

Atomistic Insights into Diamond-Rock Contacts through Molecular Modelling

by

Jagjeevan Singh Bhamra

A Thesis Submitted for the Degree of
Doctor of Philosophy

2023

Department of Mechanical Engineering
Imperial College London

Declaration of Originality

The work presented in this thesis illustrates work accomplished in the Department of Mechanical Engineering at Imperial College London and Centre for Technology Innovation, Baker Hughes Inc, Houston, Texas 77040, United States. I declare, to the best of my knowledge, that the work outlined in this thesis is my own, except where explicitly acknowledged.

Jagjeevan Singh Bhamra

08/04/2023

Copyright Declaration

The copyright of this thesis rests with the author. Unless otherwise indicated, its contents are licensed under a [Creative Commons Attribution-Non Commercial-No Derivatives 4.0 International Licence](https://creativecommons.org/licenses/by-nc-nd/4.0/) (CC BY-NC-ND).

Under this licence, you may copy and redistribute the material in any medium or format on the condition that; you credit the author, do not use it for commercial purposes and do not distribute modified versions of the work.

When reusing or sharing this work, ensure you make the licence terms clear to others by naming the licence and linking to the licence text.

Please seek permission from the copyright holder for uses of this work that are not included in this licence or permitted under UK Copyright Law.

Abstract

Understanding friction and wear properties at diamond-rock interfaces is crucial to increase the energy efficiency of not only drilling operations but several other processes. A significant proportion of the current research focuses on experimental work and continuum-level computation studies, which limits the fundamental understanding of the physicochemical mechanisms at these interfaces. Molecular modelling has been previously used to study tribological interfaces, and here, in particular, it can shed light on atomic-scale behaviour taking place at diamond-rock contacts to aid the development of new engineered surfaces and the design of new lubricants that can meet current and future demands.

In this thesis, rock drilling tribology is studied using nonequilibrium molecular dynamics (NEMD) and with a reactive forcefield (ReaxFF). Firstly, macroscale tribometer experiments reveal that a diamond-limestone (mostly calcite) gives significantly higher friction coefficients compared to granite (mostly quartz) in various humidity levels. NEMD simulations uncover the physicochemical mechanisms that lead to higher kinetic friction in the diamond-calcite system mainly due to increased interfacial bonding mostly formed through chemisorbed water molecules trapped between the tip and the substrate. For both rock types, interfacial bond formation increases exponentially with pressure, indicative of a stress-augmented thermally activated (SATA) process. The friction force is shown to be linearly dependent on the number of interfacial bonds during steady-state sliding. The agreement between the friction behaviour observed in the NEMD simulations and tribometer experiments suggests that interfacial bonding also controls diamond-rock friction at the macroscale. We anticipate that the improved fundamental understanding provided by this study will assist in the development of bit materials and coatings to minimize friction by reducing diamond-rock interfacial bonding.

Secondly, NEMD simulations of diamond-hexadecane-quartz systems show higher kinetic friction than diamond-water-quartz systems, contrary to the general understanding of lubrication at tribological contacts. This observation was corroborated by diamond-granite (mostly quartz) macroscale tribometer experiments. As previously, direct interfacial bonding between the asperity and substrate forms more readily in the diamond-hexadecane-quartz system due to little to no passivation of the quartz, which occurs with water. Again the friction force is shown to be linearly dependent on the number of interfacial bonds during steady-state sliding, and interfacial bond formation increases exponentially with pressure, suggesting that this process can be explained with pre-existing SATA models. When water is added to the diamond-hexadecane-quartz system, the kinetic friction decreases. We expect that the development of water-based lubricants will not only be more environmentally friendly but also improve the friction behaviour of diamond-rock interactions through mitigation of interfacial bonds.

Thirdly, we show that diamond wear on α -quartz involves atom-by-atom attrition of carbon atoms, which is initiated by the formation of C-O interfacial bonds, followed by C-C cleavage, and either diffusion into the substrate or further oxidation to form CO₂ molecules. The presence of interfacial water molecules, which dissociate to form surface hydroxyl groups, passivate the sliding surfaces and markedly reduce both interfacial bonding and wear. At low loads, the initial wear rate of the diamond tip increases exponentially with temperature and normal stress, consistent with stress-augmented thermally activated wear models. At higher loads, the initial wear rate becomes less sensitive to the normal stress, eventually plateauing towards a constant value. The initial wear rate versus normal stress data can be accurately described over the entire load range using the multibond wear model. Over longer sliding distances, wear also occurs through cluster detachment via tail fracture. During this phase of the simulations, wear becomes approximately proportional to the sliding distance and normal load, which is consistent with the empirical Archard model. The

normalised wear rates from the simulations are within the experimentally-measured range for single-crystal diamond on quartz glass surfaces.

Finally, in the same aforementioned system, quartz undergoes a phase transformation to a stishovite-like phase. This phase is formed through a three-step process: firstly, rupture of Si-O bonds, then a steady-state period, and finally the reformation of these bonds. Bond reformation only takes place when no water is present, and at high loads (>35 nN) and pressures (>4.5 GPa), the net number of Si-O bonds had increased at the end of the simulation when compared with the start. This phenomenon also becomes more apparent with increasing temperatures. Again, this phase transformation presents itself as a SATA process, with mechanochemical activation of Si-O bonds through sliding of the diamond asperity since this phase does not present itself with an absent asperity. We determine that the rate of bond rupture and activation volume (ΔV) both decrease when water is present, and subsequently the activation energy (E_a) increases significantly. Mitigation of this phase transformation from α -quartz to an stishovite-like region should be an effective strategy to improve the tribological performance of drill bits and other diamond tools during SiO₂-rich rocks.

Acknowledgements

I would like this moment to make acknowledgements to those who made this work possible. Firstly, Professor Daniele Dini and Dr. James P. Ewen deserve special consideration for their invaluable guidance, unrivalled knowledge, and continued trust, motivation, and encouragement.

Gratitude is also significantly expressed to Baker Hughes for making this project feasible through their sponsorship. A mention must be first made to Marc W. Bird and John A. R. Bomidi for their positive support, inspiration, and enthusiasm. Additionally, I would like to thank Eliah M Everhard Andrew Robertson for their valuable discussions and vision.

Recognitions are also due to the members of the Tribology group at Imperial College London. Not many groups are as fun, diverse, and multidisciplinary as this one.

Finally, I would like to thank my family and friends, particularly my late dog Leo who kept me company during the pandemic and now Henry, a dog that made the final stages of my PhD very memorable. Additionally, this would not have been possible without the support of my parents and my younger brother.

Thank you all.

Contents

DECLARATION OF ORIGINALITY	2
COPYRIGHT DECLARATION	3
ABSTRACT	4
ACKNOWLEDGEMENTS	7
CONTENTS	8
LIST OF FIGURES	10
ABBREVIATIONS, ACRONYMS, AND TERMINOLOGY	20
CHAPTER 1. INTRODUCTION	22
1.1. MOTIVATION	22
1.2. RESEARCH GOALS	22
1.3. LAYOUT OF THESIS	23
CHAPTER 2. DRILLING, MOLECULAR MODELLING, AND TRIBOLOGY	26
2.1. RELEVANCE OF MOLECULAR MODELLING IN TRIBOLOGY	26
2.2. DRILLING AND POLYCRYSTALLINE DIAMOND COMPACTS (PDCs)	27
2.3. MOLECULAR MODELLING	39
2.3.1. CHEMICAL REACTIONS AND MECHANOCHEMISTRY	40
2.3.2. MOLECULAR DYNAMICS	46
2.3.2.1. CLASSICAL FORCEFIELDS	51
2.3.2.2. REACTIVE FORCEFIELDS	52
2.4. FRICTION AND WEAR: MACROSCALE TO NANOSCALE	55
2.4.1. FRICTION	55
2.4.2. WEAR	59
CHAPTER 3. INTERFACIAL BONDING CONTROLS FRICTION IN DIAMOND-ROCK CONTACTS	67
3.1. INTRODUCTION	67
3.2. METHODOLOGY	69
3.3. RESULTS AND DISCUSSION	78
3.4. CONCLUSION	96
CHAPTER 4. COMPARING THE TRIBOLOGICAL PERFORMANCE OF WATER- BASED AND OIL-BASED DRILLING FLUIDS IN DIAMOND-ROCK CONTACTS	98
4.1. INTRODUCTION	98
4.2. METHODOLOGY	101
4.3. RESULTS AND DISCUSSION	107

4.4. CONCLUSION -----	120
CHAPTER 5. ATOMIC-SCALE WEAR INSIDE DIAMOND-QUARTZ CONTACTS ----	122
5.1. INTRODUCTION -----	122
5.2. METHODOLOGY -----	125
5.3. RESULTS AND DISCUSSION -----	131
5.4. CONCLUSION -----	150
CHAPTER 6. MECHANOCHEMICALLY INDUCED PHASE TRANSFORMATION OF α -QUARTZ -----	151
6.1. INTRODUCTION -----	151
6.2. METHODOLOGY -----	155
6.3. RESULTS AND DISCUSSION -----	156
6.4. CONCLUSION -----	166
CHAPTER 7. A COMPARISON OF FORCEFIELDS FOR C/O/Si/H SYSTEMS -----	168
7.1. INTRODUCTION -----	168
7.2. METHODOLOGY -----	169
7.3. RESULTS AND DISCUSSION -----	172
7.4. CONCLUSION -----	177
CHAPTER 8. CONCLUSIONS AND FURTHER WORK -----	179
8.1. CONCLUSIONS -----	179
8.2. FURTHER WORK -----	182
BIBLIOGRAPHY -----	186
APPENDIX A. SUPPORTING INFORMATION FOR CHAPTER 3 -----	222
APPENDIX B. SUPPORTING INFORMATION FOR CHAPTER 4 -----	233
APPENDIX C. SUPPORTING INFORMATION FOR CHAPTER 5 -----	237
APPENDIX D. SUPPORTING INFORMATION FOR CHAPTER 6 -----	242
APPENDIX E. SUPPORTING INFORMATION FOR CHAPTER 7 -----	244

List of Figures

Figure 2.1: Rock-crushing mechanism induced by a PDC cutter.	29
Figure 2.2: Schematic outlining the total energy of a system as a function of the reaction coordinate.	43
Figure 2.3: Simplified potential energy surface diagram for a thermal reaction without (red) and with shear (blue). Energy levels are not drawn to scale, mechanical activation can either be introduced at the reactant or transition state, and tribochemical products may be less thermodynamically stable than the reactants but kinetically stable.	45
Figure 2.4: A map to illustrate the different scales accessible in modelling tribological systems.	47
Figure 2.5: A schematic atomic-scale model of one possible thermally activated mechanism by which wear of a substrate occurs.	61
Figure 3.1: Microscopy images and energy-dispersive x-ray spectroscopy (EDS) analysis of the diamond pins after the friction experiments on granite (a) and limestone (b). EDS was performed on regions of exposed diamond and areas covered by transfer material, as shown in the middle microscopy images. Performed by Maria De La Cinta Lorenzo Martin.	71
Figure 3.2: Representative system (calcite surface with 150 water molecules) for the NEMD simulations shown before equilibration. Calcium atoms are shown in green, carbon in grey, oxygen in red, and hydrogen in light blue.	72
Figure 3.3: Comparisons of energy from ReaxFF (red) and DFT (green) for constraining of (a) Ca–O–C angle and (b) Ca–C off-diagonal. Performed by Nabankur Dasgupta.	75
Figure 3.4: Equations of state of calcite from ReaxFF (red) and DFT (green). Performed by Nabankur Dasgupta.	76

Figure 3.5: Variation in the friction force, F_f , with normal force, F_n , from the macroscale tribometer experiments with diamond–granite (black) and diamond–limestone (red) point contacts in an air environment. Dashed lines are linear fits to Amontons’ friction equation. Dotted lines are estimates for the low-load region (< 80 N) based on Hertz theory ($F_f \propto F_n^{2/3}$). Shaded regions represent 95 % confidence intervals. Performed by Evan Yu. ----- 78

Figure 3.6: Variation in friction force, F_f , with sliding time from the NEMD simulations for diamond–quartz (black) and diamond–calcite (red) interfaces with 0 (a), 50 (b), and 150 (c) water molecules. Normal force, $F_n = 35$ nN, sliding velocity, $v_x = 10$ m s⁻¹. ----- 81

Figure 3.7: Variation in the friction force, F_f , with normal force, F_n , from the NEMD simulations with diamond–quartz (black) and diamond–calcite (red) point contacts with 0 (a), 50 (b), and 150 (c) water molecules. Mean forces calculated during the final 200 ps of sliding. Dashed lines are fits to Amontons’ friction equation. Shaded areas represent 95 % confidence intervals. ----- 83

Figure 3.8. Variation in the total number of interfacial bonds between the tip and the surface during sliding for: (a) calcite with 0 water molecules, (b) quartz with 0 water molecules, (c) calcite with 50 water molecules, (d) quartz with 50 water molecules, (e) calcite with 150 water molecules, and (f) quartz with 150 water molecules. Dotted lines are fits to the function $(1 - e^{-r t})$ where r is the rate of interfacial bond formation and t is sliding time. ----- 87

Figure 3.9: Variation in rate of interfacial bond formation as sliding commences with maximum Hertz pressure for: (a) 0 water molecules, 50 water molecules, 150 water molecules. Insets show linear increase in $\ln(\text{rate})$ with pressure. Dashed lines are fits to Equation 3 used for the calculation of the activation volume. ----- 92

Figure 3.10: Type of interfacial bonds between the tip and the surface during steady-state sliding for: (a) diamond–calcite with 0 water molecules, (b) diamond–quartz with 0 water molecules, (c) diamond–calcite with 50 water molecules, (d) diamond–quartz with 50 water molecules, (e) diamond–calcite with 150 water molecules, and (f) diamond–quartz with 150 water molecules. Snapshots of each bond type are shown in the coloured boxes. Calcium atoms are shown in green, silicon in orange, carbon in grey, oxygen in red, and hydrogen in light blue. ----- 93

Figure 3.11: Correlation between the mean friction force and the mean number of interfacial bonds during steady-state sliding for diamond–calcite (a) and diamond–quartz (b). Crosses represent systems with 50 water molecules, triangles are 150 molecules, darker colours indicate higher loads. ----- 96

Figure 4.1. NEMD simulation setups for diamond-quartz contacts in air (a), water (b), and *n*-hexadecane (c) systems shown after energy minimisation/equilibration, before compression and sliding. Silicon atoms are shown in red, oxygen in blue, carbon in grey, and hydrogen in green. 104

Figure 4.2. Variation in the friction force, F_F , with normal force, F_N , from the macroscale tribometer experiments with air (purple), water- (green), and hexadecane-lubricated (red) diamond–granite contacts. Normal forces, F_N , are between 10 and 100 N and tangential velocity, $v = 0.125 \text{ m s}^{-1}$. Dashed lines are linear fits to Amontons’ friction equation. Dotted lines represent 95% confidence intervals. Performed by Eliah M Everhard. ----- 108

Figure 4.3. Variation in friction force, F_F , with sliding time from the NEMD simulations for the air (purple), water- (green), and hexadecane-lubricated (red) contacts for normal forces, F_N , between 5 and 40 nN and sliding velocity, $v_s = 10 \text{ m s}^{-1}$. ----- 109

Figure 4.4. Variation in friction force, F_F , with normal force, F_N , from the NEMD simulations for the air (purple), water- (green), and hexadecane-lubricated (red) contacts. Mean forces calculated during the final 500 ps of sliding. Dashed lines are fits to Amontons’ friction equation. Dotted lines represent 95% confidence intervals. ----- 110

Figure 4.5. Variation in the total number of interfacial bonds between the tip and the surface during sliding for the air (purple), water- (green), and *n*-hexadecane-lubricated (red) contacts across $F_N = 5 \text{ nN}$ to 40 nN . Black dashed lines are fits to the first 250 ps of interfacial bond formation data assuming first-order reactions used to calculate initial rates. ----- 112

Figure 4.6. Variation in the total number of passivated surface sites between the tip and substrate during sliding for the air (purple), water- (green), and hexadecane-lubricated (red) contacts across $F_N = 5 \text{ nN}$ to 40 nN . ----- 114

Figure 4.7. Change in the rate of interfacial bond formation with maximum Hertz pressure for air (purple), water- (green), and hexadecane-lubricated (red) contacts. Inset shows a linear increase in $\ln(\text{rate})$ with Hertz pressure. Dashed lines are fits to Equation 4.1. ----- 116

Figure 4.8. Number and type of interfacial bonds (C-O, C-O-Si or C-H-O) formed for each simulated load for the (a) air-, (b) *n*-hexadecane-, and (c) water-lubricated system. ----- 119

Figure 4.9. Correlation between the mean friction force and the mean number of interfacial bonds during steady-state sliding for (a) air, (b) hexadecane, and (c) water systems. Darker colours indicate higher loads. ----- 120

Figure 5.1: NEMD systems for the (a) dry and (b) wet (500 H₂O molecules) diamond-quartz systems before equilibration. Silicon atoms are shown in red, oxygen in blue, carbon in grey, and hydrogen in pink. ----- 129

Figure 5.2: Change in the number of wear atoms with sliding distance for the dry system at (a) varied temperatures and a constant load of 30 nN (b) varied loads and a constant temperature of 500 K. Worn atoms defined as those that have formed C-O bonds, been removed from the tip through C-C cleavage and diffused into the substrate or oxidised to form CO₂ molecules. Snapshots of the tips after 400 nm of sliding are shown in the coloured boxes. ----- 134

Figure 5.3: Number of C-O interfacial bonds formed (green), C-O interfacial bonds broken (red), and C-C wear bonds broken (purple) during sliding for the dry system at a 35 nN load and temperatures of (a) 300 K, (b) 400 K, (c) 500K, (d), 600 K, (e) 700 K, and (f) 1000 K. Black dashed lines are fits to the first 1 ns of the bond formation/breakage data assuming first-order reactions used to calculate initial rates. ----- 135

Figure 5.4: Number of C-O interfacial bonds formed (green), C-O interfacial bonds broken (red), and C-C wear bonds broken (purple) during sliding for the dry system at 500 K and loads of (a) 20 nN, (b) 25 nN, (c) 30 nN, (d) 32.5 nN, (e) 35 nN, (f) 37.5 nN, (g) 40 nN, and (h) 42.5 nN. Black dashed lines are fits to the first 1 ns of the bond formation/breakage data assuming first-order reactions used to calculate initial rates. Legend same as in Figure 5.3. ----- 137

Figure 5.5: Change in the initial rate of C-C wear in the dry (a) and wet (b) system, interfacial C-O bond formation in the dry (c) and wet (d) system, and interfacial C-O bond breaking in the dry (e) and wet (f) system with pressure. Dry systems $T = 500$ K, wet systems $T = 1000$ K. The dashed lines are exponential fits to the data used to calculate the activation volume, $\Delta V^\ddagger$, using Equation 5.2. Insets show the same data with a logarithmic y -axis. ----- 139

Figure 5.6: Change in the initial rate of C-C wear in the dry (a) and wet (b) system, interfacial C-O bond formation in the dry (c) and wet (d) system, and interfacial C-O bond breaking in the dry (e) and wet (f) system, with temperature at a constant load of 35 nN. The dotted lines are exponential fits to the data used to calculate the activation energy, ΔU , using Equation 5.2. ---- 141

Figure 5.7: Change in the number of interfacial bonds, N_{ib} , (a) and number of wear atoms, N_{wear} , (b) with normal load F_N at different simulation times for the dry system at 500 K. Dashed line is fit to Equation 5.3 in (a) and Equation 5.4 in (b) for the NEMD simulation data after 4 ns up to loads of 30 nN. Green region shows the load range where the model is applicable. ----- 144

Figure 5.8: Normalized atom wear rate (i.e., number of atoms removed from the asperity per unit time normalized by the estimated number of atoms in contact) as a function of dimensionless effective normal stress for the dry system at 500 K (a) and the wet system at 1000 K (b). The multibond wear model (Equation 4.8) is fit to the full data set. The $\tilde{\sigma}$ values are calculated using Equation 5.9. ----- 146

Figure 5.9: The normalised wear rate, dW/dL , versus normal load, F_N , for the dry system at 500 K and the wet system at 1000 K. Steady-state wear rates are calculated from linear fits through the wear versus time data shown in Figure 4.2 (dry) and Appendix C Figure 6 (wet) after the running-in period (sliding distance > 100 nm). Black dashed lines are linear fits through the data as predicted by the Archard model. ----- 148

Figure 6.1: NEMD setup for the diamond-quartz system before equilibration. Silicon atoms are shown in red, oxygen in blue, and carbon in grey. ----- 156

Figure 6.2: Change in number of Si-O bonds (a-f) and friction force (g-l) at a fixed load equal to 35 nN and temperatures between 300-1000 K. Blue and red dashed horizontal lines that indicate

where fits to the function $(1 - e^{-r})$ are fitted, where r is the rate of bond formation/breakage and t is the sliding time. ----- 156

Figure 6.3: Change in number of Si-O bonds (a-h) and friction force (i-p) at a fixed temperatures equal to 500 K and loads between 20-42.5 nN. Blue and red dashed horizontal lines that indicate where fits to the function $(1 - e^{-r})$ are fitted, where r is the rate of bond formation/breakage and t is the sliding time. ----- 158

Figure 6.4: Change in the initial rate of Si-O cleavage in the dry system for Si-O rupture (a) and formation (b) system against contact stress calculated using the atoms in contact method. The dashed lines are exponential fits to the data used to calculate the activation volume, $\Delta V^\ddagger$, using Equation 6.1. Insets show the same data with a logarithmic y-axis. ----- 159

Figure 6.5: E_a calculated for Si-O bond rupture (a) and reformation (b) using the values extracted from Figure 6.4 and equation 6.1. ----- 160

Figure 6.6: E_a calculated for with mechanochemical activation from the asperity (a) and without (b). ----- 161

Figure 6.7: Average coordination number in the uppermost layer of atoms in the quartz substrate at 300 K (a), 400 K (b), 500 K (c), 600 K (d), 700 K (e), and 1000 K (f). ----- 162

Figure 6.8: RDFs for at 300 K for bulk α -quartz (a), Si-Si (b), O-O (c), and Si-O (d) and at 1000 K for bulk α -quartz (e), Si-Si (f), O-O (g), and Si-O (h). ----- 163

Figure 6.9: Averaged bond angles for O-Si-O at 300 K (a) and 1000 K (b) and Si-O-Si at 300 K (c) and 1000 K (d). ----- 164

Figure 7.1: NEMD setup for the diamond-quartz system before equilibration. Silicon atoms are shown in red, oxygen in blue, and carbon in grey. ----- 169

Figure 7.2: A comparison of friction force, and change in the number of Si-O, C-C, and C-O bonds for the Newsome (red) and Ponomarev (black) forcefields at temperatures between 300 –

1000 K and $F_N = 35$ nN. A similar figure including the Zhang forcefield can be found at Appendix E Figure 1. ----- 172

Figure 7.3: A comparison of the number of C-O interfacial bonds form and break and the number of C-C wear atoms for the Newsome (red) and Ponomarev (black) forcefields at temperatures between 300 – 1000 K and $F_N = 35$ nN. ----- 174

Figure 7.4: Snapshots showing the dry tip wear over time for the Newsome and Ponomarev forcefields. Carbon atoms shown in black, silicon in red, and oxygen in blue. Atom-by-atom attrition occurs for all conditions via C-O interfacial bond formation, C-C breaking and either diffusion into the substrate or oxidation to form CO₂ molecules. Amorphization of the tip followed by cluster detachment at the trailing edge of the tip occurs at high temperatures and loads. This is truer for the Newsome forcefield than for Ponomarev's. ----- 176

Appendix A Figure 1: Variation in the percentage of intact water molecules with simulation time for: (a) calcite with 50 water molecules, (b) quartz with 50 water molecules, (c) calcite with 150 water molecules, and (d) quartz with 150 water molecules. The first 100 ps are equilibration at 0.1 nN, the remaining 700 ps include compression (values in legend) and sliding (10 m s⁻¹). ----- 222

Appendix A Figure 2: Comparison of vibrational frequencies of CaCO₃ from ReaxFF and DFT. Created by Nabankur Dasgupta and Adri C. T. van Duin. ----- 223

Appendix A Figure 3: Different C-O bond stretching and compression modes for CaCO₃ vibrational frequencies. Created by Nabankur Dasgupta and Adri C. T. van Duin. ----- 223

Appendix A Figure 4: Variation of the friction force with sliding distance with tip sliding velocities of 1 m s⁻¹ and 10 m s⁻¹ for: (a) calcite with 0 water molecules, (b) quartz with 0 water molecules, (c) calcite with 50 water molecules, (d) quartz with 50 water molecules, (e) calcite with 150 water molecules, and (f) quartz with 150 water molecules. The normal force is 35 nN. ----- 224

Appendix A Figure 5: Variation in the indentation depth with sliding time for: (a) calcite with 50 water molecules, (b) quartz with 50 water molecules, (c) calcite with 150 water molecules, and (d) quartz with 150 water molecules. ----- 225

Appendix A Figure 6: Variation in the indentation depth with load for: (a) calcite and quartz with 50 water molecules and (b) calcite and quartz with 150 water molecules. Mean and standard deviation (vertical bars) calculated during the final 200 ps of sliding. ----- 225

Appendix A Figure 7. Variation in the load-dependent friction coefficient (F_f/F_n) with the steady-state indentation depth with systems containing 50 and 150 water molecules. Dotted lines show the predictions from the Bowden-Tabor equation for the ploughing contribution to the friction coefficient. ----- 226

Appendix A Figure 8. Variation in the contact area, A_c , with maximum Hertz pressure, P_{max} , in the experiments and NEMD simulations. Crosses show Hertz predictions over the studies load range in the experiments (1–200 N) and simulations (2.5–40 nN). Triangles show the measured contact areas from the NEMD simulations based on the indentation depths. ----- 227

Appendix B Figure 1. Variation in the friction force, F_F , with normal force, F_N , from the macroscale tribometer experiments with air (purple), water- (green), and hexadecane-lubricated (red) diamond–granite contacts. Normal forces, F_N , are between 10 and 100 N and tangential velocity, $v = 0.095 \text{ m s}^{-1}$. Dashed lines are linear fits to Amontons’ friction equation. Dotted lines represent 95% confidence intervals. Performed by Eliah M Everhard. ----- 233

Appendix B Figure 2. Variation in the friction force, F_F , with normal force, F_N , from the macroscale tribometer experiments with air (purple), water- (green), and hexadecane-lubricated (red) diamond–granite contacts. Normal forces, F_N , are between 10 and 100 N and tangential velocity, $v = 0.15 \text{ m s}^{-1}$. Dashed lines are linear fits to Amontons’ friction equation. Dotted lines represent 95% confidence intervals. Performed by Eliah M Everhard. ----- 234

Appendix B Figure 3: Change in indentation depth with sliding time for air (purple), water (green), and hexadecane (red) lubricated contacts. ----- 234

Appendix B Figure 4: Mean indentation depth with normal force for air (purple), water (green), and hexadecane (red) lubricated contacts. ----- 235

Appendix B Figure 5: Variation in the total, formation, and rupture of interfacial bonds between the tip and the surface during sliding for the air (purple), water- (green), and hexadecane-lubricated

(red) contacts across $F_N = 5$ nN to 40 nN. Black dashed lines are fits to the first 250 ps of interfacial bond formation data assuming first-order reactions used to calculate initial rates. ----- 235

Appendix B Figure 6: Variation in the rate of interfacial bond formation as sliding commences with the atoms in contact method for pressure calculations for air (purple), water- (green), and hexadecane-lubricated (red) contacts. Inset shows a linear increase in $\ln(\text{rate})$ with pressure. --- 236

Appendix C Figure 1. Comparison between contact stress calculations using Hertz theory and the number of atoms in contact based on the number of interfacial bond for the (a) dry and (b) wet systems. Atoms in contact values are mean values over final 1 ns. ----- 237

Appendix C Figure 2. Temporal evolution of the pressure in the NEMD simulations using the atoms in contact method for (a) dry and (b) wet systems. ----- 237

Appendix C Figure 3. Snapshots showing the dry tip wear over time at (a) medium temperature/medium load, (b) medium load/high temperature, and (c) high load/medium temperature. Carbon atoms shown in black, silicon in red, and oxygen in blue. Atom-by-atom attrition occurs for all conditions via C-O interfacial bond formation, C-C breaking and either diffusion into the substrate or oxidation to form CO_2 molecules. Amorphization of the tip followed by cluster detachment at the trailing edge of the tip occurs. ----- 238

Appendix C Figure 4. Total number of C-C broken bonds with sliding distance for the dry system at (a) varied temperatures and a constant load of 35 nN (b) varied loads and a constant temperature of 500 K. ----- 239

Appendix C Figure 5. Number of carbon wear atoms as a function of a product of sliding distance and load for (a) dry and (b) wet systems. ----- 239

Appendix C Figure 6. Number of wear atoms for the wet system at (a) varied temperatures and a constant load of 30 nN and (b) varied loads and a constant temperature of 1000 K. ----- 240

Appendix C Figure 7. Change in the number of C-O (orange), C-O interfacial (red), C-C total (green), and C-C wear (purple) bonds broken/formed during sliding for the wet system at varied

temperature and a constant load of 30 nN. Black dashed lines are fits to the first 1 ns of the bond formation/breakage data assuming first-order reactions. ----- 240

Appendix C Figure 8. Change in the number of C-O (orange), C-O interfacial (red), C-C total (green), and C-C wear (purple) bonds broken/formed during sliding for the wet system at varied temperature and a constant temperature of 1000 K. Black dashed lines are fits to the first 1 ns of the bond formation/breakage data assuming first-order reactions. ----- 240

Appendix C Figure 9. Change in the number of interfacial bonds, N_{ib} , (a) and number of wear atoms, N_{wear} , (b) with normal force for the wet system. ----- 241

Appendix D Figure 1: Change in number of Si-O bonds and friction force at a fixed load equal to 35 nN and temperatures between 1000-1800 K for the wet system. Si-O rupture is fitted to the function $(1 - e^{-rt})$ are fitted, where r is the rate of bond formation/breakage and t is the sliding time. ----- 242

Appendix D Figure 2: Change in number of Si-O bonds and friction force at a fixed temperature equal to 1000 K and loads between 20-60 nN for the wet system. Si-O rupture is fitted to the function $(1 - e^{-rt})$ are fitted, where r is the rate of bond formation/breakage and t is the sliding time. ----- 242

Appendix D Figure 3: E_a (a) and $\Delta V^\ddagger$ (b) calculated for the wet system using the rates from fittings from Figure Appendix C Figure 1 and Figure Appendix C Figure 2. ----- 243

Appendix D Figure 4: Change in the number of Si-O bonds in bulk α -quartz upon heating between 300 K and 2000 K without the sliding diamond asperity. ----- 243

Appendix E Figure 1: A comparison of friction force, and change in the number of Si-O, C-C, and C-O bonds for the Newsome (red), Ponomarev (black), and Zhang (green) forcefields. --- 244

Abbreviations, Acronyms, and Terminology

μ	Friction coefficient
τ	Shear stress
A	Area
F_N	Normal force/load
F_F	Friction/tangential force
K_b	Wear coefficient
V	(Wear) volume
$\Delta E^\ddagger$	Barrier height
k_B	Boltzmann's constant
f	Effective attempt frequency
ΔG_{act}	Gibbs free energy of activation
E_a	Activation energy
$\Delta V/\Delta V_{\text{act}}$	Activation volume
ε	Depth of the potential well
G^*	Reduced shear modulus
k_{cont}	Contact stiffness
Γ_0	Pre-factor
ΔU_{act}	Stress-free activation barrier
AFM	Atomic force microscopy
LAMMPS	Large-scale atomic/molecular massively parallel simulator
MAPS	Materials and process simulation
MD	Molecular Dynamics
NEMD	Nonequilibrium Molecular Dynamics
QMD	Quantum molecular dynamics
OFM	Organic friction modifier
QC/M	Quantum chemistry/mechanics
EHL	Elastohydrodynamic lubrication
PPPM	Particle-particle, particle-mesh
JKR	Johnson, Kendall, and Roberts
DMT	Derjaguin, Muller and Toporov

ReaxFF	Reactive forcefield
vdW	van der Waals
PDC	Polycrystalline Diamond Compacts
PCD	Polycrystalline Diamond
WC	Tungsten Carbide
MC	Monte Carlo
PES	Potential energy surface
SATA	Stress-augmented thermal activation
L-J	Lennard-Jones
DODAC	Diocetyldecyldimethyl-ammonium
PBC	Periodic boundary conditions
HPC	High performance computing
NH	Nosé-Hoover
Qeq	Charge equilibration
OTG	Oleic-type triglycerides

Chapter 1. Introduction

1.1 Motivation

Understanding friction and wear properties at diamond-rock interfaces is crucial to increase the energy efficiency of not only drilling operations but several other processes. The design of new lubricants and engineered surfaces requires a fundamental understanding of atomic-scale mechanisms that underpin macroscale performance. Diamond-rock contacts are multicomponent interfaces that offer a rich physicochemical landscape. Macroscale experiments and continuum-level models can only offer so much information when trying to uncover what governs the friction and wear behaviour of diamond-rock contacts. Molecular modelling has been previously used to study tribological interfaces, and here, in particular, it can shed light on atomic-scale behaviour taking place at diamond-rock contacts to aid the development of new engineered surfaces and the design of new lubricants. Previous atomic-scale experiments and simulations reveal that macroscale friction and wear models break down on the nanoscale, while others say these models are the dominating factor.

Many areas within science and engineering are employing computer simulations to explain macroscale experiments and phenomena. This project aims to uncover the atomic-scale behaviour of diamond-granite and diamond-limestone systems using nonequilibrium molecular dynamics (NEMD) and reactive forcefields (ReaxFF). Using a simplified diamond-quartz and diamond-limestone, we aim to employ NEMD and ReaxFF to identify how these systems behave on the nanoscale in an effort to improve diamond-rock tribological performance.

1.2 Research Goals and Project Targets

The main goal of this project is to improve the tribological performance of rock drilling. To achieve our research goal, we molecularly model relevant diamond-rock systems that participate in

industrial oil drilling. We aim to further fundamental scientific knowledge and expand on recent research in order to provide a detailed understanding of how the systems interact.

Polycrystalline diamond compacts (PDCs) are not only ubiquitous in the oil drilling industry but also relevant to construction, mining, and carbon capture and storage. The physicochemical interactions of PDCs and rocks are poorly understood. Currently, much of the literature has focused on macroscale experiments and continuum-level simulations to understand the tribological performance of such systems. We aim to perform atomic-level simulations to reveal the physicochemical mechanisms that underpin these systems. Additionally, we aim to understand the role that water and other drilling fluids play in the role of improved friction and wear performance.

1.3 Thesis Layout

Initially, this thesis introduces relevant literature on PDCs, mechanochemistry, molecular modelling, and the applicability of macroscale friction and wear models on the nanoscale. The subsequent studies discuss the main findings of the project when finally, they are summarised, and final conclusions are made.

Chapter 2 begins with briefly highlighting the relevance of molecular modelling in tribology. Then a discussion on PDC friction and wear performance is presented, which heavily revolves around experimental work. Next, molecular modelling more generally is reviewed, and key studies and the inception of the technique are highlighted. Additionally, chemical reactions regarding mechanochemistry are also discussed here. This chapter concludes with a review of notable work that surrounds how macroscale friction and wear models extend to nanoscale contacts, both experimentally and computationally.

In Chapter 3 nonequilibrium molecular dynamics is used with pre-existing and a newly formulated reactive forcefield to study diamond-quartz and diamond-limestone contacts. Simulation data is compared with macroscale tribometer experiments and results from there corroborate the finding from the simulations. A range of humidity levels is tested experimentally and computationally.

In Chapter 4 the effects of drilling fluids, particularly *n*-hexadecane are compared with water lubrication in the diamond-quartz system. Here again, findings are corroborated with macroscale tribometer experiments, and a stress augmented thermally activated argument is provided for the discrepancies in each system's friction performance. We also investigate mixtures of both hexadecane and water and reveal the importance that water plays in reducing kinetic friction in diamond-quartz contacts.

In Chapter 5 nonequilibrium molecular dynamics and a reactive forcefield are used to explore the nanoscale wear of a diamond asperity on a quartz substrate. Two conditions are examined, a dry and wet system. The literature is still undecided on whether macroscale wear models are applicable at the atomic level. Here, we provide evidence that in certain conditions, different models are applicable.

In Chapter 6 we continue the investigation from Chapter 5 and focus only on the dry system. Instead of examining the asperity, we observe the initiation of a phase transformation to an stishovite-like structure in the substrate. Mechanistic details are provided along with a mechanochemical description of the process.

In Chapter 7 we compare different ReaxFF parameterisation sets for some of the key bond formation and rupture processes we observed in the previous chapters.

Finally, in Chapter 8, conclusions are drawn from all stages of the project and future work is outlined.

Chapter 2. Drilling, Molecular Modelling, and Tribology

The work presented in this chapter is partly published in *The Journal of Physical Chemistry C*,¹ currently under review at *Applied Surface Science*, and being prepared for submission to *Tribology Letters*.

This chapter firstly discusses the relevance of molecular modelling in tribology. Next, an introduction and a deep-dive examination of drilling technology with a focus on the wear mechanisms of polycrystalline diamond compact (PDC) bits and cutters are laid out. Mechanochemistry and tribochemical phenomena are detailed subsequently. A review of molecular dynamics comes after, highlighting nonequilibrium molecular dynamics and reactive forcefields. The final section concludes with an outline of how friction and wear assumptions transition across the macro to the nanoscale.

2.1 Relevance of Molecular Modelling in Tribology

Since 1966², tribology has been the science and advancement of technology in understanding friction, wear, and lubrication of surfaces in contact. Since then, a remarkable effort has gone into progressing and developing a myriad of materials, lubricant formulations, antiwear additives, and system design to combat inefficiencies in tribological performance.³ However, with current population growth and increasing energy demands, there are growing demands to significantly reduce the use of fossil fuels, initiate sustainable agendas, and improve energy efficiencies.^{4,5} End-use energy efficiency has the largest potential contribution (38%) to limit CO₂ emissions and ultimately exemplifies the impact of climate change.^{6,7} Moreover, it is currently estimated that 23% of global energy consumption arises from tribological contacts, where 20% is to overcome friction and 3% is from remanufactured equipment due to wear.³ Holmberg et al.³ also predicts that within 15 years, advancements in tribological technologies can potentially reduce friction and wear by 40%, which accounts for 1.4% of the annual global GDP. It was determined that improving

longevity, by reducing wear, is more critical than reducing friction, as it would prevent machine failure, reduce operational cost, and improve productivity.

Computer simulations are currently being employed to study several areas within science and engineering. Friction⁸ and wear⁹ in tribological systems are often governed on the nanoscale, and therefore, molecular simulations provide a great tool to study and further understand these systems. Even though contact geometry, material selection, surface topography, and lubricant formulation can impact tribological properties of a sliding interface,¹⁰ physicochemical interactions between the surfaces play an important role.¹¹ Tribochemistry is a term used to designate physicochemical phenomena at tribological contacts. The following section outlines the tribology of polycrystalline diamond compact (PDC) bits and cutters.

2.2 Drilling and Polycrystalline Diamond Compacts (PDCs)

Rock drilling is a crucial process for many areas of the energy industry, from the extraction of oil and gas¹² to the utilization of geothermal energy.¹³ Over the next decade, drilling could also play a central role to facilitate carbon capture and storage¹⁴ and the safe disposal of radioactive waste.¹⁵ Recent estimates have suggested that, in the energy industry, friction and wear account for around 40% of total energy losses.³ A significant proportion of these losses originate from the drilling of rocks, which is a rather inefficient process. Drilling efficiency is usually defined as the ratio of the rock compressive strength to the mechanical specific energy.¹⁶ At high cutting depths, the drilling efficiency is between 30 and 50%, although this can drop to 10% at low cutting depths, where most of the energy dissipation occurs through frictional contact. Drilling efficiency could be improved through the development of improved bit materials and coatings.¹⁷ This could also improve the economic feasibility of deep-well drilling (below 1.5 km), which would be beneficial for oil, gas, and particularly, geothermal applications.¹⁸ The cost of wells increases almost exponentially with increasing depth¹⁸ and drilling costs average 50% of the \$3–8 M total cost of

deep wells.¹⁹ The introduction of PDC bits during the 1970s²⁰ was a significant advancement in drilling technology.²¹ In the drilling industry, two main tools are generally employed: a roller cone with WC-Co inserts and PDC bits formed by PDC/WC-Co cutters.²² Initial investigations²³ suggested that PDC bits operate optimally in soft-to-medium rock formations through a shearing mechanism while roller cone bits are used for impact excavations in harder formations. Nevertheless, the drag bits could drill twice faster and longer than roller bits even in hard formations.²⁴

Total thickness of the PDC cutter can vary drastically, cutters larger than 50.8 mm have been made available, where they are brazed, diffusion bonded within a matrix-bit body, or bonded with a carbide stud.²⁵ This is then directly pressed into the pockets of a steel-bit body. PDC bits proved to be extremely effective in drilling soft to medium rock formations (e.g., clay, sand, shale, limestone, sandstone, and siltstone), where they achieved high rates of penetration (ROP) while also maintaining long bit life.²¹ However, in harder formations (e.g., mudstone, chert, pyrite, granite, and quartzite), both ROP and bit life were substantially reduced. The ROP is reduced by high friction coefficients at the bit–rock interface, which are 3–5 times higher for PDCs compared to other (roller cone, WC insert) drill bits.²⁶ High friction coefficients, coupled with high sliding velocities ($>1 \text{ m s}^{-1}$),²⁷ result in large temperature increase (hundreds of degrees Celcius) at the bit–rock interface,²⁷ which can promote deleterious structural transformations (graphitization) within the surfaces of PDC bits.^{28,29} These transformations, coupled with increased abrasive wear due to the higher hardness of the counter surface,³⁰ are the principal causes of reduced bit life in hard rock formations. Mechanical Specific Energy (MSE) and ROP are generally considered to be two critical evaluation metrics for determining drilling efficiency.¹⁶ ROP is commonly assumed to be the depth of cut per unit time and because it is proportional to the depth of cut per revolution, it can be thought of as the depth of cut of an individual cutter.³¹

Polycrystalline diamond (PCD) materials are considered the most capable material for the fabrication of high-performance cutting tools.³² Traditionally, WC was a commonly used material in machining applications, however, PCDs have an ultra-high hardness (~ 8000 HV), which also results in significant manufacturing costs.³² Moreover, PCD tools have prolonged tool life, high thermal conductivity, and low friction when compared with WC tools.³³ PCD originates from disc-like structures, which are manufactured from the sintering of nano/micro diamond grains, with the addition of cobalt as a binding agent, under 5 GPa pressure and >1500 °C temperatures.^{34,35} Cobalt also acts as a solvent catalyst,³⁶ where it passes through the diamond grains to form diamond-cobalt and diamond-diamond bonds³⁷ during the disc sintering process. The entire process takes place on a WC substrate when after, a PCD tool can be fabricated by brazing inserts cut from the formed discs.³⁸ PDC bits (and cutters) remove rock by either grinding, machining, or crushing.³⁹ Figure 2.1 shows a schematic adapted from Huff et al., showing the crushing mechanism of a PDC bit on a WC substrate. Here, the cutting edge of the bit propagates fractures in the direction away from the free surface of the rock.

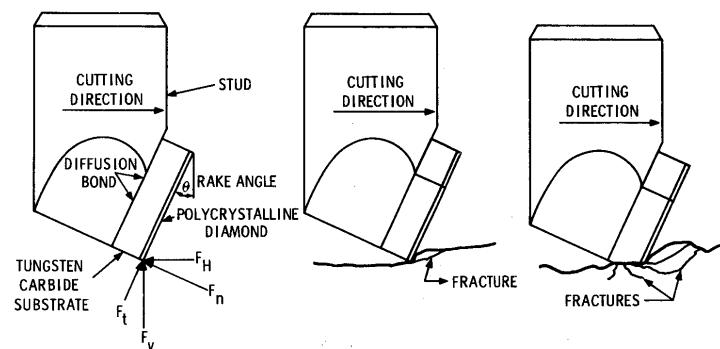


Figure 2.1: Rock-crushing mechanism induced by a PDC cutter. Used with permission from Huff et al.³⁹

Ersoy and Waller⁴⁰ suggested that the majority of damage to PDC bits was due to abrasive wear. The earth's crust is composed by 80% of hard and potentially abrasive material (e.g. alumina, silica,

hematite). This explains that the PDC bits suffer mainly from abrasive wear.⁴⁰ In fact, abrasive wear is the major wear mechanism in most tribological systems.³⁰ The Archard equation⁴¹ is the most popular empirical model to predict abrasive wear inside macroscale contacts⁴²

$$V = \frac{(K_b \cdot F_N \cdot d)}{H} \quad (2.1)$$

where V is the wear volume, K_b is the wear coefficient, F_N is the load, d is the sliding distance, and H is the hardness. The Archard equation⁴¹ has frequently been used to model the abrasive wear of PDC bits.^{43–45} The hardness of the polycrystalline diamond (PCD) used in PDC bits is at least 55 GPa.²⁷ During the drilling process, the bits can often pass through greatly varying geologies. Even within a single rock type, the properties can vary markedly and can be heterogeneous and scale-dependent. In hard rock excavation, two factors affect the material removal with the cutting tools: cutters have to penetrate deeper into existing grooves and remove additional pieces of material⁴⁶ and adjacent grooves interact with each other in a way that larger rock chips are formed.⁴⁷ The mean hardness values have been measured for several rock types, for example, calcite-rich rocks (e.g., limestone) have a mean hardness of ~ 2 GPa, while quartz-rich rocks (e.g., granite) have a mean hardness of 9–15 GPa.^{27,48} Since these are both much softer than PCD under ambient or typical wellbore temperatures (< 300 °C), low abrasive wear rates are expected from the Archard model⁴¹ for PDCs when drilling both granite and particularly, limestone rocks. However, the effective hardness of PDC can be reduced below that of quartz (but not calcite) when local cutting temperatures exceed ~ 750 °C.⁴⁹ Under these accommodating conditions, PDCs are susceptible to abrasive wear.⁵⁰ Additionally, the lifetime of diamond drill bits is generally reduced for rocks with a higher equivalent quartz content.⁴⁶ In addition to high hardness, there may also be a tribochemical component to the high wear rates observed for quartz-rich rocks. PDCs are therefore limited to drilling weaker rock formations due to their susceptibility of brittle failure.²⁵ However, in rock

cutting more generally, modes of failure of drag bits, including PDC bits, would result in a more brittle and less ductile bit as the depth of cutting increases.^{51,52} Detournay et al.³¹ described a phenomenological cutting model where a fixed wear flat (a flat contact area at the bottom of the cutter) originates at the cutter's contact area, however, the wear flat length can increase during drilling since a bit consists of several circular cutters, all experiencing distinctive wear mechanisms.^{25,53} These four distinctive wear mechanisms were laid out Lin et al.,²⁵ and consist of:

1. High mechanical and thermal loads polish diamond grains resulting in smooth wear:

Smooth wear generally occurs when drilling through homogenous rock formations, which contain both strong and abrasive components, using PDC bits with numerous cutters.⁵⁴ Since diamond has a hardness significantly higher than many rock formations, particularly, quartz, smooth wear is characterized by surface grooves in the direction of cutting as a result of high mechanical and thermal effects.⁵⁵ This combination effect originates from local friction points between the cutter and individual quartz grains, resulting in local high temperatures, which promote graphitization, oxidation, and ultimately removal of diamond without causing macroscopic fracture. Diamond also readily undergoes reactions with cobalt, iron, and other ferrous elements/compounds at elevated temperatures; this promotes graphitization and oxidation, and therefore smooth wear of PDC bits is believed to be caused primarily by a thermochemical action.²⁵ Hence, cooling of the bit wear flat during drilling operations is an effective strategy to limit smooth wear.

2. Bit-cutting forces causing microchipping:

Small flakes break off PDC cutters in a process referred to as microchipping.²⁵ Diamond fragments break off with the plane of fracture being approximately parallel to the direction of cut, and originate in the diamond table.²¹ Dunn and Lee⁵⁶ noted a significant reduction in the fracture stress of PDC cutters under cyclic loading, and subsequently indicated that

damage occurs through a thermal or mechanical fatigue-like mechanism. Lin et al.²⁵ proposed a microchipping model, where cracks (and diamond removal) are formed from tensile failure cracks initiating from the front face of the diamond table. The model heavily relies on geometrical constraints of the cutter, where a specific orientation would result in significant shearing stress on the front face of the cutter, which ultimately experiences damaging tensile stresses in the direction parallel with the front face. It is important to note that the model does not account for thermomechanical fatigue, which has been shown to play a role in crack formation and microchipping.⁵⁶

3. Gross fracturing because of extreme normal load applied to the bit:

Unlike the previous two wear mechanisms, gross fracturing generally occurs over short time periods. Gross wear occurs when formations change and the bit runs into a hard band of rock, which results in crack nucleation at the curved surface of the cutter, which propagates to the centre.⁵⁷ The fragment is generally a circular chip with a fracture plane normal to the cutting direction. The orientation of the crack indicates that gross wear is exclusively caused by normal force applied to the cutter since no wear flats have developed and the cutter has experienced mechanical overload. Wear, and failure occurs between 5-40 kN, which is significantly higher than the weight-on-bit for a typical cutter, 2.5 kN.⁵⁶ However, edge loading a cutter continuously halves the cutter's failure strength,⁵⁶ and Behr et al.⁵⁸ demonstrated, using a three-dimensional model, that when drilling through nonhomogeneous rock formations, or through rocks with strong nodules, the loading on a bit can be non-uniform, where up to 20 kN weight-on-bit can act on a single cutter. This further supports the mechanical overloading theory of gross wear.²⁵

4. Delamination between the WC substrate and diamond table:

Delamination is a result due to the mismatch between the PCD layer and the WC substrate.²⁵ The residual compressive stress forms in the PCD layer and tensile stress in the WC substrate during the PDC-WC sintering process. High tensile stresses are induced in the diamond table periods of high temperatures, such as drilling.^{28,59} It is generally accepted that high-temperature fluctuations in the cutter would reduce residual stress, however the compressive stress in the PCD layer increase. Along with gross wear, delamination causes significant wear in cutters, since large fragments of diamond are removed, which exposes the WC substrate. WC is less resilient than PCD, therefore a wear flat develops more readily when WC is left exposed.

The four processes described above all account for cutter wear. Another process, heat checking, has been discussed by Lin et al.²⁵ Here, cutters are degraded through a heating and quenching cycle that occurs unintentionally during drilling operations. During drilling, through frictional heating, cutters are subjected to extreme temperatures, that when cooled rapidly during momentary separation between the cutter and the rock, characteristic reticulate patterned cracks are formed. However, a large wear flat is necessary to generate the heat for heat checking. This follows that heat checking is only possible when one or more of the four processes described above create a sufficiently large wear flat to initiate heat checking. In 1995, Ersoy et al.⁴⁰ determined that even though PDC wear can take many forms, as described above, an abrasive wear mechanism is most common. Five key conclusions were drawn from their experiments:

1. Rocks with large soft particles that are weakly bonded results in low wear rates due to the significant pore size
2. Rocks with high silicate content induce increasingly rapid wear
3. Rocks that have a wide range of grain sizes in a hard bond of minerals and contain angular particles produce higher rates of wear
4. Mohs and Shore hardness of the rocks have specific influence on wear rates

5. An increase in the Cerchar, Dynamic Impact and F abrasivity index all increase the wear rate

A final conclusion was drawn suggesting that abrasive wear volume is linearly proportional to the weight-on-bit and torque, as predicted by Archard's law,^{40,41} as also reported by Yoshino et al.⁶⁰ It is well known that diamond can be polished with relatively soft silica particles, with the tribochemical mechanism believed to involve the formation of strong C-O bonds across the diamond-silica interface.⁶¹ This hypothesis was recently confirmed by first-principles calculations.⁶² However, it is not yet clear how diamond wears on quartz substrates.

Several studies have reported improvements in the thermal stability of PDC. Bovenkerk et al.⁶³ removed cobalt entirely or partially from PDC through a corrosion mechanism, however, the abrasive resistance, flexure strength, and bulk modulus decreased. Uedaa et al.⁶⁴ replaced the cobalt binder with MgCO_3 to increase the thermal stability but reduced the strength and toughness. Several studies have reported the synthesis of an ultrahigh strength, toughness, and thermal stability novel diamond-SiC nanomaterial.^{65–73} Jaworska et al.⁷⁴ used a wide range of ceramics as a replacement binding agent for cobalt, and Wang et al.⁷⁵ used cBN-diamond composite/mixture to enhance strength and thermal stability. Finally, Liu et al.⁷⁶ proposed a new three-layered PDC composed of a diamond-SiC composite (working layer), diamond-SiC-Co composite (intermediate layer) and WC/Co cement (substrate). However, several of these new materials come at a significant economic cost and are chemically not feasible on a larger scale.

As in many tribological systems involving direct solid–solid contact,⁸ stick-slip can occur during PDC drilling.^{77–79} In rock drilling particularly, stick-slip can be characterised by a two-phase process causing severe torsional vibrations. Firstly, a sticking phase results in the bit stopping, and a slipping phase causes the angular velocity of the bit to increase up to two times the imposed angular velocity.⁷⁸ Stick-slip is particularly critical with drag bits, which consist of fixed blades or cutters

mounted on the surface of a bit body.⁷⁷ It is believed that stick-slip originates within the constitutive properties of the frictional interface, more specifically through the dependence of the coefficient of friction, μ , on the relative velocity between the two contacting surfaces.⁸⁰ Stick-slip is highly undesirable since it leads to vibrations that can reduce both ROP and bit life.⁷⁹ Chen et al.⁷⁹ identified two types of stick-slip in drilling operations, cutting-action and friction-induced stick-slip. It was determined that if bit drilling efficiency was greater than a critical value, the cutting-action-induced stick-slip vibration is not expected in drilling. Moreover, increasing the aggressiveness of the cutting structure of a PDC bit within a limited critical depth of cut is found to be helpful to mitigate bit stick-slip vibration. Stick-slip behaviour is particularly prevalent at low rotation speed (sliding velocity) and high weight-on-bit (pressure) conditions.⁷⁸ Additionally, apart from a weight-on-bit and low ROP, the hardness of the rock, worn bit, and bit diameter can impact the likelihood of stick-slip.^{81–83} Since stick-slip occurred only when the bit on the bottom drilling head was in contact with the rock,⁸¹ it is now widely accepted that bit–rock interactions are critical to the oscillatory friction and stick-slip behaviour observed when using PDCs.^{77–79} Stick-slip is a particular problem in calcite-containing rock (e.g., limestone) formations,⁸⁴ where rock powder has been observed to strongly adhere to the PDC surface following tribometer experiments.⁸⁵ These observations suggest that stick-slip could be caused by the cooperative rupture of chemical bonds at the sliding bit–rock interface.⁸⁶ Such behaviour has previously been confirmed in atomic force microscopy (AFM) experiments of sliding silica–silica interfaces.^{87,88} Conversely, for quartz-containing rocks (e.g., granite), adhesion between the tip and rock is negligible, meaning that stick-slip is less problematic. The chemistry of the diamond–quartz interface is like that studied in previous experiments of silica AFM tips sliding on hydrogenated diamond substrates, on which stick-slip was found to be much less pronounced than for silica–silica interfaces.⁸⁷

In addition to the development of new bit materials, drilling fluids can also be used to increase performance. In the 1980s, Chilingarian and Vorabutr⁸⁹ and Darley and Gray⁹⁰ listed approximately

20 functions of drilling fluids while drilling a well. In general, this list can be summarised as the following:

1. Remove cuttings from the borehole and allow for separation at the surface to occur
2. Clean and cool the bit/cutter while in operation
3. Minimize friction and corrosion between the drill pipe and the borehole/wellbore or casing
4. Ensure the structural integrity of the borehole/wellbore remains intact
5. Prevent external fluids from entering the borehole/wellbore
6. Formulate a thin, low-permeable filter cake
7. Ensure that no damage arises to the producing formation
8. Remain non-hazardous to surrounding personnel and wildlife
9. Be considered environmentally friendly
10. Transmit hydraulic horsepower to the bit
11. Suspend drill cuttings in the event of rig shutdown so that the cuttings do not fall to the bottom of the hole and stick the drill pipe

Non-aqueous drilling fluids were introduced in the 1930s and since then, their performance has improved drastically, resulting in them being the most widely used type of fluid for drilling through petroleum formations.⁹¹ Complex fluids, including non-aqueous drilling fluids, are mixed with a multitude of different additives to form drilling muds, and the specific constituents of a drilling mud depending on the drilling method employed and the type of reservoir being drilled.⁹² The mud is a composite homogenous fluid system that is usually composed of liquids, solids, and chemical components.⁹³ Due to the multitasking performance of muds highlighted above, it is necessary to develop specific formulations of complex systems to cope with different environmental and geological situations.⁹⁴ Muds can either be classified as water-based, oil-based, synthetic-based, emulsions, invert emulsions, air, foam fluids, etc. Additionally, common bentonite

or attapulgite can be added to the borehole/wellbore to assist with fluid-loss and amplify the hole-cleaning mechanism.⁹⁵ Initially, untreated field crude oil of unknown composition was used to drill and complete producing formation.^{89,90,96,97} Soon after clay was added for viscosity in order to clean the borehole/wellbore and small amounts of fatty acids were introduced to ensure oil wetting of drilled cuttings.⁹⁸ More recently, “designer fluids” have become more common and typically consist of well-characterized synthetic hydrocarbon as the base oil of the fluid. However, oil-based muds and designer fluids have been posed with significant challenges, including high initial cost, health, safety and environmental concerns, incompatibility with elastomers, high potential for lost circulation, high sensitivity to pressure and temperature, inability to detect gas kicks, and undesirable effects on some logging tools.⁹¹ Gas- or air-based mud systems rely on the removal of drill cuttings through a high-velocity stream of air, nitrogen or natural gas.⁹⁰ This results in minimal circulation losses and increased bit life since gas- or air-based muds provide a cooling effect and rapid removal of cuttings and debris. In water-based muds, solid particles are suspended within the base fluid (e.g. water, seawater, brine, saturated brine, or moulded brine) where water is the aqueous phase and oil can be emulsified in the water.⁹⁹ Water-based muds are low-cost, environmentally friendly, the most widely used drilling mud onshore and offshore, with approximately 80% of wells being drilled with water-based muds.¹⁰⁰ Additionally, potassium chloride is commonly employed by the oil and gas industry to control rheological properties and better hydrate-resistant.¹⁰¹ However, a high concentration of potassium chloride has been shown to split the mud into a liquid and sediment phase.¹⁰² Therefore, polymers were broadened to improve rheological¹⁰³ and shale inhibition¹⁰⁴ characteristics in drilling muds. Polymers also improve high-pressure high-temperature downhole conditions,^{105,106} and synthetic polymers can be formulated for viscosity,¹⁰⁷ lubricity,¹⁰⁸ shale stability,¹⁰⁹ filtrate loss reducer,¹¹⁰ and improve yield value.¹¹¹ Furthermore rheological, thermal, and mechanical properties of muds can improve with the addition of nano-technology.¹¹² Nanosilica,¹¹³ nano-graphite,¹¹⁴ graphene oxide,¹¹⁵ carbon

nanotubes,¹¹⁶ zinc oxide,¹¹⁷ and copper oxide¹¹⁷ have all been investigated for enhancing rheological properties and shale inhibition of drilling muds.

The rheological behaviour of Newtonian fluids (e.g. water, light oil, and glycerine) is characterised as its shear stress being directly proportional to shear rate, such that, $\tau = \mu \dot{\gamma}$, where τ is the shear stress, μ is the viscosity, and $\dot{\gamma}$ is the shear rate.¹¹⁸ For non-Newtonian fluids (e.g. clays and colloids), the shear stress does not increase proportionally with shear rate, such that, $\tau = k \dot{\gamma}^n$, where n is a dimensionless fluid flow behaviour index indicating the tendency of a fluid to shear thin and k is the consistency index of the system. The Bingham plastic model, $\tau = k \tau(\dot{\gamma}) + \mu_p \dot{\gamma}$, where $\tau(\dot{\gamma})$ is the shear stress at τ and μ_p is the plastic viscosity is the most common model used to describe rheological properties of drilling fluids. The Hershel-Bulkley model, $\tau = \tau(\dot{\gamma}) + k \dot{\gamma}^n$, combines the Power Law model with Bingham's model. The Casson model, $\sqrt{\tau} = \sqrt{\tau(\dot{\gamma})} + \sqrt{\mu_p \dot{\gamma}}$, describes the flow of visco-elastic fluids with a gradual transition from Newtonian to non-Newtonian region.^{90,95}

Rehbinder et al.¹¹⁹ showed that the addition of surfactants to circulating fluids could markedly influence the ROP in hard rocks. The original mechanism offered by Rehbinder et al. was that changes in drilling performance in different environments could be a consequence of the adsorption-induced reduction in the surface energy of the solid being penetrated.¹²⁰ Subsequently, Mills et al.¹²⁰ suggested that surfactant solutions that increased the hardness of the rock surface could reduce the ploughing contribution to diamond–rock friction and thus also decrease frictional heating. Since higher temperatures result in increased wear, they suggested that solutions that increase rock surface hardness could reduce tip wear.¹²¹ This is the opposite trend to that which would be predicted using the Archard abrasive wear model.⁴¹ In a more recent study by the same authors, the influence of several other factors, such as adsorption kinetics, polarity, and surfactant concentration, on bit wear was also considered.¹²² Yoshino et al.⁶⁰ also reported an abrasive wear mechanism of single-crystal diamond machining of a quartz glass plate. They reported that

abrasion, over adhesion, is the dominating factor and the tool wear rate is significantly reduced when using either water or kerosene as a lubricant. Subsequent discussions led to a conclusion that a reduction of the friction coefficient will be effective to reduce tool wear. Controversy still remains in this area due to the complex interacting processes involved in controlling drilling performance.¹²³ The physicochemical nature of these interactions and their effects on friction for different rock types remains unclear. One plausible mechanism is that the surfactants reduce friction by passivating the sliding bit and rock surfaces and minimising interfacial bonding.¹

2.3 Molecular Modelling

Computational, and more specifically molecular, modelling is becoming an increasingly important tool in many areas of science and engineering. Molecular simulations began in the 1950s, where high-performance computers calculated representative experimental observables through interactions of molecules.¹²⁴ Molecular dynamics (MD) is a technique where the atomic trajectories of a given system are computed through the integration of Newton's equation of motion using a finite difference scheme over a series of short time steps, a deterministic method.¹²⁵ Prior to that a stochastic method was developed by Metropolis et al. known as the Monte Carlo (MC) method.¹²⁶ In the MC method, molecules are displaced by a trial random displacement usually one at a time, and the new molecule position is accepted based on the potential energy of the system. Both MD and MC are able to output thermodynamic properties of a given system, however, MD is also able to compute time-dependent processes and transport coefficients, making it more applicable to tribological systems.¹²⁴

The following sections discuss mechanochemistry, transition state theory, and molecular dynamics. The focus is given to tribochemistry with an emphasis on reactive forcefields and molecular dynamics to elucidate mechanistic and fundamental details of nanoscale friction and wear.

2.3.1 Chemical Reactions and Mechanochemistry

Conventionally, chemical reactions are thought to be activated through either a thermochemical, electrochemical, or photochemical mechanism. However, a fourth mechanism exists, mechanochemical activation of chemical reactions.¹²⁷ The first references to mechanochemical reactions were by a student of Aristotle, who mechanochemically activated the reaction of cinnabar and brass pestle to produce metallic mercury.¹²⁷ The term mechanochemistry is thought to be introduced by Ostwald,¹²⁸ however, he makes no reference to the application of a mechanical force to accelerate chemical reactions, thus the origins of the term remain obscure.

Mechanochemical phenomena occur when covalent chemical bonds are activated by the presence of an external mechanical force. Mechanical forces can predominantly trigger reactions in solid systems since other states of matter cannot support the shear strains required.¹²⁹ External shear stresses induce changes in the symmetry of molecules or solids and are therefore more effective at stimulating reactions than isotropic compression. If molecules are simplified as spheres, and in a sheared system, these spheres can become ellipsoids or their cubic symmetry becomes tetragonal or something entirely different, which will induce a chemical reaction. The molecular symmetry essentially breaks down and destabilises the electronic structure, making the material more prone to a chemical reaction. Friction, wear, solid-state synthesis, and mechanical alloying are just some examples of where mechanochemical phenomena occur.¹²⁹ Boldyrev et al.¹³⁰ were some of the first to detail the development and application of mechanochemical systems. One of their key observations was that when reactants are exposed to a thermochemical stimulus, different products are formed when the same reactants are exposed to a mechanochemical stimulus. Their account provided clarity on the mechanisms of mechanochemical reactions. Some of the early and well-documented work on mechanochemistry was by Bridgman.¹³¹ Using pressure and torsion, Bridgman showed that it was possible to decompose cross-linked polymers into compounds such as PbO and KMnO₄, and drive substitution reactions such as $2\text{Al} + \text{Fe}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$ and

$\text{Mg} + \text{SiO}_2 \rightarrow \text{MgO} + \text{Si}$. Since Bridgman's work was prior to "mechanochemistry", he determined that these reactions were athermal, as these reactions occurred at room temperature. Zharov et al.¹³² compiled numerous mechanochemical reactions, including extensions of Bridgman's work to various inorganic compounds and to polymerisation of organic monomers. The birth of modern-day mechanochemistry is thought to have begun with Matthew Carey Lea¹³³, who first reported work where he proved empirically that AgCl, AgBr, and AgI can be dissociated purely by mechanical manipulation. He then went on to produce a flurry of papers on mechanically induced chemical reactions, starting with *On Endothermic Reactions Effected by Mechanical Force (First Part)*.¹³⁴ He concluded that "Such reactions are endothermic; and it, therefore, follows that mechanical force can bring about reactions which require the expenditure of energy, which energy is supplied by mechanical force precisely in the same way that light, heat, and electricity supply energy in the endothermic changes which they bring about." Carey's work was pivotal in mechanochemistry; his macroscopic and unspecific approach in applying a mechanical force prompted the likes of Kaupp¹³⁵ and Friscic¹³⁶ in using large-scale grinding, ball-milling, compression, or mastication techniques for solids or polymeric materials.

More recently, Grandbois et al.¹³⁷ described how using an atomic force microscope (AFM), they were able to apply mechanical forces and manipulate covalent bonds in a controlled manner. By defining a bond rupture force as the maximum measured force before the bond ruptures and the cantilever snaps back to zero force, they showed that Si-C and S-Au bonds rupture at 2.0 ± 0.3 nN and 1.4 ± 0.3 nN, respectively. DFT studies corroborated their measured values, highlighting the validity of AFM studies. Simple estimates show that the magnitude of forces required to perform work on covalent chemical bonds is approximately equal to a force of 2 nN when inducing a change of 1 eV over 1 Å.¹³⁸ In contrast to AFM studies, where a surface-molecule-tip arrangement is required, sonication and photoswitching techniques can be carried out on freely moving molecules in three dimensions in solution, which create a mechanical force within

molecules. Mechanochemical reactions on the multi-nano-Newton scale are known as covalent mechanochemistry (CMC),^{138,139} and can be dubbed as “molecular nano[Newton] mechanics”. Noncovalent mechanochemistry, which governs adhesion processes and hydrogen-bonding systems, has been studied extensively, including work on cell adhesion,¹⁴⁰ unfolding proteins,¹⁴¹ ligand–receptor interactions,¹⁴² inducing chair-to-boat transitions,¹⁴³ and unzipping DNA.¹⁴⁴ Generally speaking noncovalent interactions occur on the order of 10-100 pN, meaning non-CMC and CMC reactions are separated by at least 1 order of magnitude on the force scale.¹³⁸ It is also key to note that in non-CMC interactions the chemical bonding of the system does not change, like CMC reactions and can be understood without explicitly invoking the underlying electronic structure.

Classical statistical mechanics¹⁴⁵ relies on the Maxwell-Boltzmann statistical distribution, which suggests that for some given time, reactants will spontaneously produce products. However, because the statistical probability of a spontaneous reaction is $\sim \exp[-\Delta E^\ddagger/k_B T]$, which decreases exponentially with increasing barrier height, $\Delta E^\ddagger$, it is an extremely rare occurrence. de Boer¹⁴⁶ was one of the first to study bond rupture barrier heights by invoking a Morse potential to investigate the strength of individual C–C covalent bonds in aliphatic chains. Using a derivative of the potential and analysis of the force-versus-bond distance behaviour he determined a maximum pulling force of 5-6 nN was all that a C-C bond could sustain before rupturing. Transition state theory, introduced by Henry Eyring^{147,148} described absolute reaction rates for activated processes along the reaction coordinate using statistical techniques. The formulation outlines a set of reactions that undergo a process which moves them from one stable equilibrium point (the initial state) to another (the final state). Figure 2.2 is a schematic showing the energy of a system as a function of reaction coordinate for a system undergoing a thermally activated process. The activation energy is the difference between the initial and activated complex, also known as the activated state, is the maximum during the reaction coordinate. Eyring used the statistical

mechanics techniques described above to describe the overall rate of a forward reaction k for many identical systems undergoing a thermally activated process:

$$k = f \exp\left(-\frac{\Delta G_{act}}{k_B T}\right) \quad (2.2)$$

where f the effective attempt frequency, ΔG_{act} is the Gibbs free energy of activation, k_B is the Boltzmann constant, and T is the absolute temperature.¹⁴⁹

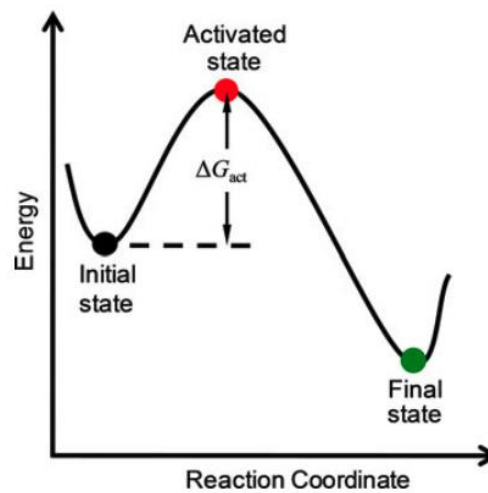


Figure 2.2: Schematic outlining the total energy of a system as a function of the reaction coordinate. Used with permission from Jacobs et al.¹⁴⁹

In his analysis, Eyring made five assumptions:¹⁵⁰

1. For a given reaction coordinate, the change from initial to final states, including intermediate and activated states is a continuous change
2. Reactions proceed along the lowest-energy path; thus, the activated state will lie at a saddle point in energy
3. If the system reaches the activated states, the probability of reaching the final state is high

4. Boltzmann statistics must be applicable and as such, the initial and activated state are at thermal equilibrium
5. The activated state possesses all degrees of freedom except vibrational motion along the reaction coordinate

Vineyard¹⁵¹ approximated system vibrations as harmonic and was able to expand on this work and formulate a general many-body problem and solve it in accordance with reaction rate theory. Eyring's model drew upon the macroscopic empirical Arrhenius model:

$$k = A \exp\left(-\frac{\Delta E_a}{k_B T}\right) \quad (2.3)$$

where A is the empirical pre-exponential factor that encapsulates the frequency at which atoms or molecules attempt to cross the reaction barrier and E_a is the activation energy (all other constants are the same as equation 2.2). However, unlike the Eyring model, the Arrhenius model breaks at very high temperatures, where it is not enough to accurately represent the regions with appreciable Boltzmann statistical weight, and at very low temperatures, where quantum mechanical tunnelling becomes the dominant transition mechanism rather than hopping over the energy barrier.¹⁵²

Bell¹⁵³ introduced the first and simplest phenomenological model for describing the increased rate of bond dissociation under external forces along a reaction coordinate x :¹⁵⁴

$$k = A \exp\left(-\frac{\Delta E_a - f \Delta x}{k_B T}\right) \quad (2.4)$$

This model is now known as the stress-augmented thermal activation (SATA) model.¹⁵⁴ This model can be understood as the application of force effectively lowering the reaction barrier, which can be seen schematically in Figure 2.3.

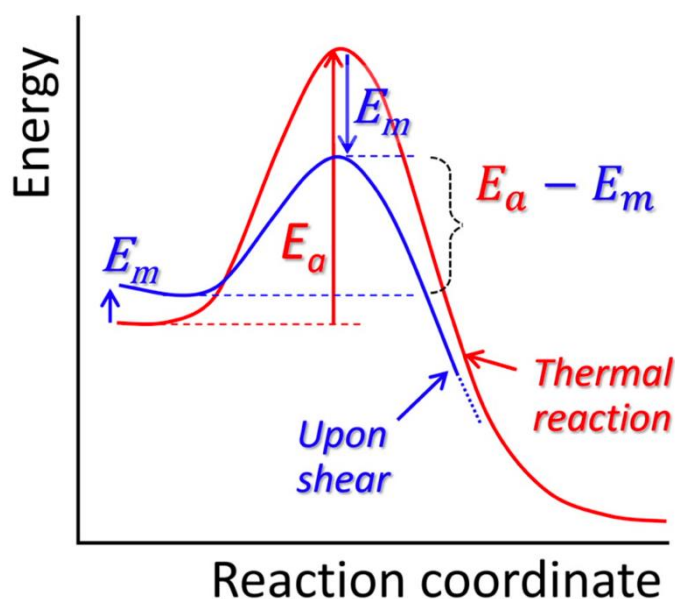


Figure 2.3: Simplified potential energy surface diagram for a thermal reaction without (red) and with shear (blue). Energy levels are not drawn to scale, mechanical activation can either be introduced at the reactant or transition state, and tribochemical products may be less thermodynamically stable than the reactants but kinetically stable. Used with permission from Martini et al.¹⁵⁵

By invoking applied shear (or mechanical) stress, τ , as an implicit parameter, equation 2.4 can be written as:

$$k = A \exp\left(-\frac{\Delta E_a - \tau \Delta V}{k_B T}\right) \quad (2.5)$$

where ΔV is the activation volume, a coupling constant between shear and the reduction in the effective energy barrier. Several other models have been used to describe CMC reactions, including a tilted potential energy surface/profile (PES) model.¹³⁸ The PES model is an improvement on the Bell model as it considers, albeit in an approximate way, that the structures of reactants and

transition states of a given reaction can be affected by a mechanical external force. A simplistic understanding of the PES model can be understood by generalising that for a given reaction coordinate, the applied force tilts the reaction profile at zero force along the mechanical reaction coordinate. Other models also exist, including electronic structure-based static methods and *ab initio* molecular dynamics models.¹³⁸

In summary, mechanochemistry plays an important role in tribological systems, particularly those involving tribochemical contacts.¹⁵⁴ The importance of mechanochemical activation is that it provides a link between nano-scale behaviour of atoms and molecules and macro-scale responses including friction and wear. SATA models are mostly used, in conjunction with non-equilibrium molecular dynamics (NEMD) simulations. These simulations allow the development of new and improved models describing friction and wear at nanoscale events and have the potential to initiate the design of molecules and surfaces to improve friction and wear performance. SATA models are able to offer a clear guided unifying principle for explaining several processes that occur at sliding tribological contacts. The next section examines how using NEMD simulation and particular forcefields, it is possible to describe macroscale tribological phenomena using nanoscale models.

2.3.2 Molecular Dynamics

As mentioned previously, computational techniques are becoming increasingly important for investigating many tribological systems. Figure 2.4 from Ewen et al.¹²⁴ highlights the different time and length scales that are accessible using such computational techniques.

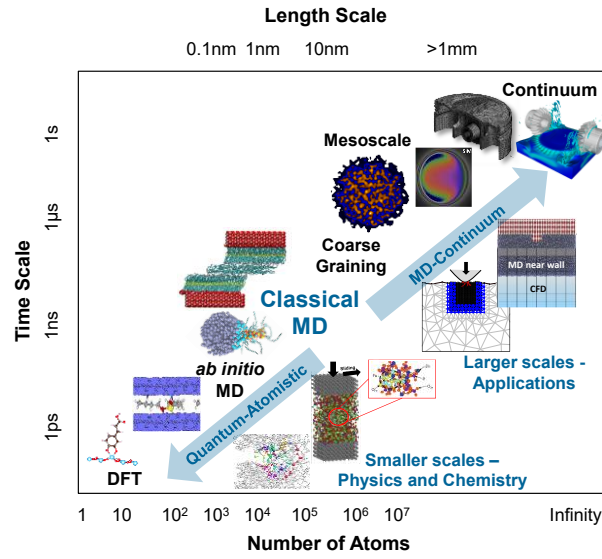


Figure 2.4: A map to illustrate the different scales accessible in modelling tribological systems.

Used with permission from Ewen et al.¹²⁴

Techniques such as DFT and *ab initio* MD can be used to investigate smaller systems to study electronic effects, classical MD (and NEMD) can be used to study rheology effects within tribological contacts, and continuum methods including finite element analysis can provide insights on the macroscale. The aim of this work is on using NEMD to investigate SATA effects, and this will be the remainder of this section's focus.

MD simulations began receiving significant attraction in the 1950s, where MD was based on the hard sphere (HS) model; the HS model represents molecules as perfectly elastic and infinitely repulsive spheres. Alder et al.¹⁵⁶ showed in 1957 that HS liquids crystallise when a certain density threshold was achieved. Soon after in 1964, Rahman¹⁵⁷ calculated the diffusion coefficient of argon atoms interacting through a Lennard-Jones (L-J) potential. The L-J potential is used to describe van der Waals interactions between two particles at a distance r :

$$E_{L-J} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2.6)$$

where ϵ is the depth of the potential well and σ is the distance at which the inter-particle energy E_{L-J} is zero. In 1970, Alder et al.¹⁵⁸ calculated viscosities of HS fluids at varying viscosities; Verlet et al.¹⁵⁹ in 1973 calculated the shear viscosity of a L-J liquid. Most of the MD simulations of liquids prior to those by Verlet and co-workers employed equilibrium MD, which follows the microcanonical or NVE ensemble, where the number of particles (N), volume (V), and energy (E) of the system remain constant. Some of the earlier work reported on MD simulations of boundary-layer lubrication was investigated by Kong Y. C., et al. in 1996.¹⁶⁰ They investigated how the rheology of dioctadecyldimethyl-ammonium chloride (DODAC) bilayers between solid surfaces changes with differing separation from opposing headgroups. Experiments have shown that the rheology of organic lubricant thin films can be considerably different from the bulk liquids.^{161–164} In order to understand why lubricants show certain friction, adhesion, etc. properties, it is fundamentally important to understand how these thin films behave on a micro- and nanoscopic level. Kong Y. C., et al. found that the friction coefficient decreases with normal force, increases with decreasing DODAC density, and increases with increasing normal forces. Soon after, NEMD simulations began appearing where strain and shear rates were imposed on systems.¹²⁴ Ashurst and Hoover¹⁶⁵ then proposed a “sliding wall” simulation setup, a setup very relevant to tribology. Periodic boundary conditions (PBC) were invoked in the x and y directions with a confining wall in the z -direction. In the 1980s, equations of motion for invoking shear motion in systems with PBCs in all cartesian directions were formulated. These DOLLS and SLLOD methods¹⁶⁶ were compatible with MD simulations that involved PBCs that accommodate shear flow of infinite extent,¹⁶⁷ sometimes referred to as “sliding brick” PBCs. In 1980, Heyes et al.¹⁶⁸ was one of the first to use Lees and Edwards PBCs¹⁶⁷ to model the shear flow in a supercooled L-J fluid.

NEMD methods can be traced back to the 1970s, however it wasn't until the mid-1980s that linear and nonlinear response theory was significantly developed to accurately predict homogenous algorithms consistent with periodic boundary conditions.¹⁶⁹ The SLLOD algorithm makes NEMD extremely useful for understanding rheological properties, as the algorithm is direct exploitation of experimental techniques for determining viscosity.¹⁶⁶ More recently NEMD has been used to predict the Newtonian viscosity of CO₂ and its derivatives to short-length polymers and lubricants.^{170,171} Bair et al.¹⁶⁹ showed the accuracy of NEMD when they compared their findings with experiment, specifically it was reported that the simulation data and experimental data followed the same time-temperature superposition and master curve.

The first to use NEMD to model OFM-like systems was by Glosli et al.¹⁷² in the 1990s. The computational inefficiency of the time meant that they were only able to observe the friction between two close-packed monolayers bound between two rigid surfaces. They found that interfacial interaction strength between the two monolayers was attribute to either a discontinuous 'plucking' mechanism, where there is a strong interaction between the layers, or a 'viscous' mechanism, where there is a weak interaction. Kong et al.¹⁶⁰ used NEMD simulations to show that the friction coefficient decreases with increasing normal force and with decreasing the headgroup area, and increased with sliding velocity. They studied dialkylammonium chloride OFM monolayers between charged solid surfaces.

To perform meaningful MD simulations, a number of factors need to be considered. Some of the most common are the availability of hardware and software, the size of the system, and the complexity of the forcefields.¹²⁴ The most significant is the accessible time and length scales in MD simulations. Tribological systems represented with MD simulations generally require several thousand individual atoms, and with classical MD force-fields requiring a time step of ~ 1 fs¹²⁵ (to ensure energy conservation), only nano- or micro-second time scales are feasible,¹⁷³ even when

performed on multiprocessor high performance computing (HPC) systems. In NEMD systems, particularly when investigating systems with shear, the main consequence of nano- or micro-second time scales is that relatively high shear rates are required to ensure the system reaches a steady state in an appropriate time frame.¹⁶⁹

NEMD simulations also led to the development of unique methods to control the temperature, including scaling atomic velocities,¹⁷⁴ coupling atoms to an external bath,¹⁷⁵ Langevin dynamics¹⁷⁶ where forces are applied to represent friction and atomic collisions with an implicit solvent, and the Nosé-Hoover (NH) thermostat,^{177,178} where the system Hamiltonian includes extra degrees of freedom for a heat reservoir that controls the temperature. However, many of these methods involve a direct thermostat within the fluid, which can influence its properties.¹⁷⁹ Alternatively, by allowing a thermal gradient to develop by applying a thermostat to the outermost atoms in either slab, prevents interference with the fluid's dynamics. Applying a Langevin thermostat to the wall atoms is more effective than an NH method in removing heat generated at the contact due to shear.¹⁸⁰ An NH barostat^{177,178} varies the system volume to control the global pressure using an NPT (constant number of atoms/particles, constant pressure, and constant temperature) ensemble. In shearing simulations, a set normal force can be applied to the top wall, before and during shearing, to control pressure.¹⁸¹ In these simulations, the system is energy minimized first before a load is applied to the top wall, and the bottom wall is fixed in space before shear is initiated. To ensure there are minimal oscillations of the inter-slab distance, a dampening term is often applied to the barostat after the load is applied.¹⁸¹ Additionally, on either wall, the outermost layer of atoms is fixed to ensure that there is no energy leakage.

MD simulations require the use of empirical forcefields which determine how individual atoms and/or molecules interact inter- and intra-molecularly. Additionally, these forcefields describe how the surface walls interact with each other and the atoms and/or molecules. Forcefields are based

on mathematics functions, like the L-J potential (equation 2.6) can be applied to various systems involving various atomic species or chemical environments. The next two subsections describe both classical and reactive forcefields.

2.3.2.1 Classical Forcefields

Classical forcefields include functional forms that are very similar to each other; these functional forms encapsulate both bonded and non-bonded terms. Bonded terms generally represent covalent bonds and include bond stretching, bending, and torsion, whereas non-bonded terms include van der Waals and electrostatic interactions.¹⁸² A typical expression for a classical forcefield can be seen in equation 2.6.¹⁸³

$$\begin{aligned}
 U = & \sum_{bonds} \frac{1}{2} k_b (r - r_0)^2 + \sum_{angles} \frac{1}{2} k_a (\theta - \theta_0)^2 \\
 & + \sum_{torsions} \frac{V_n}{2} [1 + \cos(n\phi - \delta)] + \sum_{improper} V_{imp} \\
 & + \sum_{non-bonded} \left[4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \frac{c q_i q_j}{r_{ij}} \right]
 \end{aligned} \tag{2.7}$$

The first four terms in equation 2.7 describe the intramolecular molecular contributions and the last one is the L-J non-bonded and electrostatic interactions. These terms can be either empirically parameterised to reproduce experimental observations, derived using first principle calculations, or calculated using a combination of the two. However, “cut-offs” have to be imposed to reduce computational expense when performing simulations with classical forcefields, for example, when computing van der Waals interactions, the L-J “cut-off” is set to approximately 10 Å, since at this distance the energy tends to zero. However, electrostatic interactions should not have an imposed “cut-off”, instead they should be treated using an Ewald summation¹⁸⁴ or particle-particle, particle-mesh,¹⁸⁵ which are long-range solvers that do not lead to unphysical phenomena.¹⁸⁶

Several different classical forcefield algorithms have been developed to simulate various physicochemical systems. Class I forcefields have been shown to accurately reproduce physical properties of alkanes,¹⁸⁷ which included forcefields developed from empirically fitting experimental data. Some of these forcefields include, AMBER,¹⁸⁸ CHARMM,¹⁸⁹ OPLS,¹⁹⁰ and GROMOS.¹⁹¹ Class II forcefields, such as COMPASS¹⁸⁷ were developed using *ab initio* data. For tribology more specifically, the L-OPLS-AA¹⁹² all-atom forcefield was developed as an optimization and extension of the OPLS forcefield, which is able to reproduce bulk viscosity of model lubricant *n*-hexadecane and boundary coefficients between stearic acid OFMs encapsulated by two iron slabs.¹⁸²

2.3.2.2 Reactive Forcefields

ReaxFF was developed by Adri van Duin and his colleagues at California Institute of Technology in 2001 in an effort to combat the impracticalities of using quantum chemistry/mechanics (QC/M) methods to understand the dynamic properties of larger molecules and solids.¹⁹³ The introduction and development of user-friendly software packages have made QM calculations more widely accessible in both research and industry. However, QM calculations come at a very large computational cost, and therefore only simple molecules can be studied using these methods. The limits of QC simulation scales don't allow for systems where dynamic evolution, such as diffusivity, solubility and most importantly rheology, to be studied, and thus impeding our theoretical knowledge of the general behaviour of several different materials.¹⁹⁴ ReaxFF is an empirical method where QM calculations are used to train force-fields that are orders of magnitude less computationally expensive, making ReaxFF an extremely useful tool for studying dynamic/non-equilibrium methods, however, the accuracy of calculations in ReaxFF, compared to quantum molecular dynamics (QMD), is traded-off for a less computational expense.

Like classical force-fields, ReaxFF incorporates non-reactive interactions, such as angle-strain and intermolecular forces including van der Waals, Coulombic and dispersion interactions, but with the addition of being able to describe reactive events where bonds are broken/formed. This is achieved by calculating the bond-order empirically by using the distances between molecules and considering the electronic interactions implicitly, therefore the reactive nature of systems can be studied without explicitly considering QC. In addition to the computationally inexpensive nature of ReaxFF, it also allows simulations to be conducted between solid, liquid and gas phases. ReaxFF describes each element with the same mathematical formalism, regardless of the phase or species¹⁹⁵. For example, a carbon atom in a solid diamond lattice or a gaseous methane molecule are both treated in the same manner. The energy of a ReaxFF system can be described by the following:¹⁹⁴

$$E_{system} = E_{bond} + E_{over} + E_{angle} + E_{tors} + E_{vdW} + E_{Coulomb} + E_{specific} \quad (2.8)$$

where E_{bond} is a continuous function of interatomic distance, describing the energy associated with bond formation (including σ , π , and π - π contributions). E_{angle} and E_{tors} are the energies associated with three-body angle and four-body torsional angle strain, respectively. E_{over} is an energy penalty to prevent over-coordination of atoms and is based on atomic valence rules. $E_{Coulomb}$ and E_{vdW} represent the electrostatic and dispersive interactions between all atoms in the system, irrespective of their connectivity and bond order. $E_{specific}$ represents system-specific terms required to capture properties particular to the system of interest, such as lone-pairs, conjugation, and hydrogen bonding.¹⁹⁴ The charge equilibration (Qeq) method¹⁹⁶ is used in ReaxFF simulations since the point charges on the atoms can vary dynamically during the simulation. A distinction between the covalent and ionic interactions is made by independently calculating the bond order-based and non-bonded terms. ReaxFF requires extensive parameterization and often only applies to a certain number of elements for a particular physicochemical environment. Parameters are mainly

developed with a single-parameter parabolic search method¹⁹⁴, however, more sophisticated algorithms, including genetic algorithms,¹⁹⁷ particle swarm optimization,¹⁹⁸ and the covariance matrix adaptation evolutionary strategy,¹⁹⁹ have been developed to improve parameterization efficiency.

ReaxFF has been used to study a diverse range of biological, chemical and physical phenomena, and because of its accuracy and versatility, it has been able to shed light on and describe the properties of complex processes.¹⁹⁴ Y. Zhang et al.²⁰⁰ used ReaxFF MD simulations to investigate the mechanistic details of how oleic-type triglycerides (OTG) undergo pyrolysis. OTG model used is composed of three oleic acid chains that are attached, via an ester bond, to a glycerol group. Yue et al.²⁰¹ studied the tribochemical mechanisms of amorphous silica asperities. Wen et al.²⁰² used ReaxFF to study the tribochemical wear mechanisms of silicon. Yeon et al.²⁰³ investigated how water affects the tribochemical wear of silicon oxide. Wen et al.²⁰⁴ studied copper chemical mechanical polishing in an aqueous environment. Hahn et al.²⁰⁵ used ReaxFF to examine the differences of surface wear of sodium silicate glass in dry and humid environments. Many of these studies, and several others, concluded that water plays a pivotal role in tribochemical interactions, particularly how water induces the formation of bridging bonds that subsequently reduce wear.

The subsequent chapters include studies where we model diamond-rock contacts using NEMD simulations. In these studies, we use mainly two ReaxFF forcefields to represent granite and limestone rock. For limestone, a new forcefield was developed, which is detailed in Chapter 3. For granite, we employ a forcefield developed by Newsome et al.²⁰⁶ Details of how and why granite and limestone were accurately represented are also included in Chapter 3. Comparisons of this forcefield with others parameterized for the selected elements are also included in subsequent chapters. The Newsome forcefield is an expansion of the original ReaxFF forcefield¹⁹³ but is now trained with recent quantum mechanics data of the binding energy, equation of state, and heat

formation of the SiC crystal, with the inclusion of data from previous studies that describe Si-Si, Si-O, and Si-H interactions. Newsome showed that this forcefield is capable of simultaneously describing both Si-C-O and Si-O-H bonding interactions in the ranges 500-5000 K. His initial study was to investigate the oxidation of SiC by oxygen and water. The Newsome forcefield has been recently employed by Bhati et al.²⁰⁷ to identify adhesion properties of Si/polymer interfaces, Hilbert et al.²⁰⁸ to investigate how Si doping enhances thermal stability of diamond-like carbon, Vashisth et al.²⁰⁹ who combined atomistic and continuum methods to study how temperature influences interfacial fracture in SiC/SiO₂ composites, and several others. Since the Newsome forcefield is an expansion of the original work by van Duin et al.,¹⁹³ it is able to accurately represent systems involving Si/C/H/O.

2.3.3 Summary

MD, particularly NEMD, have seen increasing use in tribology. NEMD-ReaxFF coupled simulations can elucidate mechanistic details of several tribological phenomena and can play an important role in developing a fundamental understanding at the atomic scale. Many NEMD studies have been able to accurately predict the physical properties of lubricant molecules at a range of temperatures and pressures. Moreover, reactive forcefields and ab initio techniques are able to accurately represent chemical behaviour and can be used to develop a thorough understanding of tribochemical and mechanochemical phenomena. Even though MD is limited through its system size and timescales, and even more so limited with the addition of reactive forcefields, it is still a vital tool to reveal the fundamental nature of nanoscopic wear and friction. It also provides the additional benefit of allowing more advanced surfaces and lubricants to be developed. This section has provided a description of the theory and techniques used in tribology, mainly tribochemistry. The following section outlines how friction and wear assumptions transition across from the macro to the nanoscale.

2.4 Friction and Wear: Macroscale to Nanoscale

2.4.1 Friction

Amontons' friction law,²¹⁰ formulated in 1699, states that the friction force, F_F between two macroscopic bodies is linearly proportional to the applied load, F_N , such that,

$$F_F = \mu F_N \quad (2.9)$$

where μ is the coefficient of friction. The law also stipulates that F_F is independent of the macroscopic contact area, A , however, Bowden and Tabor noted in 1950²¹¹ that a macroscopic contact is rough and in fact consists of a large number of asperities, unlike previously thought. The contact area of the sum of all the asperities, $\Sigma A_{\text{asperity}}$, is significantly smaller than A . A multi-asperity model of nanoscale contacts developed by Mo et al.²¹² shows that the frictional force is proportional to the true contact area, such that, $F_F = \tau \Sigma A_{\text{asperity}}$, where τ is an effective shear strength of the contacting bodies. They also show that the linear dependence of F_F on F_N is due to atomic roughness, small contact pressure, and that adhesion induces a transition from linear to sublinear behaviour. The friction coefficient of two sliding bodies is not an intrinsic physical property, since it is heavily dependent on the surface's specific structure, chemistry, and elastic/plastic properties, the chemical environments in which the measurements are being recorded, and the sliding history of the interface.²¹³ Therefore, several studies^{213–215} have isolated surface roughness from other physical parameters that can impact friction by focusing on individual asperities, which are assumed to be perfectly smooth. This allows a fundamental understanding of nanotribology to be developed since experiments and simulations are performed with well-defined interfaces. Experiments using a scanning force microscope (SFM) have allowed for well-defined tribological interfaces to be investigated.^{216,217} Developments in SFM technology have meant measurements in the sub-nanonewton regime have been investigated, allowing for

nanometre-scale tribological characterization of a wide range of materials in several different conditions. Atomistic simulation and MD techniques have also been used to model single-asperity contacts during sliding.²¹³

The atomic force microscope (AFM) is widely used for nanoscale single-asperity studies since it allows for a controllable, well-defined contact, which can be measured with atomic-level precision and accuracy. The design of the AFM has been extensively reviewed^{215,218,219} and we point the reader to relevant references that discuss it in great detail. Like mentioned previously, many SFM-based investigations^{215,220–224} have concluded that F_F is proportional to the real contact area, such that $F_F = \tau A$, where τ represents the frictional force per interfacial atom and A is the interfacial contact area. Hertz²²⁵ proposed that for a non-adhesive contact between homogenous, isotropic, linear elastic spheres, $A \propto F_N^{2/3}$. The single asperity studies contrast with what was proposed by Amontons, whose macroscale observation states that μ is linearly proportional to the applied load. This behaviour has been referred to as interfacial friction,²¹³ which is termed for processes whereby sliding resistance is a result of shear resistance at the contact and wear is not occurring. Macroscopically, Singer et al.^{226,227} and nanoscale studies by Christenson et al.²²⁸, Briscoe et al.²²⁹, and Israelachvili et al.²²⁷ have all observed interfacial friction. Additionally, in contrast to Hertz theory, single asperity studies show that F_F is a sublinear function of F_N ,²³⁰ $F_F \propto F_N^{2/3}$ ²³¹ and instances where the two are entirely independent.²³²

Hertz theory fails to account for adhesion, subsequently, adhesion effects between contacting bodies were studied by Johnson, Kendall, and Roberts (JKR)²³³ and Derjaguin, Muller and Toporov (DMT).²³⁴ In JKR theory, the key assumption relies upon the adhesive interactions being infinitely short in range. This means work because of adhesion can only reduce the free energy of the system for a given unit area in the contact, therefore, no attractive interactions and no reduction in free energy occurs at regions in the contact where there is greater separation. This assumption

is well applicable for covalent interactions at the atomic length scale; however, it also results in a prediction of infinite tensile stress at the contact area perimeter. DMT theory assumes that a deformed contact profile is very similar to that predicted by Hertz theory, but with an increased load globally due to adhesion. This can be thought of as adhesive interactions occurring at all separations within the contact. JKR and DMT theories are both valid but at opposite extremes of contact mechanics. For materials where there are large, induced elastic deformations when compared with attractive forces, the JKR theory is valid. For more stiff materials that have small sphere radii and weak long-range adhesive forces, the DMT theory is valid.

Even though these continuum theories provide a more accurate description of macroscale contacts, they break down on the nanoscale. The limitation of continuum theories occurs mainly when the contact contains only a few hundred atoms, and the contact radius cannot be accurately determined. In AFM studies, the contact area cannot be measured directly but can be assumed through measurements of the contact stiffness, k_{cont} , and the reduced shear modulus, G^* , such that, $k_{\text{cont}} = 8aG^*$, where a is the contact radius.²¹³ The contact area can also be estimated by measuring the electrical contact conductance. For simulated atomic-scale contacts, the contact area can be estimated by either: measuring the interatomic distance and determining if they are in contact after reaching a distance threshold;^{235,236} assuming atoms are in contact after they are subjected to a certain compressive force;²³⁷ or considering atoms to be in contact once a chemical bond has been formed.²¹² Wang et al.²³⁸ recently examined all of these proposed assumptions and concluded that neither of them was equal to the other. They concluded that the first assumption was most consistent with continuum mechanics and Hertz theory, while the last assumption was directly proportional to the frictional force, suggesting it is the most accurate for determining a material's friction properties. Here, atoms are assumed to be spherical, where a circular projected area can be defined.²³⁵ This area can be calculated using the lattice constant for the material, which determines the effective atomic area, and when multiplied by the number of contact atoms, the

atomistic contact area can be calculated. Wang et al.²³⁸ also found that this area is linearly proportional to F_N .

Luan et al.^{239,240} tested the continuum assumption that in bulk materials, continuous strain fields can replace discrete displacement of atoms, which is a function of the stress fields via elastic constants. It was reported that Hertz theory was able to accurately describe the normal displacement dependence on F_N in the elastic regime for non-adhesive contacting bodies. However, they also concluded that friction can deviate by one order of magnitude and contact area by a factor of two when compared with continuum approximations. Cha et al.²⁴¹ conducted MD investigations of single asperity contacts and reported that JKR theory is only applicable to asperity unloading when deformation is almost elastic, and not asperity loading. Wenning et al.²⁴² and Luan et al.^{239,240} reported contradictory conclusions than Gao et al.²³⁰ The former found that F_F is proportional to F_N for commensurate tips while amorphous tips result in a power law dependence and was able to describe the contact area with Hertz and DMT theories. The latter found a linear relationship between the two for both commensurate and amorphous tips. It is interesting to note that Gao and co-workers employed a more realistic forcefield on smaller tip radii, suggesting that interatomic potentials and system size are vital when investigating the limitations of continuum models. Chandross et al.²⁴³ also demonstrated the breakdown of continuum theories using MD simulations. They reported the calculated contact radius for realistic AFM tips was outside the bounds set by the JKR and DMT theories.

2.4.2 Wear

The Archard wear equation⁴¹ (equation 2.1) was developed in 1953 and has been extensively employed to describe macro and microscale contacts.²⁴⁴ Generally, equation 2.1 states that the volume removed due to wear is directly proportional to the applied load and the sliding distance. It has been applied to describe macroscale²⁴⁵ and microscale²⁴⁶ systems. Gotsmann et al.²⁴⁷ found

that the Archard equation broke down when investigating nanoscale tip wear using an AFM. Several other works have shown that the Archard equation is not applicable at the nanoscale.^{149,247–250} The Archard equation is purely empirical, and foundations are built upon simple arguments, meaning no method exists to predict the proportionality constant.²⁴⁴ Experiments by Gotsmann et al.²⁴⁷ and MD simulations by Gao et al.²⁵¹ reveal that wear on the nanoscale occurs through an atom-by-atom attrition mechanism. This was also supported by analytical models developed by D’Acunto.²⁵² D’Acunto’s theoretical approach stipulated that transitioning atoms undergo a diffusion-like hopping process. In this model, wear is either a result of van der Waals forces or shear forces and is based on an Arrhenius rate law. The atom-by-atom attrition wear mechanism relies upon bond formation and rupture across the interface, and as described in the previous section, the rate of bond formation and rupture, and subsequently atom loss is predicted to obey reaction rate theory,²⁴⁷ such that,

$$\Gamma_{\text{atom-loss}} = \Gamma_0 e^{\left(-\frac{\Delta G_{\text{act}}}{k_B T}\right)} = \left\{ \Gamma_0 e^{\left(-\frac{\Delta U_{\text{act}}}{k_B T}\right)} \right\} e^{\left(\frac{\sigma \Delta V_{\text{act}}}{k_B T}\right)} \quad (2.10)$$

where Γ_0 is a pre-factor, k_B is the Boltzmann constant, and T is the absolute temperature. As described in chapter 2.1.1, the external mechanical stress component, σ , lowers the energy barrier for a given chemical reaction such that the free energy of activation, ΔG_{act} , is reduced due to the straining of covalent bonds. ΔG_{act} can be expanded, such that, $\Delta G_{\text{act}} = \Delta U_{\text{act}} - \sigma \Delta V_{\text{act}}$, where ΔU_{act} is the stress-free activation barrier and ΔV_{act} is the activation volume. This Arrhenius analysis was also reported by Park et al.²⁵³ and Bhaskaran et al.²⁴⁸ Park and his co-workers found that the wear track growth left by a silicon nitride tip had an exponential dependence on F_N , and found that Arrhenius kinetics and transition state theory was able to model this behaviour. Sheehan²⁵⁴ was one of the first to measure changes in wear rate with temperature, and so one of the first to extract activation enthalpy. His findings were similar to that of Park et al., however, because he only

studied a limited temperature range, there was large uncertainty in his measurement of activation enthalpy. Both Park et al. and Sheehan were able to extract the activation volume by plotting a best-fit curve through measurements of wear rate as a function of stress. Kopta et al.²⁵⁵ performed AFM scanning of muscovite mica samples and were able to model the wear behaviour through thermally activated cleavage of Si–O bonds and detaching single SiO₄ tetrahedra. Transition state theory was able to derive an exponential equation that was an accurate fit to their data.

Figure 2.5 illustrates a possible model for a thermally activated wear process; for a (wear) process to be considered thermally active, the system must first obey Boltzmann statistics.¹⁴⁹

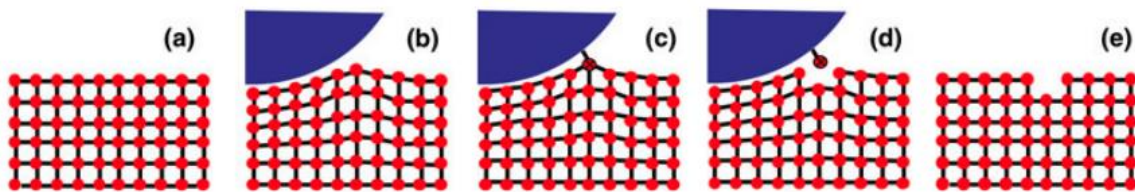


Figure 2.5: A schematic atomic-scale model of one possible thermally activated mechanism by which wear of a substrate occurs. Used with permission from Jacobs et al.¹⁴⁹

Figure 2.5 firstly shows an unperturbed surface coming into contact and creating a quasi-static equilibrium with a spherical-like sliding asperity. Figure 2.5c shows the initial stages of an unstable equilibrium state, in which the atom marked with an x is in a transition process from being sample-bonded (Figure 2.5c) to being tip-bonded (Figure 2.5d). Figure 2.5e shows the state after elastic deformation has been relaxed and before any substrate reconstruction has occurred. This entire process can be considered through transition state theory, with Figure 2.5b representing the initial state, Figure 2.5c is the activated state (highest energy state), and Figure 2.5d shows the final state. It also must be noted that the free energy difference between the activated and final states must be large enough to prevent the reverse reaction from occurring. A difficulty arises when trying to

calculate and extract these activation parameters since it can be significantly challenging to identify the transition (activated) state.¹⁴⁹ In the aforementioned studies by Park et al.²⁵³ and Sheehan²⁵⁴ it was assumed that interfacial contact stresses are the most relevant here, and relied on Hertzian contact mechanics to calculate these values. The Hertz model however relies upon frictionless surfaces and low strain rates, which is unlike what is experienced in a nanoscale adhesive contact.¹⁴⁹ Additionally, as highlighted previously, the Hertz model breaks down at the nanoscale, where the continuum contact mechanics assumption that wear occurs at the same rate for a stationary tip as a sliding tip is not applicable.¹⁴⁹ A prominent example of this was introduced by Luan and Robbins²³⁹ who examined how wear varies depending on tip geometry and roughness. They found that atoms in bulk solids showed no deviations from continuum theory, but atomic-scale surface roughness always resulted in dramatic deviations, with some individual atoms experiencing 5-6 times greater peak pressure than the average across the contact. It was concluded that the total contact area of two interfaces is in fact broken into many separate regions with a small mean radius. Additionally, Bhaskaran et al.²⁴⁸ showed that every atom inside a nanoscale contact experience a unique energy landscape and a differing identical stress state. Hirth and Nix²⁵⁶ identified another difficulty that related to changing local stresses during the sliding of a contact. In nanoscale contacts, atomic-scale wear can lead to modifications of the asperity and substrate, meaning the contact geometry, and therefore, the contact stress is constantly changing even if the load remains constant. Moreover, in relation to extracting thermodynamic quantities from nanoscale contacts becomes challenging as the pre-factor in equation 2.10 is usually approximated as the lattice vibration frequency. Most significant however is determining which stress component is the most dominant in a thermally activated process. Park et al.,²⁵³ Sheehan,²⁵⁴ and Bhaskaran²⁴⁸ do not agree on which component is most relevant, however, they were all still able to extract meaningful values even though their methodologies differed.¹⁴⁹ Jacobs and Carpick²⁴⁴ hypothesised that the mean normal stress is the controlling component during an AFM investigation of silicon tips on a diamond substrate. They also note that their analysis would also apply to other mechanisms that

consider another component that modifies the activation energy barrier. They determined an exponential dependence of the reaction rate with compressive stress, consistent with stress-assisted chemical reactions (equation 2.10).

Shao et al.²⁵⁷ introduced a multibond model of single-asperity tribochemical wear on the nanoscale based upon interfacial bond breaking due to SATA processes. They observed different wear regimes including Eyring- and Archard-like behaviours. Using the model developed by Filippov et al.⁸⁶ they captured and qualitatively explained distinct regions of single-asperity wear. The multibond wear model encapsulates three separate SATA processes. Wear is described as a series of processes; bonding firstly occurs between the asperity and substrate by overcoming the energy barrier ΔE_{on} . Next, either these newly formed interfacial bonds break as sliding occurs and the atoms remain bound to the asperity/substrate or bonds within the asperity/substrate break and atoms are transferred across the interface (i.e., wear). Both ΔE_{off} and ΔE_{wear} are associated with these events. The expected wear rate per potential bonding site is expressed as:

$$\Gamma = - \int_0^{\infty} \left(\frac{r_{\text{wear}}}{r_{\text{off}} + r_{\text{on}}} \right) \left(\frac{n_{\text{on}} v}{\Delta x} \right) \left(\frac{dP(\Delta x)}{d\Delta x} \right) d\Delta x \quad (2.11)$$

where $P(\Delta x)$ is the probability of a particular bond stretching to a distance less than Δx , and r_{on} , r_{off} and r_{wear} represent the rates of bond formation and breakage described by ΔE_{on} , ΔE_{off} and ΔE_{wear} , respectively. It was concluded that at low loads and low adhesive forces, Eyring behaviour holds true, but at higher loads, an almost rate-independent regime arises, in which wear becomes almost proportional to sliding distance, as described by Archard.⁴¹ An intermediate region also exists where wear behaviour crosses between these two regimes. Other nanoscale wear models exist like those introduced by Wang et al.²⁵⁸ In this method, a nanoscale wear event consists of two steps. Firstly, under load, the contact surfaces are compressed together and react, forming

interfacial bonds as an intermediate state in the wear event. The second step consists of atoms involved in the interfacial bonding being sheared and removed from each respective surface, which then leads to wear. These steps can be considered as a two-step SATA reaction, where interfacial bonding is assisted through normal stress and removal of atoms is assisted by shear stress. Combining reaction rate theory with this two-step reaction, the following non-empirical wear model was proposed:

$$N_{ib} = N_{rc} \exp\left(-\frac{\Delta U_{ib} - W_{\sigma}}{k_B T}\right) \quad (2.12)$$

$$N_{wear} = N_{ib} f_0 \exp\left(-\frac{\Delta U_{wear} - W_{\tau}}{k_B T}\right) t \quad (2.13)$$

where N_{rc} is the number of all atoms in the real contact surface, N_{ib} is the number of surface atoms that have one or more interfacial chemical bonds, and N_{wear} is the number of worn atoms. ΔU_{ib} and ΔU_{wear} are the activation energies of interfacial bond formation and the removal of interfacial bonding atoms, and W_{σ} and W_{τ} are the external work per atom induced by normal stress (σ) and shear stress (τ), respectively.²⁵⁸

One final area of discussion is the interpretation of the activation parameters used in developing these nanoscale wear models. Some authors argue that activation volume is similar to that of the volume of an activated species in a thermally activated process and the activation energy is that of the energy required for vacancy formation,²⁵³ while others suggest that activation volume is the volume removed during each pass of a scanning probe.²⁵⁴ However, the latter is inconsistent with transition state theory since it explicitly only considers the initial and final state and ignores the transition state. Even though interpretations of activation parameters are contested it still allows

for comparisons to be made across different thermally activated systems. They allow for atomic and MD simulations to be validated with experimental data, verify atomistic wear mechanisms, and further support the thermally activated processes inside nanoscale contacts.

While transition state theory can provide a reasonable description of nanoscale wear, some studies do not agree with this theory. Sha et al.²⁵⁹ performed MD simulations and showed that wear in diamond-like carbon obeys Archard's law at the nanoscale. They report that the rate of chemical bond formation was proportional with friction force, but not with material loss, suggesting that friction and wear follow different mechanisms. Unlike transition state theory approaches to nanoscale wear discussed above, where there is an exponential dependence of wear rate on load, Sha et al.²⁵⁹ observed a linear relationship. Here, wear was not a result of interfacial bond formation and atom-by-atom attrition, instead, shear forces induce mass accumulation at the trailing edge of the contact, which is removed by a cluster detachment process. This observation can be firstly explained by sliding velocity. Firstly, the work performed by Gotsmann et al.²⁴⁷ and Bhaskaran et al.²⁴⁸ was performed at orders of magnitude lower sliding speed than many micromechanical systems, suggesting that the thermal effects dominate in slow-speed wear but are almost non-existent in high-speed. Moreover, experimental studies are usually contaminated with various molecules, oxides and other chemical species, while the surfaces in Sha's MD study were contaminant free. Even though Jacobs and Carpick²⁴⁴ removed the outermost oxide layer from their AFM silicon tips through sliding, Maw et al.²⁴⁹ showed contaminants, including oxides and other chemical species, present in experiment studies could lead to non-linearity. It is also interesting to note that this contradiction is not due to tip geometry or inconsistencies in normal stress as Sha and co-workers used comparable tip size and normal loads to the experiments performed by Gotsmann et al.²⁴⁷ and Bhaskaran et al.²⁴⁸

In summary, there is considerable experimental and theoretical evidence to support the idea of atom-by-atom attrition wear as opposed to fracture and plastic deformation proposed by Archard and continuum studies. Some nanoscale wear studies provide contradictory evidence to those from a transition state theory perspective; however, they still do acknowledge atom-by-atom attrition, albeit not being the dominating wear mechanism. It follows that at low loads and adhesive forces, atom-by-atom attrition models and transition state theory can provide a valid explanation for nanoscale wear, but at higher loads, this fails, and Archard-like wear is observed. This has been explored and described qualitatively using a multibond model which incorporates competing SATA processes in an effort to describe this wear transition. Further experimental and theoretical work is required to support or refute the idea of using transition state theory in explaining nanoscale wear. Particularly, studies that span a large temperature range will allow researchers to elucidate the Arrhenius dependence of wear rate on temperature. Additionally, measurements of wear rate on applied load will allow for useful discussions regarding which stress component dominates a nanoscale wear event, while investigations that consider differing sliding velocities will be able to determine how this stress component varies as a function velocity and will allow for disentanglement of these interrelated phenomena.

Chapter 3. Interfacial Bonding Controls Friction in Diamond-Rock Contacts

The work presented in this chapter is partly published in *The Journal of Physical Chemistry C*.¹

Herein this chapter includes works performed by collaborators and colleagues. All experimental tribometer work, including experimental setup and data collection, was performed by Evan Yu (Baker Hughes Inc., Center for Technology Innovation, Houston, Texas 77040, U.S.A.). All microscopy and energy-dispersive x-ray spectroscopy (EDS) analyses were performed by Maria De La Cinta Lorenzo Martin (Argonne National Laboratory). All development of the CaCO₃ ReaxFF forcefield was performed by Nabankur Dasgupta and Adri C. T. van Duin (Department of Engineering Science and Mechanics, The Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.). All figures and tables created by these collaborators are clearly indicated in this chapter and in Appendix A.

3.1. Introduction

The underlying physicochemical mechanisms that control friction between sliding surfaces remain poorly understood. In some systems, friction is controlled by the formation and rupture of chemical bonds across the sliding interface.²⁶⁰ Filippov et al.⁸⁶ developed a model that directly relates macroscopic friction to the formation and rupture dynamics of interfacial bonds. Interfacial bonding has subsequently been shown to be important in a range of tribological systems. Using nonequilibrium molecular dynamics (NEMD) simulations of hydrogen-terminated amorphous carbon atomic force microscopy (AFM) tips and diamond substrates, Mo et al.²¹² showed that the kinetic friction force depended linearly on the number of atoms that chemically interact across the

sliding contact. Further AFM experiments by Li et al.⁸⁷ revealed that interfacial bonds also control static friction in silica–silica contacts. They suggested that a large amount of interfacial bonding at the nanoscale is quantitatively consistent with that required to explain the frictional ageing phenomena,⁸⁷ which is commonly observed in macroscale friction experiments of rock interfaces.²⁶¹ Interfacial bonding could also be an important factor in controlling the friction of rocks with other materials, such as diamond drill bits.

Macroscale numerical²⁶² and analytical²⁶³ modelling techniques are commonly used to investigate friction at PDC bit–rock interfaces. However, these techniques are not capable of describing the physiochemical transformations that significantly affect the tribological response of the system. NEMD simulations are becoming an increasingly useful tool to study physiochemical transformations inside tribological systems.¹²⁴ Following the seminal work of Mo et al.,²¹² NEMD simulations have been used to study the effect of interfacial bonding on friction in other systems. For example, NEMD simulations of the silica–silica interface using ReaxFF showed that friction increased due to the formation of interfacial siloxane (Si–O–Si) bridges between the sliding surfaces.²⁶⁴ Similarly, NEMD simulations using density-functional-based tight binding (DFTB) indicated that interfacial C–C bonds increased the friction between sliding diamond-like carbon (DLC) surfaces.²⁶⁵ However, NEMD simulations have not yet been used to study the diamond–rock interfaces relevant to PDC friction.

In this study, we use macroscale tribometer experiments and NEMD simulations to compare the kinetic friction of PDC bits on granite and limestone surfaces. In order to incorporate the effects of interfacial bonding, we employ the reactive force field (ReaxFF) method.¹⁹³ The computational cost of ReaxFF simulations are several orders of magnitude lower than first-principles techniques, allowing much larger time and length scales to be accessed.²⁶⁶ Unlike first-principles methods, careful parameterization is required in order to obtain reliable results. Over the last two decades,

ReaxFF parameters have been developed to study a very wide range of systems and processes.¹⁹⁴ Of particular interest to this study, ReaxFF has been widely applied to study tribochemical processes occurring between sliding surfaces.²⁶⁷ We employ published ReaxFF parameters for quartz²⁰⁶ and develop new parameters for calcite. The tribometer experiments show that friction is much higher for diamond–limestone than diamond–granite interfaces under air and aqueous environments. The NEMD simulations show that this is due to increased interfacial bonding in diamond–calcite contacts during sliding, mostly through chemisorbed water molecules.

3.2. Methodology

3.2.1. Experimental Procedure

We used a pin-on-disk rotary tribometer for the friction measurements. Previous studies²⁶⁸ have shown that the friction obtained in these experiments can be directly related to ROP in industry-standard tests such as the vertical turret lathe²¹ and the ultradeep single-cutter drilling simulator.¹⁹ Sliding contact, as studied in these experiments, is experienced by worn and shaped cutting elements that are used in some rock drilling designs. In these elements, wherein the cutting action (indentation depth) is low, interfacial friction dominates the overall energy losses.

Carthage limestone and Sierra white granite cores were, respectively, chosen as representative limestone and granite rock types. The rock samples were all ground to the same smooth surface finish prior to the tribometer experiments ($R_q \approx 12 \mu\text{m}$).²⁶⁹ Hemispherical PDC pins with a radius of 4.765 mm were employed, providing idealized point contacts. The root-mean-square surface roughness of the pins was measured using white light interferometry ($R_a = 2.86 \mu\text{m}$, $R_q = 3.65 \mu\text{m}$).^{22,40} The tests were conducted in both aqueous and air environments (average relative humidity = 70%). The experimental sliding velocity was 0.1 m s^{-1} , which is somewhat lower than that used in operational PDC drills ($2\text{--}4 \text{ m s}^{-1}$).²⁷ The load was progressively increased ($1\text{--}200 \text{ N}$) and held for 5 min at the same sliding velocity while the friction data were measured. The maximum Hertz

pressure, $P_{\max}$, is approximately 2.5 GPa for limestone ($F_n = 100$ N) and 3.3 GPa for granite ($F_n = 200$ N). Due to the roughness of the rock and diamond surfaces, the peak asperity pressures will be somewhat higher than predicted by the Hertz equation. However, the nondimensional α parameters calculated for these systems (0.01–0.03) suggest that Hertz theory provides a reasonable estimate of the contact pressure (within 5%).²⁷⁰

The velocities and loads chosen for the experiments were selected to characterize the friction response at sliding-dominated regimes, where the cutting action is relatively low. This ensured that the friction forces measured were mainly due to interfacial interactions, rather than ploughing. In addition to the friction measurements, both rock and diamond surfaces were examined using optical microscopy following the tests. No wear of the tips was measurable following the tribometer experiments.

3.2.2. Simulation Procedure

In the experiments, the mineral distribution within the granite and limestone rock substrates displays spatial heterogeneity, resulting in location-dependent surface chemistry.²⁷¹ Due to their large computational expense,²⁷² NEMD simulations with ReaxFF are limited to the study of nanoscale systems.¹²⁴ Therefore, the major constituents of granite (quartz)²⁷³ and limestone (calcite)²⁷⁴ were used as representative models of the rock substrates. The suitability of this comparison was confirmed by energy-dispersive X-ray spectroscopy analysis of the transfer film on the diamond pin after the tribometer experiments (Figure 3.1). The atomically smooth α -quartz {0001}²⁷⁵ and calcite {10.4}²⁷⁶ surfaces were selected, which have been shown to be the most thermodynamically stable in previous density functional theory (DFT) studies.

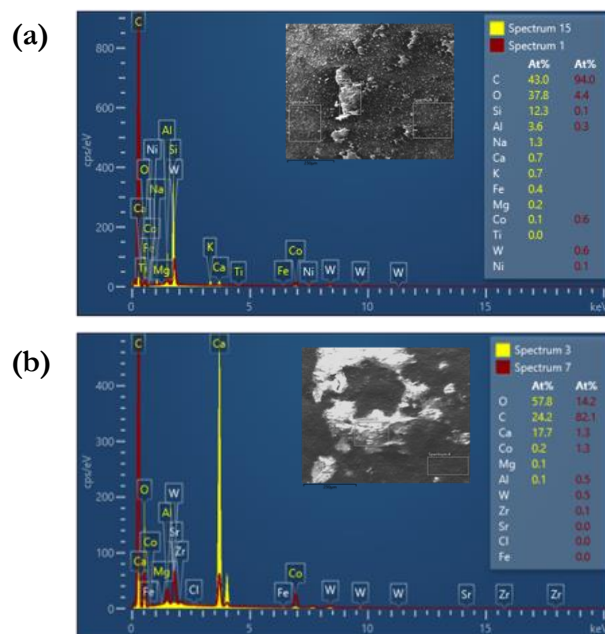


Figure 3.1: Microscopy images and energy-dispersive x-ray spectroscopy (EDS) analysis of the diamond pins after the friction experiments on granite (a) and limestone (b). EDS was performed on regions of exposed diamond and areas covered by transfer material, as shown in the middle microscopy images. Performed by Maria De La Cinta Lorenzo Martin. Used with permission from Bhamra et al.¹

Experimental evidence suggests that both quartz²⁷⁷ and calcite²⁷⁸ surfaces are hygroscopic and are likely to be covered by a water monolayer in both air and aqueous environments. Therefore, as well as the dry surfaces, we performed NEMD simulations using different numbers of water molecules to simulate humid air and aqueous environments. The NEMD simulations of the water-containing systems are expected to be more representative of the conditions in our tribology experiments and for operational PDCs. For the smaller number of water molecules,²⁶⁶ representing the air environment, the surfaces are covered by a water monolayer and most of the molecules remained chemisorbed to the surface during the equilibration phase. For the larger number of water molecules (150), representing the aqueous environment, there were additional water molecules on top of the complete water monolayer, which submerged the tip during sliding. As expected from previous DFT calculations, the adsorbed water molecules spontaneously dissociate

on both α -quartz $\{0001\}$ ²⁷⁹ and calcite $\{10.4\}$ ²⁷⁶ to form surface hydroxyl groups (Appendix A Figure 1).

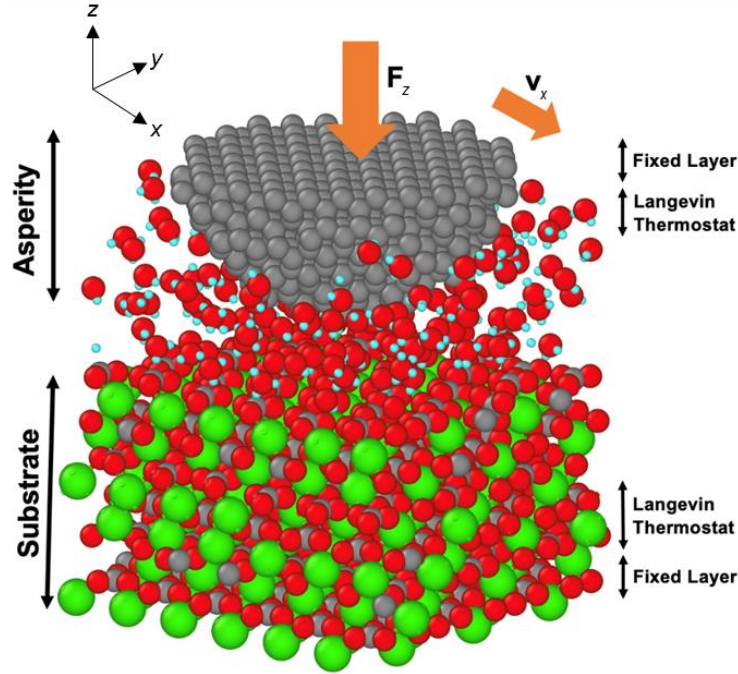


Figure 3.2: Representative system (calcite surface with 150 water molecules) for the NEMD simulations shown before equilibration. Calcium atoms are shown in green, carbon in grey, oxygen in red, and hydrogen in light blue. Rendered using OVITO.²⁸⁰ Used with permission from Bhamra et al.¹

The tip was modelled by a single-crystal diamond hemisphere with a radius of 2.0 nm.²⁰¹ A representative system for the NEMD simulations (calcite surface with 150 water molecules) is shown in Figure 3.2. The tip radius is several orders of magnitude smaller than the experimental tip radius (4.765 mm), resulting in a much lower contact area, A_c . This is not expected to significantly affect the friction coefficient, however, since the load is reduced accordingly to approximately match the mean Hertz pressure for point contacts. Previous studies have shown

that the shear stress ($\tau = F_t/A_c$) at diamond–quartz interfaces is independent of both the tip radius and tip geometry.²⁸¹

ReaxFF Parameters

ReaxFF is a bond order-based force field that was originally developed by van Duin et al.¹⁹³ to study the reactivity of hydrocarbons. The version of ReaxFF implemented in LAMMPS uses the functional form that was originally outlined by Chenoweth et al.²⁸² and was fully described by Aktulga et al.²⁸³ The general functional form of ReaxFF is given by¹⁹⁴

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{angle}} + E_{\text{tors}} + E_{\text{vdW}} + E_{\text{Coulomb}} + E_{\text{specific}} \quad (3.1)$$

where E_{bond} is a continuous function of interatomic distance, describing the energy associated with bond formation (including σ , π , and π - π contributions). E_{angle} and E_{tors} are the energies associated with three-body angle and four-body torsional angle strain respectively. E_{over} is an energy penalty to prevent over-coordination of atoms and is based on atomic valence rules. E_{Coulomb} and E_{vdW} represent the electrostatic and dispersive interactions between all atoms in the system, irrespective of their connectivity and bond order. E_{specific} represents system-specific terms required to capture properties particular to the system of interest, such as lone-pairs, conjugation, and hydrogen bonding.¹⁹⁴ The point charges on the atoms vary dynamically during the NEMD simulations and are calculated using the charge equilibration (Qeq) method.^{196,283,284}

For the α -quartz {0001} surfaces, we use the Si/O/H/C ReaxFF parameters developed by Newsome et al.²⁰⁶ to study the oxidation of silicon carbide by oxygen and water. This parameterization used a training set including previous first-principles data for silicon,²⁸⁵ silicon oxides,^{286,287} and polydimethylsiloxane.²⁸⁸ The parameters accurately reproduce the experimental density and bulk moduli of α -quartz.²⁸⁶ The relevant parameters have also been validated against

first-principles methods for the interactions between silica surfaces and water molecules.²⁸⁷ The parameters²⁰⁶ have also recently been successfully applied to study the adhesion between graphene sheets and amorphous silica substrates.²⁸⁹

A ReaxFF parameterisation is available that includes parameters for all of the elements of interest in this study.²⁹⁰ Although this includes parameters developed for CaO,²⁹¹ CaCO₃ was not included in the training set and it performs poorly for this purpose.²⁹² A previous version included parameters for CaCO₃, but this required Ca atoms to be fixed as di-cations.²⁹³ Therefore, in this study we developed new ReaxFF parameters for Ca/O/H/C using DFT that do not require fixed charges. The DFT calculations of CaCO₃ were performed with the Jaguar software²⁹⁴ using the M06-2x functional²⁹⁵ with the LACV3P++** basis set. Full geometry optimizations were performed on these clusters without using any symmetry or structural constraints. To obtain potential energy profiles, constrained geometry optimization was applied for the Ca–O–C angle (65–130°) and the Ca–C off-diagonal (1.0–4.2 Å). The vibrational frequency of CaCO₃ was also calculated using the same functional and basis set.

Periodic DFT calculations for CaCO₃ and Ca condensed phases were then performed using the Vienna ab initio simulation package (VASP).^{296–298} The DFT calculations use projector augmented wave (PAW) pseudopotentials²⁹⁹ and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional³⁰⁰ with an energy cutoff of 520 eV. All calculations were performed using spin polarization. For CaCO₃, the Brillouin zone is sampled with a (4 × 4 × 4) Monkhorst-Pack k-point mesh.³⁰¹ The equilibrium lattice constant was calculated and the equation of state was determined by deforming the lattice by ±10 %.

In this study, we have optimized the ReaxFF parameters for the Ca–O–C angle and the Ca–C off-diagonal to develop a transferable ReaxFF potential for Ca/C/O interactions, without requiring local charge constraints.²⁹³ The Ca–O parameters were obtained from Pitman and van Duin.²⁹⁰ The interaction between calcite surfaces and water molecules has previously been validated against first-principles calculations²⁹³ and the relevant parameters remain unchanged here. The new parameters were developed by training against new and existing DFT data. We used the standard ReaxFF parameter optimization strategy, which involves a weighted single-parameter search method.¹⁹⁴ Parameter correlations, which are quite extensive in ReaxFF, are captured by performing multiple loops over the optimizable force field parameters until the force field error converges. The weights depend on the relevance of a particular training set data point; in general, data points closer to the equilibrium were given higher weights.

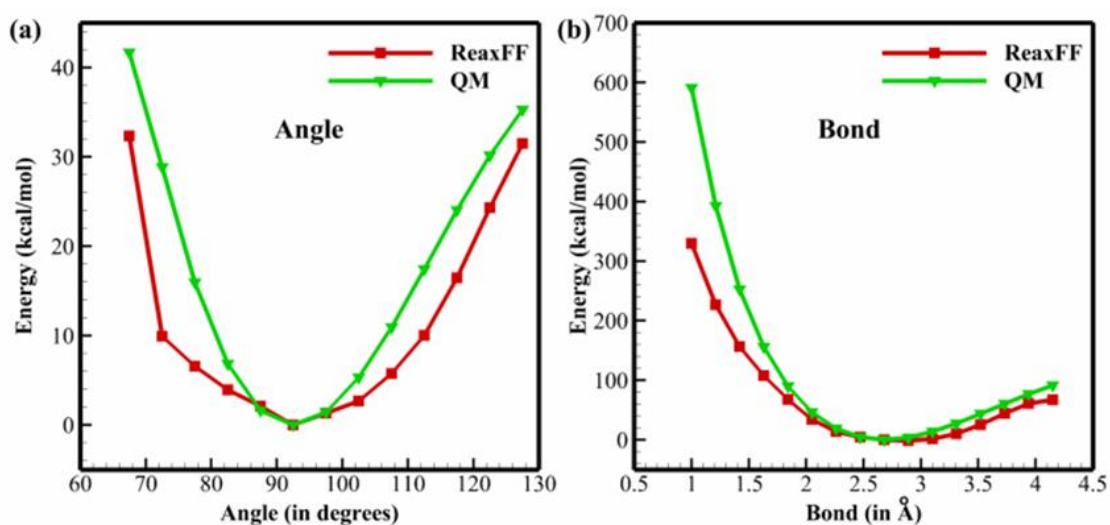


Figure 3.3: Comparisons of energy from ReaxFF (red) and DFT (green) for constraining of (a) Ca–O–C angle and (b) Ca–C off-diagonal. Performed by Nabankur Dasgupta. Used with permission from Bhamra et al.¹

Figure 3.3 shows the comparison between ReaxFF and the DFT energies for the Ca–O–C angle (a) and the Ca–C off-diagonal (b) scanning. The agreement between ReaxFF and DFT is relatively good; most of the energy differences are comparable to the typical error of DFT calculations. The mean energy deviation of ReaxFF is 5.2 kcal mol⁻¹ for the Ca–O–C angle and 7.5 kcal mol⁻¹ for the Ca–C off-diagonal. The vibrational frequencies of CaCO₃ obtained with DFT and ReaxFF are also in good agreement (Appendix A Figure 2 and Appendix A Figure S3).

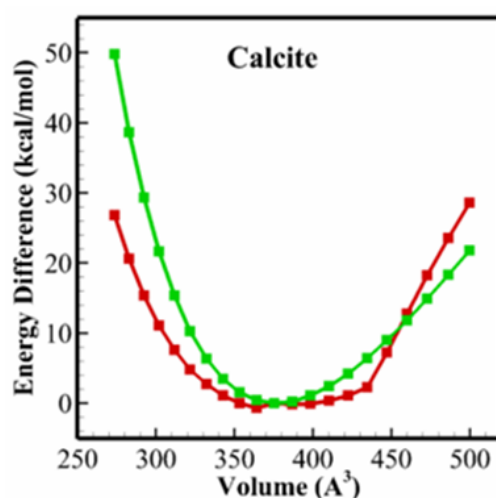


Figure 3.4: Equations of state of calcite from ReaxFF (red) and DFT (green). Performed by Nabankur Dasgupta. Used with permission from Bhamra et al.¹

The training set also included condensed phase data for the equation of state for the condensed calcite phase of CaCO₃. ReaxFF was trained against the difference in energy when the volume was varied from $\pm 10\%$ of the equilibrium value, as shown in Figure 3.4. The ReaxFF parameterisation reproduced the equilibrium density of calcite from DFT within the uncertainty of the measurements, but it slightly underestimates the volume-energy curvature close to the equilibrium density. The heat of formation and heat of reaction of calcite were also included within the training set. The ReaxFF parameters provide similar energy values for these reactions as the DFT calculations (Appendix A Table 1).

Simulation Setup

We performed NEMD simulations using the large atomic/molecular massively parallel simulator (LAMMPS) software package.³⁰² We used the velocity-Verlet integration algorithm³⁰³ with a time step of 0.25 fs. The bottom atomic layer of the substrate was frozen, and periodic boundary conditions were applied in the x - and y -directions. The temperature was maintained at 300 K using a Langevin thermostat with a coupling time of 25 fs. The thermostat was only applied to the central layers (in the z -direction) of the tip and substrate, as shown in Figure 3.1. A reflective boundary was added in the xy -plane at the top of the simulation cell to prevent desorbed species from escaping.

The systems were energy minimised, before being equilibrated at 300 K for 0.1 ns. During the equilibration, a constant normal force ($F_n = 1$ nN) was added to the outer layer of atoms in the tip to bring it in contact with the substrate. The normal force was then increased to the target value ($F_n = 2.5$ – 40 nN) and the tip was given a sliding velocity in the x -direction after equilibration ($v_x = 10$ m s⁻¹). This resulted in maximum Hertz pressures in the range $P_{\max} = 1.9$ – 3.9 GPa for diamond–calcite and $P_{\max} = 2.0$ – 4.1 GPa for diamond–quartz. We found that there was negligible difference in the change in friction force with sliding distance for sliding velocities between 1 m s⁻¹ and 10 m s⁻¹ (Appendix A Figure 4). Therefore, to reduce the computational expense, all results discussed from this point onwards refer to a tip sliding velocity of 10 m s⁻¹. The sliding simulations were performed for 0.75 ns, which was sufficient for the friction force and number of interfacial bonds to reach a steady state. Chemical bonding information was output every 1.0 ps, using a bond order cutoff of 0.3 to identify covalent bonds.²⁸² The choice of bond order cutoff only affects the post-processing analysis and does not influence the ReaxFF energy or force calculations.^{290,304}

3.3. Results and Discussion

Tribometer Experiments

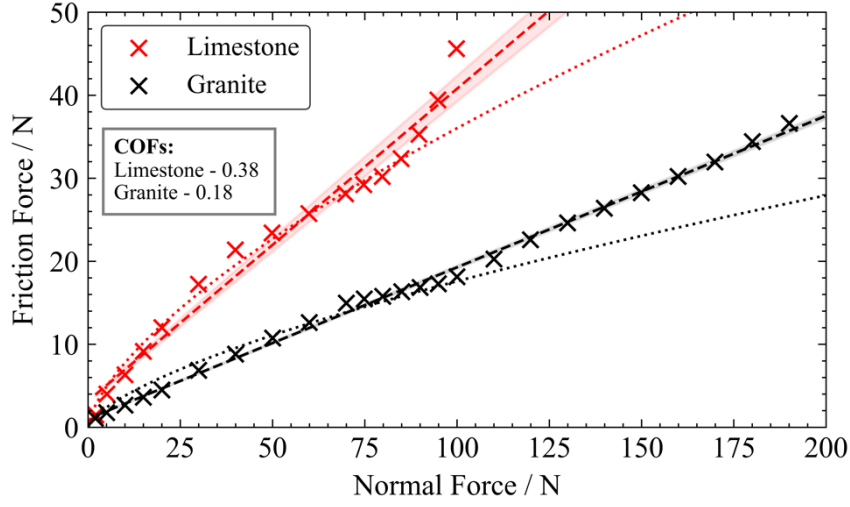


Figure 3.5: Variation in the friction force, F_f , with normal force, F_n , from the macroscale tribometer experiments with diamond–granite (black) and diamond–limestone (red) point contacts in an air environment. Dashed lines are linear fits to Amontons’ friction equation. Dotted lines are estimates for the low-load region (< 80 N) based on Hertz theory ($F_f \propto F_n^{2/3}$).²¹² Shaded regions represent 95 % confidence intervals. Performed by Evan Yu. Used with permission from Bhamra et al.¹

First, we studied the variation in the friction force, F_f , with normal force, F_n , using macroscale tribometer experiments (Figure 3.5) with diamond–granite (black) and diamond–limestone (red) point contacts in a humid air environment. For both rock types, the friction force increases roughly linearly with normal force with a near-zero intercept. This is consistent with Amontons’ friction equation, which states that the coefficient of friction (COF), $\mu = F_f/F_n$. Such a relationship is expected in macroscale contacts and is usually attributed to a linear increase in real contact area between the randomly rough surfaces.²¹² The linear fits in Figure 3.5 yield $\mu = 0.38$ for diamond–limestone and $\mu = 0.18$ for diamond–granite in an air environment. For the diamond–granite

contact, the intercept of the linear fit had an intercept of 4 N, suggesting some adhesion at the interface.²¹²

We obtained similar results in an aqueous environment, but with a slightly higher ($\sim 10\%$) friction coefficient for both rock types. Previous studies have shown that humidity can significantly affect rock friction.³⁰⁵ In the current experiments, the air relative humidity (70 %) is already sufficiently high such that there was only a slight increase in friction when changing to an aqueous environment. After the friction experiments, we observed that limestone powder strongly adhered to the diamond tip (Figure 3.1), which has previously been noted for PDCs that have been used to drill calcite-containing rocks.⁸⁵

The friction–load curves in Figure 3.5 are slightly sigmoidal, particularly for the diamond–limestone contact. At low load ($F_n < 80$ N), F_f increases sublinearly with F_n , which is consistent with Hertz theory ($F_f \propto F_n^{2/3}$),²¹² as shown by the dotted lines in Figure 3.5. At higher loads ($F_n > 80$ N), F_f increases superlinearly with F_n , which implies that the interfacial shear strength increases markedly above a critical load, corresponding to a maximum Hertz pressure of around 2 GPa. We attribute the superlinear increase of F_f with F_n at high load to interfacial bond formation, as predicted by the interfacial bonding friction model developed by Filippov et al.⁸⁶. The larger stresses encountered at higher loads increase the probability of interfacial bond formation by decreasing the activation energy.³⁰⁶ The formation of a greater number of interfacial bonds at high load, which must be ruptured for sliding to proceed, leads to higher friction than is predicted by contact mechanics theories.³⁰⁶ Superlinear friction–load behaviour has recently been observed in AFM experiments of silica–silica contacts,³⁰⁷ which are known to form interfacial bonds.⁸⁷ In summary, diamond–rock friction can be adequately described by contact mechanics theories up to a critical load (or pressure) above which interfacial bonding occurs, leading to much higher friction than would otherwise be expected. The friction–load behaviour is more sigmoidal for diamond–

calcite than diamond–quartz contacts, suggesting stronger interfacial bonding for the former. The relationship between interfacial bonding and friction was quantified and analysed using NEMD simulations.

NEMD Simulations

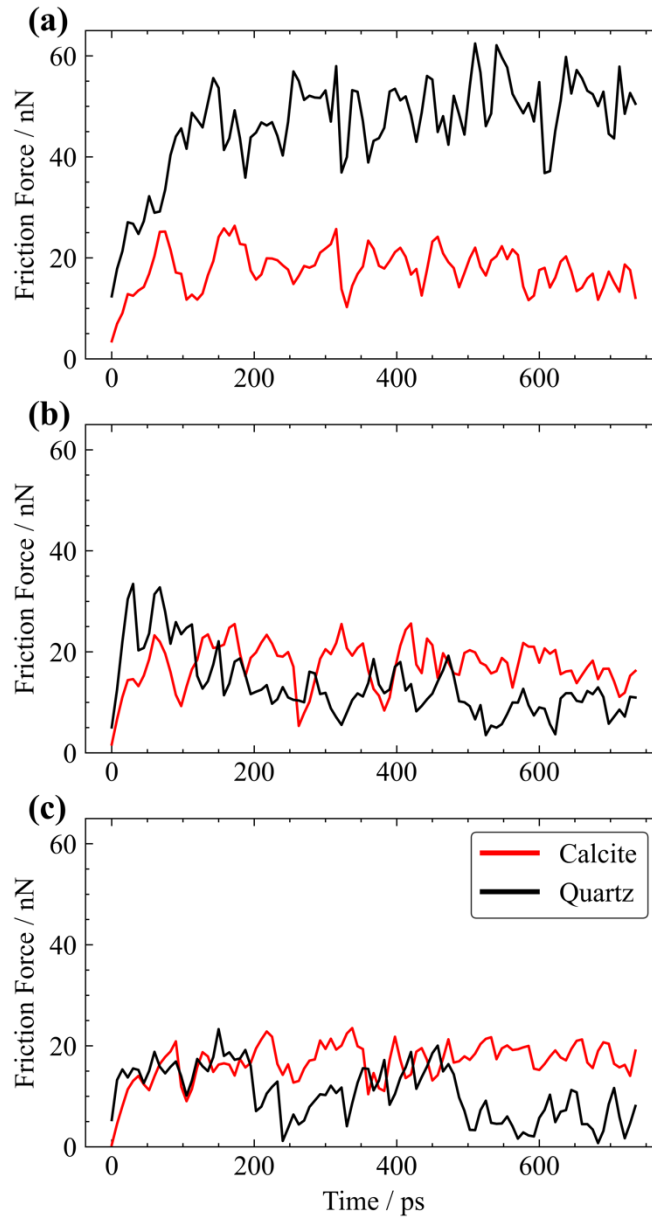


Figure 3.6: Variation in friction force, F_f , with sliding time from the NEMD simulations for diamond–quartz (black) and diamond–calcite (red) interfaces with 0 (a), 50 (b), and 150 (c) water molecules. Normal force, $F_n = 35$ nN, sliding velocity, $v_x = 10$ m s⁻¹. Used with permission from Bhamra et al.¹

Figure 3.6 shows how the friction force, F_f , changes with sliding time in the NEMD simulations. The friction force generally increases at short sliding times (< 200 ps) before reaching a steady

state. For the water-containing diamond–quartz systems, the friction force reaches a maximum before reducing to the steady-state value. Friction curves with similar shapes have been observed previously in NEMD simulations of silica–silica interfaces²⁶⁴ and tribometer experiments of quartz-containing sandstone rocks.³⁰⁸ For a subset of systems, longer simulations were performed in which there was no further change to the mean friction force. The steady-state friction force values shown from this point onwards are averaged over the final 200 ps of sliding. Stick-slip friction is observed for all the studied systems. The degree of stick-slip is more severe in the absence of water (Figure 3.6a) but is quite similar for the quartz and calcite substrates.

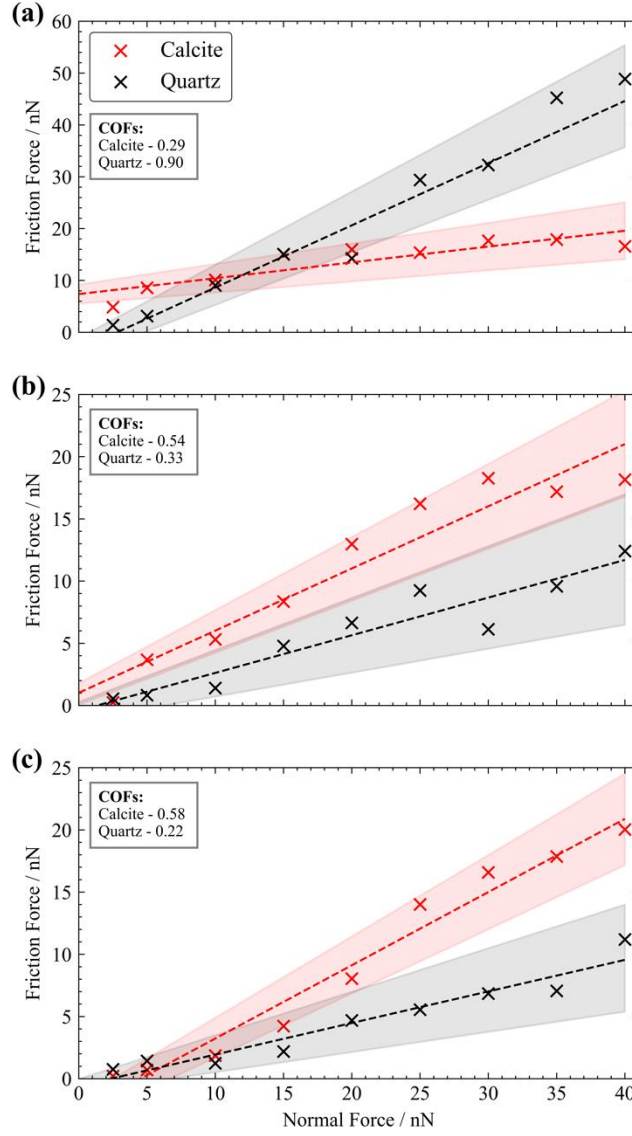


Figure 3.7: Variation in the friction force, F_f , with normal force, F_n , from the NEMD simulations with diamond–quartz (black) and diamond–calcite (red) point contacts with 0 (a), 50 (b), and 150 (c) water molecules. Mean forces calculated during the final 200 ps of sliding. Dashed lines are fits to Amontons’ friction equation. Shaded areas represent 95 % confidence intervals. Used with permission from Bhamra et al.¹

Figure 3.7 shows that F_f increases approximately linearly with F_n in all of the NEMD simulations. This is in agreement with the experimental friction results (Figure 3.5) and is consistent with

Amontons' equation.²¹² Given that a point contact geometry was used in the simulations, one might expect that $F_f \propto F_n^{2/3}$, which is consistent with Hertz theory.²¹² The linear increase in F_f with F_n observed in Figure 3.7 indicates that the interfacial shear strength increases with pressure,²¹² which we attribute to interfacial bond formation. The water-lubricated diamond–calcite contacts (Figure 3.7b and Figure 3.7c) show a superlinear increase of F_f with F_n at low loads, which can be explained by stress-assisted interfacial bonding.³⁰⁶ It is noteworthy that this behaviour occurs at a similar pressure (2 GPa) as in the experiments (Figure 3.5). The water-lubricated diamond–granite contacts show a more linear increase in F_f with F_n , which suggests that interfacial bond formation is less prolific compared to diamond–calcite interfaces. Previous single-asperity AFM friction measurements of silica–silica contacts (in which interfacial bonds are known to form⁸⁷) have shown both linear³⁰⁹ and superlinear³⁰⁷ increases in F_f with F_n , depending on the lubricating fluid.

In the absence of water (Figure 3.7a), the friction coefficient calculated using the Amontons' equation is higher for diamond–quartz ($\mu = 0.90$) than diamond–calcite ($\mu = 0.29$). This is the opposite trend observed experimentally using humid air and aqueous environments (Figure 3.5). For the dry diamond–quartz contact, the linear fit through the data has an intercept close to zero. For the dry diamond–calcite contact, the linear fit to the data has a positive intercept, which suggests that there is some adhesion between the tip and the substrate (while a negative intercept can be interpreted as repulsion, this is unlikely and an unphysical phenomenon due to limited quality of the fit in the low load region).²¹² This could explain why in both the current (Figure 3.1) and previous⁸⁵ tribometer experiments using calcite-containing rocks, carbonate material strongly adhered to the diamond surfaces. When a water monolayer is added between the tip and the substrate (Figure 3.7b), the friction coefficient of the diamond–quartz contact decreases significantly ($\mu = 0.33$), while that for diamond–calcite increases ($\mu = 0.54$). When excess water molecules are added such that the tip is submerged during sliding (Figure 3.7c), the friction coefficient of the diamond–quartz system decreases further ($\mu = 0.22$), while that for diamond–

calcite increases slightly ($\mu = 0.58$). It should be noted that the increase in friction coefficient for diamond–calcite from 50 to 150 molecules is mostly due to a decrease in friction force at low load ($F_n < 25$ nN) since the friction forces at higher load remain identical within statistical uncertainty. The intercept of the linear fits to the diamond–calcite data decreases from 9 nN for the dry case (Figure 6a) to 2 nN when 50 water molecules are present and is negligible when 150 water molecules are added. Additional simulations suggest that there is no measurable change to the friction coefficient when further water molecules (250) are added to either system. Previous experiments have shown that the friction of granite,³⁰⁵ quartzite,³⁰⁵ silicon³¹⁰ and nanocrystalline diamond³¹¹ surfaces all decrease with increased relative humidity. First-principles NEMD simulations have also shown that the presence of water molecules at the silica–silica interface significantly reduces friction by suppressing interfacial bond formation.³¹² An increase in friction in the presence of water, as observed for the diamond–calcite contact, has also been observed for some other materials, such as silicon carbide.³¹³ The friction coefficients from the water-containing NEMD simulations (Figure 3.7b and Figure 3.7c) are in qualitative agreement with those obtained experimentally in an air environment (Figure 3.5). Most importantly, the friction coefficient is much higher for the diamond–calcite than the diamond–quartz contacts.

The indentation depths in both the tribometer experiments and NEMD simulations were minimised to ensure that friction was dominated by interfacial interactions rather than ploughing. To verify that this was the case, the change in indentation depth with sliding time (Appendix A Figure 5) was monitored during the NEMD simulations.³¹⁴ The indentation depth is always deeper for calcite than quartz (Appendix A Figure 6), as expected due to the lower average hardness of the former (~ 2 GPa) compared to the latter (~ 15 GPa).³¹⁵ Through the purely geometrical arguments proposed by Bowden and Tabor,³¹⁶ higher friction coefficients are expected at deeper indentation depths because of a larger ploughing contribution. By comparing how the load-dependent friction coefficient changes with indentation depth compared to the Bowden-Tabor

prediction (Appendix A Figure 7),³¹⁶ it is clear that the ploughing contribution is relatively small for both diamond–quartz and diamond–calcite contacts. Moreover, the large differences in the friction coefficients for diamond–quartz and diamond–calcite interfaces (Figure 3.7) cannot be explained through ploughing. Assuming isotropic hardness, although the tip will indent less into the harder quartz substrate, it will also experience greater resistance to sliding at a given ploughing depth.³¹⁵

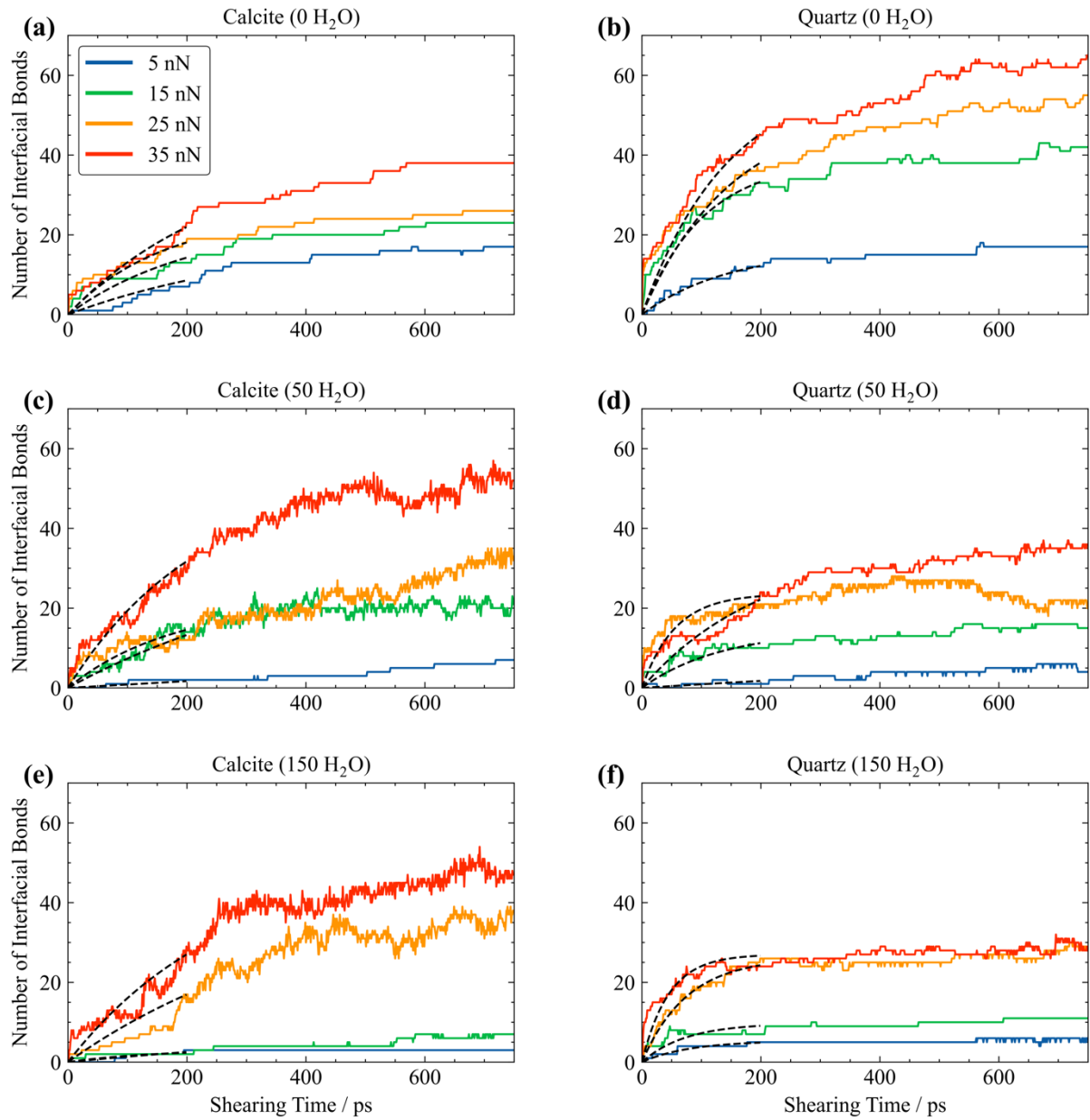


Figure 3.8. Variation in the total number of interfacial bonds between the tip and the surface during sliding for: (a) calcite with 0 water molecules, (b) quartz with 0 water molecules, (c) calcite with 50 water molecules, (d) quartz with 50 water molecules, (e) calcite with 150 water molecules, and (f) quartz with 150 water molecules. Dotted lines are fits to the function $(1 - e^{-r t})$ where r is the rate of interfacial bond formation and t is sliding time.³¹⁷

To understand the higher friction at the diamond–calcite interface than the diamond–quartz interface observed experimentally and in the water-containing NEMD simulations, the interfacial bond formation during sliding was quantified. The time evolutions of the interfacial bonding for the different systems and conditions are shown in Figure 3.8. Interfacial bonds are continuously formed and broken during sliding. As interfacial bonds break, the force on the remaining ones increases and the bond rupture becomes synchronised.⁸⁶ This cooperative rupture causes the stick-slip behaviour in the friction force observed in Figure 3.6. The oscillations in the friction force (Figure 3.6) are more pronounced than for the interfacial bonds (Figure 3.8). This suggests that the cooperative formation and rupture of the interfacial bonds are spatially localised at the leading and trailing edge of the contact region, respectively.³¹⁴ Since the formation and breaking are not temporally synchronised, the average number of interfacial bonds does not fluctuate during sliding.

In the absence of water molecules, more interfacial bonds form for diamond–quartz (Figure 3.8b) than for diamond–calcite (Figure 3.8a) (mechanism discussed later), leading to higher friction forces and more pronounced stick-slip for the former (Figure 3.7). When water molecules are added at the interface, far fewer bonds form for diamond–quartz contacts (Figure 3.8d), while the number of bonds for diamond–calcite (Figure 3.8c) remains similar to the dry case. In fact, at high load (≥ 25 nN), more diamond–quartz interfacial bonds are formed when water molecules are present (Figure 3.8e) than when they are absent (Figure 3.8a). This observation could explain why the friction coefficient decreases significantly moving from 0 (Figure 3.7a) to 50 (Figure 3.7b) and 150 (Figure 3.7c) water molecules for diamond–quartz contacts, but increases for diamond–calcite. The larger number of interfacial bonds formed for diamond–calcite contacts than for diamond–quartz when water is present could also explain the higher friction coefficient observed for the former in the NEMD simulations (Figure 3.7c) and tribometer experiments (Figure 4). Previous NEMD simulations using ReaxFF have shown that, at the interface between hydroxylated amorphous silica and oxidized silicon, the degree of atom transfer was substantially reduced when

there were sufficient water molecules present to form a complete monolayer.²⁰³ This was because the silicon atoms at the sliding interface became terminated with hydroxyl groups rather than forming interfacial bonds.²⁰³ NEMD simulations with ReaxFF have also shown that the friction of silica surfaces reduces with increasing hydroxyl group density.³¹⁸ Similarly, experiments and first-principles calculations diamond indicated that friction generally decreases with increased relative humidity due to hydrogenation and hydroxylation that passivate the surface.³¹¹ Previous DFT calculations have shown that adsorbed water molecules spontaneously dissociate on both α -quartz {0001}²⁷⁹ and calcite {10.4}²⁷⁶ to form surface hydroxyl groups (Appendix A Figure 1). Appendix A Figure 1 shows that this is more pronounced for calcite than α -quartz.

Figure 3.8 shows that interfacial bonding increases with sliding time, reaching a steady state after around 500 ps. More interfacial bonds form and the rate of interfacial bond formation increases when the load is increased. This implies that interfacial bond formation at diamond–rock interfaces is a stress-assisted, thermally activated (SATA) process.¹⁵⁴ In SATA processes, the activation energy (E_0) barrier, which determines the rates and reaction pathways, is reduced by the application of stress, such that:

$$k = Ae^{-(E_0 - N \sigma \Delta v)/(RT)} \quad (3.2)$$

where A is a prefactor, E_0 is the activation energy, N is Avogadro's number, σ is the applied stress, Δv the activation volume, R the universal gas constant, and T is the absolute temperature.¹⁵⁴ This equation predicts exponential growth in the rate with both temperature and applied stress.¹⁵⁴ The most appropriate stress component in Equation 3 has been debated for different systems. For the mechanochemical decomposition of lubricant additives, it has been proven that, at the macroscale, the shear stress, rather than the normal stress, is the most important parameter.³¹⁹ The shear stress has also been selected in nanoscale wear studies.²⁴⁷ In most previous studies, however, the normal

stress is used since this is much easier to measure and control.¹⁵⁴ The stress dependence of the rate of interfacial bond formation can be used to determine the activation volume, Δv .³¹⁷ The wear of silicon AFM tips on diamond surfaces²⁴⁴ and nano-manufacturing of silicon surfaces with a silica tip³²⁰ have also been shown to be SATA processes.¹⁵⁴ Interfacial bonding is also commonly treated as a SATA process.^{306,307}

For single-asperity Hertz contacts, the contact area, $\mathcal{A}_c$, is expected to increase with load as $\mathcal{A}_c \propto F_N^{2/3}$, although previous NEMD simulations have suggested that the real contact area, $A_{\text{real}} \propto F_N$.²¹² A higher contact area means that more atoms are close enough to participate in interfacial bonding. Some previous single-asperity studies of SATA processes have normalized the reaction rates by the number of atoms in contact,²⁴⁴ while others have not.³²⁰ The rates of interfacial bond formation are calculated over the first 200 ps of sliding (dashed lines in Figure 3.8), where the indentation depth (and thus contact area) is very similar for all of the systems and conditions studied (Appendix A Figure 5). Moreover, during steady-state sliding, the variation in contact area with load is much smaller than that predicted using the Hertz equation for both diamond–quartz and diamond–calcite contacts (Appendix A Figure 8). This is because of the microhardness values used in the Hertz calculations,³¹⁵ whereas the indentation depths in the NEMD simulations are always less than 0.5 nm (Appendix A Figure 6). It is known for many materials that hardness decreases markedly with increasing indentation depth over the first few nanometres.³²¹ For these reasons, we do not normalize the rates shown in Figure 3.9 by the contact area.

Figure 3.9 shows how the rate of interfacial bond formation varies with applied pressure. The rates are calculated using the fits shown in Figure 3.8. In all cases, the rate of interfacial bond formation increases exponentially with pressure, as predicted using SATA models.¹⁵⁴ This observation is consistent with previous experiments and NEMD simulations of dry silica–silica contacts.³²² When no water molecules are present (Figure 3.9a), the rate is higher for diamond–quartz than for

diamond–calcite. The slope of the linear increase in $\ln(\text{rate})$ with pressure, which is steeper for diamond–quartz than for diamond–calcite, yields an activation volume of $1.17 \pm 0.09 \text{ \AA}^3$ for the former and $0.59 \pm 0.11 \text{ \AA}^3$ for the latter. These values are consistent with single-atom dimensions.²⁴⁴ When 50 water molecules are present (Figure 3.9b), the rates and activation volumes are similar for both diamond–quartz and diamond–calcite, $1.33 \pm 0.09 \text{ \AA}^3$ and $1.42 \pm 0.07 \text{ \AA}^3$, respectively. This corresponds to the number of water molecules where the friction coefficients are most similar for the two substrates in Figure 3.5. When 150 water molecules are present at the interface (Figure 3.9c), the activation volume is somewhat higher for diamond–calcite ($1.84 \pm 0.02 \text{ \AA}^3$) than diamond–quartz ($1.26 \pm 0.07 \text{ \AA}^3$). This implies a greater stress-dependence of the rate of interfacial bond formation for wet diamond–calcite contacts than for diamond–quartz. The maximum Hertz pressure above which the rate of interfacial bonding accelerates exponentially in the NEMD simulations (2 GPa), corresponds to the pressure at F_f begins to increase superlinearly in with F_n in the macroscale experiments (Figure 3.5), which supports the proposed link between the two phenomena.³⁰⁶

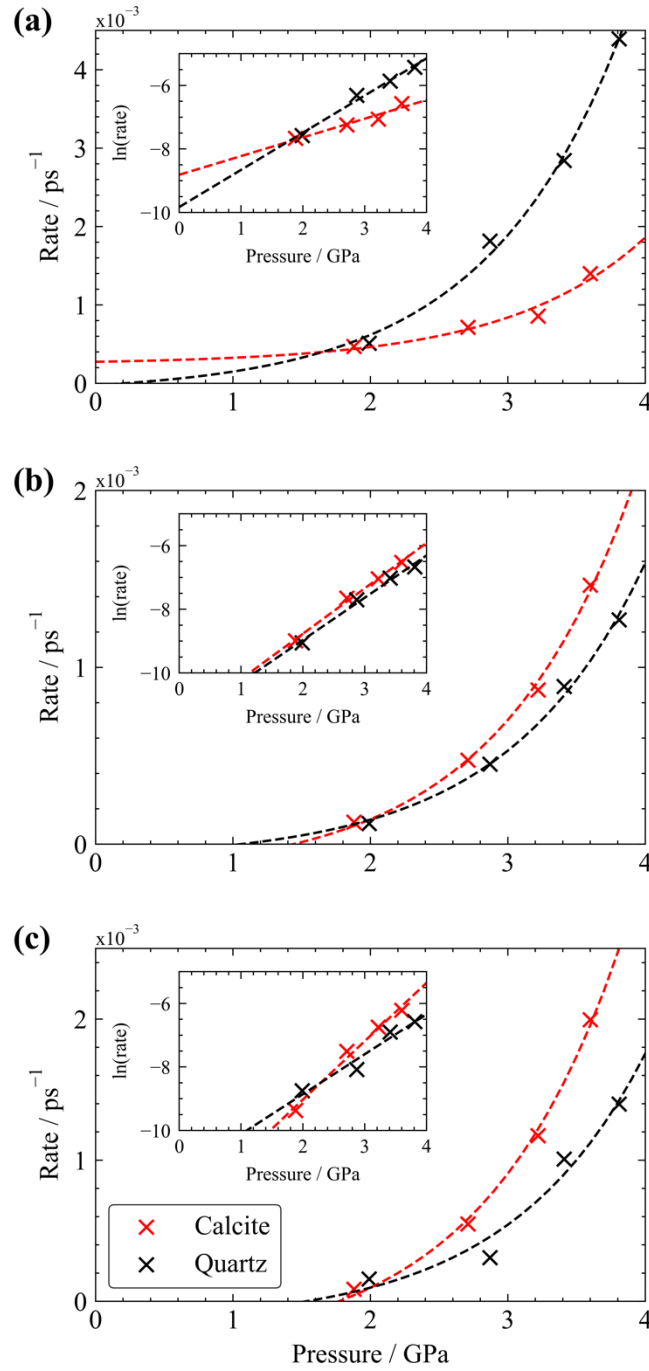


Figure 3.9: Variation in rate of interfacial bond formation as sliding commences with maximum Hertz pressure for: (a) 0 water molecules, 50 water molecules, 150 water molecules. Insets show linear increase in $\ln(\text{rate})$ with pressure. Dashed lines are fits to Equation 3 used for the calculation of the activation volume.

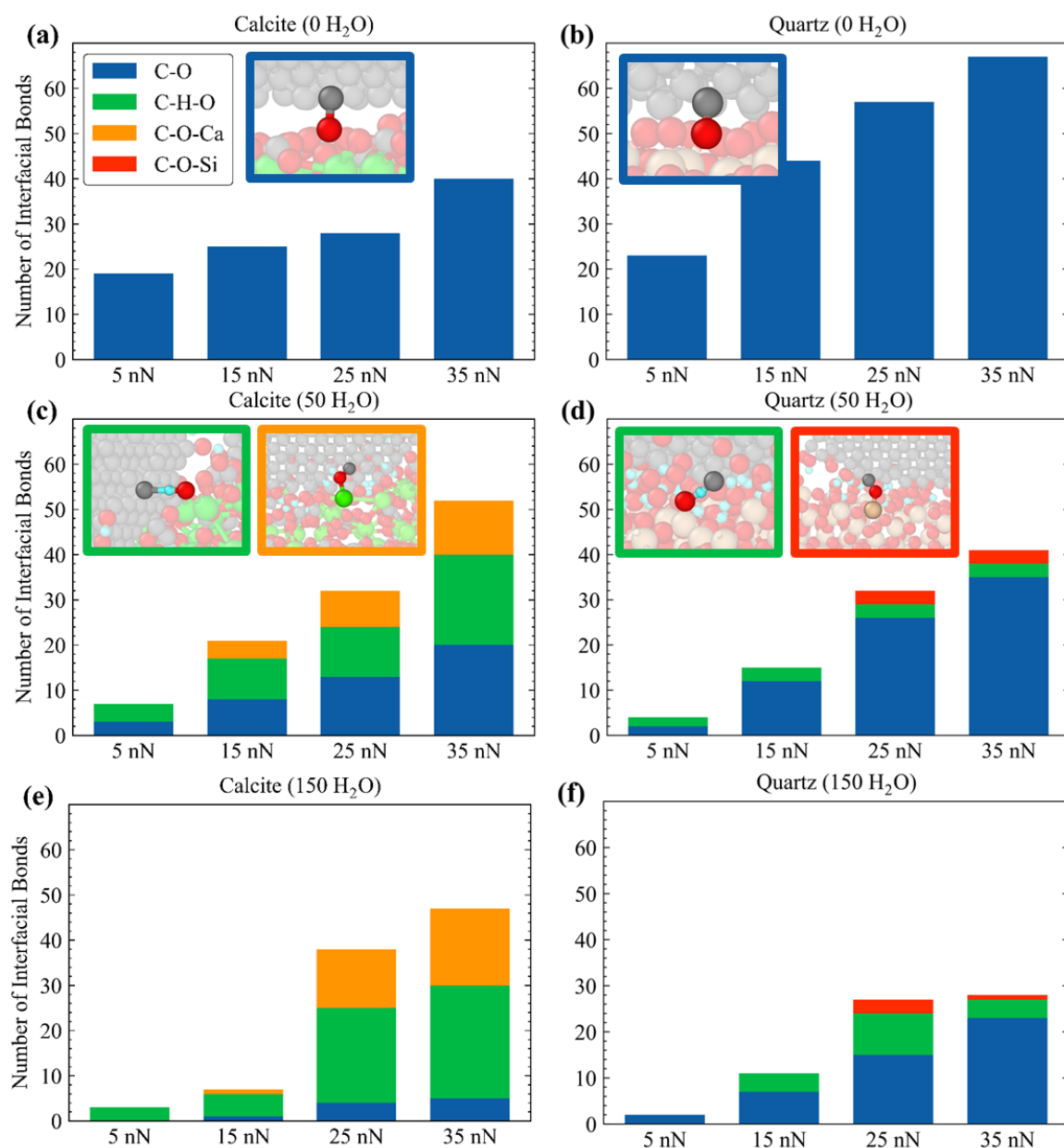


Figure 3.10: Type of interfacial bonds between the tip and the surface during steady-state sliding for: (a) diamond–calcite with 0 water molecules, (b) diamond–quartz with 0 water molecules, (c) diamond–calcite with 50 water molecules, (d) diamond–quartz with 50 water molecules, (e) diamond–calcite with 150 water molecules, and (f) diamond–quartz with 150 water molecules. Snapshots of each bond type are shown in the coloured boxes. Calcium atoms are shown in green, silicon in orange, carbon in grey, oxygen in red, and hydrogen in light blue. Rendered using OVITO.²⁸⁰

Figure 3.10 shows the variation in the steady state number of interfacial bonds with load for the different systems studied. At a nanoscale, friction is proportional to the number of the interatomic interactions between the two sliding surfaces.²¹² Negligible covalent bonding occurs between C atoms in the tip and Ca, C, (calcite) or Si (quartz) atoms in the substrates; however several C–O interfacial bonds are formed. In the absence of water molecules, only C–O bonds form across the interface for both diamond–calcite (Figure 3.10a) and diamond–quartz (Figure 3.10b). A greater number of interfacial C–O bonds are formed for quartz than calcite, which causes the higher friction (Figure 3.7). Previous NEMD simulations of dry silica–silica interfaces using ReaxFF have shown that a larger number of interfacial bonds resulted in higher friction.²⁶⁴ The force needed to break a given type of interfacial bond does not have a fixed value; it depends on the thermal state of the system and the rate at which the force is transmitted to the bond.³²³

When water is introduced at the diamond–calcite interface (Figure 3.10c and Figure 3.10e), the number of interfacial C–O bonds decreases; however, many C–O–Ca and C–H–O bridging bonds are formed. The C–O–Ca bridging bonds will be much stronger than the C–H–O hydrogen bonds.³²⁴ Although they are relatively weak, interfacial hydrogen bonds have been shown previously to enhance friction in water-lubricated silicon carbide contacts.³¹³ At low load ($F_n < 25$ nN), the total number of interfacial bonds remains similar to the dry case for diamond–calcite. At higher loads ($F_n \geq 25$ nN), the number of interfacial bonds is higher when water molecules are present at the interface. For diamond–quartz, interfacial C–O bonding substantially reduces when water is added (Figure 3.10d and Figure 3.10f) and while some C–O–Si and C–H–O bonds form, the overall number of interfacial bonds is always lower than for the dry case. The percentage of intact water molecules was also monitored during the NEMD simulations. The number of intact water molecules decreases much faster at higher loads (Appendix A Figure 1), suggesting that this could also be a SATA process.¹⁵⁴ Water dissociation occurs faster and to a greater degree at the diamond–calcite interface than diamond–quartz. This dissociation facilitates a greater degree of

interfacial bond formation through the O and H atoms at diamond–calcite interfaces than diamond–calcite without over-coordination of the O atoms.

Previous ReaxFF²⁰¹ NEMD and first-principles³¹² NEMD simulations of aqueous silica–silica contacts showed that interfacial Si–O bonds formed during sliding at high pressure, leading to increased friction. DFTB simulations of the dry diamond–silica interface have shown that both interfacial C–O and C–Si bonds form at very high pressure (5 GPa) and sliding velocity (100 m/s).⁶² Furthermore, MD simulations with ReaxFF suggested that C–Si bonding occurs at the interface between a silicon tip and a partially hydrogenated diamond substrate at high pressure.³²⁵ Accompanying transmission electron microscopy (TEM) experiments showed that adhesion at the diamond–silicon interface increased with sliding speed and applied normal stress because these variables increased the number of bonds formed,³²⁵ as predicted by the SATA model.¹⁵⁴ Here, we have shown that interfacial bonding also controls friction in aqueous diamond–quartz and particularly diamond–calcite contacts.

As a final confirmation of our hypothesis that interfacial bonding controls friction at aqueous diamond–rock interfaces, the mean number of interfacial bonding was correlated with the mean friction force for the different systems and conditions studied. Figure 3.11 shows that, for the water-containing systems, the mean friction force increases approximately linearly with the mean number of interfacial bonds for both diamond–calcite and diamond–quartz contacts. This observation is consistent with both the friction model due to Filippov et al.⁸⁶ and the NEMD simulation results of Mo et al.²¹², where the same relationship was observed for hydrogen-terminated amorphous carbon–diamond contacts. The gradient is steeper for diamond–calcite (Figure 3.11a) compared to diamond–quartz (Figure 3.11b), suggesting that the interfacial bonds are stronger and thus require more mechanical energy to break in the former case. The agreement between the friction coefficients obtained in the tribometer experiments (Figure 3.5) and NEMD

simulations with excess water present (Figure 3.7) suggest that interfacial bonding could also control friction in these systems not only at the nanoscale but also at the macroscale.

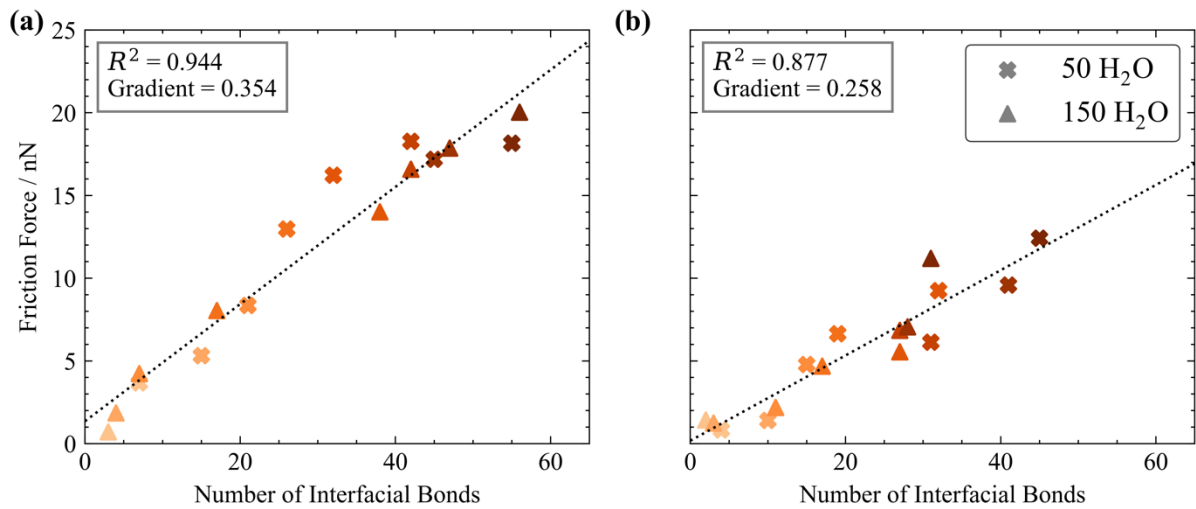


Figure 3.11: Correlation between the mean friction force and the mean number of interfacial bonds during steady-state sliding for diamond–calcite (a) and diamond–quartz (b). Crosses represent systems with 50 water molecules, triangles are 150 molecules, darker colours indicate higher loads.

3.4. Conclusion

In this study, macroscale tribometer experiments and NEMD simulations using ReaxFF have revealed why the friction of diamond–rock interfaces varies significantly depending on the rock type and the presence of water. Superlinear friction–load behavior is observed above a threshold pressure (2 GPa) in both the tribometer experiments in a humid air environment and NEMD simulations with water molecules present at the interface. The NEMD simulations show that this is due to interfacial bonding. The rate of interfacial bond formation increases exponentially with pressure, which is indicative of a SATA process. When water is present, the friction coefficient for diamond–calcite is much higher than for diamond–quartz in both the experiments and NEMD

simulations. The NEMD simulations indicate that the higher friction coefficient for diamond–calcite than diamond–quartz contacts is due to a greater amount of interfacial bonding. Finally, we show that the mean friction force is linearly dependent on the mean number of interfacial bonds during steady-state sliding. We expect that these findings will be useful to design new drill bit materials and coatings that minimise bit–rock interfacial bonding and thus friction.

Chapter 4: Comparing the Tribological Performance of Water-Based and Oil-Based Drilling Fluids in Diamond-Rock Contacts

Herein this chapter includes works performed by collaborators and colleagues. All experimental tribometer work, including experimental setup and data collection, was performed by Eliah M Everhard (Baker Hughes Inc., Center for Technology Innovation, Houston, Texas 77040, U.S.A.). All contributions by Eliah are explicitly laid out in this chapter and in Appendix B.

At the time of writing, this chapter is being prepared for submission to *Tribology Letters*.

4.1. Introduction

Drilling fluids (or drilling muds) are crucial to the safety and efficiency of drilling operations, performing around 20 different functions.³²⁶ These include facilitating the removal of cuttings from the borehole, cleaning and cooling the cutter while in operation, maintaining the stability of the wellbore, preventing the inflow of fluids from the wellbore, and forming an impermeable filter cake.³²⁶ Drilling fluids should also be non-damaging to the producing formation and non-hazardous to the environment.³²⁶ Fluids for geothermal wells, which are typically deeper than those for oil and gas, have additional requirements of high thermal stability and specific rheological properties.³²⁷ The three main classes of drilling fluid are water-based, oil-based, and gas-based.³²⁶ Water-based drilling fluids are generally the lower-cost and more environmentally friendly option compared to their oil-based alternatives. Consequently, approximately 80% of wells are drilled using water-based fluids.¹⁰⁰ The base oils used in oil-based drilling fluids have lower molecular weight and viscosity than conventional engine oils and are closer to diesel fuels. As with engine oils, mineral-based fluids are being progressively replaced by synthetics, such as poly(α -olefins), which have improved performance in a range of areas, including a lower environmental impact.³²⁸ Moreover, biodiesel-based fluids have also been studied to supplement or even replace oil-based

fluids.³²⁹ Modern drilling fluids are complex, multi-component formulations, with the base fluid containing several types of additives including salts, surfactants, polymers, and nanoparticles.¹⁰⁰ These are added to improve various properties such as viscosity, density, thermal conductivity, permeability, and friction.¹⁰⁰

The key tribological function of the drilling fluid is to minimise friction between the metal drillstring and borehole (or metal casing), as well as the cutter and the rock. One of the main benefits of oil-based drilling fluids are that they give lower friction, leading to decreased torque and drag on the drillstring,³³⁰ and thus increased drilling efficiency. In a recent review, it was stated that the friction coefficient (ratio of shear stress to normal stress) of oil-based drilling fluids is generally lower than 0.1, while for water-based drilling fluids it is often higher than 0.2.³³¹ This implies that drilling with oil-based fluids rather than water-based ones leads to 10% higher efficiency. In general, oils are better lubricants than water-based fluids, which is mainly due to the fact that the viscosity of water does not rise substantially with pressure.³³² This property is essential to the elastohydrodynamic lubrication (EHL)³³³ mechanism by which oils form lubricating films in high-pressure, non-conformal contacts of hard materials, such as gears and bearings.³³² In tribometer experiments with steel-rock contacts, which are representative of the drillstring-borehole interface, significantly lower friction is usually reported for oil-based fluids than water-based ones.^{334,335} This suggests a conventional EHL mechanism for this interface. Lower friction has also been observed for oil-based drilling fluids in rock-rock contacts.³³⁶ However, for diamond-rock contacts, which are representative of the polycrystalline diamond compact (PDC)²¹ cutter-rock interface, similar friction has been noted for oil-based and water-based drilling fluids.^{337,338} For diamond-impregnated bits on quartzite rocks, the addition of organic compounds to water that improve cutting performance actually increased the friction coefficient at the bit-rock interface.³³⁹ For certain minerals, such as magnesium oxide, much higher friction coefficients have been noted for microscratching experiments with diamond tips in *n*-hexadecane oil (0.41 to 0.65)

than in water (0.12 to 0.19).³⁴⁰ This observation was attributed to the promotion of near-surface dislocation mobility by magnesium oxide in *n*-hexadecane compared to water.³⁴¹ For most interfaces, such as zirconia-zirconia,³⁴² silicon nitride-silicon nitride,³⁴³ and silicon-silicon,³⁴⁴ *n*-hexadecane results in significantly lower friction than water. Similar comparisons for a range of ceramic-ceramic, ceramic-steel, and steel-steel contacts also showed that mineral oil was a better lubricant than water.³⁴⁵

Rehbinder¹¹⁹ showed that adding surfactants to water-based drilling fluids could markedly increase the drilling speed of hard rocks. Rehbinder suggested that this was due to an adsorption-induced reduction in surface energy of the rock.¹²⁰ Subsequently, Mills and Westwood¹²¹ proposed an alternative explanation that surfactants increase the hardness of the rock surface, reducing the ploughing contribution to friction. Controversy still remains in this area due to the complex and interacting physicochemical processes involved in controlling drilling performance. As in many areas of tribology, it is a considerable experimental challenge to studying the sliding buried interface with in situ techniques.³⁴⁶

One method that has provided a number of important insights into the behaviour inside tribological contacts is nonequilibrium molecular dynamics (NEMD) simulations.¹²⁴ Using a combination of macroscale tribometer experiments and NEMD simulations, we have recently shown that interfacial bonding can directly impact the friction behaviour of diamond-rock contacts.¹ It might reasonably be expected that drilling fluids passivate the sliding surfaces, decrease interfacial bonding, and subsequently reduce friction and wear. In this study, we use tribometer experiments and NEMD simulations to compare the kinetic friction of diamond pins on granite substrates lubricated by air, water, and *n*-hexadecane. Our aim is to uncover the fundamental tribological differences between additive-free oil-based and water-based drilling fluids. We employ the reactive forcefield (ReaxFF) method¹⁹³ to incorporate the effects of

interfacial bonding. The experiments show that friction is much higher in *n*-hexadecane than in air or water. The NEMD simulations show the same trend and reveal that *n*-hexadecane is much less effective than water at passivating the sliding surfaces and reducing interfacial bonding and thus friction.

4.2. Methodology

Experimental Procedure

We used a RTEC MFT-5000 (San Jose, California, U.S.A.) pin-on-disk rotary tribometer for the friction measurements. Previous studies²⁶⁸ have shown that the friction obtained in these experiments can be directly related to rate of penetration in industry-standard tests such as the vertical turret lathe²¹ and the ultradeep single-cutter drilling simulator.¹⁹ Sliding contact, as studied in these experiments, is experienced by worn or shaped cutting elements that are used in some rock drilling designs. In these elements, wherein the cutting action (indentation depth) is low, interfacial friction dominates the overall energy losses.

Sierra white granite cores were chosen as the rock sample. They were all ground to the same smooth surface finish prior to the tribometer experiments ($R_q \approx 12 \text{ } \mu\text{m}$).²⁶⁹ Hemispherical polycrystalline diamond pins with a radius of 5 mm were employed, providing idealized point contacts. The root-mean-square surface roughness of the pins was measured using white light interferometry ($R_q = 3.65 \text{ } \mu\text{m}$).^{22,40} Separate tests were conducted with the contact lubricated by air, water, and *n*-hexadecane. During the tests, there was an average relative humidity, $\text{RH} = 70\%$. The friction tests were run at 60 revolutions per minute (rpm) with a radial distance of 20 mm. Thus, the experimental sliding velocity was 0.125 m s^{-1} , which is somewhat lower than that used in operational PDC cutters ($2\text{--}4 \text{ m s}^{-1}$).²⁷ Additional tests were performed at radial distances of 15 mm and 25 mm, leading to sliding velocities of 0.125 m s^{-1} and 0.150 m s^{-1} , respectively. There was negligible change in the friction over this speed range. Prior to collecting the friction data, the

rock samples were run in³⁴⁷ for 5 minutes at 100 rpm with a low load of 10 N applied while the radial position was varied sinusoidally from 10 mm to 30 mm to establish a consistent smooth surface that was free from contaminants. Neither the diamond pins nor granite substrates underwent any detectable wear during the running-in phase, but it improved the repeatability of the subsequent friction measurements. During the friction tests, the load was progressively increased from 10 to 100 N at 10 N intervals and held at each load for 3 minutes while friction data was gathered. The maximum Hertz pressure,^{212,225} $P_{\max}$, varies between 0.8 to 1.8 GPa for the load range considered. Due to the roughness of the rock and diamond surfaces, the peak asperity pressures will be somewhat higher than predicted by the Hertz equation. However, the nondimensional α parameters calculated for these systems (0.01–0.03) suggest that Hertz theory provides a reasonable estimate of the contact pressure (within 5%).²⁷⁰

The velocities and loads used in the experiments were chosen to characterize the sliding-dominated friction response, where the cutting action is relatively low. This ensured that the friction forces measured were mainly due to interfacial interactions, rather than ploughing. In addition to the friction measurements, both rock and diamond surfaces were examined using optical microscopy following the tests. No wear of the tips was measurable following the tribometer experiments.

Simulation Procedure

Rocks exhibit spatial heterogeneity, which results in location-dependent surface chemistry.²⁷¹ Even though ReaxFF-based NEMD simulations are orders of magnitude less computationally expensive than first-principles techniques,¹⁹⁴ they are still limited to the study of nanoscale system sizes.¹²⁴ Therefore, α -quartz, the major constituent of granite²⁷³ is used as a representative model. Atomically smooth α -quartz{0001} is used since density functional theory (DFT) studies have previously shown it to be the most thermodynamically stable face.²⁷⁵ The x, y, z dimensions of the substrate were $13.7 \times 5.8 \times 3.7$ nm.

Experiments by Pashley and Kitchener²⁷⁷ showed that quartz is hygroscopic. Therefore, the surface of quartz will be covered by a water monolayer when exposed to air. In the NEMD simulations of the air system, 100 water molecules are added on top of the quartz substrate. This choice is consistent with previous experiments that have shown that the thickness of water films on dehydroxylated quartz is equivalent to approximately one monolayer at the ambient humidity used in the tribometer experiments (70 %).³⁴⁸ For the water system, 500 water molecules are added, to ensure full immersion of the contact interface as in the corresponding experiments. For the *n*-hexadecane system, the same number of water molecules (100) are maintained from the air systems since the tribometer experiments are not conducted in an inert atmosphere. Previous estimates have suggested that the concentration of water in *n*-hexadecane is similar to that in air.^{349,350} 25 *n*-hexadecane molecules were added to ensure that the total number of heavy atoms (C and O) was the same in the *n*-hexadecane and water systems. Given that the *n*-hexadecane molecules are expected to lie flat on the quartz surface,³⁵¹ this is sufficient to form a complete monolayer (coverage $\approx 0.3 \text{ nm}^{-2}$), as expected from experiments.³⁵² Figure 4.1 shows each of the systems after energy minimisation and equilibration, before compression and sliding.

The tip was modelled with a single-crystal diamond hemisphere with a radius of 2.5 nm.²⁰¹ The tip radius is several orders of magnitude smaller than the experiments (5 mm), resulting in a significantly reduced contact area, A_c . Therefore, the load is reduced to approximately match the mean Hertzian pressure for point contacts. Previous studies have shown that the shear stress ($\tau = F_F/A_c$) at diamond–quartz interfaces is independent of both the tip radius and tip geometry.²⁸¹

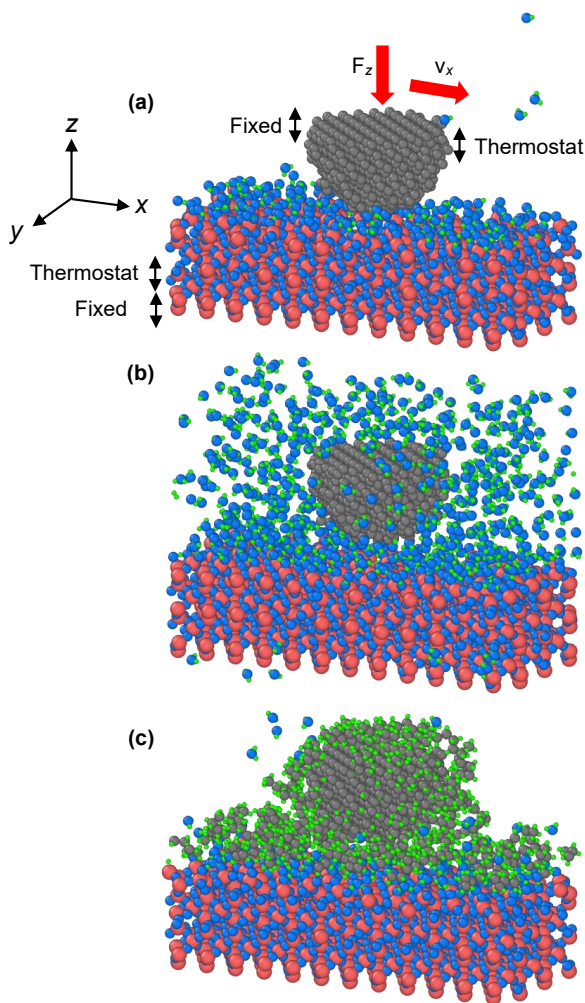


Figure 4.1. NEMD simulation setups for diamond-quartz contacts in air (a), water (b), and *n*-hexadecane (c) systems shown after energy minimisation and equilibration, before compression and sliding. Silicon atoms are shown in red, oxygen in blue, carbon in grey, and hydrogen in green. Rendered using OVITO.²⁸⁰

Figure 4.1 shows that in the air system (a), water forms a monolayer on the α -quartz surface. For the water system (b), a multilayer forms, which completely immerses to contact interface. In the *n*-hexadecane system, water still forms a monolayer on the quartz surface, since the polar molecules have a stronger affinity to the surface than the non-polar alkane molecules.³⁵³ The *n*-hexadecane molecules adsorb mostly on the diamond tip to maximise the van der Waals interactions. Budi et al³⁵³ noted through DFT studies that polar molecules that hydrogen-bond (water) adsorb more

strongly than molecules that adsorb through only dispersion forces (hexadecane) on mineral (α -quartz) surfaces. Maximisation of adsorbed species on each respective surface significantly reduces the entropy of the system and therefore minimises the energy. It was also reported that when measured experimentally, there is a reduced entropy contribution due to differing adsorption geometries.

Simulation Details

We performed NEMD simulations using the large atomic/molecular massively parallel simulator (LAMMPS) software package.²⁷² We used the velocity-Verlet integration algorithm³⁰³ with a time step of 0.25 fs. The bottom atomic layer of the substrate was frozen, and periodic boundary conditions were applied in the x - and y -directions. The temperature was maintained at 300 K using a Langevin thermostat with a coupling time of 25 fs. The thermostat was only applied to the central layers (in the z -direction) of the tip and substrate, as shown in Figure 4.1. A reflective boundary was added in the xy -plane at the top of the simulation cell to prevent desorbed species from escaping.

The systems were energy minimised, before being equilibrated at 300 K for 0.1 ns. During the equilibration, a constant normal force ($F_n = 1$ nN) was added to the outer layer of atoms in the tip to bring it in contact with the substrate. The normal force was then increased to the target value ($F_n = 5$ – 40 nN) and a sliding velocity was added to the outer layer of tip atoms in the x -direction ($v_s = 10$ m s⁻¹). This resulted in maximum Hertz pressures in the range $P_{\max} = 1.85$ – 2.85 GPa. Our previous investigation of diamond-quartz contacts¹ showed that there was negligible difference in the change in friction force with sliding velocities between 1 m s⁻¹ and 10 m s⁻¹. The sliding simulations were performed for 1.5 ns, which was sufficient for the friction force and number of interfacial bonds to reach a steady state. Chemical bonding information was output every 1.0 ps, using a bond order cutoff of 0.3 to identify covalent bonds.²⁸² The choice of bond order cutoff

only affects the post-processing analysis and does not influence the ReaxFF energy or force calculations.^{290,304}

ReaxFF Parameters

ReaxFF is a bond order-based forcefield that was developed by van Duin et al.¹⁹³ to investigate hydrocarbon reactivity. The version of ReaxFF implemented in LAMMPS uses the functional form that was originally outlined by Chenoweth et al.²⁸² and was fully described by Aktulga et al.²⁸³. The point charges on the atoms vary dynamically during the NEMD simulations and are calculated using the charge equilibration (Qeq) method.^{196,283,284}

For the α -quartz {0001} surfaces, we use the Si/O/H/C ReaxFF parameters developed by Newsome et al.²⁰⁶ to study the oxidation of silicon carbide by oxygen and water. The forcefield combines previously derived ReaxFF descriptions for hydrocarbon oxidation²⁸² and silicon/silicon oxides.^{286,287} Previous quantum mechanics data for Si/C, Si/O, Si/Si, and Si/H were also included for the silicon,²⁸⁵ silicon oxide,²⁸⁶ and poly-dimethylsiloxane ReaxFF applications.²⁸⁸ Newsome then formulated data outlining the equation of state and heat of formation of the silicon carbide crystal, in the diamond configuration, while including DFT data by Wang et al.³⁵⁴ Additionally, the Newsome calculated Si-C bond lengths, Si-C-O bond angles, and C-Si-O angle parameters using previous first principles calculations and ReaxFF data, the forcefield was not only applicable to silicon carbide materials, but also to silicon oxides, diamond, and graphite, since it also contained parameters described previously.³⁵⁵ The Newsome forcefield has been recently employed by Bhati et al.²⁰⁷ to identify adhesion properties of Si/polymer interfaces, Hilbert et al.²⁰⁸ to investigate how Si doping enhances thermal stability of diamond-like carbon, Vashisth et al.²⁰⁹ who combined atomistic and continuum methods to study how temperature influences interfacial fracture in SiC/SiO₂ composites, as well as several others. The forcefield required no additional parameterisation.

4.3. Results and Discussion

Tribometer Experiments

We investigated the variation in the friction force, F_F , with normal force, F_N , using macroscale tribometer experiments (Figure 4.2) with diamond-granite contacts in air (purple), water (green), and hexadecane (red) environments. For all three systems, F_F increases linearly with F_N with a near-zero intercept. This is consistent with Amontons' friction equation, which states that the coefficient of friction (COF), $\mu = F_F/F_N$. The near-zero intercept suggests that there is minimal adhesion between the tip and rock substrate. Since the real contact area increases linearly with F_N between randomly rough surfaces,²¹² this linear dependence of F_F on F_N expected in most macroscale contacts. The linear fits in Figure 4.2 yield $\mu = 0.15$, 0.15, and 0.36 for the air, water-, and *n*-hexadecane-lubricated contacts, respectively. There was no noticeable difference in the size of the wear scar on the granite wear scar between the three lubricants. This implies that *n*-hexadecane significantly increases friction compared to water and air. Similar friction behaviour was found at sliding velocities, v_s , ranging from 0.125 m s⁻¹ to 0.150 m s⁻¹, as shown in the Supporting Information (Appendix B Figure 1 and Appendix B Figure 2). Unlike other rocks, such as limestone,¹ minimal granite residue was found to have adhered to the diamond tip following the tribometer experiments.

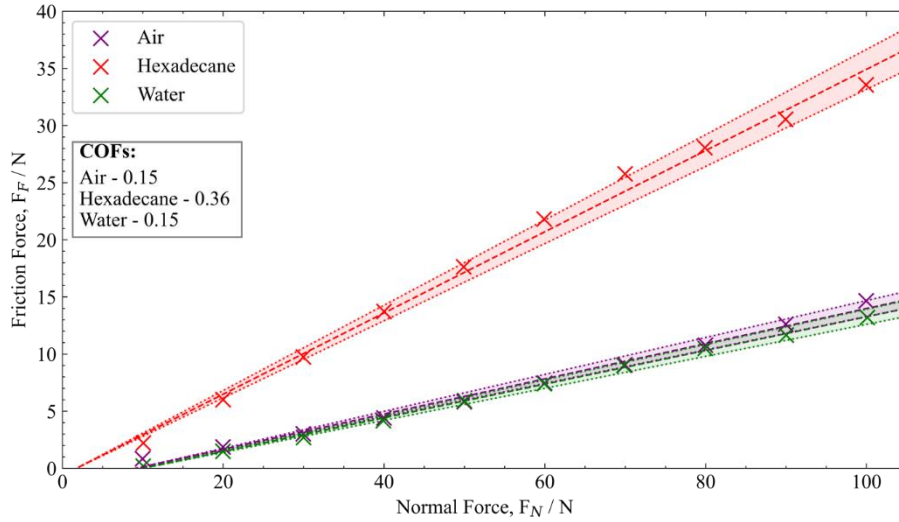


Figure 4.2. Variation in the friction force, F_F , with normal force, F_N , from the macroscale tribometer experiments with air (purple), water- (green), and hexadecane-lubricated (red) diamond–granite contacts. Normal forces, F_N , are between 10 and 100 N and tangential velocity, $v = 0.125 \text{ m s}^{-1}$. Dashed lines are linear fits to Amontons’ friction equation. Dotted lines represent 95% confidence intervals. Performed by Eliah M. Everhard.

Previous experiments of diamond-rock contacts have shown similar friction coefficients for formulated oil-based drilling fluids and water-based drilling fluids.^{337,338} However, at an equivalent normal stress, Smith et al.³³⁸ noted that the friction coefficient for a PDC cutter on shale rock was consistently higher in oil than in water. This finding refuted the common perception that oil lubricates the bit relative to the cuttings and the hole more effectively than water.³³⁸ Despite these findings, a recent review on the topic have suggested that oil-based drilling fluids give superior tribological performance.³³¹ While this may be the case when lubricating steel-steel and steel-rock contacts,^{334,335} which are representative of the drillstring-rock/casing interface, the results presented by Smith et al.³³⁸ and those shown in Figure 4.2 strongly suggests that oil-based drilling fluids give inferior performance than water-based drilling fluids at the cutter-rock interface.

One aspect that has not been considered in the current study is the effects of the various additives present in oil-based and water-based drilling fluids.³²⁶ Many of these additives are surface active, and thus they may affect the relative tribological performance, even if they are not added to explicitly reduce friction. The potential effects of surfactants on rock friction have been discussed by Reh binder¹¹⁹ and Mills and Westwood.¹²¹ Therefore, it is recommended that future work compares the friction coefficient of fully-formulated oil-based and water-based drilling fluids on a wide range of rock types to definitively establish which type of fluid gives the best tribological performance.

NEMD Simulations

To understand the unexpected results from the tribometer experiments, we performed NEMD simulations to study the atomistic behaviour at the sliding diamond-quartz interface.

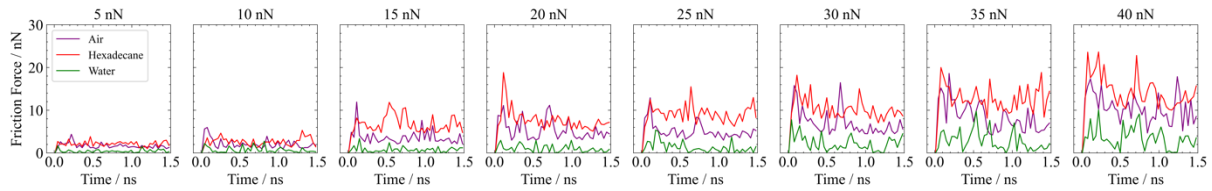


Figure 4.3. Variation in friction force, F_F , with sliding time from the NEMD simulations for the air (purple), water- (green), and hexadecane-lubricated (red) contacts for normal forces, F_N , between 5 and 40 nN and sliding velocity, $v_s = 10 \text{ m s}^{-1}$.

Figure 4.3 shows how the friction force, F_F , changes with sliding time in the NEMD simulations. The friction force generally increases rapidly at short sliding times ($< 0.25 \text{ ns}$) before reaching a steady state. There is some oscillatory behaviour around the steady state value, which is indicative of stick-slip. NEMD simulations of silica-silica interfaces²⁶⁴ and AFM experiments of SiO_2 -rich rocks⁸⁷ also showed stick-slip behaviour. The NEMD simulations revealed that stick-slip was caused by collective rupture of interfacial bonds causing an instantaneous interface slip.²⁶⁴ Longer

simulations for a subset of the systems and conditions revealed that there is no further change to the mean friction force with longer sliding times. Steady-state friction force values from this point refer to friction force averages over the last 0.5 ns of sliding. All systems and conditions display stick-slip behaviour, some more than others. The *n*-hexadecane and air simulations display the clearest stick-slip behaviour, which becomes more prominent at higher loads (> 30 nN).

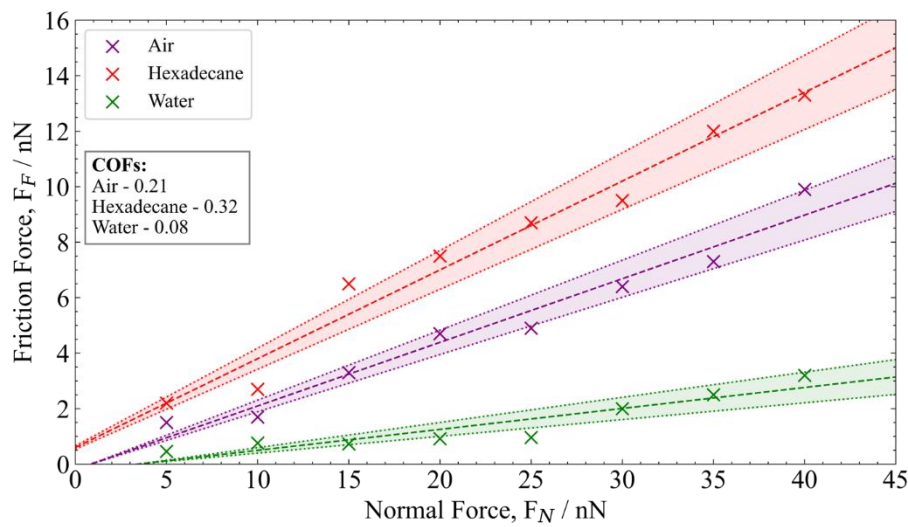


Figure 4.4. Variation in friction force, F_F , with normal force, F_N , from the NEMD simulations for the air (purple), water- (green), and hexadecane-lubricated (red) contacts. Mean forces calculated during the final 500 ps of sliding. Dashed lines are fits to Amontons' friction equation. Dotted lines represent 95% confidence intervals.

Figure 4.4 shows that F_F increases approximately linearly as a function of F_N in all the NEMD simulations, which is in agreement with the experimental data (Figure 4.2) and is consistent with Amontons' equation.^{210,212} For the idealised point contact used in our simulations, Hertz theory^{212,225} predicts that $F_F \propto F_N^{2/3}$. However, the linear relationship between F_F and F_N suggests that the interfacial shear strength behaves as a direct function of pressure, which we attribute to interfacial bond formation across the interfaces. At low loads (< 20 nN), the air and *n*-hexadecane-

lubricated contacts show a superlinear increase of F_F with F_N , which can be described using stress-assisted interfacial bonding.³⁰⁶ The water-lubricated contact shows an almost direct linear relationship between F_F and F_N , suggesting that in this system, interfacial bonding is less prolific when compared with the air and hexadecane-lubricated contacts. Single-asperity AFM friction measurements by Li et al.⁸⁷ of silica-silica contacts, where interfacial bonding occurs, has shown both linear³⁰⁹ and superlinear³⁰⁷ increases of F_F with F_N , depending on the lubricating fluid.

Figure 4.4 shows that the friction coefficient calculated using the Amontons' equation is highest for the *n*-hexadecane-lubricated system ($\mu = 0.33$), followed by air ($\mu = 0.22$), and finally water ($\mu = 0.08$). This is the same trend observed experimentally in Figure 4.2. For the *n*-hexadecane-lubricated system, the slight positive intercept suggests that there is some adhesion between the tip and substrate (while a negative intercept can be interpreted as repulsion, this is unlikely and an unphysical phenomenon due to limited quality of the fit in the low load region).²¹² Previous experiments have shown that friction coefficients of granite,³⁰⁵ quartzite,³⁰⁵ silicon,³¹⁰ and nanocrystalline diamond³¹¹ are heavily dependent on the amount of water present within the contact. In general, with increasing levels of humidity, there is a decrease in the friction coefficient. First-principles NEMD simulations have also shown that the presence of water molecules at the silica-silica³¹² and silica-diamond³⁵⁶ interfaces significantly reduces friction by suppressing interfacial bond formation. For *n*-hexadecane-lubricated mica-diamond contacts in AFM experiments, Cafolla et al.³⁵⁷ found that the formation of water nanodroplets can lead to significantly increased friction. Due to the relatively large size of the water nanodroplets (20-50 nm), this effect is not considered in the current NEMD simulations.

The indentation depths in both the tribometer experiments and NEMD simulations were minimized to ensure that friction was dominated by interfacial interactions rather than ploughing. Previous NEMD simulations of diamond-quartz contacts¹ show at these contact pressures,

indentation depths are always below 3 Å. This is also the case for the current simulations, as shown in the Supplementary Information (Appendix B Figure 3). Bowden and Tabor³¹⁶ proposed a geometrical argument implying that higher friction coefficients are expected at deeper indentation depths due to larger ploughing contributions. Quartz has a relatively large hardness (~ 15 GPa)³¹⁵ and comparisons of how load-dependent friction behaves as a function of indentation depth compared with the Bowden-Tabor prediction illustrated that there was a minimal ploughing contribution to friction in the NEMD simulations of diamond-quartz contacts.¹ Previous experiments by MacMillan et al.³⁴⁰ showed that the friction of diamond-magnesium oxide contacts was higher in *n*-hexadecane than water, which they attributed to ‘softening’ of the surface. A lower hardness would imply a greater indentation depth for *n*-hexadecane than water, which is consistent with the observations in the current NEMD simulation results show in Supporting Information. (Appendix B Figure 4). The water-lubricated system has a much lower indentation depth than the other two systems; however, the *n*-hexadecane system only has a slightly larger indentation depth. This is probably insufficient to explain the large difference in friction between the air and *n*-hexadecane-lubricated systems in the NEMD simulations.

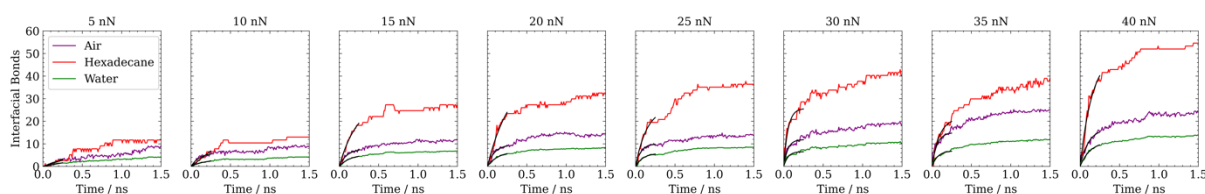


Figure 4.5. Variation in the total number of interfacial bonds between the tip and the surface during sliding for the air (purple), water- (green), and *n*-hexadecane-lubricated (red) contacts across $F_N = 5$ nN to 40 nN. Black dashed lines are fits to the first 250 ps of interfacial bond formation data assuming first-order reactions used to calculate initial rates.

To uncover why each system displayed differing friction behaviour in the NEMD simulations and tribometer experiments, we quantified the total interfacial bond formation, as shown in Figure 4.5.

Since some interfacial bonds are also broken during sliding, we also show the number of interfacial bonds formed and ruptured separately in the Supporting Information (Appendix B Figure 5). The model proposed by Filippov et al.⁸⁶ suggests that during sliding, interfacial bonds continuously form and rupture, such that, as a particular interfacial bond ruptures, the force experienced by the other bonds increases, resulting in synchronised bond formation and rupture. This dynamic behaviour of continual formation and breakage of interfacial bonds results in oscillations in the friction force, which can be seen as stick-slip behaviour (Figure 4.3). Since the oscillations in the friction force are more pronounced than they are for the interfacial bonds (Figure 4.5) as a function of sliding time, the cooperative formation and breakage of interfacial bonds can be assumed to be spatially localized at the leading and trailing edge of the asperity, respectively.³¹⁴ Additionally, the formation and breakage are not temporally synchronised, therefore, the fluctuations in the number of interfacial bonds during sliding are minimal.¹

For all the simulated loads, the number of interfacial bonds is greatest for the *n*-hexadecane-lubricated system, which results in more pronounced stick-slip behaviour (Figure 4.3), followed by the air system, and finally, with the water-lubricated system showing the lowest number of interfacial bonds. The steady-state number of interfacial bonds in the *n*-hexadecane-lubricated and air systems increases with increasing load, which could explain why the F_F increases proportionally with F_N (Figure 4.3), resulting in higher friction coefficients (Figure 4.4). This is also true for the water-lubricated contact; however, at low loads (< 25 nN) the steady-state number of interfacial bonds remains fairly consistent, and only increases proportionally at loads > 25 nN. Not only can the larger number of interfacial bonds in the *n*-hexadecane-lubricated contact provide reasoning for the higher friction coefficients in Figure 4.4, but it can also explain the observations made in the tribometer experiments (Figure 4.2). Previous NEMD simulations with ReaxFF by Yeon et al.²⁰³ have shown that when a sufficient number of water molecules to form a complete monolayer were added between hydroxylated amorphous silica and oxidized silicon interfaces, the amount of

atom transfer was reduced significantly. It was found that water passivated the sliding interface where potential reactive sites become terminated with hydroxyl groups and can no longer form interfacial bonds. Additionally, further ReaxFF simulations by Wang et al.³¹⁸ found that an increase in hydroxyl group density reduced the friction between silica surfaces. Likewise, OH and H passivation of diamond as a result of dissociative adsorption of water molecules keeps the sliding surfaces far apart, which prevents the formation of interfacial bonds.³¹¹ Li et al.²⁶⁴ also showed using NEMD and ReaxFF that an increasing number of interfacial bonds in dry silica-silica contacts results in higher friction.

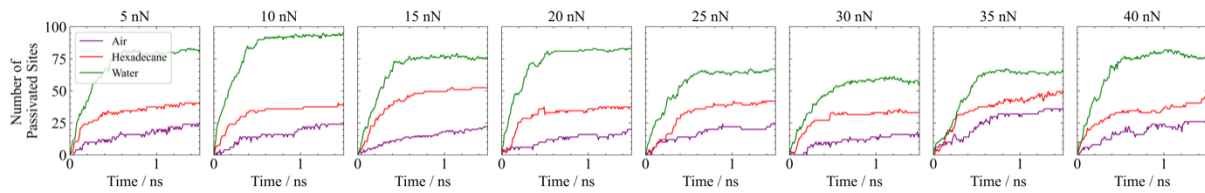


Figure 4.6. Variation in the total number of passivated surface sites between the tip and substrate during sliding for the air (purple), water- (green), and hexadecane-lubricated (red) contacts across $F_N = 5$ nN to 40 nN.

Figure 4.6 shows how the number of passivated surface sites between the tip and substrate changes as a function of time. For each simulated load, the number of passivated sites for the water-lubricated is highest, followed by the *n*-hexadecane and finally the air system. For all systems, across all loads, the number of passivated sites reaches a steady state after approximately 500 ps and remains fairly constant across the load range simulated. This suggests that water dissociation and the passivation of surface sites occurs via a spontaneous dissociative adsorption mechanism as described by Bouchet et al.³¹¹ These sites are potential interfacial bonding sites, Si and O atoms in the substrate, which are passivated to become Si-OH/Si-H and O-H, and C atoms in the tip, which are passivated to become C-OH/C-H, by dissociation of water molecules. Hydroxyl groups have been shown to form covalent bonds with silica surfaces, and when they reach a sufficiently

high level, silica surfaces have a tendency to show hydrophilic properties and form surface hydroxyls.³⁵⁸ Additionally, diamond has also been known to become OH and H passivated when exposed to water.³¹¹ In Figure 4.5, the dominating interfacial bond is direct $C_{\text{tip}}-O_{\text{substrate}}$ bonding, negligible $C_{\text{tip}}-\text{Si}_{\text{substrate}}$ and interfacial-bridging bonds¹ are found to occur.

We have previously shown that in diamond-quartz contacts, water molecule dissociation is heavily dependent on the applied load and can be considered as a stress-augmented thermally activated (SATA) process.¹⁵⁴ This suggests that the increased presence of water molecules results in a higher degree of interface passivation, which leads to less interfacial bonding, and ultimately reduced friction.^{86,212,311} It is also interesting to note the differences between the *n*-hexadecane-lubricated contact and the air system. Even though these two systems contain the same number of water molecules (100), the degree of passivation is considerably different. It can be concluded that the presence of hexadecane hinders the ability of water to dissociate and passivate each surface. Water and hexadecane have previously been shown to compete for binding sites on mica (silicate) interfaces.³⁵⁷

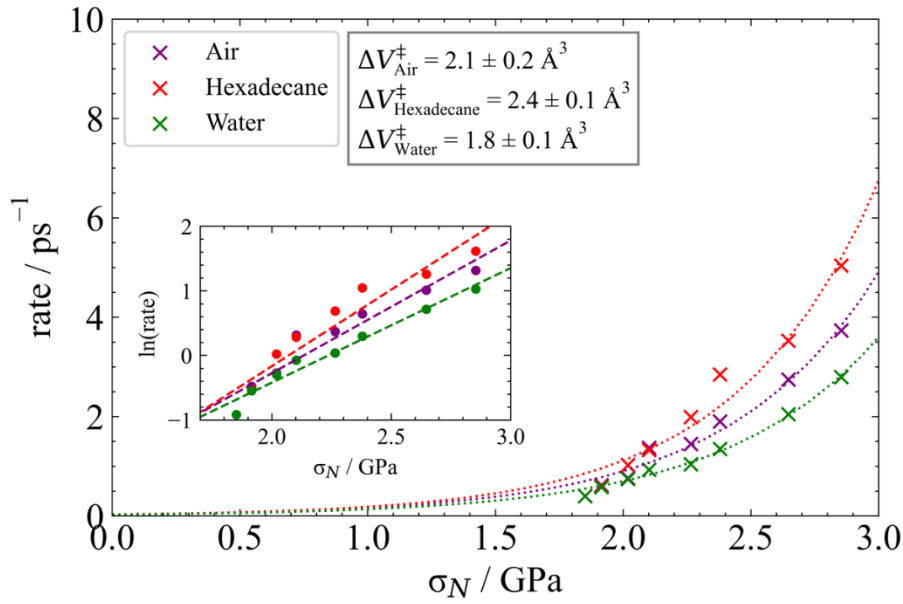


Figure 4.7. Change in the rate of interfacial bond formation with maximum Hertz pressure for air (purple), water- (green), and hexadecane-lubricated (red) contacts. Inset shows a linear increase in $\ln(\text{rate})$ with Hertz pressure. Dashed lines are fits to Equation 4.1.

The rate of interfacial bonding in all systems increases with load, suggesting that this is a SATA process.¹⁵⁴ The activation energy in SATA process is reduced with the application of stress, thus:

$$k = A \exp\left(-\frac{E_a - N\sigma\Delta V^\ddagger}{RT}\right) \quad (4.1)$$

where A is a prefactor, E_a is the activation energy, N is Avogadro's number, σ is the applied stress, $\Delta V^\ddagger$ the activation volume, R the universal gas constant, and T is the absolute temperature.¹⁵⁴ Equation 1 implies exponential growth in the rate with increased applied stress,¹⁵⁴ as seen in Figure 4.7. The stress dependence can be used to determine $\Delta V^\ddagger$. As in our previous study, we use the normal stress in Equation 1, rather than the shear stress.¹

For single-asperity Hertz contacts, the contact area, $\mathcal{A}_c$, is expected to increase with load as $\mathcal{A}_c \propto F_N^{2/3}$, although previous NEMD simulations have suggested that the real contact area, $A_{\text{real}} \propto F_N$.²¹² A higher contact area means that more atoms are close enough to participate in interfacial bonding. Some previous single-asperity studies of SATA processes have normalized the reaction rates by the number of atoms in contact,²⁴⁴ while others have not.³²⁰ The rates of interfacial bond formation are calculated over the first 250 ps of sliding (dashed lines in Figure 4.5), where the indentation depth (and thus contact area) is very similar for all of the systems and conditions studied.¹ Moreover, during steady-state sliding, the variation in contact area with load is much smaller than that predicted using the Hertz equation for diamond–quartz contacts.¹ This is because of the microhardness values used in the Hertz calculations,³¹⁵ whereas the indentation depths in the NEMD simulations are always less than 1 Å.¹ It is known for many materials that hardness decreases markedly with increasing indentation depth over the first few nanometres.³²¹ For these reasons, we do not normalize the rates shown in Figure 4.7 by the contact area. Additionally, since there is minimal wear and adhesion of the tip (Figure 4.2), we apply Hertzian contact mechanics to calculate the normal stress inside the contact. The corresponding figure, where contact stress is calculated as a function of the number of atoms in contact based on the number of interfacial bonds is shown in the Supporting Information (Appendix B Figure 6). In this method, the projected area is calculated by multiplying the lattice constant for diamond with our ReaxFF parameterisation (0.362 nm)³⁵⁹ by the number of atoms in contact.²³⁵ This method is known to result in contact pressures significantly higher than those calculated using Hertz theory.²³⁸

From Figure 4.7, the rate of interfacial bonds in the *n*-hexadecane-lubricated system is highest, followed by the air systems, and finally, the water-lubricated system. From the fits to Equation 1, Figure 4.7 yields activation volumes of $2.1 \pm 0.2 \text{ Å}^3$, $2.4 \pm 0.1 \text{ Å}^3$, and $1.8 \pm 0.1 \text{ Å}^3$, for the air, *n*-hexadecane, and water systems, respectively. These values are consistent with single-atom dimensions²⁴⁴ and are similar to what we previously reported for water-lubricated diamond-quartz

contacts.¹ This implies that the stress-dependence of interfacial bond formation is highest for the *n*-hexadecane-lubricated system. If using the atoms in contact method described above, Appendix B Figure 6 yields activation volumes of $0.52 \pm 0.04 \text{ \AA}^3$, $0.55 \pm 0.02 \text{ \AA}^3$, and $0.47 \pm 0.04 \text{ \AA}^3$, for the air, *n*-hexadecane, and water system, respectively.

Si-O interfacial bonds in aqueous silica-silica contacts have been shown to increase friction in previous ReaxFF²⁰¹ NEMD and first-principles³¹² NEMD simulations. Additionally, C-O and C-Si bonds have been shown to form at pressures of 5 GPa and sliding velocities equal to 100 m s^{-1} in DFTB studies.⁶² Even though our simulations produce no C-Si interfacial bonds, previous MD simulations have shown them to exist at the interface between a silicon tip and a partially hydrogenated diamond substrate at high pressure.³²⁵ Above we have shown that hexadecane-lubricated diamond-quartz contacts display significantly higher friction coefficients than water-lubricated contacts. We believe this to be due to water being able to passivate potential bonding sites between the tip and/or asperity with terminal OH/H groups, which prevents interfacial bonding, and subsequently reduces friction.

Figure 4.8 shows the steady-state number of interfacial bonds that form in the three systems across the load range studied. The steady-state number of interfacial bonds increases with load for all of the systems studied. The number of interfacial bonds is greatest for the *n*-hexadecane system, followed by air, and finally water. For the air system, most of the interfacial bonds are direct C-O bonds between the tip and the substrate. For the *n*-hexadecane and water systems, a significant proportion of the bonds are C-H-O hydrogen bonds from H atoms from dissociated water or *n*-hexadecane molecules. These C-H-O bonds will be much weaker than the direct C-O bonds. For all of the systems, some C-O-Si bonds form from oxygen atoms from dissociated water molecules, which will have equal strength to the direct C-O bonds.

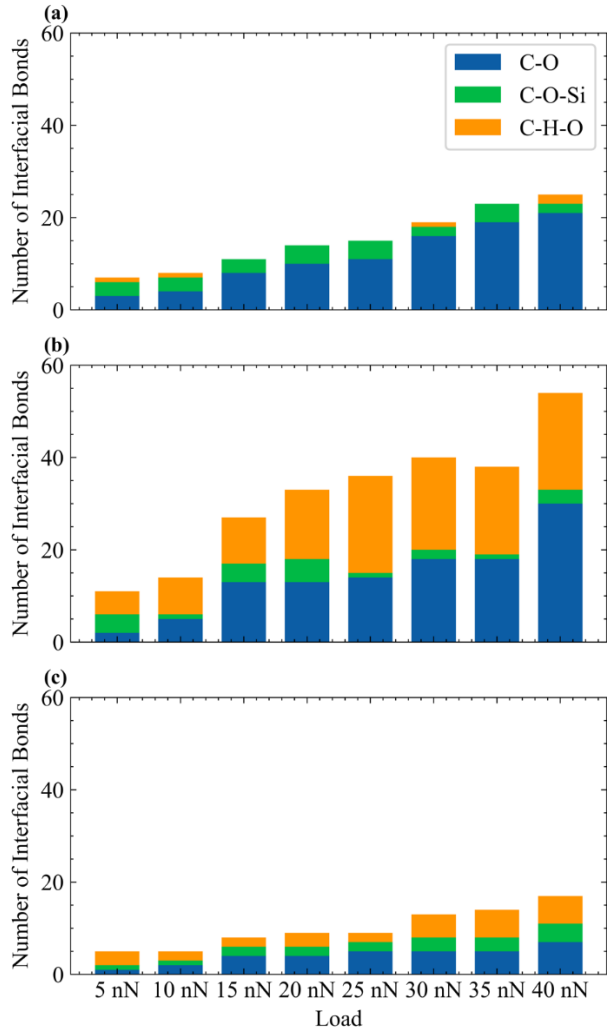


Figure 4.8. Number and type of interfacial bonds (C-O, C-O-Si or C-H-O) formed for each simulated load for the (a) air-, (b) *n*-hexadecane-, and (c) water-lubricated system.

Figure 4.9 shows the mean friction force as a function of the mean number of interfacial bonds during steady-state sliding. Consistent with both the friction model by Filippov et al.⁸⁶ and the NEMD simulations by Mo et al.²¹², all three systems show that the friction force has a linear dependence on the total number of interfacial bonds. The gradients of each line indicate the relative strength of each interfacial bond and the amount of mechanical energy required to break each bond. The slope in the air system is the steepest, since it has the lowest proportion of C-H-O bonds.

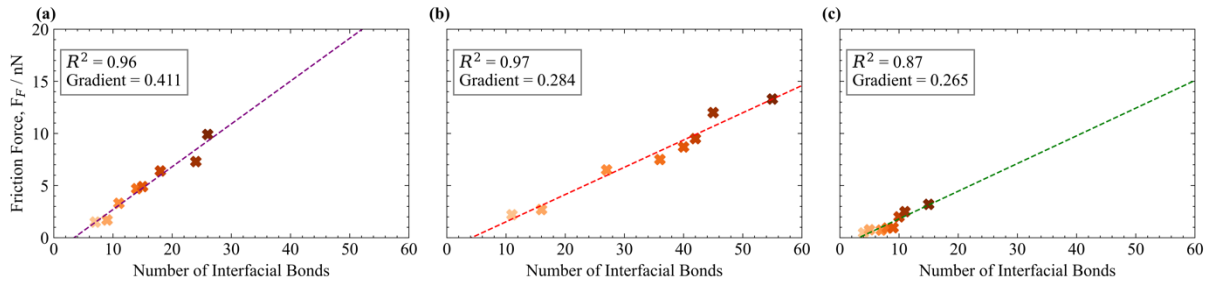


Figure 4.9. Correlation between the mean friction force and the mean number of interfacial bonds during steady-state sliding for (a) air, (b) hexadecane, and (c) water systems. Darker colours indicate higher loads.

4.4. Conclusion

In this study, we have performed macroscale tribometer experiments that have revealed that for diamond-granite interfaces, an *n*-hexadecane-lubricated contact displays unexpectedly high friction compared to air- and water-lubricated contacts. This implies that oil-based drilling fluids give poorer tribological performance at the cutter-rock contact than water-based ones. Using ReaxFF NEMD simulations of a single-crystal diamond tip sliding on α -quartz, we show the same trend in increasing friction from water-, to air-, and *n*-hexadecane-lubricated systems. The simulations suggest that the difference in friction between these systems is due to two factors: i) the indentation depth and ii) the degree of interfacial bonding. The indentation depth was much lower for the water-lubricated system, followed by air, and finally *n*-hexadecane. This suggests that *n*-hexadecane reduced the hardness of the α -quartz surface, unlike surfactants, which were shown to increase the hardness of the rock surface by Mills and Westwood.¹²¹ This has been reported previously in the microscratching of magnesium oxide with diamond asperities, where *n*-hexadecane lubricated substrates resulted in higher friction coefficients than water.³⁴⁰ Westwood et al.³⁴¹ attributed this to the promotion of near-surface dislocation mobility by magnesium oxide in *n*-hexadecane compared to water. However, for most interfaces, such as zirconia-zirconia,³⁴² silicon nitride-silicon nitride,³⁴³ and silicon-silicon,³⁴⁴ *n*-hexadecane results in significantly lower friction than

water. Similar comparisons for a range of ceramic-ceramic, ceramic-steel, and steel-steel contacts also showed that mineral oil was a better lubricant than water.³⁴⁵ Hence, oil-based drilling fluids are commonly used to reduce friction between the cutter and rock, and thus increase drilling efficiency.³³⁰ These findings are contradictory to the results from our experiments and simulations that suggest water is a better friction-reducing lubricant than *n*-hexadecane. The *n*-hexadecane system also had the highest number of interfacial bonds, followed by the air environment, and finally water with the lowest. The rate of interfacial bond formation increases exponentially with pressure for all of the systems, which is indicative of a SATA process. The activation volume is similar for all of the systems, implying a similar stress-dependence of interfacial bonding. The simulations reveal that water molecules passivate potential sites of interfacial bond formation with either hydroxyl or hydride groups on the sliding surfaces. Even though the air and hexadecane systems have an equal number of water molecules present, there are significantly fewer passivated sites in the *n*-hexadecane system, resulting in increased interfacial bond formation, and subsequently increased friction. Finally, we show that for each system, the mean friction force is linearly dependent on the mean number of interfacial bonds during steady-state sliding. We expect these findings will be useful to design new drilling fluid formulations that minimize bit-rock interfacial bonding and subsequently friction.

Chapter 5: Atomic-Scale Wear Inside Diamond-Quartz Contacts

Herein this chapter contains work submitted to *Applied Surface Science*. At the time of writing, work from this chapter is currently under review.

5.1. Introduction

Wear mitigation is critical for the long-term reliability, safety, and efficiency of devices containing moving components,³⁶⁰ from artificial hip joints³⁶¹ to automotive engines.²⁵⁰ In most tribological systems, material removal occurs mainly through abrasive wear.³⁰ The physical and chemical processes leading to wear at sliding interfaces remain quite poorly understood, so the process is usually described empirically.³⁶² Developed almost seven decades ago, the Archard equation⁴¹ remains the most popular model for abrasive wear inside macroscale contacts.⁴² It states that:

$$V = (K_b F_{\text{z}} d) / H \quad (5.1)$$

where V is the wear volume, K_b is the wear coefficient, F_{z} is the load, d is the sliding distance, and H is the material hardness. In tribological systems that follow the Archard equation, wear is thus proportional to F_{z} and d and inversely proportional to H . The equation was derived from a simplistic physical picture of wear involving plastic deformation of contacting asperities. A large number of experiments are usually required to obtain the wear coefficient, K_b , which hinders the development of low-wear materials.²⁵⁸

The lack of predictive models for wear and advances in the field of nanotechnology have motivated the detailed study of wear at the atomic level. Several atomic force microscopy (AFM) studies have

shown that nanoscale wear cannot be adequately explained using the Archard equation.^{247,248} Instead, atom-by-atom attrition occurs, which can be described by a stress-augmented thermally activated (SATA) model.^{149,244} In such processes, the wear rate increases exponentially with temperature and applied stress. A non-empirical model for atom-by-atom attrition in nanoscale contacts has also recently been proposed by Wang et al.²⁵⁸ based on quantities that can be directly obtained from nonequilibrium molecular dynamics (NEMD) simulations. This SATA-based model has been successfully applied to describe the wear of diamond-like-carbon (DLC) contacts in NEMD simulations.²⁵⁸ Another set of NEMD simulations suggested that, in addition to atom-by-atom attrition, cluster detachment via tail fracture also contributes to wear in DLC contacts, particularly at high loads.²⁵⁹ These simulations also found that wear increased linearly with normal load and sliding distance,²⁵⁹ which is consistent with the Archard model, but not SATA-based models.⁴¹ Recent nanoscale AFM experiments investigating the wear of DLC-coated tips on DLC substrates have shown that the SATA wear model can also break down under certain conditions.³⁶³ While at low loads, the stress dependence of the wear rate could be described using a SATA model, at higher loads, the wear rate was lower than predicted and eventually levelled out to a constant value. At high loads, wear was essentially proportional to the sliding distance and independent of the normal stress. In rough elastic contacts, where contact area grows linearly with normal load,²¹² this leads to behavior very similar to that described by the Archard equation. Both of these types of wear behaviour were successfully fitted using a multibond model of single-asperity wear developed by Shao et al.,²⁵⁷ which was based on the multibond friction model due to Filippov et al.⁸⁶ that describes friction through the formation and rupture of interfacial bonds. The multibond wear model considers the effects of three competing SATA processes that determine interfacial bond formation, wearless rupture, and the transfer of atoms (i.e. wear).²⁵⁷

A detailed understanding of the wear of diamond and other carbon-based materials is important due to their widespread use in high-performance cutting tools.³⁶⁴ For example, synthetic

polycrystalline diamond compact (PDC) drill bits²⁰ revolutionised the rock drilling industry due to their wide application range, high rate of penetration (ROP), and extended bit life.²¹ Accurate prediction of PDC wear is crucial for reducing the number of bit replacements, lowering rig downtime and the large associated economic costs.³⁶⁵ From the analysis of drilling experiments on a wide range of rock types, Ersoy and Waller concluded that the majority of damage to PDC bits was due to abrasive wear.⁴⁰ Consequently, the Archard equation⁴¹ has frequently been used to model the abrasive wear of PDC bits.^{43–45} The hardness of the polycrystalline diamond (PCD) used in PDC bits is at least 55 GPa.²⁷ Operationally, drill bits move through many different types of rocks that have varied and heterogenous mechanical properties. The mean hardness of calcite-rich rocks (e.g. limestone) is only around 2 GPa, while for quartz-rich rocks (e.g. granite) it is between 9-15 GPa.^{27,48} Since these rocks are much softer than PCD under ambient or typical wellbore temperatures ($< 300\text{ }^{\circ}\text{C}$), low abrasive wear rates are expected from the Archard model⁴¹ for PDCs. However, inside the contact, where local cutting temperatures can exceed $750\text{ }^{\circ}\text{C}$,³⁶⁶ where the effective hardness of PCD can be reduced to below that of granite.⁴⁹ Under these accommodating conditions, PDCs are more susceptible to abrasive wear while cutting through granite.⁵⁰ Higher PDC wear rates have been observed for granite than limestone,⁴⁰ as predicted by the Archard model. Indeed, the lifetime of diamond drill bits is generally reduced for rocks with a higher equivalent quartz content.⁴⁶ In addition to their high hardness, there may also be a tribochemical component to the high wear rates observed for quartz-rich rocks. It is well known that diamond can be polished with relatively soft silica particles, with the tribochemical mechanism believed to involve the formation of strong C-O bonds across the diamond-silica interface.⁶¹ This hypothesis was recently confirmed by first-principles calculations.⁶² Previous experimental studies have also shown that diamond tools exhibit significant wear for the machining of silicon,³⁶⁷ which will form an oxide outer layer when exposed to air. High wear rates have also been observed for diamond tools cutting through soda lime glass,³⁶⁸ whose primary constituent is silica. Significant wear of diamond AFM tips sliding on silicon surfaces has also been observed.³⁶⁹ However, it is not yet

clear to what extent tribochemical wear increases the wear of diamond sliding on crystalline α -quartz surfaces.

In this study, we use NEMD simulations to explore the wear of nanoscale diamond-quartz contacts under high temperature and pressure conditions, which are representative of those experienced during rock drilling. In order to incorporate the effects of interfacial bonding, we employ the reactive force field (ReaxFF) method.³⁵⁵ The computational cost of MD simulations with ReaxFF are several orders of magnitude lower than first-principle techniques, therefore allowing dynamic evolution of significantly larger systems over larger time scales to be explored.²⁶⁶ Unlike first-principles methods, ReaxFF requires careful parameterization to ensure validity of chemical reactivity and material properties. In recent years, ReaxFF parameters have been developed for studying a very broad range of systems and processes,¹⁹⁴ including a wide range of molecules confined between sliding surfaces to investigate tribochemical processes.²⁶⁷ In this study, using published ReaxFF parameters for silicon, oxygen, hydrogen, and carbon-containing systems,²⁰⁶ we are able to observe and quantify diamond wear in diamond-quartz contacts, which is initiated by the formation of interfacial bonds between the two surfaces. Using the multibond wear model,²⁵⁷ we can accurately describe the initial wear rate of the diamond tip at realistic bit-rock pressures (2-6 GPa). After the initial running-in period, wear increases approximately linearly with sliding distance and load, which is consistent with the Archard model.⁴¹ These new results complement our previous study that showed diamond-rock friction is governed by interfacial bonding.¹ Collectively, our NEMD simulation results suggest that reducing interfacial bonding could be an effective strategy for reducing both friction and wear during rock drilling.

5.2. Methodology

5.2.1. Simulation Setup

The mineral distributions in granite rocks display spatial heterogeneity, leading to location-dependent surface chemistry.²⁷¹ NEMD simulations paired with ReaxFF are restricted to the studying of nanoscale systems, due to the large computational cost.²⁶⁶ Therefore, α -quartz, the major constituent of granite,²⁷³ was used as a representative model for the rock substrate. The validity of this representation was confirmed in our previous study, where silicon and oxygen were confirmed as the major constituents of the transfer film formed on a diamond pin used in tribometer experiments on granite.¹ The α -quartz {0001}²⁷⁵ surface has been shown in previous density functional theory studies (DFT) to be the most thermodynamically stable, and therefore was therefore selected for this study. The x, y, z dimensions of the substrate were $13.7 \times 5.8 \times 3.7$ nm. The tip was modelled by a single-crystal diamond hemisphere with a radius of 2.5 nm.²⁰¹ The two systems used in the NEMD simulations (with and without water) are shown in Figure 5.1.

Quartz has been shown experimentally to be hygroscopic and expected to be saturated with a water monolayer in both atmospheric and aqueous environments.²⁷⁷ Consequently, as well as simulating dry surfaces, we also performed NEMD simulations with systems containing 500 water molecules. This was sufficient to fully saturate the α -quartz {0001} surface. Many of the water molecules chemisorbed to the surface during the equilibration phase. As predicted from previous DFT calculations, the chemisorbed water molecules on α -quartz {0001}²⁷⁹ spontaneously dissociate to form terminal hydroxy groups.

5.2.2. ReaxFF Parameters

ReaxFF is a bond order-based force field that was originally developed by van Duin et al.¹⁹³ to investigate the dissociation and reactivity of hydrocarbon molecules. We used the version of

ReaxFF implemented in the large atomic/molecular massively parallel simulator (LAMMPS) software.²⁷² The functional form of ReaxFF used in LAMMPS was outlined by Chenoweth et al.³⁷⁰ and fully described by Aktulga et al.²⁸³. The point charges on the atoms vary dynamically during the NEMD simulations and are calculated using the charge equilibration (Qeq) method.^{196,283,284}

We used the ReaxFF parameters developed by Newsome et al.²⁰⁶, which include Si/O/H/C interactions. This force field was originally developed to investigate the oxidation of silicon carbide by oxygen and water and included parameterizations developed from first-principles data for silicon,²⁸⁵ silicon oxides,^{286,287} and poly(dimethylsiloxane).²⁸⁸ These ReaxFF parameters predict a heat of formation of $-216 \text{ kcal mol}^{-1}$ for α -quartz, which is identical to the experimental value. Furthermore, the ReaxFF parameters predict a heat of formation for the SiC-diamond phase of $+8 \text{ kcal mol}^{-1}$, in reasonable agreement with the DFT value of $+14 \text{ kcal mol}^{-1}$. The parameters predict heats of formation for CO and CO₂ of -13 and $-88 \text{ kcal mol}^{-1}$, respectively, compared with -26 and $-94 \text{ kcal mol}^{-1}$ from experiment.²⁰⁶ Thus, the oxidation of the diamond tip is expected to be accurately modelled. The Young's modulus (1024 GPa) and lattice constant (0.362 nm) obtained using this parameter set are close to the experimental values (1065 GPa and 0.357 nm).³⁵⁹ The parameters have also been validated against first-principles methods for the interactions between silica surfaces and water molecules²⁸⁷ and experimental density and bulk moduli of α -quartz {0001}.²⁸⁶ These parameters have also been successfully applied to study adhesion and interfacial bonding in silicon-diamond³²⁵ and silica-graphene contacts,²⁸⁹ as well as the relationship between interfacial bonding and friction in dry and wet diamond-quartz contacts.¹ The parameters have also shown to satisfactorily reproduce the energy versus strain behaviour from first-principles calculations for C-C bond rupture in hydrocarbons.³⁷¹ In a recent comparison of the transferability of interatomic potentials for carbon, ReaxFF was recommended for large systems and long simulation times.³⁷² ReaxFF has also recently been applied to study the wear of DLC surfaces.^{258,373}

In summary, the chosen ReaxFF parameter set is deemed suitable for the study of the interfacial

C-O bond formation and C-C bond dissociation processes that govern the wear of diamond on quartz surfaces.

5.2.3. Simulation Details

Extreme temperatures (> 500 K) and pressures (> 200 MPa) are often encountered inside deep wells.³⁷⁴ During drilling, the local temperature (> 800 K) and pressure (> 1 GPa) conditions can be even more severe at the bit-rock interface.²⁷ These extreme conditions complicate the experimental investigation of the friction and wear of new drill bit materials on different rock types.²⁶⁸ Conversely, these extreme conditions can be directly studied using NEMD simulations. We performed NEMD coupled ReaxFF simulations using the LAMMPS software package.²⁷² We used the velocity-Verlet integration algorithm³⁷⁵ with a time step of 0.25 fs. The bottom atomic layer of the substrate was frozen and periodic boundary conditions were applied in the x - and y -directions. The temperature was maintained at temperatures ranging from 300-1800 K, depending on the system, using a Langevin thermostat¹⁷⁶ with a coupling time of 25 fs. The thermostat was selectively applied to the central layers (in the z -direction) of the tip and substrate, as shown in Figure 5.1. The thermostat was effective in maintaining the target temperature, even at the high applied sliding velocity (100 m s^{-1}). A reflective boundary was added in the xy -plane at the top of the simulation cell (10 nm above the top of the substrate) to prevent gaseous species from escaping the simulation box.

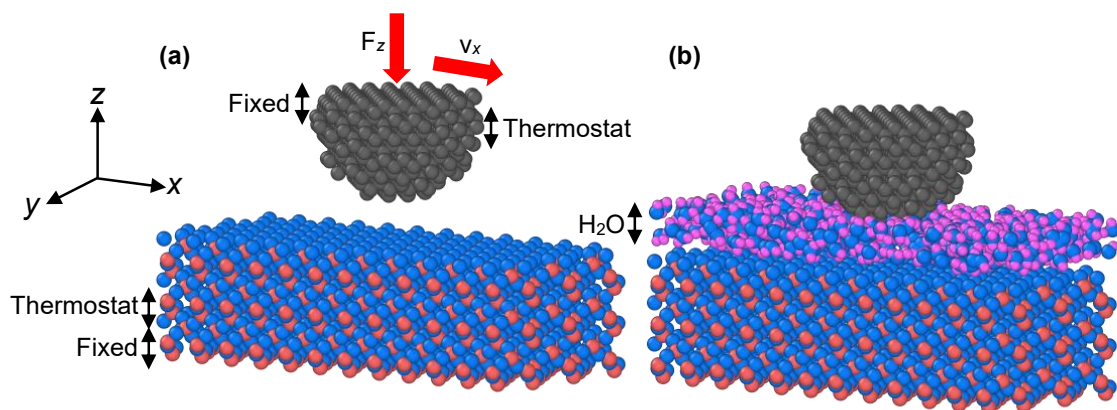


Figure 5.1: NEMD systems for the (a) dry and (b) wet (500 H₂O molecules) diamond-quartz systems before equilibration. Silicon atoms are shown in red, oxygen in blue, carbon in grey, and hydrogen in pink. Rendered using OVITO.²⁸⁰

The energy of the system was minimized using the conjugate gradient method, followed by equilibration at desired temperature (300-1800 K) for 0.1 ns. During the equilibration, a small constant normal force ($F_n = 1$ nN) was added to the top layer of atoms in the tip to bring it into contact with the substrate. The normal force was then increased to the target value ($F_n = 5-60$ nN) and a sliding velocity in the x -direction ($v_x = 100$ m s⁻¹) was added to the top layer of atoms in the tip instantaneously. The applied normal forces resulted in maximum Hertz pressure in the range $P_{\max} = 2.1-3.0$ GPa. Previous simulations have shown that atomic-scale roughness can mean that pressures are significantly underestimated by Hertz theory.²³⁹ Therefore, the contact pressures were determined based on the number of atoms in contact, which was quantified through the number of interfacial bonds formed.^{235,238} Here, the atoms are assumed to be spherical such that a circular projected area can be defined.²³⁵ The projected area is calculated by multiplying the lattice constant for diamond with our ReaxFF parameterisation (0.362 nm)³⁵⁹ by the number of atoms in contact.²³⁵ The number of atoms in contact is quantified through the number of interfacial bonds, since previous investigations have shown that this definition correlates well with friction.²³⁸ The atoms in contact method resulted in consistently higher pressures than with Hertz theory, in the range P

= 3.7-5.8 GPa for the dry system and $P = 2.1-4.5$ GPa for the wet system. A comparison of the pressure as a function of load for these two methods can be seen in the Supporting Information (Appendix C Figure 1). Wear of the tip means that it becomes increasingly non-spherical, leading to an increase in contact area. This effect is accounted for in the simulations, since the number of atoms in contact is monitored dynamically. The change in pressure from the atoms in contact method over the course of the simulations is shown in the Supporting Information (Appendix C Figure 2). Initially, the pressure rapidly drops from very high values (due to the absence of interfacial bonds) and then continues to decrease due to flattening of the tip before reaching steady-state values after approximately 3 ns. For all further analyses, we use the steady-state normal stress calculated from the number of atoms in contact.^{235,238}

To accelerate wear, a high tip sliding velocity of 100 m s^{-1} is applied in all the NEMD simulations. For NEMD simulations to be useful in terms of predictive capabilities, high shear rates are required to ensure the properties of interest reach a steady state.^{376,377} Additionally, at low shear rates, the nonequilibrium phenomena become like equilibrium fluctuations in the phase variable of interest, resulting in a low signal-to-noise ratio.^{124,166} Previous simulation studies have shown that there is negligible difference between the steady-state friction force and interfacial bonding between different sliding velocities ($1-10 \text{ m s}^{-1}$).¹ The compression and sliding phase of the simulations were performed for 4 ns, which was sufficient for friction force and number of interfacial bonds to reach a steady-state. This corresponded to 400 nm sliding distance or approximately 30 surface passes. Chemical bonding information was outputted every 1.0 ps using a bond order cutoff of 0.3 to identify covalent bonds.³⁷⁰ The choice of bond order cutoff only affects the postprocessing analysis and does not influence the ReaxFF energy or force calculations.^{290,304}

5.3. Results and Discussion

5.3.1. Wear behaviour

The number of worn atoms in the NEMD simulations was quantified in two ways. The first method was simply to quantify the number of C-C bonds broken in the diamond tip. The second method was to monitor the number of carbon atoms that formed C-O interfacial bonds, were removed from the asperity through C-C cleavage and either diffused into the α -quartz substrate or were oxidised to form gas-phase CO₂ molecules.³⁷⁸ The second method is consistent with the definition of wear in recently proposed nanoscale wear models.^{257,258} In these models, wear is treated as a multiple-step reaction where interfacial bonds first form between the tip and the substrate, followed by either wearless rupture of the interfacial bond or removal of the bonded atoms by breaking of C-C bonds within the tip. The number of worn atoms using the second method is shown as a function of sliding distance in Figure 5.2. Snapshots of the worn tips after 400 nm of sliding are shown in the coloured boxes. Additional snapshots of the tips and substrates after different sliding distances are shown in the Supporting Information (Appendix C Figure 3). These snapshots clearly show the diffusion of carbon atoms into the substrate and CO₂ formation. First-principles methods suggest that carbon diffusion through α -quartz requires temperatures in excess of 1000 K,³⁷⁹ however, the mechanical mixing due to the sliding tip is expected to significantly accelerate this process.³⁸⁰ Similar wear behaviour is observed when classifying them using the number of C-C bonds broken definition, as shown in the Supporting Information (Appendix C Figure 4). This approach includes $sp^3 \rightarrow sp^2$ transitions within the tip itself (graphitization or amorphization),³⁸¹ which should not themselves be considered as wear since the atoms are not necessarily removed from the tip. Approximately three times as many C-C bonds are broken in the tip (Appendix C Figure 3) than contribute to wear (Figure 5.2), suggesting that a significant amount of graphitization or amorphization occurs during sliding. Using both definitions, wear begins from the onset of sliding, suggesting that graphitization or amorphization

is not required to initiate wear. Instead, wear seems to be initiated by the formation of interfacial C-O bonds, which will be studied in the next section. From this point forwards, wear atoms are defined as carbon atoms that have formed interfacial C-O bonds and subsequently been removed from the diamond tip by C-C dissociation, followed by diffusion into the substrate or further oxidation to form CO₂ molecules.

In the Archard model (Equation 5.1),⁴¹ the wear volume is expected to increase linearly with the sliding distance, normal force, and hardness. From Figure 5.2, there is a sub-linear increase in the number of worn atoms with sliding distance for most of the conditions studied, which is not consistent with the Archard model. This observation is consistent with previous NEMD simulations of silica-silica contacts.³⁸² Deviations from the Archard model were also observed in previous AFM experiments analysing the wear of silicon tips on a polymer surface,²⁴⁷ silicon-doped DLC tips on silica surfaces,⁹ and silicon tips on diamond surfaces.²⁴⁴ The wear volume per unit sliding distance has frequently been found to be non-linearly dependent on the applied load and can also vary with sliding velocity.^{248,249} Furthermore, the Archard equation is purely empirical and therefore it remains difficult to extend to elucidate the observations seen in single-asperity wear.^{247–249,254} These experiments propose that, at the nanoscale, plastic deformation cannot dominate wear, as theorized by Archard, and instead atom-by-atom attrition takes place. Indeed, *in situ* transmission electron microscopy (TEM) experiments, have shown that silicon tips on a diamond substrate wear without plastic deformation or fracture.²⁴⁴ The snapshots shown in Appendix C Figure 3 confirm that atom-by-atom attrition also occurs in our NEMD simulations.

The initial wear rate (first 100 nm of sliding) in our NEMD simulations shows a significant increase with both temperature (Figure 5.2a) and load (Figure 5.2b). The hardness of diamond is only expected to decrease by around 20% between 300-1000 K.³⁸³ Thus, from the Archard model, a 20% increase in wear volume would be expected over the temperature range simulated for the dry

system. However, the initial wear rate increases by several orders of magnitude between 300 K and 1000 K, as shown in Figure 5.2a. Moreover, Figure 5.2b shows that the increase in initial wear rate with normal load is super-linear. These observations are both inconsistent with the Archard model. The number of wear atoms as a function of the product of the sliding distance and total normal load is shown in the Supporting Information (Appendix C Figure 5); this relationship is neither linear nor consistent across the different loads.²⁴⁴ Collectively, these observations further suggest that the initial wear of diamond on α -quartz cannot be adequately described by the Archard model. A sub-linear relationship between initial wear and sliding distance is also observed for the water-containing system, as shown in the Supporting Information (Appendix C Figure 6). The temperature and load dependencies of wear are also inconsistent with the Archard model. Compared to the dry systems (Figure 5.2), the amount of wear atoms was much lower for the wet systems. Indeed, measurable wear was only detected in the NEMD simulations for the wet system at high temperatures (≥ 1000 K). Previous experiments by Bowden and Scott³⁸⁴ also showed that diamond wear on silica glass was greater by two orders of magnitude in a dry atmosphere than in a humid one.

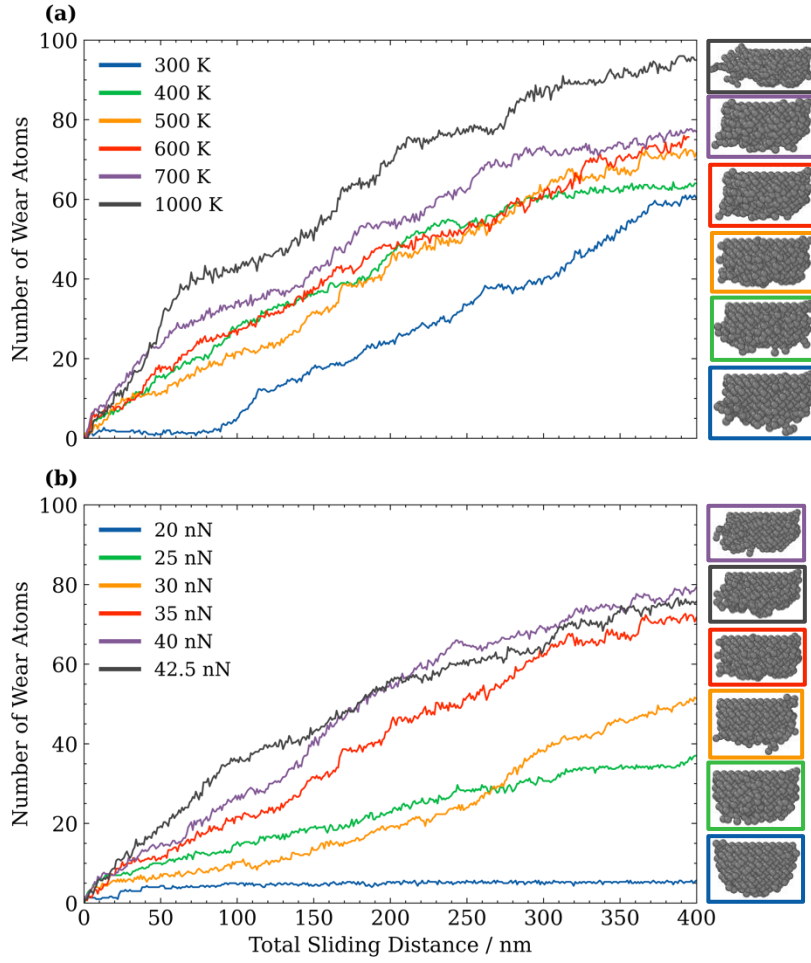


Figure 5.2: Change in the number of wear atoms with sliding distance for the dry system at (a) varied temperatures and a constant load of 35 nN (b) varied loads and a constant temperature of 500 K. Worn atoms defined as those that have formed C-O bonds, been removed from the tip through C-C cleavage and diffused into the substrate or oxidised to form CO_2 molecules. Snapshots of the tips after 400 nm of sliding are shown in the coloured boxes. Load is maintained throughout the simulation and the contact pressure reaches a steady state based on the number of interfacial bonds (Appendix C Figure 2).

Over the final 300 nm of sliding, the number of wear atoms increases approximately linearly with sliding time. Moreover, wear seems to be less dependent on temperature and load than for the initial 100 nm of sliding. In the following sections, we analyse the wear behaviour in two phases. The initial 100 nm of sliding where the wear rate is higher and the wear versus sliding distance

behaviour is strongly sub-linear is referred to as the running-in phase. The following 300 nm of sliding where the wear versus sliding distance becomes more linear (Archard-like) is referred to as the steady-state phase.

5.3.2. Bond formation and cleavage

To identify the physicochemical mechanisms leading to wear, we analysed the key bond formation and cleavage processes at different temperatures and loads. Figure 5.3 shows the number of C-O interfacial bonds formed (green), C-O interfacial bonds broken leading to wearless rupture (red), and C-C bonds broken leading to wear (purple) as a function of sliding time at constant load (35 nN) and varied temperature (300-1000 K) for the dry system. The number of interfacial C-Si bonds formed during the NEMD simulations is negligible compared to the number of interfacial C-O bonds, so these are not included in our analysis.

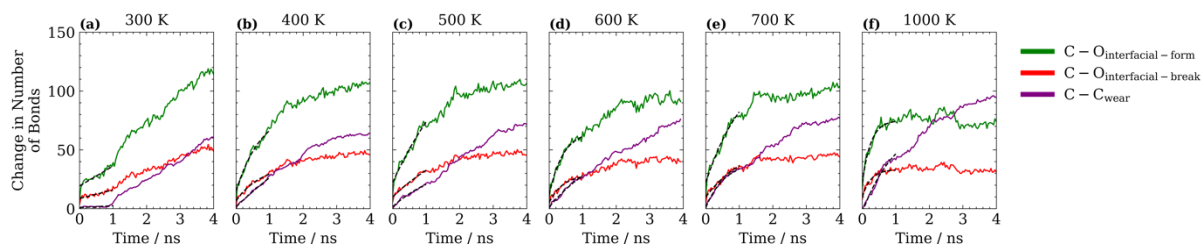


Figure 5.3: Number of C-O interfacial bonds formed (green), C-O interfacial bonds broken (red), and C-C wear bonds broken (purple) during sliding for the dry system at a 35 nN load and temperatures of (a) 300 K, (b) 400 K, (c) 500K, (d), 600 K, (e) 700 K, and (f) 1000 K. Black dashed lines are fits to the first 1 ns of the bond formation/breakage data assuming first-order reactions used to calculate initial rates.

For most of the conditions studied, the C-O interfacial bond formation and C-C wear processes begin simultaneously from the onset of sliding. At 300 K, C-O interfacial bonding occurs from

the onset of sliding, but there is a short (1 ns) induction period before wear occurs. This observation implies that wear is initiated by the formation of interfacial C-O bonds. Previous first-principles calculations have shown that wear of diamond on silica is initiated by the mechanochemical activation of C-C bonds by the formation of strong C-O interfacial bonds.⁶² The amount of C-O interfacial bond formation and C-O and C-C bond breaking increase rapidly at the start of the simulations before approaching a steady-state value. The initial rate of all three processes increases with temperature. The steady-state number of C-O interfacial bonds broken and formed remains approximately constant over the temperature range studied, since this is mostly governed by the surface area of the tip rather than the conditions.

For the water-containing systems (Appendix C Figure 7), significant C-C bond breaking and C-O bond formation was only observed at temperatures greater than 1000 K. The presence of water at the interface leads to passivation of both quartz and diamond to the formation of surface hydroxyl groups rather than interfacial bonds. With hydroxyl passivation of both the tip and substrate, the rate of C-C wear bond breaking and C-O interfacial bond formation and breaking (Appendix C Figure 8) are significantly reduced. Previous NEMD simulations using ReaxFF²⁰³ have shown that, at the interface between hydroxylated amorphous silica and oxidized silicon, the degree of atom transfer is substantially reduced when sufficient water molecules are present to form a complete monolayer. This was attributed to silicon atoms at the sliding interface becoming terminated with hydroxyl groups rather than interfacial bonds.²⁰³ Previous NEMD simulations have also shown that friction between silica surfaces³¹⁸ and diamond-quartz contacts¹ can be reduced by increasing the hydroxyl group density or adding water molecules between the sliding surfaces. This observation has also recently been recently corroborated for diamond-silica contacts using first-principles methods.³⁵⁶

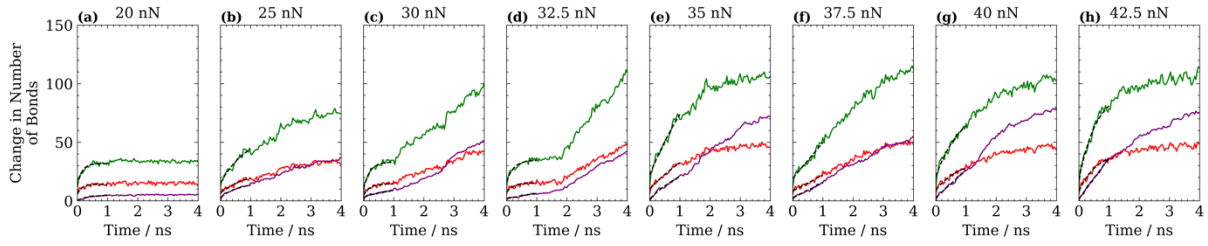


Figure 5.4: Number of C-O interfacial bonds formed (green), C-O interfacial bonds broken (red), and C-C wear bonds broken (purple) during sliding for the dry system at 500 K and loads of (a) 20 nN, (b) 25 nN, (c) 30 nN, (d) 32.5 nN, (e) 35 nN, (f) 37.5 nN, (g) 40 nN, and (h) 42.5 nN. Black dashed lines are fits to the first 1 ns of the bond formation/breakage data assuming first-order reactions used to calculate initial rates. Legend same as in Figure 5.3.

Figure 5.4 shows the change in the number of C-O interfacial and C-C wear bonds at constant temperature (500 K) and varied load (20-42.5 nN) for the dry system. The steady-state number of C-O interfacial bonds formed and broken, as well as C-C wear bonds broken, increase significantly with increasing load. The steady-state values are also reached at a higher rate as the load is increased. The addition of water molecules at the sliding interface (Appendix C Figure 8) leads to a reduction in C-O interfacial bonds formed and C-C wear bonds broken, despite the higher temperature (1000 K) than for the dry systems (500 K).

5.3.3. Wear models (running-in)

Changes in the wear rate are usually observed shortly after the start of sliding contact between fresh, unworn solid surfaces. The initial period of (usually higher) wear is known as running-in.³⁴⁷ The running-in phase often determines the subsequent steady-state friction and wear characteristics by complex interfacial pre-conditioning through processes including changes in morphology, tribochemical reactions, tribofilm formation, and structural transformations.³⁸⁵ Thus, it is important to understand during the running-in as well as the steady-state phase of the wear process.

Initial rates for these bond formation and breaking processes are calculated during the running-in phase, i.e. the first 1 ns (100 nm) of sliding. In many cases, the fits to the initial wear rate data could be extended over the entire 4 ns (400 nm). The initial rate of interfacial C-O bond formation and C-C wear increase with temperature (Figure 5.3) and load (Figure 5.4). To assess whether these processes can be described with a SATA model,¹⁵⁴ we plot the change in the initial rate of C-C wear and interfacial C-O bond formation and breaking against pressure (Figure 5.5) and temperature (Figure 5.6). The initial rates are calculated over the first 1 ns from the black dotted lines shown in Figure 5.3 and Figure 5.4, in which C-O formation and C-C cleavage are treated as first-order reactions. In SATA process, the rate constant of the process, k , can be given by:

$$k = A \exp \left(-\frac{\Delta U - N\sigma\Delta V^*}{RT} \right) \quad (5.2)$$

where A is a pre-exponential factor, ΔU is the activation energy, N is Avogadro's number, σ is the applied stress, ΔV^* the activation volume, R the universal gas constant, and T is the absolute temperature.¹⁵⁴ Equation 5.2 implies an exponential increase in the rate with increased applied stress,¹⁵⁴ as seen in Figure 5.5. The slope of the insets is used to determine ΔV^* . The most appropriate stress component in Equation 5.2 will depend upon the applied force, materials studied, and geometry of the interface. For the mechanochemical decomposition of lubricant additives, the shear stress has been shown to dominate the rate of the process.³¹⁹ Some previous nanoscale wear studies have also selected the shear stress as the key parameter.²⁴⁷ However, most previous studies have used the normal stress (pressure), mostly because it is easier to measure and control.¹⁵⁴ For simplicity and consistency with previous nanoscale wear models,^{257,258} we also use the normal stress in Equation 5.2. This was determined using the number of atoms in contact based on the number of interfacial bonds.²³⁵

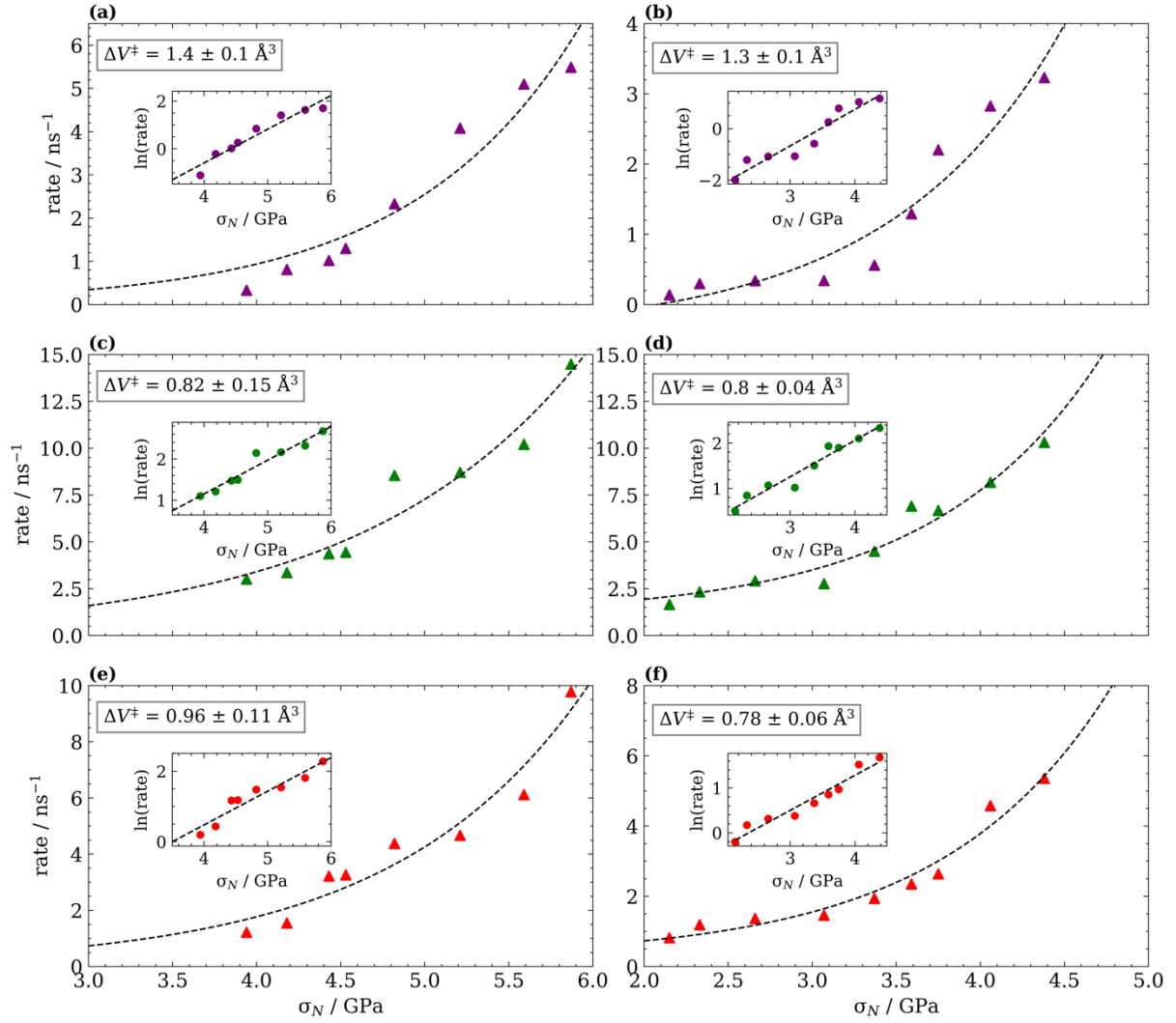


Figure 5.5: Change in the initial rate of C-C wear in the dry (a) and wet (b) system, interfacial C-O bond formation in the dry (c) and wet (d) system, and interfacial C-O bond breaking in the dry (e) and wet (f) system with pressure. Dry systems $T = 500 \text{ K}$, wet systems $T = 1000 \text{ K}$. The dashed lines are exponential fits to the data used to calculate the activation volume, $\Delta V^\ddagger$, using Equation 5.2. Insets show the same data with a logarithmic y -axis.

Figure 5.5 shows that the initial rate of C-C bond breaking leading to wear, interfacial C-O bond formation, and interfacial C-O bond breaking (wearless rupture) increase exponentially with pressure, as predicted with SATA models.¹⁵⁴ These observations are consistent with previous experiments and NEMD simulations of dry silica-silica contacts.³²² The slopes of the linear fits in the insets in Figure 5.5, yield activation volumes for C-C wear of $\Delta V^\ddagger = 1.4 \pm 0.1 \text{ \AA}^3$ for the dry

system at 500 K and $\Delta V^\ddagger = 1.3 \pm 0.1 \text{ \AA}^3$ and the wet system at 1000 K. This suggests that the normal stress-dependence of wear is similar for the wet and dry systems. The activation volumes calculated from Figure 5.5a for C-C wear are consistent with single atom or bond dimensions and are of similar magnitude to those from previous AFM experiments of wear in silica-silica contacts ($\Delta V^\ddagger = 6.7 \pm 0.3 \text{ \AA}^3$),²⁴⁴ DLC-diamond contacts ($\Delta V^\ddagger = 5.5 \pm 0.8 \text{ \AA}^3$),³⁸⁶ and oxidized DLC-silica contacts ($\Delta V^\ddagger = 10.8 \pm 0.2 \text{ \AA}^3$).³⁸⁵ The values calculated for C-C cleavage are somewhat lower than the activation volume for the graphitization of diamond at high temperature (1580-2280 K) and pressure (0-4.8 GPa) in vacuum ($\Delta V^\ddagger = 16.6 \text{ \AA}^3$).³⁸⁷ This implies that the C-C cleavage process in sliding diamond-quartz contacts is distinct from the high-temperature, high-pressure graphitization of diamond. Given that the volume of a single carbon atom is approximately $2 \text{ \AA}^3$, the activation volumes from our NEMD simulations suggests that the effect of the stress on the reaction is localised to single carbon atoms or C-C bonds. On the other hand, for previous experiments of the high-temperature, high-pressure graphitization of diamond, the applied stress likely influences the collective motion of a cluster of around eight carbon atoms.¹⁵⁵ At high pressure, the initial rate of C-C wear stops increasing exponentially with normal stress and approaches a constant value for both the dry (Figure 5.5a) and wet (Figure 5.5b) systems. This implies that standard SATA wear models²⁴⁴ are not able to describe the wear behaviour at high loads.

For C-O interfacial bond formation, the activation volume was $\Delta V^\ddagger = 0.8 \pm 0.2 \text{ \AA}^3$ for the dry system and $\Delta V^\ddagger = 0.8 \pm 0.1 \text{ \AA}^3$ for the wet system, while for C-O interfacial bond breaking, $\Delta V^\ddagger = 1.0 \pm 0.1 \text{ \AA}^3$ for the dry system and $\Delta V^\ddagger = 0.8 \pm 0.1 \text{ \AA}^3$ for the wet system. The values for C-O interfacial bond formation and rupture are also consistent with single atom or bond dimensions. The smaller activation volumes suggest these processes are less accelerated by increased normal stress compared to C-C wear.

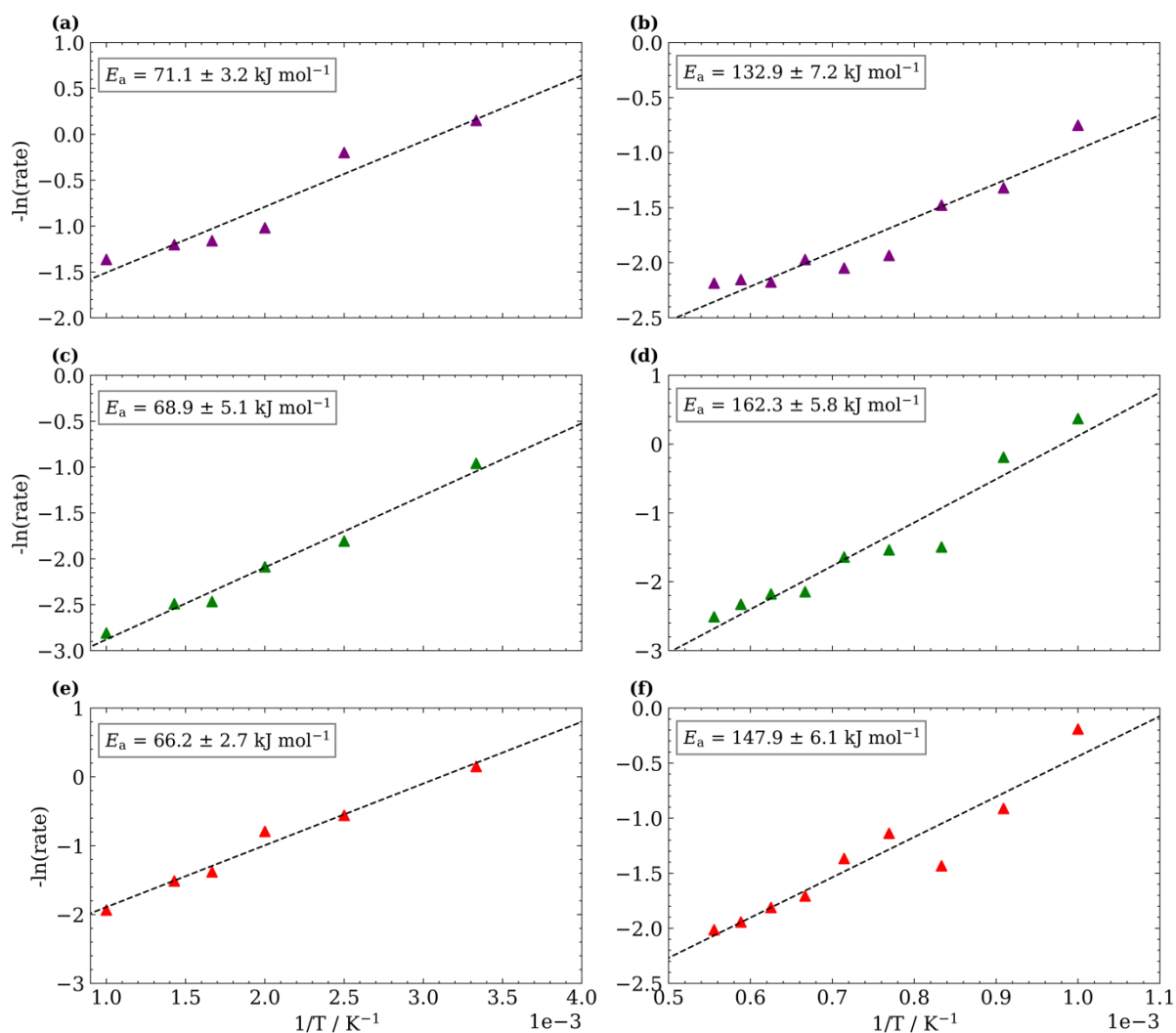


Figure 5.6: Change in the initial rate of C-C wear in the dry (a) and wet (b) system, interfacial C-O bond formation in the dry (c) and wet (d) system, and interfacial C-O bond breaking in the dry (e) and wet (f) system, with temperature at a constant load of 35 nN. The dotted lines are exponential fits to the data used to calculate the activation energy, ΔU , using Equation 5.2.

Figure 5.6 shows the exponential increase in the initial rate of C-C bond breaking leading to wear, C-O interfacial bond formation, and C-O interfacial bond breaking, with temperature. The activation energy, ΔU , of these processes was calculated using Equation 5.2 from slopes of the linear fits in Figure 5.6 and the $\Delta V^\ddagger$ from Figure 5.5. The pre-exponential factor was taken as 10^{13} s^{-1} based on atomic vibration frequencies.³⁸⁵ For C-C wear, $\Delta U = 71 \pm 3 \text{ kJ mol}^{-1}$ and $\Delta U = 133 \pm$

7 kJ mol⁻¹ for the dry and wet systems, respectively. These values are in reasonable agreement with those calculated from previous AFM experimental studies, for example: $\Delta U = 88 \pm 6$ kJ mol⁻¹ for wear in silica-silica contacts,²⁴⁴ $\Delta U = 77 \pm 77$ kJ mol⁻¹ for wear in oxidized DLC-silica contacts,³⁸⁵ and $\Delta U = 56 \pm 9$ kJ mol⁻¹ for wear in DLC-diamond contacts.³⁸⁶ In previous NEMD simulations of dry DLC-DLC contacts, the activation energy for C-C interfacial bond formation was $\Delta U = 3$ kJ mol⁻¹, while $\Delta U = 87$ kJ mol⁻¹ for C-C cleavage.²⁵⁸ Previous experiments have shown that the activation energy for the graphitization of diamond powder increases with average grain size from $\Delta U = 202$ kJ mol⁻¹ for 5 nm to $\Delta U = 365$ kJ mol⁻¹ for 35 μ m, which is close to the bond dissociation energy of C-C bonds in diamond (367 kJ mol⁻¹).³⁸⁸ Therefore, for the single-crystal diamond tip used in the NEMD simulations (radius = 2.5 nm), the α -quartz surface must significantly reduce the activation energy required for C-C bond cleavage.

For C-O interfacial bond formation, the fits in Figure 5.6 give $\Delta U = 69 \pm 5$ kJ mol⁻¹ for the dry system and $\Delta U = 162 \pm 6$ kJ mol⁻¹ for the wet system. The activation energy for diamond oxidation to form CO₂ is around 200 kJ mol⁻¹.³⁸⁹ For amorphous carbon, which is formed in the NEMD simulations during sliding, the activation energy for oxidation is reduced to approximately 130 kJ mol⁻¹.³⁹⁰ Thus, the activation energy values from our NEMD simulations are consistent with those measured experimentally for the oxidation of disordered carbon. For interfacial C-O bond breaking (wearless rupture), $\Delta U = 66 \pm 3$ kJ mol⁻¹ for the dry system and $\Delta U = 148 \pm 6$ kJ mol⁻¹ for the wet system. The presence of water increases the activation energy for all the processes studied, which is due to passivation of the sliding interface through the formation of surface hydroxyls.³⁵⁶

We also fit our NEMD data using the non-empirical wear model proposed by Wang et al.²⁵⁸ In this method, a nanoscale wear event consists of two steps. Firstly, under load, the contact surfaces

are compressed together and react, forming interfacial bonds as an intermediate state in the wear event. The second step consists of atoms involved in the interfacial bonding are sheared and removed from each respective surface, which then leads to wear. This can be considered as a two-step SATA reaction, where interfacial bonding is assisted through normal stress and removal of atoms is assisted by shear stress. Combining reaction rate theory with this two-step reaction, the following non-empirical wear model was proposed:

$$N_{ib} = N_{rc} \exp\left(-\frac{\Delta U_{ib} - W_{\sigma}}{k_B T}\right) \quad (5.3)$$

$$N_{wear} = N_{ib} f_0 \exp\left(-\frac{\Delta U_{wear} - W_{\tau}}{k_B T}\right) t \quad (5.4)$$

where N_{rc} is the number of all atoms in the real contact surface, N_{ib} , is the number of surface atoms that have one or more interfacial chemical bonds, and N_{wear} is the number of worn atoms. ΔU_{ib} and ΔU_{wear} are the activation energies of interfacial bond formation and the removal of carbon atoms that have formed interfacial bonds, and W_{σ} and W_{τ} are the external work per atom induced by normal stress, σ , and shear stress, τ , respectively.²⁵⁸ Figure 5.7 shows the change in N_{ib} (a) and N_{wear} (b) change with normal force at different simulation times for the dry system. Below 30 nN, Equation 5.3 and Equation 5.4 can be used to describe the increase in N_{ib} and N_{wear} with load. At higher loads, N_{ib} and N_{wear} level off towards constant values, which cannot be described by the model due to Wang et al.²⁵⁸. The same relationship is shown for the wet system in the Supporting Information (Appendix C Figure 9). For the wet system, the model does not provide a satisfactory fit to the data even at lower loads.

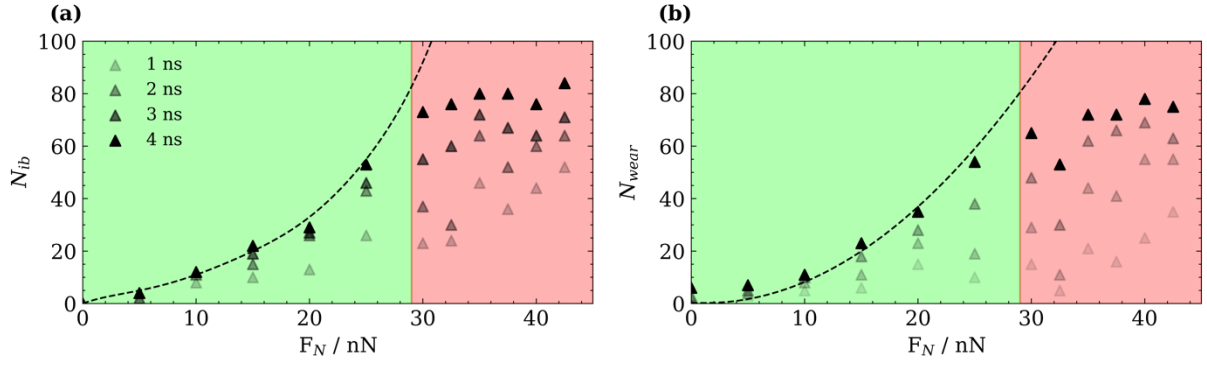


Figure 5.7: Change in the number of interfacial bonds, N_{ib} , (a) and number of wear atoms, N_{wear} , (b) with normal load F_N at different simulation times for the dry system at 500 K. The dashed lines is fit to Equation 5.3 in (a) and Equation 5.4²⁵⁸ in (b) for the NEMD simulation data after 4 ns up to loads of 30 nN. The green regions shows the load range where the model is applicable.

Changes in the wear behaviour with load have also been observed in previous experiments and simulations. From the results of their NEMD simulations, Yang *et al.*³⁹¹ suggested that an atomic-to-plastic wear transition occurs, with SATA models suitable for low loads and the Archard model suitable at high load. Shao *et al.*²⁵⁷ noted the same behaviour, but instead attributed the crossover to changes to the relative rates of competing tribochemical phenomena.

We also fit our NEMD data using the multibond wear model due to Shao *et al.*²⁵⁷, as shown in Figure 5.8. Here, three separate SATA processes are considered. Firstly, bonding occurs between the asperity and substrate by overcoming the energy barrier ΔE_{on} . Next, either these newly formed interfacial bonds break as sliding occurs and the atoms remain bound to the tip (ΔE_{off}) or bonds within the tip break and atoms are transferred across the interface (ΔE_{wear}). In the model the rates of bond formation and rupture are governed by SATA processes, such that:

$$r_{on} = \omega_0 \exp\left(-\frac{\Delta E_{on}}{k_B T}\right) \quad (5.5)$$

$$r_{off} = \omega_0 \exp\left(-\frac{\Delta E_{off} \left(1 - \frac{f_i}{f_c}\right)^\alpha}{k_B T}\right) \quad (5.6)$$

where ω_0 is the atomic attempt frequency (10^{13} s^{-1}), f_i is the tension in each bond and disappears when it reaches a critical value, f_c , and α is set at $\frac{3}{2}$, which is in accordance with the “ramped creep” condition (when the energy barrier for slipping depends on the lateral force, such that $\Delta E \sim (f_c - f)^{3/2}$, where f is the average friction). The model encapsulated a third SATA process, wear, which can be considered as an additional competing rate process, along with r_{on} and r_{off} , such that:

$$r_{\text{wear}} = \omega_0 \exp \left(- \frac{\Delta E_{\text{wear}} \left(1 - \frac{f_i}{f_w} \right)^\alpha}{k_B T} \right) \quad (5.7)$$

where f_i is the tension in the bond and f_w is the critical force for a wear event. The outcome of an interfacial bond can either be wearless rupture of the bond, described by r_{off} , or a wear event resulting in atom transfer, r_{wear} . The expected wear rate per potential bonding site is expressed as:

$$\Gamma = - \int_0^\infty \left(\frac{r_{\text{wear}}}{r_{\text{off}} + r_{\text{on}}} \right) \left(\frac{n_{\text{on}} v}{\Delta x} \right) \left(\frac{dP(\Delta x)}{d\Delta x} \right) d\Delta x \quad (5.8)$$

where $P(\Delta x)$ is the probability of a particular bond stretching to a distance less than Δx , and r_{on} , r_{off} and r_{wear} represent the rates of bond formation, wearless rupture, and the transfer of atoms, described by ΔE_{on} , ΔE_{off} and ΔE_{wear} , respectively. A full description and mathematical derivation of the model was given by Shao et al.²⁵⁷. The effective normal stress, σ , is not employed as an explicit parameter and instead assumed that the activation energy of bond formation, $\Delta E_{\text{on}} = \Delta U - \sigma \Delta V^\ddagger$, where ΔU is the activation energy and $\Delta V^\ddagger$ is the activation volume of interfacial bond formation ($0.8 \text{ \AA}^3$), is linearly dependent on normal stress. The normalized wear rate is

plotted against a function of dimensionless effective normal stress, $\tilde{\sigma}$, which is inferred from ΔE_{on} and ΔU via:

$$\tilde{\sigma} \equiv \frac{\sigma \Delta V^{\ddagger}}{\Delta U} = 1 - \frac{\Delta E_{\text{on}}}{\Delta U} \quad (5.9)$$

The calculated wear rates are normalised by the average number of atoms in contact to account for the changing geometry of the asperity. The following model parameters were all determined from the NEMD simulations: $\Delta U = 69 \text{ kJ mol}^{-1}$ and 162 kJ mol^{-1} (C-O interfacial bond formation), $\Delta E_{\text{off}} = 66 \text{ kJ mol}^{-1}$ and 148 kJ mol^{-1} (C-O wearless rupture), $\Delta E_{\text{wear}} = 71 \text{ kJ mol}^{-1}$ and 133 kJ mol^{-1} (C-C wear), $\Delta V^{\ddagger} = 1.4 \text{ \AA}^3$ and $1.3 \text{ \AA}^3$ (C-C wear), for the dry and wet systems, respectively. The bond-breaking length, $l_{\text{break}} = 3.0 \text{ \AA}$, was taken from the original frictional model.³⁹²

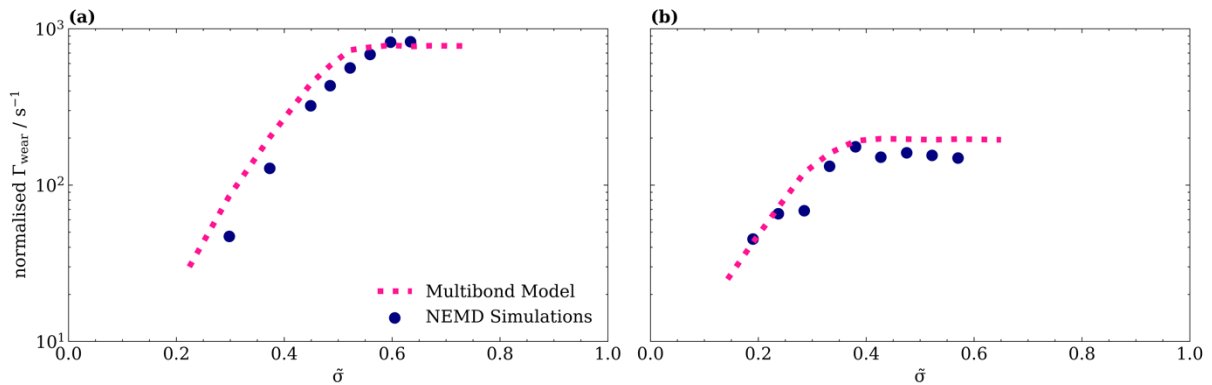


Figure 5.8: Normalized atom wear rate (i.e., number of atoms removed from the asperity per unit time normalized by the estimated number of atoms in contact) as a function of dimensionless effective normal stress for the dry system at 500 K (a) and the wet system at 1000 K (b). The multibond wear model (Equation 4.8)²⁵⁷ is fit to the full data set. The $\tilde{\sigma}$ values are calculated using Equation 5.9.

Figure 5.8 illustrates how the multibond wear model can be used to fit the initial wear data from our NEMD simulation over the entire load range studied. At low normal stress, standard SATA

models hold since there is an exponential increase in the normalised wear rate with effective normal stress. There is then a transition region before, at high stress, the normalised wear rate becomes independent of normal stress. Here, bond formation is no longer the rate-limiting step for the wear process and thus standard SATA models break down.²⁵⁷ While several other nanoscale wear models exist,^{258,322,393} they were unable to fully describe the initial wear rate data presented above.

5.3.4. Wear models (steady-state)

After the initial running-in phase (100 nm of sliding), a steady-state wear phase begins in which wear becomes almost linearly dependent on sliding distance, as shown in Figure 5.2. Here, as well as atom-by-atom attrition, cluster detachment via tail fracture occurs,²⁵⁹ as can be seen in the snapshots in Appendix C Figure 3. This implies a crossover from short sliding distances, where wear processes that can be described by SATA models, to longer sliding distances where they can be approximated using the Archard model. It should be noted, however, that the physicochemical mechanisms leading to wear are not consistent with those proposed in the Archard model, even at long sliding times.

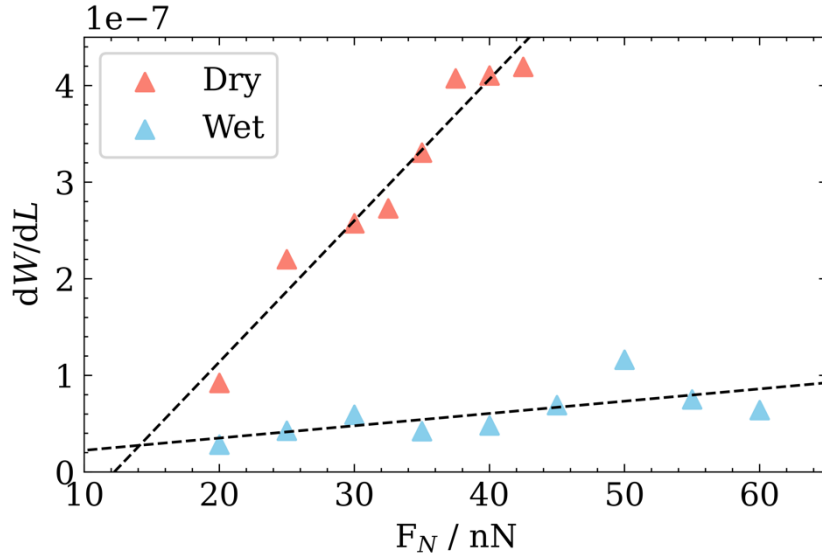


Figure 5.9: The wear rate, dW/dL , versus normal load, F_N , for the dry system at 500 K and the wet system at 1000 K. Steady-state wear rates are calculated from linear fits through the wear versus time data shown in Figure 4.2 (dry) and Appendix C Figure 6 (wet) after the running-in period (sliding distance > 100 nm). Black dashed lines are linear fits through the data as predicted by the Archard model.

To further test the applicability of the Archard model during the steady-state phase, we analysed the load-dependence of the wear rate, which should be linear. Figure 5.9 shows the variation for the wear rate, dW/dL , versus normal load F_N for the dry and wet system, where W is the worn volume per unit area and L is sliding distance. Wear rate is made unitless through volume/area/distance ($\text{m}^3/\text{m}^2/\text{m}$), this can be thought of as wear depth divided by sliding distance. The steady-state wear rates were estimated using linear fits to the wear versus time data for the dry (Figure 5.2) and wet (Appendix C Figure 6) systems after 100 nm of sliding. The linearity of dW/dL as a function of F_N further suggests that the Archard model is applicable at the nanoscale.⁴¹ This finding is consistent with previous NEMD simulations of wear in DLC-DLC contacts.²⁵⁹ However, it is in disagreement with previous AFM experiments^{149,244,247–249} that showed the non-linearity of wear as a function of both sliding distance and applied force. These differences

could be due to the much lower sliding velocities in the experiments than the NEMD simulations.²⁵⁹ On the other hand, Maw et al.²⁴⁹ showed that contaminants including oxides and other chemical species present in AFM experimental studies could lead to non-linearity in the wear versus time behaviour, which the surfaces in our simulations are free from.

Wear during the initial 100 nm of sliding can be attributed to atom-by-atom attrition that can be explained using the multibond model. From this point onwards, cluster detachment via tail fracture also occurs, as detailed by Sha et al.²⁵⁹. They noted that the average cluster size increased and few isolated atoms were lost at higher normal loads.²⁵⁹ Diffusion of the carbon atoms into the α -quartz substrate and the formation of CO₂ makes quantification of the cluster size more difficult in our simulations. However, the snapshots in Appendix C Figure 3 do seem to show an increase in cluster size with increasing normal load (and temperature). At high temperatures and loads, significant lateral atom migration takes place towards the trailing edge of the sliding asperity. Thus, it might be expected that longer simulations would lead to detachment of larger clusters.

Yoshino et al.⁶⁰ experimentally measured the wear rates of single-crystal diamond on quartz glass at 300 K. They found that the wear rate was significantly reduced when using water as a lubricant,⁶⁰ which is consistent with our NEMD simulation results for diamond on α -quartz contacts shown in Figure 5.9. Due to the considerable computational expense of our NEMD simulations, a much higher sliding velocity (100 m s⁻¹) was required compared to the experiments (3 × 10⁻⁴ m s⁻¹) and the sliding distance was also smaller in the simulations (4 × 10⁻⁷ m) than the experiments (5 × 10⁻³ m). The normalised wear rates from the experiments, dW/dL , varied considerably with indentation depth (2-38 nm) between 1.1 × 10⁻⁶ and 1.6 × 10⁻⁷. Thus, the normalised wear rates from our NEMD simulations (indentation depth ≈ 1 nm) for the dry (1 × 10⁻⁷ to 5 × 10⁻⁷) and wet (2 × 10⁻⁸ to 1 × 10⁻⁷) systems are close to the range observed experimentally. The wear rate is approximately one order of magnitude higher in the dry diamond-quartz system than when water

molecules are present at the sliding interface, which is similar to the difference noted in previous experiments.³⁸⁴ The corresponding wear coefficient, K_b , values from the Archard model (Equation 4.1) are $5.0 \pm 0.3 \times 10^{-4}$ for the dry system and $7.1 \pm 2.7 \times 10^{-7}$ for the wet system. These values are close to experimental estimates of the wear coefficient in the Archard model for a diamond AFM tip sliding on a silicon nitride substrate ($K_b \approx 10^{-5}$ - 10^{-6}),³⁹⁴ which will quickly oxidize when exposed to air and form an outer silica layer.³⁹⁵

In summary, the Archard model, the standard SATA model and the non-empirical wear model are unable to describe the initial wear behaviour of our system at the highest loads studied in our NEMD simulations. The multibond model, which considers the formation and rupture of interfacial bonds, as well as rupture of bonds withing the sliding tip, can be used to fit the initial wear data from our NEMD simulation over the entire load range studied. After the running-in phase, the wear volume becomes almost linearly proportional to the sliding distance and applied load, suggesting that the Archard wear model can be used to empirically describe the wear behaviour even in these nanoscale simulations. However, the physicochemical processes observed in the simulations are not consistent with those assumed in the Archard model.

5.4. Conclusion

We have performed NEMD simulations to quantify the wear of diamond tips on α -quartz substrates. Our results show that diamond wear on α -quartz is initiated by the formation of C-O interfacial bonds, which is followed by C-C cleavage, and either diffusion of carbon into the substrate or further oxidation to form CO₂ molecules. Amorphization of the diamond tip also occurs during sliding, but this is not essential for wear to occur. The increase in wear rate with normal stress cannot be described using standard SATA-based models at high loads. However, the multibond wear model, which encapsulates three distinct SATA processes, is able to describe

the initial wear behaviour of diamond on α -quartz over the entire load range studied. When the normal stress reaches a certain threshold, there is a transition from exponential growth of the initial wear rate with stress (as predicted by SATA models), towards stress-independent initial wear rate (as predicted by the Archard model). After the initial running-in period, tail fracture and cluster detachment occur as well as atom-by-atom attrition. Here, wear becomes approximately linearly proportional with sliding distance and load, which is consistent with the Archard model. The normalised wear rates obtained from the NEMD simulations are in good agreement with previous experiments. When water molecules are included inside the contact, interfacial bonding and wear were both significantly reduced due to passivation at the sliding interface. The multibond model can also be used to describe the initial wear behaviour for water-containing systems, but with a lower plateau wear rate. Thus, our results suggest that mitigation of interfacial bonding through passivation with water or aqueous-based lubricants should be an effective strategy to improve tribological performance of drill bits for granite rocks and other diamond tools used for cutting silica-containing materials.

Chapter 6. Mechanochemically Induced Phase Transformation of α -quartz

6.1. Introduction

As discussed in Chapter 2, mechanochemical reactions are ubiquitous at the sliding interface of solid materials and are generally termed tribochemical reactions.^{267,396} In mechanochemical reactions, an external mechanical force alters reaction energies and pathways through a flow of electrons between electronic states that results in changes to the atomic positions of the molecules involved in reactions.³¹⁷ In this chapter, we introduce and discuss the solid-solid sliding interface between diamond and α -quartz, which displaces molecular conformations from equilibrium and leads to a chemical reaction. It is also well known that at tribological interfaces, frictional heat can induce thermal reactions,¹⁵⁴ which can sometimes release triboplasma and triboemissions.³⁹⁷ However, He et al.,³⁹⁸ Gosvami et al.,²⁵⁰ and Adams et al.³⁹⁹ observed tribochemical reactions occurring without substantial heat generation, indicating that a mechanical force is directly channelled into the reaction coordinate, resulting in a change of electronic structure. As discussed in Chapter 2, this is often modelled as a SATA process,¹⁵⁴ where the reaction rate increases exponentially with applied load.

The rational design of advanced materials and coatings for drilling requires a detailed understanding of physiochemical processes occurring at the rock-bit interface.¹⁷ The temperature (> 200 °C) and pressure (> 200 MPa) conditions inside deep wells³⁷⁴ are difficult to replicate in tribometer experiments.⁴⁰⁰ Moreover, local temperatures (> 500 °C) and pressures (> 1 GPa) at the bit-rock interface during drilling can be even more severe.²⁷ Such extreme conditions complicate the experimental investigation of the friction and wear of new drill bit materials on different types of rock.²⁶⁸ A detailed understanding of silica (SiO_2) is crucial because of its

widespread use in glass manufacture and electronics. Additionally, almost all of the world's minerals originate from silica, which presents itself as mainly either α -quartz or glass. α -quartz is also the main constituent of many rocks and therefore is of high significance in many drilling technologies.

Transformations and deteriorations of rocks originates at the micro-/nano-scale and significantly impacts the characteristics at the macro-scale,⁴⁰¹ and consequently investigating the micro-mechanical behaviour of rocks can shed light onto its macroscopic behaviour.⁴⁰² In nature, silica (SiO_2) generally presents itself as quartz or glass and more than 90% of the world's minerals are composed of silicates.⁴⁰³ Studies of quartz have been investigated in various disciplines, including geology⁴⁰⁴, mechanical engineering⁴⁰⁵, biophysics⁴⁰⁶, and micro-fabrication.⁴⁰⁷ SiO_2 has significant technological importance in glass manufacture and electronics and therefore its crystal and electronic structure has been extensively investigated since the 1960s.⁴⁰⁸ The primary reason for silica-based materials in electronic devices is due to the Si- SiO_2 interface being electronically inert due to its encapsulation and passivation properties.⁴⁰⁹ Silica exists in various crystalline polymorphs, including α -/ β -quartz, coesite, α -/ β -cristobalite, keatite, tridymite, and stishovite.⁴¹⁰ However, only α -/ β -quartz, α -/ β -cristobalite, coesite and stishovite have a temperature-density field of thermodynamic stability for chemically pure SiO_2 .⁴¹⁰ Of these polymorphs α -/ β -quartz, α -/ β -cristobalite and coesite only vary in their structural arrangement of almost ideal corner-sharing $(\text{SiO}_{1/2})_4$ tetrahedra, whereas stishovite exists as distorted $(\text{SiO}_{1/3})_6$ octahedra sharing edges and corners,⁴¹¹ which facilitates a higher density. Moreover, several polymorphs of SiO_2 have an almost perfect SiO_4 tetrahedron, with the O-Si-O bond angle being almost identical to the tetrahedron bond angle of 109.5° .⁴¹²⁻⁴¹⁴ Therefore a distinguishable structural difference between the various polymorphs is the Si-O-Si bond angle, which can vary depending on the polymorph (α -quartz has a Si-O-Si bond angle equal to 143.5°).^{415,416} Most amorphous SiO_2 structures can be assumed to be

a network of randomly organised SiO_4 tetrahedra based on the Si-O-Si bond angle, and so any differences between α -quartz and amorphous SiO_2 are a result of the Si-O-Si bond angle.⁴⁰⁸

Many previous studies have shown that α -quartz can undergo phase transitions to any number of these polymorphs if subjected to appropriate conditions.^{417–419} Several polymorphs, such as α -quartz, can also undergo a crystal-to-amorphous transition, where with the application and removal of pressure, the structure can remain amorphous or return to its crystalline state.⁴²⁰ The origin of this instability is still unclear, however several possible mechanisms for this transformation have been suggested,⁴²¹ and a general consensus is that the O-O bond distances become so short that the α -quartz crystalline structure is no longer stable.⁴²² Other work has shown that the reverse transition is possible through the formation of crystal SiO_2 (coesite) from an intermediary quartz phase when amorphous SiO_2 is subjected to the correct temperatures and pressures.⁴²³ The amorphous-to-glassy transition in quartz can also be achieved via irradiation-induced damage in α -quartz.⁴²⁴ A possible mechanism for the α - β phase transformation of quartz was introduced by Grimm and Dörner.⁴²⁵ They proposed a geometric model that accounts for atomic displacements and distortions to the SiO_4 tetrahedra. They concluded that an increase in π -bond order in the Si-O bond with increasing temperature was the driving mechanism for the phase transition. Ringdalen⁴²⁶ observed that reactions containing SiO_2 generate SiO, where during heating quartz will transform to other SiO_2 modifications, mainly forming cristobalite as the stable high-temperature phase. It is noted that this transition is not readily occurring, where the rate of this transition has varied considerably across different types of quartz. Richter et al.⁴²⁷ found coesite in quartz aggregates during experiments conducted at confining pressures of 1.0-1.5 GPa and temperatures between 600 °C and 900 °C. It is interesting to note here that the mean stress was below those of the quartz-to-coesite phase transformation, yet the local maximum principal stress was in the P - T range of coesite's stability field. Coesite was also observed to transform back into quartz after deformation had occurred. Kathleen et al.⁴²⁸ demonstrated the elastic properties of α -

quartz when subjecting it to 21 GPa, observing a phase transformation, and upon decompression, noting that the structure returned to an α -quartz-like one.

In this study, we use nonequilibrium molecular dynamics (NEMD) with an α -quartz, the main constituent of granite, substrate and an atomically smooth hemispherical single-crystal diamond asperity. We employ a reactive force field under a range of temperatures and loads and observe the formation of an stishovite-like phase. This phase is formed through a three-step process: firstly, rupture of Si-O bonds, then a steady-state period, and finally the reformation of these bonds. Bond reformation only takes place when no water is present, and at high loads (>35 nN), the net number of Si-O bonds had increased at the end of the simulation when compared with the start. The global average coordination number of each Si atom had also increased. During the period of Si-O bond reformation, the friction force between the sliding surfaces was observed to increase. This is attributed to the formation of a harder material, which increases wear of the asperity and subsequently the frictional force. The rate of Si-O bond rupture and formation shows exponential growth with increasing temperature and load, indicative of SATA processes. The rate of bond rupture and activation volume ($\Delta V^\ddagger$) both decrease when water is present, and subsequently the activation energy (E_a) increases significantly. We also show how this new phase is mechanochemically induced and does not occur with no sliding asperity. Mitigation of this phase transformation from α -quartz to an stishovite-like region, with the use of water or aqueous-based lubricants should be an effective strategy to improve the tribological performance of drill bits and other diamond tools during SiO₂-rich rocks.

6.2. Methodology

Figure 6.1 shows a schematic of the system under investigation in this chapter. The methodology for this system is identical to the methodology in Chapter 4 and we refer the readers there to obtain

a detailed explanation of the system setup and conditions. This chapter is mainly focused on the dry system in Chapter 5. While the wet system is discussed, much of the data can be found in Appendix D: Supporting information for Chapter 6. Mechanochemically Induced Phase Transformation of α -quartz.

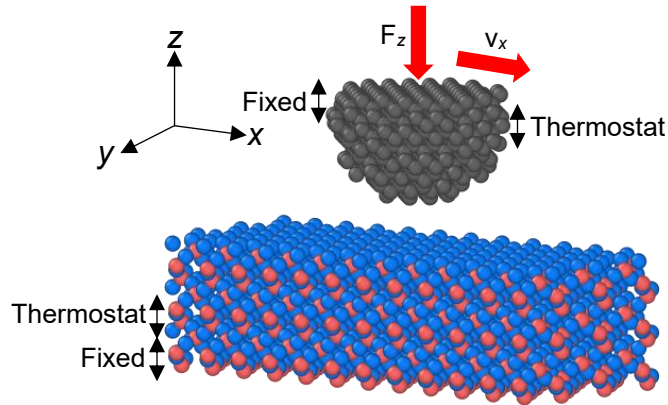


Figure 6.1: NEMD setup for the diamond-quartz system before equilibration. Silicon atoms are shown in red, oxygen in blue, and carbon in grey.

6.3. Results and Discussion

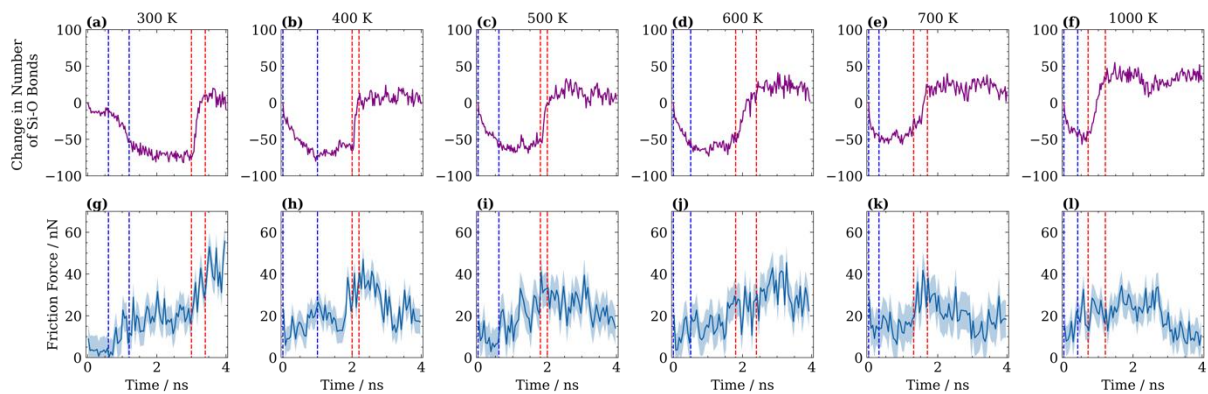


Figure 6.2: Change in number of Si-O bonds (a-f) and friction force (g-l) at a fixed load equal to 35 nN and temperatures between 300-1000 K. Blue and red dashed horizontal lines that indicate where fits to the function $(1 - e^{-t/r})$ are fitted, where r is the rate of bond formation/breakage and t is the sliding time.³¹⁷

Figure 6.2a-f shows how the number of Si-O bonds changes during the compression and sliding phase of the simulation at temperatures between 300-1000 K and a load equal to 35 nN. In all cases, the Si-O bonds initially decrease, reach a steady state (except at 1000 K), and then increase to above 0, which indicates a net increase in global Si-O bonds, before then reaching a steady state. The corresponding plots for when the temperature was fixed at 500 K and the loads varied between 20-42.5 nN can be seen in Figure 6.3a-h. When the temperature remains fixed, and the load varied, the same trend can be observed with loads >35 nN. At loads <35 nN, Si-O bonds break but do not fully reform. This is also true when water is present in the system (Figure Appendix D Figure 1) for both at fixed loads varied temperatures (except at temperatures >1700 K) and fixed temperature varied loads (Figure Appendix D Figure 2). When saturated with a water monolayer, quartz has been shown experimentally to be hydroscopic/hygroscopic in both atmospheric and aqueous environments.²⁷⁷ Water molecules have been previously shown to passivate both the diamond asperity and α -quartz substrate with hydroxyl groups, which prevents direct contact,¹ and preventing a mechanical force being directly channelled into the reaction coordinate.³¹⁷

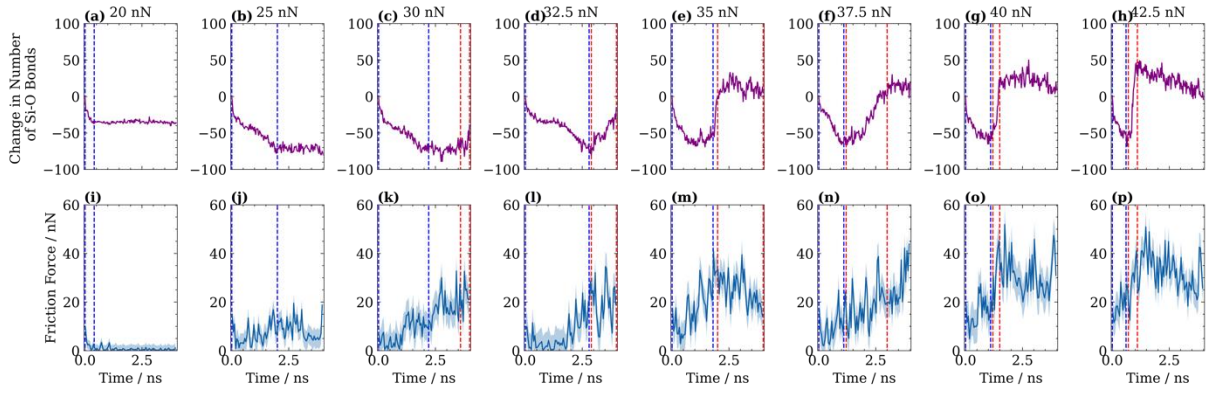


Figure 6.3: Change in number of Si-O bonds (a-h) and friction force (i-p) at a fixed temperatures equal to 500 K and loads between 20-42.5 nN. Blue (rupture region) and red (formation region) dashed vertical lines indicate where fits to the function $(1 - e^{-r})$ are fitted, where r is the rate of bond formation/breakage and t is the sliding time.³¹⁷

In all cases where Si-O bonds rupture and in the cases where Si-O bonds reform, the initial rate of rupture/formation increases with temperature (Figure 6.2a-f) and with load (Figure 6.3a-h). To determine whether these are SATA processes,¹⁵⁴ the change in Si-O bond rupture/formation rate is plotted as a function of pressure (Figure 6.4). Since there is negligible adhesion at the diamond-quartz interface¹ and the surfaces have minimal atomic-scale roughness features,²³⁹ Hertzian contact theory can be used to measure the pressure within the diamond-quartz contact. However, as described in the previous chapter, continuum theories are known to break down on the nanoscale, and therefore, to remain consistent, contact stress is calculated using an atom in contact method.²³⁵ In these methods, atoms are assumed to be spherical, where a circular projected area can be defined. This area can be calculated using the lattice constant for diamond, which determines the effective atomic area, and when multiplied by the number of contact atoms, the atomistic contact area can be calculated. In a SATA process, the rate constant of the process, k , can be given by:

$$k = A \exp\left(-\frac{E_a - N\sigma\Delta V^*}{RT}\right) \quad (6.1)$$

where $\mathcal{A}$ is a prefactor, E_a is the activation energy, N is Avogadro's number, σ is the applied stress, $\Delta V^\ddagger$ the activation volume, R the universal gas constant, and T is the absolute temperature.¹⁵⁴

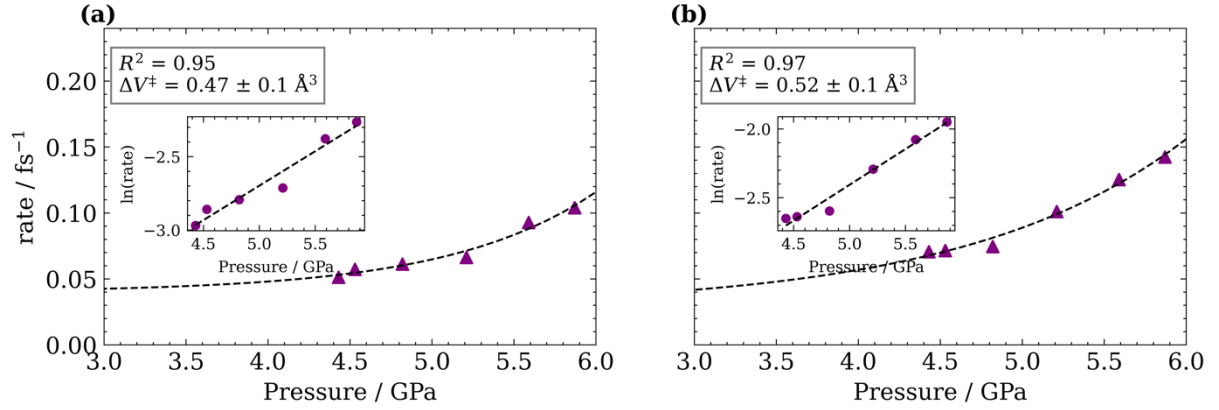


Figure 6.4: Change in the initial rate of Si-O cleavage in the dry system for Si-O rupture (a) and formation (b) system against contact stress calculated using the atoms in contact method.²³⁵ The dashed lines are exponential fits to the data used to calculate the activation volume, $\Delta V^\ddagger$, using Equation 6.1. Insets show the same data with a logarithmic y -axis.

Equation 6.1 suggests the rate increases exponentially with applied stress (Figure 6.4 and Appendix D Figure 3b), which is used to calculate $\Delta V^\ddagger$. Equation 6.1 is only used between the bond rupture regions (between blue dashed lines in Figures 6.2a-f and 6.3a-h) and the bond formation region (between red dashed lines in Figures 6.2 and 6.3). The gradient of the natural log of the rate against the pressure,¹⁵⁴ yielded Si-O bond rupturing activation volumes of $\Delta V^\ddagger = 0.47 \pm 0.1 \text{ \AA}^3$ for the dry system and $\Delta V^\ddagger = 0.24 \pm 0.2 \text{ \AA}^3$ for the wet system. For the reverse process $\Delta V^\ddagger = 0.52 \pm 0.1 \text{ \AA}^3$ in the dry case. Si-O bonds did not reform when water was present except at temperatures $>1700 \text{ K}$ due to melting of α -quartz (Appendix D Figure 4). The Si-O bond rupture rate and $\Delta V^\ddagger$ for the water-containing systems are lower than the dry ones, despite the higher temperature. We attribute this to water molecules passivating the surfaces, they then become terminated with

hydroxyl groups, which prevents direct contact between the substrate and asperity.²⁰³ This results in less interfacial bond formation, and less friction between the surfaces when water is present.³¹¹ The activation energy, E_a , of Si-O bond rupture and formation can be determined using the dependence of the initial rates of these processes using Equation 5.1 with $\Delta V^\ddagger$ values calculated in Figure 5.4 and Appendix D Figure 3b. The slopes in Figure 5.5a yield $E_a = 5.6 \pm 1.0$ kJ mol⁻¹ in the dry system and $E_a = 306.6 \pm 25.8$ kJ mol⁻¹ (Appendix D Figure 3a) in the wet system for Si-O bond rupture. For Si-O bond formation in the dry system, $E_a = -7.4 \pm 2.1$ kJ mol⁻¹ (Figure 5.5b).

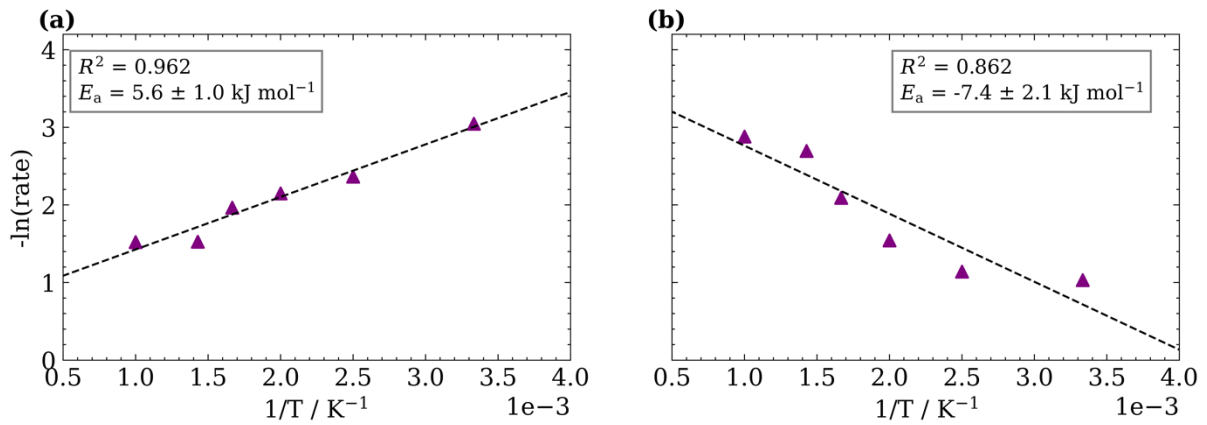


Figure 6.5: E_a calculated for Si-O bond rupture (a) and reformation (b) using the values extracted from Figure 6.4 and equation 6.1.

Figures 6.2g-l and Figures 6.3i-p suggest that during the phase transformation, the friction force between the sliding surfaces increases during the bond reformation phase (between red dashed lines). A proposed reason for this is that a stishovite-like phase has higher hardness than α -quartz,^{48,315,429} which leads to increased wear of the diamond asperity when formed.⁴³⁰ Increased wear subsequently causes a change in the asperity geometry, which increases its contact area with the substrate.^{10,210,231,431} It has been previously shown that a larger contact area can accommodate more interfacial bonding or molecular interactions by the constituent atoms through either atomistic locking (atom configuration at the contact changes continuously with sliding distance)

or dynamic locking (atom configuration discontinuously changes with sliding distance) as a result of the interatomic potential strength.⁴³² Additionally, macroscopic friction laws have been shown to break down at the nanoscale,²¹² as a result of the rough (multi-asperity) nature of a contact, where theories on roughness can be used to explain friction at the nanoscale.^{433,434}

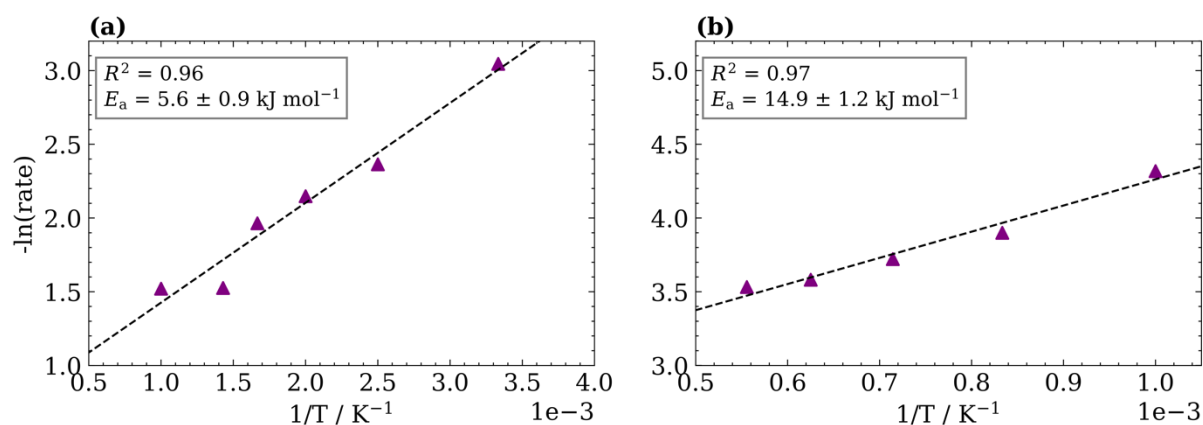


Figure 6.6: E_a calculated with mechanochemical activation from the asperity (a) and without (b).

Figure 6.6 shows how the propensity for Si-O bonds in the substrate vary with mechanochemical activation from the tip. The activation energy calculated for Si-O bond breaking in bulk α -quartz is $5.6 \pm 0.9 \text{ kJ}$ and $14.9 \pm 1.2 \text{ kJ mol}^{-1}$ with and without the diamond tip present, respectively. For bulk α -quartz without the tip, a higher temperature was required to break Si-O bonds than with the tip present (Figure Appendix D Figure 4) thus we observe an increase in activation energy ($\sim 9 \text{ kJ mol}^{-1}$ greater).⁴³⁵ A modified Arrhenius equation, with dissociation energy representing activation energy, yields that bond dissociation rate constants are a function of the external force.^{127,436,437} With applied stress from the tip sliding over α -quartz, the mechanically activated Si-O bond experiences a diminished barrier for dissociation, therefore a considerable decrease in the activation energy.¹²⁷ Several models have been used to explain this, including, a deformed Morse potential for a covalent bond,¹⁴⁷ the tilted potential energy profile model,^{139,438} where the reactants are forced into a lower energy pathway, and several others indicating a lower transition state with the application of stress.¹³⁸ Simulations were performed until 1800 K, since at this temperature, we

had exceeded the melting point for α -quartz.⁴³⁹ This can also be seen in (Figure Appendix D Figure 4), where at temperatures above 1600 K, Si-O bonds began to rearrange, rather than break.

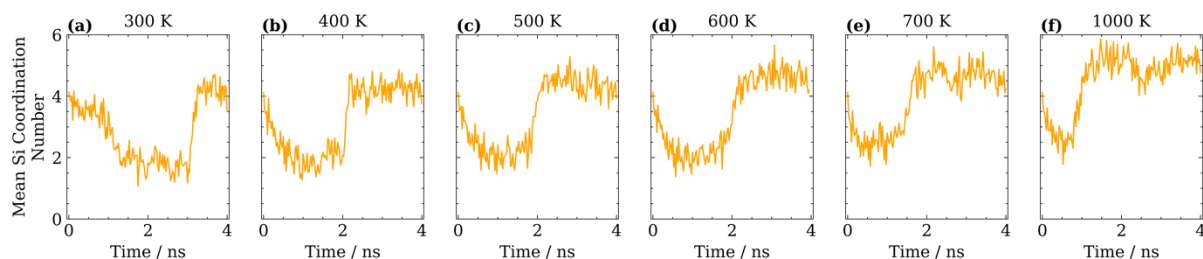


Figure 6.7: Average coordination number in the uppermost layer of atoms in the quartz substrate at 300 K (a), 400 K (b), 500 K (c), 600 K (d), 700 K (e), and 1000 K (f).

Previous work has shown that α -quartz undergoes phase transformations via refinements and distortions of the SiO_4 tetrahedra alongside an increase in the p -bond order with respect to the Si-O bond.⁴²⁵ Figure 6.7 shows how the average coordination number of Si changes throughout the simulation for a fixed load at 35 nN and varying temperatures between 300-1000 K. The coordination number of Si has only been calculated in the top layer of the substrate. In all cases, the average coordination number of Si increases and reaches a steady state above 4. Of the many crystalline polymorphs, only α -/ β -quartz, α -/ β -cristobalite, coesite and stishovite have a temperature-density field of thermodynamic stability for chemically pure SiO_2 , and all but stishovite exist as corner sharing tetrahedra (Si having a coordination number of 4).⁴¹⁰ Stishovite has six-fold octahedral coordinate geometry,⁴⁴⁰ and the global average increase in Si coordination observed in water-absent systems suggests that a phase transformation from α -quartz to stishovite-like phase is occurring. Stishovite is a high-pressure polymorph of silica occurring in the rutile structure and was the first known polymorph to be confirmed with a structure of each Si atom being coordinated with six O atoms and each O atom is bonded to three Si atoms in an octahedral fashion.⁴⁰⁹ α -quartz is known to have mechanical instability when exposed to certain conditions.⁴²⁰

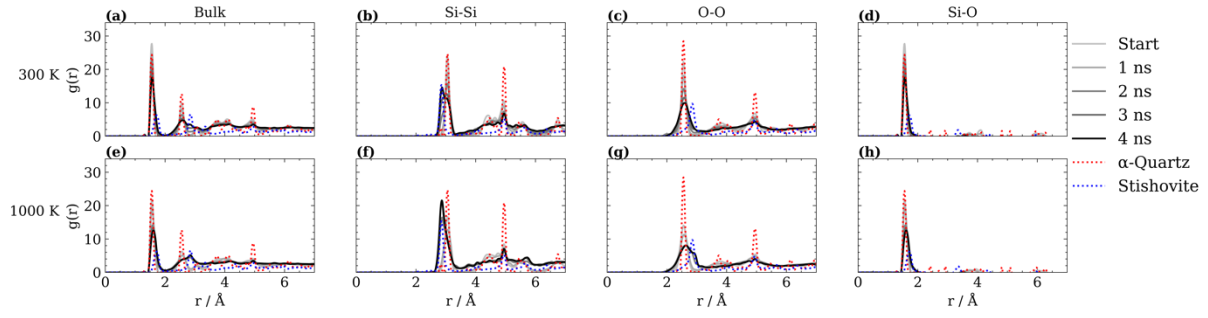


Figure 6.8: Radial distribution function (RDF) at 300 K for bulk α -quartz (a), Si-Si (b), O-O (c), and Si-O (d) and at 1000 K for bulk α -quartz (e), Si-Si (f), O-O (g), and Si-O (h).

The radial distribution function (RDF) for the substrate and for α -quartz and stishovite at 300 K and 1000 K can be seen in Figure 6.8. RDF for Si-O was calculated by subtracting the Si-Si and O-O RDFs from the bulk RDF. Comparisons of the substrate after the equilibration phase with the α -quartz reference RDF show that the substrate is predominantly α -quartz and as shearing time increases, the substrate RDF peaks shift to suggest the presence of an stishovite-like phase. This transformation is more gradual at 300 K, but at 1000 K there are shifts at: 2.55 Å to 2.65 Å (Figure 6.8e); 3.05 Å to 2.85 Å (Figure 6.8f); shoulders forming at: 1.75 Å (Figure 6.8e); 2.85 Å (Figure 6.8g); 1.80 Å (Figure 6.8h); reductions in the RDF at: 1.65 Å and 2.55 Å (Figure 6.8e); 4.95 Å (Figure 6.8f); 2.55 Å and 4.95 Å (Figure 6.8g); 1.75 Å (Figure 6.8h). The shift in $g(r)$, formation of new peaks and reduction in $g(r)$, all indicate a phase transition of α -quartz to a stishovite-like phase.^{403,410,441–443}

Previous MD studies have shown that the structure of amorphous SiO_2 becomes more octahedral-like at high pressures (~ 15 GPa).⁴⁴⁴ Even though local pressures at the diamond-quartz contact are significantly lower than stishovite's stability field,⁴⁴⁵ a well-known mechanical anomaly at 3 GPa initiates the change from tetrahedral (Si-O coordination number, $Z=4$) to octahedral (stishovite-like-structure, $Z=6$) structures in vitreous silica ($v\text{-SiO}_2$).^{446,447} DFT combined with MD revealed that at ambient pressures ($0 < p < 3$ GPa), the Si-O bonds in $v\text{-SiO}_2$ are predominantly sp^3 hybridized,

which favours the formation of SiO_4 ($Z=4$) tetrahedra.⁴⁴⁸ At $3 < p < 10$ GPa, densification of $v\text{-SiO}_2$ occurs as a result of an increase in the atomic charge Fermi energy and changes in the electronic structure. This subsequently increases the Si-O bonding ionicity and promotes the formation of higher-fold coordinated polyhedral with an accompanying higher ionic bonding contribution.⁴⁴⁹ The fraction of octahedra stishovite-like structures continually increases with pressure increase, where at $45 < p < 70$ GPa the entire network connectivity is dominated by SiO_6 . A post-stishovite-like phase (SiO_7 polyhedral) has been reported at >70 GPa.^{450,451}

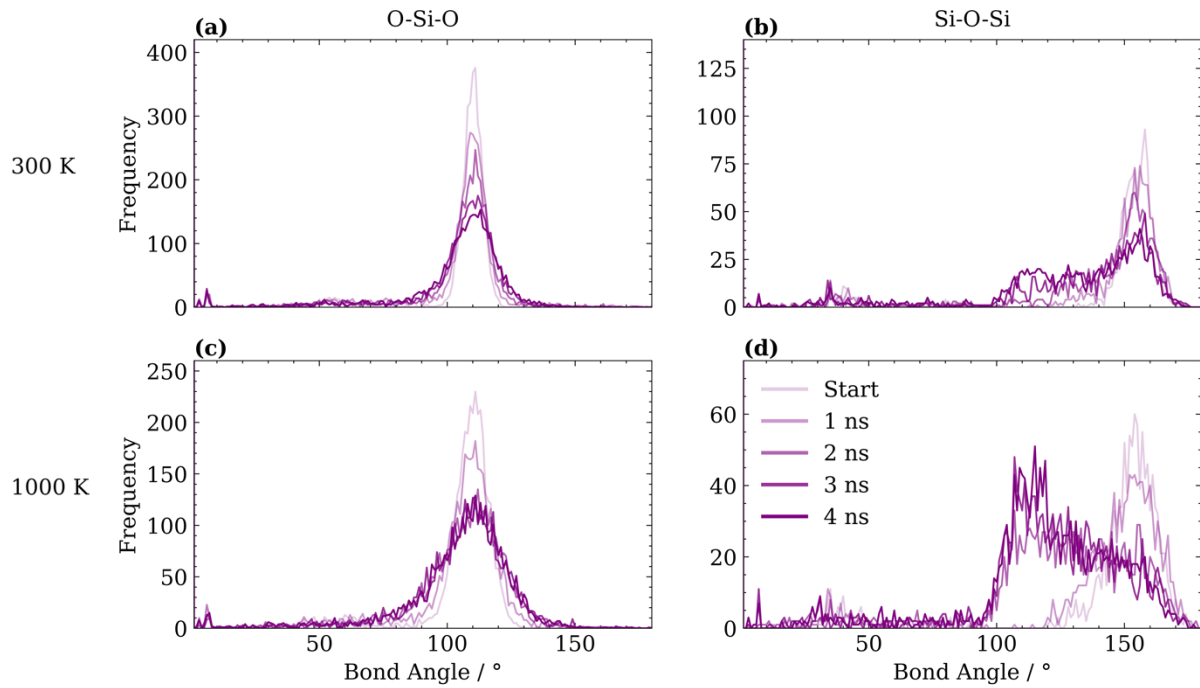


Figure 6.9: Averaged bond angles for O-Si-O at 300 K (a) and 1000 K (b) and Si-O-Si at 300 K (c) and 1000 K (d).

A final confirmation of the presence of an stishovite-like phase was observed via the bond angle distribution through the substrate (Figure 6.9). Crystallographic data of α -quartz shows broadening in O-Si-O bond angle distribution (from 108.7° - 110.4° to 100° - 130°) and a considerable reduction in Si-O-Si bond angles (143.7° to 81° , 90° , 106°).⁴¹⁰ Similar trends can be seen in Figure 6.9, more so at 1000 K (Figure 6.9d). The O-Si-O bond angle distribution is more spread with shearing

(Figure 6.9a and Figure 6.9c) and the Si-O-Si bond angle distribution is broader at 300 K (Figure 6.9b) and significantly reduced at 1000 K after shearing. At 1000 K, the Si-O-Si bond angle distribution suggests formation of the characteristic octahedral 90° bond angle geometry that is observed in stishovite.^{440,445,452} The calculated bond angles post-shearing imply the presence of an stishovite-like phase and agree with previously calculated/measured values.^{410,452,453} It is interesting to note how with a reduction in the bond angle distribution of the Si-O-Si bond (Figure 6.9d), there is lengthening in the Si-O bond seen in the distribution broadening of $g(r)$ in Figure 6.8h. Previous studies have also shown that for silicates, the Si-O-Si bond angle becomes narrower as the Si-O bond lengthens.⁴⁵⁴ Also the opening of O-Si-O bond angles allows O atoms to fill the voids as they are forced into interstitial space through rotation.⁴²⁰ The Si-O-Si angles then become compressed as a result of O-O bond distances decreasing, as seen in Figure 6.8f, essentially, SiO_4 units penetrate one another.^{420,421} Demiralp et al.⁴⁵⁵ combined a charge equilibration (QEq) and a two-body Morse stretch potential to account for short-range non-electrostatic interactions to create an MS-Q potential to investigate the quartz-to-stishovite phase transformation. They reported that α -quartz did not reform post an equilibrium/relaxing phase and a reduction in the O-Si-O bond angle as a function of pressure. This was observed in our simulations, however, the pressure applied (0-120 GPa) in Demiralp's simulations far exceeds the pressures we examined. Grady et al.⁴⁵⁶ reported an α -quartz to stishovite phase transformation occurring between 15 GPa to 40 GPa.

Previous work, using the Debye-Grüneisen theory, showed that quartz converts directly to stishovite, surpassing in-between phases (e.g. coesite) between 15 and 46 GPa.⁴⁵⁷ Several mechanisms of this transformation have been proposed, including a combination of shear-band melting of quartz and subsequent recrystallization⁴⁵⁸ and a displacive transition mechanism that leads to an increase in the coordination number,⁴⁵⁹ with the latter likely being the most dominant mechanism.⁴⁵⁷ In addition to the mechanical anomaly,^{446,447} it has been suggested that the presence

of non-hydrostatic stress, such as shearing, can shift the phase toward higher pressures with respect to the hydrostatic equilibrium.⁴⁶⁰ This accounts for why a stishovite-like phase is observed at local pressures below its stability curve. This phenomenon has also been reported in the quartz-to-coesite phase transition,⁴²⁷ where coesite was found experimentally in quartz aggregates at confining pressures of 1.0-1.5 GPa, far below the quartz-to-coesite transition. It is thought that coesite can form when the maximal principal stress, such as shear, is within the P - T stability field, even if the global mean stress was far below. In all cases reported, the maximal principal stress is entirely responsible for the quartz-to-coesite and coesite-to-quartz transitions.⁴²⁷ There are two generally accepted reasons for the mechanical instability of α -quartz.⁴²⁰ First is the Lindemann picture,⁴⁶¹ which suggests atomic displacements increase with pressure, and second is a pressure-induced generation of defects and dislocations within the lattice that cause it to collapse.⁴⁶²

6.4. Conclusion

Using NEMD simulations, we have highlighted a mechanochemically induced phase transformation of α -quartz to an stishovite-like phase. Our results show that when no water is present, the diamond asperity is able to initiate structural transformations within the substrate through a three-phase process: rupture of Si-O bonds, steady-state transitional period, and finally the reformation of Si-O bonds. When water is present, the sliding surfaces become terminated with hydroxyl groups which prevent direct contact between the tip and asperity. We have shown how for all systems, and for systems where Si-O bonds reform, the rate of the Si-O bond rupture and formation depend on both temperatures and pressure and can be assumed as SATA processes. The sliding asperity has been shown to decrease the E_a of Si-O bond breaking by a factor of three, and initiate the reformation process, indicating that this process is mechanochemically driven. The RDF for each bond (Si-Si, O-O, and Si-O) and the bulk system suggest regions of the substrate have transformed into a stishovite-like region. O-Si-O bond angles remain similarly distributed

during the entire simulation, however, the Si-O-Si bond distribution decreases, indicative of an stishovite-like phase forming. The formation of this new phase can be a cause of the increased friction observed when the Si-O bonds reform since stishovite is a harder material. We propose that mitigation of this phase transformation from α -quartz to an stishovite-like region should be an effective strategy to improve the tribological performance of drill bits and other diamond tools during SiO₂-rich rocks.

Chapter 7. A Comparison of Forcefields for C/O/Si/H Systems

7.1. Introduction

The reactive forcefield ReaxFF is an interatomic potential and very powerful computational instrument for aiding the development of new materials and investigating and optimising material properties. We refer the readers to Chapter 2 and an excellent review article by Senftle et al.,¹⁹⁴ which provides further detail on its methodology and implementation.

ReaxFF has been extensively used in all chapters to investigate diamond-rock interactions, particularly the diamond-quartz system, which relies upon accurate parameterisation for C/O/Si/H, in which many forcefields exist. For diamond-calcite (C/O/H/Ca), only a few ReaxFF parameters exist, mainly developed by Gale et al.,²⁹³ Manzano et al., and²⁹¹ Pitman et al.²⁹⁰ However, Manzano and Pitman's parameters were developed for CaO and perform poorly with CaCO₃ since it was not included in the training set. Additionally, Gale's parameters required Ca atoms to be fixed as dications and not as an atomic/molecular species, and was parameterised for aqueous CaCO₃ systems. Therefore, in Chapter 3, Dasgupta and van Duin aided in the development of a new forcefield for metal carbonate systems, which is fully transferable. Dasgupta et al.⁴⁶³ published the forcefield in 2022. The parameters for C/O/H/Ca were developed via parameterisation of the original combustion forcefield developed by Chenoweth et al.,³⁷⁰ the first generation water force field,⁴⁶⁴ and Pitman's²⁹⁰ forcefield. The forcefield had a very good agreement with DFT for equation of state comparisons for calcite, aragonite, and vaterite, which are all polymorphs of CaCO₃. Additionally, the forcefield provided heat of formation and heat of reaction values that were comparable with DFT.

As mentioned previously, for C/O/Si/H containing systems, many parameter sets exist. Newsome et al.,²⁰⁶ Ponomarev et al.,⁴⁶⁵ Zhang et al.,⁴⁶⁶ Bedrov et al.,⁴⁶⁷ Guifo et al.,⁴⁶⁸ and Yun et al.⁴⁶⁹ have all developed forcefields containing parameters for C/O/Si/H, however, the latter three were explicitly designed for modelling Li-ion-battery anode materials. In the subsequent sections, we explore three main characteristics of the Newsome, Ponomarev, and Zhang forcefields, mainly observe how the change in the number of bonds for C-C, C-O, and Si-O, as well as the friction force for the dry simulation setup discussed in Chapter 4 and Chapter 5.

7.2. Methods

7.2.1. Simulation Setup

Figure 7.1 shows a representative NEMD simulation setup used in these simulations.

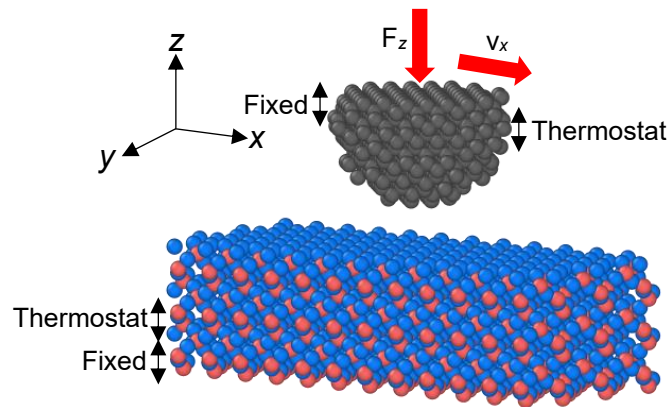


Figure 7.1: NEMD setup for the diamond-quartz system before equilibration. Silicon atoms are shown in red, oxygen in blue, and carbon in grey.

Simulation details are identical to those in Chapter 4 and Chapter 5 and we refer the reader to those chapters for a full breakdown of the simulation setup. In summary, we apply a constant load of 35 nN load and temperatures at 300 K, 400 K, 500 K, 600 K, and 1000 K, with a sliding velocity equal to 100 m s⁻¹.

ReaxFF Parameters

NEMD-coupled ReaxFF simulations have been discussed in detail in all preceding chapters. We refer the reader to previous chapters to understand the validity and implementation of ReaxFF. Below is a summary of the three C/O/Si/H ReaxFF parameters used in this study. From here onwards, the Newsome forcefield refers to the forcefield developed by Newsome et al.,²⁰⁶ Ponomarev forcefield by Ponomarev et al.,⁴⁶⁵ and Zhang forcefield by Zhang et al.⁴⁶⁶

The Newsome forcefield was developed for atoms involved in the oxidation of SiC. The forcefield combines previously derived ReaxFF descriptions for hydrocarbon oxidation²⁸² and silicon/silicon oxides.^{286,287} Previous quantum mechanics data for Si/C, Si/O, Si/Si, and Si/H were also included for the silicon,²⁸⁵ silicon oxide,²⁸⁶ and poly-dimethylsiloxane ReaxFF applications.²⁸⁸ Newsome then formulated data outlining the equation of state and heat of formation of the silicon carbide crystal, in the diamond configuration, while including DFT data by Wang et al.³⁵⁴ Additionally, the Newsome calculated Si-C bond lengths, Si-C-O bond angles, and C-Si-O angle parameters using previous QM and ReaxFF data, the forcefield was not only applicable to silicon carbide materials, but also to silicon oxides, diamond, and graphite, since it also contained parameters described previously.³⁵⁵ Using the newly developed forcefield, Newsome et al. determined that the ReaxFF and QM data for the silicon carbide equation of state for oxygen binding was in very good agreement.²⁰⁶ More importantly, the heat of formation calculated for SiO₂ α -quartz was also in good agreement with experimental values reported in NIST (-215.5 kcal/mol), and for CO and CO₂ are very comparable with the experimental values determined by Cox et al.⁴⁷⁰ The Newsome forcefield has been recently employed by Bhati et al.²⁰⁷ to identify adhesion properties of Si/polymer interfaces, Hilbert et al.²⁰⁸ investigates how Si doping enhances thermal stability of diamond-like carbon, Vashisth et al.,²⁰⁹ combined atomistic and continuum methods to study how temperature influences interfacial fracture in SiC/SiO₂ composites, and several others.

The Ponomarev forcefield was developed for silicon oxycarbide (SiCO) ceramics and its synthesis. Using the parameters for Si/C/O developed by Newsome et al.²⁰⁶ and by Srinivasan et al.⁴⁷¹ for C-C interactions, Ponomarev and co-workers were able to successfully model SiCO ceramics and describe its synthesis through inorganic polymerisation. Ponomarev reported that Newsome's forcefield failed to give an accurate description of stoichiometric SiCO, which is an intermediary species in oxidation of SiC.⁴⁷² Also, experimentally and through MD simulations, it is shown that α -SiCO is stable at temperatures up to 2600 K, however, Newsome's parameters suggest that the structure significantly breaks down at 1200 K.⁴⁶⁵ Additionally, the authors report under-coordination of C-C and C-O during bond formation and under-coordination of Si in Si-Si bonds. Takamoto et al.⁴⁷³ also report failings of the Newsome parameters in the handling of Si-C-O interactions, which occur in SiCO ceramics and polysiloxanes. Ponomarev's forcefield is able to provide stability of carbidic carbon at elevated temperatures and can model SiCO materials in melt-quench simulations when compared with DFT. However, the authors report that their forcefield can result in over-coordinated Si[3] and O[3] species and the density calculation for SiCO is heavily dependent on material composition. Additionally, private conversations with Peter Kroll (corresponding author) reveal that the forcefield has a tendency to create O-Si₃ environments, SiC build-up at accelerated rates, carbon agglomeration can occur at varying rates depending on charge equilibration parameters, and bad elastic mechanical properties.

The Zhang forcefield is also an extension of the Newsome parameters, with merged carbon parameters from Srinivasan et al.⁴⁷¹ to account for graphene modelling. Hydrocarbon chemistry was improved with the inclusion of the CHO-2016 forcefield,⁴⁷⁴ which is used to model a wide range of different hydrocarbon structures. This then allows for the interactions between Si-C, Si-H, Si-Si, C-H, and SiC-graphene to be uniformly described. The forcefield is in good agreement with DFT calculations for bond dissociation energies of Si-C and Si-H bonds, and angle distortion energies for C-C-Si, C-Si-C, Si-C-Si, C-Si-Si, Si-Si-H, C-Si-H, and H-Si-H in

select molecules.²⁸⁸ Additionally, the heat of formation for the SiC-diamond phase, as well as, the equation of state for the SiC crystal, and Si adsorption dynamics onto graphene, are all in good agreement with DFT calculations. To further validate the forcefield, the authors attempted to model multimembered carbon ring formation and reconstruction. They reported that depending on the number of carbon atoms in the ring, the forcefield can either be in good or not-so-good agreement with DFT, but it was always able to correctly identify favourable processes. The authors performed a range of simulations and found that the forcefield was well adept at modelling graphene growth on SiC substrates.

7.3. Results and Discussion

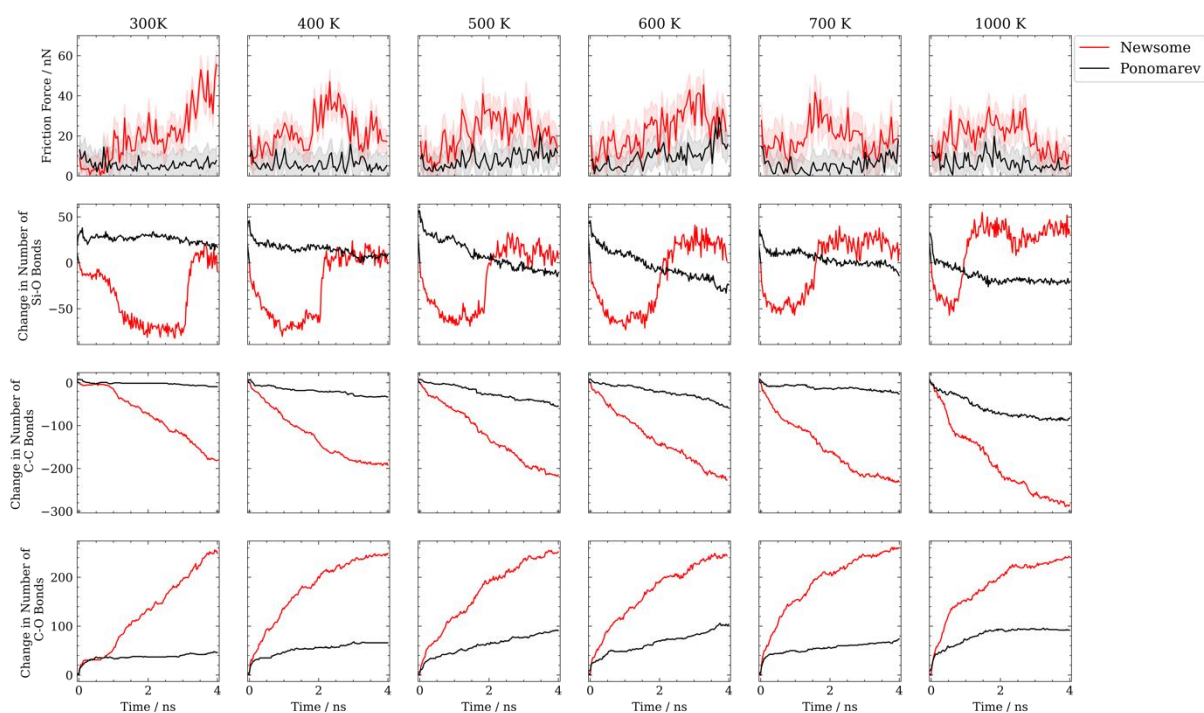


Figure 7.2: A comparison of friction force, and change in the number of Si-O, C-C, and C-O bonds for the Newsome²⁰⁶ (red) and Ponomarev⁴⁶⁵ (black) forcefields at temperatures between 300 – 1000 K and $F_N = 35$ nN. A similar figure including the Zhang⁴⁶⁶ forcefield can be found at Appendix E Figure 1.

Figure 7.2 shows the comparison of friction force, and change in the number of Si-O, C-C, and C-O bonds for the Newsome²⁰⁶ (red) and Ponomarev⁴⁶⁵ (black) forcefields at temperatures between 300 – 1000 K and $F_N = 35$ nN. A similar figure including the Zhang⁴⁶⁶ forcefield can be found at Appendix E Figure 1. Appendix E Figure 1 and OVITO²⁸⁰ trajectory files reveal that the quartz substrate is not thermodynamically stable, with a significant increase in Si-O bond when compared with the other two forcefields. Additionally, the friction force is in direct contradiction to what was observed with the Newsome and Ponomarev forcefields, particularly at high temperatures. Furthermore, the Zhang forcefield was parameterized for graphene growth, and as such, the diamond asperity was unstable and began almost immediately graphitizing. For this reason, it is not discussed in the remainder of this chapter.

Figure 7.2 shows that the friction force as a function of time for the Newsome and Ponomarev forcefields is not in direct agreement. From our findings in the previous chapter, we believe this to be due to the number of interfacial bonds forming at the interface.^{86,212} In Figure 7.2, we can see that there is a large discrepancy between the total number of C-O bonds between each forcefield, with the Newsome forcefield displaying a significantly higher number of C-O bonds being formed. Additionally, like the observations we made in Chapter 5, the Si-O bonds break with the Ponomarev forcefield, but do not reform as they did with the Newsome parameters. Additionally, across each temperature shown in Figure 7.2, the Si-O bonds with the Ponomarev forcefield almost immediately increase before they start to break.

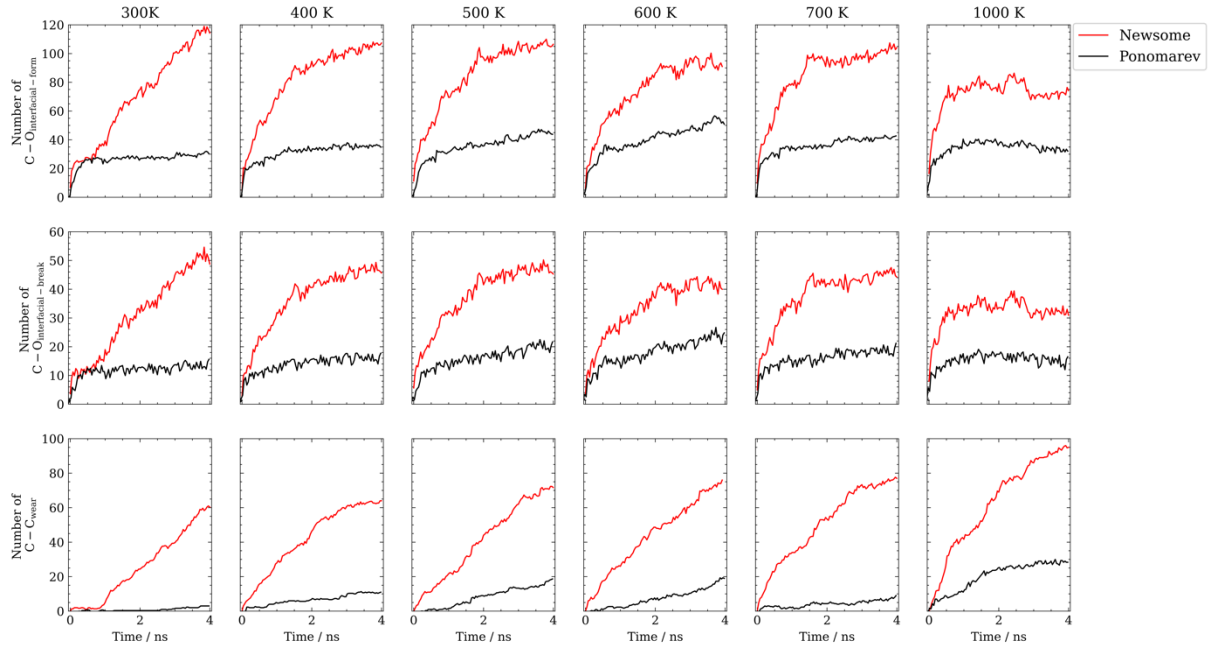


Figure 7.3: A comparison of the number of C-O interfacial bonds form and break and the number of C-C wear atoms for the Newsome²⁰⁶ (red) and Ponomarev⁴⁶⁵ (black) forcefields at temperatures between 300 – 1000 K and $F_N = 35$ nN.

To explain the differences between the friction forces produced using the two forcefields, we explore how each forcefield deals with interfacial bond formation. Figure 7.2 shows the total change in the number of C-O bonds, which includes CO₂ formation and carbon atom transfer across the interface. In Figure 7.3, we can see that the number of C-O interfacial bonds forming and breaking is significantly higher with the Newsome forcefield than Ponomarev's. The model proposed by Filippov et al.⁸⁶ suggest that during sliding, interfacial bonds continuously form and rupture, such that, as a particular interfacial bond ruptures, the force experienced by the other bonds increases, resulting in synchronised bond formation and rupture. This dynamic behaviour of continual formation and breakage of interfacial bonds results in oscillations in the friction force, which can be seen as stick-slip behaviour in Figure 7.2. Since the oscillations in the friction force (Figure 7.2) are more pronounced than they are for the interfacial bonds (Figure 7.3) as a

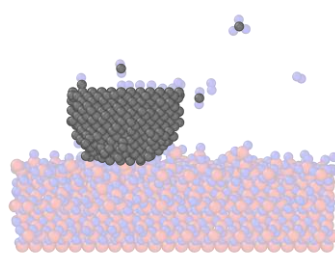
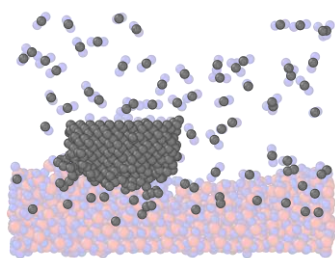
function of sliding time, the cooperative formation and breakage of interfacial bonds can be assumed to be spatially localized at the leading and trailing edge of the asperity, respectively.³¹⁴ Additionally, the formation and breakage are not temporally synchronised, therefore, the fluctuations in the number of interfacial bonds during sliding are minimal. We can see that the reduction in the interfacial bond formation and rupture with Ponomarev's forcefield results in a reduction in the friction force with sliding.

Moreover, Figure 7.3 shows how the number of C-C wear atoms change across each temperature with each forcefield. From our study in Chapter 5, it is clear that the wear behaviour is more pronounced with the Newsome forcefield than Ponomarev's. Again, this can be explained by the degree of interfacial bond formation. Using the multibond model²⁵⁷ employed in Chapter 5, it is clear that nanoscale wear events are initiated by stress-augmented thermally activated (SATA) induced interfacial bond formation and rupture. The reduced number of interfacial bonding could therefore be used to explain why there is a significant discrepancy between the two forcefields. This observation can also be seen in Figure 7.4, where Ponomarev's forcefield displays less atom-by-atom attrition and less C-C breaking to either diffuse into the substrate or oxidize to form CO₂ molecules. Additionally, less amorphization is observed in Figure 7.4 in Ponomarev's forcefield.

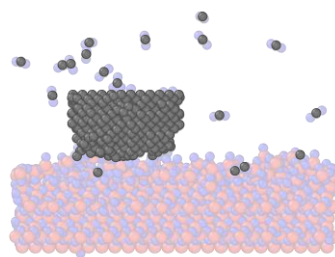
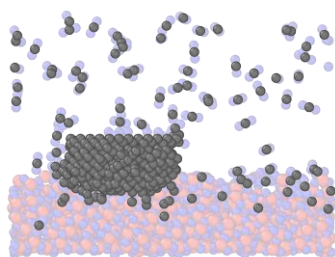
Newsome

Ponomarev

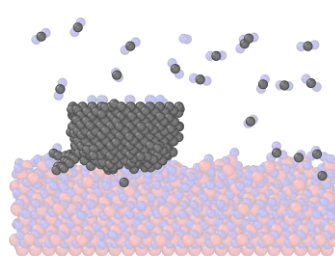
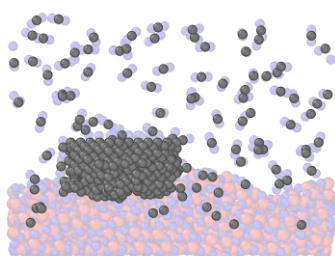
300 K



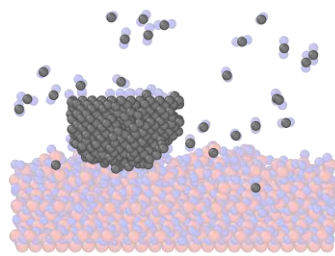
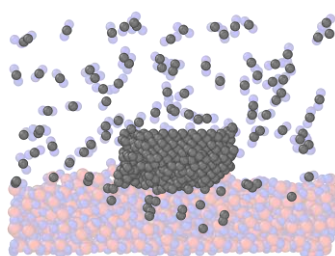
400 K



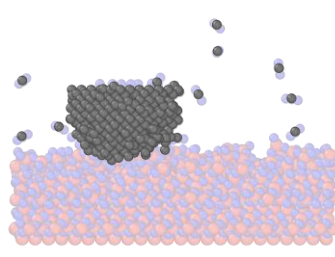
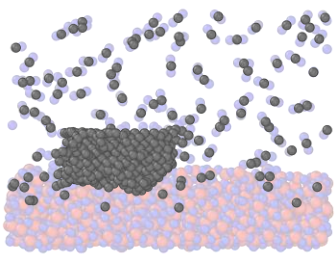
500 K



600 K



700 K



1000 K

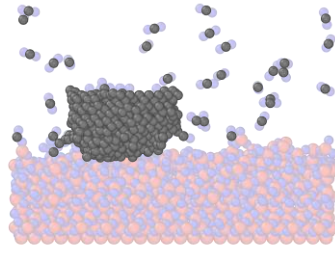
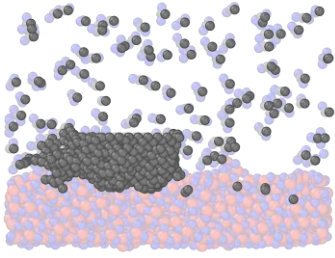


Figure 7.4: Snapshots showing the dry tip wear over time for the Newsome²⁰⁶ and Ponomarev⁴⁶⁵ forcefields. Carbon atoms shown in black, silicon in red, and oxygen in blue. Atom-by-atom attrition occurs for all conditions via C-O interfacial bond formation, C-C breaking and either diffusion into the substrate or oxidation to form CO₂ molecules. Amorphization of the tip followed by cluster detachment at the trailing edge of the tip occurs at high temperatures and loads. This is truer for the Newsome forcefield than for Ponomarev's.

In summary, both the Newsome and Ponomarev forcefield show very similar behaviour for key features observed in the previous chapters. For the features, mainly friction force, interfacial bond formation and rupture, and change in Si-O bonds, the Newsome forcefield consistently produces more pronounced features. Additionally, unlike with the Newsome forcefield, Ponomarev's does not have Si-O bond reformation at these temperatures and loads as observed in Chapter 5.

7.4. Conclusion

This chapter explored how different parameterisations for C/O/Si/H ReaxFF forcefields behave with a dry diamond-quartz system, mainly forcefields developed by Newsome et al. and Ponomarev et al. We find that both forcefields behave similarly when examining C-O interfacial bond formation and rupture, C-C wear in sliding diamond asperities, and friction force in diamond-quartz contacts. We see that even though both parameters show similar behaviour, the rates and magnitude of these processes are accelerated and larger when describing the system using Newsome's parameters. Another distinction between the two is the dynamic evolution of Si-O bonds in the quartz substrate. As we observed in Chapter 5, Si-O bonds begin to rupture with the sliding asperity, which is also apparent with Ponomarev's parameters. However, unlike Newsome's parameter set, Ponomarev's does not account for Si-O bond reformation, which is indicative of a phase transformation as discussed in Chapter 5. We believe that careful selection of parameters is

therefore critical when employing ReaxFF to describe complex systems as some processes, and the rates and magnitudes of these processes, are forcefield specific at certain conditions.

Chapter 8: Conclusions and Future Work

In this chapter, the main conclusions drawn from this project are elucidated and summarised. Additionally, work to extend this project further is discussed.

8.1. Conclusions

1. We have seen how NEMD-ReaxFF coupled simulations can elucidate the mechanistic details of several tribological phenomena, mainly by developing a fundamental understanding of friction and wear at the atomic scale. Reactive forcefields are able to accurately represent chemical behaviour and dynamic evolution of systems and have been previously used to further understand mechanochemical phenomena, even though the techniques are limited through their system size and timescales. Additionally, we have examined how there is considerable experimental and theoretical evidence to support the idea that macroscale friction and wear laws cannot be extrapolated to single asperities at the nanoscale. It follows that at low loads and adhesive forces, atom-by-atom attrition models and transition state theory can provide a valid explanation for nanoscale wear, but at higher loads, this fails, and Archard-like wear is observed.
2. We employ macroscale tribometer experiments and NEMD simulations using ReaxFF to reveal why the friction of diamond-rock interfaces varies significantly depending on the rock type and the presence of water. Superlinear friction–load behavior is observed above a threshold pressure (2 GPa) in both the tribometer experiments in a humid air environment and NEMD simulations with water molecules present at the interface. The NEMD simulations show that this is due to interfacial bonding. The rate of interfacial bond formation increases exponentially with pressure, which is indicative of a SATA process. When water is present, the friction coefficient for diamond–calcite is much higher

than for diamond–quartz in both the experiments and NEMD simulations. The NEMD simulations indicate that the higher friction coefficient for diamond–calcite than diamond–quartz contacts is due to a greater amount of interfacial bonding. We also show that the mean friction force is linearly dependent on the mean number of interfacial bonds during steady-state sliding.

3. Macroscale tribometer experiments then show how in diamond-granite contacts, a hexadecane-lubricated interface displays the highest friction behaviour, followed by an air environment, and finally shows that a water-lubricated contact produces the lowest friction coefficient over a load range 1-100 N and tangential velocities equal to 0.095 m s^{-1} . NEMD-ReaxFF coupled simulations were able to show that this is due to the degree of interfacial bonding in each system, with the *n*-hexadecane system displaying the highest number of interfacial bonds forming, followed by the air environment, and finally water with the lowest. The rate of interfacial bond formation increases exponentially with pressure, which is indicative of a SATA process. The simulations reveal that increased levels of water terminate potential sites of interfacial bond formation by passivating the interface with either OH or H bonds. We also show that the mean friction force is linearly dependent as a function of the mean number of interfacial bonds during steady-state sliding.
4. We also performed NEMD simulations to quantify wear of diamond tips on α -quartz substrates. Initially, we show that wear in these systems begins with C-O interfacial bond formation, which is followed by C-C cleavage, and either diffusion of carbon into the substrate or further oxidation to form CO_2 molecules. We also observe $sp^3 \rightarrow sp^2$ transitions within the tip itself (graphitization or amorphization), which should not themselves be considered as wear since the atoms are not necessarily removed from the tip. The increase in wear rate with normal stress cannot be described using standard SATA-based models at

high loads. However, the multibond wear model, which encapsulates three distinct SATA processes, is able to describe the initial wear behaviour of diamond on α -quartz over the entire load range studied. When the normal stress reaches a certain threshold, there is a transition from exponential growth of the initial wear rate with stress (as predicted by SATA models), towards stress-independent initial wear rate (as predicted by the Archard model). After this initial running-in period, a tail fracture or cluster detachment wear process becomes dominant, where the wear rate becomes approximately linearly proportional with sliding distance and load, which is consistent with the Archard model. We observe that when water is included in the contact, the wear rate is significantly reduced by the reduction in interfacial bonds, which is consistent with previous experimental and theoretical investigations.

5. NEMD simulations of diamond-quartz systems also reveal a mechanochemically induced phase transformation of α -quartz to an stishovite-like phase. Our results show that when no water is present, the diamond asperity is able to initiate structural transformations within the substrate through a three-phase process: rupture of Si-O bonds, steady-state transitionary period, and finally the reformation of Si-O bonds. When water is present, the sliding surfaces become terminated with hydroxyl groups which prevent direct contact between the tip and asperity. For all systems, the rate of the Si-O bond rupture and formation depend on both temperatures and pressure and can be assumed as SATA processes. The sliding asperity has been shown to decrease the E_a of Si-O bond breaking by a factor of three, and initiate the reformation process, indicating that this process is mechanochemically driven. RDFs and bond angle calculations reveal the presence of an stishovite-like phase being present.

6. Comparing two published ReaxFF parameterisations for C/O/Si/H, we observe that the presence and magnitude of some of the processes discussed above are entirely forcefield dependent. While both forcefields show similar behaviour for C-O interfacial bond formation and rupture, C-C wear, and mean friction force, albeit at different rates and magnitudes, the presence of a mechanochemically induced phase transformation of α -quartz to an stishovite-like phase is only possible with certain ReaxFF forcefields at the temperatures and load ranges studied. We believe that careful selection of parameters is therefore critical when employing ReaxFF to describe complex systems as some processes, and the rates and magnitudes of these processes, are forcefield specific at certain conditions.

8.2. Further Work

Molecular modelling techniques continue to provide valuable insights in the tribology field, and this is expected to grow in the future with the development of new and improved techniques. The field is predominantly focused on using experimental techniques, but computational advancements have meant that researchers are able to further their understanding of complex tribological phenomena. This has allowed and will continue to allow the development of the design and formulation of efficient lubricants and surfaces. The fundamental understanding of tribochemistry, triboemissions, and adhesion would benefit from modelling techniques that span multiple levels of complexity and scales. This section will focus on three main aspects for development.

8.2.1. Improved Polycrystalline Diamond Compact (PDC) Surfaces

As discussed in Chapter 2, several experimental investigations have aimed to improve the thermal stability of PDC in an effort to improve its wear behaviour, mainly studies by Bovenkerk et al.,⁶³ Uedaa et al.,⁶⁴ Jaworska et al.,⁷⁴ Wang et al.,⁷⁵ and Liu et al.⁷⁶ Experimental studies are very time-

consuming and heavily dependent on the conditions in which they are performed, and many of these investigations found that new PDC materials come at a significant economic cost and are chemically not feasible on a larger scale. ReaxFF is a promising tool for materials science and with the development of several different parameter sets becoming available, “designer” PDCs surfaces can now be modelled. Other carbon-based materials, including diamond-like carbon (DLC), can be significantly altered by doping and alloying DLC with metals, metalloids, or other elements from gaseous species, which can improve mechanical, tribological, and thermal properties.⁴⁷⁵ Like PDCs, the frictional behaviour of DLC can fluctuate drastically during sliding through tribochemical interactions.^{476,477} Work done by Heimberg *et al.* and Dickrell *et al.* confirmed that gaseous species can form physisorbed layers on the surface, and even though these layers can be mechanically removed during sliding, they can re-form rapidly.^{478,479} These tribochemical interactions is why friction coefficients of opposing DLC contacts fluctuate when sliding in atmospheric conditions. More advanced methods of synthesising films have allowed for elemental doping, elements including Ti, B, S, Si, Cr, F, W and N, and studies have shown that doping or alloys of DLC have led to improved mechanical, tribological, thermal and electrical properties.^{480,481} Doping with nitrogen, however (sometimes referred to as carbon nitride), considerably increases the hardness and friction properties of the film.^{482,483} Hilbert *et al.*⁴⁸⁴ used ReaxFF to show how Si doping enhances the thermal stability of DLC through reductions in the C-C bond length disorder. Some of the experiments mentioned previously of PDC improvements will benefit from molecular modelling techniques. Understanding molecularly why when Bovenkerk *et al.*⁶³ removed cobalt from PDC, the thermal stability improved, or when Uedaa *et al.*⁶⁴ replaced cobalt with MgCO₃ the thermal stability increased but the strength and toughness decreased, or what causes the enhanced strength and stability of PDC with a cBN-diamond composite/mixture⁷⁵ will allow for advancements in PDC technology and performance. ReaxFF parameters already currently exist for several of the systems discussed, and an initial starting point will be modelling PDC composed

of a diamond-SiC composite, which has already been shown experimentally to improve performance.⁷⁶

8.2.2. Improved Drilling Fluids

Little experimental tribometer experiments have investigated how drilling fluids impact tribological performance. We have shown how base fluids, like hexadecane, contradict much of the current knowledge of how lubricants improve friction performance. Further studies, both experimental and computational, are required to improve the fundamental understanding of diamond-rock contacts. We have shown how water can drastically improve friction and wear behaviour, yet non-aqueous drilling fluids are the most widely used type of fluid for drilling through petroleum formations.⁹¹ This is mainly due to drilling fluids (muds) having several functions, not only are they employed for reducing friction and wear but are used for a multitude of issues relating to performance as discussed in Chapter 2. However, non-aqueous drilling fluids and “designer fluids”, which consist of well-characterized hydrocarbons have been posed with significant challenges, including high initial cost, health, safety and environmental concerns, incompatibility with elastomers, high potential for lost circulation, high sensitivity to pressure and temperature, inability to detect gas kicks, and undesirable effects on some logging tools.⁹¹ Water-based muds are low-cost and environmentally friendly¹⁰⁰ and are key for the future of rock drilling. Using molecular modelling techniques, the mechanistic details of drilling fluids can lead to improved tribological performance in diamond-rock contacts and the subsequent advancement of current drilling technology.

8.2.3. Linking MD to Other Scales

Reactive forcefields, like ReaxFF, are very difficult and time-consuming to parameterise,¹⁹⁴ and as we saw in Chapter 7, the magnitude and presence of some processes are entirely forcefield dependent. To combat this, reactivity of diamond-rock surfaces can be explicitly modelled using

first principles or ab initio MD techniques. Car-Parrinello MD (CP-MD)^{485–488} and tight-binding quantum chemical MD (TB-QCMD)^{489,490} have provided valuable insights into the mechanistic reactivity details of several common friction modifiers. TB-QCMD has also been used to investigate systems with shear.⁴⁹¹ However, these techniques are several orders of magnitude more computationally expensive than classical MD, and therefore, timescales and system sizes are significantly limited. They do however provide validation for some of the processes observed using ReaxFF and can be used to reaffirm the current theoretical framework surrounding mechanochemistry and tribochemistry.

Instead of scaling systems down, coarse-grained MD (CG-MD) groups multiple atoms together to form ‘beads’, which reduces the number of interaction sites. CG-MD has been previously employed to understand the friction behaviour of polymer brushes,^{492,493} friction modifiers,⁴⁹⁴ and ionic liquids.⁴⁹⁵ Additionally, the interfacial laws of friction from the MD simulations can be used in MD-continuum coupling techniques. Two methods are generally employed depending on whether it is possible to establish scale separation between the atomic and continuum levels. Viscosity and slip information gathered from MD simulations have been used to predict film thickness and friction for strongly confined systems.^{496,497} However, if no separation between the atomic and continuum levels can be established, the respective models have to run concurrently on different spatial regions. Here, information is transferred between the MD and continuum regions.^{498–500}

References

- (1) Bhamra, J. S.; Ewen, J. P.; Latorre, C. A.; Bomidi, J. A. R.; Bird, M. W.; Dasgupta, N.; van Duin, A. C. T.; Dini, D. Interfacial Bonding Controls Friction in Diamond–Rock Contacts. *J. Phys. Chem. C* **2021**, *125*, 18395–18408.
- (2) Jost, P. Lubrication (Tribology)—A Report on the Present Position and Industry’s Needs. *London HM Station. Off.* **1966**.
- (3) Holmberg, K.; Erdemir, A. Influence of Tribology on Global Energy Consumption, Costs and Emissions. *Friction*. Tsinghua University Press September 1, 2017, pp 263–284.
- (4) McCarthy, J.; Canziani, O.; Leary, N.; Dokken, D. *Climate Change 2001: Impacts, Adaptation, and Vulnerability: Contribution of Working Group II to the Third Assessment Report of the Intergovernmental Panel On*; 2001.
- (5) Wiedmann, T. O.; Schandl, H.; Lenzen, M.; Moran, D.; Suh, S.; West, J.; Kanemoto, K. The Material Footprint of Nations. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 6271–6276.
- (6) Holmberg, K.; Kivikytö-Reponen, P.; Härkisaari, P.; Valtonen, K.; Erdemir, A. Global Energy Consumption Due to Friction and Wear in the Mining Industry. *Tribol. Int.* **2017**, *115*, 116–139.
- (7) Nosonovsky, M.; Bhushan, B. Green Tribology: Biomimetics, Energy Conservation and Sustainability. *Green Energy Technol.* **2012**, *49*.
- (8) Urbakh, M.; Klafter, J.; Gourdon, D.; Israelachvili, J. The Nonlinear Nature of Friction. *Nature* **2004**, *430*, 525–528.
- (9) Aghababaei, R.; Warner, D. H.; Molinari, J. F. Critical Length Scale Controls Adhesive Wear Mechanisms. *Nat. Commun.* **2016**, *7*, 1–8.
- (10) Vakis, A. I.; Yastrebov, V. A.; Scheibert, J.; Nicola, L.; Dini, D.; Minfray, C.; Almqvist, A.; Paggi, M.; Lee, S.; Limbert, G.; Molinari, J. F.; Anciaux, G.; Aghababaei, R.; Echeverri Restrepo, S.; Papangelo, A.; Cammarata, A.; Nicolini, P.; Putignano, C.; Carbone, G.; Stupkiewicz, S.; Lengiewicz, J.; Costagliola, G.; Bosia, F.; Guarino, R.; Pugno, N. M.; Müser, M. H.; Ciavarella, M. Modeling and Simulation in Tribology across Scales: An Overview. *Tribol. Int.* **2018**, *125*, 169–199.
- (11) Chung, Y. W. *Micro- and Nanoscale Phenomena in Tribology*; CRC Press, 2011.
- (12) Cleveland, C. J. Net Energy from the Extraction of Oil and Gas in the United States. *Energy* **2005**, *30*, 769–782.
- (13) Moore, J. N.; Simmons, S. F. More Power from Below. *Science*. **2013**, *340*, 933–934.

- (14) Bui, M.; Adjiman, C. S.; Bardow, A.; Anthony, E. J.; Boston, A.; Brown, S.; Fennell, P. S.; Fuss, S.; Galindo, A.; Hackett, L. A.; Hallett, J. P.; Herzog, H. J.; Jackson, G.; Kemper, J.; Krevor, S.; Maitland, G. C.; Matuszewski, M.; Metcalfe, I. S.; Petit, C.; Puxty, G.; Reimer, J.; Reiner, D. M.; Rubin, E. S.; Scott, Stewart, A.; Shah, N.; Smit, B.; Trusler, J. P. M.; Webley, P.; Wilcox, J.; MacDowell, N. Carbon Capture and Storage (CCS): The Way Forward. *Energy Environ. Sci.* **2018**, *11*, 1062–1176.
- (15) Krall, L.; McCartin, T.; MacFarlane, A. Siting Deep Boreholes for Disposal of Radioactive Waste: Consequences for Tight Coupling between Natural and Engineered Systems. *Environ. Sci. Technol.* **2020**, *54*, 629–646.
- (16) Teale, R. The Concept of Specific Energy in Rock Drilling. *Int. J. Rock Mech. Min. Sci.* **1965**, *2*, 57–73.
- (17) Perrott, C. M. Tool Materials for Drilling and Mining. *Annu. Rev. Mater. Sci.* **1979**, *9*, 23–50.
- (18) Lukawski, M. Z.; Anderson, B. J.; Augustine, C.; Capuano, L. E.; Beckers, K. F.; Livesay, B.; Tester, J. W. Cost Analysis of Oil, Gas, and Geothermal Well Drilling. *J. Pet. Sci. Eng.* **2014**, *118*, 1–14.
- (19) Lyons, K. D.; Honeygan, S.; Mroz, T. NETL Extreme Drilling Laboratory Studies High Pressure High Temperature Drilling Phenomena. *J. Energy Resour. Technol.* **2008**, *130*, 0431021.
- (20) Wentorf, R. H.; DeVries, R. C.; Bundy, F. P. Sintered Superhard Materials. *Science*. **1980**, *208*, 873–880.
- (21) Appl, F. C.; Wilson, C. C.; Lakshman, I.; Appl, F. C.; Wilson, C. C.; Lakshman, I. Measurement of Forces, Temperatures and Wear of PDC Cutters in Rock Cutting. *Wear* **1993**, *169*, 9–24.
- (22) Yahiaoui, M.; Paris, J. Y.; Delbé, K.; Denape, J.; Gerbaud, L.; Colin, C.; Ther, O.; Dourfaye, A. Quality and Wear Behavior of Graded Polycrystalline Diamond Compact Cutters. *Int. J. Refract. Met. Hard Mater.* **2016**, *56*, 87–95.
- (23) Cortes, J.; Besson, A. Behavior of Polycrystalline Diamond Compact Cutters While Drilling in Bottomhole Conditions-Field Applications. **1981**.
- (24) Wise, J. L.; Raymond, D. W.; Cooley, C. H.; Bertagnolli, K. Effects of Design and Processing Parameters on Performance of PDC Drag Cutters for Hard-Rock Drilling. In *Transactions - Geothermal Resources Council*; 2002; pp 201–206.
- (25) Lin, T.-P.; Hood, M.; Cooper, G. A.; Li, X. Wear and Failure Mechanisms Compact Bits of Polycrystalline Diamond. *Wear* **1992**, *156*, 133–150.

- (26) Pessier, R. C.; Fear, M. J. Quantifying Common Drilling Problems With Mechanical Specific Energy and a Bit-Specific Coefficient of Sliding Friction. In *SPE Annual Technical Conference and Exhibition*; Society of Petroleum Engineers: Washington D.C., 2007; p SPE-24584.
- (27) Wheeler, D. W. Applications of Diamond to Improve Tribological Performance in the Oil and Gas Industry. *Lubricants* **2018**, *6*, 84.
- (28) Glowka, D. A. The Thermal Response of Rock to Friction in the Drag Cutting Process. *J. Struct. Geol.* **1989**, *11*, 919–931.
- (29) Mehan, R. L.; Hibbs, L. E. Thermal Degradation of Sintered Diamond Compacts. *J. Mater. Sci.* **1989**, *24*, 942–950.
- (30) Burwell, J. T. Survey of Possible Wear Mechanisms. *Wear* **1957**, *1*, 119–141.
- (31) Detournay, E.; Defourny, P. A Phenomenological Model for the Drilling Action of Drag Bits. *Int. J. Rock Mech. Min. Sci.* **1992**, *29*, 13–23.
- (32) Li, G.; Rahim, M. Z.; Pan, W.; Wen, C.; Ding, S. The Manufacturing and the Application of Polycrystalline Diamond Tools – A Comprehensive Review. *J. Manuf. Process.* **2020**, *56*, 400–416.
- (33) Zhu, L.; Wang, J. A Study on Titanium Alloys Deep-Hole Drilling Technique. *Mater. Sci. Forum* **2006**, *532–533*, 945–948.
- (34) Abbaschian, R.; Zhu, H.; Clarke, C. High Pressure–High Temperature Growth of Diamond Crystals Using Split Sphere Apparatus. *Diam. Relat. Mater.* **2005**, *14*, 1916–1919.
- (35) Ralchenko, V. G.; Ashkihazi, E. E.; Zavedeev, E. V.; Khomich, A. A.; Bolshakov, A. P.; Ryzhkov, S. G.; Sovyk, D. N.; Shershulin, V. A.; Yurov, V. Y.; Rudnev, V. V. High-Rate Ultrasonic Polishing of Polycrystalline Diamond Films. *Diam. Relat. Mater.* **2016**, *66*, 171–176.
- (36) Bochechka, O. O. Production of Polycrystalline Materials by Sintering of Nanodispersed Diamond Nanopowders at High Pressure. Review. *J. Superhard Mater.* **2018**, *40*, 325–334.
- (37) Michaelson, S.; Ternyak, O.; Akhvlediani, R.; Hoffman, A.; Lafosse, A.; Azria, R.; Williams, O. A.; Gruen, D. M. Hydrogen Concentration and Bonding Configuration in Polycrystalline Diamond Films: From Micro-to Nanometric Grain Size. *J. Appl. Phys.* **2007**, *102*, 113516.
- (38) Olsen, R. H.; Dewes, R. C.; Aspinwall, D. K. Machining of Electrically Conductive CVD Diamond Tool Blanks Using EDM. *J. Mater. Process. Technol.* **2004**, *149*, 627–632.
- (39) Huff, C. F.; Varnado, S. G. Recent Developments in Polycrystalline Diamond Drill Bit Design. *Society* **1980**, No. SAND79-1592C, 1–28.

- (40) Ersoy, A.; Waller, M. D. Wear Characteristics of PDC Pin and Hybrid Core Bits in Rock Drilling. *Wear* **1995**, *188*, 150–165.
- (41) Archard, J. F. Contact and Rubbing of Flat Surfaces. *J. Appl. Phys.* **1953**, *24*, 981.
- (42) Kauzlarich, J. J.; Williams, J. A. Archard Wear and Component Geometry. *Proc. Inst. Mech. Eng. Part J* **2001**, *215*, 387–398.
- (43) Yahiaoui, M.; Gerbaud, L.; Paris, J. Y.; Denape, J.; Dourfaye, A. A Study on PDC Drill Bits Quality. *Wear* **2013**, *298–299*, 32–41.
- (44) Yahiaoui, M.; Paris, J. Y.; Delbé, K.; Denape, J.; Gerbaud, L.; Colin, C.; Ther, O.; Dourfaye, A. Quality and Wear Behavior of Graded Polycrystalline Diamond Compact Cutters. *Int. J. Refract. Met. Hard Mater.* **2016**, *56*, 87–95.
- (45) Wang, C.; Li, S.; Zhang, L. Evaluation of Rock Abrasiveness Class Based on the Wear Mechanisms of PDC Cutters. *J. Pet. Sci. Eng.* **2019**, *174*, 959–967.
- (46) Hamzaban, M. T.; Rostami, J.; Dahl, F.; Macias, F. J.; Jakobsen, P. D. Wear of Cutting Tools in Hard Rock Excavation Process: A Critical Review of Rock Abrasiveness Testing Methods. *Rock Mech. Rock Eng.* **2022**, *1*, 3.
- (47) Rad, P. F. Bluntness and Wear of Rolling Disk Cutters. *Int. J. Rock Mech. Min. Sci. Geomech. Abstr.* **1975**, *12*, 93–99.
- (48) Beste, U.; Lundvall, A.; Jacobson, S. Micro-Scratch Evaluation of Rock Types - A Means to Comprehend Rock Drill Wear. *Tribol. Int.* **2004**, *37*, 203–210.
- (49) Bex, P. A.; Shafto, G. R. The Influence of Temperature and Heating Time on PCD Performance. *Ind. Diam. Div. Commun.* **1978**, *44*, 128–132.
- (50) Rabinowicz, E. Abrasive Wear Resistance as a Materials Test. *Lubr. Eng.* **1977**, *33*, 378–381.
- (51) Huang, H.; Detournay, E. Intrinsic Length Scales in Tool-Rock Interaction. *Int. J. Geomech.* **2008**, *8*, 39–44.
- (52) He, X.; Xu, C.; Peng, K.; Huang, G. On the Critical Failure Mode Transition Depth for Rock Cutting with Different Back Rake Angles. *Tunn. Undergr. Sp. Technol.* **2017**, *63*, 95–105.
- (53) Appl, F. C.; Wilson, C. C.; Lakshman, I. Carbon Capture and Storage (CCS): The Way Forward. *Wear* **1993**, *169*, 9–24.
- (54) Sinor, A.; Warren, T. M. Drag Bit Wear Model. *SPE Drill. Eng.* **1989**, *4*, 128–136.
- (55) Miller, D.; Ball, A. Rock Drilling with Impregnated Diamond Microbits-An Experimental Study. *Int. J. Rock Mech. Min. Sci.* **1990**, *27*, 363–371.
- (56) Dunn, K. J.; Lee, M. The Fracture and Fatigue of Sintered Diamond Compact. *J. Mater.*

- Sci.* **1979**, *14*, 882–890.
- (57) Brett, J. F.; Warren, T. M.; Behr, S. M. Bit Whirl. A New Theory of PDC Bit Failure. *SPE Drill. Eng.* **1990**, *5*, 275–281.
 - (58) Behr, S. M.; Warren, T. M.; Sinor, L. A.; Brett, J. F. Three-Dimensional Modeling of PDC Bits. In *onepetro.org*; 1991; pp 273–281.
 - (59) Glowka, D. A.; Stone, C. M. EFFECTS OF THERMAL AND MECHANICAL LOADING ON PDC BIT LIFE. *SPE Drill. Eng.* **1986**, *1*, 201–214.
 - (60) Yoshino, M.; Nakajima, S.; Terano, M. Tool Wear of a Single-Crystal Diamond Tool in Nano-Groove Machining of a Quartz Glass Plate. *Surf. Topogr. Metrol. Prop.* **2015**, *3*, 044007.
 - (61) Thomas, E. L. H.; Nelson, G. W.; Mandal, S.; Foord, J. S.; Williams, O. A. Chemical Mechanical Polishing of Thin Film Diamond. *Carbon N. Y.* **2014**, *68*, 473–479.
 - (62) Peguiron, A.; Moras, G.; Walter, M.; Uetsuka, H.; Pastewka, L.; Moseler, M. Activation and Mechanochemical Breaking of C-C Bonds Initiate Wear of Diamond (110) Surfaces in Contact with Silica. *Carbon.* **2016**, *98*, 474–483.
 - (63) Bovenkerk, H. P.; Gigl, P. D. US Patent. 4224380, 1980.
 - (64) Akaishi, M.; Yamaoka, S. Physical and Chemical Properties of the Heat Resistant Diamond Compacts from Diamond-Magnesium Carbonate System. *Mater. Sci. Eng. A* **1996**, *209*, 54–59.
 - (65) Qian, J.; Voronin, G.; Zerda, T. W.; He, D.; Zhao, Y. High-Pressure, High-Temperature Sintering of Diamond-SiC Composites by Ball-Milled Diamond-Si Mixtures. *J. Mater. Res.* **2002**, *17*, 2153–2160.
 - (66) Pantea, C.; Gubicza, J.; Ungar, T.; Voronin, G. A.; Zerda, T. W. Dislocation Density and Graphitization of Diamond Crystals. *Phys. Rev. B* **2002**, *66*, 094106.
 - (67) Pantea, C.; Qian, J.; Voronin, G. A.; Zerda, T. W. High Pressure Study of Graphitization of Diamond Crystals. *J. Appl. Phys.* **2002**, *91*, 1957–1962.
 - (68) Qian, J.; Zerda, T. W.; He, D.; Daemen, L.; Zhao, Y. Micron Diamond Composites with Nanocrystalline Silicon Carbide Bonding. *J. Mater. Res.* **2003**, *18*, 1173–1178.
 - (69) Voronin, G. A.; Zerda, T. W.; Qian, J.; Zhao, Y.; He, D.; Dub, S. N. Diamond–SiC Nanocomposites Sintered from a Mixture of Diamond and Silicon Nanopowders. *Diam. Relat. Mater.* **2003**, *12*, 1477–1481.
 - (70) Gubicza, J.; Nauyoks, S.; Balogh, L.; Labar, J.; Zerda, T. W.; Ungár, T. Influence of Sintering Temperature and Pressure on Crystallite Size and Lattice Defect Structure in Nanocrystalline SiC. *J. Mater. Res.* **2007**, *22*, 1314–1321.

- (71) Palosz, B.; Stelmakh, S.; Grzanka, E.; Gierlotka, S.; Nauyoks, S.; Zerda, T. W.; Palosz, W. Origin of Macrostrains and Microstrains in Diamond-SiC Nanocomposites Based on the Core-Shell Model. *J. Appl. Phys.* **2007**, *102*, 074303.
- (72) Balogh, L.; Nauyoks, S.; Zerda, T. W.; Pantea, C.; Stelmakh, S.; Palosz, B.; Ungár, T. Structure of Diamond-Silicon Carbide Nanocomposites as a Function of Sintering Temperature at 8 GPa. *Mater. Sci. Eng. A* **2008**, *487*, 180–188.
- (73) Nauyoks, S.; Wieligor, M.; Zerda, T. W.; Balogh, L.; Ungar, T.; Stephens, P. Stress and Dislocations in Diamond-SiC Composites Sintered at High Pressure, High Temperature Conditions. *Compos. Part A Appl. Sci. Manuf.* **2009**, *40*, 566–572.
- (74) Jaworska, L. Diamond-Ceramic Bonding Phase Composites for Application in Cutting Tools. *Mater. Ceram.* **2011**, *63*, 131–137.
- (75) Wang, P.; He, D.; Wang, L.; Kou, Z.; Li, Y.; Xiong, L.; Hu, Q.; Xu, C.; Lei, L.; Wang, Q.; Liu, J.; Zhao, Y. Diamond-CBN Alloy: A Universal Cutting Material. *Appl. Phys. Lett.* **2015**, *107*, 101901.
- (76) Liu, S.; Han, L.; Zou, Y.; Zhu, P.; Liu, B. Polycrystalline Diamond Compact with Enhanced Thermal Stability. *J. Mater. Sci. Technol.* **2017**, *33*, 1386–1391.
- (77) Richard, T.; Germy, C.; Detournay, E. A Simplified Model to Explore the Root Cause of Stick-Slip Vibrations in Drilling Systems with Drag Bits. *J. Sound Vib.* **2007**, *305*, 432–456.
- (78) Kovalyshen, Y. Understanding Root Cause of Stick-Slip Vibrations in Deep Drilling with Drag Bits. *Int. J. Non. Linear. Mech.* **2015**, *67*, 331–341.
- (79) Chen, S.; Wisinger, J.; Dunbar, B.; Propes, C. Identification and Mitigation of Friction-And Cutting Action-Induced Stick-Slip Vibrations with PDC Bits. *SPE Drill. Complet.* **2020**, SPE-199639.
- (80) Thompson, P. A.; Robbins, M. O. Origin of Stick-Slip Motion in Boundary Lubrication. **1990**, *250*, 792–794.
- (81) Brett, J. F. The Genesis of Torsional Drillstring Vibrations. *SPE Drill. Eng.* **1992**, *7*, 168–174.
- (82) Fear, M. J.; Abbassian, F.; Parfitt, S. H. L.; McClean, A. The Destruction of PDC Bits by Severe Slip-Stick Vibration. **1997**.
- (83) Jain, J. R.; Ledgerwood, L. W.; Hoffmann, O. J.; Schwefe, T.; Fuselier, D. M. Mitigation of Torsional Stick-Slip Vibrations in Oil Well Drilling through PDC Bit Design: Putting Theories to the Test. *Proc. - SPE Annu. Tech. Conf. Exhib.* **2011**, *3*, 1815–1828.
- (84) Carpenter, C. Resolving Torsional Vibration in Limestone Reservoirs Reduces Equipment Damage. *J. Pet. Technol.* **2019**, *71*, 68–69.

- (85) Dagrain, F.; Richard, T. On the Influence of PDC Wear and Rock Type on Friction Coefficient and Cutting Efficiency. In *Eurock 2006: Multiphysics Coupling and Long Term Behaviour in Rock Mechanics*; Liege, Belgium, 2006; pp 577–584.
- (86) Filippov, A. E.; Klafter, J.; Urbakh, M. Friction through Dynamical Formation and Rupture of Molecular Bonds. *Phys. Rev. Lett.* **2004**, *92*, 135503.
- (87) Li, Q.; Tullis, T. E.; Goldsby, D.; Carpick, R. W. Frictional Ageing from Interfacial Bonding and the Origins of Rate and State Friction. *Nature* **2011**, *480*, 233–236.
- (88) Tian, K.; Gosvami, N. N.; Goldsby, D. L.; Carpick, R. W. Stick-Slip Instabilities for Interfacial Chemical Bond-Induced Friction at the Nanoscale. *J. Phys. Chem. B* **2018**, *122*, 991–999.
- (89) Chilingarian, G.; Vorabutr, P. Drilling and Drilling Fluids. **1983**.
- (90) Darley, H. C.; G. R. Gray. Composition and Properties of Drilling and Completion Fluids, 634p. *Gulf Houst.* **1998**, 1–37.
- (91) Growcock, F. B.; Patel, A. D. The Revolution in Non-Aqueous Drilling Fluids, AADE-11-NTCE-33. *AADE Natl. Tech. Conf. Exhib.* **2011**, 1–8.
- (92) Shah, S. N.; Shanker, N. H.; Ogugbue, C. C. Future Challenges of Drilling Fluids and Their Rheological Measurements. *Am. Assoc. Drill. Eng. Fluids Conf. Exhib.* **2010**, *10*, 1–16.
- (93) Vryzas, Z.; Mahmoud, O.; Nasr-El-din, H. A.; Kelessidis, V. C. Development and Testing of Novel Drilling Fluids Using Fe₂O₃ and SiO₂ Nanoparticles for Enhanced Drilling Operations. *Int. Pet. Technol. Conf. IPTC 2015* **2015**, 2015-January.
- (94) Zheng, X. Drilling Fluids, China University of Geosciences, Beijing, 2010.
- (95) Karakosta, K.; Mitropoulos, A. C.; Kyzas, G. Z. A Review in Nanopolymers for Drilling Fluids Applications. *J. Mol. Struct.* **2021**, *1227*, 129702.
- (96) American Petroleum Institute, A. *Principles of Drilling Fluid Control*, 1st ed.; University of Texas, Continuing Education Petroleum Extension Service, 2006; Vol. 12.
- (97) Bourgoyne, A. T. J.; Millheim, K. K.; Chenevert, M. E.; Young, F. S. J. *Applied Drilling Engineering. Textbook Series Vol. 2*; Society of Petroleum Engineers, 1991; Vol. 2.
- (98) Jensen, J. Recent Developments Related to Petroleum Engineering. *Trans. AIME* **1937**, *123*, 63–68.
- (99) Hossain, M. E.; Al-Majed, A. A. *Fundamentals of Sustainable Drilling Engineering*; 2015.
- (100) Aftab, A.; Ismail, A. R.; Ibupoto, Z. H.; Akeiber, H.; Malghani, M. G. K. Nanoparticles Based Drilling Muds a Solution to Drill Elevated Temperature Wells: A Review. *Renew. Sustain. Energy Rev.* **2017**, *76*, 1301–1313.
- (101) Khodja, M.; Canselier, J. P.; Bergaya, F.; Fourar, K.; Khodja, M.; Cohaut, N.; Benmounah,

- A. Shale Problems and Water-Based Drilling Fluid Optimisation in the Hassi Messaoud Algerian Oil Field. *Appl. Clay Sci.* **2010**, *49*, 383–393.
- (102) Chang, W. Z.; Leong, Y. K. Ageing and Collapse of Bentonite Gels—Effects of Li, Na, K and Cs Ions. *Rheol. Acta* **2014**, *53*, 109–122.
- (103) Guo, J.; Yan, J.; Fan, W.; Zhang, H. Applications of Strongly Inhibitive Silicate-Based Drilling Fluids in Troublesome Shale Formations in Sudan. *J. Pet. Sci. Eng.* **2006**, *50*, 195–203.
- (104) Deville, J. P.; Fritz, B.; Jarrett, M. Development of Water-Based Drilling Fluids Customized for Shale Reservoirs. *SPE Drill. Complet.* **2011**, *26*, 484–491.
- (105) Yan, L.; Wang, C.; Xu, B.; Sun, J.; Yue, W.; Yang, Z. Preparation of a Novel Amphiphilic Comb-like Terpolymer as Viscosifying Additive in Low-Solid Drilling Fluid. *Mater. Lett.* **2013**, *105*, 232–235.
- (106) Manea, M. H. Rheological Properties of Drilling Fluids Prepared with Nano Sized Polymer Additives. *Rev. Chim.* **2012**, *63*, 1132–1137.
- (107) Xie, B.; Qiu, Z.; Huang, W.; Cao, J.; Zhong, H. Characterization and Aqueous Solution Behavior of Novel Thermo-Associating Polymers. *J. Macromol. Sci. Part A* **2013**, *50*, 230–237.
- (108) Kania, D.; Yunus, R.; Omar, R.; Abdul Rashid, S.; Mohamad Jan, B. A Review of Biolubricants in Drilling Fluids: Recent Research, Performance, and Applications. *J. Pet. Sci. Eng.* **2015**, *135*, 177–184.
- (109) Zhong, H.; Qiu, Z.; Huang, W.; Sun, D.; Zhang, D.; Cao, J. Synergistic Stabilization of Shale by a Mixture of Polyamidoamine Dendrimers Modified Bentonite with Various Generations in Water-Based Drilling Fluid. *Appl. Clay Sci.* **2015**, *114*, 359–369.
- (110) Salami, O. T.; Plank, J. Preparation and Properties of a Dispersing Fluid Loss Additive Based on Humic Acid Graft Copolymer Suitable for Cementing High Temperature (200°C) Oil Wells. *J. Appl. Polym. Sci.* **2013**, *129*, 2544–2553.
- (111) Zhong, H. Y.; Qiu, Z. S.; Huang, W. A.; Cao, J.; Wang, F. W.; Zhang, X. B. An Inhibition Properties Comparison of Potassium Chloride and Polyoxypropylene Diamine in Water-Based Drilling Fluid. *Pet. Sci. Technol.* **2013**, *31*, 2127–2133.
- (112) Abdo, J.; Haneef, M. D. Clay Nanoparticles Modified Drilling Fluids for Drilling of Deep Hydrocarbon Wells. *Appl. Clay Sci.* **2013**, *86*, 76–82.
- (113) Cai, J.; Chenevert, M. E.; Sharma, M. M.; Friedheim, J. Decreasing Water Invasion into Atoka Shale Using Nonmodified Silica Nanoparticles. *SPE Drill. Complet.* **2012**, *27*, 103–112.

- (114) Nasser, J.; Jesil, A.; Mohiuddin, T.; Ruqeshi, M. Al; Devi, G.; Mohataram, S. Experimental Investigation of Drilling Fluid Performance as Nanoparticles. *World J. Nano Sci. Eng.* **2013**, *2013*, 57–61.
- (115) Kosynkin, D. V.; Ceriotti, G.; Wilson, K. C.; Lomeda, J. R.; Scorsone, J. T.; Patel, A. D.; Friedheim, J. E.; Tour, J. M. Graphene Oxide as a High-Performance Fluid-Loss-Control Additive in Water-Based Drilling Fluids. *ACS Appl. Mater. Interfaces* **2012**, *4*, 222–227.
- (116) Ismail, A. R.; Aftab, A.; Ibupoto, Z. H.; Zolkifile, N. The Novel Approach for the Enhancement of Rheological Properties of Water-Based Drilling Fluids by Using Multi-Walled Carbon Nanotube, Nanosilica and Glass Beads. *J. Pet. Sci. Eng.* **2016**, *139*, 264–275.
- (117) William, J. K. M.; Ponmani, S.; Samuel, R.; Nagarajan, R.; Sangwai, J. S. Effect of CuO and ZnO Nanofluids in Xanthan Gum on Thermal, Electrical and High Pressure Rheology of Water-Based Drilling Fluids. *J. Pet. Sci. Eng.* **2014**, *117*, 15–27.
- (118) Gupta., S. A. P. T. Y. S. D. M. R. K. Flow Behavior of Nanoparticle Stabilized Drilling Fluids and Effect of High Temperature Aging. *AADE* **2011**, *11*, 1–6.
- (119) Rehbinder, P. A.; Shchukin, E. D. Surface Phenomena in Solids during Deformation and Fracture Processes. *Prog. Surf. Sci.* **1972**, *3*, 97–187.
- (120) Westwood, A. R. C.; Ahearn, J. S.; Mills, J. J. Developments in the Theory and Application of Chemomechanical Effects. *Colloids Surf.* **1981**, *2*, 1–35.
- (121) Mills, J. J.; Westwood, A. R. C. Influence of Chemomechanically Active Fluids on Diamond Wear during Hard Rock Drilling. *J. Mater. Sci.* **1978**, *13*, 2712–2716.
- (122) Mills, J. J.; Westwood, A. R. C. Influence of Adsorption Kinetics on Chemomechanically Enhanced Hard Rock Drilling. *J. Mater. Sci.* **1980**, *15*, 3010–3016.
- (123) Cooper, G.; Berlie, J. On the Influence of the Flushing Fluid during Diamond Drilling. *J. Mater. Sci.* **1976**, *11*, 1771–1775.
- (124) Ewen, J. P.; Heyes, D. M.; Dini, D. Advances in Nonequilibrium Molecular Dynamics Simulations of Lubricants and Additives. *Friction* **2018**, *6*, 349–386.
- (125) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; 1987.
- (126) Metropolis, N.; Ulam, S. The Monte Carlo Method. *J. Am. Stat. Assoc.* **1949**, *44*, 335–341.
- (127) Beyer, M. K.; Clausen-Schaumann, H. Mechanochemistry: The Mechanical Activation of Covalent Bonds. *Chem. Rev.* **2005**, *105*, 2921–2948.
- (128) Ostwald, W. Lehrbuch Der Allgemeinen Chemie . Board 1 *Stoichiometrie*; Engelmann **1885**.
- (129) Gilman, J. J. Mechanochemistry. *Science (80-.)*. **1996**, *274*, 65.
- (130) Boldyrev, V. V.; Tkáčová, K. Mechanochemistry of Solids: Past, Present, and Prospects. *J.*

- Mater. Synth. Process.* **2000**, *8*, 121–132.
- (131) Bridgman, P. W. Explorations toward the Limit of Utilizable Pressures. *J. Appl. Phys.* **2004**, *12*, 461.
- (132) Zharov, A. A.; Kovarskii, A. L. *High Pressure Chemistry and Physics of Polymers*, 1st ed.; 1994; Vol. 1.
- (133) Lea, M. C. IV. Disruption of the Silver Haloid Molecule by Mechanical Force. *London, Edinburgh, Dublin Philos. Mag. J. Sci.* **1892**, *34*, 46–50.
- (134) Lea, M. C. On Endothermic Reactions Effected by Mechanical Force. *Am. J. Sci.* **1893**, *s3-46*, 241–244.
- (135) Kaupp, G. Mechanochemistry: The Varied Applications of Mechanical Bond-Breaking. *CrystEngComm* **2009**, *11*, 388–403.
- (136) Frišić, T. New Opportunities for Materials Synthesis Using Mechanochemistry. *J. Mater. Chem.* **2010**, *20*, 7599–7605.
- (137) Grandbois, M.; Beyer, M.; Rief, M.; Clausen-Schaumann, H.; Gaub, H. E. How Strong Is a Covalent Bond? *Science (80-.)*. **1999**, *283*, 1727–1730.
- (138) Ribas-Arino, J.; Marx, D. Covalent Mechanochemistry: Theoretical Concepts and Computational Tools with Applications to Molecular Nanomechanics. *Chem. Rev.* **2012**, *112*, 5412–5487.
- (139) Ribas-Arino, J.; Shiga, M.; Marx, D. Understanding Covalent Mechanochemistry. *Angew. Chemie Int. Ed.* **2009**, *48*, 4190–4193.
- (140) Bell, G. I. Models for the Specific Adhesion of Cells to Cells. *Science (80-.)*. **1978**, *200*, 618–627.
- (141) Rief, M.; Gautel, M.; Oesterhelt, F.; Fernandez, J. M.; Gaub, H. E. Reversible Unfolding of Individual Titin Immunoglobulin Domains by AFM. *Science* **1997**, *276*, 1109–1112.
- (142) Florin, E. L.; Moy, V. T.; Gaub, H. E. Adhesion Forces between Individual Ligand-Receptor Pairs. *Science* **1994**, *264*, 415–417.
- (143) Rief, M.; Oesterhelt, F.; Heymann, B.; Gaub, H. E. Single Molecule Force Spectroscopy on Polysaccharides by Atomic Force Microscopy. *Science* **1997**, *275*, 1295–1297.
- (144) Lee, G. U.; Chrisley, L. A.; Colton, R. J. Direct Measurement of the Forces Between Complementary Strands of DNA. *Science (80-.)*. **1994**, *266*, 771–773.
- (145) Chandler, D.; Percus, J. K. Introduction to Modern Statistical Mechanics. *Phys. Today* **1988**, *41*, 114–118.
- (146) De Boer, J. H. The Influence of van Der Waals' Forces and Primary Bonds on Binding Energy, Strength and Orientation, with Special Reference to Some Artificial Resins. *Trans.*

- Faraday Soc.* **1936**, *32*, 10–37.
- (147) Kauzmann, W.; Eyring, H. The Viscous Flow of Large Molecules. *J. Am. Chem. Soc.* **1940**, *62*, 3113–3125.
- (148) Eyring, H. The Activated Complex and the Absolute Rate of Chemical Reactions. *Chem. Rev.* **1935**, *17*, 65–77.
- (149) Jacobs, T. D. B.; Gotsmann, B.; Lantz, M. A.; Carpick, R. W. On the Application of Transition State Theory to Atomic-Scale Wear. *Tribol. Lett.* **2010**, *39*, 257–271.
- (150) Christian, J. *The Theory of Transformations in Metals and Alloys*; 2002.
- (151) Vineyard, G. H. Frequency Factors and Isotope Effects in Solid State Rate Processes. *J. Phys. Chem. Solids* **1957**, *3*, 121–127.
- (152) MILLS, G.; SCHENTER, G. K.; MAKAROV, D. E.; JÓNSSON, H. Quantum Transition State Theory. **1998**, 405–421.
- (153) Bell, G. I. Models for the Specific Adhesion of Cells to Cells. *Science*. American Association for the Advancement of Science May 12, 1978, pp 618–627.
- (154) Spikes, H. Stress-Augmented Thermal Activation: Tribology Feels the Force. *Friction* **2018**, *6*, 1–31.
- (155) Martini, A.; Kim, S. H. Activation Volume in Shear-Driven Chemical Reactions. *Tribol. Lett.* **2021**, *69*, 1–14.
- (156) Alder, B. J.; Wainwright, T. E. Phase Transition for a Hard Sphere System. *The Journal of Chemical Physics*. 1957, pp 1208–1209.
- (157) Rahman, A. Correlations in the Motion of Atoms in Liquid Argon. *Phys. Rev.* **1964**, *136*.
- (158) Alder, B. J.; Gass, D. M.; Wainwright, T. E. Studies in Molecular Dynamics. VIII. The Transport Coefficients for a Hard-Sphere Fluid. *J. Chem. Phys.* **1970**, *53*, 3813–3826.
- (159) Levesque, D.; Verlet, L.; Kürkijärvi, J. Computer “Experiments” on Classical Fluids. IV. Transport Properties and Time-Correlation Functions of the Lennard-Jones Liquid near Its Triple Point. *Phys. Rev. A* **1973**, *7*, 1690–1700.
- (160) Kong, Y. C.; Tildesley, D. J.; Alejandre, J. The Molecular Dynamics Simulation of Boundary-Layer Lubrication. *Mol. Phys.* **1997**, *92*, 7–18.
- (161) Schoen, M.; Rhykerd, C. L.; Diestler, D. J.; Cushman, J. H. Shear Forces in Molecularly Thin Films. *Science (80-.)*. **1989**, *245*, 1223–1225.
- (162) Yoshizawa, H.; Chen, Y. L.; Israelachvili, J. Fundamental Mechanisms of Interfacial Friction. 1. Relation between Adhesion and Friction. *J. Phys. Chem.* **1993**, *97*, 4128–4140.
- (163) Thompson, P. A.; Robbins, M. O. Origin of Stick-Slip Motion in Boundary Lubrication. *Science (80-.)*. **1990**, *250*, 792–794.

- (164) Schmitt, V.; Lequeux, F.; Pousse, A.; Roux, D. Flow Behavior and Shear Induced Transition near an Isotropic/Nematic Transition in Equilibrium Polymers. *Langmuir* **1994**, *10*, 955–961.
- (165) Ashurst, W. T.; Hoover, W. G. Dense-Fluid Shear Viscosity via Nonequilibrium Molecular Dynamics. *Phys. Rev. A* **1975**, *11*, 658–678.
- (166) Evans, D. J.; Morriss, G. P. Nonlinear-Response Theory for Steady Planar Couette Flow. *Phys. Rev. A* **1984**, *30*, 1528–1530.
- (167) Lees, A. W.; Edwards, S. F. The Computer Study of Transport Processes under Extreme Conditions. *J. Phys. C Solid State Phys.* **1972**, *5*, 1921–1928.
- (168) Heyes, D. M.; Kim, J. J.; Montrose, C. J.; Litovitz, T. A. Time Dependent Nonlinear Shear Stress Effects in Simple Liquids: A Molecular Dynamics Study. *J. Chem. Phys.* **1980**, *73*, 3987–3996.
- (169) Bair, S.; McCabe, C.; McCabe, C.; Cummings, P. T.; Cummings, P. T. Comparison of Nonequilibrium Molecular Dynamics with Experimental Measurements in the Nonlinear Shear-Thinning Regime. *Phys. Rev. Lett.* **2002**, *88*, 583021–583024.
- (170) Wang, B. Y.; Cummings, P. T. Nonequilibrium Molecular Dynamics Calculation of the Shear Viscosity of Carbon Dioxide. *Int. J. Thermophys.* **1989**, *10*, 929–940.
- (171) Moore, J. D.; Cui, S. T.; Cochran, H. D.; Cummings, P. T. A Molecular Dynamics Study of a Short-Chain Polyethylene Melt. I. Steady-State Shear. *J. Nonnewton. Fluid Mech.* **2000**, *93*, 83–99.
- (172) Glosli, J. N.; McClelland, G. M. Molecular Dynamics Study of Sliding Friction of Ordered Organic Monolayers. *Phys. Rev. Lett.* **1993**, *70*, 1960–1963.
- (173) Götz, A. W.; Williamson, M. J.; Xu, D.; Poole, D.; Le Grand, S.; Walker, R. C. Routine Microsecond Molecular Dynamics Simulations with AMBER on GPUs. 1. Generalized Born. *J. Chem. Theory Comput.* **2012**, *8*, 1542–1555.
- (174) Andersen, H. C. Molecular Dynamics Simulations at Constant Pressure and/or Temperature. *J. Chem. Phys.* **2008**, *72*, 2384.
- (175) Berendsen, H. J. C.; Postma, J. P. M.; Van Gunsteren, W. F.; Dinola, A.; Haak, J. R. Molecular Dynamics with Coupling to an External Bath. *J. Chem. Phys.* **1998**, *81*, 3684.
- (176) Schneider, T.; Stoll, E. Molecular-Dynamics Study of a Three-Dimensional One-Component Model for Distortive Phase Transitions. *Phys. Rev. B* **1978**, *17*, 1302.
- (177) Nosé, S. A Molecular Dynamics Method for Simulations in the Canonical Ensemble. <http://dx.doi.org/10.1080/00268978400101201> **2006**, *52*, 255–268.
- (178) Hoover, W. G. Canonical Dynamics: Equilibrium Phase-Space Distributions. *Phys. Rev. A*,

- Gen. Phys.* **1985**, *31*, 1695–1697.
- (179) Bernardi, S.; Todd, B. D.; Searles, D. J. Thermostating Highly Confined Fluids. *J. Chem. Phys.* **2010**, *132*, 244706.
- (180) Berro, H.; Fillot, N.; Vergne, P.; Tokumasu, T.; Ohara, T.; Kikugawa, G. Energy Dissipation in Non-Isothermal Molecular Dynamics Simulations of Confined Liquids under Shear. *J. Chem. Phys.* **2011**, *135*, 134708.
- (181) Gattinoni, C.; Maćkowiak, S.; Heyes, D. M.; Brańka, A. C.; Dini, D. Boundary-Controlled Barostats for Slab Geometries in Molecular Dynamics Simulations. *Phys. Rev. E - Stat. Nonlinear, Soft Matter Phys.* **2014**, *90*, 043302.
- (182) Ewen, J. P.; Gattinoni, C.; Thakkar, F. M.; Morgan, N.; Spikes, H. A.; Dini, D. A Comparison of Classical Force-Fields for Molecular Dynamics Simulations of Lubricants. *Mater. 2016, Vol. 9, Page 651* **2016**, *9*, 651.
- (183) González, M. A. Force Fields and Molecular Dynamics Simulations. *École thématique la Société Française la Neutron*. **2011**, *12*, 169–200.
- (184) Ewald, P. P. Die Berechnung Optischer Und Elektrostatischer Gitterpotentiale. *Ann. Phys.* **1921**, *369*, 253–287.
- (185) Luty, B. A.; Davis, M. E.; Tironi, I. G.; Van Gunsteren, W. F. A Comparison of Particle-Particle, Particle-Mesh and Ewald Methods for Calculating Electrostatic Interactions in Periodic Molecular Systems. *Mol. Simul.* **1994**, *14*, 11–20.
- (186) Feller, S. E.; Pastor, R. W.; Rojnuckarin, A.; Bogusz, S.; Brooks, B. R. Effect of Electrostatic Force Truncation on Interfacial and Transport Properties of Water. *J. Phys. Chem.* **1996**, *100*, 17011–17020.
- (187) Sun, H. COMPASS: An Ab Initio Force-Field Optimized for Condensed-Phase Applications Overview with Details on Alkane and Benzene Compounds. *J. Phys. Chem. B* **1998**, *102*, 7338–7364.
- (188) Nikitin, A.; Milchevskiy, Y.; Lyubartsev, A. AMBER-II: New Combining Rules and Force Field for Perfluoroalkanes. *J. Phys. Chem. B* **2015**, *119*, 14563–14573.
- (189) Brooks, B. R.; Bruccoleri, R. E.; Olafson, B. D.; States, D. J.; Swaminathan, S.; Karplus, M. CHARMM: A Program for Macromolecular Energy, Minimization, and Dynamics Calculations. *J. Comput. Chem.* **1983**, *4*, 187–217.
- (190) Jorgensen, W. L.; Tirado-Rives, J. The OPLS Potential Functions for Proteins. Energy Minimizations for Crystals of Cyclic Peptides and Crambin. *J. Am. Chem. Soc.* **1988**, *110*, 1657–1666.
- (191) Schmid, N.; Eichenberger, A. P.; Choutko, A.; Riniker, S.; Winger, M.; Mark, A. E.; Van

- Gunsteren, W. F. Definition and Testing of the GROMOS Force-Field Versions 54A7 and 54B7. *Eur. Biophys. J.* **2011**, *40*, 843–856.
- (192) Siu, S. W. I.; Pluhackova, K.; Böckmann, R. A. Optimization of the OPLS-AA Force Field for Long Hydrocarbons. *J. Chem. Theory Comput.* **2012**, *8*, 1459–1470.
- (193) Van Duin, A. C. T. T.; Dasgupta, S.; Lorant, F.; Goddard, W. A.; Goddard III, W. A. ReaxFF: A Reactive Force Field for Hydrocarbons. *J. Phys. Chem. A* **2001**, *105*, 9396–9409.
- (194) Senftle, T. P.; Hong, S.; Islam, M. M.; Kylasa, S. B.; Zheng, Y.; Shin, Y. K.; Junkermeier, C.; Engel-Herbert, R.; Janik, M. J.; Aktulga, H. M.; Verstraelen, T.; Grama, A.; Van Duin, A. C. T. The ReaxFF Reactive Force-Field: Development, Applications and Future Directions. *npj Comput. Mater.* **2016**, *2*.
- (195) Russo, M. F.; Van Duin, A. C. T. Atomistic-Scale Simulations of Chemical Reactions: Bridging from Quantum Chemistry to Engineering. In *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms*; Elsevier, 2011; Vol. 269, pp 1549–1554.
- (196) Rappé, A. K.; Goddard, W. A. Charge Equilibration for Molecular Dynamics Simulations. *J. Phys. Chem.* **1991**, *95*, 3358–3363.
- (197) Rice, B. M.; Larentzos, J. P.; Byrd, E. F. C.; Weingarten, N. S. Parameterizing Complex Reactive Force Fields Using Multiple Objective Evolutionary Strategies (MOES): Part 2: Transferability of ReaxFF Models to C-H-N-O Energetic Materials. *J. Chem. Theory Comput.* **2015**, *11*, 392–405.
- (198) Furman, D.; Carmeli, B.; Zeiri, Y.; Kosloff, R. Enhanced Particle Swarm Optimization Algorithm: Efficient Training of ReaxFF Reactive Force Fields. *J. Chem. Theory Comput.* **2018**, *14*, 3100–3112.
- (199) Trnka, T.; Tvaroška, I.; Koča, J. Automated Training of ReaxFF Reactive Force Fields for Energetics of Enzymatic Reactions. *J. Chem. Theory Comput.* **2018**, *14*, 291–302.
- (200) Zhang, Y.; Wang, X.; Li, Q.; Yang, R.; Li, C. A ReaxFF Molecular Dynamics Study of the Pyrolysis Mechanism of Oleic-Type Triglycerides. *Energy and Fuels* **2015**, *29*, 5056–5068.
- (201) Yue, D. C.; Ma, T. B.; Hu, Y. Z.; Yeon, J.; van Duin, A. C. T.; Wang, H.; Luo, J. Tribochemical Mechanism of Amorphous Silica Asperities in Aqueous Environment: A Reactive Molecular Dynamics Study. *Langmuir* **2015**, *31*, 1429–1436.
- (202) Wen, J.; Ma, T.; Zhang, W.; Psogiannakis, G.; van Duin, A. C. T.; Chen, L.; Qian, L.; Hu, Y.; Lu, X.; Wen, J.; Ma, T.; Zhang, W.; Psogiannakis, G.; van Duin, A. C. T.; Chen, L.; Qian, L.; Hu, Y.; Lu, X. Atomic Insight into Tribochemical Wear Mechanism of

- Silicon at the Si/SiO₂ Interface in Aqueous Environment: Molecular Dynamics Simulations Using ReaxFF Reactive Force Field. *ApSS* **2016**, *390*, 216–223.
- (203) Yeon, J.; van Duin, A. C. T.; Kim, S. H. Effects of Water on Tribochemical Wear of Silicon Oxide Interface: Molecular Dynamics (MD) Study with Reactive Force Field (ReaxFF). *Langmuir* **2016**, *32*, 1018–1026.
- (204) Wen, J.; Ma, T.; Zhang, W.; Van Duin, A. C. T.; Van Duin, D. M.; Hu, Y.; Lu, X. Atomistic Insights into Cu Chemical Mechanical Polishing Mechanism in Aqueous Hydrogen Peroxide and Glycine: ReaxFF Reactive Molecular Dynamics Simulations. *J. Phys. Chem. C* **2019**, *123*, 26467–26474.
- (205) Hahn, S. H.; Liu, H.; Kim, S. H.; van Duin, A. C. T. Atomistic Understanding of Surface Wear Process of Sodium Silicate Glass in Dry versus Humid Environments. *J. Am. Ceram. Soc.* **2020**, *103*, 3060–3069.
- (206) Newsome, D. A.; Sengupta, D.; Foroutan, H.; Russo, M. F.; Van Duin, A. C. T. Oxidation of Silicon Carbide by O₂ and H₂O: A ReaxFF Reactive Molecular Dynamics Study, Part I. *J. Phys. Chem. C* **2012**, *116*, 16111–16121.
- (207) Bhati, M.; Senftle, T. P. Identifying Adhesion Properties at Si/Polymer Interfaces with ReaxFF. *J. Phys. Chem. C* **2019**, *123*, 27036–27047.
- (208) Hilbert, J.; Mangolini, F.; McClimon, J. B.; Lukes, J. R.; Carpick, R. W. Si Doping Enhances the Thermal Stability of Diamond-like Carbon through Reductions in Carbon-Carbon Bond Length Disorder. *Carbon N. Y.* **2018**, *131*, 72–78.
- (209) Vashisth, A.; Mirsayar, M. M. A Combined Atomistic-Continuum Study on the Temperature Effects on Interfacial Fracture in SiC/SiO₂ Composites. *Theor. Appl. Fract. Mech.* **2020**, *105*, 102399.
- (210) Persson, B. N. J.; Sivebæk, I. M.; Samoilov, V. N.; Zhao, K. e.; Volokitin, A. I.; Zhang, Z. On the Origin of Amonton's Friction Law. *J. Phys. Condens. Matter* **2008**, *20*, 395006–395017.
- (211) Bowden, F. P.; Tabor, D. *The Friction and Lubrication of Solids*, 1st ed.; Clarendon Press, 1950; Vol. 1.
- (212) Mo, Y.; Turner, K. T.; Szlufarska, I. Friction Laws at the Nanoscale. *Nature* **2009**, *457*, 1116–1119.
- (213) Szlufarska, I.; Chandross, M.; Carpick, R. W. Recent Advances in Single-Asperity Nanotribology. *J. Phys. D. Appl. Phys.* **2008**, *41*, 123001.
- (214) Perry, S. S. Scanning Probe Microscopy Measurements of Friction. *MRS Bull.* **2004**, *29*, 478–483.

- (215) Binnig, G.; Quate, C. F.; Gerber, C. Atomic Force Microscope. *Phys. Rev. Lett.* **1986**, *56*, 930–933.
- (216) Homola, A. M.; Israelachvili, J. N.; McGuiggan, P. M.; Gee, M. L. Fundamental Experimental Studies in Tribology: The Transition from “Interfacial” Friction of Undamaged Molecularly Smooth Surfaces to “Normal” Friction with Wear. *Wear* **1990**, *136*, 65–83.
- (217) Berman, A. D.; Ducker, W. A.; Israelachvili, J. N. Origin and Characterization of Different Stick–Slip Friction Mechanisms†. *Langmuir* **1996**, *12*, 4559–4562.
- (218) Dagata, J. A. Scanning Force Microscopy with Applications to Electric, Magnetic and Atomic Forces by Dror Sarid Oxford University Press, 1991. *Scanning* **1992**, *14*, 118–120.
- (219) Carpick, R. W.; Salmeron, M. Scratching the Surface: Fundamental Investigations of Tribology with Atomic Force Microscopy. *Chem. Rev.* **1997**, *97*, 1163–1194.
- (220) Carpick, R. W.; Ogletree, D. F.; Salmeron, M. Lateral Stiffness: A New Nanomechanical Measurement for the Determination of Shear Strengths with Friction Force Microscopy. *Appl. Phys. Lett.* **1998**, *70*, 1548.
- (221) Carpick, R. W.; Agrai“tagrai“t, N.; Ogletree, D. F.; Salmeron, M. Variation of the Interfacial Shear Strength and Adhesion of a Nanometer-Sized Contact. **1996**.
- (222) Carpick, R. W. Measurement of Interfacial Shear (Friction) with an Ultrahigh Vacuum Atomic Force Microscope. *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.* **1996**, *14*, 1289.
- (223) Riedo, E.; Chevrier, J.; Comin, F.; Brune, H. Nanotribology of Carbon Based Thin Films: The Influence of Film Structure and Surface Morphology. *Surf. Sci.* **2001**, *477*, 25–34.
- (224) Enachescu, M.; Van Den Oetelaar, R. J. A.; Carpick, R. W.; Ogletree, D. F.; Flipse, C. F. J.; Salmeron, M. Observation of Proportionality between Friction and Contact Area at the Nanometer Scale. *Tribol. Lett.* **1999**, *7*, 73–78.
- (225) Hertz, H. Ueber Die Berührung Fester Elastischer Körper. *J. fur die Reine und Angew. Math.* **1882**, *1882*, 156–171.
- (226) Singer, I. L.; Bolster, R. N.; Wegand, J.; Fayeulle, S.; Stupp, B. C. Hertzian Stress Contribution to Low Friction Behavior of Thin MoS₂ Coatings. *Appl. Phys. Lett.* **1998**, *57*, 995.
- (227) Singer, I. L.; Pollock, H. Fundamentals of Friction : Macroscopic and Microscopic Processes. *Fundam. Frict. Macrosc. Microsc. Process.* **1992**.
- (228) Christenson, H. K. Adhesion and Surface Energy of Mica in Air and Water. *J. Phys. Chem.* **1993**, *97*, 12034–12041.
- (229) Briscoe, B. J.; Vans, D. C. B. E. The Shear Properties of Langmuir—Blodgett Layers. *Proc.*

- R. Soc. London. *A. Math. Phys. Sci.* **1982**, *380*, 389–407.
- (230) Gao, G.; Cannara, R. J.; Carpick, R. W.; Harrison, J. A. Atomic-Scale Friction on Diamond: A Comparison of Different Sliding Directions on (001) and (111) Surfaces Using MD and AFM. *Langmuir* **2007**, *23*, 5394–5405.
- (231) Jianping Gao, †; W. D. Luedtke, †; D. Gourdon, ‡; M. Ruths, §; J. N. Israelachvili, ‡ and; Uzi Landman*, †. Frictional Forces and Amontons' Law: From the Molecular to the Macroscopic Scale. *J. Phys. Chem. B* **2004**, *108*, 3410–3425.
- (232) Socoliuc, A.; Bennewitz, R.; Gnecco, E.; Meyer, E. Transition from Stick-Slip to Continuous Sliding in Atomic Friction: Entering a New Regime of Ultralow Friction. *Phys. Rev. Lett.* **2004**, *92*, 134301.
- (233) Johnson, K. L.; Kendall, K.; Roberts, A. D. Surface Energy and the Contact of Elastic Solids. *Proc. R. Soc. Lond. A. Math. Phys. Sci.* **1971**, *324*, 301–313.
- (234) Derjaguin, B. V.; Muller, V. M.; Toporov, Y. P. Effect of Contact Deformations on the Adhesion of Particles. *J. Colloid Interface Sci.* **1975**, *53*, 314–326.
- (235) Jacobs, T. D. B.; Martini, A. Measuring and Understanding Contact Area at the Nanoscale: A Review. *Appl. Mech. Rev.* **2017**, *69*, 060802.
- (236) Müser, M. H.; Dapp, W. B.; Bugnicourt, R.; Sainsot, P.; Lesaffre, N.; Lubrecht, T. A.; Persson, B. N. J.; Harris, K.; Bennett, A.; Schulze, K.; Rohde, S.; Ifju, P.; Sawyer, W. G.; Angelini, T.; Ashtari Esfahani, H.; Kadkhodaei, M.; Akbarzadeh, S.; Wu, J. J.; Vorlaufer, G.; Vernes, A.; Solhjoo, S.; Vakis, A. I.; Jackson, R. L.; Xu, Y.; Streator, J.; Rostami, A.; Dini, D.; Medina, S.; Carbone, G.; Bottiglione, F.; Afferrante, L.; Monti, J.; Pastewka, L.; Robbins, M. O.; Greenwood, J. A. Meeting the Contact-Mechanics Challenge. *Tribol. Lett.* **2017**, *65*, 1–18.
- (237) Pastewka, L.; Robbins, M. O. Contact between Rough Surfaces and a Criterion for Macroscopic Adhesion. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 3298–3303.
- (238) Wang, Y.; Qin, J.; Xu, J.; Sun, J.; Chen, L.; Qian, L.; Kubo, M. Definition of Atomic-Scale Contact: What Dominates the Atomic-Scale Friction Behaviors? *Langmuir* **2022**, *38*, 11699–11706.
- (239) Luan, B.; Robbins, M. O. The Breakdown of Continuum Models for Mechanical Contacts. *Nature* **2005**, *435*, 929–932.
- (240) Luan, B.; Robbins, M. O. Contact of Single Asperities with Varying Adhesion: Comparing Continuum Mechanics to Atomistic Simulations. *Phys. Rev. E - Stat. Nonlinear, Soft Matter Phys.* **2006**, *74*, 026111.
- (241) Cha, P. R.; Srolovitz, D. J.; Vanderlick, T. K. Molecular Dynamics Simulation of Single

- Asperity Contact. *Acta Mater.* **2004**, *52*, 3983–3996.
- (242) Wenning, L.; Müser, M. H. Friction Laws for Elastic Nanoscale Contacts. *Europhys. Lett.* **2001**, *54*, 693.
- (243) Chandross, M.; Lorenz, C. D.; Stevens, M. J.; Grest, G. S. Simulations of Nanotribology with Realistic Probe Tip Models. *Langmuir* **2008**, *24*, 1240–1246.
- (244) Jacobs, T. D. B.; Carpick, R. W. Nanoscale Wear as a Stress-Assisted Chemical Reaction. *Nat. Nanotechnol.* **2013**, *8*, 108–112.
- (245) Jia, K.; Fischer, T. E. Sliding Wear of Conventional and Nanostructured Cemented Carbides. *Wear* **1997**, *203–204*, 310–318.
- (246) Chung, K. H.; Kim, D. E. Fundamental Investigation of Micro Wear Rate Using an Atomic Force Microscope. *Tribol. Lett.* **2003**, *15*, 135–144.
- (247) Gotsmann, B.; Lantz, M. A. Atomistic Wear in a Single Asperity Sliding Contact. *Phys. Rev. Lett.* **2008**, *101*, 125501.
- (248) Bhaskaran, H.; Gotsmann, B.; Sebastian, A.; Drechsler, U.; Lantz, M. A.; Despont, M.; Jaroenapibal, P.; Carpick, R. W.; Chen, Y.; Sridharan, K. Ultralow Nanoscale Wear through Atom-by-Atom Attrition in Silicon-Containing Diamond-like Carbon. *Nat. Nanotechnol.* **2010**, *5*, 181–185.
- (249) Maw, W.; Stevens, F.; Langford, S. C.; Dickinson, J. T. Single Asperity Tribochemical Wear of Silicon Nitride Studied by Atomic Force Microscopy. *J. Appl. Phys.* **2002**, *92*, 5103–5109.
- (250) Gosvami, N. N.; Bares, J. A.; Mangolini, F.; Konicek, A. R.; Yablon, D. G.; Carpick, R. W. Mechanisms of Antiwear Tribofilm Growth Revealed in Situ by Single-Asperity Sliding Contacts. *Science (80-.)*. **2015**, *348*, 102–106.
- (251) Gao, G. T.; Mikulski, P. T.; Harrison, J. A. Molecular-Scale Tribology of Amorphous Carbon Coatings: Effects of Film Thickness, Adhesion, and Long-Range Interactions. *J. Am. Chem. Soc.* **2002**, *124*, 7202–7209.
- (252) D’Acunto, M. Theoretical Approach for the Quantification of Wear Mechanisms on the Nanoscale. *Nanotechnology* **2004**, *15*, 795–801.
- (253) Park, N. S.; Kim, M. W.; Langford, S. C.; Dickinson, J. T. Atomic Layer Wear of Single-Crystal Calcite in Aqueous Solution Using Scanning Force Microscopy. *J. Appl. Phys.* **1996**, *80*, 2680–2686.
- (254) Sheehan, P. E. The Wear Kinetics of NaCl under Dry Nitrogen and at Low Humidities. *Chem. Phys. Lett.* **2005**, *410*, 151–155.
- (255) Kopta, S.; Salmeron, M. The Atomic Scale Origin of Wear on Mica and Its Contribution

- to Friction. *J. Chem. Phys.* **2000**, *113*, 8249–8252.
- (256) Hirth, J. P.; Nix, W. D. An Analysis of the Thermodynamics of Dislocation Glide. *Phys. status solidi* **1969**, *35*, 177–188.
- (257) Shao, Y.; Jacobs, T. D. B. B.; Jiang, Y.; Turner, K. T.; Carpick, R. W.; Falk, M. L. Multibond Model of Single-Asperity Tribochemical Wear at the Nanoscale. *ACS Appl. Mater. Interfaces* **2017**, *9*, 35333–35340.
- (258) Wang, Y.; Xu, J.; Ootani, Y.; Ozawa, N.; Adachi, K.; Kubo, M. Non-Empirical Law for Nanoscale Atom-by-Atom Wear. *Adv. Sci.* **2020**, *8*, 2002827.
- (259) Sha, Z.-D.; Sorkin, V.; Branicio, P. S.; Pei, Q.-X.; Zhang, Y.-W.; Srolovitz, D. J. Large-Scale Molecular Dynamics Simulations of Wear in Diamond-like Carbon at the Nanoscale at the Nanoscale. *Appl. Phys. Lett.* **2013**, *27*, 073118.
- (260) Vanossi, A.; Manini, N.; Urbakh, M.; Zapperi, S.; Tosatti, E. Colloquium: Modeling Friction: From Nanoscale to Mesoscale. *Rev. Mod. Phys.* **2013**, *85*, 529–552.
- (261) Dieterich, J. H. Time-Dependent Friction in Rocks. *J. Geophys. Res.* **1972**, *77*, 3690–3697.
- (262) Menezes, P. L.; Lovell, M. R.; Avdeev, I. V.; Higgs III, C. F. Studies on the Formation of Discontinuous Rock Fragments during Cutting Operation. *Int. J. Rock Mech. Min. Sci.* **2014**, *71*, 131–142.
- (263) Cheng, Z.; Li, G.; Huang, Z.; Sheng, M.; Wu, X.; Yang, J. Analytical Modelling of Rock Cutting Force and Failure Surface in Linear Cutting Test by Single PDC Cutter. *J. Pet. Sci. Eng.* **2019**, *177*, 306–316.
- (264) Li, A.; Liu, Y.; Szlufarska, I. Effects of Interfacial Bonding on Friction and Wear at Silica/Silica Interfaces. *Tribol. Lett.* **2014**, *56*, 481–490.
- (265) Wang, Y.; Xu, J.; Ootani, Y.; Bai, S.; Higuchi, Y.; Ozawa, N.; Adachi, K.; Martin, J. M.; Kubo, M. Tight-Binding Quantum Chemical Molecular Dynamics Study on the Friction and Wear Processes of Diamond-Like Carbon Coatings: Effect of Tensile Stress. *ACS Appl. Mater. Interfaces* **2017**, *9*, 34396–34404.
- (266) Plimpton, S. J.; Thompson, A. P. Computational Aspects of Many-Body Potentials. *MRS Bull.* **2012**, *37*, 513–521.
- (267) Martini, A.; Eder, S. J.; Dörr, N. Tribochemistry: A Review of Reactive Molecular Dynamics Simulations. *Lubricants* **2020**, *8*, 44.
- (268) Dougherty, P. S. M.; Pudjoprawoto, R.; Higgs III, C. F. Bit Cutter-on-Rock Tribometry: Analyzing Friction and Rate-of-Penetration for Deep Well Drilling Substrates. *Tribol. Int.* **2014**, *77*, 178–185.
- (269) Reeves, M. J. Rock Surface Roughness and Frictional Strength. *Int. J. Rock Mech. Min. Sci.*

- 1985, 22, 429–442.
- (270) Greenwood, J. A.; Johnson, K. L.; Matsubara, E. A Surface Roughness Parameter in Hertz Contact. *Wear* **1984**, 100, 47–57.
 - (271) Lai, P.; Moulton, K.; Krevor, S. Pore-Scale Heterogeneity in the Mineral Distribution and Reactive Surface Area of Porous Rocks. *Chem. Geol.* **2015**, 411, 260–273.
 - (272) Thompson, A. P.; Aktulga, H. M.; Berger, R.; Bolintineanu, D. S.; Brown, W. M.; Crozier, P. S.; in 't Veld, P. J.; Kohlmeyer, A.; Moore, S. G.; Nguyen, T. D.; Shan, R.; Stevens, M. J.; Tranchida, J.; Trott, C.; Plimpton, S. J. LAMMPS - a Flexible Simulation Tool for Particle-Based Materials Modeling at the Atomic, Meso, and Continuum Scales. *Comput. Phys. Commun.* **2022**, 271, 108171.
 - (273) Van der Molen, I. The Shift of the α - β Transition Temperature of Quartz Associated with the Thermal Expansion of Granite at High Pressure. *Tectonophysics* **1981**, 73, 323–342.
 - (274) Levenson, Y.; Emmanuel, S. Pore-Scale Heterogeneous Reaction Rates on a Dissolving Limestone Surface. *Geochim. Cosmochim. Acta* **2013**, 119, 188–197.
 - (275) De Leeuw, N. H.; Higgins, F. M.; Parker, S. C. Modeling the Surface Structure and Stability of α -Quartz. *J. Phys. Chem. B* **1999**, 103, 1270–1277.
 - (276) Kerisit, S.; Parker, S. C.; Harding, J. H. Atomistic Simulation of the Dissociative Adsorption of Water on Calcite Surfaces. *J. Phys. Chem. B* **2003**, 107, 7676–7682.
 - (277) Pashley, R. M.; Kitchener, J. A. Surface Forces in Adsorbed Multilayers of Water on Quartz. *J. Colloid Interface Sci.* **1979**, 71, 491–500.
 - (278) Stipp, S. L. S.; Hochella, M. F. Structure and Bonding at the Calcite Surface as Observed with X-Ray Photoelectron Spectroscopy (XPS) and (LEED). *Geochim. Cosmochim. Acta* **1991**, 55, 1723–1736.
 - (279) Yang, J.; Wang, E. G. Water Adsorption on Hydroxylated α -Quartz (0001) Surfaces: From Monomer to Flat Bilayer. *Phys. Rev. B - Condens. Matter Mater. Phys.* **2006**, 73, 035406.
 - (280) Stukowski, A. Visualization and Analysis of Atomistic Simulation Data with OVITO-the Open Visualization Tool. *Model. Simul. Mater. Sci. Eng.* **2010**, 18, 015012.
 - (281) Brazil, O.; Pharr, G. M. Direct Observation of Partial Slip in Micrometre-Scale Single Asperity Contacts. *Tribol. Int.* **2020**, 106776.
 - (282) Chenoweth, K.; van Duin, A. C. T.; Goddard III, W. A. ReaxFF Reactive Force Field for Molecular Dynamics Simulations of Hydrocarbon Oxidation. *J. Phys. Chem. A* **2008**, 112, 1040–1053.
 - (283) Aktulga, H. M.; Fogarty, J. C.; Pandit, S. A.; Grama, A. Y. Parallel Reactive Molecular Dynamics: Numerical Methods and Algorithmic Techniques. *Parallel Comput.* **2012**, 38,

- 245–259.
- (284) Nakano, A. Parallel Multilevel Preconditioned Conjugate-Gradient Approach to Variable-Charge Molecular Dynamics. *Comput. Phys. Commun.* **1997**, *104*, 59–69.
 - (285) Buehler, M. J.; van Duin, A. C. T.; Goddard III, W. A. Multiparadigm Modeling of Dynamical Crack Propagation in Silicon Using a Reactive Force Field. *Phys. Rev. Lett.* **2006**, *96*, 095505.
 - (286) Van Duin, A. C. T.; Strachan, A.; Stewman, S.; Zhang, Q.; Xu, X.; Goddard, W. A. ReaxFFSiO Reactive Force Field for Silicon and Silicon Oxide Systems. *J. Phys. Chem. A* **2003**, *107*, 3803–3811.
 - (287) Fogarty, J. C.; Aktulga, H. M.; Grama, A. Y.; van Duin, A. C. T.; Pandit, S. A. A Reactive Molecular Dynamics Simulation of the Silica-Water Interface. *J. Chem. Phys.* **2010**, *132*, 174704.
 - (288) Chenoweth, K.; Cheung, S.; van Duin, A. C. T.; Goddard III, W. A.; Kober, E. M. Simulations on the Thermal Decomposition of a Poly(Dimethylsiloxane) Polymer Using the ReaxFF Reactive Force Field. *J. Am. Chem. Soc.* **2005**, *127*, 7192–7202.
 - (289) Kumar, S.; Parks, D.; Kamrin, K. Mechanistic Origin of the Ultrastrong Adhesion between Graphene and α -SiO₂: Beyond van Der Waals. *ACS Nano* **2016**, *10*, 6552–6562.
 - (290) Pitman, M. C.; van Duin, A. C. T. Dynamics of Confined Reactive Water in Smectite Clay-Zeolite Composites. *J. Am. Chem. Soc.* **2012**, *134*, 3042–3053.
 - (291) Manzano, H.; Pellenq, R. J. M.; Ulm, F. J.; Buehler, M. J.; van Duin, A. C. T. Hydration of Calcium Oxide Surface Predicted by Reactive Force Field Molecular Dynamics. *Langmuir* **2012**, *28*, 4187–4197.
 - (292) Raiteri, P.; Demichelis, R.; Gale, J. D.; Kellermeier, M.; Gebauer, D.; Quigley, D.; Wright, L. B.; Walsh, T. R. Exploring the Influence of Organic Species on Pre- and Post-Nucleation Calcium Carbonate. *Faraday Discuss.* **2012**, *159*, 61–85.
 - (293) Gale, J. D.; Raiteri, P.; Van Duin, A. C. T. A Reactive Force Field for Aqueous-Calcium Carbonate Systems. *Phys. Chem. Chem. Phys.* **2011**, *13*, 16666–16679.
 - (294) Bochevarov, A. D.; Harder, E.; Hughes, T. F.; Greenwood, J. R.; Braden, D. A.; Philipp, D. M.; Rinaldo, D.; Halls, M. D.; Zhang, J.; Friesner, R. A. Jaguar: A High-Performance Quantum Chemistry Software Program with Strengths in Life and Materials Sciences. *Int. J. Quantum Chem.* **2013**, *113*, 2110–2142.
 - (295) David Sherrill, C.; Takatani, T.; Hohenstein, E. G. An Assessment of Theoretical Methods for Nonbonded Interactions: Comparison to Complete Basis Set Limit Coupled-Cluster Potential Energy Curves for the Benzene Dimer, the Methane Dimer, Benzene-

- Methane, and Benzene-H₂S. *J. Phys. Chem. A* **2009**, *113*, 10146–10159.
- (296) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47*, 558.
- (297) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, *6*, 15–50.
- (298) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169.
- (299) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59*, 1758–1775.
- (300) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (301) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192.
- (302) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular-Dynamics. *J. Comput. Phys.* **1995**, *117*, 1–19.
- (303) Verlet, L. Computer “Experiments” on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules. *Phys. Rev.* **1967**, *159*, 98.
- (304) Ewen, J. P.; Ayestarán Latorre, C.; Gattinoni, C.; Khajeh, A.; Moore, J. D.; Remias, J. E.; Martini, A.; Dini, D. Substituent Effects on the Thermal Decomposition of Phosphate Esters on Ferrous Surfaces. *J. Phys. Chem. C* **2020**, *124*, 9852–9865.
- (305) Dieterich, J. H.; Conrad, G. Effect of Humidity on Time- and Velocity-Dependent Friction in Rocks. *J. Geophys. Res.* **1984**, *89*, 4196–4202.
- (306) Ouyang, W.; Cheng, Y.; Ma, M.; Urbakh, M. Load-Velocity-Temperature Relationship in Frictional Response of Microscopic Contacts. *J. Mech. Phys. Solids* **2020**, *137*, 103880.
- (307) Ouyang, W.; Ramakrishna, S. N.; Rossi, A.; Urbakh, M.; Spencer, N. D.; Arcifa, A. Load and Velocity Dependence of Friction Mediated by Dynamics of Interfacial Contacts. *Phys. Rev. Lett.* **2019**, *123*, 116102.
- (308) Yahiaoui, M.; Paris, J.-Y.; Delbé, K.; Denape, J.; Gerbaud, L.; Dourfaye, A. Independent Analyses of Cutting and Friction Forces Applied on a Single Polycrystalline Diamond Compact Cutter. *Int. J. Rock Mech. Min. Sci.* **2016**, *85*, 20–26.
- (309) Tian, K.; Gosvami, N. N.; Goldsby, D. L.; Liu, Y.; Szlufarska, I.; Carpick, R. W. Load and Time Dependence of Interfacial Chemical Bond-Induced Friction at the Nanoscale. *Phys. Rev. Lett.* **2017**, *118*, 076103.
- (310) Patton, S. T.; Cowan, W. D.; Eapen, K. C.; Zabinski, J. S. Effect of Surface Chemistry on

- the Tribological Performance of a MEMS Electrostatic Lateral Output Motor. *Tribol. Lett.* **2001**, *9*, 199–209.
- (311) De Barros Bouchet, M.-I.; Zilibotti, G.; Matta, C.; Righi, M. C.; Vandenbulcke, L.; Vacher, B.; Martin, J.-M. Friction of Diamond in the Presence of Water Vapor and Hydrogen Gas. Coupling Gas-Phase Lubrication and First-Principles Studies. *J. Phys. Chem. C* **2012**, *116*, 6966–6972.
- (312) Ootani, Y.; Xu, J.; Hatano, T.; Kubo, M. Contrasting Roles of Water at Sliding Interfaces between Silicon- Based Materials: First-Principles Molecular Dynamics Sliding Simulations. *J. Phys. Chem. C* **2018**, *122*, 10459–10467.
- (313) Liu, Y.; Szlufarska, I. Effect of Trace Moisture on Friction. *Appl. Phys. Lett.* **2010**, *96*, 101902.
- (314) Gao, H.; Ewen, J. P.; Hartkamp, R.; Müser, M. H.; Dini, D. Scale-Dependent Friction-Coverage Relations and Nonlocal Dissipation in Surfactant Monolayers. *Langmuir* **2021**, *37*, 2406–2418.
- (315) Broz, M. E.; Cook, R. F.; Whitney, D. L. Microhardness, Toughness, and Modulus of Mohs Scale Minerals. *Am. Mineral.* **2006**, *91*, 135–142.
- (316) Bowden, F.; Tabor, D. Friction, Lubrication and Wear: A Survey of Work during the Last Decade. *Br. J. Appl. Phys.* **1966**, *17*, 1521–1544.
- (317) Yeon, J.; He, X.; Martini, A.; Kim, S. H. Mechanochemistry at Solid Surfaces: Polymerization of Adsorbed Molecules by Mechanical Shear at Tribological Interfaces. *ACS Appl. Mater. Interfaces* **2017**, *9*, 3142–3148.
- (318) Wang, M.; Duan, F.; Mu, X. Effect of Surface Silanol Groups on Friction and Wear between Amorphous Silica Surfaces. *Langmuir* **2019**, *35*, 5463–5470.
- (319) Zhang, J.; Ewen, J. P.; Ueda, M.; Wong, J. S. S.; Spikes, H. A. Mechanochemistry of Zinc Dialkyldithiophosphate on Steel Surfaces under Elastohydrodynamic Lubrication Conditions. *ACS Appl. Mater. Interfaces* **2020**, *12*, 6662–6676.
- (320) Chen, L.; Wen, J.; Zhang, P.; Yu, B.; Chen, C.; Ma, T.; Lu, X.; Kim, S. H.; Qian, L. Nanomanufacturing of Silicon Surface with a Single Atomic Layer Precision via Mechanochemical Reactions. *Nat. Commun.* **2018**, *9*, 1542.
- (321) Tayebi, N.; Conry, T. F.; Polycarpou, A. A. Determination of Hardness from Nanoscratch Experiments: Corrections for Interfacial Shear Stress and Elastic Recovery. *J. Mater. Res.* **2003**, *18*, 2150–2162.
- (322) Vorholzer, M.; Vilhena, J. G.; Perez, R.; Gnecco, E.; Dietzel, D.; Schirmeisen, A. Temperature Activates Contact Aging in Silica Nanocontacts. *Phys. Rev. X* **2019**, *91*,

- 041045.
- (323) Ghatak, A.; Vorvolakos, K.; She, H.; Malotky, D. L.; Chaudhury, M. K. Interfacial Rate Processes in Adhesion and Friction. *J. Phys. Chem. B* **2000**, *104*, 4018–4030.
 - (324) Steiner, T. C-H···O Hydrogen Bonding in Crystals. *Crystallogr. Rev.* **2003**, *9*, 177–228.
 - (325) Milne, Z. B.; Schall, J. D.; Jacobs, T. D. B.; Harrison, J. A.; Carpick, R. W. Covalent Bonding and Atomic-Level Plasticity Increase Adhesion in Silicon-Diamond Nanocontacts. *ACS Appl. Mater. Interfaces* **2019**, *11*, 40734–40748.
 - (326) Caenn, R.; Chillingar, G. V. Drilling Fluids: State of the Art. *J. Pet. Sci. Eng.* **1996**, *14*, 221–230.
 - (327) Mohamed, A.; Salehi, S.; Ahmed, R. Significance and Complications of Drilling Fluid Rheology in Geothermal Drilling: A Review. *Geothermics* **2021**, *93*, 102066.
 - (328) Friedheim, J. E. Second-Generation Synthetic Drilling Fluids. *J. Pet. Technol.* **1997**, *49*, 724–728.
 - (329) Aboulrous, A. A.; Haddad, A. S.; Rafati, R.; Boyou, N. V.; Alsabagh, A. M. Review of Synthesis, Characteristics and Technical Challenges of Biodiesel Based Drilling Fluids. *J. Clean. Prod.* **2022**, *336*, 130344.
 - (330) Brandon, N. P.; Wood, R. J. K. The Influence of Interfacial Potential on Friction and Wear in an Aqueous Drilling Mud. *Wear* **1993**, *170*, 33–38.
 - (331) Zhao, X.; Li, D.; Zhu, H.; Ma, J.; An, Y. Advanced Developments in Environmentally Friendly Lubricants for Water-Based Drilling Fluid: A Review. *RSC Adv.* **2022**, *12*, 22853–22868.
 - (332) Lee, S.; Spencer, N. D. Materials Science: Sweet, Hairy, Soft, and Slippery. *Science (80-.).* **2008**, *319*, 575–576.
 - (333) Spikes, H. Basics of EHL for Practical Application. *Lubr. Sci.* **2015**, *27*, 45–67.
 - (334) David Ytrehus, J.; Taghipour, A.; Golchin, A.; Saasen, A.; Prakash, B. The Effect of Different Drilling Fluids on Mechanical Friction. *J. Energy Resour. Technol. Trans. ASME* **2017**, *139*.
 - (335) Zheng, Y.; Amiri, A.; Polycarpou, A. A. Enhancements in the Tribological Performance of Environmentally Friendly Water-Based Drilling Fluids Using Additives. *Appl. Surf. Sci.* **2020**, *527*, 146822.
 - (336) Yan, X.; You, L.; Kang, Y.; Li, X.; Xu, C.; She, J. Impact of Drilling Fluids on Friction Coefficient of Brittle Gas Shale. *Int. J. Rock Mech. Min. Sci.* **2018**, *106*, 144–152.
 - (337) Kuru, E.; Wojtanowicz, A. K. An Experimental Study of Sliding Friction between PDC Drill Cutters and Rocks. *Int. J. Rock Mech. Min. Sci. Geomech. Abstr.* **1995**, *32*, 277–283.

- (338) Smith, J. R.; Lund, J. B.; Galloway, R. K. Friction on PDC Cutters at High Normal Stress. *J. Energy Resour. Technol.* **2002**, *124*, 146–153.
- (339) SELIM AA; SCHULTZ CW; STREBIG KC. The Effect of Additives on Impregnated Diamond Bit Performance. *Soc. Pet. Eng. J.* **1969**, *9*, 425–433.
- (340) Macmillan, N. H.; Huntington, R. D.; Westwood, A. R. C. Chemomechanical Control of Sliding Friction Behaviour in Non-Metals. *J. Mater. Sci.* **1974**, *9*, 697–706.
- (341) WESTWOOD, A. R. C.; GOLDHEIM, D. L. Mechanism for Environmental Control of Drilling in MgO and CaF₂ Monocrystals. *J. Am. Ceram. Soc.* **1970**, *53*, 142–147.
- (342) Fischer, T. E.; Anderson, M. P.; Jahanmir, S.; Salher, R. Friction and Wear of Tough and Brittle Zirconia in Nitrogen, Air, Water, Hexadecane and Hexadecane Containing Stearic Acid. *Wear* **1988**, *124*, 133–148.
- (343) Jahanmir, S.; Fischer, T. E. Friction and Wear of Silicon Nitride Lubricated by Humid Air, Water, Hexadecane and Hexadecane + 0.5 Percent Stearic Acid. *Tribol. Trans.* **1988**, *31*, 32–41.
- (344) Reddyhoff, T.; Ku, I. S. Y.; Holmes, A. S.; Spikes, H. A. Friction Modifier Behaviour in Lubricated MEMS Devices. *Tribol. Lett.* **2011**, *41*, 239–246.
- (345) Zum Gahr, K. H. Sliding Wear of Ceramic-Ceramic, Ceramic-Steel and Steel-Steel Pairs in Lubricated and Unlubricated Contact. *Wear* **1989**, *133*, 1–22.
- (346) Marks, L. D.; Warren, O. L.; Minor, A. M.; Merkle, A. R. Tribology in Full View. *MRS Bull.* **2008**, *33*, 1168–1173.
- (347) Blau, P. J. On the Nature of Running-In. *Tribol. Int.* **2005**, *38*, 1007–1012.
- (348) Gee, M. L.; Healy, T. W.; White, L. R. Hydrophobicity Effects in the Condensation of Water Films on Quartz. *J. Colloid Interface Sci.* **1990**, *140*, 450–465.
- (349) Kinser, C. R.; Schmitz, M. J.; Hersam, M. C. Conductive Atomic Force Microscope Nanopatterning of Hydrogen-Passivated Silicon in Inert Organic Solvents. *Nano Lett.* **2005**, *5*, 91–95.
- (350) Schatzberg, P. Solubilities of Water in Several Normal Alkanes from C₇ to C₁₆. *J. Phys. Chem.* **1963**, *67*, 776–779.
- (351) Miranda, P. B.; Shen, Y. R. Liquid Interfaces: A Study by Sum-Frequency Vibrational Spectroscopy. *J. Phys. Chem. B* **1999**, *103*, 3292–3307.
- (352) Gee, M. L.; Healy, T. W.; White, L. R. Ellipsometric Studies of Alkane Adsorption on Quartz. *J. Colloid Interface Sci.* **1989**, *131*, 18–23.
- (353) Budi, A.; Stipp, S. L. S.; Andersson, M. P. Calculation of Entropy of Adsorption for Small Molecules on Mineral Surfaces. *J. Phys. Chem. C* **2018**, *122*, 8236–8243.

- (354) Wang, J.; Zhang, L.; Zeng, Q.; Gérard, V. L.; Guette, A. First-Principles Investigation on Initial Stage of 2H-SiC(001) Surface Oxidation. *Chinese Sci. Bull.* **2009**, *54*, 1487–1494.
- (355) van Duin, A. C. T.; Dasgupta, S.; Lorant, F.; Goddard III, W. A. ReaxFF: A Reactive Force Field for Hydrocarbons. *J. Phys. Chem. A* **2001**, *105*, 9396–9409.
- (356) Cutini, M.; Forghieri, G.; Ferrario, M.; Righi, M. C. Adhesion, Friction and Tribochemical Reactions at the Diamond–Silica Interface. *Carbon N. Y.* **2023**, *203*, 601–610.
- (357) Cafolla, C.; Voitchovsky, K. Impact of Water on the Lubricating Properties of Hexadecane at the Nanoscale. *Nanoscale* **2020**, *12*, 14504–14513.
- (358) Plöbß, A.; Kräuter, G. Wafer Direct Bonding: Tailoring Adhesion between Brittle Materials. *Mater. Sci. Eng. R Reports* **1999**, *25*, 1–88.
- (359) Jensen, B. D.; Wise, K. E.; Odegard, G. M. Simulation of the Elastic and Ultimate Tensile Properties of Diamond, Graphene, Carbon Nanotubes, and Amorphous Carbon Using a Revised ReaxFF Parametrization. *J. Phys. Chem. A* **2015**, *119*, 9710–9721.
- (360) Zhai, W.; Bai, L.; Zhou, R.; Fan, X.; Kang, G.; Liu, Y.; Zhou, K. Recent Progress on Wear-Resistant Materials: Designs, Properties, and Applications. *Adv. Sci.* **2021**, *8*, 2003739.
- (361) Mattei, L.; Di Puccio, F.; Piccigallo, B.; Ciulli, E. Lubrication and Wear Modelling of Artificial Hip Joints: A Review. *Tribol. Int.* **2011**, *44*, 532–549.
- (362) Meng, H. C.; Ludema, K. C. Wear Models and Predictive Equations: Their Form and Content. *Wear* **1995**, *181–183*, 443–457.
- (363) Liu, J.; Jiang, Y.; Grierson, D. S.; Sridharan, K.; Shao, Y.; Jacobs, T. D. B.; Falk, M. L.; Carpick, R. W.; Turner, K. T. Tribochemical Wear of Diamond-Like Carbon-Coated Atomic Force Microscope Tips. *ACS Appl. Mater. Interfaces* **2017**, *9*, 35341–35348.
- (364) Tönshoff, H. K.; Hillmann-Apmann, H.; Asche, J. Diamond Tools in Stone and Civil Engineering Industry: Cutting Principles, Wear and Applications. *Diam. Relat. Mater.* **2002**, *11*, 736–741.
- (365) Hossain, M. E. Drilling Costs Estimation for Hydrocarbon Wells. *J. Sustain. Energy Eng.* **2015**, *3*, 3–32.
- (366) Ortega, A.; Glowka, D. A. Frictional Heating and Convective Cooling of Polycrystalline Diamond Drag Tools During Rock Cutting. *Soc. Pet. Eng. J.* **1984**, *24*, 121–128.
- (367) Mir, A.; Luo, X.; Sun, J. The Investigation of Influence of Tool Wear on Ductile to Brittle Transition in Single Point Diamond Turning of Silicon. *Wear* **2016**, *364–365*, 233–243.
- (368) Jia, P.; Zhou, M. Tool Wear and Its Effect on Surface Roughness in Diamond Cutting of Glass Soda-Lime. *Chinese J. Mech. Eng.* **2012**, *25*, 1224–1230.

- (369) Khurshudov, A. G.; Kato, K.; Koide, H. Nano-Wear of the Diamond AFM Probing Tip under Scratching of Silicon, Studied by AFM. *Tribol. Lett.* **1996**, *24*, 345–354.
- (370) Chenoweth, K.; Van Duin, A. C. T. T.; Goddard, W. A.; Goddard III, W. A. ReaxFF Reactive Force Field for Molecular Dynamics Simulations of Hydrocarbon Oxidation. *J. Phys. Chem. A* **2008**, *112*, 1040–1053.
- (371) Nouranian, S.; Gwaltney, S. R.; Baskes, M. I.; Tschopp, M. A.; Horstemeyer, M. F. Simulations of Tensile Bond Rupture in Single Alkane Molecules Using Reactive Interatomic Potentials. *Chem. Phys. Lett.* **2015**, *635*, 278–284.
- (372) Tomas, C. De; Aghajamali, A.; Jones, J. L.; Lim, D. J.; Suarez-martinez, I.; Marks, N. A.; Maria, J. L.; de Tomas, C.; Aghajamali, A.; Jones, J. L.; Lim, D. J.; López, M. J.; Suarez-martinez, I.; Marks, N. A. Transferability in Interatomic Potentials for Carbon. *Carbon N. Y.* **2019**, *155*, 624–634.
- (373) Wang, Y.; Yamada, N.; Xu, J.; Zhang, J.; Chen, Q.; Ootani, Y.; Higuchi, Y.; Ozawa, N.; Bouchet, M. D. B.; Martin, J. M.; Mori, S.; Adachi, K.; Kubo, M. Triboemission of Hydrocarbon Molecules from Diamond-like Carbon Friction Interface Induces Atomic-Scale Wear. *Sci. Adv.* **2019**, *5*, 1–10.
- (374) Wang, H.; Ge, Y.; Shi, L. Technologies in Deep and Ultra-Deep Well Drilling: Present Status, Challenges and Future Trend in the 13th Five-Year Plan Period (2016–2020). *Nat. Gas Ind. B* **2017**, *4*, 319–326.
- (375) Verlet, L. Computer “Experiments” on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules. *Phys. Rev.* **1967**, *159*, 98.
- (376) Bair, S.; McCabe, C.; Cummings, P. T. Calculation of Viscous EHL Traction for Squalane Using Molecular Simulation and Rheometry. *Tribol. Lett.* **2002**, *13*, 251–254.
- (377) Bair, S.; McCabe, C.; Cummings, P. T. Comparison of Nonequilibrium Molecular Dynamics with Experimental Measurements in the Nonlinear Shear-Thinning Regime. *Phys. Rev. Lett.* **2002**, *88*, 058302.
- (378) Paul, E.; Evans, C. J.; Mangamelli, A.; McGlaflin, M. L.; Polvani, R. S. Chemical Aspects of Tool Wear in Single Point Diamond Turning. *Precis. Eng.* **1996**, *18*, 4–19.
- (379) Köhler, C.; Hajnal, Z.; Frauenheim, T.; Deák, P.; Suhai, S. Theoretical Investigation of Carbon Defects and Diffusion in α -Quartz. *Phys. Rev. B* **2001**, *64*, 085333.
- (380) Rigney, D. A.; Karthikeyan, S. The Evolution of Tribomaterial during Sliding: A Brief Introduction. *Tribol. Lett.* **2010**, *39*, 3–7.
- (381) Pastewka, L.; Moser, S.; Gumbsch, P.; Moseler, M. Anisotropic Mechanical Amorphization Drives Wear in Diamond. *Nat. Mater.* **2011**, *10*, 34–38.

- (382) Hu, X.; Altoe, M. V. P.; Martini, A. Amorphization-Assisted Nanoscale Wear during the Running-in Process. *Wear* **2017**, *370–371*, 46–50.
- (383) Mukhanov, V. A.; Kurakevych, O. O.; Solozhenko, V. L. Hardness of Materials at High Temperature and High Pressure. *Philos. Mag.* **2010**, *89*, 2117–2127.
- (384) Bowden, F. P.; Scott, H. G. The Polishing, Surface Flow and Wear of Diamond and Glass. *Proc. R. Soc. London. Ser. A. Math. Phys. Sci.* **1958**, *248*, 368–378.
- (385) Wang, K.; Zhang, J.; Ma, T.; Liu, Y.; Song, A.; Chen, X.; Hu, Y.; Carpick, R. W.; Luo, J. Unraveling the Friction Evolution Mechanism of Diamond-Like Carbon Film during Nanoscale Running-In Process toward Superlubricity. *Small* **2021**, *17*, 2005607.
- (386) Vahdat, V.; Ryan, K. E.; Keating, P. L.; Jiang, Y.; Adiga, S. P.; Schall, J. D.; Turner, K. T.; Harrison, J. A.; Carpick, R. W. Atomic-Scale Wear of Amorphous Hydrogenated Carbon during Intermittent Contact: A Combined Study Using Experiment, Simulation, and Theory. *ACS Nano* **2014**, *8*, 7027–7040.
- (387) Davies, G.; Evans, T. Graphitization of Diamond at Zero Pressure and at a High Pressure. *Proc. R. Soc. London. A. Math. Phys. Sci.* **1972**, *328*, 413–427.
- (388) Qian, J.; Pantea, C.; Huang, J.; Zerda, T. W.; Zhao, Y. Graphitization of Diamond Powders of Different Sizes at High Pressure–High Temperature. *Carbon N. Y.* **2004**, *42*, 2691–2697.
- (389) Sun, Q.; Alam, M. Relative Oxidation Behavior of Chemical Vapor Deposited and Type II a Natural Diamonds. *J. Electrochem. Soc.* **1992**, *139*, 933–936.
- (390) Kelemen, S. R.; Freund, H. A Comparison of O₂ and CO₂ Oxidation of Glassy Carbon Surfaces. *Carbon N. Y.* **1985**, *23*, 723–729.
- (391) Yang, Y.; Huang, L.; Shi, Y. Adhesion Suppresses Atomic Wear in Single-Asperity Sliding. *Wear* **2016**, *352–353*, 31–41.
- (392) Barel, I.; Urbakh, M.; Jansen, L.; Schirmeisen, A. Multibond Dynamics of Nanoscale Friction: The Role of Temperature. *Phys. Rev. Lett.* **2010**, *104*, 66104–66108.
- (393) Vorholzer, M.; Dietzel, D.; Cihan, E.; Schirmeisen, A. Shear-Assisted Contact Aging of Single-Asperity Nanojunctions. *Phys. Rev. B* **2022**, *105*, 195401.
- (394) Chung, K. H.; Kim, D. E. Wear Characteristics of Diamond-Coated Atomic Force Microscope Probe. *Ultramicroscopy* **2007**, *108*, 1–10.
- (395) Raider, S. I.; Flitsch, R.; Aboaf, J. A.; Pliskin, W. A. Surface Oxidation of Silicon Nitride Films. *J. Electrochem. Soc.* **1976**, *123*, 560–565.
- (396) Fischer, T. E. Tribochemistry. *Annu. Rev. Mater. Sci.* **1988**, *18*, 303–323.
- (397) Nakayama, K. Triboemission of Electrons, Ions, and Photons from Diamondlike Carbon

- Films and Generation of Tribomicroplasma. *Surf. Coatings Technol.* **2004**, 188–189, 599–604.
- (398) He, X.; Barthel, A. J.; Kim, S. H.; He, X.; Barthel, A. J.; Kim, S. H. Tribochemical Synthesis of Nano-Lubricant Films from Adsorbed Molecules at Sliding Solid Interface: Tribo-Polymers from α -Pinene, Pinane, and n-Decane. *Surf. Sci.* **2016**, 648, 352–359.
- (399) Adams, H. L.; Garvey, M. T.; Ramasamy, U. S.; Ye, Z.; Martini, A.; Tysoe, W. T. Shear Induced Mechanochemistry: Pushing Molecules Around. *J. Phys. Chem. C* **2015**, 119, 7115–7123.
- (400) Kaitkay, P.; Lei, S. Experimental Study of Rock Cutting under External Hydrostatic Pressure. *J. Mater. Process. Technol.* **2005**, 159, 206–213.
- (401) Zhu, W.; Hughes, J. J.; Bicanic, N.; Pearce, C. J. Nanoindentation Mapping of Mechanical Properties of Cement Paste and Natural Rocks. *Mater. Charact.* **2007**, 58, 1189–1198.
- (402) Gao, F.; Stead, D.; Elmo, D. Numerical Simulation of Microstructure of Brittle Rock Using a Grain-Breakable Distinct Element Grain-Based Model. *Comput. Geotech.* **2016**, 78, 203–217.
- (403) Molaei, F.; Siavoshi, H. Molecular Dynamics Studies of Thermal Conductivity and Mechanical Properties of Single Crystalline α -Quartz. *Solid State Commun.* **2020**, 320, 114020.
- (404) Skelton, A. A.; Fenter, P.; Kubicki, J. D.; Wesolowski, D. J.; Cummings, P. T. Simulations of the Quartz(1011)/Water Interface: A Comparison of Classical Force Fields, Ab Initio Molecular Dynamics, and x-Ray Reflectivity Experiments. *J. Phys. Chem. C* **2011**, 115, 2076–2088.
- (405) Wang, J.; Rajendran, A. M.; Dongare, A. M. Atomic Scale Modeling of Shock Response of Fused Silica and α -Quartz. *J. Mater. Sci.* **2015**, 50, 8128–8141.
- (406) Lopes, P. E. M.; Murashov, V.; Tazi, M.; Demchuk, E.; MacKerell, A. D. Development of an Empirical Force Field for Silica. Application to the Quartz-Water Interface. *J. Phys. Chem. B* **2006**, 110, 2782–2792.
- (407) Marcinkevičius, A.; Misawa, H.; Nishii, J.; Miwa, M.; Watanabe, M.; Juodkasis, S.; Matsuo, S. Femtosecond Laser-Assisted Three-Dimensional Microfabrication in Silica. *Opt. Lett.* Vol. 26, Issue 5, pp. 277–279 **2001**, 26, 277–279.
- (408) Griscom, D. L. The Electronic Structure of SiO₂: A Review of Recent Spectroscopic and Theoretical Advances. *J. Non. Cryst. Solids* **1977**, 24, 155–234.
- (409) Keskar, N. R.; Troullier, N.; Martins, J. L.; Chelikowsky, J. R. Structural Properties of SiO₂ in the Stishovite Structure. **1991**, 44.

- (410) Vashishta, P.; Kalia, R. K.; Rino, J. P.; Ebbsjö, I. Interaction Potential for SiO₂: A Molecular-Dynamics Study of Structural Correlations. *Phys. Rev. B* **1990**, *41*, 12197.
- (411) DR, W.; Zegers-van Duynhoven, A.; Devine, R. A. B. The Physics and Technology of Amorphous SiO₂. *Plenum Press* **1998**, 15.
- (412) Zemann, J. Crystal Structures, 2nd Edition. Vol. 1 by R. W. G. Wyckoff. *Acta Crystallogr.* **1965**, *18*, 139–139.
- (413) Bell, R. J.; Bird, N. F.; Dean, P. The Vibrational Spectra of Vitreous Silica, Germania and Beryllium Fluoride. *J. Phys. C Solid State Phys.* **1968**, *1*, 299–303.
- (414) MOZZI RL; WARREN BE. The Structure of Vitreous Silica. *J. Appl. Crystallogr.* **1969**, *2*, 164–172.
- (415) Mackenzie, J. D. Glasses from Melts and Glasses from Gels, a Comparison. *J. Non. Cryst. Solids* **1982**, *48*, 1–10.
- (416) Gaskell, P. H.; Johnson, D. W. The Optical Constants of Quartz, Vitreous Silica and Neutron-Irradiated Vitreous Silica. (II) Analysis of the Infrared Spectrum of Vitreous Silica. *J. Non. Cryst. Solids* **1976**, *20*, 171–191.
- (417) van Tendeloo, G.; van Landuyt, J.; Amelinckx, S. The $\alpha \rightarrow \beta$ Phase Transition in Quartz and AlPO₄ as Studied by Electron Microscopy and Diffraction. *Phys. status solidi* **1976**, *33*, 723–735.
- (418) Tsuneyuki, S.; Aoki, H.; Tsukada, M.; Matsui, Y. Molecular-Dynamics Study of the α to β Structural Phase Transition of Quartz. *Phys. Rev. Lett.* **1990**, *64*, 776.
- (419) Pagliari, L.; Dapiaggi, M.; Pavese, A.; Francescon, F. A Kinetic Study of the Quartz-Cristobalite Phase Transition. *J. Eur. Ceram. Soc.* **2013**, *33*, 3403–3410.
- (420) Tse, J. S.; Klug, D. D. Mechanical Instability of α -Quartz: A Molecular-Dynamics Study. **1991**, *67*, 25.
- (421) Chelikowsky, J. R.; Keskar, N. R.; Binggeli, N. The Structural Properties of Silica Using Classical and Quantum Interatomic Forces. *Mol. Eng. 1996 61* **1996**, *6*, 1–37.
- (422) Hemley, R. J.; Jephcoat, A. P.; Mao, H. K.; Ming, L. C.; Manghnani, M. H. Pressure-Induced Amorphization of Crystalline Silica. *Nature* **1988**, *334*, 52–54.
- (423) NAKA, S.; ITO, S.; INAGAKI, M. Kinetic Studies of Transitions from Amorphous Silica and Quartz to Coesite. *J. Am. Ceram. Soc.* **1974**, *57*, 217–219.
- (424) Krishnan, N. M. A.; Wang, B.; Le Pape, Y.; Sant, G.; Bauchy, M. Irradiation-Driven Amorphous-to-Glassy Transition in Quartz: The Crucial Role of the Medium-Range Order in Crystallization. *Phys. Rev. Mater.* **2017**, *1*, 53405.
- (425) Grimm, H.; Dorner, B. On the Mechanism of the α - β Phase Transformation of Quartz. *J.*

- Phys. Chem. Solids* **1975**, *36*, 407–413.
- (426) Ringdalen, E. Changes in Quartz During Heating and the Possible Effects on Si Production. *JOM* **2015**, *67*, 484–492.
- (427) Richter, B.; Stünitz, H.; Heilbronner, R. Stresses and Pressures at the Quartz-to-Coesite Phase Transformation in Shear Deformation Experiments. *J. Geophys. Res. Solid Earth* **2016**, *121*, 8015–8033.
- (428) Kingma, K. J.; Hemley, R. J.; Mao, H. K.; Veblen, D. R. New High-Pressure Transformation in α -Quartz. *Phys. Rev. Lett.* **1993**, *70*, 3927.
- (429) Klier, K.; Spirko, J. A.; Landskron, K. M. Optical Absorption Anisotropy of High-Density, Wide-Gap, High-Hardness SiO₂ Polymorphs Seifertite, Stishovite, and Coesite. *Am. Mineral.* **2015**, *100*, 120–129.
- (430) Crompton, D.; Hirst, W.; Howse, M. G. W. The Wear of Diamond. *Proc. R. Soc. London. A. Math. Phys. Sci.* **1973**, *333*, 4350454.
- (431) Weber, B.; Suhina, T.; Junge, T.; Pastewka, L.; Brouwer, A. M.; Bonn, D. Molecular Probes Reveal Deviations from Amontons' Law in Multi-Asperity Frictional Contacts. *Nat. Commun.* **2018**, *9*, 1–7.
- (432) Hirano, M.; Shinjo, K. Atomistic Locking and Friction. *Phys. Rev. B* **1990**, *41*, 11837–11851.
- (433) Müser, M. H. Rigorous Field-Theoretical Approach to the Contact Mechanics of Rough Elastic Solids. *Phys. Rev. Lett.* **2008**, *100*.
- (434) Persson, B. N. J. Theory of Rubber Friction and Contact Mechanics. *J. Chem. Phys.* **2001**, *115*, 3840–3861.
- (435) Warner, D. H.; Curtin, W. A. Origins and Implications of Temperature-Dependent Activation Energy Barriers for Dislocation Nucleation in Face-Centered Cubic Metals. *Acta Mater.* **2009**, *57*, 4267–4277.
- (436) Zhurkov, S. N.; Korsukov, V. E. Atomic Mechanism of Fracture of Solid Polymers. *J. Polym. Sci. Polym. Phys. Ed.* **1974**, *12*, 385–398.
- (437) Zhurkov, S. N. Kinetic Concept of the Strength of Solids. *Int. J. Fract.* **1984**, *26*, 295–307.
- (438) Hyeon, C.; Thirumalai, D. Can Energy Landscape Roughness of Proteins and RNA Be Measured by Using Mechanical Unfolding Experiments? *Proc. Natl. Acad. Sci.* **2003**, *100*, 10249–10253.
- (439) Ainslie, N. G.; Mackenzie, J. D.; Turnbull, D. MELTING KINETICS OF QUARTZ AND CRISTOBALITE. *J. Phys. Chem.* **2002**, *65*, 1718–1724.
- (440) Lyon, R. J. P. Infra-Red Confirmation of 6-Fold Co-Ordination of Silicon in Stishovite.

- Nat.* 1962 1964851 **1962**, 196, 266–267.
- (441) Cowen, B. J.; El-Genk, M. S. On Force Fields for Molecular Dynamics Simulations of Crystalline Silica. *Comput. Mater. Sci.* **2015**, 107, 88–101.
 - (442) Badro, J.; Teter, D. M. Theoretical Study of a Five-Coordinated Silica Polymorph. *Phys. Rev. B - Condens. Matter Mater. Phys.* **1997**, 56, 5797–5806.
 - (443) Xie, X.; Cheng, Y.; Wu, K.; Xiao, B. Study on α - β Quartz Phase Transition and Its Effect on Dielectric Properties. *J. Appl. Phys.* **2012**, 111, 104116.
 - (444) Tse, J. S.; Klug, D. D.; Page, Y. I. E. High-Pressure Densification of Amorphous Silica. *Phys. Rev. B* **1992**, 46.
 - (445) Nishiyama, N.; Wakai, F.; Ohfuji, H.; Tamenori, Y.; Murata, H.; Taniguchi, T.; Matsushita, M.; Takahashi, M.; Kulik, E.; Yoshida, K.; Wada, K.; Bednarcik, J.; Irifune, T. Fracture-Induced Amorphization of Polycrystalline SiO₂ Stishovite: A Potential Platform for Toughening in Ceramics. *Sci. Rep.* **2014**, 4.
 - (446) Tsiok, O. B.; Brazhkin, V. V.; Lyapin, A. G.; Khvostantsev, L. G. Logarithmic Kinetics of the Amorphous-Amorphous Transformations in SiO₂ and GeO₂ Glasses under High Pressure. *Phys. Rev. Lett.* **1998**, 80, 999–1002.
 - (447) Weigel, C.; Mebarki, M.; Clément, S.; Vacher, R.; Foret, M.; Rufflé, B. Pressure-Induced Densification of Vitreous Silica: Insight from Elastic Properties. *Phys. Rev. B* **2019**, 100, 094102.
 - (448) Hasmy, A.; Ispas, S.; Hehlen, & B. Percolation Transitions in Compressed SiO₂ Glasses. 62 | *Nat.* | **2021**, 599.
 - (449) Lin, J. F.; Fukui, H.; Prendergast, D.; Okuchi, T.; Cai, Y. Q.; Hiraoka, N.; Yoo, C. S.; Trave, A.; Eng, P.; Hu, M. Y.; Chow, P. Electronic Bonding Transition in Compressed SiO₂ Glass. *Phys. Rev. B - Condens. Matter Mater. Phys.* **2007**, 75, 012201.
 - (450) Sato, T.; Funamori, N. High-Pressure Structural Transformation of SiO₂ Glass up to 100 GPa. *Phys. Rev. B - Condens. Matter Mater. Phys.* **2010**, 82, 184102.
 - (451) Murakami, M.; Kohara, S.; Kitamura, N.; Akola, J.; Inoue, H.; Hirata, A.; Hiraoka, Y.; Onodera, Y.; Obayashi, I.; Kalikka, J.; Hirao, N.; Musso, T.; Foster, A. S.; Idemoto, Y.; Sakata, O.; Ohishi, Y. Ultrahigh-Pressure Form of SiO₂ Glass with Dense Pyrite-Type Crystalline Homology. *Phys. Rev. B* **2019**, 99, 045153.
 - (452) Sinclair, W.; Ringwood, A. E.; Sinclair, W.; Ringwood, A. E. Single Crystal Analysis of the Structure of Stishovite. *Natur* **1978**, 272, 714.
 - (453) Finger, L. W.; Hazen, R. M. Crystal Chemistry of Six-coordinated Silicon: A Key to Understanding the Earth's Deep Interior. *Acta Crystallogr. Sect. B* **1991**, 47, 561–580.

- (454) Boisen, M. B.; Gibbs, G. V.; Downs, R. T.; D'Arco, P. The Dependence of the SiO Bond Length on Structural Parameters in Coesite, the Silica Polymorphs, and the Clathrasils. *Am. Mineral.* **1990**, *75*, 748–754.
- (455) Demiralp, E.; Çagin, T.; Goddard, W. A. Morse Stretch Potential Charge Equilibrium Force Field for Ceramics: Application to the Quartz-Stishovite Phase Transition and to Silica Glass. *Phys. Rev. Lett.* **1999**, *82*, 1708.
- (456) Grady, D. E.; Murri, W. J.; Fowles, G. R. Quartz to Stishovite: Wave Propagation in the Mixed Phase Region. *J. Geophys. Res.* **1974**, *79*, 332–338.
- (457) Luo, S.-N.; Ahrens, T. J.; Asimow, P. D. Polymorphism, Superheating, and Amorphization of Silica upon Shock Wave Loading and Release. *J. Geophys. Res. Solid Earth* **2003**, *108*, 2421.
- (458) Ahrens, T. J.; Gregson, V. G. Shock Compression of Crustal Rocks: Data for Quartz, Calcite, and Plagioclase Rocks. *J. Geophys. Res.* **1964**, *69*, 4839–4874.
- (459) Richet, P. Superheating, Melting and Vitrification through Decompression of High-Pressure Minerals. *Nature* **1988**, *331*, 56–58.
- (460) Simha, N.; Truskinovsky, L. Shear Induced Transformation Toughening in Ceramics. *Acta Metall. Mater.* **1994**, *42*, 3827–3836.
- (461) Lindemann, F. A. The Calculation of Molecular Natural Frequencies. *Phys. Z.* **1910**, *11*, 609–612.
- (462) Cahn, R. W.; Johnson, W. L. Review: The Nucleation of Disorder. *Journal of Materials Research*. 1986, pp 724–732.
- (463) Dasgupta, N.; Chen, C.; Van Duin, A. C. T. Development and Application of ReaxFF Methodology for Understanding the Chemical Dynamics of Metal Carbonates in Aqueous Solutions. *Phys. Chem. Chem. Phys.* **2022**, *24*, 3322–3337.
- (464) van Duin, A. C. T.; Zou, C.; Joshi, K.; Bryantsev, V.; Goddard, W. A. A Reaxff Reactive Force-Field for Proton Transfer Reactions in Bulk Water and Its Applications to Heterogeneous Catalysis. *Comput. Catal.* **2014**, 223–243.
- (465) Ponomarev, I.; Duin, A. C. T. van; Kroll, P. Reactive Force Field for Simulations of the Pyrolysis of Polysiloxanes into Silicon Oxycarbide Ceramics. *J. Phys. Chem. C* **2019**, *123*, 16804–16812.
- (466) Zhang, W.; Van Duin, A. C. T. Atomistic-Scale Simulations of the Graphene Growth on a Silicon Carbide Substrate Using Thermal Decomposition and Chemical Vapor Deposition. *Chem. Mater.* **2020**, *32*, 8306–8317.
- (467) Bedrov, D.; Smith, G. D.; Van Duin, A. C. T. Reactions of Singly-Reduced Ethylene

- Carbonate in Lithium Battery Electrolytes: A Molecular Dynamics Simulation Study Using the ReaxFF. *J. Phys. Chem. A* **2012**, *116*, 2978–2985.
- (468) Olou’Ou Guifo, S. B.; Mueller, J. E.; Van Duin, D.; Talkhoncheh, M. K.; Van Duin, A. C. T.; Henriques, D.; Markus, T. Development and Validation of a ReaxFF Reactive Force Field for Modeling Silicon-Carbon Composite Anode Materials in Lithium-Ion Batteries. *J. Phys. Chem. C* **2022**, *127*.
- (469) Yun, K. S.; Pai, S. J.; Yeo, B. C.; Lee, K. R.; Kim, S. J.; Han, S. S. Simulation Protocol for Prediction of a Solid-Electrolyte Interphase on the Silicon-Based Anodes of a Lithium-Ion Battery: ReaxFF Reactive Force Field. *J. Phys. Chem. Lett.* **2017**, *8*, 2812–2818.
- (470) Cox, J.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; 1989.
- (471) Goverapet Srinivasan, S.; Van Duin, A. C. T.; Ganesh, P. Development of a ReaxFF Potential for Carbon Condensed Phases and Its Application to the Thermal Fragmentation of a Large Fullerene. *J. Phys. Chem. A* **2015**, *119*, 571–580.
- (472) Hometz, B.; Michel, H. J.; Halbritter, J. ARXPS Studies of SiC₂-SiC Interfaces and Oxidation of 6H SiC Single Crystal Si-(001) and C-(001) Surfaces. *J. Mater. Res.* **1994**, *9*, 3088–3094.
- (473) Takamoto, S.; Yamasaki, T.; Ohno, T.; Kaneta, C.; Hatano, A.; Izumi, S. Elucidation of the Atomic-Scale Mechanism of the Anisotropic Oxidation Rate of 4H-SiC between the (0001) Si-Face and ($\bar{0}00\ 1\bar{1}$) C-Face by Using a New Si-O-C Interatomic Potential. *J. Appl. Phys.* **2018**, *123*, 185303.
- (474) Ashraf, C.; Van Duin, A. C. T. T. Extension of the ReaxFF Combustion Force Field toward Syngas Combustion and Initial Oxidation Kinetics. *J. Phys. Chem. A* **2017**, *121*, 1051–1068.
- (475) Erdemir, A.; Donnet, C. Tribology of Diamond-like Carbon Films: Recent Progress and Future Prospects. *J. Phys. D. Appl. Phys.* **2006**, *39*, 311–327.
- (476) Erdemir, A. Rolling-Contact Fatigue and Wear Resistance of Hard Coatings on Bearing-Steel Substrates. *Surf. Coatings Technol.* **1992**, *54–55*, 482–489.
- (477) Donnet, C.; Belin, M.; Augé, J. C.; Martin, J. M.; Grill, A.; Patel, V. Tribochemistry of Diamond-like Carbon Coatings in Various Environments. *Surf. Coatings Technol.* **1994**, *68–69*, 626–631.
- (478) Heimberg, J. A.; Wahl, K. J.; Singer, I. L.; Erdemir, A. Superlow Friction Behavior of Diamond-like Carbon Coatings: Time and Speed Effects. *Appl. Phys. Lett.* **2001**, *78*, 2449–2451.
- (479) Dickrell, P. L.; Sawyer, W. G.; Heimberg, J. A.; Singer, I. L.; Wahl, K. J.; Erdemir, A. A

- Gas-Surface Interaction Model for Spatial and Time-Dependent Friction Coefficient in Reciprocating Contacts: Applications to near-Frictionless Carbon. *J. Tribol.* **2005**, *127*, 82–88.
- (480) Qian, F.; Craciun, V.; Singh, R. K.; Dutta, S. D.; Pronko, P. P. High Intensity Femtosecond Laser Deposition of Diamond-like Carbon Thin Films. *J. Appl. Phys.* **1999**, *86*, 2281–2290.
- (481) Garrelie, F.; Bourquard, F.; Loir, A. S.; Donnet, C.; Colombier, J. P. Control of Femtosecond Pulsed Laser Ablation and Deposition by Temporal Pulse Shaping. *Opt. Laser Technol.* **2016**, *78*, 42–51.
- (482) Fernández, A.; Fernández-Ramos, C.; Sánchez-López, J. C. Preparation, Microstructural Characterisation and Tribological Behaviour of CN_x Coatings. *Surf. Coatings Technol.* **2003**, *163–164*, 527–534.
- (483) Qi, J.; Chan, C. Y.; Bello, I.; Lee, C. S.; Lee, S. T.; Luo, J. B.; Wen, S. Z. Film Thickness Effects on Mechanical and Tribological Properties of Nitrogenated Diamond-like Carbon Films. *Surf. Coatings Technol.* **2001**, *145*, 38–43.
- (484) Hilbert, J.; Mangolini, F.; McClimon, J. B.; Lukes, J. R.; Carpick, R. W. Si Doping Enhances the Thermal Stability of Diamond-like Carbon through Reductions in Carbon-Carbon Bond Length Disorder. *Carbon N. Y.* **2018**, *131*, 72–78.
- (485) Mosey, N. J.; Woo, T. K. An Ab Initio Molecular Dynamics and Density Functional Theory Study of the Formation of Phosphate Chains from Metathiophosphates. *Inorg. Chem.* **2006**, *45*, 7464–7479.
- (486) Mosey, N. J.; Woo, T. K. Insights into the Chemical Behavior of Zinc Dialkyldithiophosphate Anti-Wear Additives in Their Isomeric and Decomposed Forms through Molecular Simulation. *Tribol. Int.* **2006**, *39*, 979–993.
- (487) Mosey, N. J.; Müser, M. H.; Woo, T. K. Molecular Mechanisms for the Functionality of Lubricant Additives. *Science* **2005**, *307*, 1612–1615.
- (488) Mosey, N. J.; Woo, T. K. Finite Temperature Structure and Dynamics of Zinc Dialkyldithiophosphate Wear Inhibitors: A Density Functional Theory and Ab Initio Molecular Dynamics Study. *J. Phys. Chem. A* **2003**, *107*, 5058–5070.
- (489) Onodera, T.; Martin, J. M.; Minfray, C.; Dassenoy, F.; Miyamoto, A. Antiwear Chemistry of ZDDP: Coupling Classical MD and Tight-Binding Quantum Chemical MD Methods (TB-QCMD). *Tribol. Lett.* **2013**, *50*, 31–39.
- (490) Onodera, T.; Morita, Y.; Nagumo, R.; Miura, R.; Suzuki, A.; Tsuboi, H.; Hatakeyama, N.; Endou, A.; Takaba, H.; Dassenoy, F.; Minfray, C.; Joly-Pottuz, L.; Kubo, M.; Martin, J.

- M.; Miyamoto, A. A Computational Chemistry Study on Friction of H-MoS₂. Part II. Friction Anisotropy. *J. Phys. Chem. B* **2010**, *114*, 15832–15838.
- (491) Loehle, S.; Matta, C.; Minfray, C.; Mogne, T. Le; Martin, J. M.; Iovine, R.; Obara, Y.; Miura, R.; Miyamoto, A. Mixed Lubrication with C18 Fatty Acids: Effect of Unsaturation. *Tribol. Lett.* **2014**, *53*, 319–328.
- (492) Singh, M. K.; Ilg, P.; Espinosa-Marzal, R. M.; Spencer, N. D.; Kröger, M. Influence of Chain Stiffness, Grafting Density and Normal Load on the Tribological and Structural Behavior of Polymer Brushes: A Nonequilibrium-Molecular-Dynamics Study. *Polym. 2016*, *Vol. 8, Page 254* **2016**, *8*, 254.
- (493) Singh, M. K.; Ilg, P.; Espinosa-Marzal, R. M.; Kröger, M.; Spencer, N. D. Polymer Brushes under Shear: Molecular Dynamics Simulations Compared to Experiments. *Langmuir* **2015**, *31*, 4798–4805.
- (494) Farrow, M. R.; Chremos, A.; Camp, P. J.; Harris, S. G.; Watts, R. F. Molecular Simulations of Kinetic-Friction Modification in Nanoscale Fluid Layers. *Tribol. Lett.* **2011**, *42*, 325–337.
- (495) Fajardo, O. Y.; Bresme, F.; Kornyshev, A. A.; Urbakh, M. Electrotunable Friction with Ionic Liquid Lubricants: How Important Is the Molecular Structure of the Ions? *J. Phys. Chem. Lett.* **2015**, *6*, 3998–4004.
- (496) Martini, A.; Liu, Y.; Snurr, R. Q.; Wang, Q. J. Molecular Dynamics Characterization of Thin Film Viscosity for EHL Simulation. *Tribol. Lett.* **2006**, *21*, 217–225.
- (497) Savio, D.; Fillot, N.; Vergne, P.; Zaccheddu, M. A Model for Wall Slip Prediction of Confined N-Alkanes: Effect of Wall-Fluid Interaction versus Fluid Resistance. *Tribol. Lett.* **2012**, *46*, 11–22.
- (498) O’Connell, S. T.; Thompson, P. A. Molecular Dynamics–Continuum Hybrid Computations: A Tool for Studying Complex Fluid Flows. *Phys. Rev. E* **1995**, *52*, R5792.
- (499) Flekkøy, E. G.; Wagner, G.; Feder, J. Hybrid Model for Combined Particle and Continuum Dynamics. *Europhys. Lett.* **2000**, *52*, 271–276.
- (500) Nie, X. B.; Chen, S. Y.; E, W. N.; Robbins, M. O. A Continuum and Molecular Dynamics Hybrid Method for Micro- and Nano-Fluid Flow. *J. Fluid Mech.* **2004**, *500*, 55–64.

Appendix A: Supporting information for Chapter 3. Interfacial Bonding Controls Friction in Diamond-Rock Contacts

The work presented in this chapter is partly published in *The Journal of Physical Chemistry C*.¹

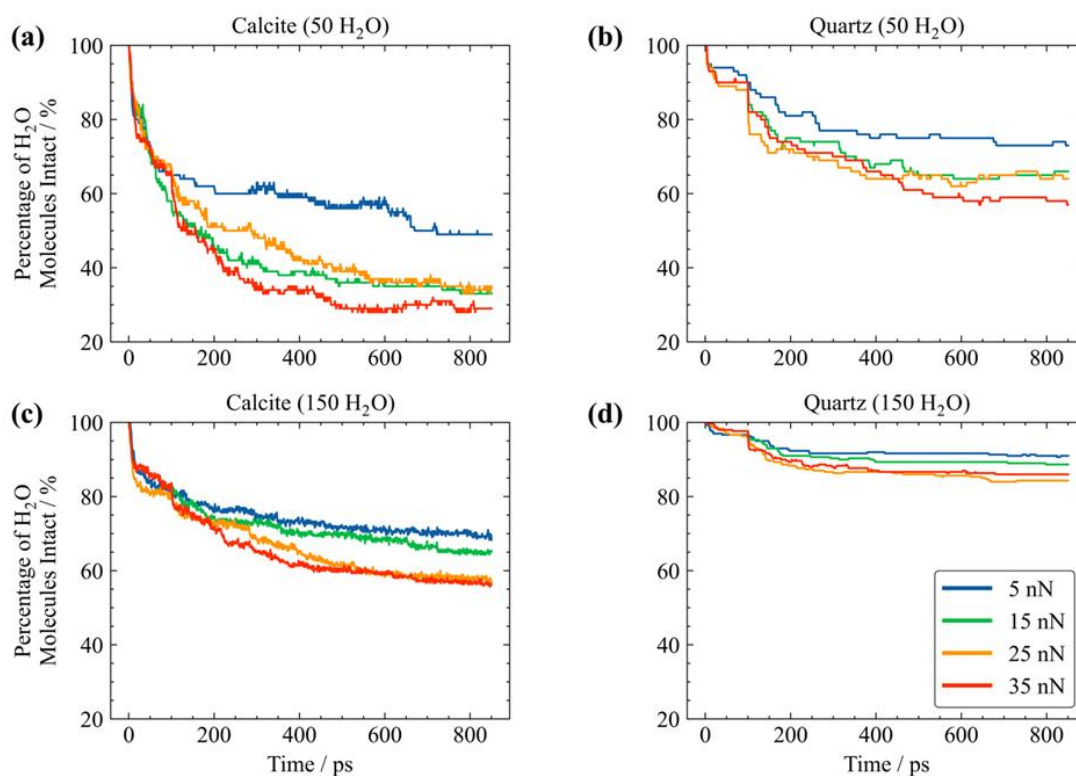


Figure 1: Variation in the percentage of intact water molecules with simulation time for: (a) calcite with 50 water molecules, (b) quartz with 50 water molecules, (c) calcite with 150 water molecules, and (d) quartz with 150 water molecules. The first 100 ps are equilibration at 0.1 nN, the remaining 700 ps include compression (values in legend) and sliding (10 m s⁻¹).

The DFT vibrational frequency range of CaCO_3 ranges from 300 cm^{-1} to 1800 cm^{-1} , as shown in Figure 2. The frequencies calculated using our ReaxFF force field are in good agreement with those obtained using DFT. Frequencies 7, 8, and 9 in Figure 1 denote the C-O bond stretching and compression in all three directions, which range between 1000 cm^{-1} and 1700 cm^{-1} . The normal modes representing mainly the C-O bond vibrations are shown schematically in Figure 3.

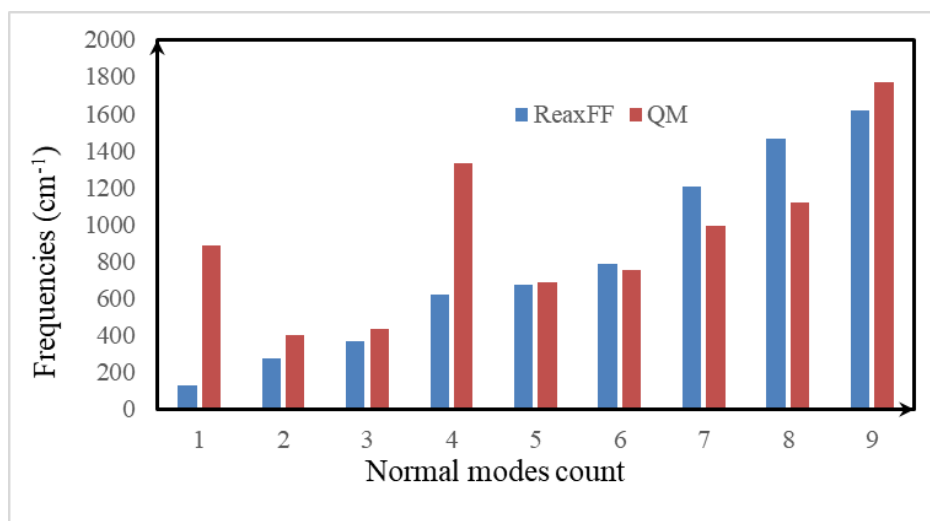


Figure 2: Comparison of vibrational frequencies of CaCO_3 from ReaxFF and DFT. Created by Nabankur Dasgupta and Adri C. T. van Duin.

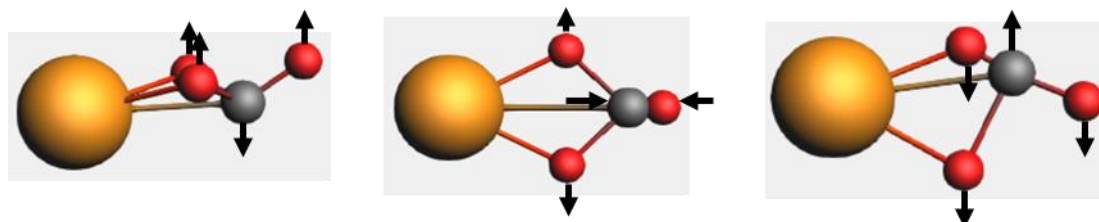


Figure 3: Different C-O bond stretching and compression modes for CaCO_3 vibrational frequencies. Created by Nabankur Dasgupta and Adri C. T. van Duin.

Reactions	DFT (kcal mol ⁻¹)	ReaxFF (kcal mol ⁻¹)
$\text{Ca} + \text{C} + \frac{3}{2}\text{O}_2 \rightarrow \text{CaCO}_3$	-288.60	-237.60
$\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$	-42.00	-50.71

Table 1: Comparisons of heat of formation and heat of reaction of CaCO_3 . Created by Nabankur Dasgupta and Adri C. T. van Duin.

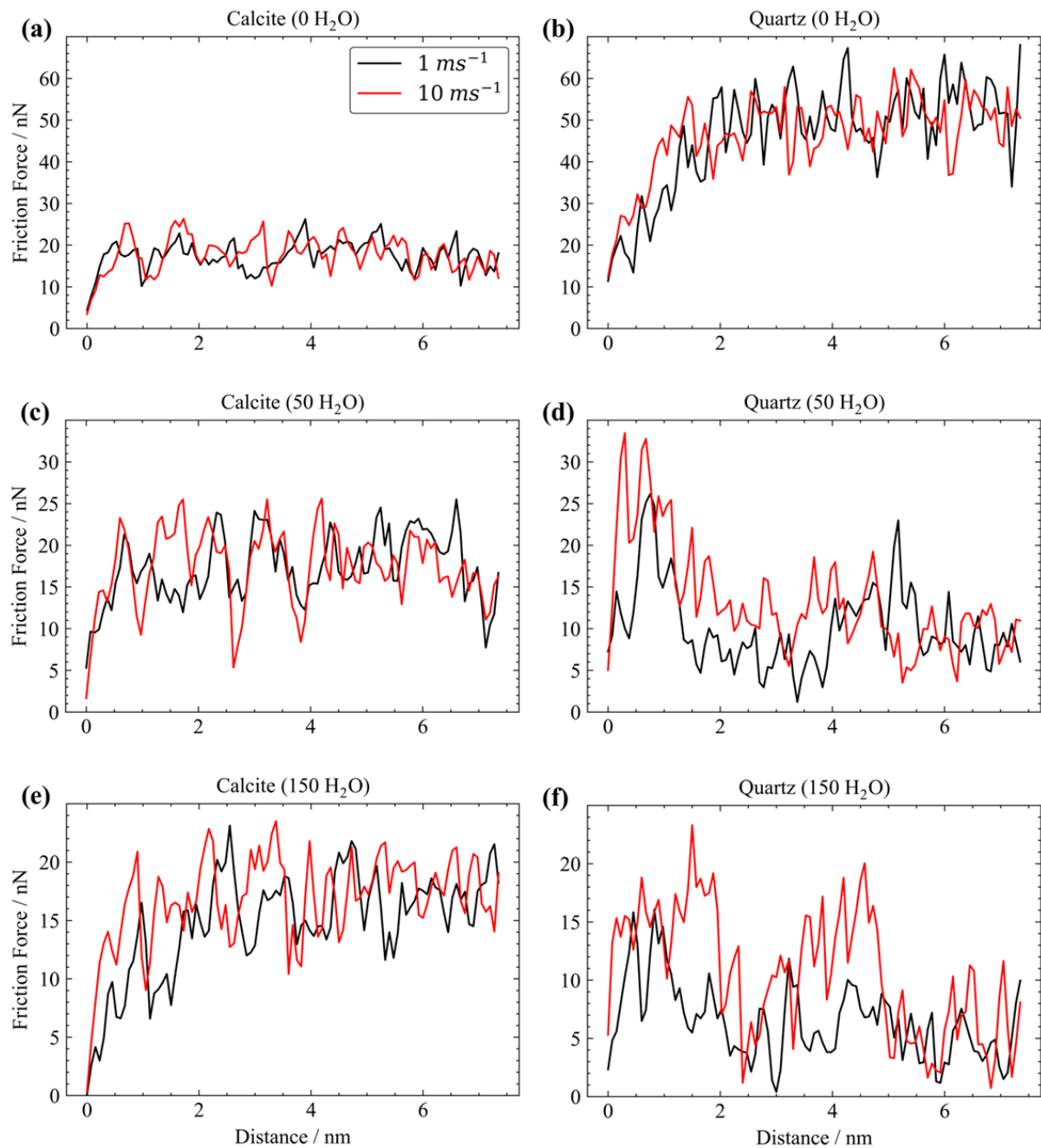


Figure 4: Variation of the friction force with sliding distance with tip sliding velocities of 1 m s^{-1} and 10 m s^{-1} for: (a) calcite with 0 water molecules, (b) quartz with 0 water molecules, (c) calcite with 50 water molecules, (d) quartz with 50 water molecules, (e) calcite with 150 water molecules, and (f) quartz with 150 water molecules. The normal force is 35 nN.

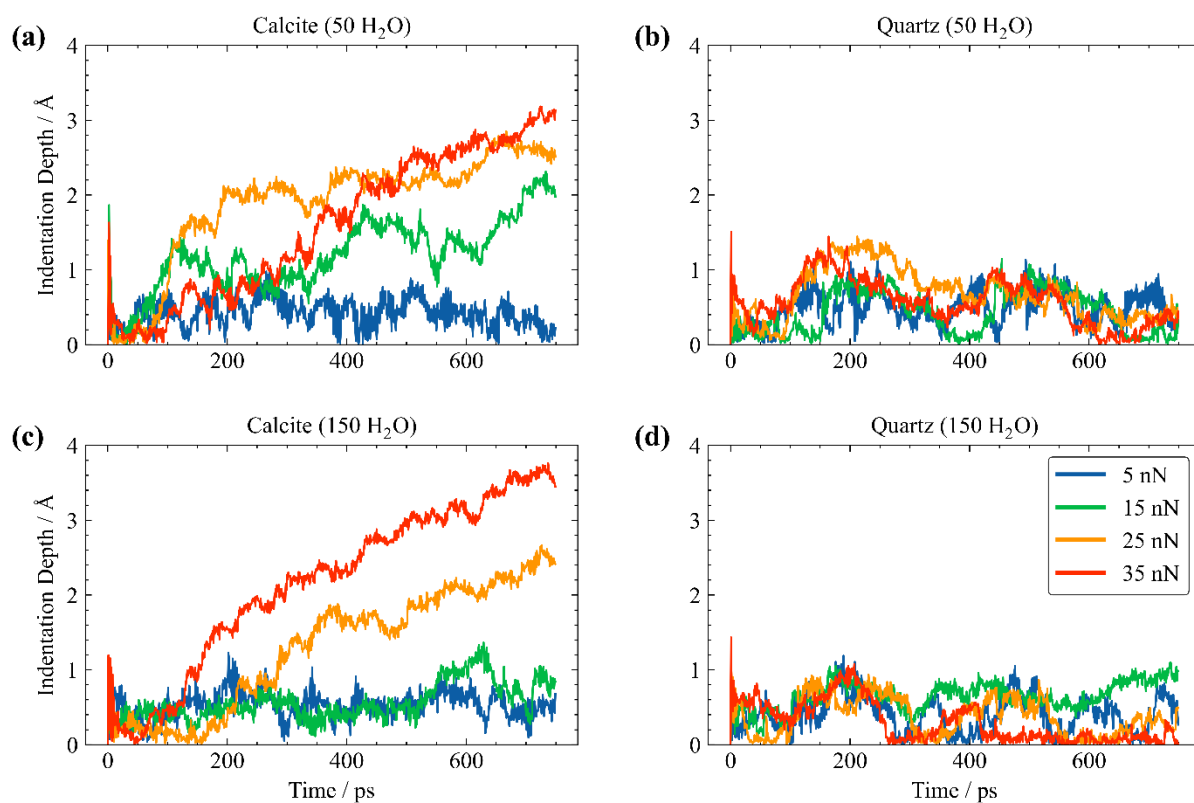


Figure 5: Variation in the indentation depth with sliding time for: (a) calcite with 50 water molecules, (b) quartz with 50 water molecules, (c) calcite with 150 water molecules, and (d) quartz with 150 water molecules.

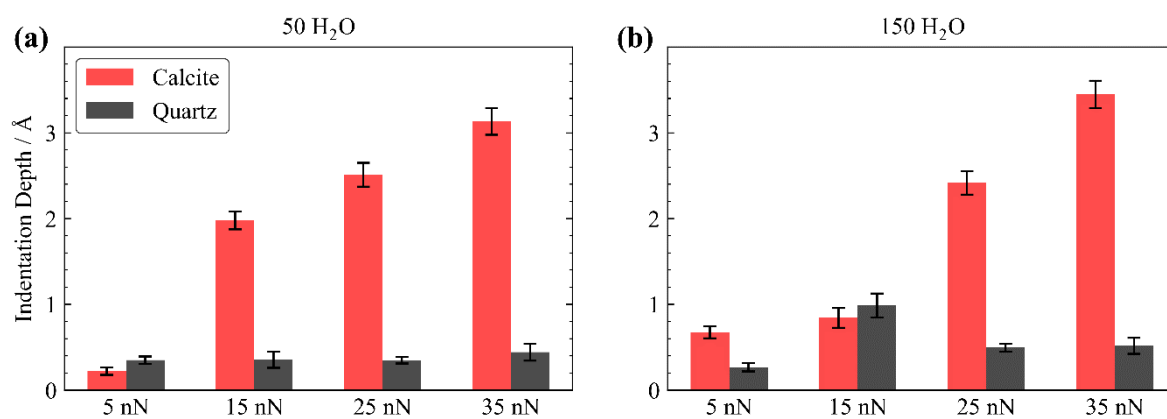


Figure 6: Variation in the indentation depth with load for: (a) calcite and quartz with 50 water molecules and (b) calcite and quartz with 150 water molecules. Mean and standard deviation (vertical bars) calculated during the final 200 ps of sliding.

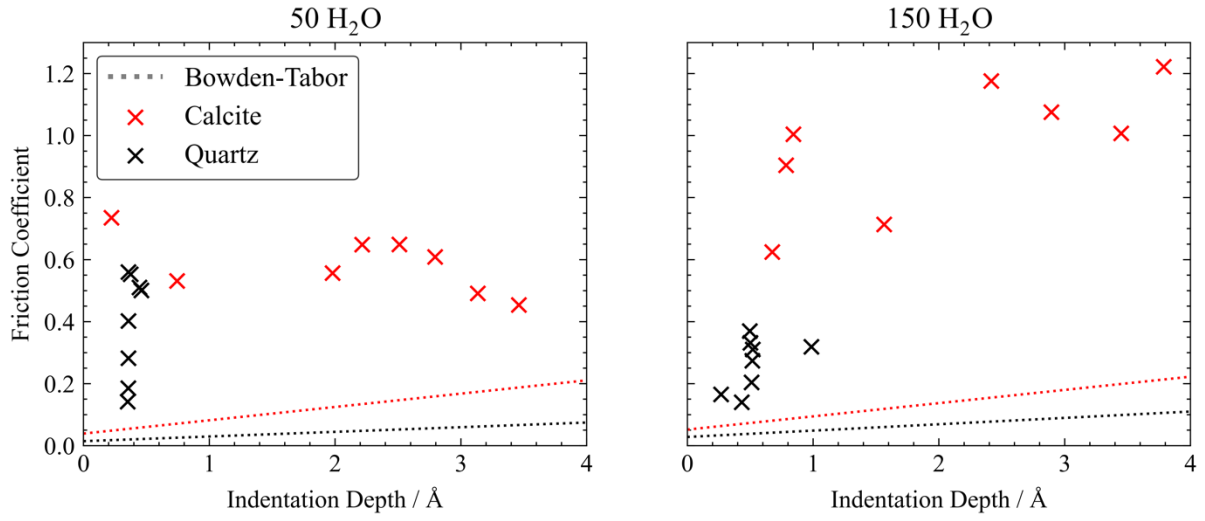


Figure 7. Variation in the load-dependent friction coefficient (F_f/F_n) with the steady-state indentation depth with systems containing 50 and 150 water molecules. Dotted lines show the predictions from the Bowden-Tabor equation for the ploughing contribution to the friction coefficient.

The ploughing contribution to the friction coefficient, μ_p , was estimated through the equation proposed by Bowden and Tabor, which calculates the ratio of the tip areas seen by the substrate in the normal, A_n , and lateral, A_l , direction, given by:

$$\mu_p = \frac{A_n}{A_l} = \frac{2\theta_s - \sin(2\theta_s)}{\pi \sin^2(\theta_s)}$$

where θ_s is the semi-angle at the centre of the spherical tip subtended by the groove and is obtained from $\cos(\theta_s) = \frac{R-d}{R}$, where d is the indentation depth.

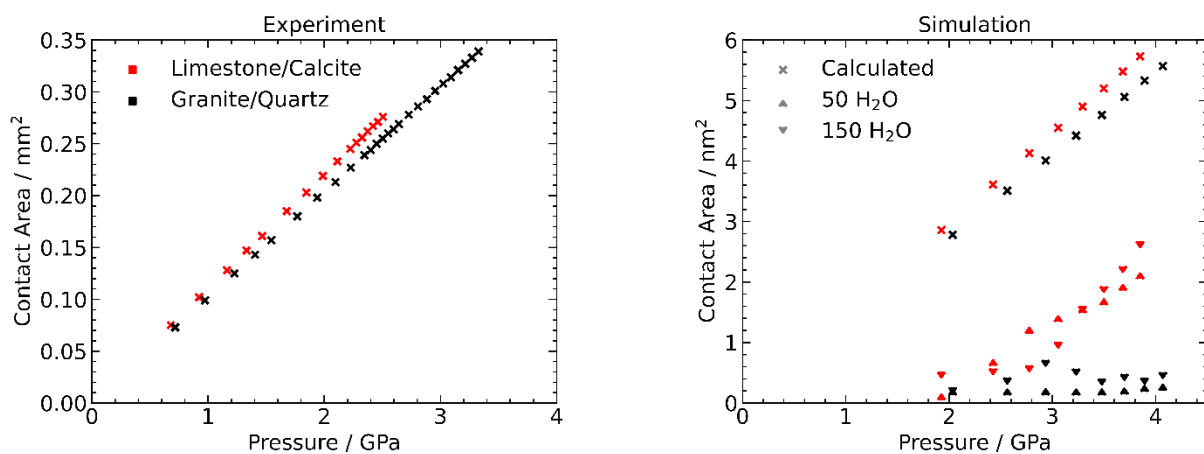


Figure 8. Variation in the contact area, $\mathcal{A}_c$, with maximum Hertz pressure, P_{max} , in the experiments and NEMD simulations. Crosses show Hertz predictions over the studies load range in the experiments (1–200 N) and simulations (2.5–40 nN). Triangles show the measured contact areas from the NEMD simulations based on the indentation depths.

ReaxFF parameters for CaCO₃

Reactive MD-force field: Ca/O/H/C

39 ! Number of general parameters
50.0000 !Overcoordination parameter
9.5469 !Overcoordination parameter
1.6725 !Valency angle conjugation parameter
1.7224 !Triple bond stabilisation parameter
6.8702 !Triple bond stabilisation parameter
60.4850 !C2-correction
1.0588 !Undercoordination parameter
4.6000 !Triple bond stabilisation parameter
12.1176 !Undercoordination parameter
13.3056 !Undercoordination parameter
-20.0000 !Triple bond stabilization energy
0.0000 !Lower Taper-radius
10.0000 !Upper Taper-radius
2.8793 !Not used
33.8667 !Valency undercoordination
6.0891 !Valency angle/lone pair parameter
1.0563 !Valency angle
2.0384 !Valency angle parameter
6.1431 !Not used
6.9290 !Double bond/angle parameter
0.3989 !Double bond/angle parameter: overcoord
3.9954 !Double bond/angle parameter: overcoord
-2.4837 !Not used
5.7796 !Torsion/BO parameter
10.0000 !Torsion overcoordination
1.9487 !Torsion overcoordination
-1.2327 !Conjugation 0 (not used)
2.1645 !Conjugation
1.5591 !vdWaals shielding
0.1000 !Cutoff for bond order (*100)
1.7602 !Valency angle conjugation parameter

0.6991 !Overcoordination parameter
 50.0000 !Overcoordination parameter
 1.8512 !Valency/lone pair parameter
 0.5000 !Not used
 20.0000 !Not used
 5.0000 !Molecular energy (not used)
 0.0000 !Molecular energy (not used)
 0.7903 !Valency angle conjugation parameter
 5 ! Nr of atoms; cov.r; valency;a.m;Rvdw;Evdw;gammaEEM;cov.r2;#
 alfa;gammavdW;valency;Eunder;Eover;chiEEM;etaEEM;n.u.
 cov r3;Elp;Heat inc.;n.u.;n.u.;n.u.;n.u.
 ov/un;val1;n.u.;val3,vval4
 C 1.3704 4.0000 12.0000 1.8907 0.1868 0.6388 1.1294 4.0000
 9.8017 2.1260 4.0000 30.0000 79.5548 4.9730 6.0000 0.0000
 1.2022 0.0000 197.2908 8.9856 34.9620 13.5366 0.8563 0.0000
 -2.8983 2.3275 1.0564 4.0000 2.9663 0.0000 0.0000 0.0000
 H 0.8930 1.0000 1.0080 1.3550 0.0930 0.8203 -0.1000 1.0000
 8.2230 33.2894 1.0000 0.0000 121.1250 3.7248 9.6093 1.0000
 -0.1000 0.0000 55.1878 3.0408 2.4197 0.0003 1.0698 0.0000
 -19.4571 4.2733 1.0338 1.0000 2.8793 0.0000 0.0000 0.0000
 O 1.2450 2.0000 15.9990 2.3890 0.1000 1.0898 1.0548 6.0000
 9.7300 13.8449 4.0000 37.5000 116.0768 8.5000 8.3122 2.0000
 0.9049 0.4056 68.0152 3.5027 0.7640 0.0021 0.9745 0.0000
 -3.5500 2.9000 1.0493 4.0000 2.9225 0.0000 0.0000 0.0000
 Ca 1.9927 2.0000 40.0870 2.7005 0.1848 0.7939 1.0000 2.0000
 10.6123 27.5993 3.0000 38.0000 0.0000 -1.9372 6.5275 0.0000
 -1.3000 0.0000 220.0000 49.9248 0.3370 0.0000 0.0000 0.0000
 -2.0000 4.0000 1.0564 6.2998 2.9663 1.4000 0.0100 13.0000
 X -0.0998 2.0000 1.0080 2.0000 0.0000 1.0000 -0.1000 6.0000
 10.0000 2.5000 4.0000 0.0000 0.0000 8.5000 1.5000 0.0000
 -0.1000 0.0000 -2.3700 8.7410 13.3640 0.6690 0.9745 0.0000
 -11.0000 2.7466 1.0338 4.0000 2.8793 0.0000 0.0000 0.0000
 10 ! Nr of bonds; Edis1;LPpen;n.u.;pbe1;pbo5;13corr;pbo6
 pbe2;pbo3;pbo4;Etrip;pbo1;pbo2;ovcorr

```

1 1 145.1104 93.6846 57.5621 -0.6831 -0.4472 1.0000 34.9350 0.3881
    0.5276 -0.1073 9.1992 1.0000 -0.0798 6.7209 1.0000 0.0000
1 2 166.2175 0.0000 0.0000 -0.5944 0.0000 1.0000 6.0000 0.5738
    5.3662 1.0000 0.0000 1.0000 -0.0572 6.9913 0.0000 0.0000
2 2 153.2532 0.0000 0.0000 -0.4600 0.0000 1.0000 6.0000 0.7300
    6.2500 1.0000 0.0000 1.0000 -0.0790 6.0552 0.0000 0.0000
1 3 157.5526 100.1654 61.2014 -0.5755 -0.3947 1.0000 18.6775 0.4110
    0.9469 -0.4198 7.9115 1.0000 -0.1708 4.9995 0.0000 0.0000
3 3 142.2858 145.0000 50.8293 0.2506 -0.1000 1.0000 29.7503 0.6051
    0.3451 -0.1055 9.0000 1.0000 -0.1225 5.5000 1.0000 0.0000
2 3 160.0000 0.0000 0.0000 -0.5725 0.0000 1.0000 6.0000 0.5626
    1.1150 1.0000 0.0000 0.0000 -0.0920 4.2790 0.0000 0.0000
1 4 0.0000 0.0000 0.0000 -0.6528 -0.3000 0.0000 36.0000 0.5000
    10.0663 -0.3500 25.0000 1.0000 -0.1000 10.0000 0.0000 0.0000
2 4 0.0000 0.0000 0.0000 -0.0203 -0.1418 1.0000 13.1260 0.0230
    8.2136 -0.1310 0.0000 1.0000 -0.2692 6.4254 0.0000 24.4461
3 4 50.8757 0.0000 43.3991 1.0000 -0.3000 1.0000 36.0000 0.0025
    0.7609 -0.2500 12.0000 1.0000 -0.0515 8.9041 1.0000 24.4461
4 4 36.9494 0.0000 0.0000 -0.0412 -0.2000 0.0000 16.0000 0.3233
    0.3708 -0.2000 10.0000 1.0000 -0.0822 4.2104 0.0000 0.0000
6 ! Nr of off-diagonal terms; Ediss;Ro;gamma;rsigma;rpi;rpi2
1 2 0.1206 1.3998 9.8420 1.1177 -1.0000 -1.0000
2 3 0.0283 1.2885 10.9190 0.9215 -1.0000 -1.0000
1 3 0.0672 1.8208 10.0991 1.4000 1.1705 1.0634
1 4 0.4000 1.8203 14.0000 -1.0000 -1.0000 -1.0000
2 4 0.0100 1.6000 13.2979 -1.0000 -1.0000 -1.0000
3 4 0.0955 1.7587 11.9417 1.9052 -1.0000 -1.0000
23 ! Nr of angles;at1;at2;at3;Thetao,o;ka;kb;pv1;pv2
1 1 1 67.2380 40.0000 0.9471 0.0000 0.6938 14.9916 1.3673
1 1 2 66.1046 14.4379 6.0443 0.0000 0.9851 0.0000 2.7063
2 1 2 68.2534 24.9110 3.7590 0.0000 1.5457 0.0000 2.9366
1 2 2 0.0000 0.0000 6.0000 0.0000 0.0000 0.0000 1.0400
1 2 1 0.0000 3.4110 7.7350 0.0000 0.0000 0.0000 1.0400
2 2 2 0.0000 27.9213 5.8635 0.0000 0.0000 0.0000 1.0400

```

1	1	3	59.2685	25.8472	1.7572	0.0000	4.4967	58.6562	1.1553
3	1	3	75.1448	11.4232	5.2677	-14.2010	1.1419	0.0000	2.2364
2	1	3	59.2133	26.6398	1.1864	0.0000	0.1245	0.0000	1.5701
1	3	1	57.8946	31.9211	0.7959	0.0000	2.4921	0.0000	1.7123
1	3	3	83.1701	45.0000	1.5698	0.0000	1.1034	68.1072	1.5349
3	3	3	87.3324	15.8235	2.7528	0.0000	2.9390	0.0000	1.0000
1	3	2	90.0000	7.3724	5.3059	0.0000	1.2146	0.0000	3.0000
2	3	3	75.6935	50.0000	2.0000	0.0000	1.0000	0.0000	1.1680
2	3	2	85.8000	9.8453	2.2720	0.0000	2.8635	0.0000	1.5800
1	2	3	0.0000	19.9767	1.1358	0.0000	0.6225	0.0000	1.0432
3	2	3	0.0000	10.7350	5.0000	0.0000	0.0000	0.0000	4.0000
2	2	3	0.0000	8.5744	3.0000	0.0000	0.0000	0.0000	1.0421
3	4	3	1.0000	4.9611	2.4541	0.0000	0.5754	0.0000	1.0000
4	3	4	9.5066	4.2640	3.1438	0.0000	1.9819	0.0000	1.6463
2	3	4	51.3829	2.5000	0.2500	0.0000	0.0500	0.0000	1.0000
3	3	4	70.0000	25.0000	1.0000	0.0000	1.0000	0.0000	1.2500
1	3	4	74.3844	25.0000	1.6739	0.0000	0.7037	0.0000	1.0000
26	! Nr of torsions;at1;at2;at3;at4;;V1;V2;V3;V2(BO);vconj;n.u;n								
1	1	1	1	-0.5000	38.4080	0.5000	-6.1117	-1.9481	0.0000
1	1	1	2	0.4247	27.7539	0.5000	-6.3112	-1.9452	0.0000
2	1	1	2	-0.5000	30.7919	0.5000	-5.8539	-3.0000	0.0000
1	1	1	3	-0.1108	80.0000	-0.5793	-5.4405	-1.1000	0.0000
2	1	1	3	-0.5732	28.8617	0.8920	-5.1112	-1.0978	0.0000
3	1	1	3	-1.7931	25.6020	-1.0000	-4.0381	-0.8614	0.0000
1	1	3	1	1.0000	59.3911	-0.5000	-2.7048	-0.9000	0.0000
1	1	3	2	-0.1141	5.0000	-1.0000	-8.1021	-0.9000	0.0000
2	1	3	1	2.5000	15.2653	0.8965	-2.5000	-0.9000	0.0000
2	1	3	2	-2.5000	37.1322	0.4144	-4.6988	-1.1000	0.0000
2	1	3	3	0.8151	100.0000	1.0000	-3.4409	-2.8274	0.0000
3	1	3	1	0.5406	16.8262	0.4979	-8.2524	-3.0437	0.0000
3	1	3	2	2.4679	16.0446	-0.3246	-2.5000	-3.0476	0.0000
1	3	3	2	-2.5000	7.3697	-1.0000	-4.1837	-2.9498	0.0000
2	3	3	2	-2.5000	-25.0000	-1.0000	-2.5000	0.0000	0.0000
1	3	3	3	2.5000	-24.1204	1.0000	-3.2189	-0.9972	0.0000

2	3	3	3	-2.0407	80.0000	-0.9677	-7.0890	0.0000	0.0000	0.0000
3	3	3	3	-2.5000	-25.0000	1.0000	-2.5000	-0.9000	0.0000	0.0000
0	1	2	0	2.0735	0.1000	0.0100	-4.0000	0.0000	0.0000	0.0000
0	2	2	0	0.0000	0.1000	0.0100	-4.0000	0.0000	0.0000	0.0000
0	2	3	0	0.0000	0.1000	0.0200	-4.0000	0.0000	0.0000	0.0000
0	1	1	0	0.0000	50.0000	0.3000	-4.0000	-2.0000	0.0000	0.0000
0	3	3	0	0.5511	25.4150	1.1330	-5.1903	-1.0000	0.0000	0.0000
1	1	3	3	-0.0002	20.1851	0.1601	-9.0000	-2.0000	0.0000	0.0000
1	3	3	1	0.0002	80.0000	-1.5000	-4.4848	-2.0000	0.0000	0.0000
3	1	3	3	-0.1583	20.0000	1.5000	-9.0000	-2.0000	0.0000	0.0000
1	! Nr of hydrogen bonds;at1;at2;at3;Rhb;Dehb;vhb1									
3	2	3		2.1200	-3.5800	1.4500	19.5000			

Appendix B: Supporting information for Chapter 4: Impact of Water on Hexadecane Lubrication in Diamond-Rock Contacts

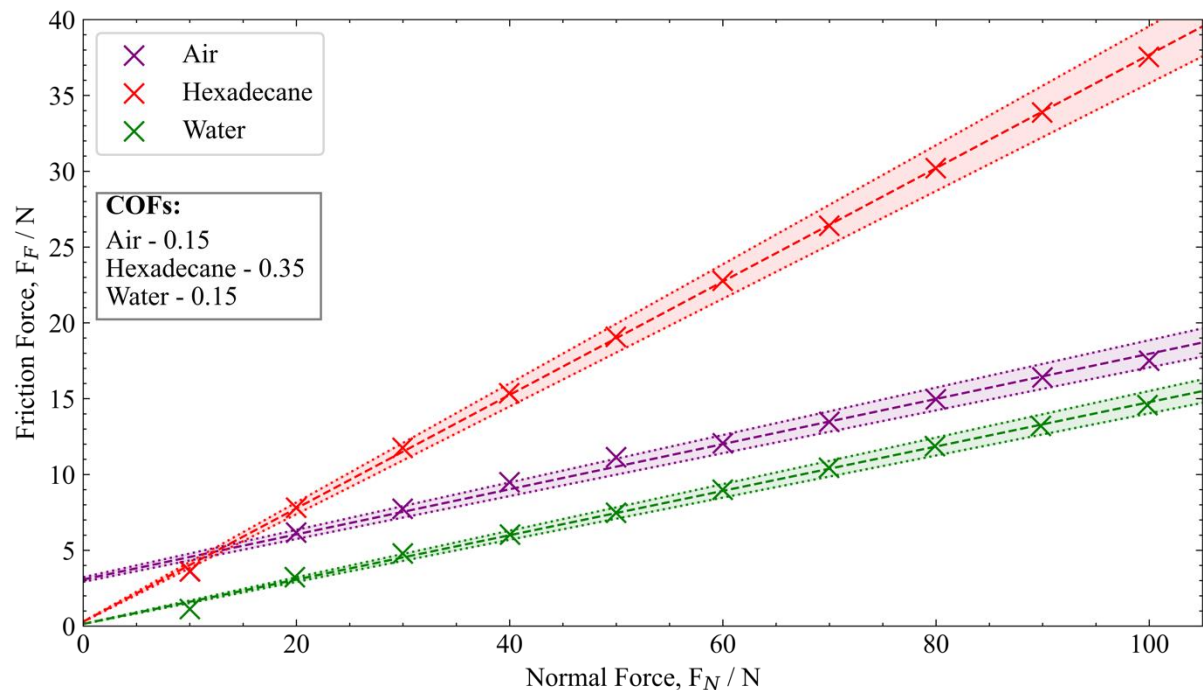


Figure 1. Variation in the friction force, F_F , with normal force, F_N , from the macroscale tribometer experiments with air (purple), water- (green), and hexadecane-lubricated (red) diamond–granite contacts. Normal forces, F_N , are between 10 and 100 N and tangential velocity, $v = 0.095 \text{ m s}^{-1}$. Dashed lines are linear fits to Amontons’ friction equation. Dotted lines represent 95% confidence intervals. Performed by Eliah M Everhard.

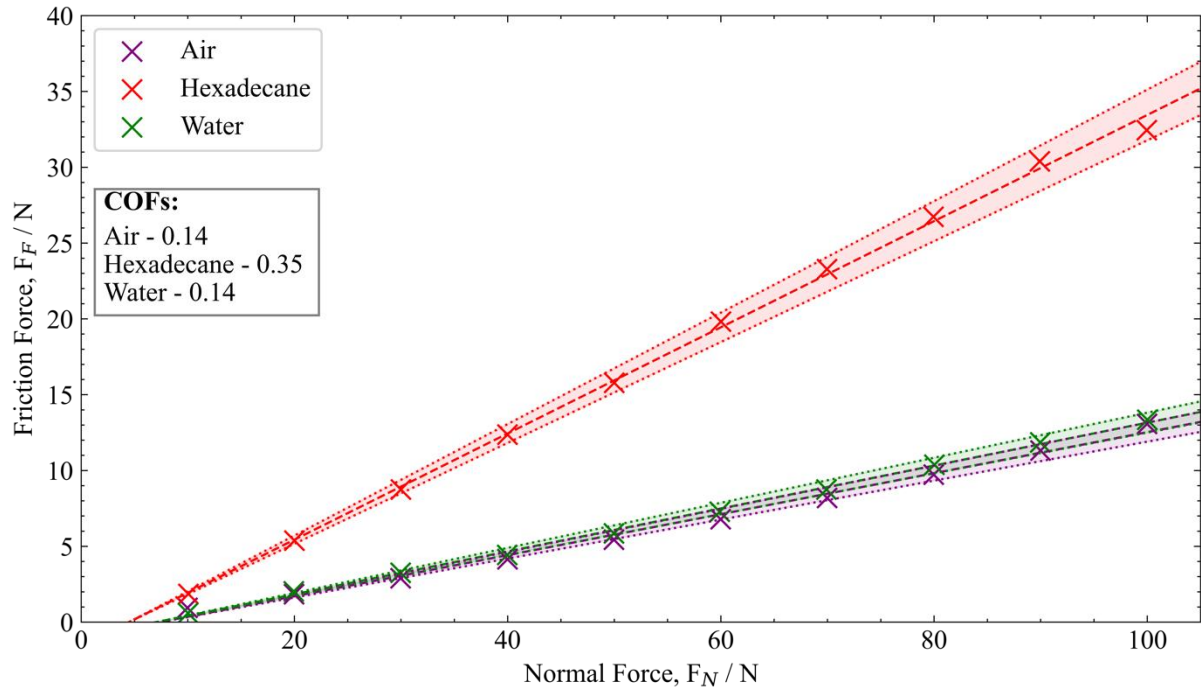


Figure 2. Variation in the friction force, F_F , with normal force, F_N , from the macroscale tribometer experiments with air (purple), water- (green), and hexadecane-lubricated (red) diamond–granite contacts. Normal forces, F_N , are between 10 and 100 N and tangential velocity, $v = 0.15 \text{ m s}^{-1}$. Dashed lines are linear fits to Amontons' friction equation. Dotted lines represent 95% confidence intervals. Performed by Eliah M Everhard.

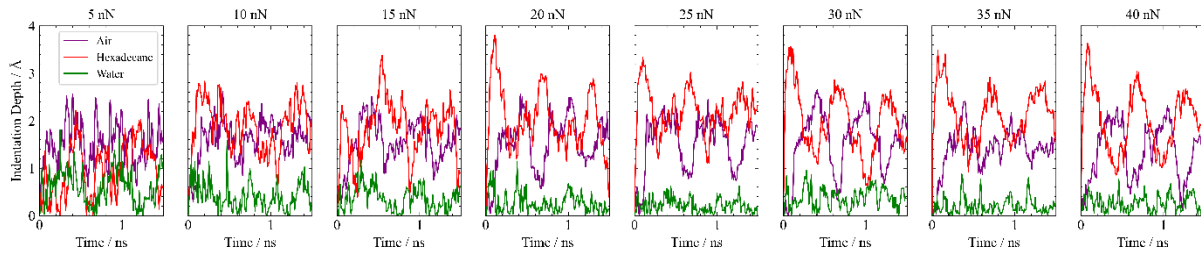


Figure 3: Change in indentation depth with sliding time for air (purple), water (green), and hexadecane (red) lubricated contacts.

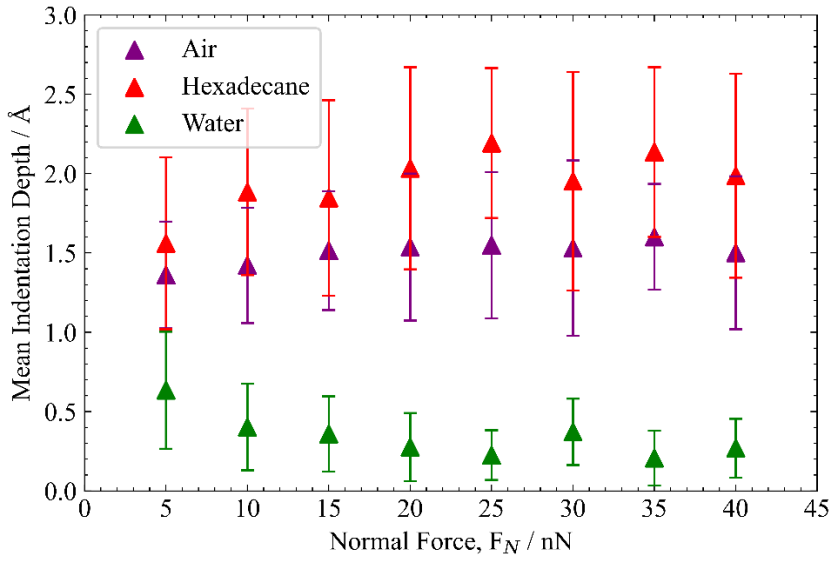


Figure 4: Mean indentation depth with normal force for air (purple), water (green), and hexadecane (red) lubricated contacts.

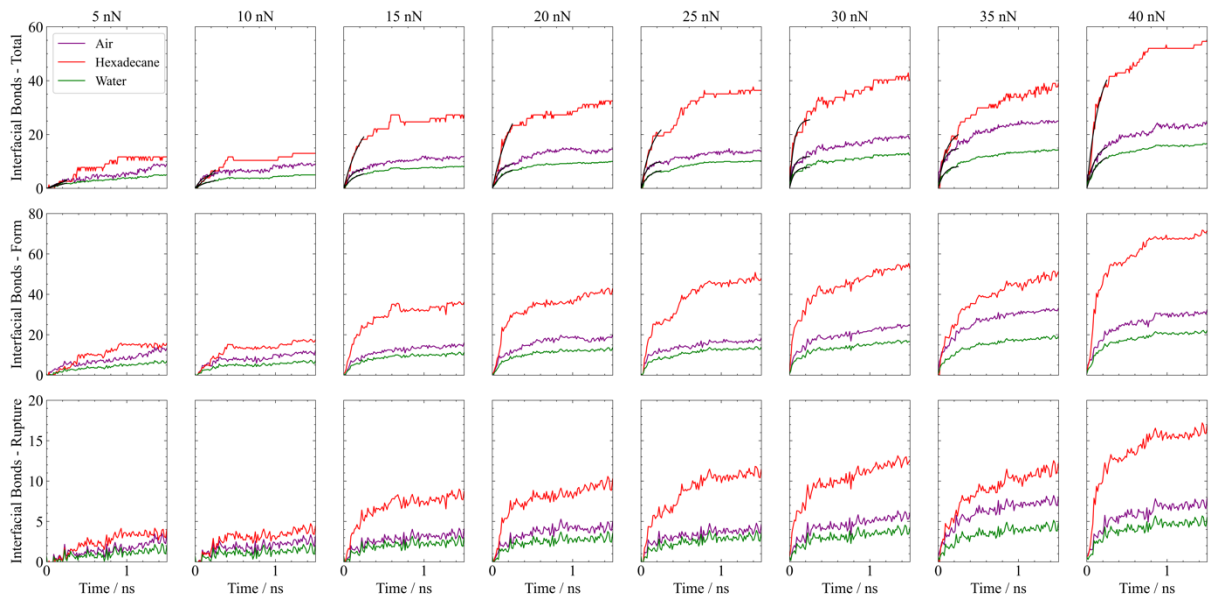


Figure 5: Variation in the total, formation, and rupture of interfacial bonds between the tip and the surface during sliding for the air (purple), water- (green), and hexadecane-lubricated (red) contacts across $F_N = 5$ nN to 40 nN. Black dashed lines are fits to the first 250 ps of interfacial bond formation data assuming first-order reactions used to calculate initial rates.

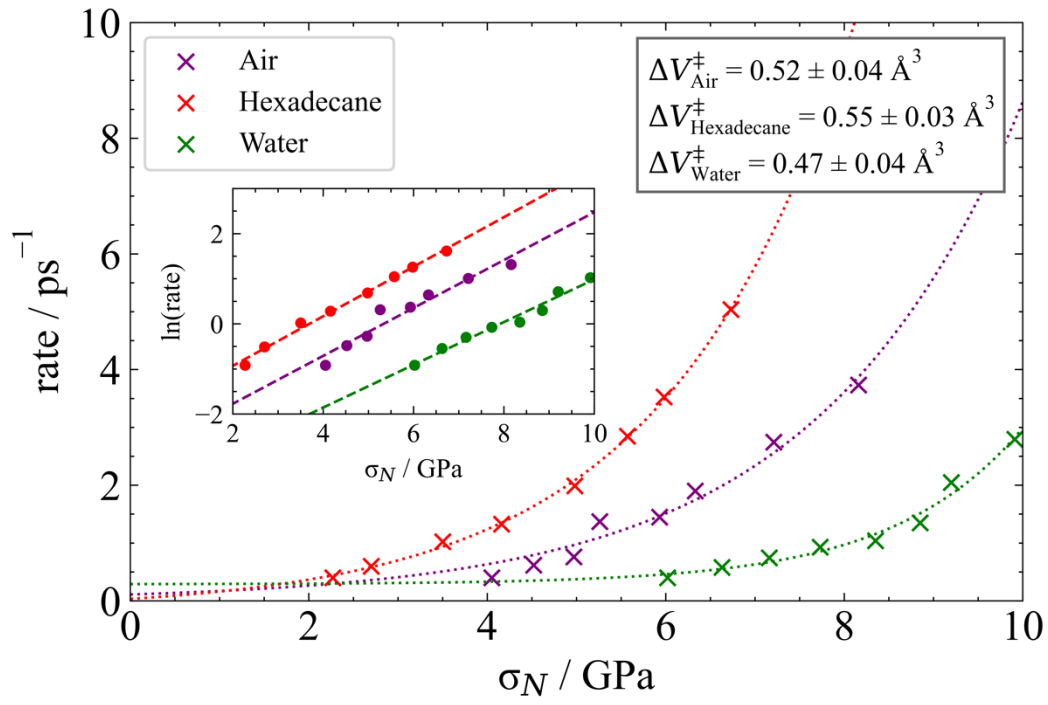


Figure 6: Variation in the rate of interfacial bond formation as sliding commences with the atoms in contact method for pressure calculations for air (purple), water- (green), and hexadecane-lubricated (red) contacts. Inset shows a linear increase in ln(rate) with pressure.

Appendix C: Supporting information for Chapter 5. Atomic-Scale Wear Inside Diamond-Quartz Contacts

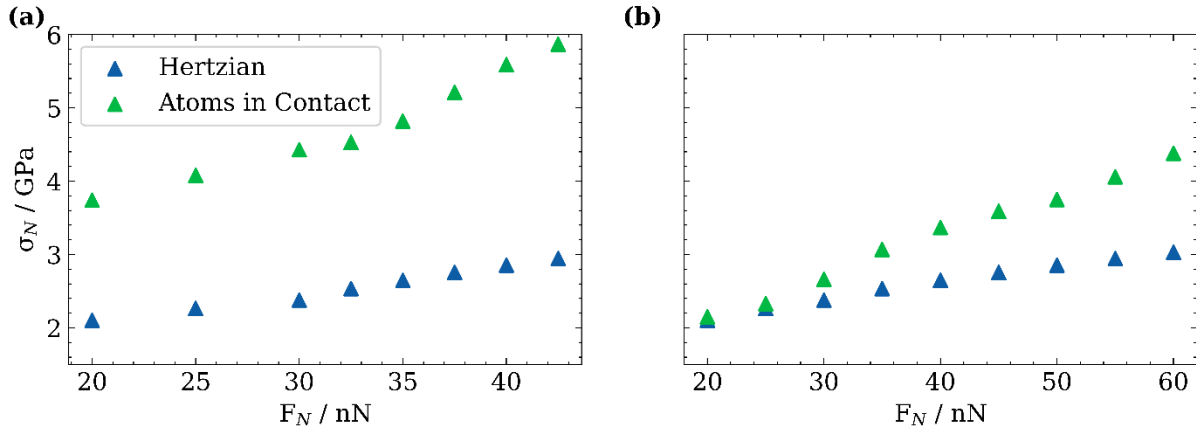


Figure 1. Comparison between contact stress calculations using Hertz theory and the number of atoms in contact based on the number of interfacial bond for the (a) dry and (b) wet systems. Atoms in contact values are mean values over final 1 ns).

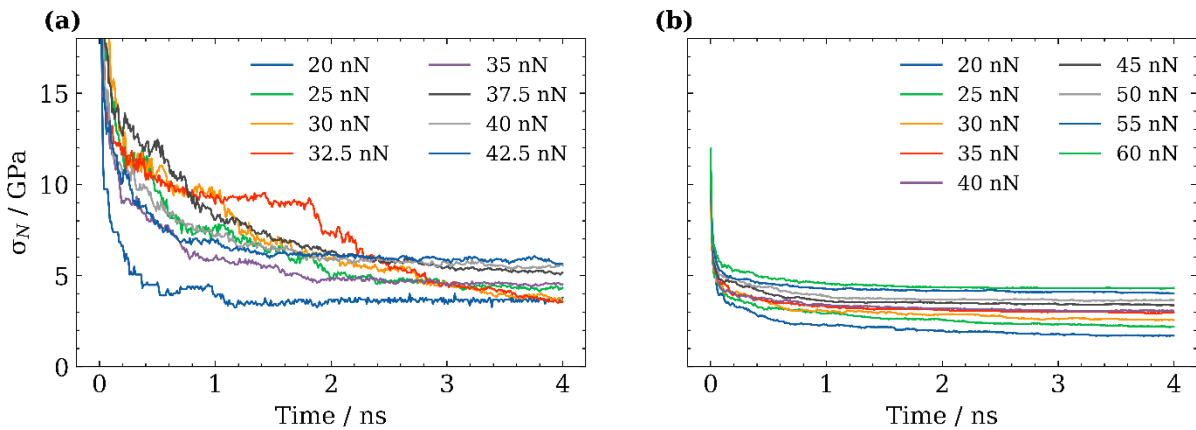


Figure 2. Temporal evolution of the pressure in the NEMD simulations using the atoms in contact method for (a) dry and (b) wet systems.

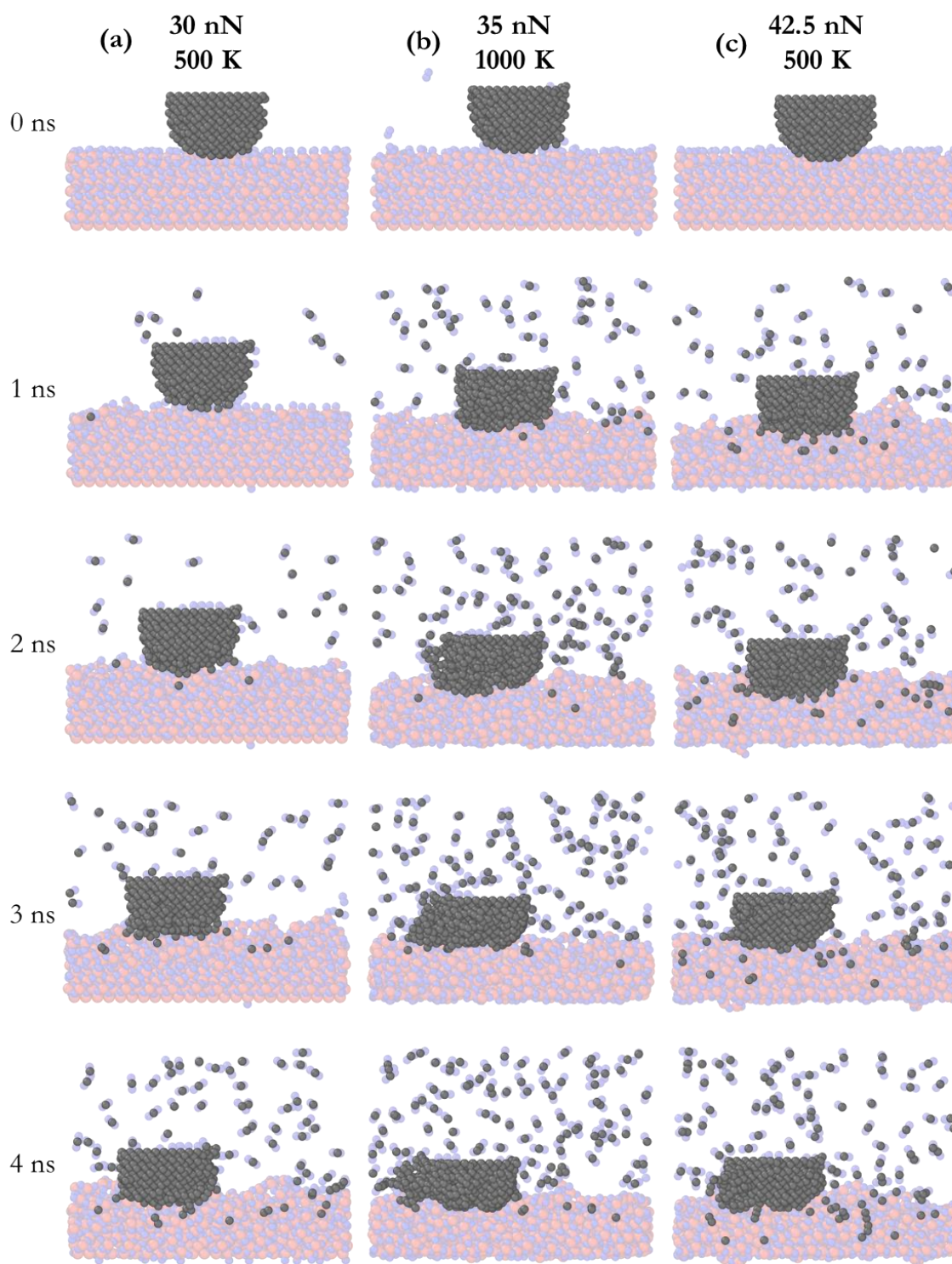


Figure 3. Snapshots showing the dry tip wear over time at (a) medium temperature/medium load, (b) medium load/high temperature, and (c) high load/medium temperature. Carbon atoms shown in black, silicon in red, and oxygen in blue. Atom-by-atom attrition occurs for all conditions via C-O interfacial bond formation, C-C breaking and either diffusion into the substrate or oxidation to form CO_2 molecules. Amorphization of the tip followed by cluster detachment at the trailing edge of the tip occurs at high temperatures and loads.

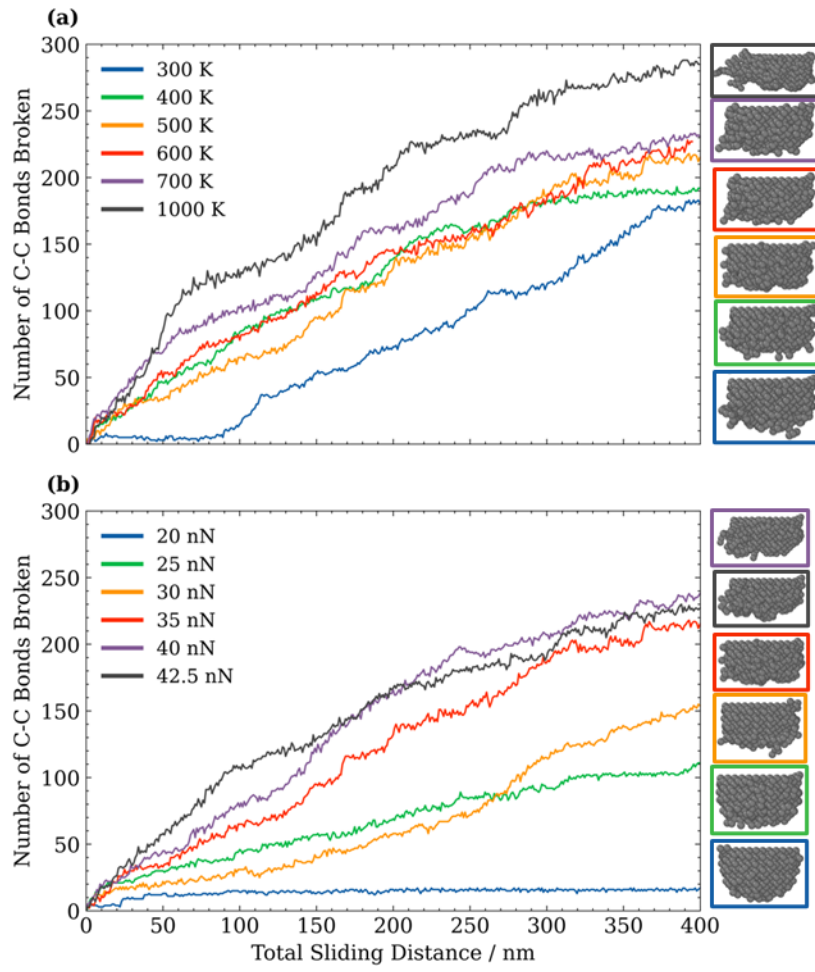


Figure 4. Total number of C-C broken bonds with sliding distance for the dry system at (a) varied temperatures and a constant load of 35 nN (b) varied loads and a constant temperature of 500 K.

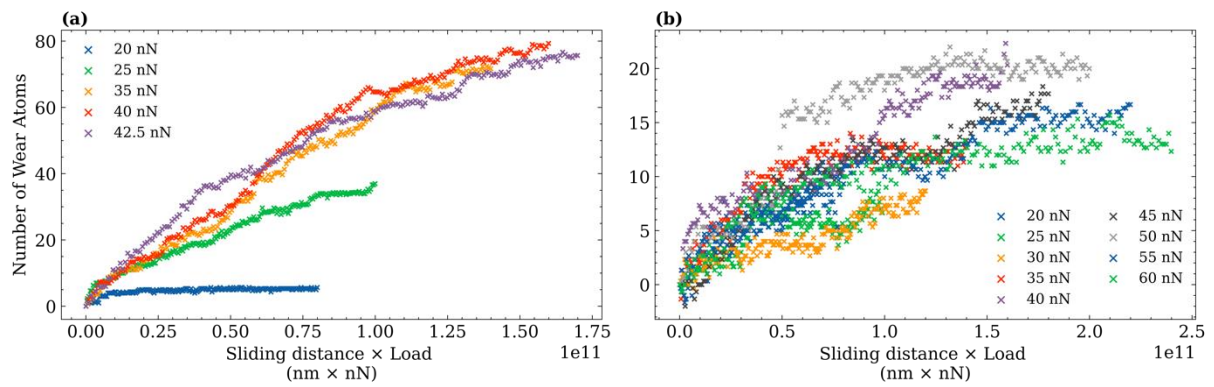


Figure 5. Number of carbon wear atoms as a function of a product of sliding distance and load for (a) dry and (b) wet systems.

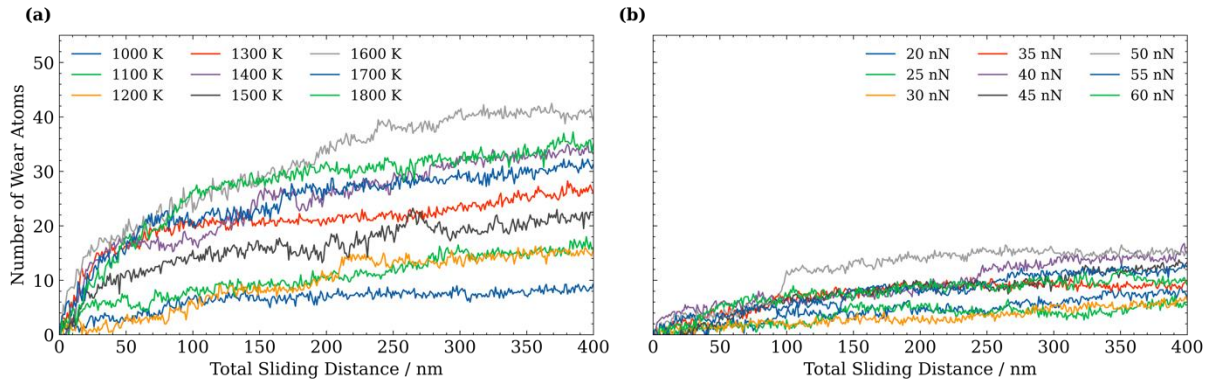


Figure 6. Number of wear atoms for the wet system at (a) varied temperatures and a constant load of 30 nN and (b) varied loads and a constant temperature of 1000 K.

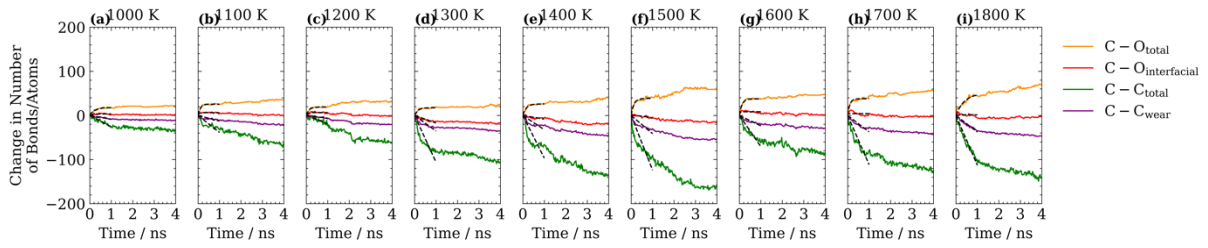


Figure 7. Change in the number of C-O (orange), C-O interfacial (red), C-C total (green), and C-C wear (purple) bonds broken/formed during sliding for the wet system at varied temperature and a constant load of 30 nN. Black dashed lines are fits to the first 1 ns of the bond formation/breakage data assuming first-order reactions.

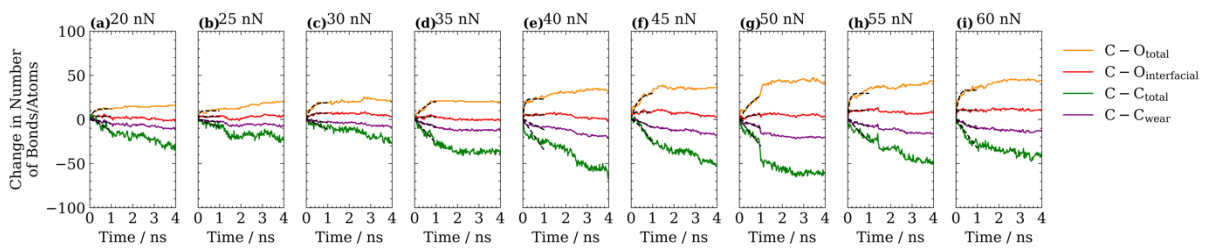


Figure 8. Change in the number of C-O (orange), C-O interfacial (red), C-C total (green), and C-C wear (purple) bonds broken/formed during sliding for the wet system at varied temperature and a constant temperature of 1000 K. Black dashed lines are fits to the first 1 ns of the bond formation/breakage data assuming first-order reactions.

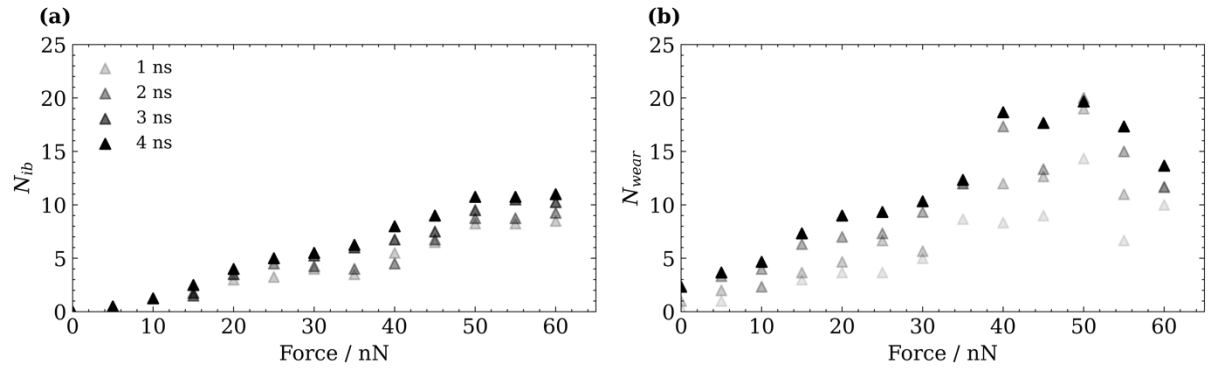


Figure 9. Change in the number of interfacial bonds, N_{ib} , (a) and number of wear atoms, N_{wear} , (b) with normal force for the wet system.

Appendix D: Supporting information for Chapter 6.

Mechanochemically Induced Phase Transformation of α -quartz

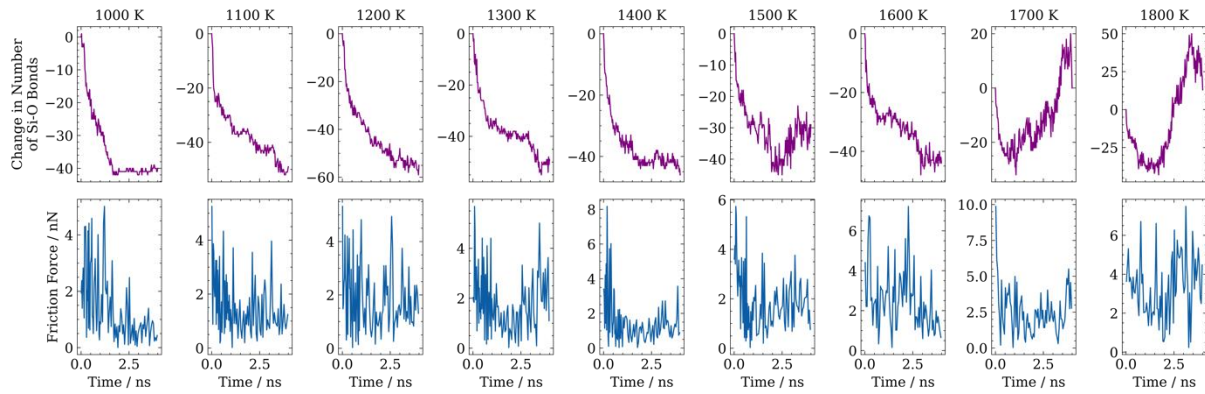


Figure 1: Change in number of Si-O bonds and friction force at a fixed load equal to 35 nN and temperatures between 1000-1800 K for the wet system. Si-O rupture is fitted to the function $(1 - e^{-rt})$ are fitted, where r is the rate of bond formation/breakage and t is the sliding time.³¹⁷

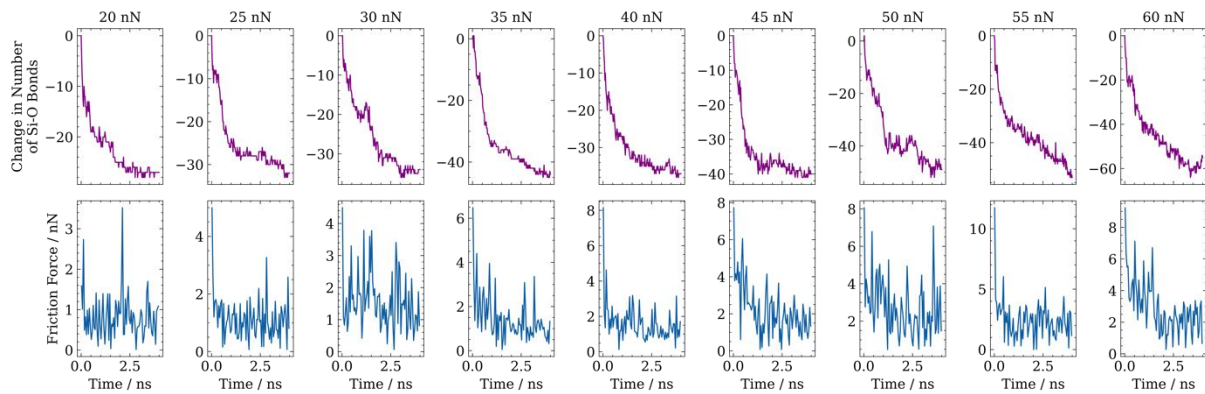


Figure 2: Change in number of Si-O bonds and friction force at a fixed temperature equal to 1000 K and loads between 20-60 nN for the wet system. Si-O rupture is fitted to the function $(1 - e^{-rt})$ are fitted, where r is the rate of bond formation/breakage and t is the sliding time.³¹⁷

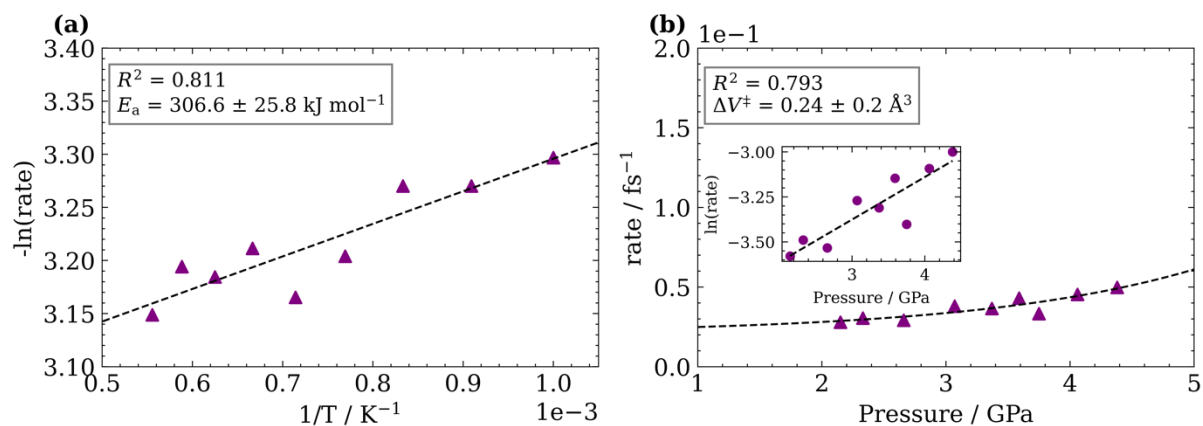


Figure 3: E_a (a) and $\Delta V^\ddagger$ (b) calculated for the wet system using the rates from fittings from Figure Appendix C Figure 1 and Figure Appendix C Figure 2.

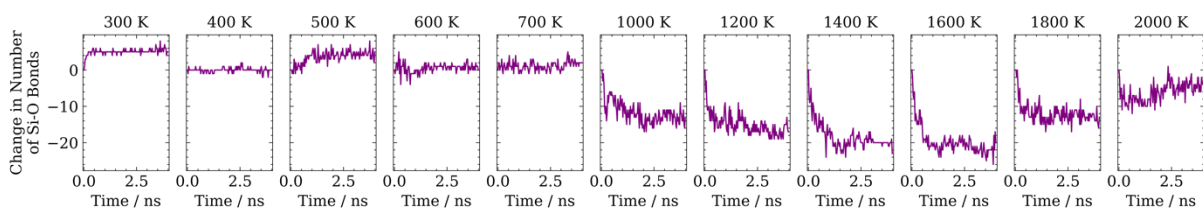


Figure 4: Change in the number of Si-O bonds in bulk α -quartz upon heating between 300 K and 2000 K without the sliding diamond asperity.

Appendix E: Supporting information for Chapter 7. A

Comparison of Forcefields for C/O/Si/H Systems

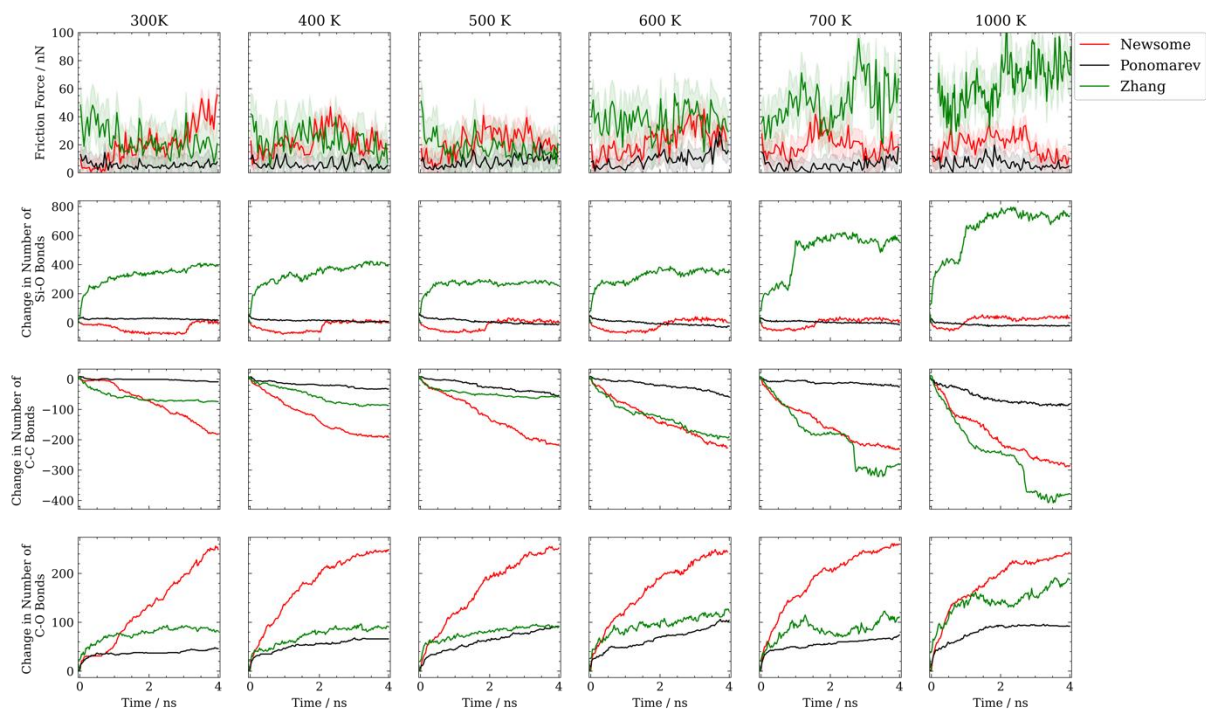


Figure 1: A comparison of friction force, and change in the number of Si-O, C-C, and C-O bonds for the Newsome²⁰⁶ (red), Ponomarev⁴⁶⁵ (black), and Zhang⁴⁶⁶ (green) forcefields.