evaluating the contribution of them to the bond strength.
Table 4.8 Bader charges (e) and charge transfer (e) of some atoms in adsorbed phosphates on the Fe$_2$O$_3$ surface. $q_i$ and $q_a$ are the charges of atoms in the isolated and adsorbed systems, respectively. For Bader charges ($q_i/q_a$), (−) means negative charge, (+) for positive charge is not shown here. For charge transfer ($\Delta q$), (−) means charge gain and (+) means charge loss. Only atoms that have significant charge differences in the CDD are presented. The order of atoms follows the order in the CDD in Figure 4.2.

<table>
<thead>
<tr>
<th>Surface atom</th>
<th>$q_i$</th>
<th>$q_a$</th>
<th>$\Delta q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1</td>
<td>1.214</td>
<td>1.416</td>
<td>+0.202</td>
</tr>
<tr>
<td>Fe2</td>
<td>1.214</td>
<td>1.404</td>
<td>+0.190</td>
</tr>
<tr>
<td>O$_1$</td>
<td>−0.841</td>
<td>−0.926</td>
<td>−0.085</td>
</tr>
<tr>
<td>O$_2$</td>
<td>−0.845</td>
<td>−0.912</td>
<td>−0.067</td>
</tr>
<tr>
<td>O$_3$</td>
<td>−0.836</td>
<td>−0.915</td>
<td>−0.078</td>
</tr>
<tr>
<td>O$_4$</td>
<td>−0.841</td>
<td>−0.888</td>
<td>−0.047</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alkali phosphate atom</th>
<th>$q_i$</th>
<th>$q_a$</th>
<th>$\Delta q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>−1.499</td>
<td>−1.319</td>
<td>+0.180</td>
</tr>
<tr>
<td>O2</td>
<td>−1.482</td>
<td>−1.359</td>
<td>+0.123</td>
</tr>
<tr>
<td>Na1</td>
<td>0.870</td>
<td>0.843</td>
<td>−0.027</td>
</tr>
<tr>
<td>Na2</td>
<td>0.853</td>
<td>0.868</td>
<td>+0.015</td>
</tr>
<tr>
<td>P1</td>
<td>3.516</td>
<td>3.606</td>
<td>+0.090</td>
</tr>
<tr>
<td>P2</td>
<td>3.541</td>
<td>3.624</td>
<td>+0.083</td>
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</table>

<table>
<thead>
<tr>
<th>Surface atom</th>
<th>$q_i$</th>
<th>$q_a$</th>
<th>$\Delta q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe1</td>
<td>1.212</td>
<td>1.401</td>
<td>+0.189</td>
</tr>
<tr>
<td>O$_1$</td>
<td>−0.841</td>
<td>−0.925</td>
<td>−0.084</td>
</tr>
<tr>
<td>O$_2$</td>
<td>−0.844</td>
<td>−0.925</td>
<td>−0.081</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alkali phosphate atom</th>
<th>$q_i$</th>
<th>$q_a$</th>
<th>$\Delta q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>−1.501</td>
<td>−1.166</td>
<td>+0.335</td>
</tr>
<tr>
<td>O2</td>
<td>−1.507</td>
<td>−1.418</td>
<td>+0.088</td>
</tr>
<tr>
<td>Na1</td>
<td>0.865</td>
<td>0.876</td>
<td>+0.011</td>
</tr>
<tr>
<td>Na2</td>
<td>0.873</td>
<td>0.860</td>
<td>−0.013</td>
</tr>
<tr>
<td>Na3</td>
<td>0.854</td>
<td>0.847</td>
<td>−0.006</td>
</tr>
<tr>
<td>P</td>
<td>3.513</td>
<td>3.510</td>
<td>−0.004</td>
</tr>
</tbody>
</table>

On the other hand, the donation/back-donation interaction mechanism results in different behaviors in Fe-O$_p$ bonds on the Fe$_2$O$_3$ surface. Apparently, BOP values of Fe-O$_p$ bonds are 0.263e, 0.265e in Fe$_2$O$_3$-Na$_4$P$_2$O$_7$ and 0.328e in Fe$_2$O$_3$-Na$_3$PO$_4$. This could be related to the interaction of O$_p$ 2p orbitals with 3dz$^2$ orbitals of Fe as CDD in Figure 4.9a and c show the shape of dz$^2$ orbital around Fe atoms. Therefore, stronger $\sigma$ bonds are supposed to form between Fe and O$_p$ through end-on binding mode, and closer Fe–O$_p$ distances are achieved i.e., 1.81 Å for MM, and 1.86/1.87 Å for BB. This also explains why oxygen O$_p$ prefers to attach on the top of Fe atoms.

4.6 Bond transformation

In tribological application, bond transformation in phosphate chains is important as it can predict the polymerization or depolymerization occurring in tribo-systems. Those structural transformations can affect friction and wear performance such as
hardening the tribofilm. In our work, during the reaction on iron surface, Na₄P₂O₇ and Na₃PO₄ undergo the molecular distortion with different levels depending on their interaction strengths and binding modes. The distortion includes changing in bond lengths as discussed in the Section 4.4, resulting in the electronic structure transformation, which is attributed to the electrons moving through the systems. Detailed calculation of electronic structure has been performed and analyzed to understand the specific transformation in the adsorbed systems.

Figure 6 presents BOP of all four P–O bonds in Na₃PO₄ in the isolated and adsorbed states of all seven Fe-Na₃PO₄ configurations. It is noted that in the isolated Na₃PO₄, BOP values for four P–O bonds are nearly the same, i.e., 0.287e, 0.30e, 0.298e and 0.302e, and they are averaged to 0.30e and denoted by black circles. On the contrary, BOP values of the adsorbed Na₃PO₄ show substantial deviations from that of the isolated ones. In fact, lower BOP values belong to P–O bonds in P–O–Fe bridges, while the higher ones represent the remaining P–O bonds in PO₄ group (Figure 4.11). The number of P–O bonds with lower BOP is exactly equal to the number of P–O–Fe bonds; in particular, one for monodentate, two for bidentate and three for tridentate. The more iron atoms bind to oxygen, the weaker P–O bonds become. For instance, in monodentate mode, the influence of the surface on P–O–Fe bonds follows the order: tridentate > bidentate > monodentate. This originates from the electron withdrawal from P–O bonds to share with Fe in Fe–O bonds as observed in CDD in Figure 4.5. Consequently, this leads to the simultaneous bond strengthening and weakening in P–O–Fe bonds of the phosphates.

![Figure 4.11 BOP (e) of P–O bonds in Na₃PO₄ in the isolated and adsorbed states. The](image-url)
BOP values after adsorption are independent in each configuration. The colors and symbols are only for the identification of different bonds. $\text{P}−\text{O}−\text{Fe}$ means the $\text{P}−\text{O}$ bonds in $\text{Fe}−\text{O}−\text{P}$ linkages, and $\text{ads. P}−\text{O}$ means the remaining $\text{P}−\text{O}$ bonds of $\text{Na}_3\text{PO}_4$.

Although $\text{P}−\text{O}$ bonds in $\text{P}−\text{O}−\text{Fe}$ are weakened significantly due to the effect of reactions on the metal surface, their BOP values are still high. For example, the lowest BOP value of $0.14e$ is found for MT configuration, and averaged values of $0.18e$, $0.24e$, and $0.27e$ for monodentate, bidentate, and tridentate binding mode respectively, which are as large as BOP magnitudes of newly formed $\text{Fe}−\text{O}$ bonds. This means that $\text{P}−\text{O}$ bonds are hardly broken even under adsorbed stage.

For $\text{Na}_4\text{P}_2\text{O}_7$, the existence of bridging oxygen ($\text{O}_b$) generates different characteristics compared to $\text{Na}_3\text{PO}_4$. BOP of isolated $\text{Na}_4\text{P}_2\text{O}_7$ presented in Figure 4.12a shows that BOP of $\text{P}−\text{O}_b$ is $0.20e$ while for other $\text{P}−\text{O}$ are considerably higher of $0.30e$, $0.34e$, and $0.36e$. This demonstrates that $\text{P}−\text{O}_b$ is the weakest bond among $\text{P}−\text{O}$ bonds, making it the easiest one to be broken in the reacted phase. BOP values of two adsorbed configurations on Fe surface: the most stable one (TP) and the one which has $\text{O}_b$ bonded to Fe (TH), and the most stable configuration on $\text{Fe}_2\text{O}_3$ surface (BB) are also collected to compare with those of the isolated state (Figure 4.12b-d). One can see that $\text{P}−\text{O}$ bonds undergo severe bond weakening analogous to what found in adsorbed $\text{Na}_3\text{PO}_4$, but there is little change occurred in $\text{P}−\text{O}_b$ bonds. In fact, in Fe-$\text{Na}_4\text{P}_2\text{O}_7$, BOP of $\text{P}−\text{O}$ bonds in $\text{Fe}−\text{O}−\text{P}$ linkages changes dramatically from $0.30e/0.36e$ to $0.23e$ or $0.17e$, while those values of $\text{P}−\text{O}_b$ are almost unchanged in TP, and drop slightly from $0.20e$ to $0.17e$ and $0.18e$ in TH when $\text{O}_b$ is bonded to Fe. Also, on the $\text{Fe}_2\text{O}_3$ surface, the BOP values of $\text{P}−\text{O}$ bonds (in $\text{Fe}−\text{O}−\text{P}$) reduce to $0.27e/0.28e$, while those of $\text{P}−\text{O}_b$ keep unchanged. However, compared to the newly formed Fe-O bonds, the BOP values of both $\text{P}−\text{O}$ bonds (in $\text{Fe}−\text{O}−\text{P}$) and $\text{P}−\text{O}_b$ in Fe-$\text{Na}_4\text{P}_2\text{O}_7$ are significantly higher while they are comparable in $\text{Fe}_2\text{O}_3$-$\text{Na}_4\text{P}_2\text{O}_7$. This emphasizes that $\text{P}−\text{O}_b$ is as stable as $\text{P}−\text{O}−\text{Fe}$ bond and it is hard to break either $\text{P}−\text{O}$ or $\text{P}−\text{O}_b$ bond even in the reaction with the surfaces. This result supports experimental finding by Cui et al. as no bond breaking or depolymerization observed in both $\text{Na}_3\text{PO}_4$ and $\text{Na}_4\text{P}_2\text{O}_7$ structures through the tribo-test.\textsuperscript{47}
Figure 4.12 BOP of P–O, P–O₆, and Fe–O bonds in the isolated and the adsorbed Na₄P₂O₇ on Fe and Fe₂O₃ surfaces. Sodium has been removed for clarity.

Overall, electronic structure calculations of bond transformation have demonstrated that both short chain orthophosphate (Na₃PO₄) and pyro-phosphate (Na₄P₂O₇) resist to polymerize on the metal surfaces although they suffer from geometrical distortion and electronic transformation, which is in accordance with the experimental results.⁴⁷

4.7 Discussion

Adsorption energies reported in Table 4.3 and Table 4.6 indicated that alkali phosphates adsorbed on Fe/Fe₂O₃ surface with lower energies than those of other phosphates on metal surfaces; for example, −1.99 eV for trimethyl phosphite on Fe(110) surface,¹⁵⁴ and −39 to −25 kJ/mol (−0.40 to −0.26 eV) by experiment,²¹⁹ but they are comparable to those for H₃PO₄ complexes on (110) goethite surface, i.e., from −3.43 to −1.48 eV.²³⁸ Generally, that data has been reported on different surfaces such as goethite surface,²³⁸ mixed Al-Fe hydro(oxide) surface²¹⁹ with various phosphate compounds. Unfortunately, experimental data for such alkali phosphate adsorption on the metal surface have not been available at the moment. However, the adsorption of sodium does contribute to the obtained low interaction energies because of electrostatic interaction between charged Na atoms and the surfaces.²⁰⁷ On the other hand, current density functional theory calculations yield excellent results of Fe–O bond length as
compared to other simulation results\textsuperscript{217-218} and experiments.

On both Fe and Fe\textsubscript{2}O\textsubscript{3} surfaces, phosphate chains are attached to the surface by Fe–O–P bonds, but the binding modes of them are rather different. In particular, phosphates bind to Fe surface through multipoint interaction of one oxygen atom (O\textsubscript{p}) and two or more Fe atoms, while on Fe\textsubscript{2}O\textsubscript{3} surface only one Fe binds to one O\textsubscript{p} atom. We suppose that this discrepancy could be resulted from the influence of different $d$ band components of Fe to 2$p$ states of oxygen O\textsubscript{p}. Therefore, PDOS of Fe on Fe(110) and Fe\textsubscript{2}O\textsubscript{3}(0001) surfaces at the free and adsorbed states are analyzed in Figure 4.13. For iron surface, the contribution of $d$ components to the hybridization area with oxygen (as shown in Figure 4.6) is relatively equal as they undergo the similar changes from the free states to the interacted ones. However, the height of $d_{xz}$ and $d_{z^2}$ curves is reduced more significantly than that of $d_{xy}$, and $d_{z^2}$-$d_{x^2}$, suggesting a slightly larger contribution from these two orbitals. Except for $d_{z^2}$ orbital which is distributed vertically in $z$ direction, other orbitals have a majority of electrons oriented horizontally in the $x$-$y$ plane. This facilitates the multiple interaction of more than one iron atom with the oxygen of phosphate. On the contrary, PDOS of iron atoms on the isolated Fe\textsubscript{2}O\textsubscript{3} surface shows that the $d$ state of Fe is split with a gap around 0.5 eV, unlike the continuous $d$ band of Fe in pure iron surface. Also, the $dz^2$ orbital is almost empty in the energy range between −3 to 0 eV (Figure 4.13c, the red line), while this energy range is occupied by other $d$ components. Instead, LUMO of Fe is located on the $dz^2$ orbital (Figure 8c, the red line), suggesting the highest possibility of receiving electrons on this orbital in the donation interaction. In fact, in the adsorbed system (Figure 4.13d), $dz^2$ orbital becomes occupied in [−2, 0] eV, and its peak at 1.5 eV is smeared and lowered as a result of charge transferred to interact with O\textsubscript{p}. The significant change in DOS of $dz^2$ compared to the other orbitals demonstrates that $dz^2$ has a major influence on the formation of Fe–O\textsubscript{p} bonds. The fact that $dz^2$ and 2$p$ interaction promotes $\sigma$ bond has been reported when molecules adsorbed on the top of the transition metals,\textsuperscript{239-240} making Fe–O\textsubscript{p} bonds shorter but stronger bonds. This explains the preferential adsorption of end-on mode due to the direct contact in the vertical direction between Fe $dz^2$ and O 2$p$ on the top of Fe atom.\textsuperscript{241}
Figure 4.13 PDOS of $d$ orbitals of Fe in (a) free Fe surface, (b) Fe-Na$_3$PO$_4$, (c) free Fe$_2$O$_3$ surface and (d) Fe$_2$O$_3$-Na$_3$PO$_4$ system. The scales are set differently for (a), (b) and (c), (d). For clarity, only energy range around Fermi level is displayed.

When compared the interaction of alkali ortho-phosphate (PO$_4$) and pyrophosphate (P$_2$O$_7$) on iron/iron oxide surfaces, the result indicated that binding strength of orthophosphate is always greater than that of pyrophosphate in all binding modes and configurations. This could be due to the better contact of atoms in short chains than those in long chains. Na$_3$PO$_4$ has more oxygen atoms that can be exposed to Fe atoms, therefore more Fe–O bonds can be formed. A correlation between adsorption energy estimated by computer simulations and wear performance measured in real engine tests has been reported with zinc dithiophosphate (DTP) additive.\(^{130-131}\) Accordingly, additive that has the larger adsorption energy provides a better wear inhibition than the smaller ones.\(^{130-131}\) Regarding this, our results lead to the similar conclusion and show a good agreement with experiment by Cui et al.\(^{47}\) However, the antiwear property of a lubricant does not only depend on its binding energy but also on the surface coverage; in particular, Ta et al.\(^{200}\) have revealed that longer chains of hydrocarbon have a higher saturated carbon density than the shorter chains despite of its weaker adsorption energy per carbon site. This point of view should not be a debatable question due to the fact that hydrocarbons are physically adsorbed on the metal surface and their linear chains
are affected by C–H bond endings. In alkali phosphates, Na-O bonds are ionic bonds that can easily be replaced by stronger covalent bonds. On the other hand, it is worth mentioning that the effects of counter surface and harsh conditions of high temperatures, severe loads and shearing were not taken into account in this work. Under those harsh conditions, bond breaking in lubricant molecules can be observed. This kind of dissociative reaction can either create a passivated layer, or promote the formation of P-rich tribofilms, which eventually reduces friction and protects the metal surface.

Another reason for the greater binding of Na$_3$PO$_4$ on the surfaces than that of Na$_4$P$_2$O$_7$ could be initiated from the existence of bridging oxygen in Na$_4$P$_2$O$_7$. In fact, there is no Fe–O$_b$ bond found on Fe$_2$O$_3$ surface while the configuration with Fe–O$_b$ connection is not the most favorable one on Fe surface. It can be possibly formed under compression and shear when P$_2$O$_7$ chain is deformed. In order to understand the chemical behavior of bridging oxygen and non-bridging oxygen (O$_b$), we analyzed PDOS of O$_b$ and O in isolated Na$_4$P$_2$O$_7$ as presented in Figure 4.14. The peaks 1, 2 and 3 from the Femi level belong to non-bonding states (lone pairs) of oxygen (Figure 4.7), as known as frontier orbitals that are the key in the reaction. Figure 4.14 reveals the highest occupied state of O$_b$ is located at the lower energy level (–0.9 eV) than that of O (–0.5 eV). 2p states of non-bridging oxygen dominate the non-bonding area which ranges from approximately –2.3 to 0 eV. It has been indicated that in the reaction, non-bridging oxygen gets easier to share its electrons to the vacancies in Fe $d$ band as LUMO of iron starts from the Fermi level. Accordingly, bridging oxygen is less chemically reactive than non-bridging oxygen, which is consistent with the thermodynamic adsorption trend observed.
The major contributions to the alkali phosphate–Fe interactions in short range are electrostatics and covalent bonds. In this case, electrostatics comes from the whole sodium phosphate molecules and surface’s atoms while Fe-O bonds contribute dominantly to the covalent part. Therefore, we argue that the main contribution to the stable binding strength of iron-phosphate film is Fe-O covalent bonds. Those interactions assure a stable adsorbed film on the working surface, which can resist surface detachment and prevent a direct metal-metal contact.

On the other hand, experiments found that alkali phosphates at the molten state together with shears and pressure and iron diffusion generated a hierarchical tribofilm containing a layer of mixed K, Na, P and Fe.$^{10, 12}$ The synergetic effect of friction, wear and oxidation reduction has been achieved by alkali phosphate lubricated surface, but the contribution of alkali metal generally remains questionable. Alkali metal doping can affect electronic states of either the surface,$^{207}$ or the glassy compound$^{69}$ by modifying HOMO, LUMO and their band gaps. In particular, increasing Na content leads to the decrease in silicate’s band gap and the dominance of non-bridging oxygen due to the breaking of silicate network.$^{69}$ If the LUMO of lubricant additives can be shifted to a comparable level with that of the surfaces, back-donation easily occurs and strengthens Fe-O bonds that eventually enhance the adhesion of additives on the surfaces. In our results, sodium forms ionic bonds with oxygen atoms of phosphates and does not affect iron–phosphate reaction significantly. However, the influence of the alkali metals in
friction and wear performance should be systematically investigated to reach a general trend. The proposal of alternative usage of alkali or alkali earth metals or their mixing in lubricant additives will be investigated in our future work.

4.8 Conclusions

DFT calculations have been performed to investigate the interactions of sodium pyro- (Na₄P₂O₇) and ortho-phosphate (Na₃PO₄) on Fe(110) and Fe₂O₃(0001) surfaces. The electronic structure of the isolated and adsorbed stages of phosphate molecules and the surfaces have been analyzed and compared to highlight the structural transformation upon adsorption. Based on the simulation results, the following conclusions can be drawn:

(i) Sodium pyro- and orthophosphate are chemisorbed on Fe(110) and Fe₂O₃(0001) surfaces through Fe–O–P linkages. Na₃PO₄ has lower interaction energy per phosphate group and greater binding strength on both iron and iron oxide surface than Na₄P₂O₇, which confirms experimental findings about their antiwear performance.

(ii) Stable covalent Fe–O bonds are formed as a result of the chemical adsorption of phosphates on Fe(110) and Fe₂O₃(0001) surfaces in different ways. On Fe surface, the interaction is likely through a donor-acceptor mechanism with multipoint contact between O_p and Fe, and the influence of d band components of Fe in Fe–O bonds is similar for dₓᵧ, dᵧz, d₂, dₓz and dₓ²ᵧ². However, the interaction occurs through a donation/back-donation mechanism on Fe₂O₃ surface by end-on adsorption mode in which d₂ orbital plays the most important role in Fe–O bond formation.

(iii) Alkali phosphates undergo a transformation in their internal structures after adsorbed on the surfaces. P–O bonds in Fe–O–P linkages are elongated and weakened as a consequence of the electron transfer to the surfaces. However, their strength is as large as that of newly formed Fe–O bonds and it is difficult to decompose the phosphate chains by breaking either P–O or P–O₈ bond.
Chapter 5. INTERACTIONS OF BORATES ON Fe$_2$O$_3$ SURFACE AT HIGH TEMPERATURE

5.1 Introduction

Surface-lubricant interactions play a crucial role in determining wear and friction reduction capability in a tribosystem. In order to adhere sufficiently well on metallic surfaces and protect underlying materials, chemical bonding is essential to secure lubricant’s persistence when two tribopairs move relative to each other. Generally, under heavy loads, shearing and high temperature, physical/chemical adsorption and tribochemical reactions occur, resulting in structural rearrangement, bond formation and dissociation, wear digestion, and cross-linking and hardening network across the interfacial region as well as inside the lubricant. These processes not only transform lubricant structure but also profoundly modify the contacting interface and induce surface complexity, which eventually affect overall lubricant effectiveness. Understanding lubricant-surface bonding nature, therefore, has been intriguing yet fundamentally important in lubrication assessment.

In a general tribology system, the surface-lubricant cohesion strength encompasses multiple contributors including van der Waals interactions, electrostatics, and covalent bonds. Physical van der Waals interactions usually dominate in hydrocarbon or long chain polymer systems. Such lubricants/additives fail to protect the surface under extreme conditions. Chemical covalent bonding based on shared electrons of two participant atoms conventionally results in a firmly attached film ubiquitously found in phosphates, silicates, borates, etc. with the formation of metal-O-P/Si linkages on oxidized surfaces. Another important contributor at the interface region is ionic interactions from free ions which are responsible for Coulombic attractions between two oppositely charged components. It has been found that the exchange of cation following the HSAB theory promotes molecular decomposition, resulting in a mixed long-chain and short-chain tribofilm. In molten inorganic lubricants and ionic liquids, alkali elements acting as free cations in a molten solution show great mobility and diffusivity which contribute to the formation of hierarchical tribofilms. The high affinity and polarity of these alkali cations towards

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2 The content of this chapter was published on Chemical Physics 2020, 529, 110548.
oxidized surfaces can thicken the protective layer by their superior attractions to lubricant molecules,\textsuperscript{11, 13, 128-129} or improve frictional activities thanks to repulsive shearing forces between similarly charged layers.\textsuperscript{249}

Sodium borate is among alkali inorganic glasses that has been widely applied as lubricants and coating materials for the metallic manufacturing fields, due to their exceptional thermal stability and oxidation resistance.\textsuperscript{14-15, 81} The presence of sodium cations in the lubricant show a remarkable lubricity compared to its sole boron oxide counterpart.\textsuperscript{16} In the bulk borates, a small amount of alkali cations helps building the units of BO$_4$ tetrahedra.\textsuperscript{70} At high temperature, the BO$_4$ groups tend to be decomposed into BO$_3$ with an accompanied non-bridging oxygen (O$^{\text{nb}}$).\textsuperscript{53, 57} Both the introduction of alkali and thermal decomposition could be the main factors for interfacial bonding. Nevertheless, melting supported by the metal substrate can exhibit more chemical complexity. Apart from thermal onset, surface catalysis plays an integral part in bond formation and dissociation activities.\textsuperscript{158, 247} However, none of these above references has characterized the alkali metal borate assembly and their bonding behaviors on a metal surface, thus raising a question on the detailed understanding of the surface-borate bonding chemistry and their contribution to the overall lubricating function.

Quantum mechanics based simulations have established reliable theoretical methods to ascertain frictional properties in the field of tribochemistry. It has been proven that the friction and wear quality of a lubricant is in accordance with its binding strength, i.e. a better surface-lubricant binding provides a superior wear resistance and surface protection than a poorer mating system.\textsuperscript{132, 159} A tribofilm made up from stable bonds requires a higher barrier to be dislodged from the metallic surface.\textsuperscript{160} An alternative way to assess metal-lubricant reaction and wear inhibition of a lubricant is by estimating the energy gap of valence electrons in lubricant and metal surface, as it represents the chemical reactivity of substances.\textsuperscript{161-163} The surface-lubricant systems with higher band gaps are less likely to exchange electrons than those with lower gaps, thus resulting in weaker electrostatic and covalent interactions. As a result, friction and wear increase.\textsuperscript{163} In this chapter, we examine how B$_2$O$_3$ and Na$_2$B$_4$O$_7$ lubricants behave in response to heat exposure and Fe$_3$O$_3$ catalysis from the quantum mechanics point of view. Time and temperature dependent configurations and their electronic structures will be thoroughly considered to compare the bonding behaviors of the two borates with the oxidized surface, and to rationalize how their interactions affect the tribological
effectiveness. In addition, the energy and transition state search is applied to find out the reaction tendency in the systems.

5.2 Simulation model

DFT and AIMD simulations were performed by the Vienna *Ab Initio* Simulation Package (VASP). A plane wave basis set and the projector augmented-wave (PAW) method (PAW potentials) were used to model core potentials. The electron exchange and correlation was estimated by using the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) exchange and correlation functional.

In order to study the interactions of sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) and boron oxide ($\text{B}_2\text{O}_3$) on iron oxide surface, the obtained sodium tetraborate and boron oxide glasses from the melt-and-quenching process were loaded on the $\text{Fe}_2\text{O}_3$ surface for AIMD simulations. The purpose of using $\text{Na}_2\text{B}_4\text{O}_7$ and $\text{B}_2\text{O}_3$ is to compare the interactions between borate systems with and without the presence of sodium with the $\text{Fe}_2\text{O}_3$ surface.

The boron oxide and sodium tetraborate glasses were equilibrated on $\text{Fe}_2\text{O}_3$ surface by AIMD simulations at 1073 K (800 °C) which is the temperature of the tribological experiments. The temperature of 1073 K was controlled using the Nose-Hover thermostat. This temperature is above the melting points of both $\text{Na}_2\text{B}_4\text{O}_7$ (525 °C) and $\text{B}_2\text{O}_3$ (450 °C) to ensure a complete molten phase of the lubricants. In the Nosé algorithm, the Nosé mass controls the frequency of the temperature oscillations every a period of 40 time steps. Due to the large size of the supercells, Brillouin zone integrations were sampled over the $\Gamma$ point, and the plane-wave expansion of the electronic wave function was truncated by setting the energy cutoff to 350 eV. An added vacuum layer of 15 Å on the top of the lubricants minimized the interaction of the image cells due to the periodic boundary condition along the z direction. In order to ensure the results are repeatable with the randomized distribution of the glass’s constituents at the $\text{Fe}_2\text{O}_3$-borate interface, for each $\text{Fe}_2\text{O}_3$-borate system, we set up two different initial configurations to perform AIMD simulations. They were selected to make sure the results provide a general tendency and do not depend on the initial configurations. As the two runs produce similar results, only results of one
configuration are discussed in this thesis. Only two initial configurations were adopted considering the large sizes of the systems and the relatively long simulation time required. All simulations were run for 40,000 MD steps corresponding to a period of 20 ps with a time step of 0.5 fs. The convergence of energies and temperatures of all systems are also reported.

DFT calculations were performed for electronic structures of the selected configurations extracted from the AIMD simulations. For these purposes, a higher accuracy standard was applied with an energy cutoff of 450 eV and Brillouin zone was sampled using Monkhorst – Pack scheme with the k-point mesh of 5 × 5 × 1. The convergence criteria of 10⁻⁴ eV and 10⁻³ eV were applied for the electronic wave function and ionic relaxation, respectively. Partial charges were estimated from DDEC6 method to describe the charge distribution in the systems.²¹¹

5.3 Melting of borate glasses

Na₂B₄O₇ and B₂O₃ systems were annealed at a high temperature of 4000 K to randomize the atomic distribution. Then they were cooled down to 300 K to create a glassy state. In order to study how the bulk materials melt, the obtained Na₂B₄O₇ and B₂O₃ at 300 K were equilibrated at their glass densities while those at 1073 K were equilibrated with the molten densities at the temperature presented in Table 5.1. Figure 5.1 shows the final configurations of Na₂B₄O₇ and their radial distribution function (RDF/g(r)) after being relaxed for 20 ps. At 300 K, the glassy form of Na₂B₄O₇ appears to be complex with planar BO₃ triangles, BO₃ in six-member boroxol rings, and BO₄ tetrahedra networking through bridging oxygen (Figure 5.1). The coexistence of the three- and four-fold coordinated boron involves the sp²- and sp³-hybridization of the element. It is worth mentioning that in an ideal crystalline alkali tetraborate bridging oxygen (O⁵⁺) atoms account for 100% oxygen, and B⁴⁺ accounts for 50% boron.⁷₀,²⁵¹ In the obtained Na₂B₄O₇ glass, there is an amount of 9.5 % Oₐᵇ which could be due to the defects from the small model size during the fast cooling process. As a result, the proportion of Oₐᵇ in the glass is slightly higher than that reported in the crystal, accompanied by a lower fraction of B⁴⁺. Na plays a role as network modifiers to neutralize the negative charges caused by the four-fold coordinated boron (B⁴⁺) and Oₐᵇ.²⁵²-²⁵³ RDF shows that the first peaks of B–O, Na–O, and O–O curves locate at
1.34, 2.25, and 2.40 Å, which correspond to the average bond lengths of B–O, Na–O, and O–O bonds (Figure 5.1), respectively. RDF of B–O bonds exhibits a tiny smear expanding from 1.34 to 1.46 Å (the circled ones in Figure 5.1c and f), representing the typical coexistence of BO₃ and BO₄ building units, as can be seen from the structural visualization in Figure 5.1a and b. These structural parameters are in good agreement with those of the tetraborate reported in the literature.⁵⁵,⁵⁷

![Structural visualization](image)

Figure 5.1 Structures of Na₂B₄O₇ (a) at 300 K and (d) at 1073 K; polyhedral presentation (b) at 300 K and (e) at 1073 K; and RDFs of Na–O, B–O, and O–O (c) at 300 K and (f) at 1073 K. Oⁿᵇ atoms are colored Blue in (a) and (d), sodium in (b) and (e) has been remove for clear visualization.

The melting of Na₂B₄O₇ at 1073 K results in a slight corruption of BO₄ compacted arrangements in the system (Figure 5.1d and e). There is a prominent transformation in the borate structure, i.e., the conversion from B⁴ to B³ accompanied by Oᵇ to Oⁿᵇ following BO₄ → BO₃ + Oⁿᵇ scheme.⁵³ The former represents the depolymerization of the network while the later is directly related to the changing in the electronic affinity caused by unshared electrons of the Oⁿᵇ. The melting of the glass at 1073 K significantly reduces the B⁴ content from 29.3 to 20.8%, and subsequently increases Oⁿᵇ/(Oⁿᵇ+Oᵇ) ratio from 9.5 to 14.3% as some Oᵇ atoms are detached from BO₄ groups. There is also a decrease in the height of the RDF’s first peaks (Figure 5.1f)
compared to the RDF’s peaks at 300 K (Figure 5.1c), indicating the delocalization in their nearest neighbors and bond lengthening. The melting structure of Na₂B₄O₇ is comparable with the result from Ohkubo et al. who reported Oⁿb/(Oⁿb+Oᵇ) ~ 11% and B⁴⁺/(B⁴⁺+B³⁺) ~ 23% in Li₂B₄O₇ at 1250 K.²⁵⁴

Table 5.1 Densities, structural parameters, and diffusion coefficients of Na₂B₄O₇ and B₂O₃ at 300 K and 1073 K.

<table>
<thead>
<tr>
<th>System/T (K)</th>
<th>Density (g cm⁻³)</th>
<th>Oⁿb/(Oⁿb+Oᵇ) (%)</th>
<th>B⁴⁺/B³⁺ (%)</th>
<th>bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂B₄O₇, 300 K</td>
<td>2.36ᵃ</td>
<td>9.52</td>
<td>29.16</td>
<td>1.35(1.46)</td>
</tr>
<tr>
<td>Na₂B₄O₇, 1073 K</td>
<td>2.09ᵃ</td>
<td>14.28</td>
<td>20.83</td>
<td>1.36(1.45)</td>
</tr>
<tr>
<td>B₂O₃, 300 K</td>
<td>1.81ᵇ</td>
<td>0.00</td>
<td>0.00</td>
<td>1.35</td>
</tr>
<tr>
<td>B₂O₃, 1073 K</td>
<td>1.50ᶜ</td>
<td>0.00</td>
<td>0.00</td>
<td>1.35</td>
</tr>
</tbody>
</table>

ᵃ From experimental data²⁵⁴ ᵇ Density of glassy B₂O₃ at 300 K²⁵⁵ ᶜ Density of glassy B₂O₃ at 1100 K²⁵⁰ ᵈ Na–O, B–O, and O–O bond lengths are taken from the position of the RDF’s first peaks, which is associated with their nearest neighbor distribution. The brackets indicate the values of the smeared peak in BO’s RDF.

Figure 5.2 describes the structures of boron oxide at the glassy and liquid states and their corresponding RDF, while average B–O and O–O bond lengths are presented in Table 5.1. In contrast to sodium tetraborate, boron oxide structure is a stoichiometric composition of corner-linked BO₃ triangles linked by B–Oᵇ bonds.⁶⁴ This is supported by the only one single sharp peak of BO’s RDF localized at a distance of 1.35 Å, specified for a highly covalent network of B₂O₃.⁶⁵ At 1073 K, a slight bond elongation occurs in B–O bonds which is pointed out by the shortening of RDF peaks (Figure 5.2c). This change could stem from the thermal expansion and atomic vibration under the heat treatment. Interestingly, although the melting of B₂O₃ at 1073 K leads to a minor bond elongation, there is neither a change in boron coordination number nor the appearance of Oⁿb in the molten B₂O₃, which indicates the thermal stability of the boron trigonal matrix.
BOP presented in Figure 5.3 describes the bonding strength of B–O bonds in Na$_2$B$_4$O$_7$ and B$_2$O$_3$. The BOP values of B–O bonds show that there are three types of B–O bonds including B$^4$–O in BO$_4$ groups, B$^3$–O, and B$^3$–O$^{nb}$ in BO$_3$ groups. Apparently, B$^4$–O (BOP = 0.32 e) is the weakest bond compared to the other two bonds B$^3$–O (BOP = 0.40 e), and B$^3$–O$^{nb}$ (BOP = 0.51 e). This makes BO$_4$ the least stable and the easier group to be decomposed at high temperature than BO$_3$ one. At 300 K, the B$_2$O$_3$ structure contains no non-bridging oxygen and the absence of the BO$_4$ complex in B$_2$O$_3$ results in a homogeneous BO$_3$ covalent network connected through B$^3$–O bonds with an averaged BOP of 0.39 e (Figure 5.3b). The BOP value is consistent with that of the B$^3$–O in Na$_2$B$_4$O$_7$ which indicates that B$_2$O$_3$ is structured in the most stable BO$_3$ form. As a result, the structure of B$_2$O$_3$ at 1073 K shows no significant changes in terms of bond length, coordination number, and B–O bonding. In particular, boron retains its three-fold coordination number and no O$^{nb}$ is generated in the system. This result, therefore, indicates the thermal stability of B–O bonds in the boron trigonal network.
Na$_2$B$_4$O$_7$ and (b) B$_2$O$_3$.

Table 5.2 Diffusion coefficients of Na, O, and B in Na$_2$B$_4$O$_7$ at 300 K and 1073 K.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Diffusion coefficient ($10^{-6}$ cm$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_{\text{Na}}$</td>
</tr>
<tr>
<td>300 K</td>
<td>0.008</td>
</tr>
<tr>
<td>1073 K</td>
<td>8.742</td>
</tr>
</tbody>
</table>

Figure 5.4 MSD of Na, B, and O at 300 K and 1073 K. The MSD values were averaged over all atoms of the same type in the system.

Mean squared displacement (MSD) and self-diffusion coefficient ($D$) were calculated to measure the mobility of atoms in the system. The MSD reflects the migration distance of an ion within a certain time while self-diffusion coefficient defines the ability to diffuse in a homogeneous system without a concentration gradient. As illustrated in Figure 5.4, at the low temperature MSD curves of Na, O and B are nearly identical as their movement is negligibly different from each other, making their diffusion coefficients close to zero (Table 5.2). When heated up, MSD magnitudes of B and O still level off at low values while that of Na increases sharply with the simulation time. Likewise, the diffusion coefficient of Na ions rises to 8.74×10$^{-6}$ cm$^2$s$^{-1}$, which is about nine times larger than that of O (0.81×10$^{-6}$ cm$^2$s$^{-1}$) and 20 times larger than that of B (0.42×10$^{-6}$ cm$^2$s$^{-1}$). This makes Na distinguish itself from the other two ions and become the most mobile ion in response to the temperature change.
In comparison, in the glassy form boron oxide appears in a homogeneous BO$_3$ trigonal network while that of the sodium tetraborate is a combination of BO$_3$ trigonal and BO$_4$ tetrahedral complexes. Thus, they possess distinguishing melting characteristics. The standout is the transformation of boron coordination number in Na$_2$B$_4$O$_7$ in favor of three-fold coordination under the thermal onset, which is absent in the B$_2$O$_3$ melt. Additionally, for sodium tetraborate, the sodium cations are extremely mobile at high temperatures compared to the other counterparts.

5.4 Interactions of Na$_2$B$_4$O$_7$ and B$_2$O$_3$ on the Fe$_2$O$_3$ surface at 1073 K

The convergence of energy and temperatures of the AIMD simulations of Na$_2$B$_4$O$_7$ on the Fe$_2$O$_3$ surface for a period of 20 ps at 1073 K is presented in Figure 5.5. It can be seen that both the potential energy and temperature converge well after the first 5 ps, and stable for the remaining simulation period.

![Figure 5.5 Potential energy and temperature of Fe$_2$O$_3$-Na$_2$B$_4$O$_7$ during the simulation at 1073 K.](image)

Snapshots of Fe$_2$O$_3$-Na$_2$B$_4$O$_7$ configurations at 1073 K, mean square of displacement (MSD), and the distances from O/Na of Na$_2$B$_4$O$_7$ to the Fe$_2$O$_3$ surface are presented in Figure 5.6. As shown in Figure 5.6a-d, at the interface Na ions that are close to the Fe$_2$O$_3$ surface quickly move toward the surface, while oxygen of Na$_2$B$_4$O$_7$ approaches the nearest Fe atoms to form Fe–O–B linkages. The migration of Na to the surface was observed at the early stage of the simulation (2 ps), and the number of Na ions on the surface increases with increasing simulation time, to a maximum of four Na ions on the Fe$_2$O$_3$ surface at 2 ps (Figure 5.6b). The Fe–O–B covalent bonding registered at the interface is based on the reaction of iron with the non-bridging oxygen
of the borate which is generated from BO$_4$ groups by thermal decomposition.$^{81}$

Figure 5.6 Snapshots of Fe$_2$O$_3$-Na$_2$B$_4$O$_7$ configurations during the simulation at 1073 K: (a) 0 ps, (b) 2 ps, (c) 5 ps, and (d) 10 ps, (e) MSD of Na$_2$B$_4$O$_7$’s atoms and (f) average distance from Na ions to the Fe$_2$O$_3$ surface during the interaction of sodium borate on the surface.

Figure 5.7 describes the atomic density profile of all elements in Fe$_2$O$_3$-Na$_2$B$_4$O$_7$ system along the z direction. The density was sampled over 100 configurations from 5 to 15 ps. It is evident that from the surface, there is a peak in Na density showing a higher concentration of Na than the rest of the borate region. This distribution results in a Na-rich layer from ~4 to 6 Å followed closely by an O-rich layer and a significant amount of boron element from 6 to 8 Å. This indicates that Na is sandwiched between two oxygen layers, one from the surface and one from the lubricant. By this way, the sodium cations play a role as a bridge holding the borate on the surface during the simulations. The similar O–Na–O stacking has been confirmed in the systems of water lubricated on silicon surface,$^{129}$ and peptide molecules adsorbed on TiO$_2$ interface,$^{257-258}$ where the adsorbate layer is greatly enriched by the alkali cation presence. Therefore,
the result suggests that sodium plays a critical role in layer-by-layer assembly at the steel-lubricant interface.

Figure 5.7 Atomic density profile of atoms across the z direction of all elements in the system. The vertical dotted line separates the surface and the lubricant areas. O is the oxygen of Na$_2$B$_4$O$_7$ and O$_S$ is the oxygen of the Fe$_2$O$_3$ surface.

The interactions on the iron oxide surface at high temperature substantially affect structural behaviors inside the lubricant. In particular, the exposure to high temperature results in the decomposition of BO$_4$ complexes into BO$_3$ forms and creates an O$^{nb}$. Table 5.3 reveals that during the interaction on the iron oxide surface at high temperature, the number of B$^4$ decreases significantly with the simulation time, i.e. from 29.2% to 16.6 %. This fraction is close to the figure of the Na$_2$B$_4$O$_7$ bulk melting, which suggests that temperature is more influential than the surface effects in terms of structural transformation inside the lubricant. However, BO$_4$$\rightarrow$BO$_3$ conversion provides O$^{nb}$ to engage in the reaction with the iron oxide surface, forming Fe–O bonds. This bonding is an essential part of the surface-lubricant adhesion because of its chemical bond strength from high Fe–O covalency. As a non-bridging atom, the unshared electrons of O$^{nb}$ atoms are located at the highest occupied state, therefore they have a higher tendency to fill up the unoccupied iron’s d band than those of the bridging oxygen.$^{159, 248}$ Compared to inorganic phosphate/silicate lubricants, the O$^{nb}/(O^{nb}+O^b)$ ratios are significantly higher than that of Na$_2$B$_4$O$_7$. As a result, Fe-O-P/Si linkages predominate the surface coverage under phosphate/silicate loading.$^{247-248}$ Because of the lower fraction of O$^{nb}$ in borate, the Fe-O$^{nb}$ bonding is less likely to occur, and the
contribution of alkali cations is more dominant in alkali borate lubricated systems.

Table 5.3 Changing of four-fold coordinated boron (B⁴) and Oⁿᵇ in Na₂B₄O₇ interacting on the iron oxide surface at 1073 K with the simulation time*, B³ is the three-fold coordinated boron.

<table>
<thead>
<tr>
<th>Time (ps)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>B³/(B⁴+B³) (%)</td>
<td>29.2</td>
<td>20.8</td>
<td>12.5</td>
<td>16.6</td>
<td>16.6</td>
</tr>
<tr>
<td>Oⁿᵇ/(Oⁿᵇ+Oᵇ) (%)</td>
<td>16.6</td>
<td>16.6</td>
<td>24.4</td>
<td>19.0</td>
<td>19.0</td>
</tr>
</tbody>
</table>

*The coordination number of boron and oxygen is identified with a cutoff radius of 1.6 Å.

An analogous AIMD simulation at 1073 K was carried out for B₂O₃ to consider its interaction with the Fe₂O₃ surface and to compare with that of Na₂B₄O₇. The convergence of the potential energy and temperature during the simulations are shows in Figure 5.8. Similar to those of Fe₂O₃-Na₂B₄O₇ system (Figure 5.5), the energy and temperature converge quickly after a few ps. Figure 5.9 shows the snapshots of B₂O₃ interacting on the iron oxide surface at 0 and 10 ps. The snapshot configuration at 10 ps shows no significant interactions between B₂O₃ and the Fe₂O₃ surface, and an interacting distance is 3.3 Å (Figure 5.9). Because of such a large gap, neither Fe–O₉ nor B–O₅ bond is formed to secure the surface-lubricant connection. Additionally, measuring the distance from the B₂O₃ block to the Fe₂O₃ surface in Figure 5.9c reveals that B₂O₃ moves up and down on the surface with the minimum distance of approximately 2.5 Å and the maximum up to 5 Å. The minimum value is around 0.5 Å longer than an ordinary Fe–O bond length,229-230 and ~1 Å longer than that of a B–O bond.55 A further relaxation produces no noticeable physical/chemical events or nor observing any B₂O₃ movement closer to the surface. The lack of bond formation that leads to the weak adsorption of B₂O₃ on the Fe₂O₃ surface can be interpreted by two factors. First, the absence of sodium element in the boron oxide reduces the surface-lubricant affinity, ruling out the electrostatic forces between free cations and surface’s oxygen. Secondly, the equilibrium of B₂O₃ structure at 1073 K produces no thermal decomposition, as B₂O₃ is a consistent network of BO₃ triangles interlinking via bridging oxygen Oᵇ.250 The bridging oxygen has been proven to be less chemically attractive to metals than its non-bridging counterpart.159 Meanwhile, Fe–Oᵇ is less likely to occur and it has been proven to be unstable at high temperature.248
Figure 5.8 Potential energy and temperature of the Fe$_2$O$_3$-B$_2$O$_3$ system during the simulation at 1073 K.

Figure 5.9 Snapshots of Fe$_2$O$_3$-B$_2$O$_3$ configurations at (a) 0 ps, (b) 10 ps, and (c) the corresponding closest distance from the B$_2$O$_3$ block to the Fe$_2$O$_3$ surface during the simulation at 1073 K.

The simulation result of Fe$_2$O$_3$-B$_2$O$_3$ is opposite to those obtained in the Fe$_2$O$_3$-Na$_2$B$_4$O$_7$ system where a stronger surface-lubricant interaction is achieved. At 1073 K sodium tetraborate interacts on the Fe$_2$O$_3$ surface through the chemical bonds between iron and the oxygen of Na$_2$B$_4$O$_7$ and the ionic bonds between oxygen of the surface and sodium cations. The favorable adsorption of sodium ions on the iron oxide surface helps
to connect the iron oxide with the borate layer and supports the experimental finding of the sodium-rich layer at the molten borate and steel interface.\textsuperscript{14-15} In contrast, B\textsubscript{2}O\textsubscript{3} appears to be weakly adsorbed. The major differences between the two systems stem from the absences of alkali constituent and O\textsuperscript{ab} species in the lone boron oxide. The current simulation provides a crucial evidence of the poor B\textsubscript{2}O\textsubscript{3}-steel adhesion that leads to the failure in friction and wear reduction in the hot tribo-test at 800 °C.\textsuperscript{16}

5.5 Binding mechanisms and charge distribution

In order to quantify the adhesion strength of the two lubricants on the oxidized surface, binding energy is calculated along the separate distance from the surface following the equation 16:

\[ E_{\text{binding}}^d = E_{\text{total}}^d - (E_{F\text{2}O\text{3}} + E_{Na\text{2}B\text{4}O\text{7}/B\text{2}O\text{3}}) \]  

(16)

Where, \( E_{\text{binding}}^d \) and \( E_{\text{total}}^d \) are the binding and the total energies at the separate distances \( d \), \( E_{F\text{2}O\text{3}} \) and \( E_{Na\text{2}B\text{4}O\text{7}/B\text{2}O\text{3}} \) are the energies of the Fe\textsubscript{2}O\textsubscript{3} surface and the lubricant.

As shown in Figure 5.10, Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} shows an extremely strong chemical interaction on Fe\textsubscript{2}O\textsubscript{3} surface with a potential well depth of 6.4 eV at 1.91 Å. As the separate distance increases, the binding energy converges to -0.4 eV instead of reaching 0 eV, indicating the existence of a long range interaction by Coulombic attraction. On the contrary, B\textsubscript{2}O\textsubscript{3} exhibits weak physical interaction with a binding energy of -0.06 eV at the equilibrium distance of 2.83 Å, and almost zero at the distance longer than 4 Å (Figure 5.10b). The absence of charged ions and bond formation at the Fe\textsubscript{2}O\textsubscript{3}-B\textsubscript{2}O\textsubscript{3} interface substantially reduces the surface–adsorbate attraction. It is worth mentioning that no van der Waals correction was used in the calculations to make it comparable with Fe\textsubscript{2}O\textsubscript{3}-Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} system, which was dominated by ionic and electrostatic interactions. Thus the remarkably low binding energy of 0.06 eV was achieved. It can be confirmed quantitatively that the binding energy of Fe\textsubscript{2}O\textsubscript{3}-Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} reflects a chemical interaction while that of the Fe\textsubscript{2}O\textsubscript{3}-B\textsubscript{2}O\textsubscript{3} system is a physical one. Considering the work of separation, the binding energy landscapes suggest that a higher energy barrier is needed to detach Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} from the iron oxide surface than that of B\textsubscript{2}O\textsubscript{3}.
Figure 5.10 Binding energies of Fe$_2$O$_3$-$\text{Na}_2\text{B}_4\text{O}_7$ and Fe$_2$O$_3$-$\text{B}_2\text{O}_3$ as a function of separate distance $d$. The scales are different in (a) and (b).

The electronic structure of the systems is analyzed to rationalize the interacting mechanisms behind distinctive binding behaviors between sodium borate and boron oxide. As shown in Figure 5.11, there is a massive surface modification with the major changes observed at the top layers of the Fe$_2$O$_3$ surface at high temperature. The charge distribution is presented as averaged partial charges for atoms at the Fe$_2$O$_3$-lubricant interface. Initially, the surface is terminated by Fe on the topmost layer. With lubricants overlay and high temperature, Fe relaxes inward into the surface and buries into an oxygen layer to preserve their coordination number with the nearest oxygen. After 10 ps only one Fe stays on the topmost layer by bonding with oxygen of Na$_2$B$_4$O$_7$ (Figure 5.11b) while there are two in the case of B$_2$O$_3$ (Figure 5.11c). As a consequence, the initial hematite (0001) surface with Fe–O$_3$–Fe termination turns into a partial oxygen-rich surface. The inward relaxation of iron on the top layer up to 57% and 79% of Fe–O bond has been reported for Fe– and O– terminated surface, respectively.\textsuperscript{259} It is worth mentioning that the Fe$_2$O$_3$(0001) surface with Fe–O$_3$–Fe termination has been acknowledged as the most stable surface morphology, followed by O–Fe–Fe and O$_3$–Fe–Fe termination.\textsuperscript{201} At some specific conditions, there are regions where Fe– and O– terminated Fe$_2$O$_3$(0001) domains coexist.\textsuperscript{260-261} This surface complex can advance the lubricant adsorption by creating a favorable chemical environment for Na, enhancing the Na adsorption strength and making sodium borate cover the surface better. Additionally, this causes a significant depletion of Fe at the surface boundary and thus reduces the exposure of Fe to the environment and the surface damage by oxidation.\textsuperscript{261} It can generally prohibit the penetration of Fe diffusing upwards, and prevent the wear loss during surface-surface collision.
Figure 5.11 Partial charge distribution of Fe$_2$O$_3$-borate systems: (a) initial Fe$_2$O$_3$ surface at 0 ps, (b) Fe$_2$O$_3$-Na$_2$B$_4$O$_7$ at 10 ps, and (c) Fe$_2$O$_3$-B$_2$O$_3$ at 10 ps. (+) means a positive charge and (−) means a negative charge. The partial charges are the averaged values over atoms of the same type in the system.

The evolution from iron-rich to oxygen-rich surface is attributed to the changing in the surface’s electronic structure. The calculated partial charges in Figure 5.11 indicate that when the conversion from Fe– to O– termination occurs, the positively charged Fe$_2$O$_3$ surface turns into the negatively charged surface. In particular, at 0 ps the topmost iron atoms of the Fe$_2$O$_3$ surface have positive charges with an average value of +0.92 e (Figure 5.11a). When the surface becomes O–terminated, it is mostly occupied by oxygen atoms carrying a negative charge of −0.65 e and −0.56 for each atom in Fe$_2$O$_3$-Na$_2$B$_4$O$_7$ and Fe$_2$O$_3$-B$_2$O$_3$, respectively (Figure 5.11b and c). At the interface of Na$_2$B$_4$O$_7$ and the Fe$_2$O$_3$ surface, Na ions carry positive charges with an average value of 0.90 e (Figure 5.11b). Thus, there expects a strong electrostatic attraction between oppositely charged components, which favors Na stabilization on the Fe$_2$O$_3$ surface. The enrichment at the surface could increase the level of polarization toward both surface and lubricants sides. In the lubricant side, there are a large number of BO$_3$ groups with O oriented toward the Na layers with partial charges of −0.82 e. This combination creates an O–Na–O interlayer where Na ions are sandwiched between two negatively charged areas of the surface and the lubricant. Such a binding mechanism has been recently proven with Ca$^{2+}$ as the cation connects peptides with TiO$_2$ surface.$^{257-258}$ According to Jarzabek et al., these alkali cations can hold water molecules on working tribopairs, allowing the system to shear over water lubricant.$^{128-129}$ Regarding frictional benefits, these cations stacking creates a protective film on the surface against heavy
loads and shearing processes.

On the other hand, Figure 5.11c shows that the negative charges of oxygen in the borate side combined with the oxygen-rich surface create two similarly charged layers in contact with each other. The average oxygen’s charges are less negative than those of the Fe$_2$O$_3$-Na$_2$B$_4$O$_7$, i.e. -0.57 and -0.71 for the oxygen of the surface and the boron oxide, respectively. Apparently, there is a repulsive force that keeps the B$_2$O$_3$ at a certain distance from the surface, which is in line with the AIMD simulation in the previous section. Furthermore, as weakly adsorbed, the material can be easily removed when a lateral force is imposed, leaving the surface unprotected. Due to the lack of the lubricated film, the two steel substrates undergo a direct metal-metal collision, which consequently induces the increasing abrasive wear in B$_2$O$_3$ lubrication.

Table 5.4 reveals the charge transfer values between the Fe$_2$O$_3$ surface and the lubricants Na$_2$B$_4$O$_7$ and B$_2$O$_3$ and how the surface-lubricant interactions influence the friction and wear performances. In particular, Na$_2$B$_4$O$_7$ and the Fe$_2$O$_3$ surface mutually transfer a substantial amount of electrons via both covalent and ionic interactions. In this case, the surface gains charges from the borate with an average value of ~ 0.7 e during the whole simulation process. In contrast, there is no electron transfer between the Fe$_2$O$_3$ surface and B$_2$O$_3$ as $\Delta q$ is almost zero for the period of 20 ps, which indicates no significant interaction between the iron oxide surface and the boron oxide. In accordance with charge transfer and binding strength, the stronger Fe$_2$O$_3$-Na$_2$B$_4$O$_7$ interaction leads to a lower coefficient of friction (COF = 0.12) and wear loss (0.04 mm$^3$) while the weaker Fe$_2$O$_3$-B$_2$O$_3$ induces higher friction (COF = 0.40 - 0.60) and wear (0.34 mm$^3$). Thus, there is a qualitative correlation between the bonding strength and friction and wear effectiveness, i.e., the more charge transfer occurs between the surface and the lubricant, the stronger their interaction and the better tribological reduction is achieved.

Overall, the binding energies and the charge analyses show a good agreement with the AIMD results in Section 5.3. More importantly, the results confirm the experimental observations on the adhesive characteristics of Na$_2$B$_4$O$_7$ and B$_2$O$_3$ on the steel surface, leading to the excellent lubricity of Na$_2$B$_4$O$_7$ and the poor performance of B$_2$O$_3$ found in the reference.
Table 5.4 Charge transfer (Δq)* between Na₂B₄O₇/B₂O₃ and the Fe₂O₃ surface of the selected configurations at 0, 5, 10, 15, and 20 ps, and friction and wear data of Na₂B₄O₇ and B₂O₃ lubricated systems collected from experiments.

<table>
<thead>
<tr>
<th>System</th>
<th>Charge transfer (e) vs time</th>
<th>Friction and wear**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (ps)</td>
<td>COF</td>
</tr>
<tr>
<td>Fe₂O₃-Na₂B₄O₇</td>
<td>Δqₛ 0.00</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Δq_NaBO 0.00</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃-B₂O₃</td>
<td>Δqₛ 0.00</td>
<td>0.40-0.60</td>
</tr>
<tr>
<td></td>
<td>Δq_BO 0.00</td>
<td></td>
</tr>
</tbody>
</table>

*Δqₛ is the charge transfer of the Fe₂O₃ surface, Δq_{NaBO} and Δq_{BO} are the charge transfer of Na₂B₄O₇ and B₂O₃ in Fe₂O₃-Na₂B₄O₇ and Fe₂O₃-B₂O₃ systems, respectively.

**Experimental measurement of friction and wear from pin-on-disk testing with a normal load of 10 N and sliding velocity of 0.1 ms⁻¹ at 800 °C.¹⁶

5.6 Bond dissociation in Fe₂O₃-Na₂B₄O₇ system

To evaluate the strength of interfacial bonding of the borate with the surface as well as the internal B-O bonds of the borate glass, we applied the Blue Moon ensemble to quantify the activation energy for the bond dissociation in the system.²⁶² The theoretical background for these methods has been reported and successfully used to locate the transition states in various complex systems that possess a large number of degrees of freedom.²⁶³²⁶⁶ In the Blue Moon method, the activation energy needed to break a bond is integrated from the mean constraint force as a function of reaction coordinate. In our model, the reaction coordinates only involve stretching the selected bonds, therefore they correspond to the bond lengths of the chosen bonds. The obtained configurations from AIMD simulations at 1073 K (presented in Figure 5.6) were pre-optimized to reach the first minimum. After that, the chosen bond was stretched from its equilibrium distance with an increment of 0.1 Å until the transition state (TS) was obtained. Constrained AIMD runs were performed at every single point of the constrained bonds at a temperature of 300 K. These settings together with the large size of the model impose a huge computation cost, therefore a relaxation time of 4000 MD steps corresponding to 2 ps with a 0.5 fs time step was chosen after optimizing the calculation time versus free energy convergence. The mean constraint force was
calculated by averaging the forces over the last 2000 MD steps of each run in order to rule out any large fluctuation due to the system instability in the early steps. The transition state is defined at the point where the mean constraint force vanishes, and the corresponding free energy of activation is obtained from the numerical integrations of the constraint force versus the reaction coordinate as follows:

$$\Delta A_{1\rightarrow 2} = \int_{\xi(1)}^{\xi(2)} d\xi \left( \frac{\partial A}{\partial \xi} \right)_{\xi^*}$$

(17)

where, \( \left( \frac{\partial A}{\partial \xi} \right)_{\xi^*} \) is the free-energy gradient at a fixed value of the reaction coordinate \( \xi^* \). The reaction coordinate for the calculations of the constraint force and activation energy was selected according to the dependence of the chosen bond on the coordinates of two atoms that form the bond. The change in the coordinate of atoms corresponds to the stretching of the bond between the two atoms. Furthermore, in the current work, only the activation energy for bond breaking was considered; there is no inclusion of additional variables such as third atoms and constraint angles. Therefore, only the reaction coordinates of the two atoms related to the chosen bond were used.

We classified the possible dissociated bonds into two groups. The first one is related to the bond between the iron of the surface and the oxygen of the borate including \( \text{Fe}–\text{O}(–\text{B}^3) \) and \( \text{Fe}–\text{O}^b \), while \( \text{O}^b \) refers to the oxygen in \( \text{B}^3–\text{O}–\text{B}^4 \). The second one involves the \( \text{B}–\text{O} \) dissociation in \( \text{B}^3–\text{O}, \text{B}^4–\text{O} \) and \( \text{B}^3–\text{O}(–\text{Fe}) \) bonds. The corresponding constraint forces along the reaction coordinates are presented in Figure 5.12. Figure 5.13 describes the dissociation and the activation energies of the bonds in the first group. After pre-optimizing, the equilibrium distances of \( \text{Fe}–\text{O}^b \) and \( \text{Fe}–\text{O}(–\text{B}^3) \) yield 2.10 and 1.84 Å (Figure 5.13a and b), respectively. From the point of force vanishing, the transition states for \( \text{Fe}–\text{O}^b \) and \( \text{Fe}–\text{O}(–\text{B}^3) \) bonds are obtained at 2.65 and 2.53 Å. After reaching the transitions state, the \( \text{BO}^3–\text{BO}^4 \) fragment retains its initial configuration (Figure 5.13b), which implies a marginal effect from \( \text{Fe}–\text{O}^b \). On the contrary, after being detached from oxygen, the iron atom moves inward away from the surface (Figure 5.13d), resembling the inward relaxation of other iron atoms. The breaking of \( \text{Fe}–\text{O}^b \) needs a low barrier of 0.13 eV, while that of \( \text{Fe}–\text{O}(–\text{B}^3) \) requires a much larger value of 0.96 eV. The energy barriers are consistent with the bond strength as the large barrier required to activate \( \text{Fe}–\text{O}(–\text{B}^3) \) bond breaking involves its high level of covalence. The low activation energy required for the \( \text{Fe}–\text{O}^b \) bond breaking relates to
the weak interaction between B$_2$O$_3$ and the Fe$_2$O$_3$ surface as only Fe–O$^b$ can be formed between these two blocks, thus B$_2$O$_3$ can easily move far away from the surface upon the heating process.$^{248}$

Figure 5.12 Constraint forces at some reaction coordinates ("ξ") for the Fe-O bond dissociation at 300 K: (a) Fe–O$^b$ bond, (b) Fe–O(B$^3$) bond, and (c) evolution of mean constraint forces of the Fe–O$^b$ and Fe–O(B$^3$) bonds along the reaction coordinates ("ξ").
Figure 5.13 Dissociative configurations and the corresponding activation energies of Fe–O bonds in the system. (a) and (d) are the initial configurations; (b) and (e) are the transition states; (c) and (f) are the corresponding free energy profiles. Sodium has been removed for clear visualization.

The dissociative configurations and the corresponding energy barriers of the B–O bond group are illustrated in Figure 5.15. The constraint forces along the reaction coordinates of these configurations are shown in Figure 5.14. For B\(^4\)–O bond, an energy barrier of 0.62 eV is needed to detach oxygen from the BO\(_4\) group. At 1073 K, the B\(^4\)–O dissociation is observed in both the bulk and the melt of Na\(_2\)B\(_4\)O\(_7\), which suggests that the heat exposure of 1073 K is sufficient to overcome the required activation energy. In this case, the bonding with Fe could play a role as an additional catalyst that can also speed up the process. The detachment of oxygen from the BO\(_3\) group needs a high barrier of 1.4 eV, which is twice as much as that of B\(^4\)–O. This value is independent upon which atom the oxygen bonds with, \(i.e.,\) 1.40 eV for B\(^3\)–O(–Fe) or 1.47 eV for B\(^3\)–O(–B\(^4\)). The barrier for B\(^3\)–O bond dissociation arises due to the stable nature of the BO\(_3\) triangle morphology, mostly governed by boron sp\(^2\) hybridization. This configuration secures the durability of the BO\(_3\) network in the pure boron oxide, which is consistent with the previous AIMD simulations of B\(_2\)O\(_3\) at 1073 K as the B\(_2\)O\(_3\) structure remains unchanged at its molten phase. Additionally, when BO\(_3\) loses one oxygen atom, it has an inherent tendency to connect with another one to recreate the
most favorable BO3 unit (Figure 5.15e and h).

Figure 5.14 Constraint forces at some reaction coordinates ("ξ") for the B–O bond dissociation at 300 K: (a) B4–O bond, (b) B3–O bond, (c) B3–O(–Fe) bond, and (d) evolution of mean constraint forces of the B4–O, B3–O, and B3–O(–Fe) bonds along the reaction coordinate ξ.
Figure 5.15 Bond dissociation and the corresponding activation energies of B–O bonds in the systems. (a), (d), and (g) are the initial configurations; (b), (e), and (h) are the transition states; (c), (f), and (i) are the corresponding energy profiles. Sodium has been removed for better visualization.

In summary, the barriers needed to activate the bond dissociation at the Fe$_2$O$_3$-borate interfacial region follows the sequence: Fe–O$^b$ < B$^4$–O < Fe–O(–B$^3$) < B$^3$–O(–Fe)/B$^3$–O(–B$^4$). Fe–O$^b$ and B$^4$–O dissociation has been observed at 1073 K, while the others remain unchanged under the surface catalysis and the heating at 1073 K.

5.7 Conclusions

The structures of Na$_2$B$_4$O$_7$ and B$_2$O$_3$ and their interactions on the iron oxide surface at 1073 K have been investigated by AIMD simulations. DFT calculations have been performed for electronic structure of selected configurations extracted from the AIMD simulations. The main conclusions can be highlighted as follows:
At high temperature, Na$_2$B$_4$O$_7$ exhibits strong chemical interactions on the iron oxide surface thanks to the ionic O–Na–O and the Fe–O covalent bonds. On the contrary, B$_2$O$_3$ weakly interacts with the Fe$_2$O$_3$ surface which accounts for its poor adhesion as a lubricant.

Charge calculations indicate that the negatively oxygen-rich Fe$_2$O$_3$ facilitates the sodium enrichment on the steel surface through Na–O ionic interactions. The better friction and wear reduction of Na$_2$B$_4$O$_7$ is associated with its larger charge transfer and the stronger interaction than those in Fe$_2$O$_3$-B$_2$O$_3$. The simulation results are in qualitatively good agreement with experimental findings of a sodium-rich layer on the steel surface and explain the superior lubrication of Na$_2$B$_4$O$_7$ over B$_2$O$_3$.

The activation energy calculations for Fe–O and B–O bonds reveal the possibility of bond dissociation following the order: Fe–O$^b$ < B$^4$–O < Fe–O(–B$^3$) < B$^3$–O(–Fe)/B$^3$–O(–B$^4$). The low Fe–O$^b$ activation energy explains the weak Fe$_2$O$_3$-B$_2$O$_3$ interaction, while the higher barriers of B$^3$–O bonds confirm a highly stable BO$_3$ network in both Na$_2$B$_4$O$_7$ and B$_2$O$_3$. 

130
Chapter 6. STRUCTURAL TRANSFORMATIONS OF SODIUM BORATES UNDER COMPRESSION

6.1 Introduction

Understanding the structural transformation of alkali borate glasses under extreme condition has been an intriguing topic that attracts tremendous attention in the fields of solid-state physics, tribochemistry, optical devices, electronic engineering and manufacturing. Borates are often considered as “anomalous” glasses because of their structural properties, coordination flexibility, and polymorphism. The ability of borate materials to adapt to various working conditions is practically versatile as it lays the foundation for widespread applications of borate-containing devices and technologies in practice. In recent years, researches on mechanical and chemical properties of borates have been reported, but little knowledge of the structural conversion in extreme conditions has been advanced.

Fundamentally, an alkali borate glass is constructed of two intrinsic components including network formers and network modifiers. The former is represented by boron atoms connecting with oxygen to create a highly cross-linking network, and the latter plays as charge compensators for \([\text{BO}_4^-]\) anions or non-bridging oxygen (O
\text{nb}). When compressed, the coordination flexibility of network forming agents is the origin of structural transformation and compressibility of inorganic glasses. Taking lithium borate glass as an example, Vegiri and Kamitsos indicated that four-fold boron is stabilized in the pressure range of 15 to 80 GPa, while five- and six-fold boron start forming from 80 to 300 GPa. When boron coordination number rises, it creates a highly compact glass, increases the degree of network connectivity as well as glass hardness. On the other hand, Svenson et al. revealed that molecular stacking instead of structural conversion is the major contribution to the borate densification. By using X-ray scattering, the nature of structural transformation of pure boron oxide at high pressure has been experimentally unveiled. Meanwhile, their response to pressure in the presence of network-modifying cations is not available. A small amount of added alkali metal oxides in the boron oxide can enhance the network connectivity, while a higher concentration inversely can contribute to the breaking of the polymerized

\(^3\)The content of this chapter was published on J. Phys. Chem. B 2020, 124, 1, 277-287.
network. As a result, their responses to external stimuli differ from mechanical-physical behaviors to chemical nature and electronic/atomic mechanism. In fact, the compressibility is composition-dependent and appears to be reversed with high and low alkali contents. Other physical and structural correlations with the corresponding alkali content have been discussed elsewhere.

As a lubricant in tribology, an alkali glass is confined between two metal substrates and subjected to compression and shear. When two surfaces rub against each other, asperity contact can result in enormous pressure variations within small contact and non-contact areas. When the pressure is sufficiently high, lubricant enters the boundary lubrication regime, lubricant molecules undergo a number of mechanical and chemical modifications in response to variations of external loads. Unlike bulk glasses where all ingredients are distributed homogeneously throughout the system, when confined between two metal substrates, sodium borates undergo a sudden change in the chemical environment at the glass-metal boundary. This effect leads to the compositional inhomogeneity and can produce a gradient-like interfacial profile as a result of free ion’s thermal mobility and diffusion. It has been found recently that high mobile sodium cations have a tendency to concentrate on the metal surface and form a sodium-rich layer when the material was subjected to shearing motion under loading, leaving the upper part with a well-polymerized borate layer. Under extreme pressure, liquid molecules at the contact interface can behave like a solid, which could alter mechanical properties such as stiffness strengthening and thereby increasing elastic modulus. For a certain stress range, mechanical load plays a role as a facilitator in activating the surface catalysis to promote surface-adsorbate reactions. Extreme pressure leads to permanent modifications in material structures, which could help to maintain the mechanical stability of the glassy film and its protective function. Nevertheless, the mechanism that leads to the polymerization in the borate glasses and the sodium enrichment at the surface has not been thoroughly studied. To understand the mechanism of structural transformation in alkali borate glasses under high pressure in detail is, therefore, essential for technological demands in chemistry and engineering practice.

In recent years, many of the atomic and electronic insights into detailed chemical reactions in tribo-systems have been increasingly investigated by computer simulations. The inclusion of external stimuli such as loading and
sliding conditions has been considered in a variety of lubricants and additives by Density Functional Theory (DFT). The advantages of parameter-free inputs and electronic level of accuracy allow the method to tackle complex systems without ad hoc parameterization in classical force fields. The theoretical model of reactions between benzene and Pt/Au surfaces upon compression using DFT has been reported.

In our work, a similar method was utilized to study the structural response of sodium borates confined between two iron oxide surfaces. Different Na$_2$O concentrations were taken into consideration to represent the sodium-rich and sodium-depleted domains in borate tribofilms. Electronic structure calculations were analyzed to understand different mechanisms of structural transformation in these sodium borate glasses which have not been proposed in previous reports.

**6.2 Simulation model**

DFT and AIMD simulations were performed using Vienna Ab Initio Simulation Package (VASP). The projector augmented-wave (PAW) method was chosen to describe electron-ion interactions, and the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) exchange and correlation functional was selected to describe exchange-correlation effects. The expansion of the plane wave was truncated using a cutoff of 450 eV in DFT calculations and 350 eV in AIMD simulations, respectively. The electronic optimization was conducted with the conjugate gradient algorithm with a convergence criterion of $10^{-4}$ eV.

The sodium borate glasses $x$Na$_2$O·$(100-x)$B$_2$O$_3$ ($x = 25, 33, 50$, and $60$ mol %) were sandwiched between two Fe$_2$O$_3$ with a minimum gap of 2.3 Å from the surface which corresponds to the ionic Na–O distance (Figure 6.1). Then the models were equilibrated at 300 K by AIMD simulations for 20 ps using the Nose-Hoover thermostat with the time step of 1 fs. After that, the systems were optimized with the z direction to obtain the equilibrium height of the supercell (d$_0$) and the corresponding energy at d$_0$. Once d$_0$ was obtained, we started compressing the systems by reducing the gap between two Fe$_2$O$_3$ surfaces stepwise by $\Delta z = 0.05$ Å. The electronic and atomic relaxations were repeated after each step of the gap reduction. The selection of step size $\Delta z$ was sufficiently small to observe every chemical occurrence in the system yet with affordable computational costs. The method is analogous to applying a vertical force on the top of the system to compress the borate layer; therefore, the average stress
was estimated based on the relative energy and distance compared to the equilibrium ones according to the following Equation 18:\textsuperscript{158}

\[
\sigma = -\frac{1}{S} \frac{\partial E}{\partial z}
\]  

(18)

where, \(\sigma\) and \(E\) are respectively the pressure applied on the z direction and the total energy of the system. \(S\) is the surface area which is equal to \(8.72 \times 10.07 \, \text{Å}^2\).

Figure 6.1 Model of sodium borates confined between two Fe\(_2\)O\(_3\) substrates for compression. In the compression, the upper surface was shifted along the z direction with a distance \(\Delta z = 0.05 \, \text{Å}\).

In practice, the contact between two working surfaces, especially two asperities can induce a flash pressure that could be orders of magnitude larger than the applied normal value.\textsuperscript{125} In our simulations, the separation distance between two Fe\(_2\)O\(_3\) surfaces was reduced until the pressure reached a high value of 10 GPa. After reaching 10 GPa, the systems were decompressed by increasing the gap distance along the z direction. The process is similar to that of the compression until the systems reverse to 0 GPa. The purpose of the decompression is to verify the stability of the pressure-induced polymerization when the applied load varies in the inverse direction.
6.3 Structures of sodium borate glasses at 300 K after cooling

Structures of sodium \( x \text{Na}_2\text{O} \cdot (100-x)\text{B}_2\text{O}_3 \) (\( x = 25, 33, 50, \) and 60 mol %) are presented in Figure 6.2. It is evident that with higher concentrations of Na\(_2\)O, the borate chains are shorter with more non-bridging oxygen atoms, which is consistent with other literature. The initial chain length and the fraction of O\(^{nb}\) are closely related to the bonding behavior with the Fe\(_2\)O\(_3\) surface and the polymerization when the systems are compressed.

Figure 6.2 Visualization structures of sodium borate glasses at 300 K obtained from the cooling process by AIMD simulation.

Figure 6.3 presents the RDFs of B−O, Na−O, and O−O pairs in \( x \text{Na}_2\text{O} \cdot (100-x)\text{B}_2\text{O}_3 \) at 300 K. B−O, Na−O, and O−O pairs feature first sharp peaks at 1.38, \( \sim 2.28 \) – 2.33 and \( \sim 2.39 \) – 2.43 Å, respectively. These values correspond to B−O bond length, Na−O ionic, and O−O distances presented in Table 6.1. The obtained values of bond distances are in a good agreement with other reported data by both experiments. The height of the first peaks in the B−O and O−O RDF reduces with the increase of Na\(_2\)O content while that of Na−O increases with the higher Na\(_2\)O concentrations. This is indicative of sodium effects to the borate network, i.e. the borate network becomes less
compact and loses its connectivity with the interference of sodium ions.

Figure 6.3 Radial distribution function g(r) of B–O, Na–O, and O–O pairs in xNa2O·(100-x)B2O3 systems at 300K. The first peaks of g(r) correspond to the bond length of each pair presented in Table 5.1.

Table 6.1 Structural parameters of xNa2O·(100-x)B2O3 at 300 K compared with experimental data (where available).

<table>
<thead>
<tr>
<th>Glass</th>
<th>AIM D</th>
<th>Exp. 277</th>
<th>[B–O]</th>
<th>Exp. 278</th>
<th>Exp. 56</th>
<th>Exp. 57</th>
<th>Exp. 58</th>
<th>Exp. 59</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na2O·3B2O3 (Na2O 25%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.41</td>
<td>2.33</td>
<td>2.40</td>
<td>2.39</td>
</tr>
<tr>
<td>Na2O·2B2O3 (Na2O 33%)</td>
<td>37.5</td>
<td>43</td>
<td>1.38/1.49</td>
<td>1.43</td>
<td>1.38/1.48</td>
<td>2.29</td>
<td>2.37</td>
<td>2.41</td>
</tr>
<tr>
<td>Na2O·1B2O3 (Na2O 50%)</td>
<td>33.3</td>
<td>34</td>
<td>1.39/1.48</td>
<td>1.43</td>
<td>1.38/1.48</td>
<td>2.29</td>
<td>2.41</td>
<td></td>
</tr>
<tr>
<td>3Na2O·2B2O3 (Na2O 60%)</td>
<td>18.8</td>
<td></td>
<td>1.40/1.50</td>
<td></td>
<td></td>
<td>2.28</td>
<td>2.43</td>
<td></td>
</tr>
</tbody>
</table>
6.4 Energetic properties under compression and decompression

The systems were optimized to obtain the equilibrium distance between the two surfaces before proceeding to reduce the distance. The equilibrium distance corresponding to the minimum energy of each system is presented in Figure 6.4. The equilibrium distances $d_0$ are 14.64, 14.34, 14.25, and 14.18 Å for FeNaB25%, FeNaB33%, FeNaB50%, and FeNaB60%, respectively. The energy at the equilibrium distance of each system is the minimum energy corresponding to zero pressure in the compression process.

![Graphs showing energetic properties](image)

Figure 6.4 Optimization of the simulation cells of FeNaB systems. The green dot is the equilibrium distance of each system. The red line is the fitted curve. The lowest energy at the distance $d_0$ in each system was shifted to zero.

The variation of energy against the separation distance during the compression and decompression is presented in Figure 6.5. One can see that, with different Na$_2$O concentrations, the systems behave differently in terms of energy variation and reaction points. Generally, as the gap decreases, the energy changes slowly at first and progressively increases with some energy drops until it dramatically increases within the separation distance from ~6 to 9 Å. For the compression, the red circles mark the points where the boron coordination number alters from three to four ($^{(3)}$B→$^{(4)}$B). For each FeNaB system, a certain pressure is required to initiate such polymerization (P$_i$),
i.e. 1.3, 4.3, 3.1 and 1.9 GPa for FeNaB25%, FeNaB33%, FeNaB50%, and FeNaB60%, respectively (Figure 6.5). Therefore, we can divide the compression into two consecutive stages I and II.\textsuperscript{63–64} The first stage (I) is the low-pressure region where only the rearrangement is observed in the sodium borate layer, and the second one (II) is the high-pressure region where the polymerization proceeds. It is worth mentioning that there is not a well-defined boundary between the two stages, thus we chose the starting point where the first $\text{BO}_3 \rightarrow \text{BO}_4$ conversion occurs in each system as the marking point. In the first stage, the gap reduction between two Fe$_2$O$_3$ substrates leads to a marginal change in the energy of the system as there are no significant modifications in the sodium borate structures except for the rearrangement of borate fragments. Borate fragments combine with sodium to adapt geometrically to the volume change as the applied loads are insufficiently high to trigger a chemical modification in the boron electronic structure. In the second stage, the conversion from $\text{BO}_3$ to $\text{BO}_4$ registers leads to several points where the energy of the system drops significantly.\textsuperscript{175} At extreme pressure (8 – 10 GPa), the energy goes up abruptly within a minor distance reduction, but no significant changes in the borate structures except for FeNaB25% system (Figure 6.5a).

Figure 6.5 Relative energy versus the gap distance during the compression (CP) and decompression (DC) processes. The zero energy is the energy of the system at the
equilibrium distance obtained from cell optimization. Each red circle represents one $^{[3]}\text{B} \rightarrow [4]\text{B}$ conversion while each green circle corresponds to one $[4]\text{B} \rightarrow [3]\text{B}$ conversion.

 Conversely, in the decompression the energy curves resemble those of the compression at the extremely high-pressure region, and start to deviate in the medium-pressure region. There are significantly fewer reaction points of $\text{BO}_4 \rightarrow \text{BO}_3$ decomposition than those of $\text{BO}_3 \rightarrow \text{BO}_4$ conversions in the compression one, which means that a majority of $\text{BO}_3 \rightarrow \text{BO}_4$ conversions induced upon compression are irreversible. Due to the permanent transformations after the compression-decompression cycle, the equilibrium volume is smaller than its original one. In addition, some $\text{BO}_4$ structures at high-pressure remain after the decompression. These structures have a higher energy than the initial $\text{BO}_3$ form, thus contributing to a higher equilibrium energy than that in the compression. The discrepancies in the energy curves between the compression and decompression depend upon the reversibility of the systems, i.e. the more $\text{BO}_4 \rightarrow \text{BO}_3$ recovers, the smaller the energy variation occurs.

 As shown in Figure 6.5, the starting pressure for the polymerization initiation varies with different $\text{Na}_2\text{O}$ concentrations used. Figure 6.6 presents the relationship between sodium content, the portion of $^{[4]}\text{B}$, and the value of $P_i$. It is worth mentioning that, in our calculations, the $^{[4]}\text{B}/(^{[4]}\text{B} + ^{[3]}\text{B})$ ratios are systematically lower than those obtained in the solid glass,\textsuperscript{280} which can be specified to the effect of small simulation cells. On the other hand, in the confined models, there is a loss of periodicity along the z direction, causing the lack of boron coordination number at the glass and $\text{Fe}_2\text{O}_3$ substrates boundary. However, it is a good agreement with the experimental measurement that the sodium borate with $x = 33\%$ $\text{Na}_2\text{O}$ contains the largest amount of $\text{BO}_4$, while this value reduces for both $x > 33\%$ and $x < 33\%$.\textsuperscript{51,280} Following the trend, $P_i$ reaches the highest value of 4.3 GPa in FeNaB33\%, and decreases following the order FeNaB50\% (3.1 GPa) > FeNaB60\% (1.9 GPa) > FeNaB25\% (1.3 GPa). This result indicates that $P_i$ depends directly on the percentage of $^{[4]}\text{B}$ at 0 GPa rather than the $\text{Na}_2\text{O}$ content. In short, the polymerization is more preferable in the system with less $^{[4]}\text{B}$ and less $\text{Na}^+$ cations.
Figure 6.6 Correlation between the percentage of $^{[4]}B$ (open symbols) and starting pressure of the polymerization (filled symbols, right axis) with different Na$_2$O concentration in FeNaB systems. DFT bulk is the results of xNa$_2$O·(100-x)B$_2$O$_3$ by AIMD for 10 ps at 300 K.

6.5 Structural transformation under compression and decompression

Figure 6.7 shows the percentages of fourfold-coordinated boron produced from compression and decompression of the FeNaB systems. At lower pressures, there is no new $^{[4]}B$ formed. From P$_i$, the portion of $^{[4]}B$ increases sharply up to 9.5 GPa. Systems with a low Na$_2$O content are more likely to be polymerized than those with higher Na$_2$O content, which is reflected by a lower P$_i$ (1.3 GPa) and a higher $^{[4]}B$ percentage (70%). The transformation from threefold to fourfold boron implies a higher connectivity in the borate glasses, and the degree of connectivity is consistently related to Na$_2$O concentration. At 10 GPa, the ratios of $^{[4]}B/(^{[4]}B+^{[3]}B)$ decrease with increasing Na$_2$O percentage; in particular, 70%, 66%, 61% and 56% $^{[4]}B$ are dominated in FeNaB25%, FeNaB33%, FeNaB50%, and FeNaB60%, respectively. This is consistent with the reduced compressibility of alkali borates with increasing alkali metal concentration reported by the experiment.\footnote{71} The fraction of $^{[4]}B$ content in the systems is in a good agreement with previous reports on borate structures at high pressure.\footnote{62, 65} Furthermore, At 10 GPa, the maximum coordination number of boron achieved in the current simulation is four. MD simulations based on classical force fields have found that four-coordinated boron is stable up to a pressure as high as 80 GPa,\footnote{65} while X-ray scattering measurement reported a minor change in $^{[4]}B$ content up to 120 GPa.\footnote{282} Higher
coordinated state such as fivefold and sixfold boron can only be achieved in more extreme conditions, i.e., from 80 to 300 GPa.\textsuperscript{65}

Figure 6.7b reveals that the ratios of fourfold boron atoms are slightly reduced with the expansion of the simulation cell along the z direction. The \( \text{BO}_3 \rightarrow \text{BO}_4 \) conversion process finishes at 2 GPa. As the pressure is released, these figures, however, do not recover to their initial values before compressed. Quantitatively, the initial percentages of \(^4\text{B}\) in FeNaB25\%, FeNaB33\%, FeNaB50\%, and FeNaB60\% systems are 12.5\%, 29.2\%, 16.7\% and 6.3\%, respectively (Figure 6.7a). After a compression-decompression loop, these figures remain remarkably high at 29.2\% for FeNaB25\% and 37.5\% for FeNaB33\% and FeNaB60\%. This confirms that pressure induces irreversible structural transformations in sodium borates in the simulation range, and agrees well with the evolution of energy in the systems.

![Figure 6.7](image_url)

**Figure 6.7** Evolution of four-coordinated boron as a function of pressure during the compression (a) and decompression processes (b). The boron coordination number was identified with a cutoff distance of 1.6 Å.

The permanent structural transformation has been observed primarily in alkali and inorganic glasses under high pressure.\textsuperscript{175, 255, 279, 283-286} The reversibility of these glasses relies on a number of factors such as the compression threshold, alkali concentration, compression/decompression rate and compression temperature.\textsuperscript{62, 279, 284, 286-287} Regarding the alkali content, our current simulation shows that systems with higher \( \text{Na}_2\text{O} \) concentrations exhibit a weaker ability to restore its original structure after being compressed. For example, after the pressure released from 10 GPa to 0 GPa, the percentage of fourfold boron in FeNaB25\% is reduced by 48\%, while they are relatively
small by 27.8% and 18.5% for FeNaB50% and FeNaB60%, respectively. The polymerization can increase the stiffness of the glassy layer, improve its ability to withstand film rupture and collapse under extreme conditions. The irreversible transitions can help maintain the stability of the applied materials. Details about the mechanisms of the polymerization will be discussed in the following sections.

6.5.1. Low pressure region: Structural reorientation

To provide more details about the structural transformation during the compression process, we analyzed the structures of the systems at low- and high-pressure regimes. At the low-pressure region, there is no polymerization observed in the borate structures as boron coordination number remains unchanged. In order to be transformed from BO$_3$ triangle to BO$_4$ tetrahedron, the BO$_3$ planar shape has to be distorted to delocalize sp$^2$ hybridization into sp$^3$ one. Simultaneously, the O–B–O angles turn from 120° to ~109° to create space for an additional oxygen atom. Therefore, a certain amount of energy is required to stimulate the electronic alteration at boron sites. A mild pressure can only result in the physical reorganization of boron oxide units to adapt to the volumetric variation of the cell. In our simulation, among the four systems with different Na$_2$O concentrations, the arrangement is more visible with higher sodium concentrations than with the lower ones. This can be interpreted by the fact that an inordinate amount of sodium can break long polymer chains into shorter ones. These short chains possess low inertia and therefore are more geometrically adaptable to their surrounding environment.

Figure 6.8 depicts the reorientation of borate fragments including BO$_3$, B$_2$O$_5$, and six-membered ring complexes in the highest Na$_2$O concentration system FeNaB60%. Some noticeable alterations are clearly visible at B1-B9 sites as noted in Figure 6.8. Initially, those fragments scatter randomly throughout the system. Under a mild compression to 1.8 GPa, those molecules reorient to adapt to the adjustment of the separation distance, forming the BO$_3$ planes that are parallel to the metal surfaces. This behavior is typical for the adaptability of borate compounds to external stimuli, which is distinct to silicates and other inorganic glassy lubricants. The reorganization is also one of the vital mechanisms of the densification to occur in glasses. In other word, it has been found that the packing of structural units rather than the polymerization is the
main mechanism for the densification of borate glass.\textsuperscript{67}

![Figure 6.8 Reorientation of borate structure in FeNaB60\%: (a) initial system at 0 GPa, (b) at 1.8 GPa. Sodium has been removed for clear visualization.](image)

The molecular rearrangement before polymerization has been largely noticed in other compressed glasses.\textsuperscript{63, 135, 279} This mechanical flexibility is essential for the resilience against structure collapse due to external forces without changing the coordination number. Therefore, the orientation of boron oxide fragments can create a locally layered structure that could support the relative movement between boron oxide units and benefit friction reduction.\textsuperscript{14-15}

### 6.5.2. High pressure region: Three Mechanism Polymerization

In the high pressure region, new \textsuperscript{[4]}B–O bond formation was observed in the systems, resulting in an alteration of boron coordination number from three to four. These reactions leading to such conversions under the compression were classified into three different reaction mechanisms M1, M2 and M3 as follows:

- **M1**: \( \text{BO}_3 + \text{O}_3 \rightarrow \text{BO}_4 \)
- **M2**: \( \text{BO}_3 + [\text{2}\text{I}_\text{O}] \rightarrow \text{BO}_4 \)
- **M3**: \( \text{BO}_3 + [\text{2}\text{I}_\text{O}] \rightarrow \text{BO}_4 \) and \( [\text{2}\text{I}_\text{O}] \rightarrow [\text{3}\text{I}_\text{O}] \)
O₃ is the oxygen of the Fe₂O₃ surface. In M1 and M2, boron connects to its nearby oxygen atoms of either the surface or the non-bridging oxygen of the borate to form a new [⁴]B–O bond and create a BO₄ tetrahedron. The former involves a chemical reaction across the interface region while the latter proceeds inside the borate glasses. Remarkably in M3, the reaction involves boron and O⁹⁺(²)O, which activates oxygen from the typical two coordinated to three coordinated state (³)O. Figure 6.9 shows the configurations that capture the bond formation that transforms BO₃ into BO₄ through the three pathways above. When the cell is mechanically reduced in thickness, not only the distances among atoms inside the borates but also those between the borate and the surface are shortened. This process can trigger electron sharing between atoms and activate chemical bonds between them. In all cases, boron atoms that are close to the oxygen of either the surface or the borates (within a distance of 2.0, 2.4 and 2.8 Å) move closer and form new [⁴]B–O bonds. These newly formed [⁴]B–O bonds with a bond length of ~ 1.5 Å, is slightly longer than a typical value of bond length in system containing tetrahedral borates, i.e., ~ 1.4 Å. Nevertheless, the new bond formation has completely altered the BO₃ planar geometry into the tetrahedral form with the addition of a new oxygen (Figure 6.9).
Figure 6.9 Ball and stick model of the selective configurations before (the left) and after (the right) the polymerization in the system following three mechanisms M1 (a) and (b), M2 (c) and (d), and M3 (e) and (f). These configurations before and after the chemical reactions were captured from two consecutive steps with $\Delta z = 0.05$ Å. Sodium has been removed for better visualization.

In order to clarify the relationship between the reaction pathways and the applied pressure, we recorded comprehensively all polymerization events in the system versus pressure when the reaction occurs (Figure 6.10). The resultant statistics indicates that the reaction pathways depend strongly on the pressure magnitudes imposed in the systems and the amount of Na$_2$O introduced. In particular, the reactions following mechanisms M1 and M2 have a tendency to start at a lower pressure i.e. 1.3 GPa for M1 in FeNaB25%, at 1.9 GPa for M2 and FeNaB60%, respectively. M1 and M2 can be
spontaneously initiated when the applied load brings oxygen and boron atoms to a sufficiently close distance. When M1 occurs, it strengthens the surface-borate binding, whereas M2 increases the compactness inside the borates by connecting borate fragments through $\text{O}^\bullet$ ($^{(2)}\text{O}$). The former occurs mostly in the system with 25% Na$_2$O while the latter usually appears in the higher Na$_2$O concentration systems of 50% and 60%. This can be understood by the fact that in the low Na$^+$ concentration systems, there is a direct contact between the borate and the surface, whereas the surface and the borate are separated by a layer of sodium atoms in the higher Na$^+$ concentration system. On the other hand, in the systems with 50% and 60% Na$_2$O, M2 is more preferable as these systems contain a remarkable amount of $\text{O}^{\text{ab}}$ available for the reactions with BO$_3$.

For M3, apart from turning $^{[3]}\text{B}$ into $^{[4]}\text{B}$, an additional amount is needed to stimulate $^{[2]}\text{O}$ into $^{[3]}\text{O}$, which is the less stable state of oxygen. Therefore, those following mechanism M3 require a higher pressure ($P > 4.3$ GPa) to eventuate, which is particularly consistent with X-ray scattering measurement of $^{[4]}\text{B}$ signature starting to dominate in B$_2$O$_3$ from 4.1 GPa, $^{61}$ and 5 GPa in Li$_2$B$_4$O$_7$. $^{288}$

![Figure 6.10 Polymerization mechanisms of sodium borates under compression as a function of pressure. M1 (black circles), M2 (red stars), and M3 (green diamonds) refer to three polymerization pathways. The dotted lines connect the first points when each mechanism was observed in each system.](image)

In order to rationalize the dependence of the polymerization mechanisms on pressure, Density of States (DOS) was performed to investigate the changing in electronic structure of boron and oxygen in the reactions. Only DOS from M2 and M3 are presented (Figure 6.11) as M1 and M2 share similar characteristics. Additionally,
both M2 and M3 can be generalized for the polymerization in the bulk systems. As can be seen in the figure, the $^3\text{B} \rightarrow ^4\text{B}$ conversions involve both $s$ and $p$ orbitals of boron and oxygen, which is associated with the modification from $sp^2$ to $sp^3$ hybridization. In all cases, DOS of both B and O are expanded indicating the delocalization of the atomic orbitals. This enables the atoms to share electrons with other atoms that engage in the reaction. When transformed from $^3\text{B}$ to $^4\text{B}$, states of boron are upshifted to higher energy levels including both B $2s$ (below $-18$ eV) and $2p$ orbitals (above $-12$ eV) due to the electron donation from O’s $p$-orbitals. As a result, boron’s orbitals are partly and fully overlapped with oxygen’s states at approximately $-10$ to $-8$ eV and $-20$ to $-18$ eV. The broadening of B $2s$ and B $2p$ bands indicates profound modifications in both boron and oxygen electronic structure. In fact, sodium borate band gaps are narrowed with the increasing pressure, as a result of band broadening in $2s$ and $2p$ states (Figure 6.12). This in turn, leads to the changes in the optical properties such as birefringence and optical anisotropy of the material.

Basically, the transition form $^3\text{B}$ to $^4\text{B}$ does not require significant effort. As an “anamalous” element, boron ($1s^22s^22p^1$) has five electrons including three valent ones. At the normal state, boron form three covalent bonds with oxygen in BO$_3$ form, creating $sp^2$ hybridization. Such hybridized configuration leaves one vacant orbital $p_z$ that is perpendicular to the BO$_3$ plane. This vacant orbital can naturally accept donor from oxygen lone pairs in either $\text{O}^\text{nb}$ or $\text{O}^\text{b}$ to become $sp^3$ hybridization, thus it requires a low energy to activate a donor-acceptor reaction between boron and oxygen to form the fourfold coordination.
Figure 6.11 Total density of state of boron and oxygen in the polymerization: (a) M2 and (b) M3. The arrows show how DOS of oxygen changes before (dash line) and after (solid line) the reaction.

Figure 6.12 Total DOS of sodium borate Na₂O.2B₂O₃ at 0, 4 and 8 GPa.

Although boron’s DOS are similar in M2 and M3, there are clear distinctions between DOS of oxygen in M2 and M3. In M2, as an non-bridging oxygen, oxygen’s
HOMO is occupied by two lone pairs $2p$. These pairs can be shared easily with the empty $2p_z$ orbital of boron through a donor-acceptor reaction.\textsuperscript{159} The reaction results in a more stable state for oxygen, making the DOS of oxygen shifted to a lower energy level (Figure 6.11a). This explains why M1 and M2 can be proceeded as a relatively low pressure. On the contrary, in M3 DOS of oxygen is upshifted by $\sim 1.0$ eV for the $s$ orbitals and by $\sim 0.4$ eV for the $p$ orbitals as marked by the arrows (Figure 6.11b). The upshift is associated with the less stable hybridization of oxygen as a consequence of the excitement to a higher energy state. Thus, the extra load compared to those of M1 and M2 is to activate oxygen state from $^{[2]}$O to $^{[3]}$O.

6.6 Sodium distribution in the compression and decompression

The distribution of sodium cations is important for transportation properties such as melt viscosity, high temperature conductivity, and lubricity. The evolution of the number of Na\textsuperscript{+} cations adsorbed on two Fe\textsubscript{2}O\textsubscript{3} substrates with pressure is presented in Figure 6.13. During the compression, the polymerization occurs, accompanied by the increase of Na\textsuperscript{+} cations moving closer to the surface. Starting from 2 GPa, the number of Na\textsuperscript{+} on the surfaces grows sharply to reach a maximum number of 12 ions at 5 GPa in FeNaB50\% and FeNaB60\%. A further compression beyond 5 GPa does not bring more sodium to the surface as the sodium number in all systems levels off from 5 to 10 GPa. The plateau regime of Na\textsuperscript{+} ions on the surface curves indicates the saturation of surface capability to adsorb free cations because both FeNaB50\% and FeNaB60\% finish with 12 adsorbed ions despite the difference in their Na\textsubscript{2}O concentrations. As discussed in the previous section, the bond formation between boron in BO\textsubscript{3} and O advances the connectivity between discrete borate units or the cross-linking between long chains. These activities inevitably reduce the modification role of Na\textsuperscript{+} inside the borate network. Na\textsuperscript{+} moves to the surfaces and creates Na-rich layers at high pressure. This phenomenon can be observed in both the upper and lower sodium borate-Fe\textsubscript{2}O\textsubscript{3} interfaces, which can clearly be seen in Figure 6.14, particularly with high concentrations of sodium. The decompression results in the desorption of Na\textsuperscript{+} cations from the surfaces starting from 4 GPa. Despite some hysteresis, the number of adsorbed sodium drops quickly to a value lower than the initial one when the pressure is released to 0 GPa.
Figure 6.13 Number of Na$^+$ ions adsorbed on Fe$_2$O$_3$ substrates during the compression (solid lines) and decompression (dotted lines). Only Na$^+$ within a distance of 2.3 Å from the surface is counted.

Figure 6.14 describes the distribution of Na$^+$ in the systems along the compression direction at two separate stages of rearrangement and polymerization. First, Na$^+$ cations distribute evenly through the system. As the cell sinks, a large number of them move to two interfaces, showing two visibly sharp peaks at the borate-metal boundaries in the density profiles from 6 to 8 GPa. This indicates a substantially higher Na$^+$ density at the interfaces compared to that in the middle of the systems. For example, the density value of Na$^+$ at the surface is double that in the core of FeNaB33% and FeNaB50%. Figure 6.14d, e, and f show ball and stick models of the systems at 6 GPa. As shown in the figure, with less Na$^+$ in the glass, there is no clear evidence of Na$^+$ at the surfaces which is, instead, replaced by B–O and Fe–O bonds between the surfaces and the sodium borate. With a higher Na$_2$O content, there is a clear layer of sodium on each Fe$_2$O$_3$ surface, resulting in a fine layer that can partially separate the borates and the Fe$_2$O$_3$. At high Na$_2$O concentrations (50 and 60%), discrete borate fragments can connect with each other to create longer borate chains, leading to the reduction of non-bridging oxygen. As a result, the network modifier role of sodium becomes less dominant than at lower pressure. On the other hand, when the volume is reduced and BO$_3$ is converted to BO$_4$, not only the connectivity but also the densification is enhanced. The connection leaves less space to accommodate such a large cation like sodium. However, in the sodium borate bulk, alkali cations are trapped in a homogeneous chemical environment and mixed with other cations or network builders. In this confined model, the glass-metal contact disrupts the periodicity in the borate glasses. The sodium cations which
are excluded from the polymerized borate are stuck at the surface, forming a sodium-rich layer on the iron oxide surface. It is noted that in this work, only static compression and decompression were performed. Therefore, the sodium distribution may not capture all types of Na motion that exist in dynamic simulations. In this case, the sodium distribution is influenced by the reduction of the gap between two Fe$_2$O$_3$ surfaces and the cross-linking of the borate network. However, in dynamic simulations, the effects of temperature, pressure and shear could activate sodium mobility; thus, sodium cations can move easily toward the interface than in the static simulation.

![Figure 6.14 Density profile of sodium ions (the yellow in the lower row) along the z direction (upper row) and ball-and-stick models at 6 GPa of FeNaB33% (a, d), FeNaB50% (b, e) and FeNaB60% (c, f) borates systems. The center of the simulation cells has been shifted to zero.](image)

Apart from increasing network connectivity by the polymerization of boron oxide clusters, Na$^+$ cations also play a part in the densification of the glass at high pressure. As shown in Figure 6.15a, the peak of Na–O radial distribution function (RDF) shifts slightly to a lower distance, i.e. from 2.36 Å at 0 GPa to 2.27 Å at 4 GPa, and remains unchanged until 10 GPa, which indicates the shortening of Na–O interacting distance in response to the severe load. Furthermore, as the portion of O$^{nb}$ is reduced (Figure 6.15b), more BO$_4$ are formed. Simultaneously, a small number of three-fold oxygen arises, suggesting that the increment of [4]B is balanced by [3]O clusters. Nevertheless, the [4]B outnumbers the [3]B, thus the role of some sodium cations as modifiers has
changed to charge compensators, especially in low Na$_2$O% systems. The appearance of $^{[3]}$O clusters is more dominant in FeNaB25% and FeNaB33%, indicating that $^{[3]}$O is more important in charge compensation mechanism in systems with less Na$^+$ content. For FeNaB50% and FeNaB60% systems, a large number of O$^{nb}$ dominates at high pressure, thus the role of Na$^+$ as network modifiers remains significant. However, the quantitative classification of Na$^+$ as a network modifier or a charge compensator is difficult as there is the interference of the surface’s oxygen. One can conclude that the formation of BO$_4^-$ is not only balanced by the formation of new oxygen triclusters, but also by Na$^+$ playing as charge compensators.

Figure 6.15 Evolution of RDFs g(r) of Na–O pair (a) and number of O$^{nb}$ (solid lines) and $^{[3]}$O (dotted lines, including $^{[3]}$O in B–O–Fe cluster, (b)) in sodium borates versus pressure during the compression. The dotted lines in (a) connect the peaks of RDF at different pressures. In (b), black (FeNaB25%), blue (FeNaB33%), green (FeNaB50%), and red (FeNaB60%).

The simulation results indicate that pressure plays a crucial role in increasing the connectivity in sodium borates as well as defining the layers of the tribofilm. The enrichment of sodium at the interface resembles the resultant sodium-rich film in the shearing motion, which was predicted as a result of flowing effects at high temperature. Complementarily, this simulation unveils that the sodium enrichment process starts from the compression stage instead of the shearing effects in previous experimental predictions. It is worth mentioning that the obtained sodium-rich film is a result of the tribotest under applied load and shear at high temperature with Na$_2$O·2B$_2$O$_3$, which corresponds to the system FeNaB33% in the current simulation. In our simulation, only pressure was considered. At high pressure, the simulation shows...
that the movement of sodium to the surface is particularly obvious as a result of increasing the degree of polymerization in the borate glass. The compression at elevated temperature mostly induces permanent transformation in the glasses, which means the interfacial texture keeps unchanged with changing conditions. Therefore, the result of the sodium-rich layer in the current compression process is also comparable to that observed in the high temperature experiment.  

6.7 Conclusions

The structural transformation of sodium borates $x\text{Na}_2\text{O} \cdot (100-x)\text{B}_2\text{O}_3$ ($x = 25, 33, 50, \text{and } 60 \text{ mol} \%$) confined between two Fe$_2$O$_3$ substrates during the compression and decompression has been investigated by DFT simulations. The compression induces the physical reorientation in borate structures before the chemical modification proceeds to polymerize the sodium borates. With various Na$_2$O mol %, the starting pressure for the polymerization ($P_i$) increases with the increase of initial $\frac{[4]B}{([3]B+([4]B)}$ fraction at 0 GPa. The polymerization process can be divided into three distinct mechanisms M1, M2, and M3. With low Na$_2$O content, M1 is more likely to occur through $\text{BO}_3 + \text{O}_s \rightarrow \text{BO}_4$, while with higher Na$_2$O concentrations, M2 arises through $\text{BO}_3 + \text{O}^{nb} \rightarrow \text{BO}_4$. Both M1 and M2 can be initiated at relatively low pressures (1.3 and 1.9 GPa). For M3 which is formed between $\text{BO}_3$ and $\text{O}^b$ by $\text{BO}_3 + [2]\text{O} \rightarrow \text{BO}_4$, a high pressure (above 4.3 GPa) is required to activate electronic structure of boron and oxygen from $[2]\text{O}$ to $[3]\text{O}$ and $[3]\text{B}$ to $[4]\text{B}$. We analyzed DOS to interpret the nature of each mechanism and their correlation with the occurred pressure. After the compression, a majority of $\text{BO}_3 \rightarrow \text{BO}_4$ transformations remain irreversible when the systems were unloaded to 0 GPa. The compression also creates a sodium-rich layer stuck at the surface-borate interfaces at high pressure, which supports the experimental results where the sodium-rich film was observed after a tribotest. The current simulation provides a full atomistic interpretation of the experimental observations and proposes the molecular mechanisms underlying the structural transformations.
Chapter 7. ALKALI BORATE GLASSES UNDER SLIDING CONDITIONS

7.1 Introduction

Shear-induced phase transitions in the bulk material and chemical reactions at the sliding interfaces can significantly affect the stability and tribological properties of the systems under severely loaded sliding. When a high load is applied, the materials can undergo amorphous to crystalline transition in MoS$_2$,\textsuperscript{245} band gap opening in graphene,\textsuperscript{291} sliding-induced graphitization.\textsuperscript{292-294} The bond formation and dissociation\textsuperscript{178-179} take place inside the bulk materials or at the binding interfaces. On the one hand, these phenomena initiate some novel properties of materials, such as an “easy-shear” layered pattern, that could benefit the frictional process. On the other hand, mechanically activated breaking of interfacial bonds is a potential source of wear debris,\textsuperscript{295} increasing friction,\textsuperscript{179, 296-297} surface degradation,\textsuperscript{298-299} and material loss or tribocorrosion.\textsuperscript{300} Thus a minor change of interfacial bonds at the sliding interface can subsequently induce huge impacts on the overall friction and wear outcomes.

The formation of layered structures during shear involves the molecular arrangement toward directional motion. This phenomenon was commonly found in 2D materials in which the absence of bonded interlayering interactions is critical to maintain the clearance among layers.\textsuperscript{170, 301-303} Likewise, in the environment with cationic interference, long-range and non-directional interactions create a more adaptable assembly when two surfaces move against each other. As a result, low friction can be expected.\textsuperscript{128-129, 249} For the systems where the lubrication is based on chemisorbed layers, bond formation and dissociation activities have been recognized as one of the most common shear-induced phenomena at the interfacial region between two working pieces.\textsuperscript{146-147, 178-179, 304} The stick-slip instability occurs at the sliding of two counter surfaces as a result of bond formation-stretching-dissociation sequences.\textsuperscript{178-179, 305} Bond dissociation at the interface due to shear promotes the generation of dangling bonds, which are generally unstable and likely to form new bonds with the nearest atoms. In some cases, dangling bonds are terminated which is known as surface reconstruction.\textsuperscript{128, 306} Otherwise, a massive bond rupture is the origin of abrasive and

\textsuperscript{4} The content of this chapter has been accepted to publish on Computational Materials Science.
adhesive wear. In the search for novel materials with excellent lubrication properties, a thorough understanding of wear formation and its mechanism in the systems is required to mitigate wear and improve the quality of end products.

Borate compounds are mechanically and thermally stable, which will benefit the working tools that are exposed to high loads. One of the most important properties of the alkali borate compounds is the mysterious contribution of the alkaline elements. Experimental works have revealed that alkali-rich tribofilms are superior in the reduction of friction and wear thanks to the ionic interfacial connection. With different alkali metals and concentrations, however, the tribological performance varies depending on the cationic field strength. This cationic effect also plays an important role in binary and mixed borate glasses, yet the contribution to interfacial interactions remains elusive. Furthermore, pressurized borates are extremely hard, with the increasing elastic modulus and viscosity, making them more resistant to external variables. It is unclear how such a highly polymerized network, which is compact and hard, can be tailored to facilitate the smooth movement. In this chapter, we used DFT simulations to study how alkali borate lubricants and their bonding behaviors at the interface respond to severely loaded sliding. The work is based on the models of sodium borates with three different concentrations of Na$_2$O and two other common alkali metal borates such as lithium and potassium borates, which could provide an insightful and comprehensive picture of the class of alkali borate lubricants.

### 7.2 Simulation details

In this chapter, in order to study the effects of alkali metals on frictional properties of alkali borate lubricated systems, five borate lubricants with different alkali metal and sodium concentrations were used including Na$_2$O·3B$_2$O$_3$ (25% Na$_2$O), Na$_2$O·2B$_2$O$_3$ (33% Na$_2$O), Na$_2$O·B$_2$O$_3$ (50% Na$_2$O), Li$_2$O·2B$_2$O$_3$, and K$_2$O·2B$_2$O$_3$. There were 72 atoms for Na$_2$O·3B$_2$O$_3$, Na$_2$O·B$_2$O$_3$, and 78 atoms for Na$_2$O·2B$_2$O$_3$, Li$_2$O·2B$_2$O$_3$, and K$_2$O·2B$_2$O$_3$. The borate glasses were created by the melt and quenching method, and then transferred to the Fe$_2$O$_3$ substrates to build confined models. In this chapter, there are five Fe$_2$O$_3$-borate systems namely FeNaB25%, FeNaB33%, FeNaB50%, FeLiB, and FeKB, corresponding to five alkali borates Na$_2$O·3B$_2$O$_3$, Na$_2$O·2B$_2$O$_3$, Na$_2$O·B$_2$O$_3$, Li$_2$O·B$_2$O$_3$, and K$_2$O·B$_2$O$_3$, respectively. In order to reduce the effects of
image interactions from the periodic boundary condition, a vacuum layer 15 Å was added on the top of the higher Fe$_2$O$_3$ surface in the Fe$_2$O$_3$-borate confined systems.

![Figure 7.1](image)

Figure 7.1 Model of alkali borate glasses confined between two Fe$_2$O$_3$ surfaces for the shearing process. Iron (blue), oxygen (red), boron (green), and sodium (yellow); the colors assignment is applied throughout this work. At each step, two surfaces are manually shifted relatively to each other along the x-direction with a distance of $\Delta x = 0.025$ Å. Therefore, the relative displacement between the two surfaces is 0.05 Å per step. At least 400 sliding steps are applied, which introduces a total relative displacement of 20 Å. The dimensions of the Fe$_2$O$_3$ surface are $8.72 \times 10.07$ Å$^2$.

First, the systems were compressed as presented in Chapter 6. Then, the sliding motion was applied when the systems were compressed to the desired pressure values of 1, or 3 GPa. To perform the shear, we manually shifted the top and the bottom Fe$_2$O$_3$ surfaces by a distance $\Delta x = 0.025$ Å in the opposite directions (Figure 7.1). The marginal distance of 0.025 Å was chosen to avoid any abrupt changes in the energy and the structure between two consecutive steps. Therefore, each time the total displacement between two Fe$_2$O$_3$ surfaces was 0.05 Å per shearing step. During the sliding motion, the gap between the two Fe$_2$O$_3$ surfaces was kept constant at a distance corresponding to the targeted pressure of 1 or 3 GPa obtained from the compression process. The electron exchange and correlation was estimated by using the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) exchange and correlation approximation.
A cutoff energy of 450 eV was used for the plane wave basis set, and the optimization with the convergence criteria of $10^{-4}$ eV and $10^{-3}$ eV were applied for the electronic wave function and ionic relaxation, respectively. The system was fully optimized with a k-point set of $3 \times 3 \times 1$ before moving to the following step. By this way, the system can arbitrarily relax to a stable stationary state and follow the minimum energy path. The shearing process was repeated 400 times, corresponding to a total shearing distance of 20 Å for each system. For FeNaB25% and FeLiB, to further observe the movement of atoms inside the systems, up to 500 steps corresponding to a distance of 27.5 Å were carried out.

The energy variation during sliding was calculated by the difference between the total energy at each step and the minimum energy of the entire shearing process by: $\Delta E = (E_i - E_0)/n$, where, $E_0$ is the minimum energy of the whole sliding process and $E_i$ is the current total energy at each sliding step. $n$ is the total number of atoms in the system. The main purpose of this process is to observe the structural responses and the bonding behaviors during the pressurized shearing movement with different Na$_2$O concentrations and with different alkali metals. Bond overlap population (BOP) calculation by the Lobster code was used to analyze the bonding behaviors during the shearing motion.

### 7.3 Energies and bonding behaviors during the shear

The energy variations at every step along the shearing distance of 20 Å is shown in Figure 7.2 and the maximum variations extracted from the highest peaks of the system energy curves are presented in Table 7.1. This energy variation corresponds to the forces required to initiate the relative displacement of the two surfaces, therefore the higher the energy variation rises, the higher friction force is induced in the system. At the start of the shearing, the energy variation gradually grows until reaching the peaks and dissipates the lateral force by dropping to a much lower value. The energy variation curves appear to be pressure-dependent as the shearing at a higher pressure requires higher energy and severer fluctuations. At 1 GPa, there is no significant difference in the maximum values of energy variation among the systems FeNaB33%, FeNaB50%, and FeKB. With a lower Na$_2$O concentration, FeNaB25% encounters a slightly higher energy variation at the maximum values than the other two systems. The shearing of FeLiB leads to the highest energy variation peaks at 70.16 meV which is almost double
that of FeNaB33% and 2.38 times larger than that of FeNaB50%. At 3 GPa, the energy variation deviates strongly in terms of changing pattern and the magnitude of the shearing energy. In particular, FeNaB50% remains shearing at as low energy variation as 1 GPa, a slight change is recorded for FeNaB33% to ~2 meV, while remarkably higher figures are indicated in FeNaB25%, FeKB, and FeLiB by approximately 10, 20, and 24 meV, respectively.

Figure 7.2 Variation of the total energy in the systems during the shear at 1 GPA and 3 GPa. The minimum energy in the whole shearing process was shifted to 0.

Table 7.1 Maximum energy variation in the systems induced by the shearing motion at 1 and 3 GPa. The maximum energy variation was calculated by the difference between the lowest and the highest peaks of the energy curve.

<table>
<thead>
<tr>
<th>System</th>
<th>(\Delta E_{\text{max}}) (meV/atom)</th>
<th>1 GPa</th>
<th>3 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNaB25%</td>
<td>39.18(^\ast)</td>
<td>49.06(^\ast)</td>
<td></td>
</tr>
<tr>
<td>FeNaB33%</td>
<td>38.42(^\ast)</td>
<td>40.50(^\ast)</td>
<td></td>
</tr>
<tr>
<td>FeNaB50%</td>
<td>29.46(^\ast)</td>
<td>28.31(^\ast)</td>
<td></td>
</tr>
<tr>
<td>FeLiB</td>
<td>70.16(^\ast)</td>
<td>94.73(^\ast)</td>
<td></td>
</tr>
<tr>
<td>FeKB</td>
<td>44.99(^\ast)</td>
<td>67.95(^\ast)</td>
<td></td>
</tr>
</tbody>
</table>

\(^\ast\) refer to low energy variation
\(^\ast\) refer to high energy variation

According to the evolution of energy variation in Figure 7.2 and the
corresponding maximum values in Table 7.1, these systems can be categorized into two groups of low and high variation energy. In the low variation energy group, FeNaB50% registers as the lowest energy variation at both 1 and 3 GPa, followed by FeNaB33% at 1 and 3 GPa, FeNaB25%, and FeKB at 1 GPa. The high variation energy group includes four systems: FeNaB25% and FeKB at 3 GPa, and FeLiB at 1 and 3 GPa. This indicates that lubricants with a higher sodium concentration have some advantages in the dissipating energy. Among alkali metals, FeNaB33% and FeKB provide similar results with a slightly lower shearing energy of sodium system at 1 GPa, while the sodium borate outperforms potassium borate at 3 GPa. The system with lithium borate results in a high energy variation at both 1 and 3 GPa which reflects the inferior performance of this lubricant.

When alkali metal borates were confined and compressed between two oxidized surfaces, the Fe$_2$O$_3$ substrates and the borates were connected mainly by the bond formation between the iron from the surfaces and oxygen from the borates (O$_B$), i.e. Fe–O$_B$ bond, or between boron with oxygen of the surface (O$_S$), i.e. B–O$_S$ bond. In order to clarify the relationship between bonding behavior and the feature of the energy variation curve during the shearing, Figure 7.3 shows the evolution of bond distance of surface-lubricant atoms and the energy variation pattern in FeNaB50% system at 1 and 3 GPa. For FeNaB50%, only Fe–O$_B$ bonds were formed due to the large portion of non-bridging oxygen. When the sliding motion is initiated, the energy variation starts to increase as the surfaces move relatively against each other. After reaching the maximum value, the energy variation drops to a lower value followed by a new increasing period. This pattern is repeated every certain distance but not identical through the whole sliding process. The changes in energy landscape represent the stick-slip motion that has largely been reported previously.\textsuperscript{178-179} The fluctuations of the energy variation curves in Figure 7.3a and c is closely associated with the Fe–O$_B$ bond stretching, bond formation and dissociation in Figure 7.3b and d, respectively.\textsuperscript{305} At a low pressure of 1 GPa, most of the Fe–O$_B$ bonds were elongated from 1.8 to 2.2 Å and only two bond dissociation events occurred. It has been indicated that an average Fe–O$_B$ bond length varies from 1.8 to 2.0 Å.\textsuperscript{159} The Fe–O$_B$ bond length measured at 1 GPa indicates that the modification at Fe–O$_B$ sites is mainly bond stretching rather than dissociation. The low energy obtained in this case could be inherited from the flexibility and molecular orientation along the sliding direction.\textsuperscript{147} In contrast, 3 GPa produces frequent bond
dissociation which is immediately followed by new bond formation across the interface regions. This is indicated by the fluctuation of Fe–O\(_B\) bonds around the covalent value of \(\sim 2.0\ \text{Å}\). When the bond distance is larger than 2.2 Å (the dotted line in Figure 7.3d), it is more likely to be dissociated and simultaneously followed by a newly formed Fe–O\(_B\) bond. As a result, the energy variation curve appears to be bumpier with larger fluctuating scales although the energy peaks remain as low as those of 1 GPa case. This is indicative that the alteration of energy dissipation pattern in the shearing process is strongly associated with the bonding behaviors in the systems.\(^{305}\) Furthermore, the bond dissociation is immediately replaced by the new bond formation, thus the borate covering could maintain throughout the process. This layer is expected to protect the underlying surface and prevent surface vacancies and direct metal-metal contacts.

Figure 7.3 Energy variation and Fe–O bond length of FeNaB50% during the shearing at 1 and 3 GPa: (a) and (c) energy variation at 1 and 3 GPa, respectively; (b) and (d) bond distance of all Fe–O\(_B\) formed between Fe and oxygen of the borate during the shearing process at 1 and 3 GPa. Different colors represent different Fe–O\(_B\) bonds. There are totally 5 and 7 Fe–O\(_B\) interfacial bonds in the system including the initial and the newly formed bonds at 1 and 3 GPa, respectively.

The number of Fe–O\(_B\) and B–O\(_S\) bonds across the surface-lubricant interface over the sliding distance of 20 Å for all systems is presented in Figure 7.4. It is consistent with the energy variation in Table 7.1 that the number of surface-lubricant bonds
follows the assigned groups of high and low variation of energy. In fact, the systems with a low variation energy, i.e., FeNaB at 1 GPa, FeNaB33% and FeNaB50% at 3 GPa, and FeKB at 1 GPa, appear with a lower number of stable interfacial bonds. At 1 GPa, there are a low number interfacial bonds with 3 or 4 bonds in all of three FeNaB systems, and this number marginally increases by 1 or 2 bonds at the end of the shearing. These figures slightly deviate when the shear is performed at 3 GPa, with stable values of FeNaB33% and FeNaB50%. In FeKB system, the number of bonds is slightly higher than those of FeNaB but remains stable with 5 or 6 bonds during the whole process at 1 GPa. In contrast, systems in the high variation energy group including FeNaB25% and FeKB at 3 GPa, FeLiB at 1 and 3 GPa, form more interfacial bonds and the number of bonds changes dramatically over the sliding process. Particularly, a large variation in the bond number was recorded in FeNaB25% with 8 bonds at 0 Å and reaches the maxima with 13 bonds at 12.5 Å. Likewise, this figure in FeKB at 3 GPa increases sharply from 4 bonds at 5 Å to 14 bonds at 12.5 Å. High bond numbers up to 17 bonds (at 7.5 Å and 3 GPa) and massive changes were found in FeLiB regardless of the sliding pressure. The noticeable changes in the number of surface-lubricant bonds indicate that bond formation and dissociation occur frequently in these systems.

![Graphs showing bond formation and dissociation](image)

Figure 7.4 Number of bonds between the Fe$_2$O$_3$ surface and the borates including Fe–$O_B$ and B–$O_S$ during the shearing. The legends are the same in (a) and (b).

As can be seen in Figure 7.3 the Fe–$O_B$ bonds in FeNaB50% form and dissociate over the sliding period but the total number of bonds experiences minor changes. The preservation of the surface-lubricant bond number provides some advantages. First it
secures surface-lubricant connection and the chemical adsorption of the lubricant on the surface. Secondly it ensures that no surface’s atoms dissociate to form a new bond with the lubricant, thus preventing wear precursors. Therefore, it is important to maintain a stable number of interfacial bonds in the system during the shearing. The initial increase and then decrease in the number of interfacial bonds could involve more atoms and be the reason for more severe bond rupture. Severe bond rupture can be directly related to the increase of the shearing energy in the system which in turn is the reason for the high friction and wear debris. On the other hand, if there is inadequate bonding connection, the interfacial bonding is lost and the lubricant can be easily dislodged from the surface as a result of poor adhesion and thus can not provide an effective protection for the wear of the surface. Furthermore, stable bonding behavior could benefit the sliding motion by stabilizing the sliding energy.

Overall, the presence of sodium and its concentrations profoundly influence the lubricant structures and their arrangement under the pressurized shearing. Low sodium content lubricant creates highly covalent glassy film which results in the drastic change in the number of interfacial bonds at the Fe₂O₃ surface. The results give clear evidence that sodium constituent in borate lubricant play the role to reduce the friction under harsh conditions reported in the experiments. In fact, Tran et al. has found that the excellent friction and wear reduction was achieved thanks to the essential formation of a sodium-rich layer. This sodium -rich layer was absent in the B₂O₃-lubricated system, which resulted in the poor frictional performance.

7.4 Formation of “easy-shear” layers

The formation of layered-like structure is only found in FeNaB50% at 1 GPa where Na₂O content accounts for 50% of the lubricant. Figure 7.5 displays the arrangement of lubricant molecules in response to the pressurized sliding. As can be seen in the figure, borate fragments in combination with sodium cations have a strong tendency to reorient and the layered structure forms from the initially disordered distribution. These layers arrange themselves parallel to the sliding direction, which results in the separate layers with a clear gap (Figure 7.5b). Figure 7.5b shows the clearance between two sodium borate layers with no interlayer bonding interactions. The lack of interlayer bonding helps to create an easy-shear model and smooth the
surface rubbing. This result is consistent with the low energy required to initiate the shearing as shown in Figure 7.2.

Figure 7.5 Rearrange ment of the lubricant under the shearing of FeNaB50% at 1 GPa: (a) initial shearing at 0 Å; (b) shearing at a distance of 12 Å; (c) The bonding network within one layer marked by the blue dotted lines in (b).

Figure 7.5c shows the top view projected from a sodium borate layer as denoted by the dotted lines in Figure 7.5b. The layer is self-balanced including borate anions in combination with sodium atoms to compensate charges for the terminated oxygen. There are three types of borate complexes found in the layer including pentaborate $B_5O_{10}$, ring-type $B_5O_6$ and chain-type ($BO_3$ chain) metaborate which are typical building units of borate glasses. These units stay isolated and they are well-defined and separated by sodium cations filling in spaces between borate units. Except for the pentaborate which contains one tetrahedral boron, the ring-type and chain-type metaborate are inherently in a planar shape. The lack of connection between layers making them easily gather in a planar manner. At the same time, the separation between borate units by a sodium cations channel blocks the approaching of the terminated oxygen to any boron available in $BO_3$ forms. Therefore, the polymerization by means of $BO_3$ to $BO_4$ conversion can be effectively eliminated. To this aspect, the contribution of cations with an adequate amount is essential to keep the structural units apart from each other. Nevertheless, due to the lack of covalent in-plane connection between separate fragments in one layer, the layer does not sustain with long sliding distance and loses its planar manner as the shear reaches 20 ps.
7.5 Fe removal from the substrates

The removal of iron atoms from the surface was found in five systems including those with a low concentration of sodium (FeNaB25%) at 1 and 3 GPa, FeLiB at 1 and 3 GPa, and FeKB at 3 GPa. These systems belong to the high variation energy group, except for FeNaB25% at 1 GPa. Figure 7.6 shows the visualization of the structures of these systems at 3 GPa at the largest displacement of the iron Fe from the surface. As can be seen in the figure, in all three models the Fe$_2$O$_3$-lubricant interfaces are well-connected by many chemical bonds including both Fe–O$_B$ and B–O$_S$. These bonds proliferate across the interface and could be the results of two factors. First, the interfacial bond formation occurs due to pressure-induced polymerization in response to the volume shrinking. This process is more profound in the systems with a low Na$_2$O content rather than those with higher one as some sodiums at the surface can partially hinder borate approaching the surface. Secondly, new bonds can be formed during the shearing when the surface’s atoms are in contact with lubricant atoms (Figure 7.4). When combined with the highly polymerized borate layer, it creates a well-adhesive surface-lubricant connection which hinders the sliding of the two surfaces. It could be found that after shearing for a certain distance, some Fe atoms form more bonds with the lubricant. This process is associated with the dissociation of the bonding with surface’s atoms, leading to the loss of the connection with the surface. The Fe atoms have a high tendency to be removed from the surface and bond with lubricant’s atoms to form clusters (circled areas in Figure 7.6).

Figure 7.6 Formation of wear particles when Fe moves up from the surface when
shearing at 3 GPa (a) FeNaB25%, (b) FeLiB, and (c) FeKB: lithium (green) and potassium (purple). The circled areas show the Fe atom moving out from the surface and forming clusters with atoms in the lubricant.

Figure 7.7 presents the distance from the surface of the highest Fe atom in each system. As can be seen in the figure, the Fe-surface height goes up gradually to the distance of ~1.5 Å except for the case FeLiB at 1 GPa. In FeNaB25%, the atom moves out gradually and has a tendency to reunite the surface as the Fe-surface distance is slightly reduced after reaching the highest peaks. At 3 GPa, the Fe-surface distance decreases to zero at the shearing distance around 15 Å, indicating the complete reunion of the Fe atom on the surface (black line in Figure 7.7b). This suggests the temporary removal of the Fe particles as it appears shortly and can disappear. However, for FeLiB and FeKB the movement of the Fe atoms occurs quickly in a short shearing distance. Remarkably, the Fe atom in FeLiB in Figure 7.7a moves far away from the surface with a distance of ~2.5 Å, which corresponds to the dissociation value of an Fe–O bond.310 Beyond that distance, the atom is unable to return to the equilibrium bond. After reaching the largest values, the Fe-surface distances in FeLiB and FeKB decrease slightly but still remain as a distance around 1.5 Å. This is indicative of the severe surface damage due to the loss of atoms, usually the Fe topmost atoms. However, in FeKB the removal occurs with the Fe atom that is initially far from the top of the surface, which suggests that severe modification could also affect the atoms in the second layer.

![Graph](image-url)

Figure 7.7 Fe-surface distance of the Fe atoms that breaks from the surface at 1 GPa (a) and 3 GPa (b). FeNaB25% (black), FeLiB (red), and FeKB (green). Only the Fe atom
that has the highest z coordinate in each system is reported. The dotted line marks the distance of 0 Å corresponding to the height of the initial surface. There is no Fe removal for FeKB at 1 GPa.

Figure 7.8 depicts the development of iron particles and bond exchange between O₈ and O₉ around Fe atoms. The initial structures in all models are the topmost Fe atoms bonding with three O₈ and one O₉. As a result of the surface cleavage and relaxation, the topmost Fe atoms share only three covalent bonds with O₈ in the Fe–O₃–Fe termination¹⁰¹ instead of the bulk-like six-fold coordination of Fe³⁺ state.³¹³⁻³¹⁴ Due to such coordination deficiency, the topmost Fe has a high tendency to fulfill its oxidation state by bonding with surrounding oxygen atoms of the lubricant. It is evident that both O₉ and O₈ contribute to the coordination number of the Fe atoms but the number of O₈ and O₉ alters along the shearing distance. After being sheared for a certain distance, the number of Fe–O₈ bonds decreases while that of Fe–O₉ increases with the shearing distance. For example, the number of Fe–O₉ bonds in FeNaB25% increase from 1 to 2, and from 2 to 4 when shearing at 1 and 3 GPa, respectively (Figure 7.8a-d). As a result, the Fe atoms end up bonding with five to six surrounding oxygen atoms including both O₈ and O₉. A noticeable feature of FeLiB and FeKB systems is that when the Fe diffuses away from the surface, it is subsequently followed by the oxygen of the surface O₈ as evidenced in Figure 7.8c, d, and h. The O₈ atoms that were complete detached from the surface denoted as O₈* in Figure 7.8f, h, and j. As shown in the figure, there are 1 O₈* in FeLiB at both 1 and 2 GPa and 2 O₈* FeKB. The subsequent removal of the surface’s oxygen suggests the severe bond rupture at the Fe₂O₃ surface. As a high coordination element, when diffusing into the lubricant, iron can create the favorable octahedral FeO₆ coordination³¹⁵⁻³¹⁶ which increases the local density at some specific points. When the interfacial bond breaking takes place at various length scales, the surface is unlikely to be healed and reconstructed to a normal finish due to the permanent loss of atoms. Unlike FeNaB25%, due to the dissociation of O₈ with the Fe atoms in FeLiB and FeKB, it hinders the capability of the surface reconstruction, thus promotes the formation of permanent wear particles and surface defects due to the atomic deficiency.²⁹⁵, ³¹⁷ These cases correspond to the extremely high energy variation presented in Figure 7.2, suggesting that the dissociation of the Fe–O₈ cluster could cause a severe abrasive wear to the system.
Figure 7.8 Snapshots of the Fe removal from the surface when shearing at 1 and 3 GPa. The snapshots were taken at the largest Fe-surface distance from Figure 7.7. Result for FeKB at 1 GPa was not shown as there is no Fe atom moving out from the surface. O$_{S}$ is the oxygen atom of the surface that completely dissociates and has no direct bonds with surface’s atoms. Fe$_{L1}$ is the Fe atoms in the top layer, and Fe$_{L2}$ is the Fe atom in the second Fe layer from the top surface. Alkali ions were removed for clear visualization.

Among FeNaB systems, the Fe removal was only observed in FeNaB25%, which is the system with the lowest Na$_2$O concentration. It can be seen in Figure 7.8a-d, the mechanism of the Fe removal in FeNaB25% is through the combination of two chemical reactions. The first one is the formation of new Fe–O$_B$ bonds, and the second one is the breaking of Fe–O$_S$ bonds. These processes are indicated by the increase in the BOP value of Fe–O$_B$ bonds and the decrease of BOP of Fe–O$_S$ bonds as shown in Table 7.2. The breaking of Fe–O$_S$ bonds suggests that the bonding between the topmost Fe
and lubricant is stronger than that with the surface’s atoms because of more O₈ approaching the surface, i.e., 2 O₈ at 1 GPa and 4 O₈ at 3 GPa (Figure 7. 8b and d). In FeNaB33% and FeNaB50%, the abundant presentation of Na⁺ in the borate, especially at the interface, can hinder the oxygen approaching Fe of the surface. Therefore, the topmost Fe atoms are not pulled off the surface and the Fe removal is effectively eliminated. This result confirms the role of alkali cations in not only supporting the sliding motion but also in preventing the formation of wear particles.

Table 7.2 Variation of BOP (e) during the shearing motion. For FeNaB25% and FeLiB, only results at 1 GPa are shown as a representative for each system. For FeKB, BOP was calculated at 3 GPa as there is no Fe removal at 1 GPa.

<table>
<thead>
<tr>
<th>Bond</th>
<th>0 Å</th>
<th>5 Å</th>
<th>10 Å</th>
<th>15 Å</th>
<th>20 Å</th>
<th>25 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNaB25%, 1 GPa</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe–O₈</td>
<td>0.004</td>
<td>0.010</td>
<td>0.012</td>
<td>0.153</td>
<td>0.321</td>
<td>0.354</td>
</tr>
<tr>
<td>Fe–O₈</td>
<td>0.782</td>
<td>0.692</td>
<td>0.566</td>
<td>0.476</td>
<td>0.482</td>
<td>0.436</td>
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<tr>
<td>O₈–Fe₁₂₂</td>
<td>1.069</td>
<td>1.147</td>
<td>1.195</td>
<td>1.079</td>
<td>1.449</td>
<td>1.514</td>
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<td>FeLiB, 1 GPa</td>
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<td></td>
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<tr>
<td>Fe–O₈</td>
<td>0.241</td>
<td>0.234</td>
<td>0.244</td>
<td>0.253</td>
<td>0.355</td>
<td>0.546</td>
</tr>
<tr>
<td>Fe–O₈</td>
<td>0.692</td>
<td>0.739</td>
<td>0.767</td>
<td>0.574</td>
<td>0.380</td>
<td>0.310</td>
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<tr>
<td>O₈–Fe₁₂₂</td>
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<td>0.858</td>
<td>0.713</td>
<td>0.637</td>
<td>0.299</td>
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<tr>
<td>O₈–B</td>
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<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.329</td>
<td>0.317</td>
</tr>
<tr>
<td>FeKB, 3 GPa</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe–O₈</td>
<td>0.000</td>
<td>0.010</td>
<td>0.228</td>
<td>0.236</td>
<td>0.296</td>
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<tr>
<td>Fe–O₈</td>
<td>0.738</td>
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<tr>
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<td></td>
</tr>
<tr>
<td>O₈–B</td>
<td>0.006</td>
<td>0.569</td>
<td>1.105</td>
<td>1.170</td>
<td>1.288</td>
<td></td>
</tr>
</tbody>
</table>

Among FeNaB systems, the Fe removal was only observed in FeNaB25%, which is the system with the lowest Na₂O concentration. It can be seen in Figure 7.8a-d, the mechanism of the Fe removal in FeNaB25% is through the combination of two chemical reactions. The first one is the formation of new Fe–O₈ bonds, and the second one is the breaking of Fe–O₈ bonds. These processes are indicated by the increase in the BOP value of Fe–O₈ bonds and the decrease of BOP of Fe–O₈ bonds as shown in Table 7. 2. The breaking of Fe–O₈ bonds suggests that the bonding between the topmost Fe and lubricant is stronger than that with the surface’s atoms because of more O₈.
approaching the surface, i.e., 2 O\textsubscript{B} at 1 GPa and 4 O\textsubscript{B} at 3 GPa (Figure 7. 8b and d). In FeNaB33\% and FeNaB50\%, the abundant presentation of Na\textsuperscript{+} in the borate, especially at the interface, can hinder the oxygen approaching Fe of the surface. Therefore, the topmost Fe atoms are not pulled off the surface and the Fe removal is effectively eliminated. This result confirms the role of alkali cations in not only supporting the sliding motion but also in preventing the formation of wear particles.

BOP in Table 7.2 explains how electrons transfer between atoms from the surface and lubricant when the systems encounter the bond formation and dissociation. In general, it is evident that both the number of Fe–O\textsubscript{B} bonds and the BOP increase with increasing shearing distance, in exchange to the corresponding quantity of Fe–O\textsubscript{S}. This confirms that the oxygen of the surface and the oxygen of the lubricant exchange their roles in coordinating with the Fe atom. There are differences between FeNaB25\% and FeLiB or FeKB for O\textsubscript{S}–Fe\textsubscript{L2} bonds. In particular with FeNaB25\%, when Fe moves out from the surface, it is not followed by any O\textsubscript{S} atoms. Therefore, when Fe–O\textsubscript{S} is broken, Os finds other nearby Fe atoms to bond, particularly with Fe atoms in the second layer, resulting in a significant increase in the BOP of Fe\textsubscript{L2}–O\textsubscript{S} bonds. On the contrary, in FeLiB and FeKB as some O\textsubscript{S} follows the Fe to break out from the surface, the BOP of Fe\textsubscript{L2}–O\textsubscript{S} dramatically decreases; for example, from 0.849 e to 0.299 e in FeLiB, and from 1.553 to 0.546 e in FeKB when the systems begin and finish the sliding. Those figures reveal the loss of connection with the underlying bulk material. Furthermore, in these two systems, there is the subsequent detachment of O\textsubscript{S*} which is the oxygen of the surface that is completely dissociated from the surface and has no explicit chemical bonds with surface atoms. Apparently, these oxygen atoms after dissociating from the surface form new bonds with boron atoms of the lubricant. These B–O\textsubscript{S*} bond formation is reflected by a noticeable rise in BOP values of B–O\textsubscript{S*} bonds, particularly in FeKB where up to 2 O\textsubscript{S*} is generated (Figure 7.8j). The fact that boron can adopt more oxygen for chemical bonds because the atom can easily switch between sp\textsuperscript{2} and sp\textsuperscript{3} hybridization for either BO\textsubscript{3} or BO\textsubscript{4} forms under a minor stimulus.\textsuperscript{50} The appearance of abundant coordinate atoms such as octahedral FeO\textsubscript{6} or tetrahedral BO\textsubscript{4} clusters collectively contribute to the density enhancement at some local points, making the interface more resistant to move than the lower density counterparts.
7.6 Effects of high temperature

The shearing process was performed at high temperature at the applied pressure of 1 GPa by AIMD simulations. The simulation process was similar to the process described in Section 7.2. However, after every step the system was shifted with a distance $\Delta x = 0.1$ Å in the opposite directions, thus the total displacement was 0.1 Å per shearing step. The system was equilibrated for 1000 MD steps, corresponding to 2 ps with a time step of 2 fs before moving to the following steps. The selection of $\Delta x = 0.1$ Å, which was larger than that used by static DFT shearing simulations due to the expensive calculation cost of AIMD simulations. The AIMD simulations were applied for only three systems including FeNaB33% (also FeNaB), FeKB and FeLiB.

Figure 7.9 presents the configurations of Fe$_2$O$_3$-alkali borate systems obtained from the shearing distance of 20 Å at 0 and 1073 K. There are no significant different in the structures at 0 and 20 Å of the three systems, except for the removal of Fe atoms in FeLiB, and the distribution of the alkali cations in FeNaB and FeKB. First, for FeLiB the iron atoms on the top layer of the surfaces were less affected by the shear at the high temperature than at the low temperature. In particular, in FeLiB system the removal of Fe at 1 GPa was discussed in detail in Section 7.5. At high temperature, the topmost Fe atoms were stable on the surface although they moved upward slightly. Secondly, the distribution of the alkali cations was homogeneous throughout the borate layer at 0 K, but more localized in the z direction at 1073 K. This observation is more clear in FeNaB and FeKB systems (Figure 7.9 e and f).
Figure 7.9 Comparison of Fe$_2$O$_3$-alkali borate structure at 0 K and 1073 K at the shearing distance of 20 Å, pressure of 1 GPa. The results at 0 K are obtained from the shear by DFT.

There is no Fe removal from the surface observed at high temperature, which could be explained by three reasons. First, the shear was applied at low pressure, while the Fe removal was observed mainly at 3 GPa (in FeKB system). Secondly, at high temperature, the lubricants melt. The melting could reduce the lubricant hardness and make them less abrasive to the surface when the lubricants move on the surface.
Thirdly, in the AIMD simulation, the system was relaxed for a period of 2 ps after being shifted 0.5 Å before moving to the next AIMD simulation. The simulation time is long enough for the system to restabilize after being modified by the displacement. This is the limitation of the simulation package which could be improved by modifying the code or using MD simulations by reactive force fields.

Figure 7.10 Z-coordinate of all Li, Na, and K ions in the systems FeLiB, FeNaB, and FeKB during the shear at 1 GPa and 1073 K. There are 12 alkali ions in each system. Different colors represent different Li/Na/K cations.

To describe to distribution of the alkali cations during the whole simulation process, Figure 7.10 reveals the z-coordinates of all alkali atoms in each system. In FeLiB systems, lithium atoms distribute almost homogeneously along the vertical direction (Figure 7.10a). The ions at the surface are more localized with a smaller fluctuation along the z direction than those in the middle of the borate layer. One remarkable feature observed in FeNaB and FeKB systems are the localized distribution of sodium and potassium cations after shearing for a certain distance. In these two systems, there are two areas where the alkali cations were concentrated, i.e. at the lower
and upper interface between the Fe₂O₃ surface and the lubricant, and one area in the middle of the borate layer. In addition, there was the movement of Na⁺ or K⁺ cations from the middle layer toward the interfaces, for instance, the atom represented by line 1 in Figure 7.10b, lines 1 to 4 in Figure 7.10c. The moving process finished at the early stage of the sliding, i.e. at 5 Å in FeNaB, and 7.5 Å in FeKB, which suggest the tendency of forming sodium-rich layers at the metal-borate interfaces. At the end of the shearing (20 Å), there were three defined layers of alkali cations with the more localized ones at the two interfaces.

Although there were some cations absorbed and stabilized on the surface, the formation of well-defined cation layers were not observed in the shear at 0 K. At high temperature, the melting of the alkali borates initiates the mobility of the alkali ions. Therefore, the alkali cations can easily diffuse through regions inside the lubricant layer. It has been reported that the surface was severely modified by exposing oxygen-rich areas at high temperature.³⁰⁷ As a result, the alkali cations can be attracted by the electrostatic interactions with these oxygen-rich areas, making them more localized on the surface. Furthermore, the localized layers of cations were less observable in FeLiB than its counterparts. This could be because of the stronger Li-O interaction which involves covalent bonding than Na-O or K-O interactions.²²⁸ Due to the less cations at the two surfaces, the fluctuation of the topmost Fe atoms was more pronounced than that of the FeNaB and FeKB.

### 7.7 Proposed interfacial layering

The current simulation provides two scenarios of shearing dynamics and surface-lubricant interactions. In the first one, the low variation of energy is associated with the stability of bonding behavior which is found in systems with high concentration of Na₂O at low pressure, i.e., FeNaB33%, FeNaB50% at 1 and 3 GPa, FeNaB25%, and FeKB at 1 GPa. In the second one, the high variation energy profile together with frequent bond formation and dissociation registers in FeLiB at both 1 and 3 GPa, FeNaB25%, and FeKB at 3 GPa.

In the first case, the surface is covered by short borate chains combined with a sodium rich region and in the second one the surface is fully covered by a well-polymerized borate layer. Results in Figure 7.5 shows that with the sufficient presence
of alkali cation in borate, basic building units of borate anions can be stable without cross-linking or polymerization. At low pressure, the layered-like assembly of sodium and borate simply involves the reorientation of separate boron-oxygen anionic units alternatively with positively charged sodium ions. This suggests the undeniable role of an alkali-rich region in the borate lubricant family. The presence of Fe removal in FeNaB25% at 1 GPa could be the effect of low sodium concentration in the system although the system encounters the low energy variation during the shearing. In the second case, two Fe₂O₃ surfaces and the borate lubricant are well-connected to form a unique system. In FeNaB25%, FeLiB, and FeKB at 3 GPa, the expectation of high energy variation as well as the removal of Fe particles dominate properties of the systems. When the systems encounter sliding and increasing applied loads, chemical bonds between iron or boron with oxygen accelerate, creating a sticky layer which could hinder the shear. In addition, the sodium-rich region can be found at the Fe₂O₃-borate interface at high temperature, pressurized conditions, and the final experimental tribofilm. Therefore, it is highly possible that the lubrication film would include multilayers of a sodium-rich region, short borate chains and long polymerized borate, which dedicate to the function of lubricant adhesion, sliding motion, and load bearing.

A schematic description of the proposed tribofilm layering is depicted in Figure 7.11. Based on the results obtained from low and high Na⁺ systems, from the oxidized surface the film is composed of three regions. Region I is the bonding region which includes Fe–O₆/B–O₆ covalent bonds and Na–O ionic interactions. The inclusion of Fe–O₆ or B–O₆ covalence at the interface is indispensable to maintain a stable covering and adhesion which compensates for the weaker ionic counterpart. Region II is the shearing region containing abundant cations mixed with short borate chains in planar form to support the shear. The alkali cations therefore play dual-role function by compensating charges for the terminated oxygen and separating borate complexes between layers to prevent possible polymerization between them. The presence of borate units in short forms of rings or chains in this region is to reduce the intramolecular binding and facilitate the sliding. Both are the short forms of borate units which are small in size and thus can either enter small gaps between two asperities and be more adaptable to the directional motion. Region III consists of the highly polymerized matrix. This layer is to withstand severe loads by extremely high hardness and elasticity of borate under extreme pressure. Therefore, this proposed model satisfies both low shearing
resistance and mechanical stability under severe loads and harsh working conditions.

Figure 7.11 Schematic description of the possible tribofilm composition and its lubricating mechanism of alkali borate.

The layering formation of the tribofilm in this work was proposed based on static DFT simulations of the compression and shear of alkali borate lubricants with various alkali concentrations. The static application of the mechanical load and shear may not account for some reactions activated at sliding interfaces or the combination of cationic movement and chemical reactions in dynamic systems. This limitation of static DFT calculations can be overcome by using dynamics simulations AIMD or QM/MM.

7.8 Conclusions

We have used DFT simulations to investigate the adaptation of alkali borate structures and bonding at the interface under the pressurised sliding with five borate lubricants: Na$_2$O·3B$_2$O$_3$, Na$_2$O·2B$_2$O$_3$, Na$_2$O·B$_2$O$_3$, Li$_2$O·B$_2$O$_3$, and K$_2$O·B$_2$O$_3$. In comparison, sodium borates Na$_2$O·2B$_2$O$_3$ and Na$_2$O·B$_2$O$_3$ show a good performance at 1 GPa, followed by Na$_2$O·3B$_2$O$_3$ and K$_2$O·B$_2$O$_3$, while only Na$_2$O·2B$_2$O$_3$ and Na$_2$O·B$_2$O$_3$
remain low shearing energy variation at 3 GPa. It has been found that Na$_2$O·B$_2$O$_3$ with higher sodium concentration facilitated the shearing motion by forming a layered-like borate while a high energy variation and atom removal were observed with a lower Na$_2$O content. Meanwhile, the high energy variations were associated with the frequent bond formation and rupture at the interface which accelerated the removal of iron particles from the surface. Based on the current results, the mechanisms of friction reduction at Fe$_2$O$_3$ sliding interface lubricated by alkali metal borates includes: (1) the bonding to secure adhesion of the lubricant and protect the surface; (2) the shearing including sodium-rich short borate complexes to support the sliding motion; (3) well-polymerized borate playing the role as a load-bearing layer. The simulation provides an atomic rationalization for low frictional results in borate-lubricated systems.
Chapter 8. GRAPHENE AND ITS MODIFICATIONS FOR HIGH TEMPERATURE LUBRICATION

8.1 Introduction

Graphite/graphene has been recognized as an excellent solid lubricant due to its exceptional lubricity and chemical stability.\textsuperscript{119, 318-319} Recent research has found that graphene provides extremely low friction at both macro- and micro-scales. In tribology, graphene has been introduced to a number of manufacturing processes in the form of graphene coatings,\textsuperscript{320} mixed powders or ionic liquids,\textsuperscript{321-323} core-shell nanoparticles,\textsuperscript{324} graphene-based nanocomposites\textsuperscript{325-327} etc., in order to improve the friction performance in harsh operating conditions of high loads and elevated temperature. For elevated temperature lubrication, the mixing of graphene with a binder or other lubricant additives could create synergistic lubricating effects such as friction and wear reduction, thermal stability, and load-bearing capacity from multi-film structures.\textsuperscript{322, 328} For example, graphene modified by phosphonium-organophosphate can reduce friction and wear at the tribointerface and avoid tribo-pairs sticking when the viscosity of the base oil declines at the temperature about 100°C.\textsuperscript{322} Shi et al. have reported that NiAl composite with 1.5 wt.% graphene showed low friction and wear rate at 100 to 200°C, but failed to maintain the lubrication film at 400°C which resulted in the increased wear rate.\textsuperscript{325} Kim et al. have found that a PTFE and graphene oxide (GO) coating provides good friction and wear performance in macro-scale tests at a high temperature of 400°C. The superior performance was linked to the combination of the high strength of GO and the low frictional property of PTFE.\textsuperscript{328} Recently, Wang et al. have found that the mixing of expanded graphite and sodium silicate showed excellent friction and wear reduction at the high temperature of 850°C.\textsuperscript{114} Such good performance is the combination of high viscosity melting sodium silicate and graphene planar structures.

Graphene possesses mechanical strength, high Young’s modulus, and thermal stability.\textsuperscript{329-330} However, one of the biggest challenges of using graphene as a high temperature lubricant is its chemical inertness that leads to the poor adhesion on the working surfaces. Berman et al. have showed that graphene provided great friction reduction at low load, but it was completely removed from the wear track under a high load of 5 N (or 0.56 GPa), or after a longer testing time.\textsuperscript{119} The reason why graphene poorly adheres on the surface is because of its perfect planar honeycomb lattice...
connected by homogeneous sp² hybridization which shares all available electrons with three other carbon nearby. Chemically modified graphene has been an effective material with desirable properties beyond its pure form. Graphene has been doped with boron, nitrogen in order to improve the adhesion and frictional performance of the lubricant additives. Ramaprabhu et al. have synthesized nitrogen-doped reduced graphene oxide which showed a significant reduction of friction up to 25%. The co-doping of nitrogen and boron was reported to create a dual effect as a boron nitride together with adsorbed graphene layers formed in the tribofilms after the test.

In order to form a chemical bond with a metal atom, atoms that possess sp³ hybridization is necessary. For this purpose, we used boron (B), phosphorus (P), sulfur (S), and silicon (Si) to dope in the graphene structure to create chemical modifications in its electronic structure and the interactions with the metal oxide surface. Besides, these doped atoms and their compounds have been proven to possess excellent adhesion which is crucial for high temperature lubricity. In an attempt to search for the best combination of lubricants/additives to work effectively at high temperature, this work aims to verify the binding of graphene and its doped structures on iron oxide surface, and the thermal stability for a wide range of temperature.

8.2 Simulation details

A 4×4 supercell containing 32 carbon atoms was built to model the monolayer graphene (G). Based on the model, the graphene doped with boron (B-G), phosphorus (P-G), sulfur (S-G), and silicon (Si-G) with the doping concentrations from 1 to 4 atoms per supercell was constructed and optimized to reach equilibrium lattice parameters (Figure 8.1). The number of dopants from 1 to 4 atoms corresponds to the doping concentrations of 1/32 (3.125%), 2/32 (6.25%), 3/32 (9.375%), and 4/32 (12.5%), respectively. In order to stack the G sheet on the Fe₂O₃ surface, the G and its doped structures have the similar size with the Fe₂O₃(0001) 2×2 supercell. The doping sites are located at the Fe topmost atoms of the surface. There are total 4 Fe atoms on the topmost layer of the surface, therefore the maximum number of impurities is 4 (Figure 8.1b and c). The chemical bonds are expected to form between the topmost Fe and the dopant atoms, thus the addition of more impurities in the graphene lattice is unnecessary and could make the system less stable.
Figure 8.1 G 4×4 supercell (a), the doping sites on the G lattice (b), and 2×2 Fe₂O₃ surface. Carbon (brown), doped atom (blue), oxygen (red), iron (navy). The blue cell in (a) shows the 1×1 G unit cell. The numbers in (b) indicate the doping positions corresponding to the number of dopants in the supercell. Green atoms in (c) represent the Fe topmost atoms.

DFT calculations were performed using VASP²⁰⁸-²⁰⁹ with GGA-PBE exchange-correlation functional.¹⁹⁴-¹⁹⁵ A plane wave basis set with a cutoff energy of 450 eV was applied to truncate the electronic wave function. The Monkhorst-Pack scheme was used with a k-points set of 5×5×1. In order to account for van der Waals interactions, DFT-D3 method was used. The stability of doped atoms in graphene lattice was evaluated by the formation energy following the equation ¹⁹:³³⁴

\[ \Delta E_F = \frac{1}{n_D} [E_{DG} - E_G - n_D \mu_D + n_D \mu_C] \quad (19) \]

where D is the doped atoms that correspond to B, P, S, or Si. \( E_{DG} \) and \( E_G \) are the total energies of graphene supercell with and without dopant atoms D, \( n_D \) is the number of doped atoms, and \( \mu_D \) and \( \mu_C \) are the chemical potentials of the doped atom and carbon. The chemical potential of C, B, P, S, and Si was calculated by the total energies per atom of pristine monolayer graphene, α-boron crystal, black phosphorus crystal, free atomic sulfur, and crystalline silicon in previous works, respectively.³³⁴-³³⁷ The binding energy of G or D-G on Fe₂O₃ surface was calculated by the equation:

\[ E_b = E_{Fe2O3} + E_{G/DG} - E_{total} \quad (20) \]

where \( E_{total} \), \( E_{Fe2O3} \), and \( E_{G/DG} \) are the total energy of the graphene or D-G adsorbed on Fe₂O₃, the Fe₂O₃ surface, and the graphene or doped graphene, respectively.
Table 8.1 Details of the graphene and doped-G models from DFT and AIMD simulations

<table>
<thead>
<tr>
<th>System</th>
<th>Supercell</th>
<th>No. atom</th>
<th>No. dopant/supercell</th>
<th>1D-G</th>
<th>2D-G</th>
<th>3D-G</th>
<th>4D-G</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. DFT optimization</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>4×4</td>
<td>32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D-G</td>
<td>4×4</td>
<td>32</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>G on Fe₂O₃</td>
<td>4×4</td>
<td>32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D-G on Fe₂O₃</td>
<td>4×4</td>
<td>32</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>2. AIMD for G and doped-G</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>8×12</td>
<td>192</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D-G</td>
<td>8×12</td>
<td>192</td>
<td>6</td>
<td>12</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. AIMD for Fe₂O₃-G/Fe₂O₃-doped-G</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃-G</td>
<td>4×12</td>
<td>216/96*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃-DG</td>
<td>4×12</td>
<td>216/96*</td>
<td>3</td>
<td>6</td>
<td>12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* the first number shows the total number of atoms in the system while the second one indicates the number of C or C and doped atoms in graphene. D is the doped atoms (B, P, S, Si).

For AIMD simulations of the pure G/doped-G and their adsorbed configurations on the Fe₂O₃ surface was studied. In the simulations of G and doped-G, the models were expanded from the fully optimized graphene and its doped structures into 192-atom 8×12 supercells. For the G/doped-G adsorbed on the Fe₂O₃ surface, 4×12 supercells containing 96 atoms were used for the pure graphene and graphene doped with 1, 2 and 4 dopant atoms. Details about the size and the number of atoms of the simulation models are presented in Table 8.1. These systems were equilibrated for 10 ps using a time step of 1 fs and canonical (NVT) ensemble at four different temperatures of 900, 1000, 1100, and 1200 K. It is worth mentioning that the simulation time is longer than that in other works, i.e., 5 ps, and sufficiently long to observe structural changes by thermal onset. The AIMD simulations were performed using Γ-point sampling and a cutoff energy of 400 eV for the plane wave functions.

8.3 Interactions of graphene with sodium borate at high temperature

In order to investigate graphene interactions with sodium and iron oxide surface at high temperature, one monolayer graphene flake (G-F) containing 6 carbon rings, and one graphene sheet (G-S) were added to Fe₂O₃-sodium borate system. The G-S has the same size with the Fe₂O₃ surface and fully covers the surface. In this work, the term
“graphene flake” indicates the small size of graphene, while “graphene sheet” is a large periodic one. The systems were equilibrated at 1000 K and 1100 K for 20 ps by AIMD simulations. Figure 8.2 shows the structures of the systems after being relaxed for 20 ps. FeBG-F and FeBG-S are Fe₂O₃-sodium borate-graphene flake and Fe₂O₃-sodium borate-graphene sheet, respectively. The interactions between Fe₂O₃ and sodium borate has been discussed in Chapters 5-7. In this chapter, we only focus on the interactions of graphene and Fe₂O₃ and/or sodium borate.

In the case of FeBG-F, the results at both 1000 and 1100 K show that the G-F was distorted when interacted on the surface. Bond formation between Fe of the surface and C or between oxygen of the borate and C occurs at the edge of the graphene flake. This can be explained by the cracking of C–C bonds that leads to the lack of covalent bonds at some C at the edge of the G-F. These carbon atoms are more chemically active and have a high tendency to react with nearby atoms, for example Fe or O. At 1100 K, there are some Na⁺ cations that diffuse from the borate layer towards the oxide surface (Figure 8.2b). These Na⁺ cations can approach the surface which is not entirely covered by the G-F. However, this did not occur when the system was relaxed at 1000 K which can be understood by the mobility of the ions at high temperature. In fact, the diffusivity of an ion increases with increasing temperature and can change significantly as the glass melts.

Figure 8.2 Interactions of G-F and G-S in Fe₂O₃-sodium borate system at 1000 and 1100 K.
1000 K for 20 ps.

In FeBG-S systems, similar results were obtained for the structures at 1000 and 1100 K (Figure 8.2c and d). First, G-S physically interacted with the Fe₂O₃ surface at a large distance of ~2.9 Å, which is in a good agreement with physical adsorption of graphene on metal surfaces. Secondly, no chemical bonds formed between G-S and Fe₂O₃ or between G-S and the sodium borate. Thirdly, after being relaxed at high temperature for 20 ps, the G-S remains as a stable sheet and shows less distortion than those of FeBG-F. This simulation result confirms the inertness of graphene sheets that has been proven in previous work.

Figure 8.3 reveals the changes in G-F and G-S structures compared to their initial configuration after fully optimized. Figure 8.3b clearly shows that after forming bonds with the Fe₂O₃ surface and the sodium borate, one C–C bond from a carbon ring was broken and the ring was opened. Another chemical modification in G-F is that one carbon ring loses one carbon atom and becomes a five-membered ring (Figure 8.3b). These chemical modifications in G-F indicate that G-F is unstable at high temperature and in the environment of the surface and lubricant catalysis. In contrast, the G-S with the physical interaction in Fe₂O₃-sodium borate systems retains its initial structure as six-membered carbon rings. Little changes were observed in G-S structure in Figure 8.3d, which confirms the stability of the graphene sheet compared to the flake counterpart. It is worth mentioning that graphene can be stable up to 500 °C in air, while the stability threshold of graphene in inert atmosphere could increase to 800 °C (1073 K). The current simulations showed that graphene sheets present no damage and defects at 1100 K, which is slightly higher than the experimental value in inert atmosphere. The reasons could be the small system size and the short simulation time that could make graphene more stable than its practical stability.
In comparison between G-F and G-S, G-F does not fully cover the surface and has chemical bonds with both the surface and the lubricant. These reactions modify significantly the G-F structure, leading to the structural distortion and breaking of carbon rings. The conversion of graphene flakes into disordered forms during sliding could result in the loss of frictional function, which leads to severe surface damage and corrosion. This is indicative of the failure of using small graphene flakes as a lubricant as it does not cover the surface evenly and loses its stable form at high temperature. Meanwhile, the use of large graphene sheets could be more stable at high temperature and with surface catalysis. This opens a promising future for using graphene combined with glass lubricants to work at elevated temperature. However, the detailed effects of graphene on frictional performance need further investigation under more practical conditions and with a wide range of glass lubricants such as alkali phosphate or silicate. Furthermore, the adhesion of graphene sheets on the metal surface is also an issue as poor adhesion could result in the removal of graphene from metal.
surfaces. The method of doping graphene structure to enhance the G-surface adhesive strength will be carried out in following sections.

8.4 Graphene doping

The doping of B, P, S and Si atoms into graphene lattice has been performed as presented in Section 8.2. The lattice parameters of these doped structures have been optimized to reach the equilibrium states. Figure 8.4 presents the optimization of doped-G scale factor according to the number of dopant atoms (D). The original graphene lattice is given the scale factor 1.0 as a reference. It is apparent that the size of the doped-G is larger with more dopant atoms added. This effect is due to the larger covalent radii of dopant atoms than that of carbon, i.e., B (0.84 Å), P (1.07 Å), S (1.05 Å), and Si (1.11 Å) while the radius of C is 0.73 Å. Therefore, B-G has a similar lattice scale with that of G, while larger factors are found for P-G and S-G, and Si-G has the largest scale factor compared to that of Gr. The equilibrium lattice parameters for 4×4 G and doped-G supercell are presented in Table 8.1. The lattice parameter of graphene is 2.464 Å. For 4×4 G supercell, our optimized lattice parameter in Table 8.1 is 9.86 Å, which is in good agreement with the literature. For other doped-G systems, the more number of dopants are added to the graphene network, the larger is the size of the supercell.

Table 8.1 Optimized lattice constants for 4×4 supercell of G and doped-G.

<table>
<thead>
<tr>
<th>System</th>
<th>Lattice constant (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n dopant</td>
</tr>
<tr>
<td>G</td>
<td>9.86</td>
</tr>
<tr>
<td>B-G</td>
<td>9.86</td>
</tr>
<tr>
<td>P-G</td>
<td>9.97</td>
</tr>
<tr>
<td>S-G</td>
<td>9.97</td>
</tr>
<tr>
<td>Si-G</td>
<td>10.07</td>
</tr>
</tbody>
</table>

* n dopant is equal to zero, corresponding to the pure graphene.
Figure 8.4 Optimization of the lattice constants for doped-G structures with the number of doping atoms: (a) B-G, (b) P-G, (c) S-G, and (d) Si-G.

The fully optimized configurations of graphene and doped-G with 4 dopant atoms are presented in Figure 8.5. These structures are those with the equilibrium lattice parameters achieved from Figure 8.4 and Table 8.1. One can see that after doped in graphene lattice, the dopant atoms form chemical bonds with carbon to form a complete network. The corresponding formation energy and bond length between carbon and the dopant atoms are presented in Table 8.2. For a single dopant, the formation energies of doped graphene are close to those obtained from other DFT calculations (Table 8.2). Among dopants, boron has the lowest formation energy, making it the easiest atom to be added to the graphene network. The order is followed by sulfur, phosphorus, and silicon, which is in line with the covalent radius. Thus the formation energy increases with the difference between the covalent radii of the dopant atoms to that of the carbon.
Figure 8.5 Top view and side view of the optimized structures of $4 \times 4$ G and doped-G supercells. Only the doping with 4 dopant atoms is shown. C (brown), B (green), P (pink), S (yellow), and Si (orange).

Table 8.2 Formation energies (eV) of doped graphene and the bond length between carbon and the dopant atoms.

<table>
<thead>
<tr>
<th>System</th>
<th>Formation energy (eV)</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 (ref.) 2 3 4 C−C C−D</td>
<td></td>
</tr>
<tr>
<td>B-G</td>
<td>1.22 1.30 1.38 1.44 1.42 1.49</td>
<td></td>
</tr>
<tr>
<td>P-G</td>
<td>3.57 3.54 3.47 3.44 1.63</td>
<td></td>
</tr>
<tr>
<td>S-G</td>
<td>1.67 0.45-3.68 1.47 1.56 1.70 1.65</td>
<td></td>
</tr>
<tr>
<td>Si-G</td>
<td>4.34 4.22 4.10 4.02 1.68</td>
<td></td>
</tr>
</tbody>
</table>

$a, b, c, d$ are formation energies from other DFT calculations $^{335-337, 341}$

The C−C bond length obtained from our calculation is 1.42 Å, similar to that obtained from other DFT calculation $^{341}$ and experimental work $^{342}$ For C−B, C−P, C−S, and C−Si, the longer bond lengths of 1.49, 1.63, 1.65, and 1.68 Å are achieved, respectively. Due to the longer bond length formed between carbon and dopant atoms, the supercells of these doped-G structures are significantly larger than the pure graphene as shown in Table 8.1.
8.5 Interactions of graphene and doped-G on Fe₂O₃ surface

The binding energy per atom of doped-G sheets on the Fe₂O₃ surface is presented in Figure 8.6. The binding energy of the graphene on Fe₂O₃ surface is 12 meV/C, which is the typical value for the physical interaction of graphene on metal surfaces, for example 40 meV for graphene on Cu(111) surface. When dopant atoms are added to the graphene structure, the binding energies increase greatly with the magnitude from 35 to 400 meV. For all systems, the binding energy increases in the systems with more dopant atoms added. The S-G systems show the strongest interaction with the Fe₂O₃ surface with the binding energy from 73 to 401 meV when the number of doped atoms rises from 1 to 4. P-G and Si-G systems show similar binding energy and from 90 to 318 meV, while B-G shows the weakest interaction with the binding energy from 35 to 147 meV. The binding energy values for B-G systems are in the range of the physical interaction while the higher energy in other systems indicates the chemical interaction between S-G/P-G/Si-G on the Fe₂O₃ surface. Compared to the adsorption of G, the addition of the dopants enhances the adsorption strength of the doped-G system significantly, which is essential for improving the adhesion of graphene on metal surfaces for applications under high pressure/shear and temperature conditions. The remarkable enhancement of binding strength on metal surface when graphene lattice was doped by boron atoms, and the binding energy increase from 35 to 121 eV/atom. These results suggest that adding suitable impurities into graphene structure is an effective method to improve graphene adhesion on metal/metal oxide surfaces.
Figure 8.6 Binding energy per atom of graphene and doped-G adsorbed on Fe$_2$O$_3$ surface. The red dot shows the binding energy of the pure graphene on Fe$_2$O$_3$ surface.

Table 8.3 presents the closest distances from G/doped-G to the Fe$_2$O$_3$ surface. The Fe$_2$O$_3$-G distance is 3.06 Å, which is consistent with the low binding energy and weak van der Waals interaction of graphene on the surface. The interacting distances are reduced with the increase in the number of dopants and the binding strength. In particular, the distances from 2.1 to 2.3 Å are found for doped-G with 4 impurity atoms. These distances correspond to covalent bond length between Fe and the dopant atoms, which is indicative of the chemical bond formation on the iron oxide surface. These chemical bonds play an important role in securing the stability of doped-G structure onto the surface in harsh operating conditions.

Table 8.3 Interacting distances from graphene and doped-G on Fe$_2$O$_3$ surface

<table>
<thead>
<tr>
<th>n dopant</th>
<th>closest distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe-G</td>
</tr>
<tr>
<td>0</td>
<td>3.06</td>
</tr>
<tr>
<td>1</td>
<td>2.67</td>
</tr>
<tr>
<td>2</td>
<td>2.34</td>
</tr>
<tr>
<td>3</td>
<td>2.35</td>
</tr>
<tr>
<td>4</td>
<td>2.27</td>
</tr>
</tbody>
</table>

The adsorption configurations and the corresponding charge density difference (CDD) of the G and doped-G adsorbed on the Fe$_2$O$_3$ surface are shown in Figure 8.7. Figure 8.7a reveals that there are no bonds formed between G and the surface, while
chemical bonds are found between Fe and the dopant atoms of the doped-G (Figure 8.7b, c, d, and e). Except for the Fe-BG system where the weaker interaction is observed, the bond formation between Fe and the dopants for Fe-P/S/SiG leads to the indent of the doped-G lattice at the doped-sites. In particular, P, S and Si atoms are relaxed downwards to the Fe$_2$O$_3$ surface and move off the initial doped-G plane. However, these dopant atoms still hold a strong connection with the graphene network by maintaining the chemical bonds at the impurity sites. These chemical modifications confirm the strong interactions with the metal oxide surface after graphene is treated with some impurities.

Figure 8.7 Adsorption configurations (top row in each sub-figure) and CDD (bottom row in each sub-figure) of graphene and doped-G on the Fe$_2$O$_3$ surface. Only doped-G configurations with 4 dopant atoms are shown in the figure. The red and blue regions in CDD signify the electron gain and loss areas, respectively.
CDD in Figure 8.7a shows that little electrons are transferred between Fe₂O₃ and graphene as the system encounters the weak van der Waals interaction. In contrast, massive electron transfer is found between Fe₂O₃-doped-G systems compared to the Fe₂O₃-G one in terms of the magnitude of the charge density and the influence to adjacent atoms. The interaction areas are mostly located around the doped atoms and the iron atom (from Fe₂O₃) that involves directly in the chemical bonds with the dopant atoms. However, some vicinity atoms of the surface or carbon of the doped-G are also influenced as some electron density redistribution is observed at these sites (the bottom rows in Figure 8.7b, c, d, and e). The shapes of the CDD in Figure 8.7b, c, d, and e indicate that Fe receives electrons to the dz² orbitals, while the dopant atoms donate electrons in the reaction. All dopant atoms B, P, S, and Si can be stable with four surrounding covalent bonds. When doped in graphene lattice, these dopant atoms are bonded to only three carbon atoms. Thus as the lone pair electrons in these atoms are available, it can facilitate the electron to the vacant d orbitals of Fe.

The calculated binding energy of doped-G on Fe₂O₃ surface indicates that doping graphene with the selected atoms can greatly improve the adhesion of graphene on the metal oxide surface. This is an important attribute to apply graphene under extreme conditions where the material undergoes shear stress at high temperatures. However, the interaction of doped-G on Fe₂O₃ surface leads to some deformations in doped-G structures, i.e., the doped atoms move toward the Fe₂O₃ surface and creating out-of-plane defects. These defects could hinder the sliding of the counter surface at the doped sites and could increase the friction compared to the sliding of two surfaces covered by pure graphene.

### 8.6 Stability of graphene and doped-G at high temperature

In this section, in order to investigate the thermal stability of graphene and doped-G at high temperature, the materials are relaxed as a monolayer sheet of G/doped-G and as the adsorbed forms on the Fe₂O₃ surface at four temperatures of 900, 1000, 1100, and 1200 K. As there is no much differences among results at 900, 1000, 1100 K, only results of 1000 and 1200 K are shown in this section. For the AIMD simulations of G/doped-Gr and their adsorbed configurations on the Fe₂O₃ surface, the G/doped-G structures were expanded to 8×12 or 4×12 supercells. For consistency, the name of the systems nD-G and Fe-nDG remains the same as the DFT systems, where n indicates the
number of dopants in the 4×4 supercell.

Figure 8.8 presents the visualization of graphene structures at 1000 and 1200 K after 10 ps equilibrium. At 1000 K, there is no bond breaking or defects in the graphene geometry. Graphene stays intact at this temperature with a weak fluctuation on the vertical direction (Figure 8.8a). At 1200 K, defects in the graphene network start with the breaking of C–C bonds. After 10 ps, only 1 defect is observed in the graphene geometry by opening two carbon rings into one large ring. It is worth mentioning that the cutoff distance for C–C bonds in Figure 8.8 is 1.6 Å, which already accounts for the 10% increase over the C–C bond length at the equilibrium state (1.42 Å). It has been experimentally reported that there is no significant damage in graphene structures up to 800°C, but graphene network starts to separate into small pieces at 1000°C. In our simulation, the limit for graphene damage is slightly higher than that of the experiment, which could be explained by the small size effects and short simulation time.

Figure 8.8 Top view and side view of graphene structures after relaxed at (a) 1000 K and (b) 1200 K for 10 ps. The number in (b) shows the defect site in the graphene lattice. The cutoff distance for C–C bonds is 1.6 Å.

The geometries of doped-G at 1000 K after the AIMD simulation for 10 ps are shown in Figure 8.9. It is indicative that the number of defect sites increases with the number of doped atoms in the network. At 1000 K, 1B-G resembles the configuration of graphene at the same temperature. However, 2B-G and 4B-G networks show some defects at the C–C bonds, but no bond breaking at C–B sites (Figure 8.9a, b, and c). In addition, boron atoms stay in-plane with the graphene network despite the slight bending of the graphene plane. A significant number of defects are observed for P-G, S-G, and Si-G, especially those with 4 dopant atoms added. The number of defects with four-dopant structures is remarkably higher than those with two or three dopants in P-G,
S-G, and Si-G configurations. In these systems, unlike B-G, the defects usually start at the doped sites by the cracking of C−P, C−S, or C−Si bonds (Figure 8.9 from d to l). Furthermore, there is a fluctuation along the out-of-plane direction at the doped sites due to the breaking of the carbon-dopant bonds. There more severe damage on the doped-G registers in 4P-G, 4S-G, and 4Si-G systems with the opening of more than two carbon rings, for example at the sites 16, 21, 23, and 24 in Figure 8.9f, or sites 18, 23, and 27 in Figure 8.9i. These are the evidence of the separation of doped-G networks into smaller pieces.329

Figure 8.9 Top view and side view of doped-G geometries from AIMD simulations at 1000 K and 10 ps. The name of the systems and number of dopant atoms remains as the 4×4 supercell for DFT optimization. n is the number of defects in the systems. The cutoff radii for C−C, C−B, C−P, C−S, and C−Si are respectively 1.60, 1.64, 1.80, 1.82,
and 1.86, which are 10% larger than the equilibrium bond lengths obtained from DFT optimization.

The geometries of doped-G obtained from the AIMD simulations at 1200 K are shown in Figure 8.10. Similar trend with that at 1000 K is achieved for doped-G structures at 1200 K with a larger scale of the vertical fluctuation of atoms and the larger number of defects. Compared to those at 1000 K, the number of defects increases slightly for B-G, S-G, and Si-G, while a huge charge is observed for P-G at 1200 K. For example, the number rises from 10 to 19, and from 29 to 30 sites in 2P-G and 4P-G at 1000 and 1200 K, respectively. It is worth mentioning that the total number of C–C and C–dopant bonds in the doped-G structures for the AIMD simulation is 288 bonds. Therefore, the broken bonds in the doped-G at 1000 and 1200 K of 4P-G, 4S-G, and 4Si-G accounts for more than 10% of the total number of bonds in the systems. This figure suggests a lower stability of doped-G structures when more dopant atoms are added in the network. The interference of foreign atoms with larger radii than that of carbon makes the graphene network less stable and more sensitive to thermal changes.
Figure 8.10 Top view and side view of doped-G geometries from AIMD simulations at 1200 K and 10 ps.

Compared to the pure graphene, B-G appears to be comparable with a small number of defects for 1B-G and 2B-G at both 1000 and 1200 K. P-G, S-G, and Si-G are less stable than the pure graphene when relaxed at high temperature. This could be explained by the larger size of these atoms compared to the carbon radius. In addition, the more dopant atoms are added into the graphene network, the less stable the system achieves. Therefore, the ideal number of dopants for a $4 \times 4$ G supercell could be 1 or 2 dopant atoms, which corresponds to the doping concentrations of 3.125 and 6.25%, respectively.

In order to compare the thermal stability of doped-G as the monolayer sheet and
the adsorbed form on the Fe₂O₃ surface, the relaxation of the doped-G on Fe₂O₃ surface at 1200 K was carried out. Figure 8.11 shows structure of these Fe-doped-G systems after equilibrated for 10 ps at 1200 K. It is evident that the number of defects in the doped-G networks reduces significantly compared to that in the doped-G sheet, except for the Fe-4SiG system. Moreover, the buckling along the vertical direction from the side views show less severe than those shown in Figure 8.9 and Figure 8.10. The reduction of the out-of-plane normal deformation could reduce static friction as found in thin sheets. In this case, the normal fluctuation in the doped-G on the Fe₂O₃ surface can be diminished by the bonding between Fe and the dopant atoms, which could constrain the bending and stretching in the doped-G lattices. In fact, the chemical bond formation between Fe and dopant atoms is the main reason to stabilise the doped-G on the surface.

However, at high temperature there is some bond dissociation occurring at the Fe-dopant sites. Under normal condition as shown in Figure 8.7, all doped atoms form chemical bonds with Fe of the surface. At 1200 K, 1B-G shows no bonds with the surface while in other systems, Fe-dopant bond dissociation occurs at some sites. Remarkably in Fe-SiG systems, the initial Fe–Si bonds disappear and Si forms new bonds with oxygen of the surface. The change of the bonding atoms laying at the second layer of the Fe₂O₃ surface leads to the elongation of the Si–C bonds, making them easier to be broken and creating more defects than other doped-G structures, especially in Fe-4SiG.
In general, the doping of B, P, S, and Si in graphene structure will improve the adhesion of the graphene on the surface, which is essential for the covering of the material on the surface under harsh tribological conditions. In addition, the interactions between the doped-G and the Fe₂O₃ surface can improve the stability of doped-G.
structure at high temperature. After being relaxed for 10 ps at 1200 K on the Fe₂O₃ surface, all doped-G with one dopant atom remain in good condition with a small number of bond breaking sites. However, with four dopant atoms, Fe-4BG, Fe-4PG, and Fe-4SG show relatively good condition while Fe-4SiG appears with a large number of defect sites. It is worth mentioning that boron, phosphorus, silicon, and sulfur have been widely used in the lubricant industry for high temperature lubrication. These atoms play a role as a binder to keep the lubricant adhered onto the working surfaces. The simulations in this work show that the adhesion of G has improved significantly when these atoms were added even at high temperature. Therefore, the results of this work open a new way to modify G structure for the applications with severe operating conditions such as metal forming.

8.7 Conclusions

The interactions of graphene with sodium borate and Fe₂O₃ surface at high temperature have been investigated by AIMD simulations. The results showed that the graphene sheet which fully covers the Fe₂O₃ surface can be stable at high temperature. The graphene flake failed to maintain its initial structure by the cracking of the six-membered carbon rings and forming bonds with the surface or with the borate. The transformation of graphene planar form into the disorder form can lead to the loss of the “easy-shear” property and result in high friction and wear rate.

The substitution of carbon in the graphene network by boron, phosphorus, sulfur, and silicon and the stability of the doped-G has been performed by DFT and AIMD simulations. The results suggest that the addition of the dopant atoms into the graphene sheet can improve the adhesion of graphene on the Fe₂O₃ surface at 0 K and at high temperature up to 1200 K. The doped-G can be stable on the Fe₂O₃ surface thanks to the chemical bonds between Fe and dopant atoms. The doping concentrations of 3.125 and 6.25 % could provide the best optimization between the adhesion and the structural stability, while higher concentration of 12.5% enhances binding strength significantly but leads to structural instability at high temperature. The improvement of graphene adhesion is beneficial for the applications under harsh operating conditions, especially high temperature lubrication in metal forming.
Chapter 9. CONCLUSIONS AND FUTURE WORK

In this work, interactions and chemical reactions between sodium phosphate/borate lubricants with iron oxide surface were studied, using DFT and AIMD simulations. Four aspects of the interaction between the lubricants and an iron oxide surface were examined, including adsorption, interactions at high temperature, under compression and under sliding motion. The AIMD simulations focused on the reactions between the sodium borate on Fe$_2$O$_3$ surface at high temperature, while DFT calculations were used to study the adsorption energy, structural transformations, and electronic structure at the lubricant-metal interface and inside the lubricants under adsorption, compression, and sliding. Electronic structure including density of state (DOS), Bader charges, charge density difference (CDD), and bond overlap population (BOP) were analyzed to provide insights into the mechanisms of the chemical reactions and structural transformations.

This chapter summarizes the finding of the DFT and AIMD simulations of the lubricant adsorption, effects of high temperature, compression, and shear on lubricant-surface chemical reactions. Conclusions with respect to the objectives in Section 2.5 are highlighted. Based on the current status of this work, recommendations for future work are also included.

9.1 Conclusions

The adsorption of sodium pyro- (Na$_4$P$_2$O$_7$) and ortho-phosphate (Na$_3$PO$_4$) on Fe(110) and Fe$_2$O$_3$(0001) surfaces was investigated. The comparison between adhesion of the two phosphate lubricants on iron and iron oxide surface was made. The results revealed that the phosphate lubricants chemisorbed on Fe(110) and Fe$_2$O$_3$(0001) surfaces through many Fe–O–P chemical bonds. The adsorption strength is correlated with the antiwear performance of the phosphate lubricants. The calculation of the adsorption energy revealed that the shorter chain orthophosphate has the lower interaction energy per phosphate group and a greater binding strength on both iron and iron oxide surface than Na$_4$P$_2$O$_7$. This binding strength explained the lubricant antiwear properties by the experiment. Therefore, in order to provide a better adhesion and wear performance, the phosphate lubricants are needed to adsorb strongly on the metal
or metal oxide surface by chemical bonds.

The effect of temperature on the interactions between sodium borate lubricants and Fe$_2$O$_3$ surface was studied by AIMD simulations. At the high temperature, Na$_2$B$_4$O$_7$ exhibits strong chemical interactions on the iron oxide surface thanks to the ionic Na–O and the Fe–O covalent bonds. On the contrary, B$_2$O$_3$ weakly interacts with the Fe$_2$O$_3$ surface which accounts for its poor adhesion as a lubricant. At high temperature, the surface was severely modified and exposed oxygen-rich areas. Charge calculations indicated that the negative oxygen-rich Fe$_2$O$_3$ facilitates the sodium enrichment on the steel surface through Na–O ionic interactions. The better friction and wear reduction of Na$_2$B$_4$O$_7$ is associated with its larger charge transfer and the stronger interaction than those in Fe$_2$O$_3$-B$_2$O$_3$. The simulation results are in qualitatively good agreement with experimental findings of sodium-rich layer on the steel surface and explained the superior lubrication of Na$_2$B$_4$O$_7$ over B$_2$O$_3$.\textsuperscript{14-15}

The structural transformations of sodium borates under the effects of high pressure were examined. Sodium borates various concentrations of Na$_2$O (25, 33, 50, and 60 mol\%) were used to compare the effects of sodium content under the compression. The reversibility of borate structure after compression to 10 GPa was examined through the decompression process.

Under mild pressure, the sodium borates underwent the physical reorientation before the polymerization occurred at high pressure. The orientation of borate fragments could benefit the frictional activities by forming local layered-like arrangement. Under further compression, the polymerization occurred through three distinct mechanisms M1, M2, and M3. With low Na$_2$O content, M1 is more likely to occur through BO$_3$ + O$_4$ $\rightarrow$ BO$_4$, while with higher Na$_2$O concentrations, M2 arises with BO$_3$ + O$^{ob}$ $\rightarrow$ BO$_4$. Both M1 and M2 can be initiated at relatively low pressures (1.3 and 1.9 GPa). For M3 which is formed between BO$_3$ and O$^{b}$ by BO$_3$ + $^{[2]}$O $\rightarrow$ BO$_4$, a high pressure (above 4.3 GPa) is required to activate electronic structure of boron and oxygen from $^{[2]}$O to $^{[3]}$O and $^{[3]}$B to $^{[4]}$B. After the compression, a majority of BO$_3$$\rightarrow$BO$_4$ transformations remain irreversible when the systems were unloaded to 0 GPa. The irreversible polymerization in the sodium borate plays an important role in supporting the loads under extreme pressure conditions. The compression also created a sodium-rich layer adsorbed at the surface-borate interfaces at high pressure, while the irreversible polymerized borate was
observed at the low Na content areas. The simulation results rationalized the mechanisms of bi-layered tribofilms observed after a tribotest.\textsuperscript{14-15}

The adaptation of alkali borate structures and the bonding at the interface under the pressurised sliding were studied. The sodium borates of 25\%, 33\% and 50\% Na\textsubscript{2}O mol\%, the lithium and potassium tetraborates were used as the lubricants. The shear was performed for 20 Å at 1 and 3 GPa, and at 1 GPa and 1073 K. The calculation of the energy in the systems revealed that the variation of the shearing energy was correlated with the changing of Fe–O and B–O bonds at the interface. The systems responded to the shear by bond stretching, bond rupture and new bond formation. The system with the lowest shearing energy variation was FeNaB50\% with the highest Na\textsubscript{2}O concentration. In this system, the formation of a layered-like borate layer was found. Meanwhile, the significant energy variation was associated with the frequent bond formation and rupture at the interface. The subsequence bond rupture occurred between surface’s atoms created severe modifications which could remove Fe atoms from the surface. The removal of Fe atoms was found in three cases: (i) in the sodium borate system with the lowest Na\textsubscript{2}O concentration (FeNaB25\%), (ii) in lithium borate system at both 1 and 3 GPa, and (iii) in the potassium borate system at 3 GPa. The shear at high temperature showed a clear evidence of cations layers mostly concentrated at the upper and lower Fe\textsubscript{2}O\textsubscript{3}-borate interfaces.

Based on the current results, the structure of sodium borate lubricated on the sliding Fe\textsubscript{2}O\textsubscript{3} interface was proposed. Thus, in order to protect the surface, support sliding motion, and loads, the film includes three consecutive regions: (1) the surface-lubricant bonding region to secure the adhesion of the lubricant and protect the surface; (2) the shearing region including sodium-rich mixed with short borate complexes to support the sliding motion; (3) the well-polymerized borate region playing the role as a load-bearing layer. The proposed layering structure of the Fe\textsubscript{2}O\textsubscript{3}-borate interface provided an atomic rationalization for low frictional results in borate-lubricated systems.

The interactions of graphene with sodium borate and Fe\textsubscript{2}O\textsubscript{3} surface at high temperature were examined by AIMD simulations. The results showed that the graphene sheet which fully covers the Fe\textsubscript{2}O\textsubscript{3} surface can be stable at high temperatures of 1000 and 1100 K. The graphene flake failed to maintain its initial structure at the
same temperature by the cracking of the six-membered carbon rings and forming bonds with the surface or with the borate.

The doping of boron, phosphorus, sulfur, and silicon into a graphene network and the interactions of the doped-G on the Fe$_2$O$_3$ surface were studied. The binding energy of the G/doped-G adsorbed on Fe$_2$O$_3$ surface revealed that doping graphene can improve the adhesion of G on the Fe$_2$O$_3$. The stability of the G/doped-G was investigated at high temperatures of 900, 1000, 1100, and 1200 K by G/doped-G sheets and their adsorbed structures on the Fe$_2$O$_3$ surface. The G and doped-G were less affected by temperature when relaxed on Fe$_2$O$_3$ surface than those relaxed without the surface. The stabilization was the result of the chemical bonds between Fe and the dopant atoms. The improvement of G adhesion is beneficial for the lubrication in metal forming under high temperature and pressure.

**9.2 Future work**

In the current work, the author investigated the interactions and the chemical reactions of sodium phosphate/borate with iron oxide surface under the conditions of adsorption, high temperature, compression and shear. In order to improve the practical conditions of the simulations, several avenues are proposed for future work:

i) The current models built with small sizes (less than 200 atoms) could not describe the formation of the tribofilms. Larger simulation models up to thousands of atoms would provide a better description of the tribofilm formation, which is more comparable with experimental observations.

ii) The current simulations do not account for the effects of dynamic conditions such as temperature, pressure, and sliding in one simulation. This issue could be improved by using more advanced simulation techniques such as coupling methods (QM/MM), using modified simulation packages to account for applied pressure and confined shear, or using MD simulations with reactive force fields.

iii) The combination of larger simulation models and advanced techniques such as QM/MM can represent simulation systems that are closer to practical experimental systems. Furthermore, the investigation of a series of systems
with different alkali metals and its concentrations could provide useful information to optimize the development and application of new lubricants for hot metal forming.

The combination of graphene with other glass lubricants or the modification of graphene structure should be investigated in the search for effective high-temperature lubricants. Frictional properties of the doped-G and its combinations will be studied to evaluate their effectiveness. Furthermore, simulations of doped-G or its combinations in tribological models with the inclusion of temperature, pressure, and sliding motion will be carried out, which can provide an overall picture of G/doped-G performance under harsh conditions.
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221


227